

Lecture 11 Highlights Phys 402

We continued to discuss the unperturbed eigenenergies and eigenfunctions of the Helium atom....

We took a detour into 1D infinite square wells to discuss the **correlations** built in to multi-particle states by the anti-symmetry constraint. Consider a 1D infinite square well between $x = 0$ and $x = a$. Put two non-interacting but identical particles into the well, and ignore the spin part of the wavefunction for now (this is very artificial!). We want to find the ground state wavefunctions and energies for the cases of two identical “Bosons” (exchange operator \hat{P} eigenvalue +1) and two identical “Fermions” (\hat{P} eigenvalue -1). The un-perturbed Hamiltonian is:

$$\mathcal{H}^0 = \frac{-\hbar^2}{2m} \left(\frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) + V(x_1) + V(x_2),$$

where $V(x)$ is the infinite square well potential. Note that this Hamiltonian commutes with the exchange operator, $[\mathcal{H}^0, \hat{P}] = 0$, hence we can find a complete set of eigenfunctions of both operators. We will write the 2-particle wavefunctions as products of single-particle states.

First suppose that they are identical Bosons ($P = +1$). One can make a symmetric space wavefunction that puts both particles in the ($n = 1$) ground state of the infinite square well, but still respects their indistinguishability:

$$\psi_{11}^S(1,2) = \frac{2}{a} \sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right),$$

where x_1 refers to the x -coordinate of particle 1, and x_2 to that of particle 2. This wavefunction is symmetric with respect to exchange of the coordinates of the particles (\hat{P} eigenvalue +1), and is an eigenfunction of the Hamiltonian with an un-perturbed energy of $E_{11}^0 = 2 \frac{\pi^2 \hbar^2}{2ma^2}$.

Now suppose they are identical Fermions. Both particles cannot occupy the same ($n = 1$) ground state of the well, due to the Pauli exclusion principle (i.e. the need to have a wavefunction with exchange operator \hat{P} eigenvalue of -1). One can write down the Fermionic ground state wavefunctions as follows. It must be anti-symmetric in space and it must put one particle in the $n = 1$ ground state and the other in the $n = 2$ first excited state. The wavefunction does this in a way that respects the indistinguishability of the two particles:

$$\psi_{12}^A(1,2) = \frac{\sqrt{2}}{a} \left[\sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{2\pi x_2}{a}\right) - \sin\left(\frac{2\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right) \right].$$

Now consider the first excited state of the two identical Bosons. This wavefunction is symmetric in space, and also puts the particles into different states:

$$\psi_{12}^S(1,2) = \frac{\sqrt{2}}{a} \left[\sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{2\pi x_2}{a}\right) + \sin\left(\frac{2\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right) \right]$$

Both of these wavefunctions have the same un-perturbed energy of $E_{12}^A = E_{12}^S = 5 \frac{\pi^2 \hbar^2}{2ma^2}$.

From the [plots](#) of $\psi_{12}^S(x_1, x_2)$ and $\psi_{12}^A(x_1, x_2)$ posted on the class web site, one can see that the probability of finding the particles at the same location $x_1 = x_2$ is significantly higher in the symmetric vs. the antisymmetric wavefunctions. This can be made quantitative by calculating the expectation value of $(x_1 - x_2)^2$ in these two states, which is a measure of how much the particles try to avoid each other. It is clear from the pictures that $\langle (x_1 - x_2)^2 \rangle_A > \langle (x_1 - x_2)^2 \rangle_S$. In other words, the two particles are likely to be found further apart in the anti-symmetric wavefunction (where $\psi_{12}^A(x_1 = x_2) = 0$) than the symmetric wavefunction. This result is derived more generally in Griffiths, section 5.1.2, beginning on page 203. This observation about the relative locations of the particles in the two eigenfunctions is known as a **correlation**. In particular these are called “exchange correlations” because they are created by the need to satisfy the exchange operator constraint.

Next, consider adding a perturbing Hamiltonian which is repulsive in nature, depending on the separation of the particles. For example take the Coulomb repulsion between two like-charges: $\mathcal{H}^1 = \frac{+e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}$, written in a form appropriate for 3D, but you get the idea. When this repulsive perturbing potential is turned on, it will leave the anti-symmetric space wavefunction at a lower energy than the symmetric space wavefunction. In other words $\langle \psi_{12}^A | \mathcal{H}^1 | \psi_{12}^A \rangle < \langle \psi_{12}^S | \mathcal{H}^1 | \psi_{12}^S \rangle$. This energy difference is called the “exchange energy” or “exchange splitting.” It will come in to play when we return to the He atom, and it influences the structure of the periodic table!

He atom wavefunctions with spin

Now, back to the He atom wavefunctions (including spin!) and eigen-energies. The ground state of He must put both of the electrons in to the lowest energy single-particle state ψ_{100} (promoting one of the two electrons to the next available state is too energetically costly). This will put the two electrons into a symmetric space wavefunction. To make the overall wavefunction anti-symmetric under exchange of all the coordinates of the two identical fermions, we must have an anti-symmetric spin wavefunction. The spin singlet wavefunction will do the trick;

$$\Psi_{He}^{GS}(1,2) = \psi_{100}(1)\psi_{100}(2)|0\ 0\rangle$$

The unperturbed eigenstate has a ground state energy of $E_T = -108.8\text{ eV}$.

Now if we include the Coulomb repulsion perturbing Hamiltonian, the first-order correction to the energy is given by;

$$\begin{aligned} E_{GS}^1 &= \langle \Psi_{He}^{GS} | \mathcal{H}^1 | \Psi_{He}^{GS} \rangle \\ &= \iiint d^3x_1 \iiint d^3x_2 \langle 0\ 0 | \psi_{100}^*(1) \psi_{100}^*(2) \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} \psi_{100}(1) \psi_{100}(2) | 0\ 0 \rangle \end{aligned}$$

This integral can be done analytically (see Griffiths, page 333), and yields $E_{GS}^1 = +34.0\text{ eV}$. The first-order corrected ground state energy of He is predicted to be $E_{GS} = E_T + E_{GS}^1 = -74.8\text{ eV}$. The measured ground state energy of He is -78.98 eV , within 5% of our estimate. We will make further improvements on the He ground state wavefunction later, when we consider the Variational Principle.

What is the first excited state of He? Clearly one of the electrons must be promoted from the $n = 1$ state to the $n = 2$ state. But now there are two choices, $\ell = 0$ (code-letter s) or $\ell = 1$ (code-letter p). The short-hand for these two states is 1s2s and 1s2p. The 1s2s configuration has a lower energy than the 1s2p for the following reason. The first electron (1s) resides in a Hydrogenic state with strong binding energy and small average radius $\langle r \rangle$. The second electron goes into an $n = 2$ state with less binding energy and a larger average radius. The $n = 2$ electron will experience a partially screened nucleus, since the 1s electron “wraps around” the nucleus and reduces its effective charge from $+2e$ to something closer to $+e$. This weakens the attraction that the $n = 2$ electron experiences with the nucleus, and is called ‘**screening**’. Now the orbital angular momentum comes in to play. An electron in an $\ell = 0$ state will spend more time traveling through the nucleus and penetrating the inner 1s screening cloud (at least classically), compared to a 2p electron that will be in more of a traditional high angular momentum classical “orbit” about the nucleus. This allows the 2s electron to enjoy a stronger attraction to the nucleus, without paying too high a price in terms of Coulomb repulsion from the 1s electron. In addition, from solutions of the radial wavefunction $R_{n,\ell}(r)$, one finds that the 1s and 2p electrons essentially reside in the same region of r , whereas the 2s electron has a significant probability of being found at larger radii. (See the radial probability densities [here](#).) This has the consequence that $\langle 1s2s | \mathcal{H}' | 1s2s \rangle < \langle 1s2p | \mathcal{H}' | 1s2p \rangle$, where \mathcal{H}' is the Coulomb repulsion perturbing Hamiltonian for the two electrons $\mathcal{H}' = \frac{+e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}$. The general idea is that electron orbitals with lower orbital angular momentum tend to have lower energy than their higher- ℓ counterparts. This explains some important features of the periodic table.

There are now numerous ways to write down the excited state wavefunctions (super-scripts “A” and “S” stand for Antisymmetric and Symmetric, respectively):

$$\Psi_{1s2s}^{SA}(1,2) = \frac{1}{\sqrt{2}} \{ \psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1) \} |0\ 0\rangle$$

$$\text{or } \Psi_{1s2s}^{AS}(1,2) = \frac{1}{\sqrt{2}} \{ \psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1) \} |1\ m\rangle, \text{ with } m = +1, \ 0, \ -1$$

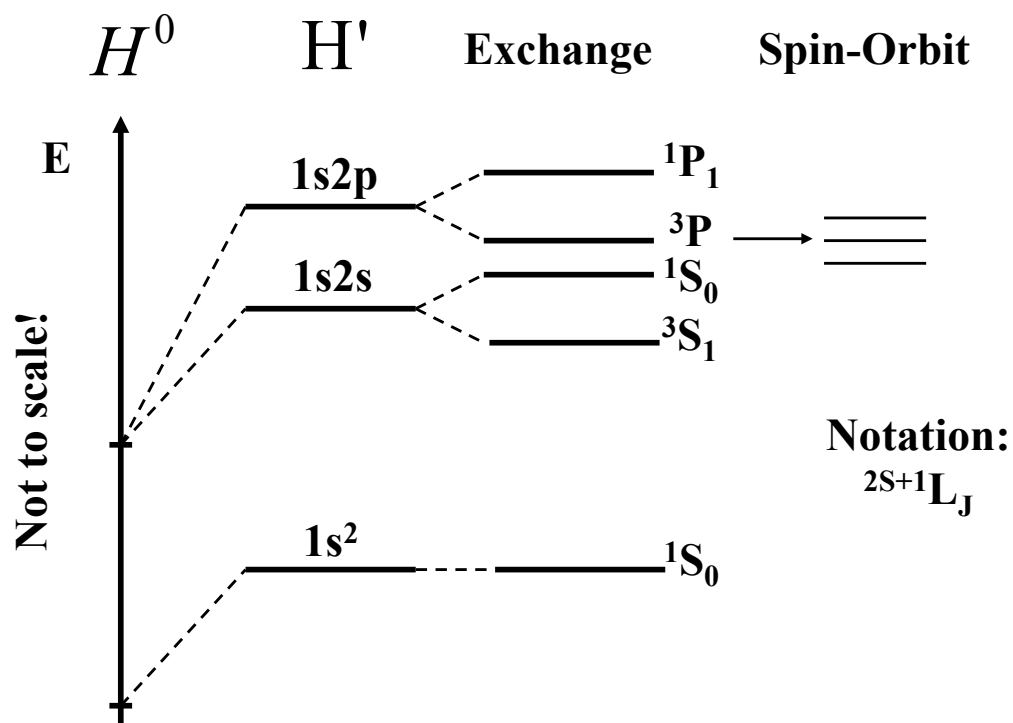
$$\text{and } \Psi_{1s2p}^{SA}(1,2) = \frac{1}{\sqrt{2}} \{ \psi_{1s}(1)\psi_{2p}(2) + \psi_{1s}(2)\psi_{2p}(1) \} |0\ 0\rangle$$

$$\text{or } \Psi_{1s2p}^{AS}(1,2) = \frac{1}{\sqrt{2}} \{ \psi_{1s}(1)\psi_{2p}(2) - \psi_{1s}(2)\psi_{2p}(1) \} |1\ m\rangle, \text{ with } m = +1, \ 0, \ -1$$

The anti-symmetric space wavefunctions will have lower energy than their symmetric counterparts because of the “exchange splitting” discussed above. The anti-symmetric space wavefunction has a zero when “ $\vec{r}_1 = \vec{r}_2$ ”, leading to an effective “exchange force” that keeps the two electrons further apart than in the symmetric space wavefunction. The wavefunctions can be labeled by the notation: $^{2S+1}L_J$, where S is the TOTAL spin angular momentum of the two electrons, L is actually a code letter (S, P, D, F, ...) for the TOTAL angular momentum of the two electrons, and J is the TOTAL angular momentum of the two electrons ($\vec{J} = \vec{L} + \vec{S}$). In addition the 3P states will be split by spin-orbit coupling.

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He Atom Low-Lying States



These energy level orderings agree with the [experimental data on He](#), as posted on the [NIST Atomic Spectra Database web site](#).