# Quantum theory of atoms, molecules and their interaction with light

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Interdiszciplináris és komplex megközelítésű digitális tananyagfejlesztés a természettudományi képzési terület mesterszakjaihoz

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Preparation of this lecture notes were suppported by **Interdisciplináris és komplex megközelítésű digitális tananyagfejlesztés a természettudományi képzési terület mesterszakjaihoz**

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# Előszó

A jelen digitális tananyag a TÁMOP-4.1.2.A/1-11/1-2011-0025 számú, "Interdiszciplináris és komplex megközelítésű digitális tananyagfejlesztés a természettudományi képzési terület mesterszakjaihoz" című projekt részeként készült el.

A projekt általános célja a XXI. század igényeinek megfelelő természettudományos felsőoktatás alapjainak a megteremtése. A projekt konkrét célja a természettudományi mesterképzés kompetenciaalapú és módszertani megújítása, mely folyamatosan képes kezelni a társadalmi-gazdasági változásokat, a legújabb tudományos eredményeket, és az info-kommunikációs technológia (IKT) eszköztárát használja.

ÚJ SZÉCHENYI TERV
MAGYARORSZÁG MEGÚJUL

# Introduction

These lecture notes have been prepared to support the study of atomic molecular physics with an emphasis on the interaction of these atomic systems with light, and in more general, with electromagnetic fields. The character of the material is theoretical, and wishes to rely on the quantum mechanical studies of the students, which is a prerequisite of being able to follow the material presented here. The first four chapters are on the border of advanced Quantum Mechanics and theoretical Atomic Physics. So this is a course definitely for MSc or PhD students. In spite of the theoretical approach based on mathematical argumentations, we tried to connect the material with experimental observations. These short notes, however cannot be considered as a replacement of courses where deeper experimental insight should be gathered.

There are several problems (~60) embedded in the text, and their solution is strongly recommended for the students. In view of the author this is a necessary condition for getting a reliable knowledge of the subject, as is the case with any other physics subject. The electronic form made it possible to include animations which may significantly improve the level of understanding, as it enabled us to couple demonstrations and interactive animations to the material which should make more easy the understanding of the rather abstract notions and laws of atomic physics. These are - as it is usual in physics - quantitative relations, the true depth and content of which can only be understood in the language of mathematics. This difficult task is intended to be promoted by the included multimedia materials. The animations can be started by clicking on the links in the tables, which visualize the problems in question.

The animations can be started by clicking on the links given in tables, which visualize the problem treated in the text. In order to start the animations the following free-ware programs need to be available on the computer:

**Java Runtime Environment**

In order to run the java interactive contents you need to download and install the **java environment (JRE)**. By clicking on the link on the left you can download the java environment that suits to your operation system. http://www.java.com/en/download/manual.jsp

**Wolfram CDF Player**

For another part of the interactive contents you need to install **Wolfram CDF Player**. Which can be downloaded by clicking on the link on left. http://www.wolfram.com/cdf-player/

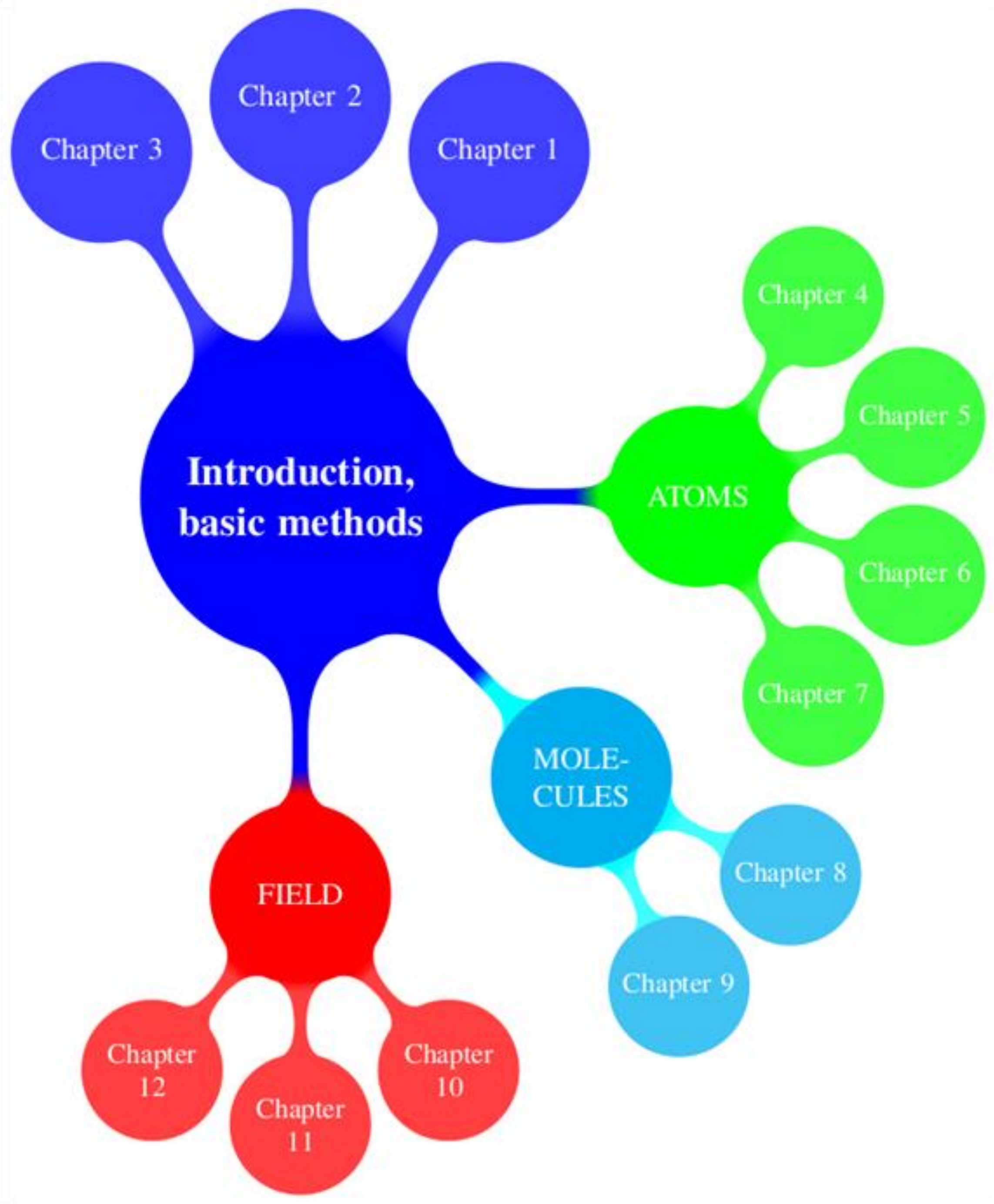
**Adobe-Flash plugin**

Flash animations of swf format can be viewed only if the appropriate **Adobe-Flash plugin** is installed for your browser. http://get.adobe.com/flashplayer

### Adobe-Shockwave plugin

There are also shochwave flash animations among the interactive materials can be viewed only if the appropriate **Adobe-Shockwave plugin** is installed for your browser. http://get.adobe.com/shockwave

The theory of atomic and molecular physics is not an easy subject, but modern technology is based more and more on the laws and properties of micro-world, so it seems necessary to understand the most important rules and methods of this field of a physics student.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# Chapter 1. The eigenvalue problem in a central force field, radial equation

**Goals:** In this chapter we recall one of the most important results of quantum mechanics, the solution of the energy eigenvalue problem of the Coulomb potential. We assume that the reader is acquainted with the basic concepts and notions of quantum mechanics: state vectors, operators, eigenvalues, and stationary states. We also assume that the problem of angular momentum in coordinate representation, i.e. the properties of the spherical harmonics are known.

**Prerequisites:** Basic QM concepts and notions: state vectors, operators, eigenvalues, and stationary states; angular momentum in coordinate representation; spherical harmonics.

## 1. Introduction

It is difficult to overestimate the significance of the Coulomb problem in atomic physics. One aspects why this is the case, is that the experimentally observed primary spectrum results here from an elegant mathematical treatment based on first principles of quantum mechanics. Secondly, the significance of angular momentum as appearing in this special case hints to its significance in quantum physics. Thirdly the results for the Coulomb problem are fundamental and ubiquitous in the whole atomic and molecular physics.

In a central field potential the Hamiltonian of a single particle takes the form:

$$H=\frac{\mathbf{P}^2}{2m}+V(|\mathbf{R}|). \qquad (1.1)$$

Using the notation $|\mathbf{R}|=R,|\mathbf{P}|=P$ we have to solve the energy eigenvalue equation:

$$\left[\frac{P^2}{2m}+V(R)\right]|\psi\rangle=\varepsilon|\psi\rangle \qquad (1.2)$$

As it is known from quantum mechanics, the square and the $z$ component of the orbital angular momentum operator $\mathbf{L}^2$ and $L_z$ commute with this Hamiltonian because the latter depends only on scalars. As it will turn out, restricting oneself to orbital motion (neglecting spin) $H$, $\mathbf{L}^2$ and $L_z$ form a CSCO.

**Problem 1.1 :** Show that the commutator of $L^2$ and $L_z$ with the Hamiltonian ( 1.1 ) vanishes

Therefore we can look for common eigenvecors of $H$, $\mathbf{L}^2$ and $L_z$. In order to do so we shall use an identity connecting $\mathbf{L}^2$ with $\mathbf{P}$ and $\mathbf{R}$.

In classical mechanics the definition of $\mathcal{L}=\mathbf{r}\times\mathbf{p}$ leads to $\mathcal{L}^2=r^2p^2\sin^2\alpha=r^2p^2(1-\cos^2\alpha)=r^2p^2-(\mathbf{r}\cdot\mathbf{p})^2$, where $\alpha$ is the - generally time dependent - angle between $\mathbf{r}$ and $\mathbf{p}$, while $(\mathbf{r}\cdot\mathbf{p})$ is the scalar product of the two vectors. Accordingly in classical mechanics we have :

$$p^2=(\mathbf{r}\cdot\mathbf{p})^2/r^2+\mathcal{L}^2/r^2=p_r^2+\mathcal{L}^2/r^2. \qquad (1.3)$$

In quantum mechanics, on the other hand, there will be a correction term of the order of $\hbar$ as the consequence of the noncommutativity of the components of $\mathbf{R}$ and $\mathbf{P}$, and we obtain for the corresponding operators:

$$\mathbf{L}^2=(\mathbf{R}\times\mathbf{P})^2=\mathbf{R}^2\mathbf{P}^2-(\mathbf{R}\cdot\mathbf{P})^2+i\hbar\mathbf{R}\cdot\mathbf{P} \qquad (1.4)$$

In order to see this, let us take into account that $\mathbf{L}^2 = L_i L_i = (\epsilon_{ijk} X_j P_k)(\epsilon_{iln} X_l P_n)$, where one has to sum for indices appearing twice. Using the identity $\epsilon_{ijk}\epsilon_{iln} = \delta_{jl}\delta_{kn} - \delta_{jn}\delta_{kl}$ we get

$$\begin{aligned} L_i &= X_j P_k X_j P_k - X_j P_k X_k P_j = X_j(X_j P_k - i\hbar\delta_{jk})P_k - X_j(X_k P_k - 3i\hbar)P_j = \\ &= X_j X_j P_k P_k - i\hbar\delta_{jk} X_j P_k - X_j X_k P_j P_k + 3i\hbar X_j P_j = \\ &= X_j X_j P_k P_k + 2i\hbar X_j P_j - X_j(P_j X_k + i\hbar\delta_{jk})P_k = \\ &= X_j X_j P_k P_k - X_j P_j X_k P_k + i\hbar X_j P_j. \end{aligned} \tag{1.5}$$

and this is just the equality ( 1.4 ) in coordinate form. From ( 1.4 ) we obtain the quantum variant of ( 1.3 ):

$$\mathbf{P}^2 = \frac{1}{\mathbf{R}^2}\left[(\mathbf{R}\cdot\mathbf{P})^2 - i\hbar\mathbf{R}\cdot\mathbf{P}\right] + \frac{1}{\mathbf{R}^2}\mathbf{L}^2. \tag{1.6}$$

**Problem 1.2 :** Prove that $-\hbar^2(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) = \left(-i\hbar\frac{1}{r}\frac{\partial}{\partial r}r\right)^2 = \left[\frac{1}{2}(\frac{\mathbf{R}}{R}\mathbf{P} + \mathbf{P}\frac{\mathbf{R}}{R})\right]^2 = P_r^2$.

**Problem 1.3 :** Prove that $P_r$ is selfadjoint by using also coordinate representation.

We present the solution of ( 1.2 ) in coordinate representation:

$$-\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) \tag{1.7}$$

and a natural choice to look for it spherical coordinates. We can separate the solution into a product of a function depending only on $r$, the distance from the center (the origin of the coordinate system) and of a function depending only on the angles assuming:

$$\psi(r,\theta,\varphi) = \mathcal{R}(r)Y_\ell^m(\theta,\phi) = \frac{u(r)}{r}Y_\ell^m(\theta,\phi). \tag{1.8}$$

Here $Y_\ell^m(\theta,\phi)$ are the spherical harmonics, the common square integrable eigenfunctions of $-i\partial_\phi$ and $-\Delta_{\theta\phi}$ :

$$\begin{aligned} -i\partial_\phi Y_\ell^m(\theta,\phi) &= mY_\ell^m(\theta,\phi) \\ \Delta_{\theta\phi}Y_\ell^m(\theta,\phi) &= -\ell(\ell+1)Y_\ell^m(\theta,\phi) \end{aligned} \tag{1.9}$$

The differential operators on the left are - apart from factors of $\hbar$ - the coordinate representations of the angular momentum operators $L_z$ and $L^2$ respectively, $\ell$ is a non-negative integer and $m$ is an integer with the $2\ell+1$ different values obeying $|m| \leq \ell$. Using the radial and the angular part of $\Delta$

$$\Delta = \Delta_r + \frac{1}{r^2}\Delta_{\theta\phi} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Delta_{\theta\phi} \tag{1.10}$$

and substituting ( 1.8 ) into ( 1.7 ) leads to an ordinary differential equation for $\mathcal{R}(r)$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\mathcal{R}(r) + \hbar^2\frac{1}{2m}\frac{\ell(\ell+1)}{r^2}\mathcal{R}(r) + V(r)\mathcal{R}(r) = \varepsilon\mathcal{R}(r)\right. \tag{1.11}$$

which is called the **radial equation**. For $u(r) = r\mathcal{R}(r)$ we get the simpler

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}u(r) + V(r)u(r) = \varepsilon u(r) \tag{1.12}$$

equation also known as the radial equation.

**Problem 1.4 :** Show that $u(r)$ obeys the equation ( 1.12 ) above.

This has the same form for $u(r)$ like a one dimensional energy eigenvalue problem on the positive semi axis, but instead of the true potential energy, we have an effective potential of the form $V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$. The term $\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ is called the coordinate representation of the **centrifugal potential** which is the analogue of the centrifugal (repelling) potential $\mathcal{L}^2/2mr^2$ in classical mechanics.

# 2. The asymptotic behaviour of the solutions

## 2.1. Asymptotics for $r \to \infty$

For $V(\infty) \to 0$, which is the usual case, for $r \to \infty$ we can omit the potential energy term and the centrifugal term in Eq.( 1.12 ) and for large $r$ the unknown function $u(r)$ obeys

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} = \varepsilon u \tag{1.13}$$

Recasting it into the form

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}\varepsilon u = 0 \tag{1.14}$$

and introducing the notation $\frac{2m}{\hbar^2}\varepsilon = k^2$, we recognize a simple equation with solutions $\sin kr$ and $\cos kr$, if $\frac{2m}{\hbar^2}\varepsilon = k^2 > 0$. As these functions are not square integrable on $[0, \infty)$, these are the **scattering** or **unbound states** corresponding to energy eigenvalues $\varepsilon > 0$, describing the physical situation when the energy is large enough (positive) so that the potential $V_{\text{eff}}(r)$ cannot keep the electron bound to the nucleus or the core. The same is true for $\varepsilon = 0$, because the solution is then a linear function, which is not square integrable again.

Square integrable solutions can be obtained only if $\varepsilon < 0$. Then we apply the notation

$$0 < -\frac{2m}{\hbar^2}\varepsilon =: \kappa^2 \tag{1.15}$$

and among the two appropriate solutions of Eq. ( 1.14 ) $e^{\kappa r}$ and $e^{-\kappa r}$, we have to choose the latter one, because now $\kappa > 0$, and therefore only $e^{-\kappa r}$ is square integrable. Then sufficiently far from the center the probability of observing the particle is exponentially decaying.

$$u(r \to \infty) \sim e^{-\kappa r}. \tag{1.16}$$

States represented by such wave functions are called **bound states**.

## 2.2. Asymptotic behaviour close to $r = 0$

We shall assume here that the potential energy $V(r)$ remains finite close to $r = 0$, or even if it diverges, this is slower than $1/r^2$. This latter case covers the Coulomb potential which goes to $\infty$ as $1/r$ close to the origin, i. e. slower than $1/r^2$. Then in the radial equation ( 1.12 ) we can omit the potential beside the dominant centrifugal term, and we can neglect the term $\varepsilon u$, as well. We then obtain the second order equation

$$\frac{d^2u}{dr^2} - \frac{\ell(\ell+1)}{r^2} = 0 \tag{1.17}$$

having the two solutions $r^{\ell+1}$ and $1/r^{\ell}$, where $\ell \geq 0$, as we know.

**Problem 1.5 :** Look for the solutions of Eq. ( 1.17 ) in the form $r^k$.

**Problem 1.6 :** Prove that the function $1/r^{\ell}$, with $\ell \neq 0$, is not square integrable on the $(0, \infty)$ interval.

The solution of the form $1/r^{\ell}$ is not square integrable between 0 and an arbitrary small positive number if $\ell > 0$. But the $\ell = 0$ case cannot be afforded, either because then in the vicinity of 0 we had $\mathcal{R}(r) = \frac{u(r)}{r} \sim \frac{1}{r}$, and applying the kinetic energy term we would obtain $\Delta\frac{1}{r} = -4\pi\delta(\mathbf{r})$ (as it is known from electrostatics: the potential of a point charge density given by $\delta(\mathbf{r})$ is $\frac{1}{4\pi r}$ according to Poisson's equation). Thus the singularity of $\delta(\mathbf{r})$ stemming from the kinetic energy in the eigenvalue equation could be compensated only by the potential energy, if the latter was also similarly singular as $V(r) \sim \delta(\mathbf{r})$. But we stipulated that the singularity of $V(r)$ should be less than that of $1/r^2$, therefore a $\delta$ singularity is not possible. This means finally that the solution $1/r^{\ell}$ cannot be good for any $\ell$ that may occur. In other words, with the prescribed condition for the potential, the function $u(r)$ must be of the form $r^{\ell+1}$ around 0:

$$u(r \to 0) \sim r^{\ell+1}, \tag{1.18}$$

which means that $u(r = 0) = 0$ and it must converge to zero as $r^{\ell+1}$.

The radial part of the wave function behaves as

$$\mathcal{R}(r) = u(r)/r \sim r^{\ell}, \tag{1.19}$$

i.e. it goes to zero if $\ell \neq 0$, and remains finite for $\ell = 0$.

We write down the radial equation that is used for finding the bound states of a central potential with $\kappa$ given by ( 1.15 ):

$$\frac{d^2u}{dr^2} - \frac{\ell(\ell+1)}{r^2}u - \frac{2m}{\hbar^2}V(r)u = -\frac{2m}{\hbar^2}\varepsilon u = \kappa^2 u. \tag{1.20}$$

It is useful to introduce the dimensionless variable

$$\kappa r = \sqrt{-2m\varepsilon/\hbar^2}r =: \varrho \tag{1.21}$$

and then the equation for $u$ - which we use for the determination of bound states, i.e. when $\varepsilon < 0$ - takes the form:

$$\left(\frac{d^2}{d\varrho^2} - \frac{\ell(\ell+1)}{\varrho^2} - \frac{V(\varrho/\kappa)}{|\varepsilon|} - 1\right)u(\varrho) = 0, \tag{1.22}$$

which is to be solved together with the two boundary conditions: $u(\varrho \to 0) \sim \varrho^{\ell+1}$ and $u(\varrho \to \infty) \sim e^{-\varrho}$.

This radial equation is often used in atomic physics, but a solution with simple elementary functions is possible only for a few exceptional forms of the potential energy $V(r)$. In most of the cases one has to rely on numerical methods to obtain the solution. We shall come back later to this point. Before doing that, however we shortly present the solution of ( 1.22 ) for one of the most important cases, the attractive Coulomb potential, when $V(r) \sim -1/r$.

## 2.3. Eigenvalue problem of the attractive Coulomb-potential, bound states

The potential energy of the electron in a the Coulomb field is

$$V(r) = -\frac{\gamma}{r}, \qquad (1.23)$$

where $\gamma > 0$. This is the potential energy of an electron in the Hydrogen (H) atom, with $\gamma = \frac{1}{4\pi\epsilon_0} q_0^2 =: e_0^2$, where $q_0$ denotes the elementary charge measured in Coulombs. In the case of Hydrogen like atoms where the number of protons is $Z$ in the nucleus binding a single electron $\gamma = \frac{1}{4\pi\epsilon_0} Z q_0^2 = Z e_0^2$. The simplest examples are the singly ionized Helium: $\mathrm{He}^+$ ( $Z = 2$ ), doubly ionized Lithium: $\mathrm{Li}^{++}$ ( $Z = 3$ ) etc. As discussed in the previous section the Hamiltonian and therefore the energy eigenvalue equation is spherically symmetric

$$H = \left( \frac{P^2}{2m} - \frac{\gamma}{R} \right) |\psi\rangle = \varepsilon \, |\psi\rangle \, . \qquad (1.24)$$

and therefore it can be solved in coordinate representation by separation in spherical coordinates:

$$\psi(r,\theta,\phi) = \mathcal{R}(r) Y_\ell^m(\theta,\phi) = \frac{u(r)}{r} Y_\ell^m(\theta,\phi). \qquad (1.25)$$

With the notations ( 1.15 ) and $\kappa r = \varrho$ the radial part determining $u(\varrho)$ is now

$$\left( \frac{d^2}{d\varrho^2} - \frac{\ell(\ell+1)}{\varrho^2} + \frac{2m\gamma}{\hbar^2\kappa}\frac{1}{\varrho} - 1 \right) u(\varrho) = 0. \qquad (1.26)$$

Let us introduce another dimensionless constant:

$$\varrho_0 = \frac{2m\gamma}{\hbar^2\kappa} \qquad (1.27)$$

then the equation take the form:

$$\left( \frac{d^2}{d\varrho^2} - \frac{\ell(\ell+1)}{\varrho^2} + \frac{\varrho_0}{\varrho} - 1 \right) u(\varrho) = 0. \qquad (1.28)$$

Based on the asymptotics (boundary conditions) discussed in the previous section it is more or less straightforward to assume a solution of the form

$$u(\varrho) = \varrho^{\ell+1} w(\varrho) e^{-\varrho}. \qquad (1.29)$$

The factor $\varrho^{\ell+1}$ ensures the correct asymptotics around 0, the exponentially decaying factor $e^{-\varrho}$ does the same at infinity, while $w(\varrho)$ is to be found so that the above form of $u(\varrho)$ be the exact solution of ( 1.28 ) everywhere in $[0,\infty)$. Inserting the form of $u$ ( 1.29 ) into ( 1.28 ), performing the differentiations and dividing by $e^{-\varrho}$, we get the following differential equation for $w$ :

$$\varrho \frac{d^2 w}{d\varrho^2} + 2(\ell + 1 - \varrho)\frac{dw}{d\varrho} + (\varrho_0 - 2(\ell+1))w = 0. \qquad (1.30)$$

Besides obeying ( 1.30 ) $w(\varrho)$ must not undo the asymptotic forms ( 1.29 ), therefore $w(\varrho)$ must have a power expansion around 0, otherwise it would destroy the correct behaviour of $u$ around 0, and for large $\varrho$ it has to grow slower than $e^{\varrho}$ to keep the exponential decay in $\infty$.

## 2.4. The confluent hypergeometric function

In order to present the solution in terms of a standard special function, we introduce here the new variable $z=2\varrho$, and obtain from ( 1.30 ) the following equation for $w(z)$:

$$z\frac{d^2w}{dz^2}+[2(\ell+1)-z]\frac{dw}{dz}-(\ell+1-\varrho_0/2)w=0 \qquad (1.31)$$

In the mathematical literature an equation of the form

$$z\frac{d^2w}{dz^2}+(b-z)\frac{dw}{dz}-aw=0 \qquad (1.32)$$

with constant $a$ and $b$ is known as **Kummer's equation**. One of the solutions of this second order equation is called the **confluent hypergeometric function**, defined as

$$F(a,b,z)=1+\frac{a}{b}z+\frac{a(a+1)}{b(b+1)}\frac{z^2}{2!}+\ldots+\frac{(a)_k}{(b)_k}\frac{z^k}{k!}\ldots=\sum_{k=0}^{\infty}\frac{(a)_k}{(b)_k}\frac{z^k}{k!} \qquad (1.33)$$

where

$$(a)_k=a(a+1)(a+2)\ldots(a+k-1),\qquad (a)_0=1 \qquad (1.34)$$

(and similarly for $(b)_k$ ) is the so called **Pochhammer symbol**.

We note that there are other frequently used notations for the confluent hypergeometric function:

$$F(a,b,z)=F_1(a,b,z)=M(a,b,z)\equiv\Phi(a,b,z) \qquad (1.35)$$

**Problem 1.7 :** Prove that $w(z)=F(a,b,z)$ is a solution of ( 1.32 ).

**Problem 1.8 :** Substitute $w=z^{1-b}w_1$ in ( 1.32 ) and prove thereby that another independent solution of this equation can be written as $w_2(z)=z_1^{1-b}F_1(a-b+1,2-b,z)$.

In our case $a=\ell+1-\varrho_0/2$, while $b=2(\ell+1)$ is a positive integer: $b\geq 2$. The latter fact shows that for such $b$, the function $w_2(z)$ is singular around $z=0$, so it cannot be an acceptable solution, as the corresponding $u$ would not obey the boundary condition $u(0)=0$. The solution we have to consider is therefore:

$$w(z)=F(\varrho_0/2-(\ell+1),\;2(\ell+1),\;z) \qquad (1.36)$$

It is obvious that $F(a,b,\,z)$ is either an infinite power series or a finite one, that is a polynomial in the latter case. Looking at ( 1.33 ) we see that this happens if and only if $a$ is zero or a negative integer to be denoted here by $-n_r$, as then all numbers $(a)_k=0$ for $k>n_r$ vanish, and F reduces to a polynomial of degree $n_r$. We show now that in order to satisfy the other boundary condition at infinity $w(z)=F(\varrho_0/2-(\ell+1),\;2(\ell+1),\;z)$ cannot be an infinite series. Suppose to the contrary that it is, then from ( 1.33 ) it is seen that the $k$ -th term is proportional to $z^k/k!$ which is the property of the power expansion of $e^z=e^{2\varrho}$. (A more detailed analysis shows that the precise asymptotic form of F is ( $\Gamma(b)/\Gamma(a)z^{a-b}e^z$. This means that in ( 1.29 ) we would have $u(\varrho)\sim e^{2\varrho}e^{-\varrho}=e^{\varrho}$ for $\varrho\to\infty$, which cannot be the case.

**Comment:** A simple way to demonstrate the exponential behaviour of the infinite series of F is to look at the quotient of the $k+1$ -th and the $k$ -th term of the series with sufficiently large $k\gg\varrho_0,\;\ell$, which is

$$\frac{(a)_{k+1}}{(a)_k}\frac{(b)_k}{(b)_{k+1}}\frac{k!}{(k+1)!}=\frac{a+k}{b+k}\frac{1}{k+1}=\frac{\varrho_0/2-(\ell+1)+k}{2(\ell+1)+k}\frac{1}{k+1}\sim\frac{1}{k+} \quad (1.37)$$

a characteristic of the ratio of the consecutive coefficients of the power series of $e^z$.

So we see that the solutions of ( 1.30 ) obeying the boundary conditions must be polynomials be of the form

$$w(z)=F(-n_r,\ 2(\ell+1),\ z) \quad (1.38)$$

which requires $\ell+1-\varrho_0/2=-n_r$, or

$$\varrho_0=2(n_r+\ell+1). \quad (1.39)$$

Where $n_r$ - the degree of the polynomial $w$ - is called the **radial quantum number**. It is easily seen that this gives the number of zeros (the number of $r$ intercepts) of the radial wave function $u(r)$. We define now the **principal quantum number** by

$$n:=n_r+\ell+1 \quad (1.40)$$

which is a *positive integer*. This is the quantum number which determines the energy eigenvalues. In order to see this we recall the definition of $\varrho_0$ Eq. ( 1.27 ), which is to be equal to $2n$

$$\varrho_0=\frac{2m\gamma}{\hbar^2\kappa}=2n, \qquad \text{yielding} \qquad \kappa_n=\frac{m\gamma}{\hbar^2}\frac{1}{n} \quad (1.41)$$

Then with $\gamma=Ze_0^2$

$$\kappa_n=Z\frac{me_0^2}{\hbar^2}\frac{1}{n}=Z\frac{1}{a_0}\frac{1}{n} \quad (1.42)$$

where the quantity

$$a_0=\frac{\hbar^2}{me_0^2}=\frac{\hbar^2}{mq_0^2}4\pi\epsilon_0 \quad (1.43)$$

is of dimension of length, and we recognize that this is just the **Bohr radius** of the first orbital in Bohr's theory of Hydrogen atom. The energy eigenvalues are obtained from ( 1.15 )

$$\varepsilon_n=-\frac{\hbar^2\kappa_n^2}{2m}=-Z^2\frac{me_0^4}{2\hbar^2}\frac{1}{n^2} \qquad n=1,2\cdots \quad (1.44)$$

or alternatively

$$\varepsilon_n=-Z^2\frac{e_0^2}{2a_0}\frac{1}{n^2} \quad (1.45)$$

Note that in the case of the Hydrogen atom $Z=1$. In the radial part of the eigenfunction ( 1.29 ) the variable $\varrho=\kappa r$ is then written as

$$\varrho=\frac{1}{n}\frac{r}{a_0}Z \quad (1.46)$$

These energy values belonging to the attractive Coulomb-potential are discrete (which is a feature of bound states) and to a very good approximation they give us the primary term structure of the Hydrogen spectrum ( $Z=1$ ), i. e. the Lyman-, Balmer etc. series. The result for the energy eigenvalues in this case coincides with the one of the Bohr model. This does not mean however that the Bohr model is correct. First, the meaning of $n$ is totally different in the quantum mechanical calculation. Second, the number of the corresponding eigenstates, the degeneracy of $E_n$, to be discussed in the next section, does not follow from the Bohr model. Third, for systems with more than one electron the Bohr model is unable to predict the energies of the stationary orbitals, while QM can treat those cases with high precision. We stress once again that in the quantum mechanical treatment the spectrum of the discrete energy eigenvalues resulted from demanding the fulfillment of the boundary conditions.

The function F for which the parameter $a$ is a negative integer is proportional to a so called **generalized Laguerre polynomial**, defined as

$$L_n^{(\alpha)}(z) := \sum_{k=0}^{n} (-1)^k \binom{n+\alpha}{n-k} \frac{z^k}{k!} = \frac{z^{-\alpha} e^z}{n!} \frac{d^n}{dx^n} \left(e^{-z} z^{n+\alpha}\right) \qquad (1.47)$$

The expression after the second equality sign is called a Rodrigues' formula. **Comment:** The particular case $\alpha = 0: \quad L_n^{(0)}(z) \equiv L_n(z)$ is called simply the $n$ -th Laguerre polynomial.

**Problem 1.9 :** Prove the validity of the above Rodrigues' formula for generalized Laguerre polynomials.

**Problem 1.10 :** Pove that $L_n^{(\alpha)}(z) = ((n+\alpha)/n) F(-n,\ \alpha+1,\ z)$.

It can be shown that

$$\int_0^\infty x^\alpha e^{-x} L_n^{(\alpha)}(x) L_m^{(\alpha)}(x) dx = \frac{\Gamma(n+\alpha+1)}{n!} \delta_{nm} \qquad (1.48)$$

which means that the set of functions $L_n^{(\alpha)}(x)$ with fixed $\alpha$ form an orthogonal system with respect to the weight function $x^\alpha e^{-x}$ on the positive real axis. Let us note that in certain books a somewhat different notion of the *associated Laguerre polynomials* is used instead of the *generalized* ones used here.

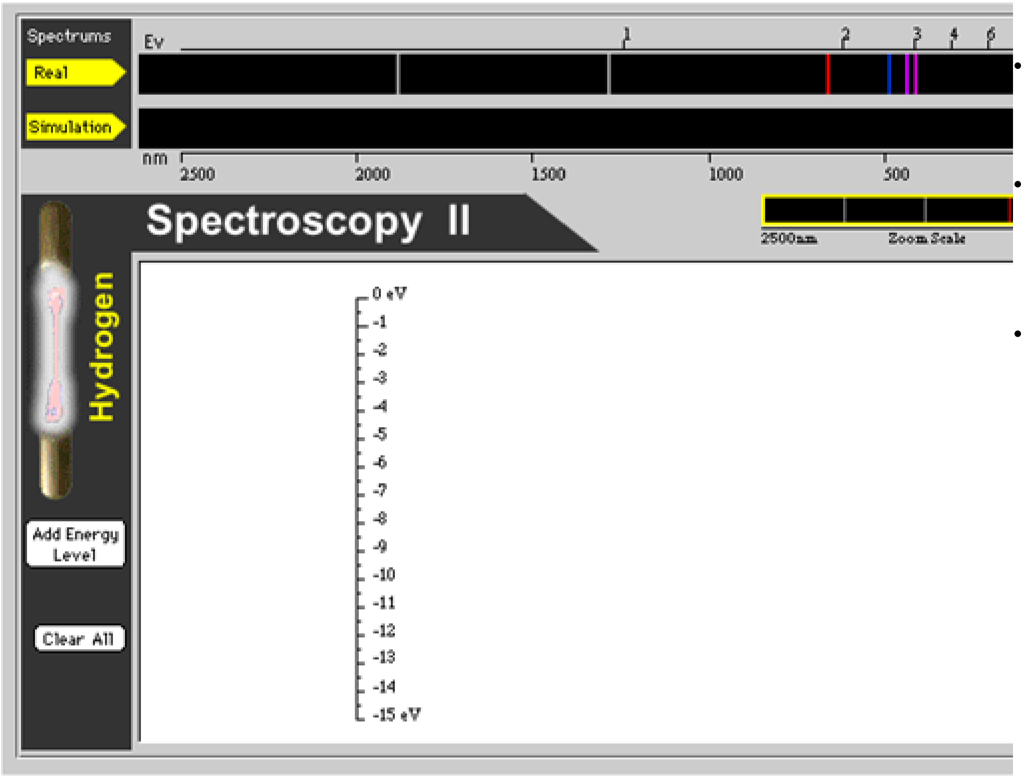
# 3. The primary spectrum of the Hydrogen atom

The result obtained in the previous section yields the primary spectrum of the H atom when $Z = 1$. We shall consider several refinements and corrections forced on us by quantum mechanics in the end of this section to obtain the real spectrum of a H atom.

**Animation:**

We can investigate the origin of spectral lines in several steps with thisn interactive shockwave animation:

- Observing the actual spectrum of



hydrogen gas

- Creating and manipulating energy levels
- Creating transitions between energy levels
- Matching trial spectral lines to those of the actual one

The energy value $\frac{me_0^4}{2\hbar^2}$ equal to $2.2 \times 10^{-18}\,\mathrm{J} = 13.6\,\mathrm{eV}$ is called 1 **Rydberg**.

$$\frac{me_0^4}{2\hbar^2} = 2.2\,\mathrm{aJ} = 13.6\,\mathrm{eV} = 1\,\mathrm{Ry}\;. \tag{1.49}$$

Sometimes one uses so called atomic units where the energy is measured in

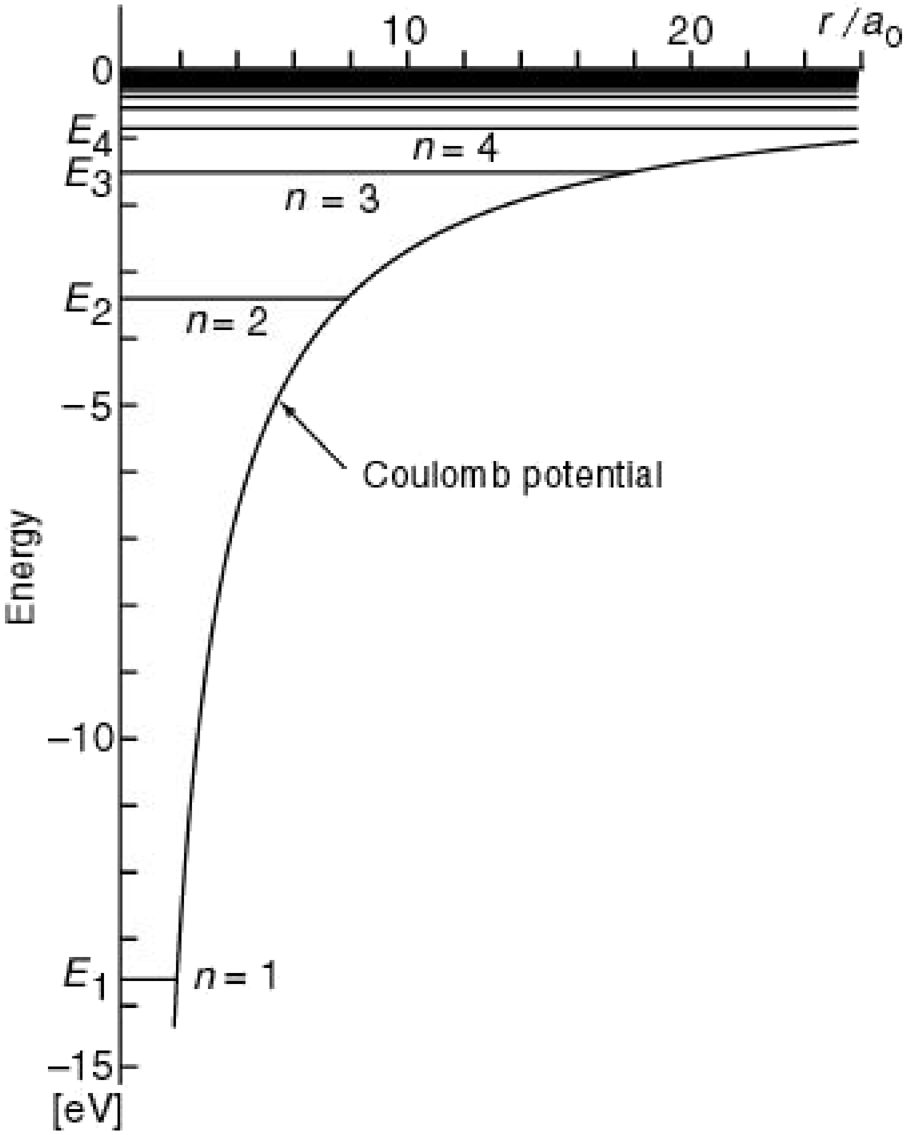
$$\frac{me_0^4}{\hbar^2} = 1\,\mathrm{a.\,u.} \tag{1.50}$$

another name used for the energy atomic unit is the Hartree, i. e. $1\,\mathrm{Ry} = \frac{1}{2}\mathrm{a.\,u} = \frac{1}{2}\,\mathrm{Hartree}$. The energy eigenvalues corresponding to the stationary bound states of the H-atom are

$$\varepsilon_n = -\frac{1}{n^2}\,\mathrm{Ry} \tag{1.51}$$

where $n$ is the principal quantum number. From the results of the previous section we have $n = n_r + \ell + 1$, where $n_r$ is the degree of a polynomial, thus a nonnegative integer. We also know that $\ell$, the orbital angular momentum quantum number is a nonnegative integer $\ell = 0, 1, 2 \dots$. It follows therefore that the possible values of $n$ are the positive integers. The stationary state having the lowest value of energy is the ground state with $n = 1$ and its energy is $-1\,\mathrm{Ry}$, compared to the state where the potential energy of the electron is 0, so that its kinetic energy also vanishes. Therefore the energy to be put in to make the electron free from the proton's attraction is at least $1\,\mathrm{Ry}$, in other words this is the ionization energy of the H atom. Increasing the value of $n$ we obtain the energies of the excited states, which rapidly approach the 0 energy level, i.e. the ionized state.

**Figure 1.1. Energy diagram of the stationary states of the Hydrogen atom. http://www.kutl.kyushu-u.ac.jp/seminar/MicroWorld2_E/2Part3_E/2P32_E/hydrogen_atom_E.htm**



Energy diagram of the stationary states of the Hydrogen atom.

We have to emphasize that the spectrum has a continuous part as well, because to each value $\varepsilon > 0$ there correspond eigenstates of the Hamiltonian ( 1.24 ). These are called scattering or unbound states. They describe a situation when a particle, say an electron with fixed energy is coming from infinity and it is scattered by the potential created by a positive nucleus and then it goes again into infinity. Quantum mechanics yields us the full machinery to calculate the amplitude, as well as the probability of scattering into different directions. The physical situation is described better if instead of stationary scattering states, which cannot be normalized and have infinite extensions, one considers the scattering of a localized wave packet. Such states, however are nonstationary, and the treatment is rather lengthy and only numerical studies are possible. We shall not consider the scattering problem here.

In the previous subsection, where we have determined the eigenvalues of the bound states, we have actually found the eigenvectors, as well. As we have been using the coordinate representation, these have been the coordinate eigenfunctions, which are to be discussed now here. The radial equation in the Coulomb potential ( 1.28 ) has $n$ linearly independent solutions, as for given $n$, according to the definition $n = n_r + \ell + 1$ the values

$$\begin{aligned} n_r &= 0, & \ell &= n-1; \\ n_r &= 1, & \ell &= n-2; \\ &\vdots & &\vdots \\ n_r &= n-1, & \ell &= 0 \end{aligned} \qquad (1.52)$$

all give different polynomials. They are labeled usually by the values of $n = n_r + \ell + 1$ and $\ell$, therefore the radial part of the eigenfunctions $\mathcal{R}_{n\ell}(r) = u_{n\ell}(\kappa r)/r$ take the form

$$\mathcal{R}_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n((n+\ell)!)^3}}(2\varrho)^\ell L_{n_r}^{(2\ell+1)}(2\varrho)e^{-\varrho} \qquad (1.53)$$

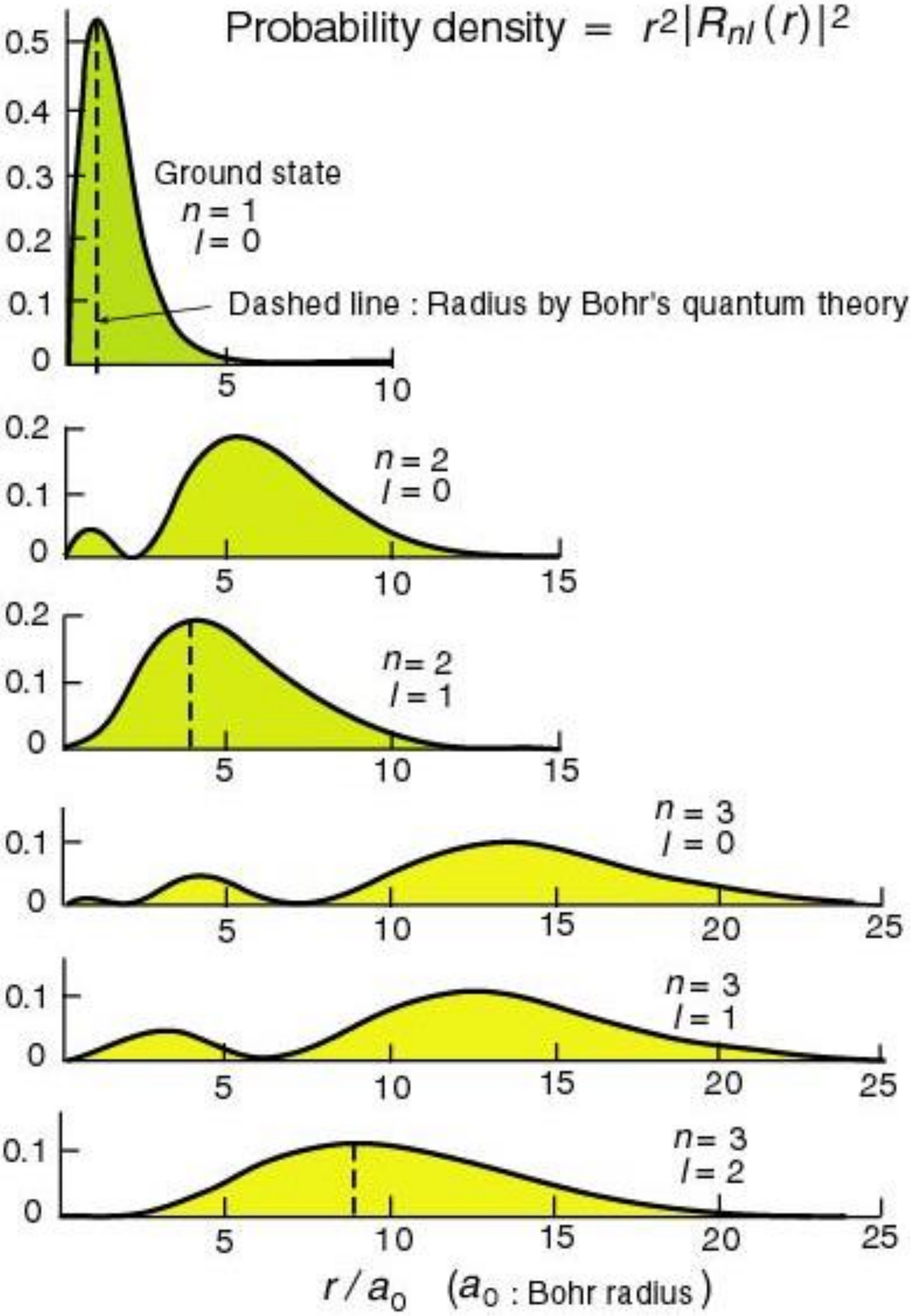
$$\mathcal{R}_{n\ell}(r) = \frac{1}{(2\ell+1)!}\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n+\ell)!}{2n(n-\ell-1)!}}(2\varrho)^\ell F(-n+\ell+1, 2\ell+2; 2\varrho)e^{-} \qquad (1.54)$$

where we have taken into consideration the previous results, among others the dimensionless radial variable

$$\varrho = \frac{r}{na_0} \qquad (1.55)$$

(in certain books $\frac{r}{na_0}$ is denoted by $\varrho/2$) this and the factor with the square root ensures proper normalization on the positive real axis. The function $\mathcal{R}_{n\ell}(r)$ is a product of a polynomial of $\frac{2r}{na_0}$ of degree $n_r + \ell = n - 1$ and of the function $e^{-\frac{r}{na_0}}$.

**Figure 1.2. The figures show the position probability densities of the electron-nucleus densties in the states ( $r^2|\mathcal{R}_{n\ell}(r)|^2$ ). http://www.kutl.kyushu-u.ac.jp/seminar/MicroWorld2_E/2Part3_E/2P32_E/hydrogen_atom_E.htm**



The figures show the position probability densities of the electron-nucleus densties in the states.

Including the angular part the form of the eigenfunctions is

$$\psi_{n\ell m}(r,\theta,\varphi) = \mathcal{R}_{n\ell}(r) Y_\ell^m(\theta,\varphi). \quad (1.56)$$

We see that whereas the energy depends only on $n$, the wave functions are determined by all three quantum numbers $n, \ell, m$. As we have seen, for a given $n$ we have the possible values of $\ell$ are $n-1, n-2, \ldots, 0$, while the number of the possible spherical harmonics for a given $\ell$ is $2\ell+1$ determined by $m = \ell, \ell-1, \ldots, -\ell$. Therefore the total number of independent eigenfunctions is $n^2$, as it follows from the summation

$$\sum_{\ell=0}^{n-1}(2\ell+1) = n^2. \tag{1.57}$$

According to this result the energy eigenvalues $\varepsilon_n$ corresponding to a given $n$, are $n^2$ times degenerate. In reality, however, we know that the electron has an additional internal degree of freedom, its intrinsic angular momentum or **spin**, given by the quantum number $j =: s = 1/2$. (We follow the custom that in case of the spin, instead of $j$ we use $s$ ). The corresponding magnetic quantum number $m_s$ can take two different values $\pm 1/2$, which means that - say - in the $z$ direction (actually in any chosen direction) the electrons intrinsic angular momentum can be measured to have only the values $\pm\hbar/2$. Therefore the degeneracy in the Coulomb field is actually

$$g_n = 2n^2. \tag{1.58}$$

The independence of $\varepsilon_n$ from $\ell$ is a specific feature of the Coulomb potential, in other spherically symmetric force fields one has $\ell$ dependent energy eigenvalues $\varepsilon_{n\ell}$. The factor 2 in ( 1.58 ) comes from the fact that neither ( 1.1 ) nor specifically ( 1.24 ) did depend on spin. This will be changed in the relativistic approach.

Here the states with different $n$, $\ell$, or $m$, as well as with different $m_s$ are not only linearly independent but also orthogonal, as they belong to different eigenvalues of the self-adjoint operators $H$, $L^2$, $L_z$, $S_z$. Using the Dirac notation and labeling the eigenstates with the corresponding quantum numbers, we have

$$\begin{aligned} H\,|n,\ell,m,m_s\rangle &= \varepsilon_n\,|n,\ell,m,m_s\rangle \\ L^2\,|n,\ell,m,m_s\rangle &= \hbar^2\ell(\ell+1)\,|n,\ell,m,m_s\rangle \\ L_z\,|n,\ell,m,m_s\rangle &= m\,|n,\ell,m,m_s\rangle \\ S_z\,|n,\ell,m,m_s\rangle &= \hbar m_s\,|n,\ell,m,m_s\rangle \end{aligned} \tag{1.59}$$

with

$$\langle n',\ell',m',m_s'\,|n,\ell,m,m_s\rangle = \delta_{n'n}\delta_{\ell'\ell}\delta_{m'm}\delta_{m_s'm_s} \tag{1.60}$$

This characterization is possible because $H,\ L^2,\ L_z,\ S_z$ form a complete set ot commuting operators (CSCO) in the subspace of the bound states with negative $\varepsilon_n$. This is the good place to emphasize that the vectors $|n,\ell,m,m_s\rangle$ are orthogonal, but do not form a complete system, as $H$ has also a continuous spectrum with positive eigenvalues $\varepsilon > 0$. Stated in another way: there exist square integrable functions of $x, y, z$ or alternatively of $r, \theta, \varphi$, which cannot be expanded in terms of the infinite set given by ( 1.56 ).

We can express the ground state energy of the Coulomb potential, $-e_0^2/r$ as

$$\varepsilon_n = -\frac{me_0^4}{2\hbar^2} = -\frac{mc^2}{2}\alpha^2\frac{1}{n^2}, \tag{1.61}$$

where $mc^2$ is the rest energy of the electron and

$$\alpha = \frac{e_0^2}{\hbar c} = \frac{1}{4\pi\epsilon_0}\frac{q_0^2}{\hbar c} = \frac{1}{137.04} = 7.297\times 10^{-3} \tag{1.62}$$

(here $q_0$ is the charge of the electron in SI units (Coulomb) a dimensionless constants introduced by A. Sommerfeld and which is called the **fine structure constant**. The origin of this name comes from the more refined relativistic theory of the H atom, where the corrections are determined by the value of $\alpha$. We shall come to this point below.

**Further reading:** Interesting speculations on the value of $\alpha$ can be found at http://en.wikipedia.org/wiki/Fine-structure_constant.

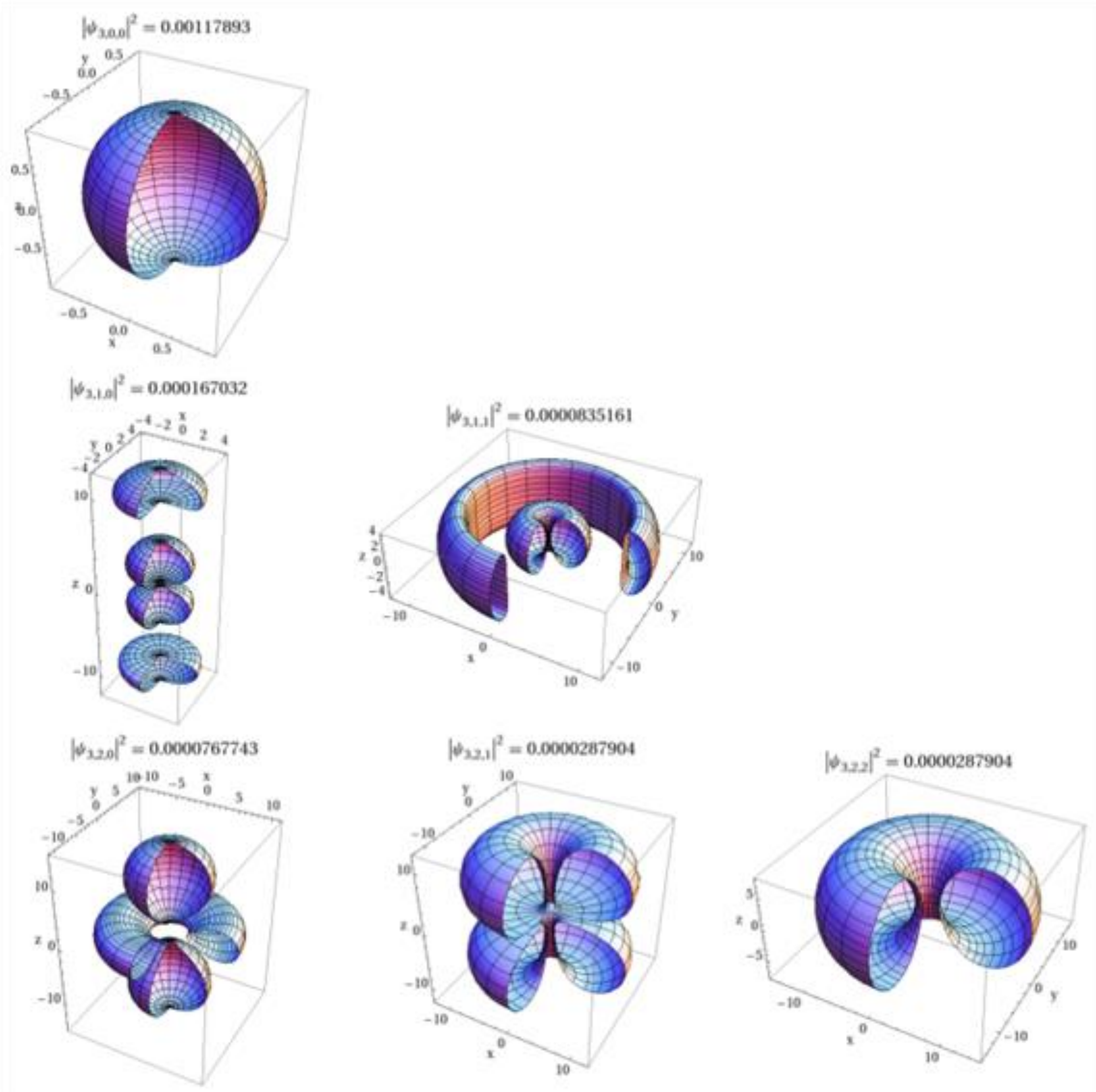
The determination of the energy spectrum and the eigenfunctions as we did it above is originally due to Erwin Schrödinger in 1926. Let us note that in the same year but a few months earlier Wolfgang Pauli did also obtain the energy eigenvalues with a purely algebraic method.

**Further reading:** The explicit forms of the eigenfunctions can be found in several books, or at the url: http://panda.unm.edu/courses/finley/P262/Hydrogen/WaveFcns.html.

We give here only the normalized wave function of the ground state:

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}. \tag{1.63}$$

**Figure 1.3. Constant surfaces of the position probability densities of the electron in the $n = 3$ stationary states of the Hydrogen**



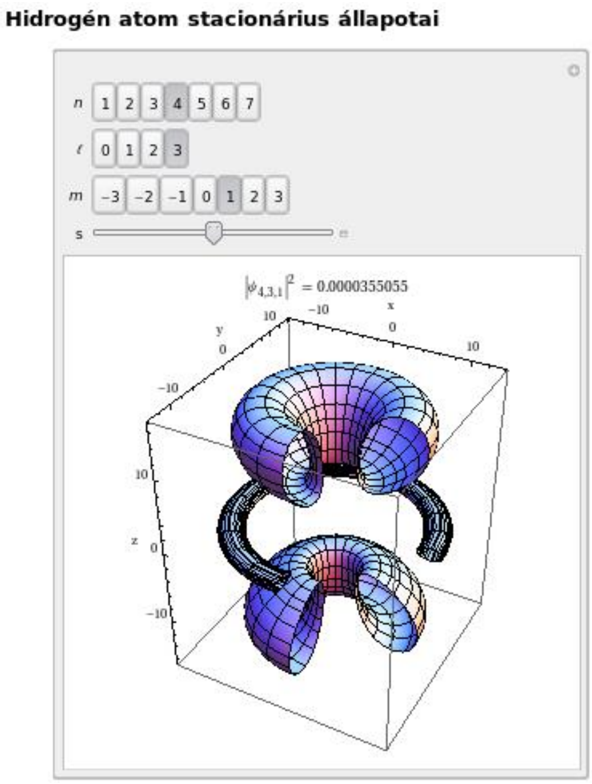
Constant surfaces of the position probability densities of the electron in the n=3 stationary states of the Hydrogen

This is a spherically symmetric state not depending on the angular variables $\theta, \phi$. The set of states $\psi_{n\ell m}$ corresponding to a given pair $n, \ell$ with all the possible $m$ -s are called **shells**, while the wave functions corresponding to the different values of the orbital angular momentum quantum number values are called **orbitals** and are denoted with letters for historical reasons:

| $\ell$ | 0 | 1 | 2 | 3 | 4 | |
|---|---|---|---|---|---|---|
| orbital | $s$ | $p$ | $d$ | $f$ | $g$ | (1.64) |

The orbitals are usually given by the value of the principal quantum number plus the letter according to the convention given in the table above. The ground state is denoted therefore as $1s$, the first excited states the $2s$, and the $2p$ orbitals, then follow the $3s, 3p, 3d$ orbitals etc. As we have noted in the simple Coulomb-potential the energy depends only on $n$, states with given $n$ but different $\ell$ -s have the same energy.

**Animation:**



**Hidrogén atom stacionárius állapotai**

n: 4

ℓ: 3

m: 1

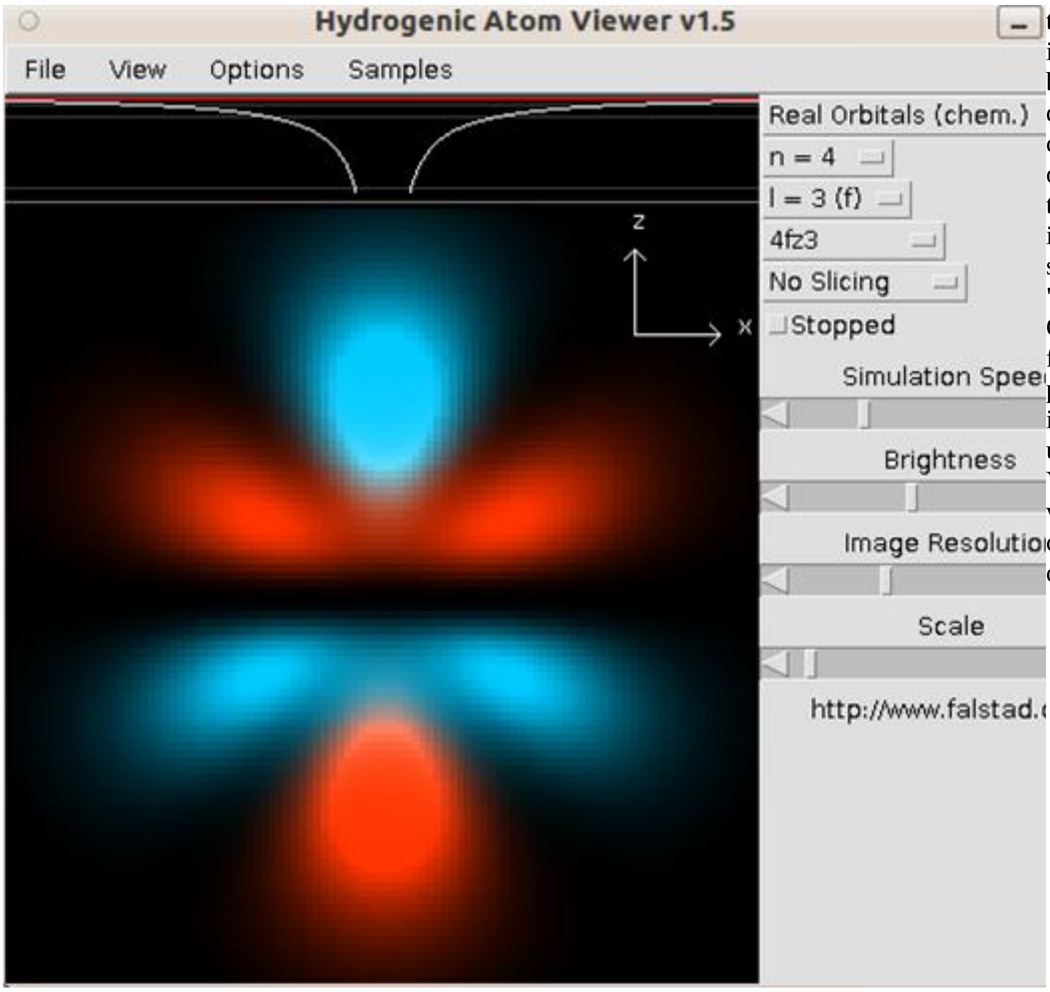
$|\psi_{4,3,1}|^2 = 0.0000355055$

The figure shows the constant surfaces of the position probability densities of the electron in certain stationary states of the Hydrogen atom. The state can be chosen by setting the quantum numbers *n*, *l*, *m*.

Sometimes an additional letter combination is added to the sign of the orbital especially if a real linear combination of states with given $\ell$ but different $m$ -s are used, which refer to the symmetry of the states with respect to rotations about specific axes in space. With respect of this directional structure of the different orbitals to visualizing web pages:

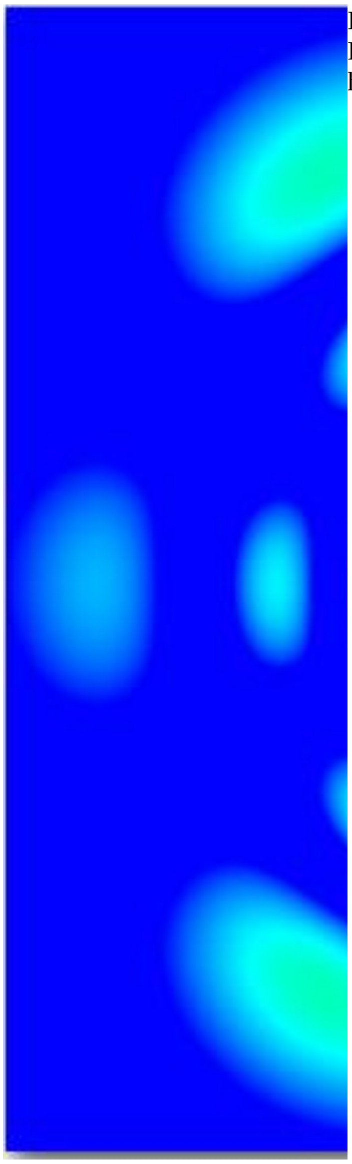
**Animation:**

This java applet displays the wave functions (orbitals) of the hydrogen atom (actually the hydrogenic atom) in 3-D. Select the wavefunction using the popup menus at the upper right. Click and drag the mouse to rotate the view. This applet displays real orbitals (as typically used in chemistry) by default; to display complex orbitals (as typically used in physics) select "Complex Orbitals" from the popup menu in the top upper right. You can also view combinations of orbitals.



Real Orbitals (chem.)
n = 4
l = 3 (f)
4fz3
No Slicing
☐ Stopped

**Further reading:**



Here you find a presentation on the different possibilities of visualizing the Hydrogen atom. http://www.hydrogenlab.de/elektronium/HTML/einleitung_hauptseite_uk.html

**Further reading:** Visit the Grand Orbital Table: http://www.orbitals.com/orb/orbtable.htm, where all atomic orbitals till $n=10$ are presented.

Another terminology calls the states with different principal quantum numbers as shells and coins a capital letter according to the convention:

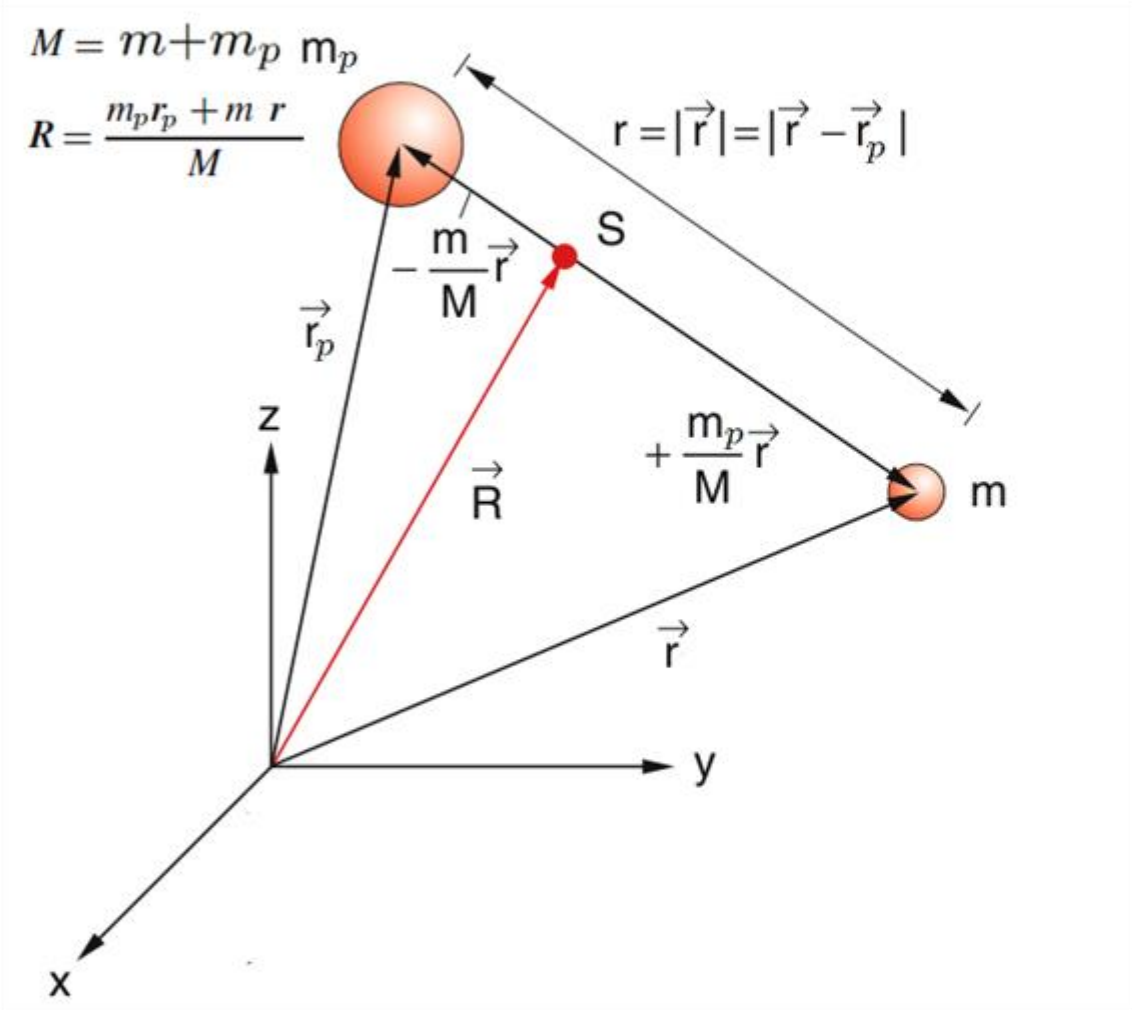
$$\begin{array}{ccccc} n & 1 & 2 & 3 & 4 \\ \text{Shell} & K & L & M & N. \end{array} \qquad (1.65)$$

# 4. Corrections to the primary spectrum of the H atom

It must be noticed that the model of an electron moving in the Coulomb potential as given by ( 1.24 ) is a very good, but still approximate description of the real Hydrogen atom. The energy spectrum derived from the Coulomb potential is the primary structure of the H atom spectrum. In reality there are other interactions not contained in ( 1.24 ), and therefore the real spectrum is different from the simple result above. Not going into the details here, we just shortly enumerate the corrections. Later on we will come to a more thorough explanation.

**1. Finite proton mass.** The H-atom is a two-body problem, as the proton mass is not infinite. One can simply show that like in classical mechanics the center of mass motion and the relative motion of the particles can be separated. The results derived above remain valid, the only difference is that wherever we had the mass of the electron we have to replace it with the reduced mass $m_r = \frac{m m_p}{m+m_p}$ where $m_p$ is the mass of the proton. As $m_p$ is much larger than the mass of the electron (1837 times) this causes a very little change in the results obtained.

### Figure 1.4. Introduction of the center of mass, and relative coordinates



Introduction of the center of mass, and relative coordinates

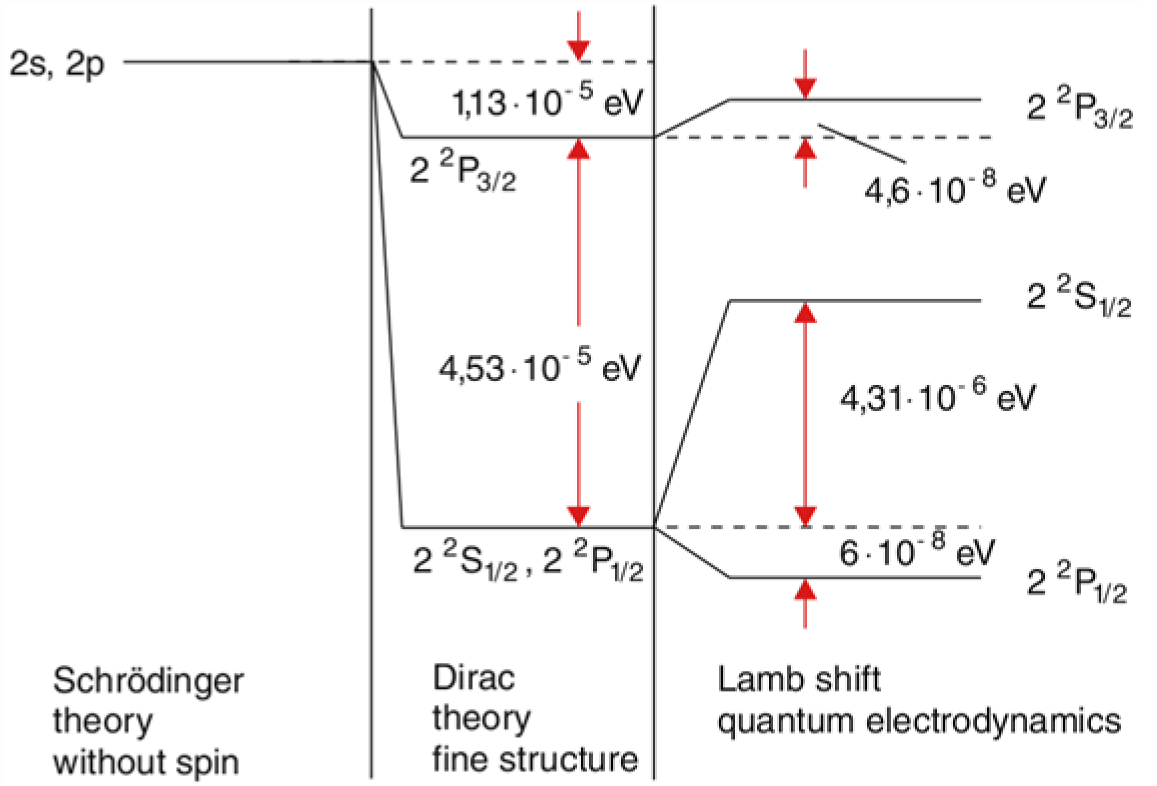
**2. Relativistic corrections.** These corrections are $\alpha^2 \approx 0.53 \times 10^{-4}$ times smaller than the typical $1\,\mathrm{Ry}$ energies of the primary spectrum. They, however, resolve the degeneracy in part, resulting in a splitting of the primary levels, which appear in a refined spectroscopic resolution. This is the **fine structure**. In the relativistic case the Hamiltonian is different from the one given by ( 1.24 ) and it becomes spin dependent and a so called spin-orbit interaction energy appears. Then the Hamiltonian and the components of the operators $\mathbf{L}$ (orbital angular momentum) and $\mathbf{S}$ the spin angular momentum do not commute separately, the latter are not constants of motion. In this case the conserved quantity is the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, which still commutes with $H$. The operator $\mathbf{J}^2$ has eigenvalues $\hbar^2 j(j+1)$ where the quantum number $j$ can be shown to take the values either $j = l + 1/2$ or $j = l - 1/2$, the latter only if $l \neq 0$. The corresponding state is denoted by $nl_j$, where $l$ is to be replaced by one of the letters $s, p, d, f$ etc. according to the numbers $l = 0, 1, 2$ shown in the table 1.64 . The spin orbit interaction causes an energy difference e.g. between the states $p_{1/2}$ and $p_{3/2}$ because here the energy is $j$ dependent. This difference between levels $2p_{3/2}$ and $2p_{1/2}$ corresponds to a frequency about 10.9 GHz. The theoretical explanation of the fine structure giving the experimental value is the great merit of P. Dirac, who constructed the correct relativistic description of the electron which also gives account of the electron spin from first principles. We come about more details later. Let us note that the first attempt to explain theoretically the fine structure of Hydrogen is due to A.

Sommerfeld. His explanation gave the correct experimental result of the splittings, but with an argument that turned out to be erroneous later.

**3. Lamb shift.** This effect got its name from W. E. Lamb who first measured it in 1947. This is a **quantum-electrodynamical** effect explained first by H. Bethe in the same year. The shift appears as the consequence of the quantum properties of the "electromagnetic vacuum" which is always present, surrounding the atom. The energies of the states $2s_{1/2}$ and $2p_{1/2}$ become a little bit different, in spite of having the same quantum number of $j = 1/2$, and therefore , according to Dirac's theory they should be of equal energy. The order of magnitude of the Lamb shift is $\alpha^3 |\ln \alpha| \approx 1.9 \times 10^{-6}$ times smaller than the differences in the primary spectrum, in the case of the states mentioned this is 1.057 GHz.

**4. Hyperfine structure.** This is caused by the magnetic interaction between the magnetic moments coupled to the spins of both the electrons and the proton. For states with $n > 1$ the hyperfine splitting is about $10^{-3}$ times smaller than the fine structure. The hyperfine interaction splits the $n = 1$ ground state, as well, where its value is 1420 MHz, much larger than for an excited states.

## Figure 1.5. The order of magnitude of the corrections



The order of magnitude of the corrections

**Problem 1.11 :** Explain qualitatively why is the hyperfine interaction larger for the ground state than for excited states? Why is this splitting twofold? Make a rough estimate of the energy of the splitting of the ground state by using the classical interaction energy of two magnetic moments. The magnetic moment of an electron is twice the Bohr magneton, and that of the proton is smaller by $5.56 \times$ electron/proton mass ratio.

# Chapter 2. Perturbation theory and applications in atomic physics

**Goals:** As we have to remember, the determination of the eigenvalues of the Hamiltonian in a quantum mechanical problem is of fundamental importance. In most of the cases this is not possible exactly with analytic methods, but approximate analytic procedures may work. One of them is perturbation theory to be introduced in this chapter. In order to understand the material one is asumed to know the most important facts about operators, eigenfunction expansions, and the significance of concept of degeneracy from quantum mechanics. **Prerequisites:** Linear operators; eigenfunction expansion; concept of degeneracy.

## 1. Introduction

In most of the cases the exact solution of the eigenvalue problem of a Hamiltonian is not possible, except for a few cases like the harmonic oscillator or the Coulomb potential. Then one has to rely on either numerical methods, or very often on *approximate* analytic procedures, that give more insight in the nature of the solutions.

One of the most important approximation methods is called perturbation theory, and we outline it here. More precisely in this chapter we restrict ourselves to the **stationary perturbation theory**, in contrast to time dependent perturbations, which we shall consider later.

The method is applicable in the case when the Hamiltonian of the system in question is of the form:

$$H = H_0 + W \qquad (2.1)$$

where we assume that the eigenvalues and the eigenvectors of $H_0$ are known while, $W$ is a *small* correction term called a perturbation to $H_0$. Our task is to find the approximate eigenvalues and eigenvectors of $H$. We write the eigenvalue equation for $H_0$ as

$$H_0|\varphi_p^i\rangle = E_p|\varphi_p^i\rangle \qquad (2.2)$$

where $p$ labels the different eigenvalues and $i$ is a degeneration index so that the set of all $|\varphi_p^i\rangle$ -s constitute complete orthonormal system with the properties:

$$\langle\varphi_{p'}^{i'}|\varphi_p^i\rangle = \delta_{pp'}\delta_{ii'}; \qquad \sum_{ip}|\varphi_p^i\rangle\langle\varphi_p^i| = 1 \qquad (2.3)$$

Equation ( 2.2 ) is called the unperturbed problem.

We assume now that the perturbation is proportional to a real number $\lambda$, and has the form of $W = \lambda\hat{W}$. $\lambda$ is called the perturbation parameter, which - in many of the cases - can be tuned from outside. We look for the spectrum of $H(\lambda) = H_0 + \lambda\hat{W}$, i.e. the solutions of the equation

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle, \qquad (2.4)$$

where we assume, that for $\lambda \rightarrow 0$ the eigenvalue $E(\lambda)$ goes **continuously** to one of the $E_p$ eigenvalues of $H_0$ and we assume that this $E_p$ belongs to the **discrete** part of the spectrum of $H_0$. Note however, that the method used here allows $H_0$ to have a continuous spectrum, as well, but we consider here only the changes in the discrete part as a consequence of the presence of $\lambda\hat{W}$. The perturbation of the continuous part of the spectrum of $H_0$, will not be treated, because it requires a procedure different from the one presented here. The requirement of the continuity with respect to $\lambda$ is not always satisfied, which raises difficulties again, and then the method to be presented here is not applicable either. So let us keep the continuity condition, which means that $E(\lambda)$ and $|\psi(\lambda)\rangle$ can be expanded in a **perturbation series** according to the powers of $\lambda$ :

$$\begin{aligned} E(\lambda) &= \varepsilon_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2 + \ldots \\ |\psi(\lambda)\rangle &= |0\rangle + \lambda\,|1\rangle + \lambda^2\,|2\rangle + \ldots \end{aligned} \qquad (2.5)$$

Our task will be the determination of the corrections $\varepsilon_q$ and $|q\rangle$, and this will be done by expressing them with the unperturbed eigenvalues and eigenvectors. We substitute these expansions into the eigenvalue equation of $H$ and we get:

$$(H_0 + \lambda\hat{W})\left[\sum_{q=0}^{\infty}\lambda^q|q\rangle\right] = \left[\sum_{q'=0}^{\infty}\lambda^{q'}\varepsilon_{q'}\right]\left[\sum_{q=0}^{\infty}\lambda^q|q\rangle\right] \qquad (2.6)$$

Consider the above equality for the different powers of $\lambda$ and rearrange the terms. Then we obtain according

$$H_0|0\rangle - \varepsilon_0|0\rangle = 0 \qquad (2.7)$$

$$(H_0 - \varepsilon_0)|1\rangle + (\hat{W} - \varepsilon_1)|0\rangle = 0 \qquad (2.8)$$

$$(H_0 - \varepsilon_0)|2\rangle + (\hat{W} - \varepsilon_1)|1\rangle - \varepsilon_2|0\rangle = 0 \qquad (2.9)$$

$$\begin{aligned} &\vdots \\ (H_0 - \varepsilon_0)|q\rangle + (\hat{W} - \varepsilon_1)|q-1\rangle - \varepsilon_q|0\rangle &= 0 \end{aligned} \qquad (2.10)$$

The equation ( 2.4 ) determines $|\psi(\lambda)\rangle$ only up to normalization, and even if we stipulate $\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$ it leaves us a free constant: a complex number of unit modulus $|\psi(\lambda)\rangle$ and $e^{i\gamma}|\psi(\lambda)\rangle$ have the same norm for real $\gamma$. Therefore we may prescribe that the inner product $\langle 0|\psi(\lambda)\rangle$ should be real, i.e. $\mathrm{Im}\langle 0|\psi(\lambda)\rangle = 0$. Now we normalize $|\psi(\lambda)\rangle$, and obtain

$$1 = \langle\psi(\lambda)|\psi(\lambda)\rangle = \langle 0|0\rangle + \lambda(\langle 1|0\rangle + \langle 0|1\rangle) + \lambda^2(\langle 2\,|0\rangle + \langle 1\,|1\rangle + \langle 0\,|2\rangle) + O(\lambda^{3} \qquad (2.11)$$

which should be valid for all $\lambda$.

The other requirement $\mathrm{Im}\langle 0|\psi(\lambda)\rangle = 0$ means that

$$0 = \mathrm{Im}\langle 0|\psi(\lambda)\rangle = \mathrm{Im}\{\langle 0\,|0\rangle + \lambda\langle 0\,|1\rangle + \lambda^2\langle 0|2\rangle + \ldots\} \qquad (2.12)$$

again to be valid for all $\lambda$. From ( 2.11 ) we have

$$\begin{aligned} \langle 0|0\rangle &= 1 \\ \langle 1|0\rangle + \langle 0|1\rangle &= 0 \\ \langle 2|0\rangle + \langle 1|1\rangle + \langle 0|2\rangle &= 0 \end{aligned} \qquad (2.13)$$

The first of this leaves the phase of $|0\rangle$ arbitrary, the second requires $\langle 1|0\rangle + \langle 0|1\rangle = \langle 0|1\rangle + \langle 0|1\rangle^* = 2\mathrm{Re}\langle 0|1\rangle = 0$. From ( 2.12 ), on the other hand, we see that in first order $\mathrm{Im}\langle 0|1\rangle = 0$ as well, therefore we have

$$\langle 0|1\rangle = \langle 1|0\rangle = 0 \qquad (2.14)$$

With a similar argument in the second order we get

$$\langle 2|0\rangle = \langle 0|2\rangle = -\frac{1}{2}\langle 1|1\rangle \tag{2.15}$$

From ( 2.7 ) it follows that $|0\rangle$ is an eigenvector of $H_0$ with an eigenvalue $\varepsilon_0$, therefore $\varepsilon_0$ belongs to the spectrum of $H_0$ We choose now a special $\varepsilon_0$, let it be $E_n^0$, the upper index refers to the unperturbed eigenvalue.

$$\varepsilon_0 = E_n^0 \tag{2.16}$$

There can be several $E(\lambda)$ -s, that goes to $E_n^0$ if $\lambda$ goes to zero, the maximum of this number is the degree of degeneracy of $E_n^0$. To determine the corrections in the sums ( 2.5 ) we distinguish between the degenerate and the nondegenerate cases.

# 2. Perturbation of a nondegenerate energy level

Let $\varepsilon_0 = E_n^0$ be nondegenerate. Then there is only one linearly independent eigenvector belonging to this eigenvalue of $H_0$, which according to ( 2.2 ) must be proportional to $|\varphi_n\rangle$, with a complex factor of unit modulus. Without loss of generality we can choose it to be 1, and accordingly we have

$$|0\rangle = |\varphi_n\rangle \tag{2.17}$$

In what follows we calculate the energy corrections up to second order and the state vector correction up to first order.

## 2.1. First order corrections

The first order energy correction obtained if we project the vector equation ( 2.8 ) on $|\varphi_n\rangle$ :

$$\langle\varphi_n|\,(H_0 - \varepsilon_0)|1\rangle + \langle\varphi_n|\,(\hat{W} - \varepsilon_1)|0\rangle = 0. \tag{2.18}$$

The first term is 0 because $H_0$ is selfadjoint and $H_0|\varphi_n\rangle = \varepsilon_0|\varphi_n\rangle$. From the second term we get

$$\varepsilon_1 = \langle\varphi_n|\,(\hat{W})|\varphi_n\rangle \tag{2.19}$$

Therefore the first order correction is $\Delta^1 E = \lambda\varepsilon_1 = \langle\varphi_n|\,(W)|\varphi_n\rangle$, and the energy eigenvalue changes according to

$$E_n^1(\lambda) = E_n^0 + \langle\varphi_n|\,(W)|\varphi_n\rangle. \tag{2.20}$$

This is an important and simple result, saying that **in the nondegenerate case the first order energy correction is the expectation value of the perturbing operator in the corresponding unperturbed eigenstate of $H_0$**. The one dimensional projection obtained in ( 2.18 ) does not yield obviously all the information contained in ( 2.8 ) because we can project the latter on the invariant subspace of $H_0$ which is orthogonal to the selected $|\varphi_n\rangle$. We do so now, and project ( 2.8 ) on each $|\varphi_p^i\rangle$ (orthogonal to $|\varphi_n\rangle$) which can be degenerate of course (that is why we keep the upper label $i$ now):

$$\left\langle\varphi_p^i\right|(H_0 - \varepsilon_0)|1\rangle + \left\langle\varphi_p^i\right|(\hat{W} - \varepsilon_1)|0\rangle = 0 \qquad |\varphi_p^i\rangle \neq |\varphi_n\rangle. \tag{2.21}$$

In the first term we can use again that $|\varphi_p^i\rangle$ is an eigenvector of the selfadjoint $H_0$, so we obtain $(E_p^0 - \varepsilon_0)\left\langle\varphi_p^i\middle|1\right\rangle$ there, while in the second term product containing $\varepsilon_1$ vanishes, because we have $\varepsilon_1\langle\varphi_p^i|0\rangle = \varepsilon_1\langle\varphi_p^i|\varphi_n\rangle = 0$ as $|\varphi_p^i\rangle$ is orthogonal to $|\varphi_n\rangle$. Rearranging the equation above we get:

$$\left\langle \varphi_p^i \middle| 1 \right\rangle = \frac{1}{E_n^0 - E_p^0} \left\langle \varphi_p^i \middle| \hat{W} \middle| 0 \right\rangle \qquad p \neq n. \tag{2.22}$$

This gives us the projection of $|1\rangle$ on all the eigenvectors of $H_0$ except for $|\varphi_n\rangle$. We know however, that $\langle \varphi_n | 1\rangle = \langle 0 | 1\rangle = 0$ according to ( 2.14 ) so the projection on $|\varphi_n\rangle$ is zero. This means that we know the components of $|1\rangle$ in the complete orthonormal basis $|\varphi_p^i\rangle$, which means that we know $|1\rangle$ itself, as according to $|1\rangle = \sum |\varphi_p^i\rangle\langle\varphi_p^i|1\rangle$ we have:

$$|1\rangle = \sum_{p \neq n} \sum_i \frac{1}{E_n^0 - E_p^0} \left\langle \varphi_p^i \middle| \hat{W} \middle| 0 \right\rangle |\varphi_p^i\rangle \; |\varphi_p^i\rangle \tag{2.23}$$

Multiplying this expression with $\lambda$, and adding it to $|\varphi_n\rangle = |0\rangle$ we get the eigenvector of $H(\lambda)$ up to first order in $\lambda$ :

$$|\psi^1(\lambda)\rangle = |\varphi_n\rangle + \sum_{p \neq n} \sum_i \frac{1}{E_n^0 - E_p^0} |\varphi_p^i\rangle \left\langle \varphi_p^i \middle| W \middle| \varphi_n \right\rangle. \tag{2.24}$$

In the correction term appears the linear combination of all the $|\varphi_p^i\rangle$ -s for which the matrix element $\langle \varphi_p^i | W | \varphi_n\rangle$ does not vanish. One says that the perturbation mixes to $|\varphi_n\rangle$ the other eigenvectors of $H_0$. We also se now, that in order to have a small correction the matrix elements $\langle \varphi_p^i | W | \varphi_n\rangle$ must be small in comparison to the energy difference $E_p^0 - E_n^0$. In other words, the perturbation approximation is the better the farther is the perturbed level from all the other ones.

## 2.2. Second order correction

We start now from ( 2.9 ) and follow the same procedure as in the first order case. We project the equation on $|\varphi_n\rangle$ :

$$\langle \varphi_n | (H_0 - \varepsilon_0) |2\rangle + \langle \varphi_n | (\hat{W} - \varepsilon_1) |1\rangle - \langle \varphi_n | \varepsilon_2 |0\rangle = 0 \tag{2.25}$$

The first term vanishes again because $H_0$ is selfadjoint and $H_0\,|\varphi_n\rangle$ gives $\varepsilon_0|\varphi_n\rangle$. In the second term the $\langle \varphi_n | \varepsilon_1 | 1\rangle = \varepsilon_1 \langle 0|1\rangle = 0$ because of ( 2.14 ) and the third is just $\varepsilon_2$.Accordingly we get $\varepsilon_2 = \langle \varphi_n | \hat{W} | 1\rangle$.

Inserting here $|1\rangle$ from ( 2.23 ) the result is:

$$\varepsilon_2 = \sum_{p \neq n} \sum_i \frac{1}{E_n^0 - E_p^0} \left\langle \varphi_p^i \middle| \hat{W} \middle| \varphi_n \right\rangle \; \left\langle \varphi_n \middle| \hat{W} \middle| \varphi_p^i \right\rangle = \sum_{p \neq n} \sum_i \frac{\left| \left\langle \varphi_p^i \middle| \hat{W} \middle| \varphi_n \right\rangle \right|}{E_n^0 - E_p^0} \tag{2.26}$$

meaning that the energy up to second order is:

$$E_n^2(\lambda) = E_n^0 + \langle \varphi_n | (W) | \varphi_n \rangle + \sum_{p \neq n} \sum_i \frac{\left| \left\langle \varphi_p^i \middle| W \middle| \varphi_n \right\rangle \right|^2}{E_n^0 - E_p^0} \tag{2.27}$$

We see that the sign of the second order correction coincides with the sign of $E_n^0 - E_p^0$, therefore one says that up to second order the levels repel each other the mor the closer they were originally, and the stronger is coupling $\left|\langle\varphi_p^i|\,W|\varphi_n\rangle\right|$. The correction of the eigenvector in the second order is obtained after projecting ( 2.9 ) on the rest of the eigenvectors of $H_0$, i.e. on the $|\varphi_p^i\rangle$ -s with $p \neq n$. We omit the formulae, and will not continue the procedure up to higher orders. An important question is whether the perturbation series is convergent, which would require further mathematical analysis. Avoiding this problem we only state that in many cases in atomic physics the second order energy corrections and the first order eigenstate corrections give results that coincide with the experimental values with great precision.

The results above need the evaluation of infinite sums and even integrals if the spectrum has - as in most of the cases - a continuous part as well. The absolute value of the second order energy correction can be estimated, however, without performing summation. Let us consider in Eq. ( 2.26 ) the denominators, and let $\Delta E = \min|E_n^0 - E_p^0|$, the minimum distance of the level in question, $E_n^0$, from all other energy levels. Let us look at the absolute value of the sum ( 2.26 ) which is certainly less or equal than the sum of the absolute values of the individual members in the sum. If we replace $\left|E_n^0 - E_p^0\right|$ in the denominators in each of the terms by $\Delta E$, we increase them, because all the nominators are nonnegative. Therefore

$$\begin{aligned}|\varepsilon_2| &\le \sum_{p\neq n}\sum_i \frac{\left|\langle\varphi_p^i|\,\hat W|\varphi_n\rangle\right|^2}{|E_n^0-E_p^0|} \le \frac{1}{\Delta E}\sum_{p\neq n}\sum_i \left|\langle\varphi_p^i|\,\hat W|\varphi_n\rangle\right|^2 = \\ &= \tfrac{1}{\Delta E}\sum_{p\neq n}\sum_i \langle\varphi_n|\,\hat W\sum_{p\neq n}\sum_i |\varphi_p^i\rangle\,\langle\varphi_p^i|\,\hat W|\varphi_n\rangle\end{aligned} \quad (2.28)$$

One observes now that $\sum_{p\neq n}\sum_i|\varphi_p^i\rangle\,\langle\varphi_p^i|$ is a projection operator on the subspace orthogonal to the one dimensional line given by the projector $|\varphi_n\rangle\,\langle\varphi_n|$, and as all the vectors $|\varphi_p^i\rangle$ with $p\neq n$ plus the single $|\varphi_n\rangle$ forms a complete orthonormal set, we have the resolution of unity:

$$|\varphi_n\rangle\,\langle\varphi_n| + \sum_{p\neq n}\sum_i|\varphi_p^i\rangle\,\langle\varphi_p^i| = \mathbf{1} \quad (2.29)$$

Therefore

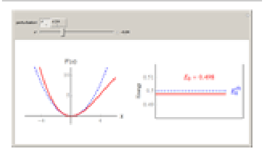
$$|\varepsilon_2| \le \frac{1}{\Delta E}\,\langle\varphi_n|\,\hat W[\mathbf{1} - |\varphi_n\rangle\,\langle\varphi_n|]\hat W|\varphi_n\rangle = \frac{1}{\Delta E}[\langle\varphi_n|\,\hat W^2|\varphi_n\rangle - \langle\varphi_n|\,\hat W|\varphi_n\rangle \quad (2.30)$$

Multiplying both sides with $\lambda^2$, we obtain the following upper bound for the second order correction:

$$|\lambda^2\varepsilon_2| \le \frac{1}{\Delta E}(\Delta W)^2_{\varphi_n} \quad (2.31)$$

where $(\Delta W)^2_{\varphi_n}$ is the variance of the perturbation operator in the unperturbed state $|\varphi_n\rangle$.

**Animation:**



This animation shows perturbation theory applied to the harmonic oscillator. We can study how the ground-state energy of the harmonic oscillator shifts as cubic and quartic perturbations are added to the potential.

# 3. Perturbation of a degenerate level

Let us assume now that - in contrast to the case considered in the previous section - the eigenvalue $E_n^0$ is degenerate, and let the degree of degeneracy be a number $g_n > 1$, but finite. In such a case the equality $\varepsilon_0 = E_n^0$ is not enough to determine the unknown $|0\rangle$ because any linear combination of the $g_n$ vectors $|\varphi_n^i\rangle$, $i = 1, 2 \ldots g_n$ obeys the eigenvalue equation ( 2.7 ) $H_0|0\rangle = \varepsilon_0|0\rangle$, and we know only that $|0\rangle$ is an element of this subspace, but it is unknown a-priori, how to get it from an arbitrarily chosen set of basis vectors in this subspace. In other words we have to determine the proper zeroth order approximation of the eigenvectors giving the limits of the possible $|\varphi(\lambda)\rangle$-s for $\lambda \to 0$. To this end we project again ( 2.8 ) to the now $g_n$ dimensional subspace corresponding to the eigenvalue $E_n^0$, as we did it in the nondegenerate case in ( 2.18 ), where $g_n$ was equal to 1.For the same reason as in ( 2.18 ) the projection of the first term vanishes and get the eigenvalue equation

$$\hat{W}^{(n)} \left|0\right\rangle = \varepsilon_1 \left|0\right\rangle \tag{2.32}$$

where $\hat{W}^{(n)}$ is the operator $\hat{W}$ restricted to the subspace in question. In more detail this means that we multiply ( 2.8 ) on a set of arbitrarily chosen orthonormal set of eigenvectors $|\varphi_n^i\rangle$ of $H_0$ : $i = 1, 2, \ldots, g_n$ belonging to $E_n^0$. The nonvanishing terms yield the $g_n$ equations:

$$\left\langle \varphi_n^i \right| \hat{W} \left|0\right\rangle = \varepsilon_1 \left\langle \varphi_n^i \middle| 0\right\rangle \tag{2.33}$$

The numbers $\langle \varphi_n^i | 0\rangle = c_i$ are the expansion coefficients of the vector $|0\rangle$ we are looking for in the chosen basis $|\varphi_n^i\rangle$. We can write therefore that

$$\left|0\right\rangle = \sum_{i'=1}^{g_n} \left|\varphi_n^{i'}\right\rangle \left\langle \varphi_n^{i'} \middle| 0\right\rangle, \tag{2.34}$$

where the summation remains in the given subspace. Plugging back this into ( 2.33 ) we obtain:

$$\sum_{i'=1}^{g_n} \left\langle \varphi_n^i \right| \hat{W} \left|\varphi_n^{i'}\right\rangle \left\langle \varphi_n^{i'} \middle| 0\right\rangle = \varepsilon_1 \left\langle \varphi_n^i \middle| 0\right\rangle, \tag{2.35}$$

which is the matrix eigenvalue equation of $\hat{W}^{(n)}$ in the $|\varphi_n^i\rangle$ representation (with a given $n$ ):

$$\sum_{i'=1}^{g_n} [\left\langle \varphi_n^i \right| \hat{W} \left|\varphi_n^{i'}\right\rangle - \varepsilon_1 \delta_{ii'}] c_{i'} = 0 \tag{2.36}$$

$c_{i'} = \left\langle \varphi_n^{i'} \middle| 0\right\rangle$. The number of the $\varepsilon_1$ eigenvalues is $g_n$, as we know, and these will be the different first order corrections to the energy eigenvalue $E_n$, while the corresponding solutions for the coefficients yield the proper zeroth order eigenvectors, using them as expansion coefficients in the basis chosen. Let $\varepsilon_1^j$ $(j = 1, 2 \ldots f_n^{(1)})$ all the *different* eigenvalues of $\hat{W}^{(n)}$, then the degenerate $E_n$ splits into a number of $f_n^{(1)}$ different sub-levels

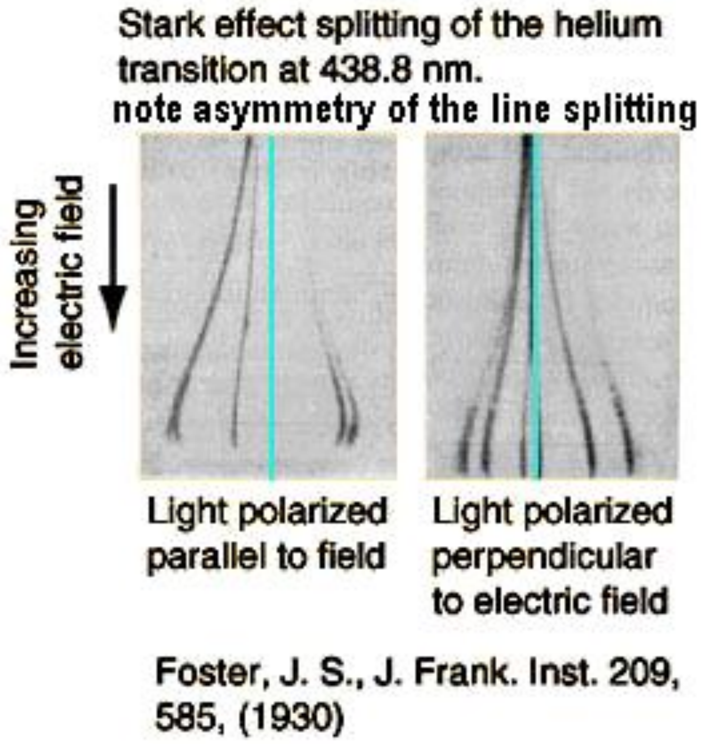
$$E_{n,j}(\lambda) = E_n^0 + \lambda \varepsilon_1^j \qquad j = 1, 2 \ldots f_n^{(1)} \leq g_n \tag{2.37}$$

as a result of the perturbation. It may occur that all the roots of the characteristic equation ( 2.36 ) are different, then $f_n^{(1)} = g_n$, and one says that the perturbation fully resolves the degeneracy. Should this not be the case, and $f_n^{(1)} < g_n$ then the degeneracy is resolved only partially. It may also turn out that $f_n^{(1)} = 1$, i.e. the degeneracy remains there fully, even after the perturbation is switched on. Higher order corrections, which are not to be treated here can further decrease or even remove the degeneracy completely.

# 4. The Stark effect of the H atom

It is known from experimental physics that if one places a gas of atoms into static electric field, a shift and splitting of the lines can be observed, this is the Stark effect. We shall consider its theoretical description in a Coulomb field, as an example of perturbation theory. The results describe very well the observations of the effect for the Hydrogen atom.

**Figure 2.1. Shift and splitting of a spectral line in static electric field in case of Helium gas.**



Shift and splitting of a spectral line in static electric field in case of Helium gas.

A perturbation operator in a homogeneous electric field is: $W = -q\boldsymbol{E}\mathbf{R}$. We choose the direction of $\boldsymbol{E}$ to be the $z$ axis, then $W = -q\mathcal{E}Z$. (where $q < 0$ for an electron) and the perturbation parameter is naturally the strength of the external field $\mathcal{E}$, we can change it externally. If $\mathcal{E}$ goes to zero the perturbation vanishes. As the ground state in the Coulomb potential is nondegenerate, while the excited states are, we treat the two cases separately.

# 5. The ground state

The diagonal matrix elements of the perturbation operator

$$\Delta^1 = \langle n,\ell,m|W|n,\ell,m\rangle = -q\mathbf{E}\langle n,\ell,m|\mathbf{R}|n,\ell,m\rangle\ . \qquad (2.38)$$

do always vanish due to parity reasons.

Let us show now a little bit more than that. The $|n,\ell,m\rangle$ eigenstates of $H_0$ are eigenstates of $L^2$, as well as that of the parity $\Pi$ with the eigenvalue $(-1)^\ell$. As parity anticommutes with the position operator: $\Pi\mathbf{R} = -\mathbf{R}\Pi$, the matrix elements obey $\langle n',\ell',m'|\Pi\mathbf{R}|n,\ell,m\rangle = -\langle n,\ell,m|\mathbf{R}\Pi|n,\ell,m\rangle$. Since $\Pi$ is selfadjoint, therefore on the left hand side $\Pi$ can act on the first factor of the inner product. We obtain

$$(-1)^{\ell'}\langle n',\ell',m'|\mathbf{R}|n,\ell,m\rangle=-(-1)^{\ell}\langle n,\ell,m|\mathbf{R}|n,\ell,m\rangle \tag{2.39}$$

We see that if $\ell-\ell'$ is even, then the two equal sides are the negative of each other, so they must be zero:

$$\text{if }\ \ell-\ell'\ \text{even, then }\ \langle n',\ell',m'|\mathbf{R}|n,\ell,m\rangle=0 \tag{2.40}$$

One can show also that there is a more strict selection rule, the matrix elements of $\mathbf{R}$ do vanish except for $\ell-\ell'=\pm 1$. The same is valid for the momentum operator $\mathbf{P}$, because it is also an odd vector operator.

**Comment:** Another proof uses coordinate representation: The integrand contains three factors: $Y_{\ell}^{m'*}$, one of the coordinates of $r(x,\ y,\ \text{or}\ z)$ and $Y_{\ell}^{m}$. The parity of the spherical harmonics is $(-1)^{\ell}$, and that of the coordinates is -1, therefore the parity of the product is $(-1)^{\ell'+\ell+1}$. If the parity of $\ell$ and $\ell'$ are equal, then $(-1)^{\ell'+\ell+1}=-1$, so the integrand is odd, and the integral vanishes.

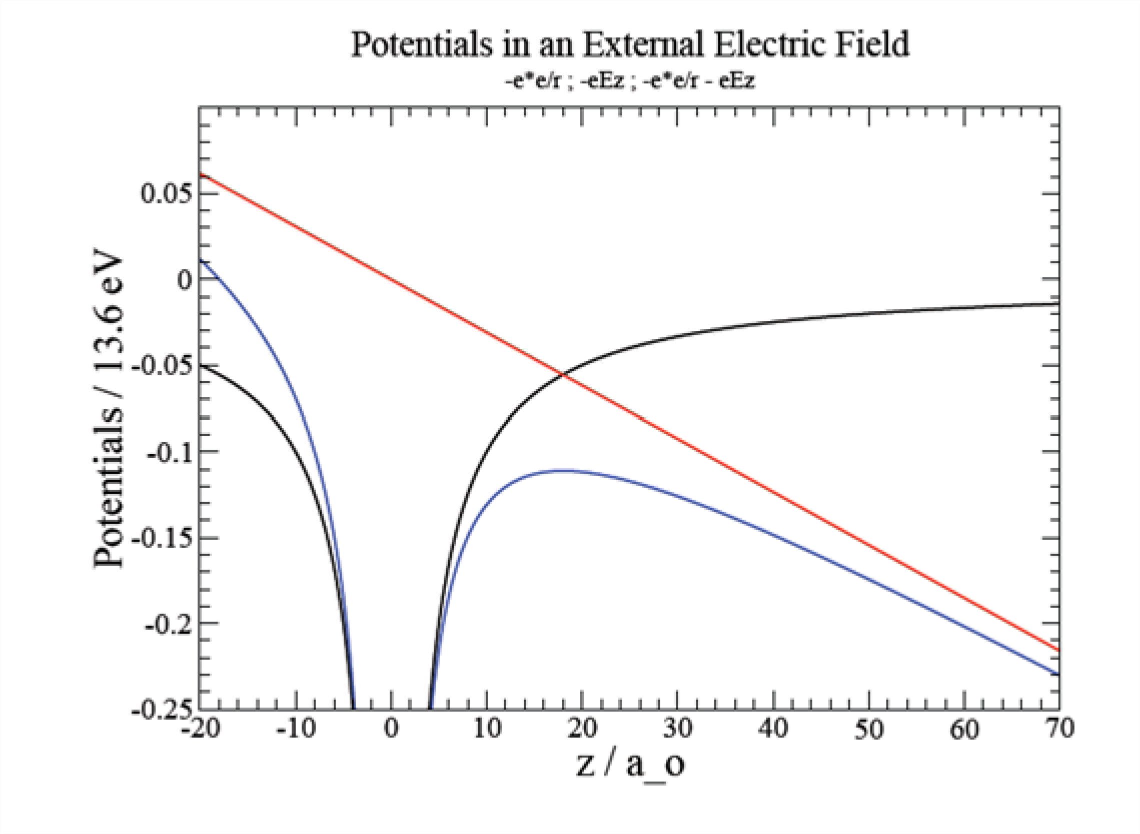
Accordingly the first order correction in the case of $\ell=\ell'=0$ does not appear, meaning that there is no first order correction to the ground state. The first nonvanishing correction is of second order:

$$\Delta^2=q^2\mathcal{E}^2\sum_{n'\neq 1,\ell=1,m=0}\frac{|\langle\varphi_{n',\ell,m}|\,Z\,|\varphi_{100}\rangle|^2}{E_1^0-E_{n'}^0} \tag{2.41}$$

where $E_1^0$ is the energy of the ground state, and the summation over all states with $n>1$ must include the continuous spectrum , as well. So in reality the correction is an infinite sum plus an integral over the states with $E>0$, where the role of the states $\varphi_{n',\ell,m}$ is taken over by the eigenvectors $\varphi_{E',\ell,m}$ belonging to the continuous spectrum of the Coulomb Hamiltonian. Nevertheless it is sufficient to perform the summation and the integration over the states with quantum numbers $\ell=1, m=0$, since the selection rules show the absence of the other terms. As $E_1^0$ is the smallest among the unperturbed eigenvalues the denominator is negative for all $n'$, as well as for the positive eigenvalues of the scattering spectrum, therefore the whole expression ( 2.41 ) is less than zero.

The experiments show, in agreement with our result, that the ground state energy of the H atom is shifted downwards in external static electric field and it goes with the square of the field strength, so the ground state Stark effect for the H atom is quadratic and negative. We note also that in the case of the Coulomb field (H atom) the sum plus integral in ( 2.41 ) can be calculated exactly. Still it is interesting that the perturbation series cannot be convergent in the case considered, because for sufficiently large $|Z|$, depending on the strength of $\mathcal{E}$, the perturbation energy $W=-q\mathcal{E}Z$ will be lower even than the ground state energy in the direction where $-q\mathcal{E}Z$ is negative. This means that the electron can tunnel out through the emerging potential barrier. This tunneling probability is so small, however, that for normal values of $E$ this will happen only in astronomical times.

**Figure 2.2. Potentials in an external electric field**



Potentials in an external electric field

# 6. Polarizability of the H atom in the ground state

With the help of perturbation theory one can also calculate an approximate value for the atomic polarizability, $\beta$ defined by the equality:

$$\mathbf{d} = \beta\varepsilon_0\mathcal{E} \tag{2.42}$$

This assumes that an atom responds linearly to the external electric field, and a dipole moment is induced in it which is proportional to the field strength. The dimension of $\beta$ is that of volume. $\varepsilon_0$ the "permittivity of the vacuum" is included according to the convention in the SI system. As the macroscopic polarization density is proportional to

$$\mathbf{P} = \mathcal{N}\mathbf{d} = \mathcal{N}\beta\varepsilon_0\mathcal{E} = \chi\varepsilon_0\mathcal{E}, \tag{2.43}$$

where $\mathcal{N}$ is the density of the atoms, (their number in unit volume), comparing Eqs. ( 2.42 ) and ( 2.43 ) the dielectric susceptibility defined by ( 2.43 ) is obtained from

$$\chi = \mathcal{N}\beta \tag{2.44}$$

which connects the atomic feature $\beta$ and the phenomenological constant $\chi$ of the gas in question. Accordingly by measuring the susceptibility of a gas of a given density or the relative permeability $\varepsilon_r = 1 + \chi$, one can determine experimentally the atomic polarizability.

In quantum mechanics the atomic dipole moment is identified with the expectation value of the operator $q_0\mathbf{R}$ in the perturbed quantum state $|\psi\rangle$ emerging under the action of the external electric field:

$$\mathbf{d} = \langle\psi|q_0\mathbf{R}|\psi\rangle \tag{2.45}$$

Here $q_0$ is taken to be the charge of the electron (negative), ensuring that the dipole moment points opposite to $\mathbf{R}$, which is the vector pointing from the nucleus to the electron. We restrict ourselves here to the determination of the polarizability in the ground state, where have

$$|\psi\rangle = |\varphi_{1,0,0}\rangle - \sum_{n'\neq 1} \frac{|\varphi_{n',\ell,m}\rangle \langle\varphi_{n',\ell,m}|\, q_0 Z\mathcal{E}\, |\varphi_{100}\rangle}{E_1^0 - E_{n'}^0} \tag{2.46}$$

keeping only the first order terms in $\mathcal{E}$ in $\langle\psi|q_0\mathbf{R}|\psi\rangle$, then

$$\langle\psi|q_0\mathbf{R}|\psi\rangle = \langle\varphi_{100}|q_0\mathbf{R}|\varphi_{100}\rangle - q_0^2\mathcal{E}2Re\sum_{n'\neq 1} \frac{\langle\varphi_{100}|\mathbf{R}\,|\varphi_{n',\ell,m}\rangle\,\langle\varphi_{n',\ell,m}|\,Z\,|\varphi_{100}}{E_1^0 - E_{n'}^0} \tag{2.47}$$

Let us note that in very strong external fields we might obtain nonlinear polarizabilities, in higher orders, which play an important role in atomic physics especially if they are time dependent, but we do not deal with such effects here. In the sum above the first term vanishes, as we have seen above. In the products of the form $\langle\varphi_{100}|q_0\mathbf{R}\,|\varphi_{n',\ell,m}\rangle\,\langle\varphi_{n',\ell,m}|\,Z\,|\varphi_{100}\rangle$ only the third the $\hat{\mathbf{z}}$ vector component remains nonzero, due to the selection rules. The second factor is different from zero only if $m = 0$. On the other hand the selection rules exclude the $X$ and $Y$ components for $m = 0$, they have nonvanishing matrix elements only if $\Delta m = \pm 1$, and in such cases the second factor is zero. This means that in the first factor only the Z component will different from zero. Physically this means that a field of direction $\hat{\mathbf{z}}$, induces a dipole moment in the same direction and not in the others. This is why an atom is electrically isotropic, which is not generally true for molecules for instance, which may posses a static dipole moment even in the absence of external fields. Polarizability is therefore a scalar (and not a tensor) as expected, and its value can be seen from the above expression:

$$d = -2q_0^2\mathcal{E}\sum_{n'\neq 1}\frac{|\langle\varphi_{100}|Z\,|\varphi_{n',\ell,m}\rangle\,|^2}{E_1^0 - E_{n'}^0} = 2q_0^2\mathcal{E}\sum_{n'\neq 1}\frac{|\langle\varphi_{100}|Z\,|\varphi_{n',\ell,m}\rangle\,|^2}{E_{n'}^0 - E_1^0} \tag{2.48}$$

With the same procedure what we did with respect to the estimation of the second order energy correction we can give an upper bound for the polarizability here. As $E_n^0 = \frac{1}{n^2}E_1^0 = -\frac{e_0^2}{2a_0}$ the denominator in each term is greater than $\frac{3}{4}\frac{e_0^2}{2a_0}$. Therefore replacing the denominators in each term by this value and using the equality $q_0^2 = e_0^2 4\pi\varepsilon_0$ (the definition of $e_0$ ) we obtain

$$\begin{aligned} d \ &\leq 2q_0^2\mathcal{E}\frac{8a_0}{3e_0^2}\sum_{n'\neq 1}|\langle\varphi_{100}|Z\,|\varphi_{n',\ell,m}\rangle\,|^2 = \\ &= 4\pi\varepsilon_0 a_0\frac{16}{3}\mathcal{E}\langle\varphi_{100}|Z\,(\mathbf{1} - |\varphi_{100}\rangle\langle\varphi_{100}|)\,Z\,|\varphi_{100}\rangle = \\ &= 4\pi\varepsilon_0 a_0\frac{16}{3}\mathcal{E}\langle\varphi_{100}|Z^2\,|\varphi_{100}\rangle \end{aligned} \tag{2.49}$$

One can easily calculate the expectation value of $Z^2$ in coordinate representation, giving: $|\langle\varphi_{100}|Z^2\,|\varphi_{1,0,0}\rangle\,| = a_0^2$, and we obtain

$$\beta \leq 4\pi a_0^3\frac{16}{3} = 5.3\times 4\pi a_0^3. \tag{2.50}$$

As we noted earlier the sum ( 2.48 ), which can be calculated exactly is identical to ( 2.41 ) gives

$$\beta = 4.5 \times 4\pi a_0^3. \tag{2.51}$$

which shows how good is the upper bound obtained above using perturbation theory.

# 7. Stark effect of the first excited state

The first excited state of the Coulomb potential is the one with principal quantum number 2. The corresponding energy eigenvalue $E_2^0 = -\frac{1}{4}\,\mathrm{Ry}$ is fourfold degenerate, ignoring spin again. The usual set of states are the simultaneous eigenstates of $L^2$ and $L_z$. with eigenvalues corresponding to $\ell = 0, m = 0$, this is the $2s$ state and the three states labeled by $\ell = 1, m = 0, \pm 1$ these are the $2p$ states. According to degenerate perturbation theory we have to find the eigenstates of the perturbing operator $W = -q\mathcal{E}Z$ in the subspace spanned by the four states above. To this end we write down the matrix of the $Z$ operator in the for basis vectors above. The matrix elements vanish for $\ell = \ell'$, we need only the elements between the $s$ and $p$ states, while we also know that only those with $m = m'$ will not vanish. So the only nonvanishing elements are those between the $2s$ state: $\ell = 0, m = 0$, and the $2p$ one with $\ell' = 1, m' = 0$. This can be easily calculated in coordinate representation and one obtains $\langle \varphi_{200} | Z \, | \varphi_{2,1,0} \rangle = 3a_0$. The original $4 \times 4$ matrix thus reduces to the following $2 \times 2$ matrix:

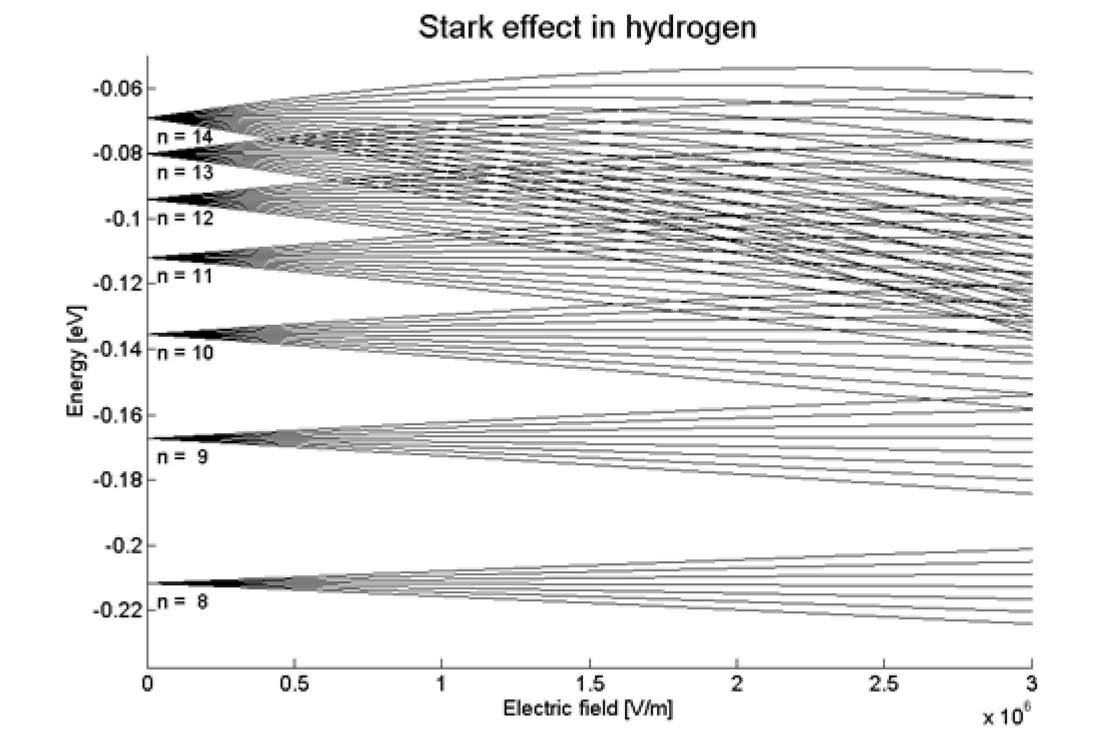
$$\begin{pmatrix} 0 & -3q\mathcal{E}a_0 \\ -3q\mathcal{E}a_0 & 0 \end{pmatrix} \tag{2.52}$$

with eigenvalues $\mp 3q\mathcal{E}a_0$, and the corresponding eigenvectors are:

$$|\mp\rangle = \frac{1}{\sqrt{2}} \left( |\varphi_{2,1,0}\rangle \pm |\varphi_{200}\rangle \right). \tag{2.53}$$

The result is a linear Stark effect that resolves partly the quartic degeneration (without spin).

**Figure 2.3. Stark effect in Hydrogen: The until then degenerate excited energy levels are split up if an exterior electric field is applied. http://en.wikipedia.org/wiki/Image:Stark_splitting.png**



Stark effect in Hydrogen: The until then degenerate excited energy levels are split up if an exterior electric field is applied.

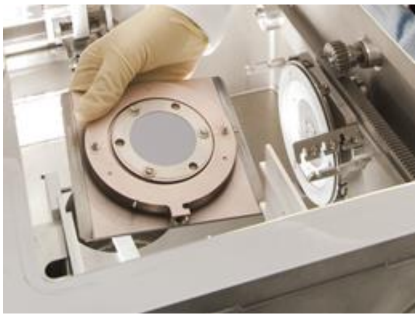
# Chapter 3. Spin and addition of angular momenta

**Goals:** In this chapter we assume that the reader is familiar with the most important points of the algebraic theory of angular momentum in quantum mechanics, which will be shortly repeated in the beginning. Then we recall the experimental evidences of the existence of spin in atomic physics. Then we turn to the problem of addition of two angular momenta, determine the possible quantum numbers $j$, and m of the resulting angular momentum

**Prerequisites:** Algebraic theory of angular momentum.

## 1. Introduction

**Animation:**



This webpage offers a two word explanation of spin. Check out the spin tab with an animated video showing basic concepts of spin. You can also find some additional information on application of spin in technology.

Let us first recall from quantum mechanics that **angular momentum is defined** as a vector operator $\mathbf{J}$ with components obeying the commutation relations

$$[J_i, J_k] = i\hbar\epsilon_{ikl}J_l, \tag{3.1}$$

where $\epsilon_{ikl}$ is the Levi-Civita symbol: the totally antisymmetric three dimensional tensor, where all the indices run over $x, y, z$. It stems from the form of orbital angular momentum $\mathbf{L} = \mathbf{R} \times \mathbf{P}$, using the canonical commutators, or more generally from the three dimensional special rotation group $SO_3$ which is the symmetry group of a sphere excluding mirror transformations. The infinitesimal generators (i. e. the Lie algebra generators) can be chosen as the infinitesimal rotations around the three Cartesian axes, and these are just the components of the angular momentum operators in units of $\hbar$.

As we know from quantum-mechanics from ( 3.1 ) follows that $\mathbf{J}^2$ and any of the components of $\mathbf{J}$ do commute, but the components themselves do not. Therefore it is customary to find the simultaneous eigenvectors of $\mathbf{J}^2$ and one of the components which is chosen traditionally to be the $z$ component $J_z$.

$$\mathbf{J}^2 \left|j,m\right\rangle = \hbar^2 j(j+1) \left|j,m\right\rangle \qquad J_z \left|j,m\right\rangle = \hbar m \left|j,m\right\rangle \tag{3.2}$$

The angular momentum quantum number $j$ can take on only nonnegative values that are half of an integer: $0,\ 1/2,\ 1,\ 3/2, \dots$, while the usual terminology calls the number $j$ as a half-integer, when it is the half of an odd number. For a given $j$ the magnetic quantum number, $m$ runs over the $2j+1$ different values from $-j$ to $j$, so $m$ is also an integer, or half-integer depending on the value of $j$.

**Problem 3.1 :** Recall the algebraic derivation of the above results from quantum mechanics.

### 1.1. Evidences of the existence of spin angular momentum

In the case of orbital motion, we use $\mathbf{L}$ instead of $\mathbf{J}$, and the corresponding quantum number is denoted by $\ell$, which is always an integer $0, 1, \ldots$. It turns out however that the half-integer value also occur in nature, which is always connected with an intrinsic property of particles, and it is called spin. The first evidence came from spectroscopy, where spectral lines in magnetic fields showed a splitting to an **even number of sublevels**. As a charged particle that has angular momentum, always has a magnetic momentum coupled to it, as well, so its energy levels will change in an external magnetic field. In the case of a magnetic field in the direction $z$, the energy proportional to $J_z$ will be different for states with different $m$s. The observed even number of sublevels corresponding to an even value of $2j+1$, meant that in that case $j$ must have been a half-integer, and as it was first proposed by S. Goudsmit and Uhlenbeck in 1925, this was due to the angular momentum of the electron called **spin**, having the value $j = 1/2$. In contrast to orbital angular momentum, this value does not depend on, and cannot be changed by any external action. It is an *intrinsic property* of the electron and as it turned out of many other particles in the microworld. In the case of the spin, one usually writes $s = 1/2$ instead of $j = 1/2$ and speaks of a spin-half particle.

As we know, there was another earlier experimental result in 1921-22, by O. Stern and W. Gerlach, who studied atomic beams of silver, and discovered that the beam is deflected in two different directions in an inhomogeneous magnetic field. It turned out only later that this phenomenon was also the sign of the electron spin. The magnetic moment of the silver atom originates from the spin of its outermost valence electron, and the two beams observed corresponded to the quantum numbers $m_s = 1/2$ and $m_s = -1/2$, where the subscript $s$ alludes to the spin.

One more experimental result was the Einstein-de Haas experiment, where a strong current impulse in a coil around a cylindric piece of iron caused the latter to rotate and gain mechanical angular momentum around its axis. The effect is attributed to the magnetic moment of the electrons in the metal, as this was aligned in the magnetic field, aligning in this way their angular momenta, as well. The cylinder as a whole then began to rotate, as it had to compensate the change of the mechanical momentum of the electrons, due to angular momentum conservation. This idea - proposed in 1910 and realized experimentally in 1914 - did prove qualitatively the reverse of Ampére's hypothesis about the existence of atomic currents in materials as the cause of their magnetism. Here the magnetism proved to create rotational motion. It was much later when the more subtle analysis of the experiment's quantitative analysis proved that the atomic angular momentum playing role in the experiment was due to the spin of the electrons.

The existence of spin and its interaction with magnetic field led W. Pauli to set up a new equation for the electron moving in three-dimensional space, which is written as:

$$i\hbar\frac{\partial\left|\Psi\right\rangle}{\partial t} = \frac{1}{2m}\left[\sigma(\mathbf{P} - q\mathbf{A})\right]^2\left|\Psi\right\rangle + q\Phi\left|\Psi\right\rangle \qquad (3.3)$$

where $\sigma$ is the Pauli spin operators, or as one often says $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ are the three Pauli matrices, connected with the spin angular momentum operator $\mathbf{S}$ as

$$\mathbf{S} = \frac{\hbar}{2}\sigma \qquad (3.4)$$

In ( 3.3 ) $\left|\Psi\right\rangle$ is a two component quantity, where each component is an element of a Hilbert space $\mathfrak{H}$ corresponding to the spinless motion. More precisely this $\left|\Psi\right\rangle$ is an element of the tensorial product $\mathfrak{H} \otimes \mathfrak{H}^2$, where $\mathfrak{H}^2$ is the two dimensional complex space representing the spin degree of freedom. In particular, in an external magnetic field $\mathbf{B}$, the Pauli equation can be written also as

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\left|\psi_+\right\rangle\\ \left|\psi_-\right\rangle\end{pmatrix} = \frac{1}{2m}\left[(\mathbf{P} - q\mathbf{A})\right]^2\begin{pmatrix}\left|\psi_+\right\rangle\\ \left|\psi_-\right\rangle\end{pmatrix} + q\Phi\begin{pmatrix}\left|\psi_+\right\rangle\\ \left|\psi_-\right\rangle\end{pmatrix} - \frac{q}{m}\mathbf{SB}\begin{pmatrix}\left|\psi_+\right\rangle\\ \left|\psi_-\right\rangle\end{pmatrix} \qquad (3.5)$$

where $\begin{pmatrix}\left|\psi_+\right\rangle\\ \left|\psi_-\right\rangle\end{pmatrix}$ is usually the basis in which $\sigma_z$ or $S_z$ is diagonal: $\sigma_z\left|\psi_\pm\right\rangle = \pm\left|\psi_\pm\right\rangle$.

**Problem 3.2 :** Derive ( 3.5 ) from ( 3.3 ).

The most important theoretical step was taken by P. Dirac, who introduced his famous equation for the quantum mechanical description of the relativistic electron, where the concept of spin emerges naturally from first principles, and the Pauli equation follows as an approximation in the case $p/mc \ll 1$ for the electron.

# 2. The problem of addition of angular momenta

It is a frequent problem in atomic physics that a system has angular momentum from different origins. In a simplest case, in a multielectron system all the electrons may have orbital angular momenta, and only the sum of these will be a conserved quantity similarly to a classical mechanical orbital problem. In quantum mechanics this means that in the case of, say, two electrons only the sum of their angular momentum operators $\mathbf{L}_1 + \mathbf{L}_2$ will commute with the total Hamiltonian.

**Problem 3.3 :** Show that for a two body problem in classical mechanics the sum of angular momenta is conserved, i. e. its time derivative is zero.

**Problem 3.4 :** Show that for a two-electron problem (say the He atom) the interaction part of the total Hamiltonian

$$H_{\text{int}} = \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_2|} \tag{3.6}$$

does not commute with the components of $\mathbf{L}_1$, and $\mathbf{L}_2$, but it does so with the sum of the two.

Another more intricate problem is if the constituents of the system possess intrinsic angular momentum i. e. a spin besides their orbital angular momentum. In such cases the Hamiltonian frequently contains a term like $H_{\text{so}} = \xi \mathbf{L}\mathbf{S}$, called the spin orbit interaction, and it turns out again that this term commutes only with the sum $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

**Problem 3.5 :** Show that $H_{\text{so}}$ commutes with the components of $\mathbf{J}$.

The situation is further complicated in atomic systems with the inclusion of the nuclear spin, $\mathbf{I}$, and one has to consider also the total angular momentum - denoted traditionally by $\mathbf{F}$ - consisting of all (orbital and spin) momenta of all constituents.

# 3. The problem of addition of two angular momenta

Now we shall consider two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$ in two different Hilbert spaces $\mathfrak{H}_1$ and $\mathfrak{H}_2$ thus we prescribe the usual commutation relations for the components of each $\mathbf{J}$ see ( 3.1 )

$$[J_{1i}, J_{1j}] = i\epsilon_{ijk}J_{1k}, \qquad [J_{2i}, J_{2j}] = i\epsilon_{ijk}J_{2k}. \tag{3.7}$$

For simplicity we use here and in the following units where $\hbar = 1$, if one still needs the original units, one can always find the correct expression including $\hbar$ by considering then the dimension of the operators in question. The two momenta are considered to be independent, therefore components with different number indices 1 and 2 commute.

$$[J_{1i}, J_{2k}] = 0 \tag{3.8}$$

In one of the spaces we can diagonalize simultaneously $\mathbf{J}_1^2$ and $J_{1z}$, while in the other the same is true for $\mathbf{J}_2^2$ and $J_{2z}$. Therefore we can consider in each of the spaces the bases $|j_1, m_1\rangle$, and $|j_2, m_2\rangle$ for which:

$$\begin{aligned} \mathbf{J}_1^2 |j_1, m_1\rangle &= j_1(j_1+1)|j_1, m_1\rangle \qquad & J_{1z}|j_1, m_1\rangle &= m_1|j_1, m_1\rangle \\ \mathbf{J}_2^2 |j_2, m_2\rangle &= j_2(j_2+1)|j_2, m_2\rangle \qquad & J_{2z}|j_2, m_2\rangle &= m_2|j_2, m_2\rangle \end{aligned} \tag{3.9}$$

Now we **fix** the values of $j_1$ and $j_2$, and then, as we know, the possible values of the corresponding $m_i$ -s are: $m_1 = -j_1, -j_1+1, \dots, j_1$, and $m_2 = -j_2, -j_2+1, \dots, j_2$, respectively. We shall consider now the space $\mathfrak{H}_1 \otimes \mathfrak{H}_2$, which is of dimension $(2j_1+1)(2j_2+1)$, and which is spanned by the basis vectors:

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle =: |j_1, m_1; j_2, m_2\rangle \tag{3.10}$$

where a simplified unambiguous notation has been introduced. These vectors are simultaneous eigenvectors of the four operators

$$\mathbf{J}_1^2 \otimes I \equiv \mathbf{J}_1^2, \quad J_{1z} \otimes I \equiv J_{1z}, \quad I \otimes \mathbf{J}_2^2 \equiv \mathbf{J}_2^2, \quad I \otimes J_{2z} \equiv J_{2z}. \tag{3.11}$$

Let us consider the operator

$$\mathbf{J} = \mathbf{J}_1 \otimes I + I \otimes \mathbf{J}_2 \tag{3.12}$$

which also acts in $\mathfrak{H}_1 \otimes \mathfrak{H}_2$, and which is written usually in the shorter form as $\mathbf{J}_1 + \mathbf{J}_2$, and its components $J_i = J_{1i} + J_{2i} (i = x, y, z)$. A short calculation shows that these $J_i$ -s obey the commutation relations defining an angular momentum according to ( 3.1 ), i.e.

$$[J_i, J_k] = i\epsilon_{ikl} J_l. \tag{3.13}$$

From this it follows that $\mathbf{J}^2 = (\mathbf{J}_1 + \mathbf{J}_2)^2$ defined according to

$$\begin{aligned}\mathbf{J}^2 \quad &:= (\mathbf{J}_1 \otimes I + I \otimes \mathbf{J}_2) \cdot (\mathbf{J}_1 \otimes I + I \otimes \mathbf{J}_2) = \mathbf{J}_1^2 \otimes I + I \otimes \mathbf{J}_2^2 + 2\mathbf{J}_1 \otimes \mathbf{J}_2 \equiv \\ &\equiv \mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1\mathbf{J}_2\end{aligned} \tag{3.14}$$

and

$$J_z = J_{1z} + J_{2z} \tag{3.15}$$

have a simultaneous eigenbasis.

Still it is interesting that $\mathbf{J}^2$ and $J_{1i}$ or $\mathbf{J}^2$ and $J_{2i}$ do not commute, because

$$\begin{aligned}[\mathbf{J}^2, J_{1i}] \quad &= [\mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1\mathbf{J}_2, J_{1i}] = 2[\mathbf{J}_1\mathbf{J}_2, J_{1i}] = \\ &= 2[J_{1k}J_{2k}, J_{1i}] = 2J_{2k}[J_{1k}, J_{1i}] = 2i\epsilon_{kil} J_{1l} J_{2k},\end{aligned} \tag{3.16}$$

and

$$\begin{aligned}[\mathbf{J}^2, J_{2i}] \quad &= [\mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1\mathbf{J}_2, J_{2i}] = 2[\mathbf{J}_1\mathbf{J}_2, J_{2i}] = \\ &= 2[J_{1k}J_{2k}, J_{2i}] = 2J_{1k}[J_{2k}, J_{2i}] = 2i\epsilon_{kil} J_{1k} J_{2l} \\ &= 2i\epsilon_{lik} J_{1l} J_{2k},\end{aligned} \tag{3.17}$$

where in the last equality we changed the summation indices $k$ and $l$. The sum of the two latter equations ( 3.16 ) and ( 3.17 ) is however zero, showing that $\mathbf{J}^2$ commutes with $J_i = J_{1i} + J_{2i}$ but not separately with the summands. At the same time

$$[\mathbf{J}^2, \mathbf{J}_1^2] = [\mathbf{J}^2, \mathbf{J}_2^2] = 0 \tag{3.18}$$

since e.g.

$$[\mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1\mathbf{J}_2, \mathbf{J}_1^2] = 2[\mathbf{J}_1\mathbf{J}_2, \mathbf{J}_1^2] = 2[J_{1k}J_{2k}, \mathbf{J}_1^2] = 0 \tag{3.19}$$

because the square commutes with each of the components. We see from this that the four operators

$$\mathbf{J}^2, J_z, \mathbf{J}_1^2, \mathbf{J}_2^2 \tag{3.20}$$

do commute again, so they must also have a common eigenbasis in the product space. These vectors will be denoted in accordance with the operators by the symbol $|j,m,j_1,j_2\rangle$. The latter is, however, not identical with the elements of the product basis $|j_1,m_1;j_2,m_2\rangle$ of ( 3.10 ), which are the simultaneous eigenvectors of the four operators

$$\mathbf{J}_1^2,\ \mathbf{J}_2^2,\ J_{1z},\ J_{2z} \tag{3.21}$$

because from the two different operator quartets ( 3.21 ) and ( 3.20 ) one can select pairs of operators that do not commute with other. These are, e.g the pair $\mathbf{J}^2$ and $J_{1z}$ or $\mathbf{J}^2$ and $J_{2z}$. One can show by explicit calculation, see the next two problems, that the vector $|j_1,m_1,j_2,m_2\rangle$ is not an eigenvector of $\mathbf{J}^2$ :

**Problem 3.6 :** Show that $\mathbf{J}^2=\mathbf{J}_1^2+\mathbf{J}_2^2+J_{1+}J_{2-}+J_{1-}J_{2+}+2J_{1z}J_{2z}$.

**Problem 3.7 :** Using the result above, prove that $|j_1,m_1;j_2,m_2\rangle$ is not an eigenvector of $J^2$, except for $m_1=j_1$ and $m_2=j_2$, or when $m_1=-j_1$ and $m_2=-j_2$.

The problem of adding two angular momenta means that we give those basis vectors $|j,m,j_1,j_2\rangle$ in which the operators $\mathbf{J}^2, J_z, \mathbf{J}_1^2, \mathbf{J}_2^2$ are all diagonal.

# 4. The possible values of the quantum numbers $j$ and $m$.

## 4.1. The possible values of $m$

Let us find now the possible values of $m$ and $j$, defining the collective basis. The elements of the product basis are eigenvectors of $J_z=J_{1z}+J_{2z}$ :

$$J_z|j_1,m_1;j_2,m_2\rangle=(J_{1z}+J_{2z})|j_1,m_1;j_2,m_2\rangle=(m_1+m_2)|j_1,m_1;j_2,m_2 \tag{3.22}$$

with eigenvalues

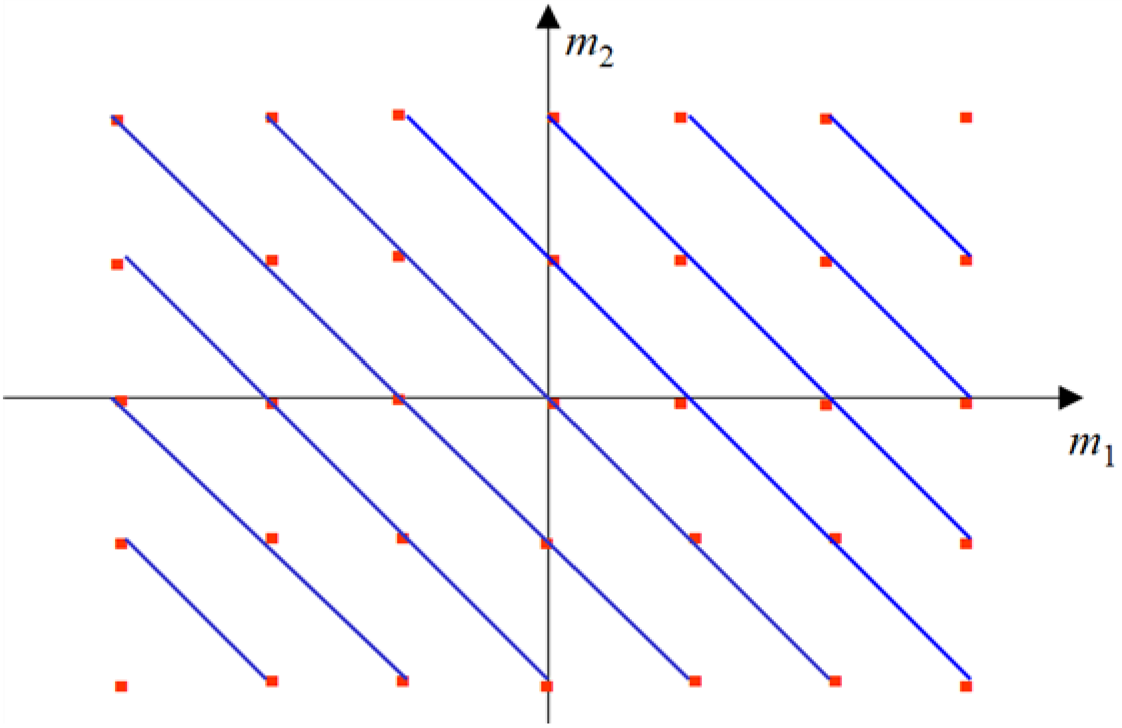
$$m=m_1+m_2 \tag{3.23}$$

Obviously all these $m$ -s are integers, if both $j_1$ and $j_2$ are integers or if both of them are half-integers. $m$ is half-integer if exactly one of the $j$ -s is half-integer. As the larest value of $m_1$ is $j_1$, and the largest $m_2$ is just $j_2$ , the maximal $m$ value is $m_+=j_1+j_2$, and for similar reason the minimal value of $m$ is $m_-=-j_1-j_2$, therefore

$$-j_1-j_2\leq m\leq j_1+j_2 \tag{3.24}$$

The eigenvalues $m$ of $J_z$ are degenerate, in general, as a given $m$ can be written in more than one way as a sum of the two numbers $m_1$ and $m_2$. In order to find the degree of degeneration of a given $m$, we plot the elements of the product basis in a two-dimensional Cartesian coordinate system with points so that the horizontal co-ordinate is $m_1$ the vertical one is $m_2$. For fixed $j_1$ and $j_2$ we get then a axially symmetric set of $(2j_1+1)(2j_2+1)$ points. The states with a given $m=m_1+m_2$ are found along the line segments with equation $m_2=-m_1+m$. Their slope is -1, and the one corresponding to a given $m$ intersects the $m_2$ axis at $m_2=m$. The number of basis vectors with a fixed $m$ is equal to the number of points on the line segment corresponding to the given $m$. Figure shows the case $j_1=3$, and $j_2=2$.

**Figure 3.1. This figure shows the case $j_1 = 3$, and $j_2 = 2$.**



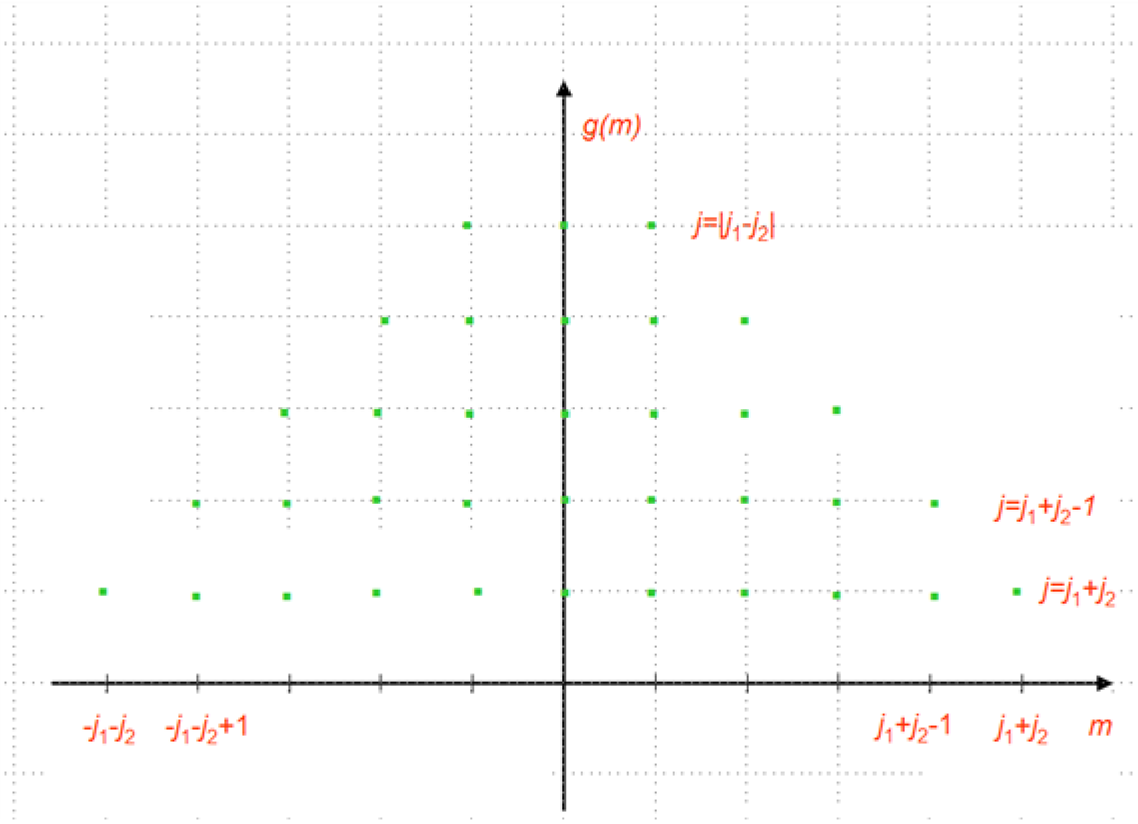
This figure shows the case where the added angularmomenta are 2 and 3 respectively.

There is only a single vector for which $m = j_1 + j_2$ this is the point in the upper right corner of the diagram and similarly a single one with $m = -j_1 - j_2$, this is the point in the lower left corner. Therefore in $\mathfrak{H}_1 \otimes \mathfrak{H}_2$ these two eigenvalues are nondegenerate: their degree of degeneracy is unity $g(m = j_1 + j_2) = 1$, and $g(m = -j_1 - j_2) = 1$. From now on we shall not write out $j_1$ and $j_2$ in the product basis states, and will denote $|j_1, m_1; j_2, m_2\rangle$ simply by $|m_1; m_2\rangle$ unless this is necessitated in order to understand the notation. Then the vector corresponding to $m = j_1 + j_2$ and $m = -j_1 - j_2$ are

$$\begin{aligned} |j_1, m_1 = j_1; j_2, m_2 = j_2\rangle &= |j_1, j_2\rangle \\ |j_1, m_1 = -j_1; j_2, m_2 = -j_2\rangle &= |-j_1, -j_2\rangle \end{aligned} \tag{3.25}$$

Let us consider now the case $m = j_1 + j_2 - 1$. There are two orthogonal vectors in the product basis belonging to this eigenvalue of $J_z$, these are $|m_1 = j_1 - 1; m_2 = j_2\rangle$, and $|m_1 = j_1; m_2 = j_2 - 1\rangle$, so $g(m = j_1 + j_2 - 1) = 2$. The space spanned by these two orthogonal vectors is two-dimensional, and **any linear combination of them belongs to the $J_z$ eigenvalue** $m = j_1 + j_2 - 1$.

**Figure 3.2. The $m \mapsto g(m)$ function corresponding to the $j_1 = 3$, $j_2 = 2$ values.**



The g(m) function corresponding to the example above.

We can continue this consideration, and find that decreasing $m$ further, its degeneracy increases until we do not reach the line segment which starts from the lower right corner where $m_2=-j_2$ and $m_1=j_1$. (See Figure 3.1 ). (We assume here that $j_1\geq j_2$, which does not restrict generality.) For all points along this line $m=j_1-j_2$, and the number of points i. e.the degree of degeneracy is $g(m=j_1-j_2)=2j_2+1$, the number of the possible $m_2$ -s. If we continue with still smaller $m$ -s: $m=j_1-j_2-1,\dots g$ does not change until we reach the smallest value of $m_1$ which is $m_1=-j_1$, and $m_2$ may still takes its largest value $m_2=j_2$, and therefore $m=-j_1+j_2$. The product basis element corresponding to $m=-j_1+j_2$ are on the line segment of slope -1 and accommodating the point in the upper left corner of the figure. The number of these points are still $g(m=-j_1+j_2)=\ 2j_2+1$. Next if $m$ decreases further one by one, the degeneracy is decreasing too, until we reach the minimal value $m=-j_1-j_2$, which is the point in the lower left corner of the figure, which is obviously nondegenerate again.

We summarize now the above statements in a more general way, including the case when $j_2>j_1$, as well:

$$\boxed{\begin{array}{lll} g(m)=j_1+j_2-m+1, & \text{if} & |j_1-j_2|\leq m\leq j_1+j_2 \\ g(m)=2\min(j_1,j_2)+1, & \text{if} & -|j_1-j_2|\leq m\leq |j_1-j_2| \\ g(m)=j_1+j_2+m+1, & \text{if} & -j_1-j_2\leq m\leq -|j_1-j_2| \end{array}} \tag{3.26}$$

Figure 3.2 shows the $m\mapsto g(m)$ function corresponding to the $j_1=3$, $j_2=2$ values, the case for which the product basis elements have been shown in Figure 3.1 . The function $g(m)$ is presented in a specific way, along the vertical line corresponding to a given $m$ discrete points with unit distance are plotted so that their number is $g(m)$. Soon we will see the advantage of this visualization.

## 4.2. The possible values of $j$

From the general theory of angular momentum it follows that the quantum numbers $j$ and $m$ corresponding to the operators representing the sum: $\mathbf{J}^2$ and $J_z$ the inequality $j \geq |m|$ must hold. Further, as $m = j_1 + j_2$ is the largest one that occur, the largest possible eigenvalue of $\mathbf{J}^2$ must be the one corresponding to the quantum number $j = j_1 + j_2$, which is $j(j+1) = (j_1 + j_2)(j_1 + j_2 + 1)$, as it could be seen straightforwardly by solving problems 3.1 and 3.2.

### 4.2.1. a) $j = j_1 + j_2, \ \ m = j_1 + j_2, \ \ j_1 + j_2 - 1, \ldots - j_1 - j_2$

We know that besides the state with $m = j$ there are additional eigenstates of $\mathbf{J}^2$ belonging to this same $j = j_1 + j_2$ quantum number, corresponding to other, smaller values of $m$, namely those with $m = j - 1, \ldots, -j$, and their number is $2j + 1 = 2(j_1 + j_2) + 1$. As we have seen in the previous subsection, such $m$-s occur actually among the eigenvalues of $J_z$, but as we have seen, there are in general **more than one such states** that belong to a given $m$, because according to ( 3.26 ) for $|m| < j_1 + j_2$, we have $g(m) > 1$.

In order to find other states that belong to the largest $j$ i.e. to $j_1 + j_2$ let us apply the operator $J_- = J_{1-} + J_{2-}$ to the state $|j = j_1 + j_2, m = j_1 + j_2\rangle$. This does not change the value of $j = j_1 + j_2$ as $[\mathbf{J}^2, J_-] = 0$, whereas it decreases the value of $m$ by one, yielding the state $|j = j_1 + j_2, m = j_1 + j_2 - 1\rangle$ and we can continue the procedure applying $k$ times $J_-$, producing in this way a vector proportional to $|j = j_1 + j_2, m = j_1 + j_2 - k\rangle$, and finally we get the zero vector for $k = 2j + 1$ $(J_-)^k$ which cannot be an eigenvector. Note that this can be visualized if we look at Figure 3.2 in a different way. The rightmost point where $m = j_1 + j_2$, and $g(m) = 1$ can be identified as a representation of the state $j = j_1 + j_2$, and $m = j_1 + j_2$. Each time we apply $J_-$ we move one step to the left and each point in the row of the $2(j_1 + j_2 + 1)$ points with $g(m) = 1$, can be considered to be one state with this same $j$ and decreasing until its final value with $m = -j_1 - j_2$.

### 4.2.2. b) $j = j_1 + j_2 - 1, \ \ m = j_1 + j_2 - 1, \ \ j_1 + j_2 - 2, \ldots - j_1 - j_2 + 1$

Let us consider now the subspace belonging to $m = j_1 + j_2 - 1$. As we have seen, this is of dimension two, (unless one of the $j_1$ and $j_2$ is not zero). In this subspace we have already found the vector $|j = j_1 + j_2, m = j_1 + j_2 - 1\rangle$ by the procedure described in the previous paragraph. But due to the twofold degeneracy there must be another one, with the same $m$, which is orthogonal to the latter for which $m = j_1 + j_2 - 1$ again. Because the $j$ and $m$ values must obey $j \geq |m|$, this $m$ can belong only to $j = j_1 + j_2$ or to $j = j_1 + j_2 - 1$. On the other hand this vector cannot be one with $j = j_1 + j_2$, because it must be orthogonal to the state with $j = j_1 + j_2, m = j_1 + j_2 - 1$. Therefore the only possible state can be only one with $j = j_1 + j_2 - 1$, and then the state $|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle$ has the largest possible $m$ for this $j$. We can apply again $J_- = J_{1-} + J_{2-}$ sufficiently many times and obtain $2(j_1 + j_2 - 1) + 1$ the vectors $|j = j_1 + j_2 - 1, m\rangle$ whose number is $2(j_1 + j_2 - 1) + 1$ as for the last one with $m = -j_1 - j_2 + 1$ the effect of $J_-$ will be zero. In Figure 3.2 the point with $g(m) = 2$ and $m = j_1 + j_2 - 1$ will be considered to represent $|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle$, and the points in the row with this same $g(m) = 2$ are those with the same $j = j_1 + j_2 - 1$, and the appropriate $m$-s.

### 4.2.3. c) $j = j_1 + j_2 - 2, \ \ m = j_1 + j_2 - 2, \ \ j_1 + j_2 - 3, \ldots - j_1 - j_2 + 2$

We can continue the procedure with vectors where $m = j_1 + j_2 - 2$. They form, in general, a three-dimensional space, where two of which have been already obtained by applying the lowering operator $J_-$ from two orthogonal starting states as described in points a) and b). These are the states $|j = j_1 + j_2, m = j_1 + j_2 - 2\rangle$, and $|j = j_1 + j_2 - 1, m = j_1 + j_2 - 2\rangle$. The third state orthogonal to the latter ones can be only the vector $|j = j_1 + j_2 - 2, m = j_1 + j_2 - 2\rangle$ because the quantum numbers $j$ and $m$ indexing a should still obey $j \geq |m|$, while there are no other states with $j > j_1 + j_2 - 2$.

Applying $J_-$ again we obtain the states with this same $j$, and $m$ decreasing till $-(j_1+j_2-2)$, and this can be interpreted by stepping down along the row with $g(m)=3$

⋮

We continue this procedure so that the rightmost point in Figure 3.2 in each row is considered to represent the state with $j=j_1+j_2-g(m)+1$, and those with the same $g(m)$ but with $m$ going down the other states.

As we see from the figure, we arrive finally at $m=|j_1-j_2|$, where the largest possible $m$ will be just this value from which $J_-$ creates the $2|j_1-j_2|+1$ orthogonal ones $|j=|j_1-j_2|,m\rangle$ , with $m=|j_1-j_2|,\dots-|j_1-j_2|$. We see that this is the smallest possible value of $j$ as we exhausted all the possibilities.

We can check that the number of orthogonal basis vectors, in the collective basis obtained in this way is the same as in the product basis. Assuming $j_1\geq j_2$, the number of the elements of the collective basis enumerating them in the reverse order, is given by $\sum_{j=j_1-j_2}^{j_1+j_2}(2j+1)$, which can be calculated as

$$\begin{aligned}\sum_{j=j_1-j_2}^{j_1+j_2}(2j+1) &= \sum_{k=0}^{2j_2}[2(k+j_1-j_2)+1] = 2\sum_{k=0}^{2j_2}k+(2j_2+1)[2(j_1-j_2)+1] \\ &= 2(2j_2+1)2j_2/2+(2j_2+1)[2(j_1-j_2)+1] = \\ &= (2j_2+1)[2j_2+2(j_1-j_2)+1] = (2j_2+1)[2j_1+1]\end{aligned} \qquad (3.27)$$

where we introduced the new summation index $k=j-(j_1-j_2)$, and made use of the well known rule $\sum_{k=0}^{n}=n(n+1)/2$. The result shows that the number of the orthogonal basis vectors in the collective basis is identical to that of the product basis as it should be.

# 5. Clebsch Gordan coefficients

The considerations given in the previous subsection provides us with an actual procedure that yields explicitly the vectors of the collective basis as linear combinations of the elements of the product basis.

As we have seen above, by fixing a possible proportionality constant of unit absolute value, we can identify $|j_1,m_1=j_1;j_2,,m_2=j_2\rangle$ with the unique collective basis vector $|j=j_1+j_2,m=j_1+j_2\rangle$. Then using

$$J_-=J_{1-}+J_{2-} \qquad (3.28)$$

we get

$$\begin{aligned}J_-|j=j_1+j_2,m=j_1+j_2\rangle &= (J_{1-}+J_{2-})|j_1,m_1=j_1;j_2,m_2=j_2\rangle = \\ &= [J_{1-}|j_1,m_1\rangle]|j_2,m_2\rangle+|j_1,m_1\rangle[J_{2-}|j_2,m_2\rangle\end{aligned} \qquad (3.29)$$

The rule

$$J_-|j,m\rangle=\sqrt{j(j+1)-m(m-1)}|j,m-1\rangle \qquad (3.30)$$

known from the theory of a single angular momentum yields normalized $|j,m-1\rangle$, if the initial $|j,m\rangle$ is normalized as well. Therefore we can explicitly calculate both sides of ( 3.29 ) and obtain for the left hand side:

$$\sqrt{j(j+1)-j(j-1)}|j,j-1\rangle=\sqrt{2j}|j,j-1\rangle \qquad (3.31)$$

with $j=j_1+j_2$, while the right hand side will be similarly

$$\sqrt{2j_1}\,|j_1, j_1-1\rangle\,|j_2, j_2\rangle + \sqrt{2j_2}\,|j_1, j_1\rangle\,|j_2, j_2-1\rangle \tag{3.32}$$

The equality of the two gives

$$|j, j-1\rangle = \sqrt{j_1/(j_1+j_2)}\,|j_1, j_1-1\rangle\,|j_2, j_2\rangle + \sqrt{j_2/(j_1+j_2)}\,|j_1, j_1\rangle\,|j_2, j_2-1 \tag{3.33}$$

We can again apply $J_-$ to the left hand side of and $J_{1-}+J_{2-}$ to the right hand side of ( 3.33 ), and using the rule ( 3.30 ) obtain the expression of $|j=j_1+j_2, m=j-2\rangle$ by the appropriate vectors of the product basis which will contain the linear combination of the vectors with $m=m_1+m_2=j_1+j_2-2$, i. e. those of $|j_1, j_1-2\rangle\,|j_2, j_2\rangle$, $|j_1, j_1, -1\rangle\,|j_2, j_2-1\rangle$, $|j_1, j_1\rangle\,|j_2, j_2-2\rangle$. Continuing this procedure through all the $2j+1$ steps, going to the left in the first row of Figure 3.2 we arrive at $|j=j_1+j_2, m=-j_1-j_2\rangle$. which the leftmost point in Figure 3.2 , and at the same time the lower left point in Figure 3.1 .

Now we go over to the second row of Figure 3.2 . Its rightmost point $|j=j_1+j_2-1, m=j_1+j_2-1\rangle$ must be orthogonal to the one represented by the point below it, which is of the same $m$, but has a different $j=j_1+j_2$. The expression of this one must be therefore in the two-dimensional subspace spanned by $|j_1, j_1-1\rangle\,|j_2, j_2\rangle$ and $|j_1, j_1\rangle\,|j_2, j_2-1\rangle$ but orthogonal to ( 3.32 ). There is a single normalized vector of this property (apart from a possible phase factor), which is thus:

$$|j=j_1+j_2-1, m=j_1+j_2-1\rangle = \sqrt{j_2/(j_1+j_2)}\,|j_1, j_1-1\rangle\,|j_2, j_2\rangle - \sqrt{j_1/(j_1+j_2)}\,|j_1, j_1\rangle\,|j_2, j_2- \tag{3.34}$$

where we simply exchanged the two coefficients and changed the sign in front of the second one, yielding an orthogonal vector to that given by ( 3.32 . We repeat now the procedure with $J_- = J_{1-}+J_{2-}$, applying them to the left and right hand sides of ( 3.34 ) respectively and obtain all the vectors $|j=j_1+j_2-1, m\rangle$ in terms of those with $|j_1, m_1\rangle\,|j_2, m_2\rangle$ where $m_1+m_2=m$ will be valid necessarily.

The first vector in the third row of the figure will be obtained (See Figure 3.2 ) again by finding the third vector with $j=m=j_1+j_2-2$, that should be orthogonal to the other two with the same $m$ but with $j=j_1+j_2$ , and $j=j_1+j_2-1$ found previously in the first two rows with this same $m$ . $J_- = J_{1-}+J_{2-}$ then yields again all vectors with this same $j=j_1+j_2-2$, but smaller $m$.

In this way all the vectors of the collective basis can be obtained as linear combinations of the elements of the product basis:

$$|j, m\rangle = \sum_{m=m_1+m_2} C^{jm}_{j_1 m_1 j_2 m_2}\,|j_1, m_1\rangle\,|j_2, m_2\rangle \tag{3.35}$$

where the coefficients $C^{jm}_{j_1 m_1 j_2 m_2} = \langle j, m\,|j_1, m_1, j_2, m_2\rangle$ are called **Clebsch-Gordan coefficients**. As can be seen from their construction they are nonzero only if $m=m_1+m_2$, and they are real numbers, due to the phase convention used above. They arose first in a different context in mathematics, the theory presented here comes from **E. Wigner**, who considered the problem of adding angular momenta in quantum mechanics. He introduced a somewhat different notion called **Wigners 3j symbols**. Their notation and connection to the Clebsch-Gordan coefficients is the following:

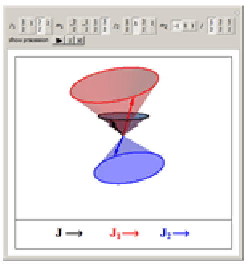
$$\begin{pmatrix} j & j_1 & j_2 \\ m & m_1 & m_2 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m}}{\sqrt{2j+1}}\langle j, m|j_1, m_1, j_2, m_2\rangle \tag{3.36}$$

There is no simple closed expression for the values of the CG coefficients or the $3j$ symbols, in general. A complicated sum can be given for them which we need not to include here, as these are tabulated in many books on atomic physics and quantum mechanics.

**Further reading:** See also the page http://www.volya.net by A. Volya, which gives the explicit values of CG coefficients and $3j$ symbols.

**Further reading:** Many of the properties of the Wigner coefficients are given in the page http://en.wikipedia.org/wiki/Wigner_3-j_symbols.

**Animation:**



Visualizations of the procedure given above is seen on this Mathematica demonstration page. Although quantum formalism is indifferent to such interpretations, the addition of angular momentum in the absence of any electric or magnetic field can be pictured by a vector model in which $\mathbf{J}_1$ and $\mathbf{J}_2$ precess about $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$, which itself precesses about a *z* axis.

**Problem 3.8 :** Perform the general procedure exposed in this section for $j_1 = j_2 = 1/2$. What are the symmetry properties of the resulting collective basis vectors with respect to the exchange of the two spins.

**Problem 3.9 :** Find the result of adding two spin half angular momenta $j_1 = j_2 = 1/2$ in another way, as well by writing up the matrix elements of $J^2$ and $J_z$ in the product basis, and diagonalize the $J_z$ matrix. Find the eigenvectors explicitly, as well.

**Problem 3.10 :** Find the result for a general $j_1 = \ell$ and $j_2 =: s = 1/2$. This is the case of spin-orbit interaction for a single electron.

**Problem 3.11 :** Add the two angular momenta $j_1 = j_2 = 1$, i.e. find all Clebsch-Gordan coefficients for this problem.

# Chapter 4. Fine and hyperfine structure of the H atom, Lamb shift

**Goals:** The energy spectrum derived from the Coulomb potential (see Chapter 1 ) is the primary structure of the Hydrogen atom spectrum. In reality there are other interactions not contained in that model. In this chapter we elaborate these interactions and explain the origin of the necessary corrections.The necessary prerequisites beyond the knowledge of the previous chapters are the most elementary facts from relativstic dynamics.

**Prerequisites:** Chapter 1 ; Chapter 2 ; Chapter 3 ; Elementary facts from relativistic dynamics.

## 1. Introduction

In this chapter we make a step forward and investigate in detail the various corrections that are necessary beyond the simplest quantum mechanical model of the H atom. We shall not follow the first principles approach based on the relativistic theory of the electron worked out by P. Dirac, which proved to be one of the greatest successes of 20-th century theoretical physics. There are a number of reasons why we do not so. The first among them is that the introduction of Dirac's theory is rather complicated and needs a longer discussion. It is usual therefore in texts on atomic physics, to present the corrections to the Schrödinger equation without proof obtained after an expansion of the Dirac Hamiltonian, and to give then the physical picture behind the terms. Another reason is that there are corrections which do not follow simply from Dirac's theory, these are the Lamb shift and the hyperfine structure, they must be included "by hand" in any way.

So we shall follow the traditional approach in atomic physics, and consider first the fine structure corrections, resulting from relativistic considerations. Then we present the Lamb shift, which is a typical quantum-electrodynamical effect, and discuss finally the hyperfine structure of Hydrogen and Hydrogen-like ions.

## 2. Fine structure in the Coulomb potential

We have seen in Chapter 1 that the eigenvalues and eigenfunctions of the Coulomb problem (H atom) with nuclear charge $Z$ and potential energy

$$V(R) = -\frac{Ze_0^2}{R} \tag{4.1}$$

are provided by the following eigenvalue equation,

$$H_0 \left|n\ell m\right\rangle = \left[\frac{P^2}{2m_e} + V(R)\right] \left|n\ell m\right\rangle = \varepsilon_n \left|n\ell m\right\rangle , \tag{4.2}$$

where we had

$$\varepsilon_n = -Z^2\frac{m_e e_0^4}{2\hbar^2}\frac{1}{n^2} = -Z\frac{e_0^2}{2a_0}\frac{1}{n^2} = -\frac{m_e c^2}{2}Z\alpha^2\frac{1}{n^2}. \tag{4.3}$$

Equation ( 4.2 ) corresponds, however, to the simplest nonrelativistic treatment. In this section we shall find explicitly the relativistic corrections by perturbation theory coming from several terms. The correct way to obtain these corrections, (see ( 4.5 ), ( 4.13 ) and ( 4.22 ) below) is to consider the relativistic equation of the electron, the Dirac equation. We do not present here the Dirac equation for electrons in a central potential, we note only that if one expands it up to first order in $\frac{p^2}{m_e^2 c^2}$, one can obtain the expressions of the corrections, reproduced here by heuristic arguments.

## 2.1. Relativistic correction to the kinetic energy

First we have to look for the first order relativistic correction to the kinetic energy:

$$T=\sqrt{m_e^2c^4+c^2p^2}-m_ec^2=\frac{p^2}{2m_e}-\frac{1}{8}\frac{p^4}{m_e^3c^2}+\dots, \tag{4.4}$$

which is the second term in the classical relativistic expansion above. As a result, we can infer the following perturbation to the kinetic energy of the electron:

$$W_t=-\frac{1}{8}\frac{P^4}{m_e^3c^2} \tag{4.5}$$

When compared with the non-relativistic kinetic energy, $\frac{p^2}{2m_e}$, one can see that,

$$W_t=-\frac{1}{2m_ec^2}\left(\frac{P^2}{2m_e}\right)^2 \tag{4.6}$$

and that the perturbation is smaller by a factor of $\frac{p^2}{2m_e^2c^2}=v^2/c^2$, which turns out to be of the order $(Z\alpha)^2$ (seen from the comparison the energy expressions $\varepsilon_1=-Z^2\frac{m_ec^2}{2}\alpha^2=-\frac{1}{2}m_ev^2$ ). This means that the correction coming from the kinetic energy is a small number until $Z\lesssim 137$. Let us note that for the heaviest natural nucleus Uranium $Z=92$. The first order perturbation expression should be obtained from finding the eigenvalues of the matrix $\langle n\ell'm'|W_t|n\ell m\rangle$, as the $\varepsilon_n$ eigenvalues are degenerate in general, as we know from Chapter 1 . The problem is not so severe, however, because $W_t$ is diagonal in the $|n\ell m\rangle$ basis. The reason is that $P^4$ is a scalar, and therefore it commutes with $\mathbf{L}^2$ as well as with $L_z$. For the explicit calculations we shall use sometimes the wave functions (coordinate representation) $\langle\mathbf{r}|n\ell m\rangle=\psi_{n\ell m}(\mathbf{r})$.

**Problem 4.1 :** Show that the vanishing commutators - $[H,L^2]=[H,L_z]=0$ - imply that all the offdiagonal elements of the matrix of $W_t$ vanish:

$$\langle nl'm'|W_t|n\ell m\rangle=\langle W_t\rangle_{n\ell m}\delta_{l'l}\delta_{m'm}. \tag{4.7}$$

Then the result of degenerate perturbation theory can be found by simply by calculating the diagonal matrix elements of $W_t$, which can be done by the following trick:

$$\begin{aligned}\langle W_t\rangle_{n\ell m}&=-\frac{1}{2m_ec^2}\left\langle\left(\frac{P^2}{2m_e}\right)^2\right\rangle_{n\ell m}=-\frac{1}{2m_ec^2}\left\langle(H_0-V(R))^2\right\rangle=\\&=-\frac{1}{2m_ec^2}\left(\left\langle H_0^2\right\rangle-2\left\langle H_0\right\rangle\left\langle V(R)\right\rangle+\left\langle V^2(R)\right\rangle\right)=\\&=-\frac{1}{2m_ec^2}\left(\varepsilon_n^2+2\varepsilon_nZe_0^2\left\langle\frac{1}{R}\right\rangle_{n\ell}+Z^2e_0^4\left\langle\frac{1}{R^2}\right\rangle_{n\ell}\right)\end{aligned} \tag{4.8}$$

**Problem 4.2 :** Show the validity of this equality, while be aware that $H_0$ and $1/R$ do not commute. Show also, that the expectation values do not depend on $m$.

In order to find the expectation value of the potential energy we shall make use the virial theorem, as formulated in the 3 problems below.

**Problem 4.3 :** Show that the expectation value of the commutator of the Hamiltonian with an arbitrary operator vanishes on the stationary states.

**Problem 4.4 :** Consider a one-dimensional problem, where $H = \frac{P^2}{2m_e} + CX^n$. Calculate the commutator $[H, XP]$. Based on the result find a simple relation between the expectation values of the kinetic and potential energies in stationary states, with given energy eigenvalues.

**Problem 4.5 :** Generalize the result for the three-dimensional case $H = \frac{\mathbf{P}^2}{2m_e} + V(X, Y, Z)$, where the potential energy is a homogeneous function of the coordinates of degree $k$. The latter means that $V(\alpha X, \alpha Y, \alpha Z) = \alpha^n V(X, Y, Z)$ for an arbitrary parameter $\alpha$. What are the consequences of this result for the harmonic oscillator in 3 dimensions and for the Coulomb problem?

From the virial theorem for the Coulomb problem we obtain $\langle E_{kin} \rangle = -\frac{1}{2} \langle V \rangle$ and consequently

$$\langle V \rangle_{n\ell m} = -\frac{Ze_0^2}{a_0} \left\langle \frac{1}{R} \right\rangle = 2\varepsilon_n = -\frac{Z}{a_0} \frac{e_0^2}{n^2}, \qquad (4.9)$$

which we use in the second term of ( 4.8 ).

In order to evaluate the third term in ( 4.8 ) we shall also need the expectation value of $\frac{1}{R^2}$, which can be obtained in the coordinate representation by using the solutions of the radial equation $u_{n\ell}(r)/r$ and calculating $\int\limits_0^\infty \frac{|u_{n\ell}|^2}{r^2} \frac{1}{r^2} r^2 dr$. The integrals for all $n$ and $\ell$ can be obtained explicitly, but another way of obtaining this expectation value will be given in the additional point and problem in the end of the next subsection. The result is

$$\left\langle \frac{1}{R^2} \right\rangle_{n\ell} = \frac{Z^2}{(\ell + 1/2) n^3 a_0^2}. \qquad (4.10)$$

Then the kinetic energy correction in first order is

$$\begin{aligned} \Delta W_t^{(1)} &= -\frac{1}{8m_e c^2} \langle P^4 \rangle_{n\ell} = -\frac{1}{2m_e c^2} \left( \varepsilon_n^2 + 2\varepsilon_n Z e_0^2 \left\langle \frac{1}{R} \right\rangle_{n\ell} + Z^2 e_0^4 \left\langle \frac{1}{R^2} \right\rangle_{n\ell} \right) = \\ &= -\frac{1}{2m_e c^2} \left( \varepsilon_n^2 - 4\varepsilon_n^2 + Z^2 e_0^4 \frac{1}{(l+1/2) n^3 a_0^2} \right) = \\ &= -\frac{m_e c^2}{2} \left( \frac{Z^2 \alpha^4}{n^4} \right) \left( \frac{n}{l+1/2} - \frac{3}{4} \right) \end{aligned} \qquad (4.11)$$

From this term alone, we expect the degeneracy between states with different values of $\ell$ of the total angular momentum "to be resolved". However, as well will see, this conclusion shall be refined below. We need to gather all terms of the same order of perturbation theory before we can reach a definite conclusion. We can, however, confirm that (as expected) the scale of the correction is of order $\Delta W_t^{(1)} / \varepsilon_n = (Z\alpha/n)^2$.

## 2.2. Spin-orbit coupling

We now turn to the second important class of corrections. As well as revealing the existence of an internal spin degree of freedom, the relativistic formulation of quantum mechanics shows that there is a further correction to the Schrödinger operator which involves a coupling between the spin and orbital degrees of freedom. For a **general spherical** potential $V(R)$, this spin-orbit coupling takes the form,

$$W_{so} = \frac{1}{2m_e^2 c^2} \frac{1}{R} \frac{dV(R)}{dR} \mathbf{L} \cdot \mathbf{S} \qquad (4.12)$$

For a Hydrogen like atom with $V(R) = -Z\frac{e_0^2}{R}$,

$$W_{so} = \frac{1}{2m_e^2c^2}\frac{Ze_0^2}{R^3}\mathbf{L}\cdot\mathbf{S} \qquad (4.13)$$

Physically, the origin of the spin-orbit interaction can be understood from the following considerations. As the electron is moving through the electric field of the nucleus then, in its rest frame, it will experience this as a magnetic field. There will be an additional energy term in the Hamiltonian associated with the orientation of the spin magnetic moment with respect to this field. We can make an estimate of the spin-orbit interaction energy as follows: If we have a classical central field, then the electric field is $q_0\mathbf{E} = -\nabla V(r) = -\hat{\mathbf{r}}\frac{dV(r)}{dr}$, and for the Coulomb field this gives $-\hat{\mathbf{r}}Ze_0^2/r^2$. (Remember we use $e_0^2 = q_0^2/4\pi\epsilon_0$.) For an electron moving with velocity $\mathbf{v}$, this electric field translates to an effective magnetic field $\mathbf{B} = -(\mathbf{v}\times\mathbf{E})/c^2$, according to the leading term in the Lorentz transformation of the field strengths. The magnetic moment of the electron associated with its spin $\mathbf{S}$ is equal to $\boldsymbol{\mu}_s = g_e\frac{q_0}{2m_e}\mathbf{S} = \frac{q_0}{m_e}\mathbf{S}$, where $g_e = 2$ the (almost) exact gyromagnetic factor of the electron spin. The interaction energy between the field and the magnetic moment is

$$-\boldsymbol{\mu}_s\mathbf{B} = \frac{q_0}{m_e}\frac{(\mathbf{v}\times\mathbf{E})}{c^2}\mathbf{S} = -\frac{1}{m_e^2}\frac{(m_e\mathbf{v}\times\hat{\mathbf{r}})}{c^2}\frac{dV(r)}{dr}\mathbf{S} = -\frac{1}{m_e^2c^2}\left(\mathbf{p}\times\frac{\mathbf{r}}{r}\right)\mathbf{S}\frac{dV(r)}{dr} = -\frac{1}{m_e^2c^2}\frac{Ze_0^2}{r^3}\mathbf{L}\cdot \qquad (4.14)$$

which - apart from the factor 1/2 - is identical to $W_{so}$. In fact, there is a relativistic effect connected with the precession of axes under rotation, called Thomas precession which multiplies the last heuristic formula by a further factor of $1/2$ giving the correct result ( 4.13 ).

Once again, we can estimate the effect of spin-orbit coupling by treating $W_{so}$ as a perturbation. In the absence of spin-orbit interaction, one may express the eigenstates of hydrogen-like atoms in the basis states of the mutually commuting operators, $H_0, L^2, L_z, S^2$, and $S_z$. However, in the presence of spin-orbit coupling, the total Hamiltonian no longer commutes with $L_z$ or $S_z$. It is therefore helpful to make use of the degeneracy of the unperturbed Hamiltonian to switch to a new basis in which the angular momentum components of the perturbed system are diagonal. This can be achieved by turning to the basis of eigenstates of the operators, $H_0, J^2, J_z, L^2$, and $S^2$, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$ denotes the total angular momentum. (For a discussion of the form of these basis states, we refer back to the previous section) Making use of the relation, $J^2 = L^2 + S^2 + 2\mathbf{LS}$, it follows

$$\mathbf{LS} = \frac{1}{2}(J^2 - L^2 - S^2). \qquad (4.15)$$

The total angular momentum can take the values $j = \ell + 1/2$, and $j = \ell - 1/2$, the latter only if $\ell \neq 0$. The corresponding basis states $|j = \ell \pm 1/2, m_j, \ell\rangle$ (with $s = 1/2$ implicit) therefore diagonalize the operator

$$\mathbf{LS}|j = \ell \pm 1/2, m_j, \ell\rangle = \frac{\hbar^2}{2}\begin{pmatrix}\ell \\ -\ell - 1\end{pmatrix}|j = \ell \pm 1/2, m_j, \ell\rangle. \qquad (4.16)$$

As for the radial dependence of the perturbation, once again, the off-diagonal matrix elements vanish circumventing the need to invoke degenerate perturbation theory. As a result, at first order in perturbation theory, one obtains

$$\langle W_{so}\rangle_{n,j=\ell\pm1/2,m_j\ell} = \frac{1}{2m_e^2c^2}\frac{\hbar^2}{2}\begin{pmatrix}\ell \\ -\ell - 1\end{pmatrix}Ze_0^2\left\langle\frac{1}{R^3}\right\rangle_{n,\ell}. \qquad (4.17)$$

The solution of the second problem in the end of this subsection gives us that for $\ell \neq 0$

$$\left\langle \frac{1}{R^3} \right\rangle_{n,\ell} = \left(\frac{m_e c Z\alpha}{\hbar n}\right)^3 \frac{1}{\ell(\ell+1/2)(\ell+1)}. \tag{4.18}$$

In this way one obtains:

$$\langle W_{so}\rangle_{n,j=\ell\pm 1/2,m_j\ell} = \frac{1}{4m_e^2c^2}\left(\frac{Z\alpha}{n}\right)^4 \frac{n}{j+1/2}\begin{pmatrix} 1/j \\ -1/(j+1)\end{pmatrix}. \tag{4.19}$$

For $\ell = 0$, the result is zero as there is no orbital angular momentum with which to couple the spin. We now rewrite the result ( 4.11 ) for $\langle W_t\rangle$ in the collective basis:

$$\langle W_t\rangle_{n,j=\ell\pm 1/2,m_j\ell} = \frac{m_e c^2}{4}\left(\frac{Z\alpha}{n}\right)^4 n\left(\frac{3}{4} - \begin{pmatrix} 1/j \\ 1/(j+1)\end{pmatrix}\right) \tag{4.20}$$

and combining both of these expressions, for $\ell > 0$, we obtain:

$$\langle W_t + W_{so}\rangle_{n,j=\ell\pm 1/2,m_j\ell} = \frac{m_e c^2}{2}\left(\frac{Z\alpha}{n}\right)^4 \left(\frac{3}{4} - \frac{n}{j+1/2}\right) \tag{4.21}$$

while for $\ell = 0$, we retain just the kinetic energy term ( 4.11 ).

**Expectation values of $1/R^2$ and $1/R^3$.**

In order to find ( 4.10 ) we take into account that the functions $u_{n\ell}$ are solutions of the radial eigenvalue equation in the variable $y = r/a_0$ : $Hu_{n\ell}(y) = \epsilon_{\ell,n_r}u_{n\ell}(y)$ where $H = -\frac{d^2}{dy^2} + \frac{\ell(\ell+1)}{y^2} + \frac{2Z}{y}$ and $\epsilon_{\ell,n_r} = -\frac{1}{(n_r+\ell+1)^2} = \epsilon_n$, (see Chapter 1 .) The expectation values can be found by taking the derivative of the eigenvalue equation with respect to $\ell$ and taking the scalar product $\langle u|\frac{\partial}{\partial\ell}(Hu)\rangle = \langle u|\frac{\partial}{\partial\ell}(\epsilon_{n_r\ell}u)\rangle$. We can express from the resulting equation $\frac{\partial H}{\partial\ell} = \frac{2\ell+1}{y^2}$ the expectation value of which will yield ( 4.10 ).

**Problem 4.6 :** Prove the form of H in the $y = r/a_0$ variable, and using the hint given in the above paragraph find the expectation value of $\frac{1}{R^2}$ in the Coulomb eigenstates.

In the next subsection we shall also need the expectation value of $1/R^3$.

**Problem 4.7 :** Follow the same procedure as in the previous problem and calculate $\left\langle u|\frac{\partial}{\partial y}(Hu)\right\rangle$, and find $\left\langle\frac{1}{R^3}\right\rangle$.

## 2.3. The Darwin term

The final contribution to the Hamiltonian from relativistic effects is known as the Darwin term, and arises from the so called "Zitterbewegung" of the electron -trembling motion in German - which smears the effective potential felt by the electron. Such effects lead to a perturbation of the form:

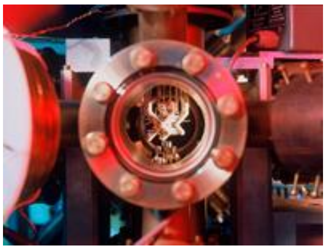
$$W_D = \frac{\hbar^2}{8m_e^2c^2}\nabla^2 V = -\frac{\hbar^2}{8m_e^2c^2}Ze_0^2\nabla^2\frac{1}{|\mathbf{r}|} = \frac{\hbar^2}{8m_e^2c^2}Ze_0^2 4\pi\delta^3(\mathbf{r}) \tag{4.22}$$

where we made use of the Poisson equation for the potential generated by the point charge density of the nucleus: $\nabla^2 V = -\varrho_{nuc}/\epsilon_0 = -q_0\delta^3(\mathbf{r})/\epsilon_0$. Since the perturbation acts only at the origin, because of the $\delta^3(\mathbf{r})$, it effects only states with $\ell = 0$, i. e. the $s$ states. As a result, one finds that

$$\langle W_D \rangle = \frac{\hbar^2}{8m_e^2c^2} Ze_0^2 |\psi_{n,\ell}(0)|^2 \delta_{\ell,0} = \frac{1}{2} m_e c^2 \left(\frac{Z\alpha}{n}\right)^4 n\delta_{\ell,0} \qquad (4.23)$$

Intriguingly, this term is formally identical to that which would be obtained from $\langle W_{so} \rangle$ at $\ell = 0$.

**Further reading:**



An article on Physics World about the successful simulation of the quivering motion of a relativistic electron by manipulating a calcium ion with a laser beam in this electrodynamic cage. http://physicsworld.com/cws/article/news/2010/jan/06/physicists-catch-sight-of-trembling-particle

## 2.4. The total fine structure correction

As a result, combining all three contributions, we obtain for the expectation value of the fine structure operator:

$$W_f = W_t + W_D + W_{so} \qquad (4.24)$$

by combining all three contributions obtained in the previous subsections the total energy shift is given simply by

$$\langle W_f \rangle = \langle W_t \rangle + \langle W_D \rangle + \langle W_{so} \rangle = \Delta\varepsilon_{n,j,m_j\ell} = \frac{m_e c^2}{2} \left(\frac{Z\alpha}{n}\right)^4 \Bigg(\frac{3}{4} - \frac{n}{j+1/2} \qquad (4.25)$$

a result that is independent of $\ell$ and $m_j$. If we express this energy in Rydbergs we have

$$\Delta\varepsilon_{n,j,m_j\ell} = \left(\frac{Z}{n}\right)^4 \alpha^2 \left(\frac{3}{4} - \frac{n}{j+1/2}\right) \mathrm{Ry} \qquad (4.26)$$

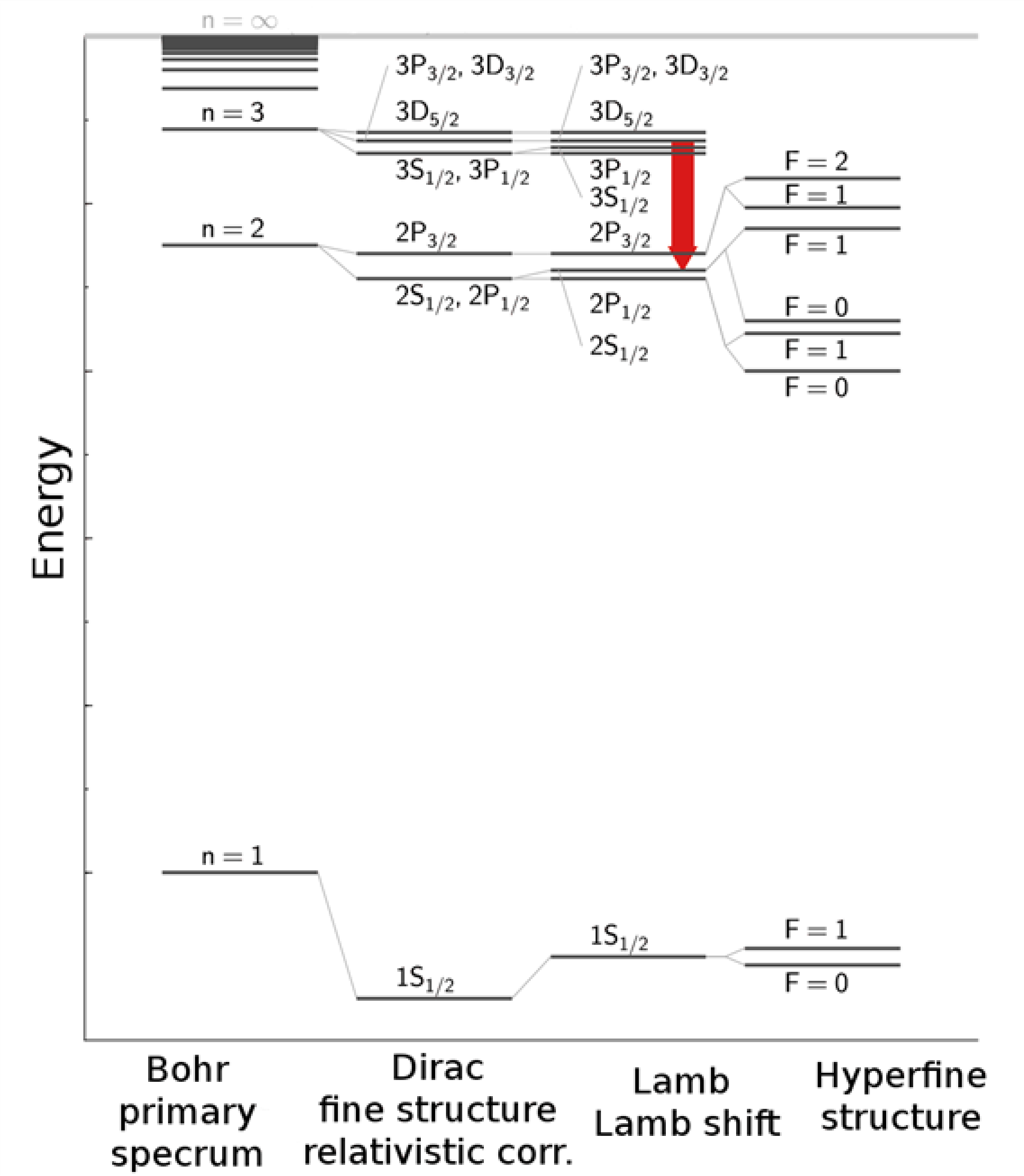
This is the first order correction called the **fine structure**. It can be written usually as $\Delta^{(1)}\varepsilon$, but as we shall see in the next section, it makes no sense to take higher order contributions, as another effect not included in Dirac's theory has an effect larger than the second order result of perturbation theory. Let us note here that the Dirac equation can be solved analytically for an electron in the Coulomb potential, and the result is ( $Z = 1$ )

$$\varepsilon_{nj} = m_e c^2 \left[ 1 + \frac{\alpha^2}{\left(n - j - 1/2 + \sqrt{(j+1/2)^2 - \alpha^2}\right)^2} \right]^{-1} \qquad (4.27)$$

**Problem 4.8 :** Expand $\varepsilon_{nj}$ in terms of $\alpha^2$, up to second order, and compare the result with ( 4.3 ) and ( 4.25 ).

In order to discuss the predicted energy shifts for particular states, it is helpful to introduce the standard nomenclature from atomic physics. For a state with principle quantum number $n$, total spin $s$, orbital angular momentum $\ell$, and total angular momentum $j$, we shall use the spectroscopic notation $n^{2s+1}\ell_j$ to define the state of the H atom, where we write $s, p, d, f$ etc. depending on the value of $\ell = 0, 1, 2, 3\ldots$. We also note here that the convention for atoms other than the Hydrogen is to use $n^{2s+1}L_j$, with capital letters $S, P, D, F$ in the place of $L$, but this latter notation is also used sometimes for the H atom. For a hydrogen-like atom, with just a single electron, $2s + 1 = 2$. In this case, the index $2s + 1$ is often just dropped for brevity. Another point that must be remembered is, that in atomic physics the quantum number for intrinsic spin is often written as a capital $S$, instead of $s$.

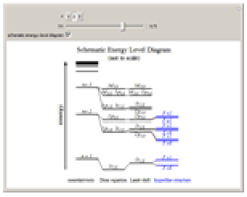
**Figure 4.1. The hierarchy of energy shifts of the spectra of hydrogen-like atoms as a result of relativistic corrections. The first column shows the primary spectrum. The second column shows the fine structure from relativistic corrections. The third column includes corrections due quantum electrodynamics and the fourth column includes interaction terms with nuclear spin The H- $\alpha$ line, particularly important in the astronomy, is shown in red**



The hierarchy of energy shifts of the spectra of hydrogen-like atoms as a result of relativistic corrections. The first column shows the primary spectrum. The second column shows the fine structure from relativistic corrections. The third column includes corrections due quantum electrodynamics and the fourth column includes interaction terms with nuclear spin. The H-alpha line, particularly important in the astronomy, is shown in red

Let us see what do we obtain for the level shifts of H like atom, if we apply the perturbative expression for the relativistic corrections ( 4.25 ). As we have seen, the non-relativistic Hamiltonian, each state of given $n$ exhibits a $2n^2$-fold degeneracy. For a given multiplet specified by $n$, the relativistic corrections depend only on $j$ and $n$. For $n = 1$, we have $\ell = 0$ and $j = 1/2$; then both $1s_{1/2}$ states, with $m_j = 1/2$ and $-1/2$, experience a negative energy shift by an amount $\Delta\varepsilon_{1,1/2,m_j,0} = -Z^4\alpha^2/4\,\mathrm{Ry}$. For $n = 2$, $\ell$ can take the values of 0 or 1. With $j = 1/2$, both the former $2s_{1/2}$ state, and the latter $2p_{1/2}$ states share the same negative shift in energy, $\Delta\varepsilon_{2,1/2,m_j,0} = \Delta\varepsilon_{2,1/2,m_j,1} = -5Z^4\alpha^2/64\,\mathrm{Ry}$ while the $2P_{3/2}$ experiences a shift of $\Delta\varepsilon_{2,3/2,m_j,1} = -1Z^4\alpha^2/64\,\mathrm{Ry}$. Finally, for $n = 3$, $\ell$ can take values of $0, 1$ or 2. Here, the pairs of states $3s_{1/2}$ and $3p_{1/2}$, and $3p_{3/2}$ and $3d_{3/2}$ each remain degenerate while the state $3d_{5/2}$ is unique. These predicted shifts are summarized in Figure 4.1 . This completes our discussion of the relativistic corrections which develop from the treatment of the Dirac theory for the hydrogen atom. However, this does not complete our description of the "real" hydrogen atom. Indeed, there are further corrections which derive from quantum electrodynamics and nuclear effects which we now turn to address.

**Animation:**



We can investigate the relativistic energy levels for Hydrogen atom with this interactive animation. The fine-structure constant can be conceptually from 0 to its actual value, or equivalently the speed of light $c$ from $\infty$ to 1 (meaning $3 \cdot 10^8\,\mathrm{m/s}$), to show the transition from nonrelativistic to relativistic energies for quantum numbers $n = 1,\ 2 \text{ and } 3$.

# 3. Lamb shift

According to the perturbation theory above, the relativistic corrections which follow from the Dirac theory for hydrogen leave the $2S_{1/2}$ state, and $2P_{1/2}$ states degenerate. However, in 47, a careful experimental study by Willis Lamb and Robert Retherford discovered that this was not in fact the case: the $2P_{1/2}$ state is slightly lower in energy than the $2S_{1/2}$ state resulting in a small shift of the corresponding spectral line - the Lamb shift. The observed shift, which was explained by Hans Bethe in the same year, provided considerable insight into quantum electrodynamics. The correct theoretical description has to take into account that an atom can absorb or emit electromagnetic radiation, and while this interaction is present naturally during the absorption or emission of photons, it is manifested also in the so-called "virtual interactions", where the atomic electron in the Coulomb field of the nucleus can absorb and then emit a photon of energy $\hbar\omega$ during a time interval $\Delta t < \hbar/\Delta E = 1/\omega$. The uncertainty relation $\Delta E \Delta t \geq \hbar$ allows such processes without violating the energy conservation law. This comes from a result in quantum electrodynamics, where the quantized radiation field has a zero-point energy equivalent to the mean-square electric field so that even in a vacuum there are fluctuations.

**Figure 4.2. Illustration of the random shaky motion of the electron due to absorption and emission of virtual photons. Motion of a free electron in a radiation field taking into account the photon recoil**

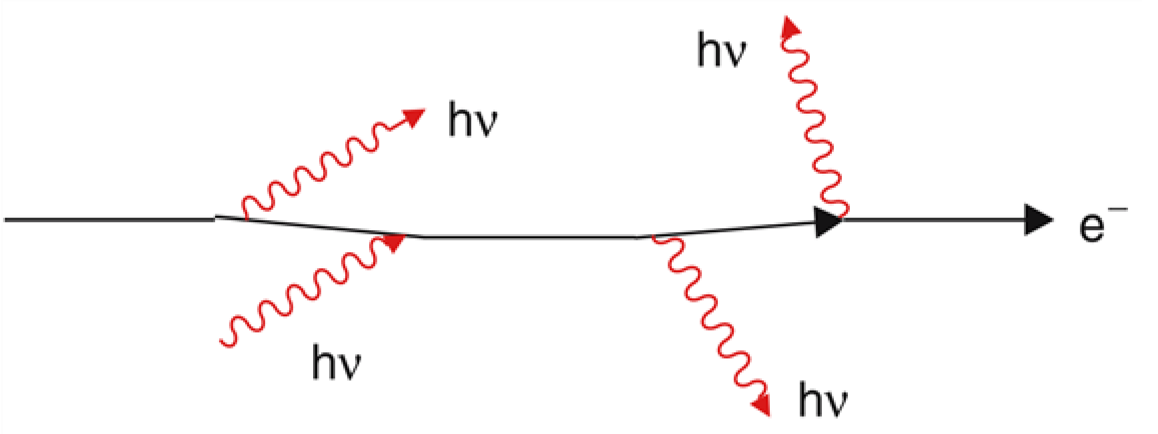
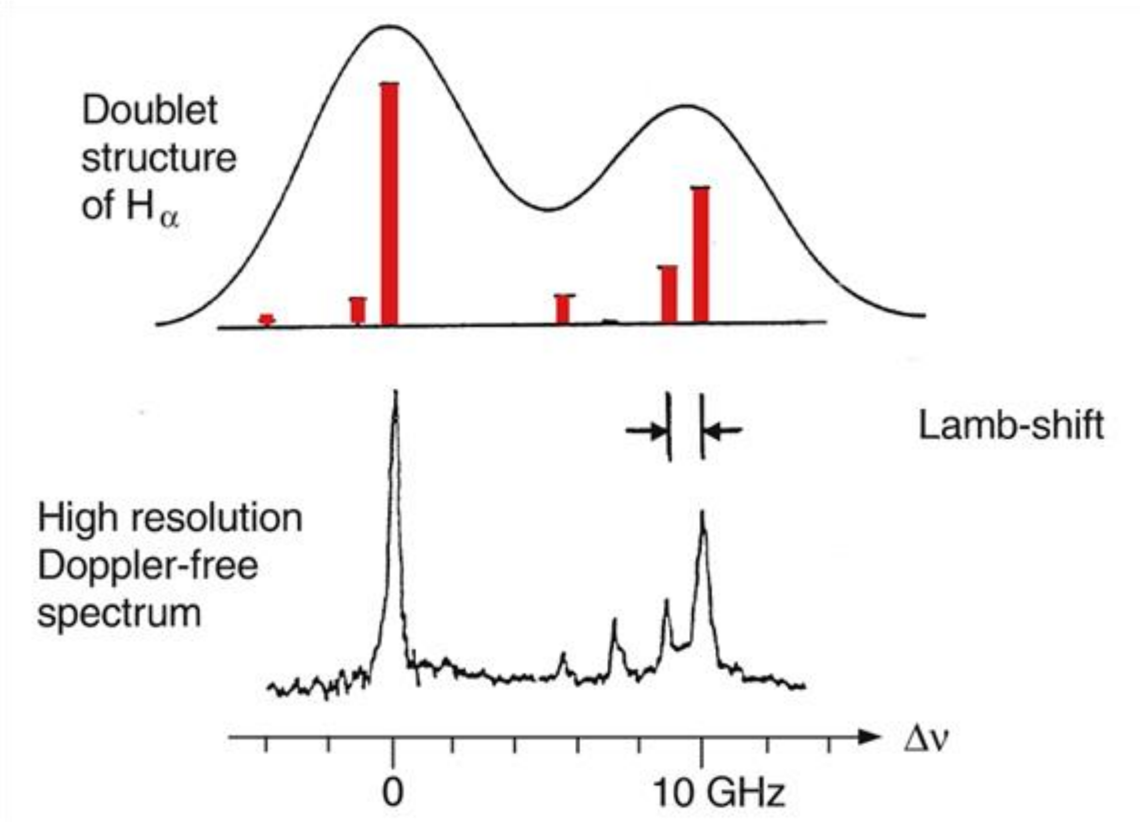


Illustration of the random shaky motion of the electron due to absorption and emission of virtual photons. Motion of a free electron in a radiation field taking into account the photon recoil

These fluctuations cause an electron to execute an oscillatory motion and its charge is therefore smeared. If the electron is bound by a non-uniform electric field (as in hydrogen), it experiences a different potential from that appropriate to its mean position. There is also a slight weakening of the force on the electron when it is very close to the nucleus, causing the $2s_{1/2}$ state (which has penetrated all the way to the nucleus) to be slightly higher in energy than the $2p_{1/2}$ electron. Taking into account these corrections, one obtains a positive energy shift for states with $\ell = 0$.

### Figure 4.3. The measured electric signal showing the Lamb shift.



The measured electric signal showing the Lamb shift.

This can be understood at least semiquantitatively as follows. The fluctuation in the electric and magnetic fields associated with the QED vacuum perturbs the Coulomb potential due to the atomic nucleus. This perturbation causes a fluctuation in the position of the electron, where the difference in the potential energy is given by

$$V(\mathbf{r}+\delta\mathbf{r})-V(\mathbf{r})=\delta\mathbf{r}\cdot\nabla V(\mathbf{r})+\frac{1}{2}(\delta\mathbf{r}\cdot\nabla)^2V(\mathbf{r})+\dots \qquad (4.28)$$

If we take the average in photon vacuum we get in the first term $\langle\delta\mathbf{r}\rangle=0$, because the fluctuations are isotropic. In the second term which is $\frac{1}{2}\sum_{i,j=1}^{3}\frac{\partial^2V}{\partial x_i\partial x_j}\delta x_i\delta x_j$, the mixed terms vanish, after the averaging while the ones containing the squares remain, giving $\frac{1}{2}\sum_{i=1}^{3}\frac{\partial^2V}{\partial x_i^2}\left\langle(\delta x_i)^2\right\rangle$, where each $\left\langle(\delta x_i)^2\right\rangle=\frac{1}{3}\left\langle(\delta\mathbf{r})^2\right\rangle$ because of isotropy again. Thus we have $\frac{1}{6}\left\langle(\delta\mathbf{r})^2\right\rangle\sum_{i=1}^{3}\frac{\partial^2V}{\partial x_i^2}=\frac{1}{6}\left\langle(\delta\mathbf{r})^2\right\rangle\nabla^2V(\mathbf{r})$. In the case of the Coulomb potential $\nabla^2V(\mathbf{r})=-Ze_0^2\nabla^2\frac{1}{r}=4\pi Ze_0^2\delta(\mathbf{r})$ where $\delta(\mathbf{r})$ is the 3D Dirac delta in the last expression. This is the reason why this shift appears only for $s$ states, where the value of the wave function is different from zero in the origin, thus the factor from the integral over the electron coordinate yields $4\pi Ze_0^2|\psi_{n\ell=0}|^2$ The calculation of $\left\langle(\delta\mathbf{r})^2\right\rangle$ in the photon vacuum needs the quantum theory of the electromagnetic field, which would take us too far, so we present only the result

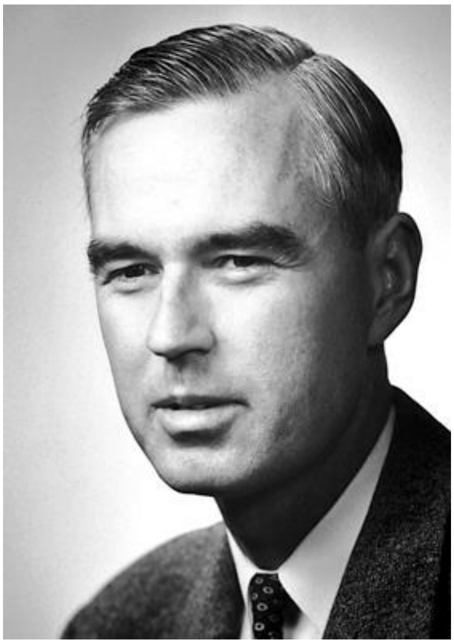
$$\Delta\varepsilon_{\text{Lamb}}=\left(\frac{Z}{n}\right)^4n\alpha^2\left(\frac{8}{3\pi}\alpha\ln\frac{1}{\alpha Z}\right)\delta_{\ell 0}\,\mathrm{Ry} \qquad (4.29)$$

As a result there is no Lamb shift for the $p$ states but there is a small increase $(\ln\frac{1}{\alpha Z}>0)$ for the $s$ state.

In the experiment of Lamb and Retherford hydrogen is thermally dissociated in a heated tungsten oven. (In modern devices, a higher degree of dissociation is achieved with a microwave discharge.) The H atoms emerging from a hole of the oven into the vacuum were collimated by an aperture into a nearly parallel atomic beam. The atoms were then excited by collisions with electrons crossing the atomic beam into the metastable $2s_{1/2}$ state of lifetime about $1\,\mathrm{second}$. (There is no dipole transition to the only lower state $1s_{1/2}$ because of the selection rule $\Delta\ell=\pm1$.) The path length of the H atoms in their excited state was therefore long enough to impinge a tungsten target, where they lost their energy, which was higher than the energy necessary to release electrons from the conduction band of W, which were collected by a detector. The rate of emitted electrons represented a small electric current that could be measured. During their flight to the detector the electrons passed a radio frequency field with a tunable frequency. When the frequency matched the energy separation $\Delta\varepsilon=\varepsilon(2s_{1/2})-\varepsilon(2p_{1/2})=4.37\times10^{-6}\,\mathrm{eV}$, corresponding to $\omega_{res}/2\pi=1.05\,\mathrm{GHz}$ (equivalent to about $\lambda_{\text{vac}}=0.3\,\mathrm{mm}$ ), then the $2s_{1/2}\to2p_{1/2}$ transition was induced by the field. As the lifetime of the $2p_{1/2}$ state is only about $2\times10^{-9}$, because it decays spontaneously into the $1s_{1/2}$ state by emitting Lyman- $\alpha$ radiation, (in contrast to the forbidden transition $2s_{1/2}\to1s_{1/2}$ ) the current in the tungsten dropped, because Hydrogen in its ground state does not excite conduction electrons in this metal. Therefore one obtained a sharp dip in the current at the resonant radio frequency, witnessing the energy difference.

The Lamb shift is very small, therefore in most cases the Schrödinger theory or its correction with the relativistic effects is sufficiently accurate to match the experimental results. Only in special cases, and in particular for high precision measurements, does the Lamb shift have to be taken into account. The presence of the Lamb shift explains, however why it makes no sense to calculate the second order correction in the perturbation expansion of the relativistic corrections ( $W_{SO}$, $W_t$, $W_D$ ), which would already be less than the Lamb shift.

**Further reading:**



The Nobel Lecture of Willis Lamb on the fine structure of the Hydrogen atom (December 12, 55), http://www.nobelprize.org/nobel_prizes/physics/laureates/1955/lamb-lecture.html

# 4. Hyperfine structure

So far, we have considered the nucleus as simply a massive point charge responsible for the large electrostatic interaction with the charged electrons which surround it. However, the nucleus has a spin angular momentum which is associated with a further set of **hyperfine corrections** to the atomic spectra of atoms. As with electrons, the protons and neutrons that make up a nucleus are fermions, each with intrinsic spin 1/2. This means that a nucleus will have some total nuclear spin which is labelled by the quantum number, $I$. Actually both the operator and the corresponding quantum number are denoted by this same letter. Thus if the operators $\mathbf{I}^2 = I_x^2 + I_y^2 + I_z^2$, and $I_z$ are diagonalized simultaneously, their eigenvectors are labelled by the quantum numbers $I$, and $M_I$ : so we can write $\mathbf{I}^2 \left|I, M_I\right\rangle = \hbar^2 I(I+1) \left|I, M_I\right\rangle$ and $I_z \left|I, M_I\right\rangle = \hbar M_I \left|I, M_I\right\rangle$.

The spin of the nucleus leads to a nuclear magnetic moment:

$$\boldsymbol{\mu}_N = g_N \frac{Zq_p}{2M_N}\mathbf{I} \qquad (4.30)$$

where $M_N$ denotes the mass of the nucleus, and $g_N$ is the nuclear gyromagnetic ratio. Since the nucleus has internal structure, the nuclear gyromagnetic ratio is not simply 2 as it (nearly) is for the electron. For the proton, the sole nuclear constituent of atomic hydrogen, $g_P = 5.56$. Even though the neutron is charge neutral, its gyromagnetic ratio is about $-3.83$. (The constituent quarks have gyromagnetic ratios of 2 (plus corrections) like the electron, but the problem is complicated by the strong interactions which make it hard to define a quark's mass.) We can compute (to some accuracy) the gyromagnetic ratio of nuclei from that of protons and neutrons as we can compute the proton's gyromagnetic ratio from its quark constituents. Since the nuclear mass is several orders of magnitude larger than that of the electron, the nuclear magnetic moment provides only a small perturbation. According to classical electromagnetism, a pointlike magnetic moment in the origin generates a magnetic field

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3}(3(\boldsymbol{\mu}_N\hat{\mathbf{r}})\hat{\mathbf{r}} - \boldsymbol{\mu}_N) + \frac{2\mu_0}{3}\boldsymbol{\mu}_N\delta(\mathbf{r}) \qquad (4.31)$$

The first term is the usual dipole field, while the second one ensures care that the divergence of $\mathbf{B}$ is zero also in the origin (see e.g. J.D. Jackson: Classical Electrodynamics). If an electron with a magnetic moment $(g_e \simeq 2)$ :

$$\boldsymbol{\mu}_e = \frac{q_0}{m_e}\mathbf{S} \tag{4.32}$$

interacts with this field, then the resulting hyperfine Hamiltonian is

$$H_{\text{hf}} = -\boldsymbol{\mu}_e\mathbf{B} = \frac{\mu_0}{4\pi r^3}(\boldsymbol{\mu}_e\boldsymbol{\mu}_N - 3(\mu_N\hat{\mathbf{r}})(\boldsymbol{\mu}_e\hat{\mathbf{r}})) - \frac{2\mu_0}{3}\boldsymbol{\mu}_N\boldsymbol{\mu}_e\delta(\mathbf{r}) - \frac{e_0}{2m_e}\frac{\mu_0}{4\pi r^3}\mathbf{L}\boldsymbol{\mu} \tag{4.33}$$

where the last term comes from the interaction of the nuclear magnetic moment and the magnetic field originating from the orbital momentum of the electron.

To explore the effect of this interaction, we shall consider the $1s$ ground state electrons, where $n=1,\ \ell=0$. Then the correction is to be calculated in the subspace corresponding to the ground state energy. This is now four dimensional, as both the electron spin and the nuclear spin are taken into account: $|n=1,\ell=0,m_\ell=0,m_S=\pm1/2,m_I=\pm1/2\rangle$ The matrix elements of the last, orbital term in $H_{\text{hf}}$ containing $\mathbf{L}$ vanishes, as $\ell=m_\ell=0$ in all of them. The first term can be shown to vanish, as well, because of the spherical symmetry of the orbital $1s$ state.

**Problem 4.9 :** Prove that the expectation value of the first term vanishes in the ground state.

Therefore the only remaining term is the one containing the Dirac $\delta(\mathbf{r})$:

$$\langle n=1,\ell=0,m_\ell=0,m'_S,m'_I| - \frac{2\mu_0}{3}\boldsymbol{\mu}_N\boldsymbol{\mu}_e\delta(\mathbf{r})\,|n=1,\ell=0,m_\ell=0,m_S,m_I \tag{4.34}$$

The importance of this term was recognized by E. Fermi, and it is called Fermi's contact term. If we go to the coordinate representation we can separate the orbital and spin parts of these matrix elements and obtain:

$$\mathcal{A}\langle m'_S,m'_I\,|\mathbf{IS}|m_S,m_I\rangle \tag{4.35}$$

where $\mathcal{A}$ is a number given by

$$\mathcal{A} = \frac{2\mu_0}{3}g_N\frac{Zq_0^2}{2M_Nm_e}\langle\psi_{100}\,|\delta^3(\mathbf{r})|\psi_{100}\rangle = \frac{2e_0^2}{3}\frac{Zg_N}{M_Nm_e}\frac{1}{4\pi}|\mathcal{R}_{10}|^2 = \frac{4}{3}g_N\frac{m_e}{M_N}m_ec^2(Z\alpha)^4\frac{1}{\hbar} \tag{4.36}$$

Now we come to the diagonalization of the operator $\mathcal{A}\mathbf{IS}$. To this end we introduce the total angular momentum $\mathbf{F}=\mathbf{I}+\mathbf{S}$. (In general we would have $\mathbf{F}=\mathbf{I}+\mathbf{S}+\mathbf{L}=\mathbf{I}+\mathbf{J}$, but $\mathbf{L}$ is not present for $s$ states.) As both $I$ and $S$ are $1/2$, (here the capital letter will be used for the spin quantum number) the values taken by $F$ can be 1, which is three times degenerate ( $M_F=0,\pm1$ ), and 0, with the only possible value $M_F=0$. Then we can use the familiar trick, and write

$$\frac{1}{2}\left(\mathbf{F}^2-\mathbf{I}^2-\mathbf{S}^2\right) = \mathbf{IS} \tag{4.37}$$

where $\mathbf{F}^2$ and $F_z$ do commute with $\mathbf{I}^2$ and $\mathbf{S}^2$ , and therefore instead of the product basis $|S=1/2,I=1/2,m_S,m_I\rangle$, it is better to use the collective basis $|F,m_F,S,I\rangle$ which are eigenvectors of $\mathbf{IS}$

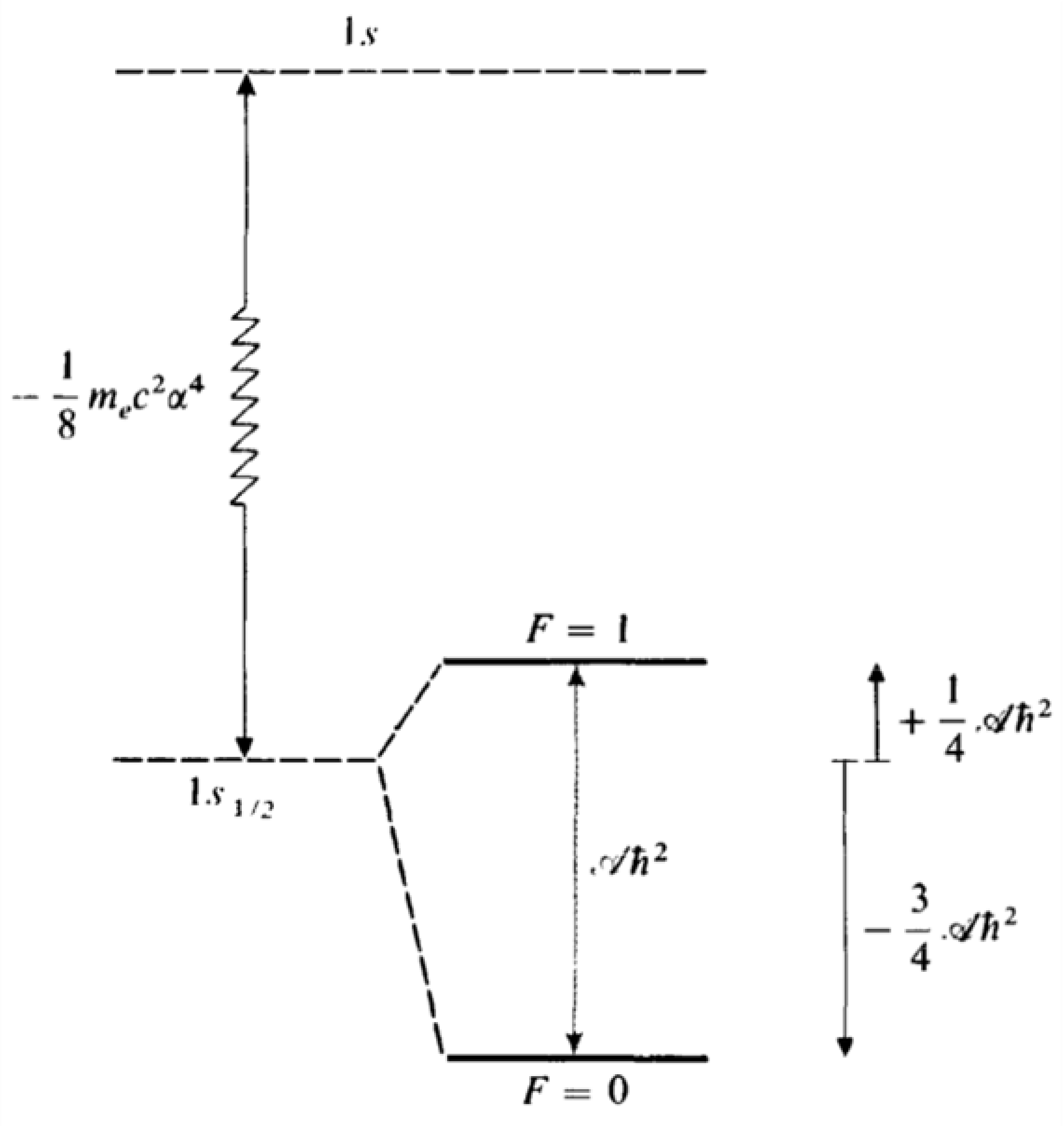
$$\begin{aligned}\mathbf{IS}|F,m_F,S,I\rangle &= \frac{1}{2}(\mathbf{F}^2-\mathbf{I}^2-\mathbf{S}^2)|F,m_F,S,I\rangle = \\ &= \frac{1}{2}\hbar^2[F(F+1)-I(I+1)-S(S+1)]|F,m_F,S,I\end{aligned} \tag{4.38}$$

Then only the diagonal matrix elements are non-zero, and we get the following corrections:

$$\begin{aligned} \frac{\mathcal{A}}{2}\hbar^2\left(2-\frac{3}{4}-\frac{3}{4}\right) &= \frac{\mathcal{A}}{4}\hbar^2, && \text{for } F=1 \ \ (2F+1=3 \text{ times degenerate} \\ \frac{\mathcal{A}}{2}\hbar^2\left(-\frac{3}{4}-\frac{3}{4}\right) &= -\frac{3\mathcal{A}}{4}\hbar^2, && \text{for } F=0, \text{ nondegenerate} \end{aligned} \tag{4.39}$$

The hyperfine splitting of the ground state is shown in Figure 4.4 .

**Figure 4.4. The effect of the fine structure Hamiltonian is a global shift down by $-m_e c^2\alpha^4/8$, with respect to the $-1\,\mathrm{Ry}$ of nonrelativistic quantum mechanics. $J$ can take only the value $J=1/2$, as $\ell=0$. When the hyperfine coupling is included, the $1s_{1/2}$ level splits into two hyperfine levels $F=1$ and $F=0$ levels. The transition between these two is the famous 21 cm line used in radioastronomy**



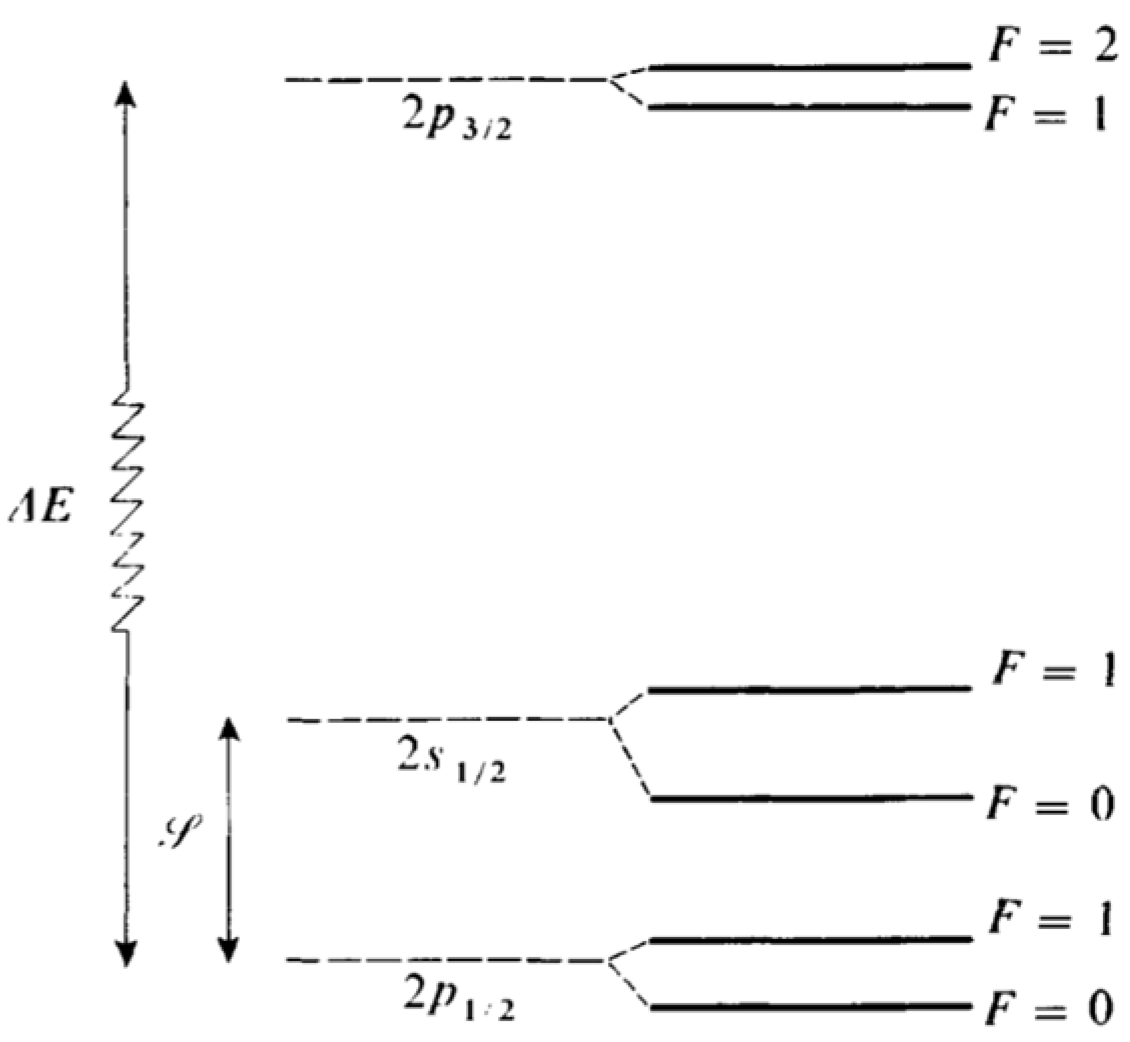
The effect of the fine structure Hamiltonian is a global shift down.

The transition frequency between the two levels $\omega = \Delta/\hbar$ is known experimentally with a very high precision, up to twelve significant digits. It is about $\omega/2\pi = 1420\,\mathrm{MHz}$ corresponding to a wavelength of $21\,\mathrm{cm}$. The frequency was measured by a Hydrogen maser. H atoms, previously sorted by magnetic methods of the Stern-Gerlach type, so as to be in their upper hyperfine state $F = 1$, are stored in a gas cell. This serves as an amplifier for the hyperfine frequency. The cell is put into a cavity that is tuned to resonance. If the losses are low enough the system becomes unstable and begins to oscillate. Its frequency can be stabilized with a high precision and yields the value of the hyperfine transition.

As cosmic space is mostly filled with atomic Hydrogen, and the energy difference between the ground state hyperfine levels is sufficiently small, a significant percent of the H atoms can be excited to the upper hyperfine state and the field emitted during the transition can be observed. Almost all information about the H distribution in space comes from these radio frequency observations.

**Problem 4.10 :** Calculate the ratio of excited H atoms at the $2.7\,\mathrm{K}$ temperature of the cosmic background radiation.

**Figure 4.5. The fine and hyperfine structure of the $n = 2$ level. The separation $\mathcal{S}$ between the two levels $2s_{1/2}$ and $2p_{1/2}$ is just the Lamb shift which is about ten times smaller than the fine structure splitting $\Delta E$ separating the two levels $2p_{1/2}$ and $2p_{3/2}$, the corresponding frequencies are $\mathcal{S} = 1057.8\,\mathrm{MHz}$ , $\Delta E = 10969.1\,\mathrm{MHz}$ . When the hyperfine splitting is taken into account, each level splits into two sublevels. The hyperfine splittings here are much smaller than for the ground state $23.7\,\mathrm{MHz}$ for $2p_{3/2}$ ; $177.56\,\mathrm{MHz}$ for $2s_{1/2}$ and $59.\,\mathrm{MHz}$ for the $2p_{1/2}$ level.**



The fine and hyperfine structure of the n=2 level. The separation S between the two levels is just the Lamb shift which is about ten times smaller than the fine structure splitting. The corresponding frequencies are 1057.8 MHz, 10969.1 MHz. When the hyperfine splitting is taken into account, each level splits into two sublevels. The hyperfine splittings here are much smaller than for the ground state .

For completeness we also show the hyperfine splitting for the $n = 2$ level of the H atom in Figure 4.5 . These can also be calculated, but we omit here the details.

A further contribution to the hyperfine structure arises if the nuclear shape is not spherical thus distorting the Coulomb potential; this occurs for deuterium and for many other nuclei.

Finally, before leaving this section, we should note that the nucleus is not point-like but has a small size. The effect of finite nuclear size can be estimated perturbatively. In doing so, one finds that the $s$ levels are those most effected, because these have the largest probability of finding it close to the nucleus. This effect is even more pronounced for the so-called muonic atoms. If a muon $\mu^-$ (which differs from the electron only by its mass, it is about 207 times heavier) is captured by an atom, the corresponding Bohr radius is 207 times smaller, thus enhancing the nuclear size effect, but the effect is still very small in hydrogen. It can be significant, however, in atoms of high nuclear charge $Z$, e.g. for lead, where the Bohr radius is already of the order of the nuclear radius, the latter being $8.5 \cdot 10^{-15}\,\mathrm{m}$.

**Problem 4.11 :** Calculate the first Bohr radius for a muon in the field of a Pb nucleus.

If one of the electrons is substituted by a muon, then it will be much closer to the lead nucleus and it is practically unaffected by the repulsion of the other electrons, which are located much.more outside. The muon will be essentially inside the nucleus and the energy corresponding to this volume effect should then be calculated by other methods. One simple model is presented in the following problem.

**Problem 4.12 :** Assume that - instead of being point-like - the proton in the H atom is a sphere of radius $r_0$, with a uniformly distributed elementary charge $q_0$. The potential energy of the electron is then

$$V(r) = \begin{cases} -\frac{e_0^2}{2r_0}\left(3 - \frac{r^2}{r_0^2}\right) & r < r_0 \\ -\frac{e_0^2}{r} & r > r_0 \end{cases} \tag{4.40}$$

where $e_0^2 = q_0^2/4\pi\epsilon_0$.

- Show the validity of this potential by using the laws of electrostatics.
- Calculate perturbatively the first order energy correction in the ground state by using coordinate representation.

# Chapter 5. Energy levels of the He atom

**Goals:** To begin the study of atoms with more than one electron, we investigate in this chapter the He atom, which represents the simplest atom with two electrons. The theory is based on the solution of the Coulomb problem, perturbation theory and the addition of angular momenta treated in the previous chapters. We shall also make use of the prescription of antisymmetry (Pauli principle) for the two-electron problem. The electronic structure of He will help us to understand the building up principle of the electron shells of atoms with several electrons. **Prerequisites:** Coulomb problem (Chapter 1 ), perturbation theory (Chapter 2 ) and the addition of angular momenta (Chapter 3 ), Pauli-principle.

## 1. Introduction

In atoms with more than one electron additional problems arise that are caused by mutual electrostatic interaction between the electrons. Another complication in quantum physics that we also have to take into account the requirement of antisymmetry of the state vector if two electrons are exchanged. We will first study these phenomena for the helium atom, which represents the simplest system with two electrons. Another reason for considering He is that He gas and liquid Helium at low temperatures are very important technological materials and show unusual macroscopic properties, the most spectacular of which is superfluidity. These can be understood only on the basis of quantum mechanics.

The electronic structure of He will help us understand the building up principle for the structure of electron shells for larger atoms. We will see that the electron configurations for all atoms can be obtained from the minimum energy principle, the correct coupling of the different angular momenta of the electrons and the observation of certain symmetry rules. This results in the determination of all possible energy states of the atoms and the characterization of these states by quantum numbers.

In this chapter we will study all the He like ions, those that have a number $Z \geq 2$ protons in their nuclei and two electrons. In the specific case of the He atom $Z = 2$. We restrict ourselves to the nonrelativistic variant of the simple perturbed Coulomb problem, where the Hamiltonian of the system takes the following form:

$$H = H_1 + H_2 + \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_2|} \tag{5.1}$$

with

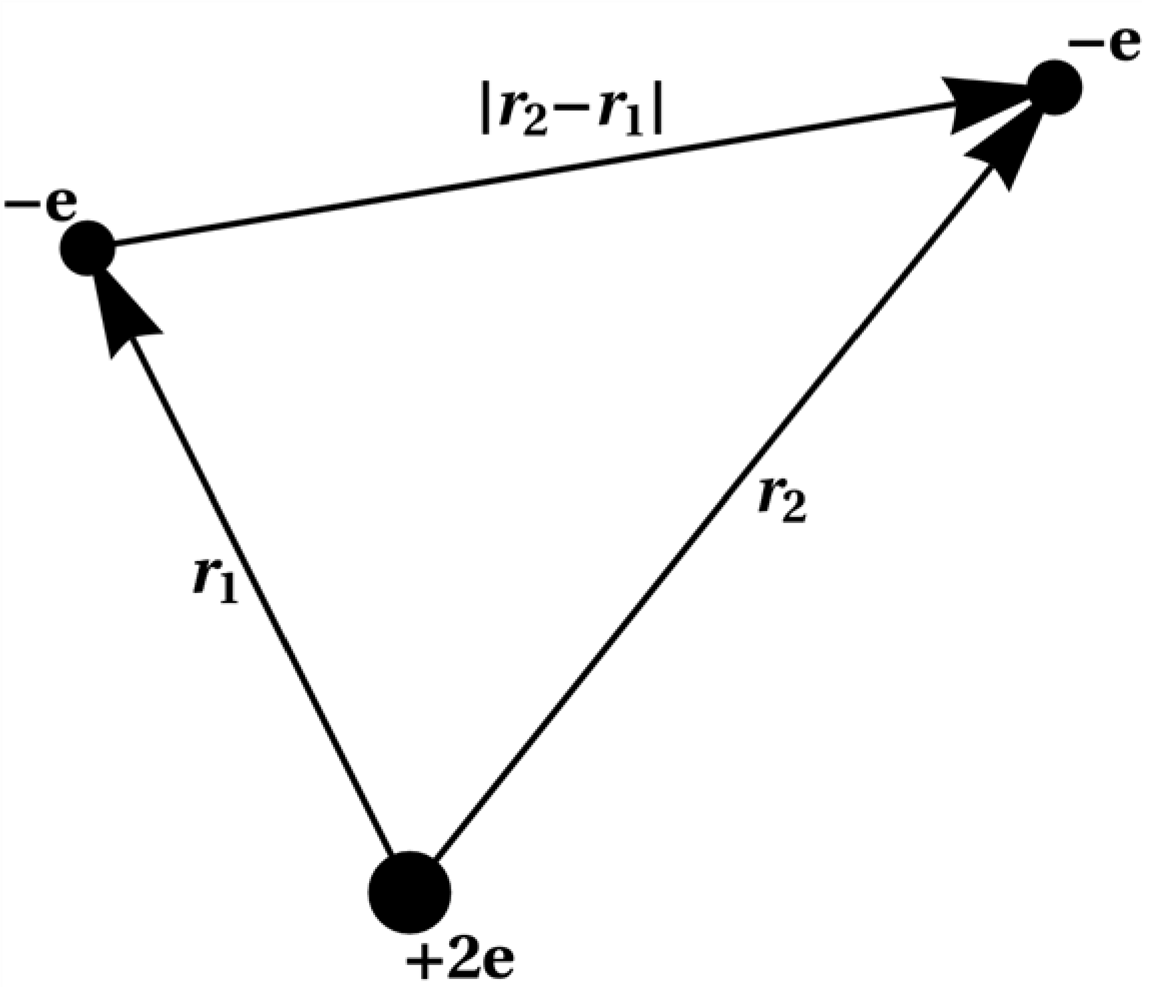
$$H_i = \frac{P_i^2}{2m} - \frac{Ze_0^2}{|\mathbf{R}_i|} \quad i = 1, 2 \tag{5.2}$$

which is the Hamiltonian of a single Hydrogen like ion with nuclear charge $Ze_0$. (We recall the convention that $e_0^2 = q_0^2/4\pi\epsilon_0$ where $q_0$ is the elementary charge measured in Coulombs, and $(4\pi\epsilon_0)^{-1} = 9 \cdot 10^9 \mathrm{Nm}^2/\mathrm{C}^2$ in SI units.) The sum $H_1 + H_2$ represent two independent electrons, and

$$W = \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_2|} \tag{5.3}$$

is the interaction between the two electrons repelling each other. We shall consider the interaction $W$ as a perturbation, and we first we recall the energy eigenvalues of $H_1 + H_2$, as well as the corresponding eigenstates with the antisymmetry principle take in to account.

**Figure 5.1. Coordinate system used for the helium atom**



Coordinate system used for the helium atom

**Problem 5.1 :** Write down the Hamiltonian in coordinate representation.

## 2. The eigenvalues in the zeroth approximation

The solution of the eigenvalue problem for each of the $H_i$ -s is known from the quantum mechanics of the simple Coulomb potential:

$$H_i \left|\psi_{n_i l_i m_i}\right\rangle = \varepsilon_{n_i} \left|\psi_{n_i l_i m_i}\right\rangle \quad (5.4)$$

where the eigenvalues are:

$$\varepsilon_{n_i} = -\frac{Z^2}{n_i^2} \quad (5.5)$$

measured in Rydbergs $(1\,\mathrm{Ry} = me_0^4/2\hbar^2)$ and the stationary states are labelled by angular momentum quantum number $0 \leq l_i < n$, and the magnetic quantum number $|m_i| \leq l_i$. If we neglect spin for a moment, then these correspond to the CSCO $H,\ L^2$ and $L_z$. As it is known the energy eigenvalue given by the principal quantum number $n_i$, is $n_i^2$ -fold degenerate without the spin.

It is obvious that the tensorial products of the solutions of the individual eigenvalue problems of the $H_i$ -s will be the solutions of the unperturbed eigenvalue problem. Using the notation $|\varphi_{n_i l_i m_i}\rangle = |n_i l_i m_i\rangle$, denoting the orbital part of the state we have:

$$(H_1 + H_2)\,|n_1 l_1 m_1\rangle\,|n_2 l_2 m_2\rangle = \varepsilon_{n_1 n_2}\,|n_1 l_1 m_1\rangle\,|n_2 l_2 m_2\rangle \qquad (5.6)$$

where

$$\varepsilon_{n_1 n_2} = \left(-\frac{Z^2}{n_1^2} - \frac{Z^2}{n_2^2}\right) \qquad (5.7)$$

The product states $|n_1 l_1 m_1\rangle\,|n_2 l_2 m_2\rangle$, however do not obey the antisymmetrization postulate valid for fermions and therefore they cannot be true eigenfunctions of a two-electron operator. We could, of course antisymmetrize these product states, but before doing so we shall have to make use of the spin degree of freedom of the electrons, as well, in spite of the fact that the Hamiltonian ( 5.1 ) is independent of the spin. The spin variable will play an implicit, but still important role in the symmetry properties of the two-particle states, which must be taken into account before we proceed.

**Problem 5.2 :** Recall the Coulomb eigenfunctions in coordinate representation and write down the explicit form of the products $|n_1 l_1 m_1\rangle\,|n_2 l_2 m_2\rangle$.

As in this nonrelativistic approximation the $H$ operator does not contain the spin operators of the electrons $H$ commutes with $\mathbf{S}_1$ and $\mathbf{S}_2$. Therefore by simply multiplying the two-electron orbital states with any of a two-electron spin state, the resulting state will remain an eigenstate of $H$.

From the point of view of antisymmetrization it is important that the collective spin states of the two electrons that are eigenstates of $\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2$, as well as of $S_z = S_{1z} + S_{2z}$, with respective eigenvalues $\hbar^2 s(s+1)$ and $\hbar m_s$, are the singlet state:

$$|\chi_a\rangle = \frac{1}{\sqrt{2}}(|+\rangle_1\,|-\rangle_2 - |-\rangle_1\,|+\rangle_2) \qquad s = 0, m_s = 0 \qquad (5.8)$$

which is antisymmetric, and the three triplet states:

$$\begin{aligned} |\chi_{s,1}\rangle &= |+\rangle_1\,|+\rangle_2 & s = 1, m_s = 1 \\ |\chi_{s,0}\rangle &= \tfrac{1}{\sqrt{2}}(|+\rangle_1\,|+\rangle_2 + |-\rangle_1\,|-\rangle_2) & s = 1, m_s = 0 \\ |\chi_{s,-1}\rangle &= |-\rangle_1\,|-\rangle & s = 1, m_s = -1 \end{aligned} \qquad (5.9)$$

that are symmetric with respect of the exchange of the two particles. Accordingly, the total state can be made antisymmetric in one of the following two ways. We symmetrize the orbital part and multiply it by the antisymmetric spin state, or we take an antisymmetrized orbital and multiply it with a symmetric spin state:

$$\left|{}^1\Psi\right\rangle = |\psi_s\rangle\,|\chi_a\rangle \qquad \left|{}^3\Psi\right\rangle = |\psi_a\rangle\,|\chi_s\rangle \qquad (5.10)$$

where $|\psi_s\rangle$ and $|\psi_a\rangle$ are obtained by symmetrizing and antisymmetrizing the product $|n_1 l_1 m_1\rangle\,|n_2 l_2 m_2\rangle$. The total state which must be always antisymmetric will be denoted by $|{}^1\Psi\rangle$ and $|{}^3\Psi\rangle$ respectively. Our notation follows the spectroscopic convention where the multiplicity of the spin state, which is equal to $2s+1$, is put as an upper left index to the sign of the state. In the case of two electrons as in He, the multiplicity is either 1: spin singlet, or $3$ : spin triplet.

Let us investigate first in more detail the state of lowest energy which is the ground state. The value given by ( 5.7 ) is the smallest when $n_1 = n_2 = 1$, and accordingly its value is:

$$\varepsilon_{1,1} = -2Z^2(\mathrm{Ry}) \qquad (5.11)$$

which in the case of the Helium atom $(Z=2)$ is $\varepsilon_{1,1} = -8\,\mathrm{Ry}$. The energy given by $n_1 = n_2 = 1$ cannot be degenerate without spin) the orbital part of the corresponding eigenvector can be only the symmetric state $|n_1=1, l_1=0, m_1=0\rangle |n_2=1, l_2=0, m_2=0\rangle = |1,0,0\rangle |1,0,0\rangle$ , which cannot be antisymmetrized.

Therefore the total ground state in the zeroth approximation is:

$$\left|1^1 S_0\right\rangle = |1,0,0\rangle\,|1,0,0\rangle\,|\chi_a\rangle \tag{5.12}$$

having a symmetric orbital part and an antisymmetric spin singlet part. The notation $1^1 S_0$ will be explained below.

Let us consider now the excited states, in which one of the principal quantum numbers $n$ must be greater than 1. It seen, however, that in growing sequence of energy first those levels come where one of the $n$ -s is increased by one, while the other remains 1:

$$\varepsilon_{n,1} = -Z^2\left(\frac{1}{n^2} + 1\right) \tag{5.13}$$

with $n = 2, 3, \ldots$. This is because all these values, including the limiting case $n = \infty$, (when it is $\varepsilon_{\infty,1} = -Z^2$ ) are smaller, than the energy value corresponding to $n_1 = n_2 = 2:\ \varepsilon_{2,2} = -Z^2/2$. The limit $n_1 = \infty, n_2 = 1$ means that the energy of one of the electrons became zero, thus it went out to infinity, so in case of $Z = 2$ the He atom is ionized, or for an ion with $Z > 2$ the ion lost an additional electron. In the case of He therefore energy is usually measured from the value $-Z^2 = -4\,\mathrm{Ry}$, rather than from 0, the latter means a state of doubly ionized He. The ground state which is $-8\,\mathrm{Ry}$ on the original scale, see ( 5.11 ) turns out then to be only $-4\,\mathrm{Ry}$, which is the energy needed to remove one of the electrons from the atom, or in other words the energy of single ionization, at lest in this zeroth approximation. The levels $n_1 = n_2 = 2$ and above this, fall into the continuous unbound energy spectrum of the singly ionized He atom: $\mathrm{He}^+$. The experimental observation of these states is not simple, because giving the appropriate resonant energy to the atom, instead of staying on the $n_1 = n_2 = 2$ level, one of the electrons goes back to the ground state, while the other one leaves the atom and takes away the rest of the energy in the form of positive kinetic energy. This process is called **autoionization**. Real bound states are therefore only those where one of principal quantum numbers is one: $n = 1$, while the other is $< \infty$. The corresponding antisymmetric states are then the following ones:

$$\begin{aligned} \left|{}^1\Psi\right\rangle &= \tfrac{1}{\sqrt{2}}\left(|1,0,0\rangle_1\,|n,l,m\rangle_2 + |1,0,0\rangle_2\,|n,l,m\rangle_1\right)|\chi_a\rangle \\ \left|{}^3\Psi\right\rangle &= \tfrac{1}{\sqrt{2}}\left(|1,0,0\rangle_1\,|n,l,m\rangle_2 - |1,0,0\rangle_2\,|n,l,m\rangle_1\right)|\chi_s\rangle \end{aligned} \tag{5.14}$$

from which we see again that the ground state - where both $n$ -s are 1 - can only be a singlet state The notation of these states is based on a convention stemming from practical spectroscopy. The sign is $n^{2s+1}L_j$ where $n$ is the principal quantum number in the kets above, In the place of $L$ we put one of the letters $S, P, D, F \ldots$ depending on the values of $l = 0, 1, 2, 3 \ldots$, $j$ is the quantum number labelling the eigenvalue of total angular momentum $\mathbf{J}^2$, which we know to be an integer now between $l + s$ and $|l - s|$, as now the value of $s$ is an integer 0 or 1. For a singlet $(s = 0)$ we have obviously $j = l$. For triplet $(s = 1)$, when $l = 0$, i. e. for an $S$ state $j$ can be only $j = s = 1$, while for $l > 0$ it may take three possible values: $j = l + 1, l, l - 1$. The possible stationary states are therefore the following ones:

## Table 5.1. Possible stationary states

| energy $(\mathrm{Ry})$ | singlet | triplet |
|---|---|---|
| $\varepsilon_{1,1} = -2Z^2$ | $1^1S_0$ | - |

| | | |
|---|---|---|
| $\varepsilon_{2,1}=-\frac{5}{4}Z^2$ | $2^1S_0,\ 2^1P_1$ | $2^3S_1,\ 2^3P_{2,1,0}$ |
| $\varepsilon_{3,1}=-\frac{10}{9}Z^2$ | $3^1S_0,\ 3^1P_1,\ 3^1D_2$ | $3^3S_1,\ 3^3P_{2,1,0}, 3^3D_{3,2,1}$ |
| $\vdots$ | $\vdots$ | $\vdots$ |

**Problem 5.3 :** Determine the degeneracy of the energy eigenvalues $\varepsilon_{n,1}$.

The energy values belonging to the states found in the same rows of the above table are identical in this zeroth i.e. nonperturbed approximation. The state $1^3S_0$ does not exist because antisymmetry ( 5.14 ) then requires the orbital part to vanish.

# 3. First order energy corrections

Let us take now into account the electron-electron interaction described by the term $\frac{e_0^2}{|R_1-R_2|}$ and calculate the first order correction perturbatively. Note that because of this interaction the total Hamiltonian $H$ does not commute any more with the components of the orbital angular momenta separately $\mathbf{L}_1$ and $\mathbf{L}_2$. Their sum is however still a constant of motion, and therefore the eigenvalues of $\mathbf{L}^2=(\mathbf{L}_1+\mathbf{L}_2)^2$ remain good quantum numbers, and the same is true for $\mathbf{S}$, as well as for the total angular momentum $\mathbf{J}=\mathbf{L}+\mathbf{S}$. As the perturbation does not depend on the spin, when we calculate the matrix elements of the interaction term, the spin parts give $\langle\chi_a|\chi_a\rangle=1$, etc. Therefore, as we will see, the spin part will influence the result only implicitly through the symmetry properties of the orbital part.

## 3.1. Ground state

The ground state is nondegenerate, and the first order energy correction is:

$$\Delta^1\varepsilon_{11}=\langle 1,0,0|_1\,\langle 1,0,0|_2\,\frac{e_0^2}{|\mathbf{R}_1-\mathbf{R}_2|}\,|1,0,0\rangle_1\,|1,0,0\rangle_2 \tag{5.15}$$

We shall calculate the explicit value of this correction in coordinate representation.

$$\begin{aligned}\Delta^1\varepsilon_{11}&=e_0^2\int\frac{\psi_{100}^*(\mathbf{r}_1)\psi_{100}^*(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3r_1d^3r_2=\\&=e_0^2\int\frac{|\psi_{100}(\mathbf{r}_1)|^2|\psi_{100}(\mathbf{r}_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\mathbf{r}_1d^3\mathbf{r}_2\end{aligned} \tag{5.16}$$

We remind that the normalized ground state wave function of the Coulomb problem (H atom) is:

$$\langle\mathbf{r}|1,0,0\rangle=\psi_{100}(\mathbf{r})=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp(-Zr/a_0), \tag{5.17}$$

where $a_0$ is the Bohr radius. Therefore

$$\Delta^1\varepsilon_{11}=\left[\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\right]^2 e_0^2\int d^3r_1d^3r_2\frac{\exp(-2Zr_1/a_0-2Zr_2/a_0)}{|\mathbf{r}_1-\mathbf{r}_2|} \tag{5.18}$$

The integral can be calculated by going over to spherical coordinates:

$$\frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^6 e^2 \int r_1^2 dr_1 \int r_2^2 dr_2 \int d\Omega_1 \int d\Omega_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \exp\left\{-2Z(r_1 + r_2)/a_0\right\} \tag{5.19}$$

Omitting the technical details, we present the result:

$$\Delta^1 \varepsilon_{11} = \frac{5}{4} Z \frac{e_0^2}{2a_0} = \frac{5}{4} Z\,\mathrm{Ry} \tag{5.20}$$

which is $\frac{5}{2}\,\mathrm{Ry}$ for He. The correction is positive as expected, because the electrons repel each other. This means that first order perturbation theory gives the following ground state energy, which is the negative of the energy of double ionization for He $(Z = 2)$:

$$\varepsilon_{11} = (-8 + \frac{5}{2})\,\mathrm{Ry} = \frac{11}{2}\,\mathrm{Ry} = -74.8\,\mathrm{eV} \tag{5.21}$$

This is to be compared with the experimental value: $-79.0\,\mathrm{eV}$. It is sometimes better to compare these values with the ground state energy of *singly* ionized He, which is $-4\,\mathrm{Ry} = -54.4\,\mathrm{eV}$. Therefore according to perturbation theory the energy necessary to ionize singly a He atom is $20.4\,\mathrm{eV}$, while the experimental value is $24.57\,\mathrm{eV}$. Below we shall see another procedure (the variational method) which yields a much better value than first order perturbation approximation.

## 3.2. Excited states, exchange interaction

As it is seen in Table 5.1 the excited states are degenerate. Then according to degenerate perturbation theory, in principle we should calculate the matrix elements of the interaction operator in the basis formed by the unperturbed states of the given degenerate energy level. These are the ones found in a single row of the table. Note that each state with a total angular momentum quantum number $j$ is still $2j + 1$ times degenerate. The corrections are the eigenvalues of the matrix of $W$. It turns out, however that the off-diagonal matrix elements of the perturbation operator all vanish in that basis, so we have to calculate only the diagonal elements. This can be seen as follows. $W$ is independent of spin, and because of the orthogonality of the spin states: $\langle \chi_a | \chi_s \rangle = 0$, the matrix elements between singlet and triplet states vanish. We write down here only the diagonal correction,which is different for the singlet and the triplet, and we do not care of the fine structure of the energy levels. The diagonal elements are then the following:

$$\begin{aligned} \Delta\varepsilon_{n1}^{1,3} &= \frac{e_0^2}{2} \int \frac{|\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \pm \psi_{100}(\mathbf{r}_2)\psi_{nlm}(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3r_1 d^3r_2 = \\ &= \frac{e_0^2}{2} 2 \int \frac{|\psi_{100}(\mathbf{r}_1)|^2 |\psi_{nlm}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3r_1 d^3r_2 \pm \\ &\pm e_0^2 2\mathrm{Re} \int \frac{\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2)\psi_{100}^*(\mathbf{r}_2)\psi_{nlm}^*(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3r_1 d^3r_2 \end{aligned} \tag{5.22}$$

where the upper $+$ or $-$ sign correspond to the singlet or the triplet state respectively. It can be shown that it is sufficient to perform the calculations for $m = 0$. The integrals can be calculated in a closed form, what is essential, however, for us is that the result can bee written as

$$\Delta\varepsilon_{n1}^{1,3} = K_{n,l} \pm J_{n,l} \tag{5.23}$$

where $K_{n,l}$ is the first term of ( 5.22 ) and this is called the Coulomb integral, while the second one, $J_{n,l}$ is the so called exchange integral. Both of them are positive. The reason of this terminology is that $K_{n,l}$ is exactly the energy of the Coulomb repulsion of two charge densities of the form $e_0 |\psi(\mathbf{r})|^2$, whereas the second term $J_{n,l}$ is a consequence of the antisymmetrization, i.e. it's appearance is a typical quantum effect, it has no classical counterpart. So while the Hamiltonian $H$ does not depend on spin, the requirement of antisymmetry of the total state leads to a dependence of the energy on whether the spin states are symmetric or antisymmetric, and in this first order approximation the energy of the triplet state is by $2J_{n,l}$ lower than that of the singlet. That is why in table ( 5.1 ) the energies belonging to the states in the right column are lower. Perturbation thus splits the unperturbed energy level, and the singlet-triplet degeneracy is resolved. The difference arising because of the exchange interaction is of the order of a few tens of electronvolts.

This result can be reformulated in another way. Let us use $\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2$ and its consequence $2\mathbf{S}_1\mathbf{S}_2 = \mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2$ for the two electron spin operators. Then we see that both $|\chi_a\rangle$ and $|\chi_s\rangle$ is an eigenvector of $2\mathbf{S}_1\mathbf{S}_2$ because they are eigenvectors of all three operators $\mathbf{S}^2$, $\mathbf{S}_1^2$, and $\mathbf{S}_2^2$, and we have:

$$2\mathbf{S}_1\mathbf{S}_2\,|\chi_{a,s}\rangle = \left(\hbar^2 s(s+1) - 2\times\frac{3}{4}\hbar^2\right)|\chi_{a,s}\rangle \tag{5.24}$$

where $s(s+1)$ takes the value 0 for $|\chi_a\rangle$ and 2 for $|\chi_s\rangle$.Then $\frac{2\mathbf{S}_1\mathbf{S}_2}{\hbar^2}$ transforms $|\chi_a\rangle$ to $-\frac{3}{2}\,|\chi_a\rangle$, and for $|\chi_s\rangle$ to $+\frac{1}{2}\,|\chi_s\rangle$. Therefore the first order correction can be written as an effective spin-dependent operator of the form:

$$\tilde{W} = K_{n,l} - \frac{J_{n,l}}{2} - \frac{2J_{n,l}}{\hbar^2}\mathbf{S}_1\mathbf{S}_2 \tag{5.25}$$

the matrix elements of which give just the required result ( 5.23 ) depending on the multiplicity (singlet or triplet) of the spin state. This effect is called exchange interaction, first recognized by Heisenberg.

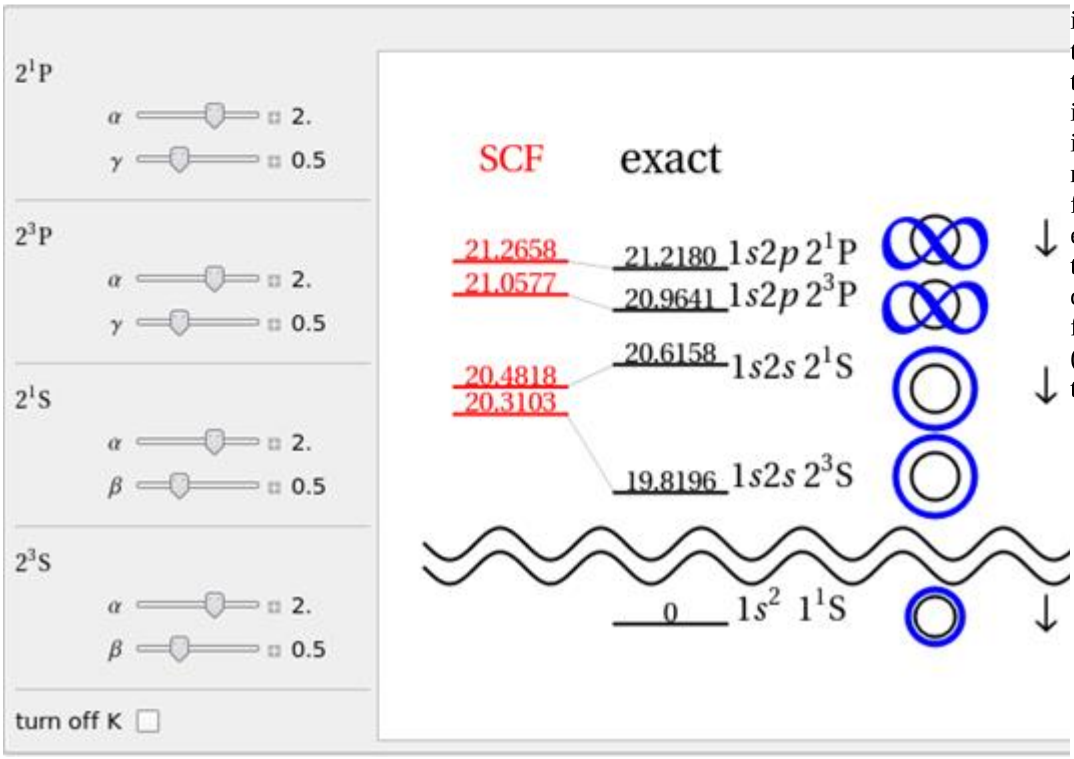
We note that this is the reason of the spin-dependent interaction of neighbouring atoms in solids, which is thus not related to the magnetic moments of the atoms depending on their spin. The magnetic interaction is many orders of magnitude smaller than $J_{n,l}$. The exchange interaction is effective through the symmetry properties of the orbital states. This interaction lies behind the ferromagnetic or antiferromagnetic behaviour in certain bulk materials, which is studied extensively in statistical physics.

As we have seen the energy levels of singlet and triplet He are different a little and only a spin dependent electromagnetic interaction could trigger a transition between them. Such interactions are extraordinary weak, so practically no such interactions can be observed. Therefore before the quantum-mechanical theory of the He, it was thought that there exist two different types of He the singlet, called parahelium and the triplet called orthohelium. The ground state is energy belongs to parahelium, and orthohelium which can be created through collisions from parahelium with close energy are very stable.

Let us add that in reality the spin orbit interaction, which is the strongest among the relativistic effects, causes an additional splitting of the triplet states, and their triplet structure, i. e. three different energy levels can be observed in the experiments. This splitting is however of the order of $10^{-4}\,\mathrm{eV}$, which is much smaller than the singlet triplet splitting $2J_{n,l}$.

**Animation:**

On this interactive animation we can investigate the lower excited states of a Helium atom. We can switch on and off the effect of exchange



$2^1$P
α 2.
γ 0.5

$2^3$P
α 2.
γ 0.5

$2^1$S
α 2.
β 0.5

$2^3$S
α 2.
β 0.5

turn off K ☐

interaction to see how this interaction is responsible for the effect of the spin degrees of freedom (singlet, triplet).

# 4. The Ritz variational method and the ground state energy of Helium

**Goals:** First we get acquainted with a simple but very powerful method -the Ritz variational method -that enables one to get a **good approximate value for the ground state energy** of a quantum mechanical system.

Than we will apply this variational method to calculate the **ground state energy of He**.

## 4.1. The Ritz method

Let us consider an arbitrary quantum system given by the Hamiltonian $H$. We show now that the expectation value $\langle\psi|H|\psi\rangle$ calculated in an **arbitrary normalized state** $\psi$**, is always larger than the smallest eigenvalue** $\varepsilon_0$ **of** $H$.

In order to prove that statement, we expand $|\psi\rangle$ in the basis formed by the complete system of the mutually orthogonal and normalized eigenvectors $|u_k\rangle$ of $H$. $|\psi\rangle=\sum_k c_k|u_k\rangle$, where $c_k=\langle\psi|u_k\rangle$. Then the following inequality can be written down:

$$\begin{aligned}\langle\psi|H|\psi\rangle = & \sum_k\langle\psi|H|u_k\rangle\langle u_k|\psi\rangle=\sum_k\varepsilon_k\langle\psi|u_k\rangle\langle u_k|\psi\rangle= \\ & =\sum_k\varepsilon_k|\langle\psi|u_k\rangle|^2\geq\varepsilon_0\sum_k|\langle\psi|u_k\rangle|^2=\varepsilon_0,\end{aligned}\qquad(5.26)$$

where $\varepsilon_0$ is the smallest eigenvalue of $H$. As a consequence, if we take an arbitrary normalized state which is now depending on an appropriately chosen set of parameters $\{\beta_i\}\equiv\boldsymbol{\beta}$, and we look for the minimum of the function $F(\boldsymbol{\beta})=\langle\psi(\boldsymbol{\beta})|H|\psi(\boldsymbol{\beta})\rangle$ of several variables, this minimum will be an upper bound of the ground state energy. By simple intuition we can expect that the more the number of the parameters we choose, the closer we get to the exact ground state energy. If accidentally the trial function coincides with the true ground state at a certain set of values $\{\beta_i^0\}=\boldsymbol{\beta}^0$ we can get in this way the true ground state energy.

As to how to choose a "good" probing function, intuition can be gained from the nature of the physical problem. In spite of the empirical observation that using sufficiently many parameters the value of $a_0$ can be approximated with a great precision, one must not think that the state providing the minimal energy is a good approximation of the ground state wave function, as well. Or, stated in another way a variational trial function and the ground state are not necessarily close at all to each other in state space, while the corresponding energies are near to each other.

# 5. The ground state energy of the He atom

We shall determine now the ground state energy of He with the variational method. As trial function we choose the product of two $1s$ type hydrogenic states, but with an effective nuclear charge $Z^*$, different from $Z=1$ or $Z=2$. We shall use coordinate representation:

$$\psi(\mathbf{r}_1,\mathbf{r}_2;Z^*)=\tilde{\varphi}_{1,0,0}(\mathbf{r}_1)\tilde{\varphi}_{1,0,0}(\mathbf{r}_2)=\left[\frac{1}{\sqrt{\pi}}\left(\frac{Z^*}{a_0}\right)^{3/2}\right]^2 e^{-Z^*(r_1+r_2)/a_0}, \tag{5.27}$$

and let $Z^*$ the variational parameter. We write the Hamiltonian in the form:

$$H=\frac{P_1^2}{2m}+\frac{P_2^2}{2m}-\frac{Ze_0^2}{R_1}-\frac{Ze_0^2}{R_2}+\frac{e_0^2}{|R_1-R_2|}=\frac{P_1^2}{2m}-\frac{Z^*e_0^2}{R_1}+\frac{P_2^2}{2m}-\frac{Z^*e_0^2}{R_2}- \\ -(Z-Z^*)e_0^2\left(\frac{1}{R_1}+\frac{1}{R_2}\right)+\frac{e_0^2}{|\mathbf{R}_1-\mathbf{R}_2|} \tag{5.28}$$

Then we obtain

$$\langle\psi|H|\psi\rangle=2\left\langle\tilde{\varphi}(1)\left|\frac{P_1^2}{2m}-\frac{Z^*e_0^2}{R_1}\right|\tilde{\varphi}(1)\right\rangle\varepsilon_1(Z^*)-2(Z-Z^*)\left\langle\tilde{\varphi}(1)\left|\frac{e_0^2}{R_1}\right|\tilde{\varphi}(1)\right\rangle+\left\langle\psi\left|\frac{e_0^2}{|\mathbf{R}_1-\mathbf{R}_2|}\right|\psi\right. \tag{5.29}$$

The factor 2 here and in the next term arises, because we have *two* identical and independent electrons in all but the last term in ( 5.28 ). The first term is just $2\varepsilon_1(Z^*)$, the exact ground state energy of a Coulomb problem corresponding to the effective nuclear charge $Z^*$. This term comes from the first four terms in ( 5.28 ). Making a small trick in the second term above, we get then

$$\langle\psi|H|\psi\rangle=2\varepsilon_1(Z^*)+2\frac{(Z-Z^*)}{Z^*}\left\langle\tilde{\varphi}(1)\left|-\frac{Z^*e_0^2}{R_1}\right|\tilde{\varphi}(1)\right\rangle+\left\langle\psi\left|\frac{e_0^2}{|\mathbf{R}_1-\mathbf{R}_2|}\right|\psi\right. \tag{5.30}$$

In the second term we have than the expectation value of $-\frac{Z^*e_0^2}{R_1}$ which is again the potential energy operator of a hydrogenic atom with effective charge $Z^*$. Knowing the ground state wave function $\tilde{\varphi}_{1,0,0}(\mathbf{r}_1)$ one can calculate it by integrating $e^{-2Z^*r_1/a_0}/r_1$ which is the product of the square of the ground state wave function and the $1/r_1$ factor coming from the potential.

The other option is to use the virial theorem stating that in any system of particles kept together with Coulomb forces the expectation value of the kinetic and potential energies are connected by the equation:

$$\langle E_{kin}\rangle=-\frac{1}{2}\langle V\rangle. \tag{5.31}$$

(More generally, if the potential is homogeneous function of order $k$ of the coordinates, then $\langle E_{kin}\rangle=\frac{k}{2}\langle V\rangle$ holds. In the case o fan oscillator $k=2$, for a Coulomb field $k=-1$.

As in the case of the potential $-\frac{e_0^2Z^*}{R_1}$ we have in the state $\tilde{\varphi}$ :

$$\langle E_{kin} + V(Z^*) \rangle = \varepsilon_1(Z^*), \tag{5.32}$$

the difference of ( 5.31 ) and ( 5.32 ) we obtain

$$\langle V \rangle = 2\varepsilon_1(Z^*) \tag{5.33}$$

therefore the second term of ( 5.29 ) gives:

$$2\frac{(Z - Z^*)}{Z^*} 2\varepsilon_1(Z^*) = -4\frac{(Z - Z^*)}{Z^*}(Z^*)^2 = -4(Z - Z^*)Z^* \tag{5.34}$$

as we know that iff expressed in Rydbergs, we know from the solution for the Coulomb problem that $\varepsilon_1(Z^*) = -1(Z^*)^2\,\mathrm{Ry}$. The third term is just the first order perturbation correction, which we have already calculated in Section 5.3 for the real nuclear charge $Z$. Here we have only to substitute $Z^*$ in place of $Z$ and we get the result:

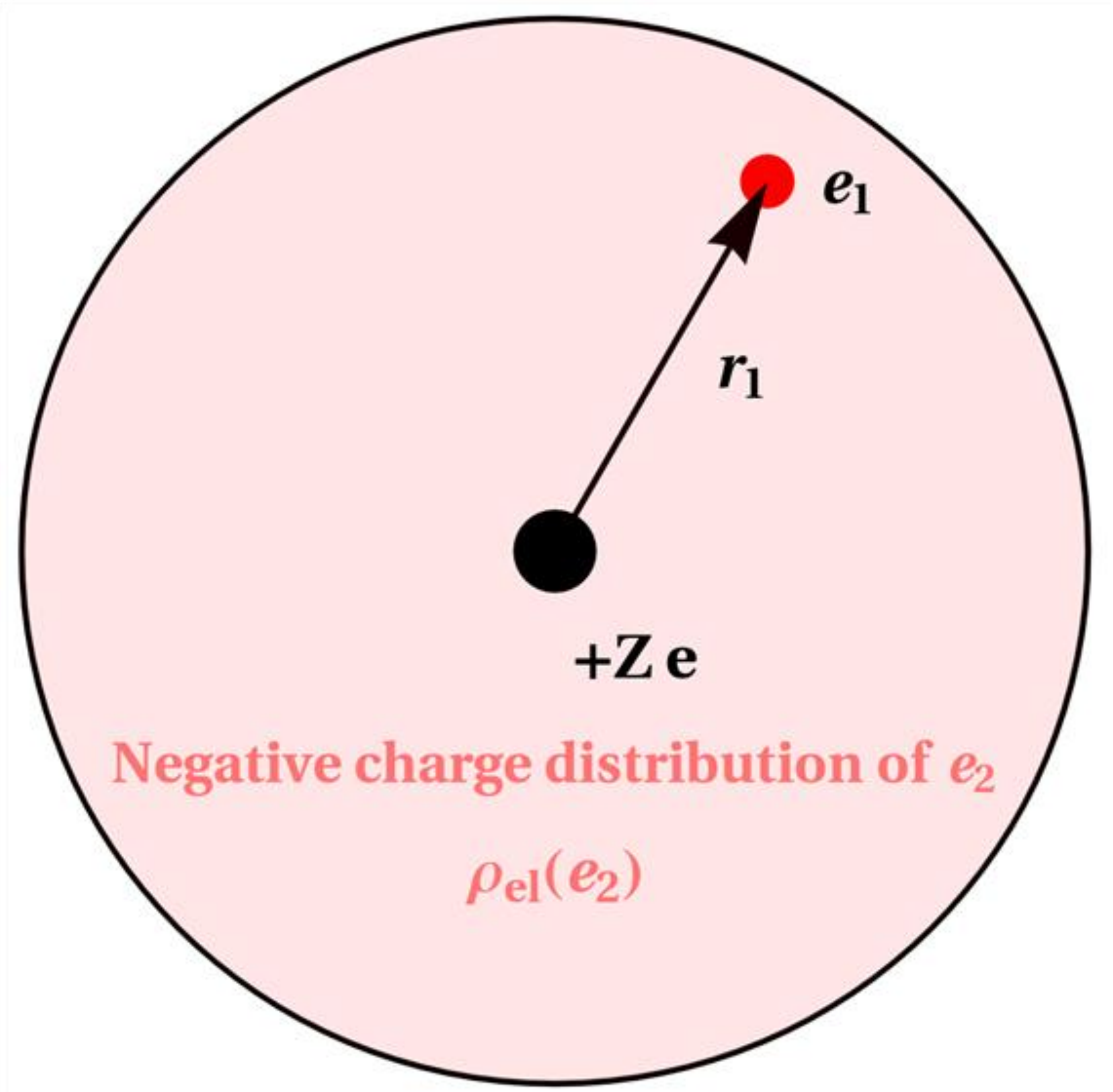
$$\left\langle \psi \left| \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_2|} \right| \psi \right\rangle = \frac{5}{4} Z^* \tag{5.35}$$

If we add now all three terms we obtain:

$$\langle \psi | H | \psi \rangle = -2(Z^*)^2 - 4(Z - Z^*)Z^* + \frac{5}{4}Z^* = 2Z^{*2} - 4ZZ^* + \frac{5}{4}Z^*. \tag{5.36}$$

We have to look for the minimum of this expression as the function of $Z^*$. It is a quadratic function, with a minimum at $Z^* = Z - \frac{5}{16}$, as it can be found by derivation or by any elementary method. So the effective nuclear charge is smaller as the real one, due to shielding of the nucleus by the other electron. In the case of Helium $Z = 2$ , we get $Z^* = 27/16$ . Putting back this value into ( 5.36 ) we obtain $\langle \psi | H | \psi \rangle_{\mathrm{min}} = -5.7\,\mathrm{Ry} = -77.4\,\mathrm{eV}$, which is much closer to the experimental value $-79.0\,\mathrm{eV}$ than the result obtained by perturbation theory in Section 5.3$-74.9\,\mathrm{eV}$.

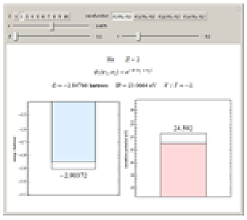
**Figure 5.2. Schematic drawing to demonstrate partial shielding of the nuclear charge $Ze$ by the other electron in Helium atom. The negative charge distribution of the other $1s$ electron is $\rho_{el}(e_2) = e|\psi_{1s}(\mathbf{r}_2)|^2$**



Schematic drawing to demonstrate partial shielding of the nuclear charge Ze by the other electron in Helium atom.

The result shows the power of the variational method used widely in quantum physics as well as in other fields of theoretical physics.

**Animation:**

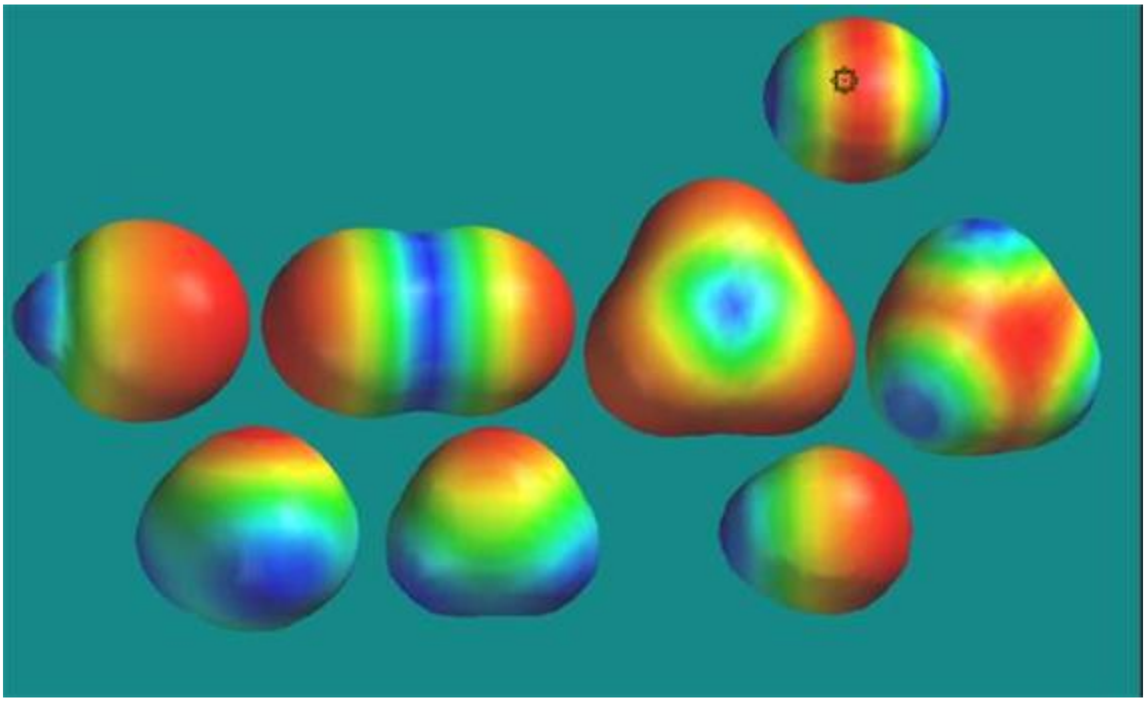


On this interactive animation we can investigate the power of variational method for determining the ground state energies of the Helium. Beside the variational method shown in this chapter (with one parameter) we see examples of other (more complicated) trial functions with more than one parameters giving better approximation for the ground state energy of the Helium. This interactive animation allows us to investigate the parameter space corresponding to these trial functions and find the best fitting of these values with the exact measurement data.

# Chapter 6. Multielectron atoms

**Goals:** In this chapter we will consider the question, how to calculate - at least in principle - the electronic structure of atoms with several electrons. We shall explain the method worked out first by D. Hartree in the 20-ies and improved a little later by V. Fock and J. Slater. This approach is called the one electron self-consistent field method. **Prerequisites:** Coulomb problem (Chapter 1 .).

**Figure 6.1. Electrostatic potential maps from Hartree-Fock calculations http://science.csustan.edu/phillips/CHEM4610 Docs/CHEM4610_All Bonds Same.htm**



Electrostatic potential maps from Hartree-Fock calculations

## 1. One electron approximation and the Hartree method

As we have noted earlier, due to the several corrections already the spectrum of simplest atom of the Hydrogen containing only one electron, shows a complicated structure. In the first approximation however the spectrum is simple, according to the result $\varepsilon_n = (-1/n^2)\,\mathrm{Ry}$ the energy depends only on the principle quantum number $n$, and this eigenvalue is $2n^2$ times degenerate.

For an atom with several electrons strictly speaking only the stationary states of the whole system of electrons exist in the field of the nucleus and each other. In the case of $N$ electrons and a single nucleus with $Z$ protons the stationary states are the solutions of the following Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2m_e} - \sum_{i=1}^{N} \frac{Zq_0^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{R}_i|} + \frac{q_0^2}{4\pi\epsilon_0} \sum_{j<i} \sum_{i=1}^{N} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} \tag{6.1}$$

where we consider the nucleus fixed. In spite of the interaction described here by the third term, a surprisingly good approximation is the independent particle model, which we shall explain in this chapter.

Our aim here is to determine the stationary states of this Hamiltonian, to be denoted by $|\Psi(1,2,3\ldots N)\rangle$ that must be a vector in the tensorial product state of the one electron spaces: $\mathfrak{H}^{\otimes N}$. To determine the exact form of such a function is impossible, even for a two electron system (He atom). Therefore we shall use the **one electron approximation**, where we assume that if we consider a single electron separately from all the others, the **electron-electron interaction term can be approximated by a potential energy of that single electron in the field of all the others**. Therefore this function, which is to be written as $v(i)$ for the $i$-th electron should depend only on the coordinate of that single electron. Mathematically this means that we make the following replacement

$$\sum_{i,j,i<j}\frac{1}{|\mathbf{R}_{ij}|} \longrightarrow \sum_i V(\mathbf{R}_i) \tag{6.2}$$

So far we do not know the explicit form of $V(\mathbf{R}_i)$, but the procedure we explain below will also yield us the expression of this potential energy. It may seem that we distinguish between the electrons by taking out one, but as we will see later, this will not be the case. We have then the following approximate Hamiltonian:

$$H^i = \sum_i h(i) \tag{6.3}$$

where

$$h(i) = \frac{\mathbf{P}_i^2}{2m} - \frac{Ze_0^2}{R_i} + V(\mathbf{R}_i) \tag{6.4}$$

is an **effective one-electron operator** that depends only on the coordinates of a single electron. This one-electron approximation, is also called as **independent particle approximation**, because the terms in $H^i$, are independent of each other. Special and mathematically correct solutions of the eigenvalue equation

$$H^i\,|\Psi\rangle = \mathcal{E}\,|\Psi\rangle \tag{6.5}$$

can be written as a product of one particle eigenstates:

$$|\Psi_H\rangle = |\varphi_{\alpha 1}\rangle\,|\varphi_{\alpha 2}\rangle \ldots |\varphi_{\alpha N}\rangle\,, \tag{6.6}$$

where each factor in this product obeys

$$h(i)\,|\varphi_{\alpha_i}\rangle = \varepsilon_{\alpha_i}\,|\varphi_{\alpha_i}\rangle \tag{6.7}$$

with

$$\langle\varphi_{\alpha_i}|\varphi_{\alpha_j}\rangle = \delta_{\alpha_i\alpha_j} \tag{6.8}$$

and

$$\mathcal{E}\sum_i \varepsilon_{\alpha_i}. \tag{6.9}$$

We shall call the state $|\Psi_H\rangle$ as the Hartree state, or Hartree function. Note that each one-particle Hamiltonian $h(i)$ in ( 6.3 ) has several eigenvalues and eigenstates, these are labeled by $\varepsilon_{\alpha_i}$ and $|\varphi_{\alpha_i}\rangle$, and as in our case all the particles are identical electrons the set of possible $\alpha_i$ -s are the same for all $i$ -s.

**Problem 6.1 :** Show the validity of ( 6.5 ).

Now the procedure is the following. We assume an **initial product** with properly chosen one electron states, these are usually the well known eigenstates of

$$h_1(i) = \frac{\mathbf{P}_i^2}{2m} - \frac{Ze_0^2}{R_i}, \tag{6.10}$$

which is the Hamiltonian of a H-like ion, as it does not contain even $v(i)$, the simplified and so far unknown electron-electron interaction. We go over now to coordinate representation. Then the Hartree product above is a function

$$\Psi_H(\mathbf{r}_1, \dots \mathbf{r}_N) = \prod_{\alpha_i} \varphi_{\alpha_i}(\mathbf{r}_k) = \varphi_{\alpha_1}(\mathbf{r}_1)\varphi_{\alpha_2}(\mathbf{r}_2)\dots\varphi_{\alpha_N}(\mathbf{r}_N), \tag{6.11}$$

which in principle must be complemented by spin states. The Hamiltonian is, however spin independent, therefore spin will be taken into account only implicitly. The Pauli principle in its **elementary form** says that in the product above all the one-electron states must be different and orthogonal, or rather because of spin, the spatial part of a pair of electrons can be the same, as they can be multiplied by the two possible eigenstates of $S_z$ . This means that if we wish to determine the ground state of the $N$ electron system we can chose those one electron states in the product which belong to the lowest one-electron eigenvalues, where orbital and spin degeneracy must be taken into account, as well.

The use of coordinate representation is useful because the potential energy of the $i$ -th single electron in the field of all others can be expressed by the spatial charge density of the other electrons:

$$\sum_{j \neq i} \varrho(\mathbf{r}_j) = \sum_{j \neq i}^{N-1} e_0^2 \left|\varphi_j(\mathbf{r}_j)\right|^2 \tag{6.12}$$

The Coulomb potential of the $i$ -th electron created by this charge density is

$$V(\mathbf{r}_i) = \sum_{j \neq i}^{N-1} \int \frac{e_0^2 \left|\varphi_j(\mathbf{r}_j)\right|^2}{R_{ij}} d^3\mathbf{r}_j \tag{6.13}$$

and this is the effective one-electron potential giving the one-electron eigenvalue equation according to ( 6.7 )

$$\left(-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze_0^2}{R_i} + V(\mathbf{r}_i)\right)\varphi_i(\mathbf{r}_i) = \varepsilon_i\varphi_i(\mathbf{r}_i). \tag{6.14}$$

The solutions to this equation yields the one-electron eigenvalues and eigenfunctions. Note that the operator on the left hand side contains the unknown functions themselves in $V(\mathbf{r}_i)$ according to ( 6.13 ). This problem can be circumvented in the following way. In the first step we take as trial functions $\varphi_j(\mathbf{r}_j)$ the exact wave functions of the Coulomb problem and calculate $V(\mathbf{r}_i)$ according to ( 6.13 ). Then we have already the potential and solve ( 6.14 ), yielding new eigenfunctions. From the latter we can again form the potential according to the prescription ( 6.13 ) and repeat the solution of Eq. ( 6.14 ). So in the $k$ -th step we use the solution obtained in $k-1$ -th step:

$$\left(-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze_0^2}{R_i} + \sum_{j \neq i}^{N-1} \int \frac{e_0^2 \left|\varphi_j^{(k-1)}(\mathbf{r}_j)\right|^2}{R_{ij}} d^3\mathbf{r}_j\right) \varphi_i^{(k)}(\mathbf{r}_i) = \varepsilon_i^{(k)}\varphi_i^{(k)}(\mathbf{r}_i \tag{6.15}$$

This iteration procedure is continued until in the final step one obtains **self consistency**, i.e. the starting ( $n-1$ -th) and the resulting ( $n$ -th) one-electron wave functions coincide with a prescribed precision. Then of course the potential $V(\mathbf{r}_i)$ will also be equal to the one in the previous step. This method is therefore a so called **self-consistent field, or shortly SCF method**, introduced by D. Hartree.

Let us find the meaning of the one-electron eigenvalues $\varepsilon_i$ obtained in this way. To this end we multiply ( 6.14 ) by $\varphi_i^*(\mathbf{r}_i)$ and integrate with respect to the coordinate. As the functions $\varphi_i(\mathbf{r}_i)$ are assumed to be normalized we obtain.

$$-\frac{\hbar^2}{2m}\int \varphi_i^*(\mathbf{r}_i)\Delta_i\varphi_i(\mathbf{r}_i) - \frac{Ze_0^2}{R_i}|\varphi_i(\mathbf{r}_i)|^2 + \int\sum_{j\neq i}^{N-1}|\varphi_i(\mathbf{r}_j)|^2\int\frac{|\varphi_j(\mathbf{r}_j)|^2}{R_{ij}}d^3\mathbf{r}_j d^3\mathbf{r}_i = \varepsilon_i\varphi_i(\mathbf{r} \qquad (6.16)$$

Here in the first integral we can use the identity $\varphi^*(\mathbf{r})\Delta\varphi(\mathbf{r}) = \nabla[\varphi^*(\mathbf{r})\nabla\varphi(\mathbf{r}_i)] - \nabla\varphi^*(\mathbf{r})\nabla\varphi(\mathbf{r})$. The volume integral of the first term vanishes, as we can apply the divergence theorem of Gauss, and assume that in infinity $\varphi^*(\mathbf{r})\nabla\varphi(\mathbf{r})$ vanish exponentially, since these the $\varphi(\mathbf{r})$ are assumed to be bound states. Therefore :

$$\varepsilon_i = \frac{\hbar^2}{2m}\int\left(|\nabla\varphi(\mathbf{r}_i)|^2 - \frac{Ze_0^2}{R_i}|\varphi_i(\mathbf{r}_i)|^2\right)d^3\mathbf{r}_i + \sum_{j\neq i}^{N} e_0^2\int\frac{|\varphi_i(\mathbf{r}_j)|^2\,|\varphi_j(\mathbf{r}_j)|^2}{R_{ij}}d^3\mathbf{r}_j d^3 \qquad (6.17)$$

Let us compare this with the total energy of the system which is to be calculated by the expectation value of the original Hamiltonian ( 6.1 ) $-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze_0^2}{R_i} + \sum_{i<j}^{N}\frac{e_0^2}{R_{ij}}$ in the state obtained in the coordinate representation in the state obtained:

$$E_{tot} := \langle H\rangle = \langle\Psi|\,H\,|\Psi\rangle = \int\prod\varphi_j^*(\mathbf{r}_j)\left[\sum_i^N\left(-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze_0^2}{R_i}\right) + \sum_{i<j}^{N}\frac{e_0^2}{R_{ij}}\right]\prod[\varphi_k(\mathbf{r}_k)d^3\mathbf{r} \qquad (6.18)$$

The one electron functions are orthonormal, therefore $\int\varphi_j^*(\mathbf{r}_j)\varphi_k(\mathbf{r}_j)d^3\mathbf{r}_j = \delta_{jk}$ and using the same trick for the kinetic energy as in getting ( 6.17 ) we obtain

$$E_{tot} = \langle H\rangle = \sum_i^N\int\left(\frac{\hbar^2}{2m}|\nabla\varphi(\mathbf{r}_i)|^2 - \frac{Ze_0^2}{R_i}|\varphi_i(\mathbf{r}_i)|^2\right)d^3\mathbf{r}_i + \sum_{i<j}^{N}\int\frac{e_0^2\,|\varphi_i(\mathbf{r}_j)|^2\,|\varphi_j(\mathbf{r}_j)|^2}{R_{ij}}d^3\mathbf{r}_j d^3 \qquad (6.19)$$

The first term here is equal to the sum of the first terms in ( 6.17 ) In the last term we can write $\sum_{i<j}^{N} = \frac{1}{2}\sum_i\sum_{j\neq i}^{N}$. Therefore the result we obtain is

$$E_{tot} = \sum_i\varepsilon_i - \frac{1}{2}\sum_i\sum_{j\neq i}^{N}\int\frac{e_0^2\,|\varphi_i(\mathbf{r}_j)|^2\,|\varphi_j(\mathbf{r}_j)|^2}{R_{ij}}d^3\mathbf{r}_j d^3\mathbf{r}_i \qquad (6.20)$$

The reason for having the last term is that in the sum $\sum_i\varepsilon_i$ we count the $\frac{e_0^2}{R_{ij}}$ interaction energy twice.

One can simplify the method by taking the spherical average of $V(\mathbf{r}_i)$ after each iteration step according to

$$\frac{1}{4\pi}\int V(\mathbf{r}_i)d\Omega_i =: V(r_i) \qquad (6.21)$$

where the integration goes over the surface of the unit square with $d\Omega = \sin\theta d\theta d\phi$. Then the solution of the partial differential equation can be reduced to a radial equation, since then the angular part of $\varphi_i(\mathbf{r}_i)$ will be one of the spherical harmonics. With his method D. Hartree could find the total energy of certain atoms with a hand driven computing machine.

## 2. The Hartree-Fock method for atoms

The SCF method of Hartree has now only a historical significance, as the naive form of the Pauli principle - stating that in the independent particle approximation all quantum numbers of the individual one-electron functions must be different - is not satisfactory. The **rigorous** prescription is that the total state must be **antisymmetric** with respect to the exchange of the electrons, as they are fermions. From this general statement the validity of the naive Pauli principle follows, but it is not true the other way round. Namely all the quantum numbers may differ in a product like ( 3.10 ), as it was supposed by Hartree, still it obviously not antisymmetric, as it expected to be. The solution to this problem came independently from V. Fock and J. Slater in 30, and it is called now the Hartree-Fock method.

The important difference is that from the one-electron functions we construct a state which is an element of the antisymmetric subspace of the tensorial product of the individual spaces. This is most easily done by writing the wave function in the form of a determinant

$$\begin{aligned}\Psi(x_1, x_2 \ldots x_N) &= \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \cdots & \varphi_1(x_N) \\ \varphi_2(x_1) & \varphi_2(x_2) & \cdots & \varphi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(x_1) & \varphi_N(x_2) & \cdots & \varphi_N(x_N) \end{vmatrix} = \\ &=: \frac{1}{\sqrt{N!}} \det |\varphi_1(x_1)\varphi_2(x_2) \ldots \varphi_N(x_N)|\end{aligned} \tag{6.22}$$

called the **Slater determinant**. We shall follow here a variational procedure to derive equations similar to those in the previous section (where we could have done the same). We take the expectation value of the Hamiltonian ( 6.1 ) and we are going to minimize it, but this time with respect of the one electron-functions in ( 6.22 ) stipulating the normalization constraint for them.

We note first that the determinant consists of $N!$ pairwise orthogonal terms and the one electron operators effect only functions of those variables on which they depend. Therefore the expectation value of the kinetic and the nuclear potential energy turns out to be the same as in the simple product case of the Hartree probe function ( 3.10 ), that is $\sum_i^N \int \left( \frac{\hbar^2}{2m} |\nabla \varphi(\mathbf{r}_i)|^2 - \frac{Ze_0^2}{R_i} |\varphi_i(\mathbf{r}_i)|^2 \right) d^3\mathbf{r}_i$. In order to find the expectation value of the two-electron operators $\sum_{i<j}^N \frac{e_0^2}{R_{ij}}$ we consider first only one term $\frac{e_0^2}{R_{12}}$ and consider its matrix element between terms that contain $\varphi_1(x_1)$ and $\varphi_2(x_2)$

$$\frac{1}{\sqrt{N!}}[\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)] \ldots \tag{6.23}$$

where " . . . " refer to the other factors. The contribution of this term to the expectation value will be

$$\frac{1}{N!} \int [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)]^* \frac{e_0^2}{r_{12}} [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)] d^3\mathbf{r}_1 d^3\mathbf{r} \tag{6.24}$$

re the expectation value All pair of functions like that of $\varphi_1(x_1)$ and $\varphi_2(x_2)$ turn up in ( 6.22 ) exactly $N!/2$ times, therefore we get

$$\left\langle \Psi | \sum_{i<j} \frac{e_0^2}{r_{ij}} \Psi \right\rangle = \frac{1}{2} \sum_{i=j} \int \frac{e_0^2}{r_{ij}} [|\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r}')|^2 - \varphi_i^*(r)\varphi_j(r')\varphi_j^*(r)\varphi_j(r)\delta_{m_i m_j}] d^3\mathbf{r} d^3 \tag{6.25}$$

where the $\delta_{m_i m_j}$ comes from the scalar product of the spin eigenfunctions with $m_i, m_j = \pm 1/2$. We obtain with the Slater determinant

$$\begin{aligned} \langle H \rangle \quad &:= \langle \Psi | H \Psi \rangle = \sum_i^N \int \left( \frac{\hbar^2}{2m} |\nabla \varphi(\mathbf{r}_i)|^2 - \frac{Z e_0^2}{R_i} |\varphi_i(\mathbf{r}_i)|^2 \right) d^3\mathbf{r}_i + \\ &+ \frac{1}{2} \sum_{ij}^N \int \frac{e_0^2 |\varphi_i(\mathbf{r}_j)|^2 |\varphi_j(\mathbf{r}_j)|^2}{r_{ij}} d^3\mathbf{r}_j d^3\mathbf{r}_i - \frac{1}{2} \delta_{m_i m_j} \sum_{ij}^N \frac{\varphi_i^*(r) \varphi_j(r') \varphi_j^*(r) \varphi_j(r)}{r_{ij}} d^3\mathbf{r}_i d^3\mathbf{r} \end{aligned} \tag{6.26}$$

which differs from the Hartree result by the last term. This term is called the **exchange energy** because it is connected with the prescribed antisymmetry of the wave function, as we have seen it already in the case of the Helium atom. $\langle H \rangle$ a functional, the energy functional of the $\varphi_i(\mathbf{r}_i)$ functions. Now we take into account the normalization of all one-electron functions, by adding the additional constraint

$$\sum_i \varepsilon_i \left( 1 - \int |\varphi_i(\mathbf{r}_i)|^2 d^3\mathbf{r}_i \right) = 0 \tag{6.27}$$

where $\varepsilon_i$ -s are Lagrange multiplicators at this stage. Now we shall minimize the sum of ( 6.26 ) and ( 6.27 )

$$\left\langle \tilde{H} \right\rangle = \langle H \rangle + \sum_i \varepsilon_i \left( 1 - \int |\varphi_i(\mathbf{r}_i)|^2 d^3\mathbf{r}_i \right), \tag{6.28}$$

with **respect to**$\varphi_i^*(r)$. This means that we set the functional derivative of this sum zero, which is defined in the case of a general functional $G[\varphi_1(\mathbf{r}_1) \cdots \varphi_N(\mathbf{r}_N)]$ by the operation

$$\frac{\delta G[\varphi_i(\mathbf{r}_i)]}{\delta \varphi_j(\mathbf{r}_j)} = \lim_{\eta \to 0} \frac{G[\varphi_i(\mathbf{r}_i) + \eta \delta_{ij} \delta(\mathbf{r}_i - \mathbf{r}_j)] - G[\varphi_i(\mathbf{r}_i)]}{\eta}. \tag{6.29}$$

The result is:

$$\left( -\frac{\hbar^2}{2m} \Delta_i - \frac{Z e_0^2}{R_i} + V(\mathbf{r}_i) \right) \varphi_i(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i), \tag{6.30}$$

where now

$$V(\mathbf{r}_i) = e_0^2 \sum_{j \neq i}^{N-1} \int \frac{|\varphi_j(\mathbf{r}_j)|^2}{R_{ij}} d^3\mathbf{r}_j - \sum_{j \neq i}^{N} \delta_{m_i m_j} \int \frac{\varphi_j^*(\mathbf{r}_j) \varphi_j(\mathbf{r}_i) \varphi_i^*(\mathbf{r}_j)}{R_{ij}} d^3\mathbf{r} \tag{6.31}$$

The system ( 6.30 )-( 6.31 ) is a system of integro-differential equations, as the unknown functions figure both as integrands in ( 6.31 ) and as solutions to be found from the differential equations ( 6.30 ). These equations are called the **Hartree-Fock equations**, and can be solved again by the self-consistent field method as explained for the Hartree method. It is often written as

$$F_i \varphi_i(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i), \tag{6.32}$$

where $F$ is called the Fock operator. It consists of four terms:

$$F_i = T_i - Z e_0^2 / R_i + K_i - J_i. \tag{6.33}$$

Her $T_i$ is the kinetic energy, the second term is the potential energy of the electron in the nuclear Coulomb field, the third, $K_i$ is the Coulomb interaction of the electron with all the others, while the last term in ( 6.31 ) $-J_i$ is an extra term called the **exchange potential**, which is negative, if present. When compared with the Hartree potential, as explained with respect to $\langle H \rangle$ , it arises because of the antisymmetry of the wave function, as it has already been noted with respect to $\langle H \rangle$ . This is a **non-local term**, as an unknown function $\varphi_i(\mathbf{r})$ appears with different arguments $\mathbf{r}_i \neq \mathbf{r}_j$ , which makes the calculation even more difficult, which is possible, of course, only numerically.

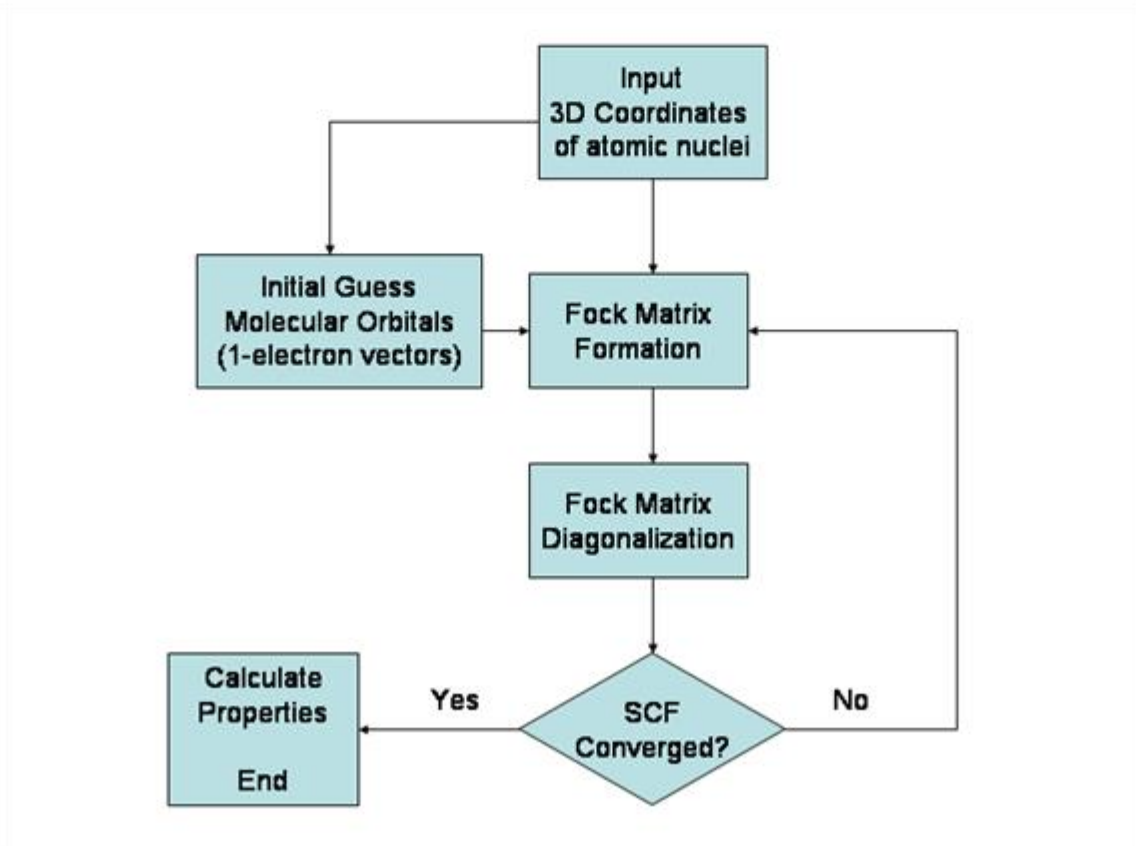
**Problem 6.2 :** Show that solutions corresponding to different $\varepsilon_i$ -s of the HF equations are orthogonal.

The physical meaning of the $\varepsilon_i$ -s that entered the formalism as Lagrange multipliers, can be seen from the following consideration. By multiplying ( 6.30 ) with $\varphi_i^*(\mathbf{r}_i)$ and integrating the resulting equation (i. e. taking the scalar product $\varphi_i$ with $H\varphi_i$ ) we obtain that $\varepsilon_i$ is equal to those terms of $\langle H \rangle$ that contain just $\varphi_i$. Therefore $-\varepsilon_i$ can be interpreted as the energy necessary for removing the particle in the state $\varphi_i$, while stipulating that all the other functions remains the same. This is called **Koopmans' theorem** obtained in 33.

**Comment:** An interesting biographical fact is that T. Koopmans received the Nobel memorial prize in economics in 75 for his studies in the theory of optimal use of resources.

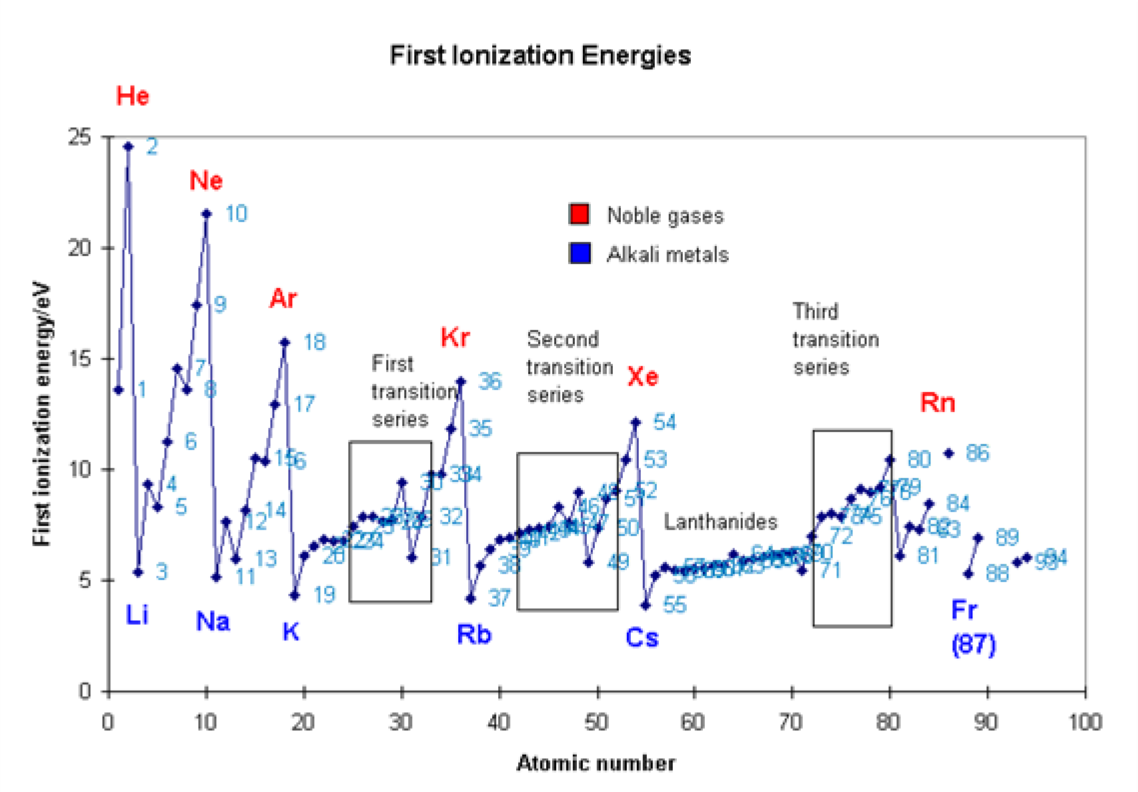
The Hartree-Fock method is called an **ab initio** (meaning: "from the beginning" in latin) calculation, because it does not use any parameter to be fitted from other considerations. By the end of the 70-s efficient program codes for atoms have been worked out to perform Hartree-Fock calculations for atoms, and the electron density of the ground states of atoms could be routinely obtained by this as well as other (non ab initio) methods to be described to some extent later. The application of the method for molecules is also possible, and will be outlined in chapter 7 .

### Figure 6.2. Simplified algorithmic flowchart illustrating the Hartree-Fock Method. http://en.wikipedia.org/wiki/Hartree-Fock_method



Simplified algorithmic flowchart illustrating the Hartree-Fock Method.

**Figure 6.3. Ionization energies of the elements. http://www.tannerm.com/first.htm**



Ionization energies of the elements.

# Chapter 7. Atomic spectra, Hund's rules, the periodic system

**Goals:** The one electron approximation works very well for atoms with several electrons, and this feature appears in their spectroscopic properties, to be considered in this chapter. In order to understand atomic spectra one has to know well the results of the quantum mechanical Coulomb problem, antisymmetrization of the many electron states, and the addition of angular momenta.

**Prerequisites:** Coulomb problem (Chapter 1 ), antisymmetrization of the many electron states, and the addition of angular momenta (Chapter 3 ).

## 1. Introduction

As we have learned in chapter 6 the one electron approximation works very well for atoms with several electrons, and this feature appears in their spectroscopic properties, as well.

A selected electron is attracted by the nucleus and repelled by all other electrons. In the one-electron approximation we solve the eigenvalue equation for only one of the electrons, where we use an effective potential $V_{\text{eff}}(\mathbf{R})$ as described in the previous chapter. In the case of atoms we can assume that $V_{\text{eff}}$ is spherically symmetric, from the point of view of the selected electron the potential originating from all the others depends only on the distance from the nucleus. In practical calculations described in the previous chapter this is achieved by a spherical averaging of the charge density in each step of the SCF process. The effective Hamiltonian can then be written as

$$H_{\text{eff}} = \frac{\mathbf{P}^2}{2m_e} - \frac{q_0^2}{4\pi\epsilon_0}\frac{Z(R)}{R}, \tag{7.1}$$

where $Z(r)q_0$ is the effective nuclear charge if the distance from the center is $r$. We prescribe that $Z(r) \to Z$ , if $r \to 0$, i.e. in the vicinity of the nucleus, and $Z(r) \to 1$, for $r \to \infty$. In the latter case the other $Z-1$ electrons **screen off** the attraction of the total nuclear charge $Zq_0$, and the electron moves effectively in the field of a single elementary positive charge $q_0$. The operator of the potential energy is obtained of course by the replacement $r \to R$.

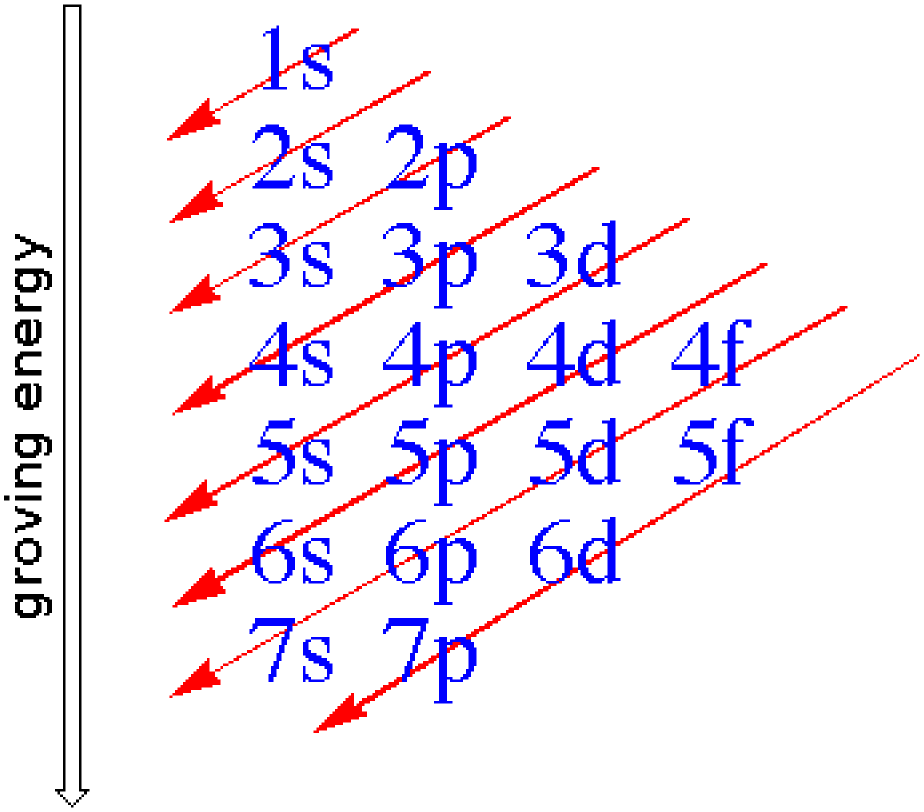
Due to spherical symmetry, the orbitals can be characterized similarly to the case of the $H$ atom. Spherical symmetry implies that $L^2$ and $L_z$ commute with $H_{\text{eff}}$ therefore their eigenvalues, $\ell$ and $m$ remain good quantum numbers. A stationary state can be characterized therefore by the energy eigenvalue (principal quantum number) and besides $\ell$ and $m$, also by $m_s$, the spin component quantum number (which can be only $\pm 1/2$ ). As in the approximation considered here $H_{\text{eff}}$ is independent of the spin, the total spin is also a good quantum number, but its value $S = 1/2$ is fixed, as an intrinsic property of the electron. The eigenstates of $H_{\text{eff}}$ are frequently called as one electron states, or orbitals, but we must be aware that this does not mean any orbit in the classical sense. The corresponding eigenvalues are the one electron energies, or orbital energies.

In the H atom the orbital energies do increase with $n$ and in the nonrelativistic approximation they are independent of $\ell$. For an atom with several electrons the situation is more complicated, because due to the electron-electron interaction the orbital energies depend also on $\ell$, so the degeneracy valid in the pure Coulomb field is **lifted**.

Accordingly we have $1s, 2s, 2p, 3s$, etc. orbitals, so that in a multielectron atom, their energies depend on the letters in the symbol. Because of the spherical symmetry, however, an energy eigenvalue labeled by $n$ and $\ell$ is still $(2\ell + 1)$ times degenerate according to the projection of orbital angular momentum along one of the axes (this is usually taken to be the $z$ axis), this is the magnetic quantum number $m$. As we know there is an additional double degeneracy because of spin, so the total degree of degeneracy is $2(2\ell + 1)$. This degeneracy is however lifted by relativistic corrections i.e. a fine structure appears, as well as hyperfine structure caused by the interaction with nuclear spin.

The results show that, as expected from the H spectrum, for a given $\ell$, the energy is higher for a larger $n$. Also for a given $n$ the energy is higher for a higher value of $\ell$. This is because, for the higher $\ell$ values, the electrons tend to lie further from the nucleus on average, and are therefore more effectively screened. The states corresponding to a particular value of $n$ are generally referred to as a **shell**, and those belonging to a particular pair of values of $n, \ell$ are usually referred to as a **subshell**. The energy levels are ordered as below (with the lowest lying on the left):

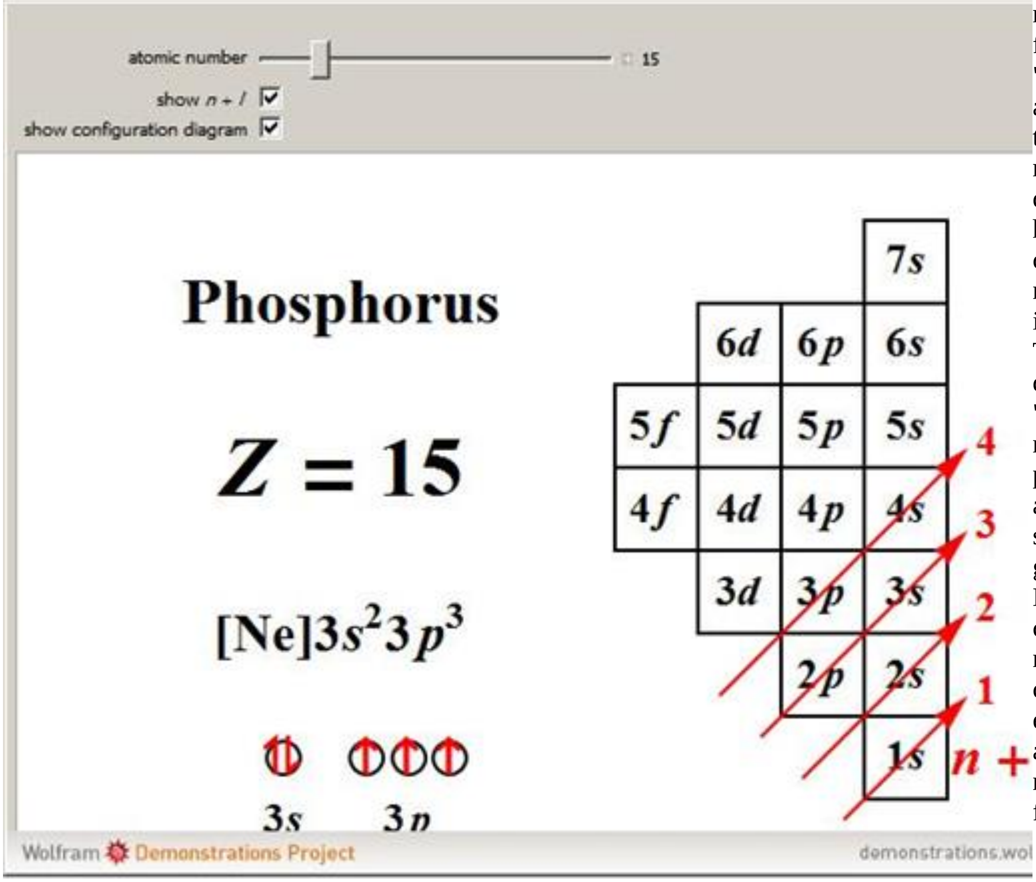
**Figure 7.1. Ordering of the atomic subshells with respect to energy. http://www.m2c3.com/c101/chemistry_in_contextx/ch2/simple_electron_configuration/electron_configuration.htm**



Ordering of the atomic subshells with respect to energy.

**Animation:**

Orbitals in atomic ground-state electron configurations are filled in the order of increasing $n+\ell$ . For equal $n+\ell$ values, the orbital with the lower $n$ is most often filled first. The "$n+\ell$ rule," also known as the Madelung rule or the diagonal rule, holds with only a small number of irregularities. The designation "diagonal rule" refers to the pattern of atomic orbitals shown in the graphic. This Demonstration covers the naturally occurring elements with atomic numbers Z from 1 to 92.



atomic number 15

show $n+l$ ☑

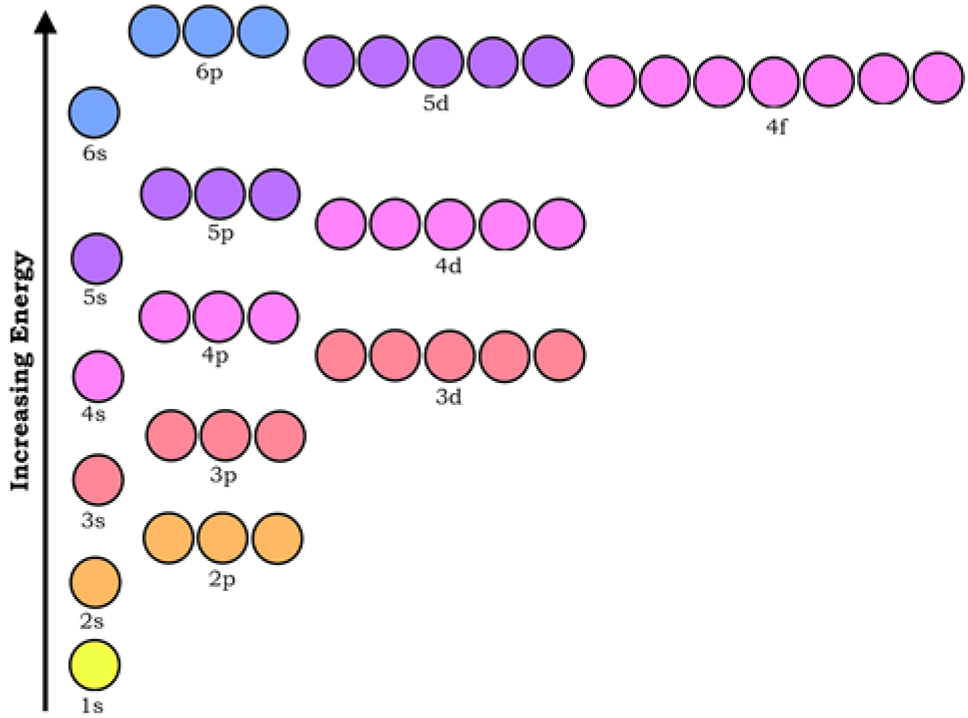
show configuration diagram ☑

Note that the values of $N$ corresponding to the noble gases, $2, 10, 18, 36$, at which the ionization energy is unusually high, now emerge naturally from this filling order, corresponding to the numbers of electrons just before a new shell $(n)$ is entered. There is a handy mnemonic to remember this filling order. By writing the subshells down as shown in Figure 7.1 , the order of states can be read off along diagonals starting from the top and going down along the diagonal arrows:

### Table 7.1. Ordering of the energy levels.

| Subshell name | 1s | 2s | 2p | 3s | 3p | 4s | 3d | 4p | 5s | 4d | … |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n$ | 1 | 2 | 2 | 3 | 3 | 4 | 3 | 4 | 5 | 4 | … |
| $\ell$ | 0 | 0 | 1 | 0 | 1 | 0 | 2 | 1 | 0 | 2 | … |
| Degeneracy | 2 | 2 | 6 | 2 | 6 | 2 | 10 | 6 | 2 | 10 | … |
| Cumulative | 2 | 4 | 10 | 12 | 18 | 20 | 30 | 36 | 38 | 48 | … |

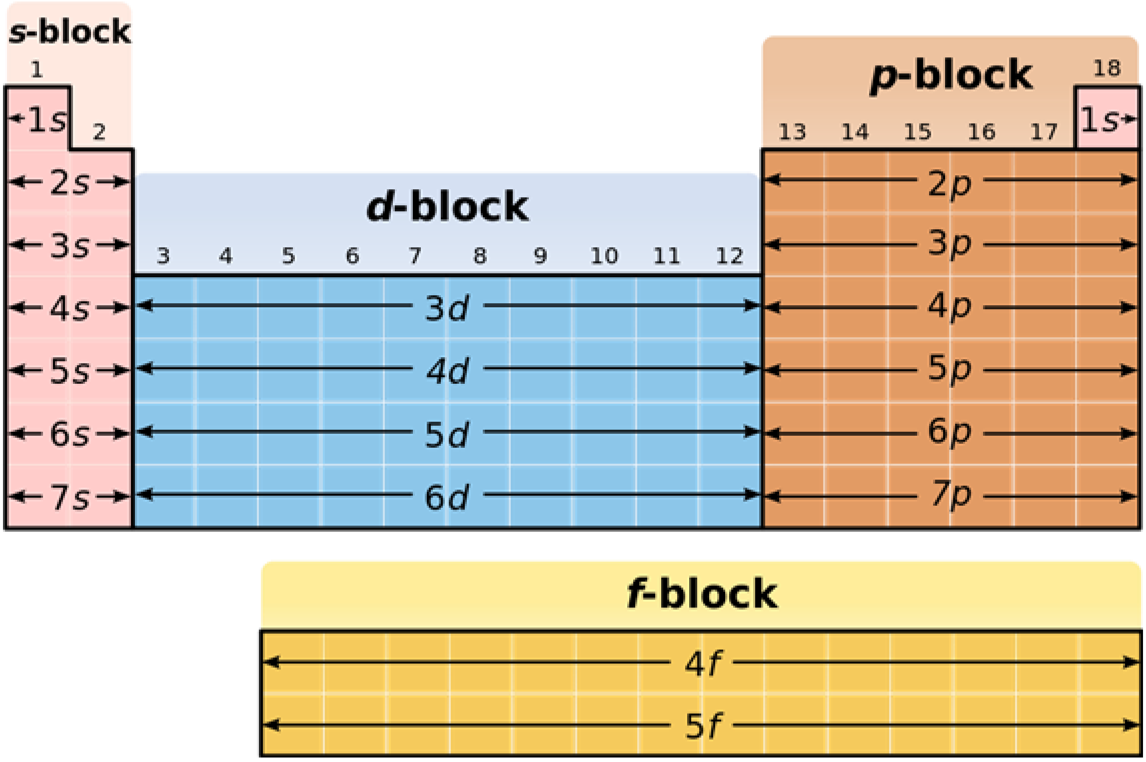
**Figure 7.2. Energies of the shells. http://commons.wikimedia.org/wiki/File:Orbital_representation_diagram.svg**



Energies of the shells.

In the ground state the electrons, whose number is $N$ fill up those one-particle states up to $N$, which follow each other along the arrows of Figure 7.1 . Accordingly the ground state can be given by the corresponding Slater -determinant at least in this one particle approximation. We can say that we put electrons one by one in the lowest lying energy levels according to the Pauli exclusion principle, until the electrons are all accommodated, this is the so called "Aufbau (build-up) principle". We can use this sequence of energy levels to predict the ground state electron configuration of atoms. An electronic configuration means that we specify the number of electrons on an orbital or level. If there are more than one electrons on the subshell given by $n$ and $\ell$, then we write this number as an exponent to $\ell$ or sometimes to the pair $(n, \ell)$.

**Figure 7.3. Outer shells in the periodic table. http://en.wikipedia.org/wiki/Electron_configuration**



Outer shells in the periodic table.

The ground state of the H-atom is $1s$. The two electrons in the He-atom in the ground state corresponds to the $1s^2$, while the first excited state of He is in the $1s2s$ configuration. The next element of the periodic system is the Lithium (Li) with 3 electrons, with ground state configuration $1s^22s$, and this is continued until Neon (Ne) with $Z=10$, and configuration $1s^22s^22p^6$, because $p$ orbitals can accommodate at most $2(2\cdot 1+1)=6$ electrons because of the Pauli principle. From Figure 7.1 we also see that the subshell $3p$ is followed by filling up $4s$ instead which is the outer shell of Potassium (K) and Calcium (Ca) having a little lower energy than that of the $3d$ orbital. Very often a closed shell, a noble gas configuration is simply denoted by the sign of the corresponding element.

Some additional examples of ground state configurations together with the resulting term in spectroscopic notation $^{2S+1}L_J$ are shown in the table below.

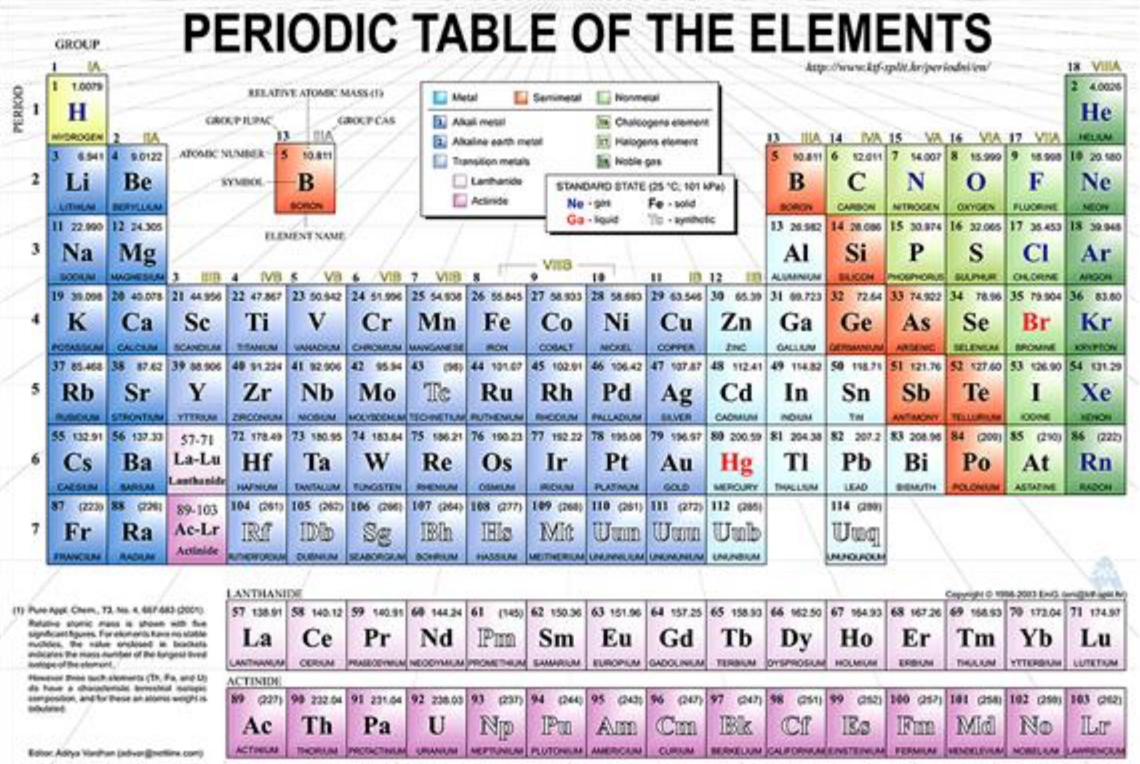
### Table 7.2. Examples of ground state configurations together with the resulting term in spectroscopic notation .

| $Z$ | Element | Config. | $^{2S+1}L_J$ | Ioniz. Energy (eV) |
|---|---|---|---|---|
| 1 | H | $1s$ | $^2S_{1/2}$ | 13.6 |
| 2 | He | $1s^2$ | $^1S_0$ | 24.6 |
| 3 | Li | He $(2s)$ | $^2S_{1/2}$ | 5.4 |
| 4 | Be | He $(2s^2)$ | $^1S_0$ | 9.3 |
| 5 | B | He $(2s^2)(2p^1)$ | $^2P_{1/2}$ | 8.3 |

| | | | | |
|---|---|---|---|---|
| 6 | C | He $(2s^2)(2p^2)$ | $^3P_0$ | 11.3 |
| 7 | N | He $(2s^2)(2p^3)$ | $^4S_{3/2}$ | 14.5 |
| 8 | O | He $(2s^2)(2p^4)$ | $^3P_2$ | 13.6 |
| 9 | F | He $(2s^2)(2p^5)$ | $^2P_{3/2}$ | 17.4 |
| 10 | Ne | He $(2s^2)(2p^6)$ | $^1S_0$ | 21.6 |
| 11 | Na | Ne $(3s)$ | $^2S_{1/2}$ | 5.1 |

Since it is generally the outermost electrons which are of most interest, contributing to chemical activity or optical spectra, one often omits the inner closed shells, and just writes O as $(2p^4)$, for example. However, the configuration is not always correctly predicted, especially in the heavier elements, where levels may be close together. It may be favourable to promote one or even two electrons one level above that expected in this simple picture, in order to achieve a filled shell. For example, Cu $(Z = 29)$ would be expected to have configuration $(4s^2)(3d^9)$, while its actual configuration is $(4s^1)(3d^{10})$. There are several similar examples in the transition elements where the d subshells are being filled, and many among the lanthanides (rare earths) and actinides where $f$ subshells are being filled.

**Figure 7.4. Periodic system of elements. https://www.phy.questu.ca/rknop/classes/enma/2010-10/wiki/images/a/aa/Periodic_table.gif**



PERIODIC TABLE OF THE ELEMENTS

| PERIOD | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | | | | | | | | | | | | | | | | | He |
| 2 | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3 | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5 | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6 | Cs | Ba | 57-71 La-Lu Lanthanide | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7 | Fr | Ra | 89-103 Ac-Lr Actinide | Rf | Db | Sg | Bh | Hs | Mt | Uun | Uuu | Uub | | Uuq | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LANTHANIDE | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| ACTINIDE | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

Periodic system of elements.

This scheme provides a basis to understand the periodic table of elements Fig. ( 7.4 ). We would expect that elements which $(ns^1)$ have similar electron configurations $(np^5)$ in their outermost shells such as Li, Na, K, Rb, Cs, Fr which all have  or F, Cl, Br, I, which all have , would have similar chemical properties, such as valency, since it is the unpaired outer electrons which especially $Z$ participate in chemical bonding. Therefore, if one arranges the atoms in order of increasing atomic number  (which $\ell$ equals the number of electrons in the atom), periodic behaviour is seen whenever a new subshell of a given  is filled.

**Animation:**

This is a nice interactive periodic table showing the basic properties of the elements.

# 2. Coupling schemes

The procedure outlined above allows us to predict the occupation of subshells in an atomic ground state. This is not in general sufficient to specify the ground state fully. If there are several electrons in a partially filled subshell, then their spins and orbital angular momenta can combine in several different ways, to give different values of total angular momentum, with different energies. In order to deal with this problem, it is necessary to consider the spin-orbit interaction as well as the residual Coulomb interaction between the outer electrons. Schematically we can write the Hamiltonian for this system as follows:

$$H \approx H_0 + \underbrace{\sum_{i<j} \frac{e_0^2}{\mathbf{R}_{ij}} - \sum_i U_i(\mathbf{R})}_{H_C} + \underbrace{\sum_i \xi_i(\mathbf{R}_i)\mathbf{L}_i\mathbf{S}_i}_{H_{SO}} \qquad (7.2)$$

where $H_0$ includes the kinetic energy and central field terms, so this is a sum of one-electron operators, $H_C$ is the residual Coulomb interaction, and $H_{SO}$ is the spin-orbit interaction with strength $\xi_i(\mathbf{R}) = \frac{1}{2m^2c^2}\frac{1}{R}\frac{\partial V}{\partial R}$

We can then consider two possibilities:

- $H_C \gg H_{SO}$ This tends to apply in the case of light atoms. In this situation, one considers first the eigenstates of $H_0 + H_C$, and then treats $H_{SO}$ as a perturbation. This leads to a scheme called $LS$ or **Russell-Saunders coupling**.
- $H_C \ll H_{SO}$ This can apply in very heavy atoms, or in heavily ionized light atoms, in which the electrons are moving at higher velocities and relativistic effects such as the spin-orbit interaction are more important. In this case, a scheme called $jj$ **coupling** applies. It is important to emphasise that both of these scenarios represent approximations; real atoms do not always conform to the comparatively simple picture which emerges from these schemes, which we now discuss in detail.

## 2.1. LS coupling scheme

In this approximation, we start by considering the eigenstates of $H_0 + H_C$. We note that this Hamiltonian must commute with the total angular momentum $\mathbf{J}^2$ (because of invariance under rotations in space), and also clearly commutes with the total spin $\mathbf{S}^2$. It also commutes with the total orbital angular momentum $\mathbf{L}^2$, since $H_C$ is a scalar, it involves only internal interactions, and must therefore be invariant under global rotation of all the electrons. Therefore the energy levels can be characterised by the corresponding total angular momentum quantum numbers $L, S, J$.

**Hund's rules.**

These are the rules determining the ordering in energy, set up by F. Hund based on spectroscopic evidence in around 25-30.

1. Combine the spins of the electrons to obtain possible values of total spin $S$. The largest permitted value of $S$ lies lowest in energy.
2. For each value of $S$, find the possible values of total angular momentum $L$. The largest value of $L$ lies lowest in energy.
3. Couple the values of $L$ and $S$ to obtain the values of $J$ (hence the name of the scheme). If the subshell is less than half full, the smallest value of $J$ lies lowest; otherwise, the largest value of $J$ lies lowest.

In deciding on the permitted values of $L$ and $S$, in addition to applying the usual rules for adding angular momenta, one also has to ensure that the total antisymmetry of the state is respected, as we will see later when considering some examples. These rules are empirical; there are exceptions, especially to the $L$ and $J$ rules (2 and 3). Nevertheless, Hund's rules are a useful guide, and we can understand their physical origin.

1. Maximising $S$ makes the spin state as symmetric as possible. This tends to make the spatial wavefunction antisymmetric, and hence reduces the Coulomb repulsion, as we saw discussing the exchange interaction in Helium.
2. Maximising $L$ also tends to keep the electrons apart. This is less obvious, though a simple classical picture of electrons rotating round the nucleus in the same or different senses makes it at least plausible.
3. The separation of energies for states of different J arises from treating the spin-orbit term $H_{SO}$ as a perturbation (fine structure).

It can be shown that the matrix element $\langle J, m_J, L, S | \sum_i \xi_i(R_i)\mathbf{L}_i\mathbf{S}_i | J, m_J, L, S\rangle$ can be written as a product of a coefficient $\zeta(L,S)$ depending only on the quantum numbers of the total momenta and a matrix element that can be calculated easily:

$$\begin{aligned}\langle J, m_J, L, S | \sum_i \xi_i(R_i)\mathbf{L}_i\mathbf{S}_i | J, m_J, L, S\rangle &= \zeta(L,S)\,\langle J, m_J, L, S | \mathbf{L}\cdot\mathbf{S} | J, m_J, L, S\rangle = \\ &= \frac{\zeta(L,S)}{2}[J(J+1) - L(L+1) - S(S+1)]\end{aligned} \tag{7.3}$$

This is the essence of the Wigner-Eckart theorem, not discussed here. Since one may show that the sign of $\zeta(L,S)$ changes according to the whether the **subshell is more or less than half-filled**, the third Hund's rule is established.

To understand the application of $LS$ coupling, it is best to work through some examples. When we discussed previously in chapter 5 the simplest multi-electron atom, helium, we have already applied implicitly the rule of the $LS$ coupling, when we considered the electron-electron interaction as the main contribution to the model beyond independent electrons.

**Problem 7.1 :** Recall the results of perturbation theory for He in Chapter 5 .

The **Helium** ground state with the $1s^2$ configuration, had $L = S = J = 0$. In fact, this is true for any completely filled subshell, as we have then $L = S = 0$ and hence $J = 0$, since the total $m_L$ and $m_S$ must equal zero if all substates are occupied. In an excited state of helium, e.g. in $(1s^1)(2p^1)$, in which one electron has been excited to the $2p$ level, we have $S = 1$ or $S = 0$, with the $S = 1$ state lying lower in energy, because of the antisymmetry of the orbital part of the wave function, and therefore a negative contribution from the exchange term. That was a clear demonstration of the reason of the first Hund rule. Combining the orbital angular momenta of the electrons yields $L = 1$ and thus, with $S = 0, J = 1$, while with $S = 1, J = 0, 1, 2$ with $J = 0$ lying lowest in energy. Once again, as with the hydrogen-like states, we may index the states of multi-electron atoms by spectroscopic term notation, ${}^{2S+1}L_J$. The superscript $2S + 1$ gives the multiplicity of $J$ values into which the level is split by the spin-orbit interaction; the $L$ value is represented by a capital letter $S, P, D$, etc., and $J$ is represented by its numerical value. Thus, for the $(1s^1)(2p^1)$ state of helium, there are four possible states, with terms: $3P_0$, $3P_1$, $3P_2$ and $1P_1$, where the three $3P$ states are separated by the spin-orbit interaction, and the singlet $1P$ state lies much higher in energy owing to the Coulomb interaction.

The separations between the $3P_2$ and $3P_1$ and the $3P_1$ and $3P_0$ should be in the ratio $2:1$. This is an example of the **Landé interval rule**, which states that the separation between a pair of adjacent levels in a fine structure multiplet is proportional to the larger of the two $J$ values involved. This is easily shown using Eq. ( 7.3 ) - the separation in energy between states $J$ and $J-1$ is

$$\Delta_{J,J-1} \sim J(J+1)-(J-1)J = 2J \qquad (7.4)$$

Actually in the case of helium the situation is a bit more complicated, because it turns out that the spin-orbit interaction between different electrons makes a non-negligible additional contribution to the fine structure. Other excited states of helium, of the form $(1s^1)(n\ell^1)$, can be handled similarly, and again separate into singlet and triplet states.

**Problem 7.2 :** Find the ground state term of **B (boron)**, with the electron configuration $(1s^2)(2s^2)(2p)$, by using Hund's rules.

We next consider the case of **C (Carbon)**, which has ground state electron configuration $(1s^2)(2s^2)(2p^2)$. This introduces a further complication; we now have two identical electrons in the same unfilled subshell, and we need to ensure that their wavefunction is antisymmetric with respect to electron exchange. The total spin can either be the antisymmetric singlet state with $S=0:\ \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2-|\downarrow\rangle_1|\uparrow\rangle_2)$, or one of the three symmetric triplet states with $S=1:\ |\uparrow\rangle_1|\uparrow\rangle_2$, $\frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2+|\downarrow\rangle_1|\uparrow\rangle_2)$, $|\downarrow\rangle_1|\downarrow\rangle_2$. We must therefore choose values of $L$ with the appropriate symmetry to partner each value of $S$. To form an antisymmetric orbital state, the two electrons must have different values of $m_\ell$, so the possibilities are as shown in the next table on the left. Inspecting the values of $m_L$ we can deduce that $L=1$.

## Table 7.3. Forming of antisymmetric orbital states.

| $m_\ell^{(1)}$ | $m_\ell^{(2)}$ | $m_L$ | $m_\ell^{(1)}$ | $m_\ell^{(2)}$ | $m_L$ |
|---|---|---|---|---|---|
| 1 | 0 | 1 | 1 | 1 | 2 |
| 1 | -1 | 0 | 1 | 0 | 1 |
| 0 | -1 | -1 | 1 | -1 | 0 |
| | | | 0 | 0 | 0 |
| | | | 0 | -1 | -1 |
| | | | -1 | -1 | -2 |

By contrast, to form a symmetric total angular momentum state, the two electrons may have any values of $m$, leading to the possibilities shown right in the table. Inspecting the values of $m_L$ we infer that $L=2$ or 0. We must therefore take $S=1$ with $L=1$ and $S=0$ with $L=2$ or 0.

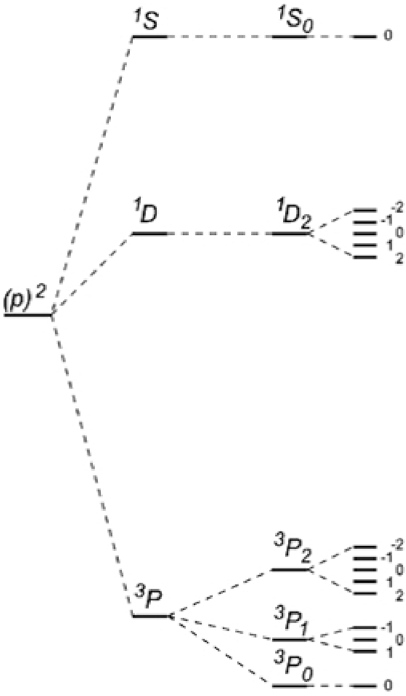
Finally, to account for the fine structure, we note that the states with $S=1$ and $L=1$ can be combined into a single $J=0$ state, three $J=1$ states, and five $J=2$ states leading to the terms $3P_0, 3P_1$, and $3P_2$ respectively. Similarly the $S=0, L=2$ state can be combined to give five $J=2$ states, $1D_2$, while the $S=0, L=0$ state gives the single $J=0$ state, $1S_0$. Altogether we recover the $1+3+5+5+1=15$ possible states with the ordering in energy as given by Hund's rules. The terms and the corresponding energies, relative to the lowest one, are shown in the table below:

## Table 7.4. Terms and the corresponding energies, relative to the lowest one.

| | $1S_0$ | $1D_2$ | $3P_2$ | $3P_1$ | $3P_0$ |
|---|---|---|---|---|---|
| $\varepsilon \sim \overline{\nu} / \mathrm{cm}^{-1}$ | 20649 | 10195 | 43 | 16 | 0 |

Here the experimental energy values are given using the conventional spectroscopic units of inverse wavelength, and the corresponding level scheme is also shown in Fig.( 7.5 ).

**Figure 7.5. Level scheme of the carbon atom $(1s^2)(2s^2)(2p^2)$. Drawing is not to scale. On the left the energy is shown without any two-particle interaction. The electron-electron interaction leads to a three-fold energy splitting with $L$ and $S$ remaining good quantum numbers. Spin orbit coupling leads to a further splitting of the states with $J$ remaining a good quantum number. Finally on the right, the levels show Zeeman splittings in an external magnetic field. In this case, the full set of 15 levels become non-degenerate.**



Level scheme of the carbon atom. Drawing is not to scale. On the left the energy is shown without any two-particle interaction. The electron-electron interaction leads to a three-fold energy splitting with L and S remaining good quantum numbers. Spin orbit coupling leads to a further splitting of the states with J remaining a good quantum number. Finally on the right, the levels show Zeeman splittings in an external magnetic field. In this case, the full set of 15 levels become non-degenerate.

Note that the Landé interval rule is approximately obeyed by the fine structure triplet, and that the separation between $L$ and $S$ values caused by the electron-electron repulsion is much greater than the spin-orbit effect. In an excited state of carbon, e.g. $(2p^1)(3p^1)$, the electrons are no longer equivalent, because they have different radial wavefunctions. So now one can combine any of $S = 0, 1$ with any of $L = 0, 1, 2$, yielding the following terms (in order of increasing energy, according to Hund's rules):

$$3D_{1,2,3}, \quad 3P_{0,1,2} \quad 3S_1 \quad 1D_2 \quad 1P_1 \quad 1S_0 \tag{7.5}$$

For **N (Nitrogen)**, the electron configuration is given by $(1s^2)(2s^2)(2p^3)$. The maximal value of spin is $S=3/2$ while $L$ can take values $3,2,1$ and 0. This result would also be apparent if we recall the that angular momentum states are eigenstates of the parity operator with eigenvalue $(-1)^\ell$. Since there are just two electrons, this result shows that both the $L=0$ and $L=2$ wavefunction must be symmetric under exchange. Since the spin wavefunction, yielding a maximal $S$ is symmetric, the spatial wavefunction must be completely antisymmetric. This demands that all three states with $m_\ell=1,0,-1$ must be involved. We must therefore have $L=0$, leading to $J=3/2$ and the term, $^4S_{3/2}$.

**Problem 7.3 :** Construct the $L=0$ state involving the addition of three $\ell=1$ angular momentum states. *Hint: make use of the total antisymmetry condition.*

As a final example, let us consider the ground state of **O (oxygen)**, which has electron configuration $(2p^4)$. Although there are four electrons in the $(2p)$ subshell, the maximum value of $S=1$. This is because there are only three available values of $m=\pm 1,0$, and therefore one of these must contain two electrons with opposite spins. Therefore, the maximum value of $m_S=1$, achieved by having electrons with $m_s=+1/2$ in both the other $m_\ell$ states. By pursuing this argument, it is quite easy to see that the allowed values of $L$, $S$ and $J$ are the same as for carbon $(2p^2)$. This is in fact a general result - the allowed quantum numbers for a subshell with $n$ electrons are the same as for that of a subshell with $n$ "holes". Therefore, the energy levels for the oxygen ground state configuration are the same as for carbon, except that the fine structure multiplet is inverted, in accordance with Hund's third rule.

# 3. jj coupling scheme

When relativistic effects take precedence over electron interaction effects, we must start by considering the eigenstates of

$$H_0 + H_{so} = H_0 + \sum_i \xi_i(R_i)\mathbf{L}_i\mathbf{S}_i. \tag{7.6}$$

These must be eigenstates of $\mathbf{J}^2$ as before, because of the overall rotational invariance, and also of $\mathbf{J}_i^2$ for each electron. Therefore, in this case, the coupling procedure is to find the allowed $j$ values of individual electrons, whose energies will be separated by the spin-orbit interaction. Then these individual j values are combined to find the allowed values of total $J$. The effect of the residual Coulomb interaction will be to split the $J$ values for a given set of js. Unfortunately, in this case, there are no simple rules to parallel those of Hund. As an example, consider a configuration $(np^2)$ in the $jj$ coupling scheme, to be compared with the example of carbon which we studied in the $\mathbf{LS}$ scheme. Combining $s=1/2$ with $\ell=1$, each electron can have $j=1/2$ or $3/2$. If the electrons have the same $j$ value, they are equivalent, so we have to take care of the symmetry of the wavefunction. We therefore have the following possibilities:

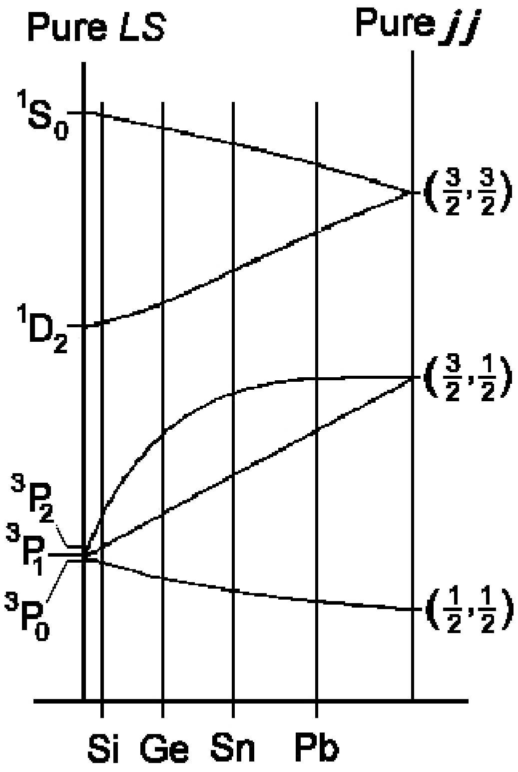
- $j_1=j_2=3/2 \Longrightarrow J=3,2,1,0$, of which $J=2,0$ are antisymmetric.
- $j_1=j_2=1/2 \Longrightarrow J=1,0$, of which $J=0$ is antisymmetric.
- $j_1=1/2$, $j_2=3/2 \Longrightarrow J=2,1$.

In $jj$ coupling, the term is written $(j_1,j_2)_J$, so we have the following terms in our example:

$$(1/2,1/2)_0 \qquad (3/2,1/2)_1(3/2,1/2)_2 \qquad (3/2,3/2)_2(3/2,3/2)_0 \tag{7.7}$$

in order of increasing energy. Note that both $LS$ and $jj$ coupling give the same values of $J$. In this case, two states with $J=0$, two with $J=2$ and one with $J=1$ and in the same order. However, the pattern of levels is different; in $LS$ coupling we found a triplet and two singlets, while in this ideal $jj$ scenario, we have two doublets and a singlet. The sets of states in the two coupling schemes must be expressible as linear combinations of one another, and the physical states for a real atom are likely to differ from either approximation. In fact, this idealized form of jj coupling is not seen in the heaviest such atom in the periodic table, lead $(6p^2)$. However, it is seen in some highly ionized states, for example in ${}_{24}\mathrm{Cr}^{18+}$, which has the same electron configuration $(2p^2)$ as carbon, but where, because of the larger unscreened charge on the nucleus, the electrons are moving more relativistically, enhancing the spin-orbit effect. However, a classic example of the transition from $LS$ to $jj$ coupling is seen in the series C-Si-Ge-Sn-Pb in the excited states $(2p)(3s)$, $(3p)(4s)$, … $(6p)(7s)$, see Fig. ( 7.6 ).

### Figure 7.6. Transition from the LS to the jj coupling as going down in the IV. (14.) column of the periodic table



Transition from the LS to the jj coupling as going down in the IV. (14.) column of the periodic table

Here, the electrons are not in the same subshell, so their wavefunctions overlap less, and the Coulomb repulsion is reduced compared to the spin-orbit interaction. Analysing this situation in the $LS$ coupling approximation, one expects a triplet and a singlet: $3P_{0,1,2}, 1P_1$, while in the $jj$ scheme one expects two doublets: $(1/2,1/2)_{0,1}, (1/2,3/2)_{2,1}$. Experimentally, C and Si conform to the $LS$ expectation and Pb to the $jj$ scheme, while Ge and Sn are intermediate.

# 4. Atomic spectra

Atomic spectra result from transitions between different electronic states of an atom via emission or absorption of photons. In emission spectra, an atom is excited by some means (e.g. thermally through collisions, or by an electric discharge), and one observes discrete spectral lines in the light emitted as the atoms relax. In absorption spectra, one illuminates atoms using a broad waveband source, and observes dark absorption lines in the spectrum of transmitted light. Of course the atoms excited in this process subsequently decay by emitting photons in random directions; by observing in directions away from the incident light this fluorescence radiation may be studied. The observation of these spectral lines is an important way of probing the atomic energy levels experimentally. In the case of optical spectra and the nearby wavebands, the excited states responsible generally involve the excitation of a single electron from the ground state to some higher level. In some cases, it may simply involve a different coupling of the angular momenta within the same electron configuration. These are the kinds of excitations which we are about to discuss. However, other types of excitations are also possible. For example, X-ray emission occurs when an electron has been removed from one of the innermost shells of a heavy atom; as electrons cascade down to fill the hole, high energy photons may be emitted. The basic theory governing stimulated emission and absorption, and spontaneous emission of photons will be outlined in detail when we study radiative transitions. Here we must anticipate some of the basic conclusions of that study. In the electric dipole approximation, the rate of transitions is proportional to the square of the matrix element of the electric dipole operator between the initial and final stationary states: $|\langle u_f|\mathbf{D}|u_i\rangle|^2$. In addition, the rate of spontaneous transitions is proportional to $\omega_{\mathrm{if}}^3$, where $\omega_{\mathrm{if}} = (E_i - E_f)/\hbar$ denotes the energy separation between the states. The symmetry properties of the dipole operator $\mathbf{D}$ (it is an odd vector operator) imply that the matrix elements may vanish identically between a large number of pairs of stationary states $u_f$ and $u_i$ This leads to a set of selection rules defining which transitions are allowed. Here we consider the simplest case of a single electron, but the principles can be generalized. We just enumerate these selection rules shortly.

- The parity must change;
- $\Delta J = \pm 1, 0$ (but $0 \leftrightarrow 0$ is not allowed) and $\Delta M_J = \pm 1, 0$

Atomic states are always eigenstates of parity and of total angular momentum, $J$, so these selection rules can be regarded as absolutely valid in electric dipole transitions. It should be emphasized again, though, that the electric dipole approximation is an approximation, and higher order processes may occur, albeit at a slower rate, and have their own selection rules.

In specific coupling schemes, further selection rules may apply. In the case of ideal $LS$ coupling, we also require:

- $\Delta S = 0$ and $\Delta M_S = 0$;
- $\Delta L = \pm 1, 0$ (but $0 \leftrightarrow 0$ is not allowed) and $\Delta M_L = \pm 1, 0$; and
- $\Delta \ell_i = \pm 1$ if only electron $i$ is involved in the transition.

In $LS$ coupling, the states are eigenstates of total spin; since the dipole operator does not operate on the spin part of the wavefunction, the rules on $\Delta S$ and $\Delta M_S$ follow straightforwardly. This, and the absolute rules relating to $J$, imply the rules for $L$ and $M_L$. The rule for $\Delta \ell_i$ follows from the parity change rule, since the parity of the atom is the product of the parities of the separate electron wavefunctions, given by $(-1)^{\ell_i}$. However, since $LS$ coupling is only an approximation, these rules should themselves be regarded as approximate.

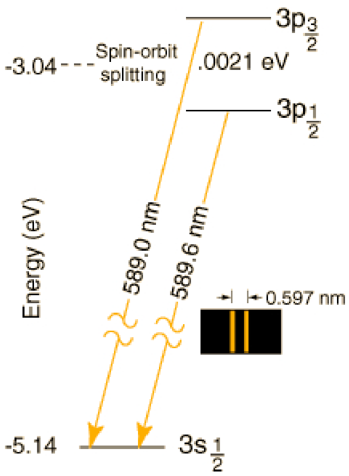
## 4.1. Single electron atoms

In this context, "single electron atoms" refer to atoms whose ground state consists of a single electron in an $s$ level, outside closed shells; it is this electron which is active in optical spectroscopy. Our discussion therefore encompasses the alkali metals, such as sodium, and also hydrogen. We take sodium, whose ground state configuration is $(3s^1)$.

- The ground state term is $2S_{1/2}$. The excited states are all doublets with $J = L \pm 1/2$, except for the $s$ states, which are obviously restricted to $J = 1/2$.
- The parity is given by $(-1)^{\ell_i}$, so the allowed transitions involve changes in $\ell$ by $\pm 1$, i.e. $s \leftrightarrow 1p, p \leftrightarrow d, d \leftrightarrow f$, etc. Changes of more than one unit in $\ell$ would violate the $\Delta J$ rule.
- The $s \leftrightarrow p$ transitions are all doublets. All the doublets starting or ending on a given $p$ state have the same spacing in energy. The transition $3s \leftrightarrow 3p$ gives rise to the familiar yellow sodium "D-lines" at 589 nm , see Figure ( 7.7 ).

**Figure 7.7. The yellow D line doublet of Na. The transition which gives rise to the doublet is from the $3p$ to the $3s$ level. The fact that the $3s$ state is lower than the $3p$ state is a good example of the dependence of atomic energy levels on orbital angular**

**momentum. The $3s$ electron penetrates the $1s$ shell more and is less effectively shielded than the $3p$ electron, so the $3s$ level is lower. The fact that there is a doublet shows the smaller dependence of the atomic energy levels on the total angular momentum. The $3p$ level is split into states with total angular momentum $J=3/2$ and $J=1/2$ by the spin-orbit interaction. http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/sodzee.html**



The yellow D line doublet of Na. The transition which gives rise to the doublet is from the 3p to the 3s level. The fact that the 3s state is lower than the 3p state is a good example of the dependence of atomic energy levels on orbital angular momentum. The 3s electron penetrates the 1s shell more and is less effectively shielded than the 3p electron, so the 3s level is lower. The fact that there is a doublet shows the smaller dependence of the atomic energy levels on the total angular momentum. The 3p level is split into states with total angular momentum J=3/2 and J=1/2 by the spin-orbit interaction.

- The $p \leftrightarrow d$ transitions involve two doublets, $2P_{1/2,3/2}$ and $2D_{3/2,5/2}$. However, the $2P_{1/2} \leftrightarrow 2D_{5/2}$ transition is forbidden by the $\Delta J$ rule, so the line is actually a triplet. In practice, the spin-orbit interaction falls quite rapidly with increasing $\ell$ (and with increasing $n$ ) as the effect of screening increases, so that the effect of the $2D_{3/2,5/2}$ splitting may not be resolved experimentally.
- As $n$ increases, the energy levels approach (from below) those for hydrogen, because the nuclear charge is increasingly effectively screened by the inner electrons. This happens sooner for the higher $\ell$ values, for which the electron tends to lie further out from the nucleus.
- In an absorption spectrum, the atoms will start from the ground state, so only the $3s \leftrightarrow np$ ines can be seen. In emission, the atoms are excited into essentially all their excited levels, so many more lines will be seen in the spectrum.

The comments above for sodium also apply for hydrogen, except that, in this case, $(2s, 2p)$, $(3s, 3p, 3d)$, etc. are degenerate. One consequence is that the $2s$ state in hydrogen is metastable - it cannot decay to the only lower lying level $1s$ by an electric dipole transition. In fact its favoured spontaneous decay is by emission of two photons; a process which is described by second-order perturbation theory. In practice, hydrogen atoms in a $2s$ state are more likely to deexcite through collision processes. During an atomic collision, the atoms are subject to strong electric fields, and we know from our discussion of the Stark effect that this will mix the $2s$ and $2p$ states, and decay from $2p$ to $1s$ is readily possible.

## 4.2. Helium and alkali earths

We next discuss atoms whose ground state consists of two electrons in an s level. Our discussion therefore covers helium $(1s^2)$, and the alkali earths: beryllium $(2s^2)$, magnesium $(3s^2)$, calcium $(4s^2)$, etc.

We start with helium, which we have already discussed from a different aspect in Chapter 5 Those results will help us to understand the present discussion

- The ground state has term $1S_0$. The excited states are of the form $(1s)(n\ell)$ (the energy required to excite both of the 1s electrons to higher states is greater than the first ionization energy, and therefore these form discrete states within a continuum of ionized $\text{He}^+ + e^-$ states). The excited states can have $m$ or $S = 1$, with $S = 1$ lying lower in energy (Hund's rule 1).

- The LS coupling approximation is pretty good for helium, so the $S = 0$ selection rule implies that the $S = 0$ and $S = 1$ states form completely independent systems as far as spectroscopy is concerned.

- The lines in the $S = 0$ system are all singlets. They can be observed in emission, and those starting from the ground state can be seen in absorption.

- The lines in the $S = 1$ system are all multiplets. They can be observed in emission only. Transitions of the form $3S_1 \leftrightarrow 3P_{2,1,0}$ are observed as triplets, spaced according to the Landé interval rule. Transitions of the form $3P_{2,1,0} \leftrightarrow 3D_{3,2,1}$ are observed as sextuplets, as is easily seen by application of the $\Delta J = \pm 1, 0$ rule. Actually, as mentioned above, the fine structure is a little more subtle in the case of helium.

The alkali earths follow the same principles. In the case of calcium, the triplet 4p state is the lowest lying triplet state, and therefore metastable. In fact a faint emission line corresponding to the $3P_1 \to 1S_0$ decay to the ground state may be observed; this violates the $\Delta S = 0$ rule, and indicates that the $LS$ coupling approximation is not so good in this case. A more extreme example is seen in Mercury, ground state $(6s^2)\ (5d^{10})$. Excited states involving promotion of one of the $6s$ electrons to a higher level can be treated just like the alkali earths. In this case the "forbidden" $3P_1 \to 1S_0$ is actually a prominent feature of the emission spectrum in the visible, implying a significant breakdown of the $LS$ approximation.

## 4.3. Multi-electron atoms

Similar principles can be used to make sense of the spectra of more complicated atoms, though unsurprisingly their structure is more complex. For example, carbon, with ground state $(2s^2)(2p^2)$, corresponds to terms $3P_{0,1,2}$, $1D_2$ and $1S_0$ as discussed above. The excited states are of the form $(2s^2)(2p^1)(n\ell^1)$, and can be separated into singlets and triplets, and in addition excitations of the form $(2s^1)(2p^3)$ can arise. Nitrogen, with ground state $(2s^2)(2p^3)$, has three unpaired electrons, so the ground state and excited states form doublets $(S = 1/2)$ and quartets $(S = 3/2)$ with correspondingly complex fine structure to the spectral lines.

# 5. Zeeman effect

## 5.1. Single-electron atoms

We are now in a position to revisit the question of how atomic spectra are influenced by a magnetic field. To orient our discussion, let us begin with the study of hydrogen-like atoms involving just a single electron. In a magnetic field, the Hamiltonian of such a system is described by $H = H_0 + H_{\text{rel}} + H_Z$, where $H_0$ denotes the non-relativistic Hamiltonian for the atom, $H_{\text{rel}}$ incorporates the relativistic corrections considered earlier and

$$\boxed{H_Z = -\frac{qB}{2m_e}(L_z + 2S_z), \qquad (7.8)}$$

denotes the Zeeman energy associated with the coupling of the spin and orbital angular momentum degrees of freedom to the magnetic field. Here, since we are dealing with confined electrons, we have neglected the diamagnetic contribution to the Hamiltonian, and assumed the approximate value $g_s = 2$. Depending on the scale of the magnetic field, the spin-orbit term in $H_{\text{rel}}$ or the Zeeman term may dominate the spectrum of the atom.

Previously, we have seen that, to leading order, the relativistic corrections lead to a fine-structure energy shift of

$$\Delta\varepsilon_{n,j} = \frac{m_e c^2}{2}\left(\frac{Z\alpha}{n}\right)^4\left(\frac{3}{4}-\frac{n}{j+1/2}\right) \tag{7.9}$$

for states $|n, j=\ell\pm 1/2, m_j, \ell\rangle$.

**For weak magnetic fields**, we can also treat the Zeeman energy in the framework of perturbation theory. Here, although states with common $j$ values (such as $2S_{1/2}$ and $2P_{1/2}$ ) are degenerate, the two spatial wavefunctions have different parity ( $\ell=0$ and 1 in this case), and the off-diagonal matrix element of $H_Z$ coupling these states vanishes. We may therefore avoid using degenerate perturbation theory. Making use of the relation

$$\langle n, j=\ell\pm 1/2, m_j, \ell|S_z|n, j=\ell\pm 1/2, m_j, \ell\rangle = \pm\frac{\hbar m_j}{2\ell+1}, \tag{7.10}$$

we obtain the following expression for the first order energy shift,

$$\Delta\varepsilon^Z_{j=\ell\pm 1/2} = \mu_B B m_j\left(1\pm\frac{1}{2\ell+1}\right) \tag{7.11}$$

where $\mu_B$ denotes the Bohr magneton. Therefore, we see that all degenerate levels are split due to the magnetic field. In contrast to the "normal" Zeeman effect, the magnitude of the splitting depends on $\ell$.

**Problem 7.4 :** Show the validity of these relations using the results of Chapter 3 .

**For strong magnetic field** the Zeeman energy becomes large in comparison with the spin-orbit contribution. In this case, we must work with the basis states $|n, \ell, m_\ell, m_s\rangle$ in which both $H_0$ and $H_Z$ are diagonal. Within first order of perturbation theory, one then finds that

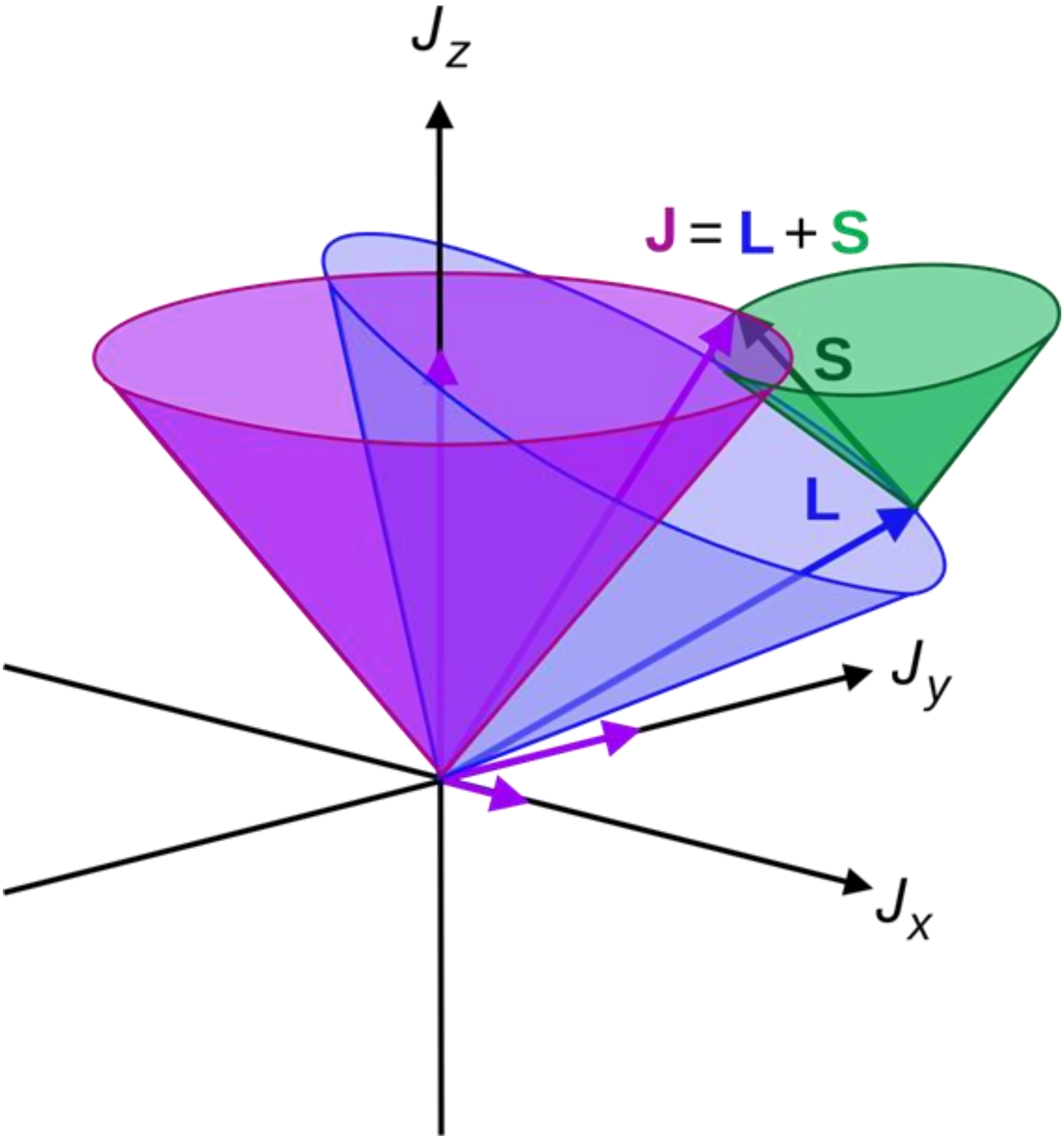
$$\Delta\varepsilon^Z_{n,\ell,m_\ell,m_s} = \mu_B B(m_\ell+2m_s)+\frac{1}{2}mc^2\left(\frac{Z\alpha}{n}\right)^4\left(\frac{3}{4}-\frac{n}{\ell+1/2}+\frac{n m_\ell m_s}{\ell(\ell+1/2)(\ell+1)}\right) \tag{7.12}$$

the first term arising from the Zeeman energy and the remaining terms from $H_{\text{rel}}$. At intermediate values of the field, we have to apply degenerate perturbation theory to the states involving the linear combination of $|n, j=\ell\pm 1/2, m_j,\rangle$. Such a calculation would lead us to far, so we refer to the literature.

## 5.2. Multi-electron atoms

For a multi-electron atom in a weak magnetic field, the appropriate unperturbed states are given by $|J, M_J, L, S\rangle$, where $J,\ L,\ S$ refer to the total angular momenta, see Figure 7.8 .

**Figure 7.8. In the weak field case, the vector model implies that the coupling of the orbital angular momentum $\mathrm{L}$ to the spin angular momentum $\mathrm{S}$ is stronger than their coupling to the external field. In this case where spin-orbit coupling is dominant, they can be visualized as combining to form a total angular momentum $\mathrm{J}$ which then precesses about the $z$ direction of the magnetic field. http://en.wikipedia.org/wiki/File:LS_coupling.svg**



In the weak field case, the vector model implies that the coupling of the orbital angular momentum L to the spin angular momentum S is stronger than their coupling to the external field. In this case where spin-orbit coupling is dominant, they can be visualized as combining to form a total angular momentum J which then precesses about the z direction of the magnetic field.

To determine the Zeeman energy shift, we need to determine the matrix element of $S_z$. To do so, we can make use once more of the identity $2\,\mathbf{L}\cdot\mathbf{S}=\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2$. This operator is diagonal in the collective basis of states, $|J,M_J,L,S\rangle$. Therefore, the matrix element of the operator

$$-i\hbar(\mathbf{S}\times\mathbf{L})=\mathbf{S}(\mathbf{L}\cdot\mathbf{S})-(\mathbf{L}\cdot\mathbf{S})\mathbf{S} \qquad (7.13)$$

must vanish.

**Problem 7.5 :** Prove the identity ( 7.13 ). *Hint: Use the fact that* $[S_i,S_j]=i\hbar\epsilon_{ijk}S_k$.

Moreover, from the identity $[\mathbf{L}\cdot\mathbf{S},\mathbf{J}]=0$, it follows that the matrix element of the vector product

$$i\hbar(\mathbf{S}\times\mathbf{L})\times\mathbf{J}=\mathbf{S}\times\mathbf{J}(\mathbf{L}\cdot\mathbf{S})-(\mathbf{L}\cdot\mathbf{S})\mathbf{S}\times\mathbf{J}-\mathbf{S}(\mathbf{L}\cdot\mathbf{J}) \tag{7.14}$$

must also vanish. If we expand the left hand side, we find that the matrix element of

$$\begin{aligned}(\mathbf{S}\times\mathbf{L})\times\mathbf{J}= & \ \mathbf{L}(\mathbf{S}\cdot\mathbf{J})-\mathbf{S}(\mathbf{L}\cdot\mathbf{J})=(\mathbf{J}-\mathbf{S})(\mathbf{S}\cdot\mathbf{J})-\mathbf{S}((\mathbf{J}-\mathbf{S})\cdot\mathbf{J})\\ = & \ \mathbf{J}(\mathbf{S}\cdot\mathbf{J})-\mathbf{S}\mathbf{J}^2\end{aligned} \tag{7.15}$$

also vanishes.

Therefore, it follows that $\langle\mathbf{S}\mathbf{J}^2\rangle=\langle\mathbf{J}(\mathbf{S}\cdot\mathbf{J})\rangle$, where the expectation value is taken over the collective basis states. Then, with $\mathbf{S}\cdot\mathbf{J}=\frac{1}{2}(\mathbf{J}^2+\mathbf{S}^2-\mathbf{L}^2)$ we have that

$$\langle S_z\rangle=\langle J_z\rangle\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \tag{7.16}$$

As a result, in first order perturbation theory the energy shift arising from the Zeeman term is given by

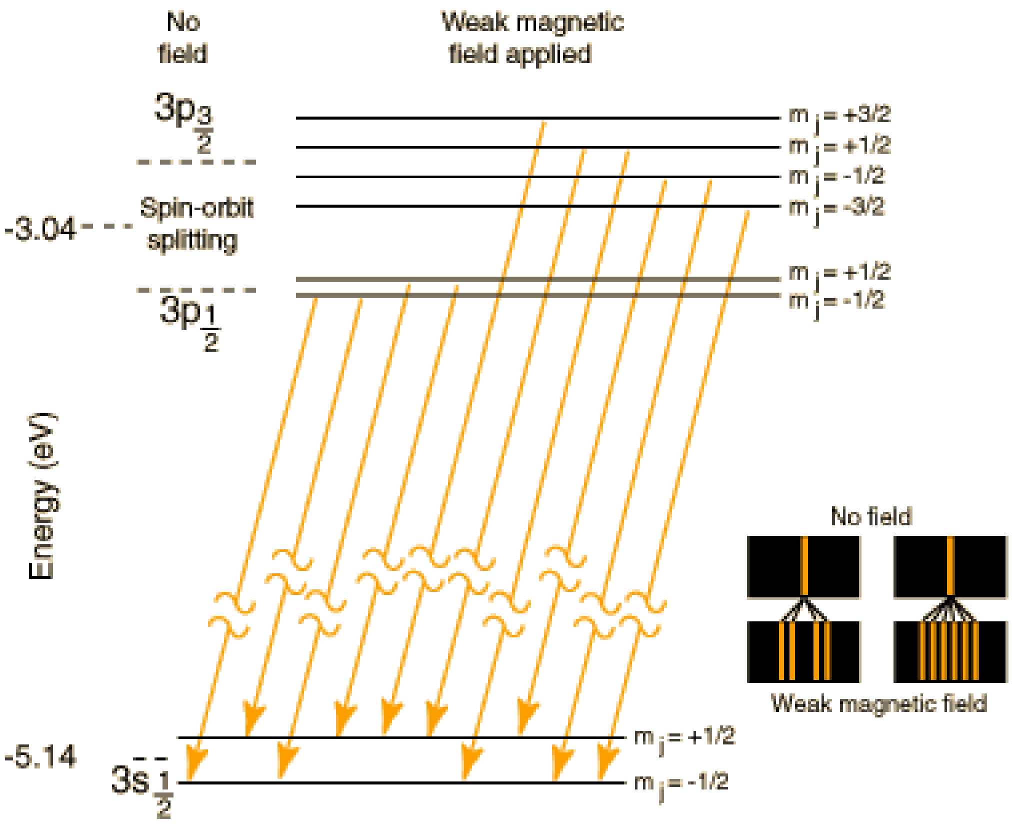
$$\Delta\varepsilon_{J,M_J,L,S}=\mu_B g_J M_J B, \tag{7.17}$$

where

$$g_J=1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \tag{7.18}$$

denotes the **effective Landé g -factor**, which lies between 1 and 2. Note that, in the special case of hydrogen, where $S=1/2$ and $J=L\pm\ 1/2$, we recover our previous result. The predicted Zeeman splitting for sodium is shown in Figure 7.9 .

**Figure 7.9. In the presence of an external magnetic field, the $3p$ levels are further split by the magnetic dipole energy, showing dependence of the energies on the z-component of the total angular momentum. The $3p_{1/2}\rightarrow 3s_{1/2}$ transition at $589.6\,\mathrm{nm}$ is split into 4, while the $3p_{3/2}\rightarrow 3s_{1/2}$ at $589.0\,\mathrm{nm}$ is split into 6 components. http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/sodzee.html**



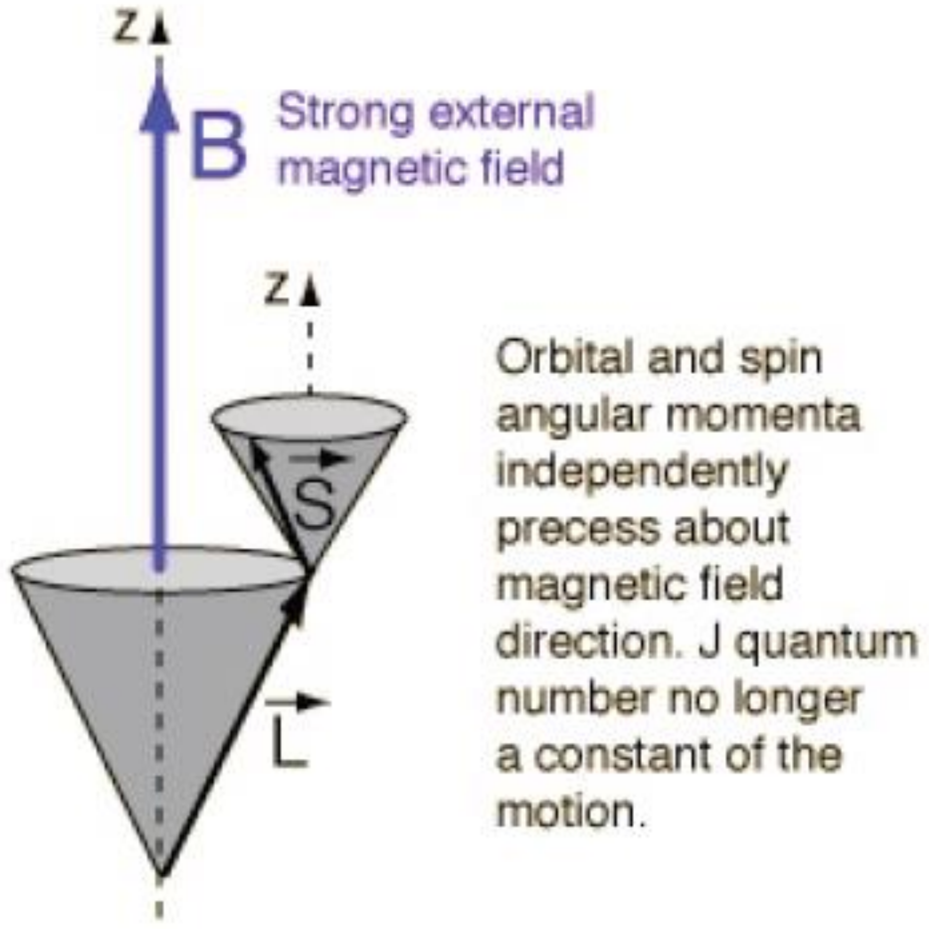
In the presence of an external magnetic field, the 3p levels are further split by the magnetic dipole energy, showing dependence of the energies on the z-component of the total angular momentum.

In the strong field limit, where the influence of Zeeman term dominates, the appropriate basis states are set by $|L, M_L, S, M_S\rangle$, in which the operators $\mathbf{L}^2, L_z, \mathbf{S}^2, S_z$, and $H_Z$ are diagonal. Not going into the details in this case, we just state that the energy splitting takes the form

$$\Delta\varepsilon^Z_{n,\ell,m_\ell,m_s} = \mu_B B(M_L + 2M_S) + \frac{1}{2}mc^2\left(\frac{Z\alpha}{n}\right)^4\left(\frac{nM_LM_S}{L(L+1/2)(L+1)}\right) \tag{7.19}$$

where the second term arises from the spin-orbit interaction.

**Figure 7.10. In the strong field case, $\mathbf{S}$ and $\mathbf{L}$ couple more strongly to the external magnetic field than to each other, and can be visualized as independently precessing about the external field direction.**

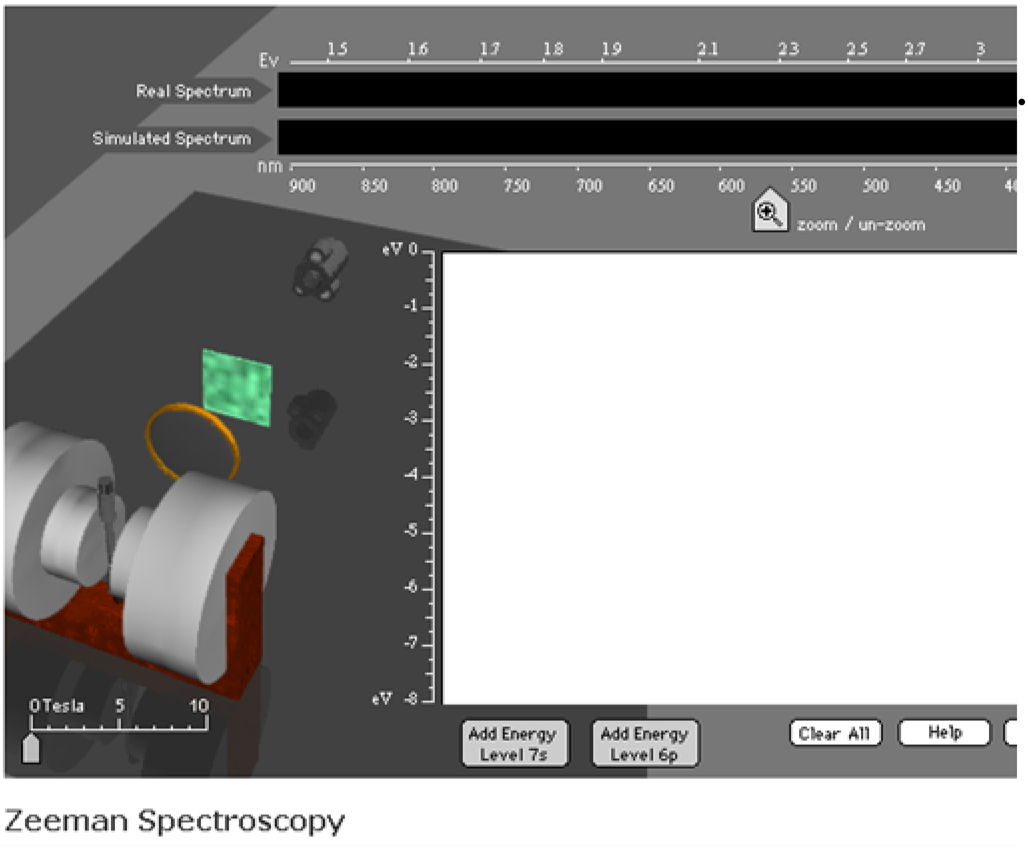


In the strong field case, S and L couple more strongly to the external magnetic field than to each other, and can be visualized as independently precessing about the external field direction.

**Animation:**

On this interactive shochwave animation we can investigate the Zeeman effect in case of mercury gas.

- Adding and manipulating energy levels
- Viewing the spectrum
- Matching trial spectral lines to those



of the actual spectrum

- Varying the magnetic field

# Chapter 8. Electronic Structure of Molecules

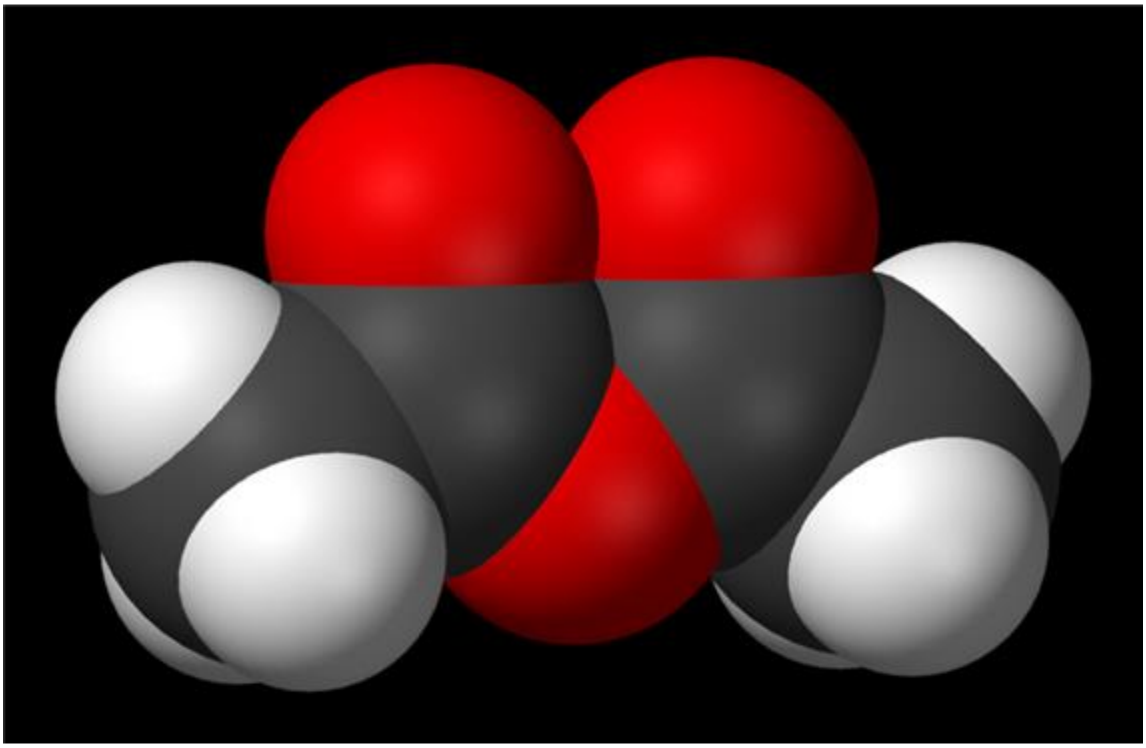
**Goals:** In this chapter we extend the methods of finding the stationary states of many electron atoms to molecules. Here two additional complications appear beyond the difficulty of having several interacting electrons. One of them is the fact that the **nuclei of a molecule are also moving relatively to each other**, and the other one is that **the potential acting on the electrons is not centrally symmetric**, and cannot even be approximated by one of having such a symmetry. Nevertheless, the large difference in the mass of the electron and the nuclei, still allows one to decouple their motion, which is called the **adiabatic approximation**, and we present here the principles of this procedure. Beginning from the second half of the 20th century, with the advent of electronic computers the Hartrre-Fock method and its extensions are performed routinely to determine the electronic structure of molecules, at least of those consisting of no more than about a few tens of atoms.

**Prerequisites:** Chapters 6 . and 7 . of the present Lecture Notes.

## 1. Introduction

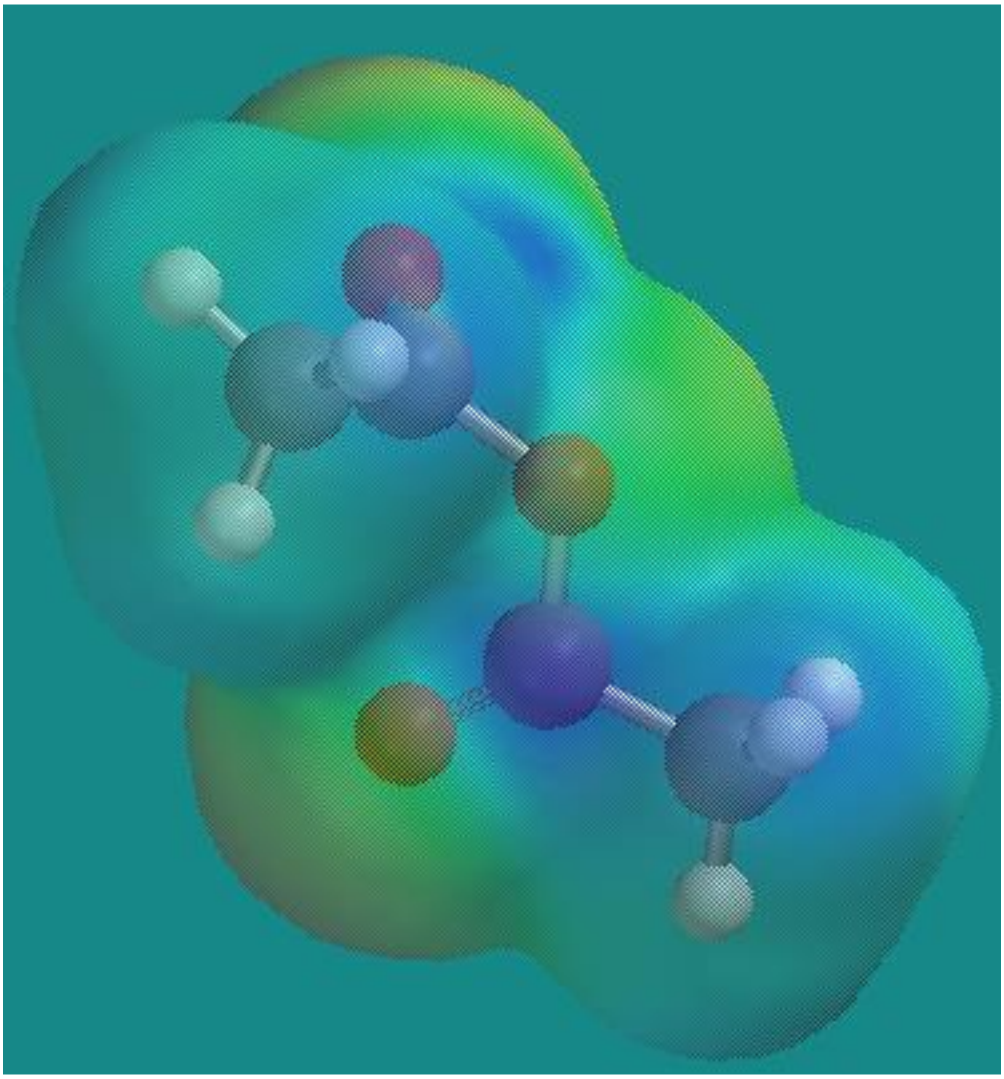
In atomic, molecular or solid state physics the composite quantum mechanical system, is considered to consist of a number of atomic nuclei, let this number be denoted by $N_n$ and of electrons their number will be denoted by $N_e$. At present we are not aware of any structure of the electron, so these particles are deemed to be elementary, while we know that nuclei are composite particles at a deeper level. We need not take this structure into account, however, because it manifests only at $\mathrm{KeV}$ or higher energies, in the domain of nuclear physics, while our aim here is to consider the chemical energy range, which is of the order of a few tens of $\mathrm{eV}$ -s or less. In most cases one can also rely on a nonrelativistic treatment, as we shall do it here.

**Figure 8.1. Acetic anhydrid. http://en.wikipedia.org/wiki/File:Acetic-anhydride-3D-vdW.png**



Acetic anhydrid.

**Figure 8.2. Electronic density of the Acetic anhydrid $(CH3CO)_2O$ molecule in the ground state. http://en.wikipedia.org/wiki/File:Acetic_anhydride_electron_density.PNG**



Electronic density of the Acetic anhydrid molecule in the ground state.

## 2. The Hamiltonian of a molecular system

The total Hamiltonian of such a system consists of the following terms:

- The kinetic energy of all the electrons:

$$T_e = \sum_i^{N_e} \frac{\mathbf{P}_i^2}{2m} \tag{8.1}$$

- The kinetic energy of all the nuclei

$$T_n = \sum_a^{N_e} \frac{\mathbf{P}_a^2}{2m_a} \tag{8.2}$$

- the electron-electron interaction

$$V_{ee} = \frac{q_0^2}{4\pi\epsilon_0}\sum_{i<j}\frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} = \frac{q_0^2}{4\pi\epsilon_0}\sum_{i<j}\frac{1}{|\mathbf{R}_{ij}|} \tag{8.3}$$

- the Coulomb interaction of the electrons with the nuclei

$$V_{en} = -\frac{q_0^2}{4\pi\epsilon_0}\sum_{i}^{N_e}\frac{Z_a}{|\mathbf{R}_i - \mathbf{R}_a|} = -\frac{q_0^2}{4\pi\epsilon_0}\sum_{i}\sum_{a}^{N_n}\frac{Z_a}{|\mathbf{R}_{ia}|} \tag{8.4}$$

- the Coulomb interaction of the nuclei

$$V_{nn} = \frac{q_0^2}{4\pi\epsilon_0}\sum_{a<b}\frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} = \frac{q_0^2}{4\pi\epsilon_0}\sum_{a<b}\frac{Z_a Z_b}{|\mathbf{R}_{ab}|}. \tag{8.5}$$

Here the $\mathbf{P}_i$ is the 3 dimensional momentum operator of the $i$ -th electron, and $m$ is its mass, which is identical for all electrons. The nuclei in the system are labeled by the subscript $a$, the $a$ -th nucleon has mass $m_a$ and a charge of $q_0 Z_a$ where $Z_a$ is the number of protons in the nucleus, and $\mathbf{P}_a$ denotes the momentum operator of the nucleus. The terms (iii), (iv), (v) correspond to the assumed pairwise Coulomb interactions of the charged constituents. $\mathbf{R}_i$ and $\mathbf{R}_a$ are the coordinate (vector) operators corresponding the positions of electrons and nuclei respectively. As it is usual in atomic physics, we shall use atomic units where

$$\hbar = 1, \quad m_e = 1, \quad \frac{q_0^2}{4\pi\epsilon_0} = 1. \tag{8.6}$$

The length, and energy units are then the Bohr radius and the atomic energy unit, called hartree

$$\begin{aligned} 4\pi\epsilon_0\frac{\hbar^2}{m_e q_0^2} &= a_0 = 0.53 \times 10^{-10}\,\text{meter} \\ \frac{q_0^2}{4\pi\epsilon_0}\frac{1}{a_0} &= 1\,\text{hartree} = 2\,\text{Rydberg} = 27.2\,\text{eV} = 4.36 \times 10^{-18}\,\text{J}\,. \end{aligned} \tag{8.7}$$

The Hamiltonian of the system is the sum of the terms above:

$$H = T_e + T_n + V_{ee} + V_{en} + V_{nn} = T_e + T_n + V, \tag{8.8}$$

where $V$ denotes the total potential energy including all the three Coulomb interactions. The task is to solve the energy eigenvalue equation of this Hamiltonian:

$$H\Phi(\mathbf{R},\mathbf{r}) = \mathcal{E}\Phi(\mathbf{R},\mathbf{r}). \tag{8.9}$$

The eigenfunction is a function of all nuclear coordinates $R$ and all electron coordinates $r$, inserted in the argument of $\Phi(\mathbf{R},\mathbf{r})$ in a contracted way. The exact solution is impossible except for a few very simple cases. Therefore one has to introduce several approximations which however can yield surprisingly good results if compared with experimental values. The first approximation we apply will be based on the huge ratio of the nuclear mass and the electron mass. This ratio is a little more than 1836 already for the lightest atom the Hydrogen, and is growing with the factor $Z_a$ for heavier atoms. We split the Hamiltonian into two parts:

$$H = (T_e + V) + T_n. \tag{8.10}$$

The first approximation step is to omit $T_n$ the nuclear kinetic energy, and consider the motion of the electrons in a possible but fixed nuclear configuration. This is justified by the fact that while the momenta of the nuclei and the electrons must of the same magnitude, because of momentum conservation, the kinetic energy of the nuclei is usually much smaller than that of the electrons, due to the mass in the denominators in $T_n$ and $T_e$.

The sum in the parentheses will be denoted by $H_e$ and will be called the electron Hamiltonian.

$$H_e = T_e + V. \tag{8.11}$$

We first look for the solution of the eigenvalue problem of $H_e$ at a given but arbitrary nuclear configuration, i. e. with a given set of $\{\mathbf{R}_a\} = \mathbf{R}$ -s, i. e. we omit here

$$H_e \Psi_\lambda(\mathbf{R}, \mathbf{r}) = E_\lambda(R) \Psi_\lambda(\mathbf{R}, \mathbf{r}). \tag{8.12}$$

The nuclear coordinates are considered as parameters here. The functions $\Psi_\lambda(\mathbf{R}, \mathbf{r})$ form an orthogonal basis set and can be normalized for any fixed $\mathbf{R}$,

$$\langle \Psi_\lambda(\mathbf{R}, \mathbf{r}) \,|\, \Psi_{\lambda'}(\mathbf{R}, \mathbf{r}) \rangle = \delta_{\lambda\lambda'}. \tag{8.13}$$

Therefore the total wave function $\Phi(\mathbf{R}, \mathbf{r})$ can be expanded in terms of $\Psi_\lambda(\mathbf{R}, \mathbf{r})$ with $\mathbf{R}$ dependent expansion coefficients, $\phi_\lambda(\mathbf{R})$, which describe the nuclear motion if we have this expansion for all possible $\mathbf{R}$ -s:

$$\Phi(\mathbf{R}, \mathbf{r}) = \sum_\lambda \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r}). \tag{8.14}$$

In order to find $\phi_\lambda(\mathbf{R})$ we substitute the expansion into the eigenvalue problem of $H$.

$$\begin{aligned} (H_e + T_n) \sum_\lambda \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r}) &= \sum_\lambda \left( \phi_\lambda(\mathbf{R}) E_\lambda \Psi_\lambda(\mathbf{R}, \mathbf{r}) + T_n \left[ \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r}) \right] \right) \\ &= \mathcal{E} \sum_\lambda \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r}) \end{aligned} \tag{8.15}$$

In the coordinate representation the term $T_n \left[ \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r}) \right]$ can be written as

$$T_n \left[ \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r}) \right] = - \sum_a \frac{1}{2M_a} \Delta_a [\phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r})], \tag{8.16}$$

where the effect of the Laplace operator on the product is given by

$$\Delta_a [\phi_\lambda \Psi_\lambda)] = \Delta_a [\phi_\lambda] \Psi_\lambda + 2 \nabla_a [\phi_\lambda] [\nabla_a \Psi_\lambda] + \phi_\lambda \Delta_a \Psi_\lambda. \tag{8.17}$$

Then using ( 8.12 ) we obtain from ( 8.15 )

$$\sum_\lambda E_\lambda \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \mathbf{r}) - \sum_\lambda \sum_a \frac{1}{2M_a} \left\{ \Delta_a [\phi_\lambda] \Psi_\lambda + 2 \nabla_a [\phi_\lambda] [\nabla_a \Psi_\lambda] + \phi_\lambda \Delta_a \Psi_\lambda \right\} = \mathcal{E} \sum_\lambda \phi_\lambda(\mathbf{R}) \Psi_\lambda(\mathbf{R}, \tag{8.18}$$

Now we project this equation to one of the eigenfunctions of $H_e$, namely $\Psi_\kappa(\mathbf{R}, \mathbf{r})$, and use their orthogonality and normalization. In other words we multiply the equation above by $\Psi^*_\kappa(\mathbf{R}, \mathbf{r})$ and integrate with respect to the electron coordinates $\mathbf{r}$ :

$$E_\kappa \phi_\kappa(\mathbf{R}) - \sum_a \frac{1}{2M_a} \Delta_a [\phi_\kappa] + \sum_\lambda \left\{ - \sum_a \frac{1}{2M_a} \left[ \int 2 \Psi^*_\kappa(\mathbf{R}, \mathbf{r}) [\nabla_a \Psi_\lambda] d\mathbf{r} \nabla_a + \int \Psi^*_\kappa(\mathbf{R}, \mathbf{r}) \Delta_a \Psi_\lambda d\mathbf{r} \right] \right\} \phi_\lambda = \mathcal{E} \phi_\kappa(\mathbf{R} \tag{8.19}$$

The term in the braces in the above equation will be denoted by $B_{\kappa\lambda}(R)$, it is an $R$ dependent matrix, and with this notation

$$(T_n + E_\kappa + B_{\kappa\kappa})\phi_\kappa + \sum_{\lambda\neq\kappa} B_{\kappa\lambda}(R)\phi_\lambda = \mathcal{E}\phi_\kappa(\mathbf{R}). \tag{8.20}$$

The last term on the right hand side couples the motion of **distinct** nuclei through the electron motion. If we neglect this term we get the **adiabatic approximation**. If in addition we neglect the diagonal term $B_{\kappa\kappa}$, we get the so called **Born-Oppenheimer (BO) approximation**, where the state of the nuclei are determined only by the energy eigenvalues $E_\kappa$, and their stationary states $\phi_\kappa$ are determined by the equation

$$(T_n + E_\kappa(R))\phi_\kappa = \mathcal{E}\phi_\kappa(\mathbf{R}). \tag{8.21}$$

This means that the electron energy eigenvalues $E_\kappa(R)$ obtained for each fixed nuclear configuration obtained from ( 8.12 ) do form an affective potential for the nuclear motion, besides their kinetic energy given by the operator $T_n$. The BO approximation fails in the vicinity of crossing points, where different $E_\kappa(R)$ eigenvalues cross or even if they get close to each other.

To summarize the results of this section, using the 3 approximations here: one first solves the electron eigenvalue equation $H_e\Psi_\lambda(\mathbf{R},\mathbf{r}) = E_\lambda(R)\Psi_\lambda(\mathbf{R},\mathbf{r})$, for a possible set of fixed nuclear positions $\mathbf{R}$, and then turns to the solution of the eigenvalue problem of the nuclear Hamiltonian: $(T_n + E_\kappa(R))\phi_\kappa = \mathcal{E}\phi_\kappa(\mathbf{R})$.

The nuclear eigenstates contain implicitly the translational motion of the center of mass of the molecule, as well as the rotational motion of the whole system. These degrees of freedom can be separated off by going over to an appropriate coordinate system, fixed to the molecule at its center of mass.

# 3. One electron approximation for molecules

The electron Hamiltonian in atomic units takes the form:

$$H_e = T_e + V = T_e = \sum_i^{N_e} \frac{\mathbf{P}_i^2}{2} - \sum_i \sum_a^{N_n} \frac{Z_a}{|\mathbf{R}_{ia}|} + \sum_{i<j} \frac{1}{|\mathbf{R}_{ij}|} + \sum_{a<b} \frac{Z_a Z_b}{|\mathbf{R}_{ab}|} \tag{8.22}$$

Intending to separate the nuclear and electron motion - as we explained above - we have to solve first the eigenvalue problem of this Hamiltonian with fixed nuclear coordinates $\mathbf{R}_a$. Then the last term is easily calculated, as it does not depend on the electronic coordinates, and adds simply a constant to the eigenvalues, we shall denote it by

$$h_0 = \sum_{a<b} \frac{Z_a Z_b}{|\mathbf{R}_{ab}|}. \tag{8.23}$$

The first two terms depend separately on the coordinates of each of the electrons, therefore they can be written as a sum of so called one-electron operators, that depend only on the coordinates of a single electron:

$$h_1(i) = \frac{\mathbf{P}_i^2}{2} - \sum_a^{N_n} \frac{Z_a}{|\mathbf{R}_{ia}|}. \tag{8.24}$$

With this notation the electron Hamiltonian is written in the form:

$$H_e = h_0 + \sum_i h_1(i) + \sum_{i<j} \frac{1}{|\mathbf{R}_{ij}|}. \tag{8.25}$$

Now an important **approximation** comes about: we **assume** that considering each of the electrons separately from all the others, the **electron-electron interaction term can be approximated by a potential energy of that single electron in the field of all the others by a function that depends only on the coordinate of that single electron**. This potential energy for the $i$ -th electron shall be written as $v(i)$. Mathematically this means that we make the following replacement:

$$\sum_{i<j} \frac{1}{|\mathbf{R}_{ij}|} \longrightarrow \sum_i v(i). \tag{8.26}$$

This procedure is called as **one-electron approximation**, or as **independent particle approximation**. So far we do not know the explicit form of $v(i)$, but the procedure we explain below, will also yield us the form of this potential energy. It may seem that we distinguish between the electrons by taking out one, but as we will see later this will not be the case. We now have an **effective one-electron operator** to be denoted by $h(i)$ that depends only on the coordinates of a single electron.

$$h(i) = h_1(i) + v(i) \tag{8.27}$$

This is a so called one electron operator, it depends only on the coordinates of one electron. We have the following approximate Hamiltonian:

$$H^i = h_0 + \sum_i h(i). \tag{8.28}$$

$H^i$ is the sum of independent Hamiltonians, therefore its eigenfunctions can be sought as an anti symmetrized product, or Slater determinant (as the electrons are fermions):

$$\Psi(x_1, x_2 \dots x_N) = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \cdots & \varphi_1(x_N) \\ \varphi_2(x_1) & \varphi_2(x_2) & \cdots & \varphi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(x_1) & \varphi_N(x_2) & \cdots & \varphi_N(x_N) \end{vmatrix} =: \frac{1}{\sqrt{N!}} \det |\varphi_1(x_1)\varphi_2(x_2)\dots\varphi_N(x_N \tag{8.29}$$

Here $\varphi_k(x_k)$ are solutions of the one particle eigenvalue equation:

$$h(i)\varphi_k(x_i) = \varepsilon_k \varphi_k(x_i) \tag{8.30}$$

By minimizing the energy functional with respect to the one electron wave functions

$$\langle \Psi | H^i | \Psi \rangle \tag{8.31}$$

with the suitable constraint prescribing normalization we obtain

$$\left( -\frac{\hbar^2}{2m}\Delta_i - \sum_a^{N_n} \frac{Z_a}{|\mathbf{R}_{ia}|} + e_0^2 \sum_{j\neq i}^{N-1} \int \frac{|\varphi_j(\mathbf{r}_j)|^2}{R_{ij}} d^3\mathbf{r}_j - \sum_{j\neq i}^{N} \delta_{m_i m_j} \int \frac{\varphi_j^*(\mathbf{r}_j)\varphi_j(\mathbf{r}_i)\varphi_i^*(\mathbf{r}_j)}{R_{ij}} d^3\mathbf{r}_j \right) \varphi_i(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i \tag{8.32}$$

These equations are essentially the same as those obtained for atoms in the previous section, and called this time as molecular Hartree Fock equations. The only difference is that in the second term the interactions with all the nuclei of the molecule are taken into account. The last two terms contain again the functions to be determined, and in addition in the last, exchange term the dependence on the functions is non-local. So the solution again needs the application of the SCF method where one iterates the one electron states as well as the potentials obtained from them.

# 4. Using a finite basis, the Roothaan-Hall method

The molecular HF equations are integro-differential equations the solution of which is very cumbersome and time consuming procedure. C. Rothaan and G. Hall proposed a method that simplifies the solution technically by a large extent. Let us write the equation ( 8.32 ) as

$$F_i\varphi_i = \varepsilon_i\varphi_i, \tag{8.33}$$

where $F_i$, the expression in the parentheses of ( 8.32 ) is called the Fock operator. We have to note that $F_i$ is a non-local operator as it depends on the orbitals themselves.

One chooses a linearly independent finite set of one electron wave functions, $b_\nu(\mathbf{r}), \nu = 1, 2, \ldots K$, which need to be neither orthogonal, nor normalized, and expand the unknown one-electron $\varphi_i$ functions in terms of these:

$$\varphi_i(\mathbf{r}) = \sum_{\nu=1}^{K} c_\nu^{(i)} b_\nu(\mathbf{r}). \tag{8.34}$$

Substituting this expansion into ( 8.33 ) and taking the inner product with one of the $b_\nu(\mathbf{r})$ functions we obtain the matrix equation

$$\sum_{\nu=1}^{K} \langle b_\mu |\, F_i \,| b_\nu\rangle\, c_\nu^{(i)} = \varepsilon_i \sum_{\nu=1}^{K} \langle b_\mu | \, b_\nu\rangle c_\nu^{(i)}, \tag{8.35}$$

or shortly:

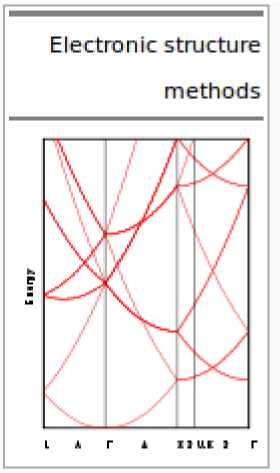
$$\sum_{\nu=1}^{K} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_\nu^{(i)} = 0, \tag{8.36}$$

where $F_{\mu\nu} = \langle b_\mu |\, F_i \,| b_\nu\rangle$ is the matrix of the Fock operator and $S_{\mu\nu} = \langle b_\mu | \, b_\nu\rangle$ is the overlap matrix between the chosen functions. We see then that the HF equations can be transformed into a matrix equation for the unknown $c_\nu^{(i)}$ coefficients, which can be solved much easier than the original integro-differential system. The problem is, however more complex than a normal secular problem solvable by diagonalization, since the Fock matrix depends upon its own eigenvectors. It is however possible to conduct the solution to a self-consistent procedure, in which at each step a generalized diagonalization procedure is to be performed in order to find the $\varepsilon_i$ values and the expansion coefficients, determining the orbitals. For the technical details we refer to the more specialized literature.

# 5. Remarks on HF theory of molecules

Finally we note that the nonlocality of the Fock operator is a major difficulty if one attempts to apply the HF method to large systems with many electrons like molecules or solids. Therefore other methods - overcoming this difficulty - have been worked out in the second half of the last century. One of the most successful among them is Density Functional Theory (DFT). The main idea behind this approach is that the important properties of the electronic structure of a quantum system is contained already in the density of the electrons, it is not necessary to know the wave function which is a probability amplitude depending on all the $\mathbf{r}_k$, $k = 1, 2, \ldots N$ positions - as random variables - of all the electrons, it can be sufficient to know the $\varrho(\mathbf{r})$ density of charges, that depend on only the single vector (3 coordinates) This idea had already been raised by Thomas and Fermi in 1927. The modern version of their approach has been established by W. Kohn and P. Hohenberg in the 1960's. The presentation of this important method is however beyond the scope of the present notes.

**Further reading:**



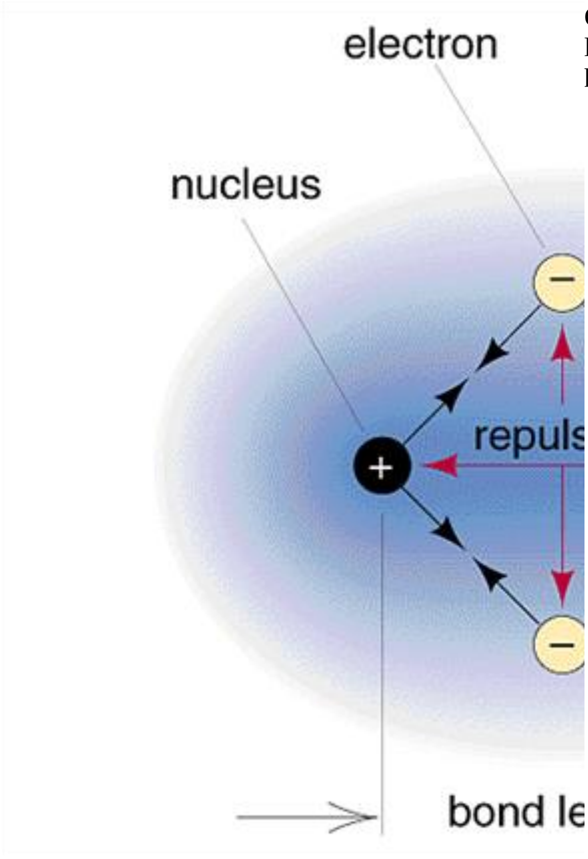
This is a Wikipedia book (collection of Wikipedia articles that can be easily saved, rendered electronically), summarizing the **Electronic structure methods**. It contains a wide range of methods for electronic structure calculations including also the methods discussed in this chapter. http://en.wikipedia.org/wiki/Book:Electronic_structure_methods

# Chapter 9. The origin of the chemical bond

**Goals:** In this chapter we consider the old problem: Why do certain atoms, which are electrically neutral, prefer to form a molecule (e.g. two H atoms a $H_2$ ). The two nuclei repel each other, as well as the two electrons. The answer can be given on quantum mechanical grounds. The total energy of the molecule must be smaller than that of two separated atoms, and this must be due to quantum mechanical effects. In order to see this we shall make use of the virial theorem.

**Prerequisites:**

**Further reading:**



On this website you can read the usual introductory level interpretation of chemical bond by chemists. http://www.chem.ufl.edu/~itl/2045/lectures/lec_13.html

# 1. Two useful theorems

## 1.1. Euler's theorem on homogeneous functions

$V(x_1, x_2 \ldots x_N)$ is called a homogeneous function of order $s$ of its coordinates, if

$$V(\mu x_1, \mu x_2, \ldots, \mu x_n) = \mu^s V(x_1, x_2, \ldots, x_n) \tag{9.1}$$

holds with a parameter $\mu$.

Euler's theorem on homogeneous functions states that if $V$ is such a function then

$$\sum_{i=1}^{n} x_i \frac{\partial V(x_1, x_2 \ldots x_N)}{\partial x_i} = sV(x_1, x_2 \ldots x_N). \quad (9.2)$$

**Problem 9.1 :** Prove Euler's theorem on homogeneous functions by differentiating the definition ( 9.1 ) with respect to $\mu$ and then substitute $\mu = 1$.

It is easy to see that the Coulomb potential is a homogeneous function of the particle coordinates with $s = -1$. This is easily seen for two charged particles *a* and *b* where the interaction potential is of the form

$$V(\mathbf{r}_a, \mathbf{r}_b) = \frac{e_a e_b}{|\mathbf{r}_a - \mathbf{r}_b|} = \frac{e_a e_b}{\sqrt{(x_a - x_b)^2 + (y_a - y_b)^2 + (z_a - z_b)^2}} \quad (9.3)$$

## 1.2. The Hellmann-Feynmann theorem

Let the Hamiltonian depend on a real parameter $\lambda$, and let us write the eigenvalue equation with normalized eigenfunctions as

$$\begin{aligned} H(\lambda)\,|\psi(\lambda)\rangle &= \mathcal{E}(\lambda)\,|\psi(\lambda)\rangle \\ \langle\psi(\lambda)\,|\psi(\lambda)\rangle &= 1, \end{aligned} \quad (9.4)$$

then

$$\frac{d}{d\lambda}\mathcal{E}(\lambda) = \left\langle \psi(\lambda) \left| \frac{d}{d\lambda} H(\lambda) \right| \psi(\lambda) \right\rangle . \quad (9.5)$$

**Problem 9.2 :** Prove the theorem by differentiating the equation $\mathcal{E}(\lambda) = \langle\psi(\lambda)|\, H(\lambda)\, |\psi(\lambda)\rangle$.

For details see: http://en.wikipedia.org/wiki/Hellmann-Feynman_theorem

# 2. The virial theorem for molecules

Consider again a molecule consisting of $N$ electrons and $N_n$ nuclei

$$H_e \Psi_\lambda(\mathbf{R}, \mathbf{r}) = E_\lambda(R) \Psi_\lambda(\mathbf{R}, \mathbf{r}) \quad (9.6)$$

where $\mathbf{R}$ denotes here the set of all operators of the nuclear positions, while $\mathbf{r}$ stands for those of the electrons. It is easy to see that the expectation value of the commutator $[H_e, A]$, where $A$ is any linear operator vanishes for all the stationary states of $H_e$, i e.

$$\langle \Psi_\lambda(\mathbf{R}, \mathbf{r}) [H_e, A] \Psi_\lambda(\mathbf{R}, \mathbf{r}) \rangle = 0. \quad (9.7)$$

**Problem 9.3 :** Prove that the expectation value of the commutator $[H_e, A]$, where $A$ is any linear operator vanishes for all the stationary states of $H_e$.

Let us now specifically choose,

$$A = \sum_i \mathbf{r}_i \mathbf{p}_i = \sum_i \sum_{\alpha = x,y,z} r_{i\alpha} p_{i\alpha} \quad (9.8)$$

where $\mathbf{p}_i$ is now the momentum operator of the $i$ -th electron and calculate the commutator

$$\begin{aligned}[H_e, A] &= \left[H_e, \sum_i \mathbf{r}_i \mathbf{p}_i\right] = \sum_i \sum_{\alpha=x,y,z} \left\{\left[H_e, r_{i\alpha}\right] p_{i\alpha} + r_{i\alpha}\left[H, p_{i\alpha}\right]\right\} = \\ &= i\hbar \sum_i \left\{-\frac{\mathbf{p}_i^2}{m} + \mathbf{r}_i \nabla_i V(\mathbf{R}, \mathbf{r})\right\}\end{aligned} \tag{9.9}$$

The second equality follows from the identity $[H, \mathbf{rp}] = H\mathbf{rp} - \mathbf{rp}H = H\mathbf{rp} - \mathbf{r}H\mathbf{p} + \mathbf{r}H\mathbf{p} - \mathbf{rp}H$ , while the third one uses the canonical commutation relations $[r_{i\alpha}, p_{j\beta}] = i\hbar\delta_{ij}\delta_{\alpha\beta}$ and the property $[V(\mathbf{R}, \mathbf{r}), \mathbf{p}_i] = i\hbar\nabla V(\mathbf{R}, \mathbf{r})$, where $\nabla_i$ denotes the gradient with respect to the **electronic** coordinate $\mathbf{r}_i$.

**Problem 9.4 :** Work out the details of the commutators above.

The first term in Eq. ( 9.9 ) is just twice the kinetic energy of the electrons times $-i\hbar$ :

$$-i\hbar \sum_i \frac{\mathbf{p}_i^2}{m} = -2i\hbar T_e. \tag{9.10}$$

In the second term we may use the Euler theorem for homogeneous functions which in this case states that

$$\sum_i \mathbf{r}_i \nabla_i V(\mathbf{R}, \mathbf{r}) + \sum_a \mathbf{R}_a \nabla_a V(\mathbf{R}, \mathbf{r}) = -V \tag{9.11}$$

as $V$ is a homogeneous function of degree $s = -1$. Therefore the second term in ( 9.9 ) is equal to $-i\hbar\left(V + \sum_a \mathbf{R}_a \nabla_a V(\mathbf{R}, \mathbf{r})\right)$. After dividing by $i\hbar$ and rearranging the result we obtain in this way:

$$\langle 2T_e + V\rangle = -\sum_a \langle \mathbf{R}_a \nabla_a V(\mathbf{R}, \mathbf{r})\rangle . \tag{9.12}$$

The expectation value on the right hand side is taken with respect to the electron coordinates, as the nuclear coordinates $\mathbf{R}$ are considered in $H_e$ as parameters. In addition, the kinetic energy $T_e$ of the electrons does not depend on the nuclear coordinates , therefore $\nabla_a V(\mathbf{R}, \mathbf{r}) = \nabla_a H_e$ and we have

$$2\langle T_e\rangle + \langle V\rangle = -\sum_a \mathbf{R}_a \langle \nabla_a H_e\rangle . \tag{9.13}$$

We can recast the theorem given by ( 9.13 ) in another form by the help of the Hellmann-Feynman theorem eq. ( 9.5 ), where the parameters are now specifically the nuclear coordinates, and write $\langle \nabla_a H_e\rangle = \nabla_a \mathcal{E}(\mathbf{R})$. Then we obtain **the quantum mechanical virial theorem for molecules** :

$$2\langle T_e\rangle + \langle V\rangle = -\sum_a \mathbf{R}_a \nabla_a \mathcal{E}(\mathbf{R}) \tag{9.14}$$

We may recast the result in the following two equivalent forms, using $\langle V\rangle + \langle T_e\rangle = \mathcal{E}$, which is valid if the expectation values are taken in the energy eigenstates:

$$\langle T_e\rangle = -\mathcal{E}(\mathbf{R}) - \sum_a \mathbf{R}_a \nabla_a \mathcal{E}(\mathbf{R}) \tag{9.15}$$

$$\langle V\rangle = 2\mathcal{E}(\mathbf{R}) + \sum_a \mathbf{R}_a \nabla_a \mathcal{E}(\mathbf{R}) \tag{9.16}$$

In other words we may calculate the expectation values of both the kinetic energy and the potential energy if we know the total energy of the molecule in an electronic state, as the function of the nuclear coordinates.

## 2.1. The virial theorem for atoms

In the special case when the potential does not depend on the nuclear positions, e.g. for an **atom with a single fixed nucleus in the center**, the term on the right hand side of the virial theorem ( 9.14 ) vanishes, and the result says:

$$\langle V\rangle = -2\langle T_e\rangle\,, \tag{9.17}$$

or as $\langle V\rangle + \langle T_e\rangle = \langle H\rangle = \mathcal{E}$ in a stationary state, we have

$$\langle H\rangle = \frac{\langle V\rangle}{2} = -\langle T_e\rangle\,. \tag{9.18}$$

Note also that - without additional refinements - ( 9.18 ), as well as ( 9.12 ) holds only for normailzable functions, i.e. only for bound states, as for scattering states the expectation values may not exist in general.

Based on the Euler's theorem for an arbitrary $s$, we can obtain a more general form of the virial theorem for a single particle problem. The theorem states that if the potential energy is a **homogeneous function** of its coordinates of degree $s$, then the following relation holds for the expectation values of the kinetic and the potential energies:

$$\langle T\rangle = \frac{s}{2}\langle V\rangle\,. \tag{9.19}$$

**Problem 9.5 :** Consider two particles in three dimensions (model of diatomic molecule) that interact with a harmonic force. Separate the problem into center of mass and relative coordinates. What is $s$ for this latter problem?

# 3. The origin of the chemical bond

Now we can come to our main task and explain the formation of molecules. Based on the virial theorem, we first consider the total energy for the case when the atoms are infinitely separated from each other. Then we may assume that $\mathcal{E}(\infty)$ does not depend on the nuclear coordinates, which means that its derivative with respect to them is zero:

$$\lim_{R_a=\infty} \nabla_a \mathcal{E}(\mathbf{R}) = 0. \tag{9.20}$$

Then taking this limit we have

$$\begin{aligned}\langle T_e\rangle_\infty &= -\mathcal{E}(\infty)\\ \langle V\rangle_\infty &= 2\mathcal{E}(\infty)\end{aligned} \tag{9.21}$$

Now we consider these values in the equilibrium configuration of the nuclei, to be denoted by $\mathbf{R}_0$. In what follows we assume that this configuration exists in reality. If that is the case then it must be at a minimum of the total energy, and we have again $\nabla_a \mathcal{E}(\mathbf{R}=\mathbf{R}_0) = 0$.

$$\begin{aligned}\langle T_e\rangle_0 &= -\mathcal{E}(\mathbf{R}_0)\\ \langle V\rangle_0 &= 2\mathcal{E}(\mathbf{R}_0)\end{aligned} \tag{9.22}$$

The energy difference between the two configurations is given by

$$\begin{aligned}\Delta\langle T_e\rangle &= \langle T_e\rangle_0 - \langle T_e\rangle_\infty = \mathcal{E}(\infty) - \mathcal{E}(\mathbf{R}_0)\\ \Delta\langle V\rangle &= \langle V\rangle_0 - \langle V\rangle_\infty = 2\mathcal{E}(\mathbf{R}_0) - 2\mathcal{E}(\infty) = -2\Delta\langle T_e\rangle\end{aligned} \qquad (9.23)$$

In order to form a bond, the changes in these energies during the formation of the molecule must obey

$$\Delta\langle T_e\rangle > 0, \qquad \Delta\langle V\rangle = -2\Delta\langle T_e\rangle \qquad (9.24)$$

so in this case the kinetic energy increases, but the potential energy decreases by twice of that increment, therefore the total energy gets lower. In the opposite case no bond is formed.

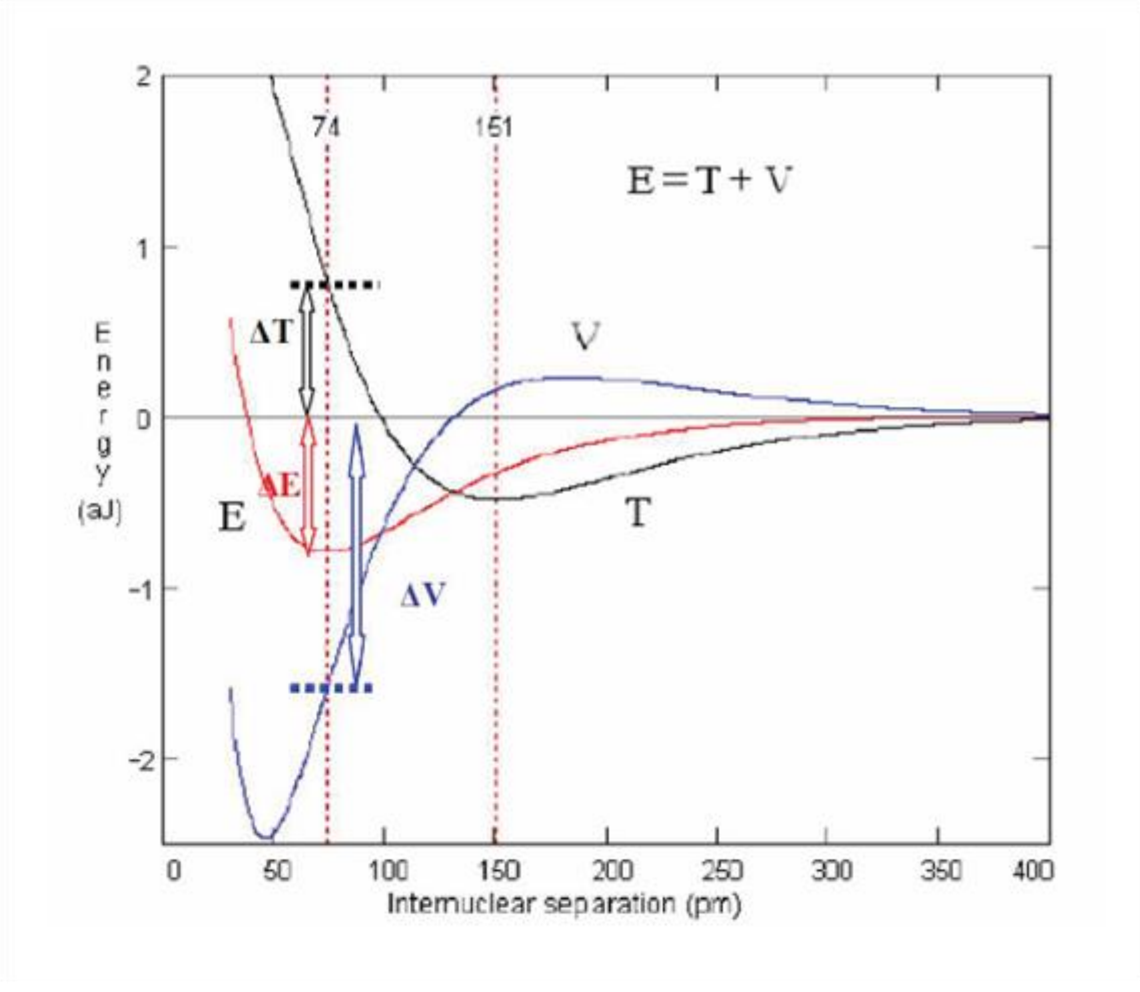
## 3.1. The example of the $H_2$ molecule

The $H_2$ molecule consists of two ptrotons (nuclei) and two electrons. Let us denote the distance between the two protons by $R$ Therefore we have $\mathcal{E}(R)$ as a function of a single variable and eqs. ( 9.15 )-( 9.16 ) take the form

$$\begin{aligned}\langle T_e\rangle &= -\mathcal{E}(R) - R\frac{d\mathcal{E}(R)}{dR}\\ \langle V\rangle &= 2\mathcal{E}(R) + R\frac{d\mathcal{E}(R)}{dR}\end{aligned} \qquad (9.25)$$

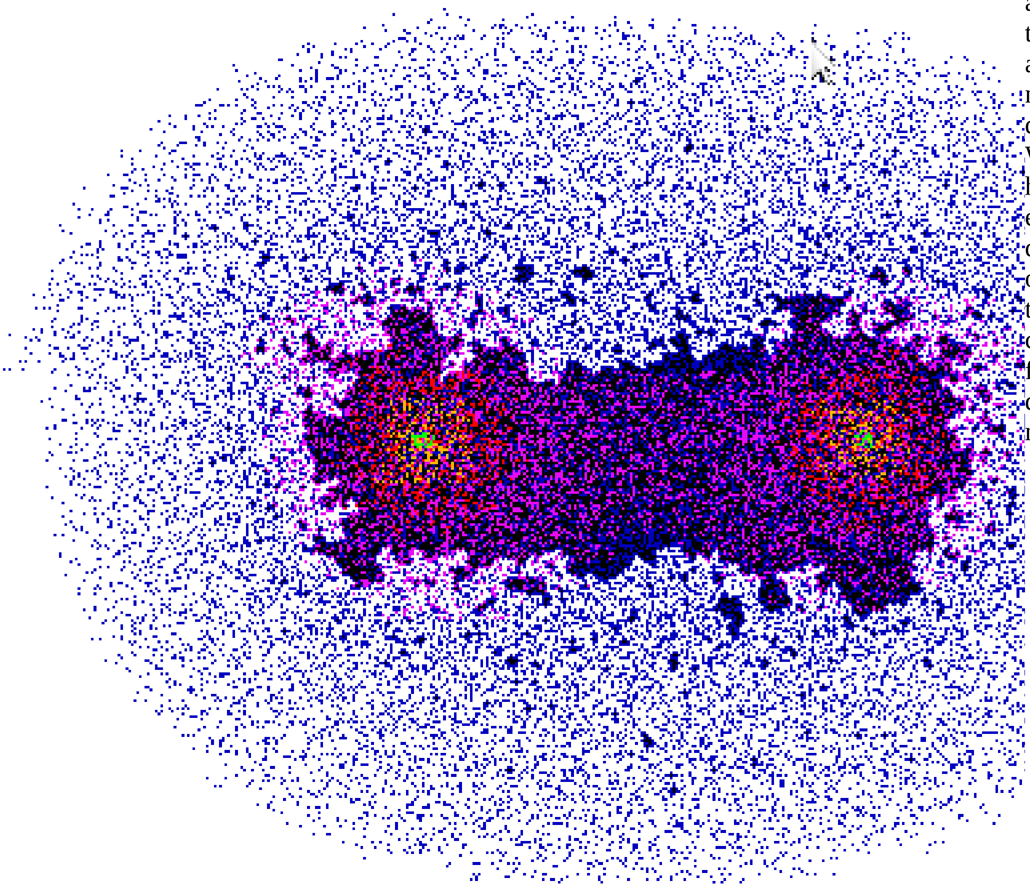
This molecule is sufficiently simple to calculate its energy for several values of the internuclear distance, with a very high precision by using hundreds of variational parameters. The results are shown in the figure where it is seen that there exists in reality an equlibriumposition where the total energy has a minimum.

**Figure 9.1. Kinetic potential and total energies, of the $H_2$ molecule. http://chemeducator.org/sbibs/s0008001/spapers/810010fr.htm**



Kinetic potential and total energies, of the Hydrogen molecule.

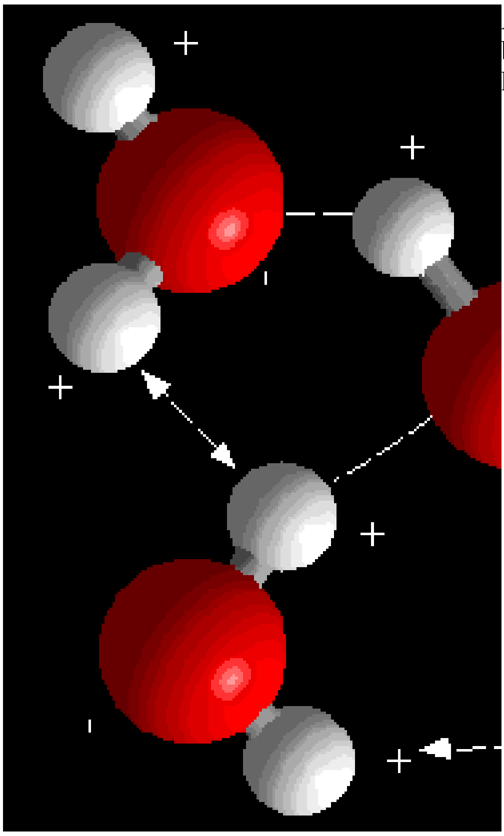
**Animation:**



On this animated gif the creation of a hydrogen molecule is demonstrated. We can se how the electron densities overlap as the two atoms get closer and form a diatomic molecule.

**Further reading:** On this page connected to the animation above you can find the technical details of creating such an animation. http://phelafel.technion.ac.il/~orcohen/h2.html

**Further reading:**

| | |
|---|---|
|  | A flash tutorial on formation of different type of chemical bonds.<br>http://bcs.whfreeman.com/thelifewire/content/chp02/02020.html |

# Chapter 10. Elements of light atom interactions with time dependent perturbation theory

**Goals:** Beginning with this chapter we turn now to the question of the interaction of atomic systems with electromagnetic field, with emphasis on the domain, where the field wavelength is between $10\,\mu\mathrm{m}$ and $10\,\mathrm{nm}$, which includes infrared, visible and uv light. This problem has very different levels of description, our approach in the whole material will be a semiclassical one, which treats the atomic systems as quantum mechanical objects, while the light field is considered to be as a classical wave. The method to be used is the **time dependent perturbation theory**, developed by P. Dirac in 1928, in order to treat the problem of light atom interactions. He used a scheme what is called now the **interaction picture**, which we will introduce first.

**Prerequisites:** Basic QM concepts and notions, Time independent perturbation theory (Chapter 2 .).

## 1. Introduction of the problem, the interaction picture

We consider a quantum mechanical system which interacts with an **external field**, which can be time dependent. So this is not a closed system, and therefore it is not conservative. We assume that the form of the Hamiltonian is the following

$$H = H_0 + K(t), \tag{10.1}$$

where $H_0$ is a time independent Hamiltonian, while $K(t)$ is a time dependent selfadjoint operator determining the effect of an external field on the system. A very important problem of this kind - to be discussed later - if an atom is placed into a time dependent external electromagnetic field. We look for the solution of the time dependent Schrödinger equation

$$i\hbar\frac{\partial\left|\Psi(t)\right\rangle}{\partial t} = \left(H_0 + K(t)\right)\left|\Psi(t)\right\rangle . \tag{10.2}$$

In the absence of $K(t)$, the system would evolve from a state

$$\left|\Psi(0)\right\rangle = \sum_n c_n(0)\left|n\right\rangle \tag{10.3}$$

into

$$\left|\Psi(t)\right\rangle = \sum c_n(0)e^{-i\frac{\varepsilon_n}{\hbar}t}\left|n\right\rangle , \tag{10.4}$$

where $\left|n\right\rangle$ denotes here the complete orthonormal basis consisting of the eigenvectors of $H_0$, and $E_n$ are the corresponding eigenvalues of $H_0$ : $H_0\left|n\right\rangle = \varepsilon_n\left|n\right\rangle$. In the case of degeneracy the value of $E_n$ can be the same for different stationary states $\left|n\right\rangle$.

Motivated by the usual ( 10.4 ) solution for the conservative system, it is straightforward to consider the effect of $K(t)$ for the time dependent solution of ( 10.2 ) in the form:

$$\left|\Psi(t)\right\rangle = \sum b_n(t)e^{-i\frac{\varepsilon_n}{\hbar}t}\left|n\right\rangle , \tag{10.5}$$

where we have now time dependent coefficients $b_n(t)$ instead of the constant values $c_n(0)$, and this time dependence can be obviously attributed to $K(t)$. W use normalized vectors (wave functions) which requires:

$$\sum_n |b_n(t)|^2 = 1 \tag{10.6}$$

similarly to the condition $\sum_n |c_n(0)|^2 = 1$ in ( 10.4 ).

In order to find the solution for $b_n(t)$ we multiply $|\Psi(t)\rangle$ by $e^{\frac{i}{\hbar}H_0 t}$, which removes the time evolution due to $H_0$ and only that part remains which is caused by $K$. This procedure is known as the application of the so called **Dirac picture or interaction picture**. We introduce accordingly

$$|\Psi(t)\rangle_S :\equiv |\Psi(t)\rangle \,, \tag{10.7}$$

which is identical to the **state in the Schrödinger picture**, used until now, although this was not explicated so far. The state in the interaction picture is defined as

$$|\Psi(t)\rangle_I := e^{\frac{i}{\hbar}H_0 t} |\Psi(t)\rangle_S = \sum b_n(t) \, |n\rangle \,. \tag{10.8}$$

We see that in the instant $t = 0$: $|\Psi(0)\rangle_I = |\Psi(0)\rangle_S$ (for the sake of simplicity we have chosen $t_0 = 0$). Let us consider now a linear operator denoted until now by $A$, and from now on by $A_S :\equiv A$, which is to be called the operator in the Schrödinger picture. If we have the mapping $A_S |\Psi_S\rangle = |\Psi'_S\rangle$, and prescribe that an analogous equation should hold for the corresponding states in the interaction picture, then we have to use a transformed expression for the operators in the interaction picture. From ( 10.8 ) we get

$$A_S \, |\Psi\rangle_S = |\Psi'\rangle_S = A_S e^{-\frac{i}{\hbar}H_0 t} \, |\Psi\rangle_I = e^{-\frac{i}{\hbar}H_0 t} \, |\Psi'\rangle_I \,. \tag{10.9}$$

If we multiply this equation by $e^{\frac{i}{\hbar}H_0 t}$ from the left, we see, that together with $A_S \, |\Psi\rangle_S = |\Psi'\rangle_S$ the equation $A_I \, |\Psi\rangle_I = |\Psi'\rangle_I$ holds, as well, if we **define**

$$A_I := e^{\frac{i}{\hbar}H_0 t} A_S e^{-\frac{i}{\hbar}H_0 t} \tag{10.10}$$

and as a consequence:

$$A_S = e^{-\frac{i}{\hbar}H_0 t} A_I e^{+\frac{i}{\hbar}H_0 t}. \tag{10.11}$$

It is simple to show that the expectation values and the commutators are invariant when we go over to the interaction picture.

**Problem 10.1 :** Show that for any state and operator $\langle \Psi_s | A_S | \Psi_s \rangle = \langle \Psi_I | A_I | \Psi_I \rangle$.

**Problem 10.2 :** Show that if $[A_S, B_S] = C_S$, then $[A_I, B_I] = C_I$ and the other way round.

The dynamical equation, that is the Schrödinger equation in the interaction picture takes the form :

$$i\hbar \frac{\partial}{\partial t} \, |\Psi(t)\rangle_I = -H_0 \, |\Psi\rangle_I + e^{\frac{i}{\hbar}H_0 t} (H_0 + K) e^{-\frac{i}{\hbar}H_0 t} \, |\Psi\rangle_I = K_I \, |\Psi\rangle_I \tag{10.12}$$

or

$$i\hbar \frac{\partial}{\partial t} \, |\Psi(t)\rangle_I = K_I \, |\Psi(t)\rangle_I \tag{10.13}$$

There is an explicit time dependence of the operators in this picture, which we obtain by differentiating( 10.10 ):

$$\frac{\partial A_I}{\partial t} = \frac{i}{\hbar} H_0 A_I - \frac{i}{\hbar} A_I H_0 + \left(\frac{\partial A_S}{\partial t}\right)_I = \frac{i}{\hbar}\left[H_0, A_I\right] + \left(\frac{\partial A_S}{\partial t}\right)_I \tag{10.14}$$

We note that there is a third picture used frequently, especially in quantum field theories, called the Heisenberg picture. We summarize the time dependence of the states and operators in the different pictures in a small table:

**Table 10.1. Time dependence of the states and operators in the different pictures. The evolution of the corresponding quantity is determined by the operator after the word "evolves".**

| | Schrödinger | Heisenberg | Interaction |
|---|---|---|---|
| state | evolves: $H_S$ | constant | evolves: $K_I$ |
| operator | constant | evolves: $H_H$ | evolves: $H_0$ |

# 2. The solution of the dynamical equation in the interaction picture

We substitute now the expansion in ( 10.8 ) into ( 10.13 ):

$$i\hbar\frac{\partial}{\partial t}\sum b_j(t)\left|n\right\rangle = K_I \sum b_j(t)\left|j\right\rangle \tag{10.15}$$

and then take the inner product from the left by $\langle k|$ :

$$i\hbar\frac{\partial}{\partial t}\left\langle k\right|\sum b_j(t)\left|j\right\rangle = \sum b_j(t)\left\langle k\right| K_I \left|j\right\rangle . \tag{10.16}$$

On the left hand side $b_j(t)$ is a number (not an operator) and $\langle k|\,j\rangle = \delta_{kj}$. On the right hand side we make use the formula ( 10.11 ) giving the transformation from the interaction picture into the Schrödinger picture yielding:

$$i\hbar\frac{\partial}{\partial t}b_k(t) = \sum_j \left\langle k\right| K_I \left|j\right\rangle b_j(t) = \sum_j \langle k|\, K_S |j\rangle e^{i\omega_{kj}t} b_j(t), \tag{10.17}$$

with $e^{+\frac{i}{\hbar}H_0 t}|j\rangle = e^{+\frac{i}{\hbar}\varepsilon_j t}|j\rangle$ and $\omega_{kn} := \omega_k - \omega_n = (\varepsilon_k - \varepsilon_n)/\hbar$. From now on we shall use the notation

$$\langle k|\, K_S(t)|j\rangle = K_{kj}(t) \tag{10.18}$$

for the matrix element of $K$. Let us remember that $K_{kj}$ is time dependent in general. With this notation we have the following system of linear differential equations for the unknown interaction picture amplitudes $b_j(t)$ :

$$i\hbar\frac{\partial}{\partial t}b_k(t) = \sum_j K_{kj} e^{i\omega_{kj}t} b_j(t). \tag{10.19}$$

## 2.1. Transformation into an integral equation, the method of successive approximations

We recast now equation ( 10.17 ) into an integral equation. This has the advantage that the equation contains explicitly the initial conditions, which we fix at $t = 0$:

$$b_k(t) = b_k(0) - \frac{i}{\hbar}\int_0^t \sum_j K_{kj}(t_1)e^{i\omega_{kj}t_1} b_j(t_1)dt_1. \qquad (10.20)$$

Although one unknown amplitude is explicit on the left hand side, it also stands, together with all the others, under the integral sign on the left hand side, so this is only formally a solution. This expression, however allows us a method of solution, called the **method of successive approximations**, which is especially useful if one has a great number of stationary states. In the case of a small finite dimensional space, when we have a few amplitudes only, there are other methods which we will explain later.

In the zeroth approximation we take the solutions to be equal to their initial values

$$b_k^{(0)}(t) = b_k(0), \qquad \forall k \qquad (10.21)$$

for all $k$ -s. This can be valid approximately only for a very short time interval after $t = 0$. The first approximation is then obtained if we replace $b_j(t_1)$ on the right hand side of ( 10.20 ) by its zeroth approximation:

$$\begin{aligned} b_k^{(1)}(t) &= b_k(0) - \frac{i}{\hbar}\int_0^t \sum_j K_{kj}(t_1)e^{i\omega_{kj}t_1} b_j^{(0)}(t_1)dt_1 = \\ &= b_k(0) - \frac{i}{\hbar}\int_0^t \sum_j K_{kj}(t_1)e^{i\omega_{kj}t_1} b_j(0)dt_1 \end{aligned} \qquad (10.22)$$

and in general

$$\begin{aligned} b_k^{(n+1)}(t) &= b_k(0) - \frac{i}{\hbar}\int\limits_0^t \sum_j K_{kj}(t_1)e^{i\omega_{kj}t_1} b_j^{(n)}(t_1)dt_1 = \\ &= b_k(0) - \frac{i}{\hbar}\int\limits_0^t \sum_{j_n} K_{kj_n}(t_n)e^{i\omega_{kj_n}t_n} b_{j_n}^{(n)}(t_n)dt_n \end{aligned} \qquad (10.23)$$

where in the last equality we simply replaced the summation index $j$ by $j_n$ for notational convenience. In this way we obtain a recursion system for the amplitudes. If we express now $b_{j_n}^{(n)}(t_n)$ according to the same formula, we have to make the replacement $n \to n-1,\ j_n \to j_{n-1}$, and $t_n \to t_{n-1}$

$$b_{j_n}^{(n)}(t_n) = b_{j_n}(0) - -\frac{i}{\hbar}\int\limits_0^{t_n} \sum_{j_{n-1}} K_{j_n j_{n-1}}(t_{n-1})e^{i\omega_{j_n j_{n-1}}t_2} b_{j_{n-1}}^{(n-1)}(t_{n-1})dt_n \qquad (10.24)$$

scheme.

Accordingly for the second approximation of the solution of ( 10.20 ):

$$\begin{aligned}b_k^{(2)}(t) &= b_k(0) - \frac{i}{\hbar}\int_0^t \sum_{j1} K_{kj_1}(t_1) e^{i\omega_{kj_1}t_1} b_{j1}^{(1)}(t_1)dt_1 = \\ &= b_k(0) - \frac{i}{\hbar}\int_0^t \sum_{j1} K_{kj_1}(t_1) e^{i\omega_{kj_1}t_1} b_j(0)dt_1 + \\ &+ \left(-\frac{i}{\hbar}\right)^2 \int_0^t \sum_{j1} K_{kj_1}(t_1) e^{i\omega_{kj_1}t_1} \int_0^{t_1} \sum_{j2} K_{j_1j_2} e^{i\omega_{j_1j_2}t_2} b_{j_2}(0)dt_2\end{aligned} \tag{10.25}$$

and so on. The result will be in general an infinite sum, the general expression of which is rather complicated:

$$b_k^{(n)}(t) = b_k^{(n)}(0) + \sum_{s=1}^{n}\left(-\frac{i}{\hbar}\right)^s \sum_{j_1,j_2,\dots,j_s} \int_0^t \int_0^{t_1} \dots \int_0^{t_s} K_{kj_1}(t_1)e^{i\omega_{kj_1}t_1} K_{j_1j_2}(t_2)e^{i\omega_{j_1j_2}t_2} \dots K_{j_{s-1}j_s} e^{i\omega_{j_{s-1}j_s}t_s} b_{j_s}^{(0)}(0)dt_s \dots dt \tag{10.26}$$

In most of the cases one makes a cut off in the approximation after the first few steps. One expects that this should give good results until the coefficients do not differ too much from their initial values. This form of time dependent perturbation theory works until this remains true. In cases when this does not work, especially if there is resonance the $b$ -s change significantly. For instance, if one of the $b$ -s change from 0 to 1 then we can apply another method just making use that all the other $b$ -s must then be close to zero. We postpone this question to the next section. It is seen that in the $r$ -th order the amplitude shall depend on the $r$ -th power of the perturbing operator $K$, therefore if we expect that the response of the system is linear to the disturbance, then it is sufficient to make a first order approximation.

## 2.2. A specific initial condition

Very often we apply the method of successive approximations in the case, when initially only one of the amplitudes is different from 1, and all the others are 0. For instance if the quantum system in question is an atom, then without external perturbation it is in its ground state, and only the ground state amplitude will be different from zero. Let the label of the initial state be $k = i$, so $b_i(0) = 1$, and then due to the normalization condition ( 10.6 ) all the other $b$ -s must be 0, i.e. $b_k(0) = \delta_{ik}$. Then the integral equation takes the following simpler form:

$$b_k^{(1)}(t) = \delta_{ik} - \frac{i}{\hbar}\int_0^t K_{ki} e^{i\omega_{ki}t_1} dt_1 . \tag{10.27}$$

Having made the first order approximation we can also go back now to the differential form of this equation by taking its time derivative, and complemented by the initial condition

$$\frac{db_k^{(1)}(t)}{dt} = -\frac{i}{\hbar} K_{ki} e^{i\omega_{ki}t}, \qquad b_k^{(1)}(0) = \delta_{ik}, \tag{10.28}$$

where we remind once more that $K_{ki} = \langle k\,|K_S|i\rangle$ are the matrix elements of the interaction operator in the Schrödinger picture and $\omega_{ki} = (\varepsilon_k - \varepsilon_i)/\hbar$ are the (circular) Bohr frequencies of the possible transitions. Now we will apply eq. ( 10.28 ) to important physical problems.

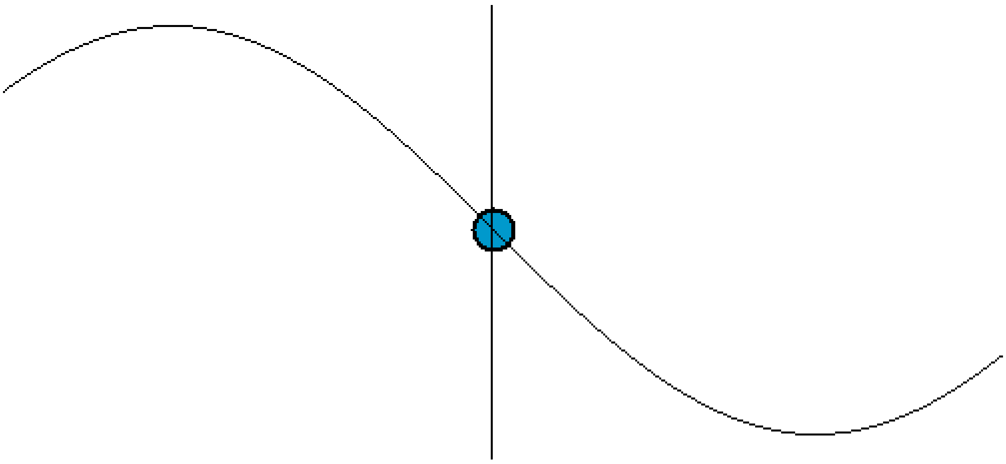
# 3. Absorption and stimulated emission

Let us assume that we place an atom into an external harmonic field, i.e. monochromatic and linearly polarized electromagnetic wave with electric field strength

$$\vec{\mathcal{E}}(t) = \mathbf{E}_0 \cos\omega t \tag{10.29}$$

of frequency $\omega$. This means that we have neglected the spatial dependence of the field strength, which is a very good approximation as long as the atomic size is much less than the wavelength of the wave. As the atomic size $a$ is smaller than 1 nm (in the case of the H atom it is only 0.05 nm) it is much less than $\lambda = 2\pi c/\omega$ which is around 500 nm for optical fields, and approaches the atomic size only down in the soft X ray domain. Therefore when $a \ll \lambda$ this approximation holds very well, as illustrated by the movie below:

**Animation:**



Placing an atom into an external harmonic field, i.e. monochromatic and linearly polarized electromagnetic wave. We can neglect the spatial dependence of the field strength when $a \ll \lambda$ as it is illustrated on this simple gif animation.

Another point here is that in a plane wave the effect of the magnetic component of the field is much less then the electric one, as then the amplitudes are related by $B_0 = E_0/c$, where $c$ is the speed of light, so the velocity dependent magnetic part of the Lorentz force $\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ on the charges in the atom becomes significant only in a relativistic treatment which we do not consider here.

It can be shown that with these approximations the Hamiltonian describing the interaction energy (in the Schrödinger picture) between the atom and the field can be written (in the Schrödinger picture) as

$$K_S = -\mathbf{D}\vec{\mathcal{E}}(t), \qquad (10.30)$$

where $D$ is the component of the **atomic dipole moment operator** parallel to the line of the polarized field. In a static case, when $\vec{\mathcal{E}}$ is not time dependent we know that this is the correct form, while for a time dependent $\vec{\mathcal{E}}(t)$ this must be proven. This can be done using the assumption $a \ll \lambda$ as above. As the interaction term contains now the dipole moment, this method is often called the **dipole approximation**.

We use now ( 10.28 ), in order to find the time dependence of the amplitude. For sake of simplicity we omit the superscript (1) in the notation of the amplitude, and write simply $b_k(t)$, instead of $b_k^{(1)}(t)$, as we are interested only in the linear response of the system. It must be kept in mind however that this is only a first order approximation. With

$$K_S = -\mathbf{D}\mathbf{E}_0 \cos\omega t, \qquad (10.31)$$

and for $k \neq i$ we get

The solution of ( 10.50 ) is:

$$b_k(t) = -\frac{i}{\hbar}\int_0^t K_{ki} e^{i\omega_{ki}t_1} dt_1 \qquad k \neq i \tag{10.32}$$

and we shall now be interested for a specific amplitude $b_f(t)$ (referring to a **final** state) For $k = f \neq i$ we get after integration

$$b_f(t) = \frac{1}{\hbar}\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2}\left(\frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega+\omega_{fi}} + \frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega}\right), \tag{10.33}$$

where

$$\mathbf{d}_{fi} = \langle f|\, \mathbf{D}_S\, |i\rangle \tag{10.34}$$

is the **matrix element of the dipole moment operator**, sometimes called as the **transition dipole moment**, which is a very important notion in atomic physics and spectroscopy, as this is the quantity that determines the probability of a transition, and in case of an emission, the intensity of the emitted radiation. It is a vector here, as the dipole moment operator is a vector itself. The amplitude of the final state,and therefore the transition probability is nonzero only if $d_{fi} \neq 0$, this is a dipole selection rule. We come back to this point below.

We see in the solution ( 10.33 ) that the two terms differ in their denominators. Take first the case if $\omega + \omega_{fi} \approx 0$. Then the first term is large because its denominator is small, note that for optical fields e.g. $\omega \simeq 10^{15} 1/s$, while $\gamma \simeq 10^8 1/s$ and in addition the nominator varies slowly in time with frequency close to zero. On the other hand, in this case the second term is small, as its denominator $|\omega_{fi} - \omega| \approx 2\omega$ and the exponent varies rapidly and has a small average over a time interval longer than $2\pi/\omega$. Therefore if $\omega + \omega_{fi} \approx 0$, we can omit the second term, and the latter equation is equivalent to

$$\varepsilon_f = \varepsilon_i - \hbar\omega, \tag{10.35}$$

which means that the final state has lower energy than the initial one, this process corresponds to **stimulated emission** driven by the external field. The atom emits a "photon" and its energy decreases. The quote marks refer to the situation that we do not treat the field as quantized so the concept of the photon makes no sense actually in this approach. We are still allowed to speak of it, as quantum electrodynamics leads essentially to the same result.

If the opposite is true i.e. when $\omega_{fi} - \omega \approx 0$, then the second term is the dominant one, the first one can be omitted and

$$\varepsilon_f = \varepsilon_i + \hbar\omega \tag{10.36}$$

interpreted now as the absorption of a "photon".

The description of the two processes are very similar, and we can write both as a single equation for $b_f$ in ( 10.33 ), where the upper sign refers to stimulated emission, while the lower one to absorption. So:

$$b_f(t) = \frac{1}{\hbar}\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2}\left(\frac{e^{i(\omega_{fi}\pm\omega)t/2} - e^{-i(\omega_{fi}\pm\omega)t/2}}{\omega_{fi}\pm\omega}\right) e^{i(\omega_{fi}\pm\omega)t/2}, \tag{10.37}$$

where we picked out a factor $e^{i(\omega_{fi}\pm\omega)t/2}$, for convenience in the next step. In order to find the probability of finding the system in the state $f$ we have to take the absolute value square of the probability amplitude, and get

$$|b_f(t)|^2 = \left(\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2\hbar}\right)^2 \frac{\sin^2\left[(\omega_{fi}\pm\omega)t/2\right]}{\left[(\omega_{fi}\pm\omega)/2\right]^2} = \left(\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2\hbar}\right)^2 4\frac{\sin^2\frac{\Delta t}{2}}{\Delta^2} \tag{10.38}$$

and is significant which is large when $(E_f - E_i)/\hbar = \omega$ (absorption) in case of the upper sign or when $(E_f - E_i)/\hbar = -\omega$, stimulated emission. For $t$ large the result cannot be valid on resonance as

$$|b_f(t)|^2 = \left(\frac{d_{fi}E_0}{2\hbar}\right)^2 t^2 \frac{\sin^2\frac{\Delta t}{2}}{(\Delta t/2)^2} \qquad (10.39)$$

$\Delta = \omega_{fi} \pm \omega$. For $\Delta = 0$ the factor $\frac{\sin^2\frac{\Delta t}{2}}{(\Delta t/2)^2} = 1$, thus the probability of finding the system in $|f\rangle$ grows as $t^2$, which cannot be the case for long times, because normalization requires $\sum_k |b_k(t)|^2 = 1$.

Still the result can be used when the atom is placed in the field like the black body radiation, which has a wide band spectrum, and the divergence in the formula above is compensated by the infinitesimal part of the spectrum where the atom emits or absorbs. In order to see this we use first the limiting form. If we consider the function $\frac{\sin^2[\Delta t/2]}{t(\Delta/2)^2} = t\frac{\sin^2[\Delta t/2]}{t^2(\Delta/2)^2}$ where , its value is $t$ for $\Delta = 0$, while it is less than $1/(t(\Delta/2)^2)$ for large $t$ -s. In addition for any smooth function $f$ the limit $\lim_{t\to\infty}\int f(\Delta)\frac{\sin^2[\Delta t/2]}{t(\Delta/2)^2}d\Delta = f(0)$, so we can write $\lim(t\to\infty)\frac{\sin^2[\Delta t/2]}{(\Delta/2)^2} = 2\pi t\delta(\Delta)$, where $\delta(\Delta)$ is Dirac's delta function. Therefore $|b_f(t)|^2 \sim t$ and the transition probability per unit time is given by:

$$w_{fi} = \frac{1}{t}|b_f(t)|^2 = \frac{(d_{fi}E_0)^2}{2\hbar^2}\pi\delta(\omega_{fi} - \omega). \qquad (10.40)$$

This result is a specific case of a more general rule called Fermi's golden rule, describing an energy conserving transition from or to a discrete level or level pairs to continuum. Here the role of the continuum is played by all the possible photon energies $\hbar\omega$. The derivation is due to Dirac, who did this earlier than Fermi.

Now if the field is polychromatic $E_0^2$ has to be replaced by $E^2(\omega)d\omega$, where $E(\omega)$ is the Fourier amplitude (spectrum) of the field at the angular frequency $\omega$, and the transition probability per unit time is obtained after integration with respect to $\omega$ :

$$w_{fi} = \int \frac{d_{ki}^2}{2\hbar^2}E^2(\omega)\delta(\omega_{ki} - \omega)d\omega = \frac{d_{ki}^2}{2\hbar^2}E_0^2(\omega_{ki}) \qquad (10.41)$$

The square of the field amplitude is proportional to the field energy density, and it will be useful to make use of this:

$$\overline{u(\omega)} = \frac{1}{2}\varepsilon_0\overline{E^2(\omega)} + \frac{1}{2\mu_0}\overline{B^2(\omega)} = \varepsilon_0\overline{E^2(\omega)} = \frac{1}{2}\varepsilon_0 E_0^2(\omega) \qquad (10.42)$$

valid for plane waves and time average of the $\cos^2\omega t$ introduces the $1/2$. Then $E_0^2\omega) = 2\overline{u(\omega)}/\varepsilon_0$ and the transition probability

$$w_{fi} = \frac{d_{ki}^2}{\varepsilon_0\hbar^2}u(\omega) \qquad (10.43)$$

We have taken $\mathbf{ED} = ED$, while in reality the relative direction of D and E is a random angle $\vartheta$, having in reality the square of $\mathbf{ED} = ED\cos\vartheta$, te average value of $\cos^2\vartheta$ is 1/3, therefore the final result is

$$w_{fi} = \frac{d_{ki}^2}{3\varepsilon_0\hbar^2}u(\omega). \qquad (10.44)$$

A similar result is obtained for the stimulated emission probability, which is also proportional to the energy density of the field $u(\omega)$. Accordingly the coefficient multiplying $u(\omega)$ is just the $B_{if}$ coefficient of Einstein (note the order of the indices is the opposite here to the one used in quantum mechanics).

We can give now determine the A coefficient as well, following the famous line of thought of Einstein, where he introduced the three elementary processes of atom field interactions. Consider now a number of atoms that are in thermal equilibrium with the field in a cavity with black body: Let $i = 2, f = 1$

$$u(\omega) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{g_1 B_{12}}{g_2 B_{21}} e^{\frac{\hbar\omega}{kT}} - 1} \qquad (10.45)$$

body radiation in it, where

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1} \qquad (10.46)$$

two level system which is in thermal equilibrium must be

Then

$$A_{21} = B_{21} \frac{\hbar\omega^3}{\pi^2 c^3} \qquad (10.47)$$

and

$$g_1 B_{12} = g_2 B_{21} \qquad (10.48)$$

In case of nondegenerate levels then

$$A_{21} = \frac{d_{ki}^2}{3\varepsilon_0 \hbar^2} \frac{\hbar\omega^3}{\pi^2 c^3} = \frac{1}{4\pi\varepsilon_0} \frac{4}{3} \frac{d_{ki}^2 \omega^3}{\hbar c^3} \qquad (10.49)$$

## 3.1. Selection rules

As we have mentioned the dipole transition matrix elements $d_{fi} = \langle u_f | D | u_i \rangle$ must be nonzero in order to have a transition in the dipole approximation. We derive now certain selection rules that determine when these matrix elements are nonzero.

In atoms the single active electron we consider is in the field of the other electrons which is assumed to be a central potential $V(r)$. This is exact in the case of Hydrogen like atoms where the potential of the unperturbed electron is the Coulomb field originating from the nucleus. In a central potential the square of the orbital angular momentum is a constant of motion, as well as any of its components are the constants of motion as the commutators $[H_0, L^2] = [H_0, L_i] = 0$ for $i = x, y, z$. This is the reason why in the case of atoms the orbital angular momentum quantum number $\ell$ as well as the magnetic quantum number $m$ are good quantum numbers, they can be used to label the eigenstates of $H_0$.

An important point also is that the angular momentum eigenstates have definite parity, i. e. on reflection with respect to the origin they are are either even or odd depending on $\ell$. In the abstract notation with the parity operator $\Pi \left| u_{n,l,m} \right\rangle = (-1)^\ell \left| u_{n,l,m} \right\rangle$, or in coordinate representation $u_{n,l,m}(-\mathbf{r}) = (-1)^\ell u_{n,l,m}(\mathbf{r})$. Laporte rule says that dipole transition is possible only between states of different parity.

# 4. The theory of linear polarizability

We shall use in this section the results of time dependent perturbation theory for a different problem, namely the quantum theory of the frequency dependent linear polarizability which is closely connected to the theory of the index of refraction. We assume here that the initial state of the atomic system is its ground state $|0\rangle$, as it must be for low enough temperatures. When considering the evolution of the atomic system there is another point here that we have to take into account. If we switch off the external field at any time then equation ( 10.28 ) says that the derivative of $b_k(t)$ is zero, so the amplitude would remain a nonzero constant forever, the value it had at the moment of switching off the field. We know, however, that in such cases the amplitudes of all stationary states decays to zero, except for the ground state where the system returns after the perturbation disappears. This is spontaneous emission, an effect which is not taken into account in the model we use, as it is caused by the quantum-electrodynamical fluctuations of the vacuum which we cannot get rid if the atom is in free space. Quantum theory can of course include this effect by treating the electromagnetic field as a quantum system, as well. But in order to keep our problem simple, we shall not do that, it will be sufficient to use a corrected version of ( 10.28 ), which takes into account the relaxation which is exponential. So instead $\frac{db_k(t)}{dt} = -\frac{i}{\hbar}K_{ki}e^{i\omega_{ki}t_1}$ we write

$$\frac{db_k(t)}{dt} = -\frac{i}{\hbar}K_{ki}e^{i\omega_{ki}t_1} - \gamma_k b_k(t) \tag{10.50}$$

where $\gamma_k$ was put in here "by hand" as a phenomenological constant, telling us that in the absence of $\mathcal{E}(t)$, all $b_k(t)$ except for the initial ground state amplitude decay exponentially to zero. In quantum electrodynamics, where also the fields are quantized, one can derive explicitly the value of $\gamma_k$, which turns out to be the order of $10/ns = 10^8 1/s$ for atoms. (Let us note the interesting fact that in its beginning and in the end the decay process is not strictly exponential.)

The solution of ( 10.50 ) is:

$$b_k(t) = -\frac{i}{\hbar}e^{-\gamma_k t}\int_0^t K_{ki}e^{i\omega_{ki}t_1}e^{\gamma_k t_1}dt_1 \qquad k \neq i \tag{10.51}$$

With $K_S = -DE_0\cos\omega t$, and for $k \neq i$ we get now

$$\begin{aligned} b_k(t) \;&= e^{-\gamma_k t}\frac{i}{\hbar}\frac{E_0}{2}\int_0^t d_{ki}e^{i\omega_{ki}t_1}e^{\gamma_k t_1}(e^{i\omega t_1} + e^{-i\omega t_1})dt_1 = \\ &= \frac{i}{\hbar}\frac{E_0}{2}d_{ki}\left[\frac{e^{i(\omega_{ki}+\omega)t} - e^{-\gamma_k t}}{i(\omega_{ki}+\omega)+\gamma_k} + \frac{e^{i(\omega_{ki}-\omega)t} - e^{-\gamma_k t}}{i(\omega_{ki}-\omega)+\gamma_k}\right] \end{aligned} \tag{10.52}$$

As we noted above, the value of $\gamma_k$ is of the order $10^8$ s$^{-1}$, this is the lifetime of an atomic excitation. Therefore if we consider excitations that are much longer than $10^{-8}$ s the terms containing $e^{-\gamma_k t}$ disappear quickly, therefore we can neglect them. If this is not the case, and we investigate light pulses the duration of which is of the order of $1/\gamma_k$, or shorter, we cannot do that, and we have to take into consideration these transients. The situation is similar to the driven and damped harmonic oscillation in mechanical systems, where one also has a short transient period of the motion. This is not accidental, as here in atomic physics the time dependence is also a kind of forced oscillation with several eigenfrequencies, the Bohr frequencies, and the external harmonic excitation is the electric field of the electromagnetic wave, which is coupled to through the atom through its dipole moment.

We consider here the **stationary case** when we neglect terms containing $e^{-\gamma_k t}$. Then

$$b_k(t) = \frac{E_0}{2}\frac{d_{ki}}{\hbar}\left[\frac{e^{i(\omega_{ki}+\omega)t}}{(\omega_{ki}+\omega) - i\gamma_k} + \frac{e^{i(\omega_{ki}-\omega)t}}{(\omega_{ki}-\omega) - i\gamma_k}\right] \tag{10.53}$$

Suppose now that the initial state is is the ground state to be denoted by $|0\rangle$, so $|i\rangle = |0\rangle$. If we treat here an atom, then $d_{00} = 0$, because of parity reasons, and as it is known, the ground state is not decaying, thus

$\gamma_0 = 0$. Then $b_i(t) = b_0(t) = 1$ in the first order, and for the other amplitudes we use the above formula with $i = 0$. The time dependent state in the Schrödinger picture in the first approximation is given by:

$$\left|\Psi_S^{(1)}(t)\right\rangle = |\varphi_0\rangle\, e^{-i\omega_0 t} + \sum b_k(t) e^{-i\omega_k t} |\varphi_k\rangle\,. \tag{10.54}$$

where the superscript (1) in $\left|\Psi_S^{(1)}(t)\right\rangle$ is shown here provisionally again to remind the reader that the result is valid only in the first approximation, but will be omitted from now on. Taking into account that $\omega_{k0} = \omega_k - \omega_0$ we get

$$\begin{aligned} |\Psi_S(t)\rangle &= |\varphi_0\rangle\, e^{-i\omega_0 t} + \textstyle\sum_k b_k(t) e^{-i\omega_k t} |\varphi_k\rangle = \\ &= |\varphi_0\rangle\, e^{-i\omega_0 t} + \textstyle\sum_k \frac{E_0}{2}\frac{d_{k0}}{\hbar}\left[\frac{e^{i(\omega_0+\omega)t}}{(\omega_{k0}+\omega)-i\gamma_k} + \frac{e^{i(\omega_0-\omega)t}}{(\omega_{k0}-\omega)-i\gamma_k}\right] |\varphi_k\rangle \end{aligned} \tag{10.55}$$

We calculate the expectation value of the dipole moment operator

$$p(t) = \langle D\rangle\,(t) = \langle\Psi_S(t)|\, D\, |\Psi_S(t)\rangle \tag{10.56}$$

Her all the diagonal matrix elements $d_{kk} = \langle k|\, D_S\, |k\rangle$ vanish, including $d_{00}$ as we mentioned referring to parity. So for the terms up to linear ones in $E$ we get:

$$\begin{aligned} p(t) &= \textstyle\sum_k 2\,\mathrm{Re}\,\frac{E_0}{2}\frac{d_{k0}}{\hbar}\left[\frac{e^{i\omega t}}{(\omega_{k0}+\omega)-i\gamma_k} + \frac{e^{-i\omega t}}{(\omega_{k0}-\omega)-i\gamma_k}\right] \langle\varphi_0|\, D\, |\varphi_k\rangle = \\ &= \textstyle\sum_k \frac{|d_{k0}|^2}{\hbar} E_0\, \mathrm{Re}\left[\frac{e^{i\omega t}}{(\omega_{k0}+\omega)-i\gamma_k} + \frac{e^{-i\omega t}}{(\omega_{k0}-\omega)-i\gamma_k}\right] \end{aligned} \tag{10.57}$$

This shows that under in the external field $E_0 \cos\omega t$, $p(t)$ also oscillates with circular frequency $\omega$, the meaning of the complex terms in the sum is a signature of $p$ being out of phase with respect to the field strength:

$$p(t) = \alpha_c E_0 \cos\omega t + \alpha_s E_0 \sin\omega t \tag{10.58}$$

If the frequency of the driving field is close to one of the resonances, $\omega \approx \omega_{k0}$, we can approximate $\omega_{k0} + \omega = 2\omega$ and the term where this $2\omega$ is in the denominator can be neglected with respect to the one where the denominator $\omega_{k0} - \omega$ is small. We get then

$$\begin{aligned} \alpha_c(\omega) &= \sum \frac{|d_{k0}|^2}{\hbar} \frac{(\omega_{k0}-\omega)}{(\omega_{k0}-\omega)^2 + \gamma_k^2} \\ \alpha_s(\omega) &= \sum \frac{|d_{k0}|^2}{\hbar} \frac{2\gamma_k}{(\omega_{k0}-\omega)^2 + \gamma_k^2} \end{aligned} \tag{10.59}$$

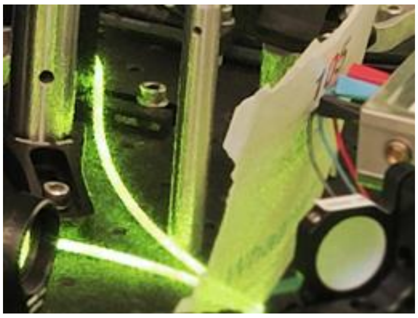
This are the dispersion formulae, as the polarizability is closely connected with the complex index of refraction. The result is very similar to the Lorentz model of the atom, where it is usually considered to be an oscillator with one resonance frequency. We see that in the linear i.e. first oder approximation quantum mechanics yields similar results, but with several resonant frequencies, these are now the transition frequencies. One has anomalous dispersion, and absorption close to resonances each time if $\omega_{k0} = \omega$. The polarizabilities corresponding to the transitions are proportional to the absolute squares of the transition dipole matrix elements divided by $\hbar$, which is obviously a difference from the classical result. We see that the validity of the Lorentz model is more or less justified by quantum mechanics, as we see from this subsection.

# Chapter 11. Field propagation in resonant media, Maxwell-Schrödinger equations and the laser

**Goals:** When presenting the material of this chapter, we assume that the reader is aware of the elementary principles of the operation of the laser. We will discuss a more advanced description, called the **semiclassical theory**, which is still not the final word, as it works without the important principle of field quantization. **Prerequisites:** Chapter 10 .; Elementary principles of the operation of the laser.

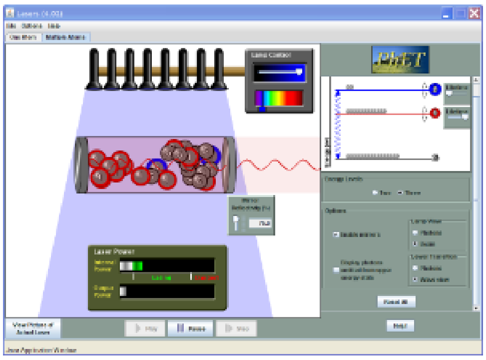
## 1. Introduction

**Animation:**



This webpage offers a two word explanation of laser principles. Check out the laser tab with an animated video explaining stimulated emission. You can find also some additional information on application of laser technology.

**Animation:**



This java animation guides you through the elementary principles of the operation of the laser. You can virtually create a laser by pumping the chamber with a photon beam and manage the energy states of the laser's atoms to control its output.

**Problem 11.1 :** Download this questionarie on "How to make a laser" to test your knowledge in lasers. http://phet.colorado.edu/en/contributions/view/2869

In our approach the interaction of atoms and radiation are described quantum mechanically, while the electromagnetic field is treated by the classical (unquantized) Maxwell equations. This method is frequently used in the description of several optical phenomena. These include the semi-classical theory of the laser, due to W.E. Lamb (the Nobel prize winner for his discovery of the Lamb shift), and other effects connected with the propagation of (quasi)monochromatic fields in resonant media. The semi classical approximation cannot give account from first principles of the noise factor that initiates the laser oscillations: spontaneous emission, but the latter can be included artificially. The intrinsic line-width of the laser field, resulting from spontaneous emission and vacuum fluctuations can only be obtained by taking into account field quantization, which is excluded from the treatment here. Another consequence of the assumption of the absence of spontaneous emission is that in the semi classical theory we have to assume that there is already a field present in the initial state of the system, for the excited atoms would not decay otherwise.

## Figure 11.1. Examples of red green and blue laser. https://en.wikipedia.org/wiki/File:RGB_laser.jpg

Examples of red green and blue laser.

We shall assume here the **two-level approximation** where only two stationary states take part in the interaction with the field. This is justified by the fact that if the frequency of the field is very close to resonance with the atomic transition in question then the other levels do not play a direct role. They can however participate in the physical process of pumping or damping indirectly, which can be taken into account by adding phenomenological terms to the fundamental quantum mechanical equations.

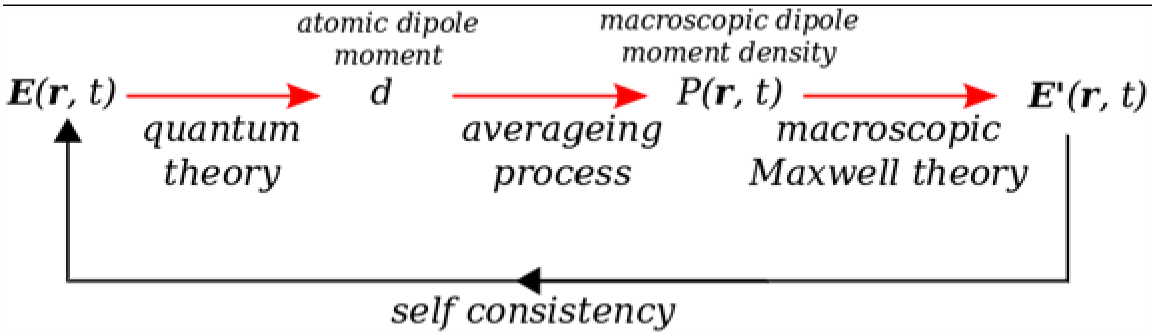
Another approximation to be exploited is the lowest order **electric dipole approximation**, as it was done in the previous chapter. For simplicity it will be also assumed that the electric field is **linearly polarized**. That means that the interaction Hamiltonian between an atom and the field has the form:

$$K_S = -DE(\mathbf{r},t)\cos\omega t \tag{11.1}$$

The amplitude of the field $E$ is space and time dependent, but the time dependence will be assumed to be slow compared with the carrier oscillations given by $\cos\omega t$. The space dependence of the field manifests only on the order of a wavelength, which is much larger then the size of the atoms, hence the dipole approximation. The absence of direct short range atomic (dipole-dipole) interactions will also be assumed, which is valid if the active atoms have a low volume density in the material, e.g. in a gas.

Other approximations to be exploited will be introduced later on.

## Figure 11.2. Visualization of self consistent field theory



Visualization of self consistent field theory

The semi-classical theory of the laser and those of other related optical processes can be considered as a self consistent field theory in the sense given in Figure 11.2 , which illustrates the approach of Lamb to the problem. As we see, the electric field $E(\mathbf{r},t)\cos\omega t$ is a factor in the interaction part of the atomic Hamiltonian. We have to solve the dynamical equation i.e. the time dependent Schrödinger equation of the atoms with this Hamiltonian, and calculate the resulting dipole moment of the atoms, which of course will turn out again time dependent. We then perform an averaging of the atomic dipoles to obtain the macroscopic polarization density $P(\mathbf{r},t)$. This now acts as a source in Maxwell's equations, which allow to calculate the field $E'(\mathbf{r},t)$ resulting from this source. The self-consistency requirement is then

$$E'(\mathbf{r},t) = E(\mathbf{r},t). \qquad (11.2)$$

This expresses the condition that the field emerging from each atom is stimulated by the average field produced by all the active atoms, to which in turn they all contribute.

The loop shown in Figure 11.2 contains the solution of the Schrödinger equation for the atoms influenced by the electromagnetic field, and the solution of the Maxwell equations for the field generated by the atoms. Therefore the coupled system of equations considered in this chapter are called the the **Maxwell-Schrödinger equations**.

# 2. The field equations

We consider first the Maxwell equations, in their usual compact vectorial form, describing the electromagnetic field in the medium. Later on we will restrict the treatment to linearly polarized fields. The phenomenological Maxwell equations are:

$$\begin{aligned} \nabla\times\mathbf{H} &= \mathbf{J}+\dot{\mathbf{D}} \\ \nabla\times\mathbf{E} &= -\dot{\mathbf{B}} \\ \nabla\mathbf{D} &= 0 \\ \nabla\mathbf{B} &= 0. \end{aligned} \qquad (11.3)$$

In the absence of macroscopic charges and currents the only source of the field strengths is the space and time dependent polarization density $\mathbf{P}(\mathbf{r},t)$ which is "hidden" in the definition of the displacement vector $\mathbf{D}$ :

$$\mathbf{P} = \mathbf{D} - \epsilon_0\mathbf{E}. \qquad (11.4)$$

The magnetic fields are supposed to be connected like in vacuum, while field losses will be introduced formally by a constant, $\sigma$, which plays a role of a fictitious "conductivity" :

$$\mathbf{B} = \mu_0\mathbf{H}, \qquad \mathbf{J} = \sigma\mathbf{E}. \qquad (11.5)$$

By taking the curl of the second Maxwell equation and the time derivative of the first one, we get for $\mathbf{E}$ :

$$\nabla\times\nabla\times\mathbf{E}+\mu_0\sigma\,\dot{\mathbf{E}}+\mu_0\epsilon_0\ddot{\mathbf{E}}=-\mu_0\ddot{\mathbf{P}}. \qquad (11.6)$$

The term containing the first derivative, $\dot{\mathbf{E}}$ is not invariant with respect to time reversal, that is why $\sigma$ can represent the losses. If the density of the material of the sample is low, e.g. in a gas, or in a weakly doped solid, $\mathbf{P}$ is a a small perturbation compared with $\epsilon_0\mathbf{E}$, so that

$$0=\nabla\mathbf{D}\approx\epsilon_0\nabla\mathbf{E}, \qquad (11.7)$$

meaning that the electric field strength is also transversal, and in the identity $\nabla\times\nabla\times\mathbf{E}=\nabla(\nabla\mathbf{E})-\Delta\mathbf{E}$ we can neglect the $\nabla(\nabla\mathbf{E})$ term. Using also $\mu_0\epsilon_0=1/c^2$ we get

$$\Delta\mathbf{E}-\mu_0\sigma\dot{\mathbf{E}}-\frac{1}{c^2}\ddot{\mathbf{E}}=\mu_0\ddot{\mathbf{P}}, \qquad (11.8)$$

which is the well known inhomogeneous damped wave equation, known also as the telegraph equation. In most cases we assume a field propagation in one direction, let it be the $z$ direction, and a linearly polarized electric field, as well as polarization density both in the $\hat{\mathbf{x}}$ direction: $\mathbf{E}(\mathbf{r},t)=E(z,t)\hat{\mathbf{x}}$, $\mathbf{P}(\mathbf{r},t)=P(z,t)\hat{\mathbf{x}}$.

Equation ( 11.8 ) now becomes:

$$\frac{\partial^2E}{\partial z^2}-\mu_0\sigma\frac{\partial E}{\partial t}-\frac{1}{c^2}\frac{\partial^2E}{\partial t^2}=\mu_0\frac{\partial^2P(z,t)}{\partial t^2}. \qquad (11.9)$$

# 3. Mode expansion of the field

In the case of a laser, the active material is put into a cavity, which has an elongated shape. This means that one of the dimensions, the length $L$ is much larger then the linear size of the cross section of the sample. We confine here our attention to the axial modes, i.e we do not care about the cross sectional (transversal) amplitude distribution of the field. The axial modes are the standing waves along the axis, with appropriate boundary conditions, and can be written as :

$$\mathrm{u}_n(z)=\sqrt{\frac{2}{L}}\sin k_nz,\quad \text{where}\quad k_n=n\pi/L=:\frac{\Omega_n}{c} \qquad (11.10)$$

corresponding to zero values of the transverse field on the surface of the mirrors. $\Omega_n$ is called the mode frequency of the empty cavity. The set of modes forms an orthonormal system:

$$\int_0^L\mathrm{u}_n(z)\mathrm{u}_{n'}(z)dz=\delta_{nn'}, \qquad (11.11)$$

and can be shown to be a basis or a complete system, in the sense that all fields, obeying the same boundary conditions, i.e. vanishing at the boundaries, can be expanded in terms of $\mathrm{u}_n(z)$.

So we can expand the field in terms of these eigenmodes and have:

$$E(z,t)=\sum_n A_n(t)\mathrm{u}_n(z)=\sqrt{\frac{2}{L}}\sum_n A_n(t)\sin k_nz, \qquad (11.12)$$

with time dependent coefficients $A_n(t)$.

Since the solution for the laser field will be practically monochromatic we can take

$$\frac{\partial^2 P}{\partial t^2} \approx -\omega^2 P, \tag{11.13}$$

where $\omega$ is the angular frequency of the oscillation of $P$ which will be later identified with the frequency $\omega_n$ of the laser field. Actually we have

$$\omega = \omega_n \approx \Omega_n \approx \omega_0, \tag{11.14}$$

where $\omega_0 := \omega_{21}$ is the atomic transition angular frequency.

Substituting ( 11.13 ) and ( 11.12 ) in ( 11.9 ) and using the orthonormality ( 11.11 ) of the modes, i.e. integrating the equation with respect to $z$, we find that the unknown time dependent mode amplitudes $A_n(t)$ obey the equation of motion for the driven and damped harmonic oscillator:

$$\ddot{A}_n + \frac{\sigma}{\epsilon_0}\dot{A}_n(t) + \Omega_n^2 A_n = \frac{\omega^2}{\epsilon_0} P_n(t). \tag{11.15}$$

The role of the driving force is played by $P_n$, which is the projection of the inhomogeneous source term $P(z,t)$ on the mode $\mathrm{u}_n(z)$ :

$$P_n(t) = \int_0^L P(z,t)\mathrm{u}_n(z)dz. \tag{11.16}$$

We shall write

$$\frac{\sigma}{\epsilon_0} = \frac{1}{\tau_n}, \tag{11.17}$$

in the absence of the driving term, as it is known from the theory of the damped oscillator. Instead of this relaxation time, one often uses the quality factor $Q_n$ for the mode, defined by

$$\tau_n \Omega_n = Q_n. \tag{11.18}$$

The value of the dimensionless $Q_n$ determines the number of oscillations of the mode during its lifetime.

# 4. Slowly varying envelope approximation

The solution of Eq. ( 11.15 ) will be sought by the method of Slowly Varying Envelope Approximation (SVEA) which means that we assume a form

$$A_n(t) = E_n(t)\cos[\omega_n t + \varphi_n(t)], \tag{11.19}$$

where both the real $E_n(t)$ and $\varphi_n(t)$ are slowly varying functions of $t$ on the time scale $2\pi/\omega_n$. This means that

$$\dot{E}_n \ll \omega_n E_n \quad \text{and} \quad \ddot{E}_n \ll \omega_n \dot{E}_n \ll \omega_n^2 E_n. \tag{11.20}$$

Then calculating the necessary time derivatives we can neglect the underlined terms in the relations below:

$$\begin{aligned}\dot A_n(t) &= -(\omega_n+\dot\varphi_n)E_n\sin(\omega_n t+\varphi_n)+\dot E_n(t)\cos(\omega_n t+\varphi_n)\\ \ddot A_n(t) &= [-(\omega_n^2+2\omega_n\dot\varphi_n+\underline{\dot\varphi_n^2})E_n+\underline{\ddot E_n}]\cos(\omega_n t+\varphi_n)-\\ &\quad -[2(\omega_n+\underline{\dot\varphi_n)\dot E_n}+\underline{\ddot\varphi_n E_n}]\sin(\omega_n t+\varphi_n).\end{aligned} \tag{11.21}$$

We now represent $P_n(t)$ in a similar way. Since $P_n$**will not in general oscillate in phase** with $A_n$, we shall take:

$$P_n(t)=C_n(t)\cos[\omega_n t+\varphi_n(t)]+S_n(t)\sin[\omega_n t+\varphi_n(t)], \tag{11.22}$$

where $C_n(t)$ and $S_n(t)$ are also slowly varying functions of the time variable, and the first term above is called the **in-phase component**, while the second one, which is obviously out of phase by $\pi/2$ with $A_n$, is called the **in-quadrature component** of $P_n$. Substituting ( 11.19 ), ( 11.21 ) and ( 11.22 ) in ( 11.15 ) and identifying $\omega$ with $\omega_n$ we find

$$\begin{aligned}&\left\{\left[\Omega_n^2-(\omega_n^2+2\omega_n\dot\varphi_n)\right]E_n+\underline{\frac{\Omega_n}{Q_n}\dot E_n}\right\}\cos[\omega_n t+\varphi_n(t)]+\\ &+\left\{-2\omega_n\dot E_n-\frac{\Omega_n}{Q_n}(\omega_n+\underline{\dot\varphi_n})E_n\right\}\sin[\omega_n t+\varphi_n(t)]=\\ &=\frac{\omega_n^2}{\epsilon_0}\{C_n(t)\cos[\omega_n t+\varphi_n(t)]+S_n(t)\sin[\omega_n t+\varphi_n(t)]\}\end{aligned} \tag{11.23}$$

and we use $1\ll Q_n$, and $\dot\varphi_n\ll\omega_n$ to neglect the underlined terms, in agreement with ( 11.20 ). Also, by ( 11.14 ) we have in the coefficient of the $\cos$ term on the left hand side:

$$\Omega_n^2-(\omega_n^2+2\omega_n\dot\varphi_n)\approx 2\omega_n(\Omega_n-\omega_n-\dot\varphi_n). \tag{11.24}$$

We require ( 11.23 ) to be valid at all times, therefore the coefficients of the cos and sin terms must be separately equal, leading to

$$(\omega_n+\dot\varphi_n-\Omega_n)E_n=-\frac{\omega_n C_n}{2\epsilon_0}, \tag{11.25}$$

$$\dot E_n+\frac{\Omega_n}{2Q_n}E_n=-\frac{\omega_n S_n}{2\epsilon_0}. \tag{11.26}$$

The first one of these, the in-phase equation, determines the **frequency** of the oscillation of the mode, while the second one, the in-quadrature equation, will allow us to determine its **amplitude**. In the following we first present the simplest solutions of the system above.

## 4.1. Free oscillations

In the absence of atomic polarization both $C_n$ and $S_n$ are absent, and the integration of the frequency equation yields:

$$\omega_n t+\varphi_n=\Omega_n t+\varphi_{n0}, \tag{11.27}$$

therefore by a suitable choice of the phase

$$\omega_n=\Omega_n. \tag{11.28}$$

Similarly Eq. ( 11.26 ) yields

$$E_n = E_{n0} \exp\left(-\frac{\Omega_n}{2Q_n}t\right), \qquad (11.29)$$

so that according to ( 11.19 ) the field corresponds to damped oscillations:

$$A_n(t) = E_{n0} \exp\left(-\frac{\Omega_n}{2Q_n}t\right) \cos(\Omega_n t + \varphi_{n0}), \qquad (11.30)$$

in agreement with the interpretation of $Q_n$ as the $Q$ factor associated with the mode $n$.

## 4.2. Linear medium

A linear medium is one for which the usual linear relationship holds between the polarization and electric field:

$$P = \epsilon_0 \chi E, \qquad (11.31)$$

where we use the complex notation $\chi = \chi' + i\chi''$ for the susceptibility. For a rarefied medium like a gas we have for the complex index of refraction

$$\tilde{\eta} = \eta + i\kappa = \sqrt{\epsilon} = \sqrt{1 + \chi' + i\chi''} \approx 1 + \frac{1}{2}(\chi' + i\chi''), \qquad (11.32)$$

where $\epsilon$ is the **relative dielectric permittivity** of the sample, and we assumed a nonmagnetic material. The corresponding linear approximation for the mode polarization is

$$\begin{aligned} P_n &= \epsilon_0 \mathrm{Re}\left\{(\chi'_n + i\chi''_n)E_n e^{-i(\omega_n t + \varphi_n)}\right\} = \\ &= \epsilon_0 \chi'_n E_n \cos(\omega_n t + \varphi_n) + \epsilon_0 \chi''_n E_n \sin(\omega_n t + \varphi_n) \end{aligned} \qquad (11.33)$$

Comparing this with ( 11.22 ) we get that

$$C_n = \epsilon_0 \chi'_n E_n, \qquad S_n = \epsilon_0 \chi''_n E_n \qquad (11.34)$$

and substituting in the frequency equation ( 11.25 ) we find

$$\omega_n + \dot{\varphi}_n - \Omega_n = -\frac{\omega_n}{2}\chi'_n, \qquad (11.35)$$

so that, by a suitable choice of phase:

$$\omega_n = \frac{\Omega_n}{1 + \chi'_n/2} = \frac{\Omega_n}{\eta_n}, \qquad (11.36)$$

where $\eta_n$ is the corresponding real refractive index given by Eq. ( 11.32 ). This result can be simply interpreted, the resonant wavelengths $\lambda_n = 2\pi/k_n$ given by ( 11.10 ) **remain unchanged**, because they are determined by the geometry, but the corresponding frequencies are now given by $\omega_n = k_n v_n = \Omega_n/\eta_n$, where $v_n = c/\eta_n$ is the phase velocity in the dielectric medium. Note that $\omega_n \approx (1 - \chi'_n/2)\Omega_n$ so that the medium has a "frequency pulling" effect. The amplitude equation ( 11.26 ) becomes:

$$\dot{E}_n + \frac{\Omega_n}{2Q_n}E_n = -\frac{\omega_n}{2}\chi''_n E_n. \qquad (11.37)$$

Thus, neglecting a small correction

$$E_n = E_{n0}\exp\left[-\frac{\omega_n}{2}\left(\frac{1}{Q_n}+\chi_n''\right)t\right], \qquad (11.38)$$

so that below threshold, in the linear approximation, the atoms give rise to an extinction coefficient associated with $\chi_n''$, as it is in a normal absorbing medium.

Multiplying equation ( 11.37 ) by $E_n$, and note that the mode energy density, $\mathcal{W}$ is proportional to $E_n^2$ we get:

$$\frac{d\mathcal{W}}{dt} = -\frac{\Omega_n}{Q_n}\mathcal{W} + \omega_n|\chi_n''|\mathcal{W}. \qquad (11.39)$$

Thereby we get the equation for the energy balance: the first term on the right hand side is the cavity loss, while the second one is the gain, assuming $\chi_n'' < 0$, which is valid if we have population inversion and therefore a "negative absorption". Then the exponent in ( 11.38 ) may turn to zero or positive when

$$-\chi_n'' = |\chi_n''| \geq \frac{1}{Q_n}. \qquad (11.40)$$

In this case the absorbing medium will change to an amplifier, the threshold given by the equality sign in the above equation. Above the threshold the amplitude of the laser oscillations would grow exponentially in time according to ( 11.38 ). This means that the linear approximation for the amplitude must be invalid beyond of a certain value, and a stable oscillation can only be obtained by taking nonlinear effects into account.

# 5. The two-level coherent resonant approximation, the optical Rabi problem

In this section we shall solve the dynamics of an atom under the influence of a given external harmonic electric field. We assume here from the very beginning that the transition takes place only between two resonant energy levels. Let us denote the two corresponding stationary states by $|u_1\rangle$ and $|u_2\rangle$ with nondegenerate energy eigenvalues $\varepsilon_1 < \varepsilon_2$ of the unperturbed Hamiltonian $H_0$. The main assumption here is that the energy difference between the two is close to $\hbar\omega$ : $\varepsilon_2 - \varepsilon_1 \approx \hbar\omega$, where $\omega$ is the circular frequency of the external electric field. This is the **two-level resonant approximation**.

According to the formalism of the previous chapter, in Eq. ( 10.5 ) we have now only two coefficients in $|\Psi(t)\rangle$ :

$$|\Psi(t)\rangle = b_1(t)e^{-i\frac{\varepsilon_1}{\hbar}t}|u_1\rangle + b_2 e^{-i\frac{\varepsilon_2}{\hbar}t}|u_2\rangle . \qquad (11.41)$$

In this section we assume that the amplitude of the linearly polarized electric field is constant at the place of the atom. Therefore we work with the interaction Hamiltonian

$$K_S = -DE_0\cos\omega t, \qquad (11.42)$$

and the equations for the coefficients see ( 10.17 ) are now:

$$\begin{aligned} i\hbar\dot{b}_1 &= -d_{11}(E_0\cos\omega t)b_1 - d_{12}e^{i\omega_{12}t}(E_0\cos\omega t)b_2 \\ i\hbar\dot{b}_2 &= -d_{21}(E_0\cos\omega t)e^{i\omega_{21}t}b_1 - d_{22}(E_0\cos\omega t)b_2. \end{aligned} \qquad (11.43)$$

The matrix elements of the components of the dipole moment operator $D := D_x$ vanish between identical stationary states : $d_{ii} = \langle u_i| D_x |u_i\rangle = 0, i = 1, 2$, because only those between states of different parities can be different from zero, according to the parity selection rule, which is valid for systems with inversion symmetry, including all the atoms. This excludes trivially $d_{11}$, and $d_{22}$. Also because the dipole moment operator is self-adjoint, the matrix elements obey $d^*_{21} = d_{12}$, the latter will be denoted by $d$. Therefore the equations can be written as:

$$\begin{aligned} i\dot{b}_1 &= -\tfrac{dE_0}{2\hbar}(e^{i\omega t} + e^{-i\omega t})e^{i\omega_{12}t}b_2 \\ i\dot{b}_2 &= -\tfrac{d^*E_0}{2\hbar}(e^{i\omega t} + e^{-i\omega t})e^{i\omega_{21}t}b_1. \end{aligned} \tag{11.44}$$

Let us note also that $\omega_{21} = -\omega_{12} > 0$. Close to resonance on the right hand side we have exponentials with

$$\omega_{21} - \omega = \Delta \ll \omega, \tag{11.45}$$

this is just the resonance condition, and also terms oscillating with frequency $\omega_{21} + \omega \approx 2\omega$. We omit the latter ones, as on integration the terms $e^{\pm i2\omega t}/2\omega$ are small and rapidly oscillating relative to those with $e^{\pm i\Delta t}/\Delta$. This is called the **rotating wave approximation** abbreviated as RWA.

Thus with the RWA we have:

$$\dot{b}_1 = i\frac{dE_0}{2\hbar}e^{i\omega t}e^{-i\omega_{21}t}b_2 = i\frac{dE_0}{2\hbar}e^{-i\Delta t}b_2 = i\frac{\Omega_0}{2}e^{-i\Delta t}b_2, \tag{11.46}$$

$$\dot{b}_2 = i\frac{d^*E_0}{2\hbar}e^{-i\omega t}e^{i\omega_{21}t}b_1 = i\frac{d^*E_0}{2\hbar}e^{i\Delta t}b_1 = i\frac{\Omega_0^*}{2}e^{i\Delta t}b_1. \tag{11.47}$$

Where we have also introduced the notation

$$\frac{dE_0}{\hbar} = \Omega_0, \tag{11.48}$$

which has the dimension of frequency. It is easily seen that the system conserves $|b_1|^2 + |b_2|^2$, which is set to be

$$|b_1|^2 + |b_2|^2 = 1 \tag{11.49}$$

as, by assumption, we have only these two levels populated.

**Problem 11.2 :** Prove that ( 11.49 ) is valid at all times ($|b_1(t)|^2 + |b_2(t)|^2 = 1$, meaning that the equations conserve the probability) if this is valid at $t = 0$, i.e. $|b_1(0)|^2 + |b_2(0)|^2 = 1$.

**Problem 11.3 :** Show that in the case of circulary polarized external field, when $\mathbf{E} = E_0(\mathbf{x}\cos\omega t + \mathbf{y}\sin\omega t)$ the rotataing wave approximation is not necessary, the equations above are exact.

The system of equations above can be easily solved by taking the second derivative of say the second equation ( 11.47 ) and substituting $\dot{b}_1$ from the first one ( 11.46 ):

$$\begin{aligned} \ddot{b}_2 &= i\tfrac{\Omega_0^*}{2}(i\Delta e^{i\Delta t}b_1 + e^{i\Delta t}\dot{b}_1) = i\tfrac{\Omega_0^*}{2}\left[i\Delta e^{i\Delta t}\left(-i\dot{b}_2\tfrac{2}{\Omega_0^*}e^{-i\Delta t}\right) + e^{i\Delta t}i\tfrac{\Omega_0}{2}e^{-i\Delta t}b_2\right] \\ &= i\Delta\dot{b}_2 - \tfrac{|\Omega_0|^2}{4}b_2 \end{aligned} \tag{11.50}$$

or

$$\ddot{b}_2 - i\Delta\dot{b}_2 + \frac{|\Omega_0|^2}{4}b_2 = 0. \tag{11.51}$$

Looking for the solution in the form $b_2 = e^{\lambda t}$ we get the characteristic equation $\lambda^2 - i\Delta\lambda + \frac{|\Omega_0|^2}{4} = 0$, and the solutions

$$\lambda_{12} = \frac{i\Delta \pm \sqrt{-\Delta^2 - |\Omega_0|^2}}{2} = \frac{i\Delta \pm i\Omega}{2}, \qquad (11.52)$$

where $\Omega = \sqrt{\Delta^2 + |\Omega_0|^2}$. The general solution is a superposition of the solutions with both eigenfrequencies yielding

$$b_2 = e^{i\Delta t/2}(b_{2+}e^{i\Omega t/2} + b_{2-}e^{-i\Omega t/2}). \qquad (11.53)$$

The solution we look for corresponds to the initial condition $b_1(0) = 1$, $b_2(0) = 0$, ie. when the system is initially in its ground state. We have then $b_2(0) = b_{2+} + b_{2-} = 0$, and therefore

$$b_2 = b_{2+}(e^{i\Omega t/2} - e^{-i\Omega t/2})e^{i\Delta t/2} = 2ib_{2+}\sin\frac{\Omega t}{2}e^{i\Delta t/2}. \qquad (11.54)$$

Than expressing $b_1$ from ( 11.47 )

$$\begin{aligned} b_1 &= -\tfrac{2}{\Omega_0^*}e^{-i\Delta t}i\dot{b}_2 = -\tfrac{2}{\Omega_0^*}e^{-i\Delta t}i\left[2ib_{2+}\left(\tfrac{\Omega}{2}\cos\tfrac{\Omega t}{2} + i\tfrac{\Delta}{2}\sin\tfrac{\Omega t}{2}\right)e^{i\Delta t/2}\right] \\ &= \tfrac{2b_{2+}}{\Omega_0^*}e^{-i\Delta t/2}\left(\Omega\cos\tfrac{\Omega t}{2} + i\Delta\sin\tfrac{\Omega t}{2}\right) \end{aligned} \qquad (11.55)$$

$b_{2+}$ can be determined with help of the initial conditions. From $b_1 = 1$ for $t = 0$ we get $1 = 2b_{2+}\frac{\Omega}{\Omega_0^*}$ and so

$$b_{2+} = \frac{\Omega_0^*}{2\Omega} = \frac{\Omega_0^*}{2\sqrt{|\Omega_0|^2 + \Delta^2}}, \qquad (11.56)$$

and we have the solution

$$\begin{cases} b_2(t) = & i\frac{\Omega_0^*}{\Omega}\sin\frac{\Omega t}{2}e^{i\Delta t/2} \\ b_1(t) = & \left(\cos\frac{\Omega t}{2} + i\frac{\Delta}{\Omega}\sin\frac{\Omega t}{2}\right)e^{-i\Delta t/2} \end{cases} \qquad (11.57)$$

The sum of absolute value squares add up to 1:

$$\frac{|\Omega_0|^2}{\Omega^2}\sin^2\frac{\Omega t}{2} + \cos^2\frac{\Omega t}{2} + \frac{\Delta^2}{\Omega^2}\sin^2\frac{\Omega t}{2} = 1 \qquad (11.61)$$

The probability of finding the system in the upper state is therefore:

$$|b_2|^2 = \frac{|\Omega_0|^2}{|\Omega_0|^2 + \Delta^2}\sin^2\frac{\Omega t}{2} = \frac{|\Omega_0|^2}{|\Omega_0|^2 + \Delta^2}\frac{1}{2}(1 - \cos\Omega t) \qquad (11.62)$$

which oscillate between 0 and $\frac{|\Omega_0|^2}{|\Omega|_0^2+\Delta^2}$ with the frequency $\Omega$. The latter is called the optical Rabi frequency after I. I. Rabi, who derived this result for magnetic resonance in 1938, and used it to determine the magnetic moments of atomic nuclei, see below.

Let us first assume that the field has a constant amplitude, $E_0$. In the case when $\Delta = 0$ the oscillation frequency is $|\Omega_0| = \frac{dE_0}{\hbar}$, and the system reaches the upper state exactly when $\Omega_0 t = \pi$. Therefore a pulse with constant amplitude and duration of $t = \pi/\Omega_0$ is called a $\pi$ pulse. On the other hand if $t = 2\pi/\Omega_0$ then the system returns to its initial ground state. this is a $2\pi$ pulse. A pulse for which $t = \frac{\pi}{2}/\Omega_0$ brings the system into an equal weight superposition of the ground and excited states, this is a $\frac{\pi}{2}$ pulse. We note that essentially the same results are valid for time dependent amplitudes, if we integrate $\frac{d}{\hbar}E_0(t)$ the amplitude of the field strength, i. e. the resonant ($\Delta = 0$) Rabi frequency with respect of time, we get:

$$\Theta = \frac{d}{\hbar}\int E_0 dt = \int \Omega_0 dt \tag{11.63}$$

and the result is an angle determining the pulse angle in the previous sense. $\Theta$ is also called the pulse area, which is characteristic to some extent to the strength of the pulse, but it is not the intensity which is proportional to $E_0^2$.

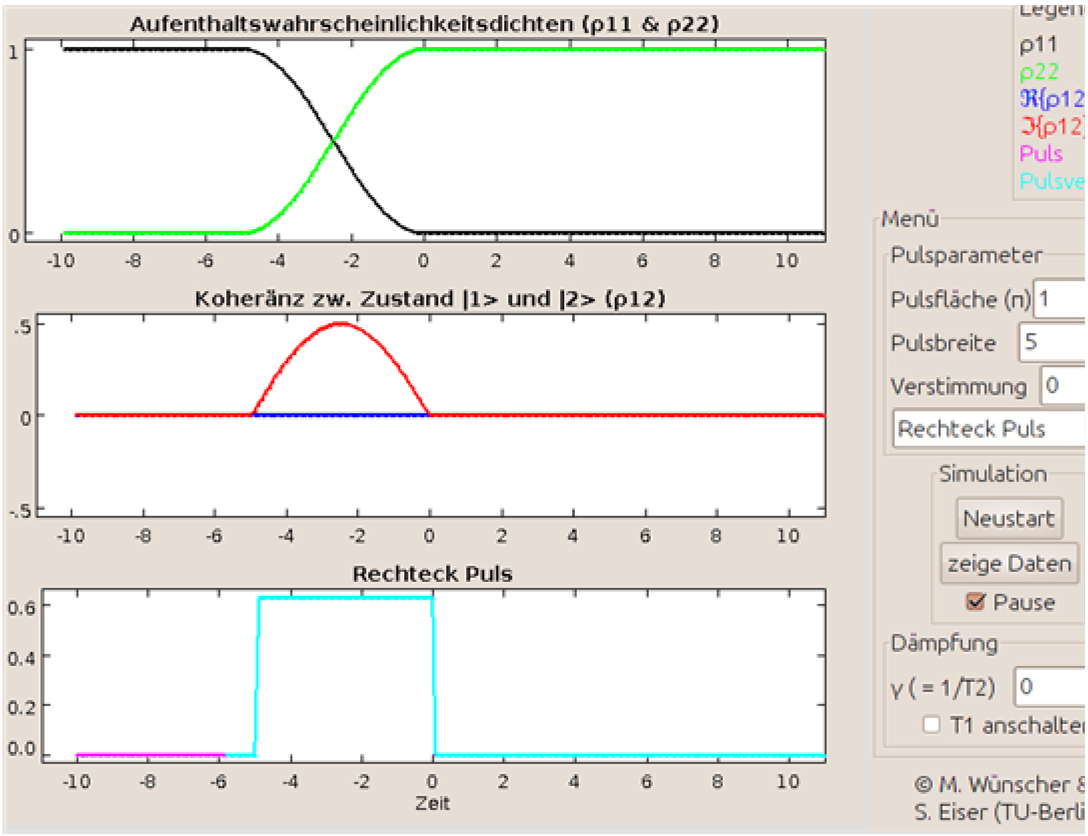
This shows that on exact resonance we can excite an atom or a system exactly to its upper state if this excitation is so fast, that the atom can be described with the Schrödinger equation for all the time. This is called a coherent excitation. It means that the atom does not interact with degrees of freedom, other then the oscillating electric field. Below we shall consider circumstances when this is not valid any more, and will complete the description with relaxation, as well as with pumping terms.

As we have mentioned, the quantum theory of the resonant interaction has been derived and used first by Rabi in his molecular beam method. In that case the levels in question were magnetic spin states in nuclei, and the transition was induced by time varying magnetic fields.

In case of atomic levels the transition is coming from an the electric dipole interaction with a time dependent electric field, as we have seen in this section. In the infrared domain the validity of these results has been proved first by G. Hocker and C. Tang in 1969, while in the visible domain by H. Gibbs with Rb atoms in 1973. In this case one speaks of the optical Rabi problem.

**Animation:**

This is a Java applet that visualizes Rabi Cycles of two-state systems (laser driven).



Pulsfläche (n) 1

Pulsbreite 5

Verstimmung 0

☑ Pause

γ ( = 1/T2) 0

☐ T1 anschalte

# 6. The polarization and the incoherent limit of the atomic equations

The Rabi oscillations cannot last forever, as we have considered an ideal situation, where the atoms did not interact with other atoms. In reality there are always collisions between the atoms and this will have an important influence on their dynamics, relaxation terms will appear. We shall also include incoherent pumping, which is different from the one by the resonant field. The pumping can be also the result of collisions with other atoms, or relaxation from levels other than the two resonant ones, or it may come directly from "non-lasing modes" propagating perpendicularly to the ones considered so far.

In order to take these effects into account, instead of the atomic amplitudes $b_i$ we shall consider quadratic functions of them, bearing a more conventional classical meaning. As we know, the probabilities to find the atom in its ground and its excited states are

$$|b_1|^2 = b_1 b_1^* =: \varrho_{11}, \qquad |b_2|^2 = b_2 b_2^* =: \varrho_{22} \qquad (11.64)$$

respectively. The notation $\varrho_{ii} = |b_i|^2$ refers to a general concept in quantum mechanics: these values are the diagonal elements of the so called atomic **density matrix** $\varrho_{ij}$, introduced by Lev Landau and independently by Janos Neumann in the second half of the 1920's. For our present purposes it is not necessary to give a more general definition of this important concept, we note only that it is an invaluable tool when considering open systems in quantum physics, like e.g. the laser

We shall also introduce the off-diagonal elements [1]of the density matrix for our two level system by

$$\varrho_{12} = b_1 b_2^* e^{i\Delta t} \qquad \varrho_{21} = b_2 b_1^* e^{-i\Delta t} = \varrho_{12}^* \qquad (11.65)$$

---

[1] We use here the interaction picture, which explains the appearance of the exponential factors $\exp(\pm i\Delta t)$, containing the detuning $\Delta$, which may seem curious at first sight.

We can easily obtain the equations of motion for the quantities: $\varrho_{ij}$. We shall assume here that the dipole matrix element between the two stationary states of $H_0$ is real:

$$d=\langle u_1|\, D\,|u_2\rangle=\langle u_2|\, D\,|u_1\rangle=d^* \qquad (11.66)$$

Let us now multiply ( 11.46 ) by $b_1^*$, and its complex conjugate by $b_1$ and add the two equations. We get then

$$\dot{\varrho}_{11}=i\frac{dE_0}{2\hbar}(\varrho_{21}-\varrho_{21}^*) \qquad (11.67)$$

A similar procedure with ( 11.47 ) yields:

$$\dot{\varrho}_{22}=-i\frac{dE_0}{2\hbar}(\varrho_{21}-\varrho_{21}^*). \qquad (11.68)$$

On the other hand, multiplying the compex conjugate of ( 11.46 ) with $b_2^*$ and ( 11.47 ) with $b_1^*$, we get from their sum

$$\dot{\varrho}_{21}=-i\Delta\varrho_{21}-i\frac{dE_0}{2\hbar}(\varrho_{22}-\varrho_{11}). \qquad (11.69)$$

Adding ( 11.67 ) and ( 11.68 ) we see that $\varrho_{11}+\varrho_{22}$ is constant in time, as it should be. If only these two levels had any role in the process, then - as in the previous section - we would have to set the constant to be $\varrho_{11}+\varrho_{22}=1$, as obviously these diagonal elements correspond to the **probabilities** that we find the atom in level 1 or 2. Therefore these values are called **level populations**.

We shall now exhibit the physical meaning of the off-diagonal term $\varrho_{21}=\varrho_{12}^*$. To this end we calculate the expectation value of the dipole moment in the time dependent state $|\Psi(t)\rangle$ of ( 11.41 )

$$|\Psi(t)\rangle=b_1(t)e^{-i\frac{\varepsilon_1}{\hbar}t}\,|u_1\rangle+b_2(t)e^{-i\frac{\varepsilon_2}{\hbar}t}\,|u_2\rangle \qquad (11.70)$$

and find:

$$\begin{aligned}\langle\Psi(t)|\, D\,|\Psi(t)\rangle &= b_1^*b_2e^{-i\omega_0t}\langle u_1|\, D\,|u_2\rangle+b_1b_2^*e^{i\omega_0t}\langle u_2|\, D\,|u_1\rangle=\\ &= d(b_1^*b_2e^{-i\omega_0t}+b_1b_2^*e^{i\omega_0t})=d(\varrho_{21}e^{-i\omega_0t+i\Delta t}+\varrho_{21}^*e^{i\omega_0t-i\Delta t})\\ &= d(\varrho_{21}e^{-i\omega t}+\varrho_{21}^*e^{i\omega t})\end{aligned} \qquad (11.71)$$

because $(\varepsilon_2-\varepsilon_1)/\hbar=\omega_0$ is the Bohr frequency of the transition, and we have assumed that the dipole matrix element (transition dipole momentum) is real, see ( 11.66 ). We made also use of the fact that the static dipole moments vanish: $\langle u_i|\, D\,|u_i\rangle=0$, which is valid for systems with inversion symmetry, including all the atoms. We see therefore that the off diagonal element $\varrho_{21}$ and its conjugate give account of how much the system is in the superposition of the two stationary states. The off-diagonal elements are often called as **coherences** of the levels in question. We see that they determine the dipole moment of the atom.

Now come to the point to determine the macroscopic polarization density from the atomic data. We consider several atoms in a sample with a volume density $\mathcal{N}$. In the simplest case we can assume that the macroscopic polarization can be obtained by multiplying the expectation value of the atomic dipole moment by $\mathcal{N}$, the number of atoms per unit volume:

$$P=\mathcal{N}\langle\Psi(t)|\, D\,|\Psi(t)\rangle=\mathcal{N}d(\varrho_{21}e^{-i\omega t}+\varrho_{21}^*e^{i\omega t}) \qquad (11.72)$$

There exist more sophisticated averaging methods, which take into account moving atoms, and instead of a single transition frequency $\omega_0$ which was assumed to be identical for all the atoms, a whole distribution of atomic frequencies (called inhomogeneous broadening) are used. We shall not go into such details here.

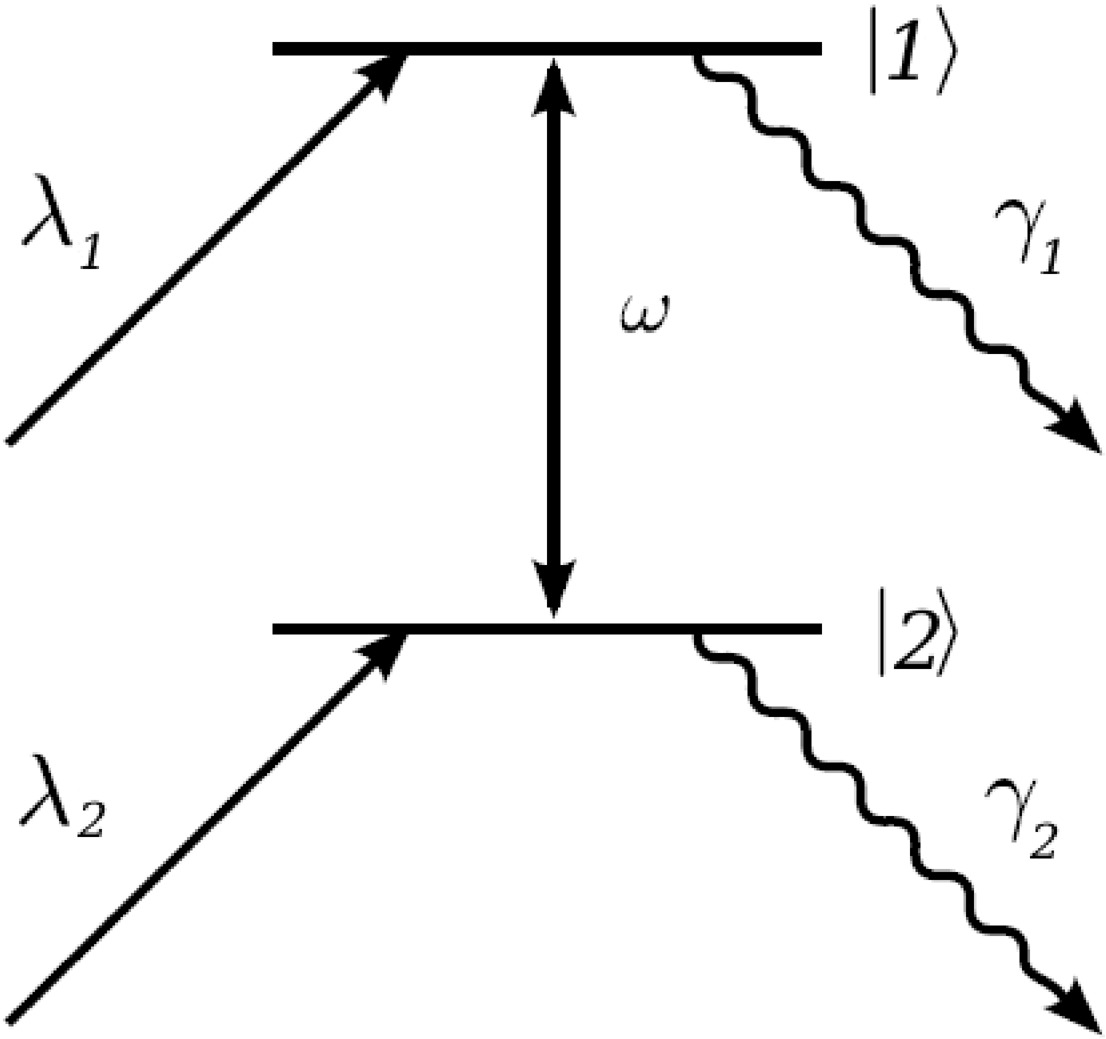
**Problem 11.4 :** Using ( 11.67 ) ( 11.68 ) and ( 11.69 ) prove that the trace of the square of the matrix $\varrho_{ij}$ is also a constant.

**Problem 11.5 :** Introduce the following three real variables: $W=\varrho_{22}-\varrho_{11}, U=\mathrm{Re}\varrho_{21}, V=-\mathrm{Im}\varrho_{21}$. Write down the differential equations for these variables and show that the length of the so called Bloch vector $\{U,V,W\}$ is a constant.

# 7. Rate equations

We come now to the point where relaxation and pumping processes, mentioned in the introduction of this section can be taken into account. First, the levels 1 and 2 may decay to other levels, which we shall assume to be exponential in time with relaxation rates $\gamma_1$ and $\gamma_2$ respectively. Pumping, on the other hand, will increase the populations, and we shall assume constant pumping rates usually denoted by $\lambda_1$ and $\lambda_2$ see Fig. 11.3 .

### Figure 11.3. Two level system with pumping and decay



Two level system with pumping and decay

Let us assume now that only a single mode, the $n$ -th one is excited in the system, thus we have only one term in the expansion ( 11.12 ) and we have to set here

$$E_0 = E_n(t)\mathfrak{u}_n(z) \tag{11.73}$$

with slowly varying $E_n(t)$, and find:

$$\begin{aligned}\dot{\varrho}_{22} &= \lambda_2 - \gamma_2\varrho_{22} - i\frac{dE_n}{2\hbar}\mathfrak{u}_n(z)(\varrho_{21} - \varrho_{21}^*)\\ \dot{\varrho}_{11} &= \lambda_1 - \gamma_1\varrho_{11} + i\frac{dE_n}{2\hbar}\mathfrak{u}_n(z)(\varrho_{21} - \varrho_{21}^*)\end{aligned} \tag{11.74}$$

We must also introduce a relaxation term $-\gamma\varrho_{21}$ into the equation of the off-diagonal element

$$\dot{\varrho}_{21} = -i\Delta\varrho_{21} - \gamma\varrho_{21} - i\frac{dE_n}{2\hbar}\mathfrak{u}_n(z)(\varrho_{22} - \varrho_{11}) \tag{11.75}$$

This term describes the loss of the phase memory between the amplitudes of the levels. For an isolated atom in vacuum this comes from the unavoidable quantum fluctuations of the electromagnetic vacuum causing spontaneous emission. In a laser material it is due to collisions with other atoms in a gas, or with phonons in a solid etc, and is therefore much faster than for an isolated atom. This process does not dissipate directly energy, as it is done by terms $-\gamma_i\varrho_{ii}$ introduced into the equations for the populations, but has only an indirect effect through the last, coherent driving terms in them. As the relaxation constant for the off-diagonal elements $\gamma$ are usually much bigger than those for the diagonal ones, the coherences vanish much faster than the populations, we can assume that $\varrho_{21}$ takes its stationary value essentially during the whole process. We note that in a gas $\gamma^{-1}$ is of the order of a few picoseconds, while $\gamma_2^{-1}$ and $\gamma_1^{-1}$ are usually in the nanosecond range. Setting $\dot{\varrho}_{21} = 0$ we obtain the stationary case for the off-diagonal element, which is:

$$\varrho_{21} = -\frac{i}{\gamma + i\Delta}\frac{dE_n}{2\hbar}\mathfrak{u}_n(z)(\varrho_{22} - \varrho_{11}) \tag{11.76}$$

This is the **incoherent limit** of our model. We introduce now the notation:

$$W = \varrho_{22} - \varrho_{11} \tag{11.77}$$

called **population inversion**. As $\varepsilon_2 - \varepsilon_1 > 0$, it must be negative for a system in thermal equilibrium, as stipulated by the Boltzmann factor $\varrho_{22} = \varrho_{11}\exp\left[-(\varepsilon_2 - \varepsilon_1)/k_BT\right]$.

A pumped system, however, can be far from equilibrium, and $W$ can be positive, this is the case when we speak of an inverted medium. In the incoherent limit we can thus write with $\Delta_n = \omega_0 - \omega_n$ :

$$\varrho_{21}(z,t) = -\frac{i}{\gamma + i\Delta_n}\frac{d}{2\hbar}E_n(t)\mathfrak{u}_n(z)W(z) \tag{11.78}$$

According to ( 11.72 ) the dipole moment density in mode $n$ is obtained then as

$$P_n(t) = -i\mathcal{N}\frac{d^2}{2\hbar}E_n(t)\bar{W}_n\frac{e^{-i(\omega_n t + \varphi_n)}}{\gamma + i\Delta_n} + c.c. \tag{11.79}$$

where $c.c.$ denotes complex conjugate, and

$$\bar{W}_n = \int W(z)\mathfrak{u}_n^2(z)dz \tag{11.80}$$

is the average spatial inversion density. Computing the coefficients of $\cos$ and $\sin$ in ( 11.79 ) and comparing with ( 11.22 ) we find

$$C_n = -\frac{d^2}{\hbar}\bar{W}_n \Delta_n \mathcal{L}(\Delta_n) E_n \qquad (11.81)$$

$$S_n = -\frac{d^2}{\hbar}\bar{W}_n \gamma \mathcal{L}(\Delta_n) E_n \qquad (11.82)$$

where

$$\mathcal{L}(\Delta_n) = \frac{1}{\gamma^2 + \Delta_n^2} \qquad (11.83)$$

is the Lorentzian line shape with the linewidth $\gamma/\pi$. This line broadening is called homogeneous broadening as it is essentially identical for all the atoms in the sample.

Equations ( 11.81 ) and ( 11.82 ), are indeed linear in $E_n$. Comparing these results with ( 11.34 ) we see that in this approximation the active atoms constitute a linear medium with complex susceptibility:

$$\chi_n = \frac{1}{\epsilon_0}\frac{d^2}{\hbar}\bar{W}_n \frac{1}{i\gamma - \Delta_n} \qquad (11.84)$$

which is the Lorentz type dispersion formula. Substituting ( 11.82 ) in the amplitude equation ( 11.38 ) we find

$$\frac{\dot{E}_n}{E_n} = -\frac{\omega_n}{2}\left[\frac{1}{Q_n} - \frac{1}{\epsilon_0}\frac{d^2}{\hbar}\bar{W}_n \gamma \mathcal{L}(\Delta_n)\right] \qquad (11.85)$$

This determines the **threshold condition** for laser oscillations at frequency $\omega_n$ :

$$\frac{1}{\epsilon_0}\frac{d^2}{\hbar}\bar{W}_n \gamma \mathcal{L}(\Delta_n) \geq \frac{1}{Q_n} \qquad (11.86)$$

We add finally that in the case when the number of exciting modes is $M$, the off-diagonal element $\varrho_{21}$ is given by the sum:

$$\varrho_{21}(z,t) = -i\frac{d}{2\hbar}\sum_{n=1}^{M}\frac{E_n(t)}{\gamma + i(\omega_0 - \omega_n)}W(z)\mathrm{u}_n(z) \qquad (11.87)$$

and the same procedure as above can be performed with essentially the same results.

## 7.1. The nonlinear theory

In the linear approximation we took $\varrho_{22} - \varrho_{11} = W(z)$ as a known time-independent function $W(z)$. The next order approximation, which will already be nonlinear is obtained by assuming that the inversion density $W(z,t)$ is a slowly varying function of time as compared to the phase of the carrier wave $\cos(\omega_n t + \varphi_n)$. We assume therefore that at any given time $\varrho_{21}(z,t)$ is still given by ( 11.87 ) but now $W(z)$ replaced by $W(z,t)$, i.e.

$$\varrho_{21}(z,t) = -i\frac{d}{2\hbar}\frac{E_n(t)}{\gamma + i\Delta_n}\mathrm{u}_n(z)W(z)e^{-i(\omega_n t + \varphi_n)} \qquad (11.88)$$

Substituting back into the equations for the population densities we get:

$$\dot{\varrho}_{22} = \lambda_2 - \gamma_2 \varrho_{22} + R(\varrho_{11} - \varrho_{22}) \tag{11.89}$$

$$\dot{\varrho}_{11} = \lambda_1 - \gamma_1 \varrho_{11} + R(\varrho_{22} - \varrho_{11}) \tag{11.90}$$

with

$$R = \frac{d^2}{2\hbar^2} \gamma \mathcal{L}(\Delta_n) E_n^2(t) \mathrm{u}_n^2(z) \geq 0 \tag{11.91}$$

in the single mode case. These equations are of the form of **rate equations** for the population densities, which can be applied in simplified treatments of light-atom interactions. The last terms in the equations represent the effects of induced emission and absorption in the sense as Einstein introduced these notions. The constants $\gamma_2$ and $\gamma_1$ include the spontaneous emission rates of isolated atoms, but in a laser material they usually contain other effects as collisions etc, and $\gamma_1 = 0$ if level 1 is just the ground state.

We see that in their original (Einstein) sense *absorption and induced emission are essentially incoherent limits of the quantum mechanical (Rabi) transition mechanism in the case, when the relaxation of the off-diagonal elements in the two-level density matrix (polarization), have already achieved their stationary values following instantaneously the time dependence of the electric field.*

The steady state solution of the rate equations is obtained by setting the derivatives equal to zero. $\dot{\varrho}_{22} = \dot{\varrho}_{11} = 0$ which leads to

$$W(z) = \varrho_{22} - \varrho_{11} = \frac{W^{(0)}}{1 + R/R_s} \tag{11.92}$$

where

$$W^{(0)} = \frac{\lambda_2}{\gamma_2} - \frac{\lambda_1}{\gamma_1} \tag{11.93}$$

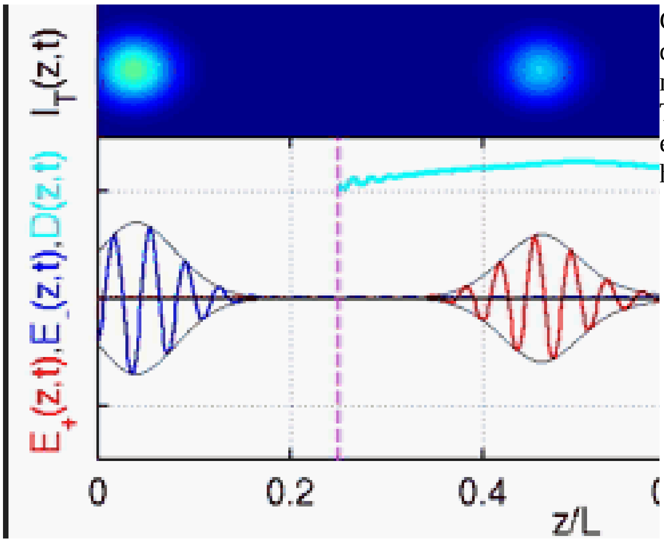
$$\frac{1}{R_s} = \frac{1}{\gamma_2} + \frac{1}{\gamma_1} \tag{11.94}$$

In the absence of radiation field, i.e for $R = 0$ we obtain $W = W^{(0)}$, thus $W^{(0)}$ represents the **zero field inversion density** resulting from the equilibrium of the pumping and the loss rates. The inversion falls to half of its zero field for $R = R_s$ therefore $R_s$ is called the **saturation rate of the system**. By ( 11.94 ) it is related to the total inverse lifetimes of the levels involved. Since $R$ is a slowly varying function of $t$ and $z$, so is $W(z, t)$ which is consistent with our initial assumption. In the presence of the field the inversion density is reduced by a factor $1 + R/R_s$, the field gains its energy from the inversion, which therefore must be smaller than in the absence of induced emission. This is the **nonlinear saturation effect** mentioned earlier, that **stops the exponential growth of the field, and ensures the stable operation of the laser**.

# 8. Concluding remarks

The coupled system of the Maxwell equations and the Schrödinger equation for the two-level atoms described by the self-consistent field method of Lamb can be used to describe many other resonant optical phenomena besides the laser. In the working principle of the laser a very important factor is the feedback coming from the presence of the resonator. In a number of other cases there is no resonator but the processes are so short (shorter than $\gamma$ ), so that the stationarity of the phenomena, as assumed in this section is not true any more, while another important factor comes into play, namely the quantum mechanical coherence between the atomic states. That is the case when the Rabi oscillations treated in section ( 11.5 ) are sustained for long enough and lead to important new phenomena. These coherent effects, however are the subjects of other specialized courses.

**Further reading:**



Check out the homepage of Freetwm, a software designed for the study of the dynamics of multisection semiconductor lasers based on the Traveling Wave approach of Maxwell Bloch equations.
http://nova.uib.es/ONL/Softwares/Softwares.html

# Chapter 12. Atoms in Strong Fields

**Goals:** The excitation of atoms by intense laser pulses is discussed. We introduce the nonlinearities which may appear, and can be divided into two broad classes. The first one involves relatively weak laser pules of long duration, while the second is the regime of strong fields and short durations. In both cases multiphoton processes do appear, but in the first case perturbation theory is sufficient for the description, while in the second one other methods are necessary.

**Prerequisites:** Coulomb problem (Chapter 1 ). Chapter 10 .

## 1. Introduction

The intensity of the laser pulse (absolute value of the Poynting vector ) is given by the amplitude of the electric field strength in it as

$$I = \frac{1}{2}\epsilon_0 E_0^2 c \qquad [\mathrm{W/cm^2}]. \tag{12.1}$$

Sometimes the intensity is given by the photon flux, which is:

$$\phi = \frac{I}{\hbar\omega} \qquad \mathrm{photon/(s \cdot cm^2)}\,. \tag{12.2}$$

The excitation of atoms by intense laser pulses can be divided into two broad regimes determined by the characteristics of the laser pulse relative to the atomic response. The first one is involves relatively weak optical fields of "long" duration $(> 1\,\mathrm{ns})$ to be referred as the "weak" long (WL) regime between $I = 10^8\,\mathrm{W/cm^2}$ and $I = 10^{13}\,\mathrm{W/cm^2}$. The second one beginning from $10^{13}\,\mathrm{W/cm^2}$ involves very strong fields, that can be realized by sufficiently short pulses $(< 10\,\mathrm{ps})$. This is the strong short (SS) regime.

In a laser field of sufficient intensity atoms and molecules begin to exhibit nonlinear response, and the emission or absorption of **several photons** may become the dominant process. We enumerate first the processes in the WL case without going into details in their description. In **Multiphoton Excitation** (MPE) the atom or molecule can undergo from a bound state which is usually, but not necessarily the ground state, to another bound state of higher energy by absorbing $n \geq 2$ photons. The reverse process is **Multiphoton Stimulated Emission** (MSE), where the final atomic state is lying lower han the initial one. One speaks of **Multiphoton Ionisation** (MPI) if several photons are absorbed in a bound state and one or possibly more electrons do leave the atomic core. **Multiphoton Dissociation** (MPD) can be considered in the case of molecules, falling into constituent atoms under the effect of several photons instead of one. **Harmonic Generation** (HG) was the first nonlinear effect observed in laser physics, when under the influence of the laser field the atom emitted photons with frequencies that were integer multiples of the frequency of the incoming field. These effects can be treated theoretically by perturbation theory up to the order $n$, where $n$ is the number of photons participating in the process. We shall not discuss all these different effects in detail, we only outline shortly the perturbative procedure for the single example of MPI.

If the intensity of the laser field becomes higher than $10^{13}\,\mathrm{W/cm^2}$ then essentially new effects appear. We will consider two of these, **Above Threshold Ionization** (ATI) and **High Harmonic Generation** (HHG). The peculiarity of these is that they cannot be understood within the framework of the perturbative approximation, the application of other methods are necessary.

## 2. Basic equations

In the dipole approximation the laser field can be characterized by a vector potential $\mathbf{A}(t)$ which depends only on the time variable, just like the electric field $\mathbf{E} = -\dot{\mathbf{A}} - \nabla\Phi$, which also means, that the space dependence of the scalar potential $\Phi$ cannot be higher than linear. We come back to this point a little later. We recall that in this approximation the magnetic field is absent, because $\mathbf{B} = \nabla \times \mathbf{A} = \mathbf{0}$, as $\mathbf{A}$ does not depend on the spatial coordinate. In the case of a linearly polarised field we can write then

$$\mathbf{E}(t) = \hat{\boldsymbol{\epsilon}} E_0 F(t) \sin(\omega t + \delta), \qquad (12.3)$$

where $\hat{\boldsymbol{\epsilon}}$ is a unit polarization vector, $E_0$ is the amplitude of the electric field strength, $F(t)$ gives us the pulse shape, the envelope, and $\delta$ is a phase constant, although in actual experiments very often both $\omega$ and $\delta$ can be time dependent, then we speak of chirped pulses.

Let us write down the equations governing the dynamics of an atom or ion interacting with a laser field given by ( 12.3 ). The staring point is the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(X,t) = H(t)\Psi(X,t), \qquad (12.4)$$

where $X := (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ denote the ensemble of the positions of the N atomic electrons. Here $H(t)$ is the Hamiltonian

$$\begin{aligned} H(t) &= \frac{1}{2m} \sum_{i=1}^{N} (\mathbf{P}_i - q_0 \mathbf{A}(t))^2 + V + q_0 \Phi \\ &= \frac{1}{2m} \sum_{i=1}^{N} \left( \mathbf{P}_i^2 - 2q_0 \mathbf{P}_i \mathbf{A}(t) + q_0^2 \mathbf{A}^2(t) \right) + V + q_0 \Phi \\ &= H_0 + K(t) = T + V + K(t). \end{aligned} \qquad (12.5)$$

The term

$$H_0 = T + V = \frac{1}{2m} \sum_{i=1}^{N} P_i^2 + V \qquad (12.6)$$

contains the kinetic energies of all the electrons while $V$ contains the sum of all the two body Coulomb interactions between all the electrons and the nucleus, as well as the sum of the electron-electron interactions. According to the dipole approximation $\mathbf{A}$ is not depending on $\mathbf{R}$, that is why we could take it identical for all the electrons. By the same token we are automatically in a Coulomb gauge, where $\nabla \mathbf{A} = 0$, and therefore in the products $\mathbf{P}_i \mathbf{A}$ the order was not relevant, as the components of $\mathbf{A}$ and $\mathbf{P}$ commute (which is not valid in general).

Let us introduce now the total momentum with

$$\mathbf{P} = \sum_{i=1}^{N} \mathbf{P}_i, \qquad (12.7)$$

so the Hamiltonian takes the form:

$$H = \frac{1}{2m} \sum_{i=1}^{N} \mathbf{P}_i^2 + V - \frac{q_0}{m} \mathbf{A}(t)\mathbf{P} + \frac{q_0^2}{2m} N \mathbf{A}^2(t) + q_0 \Phi. \qquad (12.8)$$

The Schrödinger equation for the $N$ electron atom, or ion can then be written as

$$i\hbar \frac{\partial}{\partial t} \Psi(X,t) = \left( H_0 - \frac{q_0}{m} \mathbf{A}(t)\mathbf{P} + \frac{q_0^2}{2m} N \mathbf{A}^2(t) + q_0 \Phi \right) \Psi(X,t), \qquad (12.9)$$

where $H_0$ is given by ( 12.6 ).

Still within the Coulomb gauge we can chose three further types of gauges:

**a) Velocity gauge (** $v$ **)**, or $\mathbf{PA}$ gauge defined with:

$$\Phi_v = 0, \qquad \mathbf{A}_v(t) = -\int_{-\infty}^{t} \mathbf{E}(t')dt'. \tag{12.10}$$

The Hamiltonian in this gauge is

$$H = \underbrace{\frac{1}{2m}\sum_{i=1}^{N} \mathbf{P}_i^2 + V(\mathbf{R})}_{H_0} \underbrace{-\frac{q_0}{m}\mathbf{A}_v(t)\mathbf{P} + \frac{q_0^2}{2m}N\mathbf{A}_v^2(t)}_{K_v}. \tag{12.11}$$

**b) Length gauge (** $l$ **)**, or $\mathbf{RE}$ gauge defined with

$$\mathbf{A}_l = 0, \quad \Phi_l(t) = -\mathbf{RE}(t), \tag{12.12}$$

when

$$H = \underbrace{\frac{1}{2m}\sum_{i=1}^{N} \mathbf{P}_i^2 + V(\mathbf{R})}_{H_0} \underbrace{-q_0\mathbf{RE}(t)}_{K_l}. \tag{12.13}$$

This gauge is also called as Goeppert-Mayer gauge, after Maria Goeppert-Mayer, who was the only woman winning the Nobel prize for her work in theoretical physics in 1963: for discovering the important role of spin-orbit interaction in determining the nuclear structure.

**c) Acceleration gauge (** $a$ **)** or KH gauge: Starting from the $v$ gauge we perform the unitary transformation,

$$\Psi_v(X,t) = \exp\left[-i\frac{\vec{\alpha}}{\hbar}\mathbf{P}\right]\Psi_a(X,t), \tag{12.14}$$

which is called the Kramers-Henneberger (KH) transformation, where

$$\vec{\alpha}(t) = -\frac{q_0}{m}\int \mathbf{A}_v(t')dt' \tag{12.15}$$

is a vector corresponding to a displacement of a classical electron from its oscillation center in the electric field $\mathbf{E}(t)$. The KH transformation therefore corresponds to a spatial translation, characterized by the vector $\vec{\alpha}$, to a new frame, (the KH frame), which moves with respect to the laboratory frame. Especially at high intensities and high frequencies it is useful to study the interaction in this accelerated frame.

The Schrödinger equation in this gauge becomes

$$i\hbar\frac{\partial}{\partial t}\Psi_a(X,t) = \left[\frac{1}{2m}\sum_{i}^{N}\mathbf{P}_i^2 + V\left[(\mathbf{r}_1 - \vec{\alpha}(t)),\ldots,(\mathbf{r}_N - \vec{\alpha}(t))\right]\right]\Psi_a(X, \tag{12.16}$$

so that the interaction with the laser field is now incorporated via $\vec{\boldsymbol{\alpha}}$ into the potential $V$, which thus becomes time dependent. In the case of a linearly polarized **monochromatic** field with $\hat{\boldsymbol{\epsilon}}E_0\sin(\omega t+\delta)$ this function is:

$$\vec{\boldsymbol{\alpha}}(t)=\vec{\boldsymbol{\alpha}}_0\sin(\omega t+\delta) \qquad \vec{\boldsymbol{\alpha}}_0=\alpha_0\hat{\boldsymbol{\epsilon}}, \tag{12.17}$$

where

$$\alpha_0=\frac{qE_0}{m\omega^2}. \tag{12.18}$$

# 3. Perturbation theory

As an example of the interaction in the WL regime we discuss shortly Multiphoton Ionization (MPI). Consider a noble gas, where the ionization energy is typically $\gtrsim 10\,\mathrm{eV}$, a relatively high value, when compared with other atoms, this is a witness of the stability of noble gases. Therefore light fields with common intensities in the visible regime, where the photon energy is about $1\,\mathrm{eV}$ cannot ionize a noble gas atom. However for large enough intensities, $I=10^8\,\mathrm{W/cm^2}$ or higher ionization can still appear, as the consequence of the simultaneous absorption of several, say $n$ photons. Such phenomena, studied first in the 1960's, showed, that the $n$ photon ionization rate of the electrons was proportional to $I^n$. The process can be written schematically as

$$n\hbar\omega+A^q=A^{q+1}+e^-. \tag{12.19}$$

If we are still in the WL regime as explained in the introduction, where the field strength amplitude of the external harmonic field is much smaller than the field strength of the atomic Coulomb potential stemming from the nucleus and from the electron-electron interaction, then time dependent perturbation theory can be used to study the interaction. In order to calculate the rate of an $n$ photon transition, one has to use $n$ -th order perturbation theory. Without going into the details of the derivation we simply present the result which can be obtained along the lines presented in Chapter 10 , by iterating the perturbation expansion up to $n$ -th order.

Assume that the initial atomic state is $\psi_i$ of energy $\varepsilon_i$ and the final state $\psi_f$ is in the continuum where the density of states is $\rho(\varepsilon_f)$ with respect to the ejected electron energy $\varepsilon_f=\frac{\hbar^2k_f^2}{2m}$ . The transition rate (transition probability/unit time) can be obtained as:

$$W_{if}^{(n)}=\frac{2\pi}{\hbar}\left(2\pi\alpha\hbar\right)^n I^n\,|T_{i\to f}^{(n)}|^2\,\rho(\varepsilon_f), \tag{12.20}$$

where $\alpha$ is the fine structure constant, $I$ is the intensity of the light field and $T_{i\to f}^{(n)}$ is the $n$ -th order transition amplitude, to be calculated as:

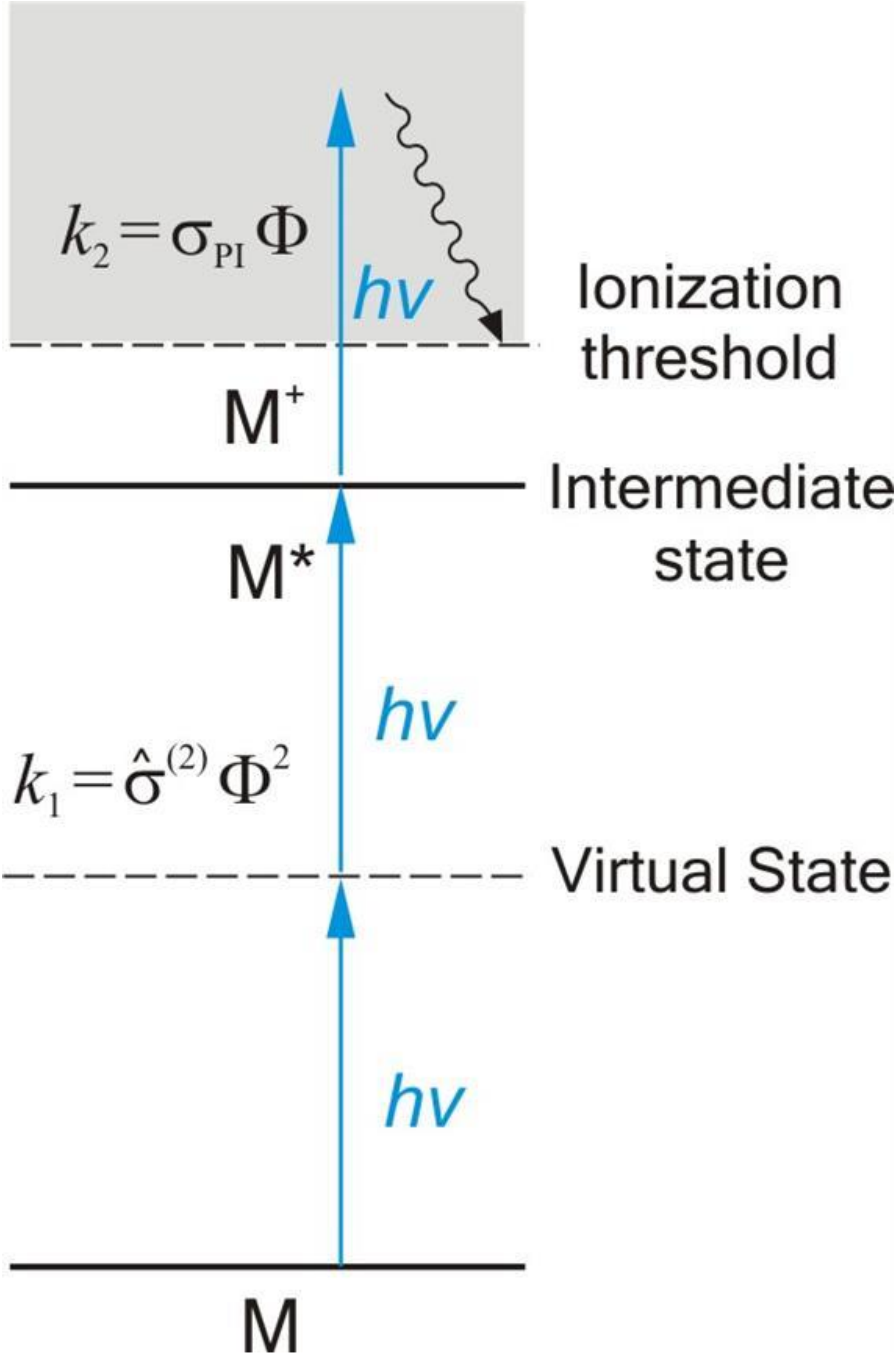
$$n=1 \qquad T_{i\to f}^{(1)}=\langle f|\,\mathbf{D}\,|i\rangle\,, \qquad \mathbf{D}=\hat{\boldsymbol{\epsilon}}q_0\mathbf{R}. \tag{12.21}$$

$$n\geq 2 \qquad T_{i\to f}^{(n)}=\langle f|\,\mathbf{D}G[\varepsilon_i+(n-1)\hbar\omega]\times\mathbf{D}G[\varepsilon_i+(n-2)\hbar\omega]\times\cdot\mathbf{D}G[\varepsilon_i+\hbar\omega]\mathbf{D} \tag{12.22}$$

$$\text{with} \quad G[\varepsilon]=\sum_j\frac{|j\rangle\,\langle j|}{\varepsilon-\varepsilon_j+i\Gamma_j/2}, \tag{12.23}$$

where $\Gamma_j$ is the line width, of the level $\varepsilon_j$. The sum over $j$ must also include an integration over the continuum for all allowed dipole transitions. For a multiphoton ionization $\omega$ can continuously vary because the final state lies in the continuum. If $\omega$ is tuned so that $\varepsilon_i+m\hbar\omega=\varepsilon_j$ for some contributing intermediate stationary state $|j\rangle$ with energy $\varepsilon_j$, or in other words the level $\varepsilon_j$ lies above the initial one by an integer number ( $m$ ) times the single photon energy, then the corresponding denominator becomes small, producing a strongly peaked resonance. Since ionization takes $k = n - m$ additional photons, the process is called an $m, k$ resonant enhanced multiphoton ionization (REMPI). Measurements of the photoelectron angular distribution in such cases are useful in characterizing the resonant intermediate state.

**Figure 12.1. Schematic drawing explaining a 2,1 resonant enhanced multiphoton ionization http://en.wikipedia.org/wiki/Resonance-enhanced_multiphoton_ionization**



Schematic drawing explaining a 2,1 resonant enhanced multiphoton ionization

This method is applicable whenever $I \ll I_a$, i.e. the field is strong but still much weaker than the atomic fields. However, when the external field approaches or getting even even stronger then the binding force in the atom, this is not a feasible way to treat the processes theoretically, since the fundamental assumption of the perturbation methods fails, and the application of nonperturbative methods are necessary. The limit can be estimated by comparing $W_{if}^{(n+1)}$ and $W_{if}^{(n)}$. It turns out that in the case of a $1\,\mathrm{eV}$ photon, the ratio of these quantities becomes close to unity around the intensity

$$I_l = 10^{13}\,\mathrm{W/cm}^2, \tag{12.24}$$

so one expects that above this value the perturbative approach should fail, as it is the case.

# 4. Nonperturbative regime

In the last 20 years or so, lasers of the intensity around and even above

$$I_a = \frac{1}{2}\epsilon_0 c \mathcal{E}_a^2 = 3.5 \times 10^{16}\,\mathrm{W/cm}^2 \tag{12.25}$$

have become available, where $\mathcal{E}_a$ corresponds to the atomic field strength which originates from the proton in the H atom in the distance of the first Bohr radius $a_0$ :

$$\mathcal{E}_a = \frac{|q_0|}{4\pi\epsilon_0}\frac{1}{a_0^2} = 5.1 \times 10^{9}\,\mathrm{V/cm}. \tag{12.26}$$

Such laser fields are therefore strong enough to overcome the Coulomb forces in the atom. Thus while multiphoton processes involving laser fields with intensities $I \lesssim I_l \ll I_a$ can be studied by perturbation theory, the effects of the laser field with intensity higher than $I_l$, and the more so for $I \simeq I_a$ must be analyzed by other, non-perturbative methods.

In the methods describing such effects we can still use the semiclassical approximation. Note that in a high intensity laser the number of photons in a laser mode is very large. For example in Nd YAG laser of the wavelength $\lambda = 1064\,\mathrm{nm}$ (which is equivalent to the photon energy $1.17\,\mathrm{eV}$ ), and of intensity $I = 10^{12}\,\mathrm{W/cm}^2$, which is still far below from peak intensities available in the first decade of the 21-st century, a coherence volume of $\lambda^3$ contains $\mathcal{N} = IV/c\hbar\omega = 2 \times 10^8$ photons. A classical description of the field seems therefore to be fully satisfactory. So once again the semiclassical approach can be applied, just like in the previous chapter. Here we will also restrict ourselves to consider nonrelativistic electrons in the dipole approximation, which is still valid up to intensities of $I = 10^{16}\,\mathrm{W/cm}^2$. We will now review shortly two possibilities to consider such strong field effects.

## 4.1. Electron in a harmonic field, the Volkov solution

In this subsection we study the dynamics of an electron in the field of a plane wave, i.e. there is no Coulomb or other static field present. Sometimes one speaks of a "free" electron in the presence of a laser field, where free is understood in the sense, that the only force comes from a time dependent external field. We restrict us here to the dipole approximation where the time dependent Schrödinger equation for a single electron ( $q_0 \leq 0$ ) takes the form:

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \frac{1}{2m}\left(\mathbf{P} - q_0\mathbf{A}(t)\right)^2\Psi(\mathbf{r},t). \tag{12.27}$$

We perform the gauge transformation:

$$\Psi(\mathbf{r},t) = \exp\left[-\frac{i}{\hbar}\frac{q_0^2}{m}\int \mathbf{A}^2(t')dt'\right]\Psi_v(\mathbf{r},t) \tag{12.28}$$

and obtain the Schrödinger equation in the velocity gauge:

$$i\hbar\frac{\partial}{\partial t}\Psi_v(\mathbf{r},t) = \left[\frac{1}{2m}\mathbf{P}^2 - \frac{q_0}{m}\mathbf{A}(t)\mathbf{P}\right]\Psi_v(\mathbf{r},t). \qquad (12.29)$$

Since $e^{i\mathbf{kr}}$ is an eigenfunction of $\mathbf{P} = -i\hbar\nabla$, with eigenvalue $\hbar\mathbf{k}$, we can look for solutions of ( 12.29 ) in the form:

$$\Psi_v(\mathbf{r},t) = e^{i\mathbf{kr}}f(t). \qquad (12.30)$$

Substituting ( 12.30 ) into ( 12.29 ) we get for the function $f(t)$ the first-order equation

$$i\hbar\frac{\partial}{\partial t}f(t) = \left[\frac{\hbar^2k^2}{2m} - \frac{q_0\hbar}{m}\mathbf{kA}(t)\right]f(t), \qquad (12.31)$$

which can be simply solved and gives:

$$f(t) = C\exp\left[-i\frac{\hbar k^2}{2m}t - i\mathbf{k}\vec{\boldsymbol{\alpha}}(t)\right], \qquad (12.32)$$

where $\vec{\boldsymbol{\alpha}}(t)$ is given by ( 12.15 ) and $C$ is an arbitrary constant, chosen usually as $C = (2\pi)^{-3/2}$. In this way we get the Volkov (or Gordon-Volkov) solution of the Schrödinger equation:

$$\Psi_v^V(\mathbf{r},t) = (2\pi)^{-3/2}\exp\left[i\mathbf{k}(\mathbf{r} - \vec{\boldsymbol{\alpha}}(t)) - i\varepsilon t/\hbar\right], \qquad (12.33)$$

where $\varepsilon = \frac{\hbar^2k^2}{2m}$ is the electron energy. This kind of solution has been found by D. M. Volkov in 1935 for the relativistic Dirac electron, we presented here the nonrelativistic limit of that result.

Going back to the solution of the original Schrödinger equation ( 12.27 ), we obtain:

$$\Psi^V(\mathbf{r},t) = (2\pi)^{-3/2}\exp\left[i\mathbf{k}(\mathbf{r} - \vec{\boldsymbol{\alpha}}(t)) - \frac{i\varepsilon}{\hbar}t - \frac{i}{\hbar}\frac{q_0^2}{2m}\int \mathbf{A}^2(t')dt'\right]. \qquad (12.34)$$

We note that in the KH frame ( $a$ gauge) the Volkov state transforms to a simple plane wave:

$$\Psi_a^V(\mathbf{r},t) = (2\pi)^{-3/2}\exp\left[i\mathbf{kr} - i\varepsilon t/\hbar\right]. \qquad (12.35)$$

The Volkov states have a number of applications in atom field interactions. They can be considered as approximate solutions of atomic electrons in strong fields, and then the Coulomb field can be considered as a perturbation.

## 4.2. Floquet theory

Floquet theory was developed originally in 1883 for the solution of differential equations with periodic coefficients. For physicists it is well known as Bloch's theorem in solid state physics, where electronic states or lattice oscillations are subject to periodic conditions in space. We shall apply the theory for electrons in time periodic fields. The first use of this method in atomic physics is due to J. Shirley in 1965.

We shall assume a monochromatic laser field, leading to a Hamiltonian with

$$H(t+T) = H(t), \qquad (12.36)$$

where $T = 2\pi/\omega$ is the period of the external field. As it is easily seen, the operator of the translation in time $\mathfrak{T}(T)$ defined by $\mathfrak{T}(T)\Psi(X,t) = \Psi(X,t+T)$ commutes with the periodic Hamiltonian, and therefore they must posses a common set of eigenfunctions. The set of nondegerate eigenfunctions of $\mathfrak{T}(T)$ are just $e^{-i\varepsilon t/\hbar}$ with eigenvalues $e^{-i\varepsilon T/\hbar}$, so we can seek the solution of the time dependent Schrödinger equation in the form

$$\boxed{\Psi(X,t) = e^{-i\varepsilon t/\hbar}\Phi(X,t), \qquad (12.37)}$$

where $\Phi(X,t)$ is a **periodic function of time of period** $T$, and $X$ denotes the set of spatial coordinates. $\varepsilon$ in the present case is called the quasi-energy. Being periodic, $\Phi(X,t)$ can be expanded into Fourier series:

$$\boxed{\Phi(X,t) = \sum_{n=-\infty}^{\infty} g_n(X) e^{-in\omega t}. \qquad (12.38)}$$

The functions $g_n(X)$ are called the harmonic components of $\Phi(X,t)$, and $\Psi(X,t)$ is written as:

$$\boxed{\Psi(X,t) = e^{-i\varepsilon t/\hbar} \sum_{n=-\infty}^{\infty} g_n(X) e^{-in\omega t}. \qquad (12.39)}$$

We can also expand the interaction Hamiltonian into Fourier components

$$\boxed{K(t) = \sum_{n=-\infty}^{\infty} K_n e^{-in\omega t} \qquad (12.40)}$$

and substitute these expansions into the Schrödinger equation. Using the orthogonality of the Fourier basis we then obtain an infinite set of coupled **time-independent** equations:

$$\boxed{(\varepsilon + n\hbar\omega - H_0) g_n(X) = \sum_{j=-\infty}^{\infty} K_{n-j} g_j(X), \qquad (12.41)}$$

with $n = 0, \pm 1, \dots$.

This infinite system is solved practically by keeping only a finite number of harmonic components, i.e. by truncating the sum over $j$ (or $n$ ) in the above equations.

In the length gauge the interaction Hamiltonian is

$$\boxed{K = -DE_0 \cos\omega t = -\frac{DE_0}{2}(e^{-i\omega t} + e^{+i\omega t}), \qquad (12.42)}$$

therefore the equation to be solved is an eigenvalue problem of a tridiagonal matrix: where $K_+$ and $K_-$ are both equal to $-DE_0/2$. The problem ( 12.41 ) is usually solved in a well selected basis of spatial functions. For atomic systems with one electron, say a H atom, a so called Coulomb-Sturmian basis is used in most of the cases:

$$\boxed{g_j(\mathbf{r}) = \sum_{n\ell m} c^j_{n\ell m} \frac{S^b_{n\ell}(r)}{r} Y^m_\ell(\hat{\mathbf{n}}) \qquad (12.43)}$$

where $Y^m_\ell(\hat{\mathbf{n}})$ are the spherical harmonics, and the radial functions $S^b_{n\ell}(r)$ are the **radial Coulomb-Sturmian basis** functions defined as

$$S^b_{n\ell}(r) = N_{n\ell}(2r/b)^{1/2}\exp(-r/b)F(-n+\ell+1, 2(\ell+1); r/b) \tag{12.44}$$

where $b$ is a fixed number, that can be chosen arbitrarily and F is the confluent hypergeometric function, introduced in chapter 1 . The functions $S^b_{n\ell}(r)$ form a **complete orthogonal system** on the positive real axis. Note, that although they are very similar in form to the bound eigenfunctions of the radial Coulomb problem, they are not identical to the latter. The reason is that in the Coulomb eigenfunctions the argument of the function depends on the energy eigenvalue, as the argument there was $\varrho = \kappa_n r = Z\frac{1}{a_0}\frac{1}{n}r$, while here in ( 12.44 ) the constant $b$ is identical for all $n$. That is why the bound Coulomb eigenfunctions do not form a complete basis set, they have to be completed by the positive energy eigenfunctions forming the continuum of ionized states. Of course, in Eq. ( 12.41 ) again only a truncated set of the infinitely many spatial basis functions is to be used.

We note here finally that the Floquet method does not exploit a kind of a rotating wave approximation (RWA) as discussed in the previous chapter, that is why both $e^{-i\omega t}$ and the $e^{+i\omega t}$ terms are present in ( 12.42 ).

# 5. Highly nonlinear effects

As we mentioned previously for intensities above $I_l = 10^{13}\,\mathrm{W/cm^2}$ the perturbation theory is not applicable any more, and what is more important, new physical effects can be observed. When energy resolved photoelectron measurements become possible in the end of the 1970's, it was observed that in the photoionization process the ejected electrons could absorb photons in excess of the minimum number required for ionisation to occur. The photoelectron spectra were seen to exhibit several peaks, separated by the photon energy $\hbar\omega$, and appearing at the energies:

$$E_s = (n+s)\hbar\omega - I_p, \tag{12.45}$$

where $n$ is the minimum number of photons to exceed the ionisation potential $I_P$, and $s = 0, 1, \dots$ where $s$ is the number of excess photons, or above threshold photons, absorbed by the electron. This process is called **above threshold ionization** (ATI).

Another effect also observed at sufficiently high intensities was high harmonic generation. Atoms interacting with a strong laser field can emit radiation at angular frequencies that are high order multiples of the angular frequency of the pump laser. Due to the inversion symmetry of atoms the harmonic circular frequencies are odd multiples of the driving, or fundamental circular frequency:

$$\Omega_n = q\omega, \qquad q = 3, 5, \dots. \tag{12.46}$$

Before going into details about this process, we introduce the important notion of the ponderomotive potential $U_P$ of the exciting field. It is the energy gained by an otherwise free electron in a harmonically oscillating field. A simple classical calculation shows that according to the equation of motion

$$m\dot{v} = q_0 E_0 \sin\omega t \tag{12.47}$$

the kinetic energy averaged over a period $2\pi/\omega$ is

$$\overline{\frac{1}{2}mv^2} = \frac{1}{2}\frac{q_0 E_0^2}{m\omega^2}\overline{\cos^2\omega t} = \frac{q_0^2 E_0^2}{4m\omega^2} =: U_P. \tag{12.48}$$

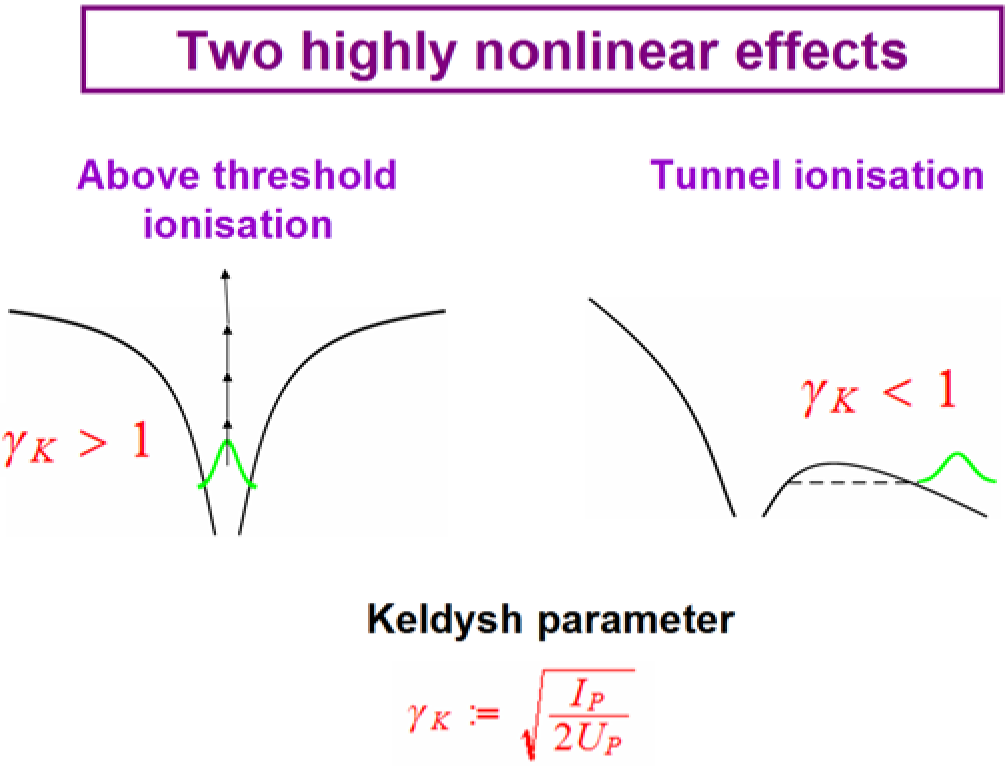
The characteristics of the response of the atom depends on the ratio of the ionisation potential $I_P$ and the ponderomotive potential through the parameter:

$$\gamma_K := \sqrt{\frac{I_P}{2U_P}} \tag{12.49}$$

introduced by L.V. Keldysh in 64, and called since then the Keldysh parameter.

The possible processes are shown in Fig 12.2 .

**Figure 12.2. The response of the atom depends on the ratio of the ionisation potential $I_P$ and the ponderomotive potential through the Keldysh parameter.**



The response of the atom depends on the ratio of the ionisation potential and the ponderomotive potential through the Keldysh parameter.

If the external field strength i. e. the square root of the incoming intensity is high enough then $\gamma_K < 1$ and the atomic potential can be significantly changed by that field as shown in the right hand side of the figure. The electron may then tunnel out through the potential barrier appearing as the sum of the atomic and external fields. The barrier can even become lower than the energy of the bound state, then we can speak of **over the barrier ionisation**. This is valid of course for a half period of the oscillating field since the external field changes sign in the next half period and the force on the electron will change its direction to the opposite. For pulses with $\gamma_K > 1$, one observes above threshold ionisation.

## 5.1. High harmonic generation (HHG)

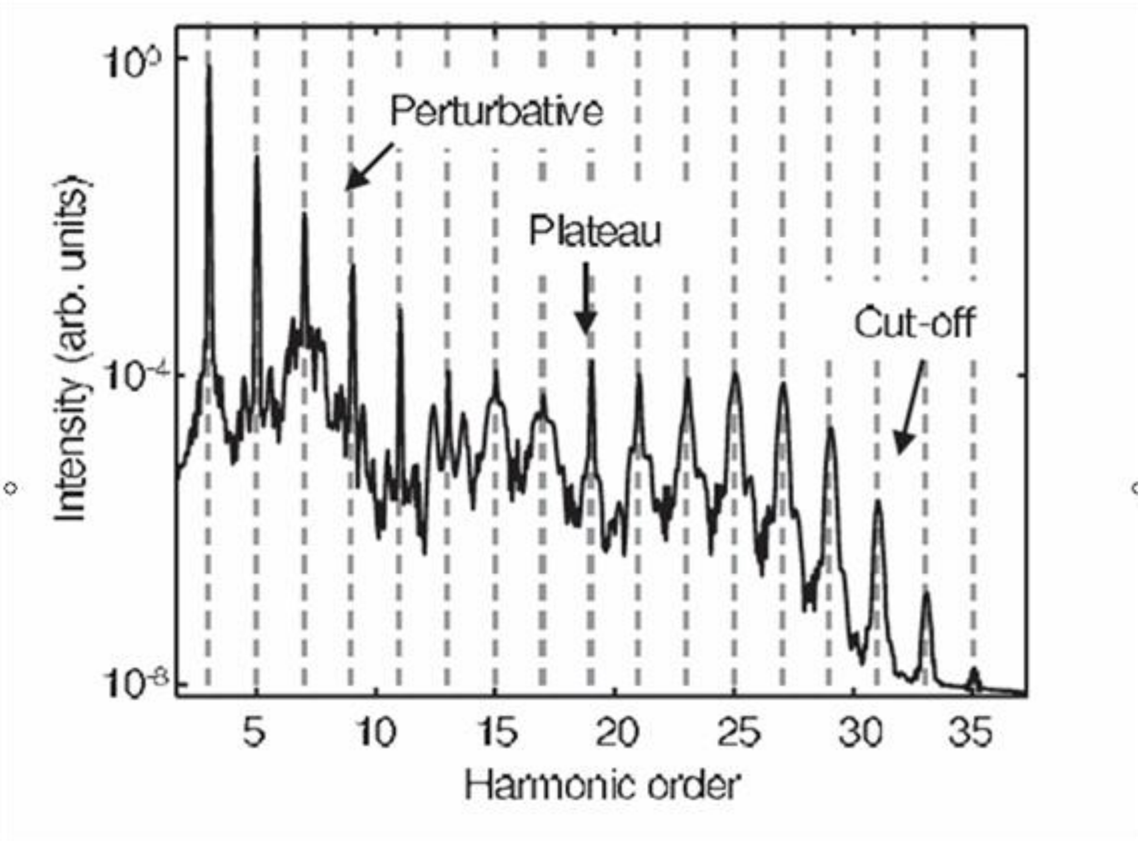
In this subsection we consider in a little more detail HHG. In the last decade in several laboratories harmonics up to around $q = 125$ were routinely generated in several laboratories, mainly in noble gas jets of Ne, Ar or Xe. The exciting laser is usually a Nd YAG laser of wavelength $1064\,\mathrm{nm}$, or more recently a Ti:sapphire laser around the wavelength $800\,\mathrm{nm}$ with a focused intensity $I = 10^{15}\,\mathrm{W/cm^2}$. The duration of these triggering pulses is around $5\,\mathrm{fs}$, so they consist of only a few cycles. The highest harmonics generated in this way fall already in the so called extreme ultraviolet (XUV), or to the X-ray domain with photon energies around $80 - 100\,\mathrm{eV}$.

**Problem 12.1 :** Calculate the wavelength and the photon energy of the 99-th harmonic of a $800\,\mathrm{nm}$.

**Problem 12.2 :** The $800\,\mathrm{nm}$ average wavelength is the carrier of a pulse of duration $5\,\mathrm{fs}$ at full width at half maximum. What is the number of cycles in the pulse within that time interval.

The distribution of the intensities of the harmonics show an interesting feature. For the first few harmonics the intensity drops, as expected from perturbation theory, but after that, beginning at a certain harmonic number a plateau appears: the intensities of the consecutive harmonics are almost the same, then finally they fall off for the highest attainable .

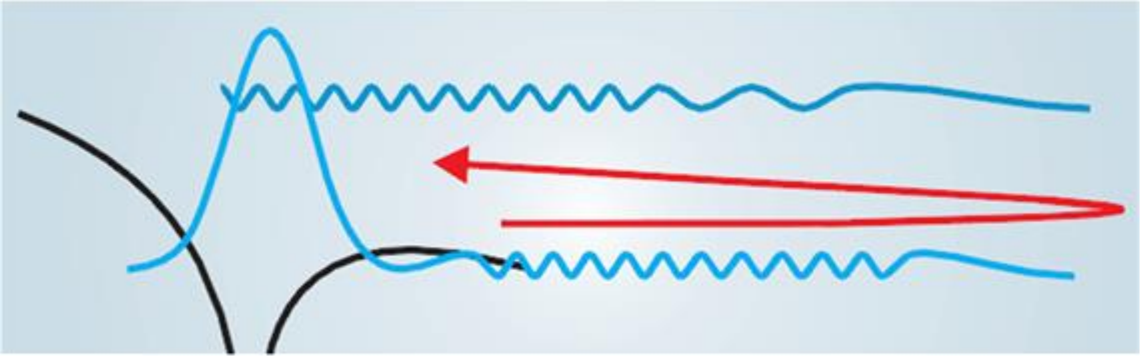
## Figure 12.3. The harmonic spectrum from Ar, laser pulse of intensity $1.4 \cdot 10^{14}\,\mathrm{W/cm^2}$



The harmonic spectrum from Ar, laser pulse

The mechanism of the process can be understood by the following three-step model. (Corkum, Schafer and Kulander 93). The electron is bound by the atomic potential which is strongly distorted in the very strong field of the external pulse, therefore the electron can tunnel out from the binding potential, and the atom is ionized temporarily, see the right hand side of Figure 12.2 . The electron then propagates practically only in the laser field, free from the atomic potential.

## Figure 12.4. The electron can tunnel out from the binding potential, and the atom is ionized temporarily



The electron can tunnel out from the binding potential, and the atom is ionized temporarily

In the second step while the field changes its direction the electron is turned back and moves towards the atomic core. Finally in the third step it recombines with the atom. If the electron recombines, its kinetic energy gained from the acceleration in the field depends on the time of tunneling and the time of recombination, and determines the energy of the emitted high energy photon. Considering the distribution of the possible tunneling times one can understand the intensity distribution of the harmonics, including the plateau, but we shall omit here the details.

An interesting consequence of these harmonics is that among favorable circumstances they can add up and produce a sequence of peaks of pulses in the attosecond range (duration $\sim 100\,\mathrm{as}$ ). This is one of the targets of the **Extreme Light Infrastructure Attosecond Light Pulse Source** (ELI-ALPS) facility to be built up in Szeged, Hungary within the next few years.

**Problem 12.3 :** Calculate and sketch the time dependence of the intensity emerging from the sum of the harmonics:

$$I(t) = \left| \sum_{q=\mathrm{odd}}^{101} A_q e^{-iq\omega t} \right|^2 \qquad (12.50)$$

Assume that all of them have identical amplitudes, as well as identical phases as it is implicitly assumed in the formula above.

## 5.2. Calculation possibilities

Although there are relatively simple approximative methods that can give account of these highly nonlinear effects, in order to reproduce the experimental results, one has to rely on extensive numerical calculations. An obvious possibility to follow the problem of strong field ionisation and to determine the energy of the emitted electrons is to solve the time dependent Schrödinger equation numerically. This has been performed by several groups since the mid 90's. The numerical complexity of the problem allows, however only the solution of single electron i.e. H like atoms. In case of more complicated systems the single active electron approximation (SAE) must be exploited, where the correlation effects between the electrons are not taken into account. More recently there were attempts to perform calculations for Helium with demanding numerical methods that include the electron-electron interaction,as well.

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