

Electron Spin and The Pauli Principle

Although the results for the hydrogen atom can in principle be extended to many-electron atoms (as we shall see in the next lecture) they are not sufficient to explain the structure of the periodic system of elements, namely, how many elements belong to one period and why. It turns out that there is one more quantum number that we have to consider and that symmetry requirements determine, which kind of wavefunctions are allowed and which not. To understand this, we have to learn about the electron spin. Let us first review the orbital angular momentum.

1. Orbital Angular Momentum and Magnetic Moment

Two important angular momentum operators \hat{L}^2 , and \hat{L}_z

According to classical mechanics, the angular momentum, or moment of momentum, \vec{L} about the origin is defined by

In Cartesian coordinates, \vec{L} has the components

$$L_x = yp_z - zp_y, L_y = zp_x - xp_z, L_z = xp_y - yp_x \quad (1)$$

Now, we will show the solutions of the Schrödinger equation are also eigenfunctions of L_z

Writing

$$p_x = -i\hbar \frac{\partial}{\partial x}, p_y = -i\hbar \frac{\partial}{\partial y} \quad (2)$$

we have

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (3)$$

Transforming this to spherical polar coordinates, we have

$$\frac{\partial}{\partial \phi} = \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z} \quad (4)$$

$$\frac{\partial}{\partial \phi} = -r \sin \theta \phi \frac{\partial}{\partial x} + r \sin \theta \cos \phi \frac{\partial}{\partial y} = -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y} \quad (5)$$

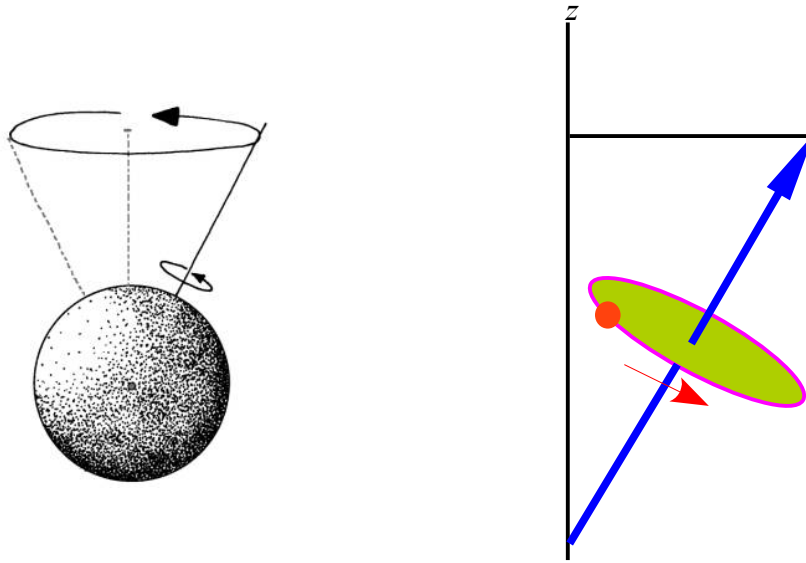
Hence

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (6)$$

Operating with this upon the ψ , we obtain

$$-i\hbar \frac{\partial \psi}{\partial \phi} = m_l \hbar \psi \quad (7)$$

Thus, the z-component of the angular momentum has the value $m_l \hbar$ in the given state ψ



In the same way, by transforming to spherical polar coordinates, it may be shown that the operator representing the total angular momentum, $\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$

$$\hat{L}^2 = L_x^2 + L_y^2 + L_z^2 \tag{8}$$

satisfies the equation $\hat{L}^2 \psi = l(l+1)\hbar^2 \psi$ (more will be given in class).

Thus, the angular momentum \hat{L} has the constant magnitude $\sqrt{l(l+1)}\hbar$ in the state ψ . For this reason, l is often called angular momentum quantum number.

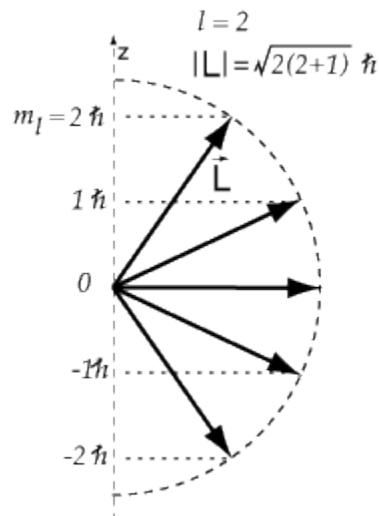
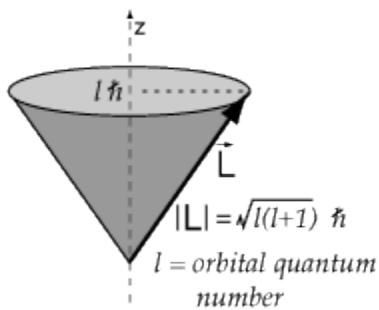
Commutation relations (this will be discussed later):

$$[\hat{H}, \hat{L}^2] = [\hat{L}^2, \hat{L}_z] = [\hat{H}, \hat{L}_z] \quad \text{Two eigenequations}$$

$$\hat{L}_z \psi = m_l \hbar \psi \tag{9}$$

$$\hat{L}^2 \psi = l(l+1)\hbar^2 \psi \tag{10}$$

Vector analysis of angular momentum



Normal Zeeman effect

The angular momentum of the electron:

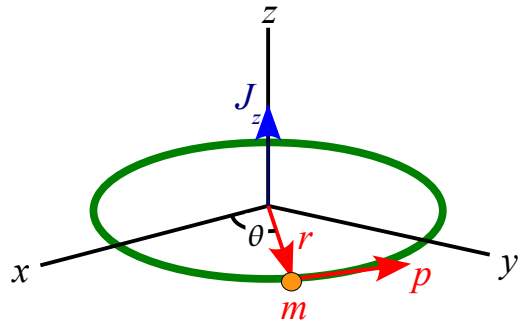
$$L_x = L_y = 0, \quad L_z = mvr$$

The motion of the electrons is equivalent to an electric current I flowing around the orbit:

$$I = \frac{-e v}{2 \pi r}$$

A current I in a small loop of area A is equivalent to a magnetic dipole of magnetic moment $I A/c$. The motion of electrons gives rise to an orbital magnetic moment whose z component is

$$\mu_z = -\frac{evr}{2c} = -\frac{e}{2mc} L_z \quad (11)$$



A magnetic dipole of moment μ has a potential energy $-\mu \cdot \mathbf{H}$ in a magnetic field \mathbf{H} . If we assume there is a magnetic field \mathbf{H} in the z direction, the electron will have a potential energy

$$\mu_z \mathbf{H} = \frac{e}{2mc} L_z H \quad (12)$$

due to the interaction of its orbital magnetic moment with the field. If the electron is moving in a central electrostatic field, its orbit will NOT in general remain in the same plane when a magnetic field is switched on, but will **precess** around the direction of the magnetic field, and the energy of the precessional motion is given by equation (12).

In quantum mechanics, the result of equation (12) remains true, except that L_z is now quantized. For a particle in a central field of force, $L_z = m_l \hbar$ and can have $2l+1$ values. Consequently, the z -component magnetic moment can have any one of the $2l+1$ values given by

$$\mu_z = -\frac{e \hbar m_l}{2mc} \quad (13)$$

And in the presence of a magnetic field \mathbf{H} in the positive z -direction, the $2l+1$ -fold degenerate level with azimuthal quantum number l will split into $2l+1$ separate levels spaces at intervals of $e \hbar \mathbf{H} / 2mc$, which gives rise to what is known as the normal Zeeman effect in atomic spectra. (some spectra lines are split into three by a magnetic field due to the operation of certain selection rules).

Bohr magnetron:

$$\mu_B = \frac{e \hbar}{2 m c} \quad (14)$$

The Schrödinger equation for an atom in a magnetic field:

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(r) - i \hbar \frac{e \mathbf{H}}{2 m c} \frac{\partial}{\partial \phi} \right] \psi = E \psi \quad (15)$$

Here, the unperturbed wavefunction $\psi_{n,l,m_l} = R_{n,l}(r) P_l^{m_l}(\cos \theta) e^{i m_l \phi}$ is also the wavefunction of the perturbed state (equation 15) because:

$$\frac{\partial}{\partial \phi} \psi_{n,l,m_l} = i m_l \psi_{n,l,m_l} \quad (16)$$

We find

$$E = E_0 + \frac{e \hbar \mathbf{H}}{2 m c} m_l \quad (17)$$

For s state, no split.

A magnetic field should have no effect upon the closed shells and sub-shells of an atom (an example of silver).

The theory failed to explain several known experimental facts, such as the fine structure of spectra (sodium D-line spectra, doublets, triplets, and multiplets), which is called the *anomalous Zeeman effect*.

2. Electronic Spin

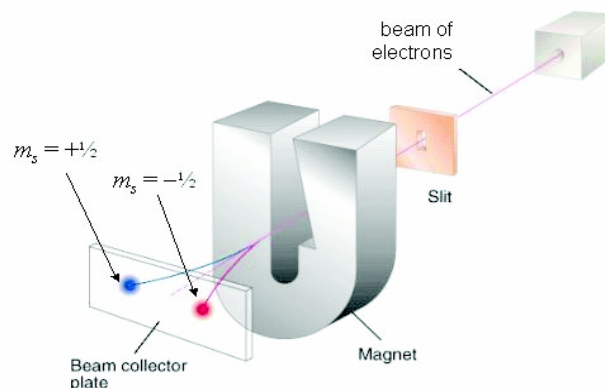
2.1 The Stern and Gerlach experiment

According to the classical electromagnetic theory, an atom with magnetic moment μ in a magnetic field will experience a force $(\mu \cdot \nabla) \mathbf{H}$ or

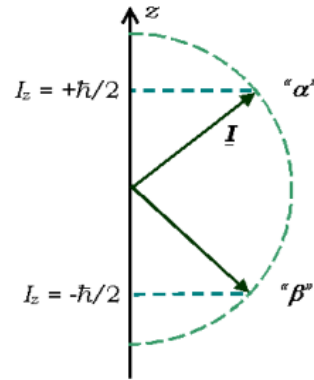
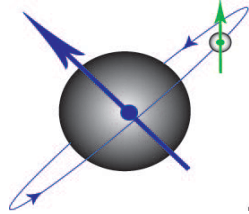
$$\left(\mu_x \frac{\partial}{\partial x} + \mu_y \frac{\partial}{\partial y} + \mu_z \frac{\partial}{\partial z} \right) \mathbf{H} \quad (18)$$

If the field is in the z-direction, and varying with z direction only, the total force will be $\mu_z d\mathbf{H}/dz$

It is clear if an atom has closed shells and sub-shells of electrons and one additional electron with



azimuthal quantum number $l=0$ (s state), no splitting is expected. But this is not the case in Stern and Gerlach's experiments. (Hydrogen, lithium, sodium, silver ..). An explanation was provided by Goudsmit and Uhlenbech in 1925 – spin momentum.



Spin angular momentum is denoted by S (cf. Orbital angular momentum L), spin magnetic moment M .

We **assume** that in the presence of a magnetic field, S_z is quantized in the same way as L_z ($2l+1=2$, which gives $l=1/2$). We may deduce that the quantized values of S_z are $m_s = -\frac{1}{2}\hbar$ and $m_s = \frac{1}{2}\hbar$ (the magnitude of S $|S| = \sqrt{I(I+1)}$), m_s is called spin quantum number. (In 1928, Dirac developed the relativistic quantum mechanics of an electron, and in his treatment electron spins arise naturally. But, in this lecture, we take this as a hypothesis).

Analogous to orbital angular momentum operator \hat{L} , we have

$$\hat{S} = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{19}$$

And

$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z, [\hat{S}_y, \hat{S}_z] = i\hbar \hat{S}_x, [\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y \tag{20}$$

$$[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y] = [\hat{S}^2, \hat{S}_z] = 0 \tag{21}$$

The eigenvalues of \hat{S}^2 are

$$s(s+1)\hbar^2, s=0, \frac{1}{2}, 1, \frac{3}{2}, \dots \tag{22}$$

And the eigenvalues of \hat{S}_z are

$$m_s \hbar, m_s = -s, -s+1, \dots, s-1, s \tag{23}$$

The quantum number s is called the **spin** of the particle. **The spin quantum numbers are capable of half-integer values.** Electrons, protons, and neutrons have $s = \frac{1}{2}$. Pions have $s = 0$. Photons have $s = 1$ (polarized light). Particles with half-integer spin are called fermions and obey the Pauli principle. Particles with integer spin are called Bosons and does not obey the Pauli Principle.

The ratio of the z-components of spin magnetic moment and spin angular momentum is

$$\frac{M_z}{S_z} = -\frac{e}{mc} \quad (24)$$

However, the ratio of the z-components of orbital magnetic moment and orbital angular momentum is

$$\frac{\mu_z}{L_z} = -\frac{e}{2mc} \quad (25)$$

The fact that these two ratios are different indicates that the picture of an electron as a spinning charged particle cannot be a true one – nonetheless, it is a useful intuitive guide.

Electron spin g-factor g_e (**gyromagnetic ratio**): $M_z = g_e \mu_B S_z$ and electron orbital g-factor g_l :
 $\mu_z = g_l \mu_B L_z \dots$

2.2 Spin Wavefunctions

Pauli spin matrices..

The electron has two states, say positive and negative spin. The electron spin eigenfunctions that correspond to these spin operator eigenvalues are denoted by α and β :

$$\hat{S}_z \alpha = +\frac{1}{2} \hbar \alpha \quad (26)$$

$$\hat{S}_z \beta = -\frac{1}{2} \hbar \beta \quad (27)$$

The terms *spin up* and *spin down* refer to $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$.

After introducing a spin quantum number m_s and a spin variable ζ , a complete designation of a one-electron state becomes:

$$\phi_{n,l,m_l,m_s}(x,y,z,\zeta) \quad (28)$$

Here, ζ is only permitted to have two values, which we will arbitrarily take as +1 and -1. (physical meaning of ζ : spin directions).

Spin-orbit coupling

An electron that is not in an s state has magnetic moment due to its orbital motion as well as its spin magnetic moment, and there must be an interaction between the two – we may picture electrons as an

elementary magnet moving in magnetic field created by its orbital motion this is called *spin-orbit coupling*.

In fact, the spin magnetic moment of the electron is forced to be in the same direction as the orbital magnetic moment or the opposite direction. However, the energy due to this effect is very small (in the order of $(e/mc)^2$). As far as the calculation of the energy of an atom, the spin-orbit coupling can be ignored. The wavefunction may be written as the product of an orbital function and a spin function: $\psi_{n,l,m_l}(x,y,z)\alpha(\zeta)$ and $\psi_{n,l,m_l}(x,y,z)\beta(\zeta)$

Q: When a magnetic field \mathbf{H} is switched on in the z-direction, how does the energy of an electron change for the α and β states respectively?

If we permit the spin functions to have only two values 0 and 1, thus

$$\alpha(1)=1, \alpha(-1)=0$$

$$\beta(1)=0, \beta(-1)=1$$

The spin functions defined above are normalized and orthogonal.

$$\int |\alpha(\zeta)|^2 d\zeta = \sum_{\zeta=\pm 1} |\alpha(\zeta)|^2 = 1 \quad (29)$$

$$\int \alpha(\zeta)\beta(\zeta) d\zeta = \sum_{\zeta=\pm 1} \alpha(\zeta)\beta(\zeta) = \alpha(1)\beta(1) + \alpha(-1)\beta(-1) = 0 \quad (30)$$

Using a vector \mathbf{x} to stand for (x, y, z, ζ) , a one electron wavefunction can be written $\phi(\mathbf{x})$ instead of $\psi(x, y, z, \zeta)$ or $\psi(\mathbf{r}, \zeta)$. $\phi(\mathbf{x})$ is referred to as a *spin-orbital*, and $d\mathbf{x} = d\mathbf{r} d\zeta$

Suppose $\phi(\mathbf{x}) = \psi(\mathbf{r})\alpha$, now, if the orbital function $\psi(\mathbf{r})$ is normalized, then the spin-orbital function is also normalized. (why?)

3. The Pauli Principle and the Symmetry of Wavefunctions

In the case of a many-electron atom it may be deduced from the experimental data that, if two electrons are in the same orbital state, they must have opposite spins. The Pauli exclusion principle states: **not more than two electrons may occupy any state.**

3.1 The symmetry of many-electron wavefunctions

We first note that electrons are indistinguishable: any interchange of the coordinates of the electrons,

including the spin coordinates, must leave the observable quantity unchanged.

Now let's consider a physically observable quantity $|\Psi|^2$. Any interchange of the coordinates (including the spin coordinates) of two electrons must leave the value of $|\Psi|^2$ unchanged:

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N)|^2 \quad (31)$$

In general, if the operator \mathbf{P} represents any one of the $N!$ different permutations of the electronic coordinates, then

$$|\Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N)|^2 = |\mathbf{P}\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 \quad (32)$$

So that

$$\Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N) = \pm \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad (33)$$

In other words, the function Ψ must be either *symmetric* or *anti-symmetric*.

Note, Ψ cannot be symmetric with respect to one pair of electrons and antisymmetric with respect to another pair. (Why?)

Whether or not they are symmetric or antisymmetric, we have to rely on experiments. A generalization of the Pauli principle states:

For a system of electrons, the total wavefunction must be antisymmetric in the electronic coordinates, including spin.

3.2 Slater Determinants

Suppose a set of one-electron wavefunctions of a system has been obtained, and they are $\phi_1(\mathbf{x}_1), \phi_2(\mathbf{x}_2), \dots, \phi_N(\mathbf{x}_N)$, where, for example $\phi_1(\mathbf{x}_1) = \psi(\mathbf{r}_1)\alpha(\zeta_1)$.

The total wavefunction of the N-electron system can be approximately written

$$\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\dots\phi_N(\mathbf{x}_N) \quad (34)$$

Any product, with the electronic coordinates rearranged in any order would be equally acceptable. The general form is

$$\sum_{\mathbf{P}} a_{\mathbf{P}} \mathbf{P} \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\dots\phi_N(\mathbf{x}_N) \quad (35)$$

Where $a_{\mathbf{P}}$ are constants, and the sum is over the $N!$ permutations. Now, taking into account the property of being antisymmetric, the total wavefunction (not normalized) becomes

$$\sum_{\mathbf{P}} (-1)^p \mathbf{P} \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\dots\phi_N(\mathbf{x}_N) \quad (36)$$

Where p is the number of interchange in the permutation. The wavefunction may be written in the

determinant form

$$\Psi = \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_1(\mathbf{x}_2) & \cdots & \phi_1(\mathbf{x}_N) \\ \phi_2(\mathbf{x}_1) & \phi_2(\mathbf{x}_2) & \cdots & \phi_2(\mathbf{x}_N) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_N(\mathbf{x}_1) & \phi_N(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix} \quad (37)$$

3.1 Expectation Value of a symmetric Operator and the Normalization of Slater determinants

The normalized total wavefunction of many-electrons is

$$\Psi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \mathbf{P} \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N) \quad (38)$$

Proof:

$$\begin{aligned} \int \Psi^* \Psi d\tau' &= \sqrt{N!} \int \Psi^* \mathbf{P} \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= \int \left[\sum_P (-1)^P \phi_1^*(\mathbf{x}_1) \phi_2^*(\mathbf{x}_2) \cdots \phi_N^*(\mathbf{x}_N) \right] \mathbf{P} \phi_1(\mathbf{x}_1) \cdots \phi_N(\mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= \int |\phi_1(\mathbf{x}_1)|^2 |\phi_2(\mathbf{x}_2)|^2 \cdots |\phi_N(\mathbf{x}_N)|^2 d\tau' \\ &= \int |\phi_1(\mathbf{x}_1)|^2 d\mathbf{x}_1 \int |\phi_2(\mathbf{x}_2)|^2 d\mathbf{x}_2 \cdots \int |\phi_N(\mathbf{x}_N)|^2 d\mathbf{x}_N = 1 \end{aligned} \quad (39)$$

For a symmetric operator \hat{F} (i.e. $\mathbf{P} \hat{F} = \hat{F}$) and normalized determinantal wavefunction Ψ , the expectation value may be written

$$\langle F \rangle = \int \Psi^* \hat{F} \Psi d\tau' = \sqrt{N!} \int \Psi^* \hat{F} \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N) d\tau' \quad (40)$$

Proof:

$$\begin{aligned} \int \Psi^* \hat{F} \Psi d\tau' &= \frac{1}{\sqrt{N!}} \int \Psi^* \hat{F} \sum_P (-1)^P \mathbf{P} \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \mathbf{P} \int (\mathbf{P}^{-1}) \Psi^* \mathbf{P} \phi_1(\mathbf{x}_1) \cdots \phi_N(\mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= \sqrt{N!} \sum_P \mathbf{P} \int \Psi^* \hat{F} \mathbf{P} \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= \sqrt{N!} \int \Psi^* \hat{F} \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N) d\tau' \end{aligned} \quad (41)$$

4. The Ground State and the Excited States of the Helium Atom

Let us consider the application of one-electron application to the helium atom, and recall that the Hamiltonian of this system is

$$\hat{H} = -\nabla_1^2 - \nabla_2^2 - \frac{4}{r_1} - \frac{4}{r_2} + \frac{2}{r_{12}} \quad (42)$$

For simplicity, we will choose hydrogenic one-electron orbitals to be eigenfunctions of this equation and treat the term e^2/r_{12} by first order perturbation theory. We are more concerned demonstrating the general effects of using a determinantal wavefunction.

4.1 Ground State

In the ground state, the electrons occupy the same 1s orbital but with different spins

$$\phi_1(\mathbf{x}) = \psi(\mathbf{r})\alpha(\zeta), \quad \phi_2(\mathbf{x}) = \psi(\mathbf{r})\beta(\zeta) \quad (43)$$

The normalized total wavefunction is

$$\begin{aligned} \Psi_0 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_1(\mathbf{x}_2) \\ \phi_2(\mathbf{x}_1) & \phi_2(\mathbf{x}_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)[\alpha(\zeta_1)\beta(\zeta_2) - \alpha(\zeta_2)\beta(\zeta_1)] \end{aligned} \quad (44)$$

The determinantal wavefunction is expressed as a product of an orbital part and a spin part. We see that the orbital part is symmetric and the spin part is antisymmetric.

The energy given by this wavefunction is

$$\begin{aligned} &\int \int \Psi_0^* \hat{H} \Psi_0 d\mathbf{x}_1 d\mathbf{x}_2 \\ &= \frac{1}{2} \sum_{\zeta_1, \zeta_2 = \pm 1} \int \int \psi^*(\mathbf{r}_1)\psi^*(\mathbf{r}_2) \hat{H} \psi(\mathbf{r}_1)\psi(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 [\alpha(\zeta_1)\beta(\zeta_2) - \alpha(\zeta_2)\beta(\zeta_1)] \\ &= \int \int \psi^*(\mathbf{r}_1)\psi^*(\mathbf{r}_2) \hat{H} \psi(\mathbf{r}_1)\psi(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (45)$$

Both electrons are in the same orbital but with different spins, and are thus non-degenerate. Non-degenerate states are known as *singlets*.

4.2 Excited States

Two orbitals with different energies (1s, 2s): the wavefunctions $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are eigenfunctions of equation 42. In this case, electrons are not required to have the same spin. We have four ways of associating spin functions with the orbitals:

$$\begin{aligned}\Psi_1 &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & 2s(1) \\ 1s(2) & 2s(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \alpha(\zeta_1) \alpha(\zeta_2)\end{aligned}\quad (46)$$

$$\begin{aligned}\Psi_2 &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1\bar{s}(1) & 2\bar{s}(1) \\ 1\bar{s}(2) & 2\bar{s}(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \beta(\zeta_1) \beta(\zeta_2)\end{aligned}\quad (47)$$

$$\begin{aligned}\Psi_3 &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & 1s(2) \\ 2\bar{s}(1) & 2\bar{s}(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \alpha(\zeta_1) \beta(\zeta_2) - \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \alpha(\zeta_2) \beta(\zeta_1)\end{aligned}\quad (48)$$

$$\begin{aligned}\Psi_4 &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1\bar{s}(1) & 1\bar{s}(2) \\ 2s(1) & 2s(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \beta(\zeta_1) \alpha(\zeta_2) - \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \beta(\zeta_2) \alpha(\zeta_1)\end{aligned}\quad (49)$$

For the unperturbed system, the four wavefunctions are degenerate, each of them corresponding to the unperturbed energies E_a and E_b .

Instead of using Ψ_3 and Ψ_4 , we may construct linear combinations of them as

$$\Psi_3 + \Psi_4 = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1)] [\alpha(\zeta_1) \beta(\zeta_2) + \alpha(\zeta_2) \beta(\zeta_1)] \quad (50)$$

$$\Psi_3 - \Psi_4 = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1)] [\alpha(\zeta_1) \beta(\zeta_2) - \alpha(\zeta_2) \beta(\zeta_1)] \quad (51)$$

The first-order perturbation energies must be obtained by setting up and solving the **secular determinant**. We construct the secular determinant in terms of the normalized wavefunctions

$$\Psi_1, \Psi_2, \frac{1}{\sqrt{2}}(\Psi_3 + \Psi_4), \frac{1}{\sqrt{2}}(\Psi_3 - \Psi_4) \quad (52)$$

It turns out that all off diagonal elements vanish, so that the perturbed energy levels are given immediately by

$$E = \int \Psi^* \hat{H} \Psi d\tau' \quad (53)$$

The first three have the antisymmetric orbital factor and the symmetric spin factor; while the remaining function has the symmetric orbital factor and the antisymmetric spin factor.

The normalized spin factor does not affect the energy values given by equation 53 (why?)

Thus there are only two perturbed energy levels, corresponding to the symmetric and antisymmetric orbital wavefunctions respectively

$$E = E_a + E_b + \frac{1}{2} \int \int \frac{2}{r_{12}} [|\psi_a(\mathbf{r}_1)|^2 |\psi_b(\mathbf{r}_2)|^2 + |\psi_a(\mathbf{r}_2)|^2 |\psi_b(\mathbf{r}_1)|^2 \pm \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) + \psi_a^*(\mathbf{r}_2) \psi_b^*(\mathbf{r}_1) \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2$$

Hence

$$E = E_a + E_b + C \pm J \quad (54)$$

C is due to coulomb interaction of electron clouds

$$C = \int \int \frac{2}{r_{12}} |\psi_a(\mathbf{r}_1)|^2 |\psi_b(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \quad (55)$$

J is called the exchange integral (the last term called exchange energy)

$$J = \int \int \frac{2}{r_{12}} \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \quad (56)$$

C and J are both positive. (why?)

The *lower* energy is therefore

$$E_l = E_a + E_b + C - J \quad (57)$$

and is triply degenerate. (Their wavefunctions are....)

The *higher* energy level is

$$E_s = E_a + E_b + C + J \quad (58)$$

and is non-degenerate.

PROBLEMS: (due March 18, 2008)

1. For a 2-electron system, prove that the spin function $\phi = \frac{\sqrt{2}}{2} [\alpha(\zeta_1)\beta(\zeta_2) + \beta(\zeta_1)\alpha(\zeta_2)]$ is an eigenfunction of the total z component of spin angular momentum, and solve for its eigenvalue.

2. Assume the 2s spin of the Li atom is α , expand the Slater determinant for the ground state of the Li atom. From the Slater determinant give a detailed expression for $\langle H \rangle$ in terms of the hydrogenic energies, and the relevant Coulomb and exchange integrals.