In this section we will see a useful method for approaching a problem that cannot be solved analytically and in the process we will learn why a product wavefunction is a logical choice for approximating a multi-electron wavefunction.

The helium atom Hamiltonian is re-written below with the kinetic and potential energy terms for each electron followed by the potential energy term for the electron-electron interaction. The last term, the electron-electron interaction, is the one that makes the Schrödinger equation impossible to solve.

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2_1 - \frac{2e^2}{4 \pi \epsilon_0 r_1} - \frac{\hbar^2}{2m} \nabla^2_2 - \frac{2e^2}{4 \pi \epsilon_0 r_2} + \frac{e^2}{4 \pi \epsilon_0 r_{12}} \label{9-9}
\]

To solve the Schrödinger Equation using this Hamiltonian, we need to make an assumption that allows us to find an approximate solution. The approximation that we consider in this section is the complete neglect of the electron-electron interaction term. Odd though it seems, this assumption corresponds mathematically to treating the helium atom as two non-interacting helium ions (with one electron each) that happen to share the same nucleus.

This approximation is called the independent-electron assumption. While this assumption might seem very drastic, it is worth trying since it also presents a straightforward path to a solution. A general strategy when solving difficult problems is to make an assumption and see how the results turn out. In this case we can compare the results we obtain using the assumption to what is known experimentally about the quantum states of helium, like the ionization energies. Are we a factor of 10 off? 10000? The latter result would probably indicate that we have hit a dead end with this method, while the former might indicate a method worth refining.

Neglecting the electron repulsion term simplifies the helium atom Hamiltonian to a sum of two hydrogen-like Hamiltonians that can be solved exactly.

\[
\hat{H}(r_1,r_2) = \hat{H}(r_1) + \hat{H}(r_2) \label{9-10}
\]

The variables (the positions of the electrons, \(r_1\) and \(r_2\)) in the Schrödinger equation separate, and we end up with two independent Schrödinger equations that are exactly the same as that for the hydrogen atom, except that the nuclear charge is +2e rather than +1e.

\[
\hat{H}(r_1) \varphi (r_1) = E_1 \varphi (r_1) \label{9-11}
\]
\[
\hat{H}(r_2) \varphi (r_2) = E_2 \varphi (r_2) \label{9-12}
\]

Exercise \(\PageIndex{1}\)

What is the specific mathematical form for \(\hat{H}(r_1)\) in Equation \(\ref{9-10}\)?

Using our previous experiences with separation of variables, we realize that the wavefunction can be approximated as a product of two single-electron hydrogen-atom wavefunctions with a nuclear charge \(Z = +2e\),

\[
\psi (r_{1}, r_{2}) \approx \varphi (r_{1}) \varphi (r_{2}) \label{9-13}
\]

Exercise \(\PageIndex{2}\)
Write the explicit mathematical expression for the ground state wavefunction for the helium atom shown in Equation \ref{9-13}).

\[ E_{\text{He}} = E_1 + E_2 \] \label{9-14}

Binding Energy

As we will show below, the energy eigenvalue associated with the product wavefunction is the sum of the one-electron energies associated with the component single-electron hydrogen-atom wavefunctions.

\[ E_{\text{He}} = E_1 + E_2 \]

The energy calculated using the Schrödinger equation is also called the total energy or the binding energy. Binding energy is the energy required to separate the particles of a system (in this case the two electrons and the nucleus) to an infinite distance apart. The binding energy should not be confused with the ionization energy, \( \langle \text{IP} \rangle \), which is the energy required to remove only one electron from the helium atom. Binding energies can be measured experimentally by sequentially ionizing the atom and summing all the ionization energies. Hence for the lithium atom with three electrons, the binding energy is

\[ E_{\text{He}} = \text{IP}_1 + \text{IP}_2 + \text{IP}_3 \]

The binding energy (or total energy) should not be confused with the ionization energy, \( \langle \text{IP} \rangle \), which is the energy required to remove a single electron from the atom.

Exercise \PageIndex{3}\)

Why was it unnecessary to differentiate the terms binding energy and ionization energy for the hydrogen atom and other one-electron systems?

To calculate binding energies using the approximate Hamiltonian with the missing electron-electron repulsion term, we use the expectation value integral, Equation \ref{9-15}). This is a general approach and we've used it in earlier chapters. The notation \( \int d\tau \) is used to represent integration over the three-dimensional space in spherical coordinates for electrons 1 and 2.

\[ \left\langle E \right\rangle = \int \varphi^*_{1s} (r_1) \varphi^*_{1s} (r_2) \left[ H(r_1) + H(r_2) \right] \varphi_{1s} (r_1) \varphi_{1s} (r_2) d\tau \] \label{9-15}

The wavefunctions in Equation \ref{9-15}) are the hydrogen atom functions with a nuclear charge of +2e. The resulting energy for the helium ground state is

\[ E_{\text{approx}} = 2Z^2 E_H = -108 \, \text{eV} \] \label{9-16}

where \( Z = +2 \) and \( E_H \) is the binding energy of the hydrogen atom (-13.6 eV). The calculated result for the binding energy can be compared to the experimental value of -78.9 eV. The difference is due to the electron-electron interaction. The experimental and calculated binding and ionization energies are listed in Table \PageIndex{1}).
Exercise 

Start with Equation \ref{9-15} and show that \(E\) in fact equals -108 eV. Rather than evaluating integrals, derive that

\[E = 2 Z^2 E_H\]

and substitute the value for \(E_H\).

The deviation of the calculated binding energy from the experimental value can be recognized as being good or bad depending on your point of view. It is bad because a 38% error is nothing to "brag about"; on the other hand, the comparison is good because the calculated value is close to the experimental value. Both the experiment and the calculation give an answer of about -100 eV for the binding energy of helium. This comparison tells you that although the electron repulsion term is important, the idea that the electrons are independent is reasonable. An independent-electron picture is reasonable because you can completely neglect the electron-electron interaction and you get a reasonable value for the binding energy, although it is not particularly accurate.

This observation is important because we can now feel justified in using the idea of independent electrons as a starting point for improved approximate solutions to the Schrödinger equation for multi-electron atoms and molecules. To find better approximate solutions for multi-electron systems, we start with wavefunctions that depend only on the coordinates of a single electron, and then take into account the electron-electron repulsion to improve the accuracy.

Getting highly accurate energies and computed properties for many-electron systems is not an impossible task. In subsequent sections of this chapter we approximate the helium atom using several additional widely applicable approaches, perturbation theory, the variational method, self consistent field theory and the Hartree-Fock approach (SCF-HF), and configuration interaction (CI). These basic computational chemistry tools are used to treat other multi-electron systems, both atomic and molecular, for applications ranging from interpretation of spectroscopy to predictions of chemical reactivity.

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