

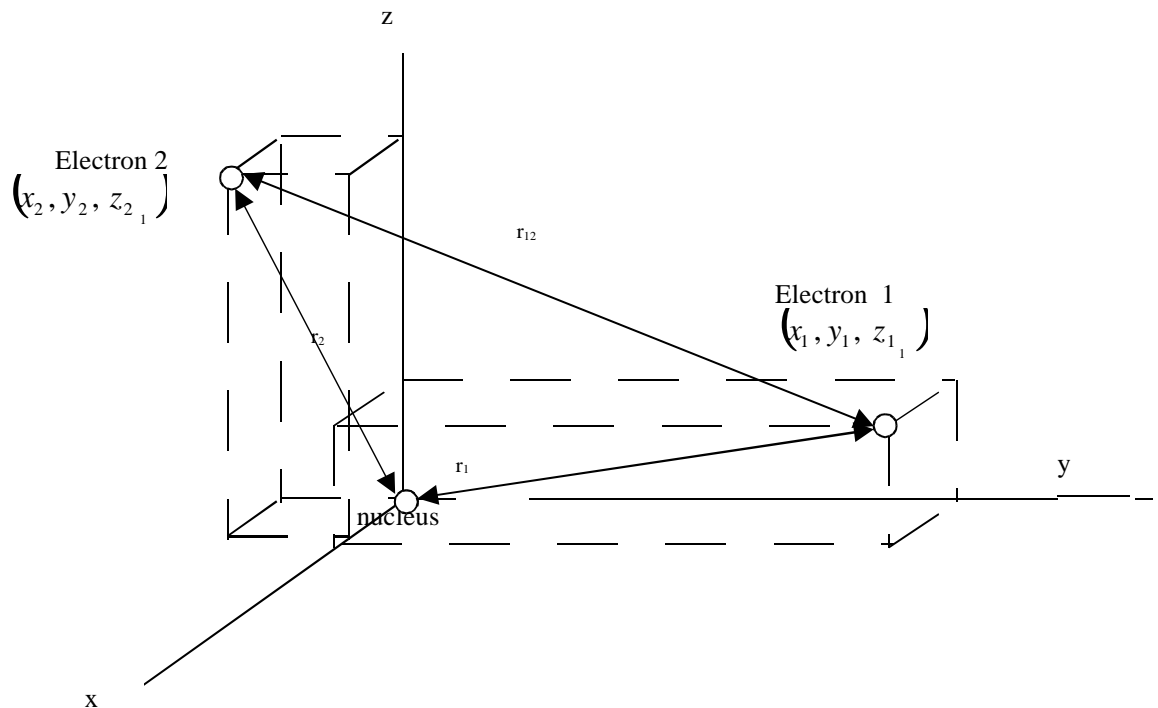
INTRODUCTION

I have decided to do a project on how to approximate the ground state of a helium atom. My project is aimed at students that have successfully completed the course of quantum mechanics one and are interested in finding out about this area quantum mechanics.

After quantum mechanics 1 students will be able to determine directly the λ functions for two particle systems such as the hydrogen atom and hydrogen like ions. In my coursework project I will show the non-relativistic Schrodinger equation for the next simplest atom the helium atom which contains three particles, cannot be solved directly. In fact the Schrodinger equation has not been solved directly for any system which contains more than two interacting particles. For all such systems one has to resort to approximation methods. In my project I have considered the method of ignoring electron repulsion, and a first order perturbation method. I wanted to write about the variation method but chose not to as I didn't want to make this project too big. Since most of the atomic and molecular systems I will deal with are relatively complicated, it is then important that I develop a few basic approximation techniques.

THE HELIUM ATOM

The helium atom, as depicted in below is a three-particle system which consist of two electrons and a nucleus whose mass is 4.0026 amu (6.6461×10^{-24} g) and whose charge is $+2e$. I will assume that here, just as in the treatment of the hydrogen atom, the total Schrodinger equation may be separated into two equations, one involving the translational energy of the atom and the other involving the relative motion of the electrons and the nucleus. I will ignore the translation energy associated with the motion of the centre of mass of the atom in space and will concentrate my attention on the relative motion of particles within the atom and on the energy of the relative motion. Furthermore, in my treatment of relative motion, I will assume that the nucleus is stationary. Although this is no exactly true, the mass of the nucleus is so much larger (about four thousand times larger) than the combined mass of the electrons that the resultant error is not significant.



1. The potential energy of attraction between the first electron and the nucleus, $-2e^2/r_1$, where r_1 is the distance between the first electron and the nucleus.
2. The potential energy of attraction between the second electron and the nucleus, $-2e^2/r_2$, where r_2 is the distance between the second electron and the nucleus.
3. The potential energy of repulsion between the two electrons $+e^2/r_{12}$, where r_{12} is the distance between two electrons.

In writing the potential energy, I have assumed that infinite separation between any particles represents zero potential energy of interaction. The total potential energy V for the atom may then be expressed as

$$V = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \quad (1)$$

Since V is not explicitly dependent on time, the force field is conservative, and we may use the nonrelativistic time-independent Schrodinger amplitude equation

$$\hat{H}\psi = E\psi, \quad (2)$$

to calculate the family of wave functions ψ and the corresponding energies of relative motion E . However, in writing the Hamiltonian operator in the model of the helium

$$\hat{H} = \frac{-h^2}{8\pi^2 m_e} \nabla_1^2 - \frac{h^2}{8\pi^2 m_e} \nabla_2^2 + V \quad (3)$$

where m_e is the mass of each electron. The first Laplacian operator, ∇_1^2 operates only on coordinates (x_1, y_1, z_1) of the first electron, and the second laplacian operator, ∇_2^2 operates only on coordinates (x_2, y_2, z_2) of the second electron, that is,

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \quad (4)$$

and

$$\nabla_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \quad (5)$$

atom, we must take into account the sum of the kinetic energies of the two particles (two electrons) and must therefore include a kinetic energy operator term for each of the particles.

Substitution of equation (1) and (3) into equation (2) yields the complete Shrodinger amplitude equation for relative motion in the helium atom:

$$\frac{-h^2}{8\pi^2 m_e} (\nabla_1^2 \psi + \nabla_2^2 \psi) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} = E\psi \quad (6)$$

Note that the Hamiltonian operator contains a Laplacian operator term for each electron and a potential energy term for each interacting pair. The general rule requiring one Laplacian operators term for each electron and one potential energy term for interacting pair also holds for other more complicated multi electron systems. By following this rule, it is not difficult to write the correct Schodinger equation for any atom we choose. The real difficulty arises in solving the eigenvalue equation. Returning to the Schrodinger equation (6) for the helium atom, we note that if we ignore the electron repulsion term $e^2\psi/r_{12}$, we would be able to separate variables and solve the eigenvalue equation directly. As it stand equation (6) has not been solved by any direct method.

FIRST APPROXIMATION: IGNORING THE ELECTRON REPULSION

Since the presence of the electron repulsion term in equation (6) prevents me from obtaining a direct solution, as a first approximation I will assume that the electrons do not repel one another and proceed with the calculations. By ignoring the total potential energy of the free helium atom is given from equation (1) as

$$V = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} \quad (7)$$

and the Schrodinger amplitude equation is

$$\left[\frac{-h^2}{8\pi^2 m_e} (\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} \right] \psi^0 = E^0 \psi^0 \quad (8)$$

where the eigenvalues E^0 are the stationary state energies of relative motion of the helium atom assuming no electron repulsion and the eigenfunction ψ^0 are the wave functions for the helium atom in which electron repulsion is ignored. The associated non repulsion Hamiltonian operator is \hat{H}^0 is then

$$\hat{H}^0 = \frac{-h^2}{8\pi^2 m_e} (\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} \quad (9)$$

so that (8) may be written as

$$\hat{H}^0 \psi^0 = E^0 \psi^0 \quad (10)$$

In order to separate the variables associated with the first electron from those associated with the second electron, I will assume that the total wave function ψ^0 may be expressed as a product of two functions, such that the first function γ_1 , depends only on the coordinates of the first electron, and the second function γ_2 , depends only on the coordinates of the second electron. That is

$$\psi^0(x_1, y_1, z_1, x_2, y_2, z_2) = \gamma_1(x_1, y_1, z_1) \gamma_2(x_2, y_2, z_2) \quad (11)$$

or more simply

$$\psi^0 = \gamma_1 \gamma_2 \quad (12)$$

Substitution of equation (12) into equation (8) followed by division of both sides by $\gamma_1 \gamma_2$ yields

$$\left[-\frac{1}{\gamma_1} \frac{h^2}{8\pi^2 m_e} \nabla_1^2 \gamma_1 - \frac{2e^2}{r_1} \right] + \left[-\frac{1}{\gamma_2} \frac{h^2}{8\pi^2 m_e} \nabla_2^2 \gamma_2 - \frac{2e^2}{r_2} \right] = E^0 \quad (13)$$

But the value of the first term in the bracket in equation (13) depends only on the coordinates of the first electron and is independent of the coordinates of the second electron, and the value of the second term in equation (13) depends only on the coordinates of the second electron and is independent of the coordinates of the first electron. Since the sum of both terms is constant and since the two terms are independent of one another, each term must separately be equal to a constant that is

$$-\frac{1}{\gamma_1} \frac{h^2}{8\pi^2 m_e} \nabla_1^2 \gamma_1 - \frac{2e^2}{r_1} = E_1 \quad (14)$$

and

$$-\frac{1}{\gamma_2} \frac{h^2}{8\pi^2 m_e} \nabla_1^2 \gamma_2 - \frac{2e^2}{r_2} = E_2 \quad (15)$$

where

$$E^0 = E_1 + E_2 \quad (16)$$

Equations (14) and (15) can be rearranged to the more familiar forms of the equations Schrodinger amplitude equation:

$$-\frac{h^2}{8\pi^2 m_e} \nabla_1^2 \gamma_1 - \frac{2e^2 \gamma_1}{r_1} = E_1 \gamma_1 \quad (17)$$

$$-\frac{h^2}{8\pi^2 m_e} \nabla_1^2 \gamma_2 - \frac{2e^2}{r_2} \gamma_2 = E_2 \gamma_2 \quad (18)$$

Equations (17) and (18) are each recognised as being identical in form to the Schrodinger equation for the hydrogen like ion, where $Z=2$. By ignoring electron repulsion we have generated a model of the helium atom which is in effect a superposition of two He^+ ions with only one nucleus however. Solving (16) and (17) yields

$$E_1 = -\frac{2\pi^2 m_e Z^2 e^4}{n_1^2 h^2} \quad (19)$$

$$E_2 = -\frac{2\pi^2 m_e Z^2 e^4}{n_2^2 h^2} \quad (20)$$

From previous knowledge I have on Quantum mechanics, I know that E_H , the energy of the hydrogen atom in the *ground state*, is given as

$$E_H = \frac{-2\pi^2 \mu e^4}{h^2}$$

I will now assume that within the accuracy of the present approximation, μ may be replaced by m_e without significant error so that

$$E_H = \frac{-2\pi^2 m_e e^4}{h^2} \quad (21)$$

and since $Z=2$ for the He^+ ions, E_1 and E_2 , as given by equations (19) and (20) may be expressed as

$$E_1 = \frac{4E_H}{n_1^2} \text{ and } E_2 = \frac{4E_H}{n_2^2}$$

so that E^0 from equation (16) becomes

$$E_1 = 4E_H \left[\frac{1}{n_1^2} + \frac{1}{n_2^2} \right] \quad (22)$$

If each of the electrons in the nonrepulsive model of the helium atom is in its ground, that is if $n_1=1$ and $n_2=1$, the ground state energy of the helium assuming no electron repulsion is

$$E^0 = 2E_{\text{He}^+} = 8E_H \quad (23)$$

where E_{He^+} is the ground state energy of a helium ion.

But E_H is -2.18×10^{-11} erg, which is equivalent to -13.6eV . Thus E^0 , the ground state energy for the helium atom in my first approximation is

$$E^0 = 8(-13.6\text{eV}) \quad (24)$$

The best experimental value for the energy E_{He} of the helium atom in the ground state is given in terms of the *first ionization potential* I , which is the *minimum* energy absorbed in the reaction in which the first electron leaves the ground state of a helium atom to become a free electron:



Since the minimum kinetic energy corresponds to an ejected electron having no translational kinetic energy, I can write the balance for equation (25) as

$$E_{\text{He}} + I = E_{\text{He}^+} \quad (26)$$

But I am able to solve the Schrodinger amplitude equation for E_{He^+} directly and show by equation 23 that

$$E_{\text{He}^+} = E^0 / 2 = -54.4\text{eV}$$

and I is experimentally determined to be 24.6eV . Thus from equation (26), the experimental value for the ground state energy of a helium atom is given as

$$E_{\text{He}} = -54.4\text{eV} - 24.6\text{eV} = 79.0\text{eV} \quad (27)$$

A comparison of E_{He} (experimental) from equation (27) with E^0 (calculated) in equation (24) indicates that in the first approximation method, the calculated value for the ground state energy of a helium atom is 38% lower (algebraically) than the experimental value. Such a large error indicates that the electron repulsion cannot be ignored.

**SECOND APPROXIMATION:
A FIRST ORDER PERTABATION METHOD**

I have shown that the correct Schrodinger wave equation for the helium atom is

$$\hat{H}\Psi = E\Psi, \quad (2)$$

Where

$$\hat{H} = \frac{-h^2}{8\pi^2 m_e} \nabla_1^2 - \frac{-h^2}{8\pi^2 m_e} \nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \quad (28)$$

Equation (2) cannot be solved directly, which means that we cannot directly evaluate the true wave function, Ψ . I have shown that if electron repulsion ignore electron repulsion is ignored, then

$$\hat{H}^0 \Psi^0 = E^0 \Psi^0 \quad (29)$$

can be directly solved where, from equation (9)

$$\hat{H}^0 = \frac{-h^2}{8\pi^2 m_e} \nabla_1^2 - \frac{h^2}{8\pi^2 m_e} \nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} \quad (30)$$

and where the eigenfunctions Ψ^0 are the wave functions for the helium atom in which electron repulsion is ignored. Substituting equation (30) into equation (28) yield

$$\hat{H} = \hat{H}^0 + \frac{e^2}{r_{12}} \quad (31)$$

and substitution of equation (31) into equation (2) yields

$$\left(\hat{H}^0 + \frac{e^2}{r_{12}} \right) \Psi = E\Psi \quad (32)$$

an equation which cannot be directly solved. I will now compare equations (29) and equations (32). The difference in the operators in the two eigenvalue equations is the repulsion term e^2/r_{12} . The smaller the value of the e^2/r_{12} the closer the two equations will be. If I let e^2/r_{12} equal zero (ignore electron repulsion) then the two equations will be the same. This means that E values are given by E^0 values and Ψ functions are given by Ψ^0 functions.

When using the perturbation method I will assume that e^2/r_{12} is small enough to be considered as a minor modification or perturbation of the operator \hat{H}^0 , an operator for which we may directly calculate the eigenfunctions Ψ^0 . I will further hope that the perturbation of the operator \hat{H}^0 will not be too different from \hat{H} (which cannot be directly evaluated)

Thus when evaluating the ground state energy of a helium atom in a given state, I will combine the use of the correct hamiltonion operator $\hat{H} = \hat{H}^0 + e^2/r_{12}$ with an incorrect wave function Ψ^0 for that state which is regarded to be fairly close to what the correct wave function should be. The nonrepulsive operator \hat{H}^0 is said to be perturbed to the first order by term e^2/r_{12} , and the present method of approximation is called a first order perturbation method. The previous approximation method in which I ignored electron repulsion altogether is called a zero order perturbation method, since I used \hat{H}^0 directly as the operator. This means that I added no perturbation terms to the nonrepulsive hamiltonion that I used. It is important to mention that for a given state, Ψ^0 is not an eigenfunction of \hat{H} and therefore the operation of \hat{H} on Ψ^0 will not yield an exact energy eigenvalue. Rather, because of the perturbation of energy due to the repulsion term, the value of E obtained by the operation \hat{H} on Ψ^0 for a given state will depend on the relative positions of the two electrons so that an approximate average value of \tilde{E} must be calculated through use of the mean value postulate as

$$\tilde{E} = \frac{\int_{-\infty}^{\infty} \Psi^{0*} \hat{H} \Psi^0 d\tau}{\int_{-\infty}^{\infty} \Psi^{0*} \Psi^0 d\tau} = \frac{\int_{-\infty}^{\infty} \Psi^{0*} (\hat{H} \Psi^0 + e^2 \Psi^0 / r_{12}) d\tau}{\int_{-\infty}^{\infty} \Psi^{0*} \Psi^0 d\tau} \quad (33)$$

Substituting of equation (29) into equation (33) yields

$$\tilde{E} = \frac{\int_{-\infty}^{\infty} \Psi^{0*} E^0 \Psi^0 d\tau + \int_{-\infty}^{\infty} \Psi^{0*} (e^2 / r_{12}) \Psi^0 d\tau}{\int_{-\infty}^{\infty} \Psi^{0*} \Psi^0 d\tau} \quad (34)$$

but since for any given state, E^0 is constant

$$\tilde{E} = E^0 + \frac{\int_{-\infty}^{\infty} \Psi^{0*} (e^2 / r_{12}) \Psi^0 d\tau}{\int_{-\infty}^{\infty} \Psi^{0*} \Psi^0 d\tau} \quad (35)$$

According to equation (35) the approximate first order energy \tilde{E} for the helium atom in a given state is given by the sum of E^0 , the energy of the nonperturbed atom in that same state in which electron repulsion is ignored (the zero order energy), and a term which is equivalent to the approximate average potential energy of electron repulsion over all space. Note that the second term of the right hand side of equation (35) would be, according to the mean value postulate, the mean value of e^2 / r_{12} if Ψ^0 were used as the correct wave function, since the quantum mechanical operator for e^2 / r_{12} is also e^2 / r_{12} .

The second term of the right hand side of equation (35) is called the perturbation energy E' . Therefore one can write

$$\tilde{E} = E^0 + E' \quad (36)$$

where the perturbation energy is

$$E' = \frac{\int_{-\infty}^{\infty} \Psi^{0*} (e^2 / r_{12}) \Psi^0 d\tau}{\int_{-\infty}^{\infty} \Psi^{0*} \Psi^0 d\tau} \quad (37)$$

Thus when using the perturbation method, one must think of the energy \tilde{E} of a given state of the helium atom as consisting of the total of E^0 , the exact sum of the kinetic energy and potential energy of the attraction in the same state calculated by ignoring repulsion, and E' , the approximate mean potential energy of repulsion, which in this case is a perturbation energy.

Since I want to evaluate E' for ground state energy of the helium atom, ($n_1=1$ and $n_2=1$), we must use 1's orbitals for each of the electrons. From tables of Normalised Hydrogen wave functions where $Z=2$

$$\tilde{a}_1 = \tilde{a}_1^* = \left(\frac{1}{\delta}\right)^{\frac{1}{2}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-2r_1/a_0} \quad (38)$$

and

$$\tilde{a}_2 = \tilde{a}_2^* = \left(\frac{1}{\delta}\right)^{\frac{1}{2}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-2r_2/a_0} \quad (39)$$

Since $\phi^0 = \tilde{a}_1 \tilde{a}_2$ and $\phi^{0*} = \tilde{a}_1^* \tilde{a}_2^*$

$$\phi^0 = \phi^{0*} = \tilde{a}_1 \tilde{a}_2 = \left(\frac{1}{\tilde{\delta}}\right) \left(\frac{2}{a_0}\right)^3 e^{-2r_2/a_0} e^{-2r_1/a_0} \quad (40)$$

$$\int_{-\infty}^{\infty} \phi_1^* \phi_1 d\hat{\delta}_1 = 1$$

$$\int_{-\infty}^{\infty} \phi_2^* \phi_2 d\hat{\delta}_2 = 1$$

and

$$\int_{-\infty}^{\infty} \phi^{0*} \phi^0 d\hat{\delta} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi_1^* \phi_1 \cdot \phi_2^* \phi_2 d\hat{\delta}_1 d\hat{\delta}_2 = 1 \quad (41)$$

Substituting equations (40) and (41) into equation (37) yields

$$E' = \left(\frac{8}{\tilde{\delta} a_0^3}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{e^2}{r_{12}} \left(e^{-2r_2/a_0} e^{-2r_1/a_0} \right) d\hat{\delta} \quad (42)$$

or, in terms of the co-ordinates of each of the particles,

$$E' = \left(\frac{8}{\tilde{\delta} a_0^3}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{e^2}{r_{12}} \left(e^{-2r_2/a_0} e^{-2r_1/a_0} \right) d\hat{\delta}_1 d\hat{\delta}_2 \quad (43)$$

$$= -\frac{5}{2} E_H = -\frac{5}{2} (-13.6\text{eV}) = +34.0\text{eV} \quad (44)$$

Substituting of the value for E^0 from equation (24) and E' from equation (44) into equation (36) yields

$$\tilde{E} = -108.8 + 34.0 = -74.8\text{eV} \quad (45)$$

for the approximate ground state energy of the helium atom, as calculated by a first order perturbation method. A comparison of \tilde{E} (-74.8eV) with the experimental value (-79.0eV) shows that the calculated value is about 5.3% too high algebraically. If I use the calculated \tilde{E} value to compute a value for the ionisation potential, then I get

$$\begin{aligned} I_{calc} &= E_{\text{He}^+} - \tilde{E} \\ &= -54.4 - (-74.8) = 20.4\text{eV} \end{aligned}$$

As compared with the experimental value of I , which is 24.6eV , the value calculated by perturbation method is 17% too low. It appears that a comparison of calculated and experimental first ionisation potentials is a more sensitive measure of the accuracy of the given approximation method than is a comparison of ground state energies, the reasons being that the ionisation potential is a measure of a difference in energy levels.