

Atomic Structure

Hydrogen-like Atoms

The Hamiltonian for a single electron atom is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{r}$$

where m is the mass of the electron (stationary nucleus) and Z is the nuclear charge (1 for hydrogen, 2 for He^+ , etc.).

The momentum operator is

$$\hat{p}^2 = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = \frac{-\hbar^2}{2m} \nabla^2$$

this is a spherically symmetric problem, so we will find the solutions more easily if we start with the operator in spherical polar coordinates

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

Next, we note that the angular part of this operator is

equal to $-\hat{L}^2 / \hbar^2 r^2$.

Therefore,
$$-\hbar^2 \nabla^2 = \frac{-\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \hat{L}^2$$

Substitution in the Hamiltonian gives

$$**** \hat{H} = \frac{-\hbar^2}{2\mu r^2} \frac{\partial^2}{\partial r^2} - \frac{Ze^2}{r} + \frac{\hat{L}^2}{2\mu r^2}$$

as the potential energy depends on only one coordinate, the eigenvalue equation is separable, and we can write the wavefunction as the product

$$\hat{h}(r) + \frac{1}{2\mu r^2} \hat{L}^2 R(r)S(\theta, \phi) = ER(r)S(\theta, \phi)$$

where $\hat{h}(r) = \frac{-\hbar^2}{2\mu r^2} \frac{\partial^2}{\partial r^2} - \frac{Ze^2}{r}$ is a radial operator.

Now, note that \hat{L}^2 commutes with the Hamiltonian. As a consequence, the wavefunctions will also be eigenfunctions of \hat{L}^2 , so the spherical harmonics $Y_{\ell,m}$ are the obvious choice for $S(\theta, \phi)$.

With this substitution we have

$$\hat{h}(r) + \frac{1}{2\mu r^2} \hat{L}^2 R(r)Y_{\ell,m} = ER(r)Y_{\ell,m}$$

As $\hat{L}^2 Y_{\ell,m} = \hbar^2 \ell(\ell + 1)Y_{\ell,m}$, this equation can be simplified to

$$\hat{h}(r) + \frac{\hbar^2 \ell(\ell + 1)}{2mr^2} R(r) = ER(r)$$

Now for some juggling with constants. We will transform to a unitless radial equation using the Bohr radius, $a_0 = \hbar^2 / me^2$, and a new dimensionless variable defined by

$$\rho = \frac{Zr}{a_0} \text{ (dimensionless)}$$

In terms of the Bohr radius, we can write the Hamiltonian as

$$\frac{-a_0 e^2}{2r^2} - \frac{Ze^2}{r} + \frac{\ell(\ell + 1)a_0 e^2}{2r^2} R(r) = ER(r)$$

Then, multiply by $-2a_0 / Z^2 e^2$

$$\frac{a_0^2}{Z^2 r^2} - \frac{r^2}{r} + \frac{2a_0}{Zr} - \frac{\ell(\ell + 1)a_0^2}{Z^2 r^2} R(r) = \frac{-2a_0 E}{Z^2 e^2} R(r)$$

Then, by the change of variable from r to ρ , we get

$$\frac{1}{2} \frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} - \frac{\ell(\ell+1)}{2r^2} R(r) = E R(r)$$

with $E = \frac{-Z^2 e^2}{2a_0}$

The result is a standard form known as Laguerre's differential equation.

Without going through math, ...

Solutions that do not become infinite as $r \rightarrow \infty$ (boundary condition) are subject to the condition

$$E = -\frac{Z^2 e^2}{2a_0 n^2}, \dots, -\frac{Z^2 e^2}{2a_0 n^2}, \dots$$

n is an integer that must be $\ell + 1$.

Thus, $n=1,2,3,\dots$; $\ell=0,1,\dots,n-1$.

Therefore,

$$*** E = \frac{-Z^2 e^2}{2a_0} = \frac{-Z^2 e^2}{2a_0} \frac{1}{n^2} = -\frac{Z^2}{n^2} R_y$$

The rigorous result is to account for the fact that the nucleus is not infinitely massive. Thus, the rigorous energy is given by

$$E_n = -\frac{Z^2}{n^2} \frac{\mu}{m_e} R_y; \quad \mu = \frac{m_e m_{\text{nucleus}}}{m_e + m_{\text{nucleus}}}$$

($Ry = \frac{e^2}{2a_0}$ = the Rydberg constant = 13.6057 eV).

This is the Bohr result !

Energy depends on n , but not on ℓ or m .

$n=1$ $\ell=0$ (1s) $m=0$ degeneracy g for $n=1$ (1s) is 1.

$n=2$ $\ell=0$ (2s) $m=0$

$n=2$ $\ell=1$ (2p) $m=-1, 0, +1$ for $n=2$,
 $g=1(2s)+3(2p)=4$.

$n=3$ $\ell=0$ (3s) $m=0$

$n=3$ $\ell=1$ (3p) $m=-1, 0, +1$

$n=3$ $\ell=2$ (3d) $m=-2, -1, 0, +1, +2$

for $n=3$, $g=1(3s)+3(3p)+5(3d)=9$.

Radial eigenfunctions for Hydrogen-like atoms

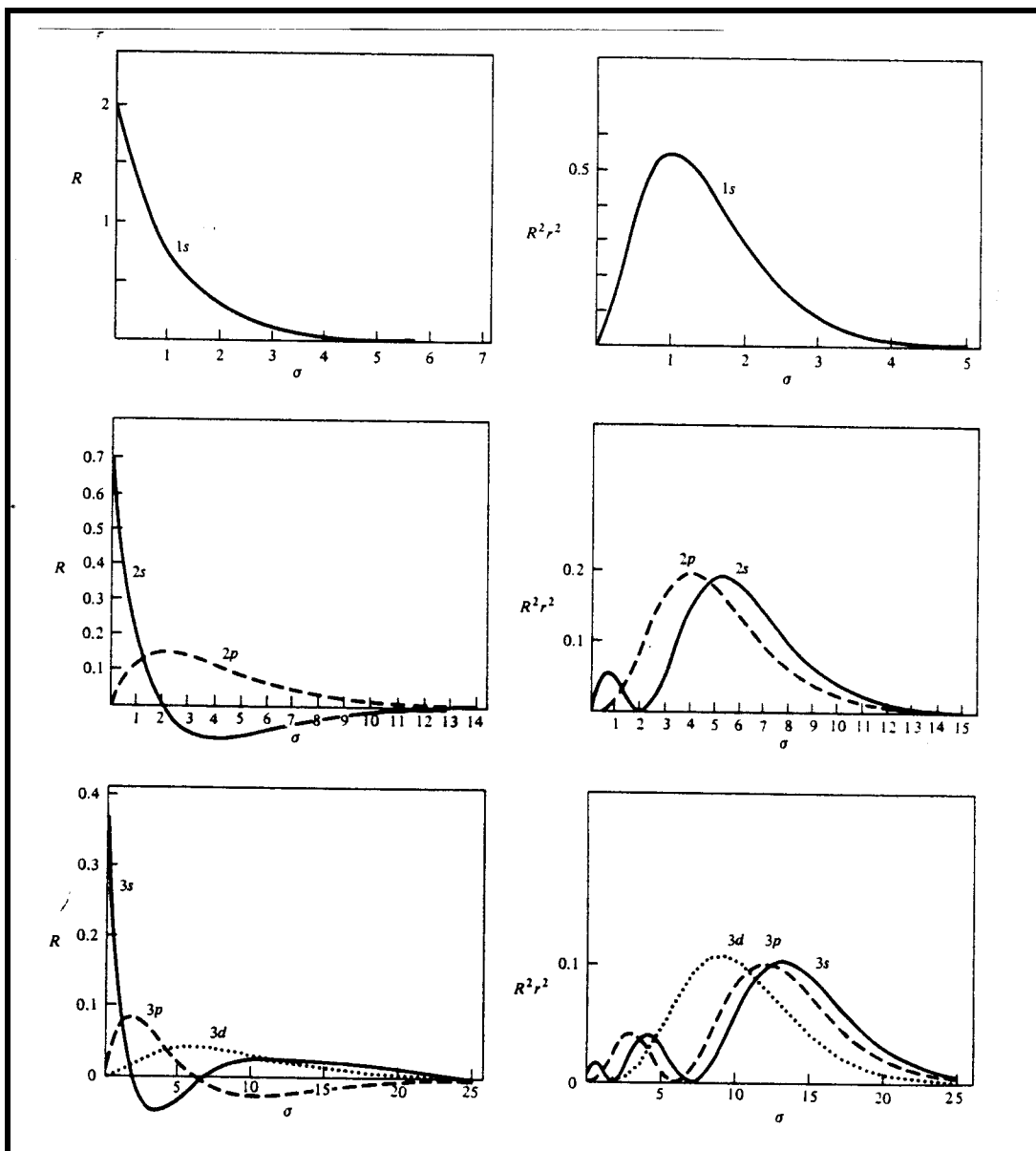
The solutions to the radial equation for hydrogen-like atoms are:

$$R_{n,\ell}(r) = \sqrt{\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-r/2} r^\ell L_{n+\ell}^{2\ell+1}\left(\frac{r}{a_0}\right)$$

where $L_{n+\ell}^{2\ell+1}\left(\frac{r}{a_0}\right)$ are the associated Laguerre polynomials, defined by the equations

$$L_k^j(\sigma) = \frac{d^j}{d\sigma^j} L_k(\sigma)$$

$$L_k(\sigma) = e^{-\sigma} \frac{d^k}{d\sigma^k} (\sigma^k e^{-\sigma}) \quad (\text{Laguerre polynomials})$$



Typical solutions (where $N = (Z\mu e^2 / \hbar^2)^{3/2}$) :
 $n=1, \ell=0$ (1s orbital)

$$R_{1,0}(r) = N2e^{-r/2} \quad \text{no node}$$

$n=2, \ell=0$ (2s orbital)

$$R_{2,0}(r) = \frac{N}{2\sqrt{2}} (2 - r) e^{-r/2}$$

one node (where $R=0$ at $r=2$)

$n=2, \ell=1$ (2p orbital)

$$R_{2,1}(r) = \frac{N}{2\sqrt{6}} r e^{-r/2} \quad \text{no node}$$

For $R_{n,\ell}$ there are $n-\ell-1$ nodes.

3s: 2 nodes; 3p: 1 node; 3d: 0 nodes; ...

Angular components for $\ell=1$: $Y_{1,0} \cos \theta$ $2p_z$

$$Y_{1,1} \sin \theta e^{i\phi}$$

$$Y_{1,-1} \sin \theta e^{-i\phi}$$

Real linear combinations of 2p orbitals

$$2p_x = R_{n,\ell} (Y_{1,1} + Y_{1,-1})$$

$$2p_y = R_{n,\ell} (Y_{1,1} - Y_{1,-1}) / i$$

Other linear combinations of note:

$$d_{1,1} \text{ and } d_{-1,1} \text{ combine to give } d_{xz} \text{ and } d_{yz}$$

$$d_{2,2} \text{ and } d_{-2,2} \text{ combine to give } d_{xy} \text{ and } d_{(x^2-y^2)}$$

$$d_{0,0} = d_{z^2}$$

Normalization.

The complete wavefunction for the hydrogen atom is given by

$$\psi_{n,\ell,m} = R_{n,\ell}(r) Y_{\ell,m}(\theta, \phi)$$

and the volume element in spherical polar coordinates is $d\tau = r^2 \sin\theta \, d\theta \, d\phi$. The spherical harmonics are usually given in a normalized form, such that

$$\int_0^{2\pi} \int_0^\pi Y_{\ell,m}^* Y_{\ell,m} \sin\theta \, d\theta \, d\phi = 1$$

therefore, the radial functions are normalized independently:

$$\int_0^\infty R_{n,\ell}^* R_{n,\ell} r^2 dr = 1$$

Orthogonality.

$$\int_0^{2\pi} \int_0^\pi Y_{\ell,m}^* Y_{\ell',m'} \sin\theta \, d\theta \, d\phi = \delta_{\ell,\ell'} \delta_{m,m'}$$

$$\int_0^\infty R_{n,\ell}^* R_{n',\ell'} r^2 dr = \delta_{n,n'} S_{\ell\ell'}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} R_{n,\ell}^* R_{n',\ell'} Y_{\ell,m}^* Y_{\ell',m'} \, d\tau = \delta_{n,n'} \delta_{\ell,\ell'} \delta_{m,m'} S_{\ell\ell'}$$

The eigenfunctions are orthogonal to all other eigenfunctions.

For a normalized wavefunction, the probability of finding the electron in a volume element $d\tau$ is

$$|\psi_{n,\ell,m}|^2 d\tau = |R_{n,\ell}|^2 |Y_{\ell,m}|^2 r^2 dr \sin\theta \, d\theta \, d\phi$$

Integration over θ and ϕ gives radial distribution function $f(r)$:

$$f(r)dr = R_{n,\ell}^* R_{n,\ell} r^2 dr$$

$f(r)dr$ is the probability of finding the electron between spheres of radius r and $r+dr$.

Consider the most probable radius for the hydrogen 1s orbital. The wavefunction is given by

$$\psi_{1,0,0} = R_{10} Y_{00} = 2a_0^{-3/2} e^{-r/a_0} \frac{1}{\sqrt{4}}$$

(First, check to see if the radial wavefunction is normalized

$$\int_0^\infty R_{1,0}^* R_{1,0} r^2 dr = \frac{4}{a_0^3} \int_0^\infty e^{-2r/a_0} r^2 dr$$

$$= \frac{4}{a_0^3} \frac{2!}{(2/a_0)^3} = 1)$$

(From integral table or integration by

parts: $\int_0^\infty e^{-qx} x^n dx = \frac{n!}{q^{n+1}})$

the radial distribution function is

$$f(r) = \frac{4}{a_0^3} e^{-2r/a_0} r^2,$$

and the most probable radius is given by the maximum of this function.

$$\frac{df(r)}{dr} = 0 = \frac{4}{a_0^3} 2r e^{-2r/a_0} - \frac{2r^2}{a_0} e^{-2r/a_0}$$

so

$$*** 2r_{\max} - \frac{2r_{\max}^2}{a_0} = 0, \quad \text{or} \quad r_{\max} = a_0$$

Since $R_{1,0}$ is normalized, the average distance from the nucleus is obtained from

$$\langle r \rangle = \int_0^{\infty} R_{1,0}^* r R_{1,0} r^2 dr$$

$$\langle r \rangle = 4a_0^{-3} \int_0^{\infty} r^3 e^{-2r/a_0} dr = 4a_0^{-3} \frac{3!}{(2/a_0)^4} = \frac{3a_0}{2}$$

Electron Spin

As noted before,

$$\hat{S}^2 = \hbar^2 s(s+1) \quad , \quad \hat{S}_z = \hbar m_s$$

for a particle with spin 1/2 it is usual to equate the function \square with $m_s=1/2$ and \square with $m_s=-1/2$.P

We also have raising and lowering operators:

$$\begin{aligned} \hat{S}_+ &= 0, & \hat{S}_- &= \hbar \\ \hat{S}_+ &= \hbar, & \hat{S}_- &= 0 \end{aligned}$$

Furthermore, we can specify the operators for the projection of spin along the x and y axes:

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$$

therefore

$$\hat{S}_x = \frac{1}{2} (\hat{S}_+ + \hat{S}_-), \quad \hat{S}_y = \frac{1}{2i} (\hat{S}_+ - \hat{S}_-)$$

The action of these operators on the spin functions gives

$$\begin{aligned} \hat{S}_x &= \frac{\hbar}{2}, & \hat{S}_y &= \frac{-\hbar}{2i} \\ \hat{S}_x &= \frac{\hbar}{2}, & \hat{S}_y &= \frac{\hbar}{2i} \end{aligned}$$

Finally, the spin functions are orthonormal

$$*** \begin{array}{l} * d_e = * d_e = 1 \\ * d_e = 0 \end{array}$$

The spin "coordinates" commute with position coordinates. Therefore, the complete wavefunction will be given by the product of spatial and spin wavefunctions. e.g., for hydrogen-like atoms

$$= \psi_{n,\ell,m} \chi_{m_s} \quad \text{or} \quad \psi_{n,\ell,m,m_s}$$

With the inclusion of spin the 1s orbital is two-fold degenerate. The degeneracies we derived above without consideration of spin have to be multiplied by 2.

The Helium Atom

We now consider He and He-like atoms (two electron atoms). The problems encountered here are common to all many-electron atoms. In addition the energies of the He atom form the basis for the "shell" picture of the atom.

The model consists of two electrons moving around a fixed nucleus of charge $+Ze$.

electron coordinates are $x_1, y_1, z_1, x_2, y_2, z_2$

or $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$

each electron has its own operators

$$\hat{p}_{x_1} = \frac{\hbar}{i} \frac{\partial}{\partial x_1}, \quad \hat{L}_{z_2} = \frac{\hbar}{i} \frac{\partial}{\partial \phi_2} \quad \text{etc.}$$

operators for particle 2 do not change the functions for particle 1 and vice versa.

Two-electron atom Hamiltonian:

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_2^2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \\ + \text{spin orbit} + \dots$$

(the terms on the second line are usually small, and will not be considered at this point)

Due to the electron-electron repulsion which depends on $r_{12} = |\vec{r}_1 - \vec{r}_2|$, this is not a separable Hamiltonian.

Note that the Hamiltonian is mostly the sum of two hydrogen-like atomic Hamiltonians:

$$*** \hat{H} = \hat{h}(1) + \hat{h}(2) + \frac{e^2}{r_{12}},$$

$$\text{where } \hat{h}(j) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_j^2} - \frac{Ze^2}{r_j}$$

We can solve this problem if we take the drastic approximation of ignoring the electron-electron repulsion

$$\hat{H}_0 = \hat{h}(1) + \hat{h}(2)$$

the Hamiltonian is separable between electron 1 and 2, and the wavefunction is then given by the product of hydrogen-like wavefunctions

$$= \psi_{n_1, \ell_1, m_1}(1) \psi_{n_2, \ell_2, m_2}(2), \quad \text{where } (j) = (n_j, \ell_j, m_j)$$

The energy is the sum of the one-electron energies:

$$E^{(0)} = -Z^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \frac{e^2}{2a_0}$$

Lowest energy eigenfunction = ground state = 1s(1)1s(2)

$$E^{(0)} = -2^2 \left(\frac{1}{1} + \frac{1}{1} \right) \text{Ry} = -8 \text{Ry}$$

to compare with experiment, consider the first ionization energy (He^+ , $n_1 = 1, n_2 = \infty$)

$$\text{I.P.} = E(\text{He}^+) - E(\text{He}) = -4 \text{ Ry} + 8 \text{ Ry} = 4 \text{ Ry}$$

model gives 54.4 eV vs the measured value of 24.6 eV. This is a very poor approximation!

A better approximation is obtained from Perturbation Theory -

We know that we can write the Hamiltonian as the sum of an operator whose wavefunctions we can find, \hat{H}_0 , and an operator for which we cannot find solutions.

$$*** \hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\hat{H}_0 = \hat{h}(1) + \hat{h}(2) \quad (\text{just solved above}). \text{ solution}$$

0

$$\hat{H}_1 = e^2 / r_{1,2} \quad (\text{for the present problem})$$

The mean value or expectation value theorem can be used to approximate the energy contributed by the \hat{H}_1 term:

$$*** E^{(1)} = \langle \hat{H}_1 \rangle = \frac{\int \psi_0^* \hat{H}_1 \psi_0 d\tau}{\int \psi_0^* \psi_0 d\tau}$$

this is the result from "first order perturbation theory", the wavefunctions used are the eigenfunctions of \hat{H}_0 ("zeroth order wavefunctions").

The total energy is then $E = E^{(0)} + E^{(1)}$

For the ground state of He we will be interested in the correction

$$\left\langle \frac{e^2}{r_{1,2}} \right\rangle_{1s} = \frac{\int \left(e^{-2r_1/a_0} e^{-2r_2/a_0} \right)^2 \frac{e^2}{r_{1,2}} d\tau}{\int \left(e^{-2r_1/a_0} e^{-2r_2/a_0} \right)^2 d\tau}$$

the above integrals can be evaluated analytically (but not easily). The result is

$$\left\langle \frac{e^2}{r_{1,2}} \right\rangle_{1s} = 2.5 \text{ Ry}$$

which gives $E = E^{(0)} + E^{(1)} = -5.5 \text{ Ry}$ and the ionization energy is $1.5 \text{ Ry} = 20.4 \text{ eV}$ - much better but still not good enough. (Can do higher order perturbation theory.)

Extra credit homework problem

Calculate the coulomb repulsion energy using the most probable and average distances an electron in a 1s orbital and assume that the two electrons stay as far away from each other as geometrically possible. Is the result better than 1st order PT? Discuss.

Variation Theory - another approximation scheme.

For this method we start with a "guessed" trial wavefunction, ψ , and estimate the energy of the system by

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$

We can show that E_0 (the true lowest eigenvalue) for any trial function ψ . To do this, first expand the trial function in terms of the true (orthonormalized) eigenfunctions (we don't need to know the eigenfunctions to do this. We only need to know that they exist). If

$$\hat{H} \psi = E \psi \quad \text{then} \quad \psi = \sum_i a_i \phi_i$$

To simplify matters we will normalize the trial function. It then follows that

$$\int \psi^* \psi = 1 = \left(\sum_i a_i^* \right) \left(\sum_j a_j \right) = \sum_i a_i^* a_i$$

Next, evaluate the trial energy from

$$\begin{aligned} E &= \left(\sum_i a_i^* \right) \hat{H} \left(\sum_j a_j \phi_j \right) \\ &= \left(\sum_i a_i^* \right) \sum_j a_j E_j \\ &= \sum_i a_i^* a_i E_i = |a_0|^2 E_0 + |a_1|^2 E_1 + |a_2|^2 E_2 + \dots \end{aligned}$$

Now, as $E_0 < E_1 < E_2 < \dots$, it follows from the normalization condition that $E \geq E_0$. If $E = E_0$, this implies that the trial function is the true ground state eigenfunction.

(Variation principle)

Given that $\langle H \rangle$ is always an upper bound, improved estimates of the ground state energy may be obtained by including variable parameters in the trial function that may be adjusted to give the smallest value for $\langle H \rangle$

Write $\langle H \rangle$ as $\langle H \rangle = f(r, \dots; c_1, c_2, c_3, \dots)$

where the c_n 's are adjustable parameters (variation parameters). The best estimate for the energy is found from

$$\frac{\partial \langle H \rangle}{\partial c_1} = 0, \quad \frac{\partial \langle H \rangle}{\partial c_2} = 0, \text{ etc.}$$

which gives n equations in n unknowns. Solution of the simultaneous equations yields the "best" parameter values.

This is called the variation method.

Returning to the Helium-like atom, we can use a trial function that is the product of the one-electron hydrogen-like orbitals

$$(1,2;Z') = \psi_{1s}(1) \psi_{1s}(2) e^{-Z' r_1/a_0} e^{-Z' r_2/a_0}$$

Here we consider Z' as a variation parameter.

Substitution of this function in the variational equation

$$\frac{\partial \langle H \rangle}{\partial Z'} = 0 \text{ gives}$$

$$= -2Ry(Z')^2, \quad \text{where } Z' = Z - \frac{5}{16}$$

For He, $Z=2$, $Z'=27/16$, $\square=-5.70Ry$, $iP=23.1eV$. The effective nuclear charge is reduced because the electrons "screen" one another.

Pauli Exclusion Principle

The complete wavefunction for the He atom must include the spin functions. For the ground state there are four possibilities:

$$\begin{array}{l} a = 1s(1) \ 1s(2) \ (1) \ (2) \\ b = 1s(1) \ 1s(2) \ (1) \ (2) \\ c = 1s(1) \ 1s(2) \ (1) \ (2) \\ d = 1s(1) \ 1s(2) \ (1) \ (2) \end{array}$$

The Pauli exclusion principle: "Electrons in the same orbital must have opposite spins."

Functions a and d are unsuitable on the basis of the Pauli principle.

At a more fundamental level, systems of electrons (and all other half-integer spin "particles"=Fermi particles) are subject to the restriction that the complete wavefunction must be anti-symmetric for the exchange

of any two indistinguishable (identical) particles (another expression of the Pauli principle). To examine this we define a permutation operator

$$\hat{P}_{i,j} (1, 2, \dots, i, j, \dots) = p (1, 2, \dots, j, i, \dots)$$

As two applications of the permutation operator will give the original function, $p = \pm 1$ (even or odd). For Fermions Only wavefunctions having $p = -1$ are allowed.

Also note that $[\hat{H}, \hat{P}_{i,j}] = 0$. The permutation operator commutes with the Hamiltonian. Therefore, permuting the electrons will not change the energy of the system.

Viewed in terms of the symmetry of the wavefunction, \square_a and \square_d are not suitable as they are symmetric (even, $p = 1$) with respect to permutation

$$\begin{aligned} \hat{P}_{1,2} \square_d &= \hat{P}_{1,2} \square_{1s(1) 1s(2)} (1) (2) \\ &= \square_{1s(2) 1s(1)} (2) (1) = \square_d \end{aligned}$$

Functions \square_b and \square_c are neither even nor odd; they assign distinguishable characteristics to fundamentally indistinguishable particles. These problems can be removed by using the linear combinations

$$\begin{aligned} \square_+ &= \square_b + \square_c \\ &= \square_{1s(1) 1s(2)} [(1) (2) + (2) (1)] \end{aligned}$$

and

$$\begin{aligned} \square_- &= \square_b - \square_c \\ &= \square_{1s(1) 1s(2)} [(1) (2) - (2) (1)] \end{aligned}$$

For these functions it is easily shown that

$$\hat{P}_{1,2}^{\pm} = \pm$$

Hence, only \square_{-} is acceptable from the Pauli principle. Thus this is the ground state of the He atom. Note that we have an symmetric (even) spatial function, and an anti-symmetric (odd) spin function. For other situations we will also find odd spatial functions combined with even spin functions.

Excited States of He.

First, consider the states arising from the configuration $1s2s$.

The wavefunctions $1s(1)2s(2)$ or $1s(2)2s(1)$ are not suitable because they suggest that the electrons are distinguishable. Appropriate linear combinations of these functions are:

$$\begin{aligned} a &= (1s(1)2s(2) + 1s(2)2s(1)) \quad [\text{symmetric}] \\ b &= (1s(1)2s(2) - 1s(2)2s(1)) \quad [\text{anti - symmetric}] \end{aligned}$$

To form complete wavefunctions that are anti-symmetric, we may combine the symmetric spatial function with the anti-symmetric spin function (a singlet state, i.e. $s=0$)-

$$*** \square_{0,0} = a \left(\begin{matrix} (1) \\ (2) \end{matrix} - \begin{matrix} (2) \\ (1) \end{matrix} \right)$$

(the numerical subscripts are s and m_s .)

Alternatively, we can combine the anti-symmetric spatial function with the symmetric spin functions (a triplet state, i.e. $s=1$)-

$$\begin{aligned}
 & \text{***} \quad \psi_{1,1} = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)) \\
 & \text{***} \quad \psi_{1,0} = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)) \\
 & \text{***} \quad \psi_{1,-1} = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2))
 \end{aligned}$$

Next, consider the energies of the singlet and triplet states. For this purpose we can ignore the spin functions as the Hamiltonian we are using does not contain any spin operators.

For the zeroth-order approximation, we ignore the electron-electron repulsion. Both ψ_a and ψ_b have the same zeroth-order energy -

$$E^{(0)} = -4Ry \left(\frac{1}{1} + \frac{1}{4} \right) = -5Ry$$

1st order perturbation theory for the singlet state (ψ_a) gives

$$\left\langle \frac{e^2}{r_{12}} \right\rangle_a = \frac{e^2}{r_{12}} (1s(1)2s(2) + 1s(2)2s(1))^2 d_1 d_2$$

$$\begin{aligned}
 &= \frac{e^2}{r_{12}} (1s(1)2s(2))^2 d_1 d_2 \\
 &+ \frac{e^2}{r_{12}} (1s(2)2s(1))^2 d_1 d_2 \\
 &+ 2 \frac{e^2}{r_{12}} 1s(1)1s(2)2s(1)2s(2) d_1 d_2
 \end{aligned}$$

the first two terms are known as the **Coulomb integral $J_{1s,2s}$** (corresponding to classical Coulombic interaction between the electron distribution $(1s(1)2s(2))^2$ and $(1s(2)2s(1))^2$) and the last term is the **Exchange integral $K_{1s,2s}$** (purely quantum effect, no classical counterpart).

Hence,
$$E_a^{(1)} = J_{1s,2s} + K_{1s,2s} = 0.839\text{Ry} + 0.088\text{Ry}$$

and
$$E_a = -5\text{Ry} + 0.927\text{Ry} = -4.043\text{Ry}$$

The first-order correction to the energy for the triplet state is given by

$$\left\langle \frac{e^2}{r_{12}} \right\rangle_b = \frac{e^2}{r_{12}} (1s(1)2s(2) - 1s(2)2s(1))^2 d_1 d_2$$

expansion of this integral gives

$$E_b^{(1)} = J_{1s,2s} - K_{1s,2s} = 0.751\text{Ry}$$

and
$$E_b = -4.249\text{Ry}$$

Hence the triplet state is at a lower energy than the singlet. (Typically, for a given electron configuration the triplet states will lie below the singlet states)

Now consider excited states involving the 2p orbitals. For the configuration 1s2p there will be six allowed spatial functions. The symmetric spatial functions are given by

$$\begin{aligned} a &= 1s(1)2p_1(2) + 1s(2)2p_1(1) \\ b &= 1s(1)2p_0(2) + 1s(2)2p_0(1) \\ c &= 1s(1)2p_{-1}(2) + 1s(2)2p_{-1}(1) \end{aligned}$$

and the anti-symmetric spatial functions are

$$\begin{aligned} d &= 1s(1)2p_1(2) - 1s(2)2p_1(1) \\ e &= 1s(1)2p_0(2) - 1s(2)2p_0(1) \\ f &= 1s(1)2p_{-1}(2) - 1s(2)2p_{-1}(1) \end{aligned}$$

Again, when these functions are combined with the spin functions we will have singlet and triplet states. The symmetric spatial functions combine with the antisymmetric spin function to yield three "singlet P" functions. The three anti-symmetric spatial functions combine with the three symmetric spin functions to give nine "triplet P" functions.

As in the previous example, the zeroth order energies of the triplet and singlet states are the same (still $-5Ry$)

When the first-order corrections to the energy are calculated, it is found that the Coulomb and exchange integrals for $1s2p$ are not the same as those for $1s2s$ (no surprise as the s and p orbitals have very different shapes). First-order perturbation calculations give

$$\begin{array}{l} E(^1P) = -5Ry + J_{1s2p} + K_{1s2p} \\ E(^3P) = -5Ry + J_{1s2p} - K_{1s2p} \end{array}$$

Note that the $1s2p$ states lie above the $1s2s$ states. This comes from the fact $J_{1s2p} > J_{1s2s}$. The energy now depends on ℓ as well as n (this was not the case for one-electron atoms).

Many-Electron Atoms - Vector Model.

When more than two electrons are involved, the problem of solving the atomic Hamiltonian becomes extremely complex. However, the patterns of energy levels that occur can be understood by considering the angular momentum associated with each state.

The total angular momentum (J) of an isolated system of orbiting electrons is a well defined (conserved) property. However, there are different ways in which the angular momenta associated with each electron may be combined to determine J .

We consider the two most important coupling schemes.

In the following, small letters will be used to indicate the momenta associated with individual electrons, capital letters will be used to represent the properties of the entire atom.

1. LS (Russell-Saunders) coupling.

[This scheme is suitable for light atoms, where spin-orbit coupling is relatively weak]

The individual spins of the electrons are added together to give the total spin angular momentum

$$**** \boxed{\vec{S} = \sum_i \vec{S}_i}$$

(the sum is over the # of electrons in the atom)

The orbital angular momenta of the electrons are added together to give the total orbital angular momentum

$$*** \boxed{\vec{L} = \sum_i \vec{\ell}_i}$$

Then the spin and orbital angular momenta are added to give the conserved total angular momentum

$$*** \boxed{\vec{J} = \vec{L} + \vec{S}}$$

2. j-j coupling.

[This works well for systems where spin-orbit coupling is strong. The disadvantage is that it provides less physical insight than the LS model]

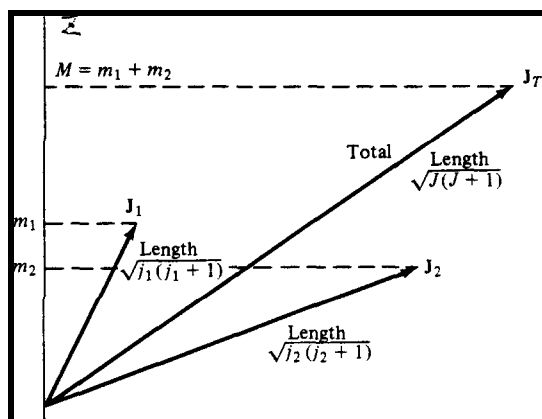
For each electron we combine the spin and orbital angular momenta to give the resultant

$$\boxed{\vec{j}_i = \vec{\ell}_i + \vec{s}_i}$$

the individual j values are then added to obtain the total

$$\boxed{\vec{J} = \sum_i \vec{j}_i}$$

Addition of Two Angular Momentum Vectors



Russell-Saunders Coupling

Consider two electrons:

Orbital angular momentum

$$L = (\ell_1 + \ell_2), (\ell_1 + \ell_2 - 1), (\ell_1 + \ell_2 - 2), \dots, (|\ell_1 - \ell_2|)$$

Spin angular momentum

$$S = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, (|s_1 - s_2|)$$

Total angular momentum

$$J = (L + S), (L + S - 1), (L + S - 2), \dots, (|L - S|)$$

Term Symbols are given as

$$**** \boxed{2S+1 L_J}$$

where $2S+1$ is the spin multiplicity. L is represented by the usual letter notation:

$$\begin{array}{cccccc} L = & 0, & 1, & 2, & 3, & 4 \dots \\ & S, & P & D & F & G \end{array}$$

Consider the configuration $1s2p$

$$\boxed{\ell_1 = 0, \ell_2 = 1; \quad L = 1}$$

$$\boxed{s_1 = 1/2, s_2 = 1/2; \quad S = 1, 0}$$

With $L=1$ and $S=1$, we have $J=2, 1, 0$. The term symbols are given by

Term	$\boxed{{}^3P_0}$	$\boxed{{}^3P_1}$	$\boxed{{}^3P_2}$	
Degeneracy	1	3	5	(total 9=3x3)
$g_J=(2J+1)$				

For $L=1, S=0$ we have $J=1$, and the term symbol is

$$\boxed{{}^1P_1} \quad (g_J=3)$$

Note that the total degeneracy of the $1s2p$ configuration is $1+3+5+3=12$. This is the same as the number of different ways that the two electrons may be arranged in the orbitals

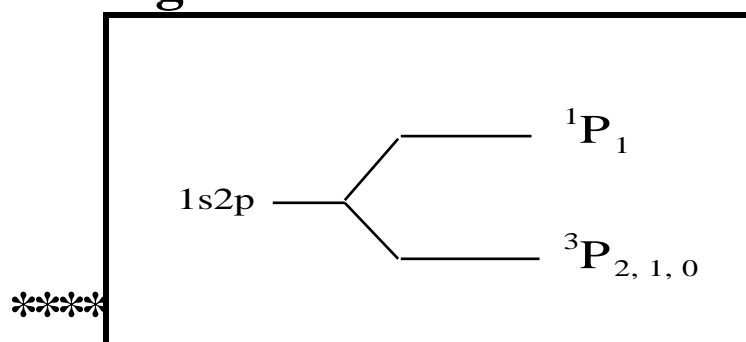
1s	2p ₁	2p ₀	2p ₋₁	M _L	M _S	M _J
		–	–	1	1	2a
	–		–	0	1	1a
	–	–		–1	1	0a
		–	–	1	0	1b
	–		–	0	0	0b
	–	–		–1	0	–1c
		–	–	1	0	1c
	–		–	0	0	0c

-	-	-	-1	0	-1	b
-	-	-	1	-1	0	d
-	-	-	0	-1	-1	a
-	-	-	-1	-1	-2	a

$$a = \boxed{{}^3P_2} \quad b = \boxed{{}^3P_1} \quad c = \boxed{{}^1P_1} \quad d = \boxed{{}^3P_0}$$

Care is needed in determining term symbols from the above, which is a table of micro states. The quantum numbers M_L and M_S are physically significant only for the micro-states corresponding to the maximum and minimum values of M_J . In this example, we can tell from the first line of the table that we have a triplet P state. This accounts for 9 micro-states ($J=2, M_J=2, 1, 0, -1, -2$; $J=1, M_J=1, 0, -1$; $J=0, M_J=0$). The remaining $J=1$ micro-states must then belong to the singlet P.

Finally, note that the singlet and triplet states will have different energies



Next, consider the more complex configuration $2p3p$ (two p electrons in different sets of p orbitals).

The various ways that the electrons may be assigned to the p-orbitals and spin states gives $6 \times 6 = 36$ micro-states. We do not need to develop a table of micro-states to determine the term symbols. We only need to examine the ways in which the angular momentum quantum numbers may be combined

$$\begin{array}{l} \ell_1 = 1, \ell_2 = 1; \quad L = 2, 1, 0 \\ s_1 = 1/2, s_2 = 1/2; \quad S = 1, 0 \end{array}$$

J values and term symbols, triplet states

For $L=2, S=1, J=3, 2, 1$

Terms -	3D_3	3D_2	3D_1
degeneracies	7	5	3

For $L=1, S=1, J=2, 1, 0$

Terms -	3P_2	3P_1	3P_0
degeneracies	5	3	1

For $L=0, S=1, J=1$

Term-	3S_1
degeneracy	3

J values and term symbols, singlet states

For $L=2, S=0, J=2$. Term 1D_2 , degeneracy = 5

For $L=1, S=0, J=1$. Term 1P_1 , degeneracy = 3

For $L=0, S=0, J=0$. Term $\boxed{^1S_0}$, degeneracy = 1

Total degeneracy of triplet and singlet states

$$7+5+3 +5+3+1 +3 +5 +3 +1 = 36$$

Equivalent electrons

If the electrons are assigned to the same p-orbitals, the Pauli Exclusion principle must be considered. There are then fewer than 36 allowed sub-states.

Consider the example presented by the ground state of atomic carbon.

Configuration $1s^2 2s^2 2p^2$

To begin, note that closed shells and closed subshells have zero orbital and spin angular momentum. Hence for $1s^2$ and $2s^2$, $L=S=0$.

We need only examine $2p^2$ (two electrons in the same p orbitals, or equivalent p electrons) to determine the term symbols. The micro-state table for this is:

$2p_1$	$2p_0$	$2p_{-1}$	M_L	M_S	M_J
	–	–	2	0	2a
–		–	0	0	0e
–	–		–2	0	–2a
		–	1	1	2b

	–		0	1	1b
–			–1	1	0b
		–	1	0	1a
	–		0	0	0a
–			–1	0	–1a
		–	1	0	1c
	–		0	0	0c
–			–1	0	–1c
		–	1	–1	0d
	–		0	–1	–1b
–			–1	–1	–2b

$a = \boxed{^1D_2}$. This is the only possible assignment for this micro state. We then eliminate from the table five micro states associated with this term.

Once this has been done, identify the highest remaining M_J value. In this example it is $M_J=2$. With $M_L=1$ and $M_S=1$ this must be the $J=2$ component of $\boxed{^3P_2}$.

Therefore, we must also have $\boxed{^3P_1}$ and $\boxed{^3P_0}$. These terms account for 9 of the micro states (b, c, and d).

We are left with a single state, which must be $\boxed{^1S_0}$

Finally, we see that the term symbols arising from the ground state of atomic carbon are



In general, if we are dealing with a shell that is more than half-filled, the term symbols can be derived by treating the holes as if they were the only electrons

thus p^2 p^4 , d^6 d^4 , d^9 d^1 , etc.

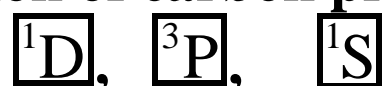
Determination of the ground state term symbol(What is the ground state out of all possible terms?) -

Hund's Rules.

1. The ground state of the lowest energy configuration will be a state of maximum spin multiplicity

2. If several states have the maximum spin multiplicity, the ground state will be the state with the highest value of L

For example, we have seen that the lowest energy configuration of carbon produces the states



Hund's rules predict that ${}^3\text{P}$ is the ground state.

The ground state terms can often be determined by assigning electrons to the orbitals in a manner that will yield the maximum orbital angular momentum for the maximum spin. To do this, it is sufficient to ensure that the z-components of the angular momenta are maximized. Thus for two equivalent p electrons.

$$\begin{array}{cccccc}
 p_1 & p_0 & p_{-1} & M_L & & M_S \\
 & & - & 1 & 1 &
 \end{array}$$

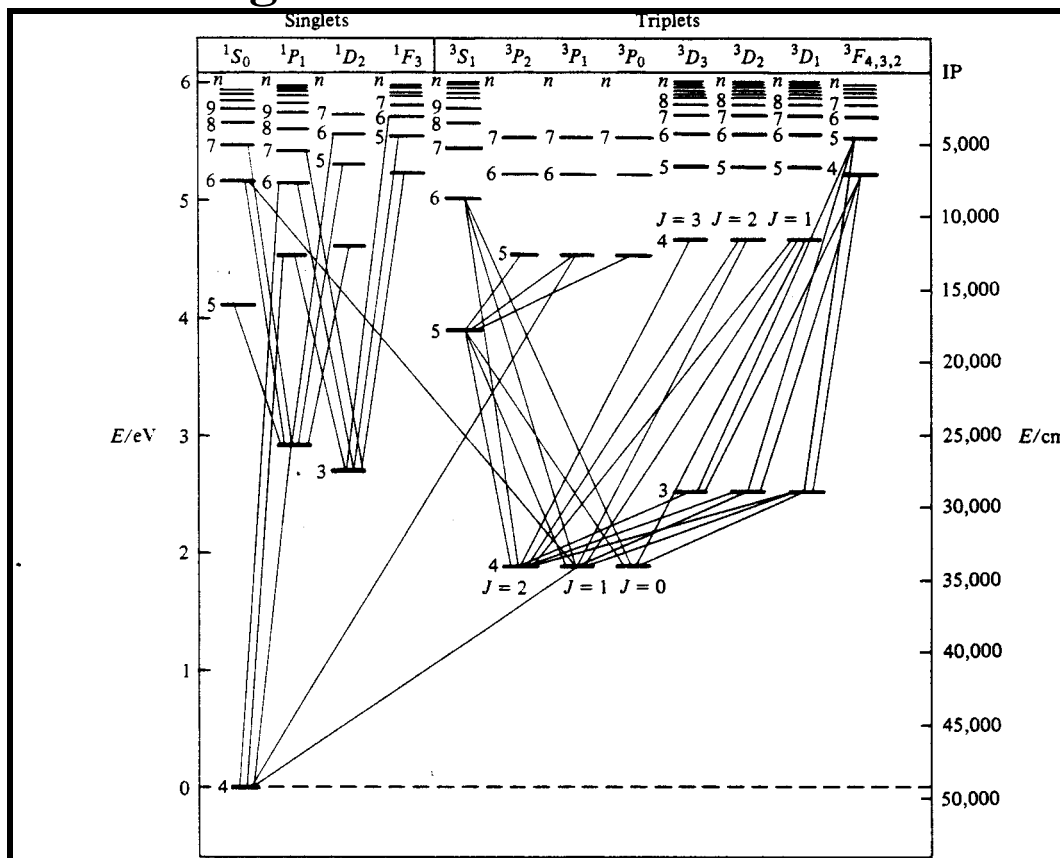
This arrangement gives $L=M_L=1$, $S=1$:- $\boxed{^3P}$

For two non-equivalent p electrons, npmp

$$\begin{array}{cccccc}
 mp_1 & np_1 & & M_L & & M_S \\
 & & & 2 & 1 &
 \end{array}$$

Here the ground state is $\boxed{^3D}$.

Trem Diagram of Ca



Spin-Orbit coupling

So far, the Hamiltonian we have considered does not have terms that couple the spin and spatial coordinates. Thus, at this level of approximation the spin components of a multiplet all have the same energy. e.g. for a ^3P state the $^3\text{P}_2$, $^3\text{P}_1$, and $^3\text{P}_0$ components would be degenerate. This degeneracy is removed by spin-orbit coupling. The spin-orbit interaction is given by-

$$\hat{H}_{\text{s.o.}} = hcA\hat{L} \hat{S}$$

where A is the spin-orbit coupling constant. For evaluation of the energies associated with spin-orbit coupling, it is convenient to expand the operator in the following way :-

$$\hat{J} = \hat{L} + \hat{S}$$

therefore,
$$\hat{J}^2 = (\hat{L} + \hat{S})^2 = \hat{L}^2 + 2\hat{L} \hat{S} + \hat{S}^2$$

or
$$\hat{L} \hat{S} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

so that

$$\hat{H}_{\text{s.o.}} = \frac{hcA}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

with the operator in this form the spin-orbit interaction energy can be calculated from first order perturbation theory:

$$\frac{E_{\text{s.o.}}}{hc} = \frac{A}{2} (J(J+1) - L(L+1) - S(S+1))$$

Note that for a given term L and S are constant. The intervals between the multiplet states are governed by J .

For a triplet P state
$$\frac{E_{\text{s.o.}}}{hc} = \frac{A}{2} (J(J+1) - 4)$$

$$E_{J+1} - E_J = A(J+1) \quad (\text{Landé interval rule}).$$

Atomic Spectra - Selection Rules

1. The most intense transitions are associated with "jumps" made by a single electron

e.g. $1s^2 \quad 1s2p$

(Transitions involving two or more electrons can occur, but they are very low probability events).

2. There is no restriction on the change in the principal quantum number, n , but the intensity decreases as $|n|$ increases.

3. For light atoms $S=0$. This rule is often broken due to spin-orbit coupling.

4. $L=\pm 1$. S P, P D, etc.

5. $J = 0, \pm 1$

6. Transitions between terms arising from the same configuration do not occur.

For examples of the application of these selection rules see Noggle, Chapter 12, figs 12.14 and 12.15.

Magnetic Moments

Classically, an orbiting electron is equivalent to a circulating current. It will generate a magnetic dipole moment given by

$$\vec{\mu}_L = \frac{e}{2mc} \vec{L}$$

In the quantum mechanics version of this equation we cannot define the direction of \vec{L} , but we do know its magnitude and projection along the z-axis. Hence,

$$\mu_{L_z} = \frac{e\hbar}{2mc} M_L = \mu_B M_L \quad *$$

and

$$|\vec{\mu}_L| = \mu_B \sqrt{L(L+1)}$$

where the collection of constants μ_B is known as the Bohr magneton (9.274×10^{-21} erg/gauss).

The spin magnetic dipole is given by similar equations

$$|\bar{\mu}_s| = g\mu_B\sqrt{S(S+1)}$$

where $g=2.002322$ is an intrinsic constant associated with the spin moment.

The magnetic dipole for an electron with both spin and orbital angular momentum is formally determined by the vector sum

$$\bar{\mu}_J = \bar{\mu}_L + \bar{\mu}_S$$

a quantum treatment yields

$$|\bar{\mu}_J| = g_L\mu_B\sqrt{J(J+1)}, \quad \mu_{J_z} = g_L\mu_B M_J$$

where

$$g_L = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

is the Landé g factor

We now have the basic information required to predict the effects of an externally applied magnetic field on various atomic states.

Classically, the energy of interaction between a magnetic dipole and an applied field is given by

$$E = -\bar{\mu} \cdot \bar{B}$$

Consider a uniform field directed along the z -axis:

$$\bar{B} = \bar{k}B_0$$

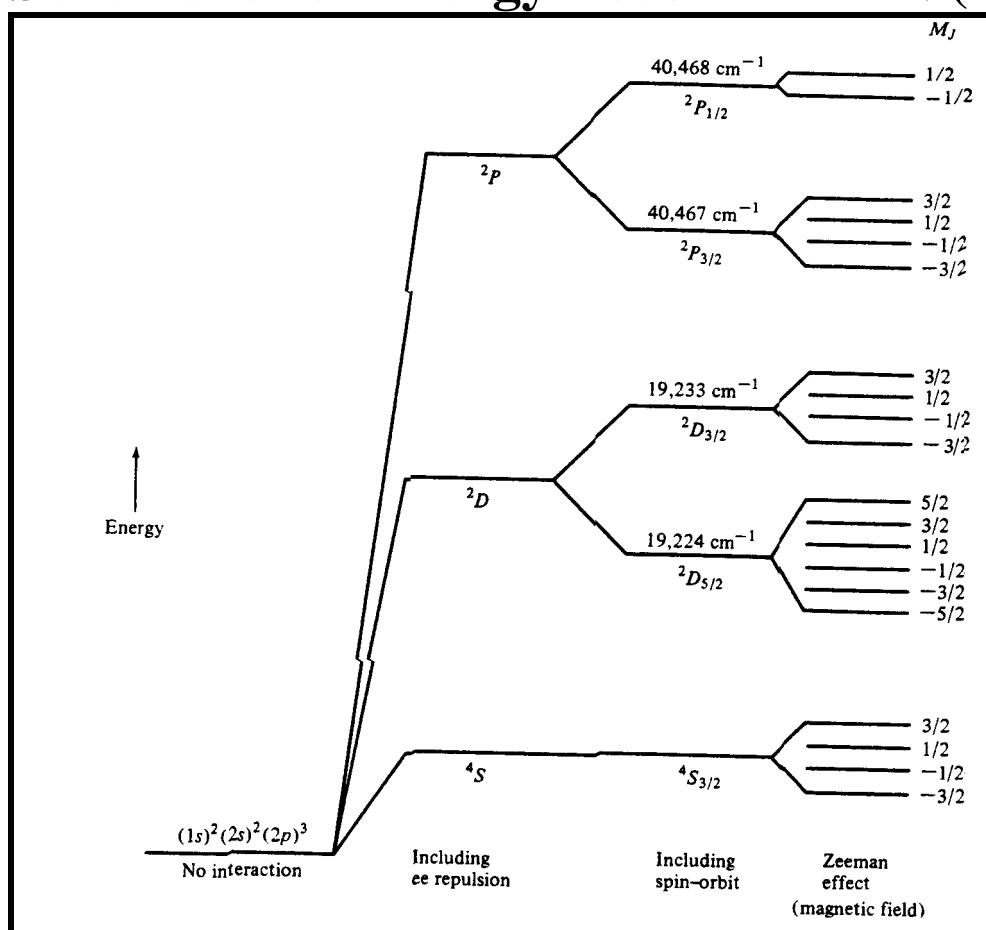
the interaction energy will be determined by the z-axis projection of the atomic dipole

$$E = -M_J g_L \mu_B B_0$$

This result predicts that J states will be split into $2J+1$ equally spaced components by a magnetic field.

The number of components can be used to find J , while the separations at a given field strength can provide g_L .

Schematics of Energy Levels -- Ex. N $(1s)^2(2s)^2(2p)^3$



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