Lecture 17 Highlights

We wish to find the eigenenergies and eigenfunctions of the Helium atom. 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:

$$\mathrm{H}^0 = -\frac{\hbar^2}{2m}\nabla_1^2 + \frac{(-e)(+2e)}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 + \frac{(-e)(+2e)}{4\pi\varepsilon_0 r_2} \qquad (1)$$

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:

$$\mathrm{H}' = \frac{(-e)(-e)}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \qquad (2)$$

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

$$\mathrm{H}^0\Psi^0 = E_T\Psi^0 \qquad (3)$$

where $\Psi^0 = \Psi^0(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$. We try 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. Putting this ansatz into (3) and dividing through by the product wavefunction gives two Hydrogenic Schrödinger equations and an algebraic constraint:

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 + \frac{(-e)(+2e)}{4\pi\varepsilon_0 r_1}\right)\psi_a(1) = E_a\psi_a(1)$$

$$\left(-\frac{\hbar^2}{2m}\nabla_2^2 + \frac{(-e)(+2e)}{4\pi\varepsilon_0 r_2}\right)\psi_b(2) = E_b\psi_b(2)$$

with $E_T = E_a + E_b$. 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 ($Z = 2$ here). This changes the unperturbed energy levels to $E_n = -Z^2\, 13.6eV/n^2$.

Thus it would appear that we have solved the un-perturbed 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 loose 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.

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

$$P\Psi(1,2) = \Psi(2,1)$$

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

$$P^2\Psi(1,2) = P\Psi(2,1) = \Psi(1,2)$$

In other words, this says that $P^2 = 1$, or that the eigenvalues of P are ± 1. If in addition we have a symmetric potential for the two particles: $V(\vec{r}_1,\vec{r}_2) = V(\vec{r}_2,\vec{r}_1)$, then P and H are compatible operators ($[P,\mathrm{H}] = 0$) and we can form 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.

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

Going back to He, because the two identical electrons are spin-1/2 particles, we need to construct an antisymmetric wavefunction. One possibility is this:

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

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.