

HELIUM ATOM

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So far, we've looked at identical particles only in the non-interacting case. In real life, of course, most particles interact with each other, so the Schrödinger equation must take this into account. For an atom with Z protons and Z electrons, each electron experiences an electric interaction with the nucleus, and with all the other electrons. The Schrödinger equation in this case is therefore

$$H\psi = E\psi \quad (1)$$

where

$$H = \sum_{j=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{Ze^2}{4\pi\epsilon_0 r_j} \right] + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{j \neq k} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|} \quad (2)$$

The first term in the first sum is the kinetic energy of the electrons (we're assuming the atom as a whole is at rest, so there is no contribution from the kinetic energy of the nucleus), the second term gives the interaction between the electrons and the nucleus, and the last sum gives the electron-electron interactions.

Needless to say, solving this equation is very difficult and in fact, there is no known exact solution except in the case of hydrogen, where $Z = 1$ and the last term vanishes.

If we *could* find a solution, however, we'd need to form a completely anti-symmetric function from it, since electrons are fermions. The general solution would have the form

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_Z) \quad (3)$$

Since the hamiltonian is completely symmetric with respect to the Z vectors \mathbf{r}_i , any permutation of the vectors in the solution is also a solution, so any linear combination of solutions is also a solution, and will have the same energy.

Since the anti-symmetry results from interchanging position vectors, we can apply the same process as that used to find anti-symmetric wave functions from stationary states. This time, however, we apply the anti-symmetrization

to the order of the vectors in the argument list, rather than to individual stationary states. Thus, we'd get

$$\psi_f = A \left[\sum_{\text{even}} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_Z) - \sum_{\text{odd}} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_Z) \right] \quad (4)$$

where the first sum is over all even permutations of the vectors and the second is over all odd permutations. The constant A is determined by normalization.

If we formed an anti-symmetric function of the position vectors, then the spin portion of the wave function would have to be symmetric. Conversely, if we formed a symmetric function of position, then the spin would have to be anti-symmetric.

In the case of bosons we just replace the minus sign by a plus sign, which results in a sum over all permutations

$$\psi_b = A \sum_{\text{all}} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_Z) \quad (5)$$

This would, of course, not apply to the hamiltonian above, since electrons are not bosons, but if we did have a hamiltonian that applied to a collection of bosons, we could use the same procedure to generate a symmetric wave function. In the boson case, we would need to pair a symmetric spatial wave function with a symmetric spin function, and an anti-symmetric spatial function with an anti-symmetric spin function.

The simplest atom larger than hydrogen is helium, with 2 electrons. In this case, the hamiltonian is

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (6)$$

A very crude approximation is to ignore the electron-electron interaction. Although this doesn't give very accurate results, it does at least allow us to solve the Schrödinger equation exactly, since r_1 and r_2 are separated in the hamiltonian. The solution is just the product of hydrogen-like wave functions, so the ground state would be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \quad (7)$$

where the wave functions on the RHS now each have an energy of

$$E_1 = Z^2 E_{1H} = 4 \times (-13.6 \text{ eV}) = -54.4 \text{ eV} \quad (8)$$

The total energy is just the sum of the two energies for each electron, so

$$E_{1He} = -108.8 \text{ eV} \quad (9)$$

The actual energy is measured to be -78.975 eV so this crude model isn't very good.

Since this ground state consists of the product of two identical functions, we can't anti-symmetrize it (ψ_f as calculated from 4 just gives zero), so to get an anti-symmetric total wave function, we have to multiply the spatial function by an anti-symmetric spin function.

Using this crude model, we can investigate the behaviour of a helium atom with both electrons in the $n = 2$ state. Experimentally, what happens in this case is that one electron decays back down to the ground state and instead of emitting a photon, it imparts the energy from this decay to the other electron. The $n = 2$ state has an energy of $E_2 = Z^2 E_{2H} = 4 \times (-13.6/4) = -13.6 \text{ eV}$ so the energy emitted by the decaying electron is $-13.6 - (-54.4) = +40.8 \text{ eV}$. Transferring this energy to the other electron gives it an energy of $40.8 - 13.6 = +27.2 \text{ eV}$. Since this energy is positive, the electron leaves the atom, resulting in a helium ion.

The spectrum of the helium ion can be calculated from the Rydberg formula:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (10)$$

where n_f is the final state and n_i is the initial state of the electron, and R is the Rydberg constant, which for helium is $Z^2 R_H = 4R_H$, or 4 times the Rydberg constant for hydrogen. As a result, the spectrum of the helium ion is the same as that of hydrogen, except all the wavelengths are a quarter of those in hydrogen.

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