The second element in the periodic table provides our first example of a quantum-mechanical problem which cannot be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The successive removal of the two electrons can be diagrammed as

$$\ce{He} \xrightarrow{I_1} \ce{He}^+ + e^- \xrightarrow{I_2} \ce{He}^{++} + 2e^- \label{1}$$

The first ionization energy $I_1$, the minimum energy required to remove the first electron from helium, is experimentally 24.59 eV. The second ionization energy, $I_2$, is 54.42 eV. The last result can be calculated exactly since $\ce{He}^+$ is a hydrogen-like ion. We have

$$I_2 = -E_{1s}(\ce{He}^+) = \frac{Z^2}{2n^2} = 2 \text{ hartrees} = 54.42 \text{ eV} \label{2}$$

The energy of the three separated particles on the right side of Equation $\eqref{1}$ is, by definition, zero. Therefore the ground-state energy of helium atom is given by $E_0 = -(I_1 + I_2) = -79.02 \text{ eV} = -2.90372 \text{ hartrees}$. We will attempt to reproduce this value, as close as possible, by theoretical analysis.

### Schrödinger Equation and Variational Calculations

The Schrödinger equation for He atom, again using atomic units and assuming infinite nuclear mass, can be written

$$\left\{-\frac{1}{2}\nabla^2_1 - \frac{1}{2}\nabla^2_2 - \frac{Z}{r_2} + \frac{1}{r_{12}}\right\}\psi(r_1, r_2) = E\psi(r_1, r_2) \label{3}$$

The five terms in the Hamiltonian represent, respectively, the kinetic energies of electrons 1 and 2, the nuclear attractions of electrons 1 and 2, and the repulsive interaction between the two electrons. It is this last contribution which prevents an exact solution of the Schrödinger equation and which accounts for much of the complication in the theory. In seeking an approximation to the ground state, we might first work out the solution in the absence of the $1/r_{12}$-term. In the Schrödinger equation thus simplified, we can separate the variables $r_1$ and $r_2$ to reduce the equation to two independent hydrogen-like problems. The ground state wavefunction (not normalized) for this hypothetical helium atom would be

$$\psi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2) = e^{-Z(r_1 + r_2)} \label{4}$$

and the energy would equal $(2 \times (-Z^2/2) = -4)$ hartrees, compared to the experimental value of $-2.90$ hartrees. **Neglect of electron repulsion evidently introduces a very large error.**

A significantly improved result can be obtained with the functional form (Equation $\eqref{4}$), but with $Z$ replaced by an adjustable parameter $\alpha$, thus:

$$\tilde{\psi}(r_1, r_2) = e^{-\alpha(r_1 + r_2)} \label{5}$$
Using this function in the variational principle [cf. Eq (4.53)], we have

$$\tilde{E} = \frac{\int \psi(r_1,r_2) \hat{H} \psi(r_1,r_2) d\tau_1 d\tau_2}{\int \psi(r_1,r_2) \psi(r_1,r_2) d\tau_1 d\tau_2} \tag{6}$$

where \(\hat{H}\) is the full Hamiltonian as in Equation (ref{3}), including the \(1/r_{12}\)-term. The expectation values of the five parts of the Hamiltonian work out to

$$\left\langle -\frac{1}{2} \nabla^2_1 \right\rangle = \left\langle -\frac{1}{2} \nabla^2_2 \right\rangle = \frac{\alpha^2}{2}, \left\langle -\frac{Z}{r_1} \right\rangle = \left\langle -\frac{Z}{r_2} \right\rangle = -Z\alpha, \left\langle \frac{1}{r_{12}} \right\rangle = \frac{5}{8}\alpha \tag{7}$$

The sum of the integrals in Equation (ref{7}) gives the variational energy

$$\tilde{E}(\alpha) = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha \tag{8}$$

This will be always be an upper bound for the true ground-state energy. We can optimize our result by finding the value of \(\alpha\) which minimizes the energy (Equation (ref{8})). We find

$$\frac{d\tilde{E}}{d\alpha} = 2\alpha - 2Z + \frac{5}{8} = 0 \tag{9}$$

giving the optimal value

$$\alpha = Z - \frac{5}{16} \tag{10}$$

This can be given a physical interpretation, noting that the parameter \(\alpha\) in the wavefunction (Equation (ref{5})) represents an effective nuclear charge. Each electron partially shields the other electron from the positively-charged nucleus by an amount equivalent to \(5/8\) of an electron charge. Substituting Equation (ref{10}) into Equation (ref{8}), we obtain the optimized approximation to the energy

$$\tilde{E} = -(Z - \frac{5}{16})^2 \tag{11}$$

For helium \((Z = 2)\), this gives \(-2.84765\) hartrees, an error of about \(2\%\) \((E_0 = -2.90372)\). Note that the inequality \(\tilde{E} > E_0\) applies in an algebraic sense.

In the late 1920’s, it was considered important to determine whether the helium computation could be improved, as a test of the validity of quantum mechanics for many electron systems. The table below gives the results for a selection of variational computations on helium.

<table>
<thead>
<tr>
<th>wavefunction</th>
<th>parameters</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e^{-Z(r_1+r_2)})</td>
<td>(Z=2)</td>
<td>(-2.75i)</td>
</tr>
<tr>
<td>(e^{-\alpha(r_1+r_2)})</td>
<td>(\alpha=1.6875)</td>
<td>(-2.84765)</td>
</tr>
<tr>
<td>(\psi(r_1)\psi(r_2))</td>
<td>best (\psi(r))</td>
<td>(-2.86168)</td>
</tr>
</tbody>
</table>
The third entry refers to the self-consistent field method, developed by Hartree. Even for the best possible choice of one-electron functions \(\psi(r)\), there remains a considerable error. This is due to failure to include the variable \(r_{12}\) in the wavefunction. The effect is known as electron correlation.

The fourth entry, containing a simple correction for correlation, gives a considerable improvement. Hylleraas (1929) extended this approach with a variational function of the form

\[
\psi(r_1, r_2, r_{12}) = e^{-\alpha(r_1+r_2)} \times \text{polynomial in } r_1, r_2, r_{12}
\]

and obtained the nearly exact result with 10 optimized parameters. More recently, using modern computers, results in essentially perfect agreement with experiment have been obtained.

Spinorbitals and the Exclusion Principle

The simpler wavefunctions for helium atom in Equation \(\text{(5)}\), can be interpreted as representing two electrons in hydrogen-like 1s orbitals, designated as a 1s\(^2\) configuration. According to Pauli's exclusion principle, which states that no two electrons in an atom can have the same set of four quantum numbers, the two 1s electrons must have different spins, one spin-up or \(\alpha\), the other spin-down or \(\beta\). A product of an orbital with a spin function is called a spinorbital. For example, electron 1 might occupy a spinorbital which we designate

\[
\phi(1) = \psi(1s) \alpha(1) \text{ or } \psi(1s) \beta(1)
\]

Spinorbitals can be designated by a single subscript, for example, \(\phi_a\) or \(\phi_b\), where the subscript stands for a set of four quantum numbers. In a two-electron system the occupied spinorbitals \(\phi_a\) and \(\phi_b\) must be different, meaning that at least one of their four quantum numbers must be unequal. A two-electron spinorbital function of the form

\[
\Psi(1, 2) = \frac{1}{\sqrt{2}} \left( \phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2) \right)
\]

automatically fulfills the Pauli principle since it vanishes if \(a = b\). Moreover, this function associates each electron equally with each orbital, which is consistent with the indistinguishability of identical particles in quantum mechanics. The factor \(1/\sqrt{2}\) normalizes the two-particle wavefunction, assuming that \(\phi_a\) and \(\phi_b\) are normalized and mutually orthogonal. The function (Equation \(\text{(13)}\)) is antisymmetric with respect to interchange of electron labels, meaning that

\[
\Psi(2, 1) = -\Psi(1, 2)
\]

This antisymmetry property is an elegant way of expressing the Pauli principle.
We note, for future reference, that the function in Equation \(\ref{13}\) can be expressed as a \(2 \times 2\) determinant:

\[
\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix} \tag{15}
\]

For the \(1s^2\) configuration of helium, the two orbital functions are the same and Equation \(\ref{13}\) can be written

\[
\Psi(1, 2) = \psi_{1s}(1)\psi_{1s}(2) \times \frac{1}{\sqrt{2}} \left( \alpha(1)\beta(2) - \beta(1)\alpha(2) \right) \tag{16}
\]

For two-electron systems (but not for three or more electrons), the wavefunction can be factored into an orbital function times a spin function. The two-electron spin function

\[
\sigma_{0,0}(1, 2) = \frac{1}{\sqrt{2}} \left( \alpha(1)\beta(2) - \beta(1)\alpha(2) \right) \tag{17}
\]

represents the two electron spins in opposing directions (antiparallel) with a total spin angular momentum of zero. The two subscripts are the quantum numbers \(S\) and \(M_S\) for the total electron spin. Equation \(\ref{16}\) is called the singlet spin state since there is only a single orientation for a total spin quantum number of zero. It is also possible to have both spins in the same state, provided the orbitals are different. There are three possible states for two parallel spins:

\[
\sigma_{1,1}(1, 2) = \alpha(1)\alpha(2) \\
\sigma_{1,0}(1, 2) = \frac{1}{\sqrt{2}} \left( \alpha(1)\beta(2) + \beta(2)\alpha(2) \right) \\
\sigma_{1,-1}(1, 2) = \beta(1)\beta(2) \tag{18}
\]

These make up the triplet spin states, which have the three possible orientations of a total angular momentum of 1.

**Excited States of Helium**

The lowest excited state of helium is represented by the electron configuration \(1s \ 2s\). The \(1s \ 2p\) configuration has higher energy, even though the \(2s\) and \(2p\) orbitals in hydrogen are degenerate, because the \(2s\) penetrates closer to the nucleus, where the potential energy is more negative. When electrons are in different orbitals, their spins can be either parallel or antiparallel. In order that the wavefunction satisfy the antisymmetry requirement (Equation \(\ref{14}\)), the two-electron orbital and spin functions must have opposite behavior under exchange of electron labels. There are four possible states from the \(1s \ 2s\) configuration: a singlet state

\[
\Psi^+ (1, 2) = \frac{1}{\sqrt{2}} \left( \psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2) \right) \sigma_{0, 0}(1, 2) \tag{19}
\]

and three triplet states

\[
\Psi^-(1, 2) = \frac{1}{\sqrt{2}} \left( \psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2) \right) \begin{cases} \sigma_{1,1}(1, 2) \\ \sigma_{1,0}(1, 2) \\ \sigma_{1,-1}(1, 2) \end{cases} \tag{20}
\]

Using the Hamiltonian in Equation \(\ref{3}\), we can compute the approximate energies

\[
\langle E^\pm \rangle = \iint \Psi^\pm (1, 2) \hat{H} \Psi^\pm (1, 2) d\tau_1 d\tau_2 \tag{21}
\]
After evaluating some fierce-looking integrals, this reduces to the form
\[ E^\pm = I(1s) + I(2s) + J(1s, 2s) \pm K(1s, 2s) \]

in terms of the one electron integrals
\[ I(a) = \int \psi_a(\mathbf{r}) \left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} \right\} \psi_a(\mathbf{r}) d\tau \]

the Coulomb integrals
\[ J(a, b) = \iint \psi_a(\mathbf{r}_1)^2 \frac{1}{r_{12}} \psi_b(\mathbf{r}_2)^2 d\tau_1 d\tau_2 \]

and the exchange integrals
\[ K(a, b) = \iint \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_1) \frac{1}{r_{12}} \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_2) d\tau_1 d\tau_2 \]

The Coulomb integral represents the repulsive potential energy for two interacting charge distributions \( \psi_a(\mathbf{r}_1)^2 \) and \( \psi_b(\mathbf{r}_2)^2 \). The exchange integral, which has no classical analog, arises because of the exchange symmetry (or antisymmetry) requirement of the wavefunction. Both \( J \) and \( K \) can be shown to be positive quantities. Therefore the lower sign in (22) represents the state of lower energy, making the triplet state of the configuration 1s 2s lower in energy than the singlet state. This is an almost universal generalization and contributes to Hund's rule, to be discussed in the next Chapter.

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