The Helium Atom

James Saslow

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Abstract—The purpose of this research is to investigate the intricacies of the Helium atom by examining the obstacles that are not necessarily present in solving the Schrodinger equation for the Hydrogen atom. For instance, the presence of 2 electrons in Helium introduces a repulsion term between them in the potential, which makes the Schrodinger equation for Helium impossible to solve analytically. This repulsion, in fact serves as a basis for quantum entanglement. This paper also talks about the Helium Ground state, the different spin states in Helium (namely ortho/parahelium) and spin state's effect on energy levels. Although the transition from analyzing Hydrogen to Helium may seem like a minute one at first glance, it is actually a tremendous jump in difficulty.

I. MULTI-PARTICLE SCHRODINGER EQUATION

We can write the Schrodinger Equation in its most general form as the eigenvalue problem.

$$H\psi = E\psi \tag{1}$$

where H is the *Hamiltonian* and E is the *total energy* of the system. We can express the Hamiltonian as the sum of kinetic energies T and potential energies V.

$$H = T + V \tag{2}$$

A. Potential Energy

Suppose our potential energy V is a function of the position of each electron. Let $\mathbf{r}_i$ be the position vector of the *ith* electron. Let's also measure $\mathbf{r}_i$ from the nucleus of the atom. If our multi-electron atom consisted of N electrons, we could then write V as

$$V = V(\mathbf{r}_1, .., \mathbf{r}_i, .., \mathbf{r}_N) \tag{3}$$

For now, we will leave V as an arbitrary potential as it is in eq. (3)

B. Kinetic Energy

We can describe the kinetic energy of the *ith* particle as $T_i = \mathbf{p}_i \cdot \mathbf{p}_i/(2m)$. Since the momentum operator is defined as $\mathbf{p}_i = -i\hbar\nabla_i$ [7], we can rewrite the kinetic energy of each individual particle as

$$T_i = -\frac{\hbar^2}{2m_i}\nabla_i^2 \tag{4}$$

The Laplacian operator ∇_i^2 acts on the *ith* particle. For instance, in a Cartesian basis, $\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$.

To obtain the total kinetic energy of all the particles, we must sum eq. (4) over all N electrons,

$$T = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i}\nabla_i^2 \tag{5}$$

C. Hamiltonian

Equation (2) says we can add eq. (3) and eq. (4) together to get the multi-particle Hamiltonian.

$$H = V(\mathbf{r}_1, .., \mathbf{r}_i, .., \mathbf{r}_N) + \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i}\nabla_i^2 \tag{6}$$

D. Time Independent Schrodinger Equation

To formulate the multi-particle Schrodinger Equation, we must let some wavefunction ψ act on H and on E as described in eq. (1). For this to make mathematical sense, the wavefunction ψ must also be a function of each particle's position vector. This means $\psi = \psi(\mathbf{r}_1, ..., \mathbf{r}_i, ...\mathbf{r}_N)$. By substituting eq. (6) into (2), we get a generalized form of the time independent multi-particle Schrodinger equation (7) **[9]**.

$$V(\mathbf{r}_1, .., \mathbf{r}_N)\psi(\mathbf{r}_1, .., \mathbf{r}_N) - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2\psi(\mathbf{r}_1, .., \mathbf{r}_N) = E\psi(\mathbf{r}_1, .., \mathbf{r}_N) \tag{7}$$

Note that the solution to the time independent Schrodinger equation ψ Is a $3 \times N$ dimensional function. This is because the wavefunction holds N number of position vectors $\psi = \psi(\mathbf{r}_1, .., \mathbf{r}_N)$ and each position vector has 3 components to describe where the electron's position is in 3 dimensional space. For instance, we can describe our position vector of some electron in the Cartesian basis as $\mathbf{r}_i = x_i\hat{\mathbf{x}} + y_i\hat{\mathbf{y}} + z_i\hat{\mathbf{z}}$, which has 3 components, x,y, and z.

Since $N = 1$ for Hydrogen, its wave function is a function of 3 variables. $N = 1$ atoms are magnitudes of effort easier to represent graphically because we can simply use a 3d plot or surface plots to represent them.

The wavefunction for multi-electron atoms ($N \geqslant 2$) on the other hand, cannot be physically represented using a graphing tool or imagined as easily since their wavefunction is a high dimensional structure **[8]**. In fact, the time independent wavefunction for Helium is a 6 dimensional function since it is a function of 6 variables $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2)$. Another way of saying this is that ψ for Helium is in a 6 dimensional configuration space. If we account for time dependence, the Helium wavefunction is then in 7 dimensional configuration space.

E. Time Dependent Schrodinger Equation

If we would like to account for time dependence in our Schrodinger Equation, we would simply append an additional dimension of time t to both our wavefunction ψ and to our potential energy V. The time dependent multi-particle Schrodinger equation looks like this:

$$V(\mathbf{r}_1, .., \mathbf{r}_N, t)\psi(\mathbf{r}_1, .., \mathbf{r}_N, t) \\ - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 \psi(\mathbf{r}_1, .., \mathbf{r}_N, t) = E\psi(\mathbf{r}_1, .., \mathbf{r}_N, t) \quad (8)$$

However, for the sake of simplicity, we will not account for time dependence when dealing with Helium in this paper.

II. SCHRODINGER EQUATION FOR HELIUM

A. Helium Hamiltonian

If we would like to examine the Hamiltonian for Helium, we can take the $N = 2$ case of eq. (6). Since each electron in our Helium atom has equivalent mass $m_i = m_e = constant$, we can take m_e outside of the summation.

$$H = V(\mathbf{r}_1, \mathbf{r}_2) - \sum_{i=1}^{2} \frac{\hbar^2}{2m_i}\nabla_i^2 \quad (9)$$

The potential energy of the system is due to the Coulomb interaction between the the nucleus and the 2 electrons *(Figure 1)*.
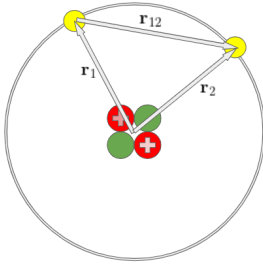

Figure 1: Bohr Model of the Helium-4 atom.

We define the charge of an atom's nucleus to be $Q_{nucleus} \equiv Ze$. Where e is the electron charge and Z is the number of protons within the nucleus. For Helium, $Z = 2$.

We have 3 electrostatic potential interactions in Helium, let's list them all. **[5]**

Electron 1 with nucleus : $V_1(\mathbf{r}_1) = -\dfrac{1}{4\pi\epsilon_0}\dfrac{Ze^2}{r_1}$ *(Attraction)*

Electron 2 with nucleus : $V_2(\mathbf{r}_2) = -\dfrac{1}{4\pi\epsilon_0}\dfrac{Ze^2}{r_2}$ *(Attraction)*

Electron 1 with Electron 2 : $V_{12}(\mathbf{r}_1, \mathbf{r}_2) = \dfrac{1}{4\pi\epsilon_0}\dfrac{e^2}{r_{12}}$ *(Repulsion)*

We can write the total potential in the Helium atom V as a summation of these 3 electrostatic potential energy interactions listed above. **[5]**

$$V(\mathbf{r}_1, \mathbf{r}_2) = V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2) + V_{12}(\mathbf{r}_1, \mathbf{r}_2) \quad (10)$$

$$V(\mathbf{r}_1, \mathbf{r}_2) = -\frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} \quad (11)$$

We can compactly write eq. (11) using a summation.

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} - \frac{Ze^2}{4\pi\epsilon_0}\sum_{i=1}^{2}\frac{1}{r_i} \quad (12)$$

Then, we can substitute our potential above in eq. (12) into our Hamiltonian for Helium in eq. (9) to get:

$$H = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} - \sum_{i=1}^{2}\left(\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i} + \frac{\hbar^2}{2m_e}\nabla_i^2\right) \quad (13)$$

$$H \quad = \quad \text{repulsion} \quad - \quad (\text{attraction} + \text{Kinetic energy})$$

As expected, the Hamiltonian H is composed of 3 terms, an electrostatic repulsion, an electrostatic attraction, and a kinetic energy term. Notice that if the repulsion term went to 0, the Hamiltonian would describe two independent electrons that interact with only the nucleus, but not with each other. Solving the Schrodinger equation with the electron-electron interaction term set to 0 ($\frac{1}{r_{12}} = 0$) in our Hamiltonian will give us a product of 2 wavefunctions for Hydrogen. Thus, the attraction + kinetic energy terms must be Hamiltonians for Hydrogen-like systems. We can write eq. (13) in terms of the Hydrogen-like Hamiltonians eq. (14) and in terms of a perturbation term [4] eq. (15)

$$h_i \equiv -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i} - \frac{\hbar^2}{2m_e}\nabla_i^2 \quad (14)$$

$$h^{(1)} \equiv \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} \quad (15)$$

So the Hamiltonian for Helium in eq. (13) becomes

$$H = h^{(1)} + \sum_{i=1}^{2} h_i \quad (16)$$

B. Multi-electron Hamiltonian

Since we have eq. (13) nicely written with summations, we can generalize the Hamiltonian to be a "one size fits all" expression for any multi-electron atom.

The Hamiltonian for any general multi-electron atom looks like this **[5]**

$$H = \sum_{i\neq j}^{N,N}\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\left(\frac{\hbar^2}{2m_e}\nabla_i^2 + \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i}\right) \quad (17)$$

C. Schrodinger Equation For Helium

To write the Schrodinger Equation for Helium, we can substitute the Hamiltonian for Helium in eq. (16) into eq. (1)

$$H\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{18}$$

Again, notice how ψ is a function of two position vectors $\mathbf{r}_1 = x_1\hat{\mathbf{x}} + y_1\hat{\mathbf{y}} + z_1\hat{\mathbf{z}}$ and $\mathbf{r}_2 = x_2\hat{\mathbf{x}} + y_2\hat{\mathbf{y}} + z_2\hat{\mathbf{z}}$, which is in total, a function of 6 variables. I shall paraphrase from Schroeder [3]: "For a multi-electron atom, one wavefunction describes the entire system of electrons." This means we can't "break up" or separate the wavefunction into a product of wavefunctions for each individual particle. This means $\psi(\mathbf{r}_1, \mathbf{r}_2) \neq \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$. When we can't separate the wavefunction like this the wavefunction is considered to be entangled [3]. Remember, the primary reason for why this wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is entangled in the first place is because of the electrostatic repulsion term $1/r_{12}$ between the 2 electrons in our potential eq. (11). This repulsion term is the main culprit in making the Helium quantum 3-body problem extremely challenging.

D. Independent Electron Approximate Solution for the Helium Schrodinger equation

Since it is impossible to find a analytical, closed form solution to the Schrodinger Equation for Helium, the best we can do is find an approximate wavefunction. A very crude approximation is to set the perturbation term responsible for the wavefunction entanglement equal to 0. $h^{(1)} = 0$. This is obviously a very bad approximation, since it does not accurately reflect the intricacies of the Helium problem. By doing this, we are avoiding the coulomb repulsion of electrons which isn't very realistic and it's what makes the Helium atom interesting in the first place. However this is the only way we can "untangle" the entangled wavefunction. In other words, with this approximation, we can separate our wavefunction into two wavefunctions, one for each electron. This means the wavefunction is no longer entangled. $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$ then becomes a valid ansatz where $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$ are Hydrogen-like wave functions.

E. Better Approximations

Obviously, the Independent Electron approximation does not provide a sufficient representation for what is actually happening in Helium, since it neglects the $1/r_{12}$ electron - electron repulsion term. We can use other methods that *account* for electron entanglement. However, many of these other algorithms are too computationally expensive to be done by hand, so they are often left as tasks in the world of computational physics. One of these algorithms makes use of the Chemical Formula Theory for atoms. **[9]**. The procedure looks like this:

1 : Write the Hamiltonian for a multi-electron atom eq.(17)

2 : Expand the ground wavefunction as a sum of wavefunctions times arbitrary coefficients $\psi_{approx} = \sum c_i \phi_i$

3 : After applying the **variational method** for quantum mechanics to solve for our c_i arbitrary coefficients

4 : We can then make use of **Hartree - Fock approximation** scheme to solve for our ϕ_i wavefunctions.

This gives us an approximation for the wavefunction in the ground state. I will discuss the Variational Principle further in depth later in the paper when we get to the ground state energy of Helium in section V.

III. HELIUM SPIN STATES

A. Spatial and Spin Wavefunctions

So far, the wavefunction that we have dealt with was concerned with spacial probability. It turns out, the total wavefunction that describes Helium is the product of the spacial wavefunction times the spin wave function **[8] [2]**.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)\sigma(1, 2) \tag{19}$$

where ψ is the spatial part of the wavefunction and σ is the spin part. (*Warning! Do not confused capital psi Ψ for lowercase psi ψ.*)

B. Antisymmetry of Fermion Wavefunctions

If we have some entangled wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ that describes electron 1 and electron 2 respectively in the Helium atom, then we can find the probability density by squaring the wave function.

The probability density for Helium is

$$\mathbb{P}(\mathbf{r}_1, \mathbf{r}_2) = |\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2 \tag{20}$$

Logically, if we swap the labels on electron 1 and on electron 2, this should have no effect on the probability distribution **[8]**,**[3]**. In other words, the probability distribution doesn't care what we name electron 1 and electron 2, or in what order. This must mean, after we square root both sides of the probability distribution, that $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\Psi(\mathbf{r}_2, \mathbf{r}_1)$. So, Ψ has to either be *symmetric* $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$, or it must be *antisymmetric* $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$. The **Spin Statistics Theorem** can help us figure out if the wavefunction for helium is symmetric or antisymmetric. I shall paraphrase this theorem stated on the MIT Open Course ware Notes **[4]**.

Spin Statistics Theorem (*paraphrased*)

Fermion Rule: A wavefunction involving identical *fermions* (integer spin $\frac{1}{2}$ particles) must be *antisymmetric* upon permutating variables in the wavefunction.

Boson Rule: A wavefunction involving identical *bosons* (integer spin particles) must be *symmetric* upon permutating variables in the wavefunction.

Since we are only concerned with the 2 electrons, which are fermions, the *total wavefunction* must be *antisymmetric* by the spin statistics theorem. This means that

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1) \tag{21}$$

Essentially, the wavefunction does not care which electrons are labeled *electron 1* and *electron 2*. There will be an antisymmetry in the wavefunction as a result of swapping electron names. It has no effect on the probability distribution.

Because the spin statistics theorem applies to the total wavefunction, we need to consider both the spatial and spin parts $\Psi = \psi\sigma$ eq. (19). In order to ensure that Ψ is antisymmetric, ψ must be symmetric and σ must be antisymmetric (*case 1*) **or** ψ must be symmetric and σ must be antisymmetric (*case 2*).

C. Parahelium Formalism

Case 1 we require that ψ to be symmetric and σ to be antisymmetric. So, $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1)$. Now we need to come up with an antisymmetric expression for σ. The spin wavefunction depends on total spin S of each electron. $S = s_1 + s_2$ and the total spin quantum number of each electron $M_s = M_{s1} + M_{s2}$. We can write σ as $\sigma_{Ms}^S(1,2)$ where (1,2) are just labels for each electron.

For *case 1*, let's consider $\sigma_0^0(1,2)$ **[8]**

$$\sigma_0^0(1,2) = |S = 0, M_s = 0> = \frac{1}{\sqrt{2}}(|\uparrow\downarrow> - |\downarrow\uparrow>) \tag{22}$$

I will explain what this notation means. $|>$ represents a ket, Dirac notation for a vector in quantum mechanics. In this case, our ket vector holds information about each electron's spin. If we just look at $|\uparrow\downarrow>$, we can interpret the first up arrow as the spin state of the first electron, and the following down arrow as the spin state of the second electron. We can show that $\sigma_0^0(1,2)$ is antisymmetric by swapping the arrows in each ket in eq. (22) and observing what happens as a result.

$$\sigma_0^0(2,1) = \frac{1}{\sqrt{2}}(|\downarrow\uparrow> - |\uparrow\downarrow>) = \\ -\frac{1}{\sqrt{2}}(|\uparrow\downarrow> - |\downarrow\uparrow>) = -\sigma_0^0(1,2) \tag{23}$$

We prove in eq.(23) that $\sigma_0^0(1,2)$ is antisymmetric. This means

$$\sigma_0^0(1,2) = -\sigma_0^0(2,1) \tag{24}$$

This happens to be the only antisymmetric spin wavefunction, so it is called the **singular state**. As you may have noticed in eq. (23), $S = 0$. This is only possible if the spin vectors add to 0. So, the spin vectors must be pointing in opposite directions. Such a configuration is known as **Parahelium**. (*Figure 2*).
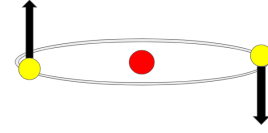
Figure 2: Parahelium.

D. Orthohelium Formalism

Case 2 we require that $\psi(\mathbf{r}_1, \mathbf{r}_2)$ to be antisymmetric and $\sigma_{Ms}^S(1,2)$ to be symmetric. This means that $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$ and $\sigma_{Ms}^{\mathbf{S}}(1,2) = \sigma_{Ms}^S(2,1)$.

For *Case 2*, let's consider the following spin wavefunctions. **[8]**

$$\sigma_1^1(1,2) = |S = 1, M_s = 1> = |\uparrow\uparrow> \tag{25}$$

$$\sigma_0^1(1,2) = |S = 1, M_s = 0> = \frac{1}{\sqrt{2}}(|\uparrow\downarrow> + |\downarrow\uparrow>) \tag{26}$$

$$\sigma_{-1}^1(1,2) = |S = 1, M_s = -1> = |\downarrow\downarrow> \tag{27}$$

It is trivial to prove the spin wavefunction symmetry in eqs. (25), (26), and (27). (i.e. it's trivial to show that $\sigma_1^1(1,2) = \sigma_1^2(2,1)$, $\sigma_0^1(1,2) = \sigma_0^1(2,1)$, and $\sigma_{-1}^1(1,2) = \sigma_{-1}^1(2,1)$) *(We can show this by simply swapping the arrows in each equation!)*

These are the only three spin symmetric wavefunctions so, we call it the **triplet state**. Because $S = 1$ in eqs. (25), (26), (27), the spin contribution from each electron must constructively add. This means that the spin of electron 1 and the spin of electron 2 must be pointing in the same direction. This configuration of Helium is called **Orthohelium**. (*Figure 3*).
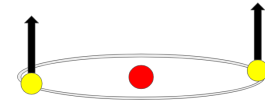
Figure 3: Orthohelium.

E. Energy states of Orthohelium & Parahelium

The energy states for the triplet states of Helium are less than the energy for the singlet states. **[6]**. Since triplet states have electrons with identical spin, the electrons can never be in the same energy orbital.(*Figure 4*). If they were, it would be a violation of the Pauli Exclusion Principle which states 2 fermions can not have identical quantum numbers. So, electrons in orthohelium have to be in separate orbitals. Whereas electrons in parahelium can be paired in the same orbital or in separate orbitals. (*Figure 4*). This means on average, the electrons in orthohelium will be further away than the electrons in parahelium. The total energy decreases when the electrons are further apart since the Hamiltonian is inversely proportional to the electrostatic repulsion in eq. (17) $H \propto \frac{1}{r_{12}} - (\textit{Kinetic Energy term} + \textit{Attraction term})$.
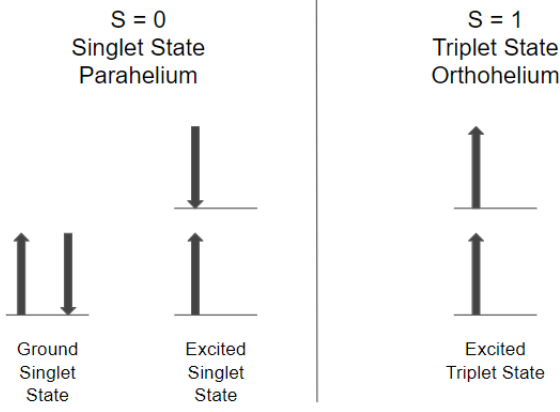
Figure 4: Possible Singlet and Triplet States.

IV. QUANTUM ENTANGLEMENT IN THE HELIUM ATOM

A. What is Quantum Entanglement?

Quantum entanglement describes how the states of 2 fermions are correlated. In the case of Helium, the entangled fermions are the 2 surrounding electrons. **[2]**.

B. The Results of Quantum Entanglement in Helium

To summarize the findings of **[2]**, entanglement between the two electrons in Helium tends to increase with an increase in the energy state. Singlet states are generally more entangled than triplet states because singlet states have more energy than triplet states.

V. GROUND STATE ENERGY

Like the wavefunction for Helium, the ground state energy is not something that can be analytically determined, but it can be approximated. A way we can estimate the ground state energy is by calculating the ionization energies of electron 1 and electron 2. Namely, we can consider the following processes for ionizing Helium:

$$He \rightarrow He^+ + e^- \quad \textit{(1st Ionization)}$$
$$He^+ \rightarrow He^{+2} + e^- \quad \textit{(2nd Ionization)}$$
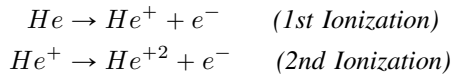
We know the experimental/accepted values for Helium ionization energy to be **[4]**. $I_1^{exp} = 24.6eV, I_2^{exp} = 54.4eV$, $I^{exp} = 79eV$

Out of the 2 ionizations, it is by far easier to compute the 2nd ionization compared to the 1st ionization. The reason being He^+ is a hydrogen-like atom with central charge $= Ze$. We can approach the 2nd ionization using nothing but Bohr theory for atoms! The 1st ionization on the other hand, is not as simple. For the first ionization, we must consider the electron-electron repulsion which is a nuisance to account for. In order to calculate the 1st ionization, we must resort to approximations.

A. The Second Ionization

We can calculate the second ionization energy I_2 to be

$$I_2 = 54.5eV \quad (28)$$

1) Derivation: We can directly derive this from Bohr theory. We can use Newton's second law on a an electron orbiting a central nucleus of charge Ze.

$$\sum F = \frac{kZe^2}{r^2} = \frac{mv^2}{r} \quad (29)$$

We can write (29) in terms of p^2 and isolate for that. We get:

$$p^2 = \frac{kZme^2}{r} \quad (30)$$

The de Brogile Hypothesis states that angular momentum is quantized $L = n\hbar = pr$.

We can combine our momentum equation with the de Brogile hypothesis to get:

$$r = \frac{n^2}{Z}\frac{4\pi\epsilon_0\hbar^2}{me^2} = \frac{n^2}{Z}a_0 \quad (31)$$

Where a_0 is the Bohr radius. The total energy is the sum of the kinetic energy and the potential energy.

$$E = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0} \quad (32)$$

We can combine equation (30) with (32) to get

$$E = -\frac{1}{2}\frac{Z^2e^2}{4\pi\epsilon_0 a_0}\frac{1}{n^2} = -\frac{Z^2}{n^2}|E_1| \quad (33)$$

Where E_1 is the ground state energy of Hydrogen. $E_1 = -13.6eV$

We can evaluate I_2 in equation (33) by setting $Z = 2$, and $n = 1$. In other words, $I_2 = 4|E_1|$ the 2nd ionization energy of Helium is equivalent to 4 times the Hydrogen ground state energy.

B. The First Ionization (No electron repulsion)

When we try to analyze the first ionization, we now have to consider the presence of two electrons. The easiest yet most ineffective way to deal with this problem is to ignore the electron repulsion entirely. Again, this strategy provides a poor representation of what the actual Helium ground state energy actually is, but perhaps it can help us gain insight on what value the true total Helium ionization energy could take on.

If we have no electron repulsion then,

$$I_1 \approx I_2 = 54.5eV \quad (34)$$

So, our approximate total approximate ionization energy must be $I = 109eV$ **[4]**

Consider this:

If the electron repulsion is present, then one electron will push the other electron towards infinity, lessening the amount

of work the ionization energy I_1^{exp} needs to do to ionize the electron. But if we don't consider electron repulsion, then the ionization energy I_1 needs to provide more energy than I_1^{exp} to the electron to ionize it since it's not getting the extra helpful electrostatic "boost" from the other electron.

From this analysis, we can construct an interval for the possible values of I^{exp}

$$I_1 < I^{exp} < I$$
$$54.5eV < I^{exp} < 109eV$$

And as we expect, the accepted value of the magnitude of the ground state of Helium falls within this interval. $I^{exp} = |E_1| = 79eV$

If we want a better approximation of the Helium ground state energy, we can use the Variational Method.

C. The Variational Method

The variational method is a scheme to determine a better approximation for the ground state energy. The variational method considers an educated guess for what the ground state wavefunction might look like, and gives us back an optimized energy. For example, we know that the solution for an infinite square well is a sinusoidal wavefunction. But suppose we didn't know this. We could guess that the ground state wavefunction might look like a parabola and use the variational method to get an approximate ground state energy for our parabola guess. The guessed wavefunction is called a *trial wavefunction*. The better the guess for the trial wavefunction, the more accurate our trial energy will become.

Luckily for us, we have an approximate wavefunction for the Helium atom. We found in section II C that if we assumed no entanglement in our wavefunction, we could treat the wavefunction for Helium as the product of two Hydrogen wavefunctions. Since we're interested in the ground state, our trial wavefunction should be the product of two ground state Hydrogen-like wavefunctions. **[10]**

$$\phi_{trial} = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \tag{35}$$

Where $\psi_{1s}(\mathbf{r}) = \frac{1}{\sqrt{2\pi}a_0^{3/2}}e^{-2r/a_0}$ is the ground state wavefunction for a Hydrogen-like atom with a central nucleus charge of $2e$.

Now that we have a trial wavefunction, we can use the variational method to get a trial energy. The variational method is **[11]**

$$E_{trial} = \frac{<\phi_{trial}|H|\phi_{trial}>}{<\phi_{trial}|\phi_{trial}>} \tag{36}$$

where the denominator is a normalization factor of ϕ_{trial}. This is once again Dirac notation as seen in section III C. I will elaborate what exactly this notation represents. $<\phi_{trial}|\phi_{trial}>$ is asking us to integrate the trial wavefunction over all space.

$$<\phi_{trial}|\phi_{trial}> = \int_{allspace}\phi_{trial}\phi_{trial}d^6r \tag{37}$$

And the numerator $<\phi_{trial}|H|\phi_{trial}>$ is

$$<\phi_{trial}|H|\phi_{trial}> = \int_{allspace}\phi_{trial}(H\phi_{trial})d^6r \tag{38}$$

Where H is the Hamiltonian for Helium in equation (13).

After doing this computation, we find $E_{trial} = -77.5eV$, which is not very far off from the accepted ground state energy of $-79eV$. **[10]**

VI. FUTURE RESEARCH

Some other interesting topics for future research on quantum Helium would include but are not limited to:

1) **1 Dimensional Helium** – This is analyzing the Helium problem except the particles are confined to one dimension. There are 2 different configurations of 1D Helium eZe and eeZ **[1]**

2) **Computational Methods** – Using computational methods for evaluating an approximate Helium wavefunction and Ground state energy.**[9]**

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