

# Solving for the Helium Atom Energies with the Variational Method

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The non-relativistic ground state and four excited state energies of the helium atom are solved to reasonable accuracy using the variational method with Hylleraas' basis states. The ground state parahelium energy agrees well with the literature to within 0.0008%. We find that using negative, fractional powers in the Hylleraas coordinates does not provide any advantage to the minimisation unless these are selected suitably such as in the three basis case. This is contrary to the literature where these basis state forms appear to give an advantage. The wave functions are reconstructed and we learn that the weighting of the basis states is very sensitive to the basis states chosen. Ultimately, there is no substitute for using a high number of basis states if very high accuracy is required.

## 1. Introduction

The helium atom is the simplest quantum mechanical system which cannot be solved for analytically, unlike the hydrogen atom [1]. This is because it is a multi-electron system whereby the electron-electron term in the Hamiltonian prevents the wave function or energies from being solved easily. By approximating the nucleus as having an infinite mass we can write the Hamiltonian in terms of the positions of the two electrons  $\vec{r}_1$  and  $\vec{r}_2$  as seen in Eq.1 where the inseparable coulomb repulsion term can be seen as the last term. The  $\frac{1}{4\pi\epsilon_0}$  prefactors have been absorbed into the definition of the electric charge. This equation approximates the system by ignoring fine structure (or hyperfine structure) terms such as relativistic corrections or spin-orbit coupling.

$$H = -\frac{\hbar^2}{2m_e}(\Delta_1 + \Delta_2) - \frac{Ze^2}{|\vec{r}_1|} - \frac{Ze^2}{|\vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \quad (1)$$

Finding the non-relativistic energy levels of the helium atom to high accuracy is important for various applications in physics such as studying antiprotonic helium atoms and finding the critical nuclear charge for two-electron atoms [2]. The non-relativistic energies can also be used as the building blocks for comparing numerical methods to experimental methods when investigating the spectrum of the helium atom or other atoms and molecules. Physical properties of the helium atom, like the average distance between the electrons, can be inferred from the wave functions.

In this report we employ the variational method to solve for the energies using Hylleraas' basis states which were first used in 1929 [3]. It is assumed that the eigenstates  $\Psi_n$  of the Hamiltonian can be written as a linear combination of basis states  $\Phi_i$  which are not necessarily eigenstates themselves. Taking the expectation value of the eigenstates with the Hamiltonian and dividing by the inner product gives the energy of the eigenstate as shown in Eq.2.

$$E_n = \frac{\langle \Psi_n | H | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} \quad (2)$$

Since  $E_n \geq E_0$  where  $E_0$  is the ground state energy, minimising the energy of the wave function gives the best approximation to the ground state energy. The energies of the eigenstates orthogonal to that wave function give the excited state energies. The basis states originally used by Hylleraas are of the following form:

$$\tilde{\Phi}_{jkm}(\vec{r}_1, \vec{r}_2) = (r_1 + r_2)^j (r_1 - r_2)^k |\vec{r}_1 - \vec{r}_2|^m \exp\left[-\frac{Z}{\kappa r_0}(r_1 + r_2)\right] \quad (3)$$

The exponent of the wave function resembles two hydrogenic wave functions multiplied with a  $\kappa$  constant which can mimic the shielding effect of the electrons. The  $(r_1 - r_2)^k$  term allows us to make the wave function symmetric or anti-symmetric depending on whether  $k$  is an even or odd power. This is important when we consider the two states of helium; parahelium and orthohelium. Parahelium is the singlet state with an antisymmetric spin wave function while orthohelium is the triplet state with a symmetric spin wave function [1]. Pauli's principle states that fermionic wave functions must be antisymmetric forcing parahelium to have a symmetric spatial wave function and orthohelium to have an antisymmetric wave function.

There have been many alterations made over time to Hylleraas' basis states by including logarithmic terms to the basis states, half integer powers, double or triple exponents and more [4]. The significant advancements in computational power have vastly improved the energy calculations in the time this problem has been around. Up to 22,000 basis states have been used in some calculations and the best estimates claim to reach accuracy of up to 40 significant figures [2] [4]. High accuracy has also been reached for the excited state wave functions, which are more difficult to calculate, with values reaching 27-28 correct significant figures [2].

In this paper we look at how closely we can predict the accepted values in the literature with lower numbers of basis states (1-200 states) as these are reported upon less. Different forms of the basis states are considered and their convergent rates are compared. The wave functions are reconstructed by finding the coefficients of the basis states and we learn that the weighting of the basis states is unpredictable with no pattern to exploit. We also look at the physical implications of our results.

## 2. Method

A trial wave function, which we assume to be an eigenstate of the Hamiltonian, is constructed from a linear combination of the basis states in Eq.3 which depend on a parameter  $\kappa$ . The wave function is shown in Eq.4 where the tilde indicates that the basis states are not orthogonal.

$$\Psi(\vec{r}_1, \vec{r}_2) = \sum_{j,k,m} \tilde{a}_{jkm} \tilde{\Phi}_{jkm}(\vec{r}_1, \vec{r}_2) \quad (4)$$

We can turn the problem into an eigenvalue equation which when solved gives the ground state energies and excited state energies. This equation is shown in Eq.5 where  $\hat{H}$  is

a matrix with the expectation values of the basis states with the Hamiltonian as its entries.  $\tilde{A}$  is a column vector with the basis state coefficients as its elements,  $E$  is the energy eigenvalue and  $N$  is a matrix, the entries of which are the possible combinations of inner products between the basis states.

$$\tilde{H}\tilde{A} = E\tilde{N}\tilde{A} \quad (5)$$

The best estimate of the energy is found by minimising the energy distribution with respect to  $\kappa$ . Fig.1 shows the energy distribution for different numbers of basis states.

Three different basis sets were used in this paper which are compared in the results and discussion. These differ through the forms of the powers  $j$ ,  $k$ ,  $m$  shown in Eq.3. Basis A uses the original basis state forms which Hylleraas used including positive integer powers for  $j$ ,  $k$ ,  $m$ . Basis B includes negative powers for  $j$  and basis C includes negative fractional powers which increase in increments of  $\frac{1}{2}$ . These bases are created in order of the sum of  $j,k,m$  such that the state  $[1,0,0]$  will appear before  $[1,0,1]$  when a certain number of states are chosen.

The coefficients of the basis states in the wave function can be recovered by using the eigenvalues and eigenvectors of the matrix  $N$ . With some algebraic manipulation we find that the coefficients can be returned as the entries of an eigenvector  $\tilde{A}$  where  $Y$  is a matrix with the eigenvectors of  $N$  as its columns, and  $\beta^{-\frac{1}{2}}$  is a matrix, the diagonal elements of which are the inverse eigenvalues of  $N$  to the power  $-\frac{1}{2}$ .  $Z$  is found by solving for the eigenvalues of  $P$ , another matrix given by  $P = \beta^{-\frac{1}{2}}Y^T\tilde{H}Y\beta^{-\frac{1}{2}}$ .

$$\tilde{A} = Y\beta^{-\frac{1}{2}}Z \quad (6)$$

### 3. Results and Discussion

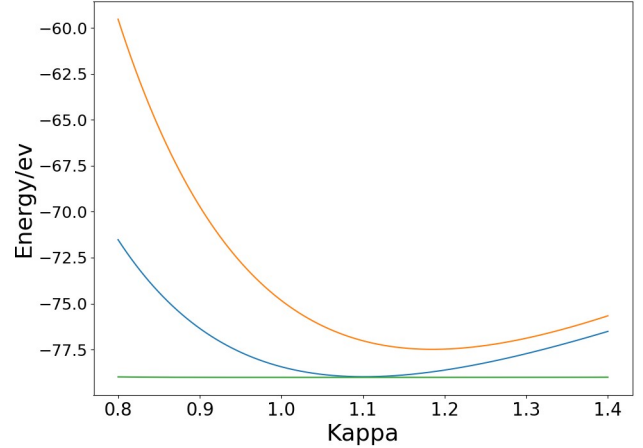
#### 3.1. Ground state and excited state energies

Table I shows the results for the energies using the variational method in the cases of parahelium and orthohelium. These are in reasonable agreement with the literature values for the non-relativistic case, also shown. The states with low principal quantum numbers show the best agreement such as the parahelium ground state energy which is within 0.0008% of the accepted value and the first excited state energy for orthohelium which is within 0.03% of the accepted value [2]. Basis B with 200 basis states was used as it returned the lowest energies. These energies are for S states only as there is no angular dependence in the wave functions ( $l=0$ ).

**TABLE I:** Ground state and excited state energies for parahelium(total spin  $S=0$ ) and orthohelium(total spin  $S=1$ ). The states are labelled in the format  $n^{2S+1}l_J$ .

State	Energy/ev	
	Literature [2]	Best estimate
$1^1S_0$	-79.0144	-79.0150
$2^1S_0$	-58.3949	-58.3764
$2^3S_1$	-59.1910	-59.1741
$3^1S_0$	-56.0901	-54.8959
$3^3S_1$	-56.2917	-55.3307

The best estimates for the energies were found by minimising the energy eigenvalues returned from Eq.5 with respect to  $\kappa$ , of which the dependence can be seen in Eq.3. The  $\kappa$  dependence decreases significantly as more basis states are used as can be seen with the correspondingly shallower plots in Fig.1. At higher numbers of basis states, the wave function's form has more variation through the weighting of the basis states (with their coefficients) and this allows a better approximation of the energy.



**FIG. 1:** The parahelium distribution of energy with  $\kappa$ , of which the minima give the best guess for the ground state energy. The 1, 3 and 32 basis states case are shown in orange, blue and green respectively.

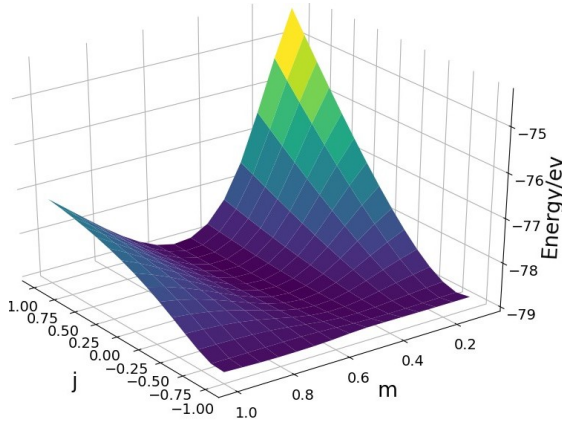
An unusual result of our calculated value for the ground state energy is that it is lower than the accepted value in the literature. In the variational method, minimising the energy returns the best estimate and so going lower than the accepted value suggests it would be a better estimate, which is unlikely.

It was thought that this could have been caused by a lack of precision in one of the physical constants, an error which could have propagated through the calculations. However, changing the last digit of this constant only shifted the energy value at the sixth decimal place mark whereas the difference between the two can be seen at the third decimal place. The difference was not resolved.

#### 3.2. Different forms of basis states

Fig. 1 shows the clear numerical convergence of our results as we increase the number of basis states. However, changing the form of the basis states which make the wave function can also improve convergence. Fig.2 shows how taking fractional (including negative) values for  $j$  and  $m$  can significantly improve the minimisation of the energy for the three basis case [5].

The lowest energies in Fig.2 lie amongst fractional values for  $j$  and  $m$ . The minimum is at  $j = -0.143$  and  $m = 0.164$  and takes the three basis case to below -79ev (-79.006ev). Although using fractional values for  $j$  and  $m$  is arbitrary (the wave function is decided by us) it is unclear what advantage it provides to the minimisation process. There is the appeal to 'flexibility' in the wave function when using fractional values but as Schwartz puts it, this "is just armwaving; it lacks any mathematical foundation" [6]. It is not always obvious which fractional values will be advantageous. Creating a contour plot to see which  $j$  and  $m$  values work best at

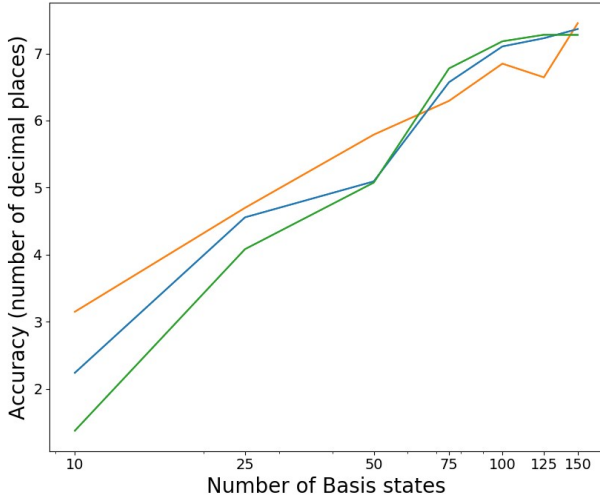


**FIG. 2:** The variation in ground state energy for parahelium in the three-basis case of  $[j,0,0]$ ,  $[0,2,0]$ ,  $[0,0,m]$  where  $j$  and  $m$  are varied.  $j$  takes values between -1 and 1 in 15 intervals and  $m$  takes values between 0 and 1 in 15 intervals.

higher numbers of basis states requires either a lot of computer power or time.

### 3.3. Numerical convergence of different basis states

Fig.3 shows the variation between number of basis states and accuracy (correct number of decimal places compared to our best estimate) for our three different bases A,B and C which each have different selection rules. It was decided to change  $j$  as it has the fewest constraints in the calculations ( $m$  must be positive and  $k$  has to be even or odd and thus integer) and shows the best minimisation in the literature [6]. Similar selection rules were used in the literature however only at higher numbers of basis states so here we discuss the results at lower numbers of basis states [6].



**FIG. 3:** The accuracy of three different sets of basis states. Accuracy gives the number of decimal places in agreement with our best estimate at 200 basis states. The line in orange is basis A with positive, integer  $j$ , the line in blue is basis B including negative  $j$  and the line in green is basis C including negative, fractional  $j$ . The x axis has a logarithmic scale.

The accuracy values used in Fig.3 are from an empirical relationship between calculated results and our best estimate at 200 basis states. They are given by  $\log\left(\frac{E^*}{E^* - E}\right) - 1$  where  $E^*$  is the best estimate at 200 basis states (from basis B) and  $E$  is the calculated result at a particular number of

basis states. This equation was used by Schwartz and has been modified to better suit our data [6]. Using Hartrees as a unit the accuracy gives the number of decimal places in agreement with the best estimate. The advantage of this method is it can distinguish how closely the last decimal place agrees with the accepted result.

By looking at Fig.3 it is not clear that including negative or fractional basis states provides an advantage in our method at lower numbers of basis states. The accuracies of the different methods appear to converge quite closely at 150 basis states with basis A being closest to our lowest calculated result. The lowest calculated result was found with basis B at 200 basis states. These results are in partial agreement with the literature, with our results being slightly lower. Schwartz reports that with number of basis states  $N = 125$ , basis A gave an accuracy of 6.9 compared to our 6.5, basis B gave 7.7 compared to our 7.2, while at  $N = 139$  basis C gave 8.5 compared to our 7.3 at  $N=125$  [6]. It seems that at lower numbers of basis states the basis used does not significantly affect the outcome.

The forms used for bases B and C in the literature differ slightly from ours and may have provided an advantage we overlooked. Whereas our powers  $j,k,m$  are independent, in the literature they are combined as shown in Eq.7 where  $s = (r_1 + r_2)$ ,  $t = (r_1 - r_2)$  and  $u = |\vec{r}_1 - \vec{r}_2|$ .

$$\tilde{\Phi} = s^{j+\frac{1}{2}} (u/s)^k (t/s)^m \exp\left[-\frac{Zs}{\kappa r_0}\right] \quad (7)$$

The  $s^{\frac{1}{2}}$  is ignored for negative integer powers but is kept for including fractional powers.  $J,k,m$  are kept as integers this way. Using this form for the basis states appears to lead to quicker numerical convergence in the literature and could have been something to explore further [6].

Fig.3 shows the general correlation between higher number of states and higher accuracy but this not a strict relationship. Basis A for example shows a decrease in accuracy from 100 to 125 basis states. The trends appear linear but are quite discontinuous and it would have been useful to calculate the energies at smaller numbers of basis state intervals. As discussed in the next section it was not clear if certain basis states offered advantages to the minimisation. The process in which the basis states were created meant that basis states with different forms were picked even though the sum of their elements were the same. This could have had an effect on the accuracy.

### 3.4. Choice of basis states

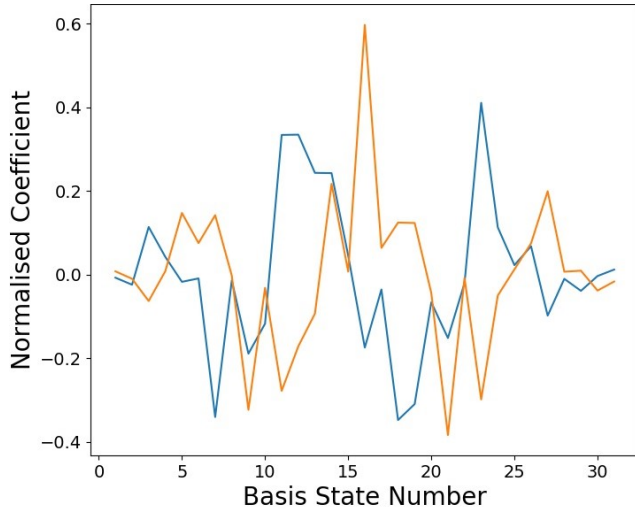
The importance of choosing basis states, as opposed to increasing the sum of  $j,k,m$  in the basis states consecutively, was also investigated to see if certain states can improve the estimate. Table II shows that in the three basis states case where combinations of three out of the six possible states are considered, some states such as  $[0,0,0]$  and  $[1,0,0]$  give better estimates. These states also have low standard deviations between the combinations. However, this is not an indication that these states are being more strongly weighted. Also shown in Table II are the normalised coefficients of the wave function in the six basis states case where the states we expected to be more heavily weighted were not necessarily so. When looking at the weighting of the basis states at increasing numbers there was no clear pattern where some

states were always weighted strongly or weakly. This implies what is more important is the way in which the basis states interact with each other.

**TABLE II:** Mean ground state energy for the three basis states case where combinations of two of the five other basis states are considered. The normalised coefficients are also given for each basis state in the six basis states case.

Basis State	Mean Energy/ev	Norm. Coefficient
[0,0,0]	-78.57	0.822
[0,0,1]	-76.03	0.424
[0,2,0]	-75.71	0.375
[1,0,0]	-77.51	-0.055
[1,0,1]	-75.73	0.008
[1,2,1]	-75.62	0.012

Fig.4 illustrates how the coefficients change for the wave function with 32 and 31 basis states (only 31 states are compared between them). Adding just one more basis state considerably changes the weighting of all the states, some coefficients even change sign with the addition of the extra state. This shows how the weighting of the basis states is very dependent on which are included. It was difficult to know which basis states worked well with others, especially at higher numbers. It was decided to keep the selection rules aforementioned.



**FIG. 4:** The normalised coefficients of the wave function for the 32 and 31 basis states cases. The 32 basis states wave function coefficients are shown in orange and the 31 basis states wave function coefficients are shown in blue. Only 31 of the basis states are included so that all coefficients can be compared. Basis state number is arbitrary and indicates which are being compared.

### 3.5. Physical implications

Calculating the groundstate for the helium atom is useful for various applications, even with the non-relativistic case. One use of the variational method is in determining the critical nuclear charge required to bind a nucleus for two electron atoms [2]. Applications such as these require high-precision methods. It is clear from the literature that at high numbers of basis states the energy can be calculated to high numbers of decimal places but it is less certain at lower numbers of states. The effects of employing tech-

niques like using negative or fractional powers are not realised as much at lower numbers of states which prevents quicker convergence. However, there are other ways of using the variational method and different basis state forms used which are not considered in this paper.

It is also difficult to compare the wave functions to the one-electron case because the weightings of the basis states change greatly depending on the number of states used. The coefficient of the wave function for the [0,0,0] basis state for example has a high weighting for low numbers of basis states but it is considerably lower at higher numbers of basis states. Other basis states have even greater variation and it is difficult to infer any pattern.

However, reconstructing the wave functions is useful for finding physical properties of the system. The average distance between the two electrons can be found by computing  $\langle |\vec{r}_1 - \vec{r}_2| \rangle$ . This involves summing the different combinations of inner products of all the basis states in the wave function, which can only be done for the one basis state case in our method otherwise more  $|\vec{r}_1 - \vec{r}_2|$  terms enter the inner product calculations than necessary. A value of 0.6860 was calculated which is in very good agreement with the analytic solution. This shows how other quantities which may be harder to compute analytically could be found with these numerical computations.

## 4. Conclusions

In conclusion, the ground state energies and excited state energies for helium can be calculated to considerable accuracy with the variational method presented in this report. Our value for the ground state parahelium energy agrees with the accepted value to 0.0008% and the first excited state of orthohelium agrees with the literature to 0.03% [2]. Our parahelium ground state energy is in fact lower than the accepted value and we would have liked to investigate further why this was the case. At low numbers of basis states the energies may not reach the required high accuracy in certain applications, however we have seen that this improves with higher numbers of basis states. Apart from in the three basis states case where choosing negative fractional powers for the wave function was advantageous, we saw that using different bases did not provide any improvements to the energy estimations. However, different forms were used in the literature which, given more time on the project we would have liked to implement at lower numbers of basis states [6]. It was found that, generally, choosing the basis states is impractical because the weighting of the states is highly sensitive to which basis states are used. Reconstructing the basis states can be useful for finding properties of the system such as the average distance between the electrons which was calculated to excellent agreement with the analytic calculations and shows that other properties which are difficult to compute analytically could be done in a similar way. Transition probabilities between different states are something we would have liked to investigate.

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