

## MANY ELECTRON ATOMS

Thus far, we have learned that the independent particle model (IPM) gives a qualitatively correct picture of the eigenstates of the helium atom. What about atoms with more than two electrons, such as lithium or carbon? As it turns out, the IPM is capable of giving a realistic picture of atomic structure in essentially an analogous fashion to the helium case. To begin with, we set up our coordinates so that the nucleus is at the origin and the  $N$  electrons are at positions  $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N$ . In terms of these variables, we can quickly write down the many-electron Hamiltonian (in atomic units):

$$\hat{H} = \underbrace{-\frac{1}{2} \sum_{j=1}^N \nabla_j^2}_{\text{Kinetic Energy}} \underbrace{- \sum_{j=1}^N \frac{Z}{\hat{\mathbf{r}}_j}}_{\text{Electron-Nuclear Attraction}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}}_{\text{Electron-Electron Repulsion}}$$

Thus, the Hamiltonian has the same three sources of energy as in the two electron case, but the sheer number of electrons makes the algebra more complicated. As before, we note that we can make the Hamiltonian separable if we neglect the electron-electron repulsion:

$$\hat{H}_{NI} = -\frac{1}{2} \sum_{j=1}^N \nabla_j^2 - \sum_{j=1}^N \frac{Z}{\hat{\mathbf{r}}_j} = \sum_{j=1}^N \left( -\frac{1}{2} \nabla_j^2 - \frac{Z}{\hat{\mathbf{r}}_j} \right) \equiv \sum_{j=1}^N \hat{h}_j$$

where each of the independent Hamiltonians  $\hat{h}_i$  describes a single electron in the field of a nucleus of charge  $+Z$ . Based on our experience with separable Hamiltonians, we can immediately write down the eigenstates of this Hamiltonian as products with energies given as sums of the independent electron energies:

$$\Psi = \psi_{k_1}(1) \psi_{k_2}(2) \psi_{k_3}(3) \dots \psi_{k_N}(N) \quad E = E_{k_1} + E_{k_2} + E_{k_3} + \dots + E_{k_N}$$

Where (1) is a shorthand for  $(\mathbf{r}_1, \sigma_1)$  and  $k_i \equiv \{n_i, l_i, m_i, s_i\}$  specifies all the quantum numbers for a given hydrogen atom eigenstate. Of course, there is a problem with these eigenstates: they are not antisymmetric. For the Helium atom, we fixed this by making an explicitly antisymmetric combination of two degenerate product states:

$$\frac{1}{\sqrt{2}} (\psi_{1s\alpha}(1) \psi_{1s\beta}(2) - \psi_{1s\alpha}(2) \psi_{1s\beta}(1)) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s\alpha}(1) & \psi_{1s\alpha}(2) \\ \psi_{1s\beta}(1) & \psi_{1s\beta}(2) \end{vmatrix}$$

where on the right we have noted that this antisymmetric product can also be written as a determinant of a  $2 \times 2$  matrix. As it turns out, it is straightforward to extend this idea to generate an  $N$  particle antisymmetric state by computing an  $N \times N$  determinant called a **Slater Determinant**:

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_3}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_3}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_3}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_3}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix}$$

As you can imagine, the algebra required to compute integrals involving Slater determinants is extremely difficult. It is therefore most important that you realize several things about these states so that you can avoid unnecessary algebra:

- **A Slater determinant corresponds to a single stick diagram.** This is easy to see by example:

$$\begin{array}{l} 2p_x \uparrow \\ 2s \uparrow \\ 1s \uparrow\downarrow \end{array} \Rightarrow \Psi(1,2,3,4) = \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) & 2p_x\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) & 2p_x\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) & 2p_x\alpha(3) \\ 1s\alpha(4) & 1s\beta(4) & 2s\alpha(4) & 2p_x\alpha(4) \end{vmatrix}$$

It should be clear that we can extend this idea to associate a determinant with an arbitrary stick diagram. Further, recall that for the excited states of helium we had a problem writing certain stick diagrams as a (space) $\times$ (spin) product and had to make linear combinations of certain states to force things to separate. Because of the direct correspondence of stick diagrams and Slater determinants, the same pitfall arises here: **Slater determinants sometimes may not be representable as a (space) $\times$ (spin) product, in which case a linear combination of Slater determinants must be used instead.**

This generally only happens for systems with unpaired electrons, like the  $1s\uparrow 2s\downarrow$  configuration of helium or the  $\dots 2p_x\uparrow 2p_y\downarrow$  configuration of carbon.

- **A Slater determinant is antisymmetric upon exchange of any two electrons.** We recall that if we take a matrix and interchange two its rows, the determinant changes sign. Thus, interchanging 1 and 2 above, for example:

$$\Psi(2,1,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_3}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_3}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_3}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_3}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix}$$

$$\xrightarrow{\text{Interchange Rows 1\&2}} -\frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_3}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_3}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_3}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_3}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix} = -\Psi(1,2,\dots,N)$$

A similar argument applies to any pair of indices, and so the Slater determinant is antisymmetric under any  $i \leftrightarrow j$  interchange.

- **The determinant is zero if the same orbital appears twice.** We recall that if we take a matrix and interchange two of its columns, the determinant also changes sign. Assuming  $k_1=k_3$  above:

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_1}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_1}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_1}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_1}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix}$$

$$\xrightarrow{\text{Interchange Columns 1\&3}} -\frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_1}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_1}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_1}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_1}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix} = -\Psi(1,2,\dots,N)$$

The only way a number can be equal to its opposite is if it is zero. Thus, in enforcing antisymmetry the determinant also enforces the **Pauli exclusion principle**. Thus, Slater determinants immediately lead us to the aufbau

principle we learned in Freshman chemistry: because we cannot place two electrons in orbitals with the same quantum numbers, we are forced to fill up orbitals with successively higher energies as we add more electrons:  $1s\uparrow, 1s\downarrow, 2s\uparrow, 2s\downarrow, \dots$ . This filling up is dictated by the fact that the wavefunction is antisymmetric, which, in turn, results from the fact that the electron is spin- $\frac{1}{2}$ . As it turns out, all half-integer spin particles (Fermions) have antisymmetric wavefunctions and all integer spin particles (Bosons) have symmetric wavefunctions. Imagine how different life would be if electrons were Bosons instead of Fermions!

- $\Psi$  is normalized if the orbitals  $\psi_{k_i}$  are normalized and two determinants are orthogonal if they differ in any single orbital. These two facts are relatively tedious to prove, but are useful in practice.
- The non-interacting energy of a Slater determinant is the energy of the orbitals that make it up. Just as was the case for helium, our antisymmetric wavefunction is a linear combination of degenerate non-interacting eigenstates:

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} (\psi_{k_1}(1)\psi_{k_2}(2)\psi_{k_3}(3)\dots\psi_{k_N}(N) - \psi_{k_1}(2)\psi_{k_2}(1)\psi_{k_3}(3)\dots\psi_{k_N}(N) \\ + \psi_{k_1}(3)\psi_{k_2}(1)\psi_{k_3}(2)\dots\psi_{k_N}(N) - \psi_{k_1}(1)\psi_{k_2}(3)\psi_{k_3}(2)\dots\psi_{k_N}(N) \dots)$$

Thus the determinant itself is an eigenstate of the non-interacting Hamiltonian with the same eigenvalue as each state in the sum:

$$E_{\Psi} = E_{k_1} + E_{k_2} + E_{k_3} + \dots + E_{k_N}$$

We have only completed half of the independent particle picture at this point. We have the noninteracting energy; what remains is the computation of the average energy. To compute this, we would need to do a  $2N$ -dimensional integral involving a Slater Determinant on the left, the Hamiltonian in the middle (including all interaction terms) and a Slater Determinant on the right. The book-keeping is quite tedious, but can be worked out in the most general case. The result is that the energy breaks down into terms that we already recognize:

$$\langle \hat{H} \rangle = \underbrace{\sum_{i=1}^N E_i}_{\text{Noninteracting Energy}} + \underbrace{\sum_{i<j}^N \tilde{J}_{ij} - \tilde{K}_{ij}}_{\text{Average Repulsion}}$$

$$\tilde{J}_{ij} \equiv \iint \psi_{k_i}^*(1)\psi_{k_j}^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{k_i}(1)\psi_{k_j}(2) d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2$$

$$\tilde{K}_{ij} \equiv \iint \psi_{k_i}^*(1)\psi_{k_j}^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{k_i}(2)\psi_{k_j}(1) d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2$$

This energy expression has a nice intuitive feel to it: we get contributions from the interaction of each electron orbital with the nucleus (first term) as well as from the mutual repulsion of each pair of orbitals (second term). The repulsion has the characteristic "Coulomb **minus** Exchange" form because of the antisymmetry of the Slater determinant, which leads to a minus sign every time we exchange 1 and 2. For example, when we expand the determinant in terms of product functions, we will have a term like:

$$X \equiv \psi_{k_1}(1)\psi_{k_2}(2)\psi_{k_3}(?)\cdots\psi_{k_N}(?)$$

we will have a corresponding term with **1↔2 with a minus sign**:

$$Y \equiv \psi_{k_1}(2)\psi_{k_2}(1)\psi_{k_3}(?)\cdots\psi_{k_N}(?)$$

When we compute the average repulsion we will have:

$$\left\langle \frac{1}{r_{12}} \right\rangle \approx \iint (X - Y \dots) \frac{1}{r_{12}} (X - Y \dots) d\mathbf{r}_1 d\mathbf{r}_2 \dots$$

The +XX and +YY terms will give us Coulomb integrals and the cross terms -XY and -YX will give us exchange integrals. We note that, as defined, the Coulomb and Exchange terms are both positive, so that the exchange integral always reduces the repulsion energy for a Slater determinant. These arguments do not constitute a proof of the energy expression above - they are merely intended to give you a general feeling that this expression is plausible. Deriving the average energy actually takes quite a bit of time and careful bookkeeping of different permutations (e.g. 1↔2↔4 versus 4↔2↔3 ...). If you want to delve deeper into these kinds of things, we recommend you take 5.73, which covers much of the material here in greater depth.

In any case, most of the time we need not worry about the details of how the average energy expression is derived for a general determinant. Usually what we want to do is *use* the formula to compute something interesting rather than re-derive it. Toward this end we note that the Coulomb and exchange integrals above involve integration over spin variables, which can be done trivially. Basically, the integration over  $\sigma_1$  ( $\sigma_2$ ) will give unity if the left and right functions for electron 1 (electron 2) have the same spin, and zero otherwise. For the Coulomb integral, the left and right functions are the same, so the spin integration always gives 1 and we can get rid of the spin integration:

$$J_{ij} = \iint \psi_i^*(1)\psi_j^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_i(1)\psi_j(2) d\mathbf{r}_1 d\mathbf{r}_2$$

where here we use the shorthand  $i \equiv \{n_i, m_i, l_i\}$  to represent all the spatial quantum numbers for the  $i^{\text{th}}$  orbital, and similarly for the  $j^{\text{th}}$  one. For the exchange integrals, the left and right functions are different, and so the exchange integral is only nonzero if the  $i^{\text{th}}$  orbital and the  $j^{\text{th}}$  orbital have the same spin part:

$$K_{ij} = \begin{cases} \iint \psi_i^*(1) \psi_j^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_i(2) \psi_j(1) d\mathbf{r}_1 d\mathbf{r}_2 & \text{if } s_i = s_j \\ 0 & \text{Otherwise} \end{cases}$$

In practice (for example on a Problem Set) it is useful to begin with the general expression for the independent particle energy and then integrate out the spin part to get a final expression that only involves the spatial integrals  $J$  and  $K$  rather than the space-spin integrals  $\tilde{J}$  and  $\tilde{K}$ . For example, say we are interested in the  $1s\uparrow 1s\downarrow 2s\uparrow$  configuration of lithium. The energy is given by:

$$\begin{aligned} \langle \hat{H} \rangle &= \sum_{i=1}^N E_i + \sum_{i < j} \tilde{J}_{ij} - \tilde{K}_{ij} \\ &= E_{1s} + E_{1s} + E_{2s} + \tilde{J}_{1s\alpha; 1s\beta} - \tilde{K}_{1s\alpha; 1s\beta} + \tilde{J}_{1s\alpha; 2s\alpha} - \tilde{K}_{1s\alpha; 2s\alpha} + \tilde{J}_{1s\beta; 2s\alpha} - \tilde{K}_{1s\beta; 2s\alpha} \\ &= 2E_{1s} + E_{2s} + J_{1s1s} + 2J_{1s2s} - K_{1s2s} \end{aligned}$$

Thus, in going from space-spin integrations to space integrations, we acquire a few factors of 2, but the formula still looks similar to the expressions we've seen before.

The independent particle energy expression is extremely powerful: it allows us to make rough predictions of things like atomic ionization energies and excitation energies once we have the Coulomb and exchange integrals. The independent particle energy also gives us a rigorous explanation of another freshman chemistry effect: shielding. As we know, while  $2s$  and  $2p$  are degenerate for the hydrogen atom they are not degenerate as far as the order of filling up orbitals.  $2s$  comes first and  $2p$  comes second. As you know, physically this arises because the  $2s$  orbital sees an effective nuclear charge that is bigger than  $2p$  because it is shielded less by the  $1s$  orbital. It turns out that the IPM has a simple means of explaining this result. If we look at the  $1s\uparrow 1s\downarrow 2p_x\uparrow$  configuration of lithium and go through exactly the same manipulations as we did above for  $1s\uparrow 1s\downarrow 2s\uparrow$  we get:

$$\langle \hat{H} \rangle = 2E_{1s} + E_{2p_x} + J_{1s1s} + 2J_{1s2p_x} - K_{1s2p_x}$$

taking the difference between  $1s\uparrow 1s\downarrow 2p_x\uparrow$  and  $1s\uparrow 1s\downarrow 2s\uparrow$  gives:

$$\begin{aligned}
 \Delta E = E_{1s^2 2p} - E_{1s^2 2s} &= \cancel{2E_{1s}} + \cancel{E_{2p_x}} + \cancel{J_{1s1s}} + 2J_{1s2p_x} - K_{1s2p_x} - \\
 &\quad \left( \cancel{2E_{1s}} + \cancel{E_{2s}} + \cancel{J_{1s1s}} + 2J_{1s2s} - K_{1s2s} \right) \\
 &= 2J_{1s2p_x} - 2J_{1s2s} + K_{1s2s} - K_{1s2p_x} \neq 0
 \end{aligned}$$

Thus, while  $1s\uparrow 1s\downarrow 2p_x\uparrow$  and  $1s\uparrow 1s\downarrow 2s\uparrow$  give the same energies if the electrons do not interact, **they give different energies once we include the average interaction.** Further, it is clear from the above expression that the relevant interactions are between the 1s and 2p orbitals on the one hand and the 1s and 2s orbitals on the other. Using our physical argument of shielding, we assert that the 1s and 2s orbitals will repel each other less than the 1s and 2p orbitals, leading to a net stabilization of  $1s\uparrow 1s\downarrow 2s\uparrow$  relative to  $1s\uparrow 1s\downarrow 2p_x\uparrow$ . We explore this idea in more detail on the problem set.