PHYSNET

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THE HELIUM ATOM:
AN INTUITIVE APPROACH

Project PHYSNET Physics Bldg. Michigan State University East Lansing, MI

THE HELIUM ATOM: AN INTUITIVE APPROACH
by
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Title: **The Helium Atom: An Intuitive Approach**

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Input Skills:

1. Skills from "The Uncertainty Relations" (MISN-0-241).
2. Skills from "The Schroedinger Equation in One Dimension: Quantization of Energy" (MISN-0-242).

Output Skills (Knowledge):

K1. Write the classical expression for the energy of an n-electron atom and write the corresponding Schrödinger Equation.

K2. Explain how the average coulomb and kinetic energies of an arbitrary Hydrogen wave function depend on the diameter of the region containing the wave function and explain hot this determines the size of the region containing the ground state wave function.

K3. Explain why the wave functions of Helium should be symmetric upon interchange of the coordinates of electron 1 and electron 2.

K4. Explain the meaning, in terms of probability, of the expression $|\psi|^2\,dV_1\,dV_2$.

K5. Describe the simplification in the Schroedinger equation that results from setting $V_{12} = 0$. Show that the Schrödinger equation reduces to two separate hydrogen-like equations whose solutions can be combined to give an approximate solution to for Helium.

K6. Describe the "full shielding" approximation and show results for the case $V_{12} = k_e e^2/r_1$ for the electron 1 and $V_{12} = k_e e^2/r_2$ for the electron 2, similar to (8) above.

K7. Describe why the "best shielding" approximation is better than those of K8 and K9 above.

External Resources (Optional):

1. Readings in K. Ford, *Classical and Modern Physics*, Vol. 3. For access see the "Readings" section of this module's *Local Guide*.
2. Readings in *Introduction to Quantum Mechanics*, L. Pauling and E. Bright Wilson, Mc-Graw Hill, 1935. For access, see the "Book" section of this module's *Local Guide*.

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1. Introduction

We will examine the ground state of the helium atom, the simplest atom beyond hydrogen. At little cost in effort and considerable gain in generality, we will formulate the problem for any 2-electron atom or ion by allowing the number, Z, of protons to differ from 2. So by the word "atom" we may also mean "ion."

To good approximation, each of the 2 electrons moves independently of the other, and they occupy individual wave functions of the same shape, that is, a nodeless wave function of spherical symmetry. We will obtain a succession of better approximations to the exact wave function. The methods developed here can also be used for excited states, by introducing a few additional concepts.

2. The Size of the Atom

[Note: A different presentation of the material in this section is given in Section 23.12 of Ford.[1]]

We want to illustrate the trade-off between kinetic energy and potential energy in an atom which leads to a minimum energy (bound) state for the atom. For hydrogen-like atoms the classical energy is:

$$E = E_k + E_p \,,$$

where E_k is the kinetic energy,

$$E_k = p^2/(2m) \,, \tag{1}$$

and E_p is the potential energy

$$E_p = -k_e e^2 Z/r \,.$$

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[1] K. Ford, *Classical and Modern Physics*, Vol. 3. For access see the "Readings" section of this module's *Local Guide*.

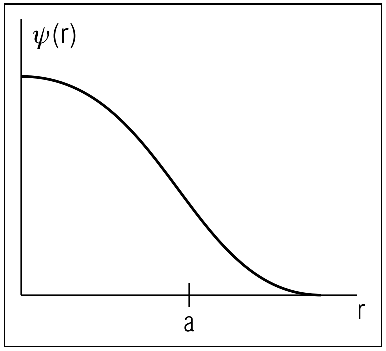

Figure 1. .

In the above equations, p, m, e are the momentum, mass and charge of the electron and Z is the number of protons in the nucleus.

We obtain the Schrödinger equation from that energy by making this substitution for $p^2 = p_x^2 + p_y^2 + p_z^2$:

$$p_x \Rightarrow -i\hbar \frac{\partial}{\partial x} \,, \tag{2}$$

and similarly for the other two components.

To understand the trade-off between the mean kinetic energy $\overline{E_k}$ (always positive) and the mean potential energy $\overline{E_p}$ (always negative) let us assume a spherically symmetric wave function $\psi(r)$ exists of approximate radius a (see Fig. 1), where we need not know much about its exact shape, and make crude estimates of how $\overline{E_k}$ and $\overline{E_p}$ will vary as a varies. The mean kinetic energy is $\overline{E_k} = \overline{p^2}/2m$ and since $\overline{p} = 0$, (the wave function is centered at the nucleus), $(\Delta p)^2 = \overline{p^2}$. But the uncertainty relation gives for this wave function the approximate result:

$$\Delta p_x =\geq \hbar/2a \,, \tag{3}$$

because $\Delta x \approx a$.

Then $\overline{p^2} = 3\hbar^2/4a^2$.

▷ Where does the "3" come from? Why is there "≈" instead of "≥"?

Let us replace the above expression with:

$$\overline{p^2} = t3\hbar^2/4a^2 \,, \tag{4}$$

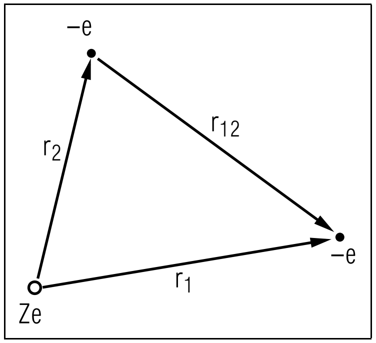

Figure 2. .

where t is a positive number near unity which allows for the sloppy reasoning in the above arguments. Similarly, we write:

$$E_p = v k_e e^2 Z/a\,, \tag{5}$$

where v is a positive number near unity.

Then,

$$\overline{E} = t3\hbar^2/8ma^2 - v k_e e^2 Z/a\,. \tag{6}$$

Exercise: Draw $\overline{E_k}$, $\overline{E_p}$, $\overline{E}$ vs. a and show there must be a minimum value of $\overline{E}$ at some value of $a \neq 0, \infty$.

To find the size, a, of the atom which gives a minimum in $\overline{E}$, set $\partial\overline{E}/\partial a = 0$, and find that the value of a is:

$$a = \frac{4v^2}{3t}\, a_0\,, \tag{7}$$

where $a_0 = \hbar^2/(m k_e e^2 Z)$, the Bohr value for the ground state energy of the hydrogen atom. The quantity $4v^2/3t$ is near unity, and so the size of the hydrogen atom is determined largely by a compromise; low potential energy would result from the electron being near the nucleus, but this would require large kinetic energy.

3. The Schrödinger Equation

We draw a diagram of the the He atom. The classical expression for the energy of this three point-charge system is:

$$E = E_{k,1} + E_{k,2} + E_{p,1} + E_{p,2} + E_{p,12}\,. \tag{8}$$

We assume the (massive) nucleus is fixed at the center of mass. The subscripts 1 and 2 refer to the 2 electrons "by name," and the electron-electron repulsive coulomb energy, is:

$$E_{p,12} = k_e e^2/r_{12}\,. \tag{9}$$

Magnetic energies should also be included because we have moving charges, but the magnetic energies are very small (on the order of v^2/c^2 as large as the coulomb energies) so they are neglected.

We imagine the electrons are point objects with instantaneous positions and velocities, but these must remain unknown to us and we can only find the wave function of the system, $\psi(r_1, r_2)$ such that $|\psi|^2 dV_1\, dV_2$ gives the probability that electron 1 is in an element of volume dV_1 at r_1 and electron 2 is in dV_2 at r_2. Actually, we must not suppose that we can identify which electron is "1" and which is "2" so $|\psi|^2$ must remain unchanged upon interchanging coordinates r_1 and r_2. This choice of wave function implies that the two electrons have their spins anti-parallel. We obtain the Schrödinger equation from Eq. (9) by the replacements $p_{x1} = -i\hbar\partial/\partial x_1$, etc. for y_1 and z_1 of electron 1 and similarly for electron 2. The resulting Schrödinger equation looks deceptively simple. The term $E_{p,12}$, containing $1/r_{12}$, however, is awkward to express in terms of r_1 and r_2 and obtaining the exact solution of this Schrödinger equation is far from trivial.

Now $\psi(\vec{r_1}, \vec{r_2})$ is a function of six coordinates (x_1, y_1, z_1, x_2, y_2, z_2) and could be "drawn" in 7-dimensional space. Elsewhere it is shown[2] that the one-electron approximation is good and write $\psi(\vec{r_1}, \vec{r_2}) = \psi(\vec{r_1})\,\psi(\vec{r_2})$. That is, each electron has its own wave function independent of the other's, and the wave function of the system is the product of these individual wave functions.

Let us start to find the ψ's by ignoring the pesky term, by setting $E_{p,12} = 0$, thereby reducing the problem to a trivial form:

$$E = E_1^{(0)} + E_2^{(0)} = (E_{k,1} + E_{p,1}) + (E_{k,2} + E_{p,2})\,. \tag{10}$$

That is, there are two non-interacting atoms superposed at the same point in space. The solutions are then those of hydrogen-like atoms, with energies $E_n = -RZ^2/n^2$. The ground state is:

$$\psi_0(r_1, r_2) = \psi_0(r_1)\,\psi_0(r_2)\,, \tag{11}$$

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[2] See *Introduction to Quantum Mechanics*, L. Pauling and E. Bright Wilson, McGraw Hill, 1935. For access, see the "Book" section of this module's *Local Guide*.

where

$$\psi_0(r) = N\,e^{-\alpha r}, \qquad E = -\frac{\alpha^2}{2}\,.$$

We will call this the "zero-th approximation."

Exercise: Suppose there are two electrons confined to a one-dimensional box of length a. Make a perspective drawing of $\psi(x_1, x_2) = \psi(x_1)\,\psi(x_2)$ against orthogonal axes x_1 and x_2 under each of the following cases:

1. Both electrons are in the ground state.
2. Both electrons are in the first excited state.

4. Approximate Wave Functions

Let us improve on the wave functions $\psi_0 = N\,e^{-\alpha r}$. We expect that they are too compact, because setting $E_{p,12} = 0$ turned off a coulomb repulsion that would have pushed each electron away from the other, and thus away from the nucleus. We can attempt to account for this repulsion by assuming that electron 1 moves as if electron 2 is permanently located on the nucleus, so the net nuclear charge is $Z = 1$, not 2. That is, electron 2 shields electron 1 from the full coulomb effect of the nuclear charge. (In what follows, we will be trying to get a good wave function for electron 1 by making crude assumptions about the average value of the interaction potential, $\overline{(E_{p,12})}$, set up by the charge distribution $-e|\psi(r_2)|^2$ of electron 2. However, all arguments must be symmetrical when the names "1" and "2" are interchanged. After getting a wave function for electron 1, electron 2 is assumed to have an identical wave function, except with opposite spin.

Again, the solution is trivial, of the form in Eq. (11) but with a new value for a. We will call this the "full shielding" approximation.

Exercise: Compare the ionization energies (i.e. the energy required to remove one more electron from the ion, as predicted by the above approximation) for the cases $Z = 1$, 2 and 92.

It is easy to see that the "full shielding" approximation has overemphasized the shielding. The potential energy $\overline{(E_{p,12})}$ can be approximated as:

$$\overline{(E_{p,12})} = \frac{k_e e^2 \sigma}{r_1}\,, \tag{12}$$

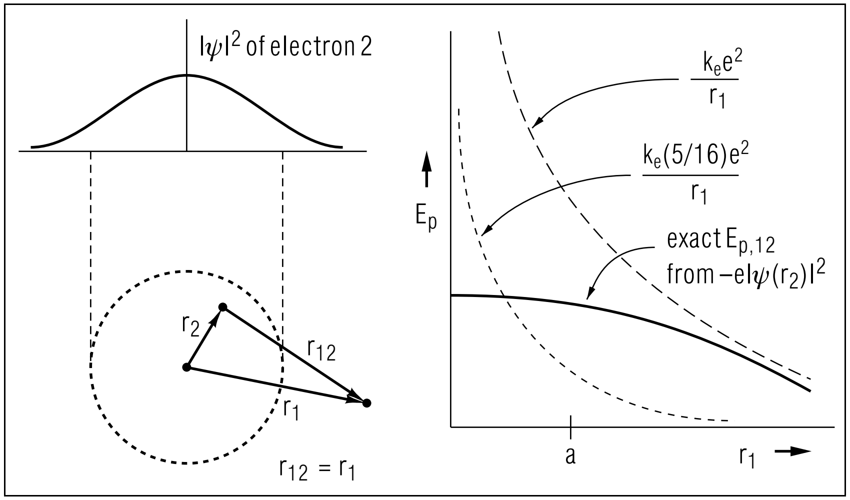

Figure 3. .

where σ is the "shielding parameter" and for "full shielding" we chose $\sigma = 1$. This is actually a good approximation to the exact $E_{p,12} = k_e e^2/r_{12}$ when $r_1 \gg r_2$.

Elsewhere it is shown[3] that the best value of σ is 5/16, by calculations that include exact evaluations of the mean potential energy, $\overline{(E_{p,12})}$. The curve implied by Eq. (12), with = 5/16, has a widely different shape than the curve it is supposed to be approximating, $\overline{(E_{p,12})}$. However, deviations for distances $r_1 \gg a$ don't matter much since electron 1 is rarely out there. Deviations for $r_1 \leq a$ look at first glance to be serious, but they are not.

Exercise: Compare the ground state wave functions, ψ, for the particle in a box, the hydrogen atom, and the cut-off harmonic oscillator. Locate "funny points" in E_p (infinities, discontinuities in E_p and its derivatives) and note the effect these have on ψ.

From the exercise, we see that wave functions, especially ground state ones, react chiefly to the average shape and size of the potential, not to its details. This is a general result for wave properties and can be seen as another manifestation of the trade-off between minimizing the (positive) kinetic energy and maximizing the (negative) potential energy.

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[3] See *Introduction to Quantum Mechanics*, L. Pauling and E. Bright Wilson, McGraw Hill, 1935. For access, see the "Book" section of this module's *Local Guide*.

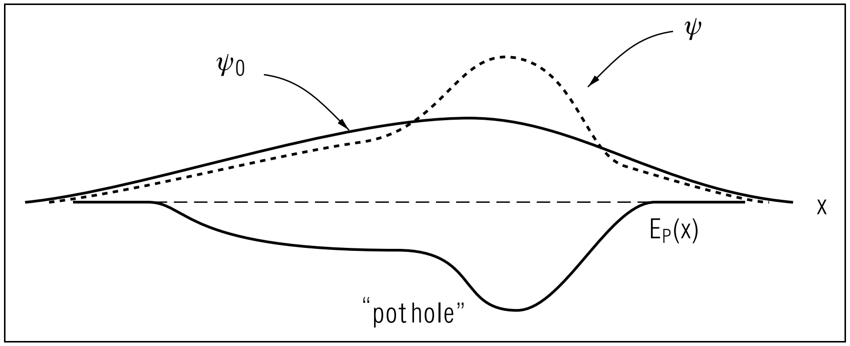

Figure 4. .

Suppose the potential has a deep "pot hole." We have drawn a "correct" ψ_0 for a particle trapped in the potential well. Why can't ψ be the correct one, where ψ has "humped up" in the region of the pot hole and thus lessened its average potential? In order to do so, it must curve sharply in the region, and thus develop a large $d^2\psi/dx^2$ or kinetic energy. The price is too high to pay. Returning to the approximation of Eq. (12) for $\overline{(E_{p,12})}$, we see the shape from Eq. (12) is not very important, but that its average value should equal that of $\overline{(E_{p,12})}$ in the region $r_1 \leq a$, which occurs for $\sigma = 5/16$.

Exercise: Complete the analysis of ionization energies you started by adding the case $\sigma = 5/16$ to those of $\sigma = 0$ and $\sigma = 1$.

Acknowledgments

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LOCAL GUIDE

The readings for this unit are on reserve for you in the Physics-Astronomy Library, Room 230 in the Physics-Astronomy Building. Ask for them as "The readings for CBI Unit 247." Do **not** ask for them by book title.

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