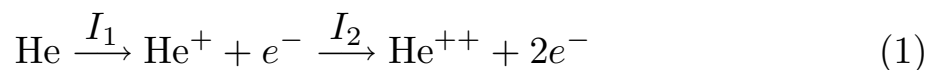


CHAPTER 8

THE HELIUM ATOM

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



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 He^+ is a hydrogenlike ion. We have

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

The energy of the three separated particles on the right side of Eq (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

$$\left\{ -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right\} \psi(\mathbf{r}_1, \mathbf{r}_2) = E \psi(\mathbf{r}_1, \mathbf{r}_2) \quad (3)$$

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 \mathbf{r}_1 and \mathbf{r}_2 to reduce the equation to two independent hydrogenlike problems. The ground state wavefunction (not normalized) for this hypothetical helium atom would be

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(r_1)\psi_{1s}(r_2) = e^{-Z(r_1+r_2)} \quad (4)$$

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 (4), but with Z replaced by a adjustable parameter α , thus:

$$\tilde{\psi}(r_1, r_2) = e^{-\alpha(r_1+r_2)} \quad (5)$$

Using this function in the variational principle [cf. Eq (4.53)], we have

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

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

$$\begin{aligned} \left\langle -\frac{1}{2}\nabla_1^2 \right\rangle &= \left\langle -\frac{1}{2}\nabla_2^2 \right\rangle = \frac{\alpha^2}{2} \\ \left\langle -\frac{Z}{r_1} \right\rangle &= \left\langle -\frac{Z}{r_2} \right\rangle = -Z\alpha, \quad \left\langle \frac{1}{r_{12}} \right\rangle = \frac{5}{8}\alpha \end{aligned} \quad (7)$$

The sum of the integrals in (7) gives the variational energy

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

This will be always be an upper bound for the true ground-state energy. We can optimize our result by finding the value of α which *minimizes* the energy (8). We find

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

giving the optimal value

$$\alpha = Z - \frac{5}{16} \quad (10)$$

This can be given a physical interpretation, noting that the parameter α in the wavefunction (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 (10) into (8), we obtain the optimized approximation to the energy

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

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.

wavefunction	parameters	energy
$e^{-Z(r_1+r_2)}$	$Z = 2$	-2.75
$e^{-\alpha(r_1+r_2)}$	$\alpha = 1.6875$	-2.84765
$\psi(r_1)\psi(r_2)$	best $\psi(r)$	-2.86168
$e^{-\alpha(r_1+r_2)}(1 + cr_{12})$	best α, c	-2.89112
Hylleraas (1929)	10 parameters	-2.90363
Pekeris (1959)	1078 parameters	-2.90372

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, for example (5), can be interpreted as representing two electrons in hydrogenlike $1s$ 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 α , the other spin-down or β . A product of an orbital with a spin function is called a *spinorbital*. For example, electron 1 might occupy a spinorbital which we designate

$$\phi(1) = \psi_{1s}(1)\alpha(1) \quad \text{or} \quad \psi_{1s}(1)\beta(1) \quad (12)$$

Spinorbitals can be designated by a single subscript, for example, ϕ_a or ϕ_b , where the subscript stands for a *set* of four quantum numbers. In a two electron system the occupied spinorbitals ϕ_a and ϕ_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

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \left(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2) \right) \quad (13)$$

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 ϕ_a and ϕ_b are normalized and mutually orthogonal. The function (13) is *antisymmetric* with respect to interchange of electron labels, meaning that

$$\Psi(2, 1) = -\Psi(1, 2) \quad (14)$$

This antisymmetry property is an elegant way of expressing the Pauli principle.

We note, for future reference, that the function (13) can be expressed as a 2×2 determinant:

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix} \quad (15)$$

For the $1s^2$ configuration of helium, the two orbital functions are the same and Eq (13) can be written

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

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

$$\sigma_{0,0}(1, 2) = \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) - \beta(1)\alpha(2) \right) \quad (17)$$

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. Eq (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:

$$\begin{aligned} \sigma_{1,1}(1, 2) &= \alpha(1)\alpha(2) \\ \sigma_{1,0}(1, 2) &= \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) + \beta(1)\alpha(2) \right) \\ \sigma_{1,-1}(1, 2) &= \beta(1)\beta(2) \end{aligned} \quad (18)$$

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 $1s2s$. The $1s2p$ 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 (14), the two-electron orbital and spin functions must have *opposite* behavior under exchange of electron labels. There are four possible states from the $1s2s$ configuration: a singlet state

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

and three triplet states

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

Using the Hamiltonian in Eq(3), we can compute the approximate energies

$$E^\pm = \int \int \Psi^\pm(1, 2) \hat{H} \Psi^\pm(1, 2) d\tau_1 d\tau_2 \quad (21)$$

After evaluating some fierce-looking integrals, this reduces to the form

$$E^\pm = I(1s) + I(2s) + J(1s, 2s) \pm K(1s, 2s) \quad (22)$$

in terms of the one electron integrals

$$I(a) = \int \psi_a(\mathbf{r}) \left\{ -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right\} \psi_a(\mathbf{r}) d\tau \quad (23)$$

the Coulomb integrals

$$J(a, b) = \int \int \psi_a(\mathbf{r}_1)^2 \frac{1}{r_{12}} \psi_b(\mathbf{r}_2)^2 d\tau_1 d\tau_2 \quad (24)$$

and the exchange integrals

$$K(a, b) = \int \int \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_1) \frac{1}{r_{12}} \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_2) d\tau_1 d\tau_2 \quad (25)$$

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 $1s2s$ 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.

The Variational Principle

Except for a small number of intensively-studied examples, the Schrödinger equation for most problems of chemical interest *cannot* be solved exactly. The variational principle provides a guide for constructing the best possible approximate solutions of a specified functional form. Suppose that we seek an approximate solution for the ground state of a quantum system described by a Hamiltonian \hat{H} . We presume that the Schrödinger equation

$$\hat{H} \psi_0 = E_0 \psi_0 \quad (52)$$

is too difficult to solve exactly. Suppose, however, that we have a function $\tilde{\psi}$ which we think is an approximation to the true ground-state wavefunction. According to the variational principle (or variational theorem), the following formula provides an *upper bound* to the exact ground-state energy E_0 :

$$\tilde{E} \equiv \frac{\int \tilde{\psi}^* \hat{H} \tilde{\psi} d\tau}{\int \tilde{\psi}^* \tilde{\psi} d\tau} \geq E_0 \quad (53)$$

Note that this ratio of integrals has the same form as the expectation value $\langle H \rangle$ defined by (29). The better the approximation $\tilde{\psi}$, the lower will be the computed energy \tilde{E} , though it will still be greater than the exact value. To prove Eq (53), we suppose that the approximate function can, in concept, be represented as a superposition of the actual eigenstates of the Hamiltonian, analogous to (24),

$$\tilde{\psi} = c_0 \psi_0 + c_1 \psi_1 + \dots \quad (54)$$

This means that $\tilde{\psi}$, the approximate ground state, might be close to the actual ground state ψ_0 but is “contaminated” by contributions from excited states ψ_1, \dots . Of course, none of the states or coefficients on the right-hand side is actually known, otherwise there would no need to worry about approximate computations. By Eq (25), the expectation value of the Hamiltonian in the state (54) is given by

$$\tilde{E} = |c_0|^2 E_0 + |c_1|^2 E_1 + \dots \quad (55)$$

Since all the excited states have *higher* energy than the ground state, $E_1, E_2 \dots \geq E_0$, we find

$$\tilde{E} \geq (|c_0|^2 + |c_1|^2 + \dots) E_0 = E_0 \quad (56)$$

assuming $\tilde{\psi}$ has been normalized. Thus \tilde{E} must be greater than the true ground-state energy E_0 , as implied by (53)

As a very simple, although artificial, illustration of the variational principle, consider the ground state of the particle in a box. Suppose we had never studied trigonometry and knew nothing about sines or cosines. Then a reasonable approximation to the ground state might be an inverted parabola such as the normalized function

$$\tilde{\psi}(x) = \left(\frac{30}{a^5}\right)^{1/2} x(a-x) \quad (57)$$

Fig. 1 shows this function along with the exact ground-state eigenfunction

$$\psi_1(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{\pi x}{a} \quad (58)$$

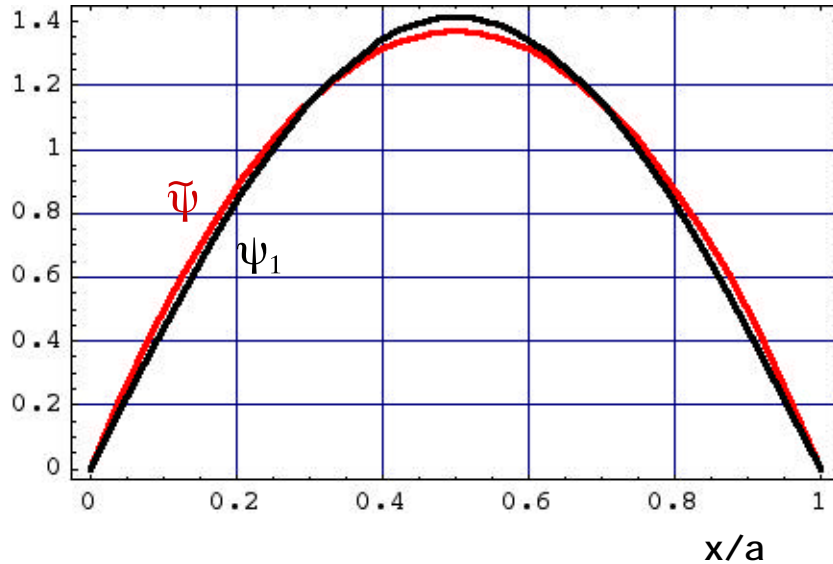


Figure 1. Variational approximation for particle in a box.

A variational calculation gives

$$\begin{aligned} \tilde{E} &= \int_0^a \tilde{\psi}(x) \left(-\frac{\hbar^2}{2m}\right) \tilde{\psi}''(x) dx = \\ &= \frac{5}{4\pi^2} \frac{\hbar^2}{ma^2} = \frac{10}{\pi^2} E_1 = 1.01321 E_1 \quad (59) \end{aligned}$$

in terms of the exact ground state energy $E_1 = \hbar^2/8ma^2$. In accord with the variational theorem, $\tilde{E} > E_1$. The computation is in error by about 1%.