Chapter 12

Identical Particles

12.1 Theoretical ideas

We now apply these quantum mechanical methods we have developed to multi-electron atoms.

We will create a model to handle these atoms that follows from the one-electron case considered earlier. These systems are very complex and all the results that we derive will be approximations.

If we consider an atom or system of N particles, the wave function

$$\begin{aligned}\psi(1,2,3,4,.....,N,t) &= \psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \vec{r}_3 s_3, \vec{r}_4 s_4, ..., \vec{r}_N s_N, t) \\ &= \langle 1,2,3,4,.....,N,t \mid \psi \rangle \qquad (12.1)\end{aligned}$$

where $\vec{r}_j s_j =$ (radius vector,spin) of the j^{th} particle

describing the system will be a function of $3N$ spatial coordinates, time and all of the particle spin variables. The $3N$ spatial coordinates form a multi-dimensional configuration space.

The Hamiltonian of the system is given by

$$\hat{H} = \hat{T} + \hat{V} \tag{12.2}$$

where

$$\hat{T} = \sum_{j=1}^{N} \hat{T}_j = -\sum_{j=1}^{N} \left(\frac{\hbar^2}{2m_j} \nabla_j^2 \right) \text{ and } \hat{V} = \hat{V}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) \tag{12.3}$$

The time-dependent Schrodinger equation is

$$\hat{H}\psi(1,2,3,4,....., N,t) = i\hbar \frac{\partial}{\partial t} \psi(1,2,3,4,....., N,t) \tag{12.4}$$

The probability density is defined as

$$\rho(1,2,3,4,....., N,t) = \psi^*(1,2,3,4,....., N,t)\psi(1,2,3,4,....., N,t) \tag{12.5}$$

so that

$\rho(1,2,3,4,....., N,t) d^3\vec{r}_1 d^3\vec{r}_2 ..... d^3\vec{r}_N =$ probability of finding particle 1 at $\vec{r}_1$ in $d^3\vec{r}_1$, and particle 2 at $\vec{r}_2$ in $d^3\vec{r}_2$, ..., and particle N at $\vec{r}_N$ in $d^3\vec{r}_N$ all at time time t

We assume that the N-particle wave function is normalized.

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The energy eigenstates or stationary states are solutions of

$$\hat{H}\psi_E(1,2,3,4,.....,N) = E\psi_E(1,2,3,4,.....,N) \tag{12.6}$$

which implies the time dependence

$$\psi(1,2,3,4,.....,N,t) = \psi_E(1,2,3,4,.....,N)e^{-i\frac{E}{\hbar}t} \tag{12.7}$$

where E is the energy of the system.

When we consider an $N-$electron atom, the system really has $N+1$ particles (we must include the nucleus). However, the nucleus is so much more massive than the electrons that we can make the approximation that it has infinite mass and is fixed.

We put the nucleus of charge Ze at the origin and define

$\vec{r}_j =$ position vector of the j^{th} electron

$r_{jk} = |\vec{r}_j - \vec{r}_k| =$ separation between the j^{th} and k^{th} electrons

The potential energy is

$$V(1,2,3,.....,N) = -\sum_{j=1}^{N}\frac{Ze^2}{r_j} + \sum_{j=1}^{N}\sum_{i>j}^{N}\frac{e^2}{r_{ij}} \qquad (12.8)$$

$$= \text{Coulomb energy between nucleus and electrons}$$

$$+ \text{Coulomb energy between electrons}$$

We will assume no spin-dependence or time dependence in the potential energy.

All electrons in the atom are considered to be *identical* or *indistinguishable*. This means that there are no interactions that can, in any way, distinguish them from each other.

Alternatively, we can say that, if we interchange the coordinates and spins of two particles, then it is not possible to determine via any physical measurement that any change was made in the system.

This says that all measurable quantities or the operators representing them must remain unchanged by the interchange of indistinguishable particles.

In particular, the Hamiltonian must remain unchanged, i.e., we must have

$$\hat{H}(1,2,3,4,...,j,k,...,N) = \hat{H}(1,2,3,4,...,k,j,...,N) \qquad (12.9)$$

This property of $\hat{H}$ is called *exchange symmetry.* Operators that have this property are *symmetric* functions of their indices $1, 2, 3, 4, ..., N$ and they are called *symmetric* operators.

Now, every symmetry of a physical system must be represented by an operator that commutes with $\hat{H}$. In this case, we introduce the *particle interchange* or *permutation operator* $\hat{P}_{ij}$ such that

$$\begin{aligned}\hat{P}_{ij}\psi(1,2,3,.....,i,j,.....,N) &= \langle 1,2,3,.....,i,j,.....,N|\,\hat{P}_{ij}\,|\psi\rangle \\ &= \langle 1,2,3,.....,j,i,.....,N\,|\,\psi\rangle = \psi(1,2,3,.....,j,i,.....,N)\end{aligned}$$

In words, we say

$\hat{P}_{ij}\psi(1,2,3,.....,i,j,.....,N)$ gives the amplitude for
finding the j^{th} particle at $\vec{r}_i$ with spin s_i
and i^{th} particle at $\vec{r}_j$ with spin s_j

Now, the transformed Hamiltonian operator is given by

$$\hat{H}' = \hat{P}_{ij}\hat{H}\hat{P}_{ij}^{-1} = \hat{H} \text{ (by assumption)} \tag{12.10}$$

This implies that

$$\hat{P}_{ij}\hat{H} = \hat{H}\hat{P}_{ij} \rightarrow \left[\hat{H}, \hat{P}_{ij}\right] = 0 \tag{12.11}$$

as we expected. The same result holds for all symmetric operators.

Now, suppose that the state vector $|\psi\rangle$ is an eigenvector of the symmetric, $N-$particle $\hat{H}$ with energy E. We then have

$$\hat{H}|\psi\rangle = E|\psi\rangle \tag{12.12}$$

$$\hat{H}\hat{P}_{ij}|\psi\rangle = \hat{P}_{ij}\hat{H}|\psi\rangle = E\hat{P}_{ij}|\psi\rangle \tag{12.13}$$

which says that

$$\hat{P}_{ij}|\psi\rangle \text{ is also an eigenvector of } \hat{H} \text{ with the same energy} \tag{12.14}$$

This holds for any pair (i,j). So $\hat{H}$ and $\hat{P}_{ij}$ share a common eigenbasis as expected. This phenomenon is called *exchange degeneracy.*

For simplicity, we assume that $N = 2$. We then have

$$\hat{H}(1,2) \text{ and } \psi(1,2) \tag{12.15}$$

and

$$\left[\hat{H}, \hat{P}_{12}\right] = 0 \tag{12.16}$$

What are the simultaneous eigenfunctions? We have

$$\hat{P}_{12}\psi(1,2) = \psi(2,1)$$

$$\hat{P}_{12}^2\psi(1,2) = \hat{P}_{12}\psi(2,1) = \psi(1,2)$$

which says that

$$\hat{P}_{12}^2 = \hat{I} \tag{12.17}$$

and that $\hat{P}_{12}$ has eigenvalues ± 1. Now if

$$\hat{H}\psi(1,2) = E\psi(1,2) \tag{12.18}$$

then

$$\hat{H}\psi(2,1) = E\psi(2,1) \tag{12.19}$$

and these two state functions are degenerate. Then, we can write

$$\psi_S(1,2) = \psi(1,2) + \psi(2,1) \rightarrow \text{ symmetric wave function}$$
$$\psi_A(1,2) = \psi(1,2) - \psi(2,1) \rightarrow \text{ antisymmetric wave function}$$

which are the simultaneous eigenfunctions with

$$\hat{H}\psi_S = E\psi_S \qquad \hat{H}\psi_A = E\psi_A \tag{12.20}$$

$$\hat{P}_{12}\psi_S = +\psi_S \qquad \hat{P}_{12}\psi_A = -\psi_A \tag{12.21}$$

It is an *experimental fact* that the behavior of wave functions under pairwise particle interchange depends only on the kind of particles involved, in particular on their *spin*.

All known particles divide themselves in to *two classes*:

1. Bosons → particles with integer spin, $s = 0, 1, 2, 3, 4, ...$
2. Fermions → particles with half-integer spin, $s = 1/2, 3/2, 5/2, ...$

and

1. Fermions have antisymmetric wave functions under particle interchange
2. Bosons have symmetric wave functions under particle interchange

This relationship between spin and wave function symmetry cannot be proved in non-relativistic quantum mechanics. It can, however, be proved if we add relativity and construct the relativistic waves equations for bosons and fermions.

As we shall see, this symmetry/antisymmetry connection of spin and wave functions will generalize to more complex systems with more particles.

Before proceeding to study real atoms with N electrons, let us see what we can learn from a one-dimensional systems containing either two identical bosons or two identical fermions.

The general Hamiltonian for a one-dimensional two-particle system is

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{U}(x_1 - x_2) \tag{12.22}$$

$$\hat{H}_1 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} + \hat{V}(x_1) \tag{12.23}$$

$$\hat{H}_2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + \hat{V}(x_2) \tag{12.24}$$

where

$$\hat{U}(x_1 - x_2) = \text{ the particle - particle interaction} \tag{12.25}$$

We will assume that $\hat{U}(x_1 - x_2)$ is small enough that we can apply perturbation theory. We then use direct product states and write

$$\hat{H} = \hat{H}_0 + \hat{U} \tag{12.26}$$

$$\hat{H}_1\psi_{n_1}^{(0)}(x_1) = E_{n_1}^{(0)}\psi_{n_1}^{(0)}(x_1) \tag{12.27}$$

$$\hat{H}_2\psi_{n_2}^{(0)}(x_2) = E_{n_2}^{(0)}\psi_{n_2}^{(0)}(x_2) \tag{12.28}$$

$$\begin{aligned}\hat{H}\psi_{n_1n_2}^{(0)}(x_1,x_2) &= \hat{H}_0\psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2)\\ &= (\hat{H}_1 + \hat{H}_2)\psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2)\\ &= (E_{n_1}^{(0)} + E_{n_2}^{(0)})\psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2)\\ &= E_{n_1n_2}^{(0)}\psi_{n_1n_2}^{(0)}(x_1,x_2)\end{aligned} \tag{12.29}$$

We will construct the unperturbed(zero order) eigenfunctions and energies from these direct product states.

For the moment, we will also ignore spin.

The simple direct product states will not work for a description of the two particle system since the eigenfunctions of $\hat{H}_0$ must be either symmetric or antisymmetric under particle interchange.

The correct choice is ψ_S or ψ_A where

$$\psi^{(0)S}_{n_1 n_2} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) + \psi^{(0)}_{n_1}(x_2)\psi^{(0)}_{n_2}(x_1)\right] \tag{12.30}$$

$$\psi^{(0)A}_{n_1 n_2} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) - \psi^{(0)}_{n_1}(x_2)\psi^{(0)}_{n_2}(x_1)\right] \tag{12.31}$$

Both of these states have energy $E^{(0)}_{n_1 n_2} = E^{(0)}_{n_1} + E^{(0)}_{n_2}$.

12.2 Bosons with Spin = 0

We assume that $s_1 = s_2 = 0$. This says that there are no new degrees of freedom and hence no reason to change the wave functions.

Indistinguishable bosons of spin = 0 require a symmetric wave function and thus we choose as the properly *symmetrized* zero-order wave functions

$$\psi^{(0)S}_{n_1 n_2} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) + \psi^{(0)}_{n_1}(x_2)\psi^{(0)}_{n_2}(x_1)\right] \tag{12.32}$$

The ground state corresponds to $n_1 = n_2 = 1$ or

$$\psi^{(0)S}_{11} = \psi^{(0)}_{1}(x_1)\psi^{(0)}_{1}(x_2) \tag{12.33}$$

In perturbation theory, the first order energy is then

$$\begin{aligned} E_{11} &= 2E^{(0)}_1 + \left\langle \psi^{(0)S}_{11} \middle| \hat{U}(x_1 - x_2) \middle| \psi^{(0)S}_{11} \right\rangle \\ &= 2E^{(0)}_1 \\ &\quad + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx_1 dx_2 dx'_1 dx'_2 \\ &\quad \times \left\langle \psi^{(0)S}_{11} \middle| \left(\left| \psi^{(0)}_{1}(x_2) \right\rangle \left| \psi^{(0)}_{1}(x_1) \right\rangle \left\langle \psi^{(0)}_{1}(x_1) \right| \left\langle \psi^{(0)}_{1}(x_2) \right| \right) \right. \\ &\quad \left. \times \hat{U}(x_1 - x_2) \left(\left| \psi^{(0)}_{1}(x'_1) \right\rangle \left| \psi^{(0)}_{1}(x'_2) \right\rangle \left\langle \psi^{(0)}_{1}(x'_1) \right| \left\langle \psi^{(0)}_{1}(x'_2) \right| \right) \middle| \psi^{(0)S}_{11} \right\rangle \end{aligned} \tag{12.34}$$

Now

$$\left\langle \psi_1^{(0)}(x_1) \right| \left\langle \psi_1^{(0)}(x_2) \right| \hat{U}(x_1 - x_2) \left| \psi_1^{(0)}(x_1') \right\rangle \left| \psi_1^{(0)}(x_2') \right\rangle$$
$$= U(x_1 - x_2)\delta(x_1 - x_1')\delta(x_2 - x_2') \tag{12.35}$$

which implies that

$$E_{11} = 2E_1^{(0)} + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx_1 dx_2 \left\langle \psi_{11}^{(0)S} \right| \left(\left| \psi_1^{(0)}(x_2) \right\rangle \left| \psi_1^{(0)}(x_1) \right\rangle \right)$$
$$\times U(x_1 - x_2) \left(\left\langle \psi_1^{(0)}(x_1) \right| \left\langle \psi_1^{(0)}(x_2) \right| \right) \left| \psi_{11}^{(0)S} \right\rangle \tag{12.36}$$

or

$$E_{11} = 2E_1^{(0)} + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx_1 dx_2 \left| \psi_1^{(0)}(x_1) \right|^2 U(x_1 - x_2) \left| \psi_1^{(0)}(x_2) \right|^2 \tag{12.37}$$

For later use we define the general direct integral

$$J_{n_1 n_2} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx_1 dx_2 \left| \psi_{n_1}^{(0)}(x_1) \right|^2 U(x_1 - x_2) \left| \psi_{n_2}^{(0)}(x_2) \right|^2 \tag{12.38}$$

In this case, we have

$$E_{11} = 2E_1^{(0)} + J_{11} \tag{12.39}$$

Now we look at the first excited state of this system. We assume that for the zero-order states, the first excited state corresponds to $n_1 = 1$ and $n_2 = 2$. Therefore, the zero-order symmetric wave function for the first excited state is

$$\psi_{12}^{(0)S} = \frac{1}{\sqrt{2}}\left[\psi_1^{(0)}(x_1)\psi_2^{(0)}(x_2) + \psi_1^{(0)}(x_2)\psi_2^{(0)}(x_1)\right] \tag{12.40}$$

and the first order energy is

$$E_{12} = E_1^{(0)} + E_2^{(0)} + \left\langle \psi_{12}^{(0)S} \middle| \hat{U}(x_1 - x_2) \middle| \psi_{12}^{(0)S} \right\rangle \tag{12.41}$$

Using the same procedure as before we get

$$E_{12} = E_1^{(0)} + E_2^{(0)} + J_{12} + K_{12} \tag{12.42}$$

where

$$K_{n_1 n_2} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx_1 dx_2 \psi_{n_1}^{(0)*}(x_1)\psi_{n_2}^{(0)}(x_1)U(x_1 - x_2)\psi_{n_2}^{(0)*}(x_2)\psi_{n_1}^{(0)}(x_2) \tag{12.43}$$

is called the *exchange integral.*

Now let us look at a possible physical meaning of these direct and exchange integrals.

We define

$$\left|\psi_{n_1}^{(0)}(x_1)\right|^2 = \rho_1 = \text{ probability density for particle 1 in state } n_1 \tag{12.44}$$

and

$$\left|\psi_{n_2}^{(0)}(x_2)\right|^2 = \rho_2 = \text{ probability density for particle 2 in state } n_2 \tag{12.45}$$

Therefore, the direct integrand takes the form

$$\rho_1 \rho_2 U(r_{12}) \tag{12.46}$$

To see what this means let

$$U(r_{12}) = \frac{e^2}{r_{12}} \tag{12.47}$$

which corresponds to a repulsive Coulomb potential. The direct integral is then

$$\int\int \frac{(e\rho_1)(e\rho_2)}{r_{12}}\, dx_1\, dx_2 \tag{12.48}$$

This represents the total energy of two classical charge distributions interacting with the potential energy $U(r_{12})$.

The exchange integral, however, has no such classical counterpart. It is the result of symmetrizing the wave function and therefore arises because of the invariance of $\hat{H}$ with respect to particle interchange.

The energy level diagram to first order might look like Figure 12.1 below.

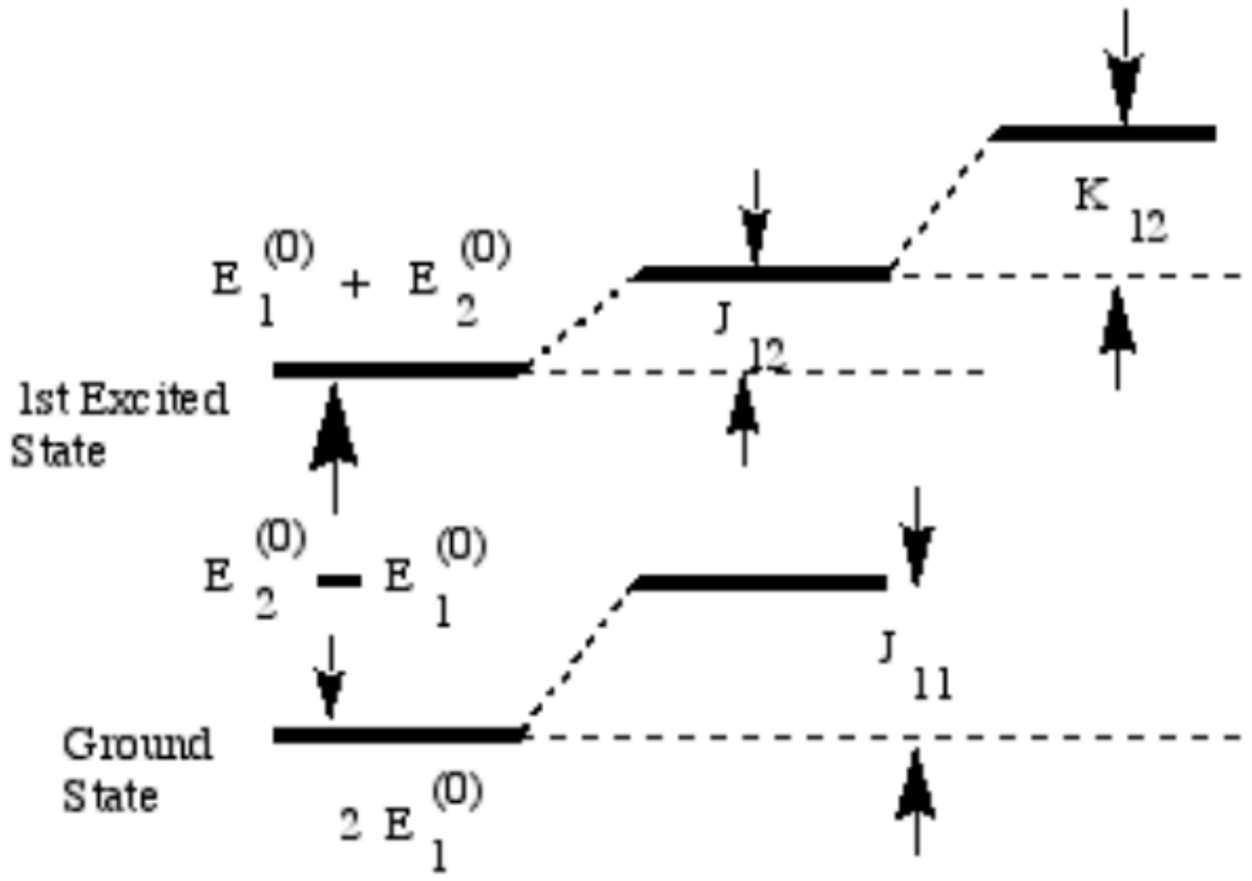


Figure 12.1: Typical Boson Energy Level Diagram

The more interesting case is a two spin = 1/2 fermion system (since electrons are spin = 1/2 fermions).

12.3 Spin = 1/2 Fermions

The particles now have internal degrees of freedom. The single particle state vectors must now have both spatial and spin parts

$$|space\rangle\,|spin\rangle \tag{12.49}$$

For example,

$$\left|\psi_{n_1}^{(0)}\right\rangle|+\rangle_1 \tag{12.50}$$

presents a fermion in the $\psi_{n_1}^{(0)}$ spatial state with spin *up*.

We write the corresponding wave function as

$$\left\langle x_1 \,\middle|\, \psi_{n_1}^{(0)}\right\rangle|+\rangle_1 = \psi_{n_1}^{(0)}(x_1)\alpha(1) \tag{12.51}$$

and so on, where we define the labels $\alpha(j) = |+\rangle_j$ and $\beta(j) = |-\rangle_j$.

We must choose the antisymmetric combination for the zero-order wave functions. We have 4 possible direct product states given n_1 and n_2, i.e.,

$$\psi_1(1,2) = \psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2)\alpha(1)\alpha(2) \tag{12.52}$$

$$\psi_2(1,2) = \psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2)\alpha(1)\beta(2) \tag{12.53}$$

$$\psi_3(1,2) = \psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2)\beta(1)\alpha(2) \tag{12.54}$$

$$\psi_4(1,2) = \psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2)\beta(1)\beta(2) \tag{12.55}$$

These are not antisymmetric, however. A useful operator allows us to construct antisymmetric states. Consider the operator

$$\hat{R} = \frac{1}{\sqrt{2}}(1 - \hat{P}_{12}) \tag{12.56}$$

Now for any function $A(1,2)$ we have

$$\hat{R}A(1,2) = \frac{1}{\sqrt{2}}(1 - \hat{P}_{12})A(1,2) = \frac{1}{\sqrt{2}}\left[A(1,2) - A(2,1)\right] \tag{12.57}$$

which is antisymmetric. The factor $1/\sqrt{(2)}$ keeps the state normalized. We now use $\hat{R}$ to construct four antisymmetric states from the four direct product states (12.52).

$$\begin{aligned}\psi^{(0)}_{n_1 n_2 ++}(x_1, x_2) &= \frac{1}{\sqrt{2}}(1 - \hat{P}_{12})\psi_1(1,2) \\ &= \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2)\alpha(1)\alpha(2) - \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\alpha(1)\alpha(2)\right]\end{aligned} \tag{12.58}$$

$$\begin{aligned}\psi^{(0)}_{n_1 n_2 +-}(x_1, x_2) &= \frac{1}{\sqrt{2}}(1 - \hat{P}_{12})\psi_2(1,2) \\ &= \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2)\alpha(1)\beta(2) - \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\alpha(2)\beta(1)\right]\end{aligned} \tag{12.59}$$

$$\psi^{(0)}_{n_1 n_2 -+}(x_1, x_2) = \frac{1}{\sqrt{2}}(1 - \hat{P}_{12})\psi_3(1,2)$$

$$= \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2)\beta(1)\alpha(2) - \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\alpha(1)\beta(2)\right] \quad (12.60)$$

$$\psi^{(0)}_{n_1 n_2 --}(x_1, x_2) = \frac{1}{\sqrt{2}}(1 - \hat{P}_{12})\psi_4(1,2)$$

$$= \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2)\beta(1)\beta(2) - \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\beta(1)\beta(2)\right] \quad (12.61)$$

where the subscripts imply

+ + means both spins *up*

+ - or - + means one spin *up* and one spin *down*

- - means both spins *down*

Each of these wave functions is antisymmetric and each is an eigenfunction of $\hat{H}_0$ (since $\hat{H}_0$ does not contain any spin dependent terms) with the same energy. This implies that, at this point, we have a 4-fold degenerate zero-order system with energy $E^{(0)}_{n_1} + E^{(0)}_{n_2}$.

We could use these states as the zero-order wave function to start perturbation theory. It would be like doing the spin-orbit calculation using the $|\ell s m_\ell m_s\rangle$ basis, rather than the $|\ell s j m_j\rangle$ basis where $\hat{H}_{so}$ is diagonal. It is always important to choose zero-order wave functions, if it is not to difficult to do, that incorporate as much of the symmetry of the system as possible. In other words, choose zero-order wave functions that are simultaneous eigenstates of the maximal set of commuting observables. This will hopefully produce a diagonal perturbation matrix or at least so many zeros that it is easy to diagonalize the rest of the matrix.

In this case, we not only have $[\hat{H}, \hat{P}_{12}] = 0$ which told us to choose antisymmetric zero-order states, but we also have $[\hat{H}, \vec{S}_{op}^{\,2}] = 0$ and $[\hat{H}, \hat{S}_z] = 0$ where

$\vec{S}_{op} = \vec{S}_{1,op} + \vec{S}_{2,op} =$ the total spin angular momentum

$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z} =$ the z - component of the total spin angular momentum

Therefore we should choose antisymmetric state functions which are also eigen-functions of $\hat{H}_0$, $\vec{S}_{op}^{\,2}$ and $\hat{S}_z$ as our zero-order states.

From our earlier work we know that the possible values of the total spin are $S = 0, 1$ and the state vectors that are eigenstates of $\vec{S}_{op}^{\,2}$ and $\hat{S}_z$ are

$$|1,1\rangle = \alpha(1)\alpha(2) = \chi_{11} \tag{12.62}$$

$$|1,0\rangle = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \alpha(2)\beta(1)\right) = \chi_{10} \tag{12.63}$$

$$|1,-1\rangle = \beta(1)\beta(2) = \chi_{1,-1} \tag{12.64}$$

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) = \chi_{00} \tag{12.65}$$

Notice that the $\chi_{1,m=\pm1,0}$ are symmetric under $\hat{P}_{12}$ and χ_{00} is antisymmetric.

Therefore, we will maintain overall antisymmetry by writing the wave functions as products of spatial wave function and spin functions such that the spatial function is symmetric when combined with χ_{00} and the spatial function is antisymmetric when combined with $\chi_{1,m=\pm1,0}$.

The symmetric spatial function is

$$\psi^{(0)S}_{n_1 n_2} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) + \psi^{(0)}_{n_1}(x_2)\psi^{(0)}_{n_2}(x_1)\right] \tag{12.66}$$

and the antisymmetric spatial function is

$$\psi^{(0)A}_{n_1 n_2} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) - \psi^{(0)}_{n_1}(x_2)\psi^{(0)}_{n_2}(x_1)\right] \tag{12.67}$$

The four zero-order wave functions, which are now eigenfunctions of $\hat{P}_{12}$, $\hat{H}_0$, $\vec{S}^2_{op}$ and $\hat{S}_z$ are then

$$\psi^{(0)}_{n_1 n_2 00} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) + \psi^{(0)}_{n_1}(x_2)\psi^{(0)}_{n_2}(x_1)\right]\chi_{00} \tag{12.68}$$

$$\psi^{(0)}_{n_1 n_2 1 m_s} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) - \psi^{(0)}_{n_1}(x_2)\psi^{(0)}_{n_2}(x_1)\right]\chi_{1 m_s} \quad m_s = \pm 1, 0 \tag{12.69}$$

Notice that if we have identical spatial states, i.e., $n_1 = n_2$, the $S = 1$ states vanish identically. This says that two fermions in an $S = 1$ spin state cannot be in the same spatial state(the wavefunction vanishes). This is the first example of a general principle we will discuss later called the *Pauli Exclusion Principle.*

An alternative way to find these zero-order wave functions is to go back to first principles and use CG coefficients. For example

$$\psi^{(0)}_{n_1 n_2 s m_s} = \sum_{\substack{m_{s_1}, m_{s_2} \\ m_{s_1} + m_{s_2} = m_s}} a_{m_{s_1}, m_{s_2}} \psi^{(0)}_{n_1 n_2 m_{s_1} m_{s_2}} \tag{12.70}$$

where

$$a_{m_{s_1} m_{s_2}} = \langle s_1 s_2 m_{s_1} m_{s_2} \mid s_1 s_2 s m_s \rangle \tag{12.71}$$

Now

$$\left\langle \frac{1}{2}\frac{1}{2} m_{s_1} m_{s_2} \,\middle|\, \frac{1}{2}\frac{1}{2} 11 \right\rangle = \delta_{m_{s_1},\frac{1}{2}} \delta_{m_{s_2},\frac{1}{2}} \tag{12.72}$$

which implies that

$$\psi^{(0)}_{n_1 n_2 11} = \psi^{(0)}_{n_1 n_2 ++} \tag{12.73}$$

as written above.

Similarly, for $s = 1, m_s = 0$, the only nonzero CG coefficients are

$$\left\langle \frac{1}{2}\frac{1}{2}\frac{1}{2} -\frac{1}{2} \,\middle|\, \frac{1}{2}\frac{1}{2} 10 \right\rangle = \frac{1}{\sqrt{2}} = \left\langle \frac{1}{2}\frac{1}{2} -\frac{1}{2}\frac{1}{2} \,\middle|\, \frac{1}{2}\frac{1}{2} 10 \right\rangle \tag{12.74}$$

which implies that

$$\psi^{(0)}_{n_1 n_2 10} = \frac{1}{\sqrt{2}} \psi^{(0)}_{n_1 n_2 +-} + \frac{1}{\sqrt{2}} \psi^{(0)}_{n_1 n_2 -+}$$

$$= \frac{1}{\sqrt{2}} \left[\psi^{(0)}_{n_1}(1) \psi^{(0)}_{n_2}(2) - \psi^{(0)}_{n_1}(2) \psi^{(0)}_{n_2}(1) \right] \chi_{10} \tag{12.75}$$

as written above. We now have the appropriate zero-order wave functions and can apply perturbation theory to the two fermion system.

As with the two boson case, the zero-order ground state for two fermions corresponds to $n_1 = n_2 = 1$ with zero-order energy $2E_1^{(0)}$. Since the $S = 1$ or triplet states have identically zero state functions in the case (since the spatial function are antisymmetric), we have $\psi^{(0)}_{11,1m_s} = 0$. The unperturbed ground state must then have $S = 0, S_z = 0$ or it is $\psi^{(0)}_{11,00}(1,2)$. This involves a singlet state with $m_s = 0$ only

$$\chi_{00} = \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) - \beta(1)\alpha(2) \right) \tag{12.76}$$

In this state, the particle spins are always opposite or antiparallel.

The ground state energy to first order is

$$\begin{aligned} E_{11} &= 2E_1^{(0)} + \left\langle \psi_{11,00}^{(0)} \middle| \hat{U}(x_1 - x_2) \middle| \psi_{11,00}^{(0)} \right\rangle \\ &= 2E_1^{(0)} + J_{11} \end{aligned} \tag{12.77}$$

which is the *same* energy as in the two boson system(we are assuming the *same Hamiltonian* applies).

The spatial part of the wave function is the same also, namely,

$$\psi_1^{(0)}(1)\psi_2^{(0)}(2) \tag{12.78}$$

We must use a symmetric spatial wave function here because the spin vector is antisymmetric in the ground state of two fermions. The presence of the spin internal degrees of freedom(and the Pauli principle) has a more dramatic effect on the first excited state for two fermions.

We again assume that the first excited state corresponds to $n_1 = 1, n_2 = 2$. This gives the energy to first order as

$$E_{12} = E_1^{(0)} + E_2^{(0)} + \left\langle \psi_{12,sm_s}^{(0)} \middle| \hat{U}(x_1 - x_2) \middle| \psi_{12,sm_s}^{(0)} \right\rangle \tag{12.79}$$

We can write the energy this way, i.e., we do not need to write a 4×4 matrix $\langle \hat{U} \rangle$ and diagonalize it because the $\langle \hat{U} \rangle$ matrix is already diagonal in this basis due the orthogonality of the spin functions and the fact that the perturbing potential does not depend on spin. This first order energy is different for the triplet and singlet states. If we do the integrals (they are the same as the boson case) we get

$$E_{12} = E_1^{(0)} + E_2^{(0)} + J_{12} \pm K_{12} \tag{12.80}$$

where

$$+ \rightarrow \text{ singlet } s = 0, m_s = 0$$
$$- \rightarrow \text{ triplet } s = 1, m_s = \pm 1, 0$$

All the triplet states have the same energy because they have the same spatial wave function and the perturbing potential does not depend on spin.

We thus get the energy level structure shown in Figure 12.2 below.

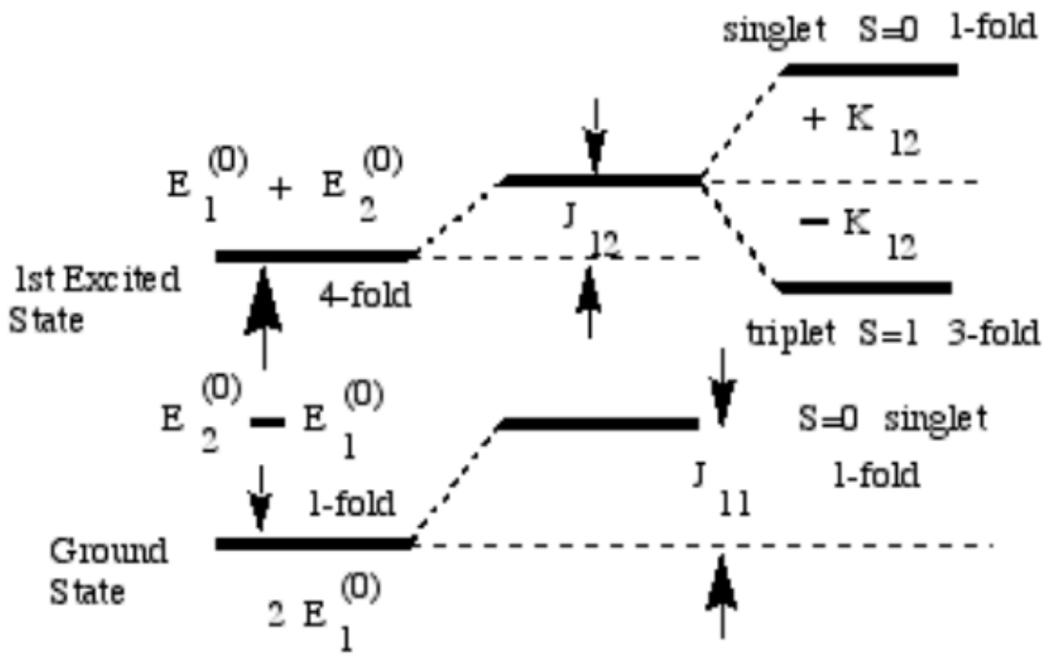


Figure 12.2: Typical Fermion Energy Level Diagram

The energies now depend on the total spin S *even though* the Hamiltonian $\hat{H}$ *does not* explicitly depend on spin. A very dramatic effect!!

This level splitting is not due to any additional terms added to the Hamiltonian such as $\hat{H}_{so}$ or $\hat{H}_{Zeeman}$. This effect is strictly due to *symmetry* requirements. The requirement of symmetry or antisymmetry forced on the spatial wave functions by the symmetry or antisymmetry of the spin vectors causes this level splitting. The entire effect is due to the invariance of the Hamiltonian under pairwise particle interchange.

Physically, we can argue as follows:

1. symmetric spatial functions are large for $x_1 \approx x_2$, while antisymmetric spatial functions are ≈ 0 for $x_1 \approx x_2$

2. $U(x_1 - x_2)$ is expected to be largest for $x_1 \approx x_2$

3. this implies that for $S = 1$ fermions $\langle \hat{U} \rangle$ is relatively small while for $S = 0$ fermions $\langle \hat{U} \rangle$ is relatively large

4. two identical fermions with antiparallel spins have a large probability of being close together – they *attract* each other

5. two identical fermions with parallel spins have zero probability of being close together – they *repel* each other

This *repulsion* is spin dependent and not due to the Coulomb repulsion between the electrons.

The first order energy for the singlet state is larger than for the triplet states because the repulsive interaction is enhanced in the singlet state. This overall effect is called *spin pairing* and it is a purely quantum mechanical effect.

stop

12.4 The N-Electron Atom

We now extend our discussion to a system with N electrons (fermions). We write

$$\hat{H} = \hat{H}_0 + \hat{H}' \tag{12.81}$$

where

$$\hat{H}_0 = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + \hat{V}(\vec{r}_i) \right] \tag{12.82}$$

$$\hat{H}' = \sum_{i=1}^{N} \sum_{j>i}^{N} \hat{U}(\vec{r}_i - \vec{r}_j) \tag{12.83}$$

The energy eigenstates for the $N-$electron atom are solutions of the time independent Schrodinger equation

$$\hat{H}\psi_E = E\psi_E \tag{12.84}$$

where $\psi_E = \psi_E(1, 2, 3, 4, ..., N)$ and $1 = (\vec{r}_1, s_1)$ and so on.

The indistinguishability of the N electrons implies that

$$\left[\hat{H}, \hat{P}_{ij}\right] = 0 \qquad i, j = 1, 2, 3, 4, ..., N \; ; \; i \neq j \tag{12.85}$$

where the $\hat{P}_{ij}$ interchange *all attributes* of the electrons, i.e., both the spatial and spin degrees of freedom.

The wave function must be antisymmetric under pairwise electron interchange

$$\hat{P}_{ij}\psi_E = -\psi_E \qquad i, j = 1, 2, 3, 4, ..., N \; ; \; i \neq j \tag{12.86}$$

The general problem of N interacting electrons is very complex. At this stage we only want to extract general properties that will also hold in real 3–dimensional atomic systems. It turns out to be instructive to consider the case of non-interacting electrons - the so-called independent particle model. In this model we neglect the electron-electron interactions and look only at the zeroth order.

In particular, we consider N identical non-interacting particles in a potential well $V(\vec{r})$. The Hamiltonian for any particle in the well is

$$\hat{H}_0(k) = \frac{\vec{p}_{k,op}^{\,2}}{2m} + V(\vec{r}_k) \tag{12.87}$$

where

$$\hat{H}_0(k)\phi_n(\vec{r}_k) = \varepsilon_n\phi_n(\vec{r}_k) \qquad n = 0, 1, 2, 3, 4, ... \tag{12.88}$$

Thus, any single particle sees the energy level structure as shown in Figure 12.3 below.



Figure 12.3: Single Particle Energy Level Structure

The N-particle Hamiltonian is then

$$\hat{H} = \hat{H}_0(1) + \hat{H}_0(2) + \hat{H}_0(3)..... + \hat{H}_0(N) \tag{12.89}$$

with solutions given by

$$\hat{H}\psi(1, 2, 3, ..., N) = E\psi(1, 2, 3, ..., N) \tag{12.90}$$

where

$$\psi(1, 2, 3, ..., N) = \phi_a(1)\phi_b(2).....\phi_n(N) \tag{12.91}$$

and

$$E = \varepsilon_a + \varepsilon_b + ... + \varepsilon_n \tag{12.92}$$

This solution implies that

particle 1 is in state a with energy ε_a

particle 2 is in state b with energy ε_b

.....

.....

.....

particle N is in state n with energy ε_n

Electrons have spin = 1/2. Thus, corresponding to any single particle energy level, say a, there are two possible single particle states, namely,

$$\phi_a(1)\alpha(1) \text{ and } \phi_a(1)\beta(1) \tag{12.93}$$

From now on when we write $\phi_a(1)$, where the subscript a will be understood to also include the spin information.

The simple product state solutions are not physically admissible solutions since they are not antisymmetric under particle interchange for any two particles.

All such states with particles interchanged pairwise have the same energy. In fact, any permutation of the indices produces a state with the same energy. We need to construct a completely antisymmetric linear combination of all of these solutions.

If these were bosons we would have to construct a completely symmetric linear combination of all these solutions.

If we define

$$\wp\psi(1,2,3,4,.....,N) = \text{ a permutation of the particles} \tag{12.94}$$

then, the completely symmetric state is easy to construct. It is

$$\psi_S(1,2,3,.....,N) = \sum_{\wp} \wp\psi(1,2,3,4,.....,N) \tag{12.95}$$

where the sum means a sum over all possible permutations or arrangements. There are $N!$ such permutations.

Examples

$$N = 2 \rightarrow N! = 2$$
$$\psi_S(1,2) = \phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)$$
$$N = 3 \rightarrow N! = 6$$
$$\psi_S(1,2,3) = \phi_1(1)\phi_2(2)\phi_3(3) + \phi_1(2)\phi_2(1)\phi_3(3) + \phi_1(3)\phi_2(2)\phi_3(1)$$
$$+ \phi_1(1)\phi_2(3)\phi_3(2) + \phi_1(3)\phi_2(1)\phi_3(2) + \phi_1(2)\phi_2(3)\phi_3(1)$$

How do we construct a completely antisymmetric state? Let us define a general permutation operator by (illustrate for $N = 5$)

$$\hat{\wp}_{13452}\psi(1,2,3,4,5) = \psi(3,1,4,5,2)$$
$$\hat{\wp}_{23451}\psi(1,2,3,4,5) = \psi(2,3,4,5,1)$$

Any such permutation operator can be written as the product of the 2–particle interchange operators $\hat{P}_{ij}$, i.e.,

$$\begin{aligned}\psi(2,3,1) &= \hat{\wp}_{231}\psi(1,2,3) \\ &= \hat{P}_{12}\psi(3,2,1) = \hat{P}_{12}\hat{P}_{13}\psi(1,2,3)\end{aligned}$$

Thus, any permutation $\hat{\wp}$ can be written in terms of an odd or even number of pair interchanges or pair permutations and we call it an odd or even permutation accordingly. All pair permutations are odd.

Therefore, for a completely antisymmetric state we must have

$$\hat{\wp}\psi_A = \begin{cases} +\psi_A & \text{if } \hat{\wp} \text{ is an even permutation} \\ -\psi_A & \text{if } \hat{\wp} \text{ is an odd permutation} \end{cases} \tag{12.96}$$

We therefore form a completely antisymmetric state as follows. We let

$$(-1)^{\hat{\wp}} = \begin{cases} +1 & \text{if } \hat{\wp} \text{ is an even permutation} \\ -1 & \text{if } \hat{\wp} \text{ is an odd permutation} \end{cases} \tag{12.97}$$

and then

Examples

$$N = 2 \rightarrow N! = 2$$

$$\psi_A(1,2) = \phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)$$

$$N = 3 \rightarrow N! = 6$$

$$\psi_A(1,2,3) = \phi_1(1)\phi_2(2)\phi_3(3) - \phi_1(2)\phi_2(1)\phi_3(3) - \phi_1(3)\phi_2(2)\phi_3(1)$$
$$- \phi_1(1)\phi_2(3)\phi_3(2) + \phi_1(3)\phi_2(1)\phi_3(2) + \phi_1(2)\phi_2(3)\phi_3(1)$$

It is clear that if any two states are identical (put 2 = 3 above), then ψ_A is identically = 0 as it should be for fermions.

This implies that we can put at most 2 electrons in each energy level of the potential well. The two electrons in the k^{th} level would then have wave functions

$$\phi_k\alpha \text{ and } \phi_k\beta \tag{12.98}$$

i.e., they must have opposite spins. This says that N spin = 1/2 fermions must occupy at least $N/2$ different states in the well.

This is very different than for bosons where all the N bosons can be in any energy level.

Another way to write the completely antisymmetric wave function for fermions is the so-called Slater determinant

$$\psi_A(1,2,3,.....,N) = \begin{vmatrix} \phi_a(1) & \phi_a(2) & . & \phi_a(N) \\ \phi_b(1) & \phi_b(2) & . & \phi_b(N) \\ . & . & . & . \\ \phi_n(1) & \phi_n(2) & . & \phi_n(N) \end{vmatrix} \qquad (12.99)$$

The last thing we must do is to normalize these state vectors.

$$\langle \psi_A \mid \psi_A \rangle = \sum_{s_1,s_2,\ldots,s_N} \int d^3\vec{r}_1 \ldots\ldots d^3\vec{r}_N \times \sum_{\wp\wp'} (-1)^{\wp}(-1)^{\wp'} [\wp\phi_a^*(1)\ldots.\phi_n^*(N)][\wp'\phi_a(1)\ldots.\phi_n(N)]$$

Now if $\wp \neq \wp'$, then $[\wp\phi_a(1)\ldots.\phi_n(N)]$ and $[\wp'\phi_a(1)\ldots.\phi_n(N)]$ are orthogonal and the integration for that term is zero.

Therefore, we get

$$\langle \psi_A \mid \psi_A \rangle = \sum_{s_1,s_2,\ldots,s_N} \int d^3\vec{r}_1 \ldots\ldots d^3\vec{r}_N \sum_{\wp} \wp\, |\phi_a(1)|^2 \ldots. |\phi_n(N)|^2 \qquad (12.100)$$

But

$$\sum_{s_k} \int d^3\vec{r}_k \, |\phi_k(j)|^2 = 1 \qquad (12.101)$$

so we finally get

$$\langle \psi_A \mid \psi_A \rangle = \sum_{\wp} 1 = \text{ number of possible permutations } = N! \tag{12.102}$$

and therefore, the properly normalized completely antisymmetric wave function is

$$\psi_A(1,2,3,.....,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & . & \phi_a(N) \\ \phi_b(1) & \phi_b(2) & . & \phi_b(N) \\ . & . & . & . \\ \phi_n(1) & \phi_n(2) & . & \phi_n(N) \end{vmatrix} \tag{12.103}$$

In a similar manner

$$\langle \psi_S \mid \psi_S \rangle = \frac{N!}{N_a!.....N_n!} \tag{12.104}$$

where

$N_k =$ the number of times the single particle state ϕ_k occurs

What is the difference between the ground state of N fermions and N bosons?

For N bosons, all N particles occupy the lowest level ϕ_0 and the wavefunction is

$$\psi_S(1,2,3,....,N) = \phi_0(1)\phi_0(2)\phi_0(3).....\phi_0(N) \tag{12.105}$$

with energy

$$E_0 = N\varepsilon_0 \tag{12.106}$$

This is true no matter how large N might be, even for macroscopic systems where $N \approx 10^{23}$. As we shall see in later discussions, this is one of the physical requirements for phenomena like superconductivity, superfluidity and Bose-Einstein condensation.

Such a state is not allowed for fermions however. We must have

N even	N odd
2 in ϕ_0	2 in ϕ_0
2 in ϕ_1	2 in ϕ_1
.....	.....
2 in $\phi_{\frac{N}{2}-1}$	2 in $\phi_{\frac{N-1}{2}}$
2 in $\phi_{\frac{N}{2}}$	1 in $\phi_{\frac{N+1}{2}}$

This difference for systems with even or odd numbers of fermions will lead to dramatic physical consequences later for some atomic systems.

The ground state energy for N fermions is

$$2(\varepsilon_0 + \varepsilon_1 + ... + \varepsilon_{\frac{N}{2}}) \qquad \text{for } N \text{ even}$$
$$2(\varepsilon_0 + \varepsilon_1 + ... + \varepsilon_{\frac{N-1}{2}}) + \varepsilon_{\frac{N+1}{2}} \qquad \text{for } N \text{ odd}$$

Either of these two energies is always greater than the N boson ground state energy.

The extra energy is called the *zero point energy* and it arises from particle interchange invariance or it arises from the *Pauli Exclusion Principle* which states

> No two identical fermions in a physical system
> can have the same set of quantum numbers

It is equivalent to the antisymmetry of the wave function requirement for fermions.

12.5 The Helium Atom

We now consider the simplest multielectron atom, namely, helium, which has two electrons. The Hamiltonian is

$$\hat{H} = \hat{H}(1) + \hat{H}(2) + \hat{V} = \frac{\vec{p}_{1,op}^{\,2}}{2m} - \frac{Ze^2}{r_1} + \frac{\vec{p}_{2,op}^{\,2}}{2m} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \qquad (12.107)$$

where

$\hat{H}(i) =$ hydrogen atom Hamiltonian with nuclear charge Ze (instead of e)

$\hat{V} =$ electrostatic repulsion between the electrons

We start by neglecting the electrostatic repulsion between the electrons. This gives us a zero-order solution that we can use in perturbation theory. This is equivalent to the independent particle model we just discussed.

Since $\hat{H} = \hat{H}(1) + \hat{H}(2)$ in this model, we can write

$$|\psi\rangle = |n_1\ell_1 m_1\rangle\,|n_2\ell_2 m_2\rangle \qquad (12.108)$$

where

$$\hat{H}(1)\,|n_1\ell_1 m_1\rangle = E_{n_1}^{(0)}\,|n_1\ell_1 m_1\rangle \text{ and } \hat{H}(2)\,|n_2\ell_2 m_2\rangle = E_{n_2}^{(0)}\,|n_2\ell_2 m_2\rangle$$

$$\hat{H}\,|\psi\rangle = (\hat{H}(1) + \hat{H}(2))\,|\psi\rangle = (\hat{H}(1) + \hat{H}(2))\,|n_1\ell_1 m_1\rangle\,|n_2\ell_2 m_2\rangle$$

$$= E_{n_1 n_2}^{(0)}\,|\psi\rangle = (E_{n_1}^{(0)} + E_{n_2}^{(0)})\,|n_1\ell_1 m_1\rangle\,|n_2\ell_2 m_2\rangle = (E_{n_1}^{(0)} + E_{n_2}^{(0)})\,|\psi\rangle$$

and

$$E_n^{(0)} = -\frac{Z^2 e^2}{2a_0 n^2} \qquad (\text{Z} = 2 \text{ for helium}) \qquad (12.109)$$

We will be working out the numbers in this problem so that we can compare our results to experiment. The zero order energies are shown in Table 12.1 below:

n_1	n_2	$E^{(0)}_{n_1 n_2}(Ry)$	$E^{(0)}_{n_1 n_2}(eV)$
1	1	-8	-108.8
1	2	-5	-68.0
1	3	-40/9	-64.4
1	..	..	..
1	..	-4	-54.5
2	2	-2	-27.2

Table 12.1: Zero Order Energies

where

$$1 \text{ Ry(Rydberg)} = \frac{e^2}{2a_0} = 13.6\, eV \tag{12.110}$$

The ground state energy is

$$E_{gs} = E^{(0)}_{11} = 2E^{(0)}_{1} = -8\, Ry \tag{12.111}$$

and the energy of the system when one electron has been ionized (no longer bound) is

$$E_{ion} = E^{(0)}_{1} + E^{(0)}_{\infty} = -4\, Ry \tag{12.112}$$

Therefore, it requires the addition of $4\, Ry$ to create singly ionized helium. Notice that the $(2,2)$ state has an energy greater than E_{ion}, which implies that it is not a bound state of the helium atom. All the states $(1,n)$ are bound states. The energy level spectrum looks as shown in Figure 12.4 below.

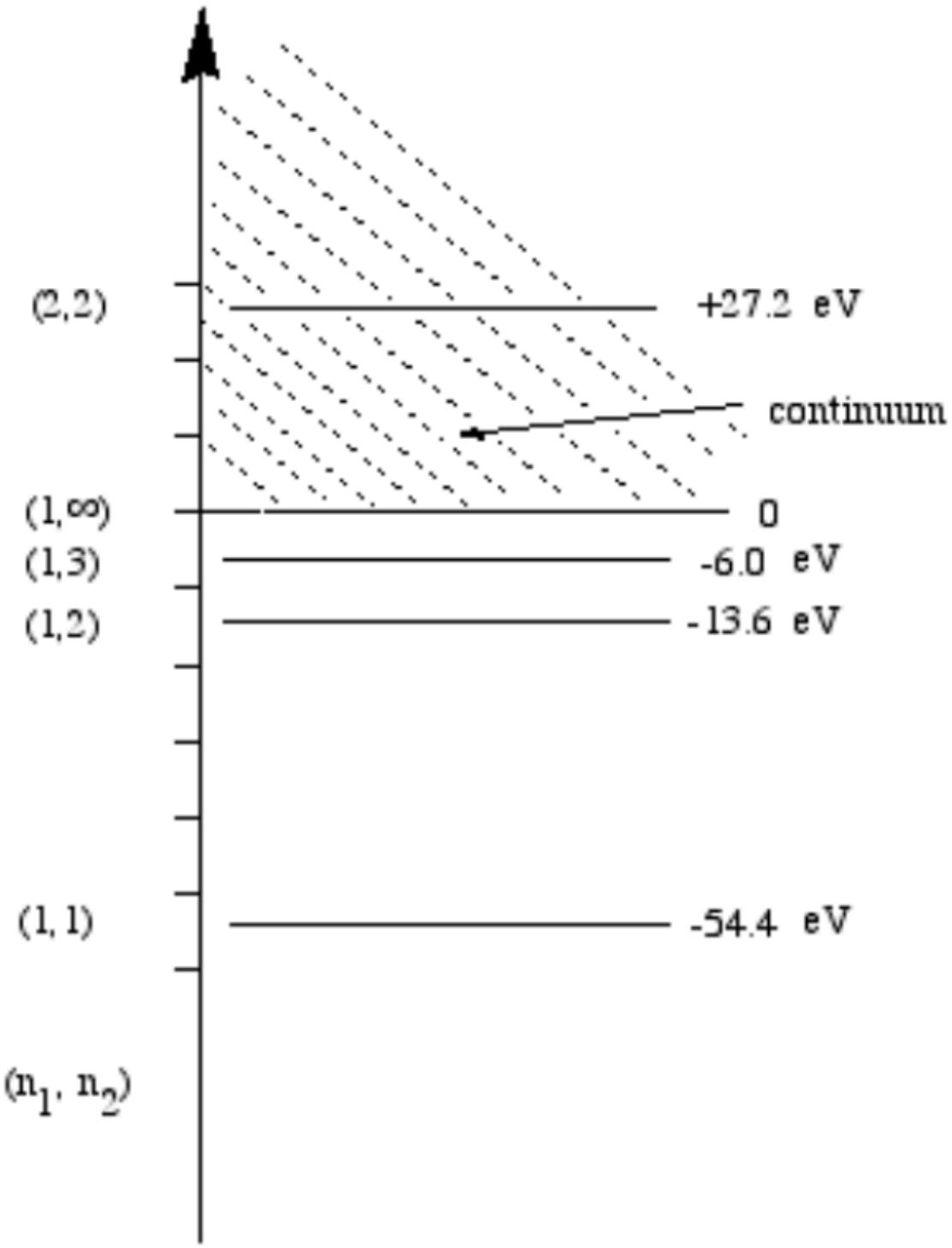


Figure 12.4: Helium Energy level Spectrum

Since the particles are electrons we must antisymmetrize the wave functions. We have two spin = 1/2 fermions. The spin functions are

$$|s, m_s\rangle = \begin{cases} |1, (\pm 1, 0)\rangle & \rightarrow \text{symmetric} \\ |0, 0\rangle & \rightarrow \text{antisymmetric} \end{cases} \tag{12.113}$$

The spatial part of the wave function must be of opposite symmetry to the spin functions so that the product is antisymmetric. By convention we label the states as follows:

Parahelium

$$\begin{gathered} (\text{symmetric space part})\chi_{00} \\ (|100\rangle\,|100\rangle)\,|00\rangle \\ \frac{1}{\sqrt{2}}\left[|100\rangle\,|2\ell m\rangle + |2\ell m\rangle\,|100\rangle\right]\chi_{00} \end{gathered}$$

and so on.

Orthohelium

$$\begin{gathered} (\text{antisymmetric space part})\chi_{1m_s} \\ \frac{1}{\sqrt{2}}\left[|100\rangle\,|2\ell m\rangle - |2\ell m\rangle\,|100\rangle\right]\chi_{1m} \end{gathered}$$

and so on.

These are the zero-order wave functions. We now handle the

$$\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} = \frac{e^2}{r_{12}} \tag{12.114}$$

term by perturbation theory.

The first order ground state energy correction is

$$\begin{aligned}\Delta E &= \langle 100| \langle 100| \frac{e^2}{r_{12}} |100\rangle |100\rangle \langle 00 \mid 00\rangle \\ &= e^2 \int \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{|\psi_{100}(\vec{r}_1)|^2 |\psi_{100}(\vec{r}_2)|^2}{r_{12}}\end{aligned} \tag{12.115}$$

where

$$\psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}} \tag{12.116}$$

Therefore,

$$\Delta E = \frac{1}{\pi^2} \left(\frac{Z}{a_0}\right)^3 e^2 \int_0^\infty dr_1 r_1^2 e^{-\frac{2Zr_1}{a_0}} \int_0^\infty dr_2 r_2^2 e^{-\frac{2Zr_2}{a_0}} \int \int d\Omega_1 d\Omega_2 \frac{1}{r_{12}} \tag{12.117}$$

Even though this calculation does not give a very accurate result, it is still very instructive to learn the tricks necessary to evaluate the integrals.

We first need to find a useful expression for $1/r_{12}$. We have

$$r_{12} = |\vec{r}_1 - \vec{r}_2| = \sqrt{(\vec{r}_1 - \vec{r}_2)\cdot(\vec{r}_1 - \vec{r}_2)} \tag{12.118}$$

$$r_{12}^2 = (\vec{r}_1 - \vec{r}_2)\cdot(\vec{r}_1 - \vec{r}_2) = r_1^2 + r_2^2 - 2\vec{r}_1\cdot\vec{r}_2$$

$$= r_1^2 + r_2^2 - 2r_1 r_2 \cos\beta \tag{12.119}$$

where

$$\beta = \text{ angle between } \vec{r}_1 \text{ and } \vec{r}_2 \tag{12.120}$$

Therefore,

$$\frac{1}{r_{12}} = \frac{1}{\left(r_1^2 + r_2^2 - 2r_1 r_2 \cos\beta\right)^{1/2}} \tag{12.121}$$

In the subsequent development, we let the larger of r_1, r_2 be called $r_>$ and the smaller be called $r_<$. We then have

$$\frac{1}{r_{12}} = \frac{1}{r_>\left(1 - 2\frac{r_<}{r_>}\cos\beta + \left(\frac{r_<}{r_>}\right)^2\right)^{1/2}}$$

$$= \frac{1}{r_>} + \frac{1}{2r_>}\left(2\frac{r_<}{r_>}\cos\beta - \left(\frac{r_<}{r_>}\right)^2\right) - \frac{3}{8r_>}\left(2\frac{r_<}{r_>}\cos\beta - \left(\frac{r_<}{r_>}\right)^2\right)^2$$

$$+ \frac{15}{48r_>}\left(2\frac{r_<}{r_>}\cos\beta - \left(\frac{r_<}{r_>}\right)^2\right)^3 - \ldots \tag{12.122}$$

or

$$\frac{1}{r_{12}} = \frac{1}{r_>}\left[1 + \frac{r_<}{r_>}\cos\beta + \left(\frac{r_<}{r_>}\right)^2\left(\frac{3}{2}\cos^2\beta - \frac{1}{2}\right) + \ldots\right] \tag{12.123}$$

$$= \frac{1}{r_>}\left[P_0(\cos\beta) + \frac{r_<}{r_>}P_1(\cos\beta) + \left(\frac{r_<}{r_>}\right)^2 P_2(\cos\beta) + \ldots\right] \tag{12.124}$$

Therefore,

$$\frac{1}{r_{12}} = \frac{1}{r_>}\sum_{\lambda=0}^{\infty}\left(\frac{r_<}{r_>}\right)^\lambda P_\lambda(\cos\beta) \tag{12.125}$$

Now, the addition theorem for spherical harmonics, which is proved at the end of this chapter, gives

$$P_\lambda(\cos\beta) = \frac{4\pi}{2\lambda+1}\sum_{m=-\lambda}^{\lambda} Y_{\lambda m}(\Omega_1)Y^*_{\lambda m}(\Omega_2) \tag{12.126}$$

Therefore, we finally have

$$\frac{1}{r_{12}} = \frac{1}{r_>}\sum_{\lambda=0}^{\infty}\left(\frac{r_<}{r_>}\right)^\lambda \frac{4\pi}{2\lambda+1}\sum_{m=-\lambda}^{\lambda} Y_{\lambda m}(\Omega_1)Y^*_{\lambda m}(\Omega_2) \tag{12.127}$$

Now, the factor

$$\int\int d\Omega_1 d\Omega_2 \frac{1}{r_{12}} \tag{12.128}$$

contains terms like

$$\int\int d\Omega_1 d\Omega_2 Y_{\lambda m}(\Omega_1)Y^*_{\lambda m}(\Omega_2) \tag{12.129}$$

and

$$\int d\Omega Y_{\lambda m}(\Omega) \propto \int d\Omega Y_{\lambda m}(\Omega) Y_{00}(\Omega) = \delta_{\lambda 0}\delta_{m0} \tag{12.130}$$

Therefore, the only term that contributes from the sum is $\lambda = m = 0$ and we get

$$\int\int d\Omega_1 d\Omega_2 \frac{1}{r_{12}} = \frac{1}{r_>} \tag{12.131}$$

and therefore we have

$$\Delta E = \frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^3 e^2 \int_0^\infty dr_1 r_1^2 e^{-\frac{2Zr_1}{a_0}} \int_0^\infty dr_2 r_2^2 e^{-\frac{2Zr_2}{a_0}} \frac{1}{r_>} \tag{12.132}$$

or

$$\begin{aligned}\Delta E = &\frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^3 e^2 \int_0^\infty dr_1 r_1^2 e^{-\frac{2Zr_1}{a_0}} \int_0^{r_1} dr_2 r_2^2 e^{-\frac{2Zr_2}{a_0}} \frac{1}{r_1} \\ &+ \frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^3 e^2 \int_0^\infty dr_1 r_1^2 e^{-\frac{2Zr_1}{a_0}} \int_{r_1}^\infty dr_2 r_2^2 e^{-\frac{2Zr_2}{a_0}} \frac{1}{r_2}\end{aligned} \tag{12.133}$$

which gives

$$\Delta E = \frac{5}{8}\frac{Ze^2}{a_0} = J_{1s,1s} = J_{10,10} = 2.5\ Ry = 34\ eV \tag{12.134}$$

for $Z = 2$.

The ground state energy corrected to first order is then

$$E_{11} = E_{11}^{(0)} + \Delta E = -74.8\ eV = -5.5\ Ry \tag{12.135}$$

The experimental value is

$$(E_{11})_{exp\,t} = -78.975\ eV = -5.807\ Ry \tag{12.136}$$

This first order result is amazingly good for this complex system!

Now we deal with the first excited state.

The first order energy shifts are once again given by standard perturbation theory since the $\langle V \rangle$ matrix is diagonal in this basis due to the orthonormality of the spin vectors and the fact that $\hat{V}$ is independent of spin.

We thus have

$$\Delta E_{n\ell}^{s,t} = \frac{1}{2} \int \int d^3\vec{r}_1 d^3\vec{r}_2 \left|\psi_{100}(1)\psi_{n\ell 0}(2) \pm \psi_{100}(2)\psi_{n\ell 0}(1)\right|^2 \frac{e^2}{r_{12}} \tag{12.137}$$

where $s,t \rightarrow$ singlet, triplet $\rightarrow S = 0,1 \rightarrow -,+$. As shown before, we need only calculate the $m = 0$ case because $[\vec{L}_{op}, \hat{V}] = 0$ where

$$\vec{L}_{op} = \vec{L}_{1,op} + \vec{L}_{2,op} = \text{ total orbital angular momentum} \tag{12.138}$$

which implies that the result is independent of m.

Therefore

$$\Delta E_{n\ell}^{s,t} = e^2 \int\int d^3\vec{r}_1 d^3\vec{r}_2 \left|\psi_{100}(1)\right|^2 \left|\psi_{n\ell 0}(2)\right|^2 \frac{1}{r_{12}} \tag{12.139}$$

$$+ e^2 \int\int d^3\vec{r}_1 d^3\vec{r}_2 \psi_{100}^*(1)\psi_{n\ell 0}^*(2)\psi_{100}(2)\psi_{n\ell 0}(1)\frac{1}{r_{12}} = J_{n\ell} \pm K_{n\ell}$$

where

$J_{n\ell}$ = electrostatic repulsion between two charge distributions

$\left|\psi_{100}(1)\right|^2$ and $\left|\psi_{n\ell 0}(2)\right|^2$ = the direct integral

and

$K_{n\ell}$ = the exchange integral which arises from

antisymmetrization of the wave function

with

$+$ = singlet and $-$ = triplet

A convenient way of representing this result is as follows.

$$\vec{S}_{op} = \vec{S}_{1,op} + \vec{S}_{2,op}$$

$$\rightarrow 2\vec{S}_{1,op} \cdot \vec{S}_{2,op} = \vec{S}_{op}^2 - \vec{S}_{1,op}^2 - \vec{S}_{2,op}^2 = \hbar^2 (S(S+1) - \frac{3}{2}) \tag{12.140}$$

$$2\vec{S}_{1,op} \cdot \vec{S}_{2,op} = \hbar^2 \begin{cases} +\frac{1}{2} & \text{triplet} \\ -\frac{3}{2} & \text{singlet} \end{cases} \tag{12.141}$$

and therefore

$$\Delta E_{n\ell}^{s,t} = J_{n\ell} - \frac{1}{2\hbar^2}(1 + 4\vec{S}_{1,op} \cdot \vec{S}_{2,op}) K_{n\ell} \tag{12.142}$$

The calculation results (in eV) are shown in Table 12.2 below and the energy levels are shown in Figure 12.5 below. Not bad!!

State	1s2s		1s2p	
$n\ell$	10,20	10,20	10,21	10,21
	singlet	triplet	singlet	triplet
0^{th} order	-68.0	-68.0	-68.0	-68.0
J	11.4	11.4	13.2	13.2
K	1.2	1.2	0.9	0.9
1^{st} order	-55.4	-57.8	-53.9	-55.7
E_{expt}	-58.4	-59.2	-57.8	-58.0
error	3.0=5.1%	1.4=2.4%	3.9=6.7%	2.3=4.0%

Table 12.2: Calculation Results

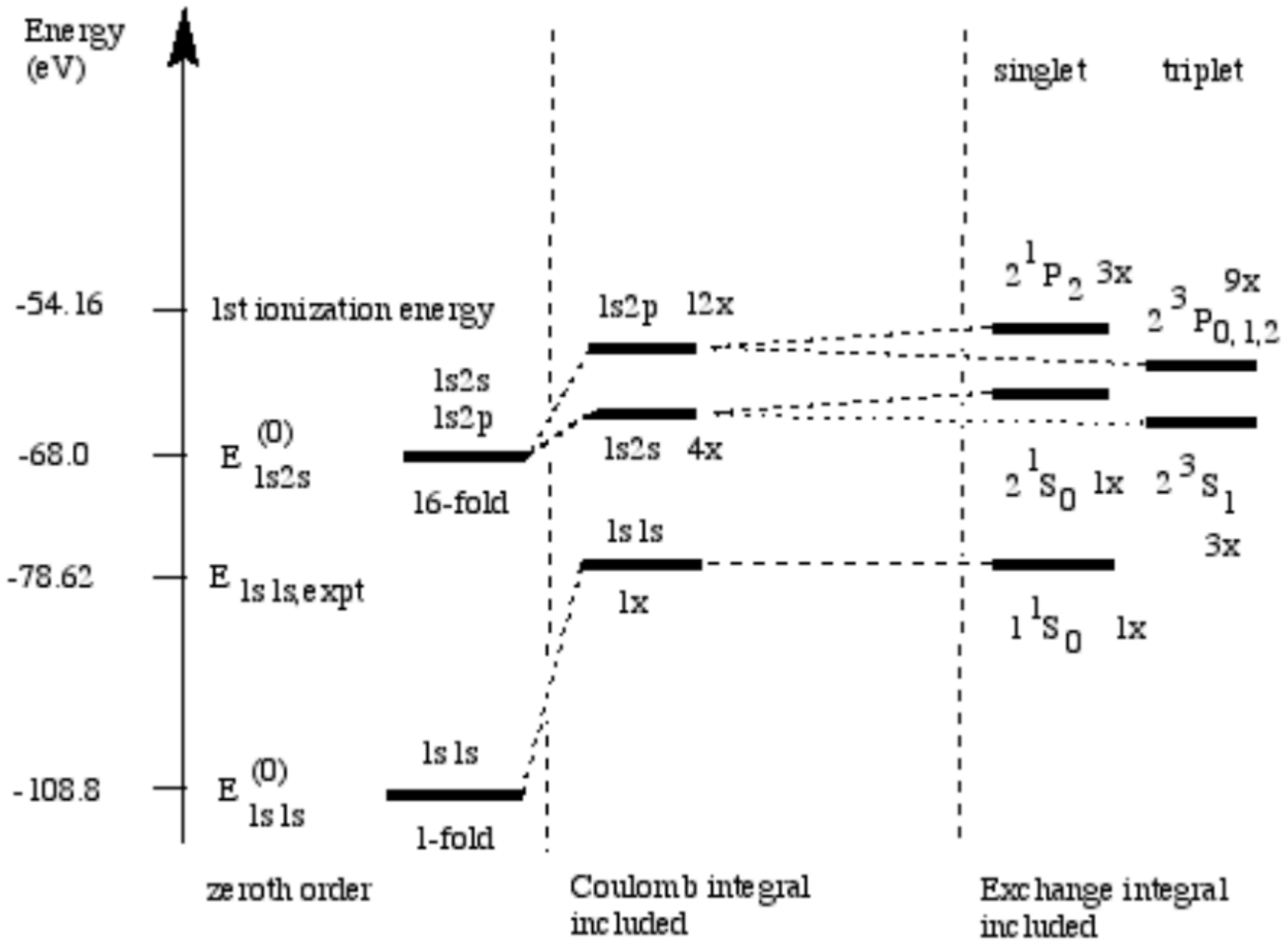


Figure 12.5: Helium Energy Levels

For comparison, we will also calculate the ground state energy using the variational method. We neglect spin in this case. The simplest choice of a trial function is the product of two hydrogen atom wave functions as in (12.143) below, which would be an exact solution if the electron-electron repulsion was neglected.

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr_1}{a_0}} \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr_2}{a_0}} \tag{12.143}$$

Since we expect the true wave function to be approximately represented by the above function, we change Z to α and thus obtain the best possible value for E_0 for this type of trial function.

We do the calculation as follows. We write

$$\begin{aligned}
\hat{H} &= \hat{H}_Z(1) + \hat{H}_Z(2) + \hat{V} = \frac{\vec{p}_{1,op}^2}{2m} - \frac{Ze^2}{r_1} + \frac{\vec{p}_{2,op}^2}{2m} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \\
&= \frac{\vec{p}_{1,op}^2}{2m} - \frac{\alpha e^2}{r_1} + \frac{\vec{p}_{2,op}^2}{2m} - \frac{\alpha e^2}{r_2} + \frac{(\alpha - Z)e^2}{r_1} + \frac{(\alpha - Z)e^2}{r_2} + \frac{e^2}{r_{12}} \\
&= \hat{H}_\alpha(1) + \hat{H}_\alpha(2) + \frac{(\alpha - Z)e^2}{r_1} + \frac{(\alpha - Z)e^2}{r_2} + \frac{e^2}{r_{12}}
\end{aligned} \tag{12.144}$$

Now

$$\hat{H}_\alpha(1)\psi_{100}^\alpha(1) = E_{100}^{(0)}(\alpha)\psi_{100}^\alpha(1) = -\alpha^2\psi_{100}^\alpha(1) \tag{12.145}$$

$$\hat{H}_\alpha(2)\psi_{100}^\alpha(2) = E_{100}^{(0)}(\alpha)\psi_{100}^\alpha(2) = -\alpha^2\psi_{100}^\alpha(2) \tag{12.146}$$

in Rydbergs. Therefore

$$\begin{aligned}
f(\alpha) = -2\alpha^2 &+ \langle\psi_{100}^\alpha(1)| \frac{(\alpha - Z)e^2}{r_1} |\psi_{100}^\alpha(1)\rangle \\
&+ \langle\psi_{100}^\alpha(2)| \frac{(\alpha - Z)e^2}{r_2} |\psi_{100}^\alpha(2)\rangle + \langle\psi(\alpha)| \frac{e^2}{r_{12}} |\psi(\alpha)\rangle
\end{aligned} \tag{12.147}$$

But

$$\langle\psi^{\alpha}_{100}(1)|\,\frac{(\alpha-Z)e^2}{r_1}\,|\psi^{\alpha}_{100}(1)\rangle = \langle\psi^{\alpha}_{100}(2)|\,\frac{(\alpha-Z)e^2}{r_2}\,|\psi^{\alpha}_{100}(2)\rangle$$
$$= \langle 100|\,\frac{(\alpha-Z)e^2}{r}\,|100\rangle \qquad (12.148)$$

Therefore,

$$f(\alpha) = -2\alpha^2 + 2e^2(\alpha-Z)\,\langle 100|\,\frac{1}{r}\,|100\rangle + \langle 100|\,\langle 100|\,\frac{e^2}{r_{12}}\,|100\rangle\,|100\rangle \qquad (12.149)$$

Using some earlier calculations we get

$$f(\alpha) = -2\alpha^2 + 4\alpha(\alpha-Z) + \frac{5}{4}\alpha \qquad (12.150)$$

Minimizing

$$\frac{df}{d\alpha} = 0 = -2\alpha + 2Z - \frac{5}{8} \qquad (12.151)$$

or

$$\alpha = Z - \frac{5}{16} \qquad (12.152)$$

and

$$E_0^{\text{variational}} = f(Z-\frac{5}{16}) = -2(Z-\frac{5}{16})^2 = -2Z^2 + \frac{5}{4}Z - 2(\frac{5}{16})^2 \qquad (12.153)$$

The first two terms are just the first order perturbation theory result. The third term lowers the energy relative to perturbation theory.

For $Z = 2$, we get

$$E_0^{variational} = -5.7\ Ry = -77.48\ eV$$
$$E_0^{experimental} = -78.975\ eV$$
$$E_0^{perturbation\ theory} = -74.8\ eV$$

Even with the simple trial function, we get a significantly better result using the variational method. The reduction in the value of Z represents the effect of the inner electron screening the outer electron so it see a smaller nuclear charge.

12.6 Multielectron Atoms

We now return to the case of N electrons ($N > 2$). We have

$$\hat{H}\psi_\alpha = E_\alpha \psi_\alpha \tag{12.154}$$

where α = all quantum numbers needed to specify the N-electron state and the Hamiltonian $\hat{H}$ is

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{r_i}\right] + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{r_{ij}} \tag{12.155}$$

For the moment we are neglecting many small(weak) interactions (spin-orbit, etc). We are also not including the electromagnetic field at this stage. We will consider it later when we talk about time-dependent perturbation theory and we will see that its presence leads to instability of atoms with respect to photon absorption/emission.

The electrons are all indistinguishable, which says that

$$\left[\hat{H}, \hat{P}_{ij}\right] = 0 \quad i, j = 1, 2, 3, ..., N \; ; \; i \neq j \tag{12.156}$$

This implies, since electrons are fermions, that the wave functions must be completely antisymmetric, i.e.,

$$\hat{P}_{ij}\psi_\alpha = -\psi_\alpha \quad i, j = 1, 2, 3, ..., N \; ; \; i \neq j \tag{12.157}$$

The full Hamiltonian is much too complex to solve exactly. We will approach the solution as a series of increasingly better approximations and obtain a qualitative picture of the energy level structure of these complex atoms.

Since the difficulties arise from the e^2/r_{ij} terms that represent the electron-electron repulsion, we start with a model where each electron moves independently of all the other electrons (an independent particle model). In this model each electron will be described by a single-particle wavefunction called an orbital.

This leads us to write an approximate Hamiltonian in terms of the single particle Hamiltonians

$$\hat{H}_{0i} = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \hat{V}_i(\vec{r}_i) \tag{12.158}$$

where we assume that the potential energy of the i^{th} electron $\hat{V}_i(\vec{r}_i)$ does not depend on the coordinates of the other $N-1$ electrons. We then have the approximate Hamiltonian for the entire system

$$\hat{H}_0^A = \sum_{i=1}^{N} \hat{H}_{0i} = \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \hat{V}_i(\vec{r}_i)\right] \tag{12.159}$$

This Hamiltonian is separable, i.e., we can assume that the system wavefunction is a product of single-particle wavefunctions or orbitals.

$$\psi_\alpha = \psi_{\varepsilon_1}(\vec{r}_1)\psi_{\varepsilon_2}(\vec{r}_2)\psi_{\varepsilon_3}(\vec{r}_3).....\psi_{\varepsilon_N}(\vec{r}_N) \tag{12.160}$$

where the subscript ε_k represents all applicable single particle quantum numbers for the k^{th} electron, that is,

$$\varepsilon_k = (n_i \ell_i m_{\ell_i} m_{s_i}) \tag{12.161}$$

Each single particle wave function is a product of the form

$$\psi_\varepsilon = (\text{spatial wave function})(\text{spin vector}) \tag{12.162}$$

We will assume that the system wavefunction is a completely antisymmetric combination of the product states ψ_α.

Each term in $\hat{H}_0^A$ has an eigenvalue equation of the form

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \hat{V}_i(\vec{r}_i)\right]\psi_{n_i\ell_i m_{\ell_i} m_{s_i}} = E_{n_i\ell_i m_{\ell_i} m_{s_i}}\psi_{n_i\ell_i m_{\ell_i} m_{s_i}} \tag{12.163}$$

and there are N such equations.

To solve these equations, we must know the potential energy functions $\hat{V}_i(\vec{r}_i)$. As a first approximation within the orbital approximations, we ignore the electron-electron repulsion so that the electrons only interact with the nucleus and we have

$$\hat{V}_i(\vec{r}_i) = \hat{V}(r_i) = -\frac{Ze^2}{r_i} \tag{12.164}$$

In this approximation, all the other electrons do not matter at all and each electron satisfies

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{r_i}\right]\psi_{n_i\ell_i m_{\ell_i} m_{s_i}}(\vec{r}_i) = E_{n_i\ell_i m_{\ell_i} m_{s_i}}\psi_{n_i\ell_i m_{\ell_i} m_{s_i}}(\vec{r}_i) \tag{12.165}$$

This is a hydrogen atom with charge Ze. The single-particle wavefunctions are given by

$$\psi_{n\ell m_\ell m_s}(\vec{r}) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\varphi)\chi_{sm_s} = \psi_\varepsilon(\vec{r}) \tag{12.166}$$

where

$$E_{n_k} \approx -\frac{m_e Z^2 e^4}{2\hbar^2 n_k} \qquad n_k = 1, 2, 3, ... \tag{12.167}$$

The wave function corresponding to a set of orbitals $(\varepsilon_1, \varepsilon_2, ..., \varepsilon_N)$ is then properly antisymmetrized by writing it as

$$\psi_\alpha = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{\varepsilon_1}(1) & \psi_{\varepsilon_2}(1) & .. & \psi_{\varepsilon_N}(1) \\ \psi_{\varepsilon_1}(2) & .. & .. & .. \\ .. & .. & .. & .. \\ \psi_{\varepsilon_1}(N) & .. & .. & \psi_{\varepsilon_N}(N) \end{vmatrix} \tag{12.168}$$

where

$$E_\alpha = E_{\varepsilon_1} + E_{\varepsilon_2} + ... + E_{\varepsilon_N} \tag{12.169}$$

We certainly can write down an answer in this approximation but the result, not surprisingly, is terrible. Any real electron is dramatically affected by the others, even when there is only one other electron as we saw in helium.

We move on by making the next incrementally better approximation. This involves the concept of screening.

12.6.1 Screening

Any electron, on the average, if it is far from the nucleus, does not feel all of the nuclear charge Ze and hence has a weaker Coulomb attraction then we have assumed. This is clear in the helium variational calculation where we found that the best value of the charge variational parameter Z' was

$$Z' = Z - \frac{5}{16} \tag{12.170}$$

This implies that, on the average, the distant electrons are *shielded* or *screened* from the nucleus by the other electrons.

What is the simplest correction that we can make to take this effect into account for multi-electron atoms and still leave us with solvable equations?

Suppose we write

$$V_i(r_i) = -\frac{Ze^2}{r_i} + V_i^{eff}(r_i) \tag{12.171}$$

where $V_i^{eff}(r_i)$ includes the screening effects of the other $N-1$ electrons. An important feature of this assumption is that $V_i^{eff}(r_i)$ is independent of (θ, φ). This says that the angular part of the wave function is still

$$Y_{\ell_i m_{\ell_i}}(\theta, \varphi) \tag{12.172}$$

The radial function, however, now satisfies a modified equation

$$\frac{1}{r_i^2}\frac{d}{dr_i}\left[r_i^2\frac{d}{dr_i} - \frac{\ell(\ell+1)}{r_i^2} + \frac{2m_e}{\hbar^2}\left(E_{n_i} - V_i(r_i)\right)\right]R_{n_i\ell_i}(r_i) = 0 \tag{12.173}$$

This is called the *central field approximation.* We still have N difficult equations to solve.

Hartree proposed the following solution using a successive approximations technique.

1. an initial potential function is guessed (a very educated guess)
2. this potential function is used to derive new wave functions
3. the new wave functions generate a new potential energy function
4. the procedure is continued until the final wave functions determine a *self-consistent* potential, i.e., it stops changing as we iterate

The Hartree method is equivalent to a variational calculation, where the trial function is taken to be a simple product of single-particle orbitals and the variation is performed by varying each orbital in an arbitrary way.

Using single-particle wave functions, however, we are still neglecting the correlations between the electrons. Although the simple single-particle orbital product functions ignore antisymmetry, some effect of the Pauli exclusion principle (PEP) can be included in the calculations by choosing the single-particle quantum numbers so they do not violate the PEP.

If we make the calculation more complicated, we can include antisymmetry by using Slater determinant wave functions. This is called the Hartree-Fock theory. Correlation effects arising from the $1/r_{ij}$ terms can then be added using perturbation theory. At the level of this text, we assume that this can be done

12.6.2 Shell Structure

The hydrogen atom solution exhibited a kind of shell structure. We found that the energy levels were given by

$$E_n = -\frac{Z^2 e^2}{2a_0 n^2} \tag{12.174}$$

and each level had a degeneracy equal to n^2 arising from the allowed ranges

$$\ell = 0, 1, 2, ..., n-1$$
$$m_\ell = -\ell, ..., \ell$$

We say that each n value defines a shell with energy E_n and within each shell we have subshells defined by ℓ. Thus,

$$n = 1 \rightarrow \ell = 0 \rightarrow 1s\text{subshell}$$
$$n = 2 \rightarrow \ell = 0, 1 \rightarrow 2s, 2p\text{subshells}$$
$$n = 3 \rightarrow \ell = 0, 1, 2 \rightarrow 3s, 3p, 3d\text{subshells}$$

We can generalize this idea to N electron atoms.

We assume that the atom consists of shells (n) and subshells $(n\ell)$. Electrons are placed into these shells so that we do not violate the PEP, that is, since the electrons are fermions only two electrons can be in each energy level. We define in this model

$$\langle r \rangle_{n0} = \textit{radius} \text{ of a shell}$$
$$\langle r \rangle_{n\ell} = \textit{radius} \text{ of a subshell}$$

and we have

$$E_{n\ell} = E_{n\ell'} \text{ (degenerate)} \tag{12.175}$$

(this is not true in the central field approximation).

For $n > 1$, the $s-$orbital has a nonzero probability near the origin $r = 0$ (the nucleus). This implies that it *penetrates* the $n = 1$ shell more than the corresponding $p-$orbitals do. This implies that the s subshell electrons feel a stronger nuclear charge then the p subshell electrons.

Therefore, we expect in this model that the energy levels will look like Figure 12.6 below.

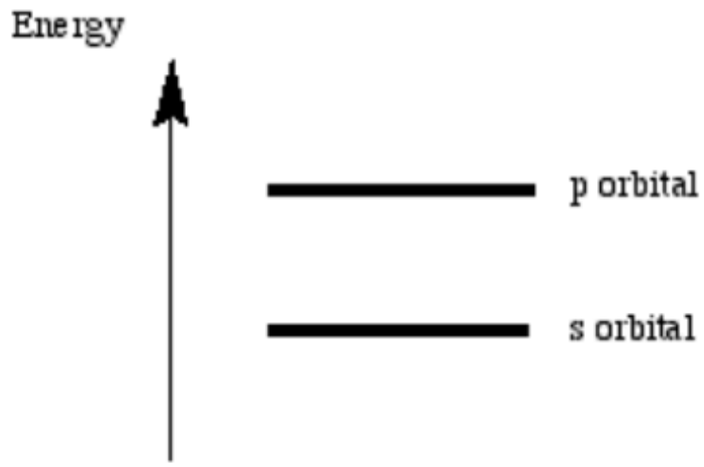


Figure 12.6: Expected Level Structure

which is the *screening* effect.

Complex screening arguments of this type lead to the *Aufbau* principle, which tells us how electrons fill shells.

We see how it works by figuring out the ground state of an N electron atom. The ground state corresponds to that state where all the *lowest energy levels* are filled with a *maximum* of two electrons per level. It is clear that this is the state of lowest energy.

The single-particle Hamiltonian in the central field approximation commutes with ℓ_{iz} and s_{iz} which implies that the energy levels are independent of m_{ℓ_i} and m_{s_i}. Each energy level is therefore characterized by the $2N$ quantum numbers

$$n_i, \ell_i \quad i = 1, 2, 3, ..., N \tag{12.176}$$

We define the electronic configuration of an atomic state as the set of quantum numbers (n_i, ℓ_i) for all the electrons in the atom. We use the symbolic representation

$$shell - label = (n - label)(\ell - label)^{number\ of\ electrons} \tag{12.177}$$

i.e.,

$$ground\ state\ of\ hydrogen = 1s^1 = 1s$$
$$(a\ superscript\ 1\ is\ always\ understood)$$
$$ground\ state\ of\ helium = 1s^2$$
$$ground\ state\ of\ lithium = 1s^2 2s$$

The electronic configuration of helium is an example of a *closed* or *full* shell. The $1s$ subshell has the maximum number electrons as allowed by the PEP, i.e.,

$$n = 1, \ell = 0, m_\ell = 0, s = \frac{1}{2}, m_s = \pm\frac{1}{2} \tag{12.178}$$

The Aufbau principle says that we fill the shells so that we obey the PEP or in the order

$$1s, 2s, 2p, 3s, 3p, 3d, 4s, \ldots\ldots\ldots\ldots$$

with energy increasing from left to right.

The screening arguments of the type we just discussed imply that for a given n (a given shell) the energy order is $s, p, d, \ldots..$ and generally the energy of a shell increases with n = the principal quantum number. The closed shells correspond to

$$\begin{aligned} s - shell \rightarrow & \text{ maximum number of electrons} = 2 \\ & = 2(2\ell + 1) \\ p - shell \rightarrow & \text{ maximum number of electrons} = 6 \\ d - shell \rightarrow & \text{ maximum number of electrons} = 10 \end{aligned}$$

and so on.

Electrons in the shell beyond the last closed shell are called *valence* electrons.

Much of the form and shape of the periodic table is determined by the Aufbau principle. For instance

number of valence electrons → chemical properties

The valence electrons are the ones that participate in bonding and chemical reactions.

This implies that

$$carbon \rightarrow 1s^2 2s^2 2p^2$$

and

$$silicon \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^2$$

which each have two p valence electrons should have similar chemical properties, which is the case.

As with all simple principles of this type, anomalies and breakdowns soon appear. For the Aufbau principle this occurs at the $n = 3$ shell.

In real atoms, when the $3d$ and $4s$ subshells are partially full, the $4s$ level fills ups before the $3d$ level. This means that

$$potassium \rightarrow 1s^2 2s^2 2p^2 3s^2 3p^6 4s$$

$$\text{and not} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 3d$$

The $4s$ state has a larger probability of being near $r = 0$ then the $3d$ state and hence its energy is lower.

For neutral atoms, an experimental ordering scheme is

shell	increasing energy $\rightarrow$									
$n = 1$	$1s$									
$n = 2$		$2s$	$2p$							
$n = 3$				$3s$	$3p$		$3d$			
$n = 4$						$4s$		$4p$	$4d$	$4f$
$n = 5$							$5s$	$5p$	$5d$	
$n = 6$										$6s$ $6p$

At the level of this text we will not be doing any actual energy calculations.

12.7 Angular Momentum Coupling

The N electrons each have spin and orbital angular momentum and thus have associated magnetic moments.

For the full Hamiltonian $\hat{H}$ including the electron-electron repulsion terms we have

$$\left[\hat{H}, \vec{\ell}_{i,op}\right] \neq 0 \quad i = 1, 2, 3, ..., N \tag{12.179}$$

However,

$$\left[\hat{H}, \vec{L}_{op}\right] = 0 \tag{12.180}$$

where

$$\vec{L}_{op} = \sum_{i=1}^{N} \vec{\ell}_{i,op} = \text{ the total orbital angular momentum} \tag{12.181}$$

Therefore, the individual ℓ_i are not conserved, but $\vec{L}$ is conserved.

Thus, the electron-electron repulsion or electrostatic terms in the Hamiltonian couple the electron orbital angular momenta.

In addition, we must add in spin-orbit and other magnetic interactions (spin-spin, etc).

The spin-orbit interaction leads to terms of the form $\vec{\ell}_i \cdot \vec{s}_i$ and thus couple a particle's orbital and spin angular momentum leading to (j_i, m_{j_i}) values, where $\vec{j}_i = \vec{\ell}_i + \vec{s}_i$ as we saw earlier in hydrogen.

In most light atoms, the magnetic interactions are usually weaker than the electrostatic interactions, i.e., electrostatic $\approx 1\ eV$ and spin-orbit $\approx 10^{-4} - 10^{-5}\ eV$.

The angular momentum coupling in a light atom goes like:

1. the orbital angular momenta $\vec{\ell}_i$ couple to form a total orbital angular momentum

$$\vec{L}_{op} = \sum_{i=1}^{N} \vec{\ell}_{i,op} \tag{12.182}$$

2. the spin angular momenta $\vec{s}_i$ couple to form a total spin angular momentum

$$\vec{S}_{op} = \sum_{i=1}^{N} \vec{s}_{i,op} \tag{12.183}$$

   These two couplings occur when we include the electrostatic interactions in the Hamiltonian $\hat{H}$.

3. the weaker magnetic interactions then couple $\vec{L}$ and $\vec{S}$ to form the total angular momentum of the atom

$$\vec{J} = \vec{L} + \vec{S} \tag{12.184}$$

This coupling scheme or order where the electrostatic interactions dominate the magnetic interactions is called LS or *Russell-Saunders* coupling.

In heavy atoms, the spin-orbit magnetic interactions dominate the electrostatic interactions and we get an alternative coupling scheme:

1. each electron's $\vec{\ell}_i$ and $\vec{s}_i$ couple via the magnetic interactions to form

$$\begin{aligned}\vec{j}_i &= \vec{\ell}_i + \vec{s}_i \\ &= \text{the total angular momentum for the } i^{th} \text{ electron}\end{aligned}$$

2. the electrostatic interactions then couple the $\vec{j}_i$ to form

$$\vec{J}_{op} = \sum_{i=1}^{N} \vec{j}_{i,op} \tag{12.185}$$

This scheme is called *jj-coupling*.

We will now investigate the energy level structure in detail for these two different schemes.

Our discussion of helium has shown that exchange symmetry, which requires that the wave functions are completely antisymmetric, has dramatic observable consequences. We saw a spin-spin correlation energy that is characterized by the rule:

> There is a tendency for electrons with parallel spins to repel (avoid) each other. This fact, together with the electrostatic repulsion between electrons implies a strong exchange correlation that cause the spins to tend to align with each other

12.7.1 LS Coupling

In this regime we have the observables and quantum numbers as shown in Table 12.3 below:

Operator	Quantum Number
$\vec{L}^2_{op}$	L
$\vec{J}^2_{op}$	J
$\vec{S}^2_{op}$	S
$\hat{L}_z$	M_L
$\hat{S}_z$	M_S

Table 12.3: LS Coupling Quantum Numbers

When we discussed the spin-orbit interaction in hydrogen we found

1. when we neglect $\hat{H}_{so}$ we can use either $|n, L, S, M_L, M_S\rangle$ or $|n, L, S, J, M_J\rangle$ as basis states

2. when we add in $\hat{H}_{so}$, M_L and M_S are no longer conserved (not good quantum numbers) and therefore we must use $|n, L, S, J, M_J\rangle$ as basis states

Now in the orbital approximation we have

$$M_L = \sum_{i=1}^{N} m_{\ell_i} \quad , \quad M_S = \sum_{i=1}^{N} m_{s_i} \tag{12.186}$$

and

$$\hat{L}_z \psi_\alpha = \hbar M_L \psi_\alpha \qquad \hat{S}_z \psi_\alpha = \hbar M_S \psi_\alpha$$

What are the possible L, S values? We can use our addition of angular momentum rules to find out.

Consider two $p-$electrons , i.e., an vp^2 configuration. We have

$$\ell_1 = \ell_2 = 1 \rightarrow L = 0, 1, 2$$
$$s_1 = s_2 = \frac{1}{2} \rightarrow S = 0, 1$$

and

$$\text{for a given } L \quad M_L = -L, ..., L$$
$$\text{for a given } S \quad M_S = -S, ..., S$$

and

$$M_J = M_L + M_S$$
$$J = |L - S|, ..., L + S$$

Therefore we get the possibilities shown in Table 12.4 below:

L	S	J	State(s)
0	0	0	$^1S_0$
0	1	1	$^3S_1$
1	0	1	$^1P_1$
1	1	0,1,2	$^3P_{0,1,2}$
2	0	2	$^1D_1$
2	1	1,2,3	$^3D_{1,2,3}$

Table 12.4: Possible States

We will discuss the state notation shortly.

For a closed shell we must have $L = S = 0$ or we would violate the PEP. For example,

$$s^2 \rightarrow \ell_1 = \ell_2 = 0 \rightarrow L = 0$$

$$s_1 = s_2 = \frac{1}{2} \rightarrow S = 0 \; or \; 1$$

However, there is only one way to choose the m quantum numbers without violating the PEP which is shown in Table 12.5 below.

m_{ℓ_1}	m_{ℓ_2}	m_{s_1}	m_{s_2}
0	0	1/2	-1/2

Table 12.5: s^2 m-values

We therefore have $M_L = M_S = 0$ (only possibility) which implies that

$$L = S = J = 0 \rightarrow {}^1S_0 \text{ state} \tag{12.187}$$

For

$$p^6 \rightarrow \ell_1 = \ell_2 = \ell_3 = \ell_4 = \ell_5 = \ell_6 = 1$$

$$s_1 = s_2 = s_3 = s_4 = s_5 = s_6 = \frac{1}{2}$$

Once again it turns out there is only one way to choose the values without violating the PEP. This is shown in Table 12.6 below.

m_{ℓ_1}	m_{ℓ_2}	m_{ℓ_3}	m_{ℓ_4}	m_{ℓ_5}	m_{ℓ_6}	m_{s_1}	m_{s_2}	m_{s_3}	m_{s_4}	m_{s_5}	m_{s_6}
1	1	0	0	-1	-1	1/2	-1/2	1/2	-1/2	1/2	-1/2

Table 12.6: p^6 m-values

We therefore have $M_L = M_S = 0$ (only possibility) which implies that

$$L = S = J = 0 \rightarrow {}^1S_0 \text{ state} \tag{12.188}$$

This result is true for *all* closed shells.

In the presence of $\hat{H}_{so}$ the energy levels will depend on L, S and J but not on M_L, M_S or M_J, which is why we label their *atomic terms* by

$$^{2S+1}L_J \tag{12.189}$$

where

$$S, P, D, F, \ldots\ldots\ldots \text{ means } L = 0, 1, 2, 3, \ldots\ldots \tag{12.190}$$

The superscript $2S + 1$ s the *multiplicity* of the level (singlet, doublet, triplet, etc).

If we ignore $\hat{H}_{so}$ then we have $(2S + 1)(2L + 1)$ degeneracy for a given level.

Adding $\hat{H}_{so}$ splits the J states. Each term $^{2S+1}L_J$ remains $2J+1$ degenerate (the M_J values).

This degeneracy is removed by an external magnetic field which splits the $2J+1$ M_J levels(Zeeman effect).

How do we determine the ground state for a particular atom in this scheme?

First, we fill up as many closed shells as possible. The remaining (valence) electrons determine the ground state configuration.

Let us consider carbon which has two equivalent (same subshell) $2p$-electrons in the unfilled shell. We have

$$2p^2 \rightarrow \ell_1 = \ell_2 = 1 \rightarrow L = 0, 1 \; or \; 2$$

$$s_1 = s_2 = \frac{1}{2} \rightarrow S = 0 \; or \; 1$$

We get Table 12.7 below by applying these rules:

L	S	J	Term	Sublevels
0	0	0	^1S	$^1S_0$
1	0	1	^1P	$^1P_1$
2	0	2	^1D	$^1D_2$
0	1	1	^3S	$^3S_1$
1	1	0,1,2	^3P	$^3P_{0,1,2}$
2	1	1,2,3	^3D	$^3D_{1,2,3}$

Table 12.7: Possible States from LS Rules

Not all of these sublevels are allowed by the PEP however. To see this we must look at the individual electron quantum numbers. Table 12.8 below shows those $m_{\ell_1}, m_{\ell_2}, m_{s_1}, m_{s_2}$ values allowed by the PEP (i.e., no two electrons have the same set of quantum numbers).

Before proceeding to the table, in this case, we can use symmetry arguments to determine the allowed levels. In the special case of only two electrons in an unfilled shell, we can easily determine the symmetry of the spin vectors

$$S = 0 \rightarrow \text{ antisymmetric spin function}$$
$$S = 1 \rightarrow \text{ symmetric spin function}$$

We also know the symmetry of the spatial state in general. The symmetry follows from the symmetry of the angular part of the 2–electron wave function. Since we have a central field approximation, the angular part of the wave function is given by the Y_{LM_L} spherical harmonics. The radial function is always symmetric. The symmetry of the spherical harmonics is $(-1)^L$. Therefore,

$$L = odd \rightarrow \text{ antisymmetric space function}$$
$$L = even \rightarrow \text{ symmetric space function}$$

The product of the spin vector and the spatial function must always be anti-symmetric. Therefore we have

$$S = 0 \text{ always combines with even } L$$
$$S = 1 \text{ always combines with odd } L$$

This method is only simple to carry out for 2–electron unfilled shells. In the case of carbon we get the allowed states

$$L = 2, S = 0 \rightarrow 5 \text{ states } = (2L+1)(2S+1)$$
$$L = 1, S = 1 \rightarrow 9 \text{ states}$$
$$L = 0, S = 0 \rightarrow 1 \text{ states}$$

for a total of 15 allowed states. The individual quantum numbers table corresponding to these 15 states is

Entry	$m_\ell = -1$	$m_\ell = 0$	$m_\ell = +1$	M_L	M_S
1	↑↓			-2	0
2		↑↓		0	0
3			↑↓	2	0
4	↑	↑		-1	1
5	↑	↓		-1	0
6	↓	↑		-1	0
7	↓	↓		-1	-1
8	↑		↑	0	1
9	↑		↓	0	0
10	↓		↑	0	0
11	↓		↓	0	-1
12		↑	↑	1	1
13		↑	↓	1	0
14		↓	↑	1	0
15		↓	↓	1	-1

Table 12.8: Individual Quantum Numbers

Any other combinations will violate the PEP. This table can be constructed just using the PEP.

We now construct an implied terms table which tells us how many states exist with a particular pair of (M_L, M_S) values. It is shown as Table 12.9 below.

M_L/M_S	1	0	-1
2	0	1	0
1	1	2	1
0	1	3	1
-1	1	2	1
-2	0	1	0

Table 12.9: Implied terms

We use this table to determine which atomic terms are allowed for carbon. The steps are as follows:

1. Consider the largest possible values of L and S, $L = 2, S = 1$ which correspond to the ${}^3D$ terms.

   Now if a ${}^3D$ atomic term existed , then we would necessarily have $M_L = 2, M_S = 1$ terms. However, there are no such terms, which implies that the ${}^3D$ term is not allowed and thus the sublevels ${}^3D_1, {}^3D_2, {}^3D_3$ are ruled out by the PEP.

2. We now look at the next largest values, namely, $L = 2, S = 0$ or the ^1D term. A $L = 2, S = 0$ term requires $M_L = 2, M_S = 0$ terms which do exist. Therefore the ^1D term and the sublevel $^1D_2$ exist. This has $J = 2$ and thus $2J + 1 = 5$ M_J levels. This accounts for 5 of the 15 entries in the table.

3. We subtract these 5 states to get a *second-implied terms* table

M_L/M_S	1	0	-1
2	0	0	0
1	1	1	1
0	1	2	1
-1	1	1	1
-2	0	0	0

Table 12.10: Implied terms

4. We now look at the next largest values, namely, $L = 1, S = 1$ or the ^3P term. Since entries with $M_L = -1, 0, +1$ and $M_S = -1, 0, +1$ still exist in the new table, the ^3P term and the sublevels $^3P_2, ^3P_1, ^3P_0$ are allowed. These correspond to a total of $(2L + 1)(2S + 1) = 5 + 3 + 1 = 9$ states.

5. We subtract these 9 states to get the *third-implied terms* table

M_L/M_S	1	0	-1
2	0	0	0
1	0	0	0
0	0	1	0
-1	0	0	0
-2	0	0	0

Table 12.11: Implied terms

Only one state is left with $M_L = M_S = 0$, which is a ^1S atomic term. Therefore the $^1S_0$ sublevel is allowed.

This accounts for all the 15 entries in the table. No more states are allowed, which means that the ^3S and ^1P atomic terms and their associated sublevels are forbidden by the PEP. This result agrees with the allowed states we obtained from symmetry arguments.

We always need to use the implied-terms tables in the general cases (more than 2 electrons in an unfilled shell) because the corresponding symmetry arguments are very complex to apply.

Finally, for carbon we have the ^1S, ^3P and ^1D allowed by the PEP.

This result is true for all atoms with 2 equivalent $p-$electrons outside closed subshells.

To complete the picture, we must now determine how the allowed terms are ordered in energy.

stop

12.7.2 Hund's Rules

Each sublevel in carbon $^1S_0$, $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ has a different energy when $\hat{H}_{so}$ is included in $\hat{H}$.

A set of rules exists for qualitatively ordering the levels. They are called *Hund's rules.*

Hund's rules apply when we are ordering the energy levels and sublevels for equivalent electrons in the ground state.

Rule 1 Terms in the ground state configuration with maximum multiplicity $2S + 1$ lie lowest in energy.

This follows from the fact that same spins (unpaired spins) *repel* and different spins (paired spins) *attract.*

High multiplicity implies a greater number of electrons with parallel spin than low multiplicity in multielectron atoms. Since parallel spin electrons avoid each other, the e^2/r_{ij} effect decreases and the energy of high multiplicity states lies below that of low multiplicity states.

Rule 2 Of several levels with the same multiplicity S, the one with maximum L lies lowest in energy

In some sense, the maximum L state implies that all electrons are *orbiting in the same direction*. These electrons tend to remain separated from each other and so have a lower energy than those *orbiting in the opposite direction*, which get close to each other some of the time.

Rule 3 Of several sublevels with the same multiplicity S and same L

1. the sublevel with the minimum value of J lies lowest in energy if the shell is less than half-filled. These are called *regular multiplets*
2. the sublevel with the maximum value of J lies lowest in energy if the shell is more than half-filled. These are called *inverted multiplets*

This results follows from $\hat{H}_{so}$ and the fact that $-e^2/r$ increases as $r \to \infty$. Applying Hund's rules to an np^2 configuration we get the energy level scheme in Figure 12.7 below.

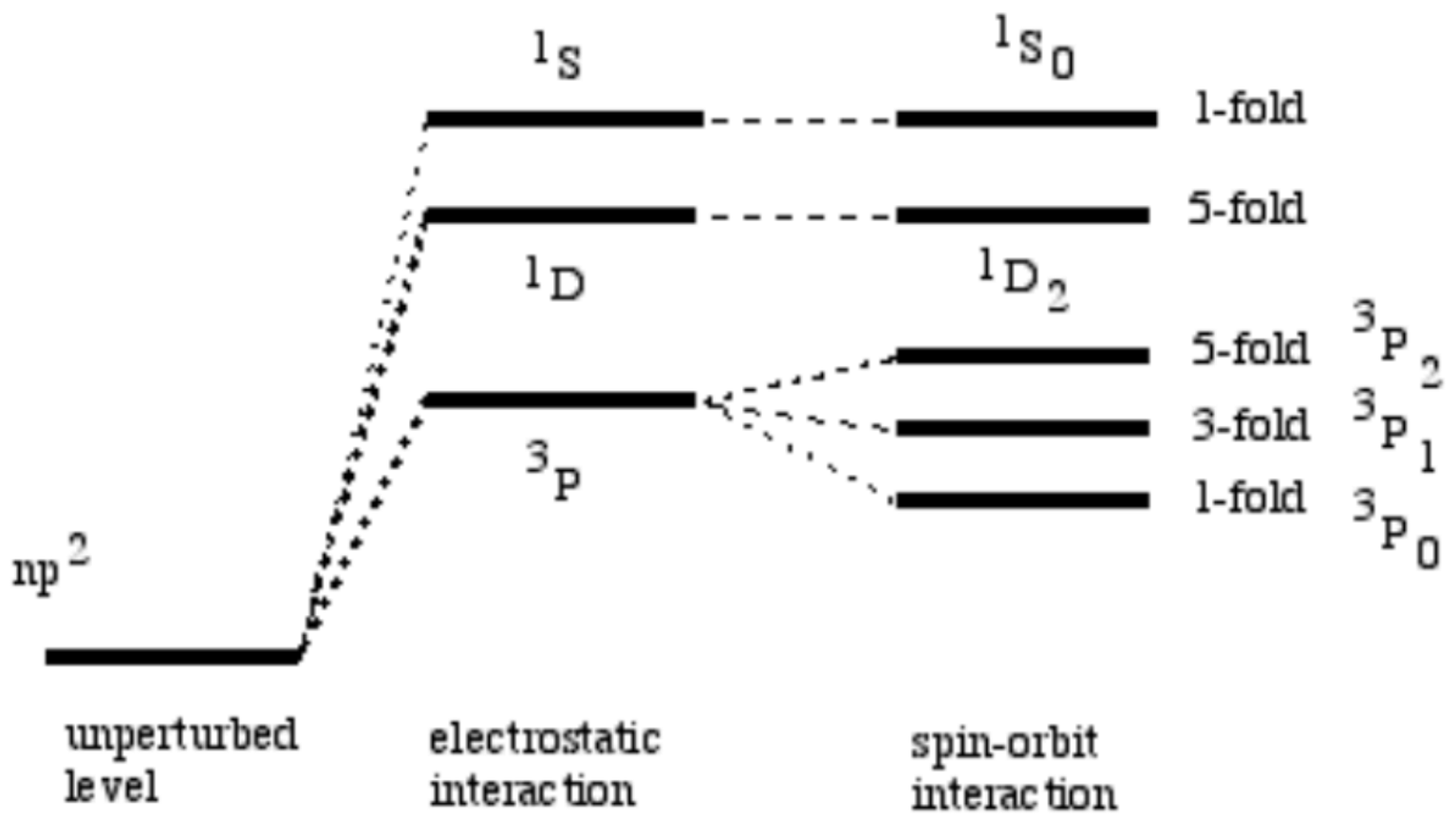


Figure 12.7: np^2 Level Scheme

Hund's rules are not perfect since they are based on the orbital approximation.

To determine an electronic configuration, we must specify how the electrons are placed into subshells. It turns out there is a phenomenon called configuration interaction or configuration mixing which forces the quantum mechanical state to sometimes be a mixture of more than one configuration.

12.7.3 JJ-Coupling

In heavy atoms, the magnetic interactions which couple the $\vec{\ell}_i$ and $\vec{s}_i$ together into the $\vec{j}_i$, dominate over the electrostatic interactions which led to LS coupling. The configurations are then better described by the so-called *jj-coupling* scheme.

Since $s_i = 1/2$ for all electrons, we have for $\ell_i \geq 1$

$$j_i = \ell_i \pm \frac{1}{2}$$
$$m_{j_i} = -j_i, \ldots\ldots, j_i$$

The individual $\vec{j}_i$ then couple together to give the total $\vec{J}$.

In a two-electron configuration the levels are labelled by J, j_1, j_2, M_J where

$$J = |j_1 - j_2|, \ldots\ldots, j_1 + j_2$$
$$M_J = -J, \ldots\ldots, J$$

Let us consider the Pb (lead) atom, which has np^2 valence electrons (built on many closed shells). We have

$$\ell_1 = \ell_2 = 1$$
$$\rightarrow j_1 = \frac{1}{2}, \frac{3}{2} \text{ and } j_2 = \frac{1}{2}, \frac{3}{2}$$

The possible total J values are then

$$\frac{3}{2} \otimes \frac{3}{2} = 3, 2, 1, 0$$
$$\frac{1}{2} \otimes \frac{3}{2} = 2, 1$$
$$\frac{1}{2} \otimes \frac{1}{2} = 1, 0$$

Not all of these states are allowed by the PEP. For example,

$$J = 3, M_J = 3 \rightarrow j_1 = j_2 = \frac{3}{2}, m_{j1} = m_{j2} = \frac{3}{2}$$
$$\ell_1 = \ell_2 = 1, m_{\ell 1} = m_{\ell 2} = 1$$
$$s_1 = s_2 = \frac{1}{2}, m_{s1} = m_{s2} = \frac{1}{2}$$

Both electrons need to have identical quantum numbers for this state to exist. Thus, this state is not allowed. In a similar manner,

$$J = 3 \quad , \quad j_1 = j_2 = \frac{3}{2}$$
$$J = 1 \quad , \quad j_1 = j_2 = \frac{1}{2}$$

can be shown to be forbidden by the PEP. Therefore we have

$$\frac{3}{2} \otimes \frac{3}{2} = 2, 0$$
$$\frac{1}{2} \otimes \frac{3}{2} = 2, 1$$
$$\frac{1}{2} \otimes \frac{1}{2} = 0$$

Usually, the level with the lowest J for a given pair (j_1, j_2) has the lowest energy (this is not a strict rule).

For medium weight atoms, neither LS nor jj coupling is valid.

There is a connection between the levels in the two schemes as illustrated by the energy level diagram in Figure 12.8 below.

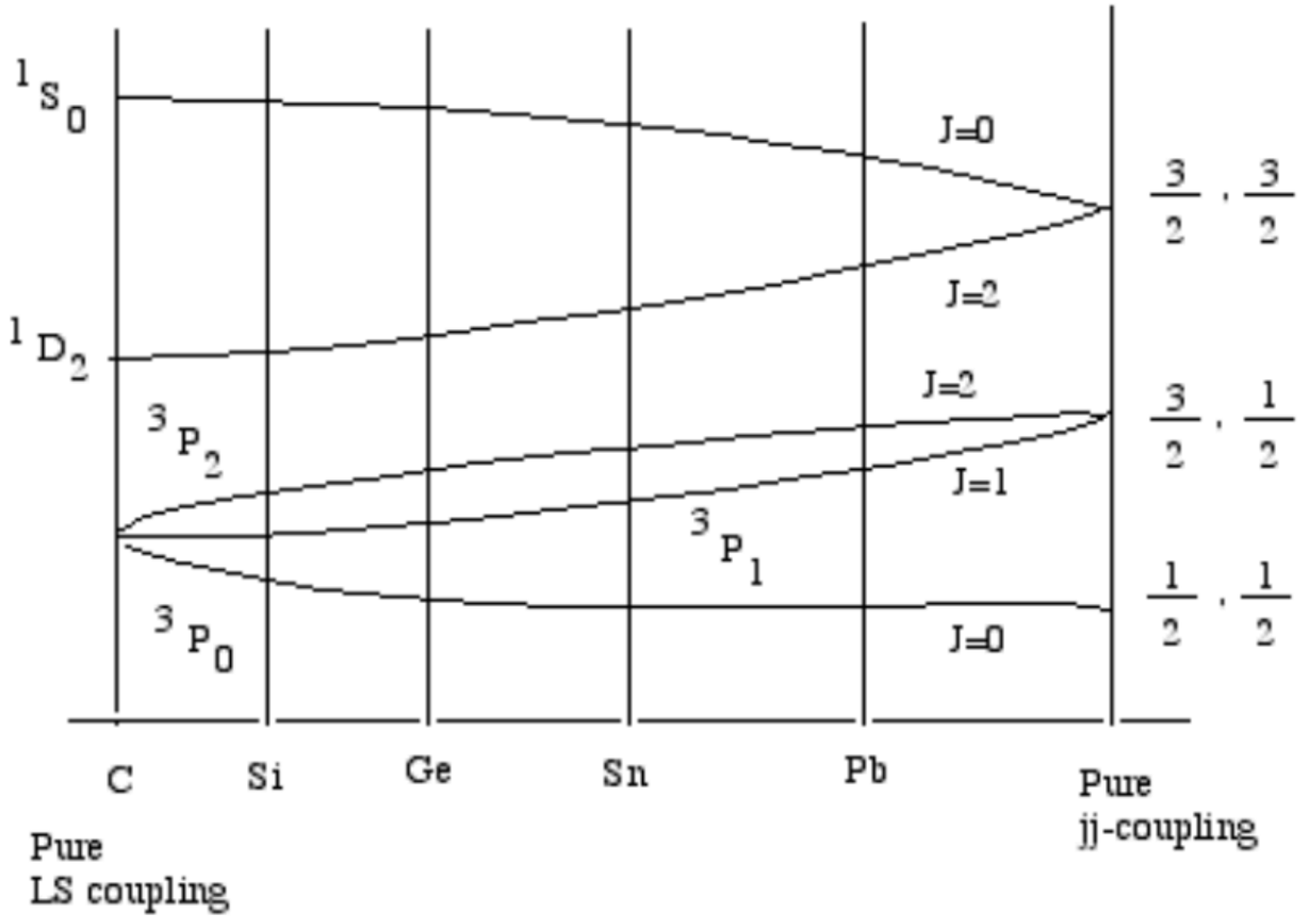


Figure 12.8: LS - jj Energy Level Connection

The connection between the two schemes is clear.

The spacing between J-levels in LS coupling is given as follows.

$$\left\langle \hat{H}_{so} \right\rangle = \frac{1}{2} C \left[(J(J+1) - L(L+1) - S(S+1) \right] \qquad (12.191)$$

For the same L, S we have

$$\begin{aligned} E_{J+1} - E_J &= \frac{1}{2} C \left[(J+1)(J+2) - J(J+1) \right] \\ &= C(J+1) \end{aligned} \qquad (12.192)$$

This says that the spacing between consecutive levels of a fine structure multiplet is proportional to the larger J value involved. This is the *Lande interval rule.*

We end this discussion with an example of two electrons that are not equivalent(in different shells). The discussion is more straightforward since we do not have to worry about the PEP (all possibilities are allowed).

We consider two electrons in a $4p4d$ configuration. In the LS coupling scheme we have:

$$\ell_1 = 1\ ,\ \ell_2 = 2 \rightarrow L = 1, 2, 3$$

$$s_1 = s_2 = \frac{1}{2} \rightarrow S = 0, 1$$

$$3 \otimes 1 \rightarrow J = 4, 3, 2$$

$$3 \otimes 0 \rightarrow J = 3 \rightarrow 7 \text{ states}$$

$$2 \otimes 1 \rightarrow J = 3, 2, 1 \rightarrow 16 \text{ states}$$

$$2 \otimes 0 \rightarrow J = 2 \rightarrow 5 \text{ states}$$

$$1 \otimes 1 \rightarrow J = 2, 1, 0 \rightarrow 9 \text{ states}$$

$$1 \otimes 0 \rightarrow J = 1 \rightarrow 3 \text{ states}$$

or

$$J = 4 \quad in \quad 1 \quad level$$

$$J = 3 \quad in \quad 3 \quad levels$$

$$J = 2 \quad in \quad 4 \quad levels$$

$$J = 1 \quad in \quad 3 \quad levels$$

$$J = 0 \quad in \quad 1 \quad level$$

Thus, we have 12 total levels. The LS coupling energy level diagram is shown in Figure 12.9

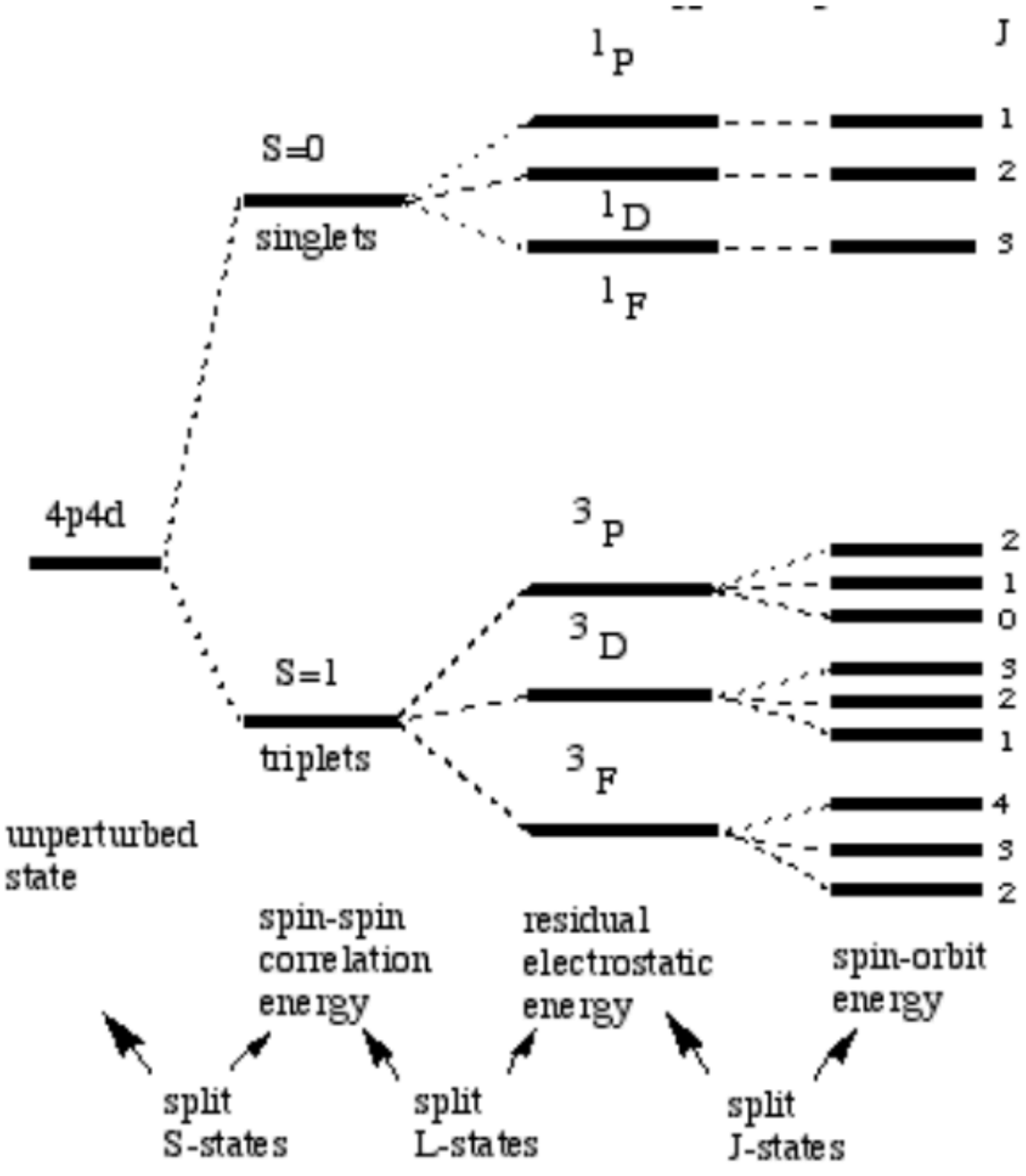


Figure 12.9: LS 4p4d Energy Levels

In the jj-coupling scheme the energy level diagram is shown in Figure 12.10

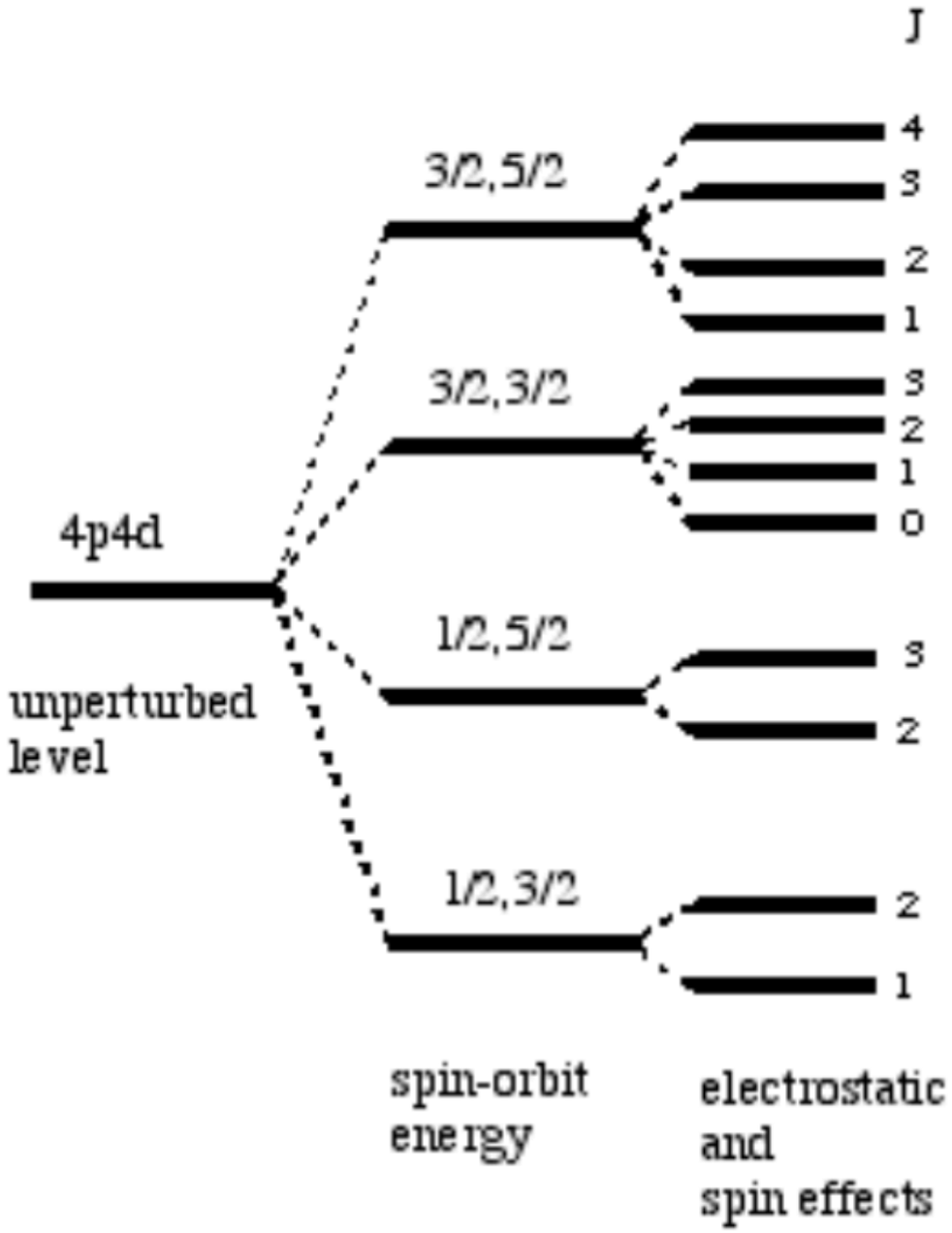


Figure 12.10: jj 4p4d Energy Levels

Notice that the final J values are identical, but their arrangement in energy is very different.

12.8 Spherical Harmonics Addition Theorem

In Chapter 7 we defined the properties of the spherical harmonics. We found the following results.

12.8.1 Orbital Angular Momentum

Abstractly,

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \text{ and } \left[\hat{L}_{op}^2, \hat{L}_j\right] = 0 \tag{12.193}$$

$$\hat{L}_{op}^2 |\ell m\rangle = \hbar^2 \ell(\ell+1) |\ell m\rangle \text{ and } \hat{L}_3 |\ell m\rangle = \hbar m |\ell m\rangle \tag{12.194}$$

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \tag{12.195}$$

$$\ell = \frac{\text{integer}}{2} \geq 0 \tag{12.196}$$

For a given value of ℓ, m takes on the $2\ell+1$ values

$$m = -\ell, -\ell+1, -\ell+2, \ldots\ldots\ldots, \ell-2, \ell-1, \ell$$

In ordinary 3–dimensional space, if we define

$$Y_{\ell m}(\theta, \varphi) = \langle \theta\varphi \mid \ell m\rangle = \textit{spherical harmonic} \tag{12.197}$$

then we have the defining equations for the $Y_{\ell m}(\theta, \varphi)$ given by

$$\begin{aligned} \langle\theta\varphi|\, \vec{L}_{op}^2 \,|\ell m\rangle &= \vec{L}_{op}^2 \langle\theta\varphi \mid \ell m\rangle = \vec{L}_{op}^2 Y_{\ell m}(\theta, \varphi) \\ &= \hbar^2\ell(\ell+1) \langle\theta\varphi \mid \ell m\rangle = \hbar^2\ell(\ell+1) Y_{\ell m}(\theta, \varphi) \end{aligned} \tag{12.198}$$

$$\begin{aligned} \langle\theta\varphi|\, \hat{L}_3 \,|\ell m\rangle &= \hat{L}_3 \langle\theta\varphi \mid \ell m\rangle = \hat{L}_3 Y_{\ell m}(\theta, \varphi) \\ &= \hbar m \langle\theta\varphi \mid \ell m\rangle = \hbar m Y_{\ell m}(\theta, \varphi) \end{aligned} \tag{12.199}$$

The general result is

$$Y_{\ell m}(\theta,\varphi) - \frac{(-1)\ell}{2^\ell \ell!}\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell+m)!}{(\ell-m)!}}\frac{e^{im\varphi}}{(\sin\theta)^m}\left(\frac{d}{d\cos\theta}\right)^{\ell-m}(\sin\theta)^{2\ell} \quad (12.200)$$

Some examples are:

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \quad (12.201)$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \ , \ Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\theta \quad (12.202)$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \ , \ Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi} \quad (12.203)$$

$$Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi} \quad (12.204)$$

Some Properties

Complex Conjugate

$$Y_{\ell,-m}(\theta,\varphi) = (-1)^m Y^*_{\ell,m}(\theta,\varphi) \quad (12.205)$$

Under the parity operation

$$\vec{r} \to -\vec{r} \quad or \quad r \to r, \theta \to \pi - \theta, \varphi \to \varphi + \pi$$

which says that

$$e^{im\varphi} \to e^{im\varphi}e^{im\pi} = (-1)^m e^{im\varphi}$$
$$\sin\theta \to \sin(\pi - \theta) \to \sin\theta$$
$$\cos\theta \to \cos(\pi - \theta) \to -\cos\theta$$

which imply that

$$Y_{\ell,m}(\theta,\varphi) \to (-1)^\ell Y_{\ell,m}(\theta,\varphi) \tag{12.206}$$

Therefore,

if ℓ is even, then we have an even parity state
if ℓ is odd, then we have an odd parity state

Since they form a complete set, any function of (θ,φ) can be expanded in terms of the $Y_{\ell,m}(\theta,\varphi)$ (the $Y_{\ell,m}(\theta,\varphi)$ are a basis), i.e., we can write

$$f(\theta,\varphi) = \sum_{\ell,m} f_{\ell m} Y_{\ell,m}(\theta,\varphi) \tag{12.207}$$

where

$$f_{\ell m} = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta Y^*_{\ell' m'}(\theta,\varphi) f(\theta,\varphi) \tag{12.208}$$

and we have used the orthonormality relation

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta Y^*_{\ell' m'}(\theta,\varphi) Y_{\ell m}(\theta,\varphi) = \delta_{\ell'\ell}\delta_{m'm} \tag{12.209}$$

The spherical harmonics also satisfy these relations:

Closure:

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y^*_{\ell m}(\theta,\phi) Y_{\ell m}(\theta',\phi') = \frac{\delta(\theta-\theta')\delta(\phi-\phi')}{\sin\theta} \equiv \delta(\hat{r},\hat{r}') \tag{12.210}$$

i.e., the solid angle delta function is equal to zero unless the two vectors $\hat{r}(\theta,\phi)$, $\hat{r}'(\theta',\phi')$ coincide. It has the property

$$\int f(\hat{r}')\delta(\hat{r},\hat{r}')d\Omega' = f(\hat{r}) \tag{12.211}$$

for any function $f(\vec{r})$ of the spatial direction specified by θ, φ.

Recursion:

$$\hat{L}_{\pm} Y_{\ell m} = \left[\ell(\ell+1) - m(m\pm 1)\right]^{1/2} Y_{\ell,m\pm 1}$$
$$= \left[(\ell \mp m)(\ell + 1 \pm m)\right]^{1/2} Y_{\ell,m\pm 1} \qquad (12.212)$$

$$\cos\theta Y_{\ell m} = \left[\frac{(\ell+1+m)(\ell+1-m)}{(2\ell+1)(2\ell+3)}\right]^{1/2} Y_{\ell+1,m}$$
$$+ \left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right]^{1/2} Y_{\ell-1,m} \qquad (12.213)$$

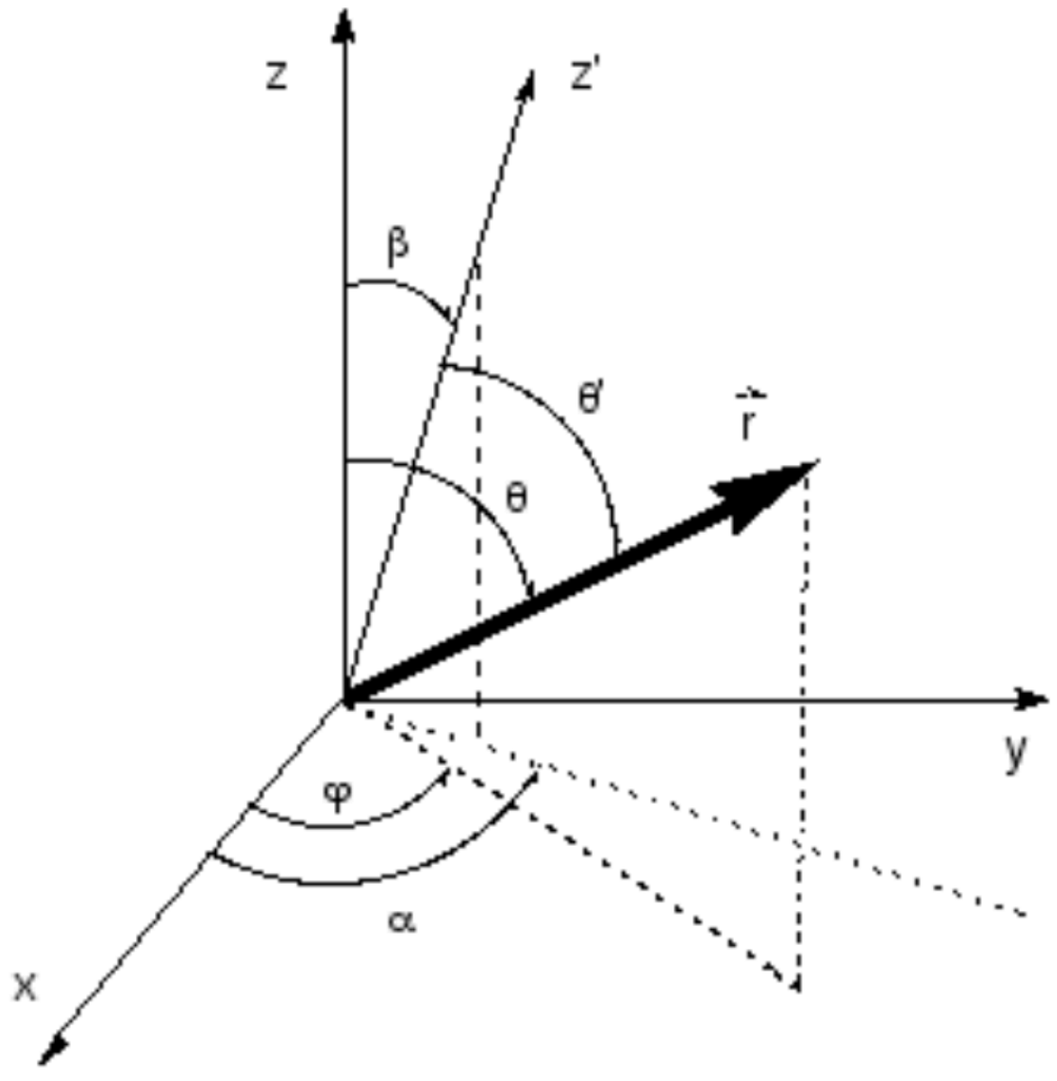


Figure 12.11: Angles Used in the Addition Theorem

12.8.2 The Addition Theorem

Consider two coordinate systems xyz and $x'y'z'$. The addition theorem is the formula expressing the eigenfunction $P_\ell(\cos\theta')$ of the angular momentum $\hat{L}_{z'}$ about the $z'-$axis in terms of the eigenfunctions $Y_{\ell,m}(\theta,\varphi)$ of $\hat{L}_z$. . See Figure 12.11above for orientations.

The angles α and β are the azimuth and the polar angles of the z' axis in the Cartesian xyz coordinate frame. They are also the first two Euler angles specifying the orientation of the Cartesian coordinate system $x'y'z'$ with respect to xyz. The third Euler angle γ is left unspecified here and the x' and y' axes are not shown. The projections of the z' axis and the radius vector on the xy plane are dashed lines.

As we can see the position vector $\vec{r}$ has angular coordinates θ,φ and θ',φ' in the two coordinate systems.

The direction of the z' axis in space is specified by its polar angle β and its azimuth angle α with respect to the xyz system.

Since P_ℓ is an eigenfunction of $\vec{L}^2_{op}$, only spherical harmonics with the same subscript ℓ can appear in the expansion.

An interchange of θ,φ and β,α is equivalent to the transformation $\theta \to -\theta'$ and must leave the expansion unchanged because $P_\ell(\cos\theta')$ is an even function of θ'. This means that $P_\ell(\cos\theta')$ must be a function of $\varphi-\alpha$.

All of these requirements are satisfied only if we write

$$P_\ell(\cos\theta') = \sum_{m=-\ell}^{\ell} c_m Y_{\ell,-m}(\beta,\alpha) Y_{\ell,m}(\theta,\phi) \tag{12.214}$$

We determine the coefficients c_m using the conditions

$$\hat{L}_{z'} P_\ell(\cos\theta') = 0 \tag{12.215}$$

We also use the identity (from rotation of a vector component)

$$\begin{aligned}\hat{L}_{z'} &= \sin\beta\cos\alpha\hat{L}_x + \sin\beta\sin\alpha\hat{L}_y + \cos\beta\hat{L}_z \\ &= \frac{1}{2}\sin\beta e^{-i\alpha}\hat{L}_+ + \frac{1}{2}\sin\beta e^{i\alpha}\hat{L}_- + \cos\beta\hat{L}_z\end{aligned} \tag{12.216}$$

and invoke the linear independence of the spherical harmonics to obtain (after some algebra)

$$c_{m\pm1} = -c_m \rightarrow c_m = (-1)^m c_0 \tag{12.217}$$

so that we only need to determine c_0. We specialize to $\beta = 0$ or $\theta' = \theta$ so that we have the relations

$$Y_{\ell m}(0,\phi) = \sqrt{\frac{2\ell+1}{4\pi}}\delta_{m0} \tag{12.218}$$

$$Y_{\ell 0}(\theta,\phi) = \sqrt{\frac{2\ell+1}{4\pi}} P_\ell(\cos\theta) \tag{12.219}$$

We then have

$$P_\ell(\cos\theta) = \sum_{m=-\ell}^{\ell} c_m Y_{\ell,-m}(0,\alpha) Y_{\ell,m}(\theta,\phi) = \sum_{m=-\ell}^{\ell} c_m \sqrt{\frac{2\ell+1}{4\pi}} \delta_{m0} Y_{\ell,m}(\theta,\phi)$$

$$= c_0 \sqrt{\frac{2\ell+1}{4\pi}} Y_{\ell,0}(\theta,\phi) = c_0 \sqrt{\frac{2\ell+1}{4\pi}} \sqrt{\frac{2\ell+1}{4\pi}} P_\ell(\cos\theta) \qquad (12.220)$$

or

$$c_0 = \frac{4\pi}{2\ell+1} \qquad (12.221)$$

and we end up with the addition theorem

$$P_\ell(\cos\theta') = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} c_m Y^*_{\ell m}(\beta,\alpha) Y_{\ell,m}(\theta,\phi) \qquad (12.222)$$

where θ' = angle between the directions (β,α) and (θ,φ).

If we combine the closure relation with the addition theorem we get the identity

$$\sum_{\ell=0}^{\infty} (2\ell+1) P_\ell(\hat{r}\cdot\hat{r}') = 4\pi\delta(\hat{r},\hat{r}') \qquad (12.223)$$

Since we can write

$$\delta(\vec{r}-\vec{r}') = \frac{\delta(r-r')}{r^2} \delta(\hat{r},\hat{r}') \qquad (12.224)$$

we then have the identity

$$\delta(\vec{r}-\vec{r}') = \frac{\delta(r-r')}{r^2}\sum_{\ell=0}^{\infty}\frac{2\ell+1}{4\pi}P_\ell(\hat{r}\cdot\hat{r}') \tag{12.225}$$

Another useful relation is

$$e^{ikz} = \sum_{\ell=0}^{\infty}(2\ell+1)i^\ell j_\ell(kr)P_\ell(\cos\theta) \tag{12.226}$$

or, in general

$$e^{ik\cdot\vec{r}} = 4\pi\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} i^\ell j_\ell(kr)Y^*_{\ell m}(\theta_{\vec{k}},\phi_{\vec{k}})Y_{\ell m}(\theta_{\vec{r}},\phi_{\vec{r}}) \tag{12.227}$$

done