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Numerical calculation of the ground state of Helium atom using Hyllerass algorithm

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Abstract

Hylleraas did the calculation of the ground state in* 1926 *using the variational parameter* α*. In this paper we trace Hylleraas historic calculation, the use of computer enables us to improve the approximation found by Hylleraas . The program was written in FORTRAN language, designed in such away that for a particular value of dimension D, we varied the variational parameter* α *and the corresponding minimum energy was computed. The optimal value of the dimension D, that is D =*20*, and for all possible values of the basis state, the variational parameter* α*=1.05 has the lowest energy of –*79.015104*eV; compared with the historic calculation of Hylleraas the difference is only* 0.0329*eV. (*0.02%*)

1.0 Introduction

The Helium atom consists of a nucleus of charge 2*e* and two electrons which we label 1 and 2. Each electron is attracted to the nucleus and the two electrons repel each other. We assume, this will turn out to be correct, that no forces, other than the electromagnetic ones (Coulomb to a very good approximation) are necessary to describe the dynamic of the Helium atom with the help of quantum mechanics [6].

The largest quantities of Helium are obtained from natural gas. The low solubility of Helium in water, and thus in the body fluids is the reason for using helium to replace nitrogen in "air" breathed by divers and other working in high-pressure atmosphere in order to prevent the "bends". The melting point of Helium is -272.2^0C and the boiling point of Helium is -268.6^0 C with density of $0.178 kgm^{-2}$, [[1]].

These atoms have the simplest energy level schemes. In this case we find it necessary to take into account the Coulomb repulsion between the two valence electrons rather more explicitly [2], and not merely represent it by an average field. All the features of the energy level spectra of atoms with two valence electrons are brought out by the example of helium and as in this case, we have the additional simplification of knowing precisely what the central field is namely just that due to the nucleus, we shall confine our attention to this case.

2.0 Solution of Helium atom problem by the Hylleraas method

If these were no interaction between the electrons, one could determine the ground state wave function for the helium atom analytically [9]. One would only have to put each

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electron into the ground state of the Schrödinger equation for the one-electron problem. One would have

$$\Phi_G(r_1, r_2) = \exp\left(\frac{-z}{r_0}(r_1 + r_2)\right) \tag{2.1}$$

where $$r_0 = \frac{4\pi\varepsilon_0\eta}{me^2} = 0.52917\,\overset{o}{A}$$

is the Bohr radius. From now on we use the abbreviation r_1 and r_2 for $|r_1|$ and $|r_2|$. If one calculates the expectation values of the Hamilton operator with the normalized state equation (1.1), this corresponds to the perturbation calculation, one certainly obtains an estimate of the binding energy, but it still differs from the true value by several *eV*.

The estimate can be improved by taking account of the fact that each electron shields the other electron from a portion of the nucleus-electron interaction. This is most easily achieved by replacing the nuclear charge number *Z* in equation (2.1) by an effective nuclear charge number $Z' = Z/\alpha$

$$\Phi'_G(r_1, r_2) = \exp\left(\frac{-z'}{\alpha r_0}(r_1 + r_2)\right) \tag{2.2}$$

The expression in equation (2.2), however, does not take account of the fact that, because of their mutual repulsion, the electron have reduced probability of being close together, as this expression is purely a product of single particle wave functins.however, one can take equation (2.2) as a starting point for the construction of a function basis, by multiplying $\Phi_{\overline{G}}$ by suitable factors. Hylleraas introduced the following basis functions, obtained in this way [4].

$$\hat{\Phi}_{jkm}(r_1, r_2) = (r_1 + r_2)^j (r_1 - r_2)^k \left|r_1 - r_2\right|^m \Phi'_G(r_1, r_2) \qquad (j, k, m \geq 0) \tag{2.3}$$

The tilde indicates that basis functions are not orthogonal to one another. Only even values are allowed for *k* [10], because the space wave function in the ground state must be symmetric with regard to interchange of the two electrons .The wave function is written as

$$\psi(r_1, r_2) = \sum_{j,k,m} \hat{a}_{jkm} \hat{\Phi}_{jkm}(r_1, r_2) \tag{2.4}$$

The elements of the function basis with $m > 0$ enable us to allow approximately for the effect of the mutual repulsion of electrons. In his historic calculation Hylleraas used only three states, namely (*j, k, m*)=(0,0,0), (0,0,1), (0, 2,0). In what follows we shall, for the sake of brevity, often denote the triad (*j, k, m*) by *n* [5].

The representation of the Schrodinger equation on the non-orthogonal basis equation (2.3) leads to the general eigenvalue equation

$$\sum_{n'} \left(\hat{H}_{nn'} - EN_{nn'}\right) \hat{a}_{n'} = 0 \tag{2.5}$$

with $$\hat{H}_{nn'} = <\hat{\Phi}_n \left| H \right| \hat{\Phi}_{n'}> \tag{2.6}$$

and $$\mathrm{N}_{nn'} = <\hat{\Phi}_n \left| \hat{\Phi}_{n'} \right.> \tag{2.7}$$

The matrix *N* occurring in equations (2.5) and (2.7) is called the ***norm matrix***. It contains all the information on the non-orthogonal of function basis equation (2.3). The matrix *N* is real

and symmetric [7]. Because of the linear independence of the basis it is also positive definite, i.e. all its eigenvalues are greater than zero. Also $N^{-1}N^{+½}$ and $N^{-½}$ therefore exist. With the matrix $N^{-½}$ we can orthonormalize the basis equation (2.3). We set

$$\Phi_n = \sum (N^{-1/2})_{nn'} \Phi_{n'} \tag{2.8}$$

where $(N^{-½})_{nn'}$ denote the nn' matrix element of the matrix $N^{-½}$ .The basis of the transformed states Φ_n is orthonormal.

$$< \Phi_n | \Phi_{n'} >= \sigma_{nn'} \tag{2.9}$$

For the matrix elements of *H* on the orthonormalised basis we obtain,

$$H_{nn'} =< \Phi | H | \Phi_{n'} >= \left(N^{-1/2} \hat{H} N^{-1/2} \right)_{nn'} \tag{2.10}$$

The last expression is again the nn' element of the matrix product in brackets. Finally we transform the co-efficient $\hat{a}_n$ occurring in equations (2.4) and (2.5). From

$$\psi = \sum_n \hat{a}_n \Phi_n = \sum_n a_n \Phi_n \tag{2.11}$$

And the transformation equation (2.8) one obtains,

$$\begin{aligned} \hat{a}_n &= \sum_{n'} (N^{-1/2})_{nn'} a_{n'}, \\ \hat{a}_n &= \sum_{n'} (N^{1/2})_{nn'} \hat{a}_{n'} \end{aligned} \tag{2.12}$$

We can now see how the basis transformation equation (2.8) affects the general eigenvalue equation (2.5). In matrix notation equation (2.5) read

$$(\hat{H} - NE)\hat{a} = 0 \tag{2.13}$$

where $\hat{a}$ denotes the column vector formed with the components $\hat{a}_n$. We insert the unit matrix in the form $1=N^{-½}NN^{½}$ in equation (2.10) between $(\hat{H} - NE)$ and $\hat{a}$, multiply by $N^{½}$ from the left and obtain $\left(N^{-1/2} \hat{H} N^{-1/2} - E N^{-1/2} N N^{-1/2} \right) N^{+1/2} \hat{a} = 0$ (2.14)

The expression $N^{-1/2} \hat{H} N^{-1/2}$ is equal to the matrix (Hnn') appearing in equation (2.7), the expression $N^{-1/2} \mathrm{N} N^{-1/2}$ is the unit matrix, and $N^{-1/2} \hat{a}$ is according to equation (2.12) equal to the column vector a with the components a_n.

Over the years since Hyllerass' original work, tremendous efforts have been made to improve upon that work, using larger and larger expansions, adding more complicated terms, etc., with the net result that the non-relativistic ground state energy of Helium's electrons is now known, to 35 significant figures to be [3] E = −2.903 72 . . . *a.u.*, a truly remarkable result. The orthonormalisation of the basis (2.4) has led from the general eigenvalue equation (2.5) via equation (2.1). Not only the eigenvalues but also the wave function ψ calculated from the eigenvectors is the same for both equations. With equation (2.1) we have also obtained a scheme by which the general eigenvalue equation can be solved numerically [8]. We shall therefore not explicitly carry out the orthonormalisation of the basis (2.1) in our program; instead we shall set up the general eigenvalue equation (2.2) and write a subroutine for the solution which works essentially according to the scheme of equation (2.11). The subroutine will have independent of the particular example that we are considering.

As matrix elements of the Hamilton operator we now have

$$\hat{H}_{nn'} = \hat{T}_{nn'} + \hat{C}_{nn'} + \hat{W}_{nn'} \qquad (3.15)$$

3.0 Results

Hylleraas constructed a relatively small number of basis states that are suited to the physical problem. The basis states contain a non-linear parameter α which may be freely varied .The matrix elements of the Hamilton operator depend on the variation parameter α, accordingly all the eigenvalues *Ej* and all the associated eigenvectors (a_n)j depend on the parameter α

We now applied the theorem of Hylleraas which states that the eigenvalues *Ej* of $\sum H_{nn'} a_{n'} = E_{ij} a_{nj}$, n=1,L ,D cannot be lower than the exact eigenvalues of the Schrödinger equation, regardless also of the dimension D and of the variation parameter α.[6].

The theorem of Hylleraas [5] is used not only to find the best approximation for the true eigenvalues, but also to assess the quality of the approximation. The calculation of the eigenvalues from $\sum H_{nn'} a_{n'} = E_{ij} a_{nj}, n = 1;\text{L}\ , D$ for various values of the variation parameter α and obtain the minimum for the eigenvalues in which we are interested. The minimum for the Dimension is 1 and the maximum is 20 in the program, otherwise the program will not run (The program will read error or it will be terminated). The basis state (*j, k, m*) must not be more than 3, which is $(j+k+m) \leq 3$.

For D = 1 using the basis state with the indices (*j, k, m*) = (0, 0, 1), (0, 2, 0) and (0, 0, 0) was used to plot the graph of energy against variation parameter (α) as shown in Figure 3.1 [9].

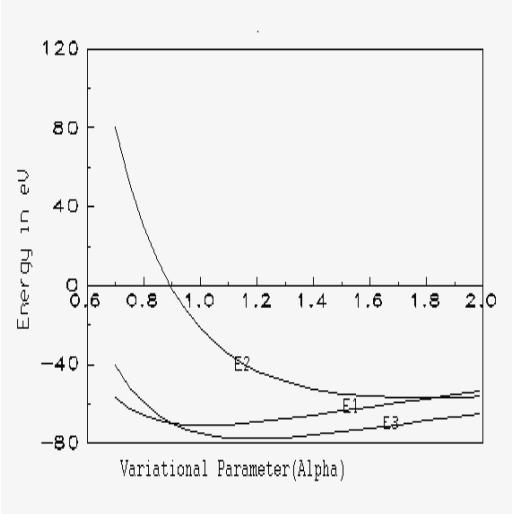

Figure 3.1: The graph of energy versus variation parameter α for the basis state (0,0,1), (0,2,0) and (0,0,0)

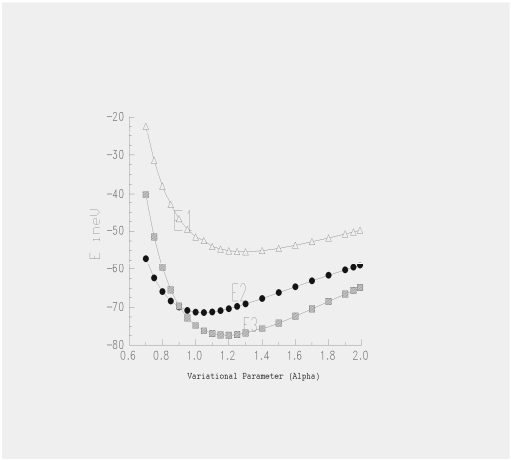

Figure 3.2: The graph of energy versus variation parameter α for the basis state the basis state (*j, k, m*) = (0,0,1), (0,2,0) for E1, for E2 with indices (0,1,1), (1,1,1) and for E3 with the indices (0,0,0), (0,1,0)

In figure 3.1, (E1) is a graph for basis state (0,0,1), the values of energy eigenvalues start from –56.808255*eV* at variation parameter α 0.70. The minimum values of the variation parameter lie at 1.00 of the eigenvalue –70.865695*eV* from the value its increase up to –53.752062*eV*.

In the above graph (E2) shows the basis state with the indices (0,2,0) which has positive values of the energy eigenvalue of all the basis state with dimension D = 1.The graph cut the variation parameter at 0.9,its increases up to –56.178614 of the eigenvalue.

The curve (E3) is a graph of the basis state (0, 0, 0), which enables us to treat the electron-electron interaction in the first order perturbation theory. As we can see at $\alpha = 1$ the basis state with the indices (j, k, m) = (0, 0, 0) we got the value calculated for the first order perturbation theory, which is –74.834174*eV* at the variation parameter of 1.00

For $D = 2$ with the basis state (j, k, m) = (0,0,1), (0,2,0) for E1, for E2 with indices (0,1,1), (1,1,1) and for E3 with the indices (0,0,0), (0,1,0) and we plot the graph of variation parameter (α) against the energy eigenvalues E in (electron Volts) as shows in figure 3.2

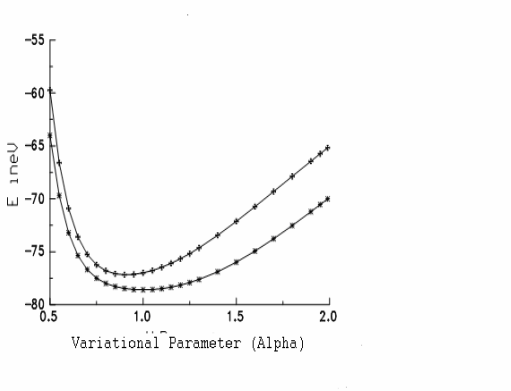

Figure 3.3: The graph energy versus variation parameter α for the basis state (j, k, m) = (2,0,0), (0,2,0), (0,0,2), (1,0,0), (0,1,0), (0,0,1) for E1 and (0,0,0), (1,1,1), (2,1,0), (1,0,2), (0,0,2), (1,0,1) for E2

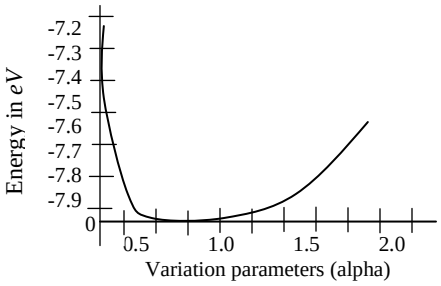

Figure 3.4: The graph energy versus variation parameter α for basis the basis state (j, k, m) = (0,0,0), (0,0,1), (0,1,0), (1,0,0), (2,0,0), (0,2,0), (0,0,2), (2,1,0), (2,0,1), (0,2,1), (0,1,2)

The minimum energy eigenvalue is -79.00679*eV* at $\alpha = 1.15$, which is almost the value, got by the experimental calculation of the ground state energy of the helium atom

For $D = 6$ at the basis state (j, k, m) = (2,0,0), (0,2,0), (0,0,2), (1,0,0), (0,1,0), (0,0,1) for E1 and (0,0,0), (1,1,1), (2,1,0), (1,0,2), (0,0,2), (1,0,1) for E2, we plot a graph of energy versus variation parameter α as shown in figure 3.3.

The minimum for El is -77.173893 at α=0.90 and for E2 is -78.593471 at α=1.00.

For $D = 13$with the basis state (j, k, m) = (2,1,0), (2,0,1), (0,2,1), (1,0,2), (0,1,2), (1,2,0), (0,0,0), (1,1,1), (1,1,0), (1,0,1), (0,1,1), (1,0,0), (0,0,1) the energy-variation parameter curve is as shown in figure 3.4.

Lastly for $D = 20$, which is the maximum value of dimension , we make use of all the possible values that (j,k,m) can accommodate which are between 0 and 3.The basis state are as follows (0,0,0), (0,0,1), (0,1,0), (1,0,0), (1,1,1), (1,1,0), (1,0,1), (0,1,1), (2,0,0), (0,2,0), (0,0,2), (1,2,0), (2,1,0), (2,0,1), (0,2,1), (1,0,2), (3,0,0), (0,3,0), (0,0,3), (0,1,2).

Using these we plot a graph of energy eigenvalue against variation parameter α as shown in figure 3.5.

The minimum of the ground state energy lies at $\alpha = 1.05$ and has the value -79.015104*eV*. Comparing with the historic calculation of Hylleraas the difference is only 0.0329*eV*, compared with the first order perturbation calculation the difference of about 4.2*eV*.

4.0 Conclusion

In general the basis state with $k = 0$ or 3 has no component of eigenvector. The element of the function basis with $m > 0$ enables us to allow approximation for the effect of the mutual repulsion of the electrons. We have seen that there is an improvement of the estimate for the energy obtained with $m > 0$ or $k > 0$, whereas the terms with $m = 0$, $k = 0$, $j > 0$ make little contribution. Even if we could solve the Schrödinger equation exactly, our ground state energy

would therefore differ from the experimental one by few hundredths of an *eV*. Since the experimental value for the ground state energy is -79.0*eV*, we have therefore already achieved the best possible agreement with a computational value of -79.015104*eV*.

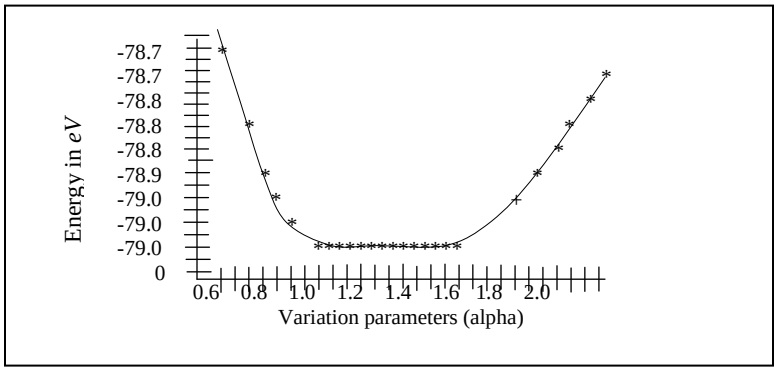

Figure 3.5: The graph energy versus variation parameter α for basis state are as follows (0,0,0), (0,0,1), (0,1,0), (1,0,0), (1,1,1), (1,1,0), (1,0,1), (0,1,1), (2,0,0), (0,2,0), (0,0,2), (1,2,0), (2,1,0), (2,0,1), (0,2,1), (1,0,2), (3,0,0), (0,3,0), (0,0,3), (0,1,2)

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