

Structure of Matter 1

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Block IIa, 2020/2021

1 Recap of General QM

1.1 The Schrödinger equation

We of course all know the Schrödinger equation:

$$H\psi = E\psi$$
$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi$$

When generalizing to 3 dimensions, momentum becomes:

$$\mathbf{p} \rightarrow \frac{\hbar}{i} \nabla$$

Thus:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi.$$

Here

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

of course is the **Laplacian**. The potential energy and the wave function now are functions of $\mathbf{r} = (x, y, z)$ and t . The normalization condition now reads

$$\int |\Psi|^2 d^3\mathbf{r} = 1$$

with the integral taken over all space and the infinitesimal volume $d^3\mathbf{r} = dx dy dz$. If the potential is independent of time we can still use the separation of variables and there will be a complete set of stationary states:

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-iE_n t/\hbar}.$$

And the the time-independent Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

1.1.1 Separation of Variables

To make our lives easier in the long run we want to adopt **spherical coordinates**, (r, θ, ϕ) ,

$$x = r \sin \theta \cos \phi,$$

$$y = r \sin \theta \sin \phi,$$

$$z = r \cos \theta.$$

In spherical coordinates the Laplacian takes the form

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}.$$

In spherical coordinates, then, the time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + V\psi = E\psi$$

We begin by looking for solutions that are separable into products:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Some derivation later gives us two equations, one that only depends on r and one that depends on θ and ϕ . Both must be a constant, we will write this “separation constant” in the form $l(l+1)$:

$$\begin{aligned} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] &= l(l+1); \\ \frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] &= -l(l+1). \end{aligned}$$

1.2 Angular and radial wavefunctions

1.2.1 The Angular Equation

First we will look at the angular equation, that depends on θ and ϕ . For this equation we can once again use separation of variables:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi).$$

This again gives us two equations, one that only depends on θ and one that only depends on ϕ . Again both must be a constant, this time we will call the separation constant m^2 :

$$\begin{aligned} \frac{1}{\Theta} \left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta &= m^2; \\ \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} &= -m^2. \end{aligned}$$

The general solution of $\Phi(\phi)$ then is

$$\Phi(\phi) = e^{im\phi},$$

here m is an *integer* that can be positive and negative. Also it is natural to require that

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

The general solution of $\Theta(\theta)$ isn't that easy. The solution is

$$\Theta(\theta) = AP_l^m(\cos \theta),$$

here P_l^m is the associated **Legendre function**, defined by

$$P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x),$$

and $P_l(x)$ is the l th **Legendre polynomial**, defined by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l.$$

Important to note is that l must be a nonnegative *integer* and that the values of m range from $-l$ to l , with integer intervals, because of this for any given l there are $(2l + 1)$ possible values of m . Mathematically speaking there exist solutions for *any old* values of l and m , but physically speaking some solutions are unacceptable.

The normalized angular wave functions are called **spherical harmonics**:

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos\theta),$$

here $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. These are automatically orthogonal, so

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin\theta d\theta d\phi = \delta_{ll'} \delta_{mm'}.$$

For historical reasons, l is called the **azimuthal quantum number**, and m the **magnetic quantum number**.

1.2.2 The Radial Equation

Notice that the *angular* part of the wave function, $Y(\theta, \phi)$, is the same for all spherically symmetric potentials; the actual shape of the potential, $V(r)$, affects only the *radial* part of the wave function, $R(r)$.

The **radial equation** is given by

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V \right] P_{nl}(r) = EP_{nl}(r)$$

here the m 's are masses and

$$P_{nl}(r) \equiv rR(r).$$

As you can see the radial equation is *identical in form* to the one-dimensional Schrödinger equation, except that the effective potential contains an extra term called the **centrifugal term**. It tends to throw the particle outward (away from the origin).

For the radial equation the normalization condition becomes

$$\int_0^\infty |P_{nl}|^2 dr = 1.$$

This is all we can do with the radial part of the wave function until a specific potential $V(r)$ is provided.

1.3 Basic quantum numbers

Due to different energy levels, the separation of variables and spin multiple quantum numbers are introduced:

Name	Symbol	Orbital meaning	Range of values	Value examples
Principal quantum number	n	shell	$1 \geq n$	$n = 1, 2, 3, \dots$
Azimuthal quantum number (angular momentum)	l	subshell	$0 \leq l \leq n - 1$	for $n = 3$: $l = 0, 1, 2$
Magnetic quantum number (projection of angular momentum)	m_l	energy shift	$-l \leq m_l \leq l$	for $l = 2$: $m_l = -2, -1, 0, 1, 2$
Spin quantum number	m_s	spin of the electron	$-s \leq m_s \leq s$	for $s = \frac{1}{2}$: $m_s = -\frac{1}{2}, \frac{1}{2}$

In the spectroscopic notation l gets assigned letters in place of the numbers:

$$\begin{aligned} l = 0 &\rightarrow s \\ l = 1 &\rightarrow p \\ l = 2 &\rightarrow d \\ l = 3 &\rightarrow f \\ l = 4 &\rightarrow g, \text{ etc.} \end{aligned}$$

After this the order follows the alphabet, with either **i** or **j**. The electron shells get filled according to this table.

$n \backslash l$	s	p	d	f	g
1	2	-	-	-	-
2	2	6	-	-	-
3	2	6	10	-	-
4	2	6	10	14	-

The numbers in the table indicate the total number of atoms that each shell can hold and the arrows indicate the order in which the shells get filled, so the $1s$ shell gets filled first, then $2s$, $2p$, $3s$ and so on. Another way to express the state of an atom is using the following notation:

$$^{2S+1}L_J,$$

with S as the total spin, L as the total orbital angular momentum and J as the grand total (orbital plus spin).

Only the quantum number n is needed to specify the energy of an electron in a hydrogen atom, but to specify the motion of an electron moving in three dimensions the value of the square of the angular momentum \mathbf{l}^2 and the z -component of the angular momentum l_z are also needed.

1.3.1 The Orbital Angular Momentum

The eigenvalues of \mathbf{l}^2 and l_z are given by

$$\mathbf{l}^2 f_l^m = l(l+1)\hbar^2 f_l^m \quad \text{and} \quad l_z f_l^m = m_l \hbar f_l^m,$$

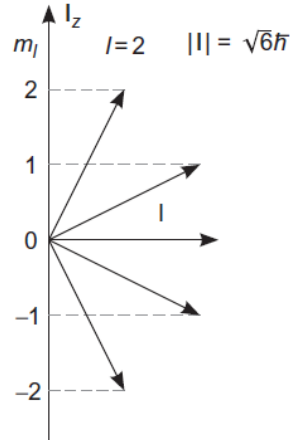
where

$$l = 0, 1/2, 1, 3/2, \dots; \quad m_l = -l, -l+1, \dots, l-1, l,$$

and the eigenfunctions are characterized by the numbers l and m . For a given value of l , there are $2l+1$ different values of m_l (i.e., $2l+1$ “rungs” on the “ladder”). The magnitude of l is given by

$$|l| = \sqrt{l(l+1)}\hbar$$

The orientations in space of the vector \mathbf{l} correspond to the different values of $m_l \hbar$. The cosine of the angle between \mathbf{l} and the z -axis is $l_z/|\mathbf{l}|$, which is equal to $m_l/\sqrt{l(l+1)}$. Quantum theory thus predicts that for a given value of l only certain orientations of the angular momentum vector in space are allowed. This is called **space quantization**.



1.3.2 Spin of the Electron

Spin works in a very similar way to angular momentum. The eigenvalues of \mathbf{s}^2 and s_z are given by

$$\mathbf{s}^2 f_l^m = s(s+1)\hbar^2 f_l^m \quad \text{and} \quad s_z f_l^m = m_s \hbar f_l^m,$$

where

$$s = 0, 1/2, 1, 3/2, \dots; \quad m_s = -s, -s+1, \dots, s-1, s,$$

and the eigenfunctions are characterized by the numbers s and m . For a given value of s , there are $2s+1$ different values of m_s (i.e., $2s+1$ “rungs” on the “ladder”). The magnitude of s is given by

$$|s| = \sqrt{s(s+1)}\hbar$$

The orientations in space of the vector \mathbf{s} correspond to the different values of $m_s \hbar$. The cosine of the angle between \mathbf{s} and the z -axis is $s_z/|\mathbf{s}|$, which is equal to $m_s/\sqrt{s(s+1)}$. Quantum theory thus predicts that for a given value of s only certain orientations of the angular momentum vector in space are allowed.

2 The Hydrogen Atom and (Quasi-) One-Electron Systems

The hydrogen atom is the simplest of all: it consists of a heavy, essentially motionless proton, of charge e , together with a much lighter electron (charge $-e$) that orbits around it, bound by the mutual attraction of opposite charges. From Coulomb’s law, the potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

All atoms with a similar structure, of a nucleus with 1 electron, are called hydrogen like, or hydrogenic. Some examples include He^+ , O^{7+} and U^{91+} .

2.1 The Radial Wavefunction

The angular wavefunction stays the same as in the general case

The radial equation now is

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] P_{nl} = EP_{nl},$$

and we will be looking at the discrete *bound* states, representing the hydrogen atom.

The allowed energies of this equation are given by the **Bohr formula**:

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \text{ with } n = 1, 2, 3, \dots$$

The energy of the **ground state** is given by:

$$E_1 = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV}$$

Evidently the **binding energy** of hydrogen (the amount of energy you would have to impart to the electron in the ground state in order to ionize the atom) is 13.6 eV.

The most probable distance between the nucleus and the electron in a hydrogen atom in its ground state is the so-called **Bohr radius** and is given by

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m}$$

2.1.1 Plots of the Radial Wavefunction

Plots of the radial part will have $n - l - 1$ nodes. By a node, we mean a zero crossing of the function other than the zero at the origin. So the principal quantum number n can be expressed as:

$$n = l + \nu + 1$$

where ν is the number of nodes.

2.1.2 The Wave Functions of Hydrogen

The normalized hydrogen wave functions are

$$\begin{aligned} \psi_{nlm}(r, \theta, \phi) &= R_{nl}(r)Y_l^m(\theta, \phi) \\ &= \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l [L_{n-l-1}^{2l+1}(2r/na)] Y_l^m(\theta, \phi). \end{aligned}$$

Here

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

is an **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$$

is the q th **Laguerre polynomial**.

The ground state of hydrogen is given by

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

2.1.3 Basic quantum numbers

We already went over these lol

2.1.4 The Energy Levels of Hydrogen and Bohr's Approximation

The energy of an electron in the hydrogen atom is given by the following equation:

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

where the principal quantum number n has the possible values, $n = 1, 2, 3, \dots$. Bohr's approximation expands this formula to all one-electron systems:

$$E_{nlm} \approx E_n = -13.6 \frac{Z^2}{n^2} [\text{eV}]$$

2.2 Selection Rules

The selection rules for radiative transitions are:

$$\Delta l = \pm 1 \text{ for all polarizations}$$

$$\Delta m_l = \begin{cases} 0 & \text{for z-polarized light,} \\ \pm 1 & \text{for x- and y-polarized light} \end{cases}$$

2.3 The Fine Structure of Hydrogen

2.3.1 The Magnetic Moment of the Electron

An electron circulating about the nucleus of an atom can be expected to behave like a current loop which interacts with an external magnetic field. This current gives rise to a magnetic dipole moment, which has a magnitude given by $|\mu_l|$.

$$\mu_l = \frac{-e}{2m_e} |\mathbf{l}|$$

The ratio of a magnetic moment to the angular momentum giving rise to the magnetic moment is called the **gyromagnetic ratio**.

$$\frac{|\mu_l|}{|\mathbf{l}|} = \frac{e}{2m_e}$$

Looking at the z component of the magnetic moment and substituting in the z component of the angular momentum gives the **Bohr magneton**:

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} \text{ JT}^{-1}$$

2.3.2 The Spin of the Electron

An atomic electron has a magnetic moment due to its spin just as the electron has a magnetic moment due to its orbital motion. The magnetic moment associated with the spin of the electron is given by the following equation:

$$\mu_s = \frac{-e}{2m_e} g_s |\mathbf{s}|$$

Here the constant g_s is called the **g -value** of the spin. Angular momentum also has a g -value; $g_l = 1$. The gyromagnetic ratio associated with the spin of the electron is

$$\frac{|\mu_s|}{|\mathbf{s}|} = \frac{-eg_s}{2m_e}$$

The total magnetic moment of the electron is given by

$$\mu = \frac{-e}{2m_e} (\mathbf{l} + g_s \mathbf{s})$$

Since the electron and the nucleus are charged particles, their relative motion gives rise to magnetic fields which are a property of the atom itself. This magnetic field interacts with the magnetic moment associated with the spin of the electron, this interaction is called the spin-orbit interaction. If one takes g_s equal to two, the spin-orbit interaction of an electron with a potential energy $V(r)$ is described by the following Hamiltonian:

$$h_{s-o} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{s} \cdot \mathbf{l}$$

2.3.3 The Total Angular Momentum

The total angular momentum \mathbf{j} is the sum of \mathbf{s} and \mathbf{l} :

$$\mathbf{j} = \mathbf{l} + \mathbf{s}$$

It can take the following range of values, jumping only in integer steps:

$$|l - s| \leq j \leq l + s$$

2.3.4 The Fine Structure

Using the potential energy of the hydrogen atom the spin-orbit interaction can be written as

$$h_{s-o} = \frac{1}{2m^2c^2} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^3} \mathbf{s} \cdot \mathbf{l}$$

With the average value of $1/r^3$ the spin-orbit interaction can be written as

$$h_{s-o} = \zeta \mathbf{s} \cdot \mathbf{l}$$

With the **spin-orbit constant**

$$\zeta = \frac{1}{2m^2c^2} \frac{1}{4\pi\epsilon_0} Ze^2 \left\langle \frac{1}{r^3} \right\rangle$$

and

$$\mathbf{s} \cdot \mathbf{l} = \frac{1}{2} (\mathbf{j}^2 - \mathbf{s}^2 - \mathbf{l}^2)$$

2.3.5 The Zeeman Effect

Interaction with a magnetic field also gives splitting due to the **Zeeman effect**. The interaction of the magnetic moment of the electron with the magnetic field may be described by the magnetic potential energy

$$\begin{aligned} V_{\text{mag}} &= -\boldsymbol{\mu} \cdot \mathbf{B} \\ &= (e/2m)(\mathbf{l} + g_s \mathbf{s}) \cdot \mathbf{B} \\ &= (e/2m)B(l_z + g_s s_z) \end{aligned}$$

We can make the following two replacements:

$$\begin{aligned} l_z &\rightarrow \frac{(\mathbf{j}^2 + \mathbf{l}^2 - \mathbf{s}^2)j_z}{2j(j+1)\hbar^2} = \frac{j(j+1) + l(l+1) - s(s+1)}{2j(j+1)} j_z \\ s_z &\rightarrow \frac{(\mathbf{j}^2 - \mathbf{l}^2 + \mathbf{s}^2)j_z}{2j(j+1)\hbar^2} = \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} j_z \end{aligned}$$

This then gives

$$V_{\text{mag}} = g_j (e/2m) B j_z,$$

with

$$g_j = \frac{j(j+1) + l(l+1) - s(s+1)}{2j(j+1)} + g_s \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}.$$

Important to note:

$$\begin{aligned} l = 0 &\rightarrow j = s, & g_j = 2 = g_s \\ s = 0 &\rightarrow j = l, & g_j = 1 = g_l \end{aligned}$$

This gives the following splitting of the energy levels:

$$\Delta E = g_j(e/2m)Bm_j\hbar.$$

Or, with the Bohr magneton $\mu_B = e\hbar/2m$:

$$\Delta E = g_j\mu_B Bm_j.$$

There are two types of Zeeman effect:

- Normal Zeeman effect, the special type, $S = 0$
- Anomalous Zeeman effect, the common type, $S \neq 0$

2.3.6 The Paschen Back effect

If B_{ext} is bigger than B_{int} we get the Paschen Back effect. Here \mathbf{l} and \mathbf{s} divorce, thus s-o coupling breaks apart. Then:

$$\begin{aligned} V &= -\mu_l \cdot \mathbf{B} - \mu_s \cdot \mathbf{B} \\ &= g_l m_l \mu_B B + g_s m_s \mu_B B \\ &= (m_l + 2m_s)\mu_B B \end{aligned}$$

3 Many-electron atoms

Next we gonna look at many-electron systems. This means 2 or more electrons. We're going to look at a strategy example; the independent particle model with 2 electrons.

3.1 Independent particle model

3.1.1 Wavefunctions

The Hamiltonian for a two-electron atom may be written as:

$$\begin{aligned} H = & -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_2} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{12}} \\ & E_{\text{kin},1} \quad E_{\text{p},1} \quad E_{\text{kin},2} \quad E_{\text{p},2} \quad \text{el-el interaction} \end{aligned}$$

r_1 is the distance of the first electron from the nucleus and r_2 is the distance of the second electron from the nucleus. The distance between the two electrons is denoted by r_{12} .

We can't solve this Hamiltonian in the general way, so we want approximations.

The **independent particle model** approximates that each electron moves independently in an average potential due to the nucleus and the electrons. This gives:

$$\begin{aligned} H_0 &= -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_1} + u(\mathbf{r}_1) - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_2} + u(\mathbf{r}_2) \\ &= h_0(1) + h_0(2) \end{aligned}$$

Then the simplest wave function, which describes the two electrons, is the product function

$$\Phi = \phi_a(1)\phi_b(2)$$

with a being the quantum numbers of the first electron and b being those of the second one.

3.1.2 Pauli exclusion principle

The wave functions of an atom must have the property that no two electrons are in the same state $nlm_l m_s$. This property is called the **Pauli exclusion principle**. Due to this, a wave function can only be formed by taking an antisymmetric combination of wave functions:

$$\Psi = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1) & \phi_a(2) \\ \phi_b(1) & \phi_b(2) \end{vmatrix}$$

All these ideas can be generalised for N electrons:

$$H_0 = h_0(1) + h_0(2) + \dots + h_0(N)$$

$$h_0(i) = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} + u(\mathbf{r}_i)$$

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & \dots & \phi_a(N) \\ \phi_b(1) & \phi_b(2) & \dots & \phi_b(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(1) & \phi_n(2) & \dots & \phi_n(N) \end{vmatrix}$$

This last wave function is called a **Slater determinant**.

3.1.3 Central field approximation

The central-field approximation assumes that the potential is spherically symmetric. This approximates $u(\mathbf{r}_i)$ as $u(r_i)$;

$$h_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_1} + u(r).$$

Then as the radial part of the wave function:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} + u(r) \right] P_{nl}(r) = EP_{nl}(r).$$

Together $-\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$ and $u(r)$ become:

$$-\frac{Z_{\text{eff}}e^2}{4\pi\epsilon_0} \frac{1}{r_i}$$

Here Z_{eff} is the effective nuclear charge that the electron "sees".

In single-electron atoms, the energy only depends on the quantum number n . However, for electrons with more than one electron, this doesn't hold anymore. The difference between the energies of electrons with the same value of n and a different value of l (the orbital angular momentum) originates from the motion of the electrons in the charge distribution of the atom. Electrons with a smaller value of the angular momentum come closer to the nucleus and see a larger effective nuclear charge. Since they move under the influence of a larger effective charge, the lower angular momentum states of a many-electron atom are more tightly bound.

3.2 Shell structure and the Periodic Table

Due to different energy levels, the separation of variables and spin multiple quantum numbers are introduced:

Name	Symbol	Orbital meaning	Range of values	Value examples
Principal quantum number	n	shell	$1 \geq n$	$n = 1, 2, 3, \dots$
Azimuthal quantum number (angular momentum)	l	subshell	$0 \leq l \leq n - 1$	for $n = 3$: $l = 0, 1, 2$
Magnetic quantum number (projection of angular momentum)	m_l	energy shift	$-l \leq m_l \leq l$	for $l = 2$: $m_l = -2, -1, 0, 1, 2$
Spin quantum number	m_s	spin of the electron	$-s \leq m_s \leq s$	for $s = \frac{1}{2}$: $m_s = -\frac{1}{2}, \frac{1}{2}$

In the spectroscopic notation l gets assigned letters in place of the numbers:

$$\begin{aligned}
 l = 0 &\rightarrow s \\
 l = 1 &\rightarrow p \\
 l = 2 &\rightarrow d \\
 l = 3 &\rightarrow f \\
 l = 4 &\rightarrow g, \text{ etc.}
 \end{aligned}$$

After this the order follows the alphabet, with either **i** or **j**. The electron shells get filled according to this table.

$n \backslash l$	s	p	d	f	g
1	2	-	-	-	-
2	2	6	-	-	-
3	2	6	10	-	-
4	2	6	10	14	-

The numbers in the table indicate the total number of atoms that each shell can hold and the arrows indicate the order in which the shells get filled, so the $1s$ shell gets filled first, then $2s$, $2p$, $3s$ and so on.

Due to the Pauli exclusion principle, a subshell with quantum numbers n and l can contain no more than $2(2l + 1)$ electrons. A subshell which has all orbitals occupied is said to be filled or closed, while a partially filled subshell is said to be open. The lowest energy for a particular atom can be obtained by successively filling the lowest-lying subshells. The electron configuration of the lowest state, which is called the ground configuration, would then consist of a number of closed subshells and at most one open subshell. This leads to the historically important building-up principle or Aufbau principle. Due to changes in the average central field and Coulomb interaction, the electrons depart from the central field description in some ways.

Filled shells have $L = 0$; $S = 0$.

3.3 LS and jj coupling schemes

The LS and jj coupling schemes differ a bit from each other, using an example this difference will be shown. In this example we have a p electron with $l_1 = 1$ and $s_1 = 1/2$ and an s electron with $l_2 = 0$ and $s_2 = 1/2$.

3.3.1 jj coupling

$$\begin{array}{r}
 l_1 + l_2 + l_3 + \cdots = L \\
 + \quad + \quad + \\
 s_1 + s_2 + s_3 + \cdots = S \\
 \downarrow \quad \downarrow \quad \downarrow \\
 j_1 + j_2 + j_3 + \cdots = J
 \end{array}$$

Then the example gives:

$$\begin{aligned}
 j_1 &= 1 + 1/2 = 1/2, 3/2 \\
 j_2 &= 0 + 1/2 = 1/2 \\
 J &= 1/2 + 1/2 = 0, 1 \\
 \text{or } J &= 3/2 + 1/2 = 1, 2
 \end{aligned}$$

This then gives the states:

$$\left(\frac{1}{2}, \frac{1}{2} \right)_{0,1} \quad \text{and} \quad \left(\frac{3}{2}, \frac{1}{2} \right)_{1,2}$$

You get the same J levels, but the grouping is clearly different, in the jj-case you get two groups of 2 and in the LS-case you get one group of one and one group of three. In real atoms jj-coupling will be present in heavy atoms.

3.3.2 LS coupling

LS, or Russel-Saunders coupling is given by:

$$\begin{array}{r}
 l_1 + l_2 + l_3 + \cdots = L \\
 + \\
 s_1 + s_2 + s_3 + \cdots = S \\
 \downarrow \\
 J
 \end{array}$$

Then the example gives:

$$\begin{aligned}
 L &= 1 + 0 = 1 \\
 S &= 1/2 + 1/2 = 0, 1 \\
 J &= 1 + 0 = 1 \\
 \text{or } J &= 1 + 1 = 0, 1, 2
 \end{aligned}$$

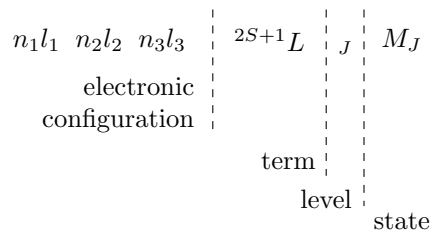
This then gives the states:

$${}^1P_1 \quad \text{and} \quad {}^3P_{0,1,2}$$

You get the same J levels, but the grouping is clearly different, in the jj-case you get two groups of 2 and in the LS-case you get one group of one and one group of three. In real atoms LS-coupling will be present in light atoms.

We use LS in SoM, unless stated otherwise.

The state of an electron is split into different parts



$$M_L = m_{l_1} + m_{l_2} + m_{l_3} + \dots$$

$$M_S = m_{s_1} + m_{s_2} + m_{s_3} + \dots$$

$$M_J = M_L + M_S$$

3.4 Hund's rules

For 2 and 2 electrons only Pauli is satisfied if $L + S = \text{even}$.

Hund's rules are only applicable to find the ground term of the ground electronic configuration. The rules:

1. Only partially filled shells
2. the term with maximum multiplicity has the lowest energy, which is the term with maximum S , and maximum number of unpaired electrons.
3. For a given multiplicity, the term with the largest value of the total orbital angular momentum quantum number L , has the lowest energy.
4. The ground level is found by:
 - If the outermost subshell is half-filled or less, then the lowest J lies lowest in energy.
 - If the outermost shell is more than half-filled, the level with the highest value of J , is lowest in energy.