

## 15.6: Multielectron Atoms and Exchange

Having exhausted our investigations into hydrogen, we now study helium as the next element on the periodic table. This atom has two electrons to balance out the nuclear charge of  $Z = +2$ . Due to the extra electron we now must solve a larger Schrödinger equation with a Hamiltonian that more than doubles in size:

$$\hat{H}(1, 2) = \frac{-\hbar^2}{2\mu r_1^2} \nabla_1^2 + \frac{-\hbar^2}{2\mu r_2^2} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|}$$

where  $\nabla$  is called the “Laplacian” operator that returns all the kinetic energy including rotational. The reason that the Hamiltonian more than doubles is because there is an electron-electron repulsive (energy raising) term:  $\frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|}$ , which unfortunately creates a problem for solving the wavefunctions. To explain, note that without this part the Hamiltonian can be separated into terms for either electron 1 or 2 only. Thus, the total wavefunction is separable into the product of two individual states:

$$\psi_{total}(1, 2) = \psi_1(1)\psi_2(2)$$

where the “[GrindEQ\_1]” and “[GrindEQ\_2]” are labels for the first and second electron and the subscripts on  $\psi_1$  and  $\psi_2$  refers to what type of orbital (1s, 2p<sub>x</sub> etc.) that the electron resides. We expect that the individual electron states are the same as the hydrogen atom albeit with a higher nuclear charge of  $Z=+2$ . The He wavefunction for the ground state 1s<sup>2</sup> configuration should be  $\psi_{1s}(1)\psi_{1s}(2)$ .

However, none of this is true because the  $\frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|}$  term completely negates the ability to separate the Hamiltonian into “mini” Schrödinger equations for electrons 1 and 2. Maybe you are expecting us to introduce a clever math trick that allows us to derive the real wavefunctions- actually there isn’t one. *We don’t know what the real wavefunctions are for any atom or molecule with more than one electron.*

Even though the separation solution  $\psi_{total}(1, 2) \approx \psi_1(1)\psi_2(2)$  isn’t correct, we use it anyways due to the fact that we are confronted with a problem with no simple solution. This approximation requires us to employ a variety of different approaches for developing a quantum-based understanding of multielectron atoms. For example, since a separated solution is not an eigenstate of the multielectron Hamiltonian:

$$\hat{H}\psi_1(1)\psi_2(2) \neq E \cdot \psi_1(1)\psi_2(2)$$

we cannot use the eigenvalue way of solving the energy. However, we can employ the expectation value approach:  $\langle E \rangle = \int \psi^* \hat{H} \psi$ . While it is comforting that we have some mathematical tools at our disposal, the expectation value nonetheless is not real energy of the atom because the separated wavefunctions allow the two electrons to partially overlap each other in the same space at the same time. This energy raising mistake is called the “correlation error”, and it causes  $\langle E \rangle$  to be higher than the real energy. Methods to mitigate the correlation error can be complex and are usually introduced in graduate-level courses in quantum mechanics.

**15.6.1 The Variational Principle.** The use of an approximate  $\psi$  solution to the multielectron Hamiltonian causes the  $\langle E \rangle$  expectation value to always be greater than the true energy:

$$\int \psi^* \hat{H} \psi > E_{exact}$$

This provides an interesting approach to create better wavefunctions for multielectron atoms and molecules using what is called the Variational Principle. What we do is alter and adjust our “best guess” separated wavefunctions to achieve the lowest  $\langle E \rangle$  possible, as any change that results in a lower energy is better. Here is an example; if we are trying to optimize a quantum mechanical description for the helium atom ground state using a separated solution:  $\psi_{total}(1, 2) \approx \psi_{1s}(1)\psi_{1s}(2)$ , we first re-derive the hydrogen  $\psi_{1s}$  using the variable  $Z$  for the atomic number. These are called “hydrogen-like” wavefunctions, which for the 1s state is:

$$\psi_{1,0}(r, Z) = 2 \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

(recall that  $Z = +1$  for hydrogen). Next, we insert this function for electrons 1 and 2 and apply it to calculate the  $\langle E \rangle$  expectation value for the helium atom. The result is a function of  $Z$ , which we then adjust to achieve the lowest energy possible. To do so we find the best  $\langle E \rangle$  by applying standard calculus definition of the minimum of a function:

$$\frac{\partial}{\partial Z} \int \psi_{1s}(1)^* \psi_{1s}(2)^* \hat{H} \psi_{1s}(1) \psi_{1s}(2) = 0 @ Z_{opt}$$

While  $Z = +2$  for helium, applying the above method we find that  $Z_{opt} = +1.7$ . While the lower atomic charge may seem arbitrary, in fact one can understand why such alterations make sense based on physical grounds. In this example, reducing the effect of the nuclear charge in the helium atom wavefunction means that the electrons screen each other from the nucleus. This has a substantial effect on atomic energies as discussed below. And while changing the apparent nuclear charge improves our description of the multielectron wavefunction, it’s not a perfect solution and further optimizations are necessary. In fact, this is one of the most active areas of research in chemical theory.

**15.6.2 Shielding.** An electron’s attraction to the nucleus is offset by repulsive interactions with other electrons. This is easy to imagine for electrons in different shells because one electron is closer to the nucleus than the other. As a result, one can say that the higher shell electron is “shielded” from the positive nuclear charge. The shielding effect also operates within the  $l$  states (s, p, d etc.) of the same  $n$  shell, which results in a loss of their degeneracy. The reason for this can be seen in the 2s and 2p wavefunctions in Figure 15.4, where the 2s has amplitude near  $r = 0$  while the 2p doesn’t. As a result, in a multielectron atom the 2s electron’s energy is lowered at the expense of the 2p.

This trend continues across states of increasing angular momentum, and as a result the 3s state is lower in energy than the 3p, which in turn is lower in energy than the 3d. In fact, the effect of shielding is so substantial the 4s state is lower in energy than the 3d! Let’s use radial wavefunctions to demonstrate. At first, the reordering of  $4s < 3d$  appears incorrect because the average electron-nuclear distance of a hydrogenic 4s state is  $\langle r \rangle_{4s} = \int_0^\infty R_{4s}^* \cdot r \cdot R_{4s}(r) \cdot r^2 dr = 24 \cdot a_0$ , which is much longer than  $\langle r \rangle_{3d} = 10.5 \cdot a_0$  of a 3d electron. The 4s electron’s greater  $\langle r \rangle$  implies that it is higher in energy than the 3d. However, the shielding effect occurs close to the nucleus. Thus we must alter our approach by calculating  $|R_{4s}(r)|^2$  and  $|R_{3d}(r)|^2$  over the shorter distance range of  $0 \rightarrow a_0$ . Integral of the absolute value of the 4s wavefunction yields:  $\int_0^{a_0} R_{4s}^* \cdot R_{4s}(r) \cdot r^2 dr =$

$\frac{1}{16}$

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$\int_0^{a_0} R_{3d}^* \cdot R_{3d}(r) \cdot r^2 dr = \frac{1}{16}$

When we perform the same calculation using the 3d radial wavefunction we find:

$\int_0^{a_0} R_{3d}^* \cdot R_{3d}(r) \cdot r^2 dr = \frac{1}{16}$

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$\int_0^{a_0} R_{3d}^* \cdot R_{3d}(r) \cdot r^2 dr = \frac{1}{16}$

As a result, the 4s electron is more likely to be within  $0 \rightarrow a_0$  of the nucleus by a factor of  $\sim 630 \times$  compared to the 3d. In turn the 4s electron soaks up more Coulombic energy by  $\sim 1000 \times$ , which is why a multielectron atom has a lower energy 4s orbital compared to 3d. Don’t forget, however, that 4s is higher in energy than the 3d in a 1-electron hydrogenic atom as shielding only occurs if there are multiple electrons.

When applied across all elements shielding reorders the periodic table into its familiar form shown in Figure 15.8. A diagram to remember the state ordering is also presented. We conclude this section with one last effect on atomic structure due to the effects of relativity. For very heavy elements such as gold ( $Z=79$ ), the 1s electrons experience an extremely high positive nuclear charge that

considerably increases the electrons' kinetic energy. Thus, the velocities approach that of light, which causes an increase in mass and a contraction of the 1s orbital's radius. This is consistent with the fact that the Bohr unit of length is inversely proportional to mass. This relativistic effect causes gold and other heavy elements of the 6<sup>th</sup> and 7<sup>th</sup> row to reverse erstwhile normal trends of the periodic table concerning electron binding energies and oxidation states. The relativistic effect has also been used to explain why the periodic table appears to come to an end. If the atomic number  $Z$  becomes too high then 1s electrons simply become too unstable such that the element can't exist.

**15.6.3 The Pauli exclusion principle and Slater determinants.** In Ch. 14 it was discussed how spin is an angular momentum-like property of an electron. The spin wavefunctions are  $\psi_{spin} = \alpha$  (the "up"  $\uparrow$  state) and  $\psi_{spin} = \beta$  (the "down"  $\downarrow$  state). The  $\hat{S}_z$  operator acts upon them as:

$$\hat{S}_z \alpha = s_z \cdot \alpha = \frac{1}{2} \hbar \cdot \alpha \text{ and } \hat{S}_z \beta = s_z \cdot \beta = -\frac{1}{2} \hbar \cdot \beta$$

Likewise  $\hat{S} \alpha = \sqrt{s(s+1)} \hbar \cdot \alpha$  and  $\hat{S} \beta = \sqrt{s(s+1)} \hbar \cdot \beta$ . Last, we note that the spin states are orthonormal:

$$\int \alpha^* \alpha = \int \beta^* \beta = 1 \text{ and } \int \alpha^* \beta = \int \beta^* \alpha = 0$$

Electrons are assigned spin wavefunctions by labeling them as such; for example,  $\psi_{spin} = \alpha(1) \beta(2)$  for an orbital with an up and down electron ( $\uparrow\downarrow$ ).

One "rule" of the Universe is that particles with  $\frac{1}{2}\hbar$  spin angular momentum cannot occupy the same quantum state at the same time. This is called the Pauli exclusion principle, and it is the reason why you can't have an atomic orbital hold two electrons of the same spin:  $\uparrow\uparrow = \alpha(1) \alpha(2)$ . Rather they must have opposite  $s_z$  as:  $\uparrow\downarrow = \alpha(1) \beta(2)$ . To include spin into our multielectron wavefunction we simply express it as the product of space and spin. Consequently, it would appear that the multielectron wavefunction for helium's  $1s^2 \uparrow\downarrow$  configuration is:

$$\psi(1, 2) = \psi_{space}(1, 2) \psi_{spin}(1, 2) = \psi_{1s}(1) \alpha(1) \cdot \psi_{1s}(2) \beta(2)$$

However, this approach easily allows us to create a wavefunction for a  $1s^2 \uparrow\uparrow$  configuration that violates the Pauli principle:  $\psi(1, 2) = \psi_{space}(1, 2) \psi_{spin}(1, 2) = \psi_{1s}(1) \alpha(1) \cdot \psi_{1s}(2) \alpha(2)$ . This cannot be correct, which causes us to enforce the Pauli principle by imparting a mathematical property called "inversion to interchange" defined by:

$$\psi(1, 2) = -\psi(2, 1)$$

This means that, upon exchanging the labels on an electron pair, the wavefunction should become the opposite of its former self. Any multielectron wavefunction that has this property satisfies the Pauli exclusion principle as shown below.

**15.6.3.1 Singlet States.** A singlet state is one with an even number of electrons that are equally split between up and down spins. This is called a "low spin" configuration and is diamagnetic; most chemical compounds have low spin electronic ground states. We will demonstrate the effects of the Pauli exclusion principle by developing an appropriate singlet  $1s^2 \uparrow\downarrow$  ground state helium wavefunction. While it appears that the inversion to interchange property:  $\psi(1, 2) = -\psi(2, 1)$  might be mathematically intractable, in fact this is trivial to engineer. Beginning with the total wavefunction divided into space and spin components as:

$$\psi_{total}(1, 2) = \psi_{space}(1, 2) \cdot \psi_{spin}(1, 2)$$

We create the inversion to interchange property within the spin manifold as:

$$\psi_{spin}(1, 2) = \alpha(1) \beta(2) - \alpha(2) \beta(1)$$

To verify, we exchange the electron's labels to find:

$$\psi_{spin}(2, 1) = \alpha(2) \beta(1) - \alpha(1) \beta(2) = -(\alpha(1) \beta(2) - \alpha(2) \beta(1)) = -\psi_{spin}(1, 2)$$

This is antisymmetry property we are looking for. The total singlet ground state wavefunction with space and spin is therefore:

$$\psi(1, 2) = \psi_{space} \psi_{spin} \approx \psi_1(1) \psi_2(2) \left\{ \frac{\alpha(1) \beta(2) - \alpha(2) \beta(1)}{\sqrt{2}} \right\}$$

where the  $\frac{1}{\sqrt{2}}$  is a normalization factor. It is now evident how the creation of an "illegal"  $1s^2 \uparrow\uparrow$  configuration for helium is avoided:

$$\psi(1, 2) = \psi_1(1) \psi_2(2) \left\{ \frac{\alpha(1) \alpha(2) - \alpha(2) \alpha(1)}{\sqrt{2}} \right\} = 0$$

due cancellation of the spin wavefunctions. There is one more property that is required, which is that it shouldn't be possible to distinguish between the two electrons. This is accomplished by altering the real space orbital manifold as:

$$\psi(1, 2) = \psi(2, 1)$$

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$$\psi(1, 2) = \psi_1(1) \psi_2(2) + \psi_1(2) \psi_2(1)$$

This works because electron 1 can be in either the first or second spatial orbital, and the same is true for the 2<sup>nd</sup> electron. As a result they are not identifiably different.

**15.6.3.2 Triplet states.** A high spin electronic configuration has an unbalanced number of up and down electrons. The triplet is the most common example and occurs when the number of spin up and down electrons differ by 2. In Chapter 14 we discussed how spin angular momenta add to create three possible triplet spin wavefunctions:

$$\psi_{spin} = \alpha(1) \alpha(2) \quad \psi_{spin} = \beta(1) \beta(2) \quad \psi_{spin} = \frac{1}{\sqrt{2}} \{ \alpha(1) \beta(2) + \alpha(2) \beta(1) \}$$

The above are symmetric with respect to interchange of the electron's labels, we must impart antisymmetry to the spatial wavefunctions as follows:

$$\psi(1, 2) = -\psi(2, 1)$$

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$$\psi(1, 2) = \frac{1}{\sqrt{2}} \{ \alpha(1) \beta(2) - \alpha(2) \beta(1) \}$$

It is very uncommon to observe molecules with triplet ground states as the Pauli principle forbids two up or down spins from occupying the same space orbital. However, it is more frequently observed in excited electronic states, especially as a high spin configuration can be lower in energy compared to an equivalent singlet state as discussed below. An exception is molecular oxygen that is a ground state triplet. This fact dictates much about  $O_2$ 's reactivity with organics, which has important implications for oxidation of biological molecules and materials.

**15.6.3.3 Slater Determinants.** While the ability to write antisymmetrized wavefunctions for two electrons isn't particularly difficult, one runs into greater complexity when trying to do the same for more electron rich systems. For example, in the case of a three electron atom, the principle of antisymmetry requires the permutation of any pair of electrons result in a negative wavefunction:

$$\psi(1, 2, 3) = -\psi(2, 1, 3) = -\psi(1, 3, 2) = \psi(3, 2, 1)$$

It isn't clear how to mathematically engineer these relationships into a single wavefunction. In 1929 John Slater developed a method to do so using matrices, where the orbital identity change down the column while the electron identity moves to the right across the row. The wavefunction is the normalized determinant of this configuration. Let's practice by creating a helium two electron  $1s^1 2s^1$  triplet state the wavefunction:

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

Expanding the determinant reveals:

$$3\Psi = \frac{1}{\sqrt{2}} \{ \psi_{1s}(1)\alpha(1)\psi_{2s}(2)\alpha(2) - \psi_{2s}(1)\alpha(1)\psi_{1s}(2)\alpha(2) \}$$

This expression is equal to:  $\frac{1}{\sqrt{2}} \{ \psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2) \} \alpha(1)\alpha(2)$ , exactly as we determined previously. The singlet  $1s^2 \uparrow\downarrow$  ground state configuration of helium requires two determinants:

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

Simplification yields:

$$\frac{1}{2} \{ \psi_{1s}(1)\psi_{1s}(2) + \psi_{1s}(1)\psi_{1s}(2) \} \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \}$$

which is identical to the expression derived earlier.

Next on the periodic table is lithium, which has a  $1s^2 2s^1$  configuration for its three electrons. The wavefunction in the determinant form is:

$$\Psi = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(1)\beta(1) & \psi_{2s}(1)\alpha(1) \\ \psi_{1s}(2)\alpha(2) & \psi_{1s}(2)\beta(2) & \psi_{2s}(2)\alpha(2) \\ \psi_{2s}(3)\alpha(3) & \psi_{2s}(3)\beta(3) & \psi_{2s}(3)\gamma(3) \end{vmatrix}$$

We won't expand the determinant here; however, if we did so and switched any two electron labels, we would find that the resulting total wavefunction has picked up a "-" sign as required by the Pauli principle. The addition of more electrons creates an even more complex state, which is why one needs supercomputers to model large molecules such as proteins using quantum mechanics.

**15.6.4 Exchange energy and magnetism.** The effects of Pauli principle are substantial due to the antisymmetry of wavefunctions. This in turn affects energetic ordering of excited states as a function of spin. To demonstrate we will study the dynamics of excitation of the helium atom shown in Figure 15.9A. The singlet  $1s^2$  ground state transitions into the singlet  $1s^1 2p_z^1$  excited state of helium after absorption of z-polarized light due to the angular momentum selection rule. While a spin selection rule stipulates  $\Delta m_s = 0$  for excitation to the triplet state, the excited singlet may intersystem cross into a high spin  $1s^1 2p_z^1$  configuration nonetheless. As a result we will study the difference in the singlet and triplet state energies by applying the antisymmetrized wavefunction to the electron-electron Coulomb operator:

$$\int \Psi^* \hat{V} \Psi \, d\tau$$

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$$\int \Psi^* \hat{V} \Psi \, d\tau$$

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$$\int \Psi^* \hat{V} \Psi \, d\tau$$

These integrals are evaluated in full in the Appendix, where we demonstrate that the many terms collapse into the form  $K + J$ , where the term  $K$  is the Coulomb integral:

$$K = \int \psi_1^*(1)\psi_2^*(2) \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} \psi_1(1)\psi_2(2) \cdot d\tau = \int |\psi_1(1)|^2 \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} |\psi_2(2)|^2 \cdot d\tau$$

This describes the probability density of the first electron in the first orbital,  $|\psi_1(1)|^2$ , electrostatically interacting with the same for the second electron  $|\psi_2(2)|^2$ . This is essentially identical to what was taught to you in Physics II Electromagnetism. Where this story gets more complex is that there is a second term found in the Coulombic interaction. It is called the exchange term and is usually abbreviated  $J$ :

$$J = \pm \int \psi_1^*(1)\psi_2(2) \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} \psi_2^*(2)\psi_1(1) \cdot d\tau$$

where + is for the singlet and - is for the triplet. Consequently, the excited triplet state of helium is slightly lower in energy as shown in Figure 15.9.

The exchange term describes electrons as being in two places at once. While this is hard to understand, the effect is very much real as the fact that the excited triplet state is lower in energy than the singlet has been verified experimentally. One reason for this is the "odd" space symmetry of the triplet state. Take for example diatomic  $H_2$  that shares two electrons as shown in Figure 15.9B. The even symmetry of the singlet allows the electrons to become closer together while the triplet does the opposite, which would energetically favor the triplet. It should be noted that wavefunctions become increasingly complex as atoms gain more electrons and form molecules. As a result there is no simple rule about the ordering of the energies of excited states although one often hears "triplets are lower in energy than singlets". While this is often the case, especially for organics, in reality nothing is assured pending a full quantum chemical analysis.

Tipping the energy balance between high spin triplet states and low spin singlets due to the exchange interaction has many significant effects. For one, if an excited organic molecule intersystem crosses into a triplet state it will vigorously react with oxygen as  $O_2$  is also triplet. Furthermore, the unpaired electron configuration of a high spin state imparts magnetic properties such as ferromagnetism. This phenomenon occurs when the constituent atoms of a solid piece of metal align their magnetic moments in parallel, which massively augments the high spin magnetic character. This is due to the strength of the exchange interaction, which is a function of atomic geometry because of the unusual nature of the exchange integral. This is why some metals are magnetic and some are not; the crystal structure and interatomic distances of some materials don't allow for enough exchange to impart a net magnetic field.

**15.6.4 Spin-orbit mixing, intersystem crossing and phosphorescence.** Any molecular dynamics that require a change of the overall spin state is formally not allowed, and such processes are usually referred to as "spin forbidden". However, the spin-orbit effect relaxes this prohibition. For example, most molecules have singlet ground states, and as such upon absorption of light the final state must also be a singlet due to the spin selection rule. This is also consistent with the fact that a photon does not have any spin-type angular momentum. Once an excited state singlet is created, however, the spin-orbit effect allows that state to intersystem cross into the lower energy triplet as shown in Figure 15.10A. This is because the forbidden nature of the transition is lifted by spin-orbit coupling, which mixes the spin states together as shown in Figure 15.10B. Here, spin-orbit coupling rotates a triplet state eigenvector into the singlet electronic state space causing it to gain some singlet character. The same is true for the singlet, and as a result an excited singlet state can become a triplet given that it already has some triplet character. Phosphorescence, which is the emission of light from an excited triplet state back to a ground singlet state, is also allowed due to the spin-orbit effect.

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