

Three particle systems in quantum mechanics; the Helium wave function

Department of Physics, Durham University

Introduction

Helium was first discovered in 1868 from observations of its line in the Sun's spectrum, deriving its name from the Greek "Helios", and it was first isolated on Earth in 1895 [1]. However predicting the spectra of helium is not possible analytically, instead we must use numerical methods. The Hamiltonian for the electrons in the Helium atom is the sum of the kinetic energy of both electrons, their mutual repulsion, and their repulsion from the nucleus,

$$\hat{H} = \underbrace{\frac{\hat{p}_1^2 + \hat{p}_2^2}{2m_e}}_{\text{kinetic energy}} - \underbrace{\frac{2e^2}{4\pi\epsilon_0} \left(\frac{2}{|\hat{r}_1|} + \frac{2}{|\hat{r}_2|} \right)}_{\text{nuclear repulsion}} - \underbrace{\frac{1}{|\hat{r}_2 + \hat{r}_1|}}_{\text{mutual repulsion}}. \quad (1)$$

There is no analytic solution to Schrodinger's equation for this Hamiltonian, however, the Rayleigh Ritz variational method can be used to find the energy eigenvalues and corresponding wave functions [2].

The Rayleigh Ritz variational method

The fundamental idea behind the Rayleigh Ritz variational method is that

$$\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle \geq E_0, \quad (2)$$

this is a consequence of the fact that the ground state has the smallest allowed energy value. We can use this to find an upper bound on the ground state energy. We want to find the best estimate of E_0 , IE the smallest values of $\langle E \rangle$. A good way of doing this is by varying the wave function with respect to an arbitrary parameter, and minimizing $\langle E \rangle$. However there is a better way, the method can be extended as follows.

Given an orthonormal basis, $\{|\phi_n\rangle\}$, that span a subspace of the Hilbert space. Hylleraas and Undheim showed that the eigenvalues, \tilde{E} , of the projection of the Hamiltonian in that subspace, $\tilde{\underline{\underline{H}}}$, are greater than or equal to the actual energy eigenvalues, E .

$$\tilde{\underline{\underline{H}}} \underline{\underline{a}} = \tilde{E} \underline{\underline{a}}, \quad E \leq \tilde{E}, \quad (3)$$

where the elements of $\tilde{\underline{\underline{H}}}$ are defined as $\tilde{H}_{nn'} = \langle \phi_n | \hat{H} | \phi_{n'} \rangle$. More generally for non-orthonormal basis vectors, instead of equation 3, we have

$$\tilde{\underline{\underline{H}}} \underline{\underline{a}} = \tilde{E} \underline{\underline{N}} \underline{\underline{a}}, \quad (4)$$

where the elements of $\underline{\underline{N}}$ are defined as $N_{nn'} = \langle \phi_n | \phi_{n'} \rangle$. This equation is no longer in the form of an eigenvalue equation, so we have to rearrange it. By observing that $\underline{\underline{N}}$ is hermitian and so diagonalizable, we can substitute $\underline{\underline{N}}$ with $\underline{\underline{Y}} \underline{\underline{\beta}} \underline{\underline{Y}}^T$, and rearrange to get

$$\underbrace{\underline{\underline{\beta}}^{-\frac{1}{2}} \underline{\underline{Y}}^T \tilde{\underline{\underline{H}}} \underline{\underline{Y}} \underline{\underline{\beta}}^{-\frac{1}{2}}}_{\underline{\underline{P}}} \underbrace{\underline{\underline{\beta}}^{\frac{1}{2}} \underline{\underline{Y}}^T \underline{\underline{a}}}_{\underline{\underline{z}}} = \tilde{E} \underbrace{\underline{\underline{\beta}}^{\frac{1}{2}} \underline{\underline{Y}}^T \underline{\underline{a}}}_{\underline{\underline{z}}} \quad (5)$$

. And so we can recover another eigenvalue equation, $\underline{\underline{P}} \underline{\underline{z}} = \tilde{E} \underline{\underline{z}}$. So for any basis, we can construct $\underline{\underline{P}}$, find its eigenvalues, to determine an upper bound on the ground state energy [3].

Our Choice of Basis

we want to choose basis vectors that give us a projection of the Hamiltonian that we can calculate analytically. A good choice of wave functions is

$$\phi_{jkm}(r_1, r_2) = (r_1 + r_2)^j (r_1 - r_2)^k |r_1 - r_2|^m e^{-\frac{Z}{\kappa r_0}(r_1 + r_2)}, \quad (6)$$

where the j, k, m are positive integers, and the κ is the parameter to be varied. For these wave functions both the $\underline{\underline{H}}$ and $\underline{\underline{N}}$ matrices can be calculated analytically [3].

It is important that our basis wave functions have the same symmetries as the state we are trying to find. For the ground state of helium, when we swap the positions of the electrons, r_1 and r_2 , the wave function is unchanged. This means we should choose basis vectors that have this symmetry. Because of this, k , must be even. The original basis vectors used by Hylleraas' are $((j, k, m) = (0, 0, 0), (0, 0, 1), (0, 2, 0))$, and they satisfy this symmetry. Unfortunately These wave functions have no θ or ϕ dependence, and so are not suitable to represent states of Helium with angular momentum.

Results

For Hylleraas' original basis the E_0 values were calculated for a range of κ , these values are plotted in figure 1.

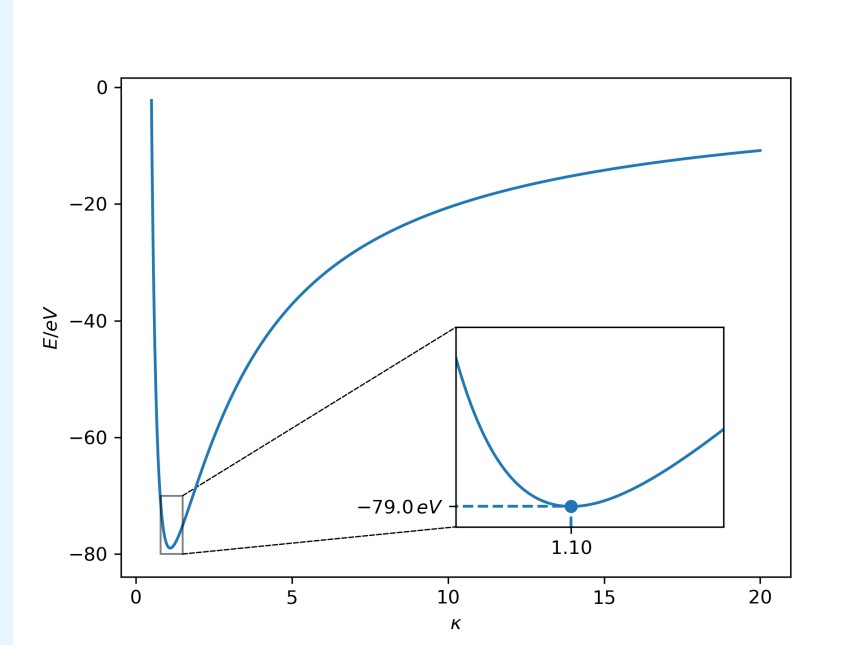


Figure 1. A plot of the upper bound on the ground state energy of Helium, for a range of κ . The minimum is shown in the magnified region.

So our estimate of the ground state energy of helium is $E_0 = -78.97920 \text{ eV}$, which is within 0.04% of the experimentally measured value of $79.005168 \pm 0.000006 \text{ eV}$ [4]. This curve has a single minimum, and as we increase the number of basis states used the minimum becomes more spread out as shown in figure 2, this suggests that the minimum is converging to E_0 .

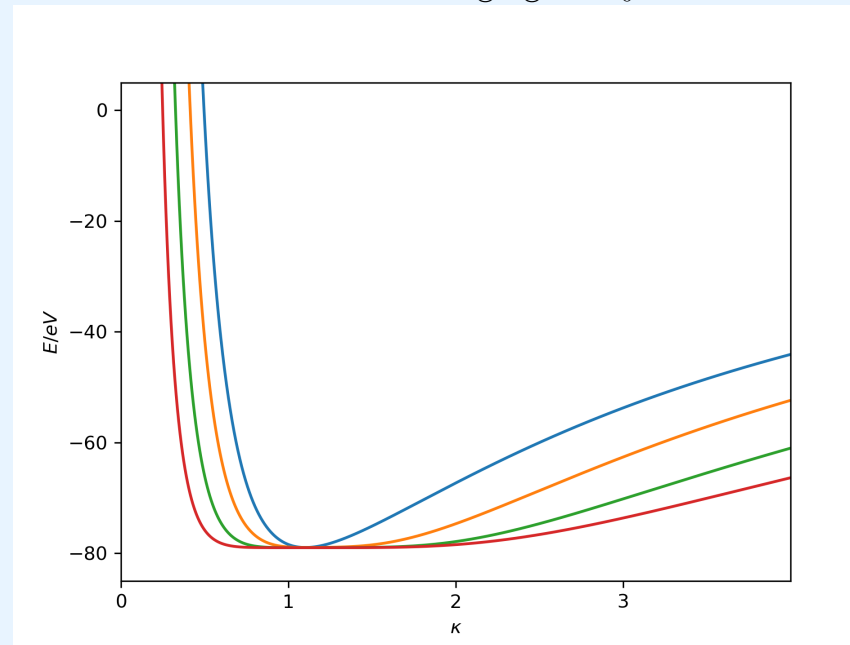


Figure 2. A plot of the upper bound on the ground state energy of Helium against κ for an increasing number of basis states: 3, 5, 11, then 81.

Conclusion and Future Work

We have successfully used Rayleigh Ritz variation to find Helium's ground state energy level. We then calculated the ground state wave function. Our value of the ground state energy level was within 0.01 of the experimentally measured value.

Further work could include, adding in a relativistic correction, calculating higher energy levels of helium, or calculating the dipole moment.

The minimum of these curves gives -79.01394 eV , which is within 0.01% of the experimental value. This error can be explained by our non-relativistic treatment of the helium atom. The amplitude of the ground state in its basis functions from Hylleraas' original basis is shown in the table 1.

(j, k, m)	a
$(0, 0, 0)$	0.81050483
$(0, 0, 1)$	0.3786262
$(0, 2, 0)$	0.44690505

Table 1. The amplitudes of Helium's ground state in the Hylleraas' original basis.

These can be used to approximate the Helium wave function, this is shown in figure 3

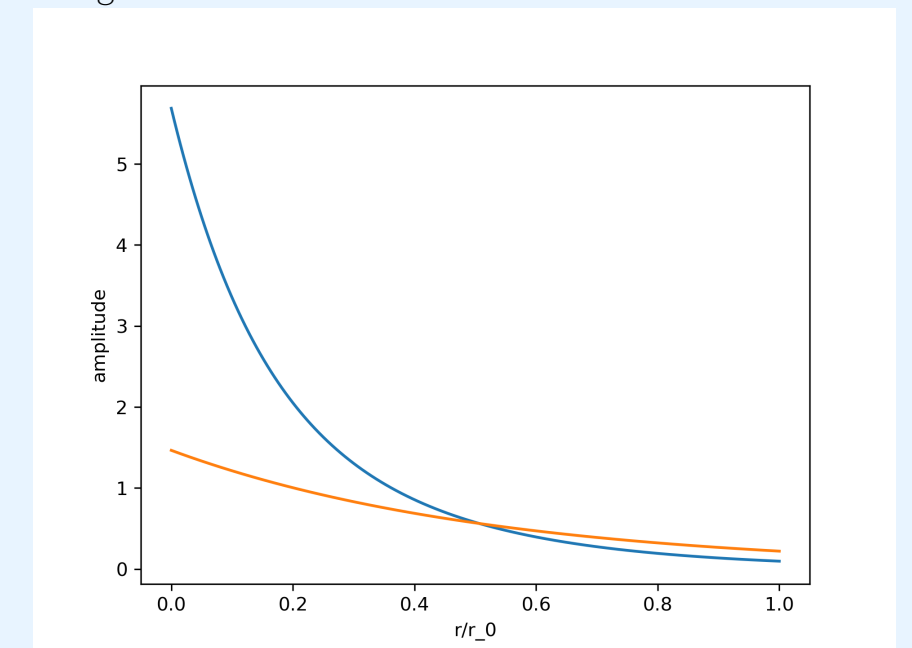


Figure 3. The amplitude that an electron is found a distance r from the nucleus, Helium's ground state is shown in blue, and Hydrogen's is shown in orange.

Both curves have a similar shape, they are both exponential, however the electrons in the Helium ground state are closer to the nucleus, this is because of the stronger nuclear charge.

References

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- [3] Egil A. Hylleraas and Bjarne Undheim. Numerische berechnung der 2s-terme von ortho- und par-helium. *Zeitschrift für Physik*, 65(11–12):759–772, doi:10.1007/bf01397263.
- [4] W. C. Martin. Energy levels of neutral helium (4he i). *Journal of Physical and Chemical Reference Data*, 2:257–266, doi:10.1063/1.3253119.