

# THE HELIUM ATOM

Now we have 3 particles: the nucleus and 2 electrons.

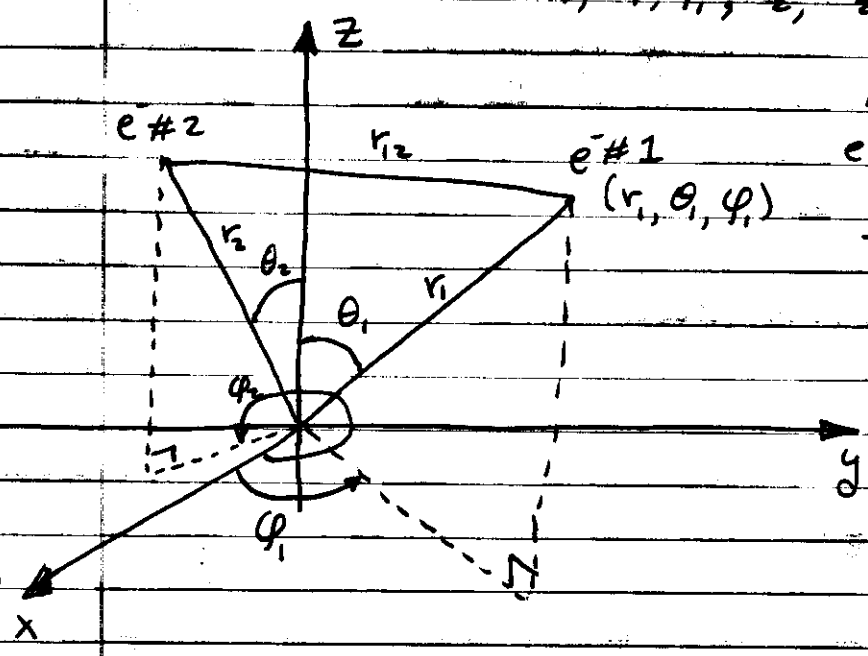
We begin by making a minor approximation (for which corrections may be made later on): we treat the nucleus as being infinitely massive, and locate it at the center of the coordinate system. Then, as the electrons orbit the nucleus it remains fixed in space. Because  $m_N \gg m_e$ , this is not severe.

We now need to obtain the wavefunction for the two electrons. In principle, this will be a function of six variables, which are needed to describe the locations of the two electrons (relative to the nucleus, which lies at the origin). We could write:

$$\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$$

Given the symmetry of the system, however, it makes more sense to use polar coordinates:

$$\Psi = \Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$



Now, the kinetic energy is easily written as

$$\begin{aligned} \hat{T} &= \frac{1}{2m_e} (\hat{p}_1^2 + \hat{p}_2^2) \\ &= \frac{-\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right. \\ &\quad \left. + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right) \end{aligned}$$

And this may be written conveniently in spherical polar coordinates as well.

The problem lies in the potential energy, which now has 3 terms:

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Attraction of electron 1 to the nucleus

Attraction of electron 2 to the nucleus

Repulsion between electrons 1 and 2.

We can abbreviate  $\frac{d^2}{dx_1^2} + \frac{d^2}{dy_1^2} + \frac{d^2}{dz_1^2}$  as  $\nabla_1^2$

and similarly abbreviate  $\frac{d^2}{dx_2^2} + \frac{d^2}{dy_2^2} + \frac{d^2}{dz_2^2}$  as  $\nabla_2^2$

so we may write the Schrödinger equation as:

$$\left[ -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \psi = E\psi$$

The big problem is the e<sup>-</sup>-e<sup>-</sup> repulsion. If this term were absent, then  $\hat{H}$  would break into a sum of pieces involving electron 1  $(-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1})$  and a sum of pieces involving electron 2  $(-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2})$ . Then, we could use the separation of variables method to write  $\psi$  as a product of a wavefunction for electron 1 and a wavefunction for electron 2. Let's just try ignoring this  $\frac{e^2}{4\pi\epsilon_0 r_{12}}$  term to see how this would work.

$$\left[ \left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right) + \left( -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right) \right] \psi(1,2) = E\psi(1,2)$$

Now, let  $\psi(1,2) = \psi_1(1) \psi_2(2)$  and substitute this into the differential equation:

$$\left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right) \psi_1(1) \psi_2(2) + \left( -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right) \psi_1(1) \psi_2(2) = E \psi_1(1) \psi_2(2)$$

Acts only on electron 1

Acts only on electron 2

$$\psi_2(2) \left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right) \psi_1(1) + \psi_1(1) \left( -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right) \psi_2(2) = E \psi_1(1) \psi_2(2)$$

Dividing by  $\psi_1(1) \psi_2(2)$ :

$$\frac{1}{\psi_1(1)} \left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right) \psi_1(1) + \frac{1}{\psi_2(2)} \left( -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right) \psi_2(2) = E$$

A function of the coordinates of electron 1 only, this has no dependence on the coordinates of electron 2

A function of the coordinates of electron 2 only, this has no dependence on the coordinates of electron 1

A constant, independent of the coordinates of both electrons.

How can a function of  $x_1, y_1, z_1$  be added to a function of  $x_2, y_2, z_2$  and get a constant? These coordinates are independent variables! A function of  $x_1, y_1, z_1$  cannot have its dependence on these variables cancelled out by a function which doesn't depend on them! The only way these two things can add up to give a constant is if they are each equal to a constant themselves. Let's call the constants  $E_1$  and  $E_2$ , which must add to give  $E$ :

$$\frac{1}{\psi_1(1)} \left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right) \psi_1(1) = E_1 \quad \frac{1}{\psi_2(2)} \left( -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right) \psi_2(2) = E_2$$

$$\left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right) \psi_1(1) = E_1 \psi_1(1) \quad \left( -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right) \psi_2(2) = E_2 \psi_2(2)$$

Each of these is the Schrödinger equation for an H-atom, for which we know the solution!

Ignoring the  $e^-e^-$  repulsion this gives

$$\Psi(1,2) = \Psi_1(1) \Psi_2(2)$$

$$= \Psi_{n_1, l_1, m_1}(r_1, \theta_1, \phi_1) \Psi_{n_2, l_2, m_2}(r_2, \theta_2, \phi_2)$$

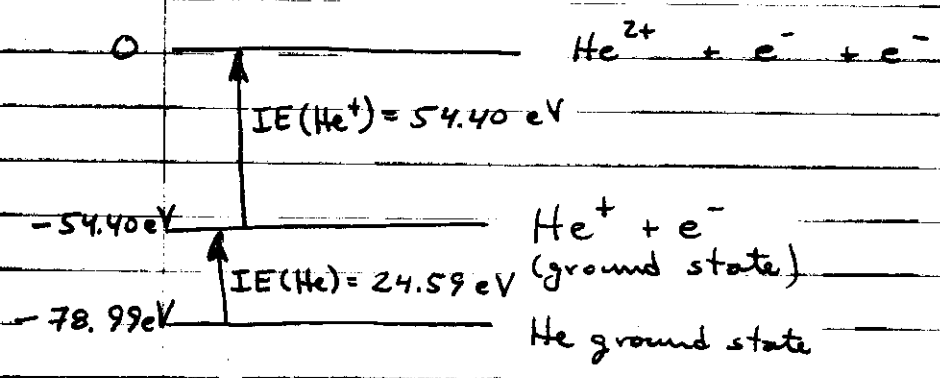
and of course  $E = E_1 + E_2$

$$= -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

Ground state has both  $e^-$  in 1s orbital, so  $n_1 = n_2 = 1$ , giving

$$E = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0} (2) = -108.8 \text{ eV.}$$

This is the energy calculated for the ground state of He, relative to the zero of energy. Examining the potential energy, we find  $V=0$  only when all three particles are separated out at infinity. Thus, our energy scale is:



Experimentally, the energy of the He ground state may be measured as the negative of the sum of the two ionization energies, listed on the arrows. This gives the energy of ground state He as  $-78.99 \text{ eV}$ .

Why is our He ground state energy lower than this (we get  $-108.8 \text{ eV}$ )? Doesn't the variational theorem guarantee that our calculated energy lies above the true energy?

THE REASON FOR THIS FAILURE IS THAT WE DIDN'T PROPERLY USE THE VARIATIONAL THEOREM!

Our value,  $E = -108.8 \text{ eV}$ , results when a trial wavefunction  $\Phi(1,2) = 1s(1)1s(2)$  is used to calculate the variational integral

$$W = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}$$

using the incomplete Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

when the correct Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$

is properly used, then an estimated energy of

$$W = -74.80 \text{ eV} \text{ is obtained.}$$

This does satisfy the requirement  $W \geq E_0$  because

$$-74.80 \text{ eV} \text{ is greater than } -78.99 \text{ eV.}$$

The error in this calculation is  $4.19 \text{ eV}$ , or  $5.3\%$ , which is not too bad. However in absolute terms it is horrendous!  $4.19 \text{ eV}$  is equal to  $96.6 \text{ kcal/mole}$ , or  $404.29 \text{ kJ/mol}$ . To put this in perspective the bond energy of  $\text{H}_2$  is  $4.48 \text{ eV}$ . Errors of this magnitude are absolutely intolerable if we are to obtain chemically useful information from a calculation.

How can we improve our trial wavefunction  $\Phi$ ?

The trial wavefunction we have used is

$$\phi = \psi(1)\psi(2) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_1/a_0} \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_2/a_0}$$

where we have used  $Z=2$ , since this is the charge of the He nucleus.

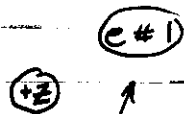
Let's try the same functional form, but let  $Z$  be a parameter, which we may call  $Z_{eff}$ :

$$\phi = \left(\frac{Z_{eff}^3}{\pi a_0^3}\right)^{1/2} e^{-Z_{eff} r_1/a_0} \left(\frac{Z_{eff}^3}{\pi a_0^3}\right)^{1/2} e^{-Z_{eff} r_2/a_0}$$

$$\phi = \left(\frac{Z_{eff}^3}{\pi a_0^3}\right) \exp\left[-\frac{Z_{eff}}{a_0}(r_1 + r_2)\right]$$

Now our <sup>trial</sup> wavefunction has a parameter that we may vary to optimize the resulting value of  $W$ . In fact, there is a simple physical rationale for letting  $Z$  vary in our trial wavefunction.

The electron feels the full nuclear charge when it is close to the nucleus and the other electron is far away:



This electron feels the full  $+Z$  charge of the nucleus



But this electron feels an attraction to the nucleus which is much weaker because it's attraction is shielded by the presence of another electron

Based on this idea, we expect an optimal value of  $Z_{eff}$  to lie in the range between  $Z$  (the full nuclear charge) and  $Z-1$  (the nuclear charge shielded by one electron).

Using the trial wavefunction (which has the parameter  $Z_{eff}$ ), but using the true Hamiltonian (which has the attraction to a nucleus of charge  $Z$ , as well as the  $\frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$  electron-electron repulsion),

the variational integral may be evaluated to give:

$$W(Z_{eff}) = \left[ (Z_{eff})^2 - 2Z(Z_{eff}) + \frac{5}{8} Z_{eff} \right] \frac{e^2}{8\pi\epsilon_0 a_0}$$

Note: Often,  $Z_{eff}$  is given the symbol  $\zeta$ .

Minimizing  $W(Z_{eff})$ , we set  $\frac{\partial W}{\partial Z_{eff}} = 0$ , giving

$$2 Z_{eff} - 2Z + \frac{5}{8} = 0$$

$$Z_{eff} = Z - \frac{5}{16}, \text{ which lies between } Z \text{ and } Z-1, \text{ as expected.}$$

Inserting this back into  $W(Z_{eff})$ , we get

$$W = -77.48 \text{ eV} \quad \Rightarrow \text{ compared to } -78.99 \text{ eV (expt.)}$$

This is a major improvement, as the error is now only  $1.51 \text{ eV} = 34.8 \text{ kcal/mole} = 145 \text{ kJ/mole}$ .

We may add additional degrees of flexibility to our  $1s$  function for helium, still taking our trial wavefunction to be of the form

$$\psi(1,2) = 1s(1) 1s(2)$$

No matter how much adjustability we build into our trial function, however, the best we can do

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with a trial wavefunction of this form is

$$W = -77.86 \text{ eV} \quad \text{vs} \quad E = -78.99 \text{ (expt.)}$$

What is wrong? we've used what amounts to a complete set in describing the 1s function, and have taken

$$1s(r) = (c_0 + c_1 r + c_2 r^2 + c_3 r^3 + \dots) e^{-Z_{\text{eff}} r}$$

The problem is that we have assumed our wavefunction factors into a product

$$\Phi = 1s(1) 1s(2)$$

and this is not the most general form of a wavefunction for two particles. Even worse, it assumes that the motion of the particles is uncorrelated. This may be illustrated by constructing the probability density:

$$P(1,2) = |\Phi|^2 = |1s(1)|^2 |1s(2)|^2$$

When a probability of two events factors into the probability of one event times the probability of the second event, the two events are uncorrelated. A good example is the probability of tossing a coin and getting HH. If the probability of getting H on each toss is 0.5 and the events are uncorrelated, then the probability of getting HH is the product of the probabilities for each event, or  $(0.5)(0.5) = 0.25$ .

Here, by writing the wavefunction as a product  $\Phi = 1s(1) 1s(2)$  we are saying that the probability of finding electron 1 at a certain position is

Variation of the trial wavefunction, taken as the product

$$\Psi(1,2) = 1s(1)1s(2),$$

where the 1s function is a function of r only, over all possible radial functions still does not give the experimental energy. This generalized trial wavefunction could be written out as

$$\Psi(1,2) = \left\{ [c_0 + c_1 r_1 + c_2 r_1^2 + c_3 r_1^3 + \dots] e^{-Z_{eff} r_1/a} \right\} \times \left\{ [c_0 + c_1 r_2 + c_2 r_2^2 + c_3 r_2^3 + \dots] e^{-Z_{eff} r_2/a} \right\}$$

Including many terms in the sum, and varying the coefficients  $c_0, c_1, c_2, \dots$  and  $Z_{eff}$  leads to what is effectively a search over all possible trial wavefunctions of the form  $\Psi(1,2) = 1s(1)1s(2)$ .

This procedure was followed in the early 1930's and the best product function was investigated by Douglas R. Hartree, with the assistance of his father, W. Hartree, who enjoyed numerical computation as a hobby!

By varying  $\Psi(1,2) = 1s(1)1s(2)$  over all possible spherically symmetric 1s functions, Hartree and his father discovered that a minimum value of W could be obtained, but that this still was above the true ground state energy. This limit is called the Hartree limit, and the difference between this limit and the true energy is defined as the correlation energy, since it can only be obtained by having the motions of the electrons correlated in some way.

Here is a summary of our calculated results so far:

-74.80 eV using  $\varphi(1,2) = \left(\frac{Z^3}{\pi a_0^3}\right) \exp\left[-\frac{Z}{a_0}(r_1+r_2)\right]$   
 with  $Z=2$

HARTREE  
LIMIT →

-77.5 eV using  $\varphi(1,2) = \left(\frac{Z_{eff}^3}{\pi a_0^3}\right) \exp\left[-\frac{Z_{eff}}{a_0}(r_1+r_2)\right]$   
 -77.9 eV  
 -78.99 eV [Experiment]

and optimizing  $Z_{eff}$  to give  $Z_{eff} = 1\frac{11}{16} = 1.6875$

using best product function  $\varphi(1,2) = 1s(1)1s(2)$

The problem is that even the very best product function [ $\varphi(1,2) = 1s(1)1s(2)$ ] still does not allow the wavefunction to vary in all possible ways. As described above, it corresponds to a situation in which the probability distribution for finding electrons 1 and 2 simultaneously at some given locations is simply the product of the two probabilities. This means that the motions of the electrons are uncorrelated, which goes against common sense.

How can we correlate the motions of the electrons?  
 One method is to introduce an extra factor into our wavefunction which explicitly reduces the probability that the two electrons will be found near one another. Thus, we might take

**HYLLERAAS  
METHOD**

$\varphi(1,2) = 1s(1)1s(2)g(r_{12})$ , where  $g(r_{12})$  is a function of the distance between the two electrons that gets small as  $r_{12}$  gets small. This approach was employed by Egil Hylleraas (1928-1930) to obtain  $W = -78.98$  eV in a stunning confirmation of quantum mechanics. This was truly the first major success of quantum mechanics, and it suggested that the theory was in hand that could explain all of chemistry.

More recently this method has been extended by including a sum of 1078 terms that depend explicitly on  $r_{12}$ , and the resulting variational function was used to calculate the ionization energy of He as:

$$\begin{aligned} IE(\text{He}) &= 198,310.69 \text{ cm}^{-1} \text{ (calculated)} \\ \text{vs. } IE(\text{He}) &= 198,310.82 \pm 0.15 \text{ cm}^{-1} \text{ (measured)} \end{aligned}$$

It seems that we can now calculate two-electron atoms to fantastic accuracy! The problem is that this method becomes very cumbersome when it is applied to more than 2 electrons. It is not readily generalized.

The alternative method to go beyond the product function  $\phi(1,2) = 1s(1)1s(2)$  is to simply add additional terms, with coefficients which may be varied:

CONFIGURATION  
INTERACTION

$$\phi(1,2) = c_1 [1s(1)1s(2)] + c_2 [2s(1)2s(2)] + c_3 [2p(1)2p(2)]$$

When evaluating  $P(1,2) = |\phi(1,2)|^2$  we now obtain a more complicated expression than simply  $|1s(1)|^2 |1s(2)|^2$ . Our result cannot be factored into a function of electron 1 times a function of electron 2. By mixing in higher energy configurations into our wavefunction we allow the electron motions to be correlated, and this reduces the overall energy of the ground state. This method of improving our wavefunction is called configuration interaction, and it has the advantage of being readily extended to systems with more than two electrons. Although it seems counterproductive to introduce higher energy configurations (such as  $2s(1)2s(2)$ ) into our wavefunction, the variational method guarantees that they can never hurt us. If such a term would worsen

our ground state energy, its optimized coefficient would be zero. Often, the leading configuration in such a configuration interaction calculation has a contribution to the overall wavefunction (denoted by  $|c_0|^2$ ) of approximately 95% ( $|c_0|^2 = 0.95$ ). Nevertheless, these higher terms are necessary to obtain chemical accuracy in many quantum chemical calculations.

For some particularly nasty systems, however, a very large number of excited configurations must be included to get anything approaching an accurate description of the molecule. For the chromium dimer ( $Cr_2$ ), for example, the leading configuration contributes at most 12% to the overall wavefunction. Further, it has been estimated that a sum over more than 57 million configurations would be required to calculate the properties of  $Cr_2$  to reasonable accuracy.

Proceeding further into the periodic table, we may attempt to calculate the ground state energy of Li, which has 3 electrons. Attempts to do this using the very reasonable trial wavefunction:

$$\psi(1,2,3) = \psi(1)\psi(2)\psi(3)$$

are dismal failures, however. To get this system correct we must introduce two more postulates of quantum mechanics. These will yield the familiar Pauli principle as a result.