XI. <u>Identical Particles</u>

a. <u>The Product Basis</u>

We have already dealt with multiple particles implicitly. For example, when we were doing inelastic scattering calculations, our basis states involved specifying the state of the electron **and** the molecule, $|\psi;n\rangle$. Although we did not stress it at the time, these basis states are equivalent to **products**: a state for the electron times a state for the molecule:

$$|\psi;n\rangle = |\psi\rangle|n\rangle$$

To verify this, we act on the right hand state with the zeroth order Hamiltonian:

$$\hat{H}_0|\psi\rangle|n\rangle = -\tfrac{1}{2}\nabla^2 + \omega\left(\hat{n} + \tfrac{1}{2}\right)|\psi\rangle|n\rangle = \left(\tfrac{k^2}{2} + \omega\left(n + \tfrac{1}{2}\right)\right)|\psi\rangle|n\rangle$$

and we see that these are, indeed, eigenfunctions of $\hat{H}_0$ as advertised. This is a general rule: one can conveniently build a many particle wavefunction that describes the state of particles A, B, C, D,… by considering a product of states for A, B, C, D,… individually:

$$|\Psi\rangle \equiv |\psi_A\psi_B\psi_C\psi_D...\rangle = |\psi_A\rangle|\psi_B\rangle|\psi_C\rangle|\psi_D\rangle...$$

Many Particle ψ   Single Particle ψ's

where from here on out we will use capitol Greek letters to denote many particle states and lower case Greek letters when representing one-particle states. The particles A, B, C, D,… can be **any** set of distinct particles (e.g. A=H$_2$O, B=He+, C= H$_2$O+, D=He,…). Then $|\psi_A\rangle$ would be a wavefunction that represents the state of the water molecule, $|\psi_B\rangle$ would represent the state of the He+, etc.

What do these product states mean? To look at this question, lets assume the Hamiltonian can be decomposed into a Hamiltonian that acts just on A plus one for B plus one for C …:

$$\hat{H} = \hat{h}_A + \hat{h}_B + \hat{h}_C + \hat{h}_D + ...$$

This Hamiltonian describes independent particles (because it lacks coupling terms $\hat{h}_{AB}$ that depend on A and B simultaneously). Now, the eigenstates of this independent particle Hamiltonian can always be chosen to be product states, for which:

$$\hat{H}|\Psi\rangle = \left(\hat{h}_A + \hat{h}_B + \hat{h}_C + \hat{h}_D + ...\right)|\psi_A\rangle|\psi_B\rangle|\psi_C\rangle|\psi_D\rangle$$
$$= \left(e_A + e_B + e_C + e_D + ...\right)|\psi_A\rangle|\psi_B\rangle|\psi_C\rangle|\psi_D\rangle = E|\Psi\rangle.$$

Thus, product states describe particles that are independent of, or uncorrelated with, one another. One consequence of this fact is that a measurement on A will not affect the state of B and vice versa. For this reason, product states are also sometimes called "independent particle" states, which is appropriate since they describe the state of each particle **independently**.

Note that just because product states happen to describe many particles, it does not follow that **every** many particle wavefunction can be written in this form. In fact, it is easy to build a many particle wavefunction that is **not** of product form. For example:

$$|\Psi_2\rangle \equiv c_1|\psi_{1A}\rangle|\psi_{1B}\rangle|\psi_{1C}\rangle|\psi_{1D}\rangle + c_2|\psi_{2A}\rangle|\psi_{2B}\rangle|\psi_{2C}\rangle|\psi_{2D}\rangle$$

cannot be written as a product of one particle wavefunctions. In particular, for this state, a measurement on A influences the outcome of measurements on B, C and D: if we find that A is in state 1, B,C and D must collapse to state 1, while A in state 2 implies B, C and D will collapse to state 2. This strange correlation between different particles is called entanglement and plays a very important role in many-particle quantum mechanics. Meanwhile, the state

$$|\Psi'\rangle \equiv \left(c_1|\psi_{1A}\rangle + c_2|\psi_{2A}\rangle\right)\left(c_1|\psi_{1B}\rangle + c_2|\psi_{2B}\rangle\right)\left(c_1|\psi_{1C}\rangle + c_2|\psi_{2C}\rangle\right)\left(c_1|\psi_{1D}\rangle + c_2|\psi_{2D}\rangle\right)$$

| Particle A | Particle B | Particle C | Particle D |
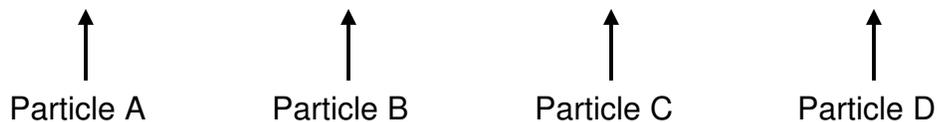
is of product form by construction, but if we expand it out, we find:

$$|\Psi'\rangle \equiv c_1{}^4|\psi_{1A}\rangle|\psi_{1B}\rangle|\psi_{1C}\rangle|\psi_{1D}\rangle$$

$$+ c_1{}^3 c_2 \left(\begin{array}{l} |\psi_{2A}\rangle|\psi_{1B}\rangle|\psi_{1C}\rangle|\psi_{1D}\rangle + |\psi_{1A}\rangle|\psi_{2B}\rangle|\psi_{1C}\rangle|\psi_{1D}\rangle + \\ |\psi_{1A}\rangle|\psi_{1B}\rangle|\psi_{2C}\rangle|\psi_{1D}\rangle + |\psi_{1A}\rangle|\psi_{1B}\rangle|\psi_{1C}\rangle|\psi_{2D}\rangle \end{array} \right)$$

$$+ c_1{}^2 c_2{}^2 (...) + ...$$

This looks very complicated in the many particle space, and it clearly points out why $|\Psi_2\rangle$ could not be written in product form: it lacks the necessary cross terms! The important property that distinguishes $|\Psi_2\rangle$ as describing independent particles is that measurements on A will not influence the state of B, C or D.

Now, while $|\Psi'\rangle$ looks very complicated in our many particle basis, this is really a symptom of the fact that we have chosen the wrong *one particle basis* for this product state. If we instead define the basis functions

$$|\psi_A'\rangle = c_1|\psi_{1A}\rangle + c_2|\psi_{2A}\rangle \qquad |\psi_B'\rangle = c_1|\psi_{1B}\rangle + c_2|\psi_{2B}\rangle$$

$$|\psi_C'\rangle = c_1|\psi_{1C}\rangle + c_2|\psi_{2C}\rangle \qquad |\psi_D'\rangle = c_1|\psi_{1D}\rangle + c_2|\psi_{2D}\rangle$$

Then, $|\Psi'\rangle$ takes the simple form

$$|\Psi'\rangle = |\psi_A'\rangle|\psi_B'\rangle|\psi_C'\rangle|\psi_D'\rangle .$$

Thus, a change in our one particle basis states (e.g. from the $|\psi_{1A}\rangle,|\psi_{2A}\rangle,|\psi_{1B}\rangle$... basis to the $|\psi_A'\rangle,|\psi_B'\rangle$... basis) has a **very complicated** effect on our many particle product space. In general if we change our basis so that

$$|\psi_A'\rangle = \sum_i a_i|\psi_{iA}\rangle$$

$$|\psi_B'\rangle = \sum_i b_i|\psi_{iB}\rangle$$

...

then we can write $|\Psi'\rangle$ in the new basis as:

Old Many-Particle Basis function

$$|\Psi'\rangle = |\psi_A'\rangle|\psi_B'\rangle|\psi_C'\rangle|\psi_D'\rangle...$$

$$= \left(\sum_i a_i|\psi_{iA}\rangle\right)\left(\sum_j b_j|\psi_{jB}\rangle\right)\left(\sum_k c_k|\psi_{kC}\rangle\right)\left(\sum_l d_l|\psi_{lD}\rangle\right)... .$$

$$= \sum_{ijkl...} a_i b_j c_k d_l...|\psi_{iA}\rangle|\psi_{jB}\rangle|\psi_{kC}\rangle|\psi_{lD}\rangle...$$

Coefficients

New Many-Particle Basis function

Note that in either basis, $|\Psi'\rangle$ is still a product state. This is true in general; changing our one particle basis cannot turn a product state into a non-product state (or vice versa) – it only makes the structure of a given product state more or less simple.

The most important thing about product states is that they form a complete many-particle basis. Thus, assume we have complete basis, $|\psi_{iA}\rangle$, so that any one-particle wavefunction for A can be written as a linear combination of the basis functions:

$$|\psi_A\rangle = \sum_i a_i |\psi_{iA}\rangle$$

and similarly for B, C, D,…. Then any ***many particle*** state for A, B, C, D… can be written as a linear combination of products of these basis functions:

$$|\Psi\rangle = \sum_{ijkl\dots} C_{ijkl}\dots |\psi_{iA}\rangle|\psi_{jB}\rangle|\psi_{kC}\rangle|\psi_{lD}\rangle\dots .$$

Note that in the case of a single particle transformation, the coefficients always decomposed as products; that is

$$C_{ijkl}\dots = a_i b_j c_k d_l \dots .$$

Finally, we should stress that the many particle basis will be much bigger than the single particle basis. For example, suppose we require 100 basis functions to make a "complete" basis (within numerical precision) for A and similarly for B,C and D. The number of 4 particle basis states we can specify is the ***product*** of the numbers of single particle functions. Hence the many particle basis will have 100x100x100x100=100,000,000 basis functions! Hence we immediately see the need for physical approximations for many-particle systems.

b. Symmetry Under Exchange

Up to now, we have been dealing with several particles that are all of different character. In many cases, we want to deal with the situation where some or all of the particles are identical (e.g. to describe the many electrons in an atom or molecule). For simplicity, in what follows we will assume all the particles are identical; if there are several classes of identical particles (e.g. some electrons, some protons and some neutrons) one can always build an appropriate

wavefunction as the product of a wavefunction for the electrons times a wavefunction for the protons times….

What do we mean when we say that particles are identical? Notice that in order to keep track of the particles, I need to put labels on them: so, one of the electrons will be particle "1" and the other particle "2." If the particles are identical, these labels are completely arbitrary, and if I switch them it must not change any experimental observable. Hence, if I swap "1" and "2", I better get the same wavefunction back (up to, perhaps, a constant factor). For two particles, I can put an equation to this by defining an operator, $\mathcal{P}$, that permutes the two labels; for example if I have a product state:

$$\mathcal{P}|\psi_1(1)\rangle|\psi_2(2)\rangle = |\psi_1(2)\rangle|\psi_2(1)\rangle$$

where $|\psi_i(j)\rangle$ indicates that the jth electron is in the ith state. For identical particles, we concluded that we must have

$$\mathcal{P}|\Psi\rangle = c|\Psi\rangle$$

which means that the wavefunction for identical particles must be an eigenstate of $\mathcal{P}$. Now, it is clear that $\mathcal{P}^2 = 1$ (i.e. if we switch the particles and then switch them back, we get the same state). As a result, the eigenvalues of $\mathcal{P}$ must be ± 1 and so for identical particles, we have the restriction that

$$\mathcal{P}|\Psi\rangle = \pm|\Psi\rangle$$

The two signs relate to a wavefunction that is symmetric (+) or antisymmetric (-) with respect to the interchange of the particles.

Now, there is a rather deep result, called the spin statistics theorem that proves two things:

   1) All particles fall into two classes; Fermions, which are **always** antisymmetric under exchange and Bosons, which are **always** symmetric under exchange.

   2) Fermions always have half-integer spin (e.g. electrons, protons, He^3, etc.). Bosons always have integer spin (e.g. photons, He^4, etc.).

Proving this theorem is *definitely* beyond the scope of this course, so we will just take it as a given. We will primarily be interested in

electrons (Fermions) and photons (Bosons) in this course, but it is important to realize that composite particles (like a proton or a helium atom) also obey the spin statistics theorem.

How do we construct functions that obey the appropriate exchange symmetry? First, notice that product functions do not work because, as we showed above

$$\mathcal{P}|\psi_1(1)\rangle|\psi_2(2)\rangle = |\psi_1(2)\rangle|\psi_2(1)\rangle \neq \pm|\psi_1(1)\rangle|\psi_2(2)\rangle .$$

However, it is easy to see that the states

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|\psi_1(1)\rangle|\psi_2(2)\rangle \pm |\psi_1(2)\rangle|\psi_2(1)\rangle\right)$$

have the proper symmetry, since

$$\mathcal{P}|\Psi\rangle = \frac{1}{\sqrt{2}}\left(\mathcal{P}|\psi_1(1)\rangle|\psi_2(2)\rangle \pm \mathcal{P}|\psi_1(2)\rangle|\psi_2(1)\rangle\right)$$

$$= \frac{1}{\sqrt{2}}\left(|\psi_1(2)\rangle|\psi_2(1)\rangle \pm |\psi_1(1)\rangle|\psi_2(2)\rangle\right) = \pm|\Psi\rangle$$

Hence, these states are the appropriate product basis functions for two identical particles. We can generalize this concept to arbitrary numbers of particles as follows: for Fermions, we define the **Slater Determinant** by:

$$\left|\psi_i\rangle|\psi_j\rangle|\psi_k\rangle...\right| = \frac{1}{\sqrt{N!}}\begin{vmatrix} |\psi_i(1)\rangle & |\psi_i(2)\rangle & |\psi_i(3)\rangle & . & . \\ |\psi_j(1)\rangle & |\psi_j(2)\rangle & |\psi_j(3)\rangle & . & . \\ |\psi_k(1)\rangle & |\psi_k(2)\rangle & & . & . \\ . & . & . & . & \\ . & . & . & & \end{vmatrix}$$

It is easy to verify that this wavefunction is antisymmetric – permuting two of the ψ's corresponds to interchanging two of the rows, which our linear algebra textbook tells us multiplies the whole Determinant by -1. Further, we note no two of the ψ's can be the same because this would make two of the rows equal, which would make the whole determinant zero. This is the **Pauli Exclusion Principle.**

The nice thing about determinants is that they play the same role for Fermions that product states play for distinguishable particles; they form a complete basis for the many-particle space. Thus, if we have

a complete one particle basis $|\phi_i\rangle$ then any many particle function can be written

$$|\Psi\rangle = \sum_{ijkl\dots} c_{ijkl\dots} \big\| \phi_i \rangle \big| \phi_j \rangle \big| \phi_k \rangle \big| \phi_l \rangle \dots \big|$$

In fact, because the particles are identical, we can always permute the indices in the determinant so that they are in increasing order without changing the physical state, which means we can write

$$|\Psi\rangle = \sum_{i \le j \le k \le l \dots} c_{ijkl\dots} \big\| \phi_i \rangle \big| \phi_j \rangle \big| \phi_k \rangle \big| \phi_l \rangle \dots \big|$$

Since we have the Pauli Exclusion principle, we can even go one step further and note that none of the indices can be equal, so

$$|\Psi\rangle = \sum_{i < j < k < l \dots} c_{ijkl\dots} \big\| \phi_i \rangle \big| \phi_j \rangle \big| \phi_k \rangle \big| \phi_l \rangle \dots \big| .$$

For Bosons, the appropriate many-particle basis functions are a bit more obtuse. Intuitively, we can tell that the right state will look just like a Slater determinant, except that everywhere there is a minus sign in the former, we to replace it with a plus sign. In order to accomplish this, what is typically done is to simply **define** an object (a "permanent") that is just a determinant with plus signs. We will denote this by

$$|\Psi\rangle = \big\| \psi_1 \rangle \big| \psi_2 \rangle \dots \big| \psi_N \rangle \big|_+ .$$

Clearly, a permanent is symmetric, by construction. However, note that it does not obey any kind of exclusion principle; one can put as many Bosons into a given state as you like. As an example:

$$|\Psi\rangle = \big\| \psi_1 \rangle \big| \psi_1 \rangle \big| \psi_1 \rangle \dots \big|_+ = \big| \psi_1 \rangle \big| \psi_1 \rangle \big| \psi_1 \rangle \dots$$

is manifestly symmetric under exchange, and it describes a state where all the Bosons are piled into the same one particle state. This is actually the wavefunction that describes a Bose-Einstein condensate.

Similar to determinants, permanents form a complete many-particle basis. So we can write any many-Boson wavefunction as

$$|\Psi\rangle = \sum_{i \le j \le k \le l \dots} c_{ijkl\dots} \big\| \phi_i \rangle \big| \phi_j \rangle \big| \phi_k \rangle \big| \phi_l \rangle \dots \big|_+ .$$

Note that we **must** include the $i = j$ and $k = l$ kinds of terms in this sum specifically because Bosons do not obey any exclusion principle.

Finally, we note that determinants and permanents share one other important feature in common with product states: the eigenfunctions of a Hamiltonian that describes many independent Fermions (Bosons) can always be written as a determinant (permanent). To see this, we first note that because the particles are **identical**, the Hamiltonian for particle i must be the same as that for j. Thus, an independent particle $\hat{H}$ for N identical particles must take the form:

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(i)$$

where $\hat{h}(i)$ is just the Hamiltonian for the ith particle and clearly each particle "feels" the same Hamiltonian. Now, if we expand out the state $\left. \left| \phi_i \right\rangle \left| \phi_j \right\rangle \left| \phi_k \right\rangle ... \right|_{\pm}$, we find a sum that contains the state

$\left| \phi_i(1) \right\rangle \left| \phi_j(2) \right\rangle \left| \phi_k(3) \right\rangle ...$ plus (or minus) other states like $\left| \phi_i(2) \right\rangle \left| \phi_j(1) \right\rangle \left| \phi_k(3) \right\rangle ...$ and $\left| \phi_i(3) \right\rangle \left| \phi_j(1) \right\rangle \left| \phi_k(2) \right\rangle ...$ that involve the same one particle states, but in a different order. However, these are all eigenfunctions of our Hamiltonian **with the same eigenvalue**:

$$\hat{H} \left| \phi_i(1) \right\rangle \left| \phi_j(2) \right\rangle \left| \phi_k(3) \right\rangle ... = \left(\hat{h}(1) + \hat{h}(2) + \hat{h}(3) ... \right) \left| \phi_i(1) \right\rangle \left| \phi_j(2) \right\rangle \left| \phi_k(3) \right\rangle ...$$

$$= \left(e_i + e_j + e_k ... \right) \left| \phi_i(1) \right\rangle \left| \phi_j(2) \right\rangle \left| \phi_k(3) \right\rangle ...$$

$$\hat{H} \left| \phi_i(2) \right\rangle \left| \phi_j(1) \right\rangle \left| \phi_k(3) \right\rangle ... = \left(\hat{h}(1) + \hat{h}(2) + \hat{h}(3) ... \right) \left| \phi_i(2) \right\rangle \left| \phi_j(1) \right\rangle \left| \phi_k(3) \right\rangle ...$$

$$= \left(e_j + e_i + e_k ... \right) \left| \phi_i(2) \right\rangle \left| \phi_j(1) \right\rangle \left| \phi_k(3) \right\rangle ...$$

....

Thus, since a determinant or permanent is a sum of degenerate eigenstates of $\hat{H}$, we conclude that it is, itself, an eigenstate with the same eigenvalue:

$$\hat{H} \left. \left| \phi_i \right\rangle \left| \phi_j \right\rangle \left| \phi_k \right\rangle ... \right|_{\pm} = \left(e_i + e_j + e_k ... \right) \left. \left| \phi_i \right\rangle \left| \phi_j \right\rangle \left| \phi_k \right\rangle ... \right|_{\pm}$$

Hence, we see that determinants and permanents are the functional analogs of product states when we are dealing with many identical particles.

c. Two Electron Atoms

As an application of the formalism we have just developed, we consider Helium-like atoms (i.e. He, Li+ …). Assuming the nucleus is infinitely massive, the Hamiltonian for the two electrons is given by

$$\hat{H} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Kinetic Energy   Electron-Nuclear   Electron-Electron
                    Attraction   Repulsion

where "1" and "2" denote the two different electrons. It is convenient to separate the parts Hamiltonian that depend only on particle "1" or "2", independently:

$$\hat{h}(1) \equiv -\tfrac{1}{2}\nabla_1^2 - \frac{Z}{r_1} \qquad \hat{h}(2) = -\tfrac{1}{2}\nabla_2^2 - \frac{Z}{r_2}$$

note that, as advertised, these operators are identical. It is then conventional to then separate the Hamiltonian into a zeroth order part that describes the electrons moving independently in the field of the nucleus and a perturbation that consists of the electron-electron interaction:

$$\hat{H}_0 \equiv \hat{h}(1) + \hat{h}(2) \qquad \hat{V}_{12} \equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_{12}}$$

Note that the electron-electron repulsion is typically of the same order of magnitude as the independent particle energy, and so this will not generally be a good approximation. However, it is **convenient** because we know the eigenstates of $\hat{H}_0$ and we can therefore do perturbation theory.

In accordance with the previous section, we conclude that the eigenfunctions of $\hat{H}_0$ are determinants:

$$\left|\Psi^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_1\right\rangle\left|\psi_2\right\rangle - \left|\psi_2\right\rangle\left|\psi_1\right\rangle\right).$$

The one electron functions in this expression are generically called orbitals. First of all, we note that our orbitals certainly cannot neglect the spin of the electron; the Pauli exclusion principle tells us that we cannot have more than one electron in the same overall state, but we can effectively fit two electrons in each **spatial** orbital – one with spin "up" and one with spin "down". This is most easily dealt with by writing the determinant in terms of **spin** orbitals, which are products of a space part and a spin part, i.e.

$$\left|1s\uparrow\right\rangle \equiv \left|1s\right\rangle\left|\uparrow\right\rangle.$$

We will also use the shorthand notation

$$|\psi\rangle \equiv |\psi\rangle|\uparrow\rangle \qquad |\bar{\psi}\rangle \equiv |\psi\rangle|\downarrow\rangle .$$

We can easily guess the ground state of $\hat{H}_0$; one merely puts two electrons in the $1s$ orbital. We can write this wavefunction in three ways

$$\left|\Psi^{(0)}\right\rangle = \left\|1s\right\rangle\left|1\bar{s}\right\rangle\|$$

$$= \frac{1}{\sqrt{2}}\left(\left|1s\uparrow\right\rangle\left|1s\downarrow\right\rangle - \left|1s\downarrow\right\rangle\left|1s\uparrow\right\rangle\right)$$

$$= \left|1s\right\rangle\left|1s\right\rangle\frac{1}{\sqrt{2}}\left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right)$$

The first representation is the most economical and stresses that this is a determinant. The last expression is interesting because it factorizes into the form $\left|\Psi_{space}\right\rangle\left|\Psi_{spin}\right\rangle$, which allows us to make several observations. First, note that for this case, this spin part is just the wavefunction for a singlet (S=0) state. This is encouraging, because (in the absence of spin-orbit coupling) the true electronic states can **always** be chosen to be spin eigenfunctions because $\left[\hat{H},\hat{S}^2\right]=0$. The fact that the zeroth order eigenfunction is also a spin eigenfunction therefore makes it a convenient starting point. Second, we notice that the space part is symmetric and the spin part is antisymmetric, giving an overall antisymmetric state. In general, the exchange symmetry of spin eigenfunctions is $(-1)^{S+1}$, so singlets have symmetric spatial parts, triplets have antisymmetric spatial parts…

Now, this determinant should in no way be confused with the **true** ground state of the Hamiltonian; it is merely a convenient **approximation** that has the right symmetry properties (i.e. it is a singlet with no angular momentum,…) but completely neglects the interaction between the electrons. To see how good or bad this state is, we compute its zero-order eigenvalue:

$$\hat{H}_0\left|\Psi^{(0)}\right\rangle = \left(-\tfrac{1}{2}\nabla_1^{\,2} - \frac{Z}{r_1}\right) + \left(-\tfrac{1}{2}\nabla_2^{\,2} - \frac{Z}{r_2}\right)\left|1s\right\rangle\left|1s\right\rangle\frac{1}{\sqrt{2}}\left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right)$$

$$= \left(-\frac{Z^2}{2}\right) + \left(-\frac{Z^2}{2}\right)\left|1s\right\rangle\left|1s\right\rangle\frac{1}{\sqrt{2}}\left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right) = -Z^2\left|\Psi\right\rangle$$

Now, for Helium, this corresponds to an energy of $-2^2 = -4$ E_h = -108.8 eV, which compares to the experimental value of -78.86 eV! This is terrible! There are three primary ways to improve this result.

1) **Hartree-Fock**

The first approach still uses a single determinant state, but recognizes that the zeroth order orbitals will not generally be the optimal choice. One realizes physically that each electron will not "see" the bare Coulomb field of the nucleus, but it will be "shielded" from the core because it will be repelled by the other electron. This will of course cause some distortion of the wavefunction, even at the independent particle level. In order to find the best possible one particle functions, we have to do a variational calculation that minimizes:

$$\langle \psi\, \bar{\psi} \| \hat{H} \| \psi\, \bar{\psi} \rangle = \frac{1}{2} \left(\langle \uparrow |\langle \downarrow | - \langle \downarrow |\langle \uparrow | \right)\left(|\downarrow\rangle|\uparrow\rangle - |\uparrow\rangle|\downarrow\rangle \right) \langle \psi |\langle \psi |\hat{H}|\psi\rangle|\psi\rangle$$

$$= \langle \psi |\langle \psi |\hat{H}|\psi\rangle|\psi\rangle$$

where in the second line we have noted that overlap of the spin functions is 1. To minimize this, we can expand the orbitals in a complete basis of, say, hydrogenic eigenstates:

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle$$

We can then write out the variational condition:

$$0 = \frac{\partial}{\partial c_i^*} \frac{\langle \psi |\langle \psi |\hat{H}|\psi\rangle|\psi\rangle}{\langle \psi |\langle \psi \|\psi\rangle|\psi\rangle} = \frac{\dfrac{\partial \langle \psi |}{\partial c_i^*}\langle \psi |\hat{H}|\psi\rangle|\psi\rangle}{\langle \psi |\langle \psi \|\psi\rangle|\psi\rangle} + \frac{\langle \psi |\dfrac{\partial \langle \psi |}{\partial c_i^*}\hat{H}|\psi\rangle|\psi\rangle}{\langle \psi |\langle \psi \|\psi\rangle|\psi\rangle}$$

$$- \frac{\partial \langle \psi |}{\partial c_i^*}\langle \psi \|\psi\rangle|\psi\rangle \frac{\langle \psi |\langle \psi |\hat{H}|\psi\rangle|\psi\rangle}{\left(\langle \psi |\langle \psi \|\psi\rangle|\psi\rangle \right)^2}$$

$$- \langle \psi |\frac{\partial \langle \psi |}{\partial c_i^*}|\psi\rangle|\psi\rangle \frac{\langle \psi |\langle \psi |\hat{H}|\psi\rangle|\psi\rangle}{\left(\langle \psi |\langle \psi \|\psi\rangle|\psi\rangle \right)^2}$$

.

We now enforce normalization ($\langle \psi |\langle \psi \|\psi\rangle|\psi\rangle = 1$) and define the

energy ($E = \dfrac{\langle \psi |\langle \psi |\hat{H}|\psi\rangle|\psi\rangle}{\langle \psi |\langle \psi \|\psi\rangle|\psi\rangle}$) which allows us to simplify:

$$0 = \frac{\partial \langle \psi|}{\partial c_i^*} \langle \psi|\hat{H}|\psi\rangle|\psi\rangle + \langle \psi| \frac{\partial \langle \psi|}{\partial c_i^*} \hat{H}|\psi\rangle|\psi\rangle - \frac{\partial \langle \psi|}{\partial c_i^*} \langle \psi \| \psi\rangle|\psi\rangle E - \langle \psi| \frac{\partial \langle \psi|}{\partial c_i^*} |\psi\rangle|\psi\rangle E$$

$$= \frac{\partial \langle \psi|}{\partial c_i^*} \langle \psi|\hat{H}-E|\psi\rangle|\psi\rangle + \langle \psi| \frac{\partial \langle \psi|}{\partial c_i^*} \hat{H}-E|\psi\rangle|\psi\rangle$$

$$= \langle \phi_i|\langle \psi|\hat{H}-E|\psi\rangle|\psi\rangle + \langle \psi|\langle \phi_i|\hat{H}-E|\psi\rangle|\psi\rangle$$

We want to write this in terms of $\hat{h}_1, \hat{h}_2$ and $\hat{V}_{12}$, so consider the first term on the right hand side:

$$\langle \phi_i|\langle \psi|\hat{H}-E|\psi\rangle|\psi\rangle = \langle \phi_i|\langle \psi|\hat{h}_1-E|\psi\rangle|\psi\rangle + \langle \phi_i|\langle \psi|\hat{h}_2|\psi\rangle|\psi\rangle + \langle \phi_i|\langle \psi|\hat{V}_{12}|\psi\rangle|\psi\rangle$$

$$= \langle \psi|\hat{h}_1-E|\psi\rangle\langle \phi_i|\psi\rangle + \langle \phi_i|\hat{h}_2|\psi\rangle\langle \psi|\psi\rangle + \langle \phi_i|\langle \psi|\hat{V}_{12}|\psi\rangle|\psi\rangle$$

$$= \langle \psi|\hat{h}_1-E|\psi\rangle c_i + \sum_j \left(\langle \phi_i|\hat{h}_2|\phi_j\rangle + \langle \phi_i|\langle \psi|\hat{V}_{12}|\psi\rangle|\phi_j\rangle \right) c_j$$

At this point we make two definitions. First, we define an effective energy for electron "2", ε_2, as the difference between the total energy and the average value of $\hat{h}_1$: $\varepsilon_2 \equiv E - \langle \psi|\hat{h}_1|\psi\rangle$. Second, we define the **Fock matrix** as:

$$F_{ij}(\psi) = \langle \phi_i|\hat{h}_2|\phi_j\rangle + \langle \phi_i|\langle \psi|\hat{V}_{12}|\psi\rangle|\phi_j\rangle$$

Hamiltonian for electron "2" by itself

Repulsion of electron "2" by the average field from electron "1"

We include the "(ψ)" to remind ourselves that this operator for electron "2" depends implicitly upon the state of the other electron; electron "2" moves in the average field produced by electron "1" and vice versa. If we write the second term in real space, this becomes more clear

$$\langle \phi_i|\langle \psi|\hat{V}_{12}|\psi\rangle|\phi_j\rangle = \iint \phi_i(r_2)^*\psi(r_1)^* \frac{1}{r_{12}} \psi(r_1)\phi_j(r_2) d^3r_1 d^3r_2$$

$$= \int \phi_i(r_2)^* V_{avg}(r_2)\phi_j(r_2) d^3r_2$$

where in the second line we have identified the average potential

$$V_{avg}(r_2) \equiv \int \frac{|\psi(r_1)|^2}{r_{12}} d^3r_1$$

which is literally the classical expression for the potential exerted by a charge density $\rho(r_1) = |\psi(r_1)|^2$.

In any case, in terms of ε_2 and $F_{ij}(\psi)$ we can write

$$\langle \phi_i | \langle \psi | \hat{H} - E | \psi \rangle | \psi \rangle = \sum_j F_{ij}(\psi) c_j - \varepsilon_2 c_i$$

The second term in the variational equation ($\langle \psi | \langle \phi_i | \hat{H} - E | \psi \rangle | \psi \rangle$) turns out to be identical to the first, because we have constrained the spatial wavefunctions for electrons "1" and "2" to be equal. As a result, the full variational equation implies the above expression is zero, which is equivalent to the matrix equation

$$\mathbf{F}(\psi) \cdot \mathbf{c} = \varepsilon \, \mathbf{c}$$

where we have dropped the subscript "2" on ε because the equations for electrons "1" and "2" are identical. These are known as the **Hartree-Fock** (HF) equations. They determine the unknown c_i's that describe the **optimal** one particle orbitals, which take into account all of the screening effects discussed above. It is clear from the matrix form that the correct c_i's are an eigenvector of the Fock matrix $\mathbf{F}(\psi)$, which describes the motion of each electron in the average (or mean) field produced by the other electron. Solving these equations is complicated by the fact that $\mathbf{F}$ *depends on* the c_i's, since $\mathbf{F}(\psi)$ depends on the form of ψ. In practice, this equation must be solved iteratively; one guesses ψ (for example a 1s orbital) and then computes $\mathbf{F}(\psi)$, which is diagonalized to give a new set of c_i's which are used to build a new ψ, which is then used to compute a new $\mathbf{F}(\psi)$, which is diagonalized to give a new set of c_i's…. These iterations are known as self-consistent field iterations, because one is looking for the orbital ψ that is consistent with (i.e. is an eigenstate of) its own Fock matrix $\mathbf{F}(\psi)$.

For helium, HF results in a ground state energy of -77.8 eV, which is still too far away from the experimental result, but much better than the independent particle answer. Time permitting, we will discuss Hartree-Fock theory in more detail later, but for now suffice it to say that the residual error results from the fact that our wavefunction still describes **independent** particles (albeit in modified orbitals). In practice, the electrons are not independent because they repel one another.

2) **Perturbation Theory**

Another approach is to really apply the perturbation expansion we have set up; i.e. to use the zeroth order eigenfunction as our starting point and include corrections due to the electron-electron interaction that will look like first, second, third,… powers of $\hat{V}_{12}$. If we want to treat this interaction to first order, we need to compute:

$$E^{(1)} = \left\langle \left\| 1s\ 1\bar{s} \right\| \hat{V}_{12} \left\| 1s\ 1\bar{s} \right\| \right\rangle$$

This is a fairly complicated 6 dimensional integral, but it can be evaluated, and the resulting first order correction is +5/2 E_h = 34 eV (note that the sign is **positive**, as it should be for electron repulsion). Thus, at first order the total energy is -108.8+34=-74.8 eV, which is worse than Hartree-Fock. However, one can continue to second, third, fourth… orders to more closely approximate the experimental results. For example, the second order correction looks like

$$E^{(2)} = \sum_{\substack{nlm \\ n'l'm'}} \frac{\left\langle \left\| 1s;1\bar{s} \right\| \hat{V}_{12} \left\| nlm;\bar{n}'\bar{l}'\bar{m}' \right\| \right\rangle \left\langle \left\| nlm;\bar{n}'\bar{l}'\bar{m}' \right\| \hat{V}_{12} \left\| 1s;1\bar{s} \right\| \right\rangle}{E_n + E_{n'} + Z^2}$$

which can be numerically evaluated to give a second order correction of -3.8 eV. This yields an approximate ground state energy of -74.8-3.8=-78.6 eV, which is starting to look respectable. What we are doing physically when we do these calculations is accounting for the fact that the electrons **are not independent** but rather they tend to avoid each other to minimize the Coulombic repulsion. In practice, perturbation theory works quite well for the ground state of Helium-like systems.

3) **Configuration Interaction**

There is one final deficiency of a single determinant as an approximate eigenstate; it sometimes lacks the proper symmetry possessed by the true eigenstate. As an example, consider not the ground state but the first excited singlet state of a two electron atom. The independent particle eigenstate can be written $\left\| 1s2\bar{s} \right\|$. [Aside: note that $\left\| 1s2\bar{p} \right\|$ is technically degenerate with this state if we neglect the interaction, but we know that once the electron-electron repulsion

is included the $2s$ orbital will be less shielded than $2p$ and so this will be the lower Hartree-Fock state.] Now, this state **is not** a spin eigenfunction:

$$\left\|1s2\bar{s}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|1s\uparrow\right\rangle\left|2s\downarrow\right\rangle - \left|2s\downarrow\right\rangle\left|1s\uparrow\right\rangle\right) \neq \left|\Psi_{space}\right\rangle\left|\Psi_{spin}\right\rangle$$

In order to get a state that is a spin eigenfunction, we need to add two different determinants:

$$\frac{1}{\sqrt{2}}\left(\left\|1s2\bar{s}\right\rangle - \left\|1\bar{s}2s\right\rangle\right) = \frac{1}{2}\left(\left|1s\uparrow\right\rangle\left|2s\downarrow\right\rangle - \left|2s\downarrow\right\rangle\left|1s\uparrow\right\rangle - \left|1s\downarrow\right\rangle\left|2s\uparrow\right\rangle + \left|2s\uparrow\right\rangle\left|1s\downarrow\right\rangle\right)$$

$$= \frac{1}{2}\left(\left|1s\right\rangle\left|2s\right\rangle + \left|2s\right\rangle\left|1s\right\rangle\right)\left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right) = \left|\Psi_{space}\right\rangle\left|\Psi_{spin}\right\rangle$$

Likewise, in order to get a wavefunction that is an eigenfunction of the total angular momentum ($\hat{\mathbf{J}}^2$) we will need to take a linear combination of different determinants as well. In atomic spectroscopy, these determinants are called **microstates** and the correct linear combinations that make eigenfunctions are called **macrostates**. In electronic structure theory, these determinants are called **configurations** and the process of obtaining the best linear combination of these determinants is called **configuration interaction** (CI).

In practice, CI can be used not only to get the correct symmetry, but also the energy shift due to the Coulomb repulsions, in like manner to perturbation theory. To do this, we use the complete expansion:

$$\left|\Psi\right\rangle = \sum_{\substack{n_1l_1m_1 \\ n_2l_2m_2}} C_{n_1l_1m_1n_2l_2m_2}\left\|n_1l_1m_1;n_2l_2m_2\right\rangle.$$

The problem of finding the optimal coefficients $C_{n_1l_1m_1n_2l_2m_2}$ is then equivalent to finding the eigenvectors and eigenvalues of the matrix

$$H_{n_1l_1m_1n_2l_2m_2;n_1'l_1'm_1'n_2'l_2'm_2'} \equiv \left\langle n_1'l_1'm_1';n_2'l_2'm_2'\right\|\hat{H}\left\|n_1l_1m_1;n_2l_2m_2\right\rangle$$

By definition, this is an exact eigenfunction of $\hat{H}$. However, even for this simple two electron problem, the difficulty of doing full CI calculations is apparent.