

Lecture 10 Highlights Phys 402

The Helium Atom

Let's move beyond Hydrogen to the next interesting case, the Helium atom. The neutral ${}^4\text{He}$ atom has two electrons bound to a nucleus made up of two protons and two neutrons. We wish to find the eigenenergies and eigenfunctions of the Helium atom. In doing so we will discover some interesting new physics.

There are two electrons orbiting a nucleus of charge $+2e$. We shall treat this as a perturbation problem. The un-perturbed Hamiltonian is that of the two electrons independently orbiting the same nucleus:

$$H^0 = -\frac{\hbar^2}{2m} \nabla_1^2 + \frac{(-e)(+2e)}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m} \nabla_2^2 + \frac{(-e)(+2e)}{4\pi\epsilon_0 r_2}, \quad (1)$$

where the Laplacian operators only operate on the spherical coordinates of either particle 1 or particle 2. Note that the electrons are identical, they have exactly the same mass and charge.

What remains is the Coulomb repulsion between the two electrons. We shall treat this as a perturbation:

$$H' = \frac{(-e)(-e)}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \quad (2)$$

The solution to the un-perturbed Schrödinger equation is a wavefunction that depends on 6 coordinates:

$$H^0 \Psi^0 = E_T \Psi^0 \quad (3)$$

where $\Psi^0 = \Psi^0(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$. This wavefunction has the following probabilistic interpretation. $|\Psi^0(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)|^2 d^3x_1 d^3x_2$ is the probability of finding particle 1 within a differential volume d^3x_1 of location (r_1, θ_1, ϕ_1) and finding particle 2 within a differential volume d^3x_2 of location (r_2, θ_2, ϕ_2) .

Unlike the Hydrogen atom, there is no exact analytical solution to the Helium atom Schrodinger equation. This is related to the fact that the classical 3-body problem cannot be solved analytically either. In other words, for the [classical 3-body problem](#) no general closed-form solution exists. Ultimately, we must use either numerical methods or approximation schemes to solve the Helium atom Schrodinger equation.

To proceed, we try an *ansatz* which we believe will lead to separation of variables as

$$\Psi^0(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \psi_a(1) \psi_b(2)$$

where “1” and “2” represent all of the coordinates of particles 1 and 2, respectively, and “a” and “b” are different lists of quantum numbers, in general. This assigns electron 1 to state “a” and particle 2 to state “b”. Putting this ansatz into (3) and dividing through by the product wavefunction gives two Hydrogenic Schrödinger equations and an algebraic constraint:

$$\left(-\frac{\hbar^2}{2m} \nabla_1^2 + \frac{(-e)(+2e)}{4\pi\epsilon_0 r_1} \right) \psi_a(1) = E_a \psi_a(1)$$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \frac{(-e)(+2e)}{4\pi\epsilon_0 r_2} \right) \psi_b(2) = E_b \psi_b(2)$$

with the constraint $E_T = E_a + E_b$. Note that the solutions to these equations are the hydrogen atom wavefunctions with r/a_0 replaced by Zr/a_0 , where Ze is the nuclear charge ($Z = 2$ for Helium). This changes the unperturbed energy levels to $E_n^0 = -Z^2 13.6 \text{ eV}/n^2$.

Thus it would appear that we have solved the unperturbed Schrödinger equation for the Helium atom as $\Psi^0 = \psi_a(1)\psi_b(2)$. However there is an important inconsistency in this argument. The solution has implicitly assumed that we can distinguish which electron is in which state (“a” or “b” in this case). However when two electrons “collide” (i.e. their wavefunctions overlap, as in the He atom) they lose their unique identity. They are not only identical but indistinguishable. Indistinguishability is a tremendously important concept in quantum mechanics. It means that when we construct multi-identical-particle wavefunctions (in which the particles have overlapping wavefunctions) we must be very careful to honor their *indistinguishability*. For example we cannot insist that electron 1 is in state “a” while electron 2 is in state “b” in the He atom. If one of the electrons is subsequently ionized from the atom we cannot tell which one it “originally” was.

When two identical particles “collide” we must make a new kind of wavefunction that describes the composite state. Note that perfect distinguishability is implicitly assumed in much of classical physics.

For a clue as to how to proceed we re-examined the wavefunctions created when combining 2 identical spin-1/2 particles covered in discussion 3. These are the spin triplet wavefunctions ($|1\ 1\rangle, |1\ 0\rangle, |1\ -1\rangle$) and the spin singlet wavefunction ($|0\ 0\rangle$). These 4 wavefunctions respect the indistinguishability of the two particles. If you extract one particle from any of these states and ask what is its spin orientation, you will get an answer which treats the two particles on equal footing. You will not be able to say “aha, particle 1 was in the ‘up’ state in $|1\ 0\rangle$ ” for example. The four eigenstates do not give any preference to either of the two particles. It respects their indistinguishability. We need to use this idea to make a better Helium atom wavefunction than $\Psi^0 = \psi_a(1)\psi_b(2)$.

Consider a 2-identical-particle wavefunction $\Psi(1,2)$. Define a permutation (or “exchange”) operator $\hat{P}$ that exchanges all of the coordinates of two particles in the wavefunction:

$$\hat{P}\Psi(1,2) = \Psi(2,1)$$

If we apply this operator twice, we get back to the same wavefunction:

$$\hat{P}^2\Psi(1,2) = \hat{P}\Psi(2,1) = \Psi(1,2)$$

In other words, this says that $\hat{P}^2 = \hat{1}$, or that the eigenvalues of $\hat{P}$ are ± 1 . If in addition we have a symmetric potential for the two identical particles: $V(\vec{r}_1, \vec{r}_2) = V(\vec{r}_2, \vec{r}_1)$, then $\hat{P}$ and $\hat{H}$ are compatible operators ($[\hat{P}, \hat{H}] = 0$) and we can form a complete set of simultaneous eigenfunctions that will have the property: $\Psi(1,2) = \pm \Psi(2,1)$. The plus sign denotes symmetric wavefunctions, while the minus sign denotes anti-symmetric wavefunctions. Thinking back to the problem of two (identical) spin-1/2 particles in the coupled representation, recall that we found two classes of states, the triplet states ($|1\ 1\rangle, |1\ 0\rangle, |1\ -1\rangle$) and the singlet state ($|0\ 0\rangle$). Note that the triplet states have

eigenvalue +1 under the $\hat{P}$ operator, while the singlet state has eigenvalue -1 under $\hat{P}$. Hence, these states also respect the indistinguishability of the two particles involved.

The spin-statistics theorem states that all particles with integer spin (called Bosons) have overall symmetric wavefunctions for multi-identical-particle systems. Also, particles with half-integer spin (called Fermions) have overall anti-symmetric wavefunctions for multi-identical-particle systems.

Going back to Helium, because the two identical electrons are spin-1/2 particles, we need to construct an overall antisymmetric wavefunction. One possibility (for the space part of the wavefunction) is this:

$$\Psi_A^0(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1))$$

Check to see that $\Psi_A^0(1,2) = -\Psi_A^0(2,1)$, as advertised. Note that this wavefunction puts electrons into states “a” and “b” of the He atom, but does not make the mistake of saying explicitly which electron is in which state. It maintains the anonymity and indistinguishability of the two electrons. Learning how to write down such wavefunctions is an art form that you must learn (the homework problems will give you some guidance).

Note that the anti-symmetric space wavefunction:

$$\Psi_A^0(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1))$$

has a peculiar property. If both particles are in the same single-particle state (i.e. the lists of quantum numbers $a = b$), then the wavefunction is zero! This remarkable property is shared by much more sophisticated multi-identical-particle Fermionic wavefunctions and is called the **Pauli Exclusion Principle**. It says that no two Fermions in a multi-identical-particle composite Fermion (overall anti-symmetric) wavefunction can occupy the same exact single-particle quantum state.

This principle now constrains the types of He atom wavefunctions we can write down. If we now explicitly include spin of the electrons, and assume the wavefunctions are product states of space and spin wavefunctions, they can only be of the form:

$$\Psi^0(1,2) \sim \psi_{\text{Symmetric}}(1,2)\chi_{\text{Anti-Symmetric}}(1,2),$$

or

$$\Psi^0(1,2) \sim \psi_{\text{Anti-Symmetric}}(1,2)\chi_{\text{Symmetric}}(1,2),$$

where ψ represents the space-part of the wavefunction and χ represents the spin part of the wavefunction (here it is assumed that the He-atom wavefunction can be factorized like this). A symmetric space wavefunction that respects indistinguishability can be written in this way, for example (inspired by the spin-triplet state $|1\ 0\rangle$):

$$\Psi_S^0(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1))$$

But what about symmetric and anti-symmetric spin wavefunctions χ ? It turns out that we already have them, at least for the combination of two identical spin-1/2 particles. The spin triplet states ($|11\rangle, |10\rangle, |1-1\rangle$) are symmetric under permutation (also called exchange) of the two particles, while the spin singlet state ($|00\rangle$) is antisymmetric. Fantastic!

We now have 4 candidate He atom wavefunctions:

$$\Psi_{He}^0(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)) \parallel 11 \rangle$$

or

$$\Psi_{He}^0(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)) \parallel 10 \rangle$$

or

$$\Psi_{He}^0(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)) \parallel 1-1 \rangle$$

or

$$\Psi_{He}^0(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)) \parallel 00 \rangle$$