The Variational Method for Finding Energy Eigenstates: An Illustration Finding the Approximate Ground State and First Excited State of Helium

Last update: 28/1/10

1. The Method for the Ground State

For a given Hamiltonian, H, we want to find a means of approximating the ground state energy and the corresponding wavefunction when the problem is too difficult to solve exactly. The secret is that the ground state energy is lowest possible expectation value of the Hamiltonian. Of course, if we confine attention just to the energy eigenstates, then the fact that the ground state has the lowest energy is merely its definition. However, the statement just made is much stronger. For *any* function, ψ , not necessarily an eigenfunction, the expectation value for the energy, $\langle\psi|\hat{H}|\psi\rangle = \int \psi^* \hat{H}\psi \cdot dV$, must exceed the ground state energy. This is proved by recalling that the eigenstates of an Hermetian operator (such as the Hamiltonian) form a complete set. This means that an arbitrary function can be written as a linear superposition of eigenstates. Hence our arbitrary function can be expressed,

$$|\psi\rangle = \sum A_n |n\rangle \tag{1}$$

where $|n\rangle$ is the nth energy state, using as many quantum numbers as necessary. Normalisation ensures that,

$$\sum |A_n|^2 = 1 \tag{2}$$

But (1) means that,

$$\langle\psi|\hat{H}|\psi\rangle = \sum_{n,m} \langle m|A_m^* \hat{H} A_n|n\rangle = \sum_{n,m} \langle m|A_m^* E_n A_n|n\rangle = \sum_{n,m} \delta_{nm} A_m^* E_n A_n = \sum_n |A_n|^2 E_n \tag{3}$$

By virtue of (2) it is clear that (3) is a weighted average of the contributing energies, with the coefficients $|A_n|^2$ as the weighting factors. But this can only exceed the smallest energy contributing to the sum in (3), and hence must exceed the ground state energy, E_1.

This provides the basis of the variational method for approximating the ground state. A wavefunction $\psi(\bar{r}_1, \bar{r}_2, \ldots .a, b, \ldots)$ is postulated which, as well as depending upon the particle positions, $\bar{r}_1, \bar{r}_2, \ldots$ also depends upon some unspecified constants, a, b,… It follows that the best approximation to the ground state which has this postulated algebraic form is that which minimises the expectation value of the Hamiltonian with respect to variations in these constants. Hence, the variational method consists of evaluating $\langle\psi|\hat{H}|\psi\rangle = \int \psi^* \hat{H}\psi \cdot d^3r_1 d^3r_2 \ldots$ for the trial function and then requiring that,

$$\frac{\partial\langle\psi|\hat{H}|\psi\rangle}{\partial a} = \frac{\partial\langle\psi|\hat{H}|\psi\rangle}{\partial b} = \ldots = 0 \tag{4}$$

(and, of course, ensuring that this turning point is a minimum, not a maximum). In practice the method will only work well if a good choice of trial function is made. This should be inspired by what is known about the problem and hence what shape the wavefunction is likely to take.

2. Illustration: The Ground State of Helium

The workings of the method will be laid out in detail for the first excited state of helium later. Hence we only show the bare bones of the method for the ground state (which involves far simpler algebra). The Hamiltonian is,

$$\hat{H} = -\frac{\hbar^2}{2}\left(\nabla_1^2 + \nabla_2^2\right) - 2\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \qquad (5)$$

The first term in (5) is the sum of the kinetic energies of the two electrons. The second term is the sum of the potential energies of the two electrons due to their electrostatic attraction to the helium nucleus. The latter has charge 2*e*, hence the factor of 2 in front of this term. The attractive potential is negative in sign. The last term is what prevents us from finding the exact solution. It is the potential due to the mutual electrostatic repulsion between the electrons (and hence is positive in sign). It depends upon the distance between the two electrons, $r_{12} = \left|\bar{r}_1 - \bar{r}_2\right|$.

[*Henceforth we shall drop the factors of* $4\pi\varepsilon_0$ *in the denominators, which merely define the units. They can be reinstated later if desired*].

We know that the ground state solution for a single electron orbiting a nucleus of charge *Ze* is,

$$\psi_1(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \qquad (6)$$

where $a_0 = \frac{\hbar^2}{me^2}$ is the Bohr radius (0.53 x 10^{-10} m). This motivates the use of a trial function which has identical form to (6), for both electrons, i.e.,

$$\psi_{GS}^{He}(r_1, r_2) = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-Z(r_1+r_2)/a_0} \qquad (7)$$

However, we allow the parameter *Z* to differ from the value 2 it would have for a single electron. This is because we anticipate that the nuclear charge experienced by one electron will be partly shielded by the other electron. Thus we anticipate that *Z* will turn out to be less than 2. The expectation value of the energy is found by substituting (5) and (7) into,

$$\langle E \rangle = \int\int \psi_{GS}^{He*}(r_1, r_2)\hat{H}\psi_{GS}^{He}(r_1, r_2) d^3r_1 d^3r_2 \qquad (8)$$

The result is,

$$\langle E \rangle = \frac{e^2}{a_0}\left(Z^2 - \frac{27}{8}Z\right) \qquad (9)$$

The minimum of $\langle E \rangle$ with respect to variations in *Z* is thus at $Z = \frac{27}{16}$ and is,

$$\langle E \rangle_{\min} = -2.85\frac{e^2}{a_0} \approx E_{GS} \qquad (10)$$

This is our approximation to the ground state energy. The actual value is $-2.904\frac{e^2}{a_0}$, so (10) is a good approximation given the simplicity of the trial function.

As expected, the optimal value for Z is indeed less than 2.

3. The Variational Method for the First Excited State

The method is essentially the same for the first excited state as for the ground state. The only difference is that we must now confine attention to the space of functions which are orthogonal to the ground state function. We know this must include the first excited state (indeed, all the excited states). The sum, (1), now excludes the ground state, *n* = 1. But the first excited state has the smallest energy of all eigenstates in this sub-space. Hence, by the same argument as before, there is no function in this sub-space with as low an energy as the first excited state. Hence we can again use a trial function and minimise its expectation energy with respect to free parameters as a means of approximating the first excited state – provided that we have already found a suitable approximation for the ground state wavefunction and ensure that the trial wavefunction for the excited state is constrained to be orthogonal to it.

4. The First Excited State of Helium

4.1 The Form of the Trial Wavefunction

We start from a knowledge of the ground state, which is approximately,

$$\psi_{GS}^{He}(r_1, r_2) = \frac{1}{\pi}\left(\frac{Z_0}{a_0}\right)^3 e^{-Z_0(r_1+r_2)/a_0} \qquad (11)$$

The subscript denotes that we have fixed the *Z* parameter appearing in the ground state wavefunction to be $Z_0 = \frac{27}{16}$. We must now find a trial wavefunction for the first excited state. It is reasonable to assume that this will involve one of the electrons remaining in a $1S$ state whilst the other is excited to a $2S$ state. This means that it is reasonable to use, as a trial function for the first electron, a function like (6). Note, though, that the *Z* parameter might differ from Z_0 because the fact that the second electron is likely to be further away from the nucleus will mean that it shields less the first electron from the nucleus. Calling the Z parameter for the first electron Z_1, we expect that $Z_1 > Z_0$. However, in addition to the *Z* parameter being different, the radius parameter, a_0, might be different as well. Hence we write the wavefunction of the first electron as,

$$\psi_1(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z_1}{a_1}\right)^{3/2} e^{-Z_1 r/a_1} \qquad (12)$$

The 2*S* state in hydrogen is given by a wavefunction,

$$\psi_2(r) = \frac{1}{\sqrt{4\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2 - \frac{Z}{a_0}r\right)e^{-Zr/2a_0} \qquad (13)$$

Hence it is reasonable to use this functional form for the second (excited) electron. Again the parameters *Z* and/or a_0 will be varied to find the minimum energy, so we write the state of the second electron as,

$$\psi_2(r) = \frac{1}{\sqrt{4\pi}} \left(\frac{Z_2}{2a_2} \right)^{3/2} \left(2 - \frac{Z_2}{a_2} r \right) e^{-Z_2 r / 2a_2} \tag{14}$$

Note that (12) and (14) are normalised. But they would only be orthogonal if $\frac{Z_2}{a_2} = \frac{Z_1}{a_1}$. Because the second electron is further away from the nucleus than the first electron, we actually expect $\frac{Z_2}{a_2} < \frac{Z_1}{a_1}$. So (12) and (14) are *not* orthogonal. However, this is not as serious as it seems, because (12) and (14) are not yet a viable form of wavefunction.

The reason is that multi-electron wavefunctions must be anti-symmetric under interchange of any pair of electrons. This follows from the fact that electrons are fermions, and the spin-statistics theorem – and is essentially a generalisation of the Pauli Exclusion Principle. In addition, we have not yet specified the spin part of the wavefunction. Let us do that first. There are four possible spin states of two electrons. They are,

Spin 0 – the singlet state:

$$|\psi_S\rangle = \frac{1}{\sqrt{2}} \left[|\uparrow\rangle|\downarrow\rangle - |\uparrow\rangle|\uparrow\rangle \right] \tag{15}$$

Spin 1 – the triplet of states,

$$|\psi_{T+}\rangle = |\uparrow\rangle|\uparrow\rangle; \qquad |\psi_{T0}\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle \right); \qquad |\psi_{T-}\rangle = |\downarrow\rangle|\downarrow\rangle \tag{16}$$

which respectively have z-components of spin of +1, 0 and -1. In each term, the first ket represents the first electron, and the second ket the second electron. So it is clear that the singlet spin state, (15), is anti-symmetric under interchange of the two electrons, whereas the triplet states are all symmetric under interchange.

However, it is the *overall* wavefunction – the product of both the spatial and the spin parts – which must be anti-symmetric. Consequently, because the ground state spatial wavefunction, (11), is symmetric under interchange, it must be paired with the anti-symmetric singlet spin state (i.e., the ground state has spin zero). Hence, the complete expression for the ground state is,

$$\psi_{GS}^{He}(r_1, r_2)|\psi_S\rangle \tag{17}$$

We can make both a symmetric and an anti-symmetric spatial wavefunction out of (12) and (14), as follows,

$$\psi_{\pm}(r_1, r_2) = \frac{1}{\sqrt{2}} \left[\psi_1(r_1)\psi_2(r_2) \pm \psi_1(r_2)\psi_2(r_1) \right] \tag{18}$$

Whilst r_1 and r_2 label the positions of the first and second electron respectively, we have no way of knowing which is which because they are identical. Hence both terms in (17) are equally possible – but the spin-statistics theorem tells us that the overall wavefunction must be anti-symmetric. We can achieve this in two ways,

Singlet:

$$\psi_+(r_1, r_2)|\psi_S\rangle \tag{19}$$

Triplet:

$$\psi_-(r_1, r_2)|\psi_T\rangle \tag{20}$$

The singlet state, (19), is the product of a symmetric spatial state and an anti-symmetric spin state – so is anti-symmetric overall. The triplet states, (20), are products of an anti-symmetric spatial state and one of the symmetric triplet spin states – so they are again anti-symmetric overall.

Which of (19) or (20) do we need? At this stage we do not know, and so we will work with both of them.

4.2 Orthogonality

We require our trial wavefunction for the excited state to be orthogonal to the ground state wavefunction given by (11) and (17) – and this must be true for arbitrary values of the variable parameters (because we do not yet know what values they will take). It is easy to see that the triplet states, (20), are orthogonal to the ground state. The orthogonality of the spin states is enough to ensure this. But the spatial parts of the states are also orthogonal, by virtue of their product being an anti-symmetric function it must vanish when integrated over the whole product volume $d^3r_1d^3r_2$.

We need to work harder to see if the singlet state, (19) is orthogonal to the ground state, (17). The spin states are the same and so their scalar product is unity. Hence we require $\int\psi_{GS}^{He}(r_1,r_2)\psi_+(r_1,r_2)d^3r_1d^3r=0$. Substituting (11, 12, 14, 18) into this gives,

$$\begin{aligned}
\int\psi_{GS}^{He}(r_1,r_2)\psi_+(r_1,r_2)d^3r_1d^3r &= \frac{1}{4\pi^2}\left(\frac{Z_1Z_2}{a_1a_2}\right)^{3/2}\left(\frac{Z_0}{a_0}\right)^3\int\left(2-\frac{Z_2}{a_2}r\right)e^{-Z_0(r_1+r_2)/a_0}e^{-Z_2r_2/2a_2}e^{-Z_1r_1/a_1}d^3r_1d^3r_2\\
&=4\left(\frac{Z_1Z_2}{a_1a_2}\right)^{3/2}\left(\frac{Z_0}{a_0}\right)^3\int\left(2-\frac{Z_2}{a_2}r\right)e^{-Z_0(r_1+r_2)/a_0}e^{-Z_2r_2/2a_2}e^{-Z_1r_1/a_1}r_1^2dr_1r_2^2dr_2\\
&=4\left(\frac{Z_1Z_2}{a_1a_2}\right)^{3/2}\left(\frac{Z_0}{a_0}\right)^3\cdot 2\left(\frac{Z_0}{a_0}+\frac{Z_1}{a_1}\right)^{-3}\left\{4\left(\frac{Z_0}{a_0}+\frac{Z_2}{2a_2}\right)^{-3}-6\frac{Z_2}{a_2}\left(\frac{Z_0}{a_0}+\frac{Z_2}{2a_2}\right)^{-4}\right\}\\
&=8\left(\frac{Z_1Z_2}{a_1a_2}\right)^{3/2}\left(\frac{Z_0}{a_0}\right)^3\left(\frac{Z_0}{a_0}+\frac{Z_1}{a_1}\right)^{-3}\left(\frac{Z_0}{a_0}+\frac{Z_2}{2a_2}\right)^{-4}\left\{4\left(\frac{Z_0}{a_0}+\frac{Z_2}{2a_2}\right)-6\frac{Z_2}{a_2}\right\}\\
&=32\left(\frac{Z_1Z_2}{a_1a_2}\right)^{3/2}\left(\frac{Z_0}{a_0}\right)^3\left(\frac{Z_0}{a_0}+\frac{Z_1}{a_1}\right)^{-3}\left(\frac{Z_0}{a_0}+\frac{Z_2}{2a_2}\right)^{-4}\left\{\frac{Z_0}{a_0}-\frac{Z_2}{a_2}\right\}
\end{aligned}\tag{21}$$

where we have used some standard integrals which will be derived later. We see that the requirement that (21) be zero can be met only if,

$$\frac{Z_2}{a_2}=\frac{Z_0}{a_0}\tag{22}$$

Consequently we have two possibilities for the first excited state. We can use the triplet state, (20), in which case we can minimise with respect to both variations in $\frac{Z_1}{a_1}$ and in $\frac{Z_2}{a_2}$, because the triplet state is orthogonal to the ground state for arbitrary values of both these parameters. Alternatively, we can use the singlet state, (19), but in this case we are allowed to minimise with respect to variations in $\frac{Z_1}{a_1}$ only, because the value of $\frac{Z_2}{a_2}$ is fixed to equal that for the ground state, by (22). It is not clear which might give the smallest minimum energy so we pursue both options.

4.3 Standard Integrals

4.3.1 Radial Integrals

Our task will be to evaluate the expectation value of the Hamiltonian in (5) for the state given by either (19) or (20). Since the Hamiltonian (at least in our approximation) is not dependent upon spin, this becomes evaluation of,

$$\langle E\rangle_{\pm} = \int \psi_{\pm}(r_1, r_2)\left[-\frac{\hbar^2}{2}\left(\nabla_1^2 + \nabla_2^2\right) - 2\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]\int \psi_{\pm}(r_1, r_2)d^3r_1 d^3r_2 \quad (23)$$

The first two terms, the kinetic energy and the attractive potential energy, can be evaluated in terms of radial integrals of the form,

$$I_n = \int_0^\infty r^n e^{-\alpha r} dr \quad (24)$$

It is simple to show $\qquad I_0 = \frac{1}{\alpha} \qquad (25)$

Integration by parts gives the induction formula $I_n = \frac{n}{\alpha} I_{n-1}$, so that we find,

$$I_1 = \frac{1}{\alpha^2} \qquad I_2 = \frac{2}{\alpha^3} \qquad I_3 = \frac{6}{\alpha^4} \qquad I_4 = \frac{24}{\alpha^5} \quad (26)$$

We have already used the results for I_2 and I_3 in evaluating (21).

Evaluation of the last term in (23), the electron-electron interaction, also requires radial integrals over a finite range. These are also easily evaluated by parts and are,

$$\int_0^r x e^{-\alpha x} dx = \frac{1}{\alpha^2} - \left(\frac{1}{\alpha^2} + \frac{r}{\alpha}\right)e^{-\alpha r} \qquad \int_r^\infty x e^{-\alpha x} dx = \left(\frac{1}{\alpha^2} + \frac{r}{\alpha}\right)e^{-\alpha r} \quad (27)$$

$$\int_0^r x^2 e^{-\alpha x} dx = \frac{2}{\alpha^3} - \left[\frac{2}{\alpha^3} + \frac{2r}{\alpha^2} + \frac{r^2}{\alpha}\right]e^{-\alpha r} \qquad \int_r^\infty x^2 e^{-\alpha x} dx = \left[\frac{2}{\alpha^3} + \frac{2r}{\alpha^2} + \frac{r^2}{\alpha}\right]e^{-\alpha r} \quad (28)$$

$$\int_0^r x^3 e^{-\alpha x} dx = \frac{6}{\alpha^4} - \left[\frac{6}{\alpha^4} + \frac{6r}{\alpha^3} + \frac{3r^2}{\alpha^2} + \frac{r^3}{\alpha}\right]e^{-\alpha r} \quad \int_r^\infty x^3 e^{-\alpha x} dx = \left[\frac{6}{\alpha^4} + \frac{6r}{\alpha^3} + \frac{3r^2}{\alpha^2} + \frac{r^3}{\alpha}\right]e^{-\alpha r}$$

(29)

4.3.2 Angular Integrals

Only the third term in (23), the electron-electron interaction, will require angular integration. It turns out that the angular integral can be accomplished painlessly by making use of the following expansion in terms of the Legendre polynomials,

$$\frac{1}{r_{12}}=\frac{1}{r_L}\sum_{l=0}^{\infty}\left(\frac{r_S}{r_L}\right)^l P_l(\cos\theta) \tag{30}$$

where θ is the angle between the two position vectors, $\cos\theta=\hat{r}_1\cdot\hat{r}_2$, and r_L, r_S refer to the larger and the smaller of r_1, r_2 respectively. The use of (3) together with the addition theorem for the Legendre functions, and their orthogonality, reveals that only the $l=0$ term is non-zero in double-volume integrals of functions of the form $f(r_1,r_2)/r_{12}$. Specifically,

$$\iint\frac{f(r_1,r_2)}{r_{12}}d^3r_1d^3r_2=(4\pi)^2\int_0^\infty\int_0^\infty\frac{f(r_1,r_2)}{r_L}r_1^2r_2^2dr_1dr_2 \tag{31}$$

To evaluate the RHS it is necessary to split the inner integral into two finite ranges, according to whether r_L equates to r_1 or r_2. So we get,

$$\iint\frac{f(r_1,r_2)}{r_{12}}d^3r_1d^3r_2=(4\pi)^2\left[\int_0^\infty r_2dr_2\int_0^{r_2}f(r_1,r_2)r_1^2dr_1+\int_0^\infty r_2^2dr_2\int_{r_2}^\infty f(r_1,r_2)r_1\,dr_1\right] \tag{32}$$

The inner integrals are evaluated with the aid of (27-29).

4.4 Evaluation of the Kinetic Energy

Because the wavefunctions have no angular dependence, the kinetic energy operator reduces to,

$$\hat{K}=-\frac{\hbar^2}{2m}\left[\frac{1}{r_1^2}\partial_{r_1}\left(r_1^2\partial_{r_1}\right)+\frac{1}{r_2^2}\partial_{r_2}\left(r_2^2\partial_{r_2}\right)\right] \tag{33}$$

But we shall be evaluating the expectation value for states which are symmetric or anti-symmetric when $r_1\leftrightarrow r_2$, so that both terms in (33) give equal results. So for this purpose we can effectively replace $\hat{K}$ by,

$$\hat{K}=-\frac{\hbar^2}{m}\frac{1}{r_1^2}\partial_{r_1}\left(r_1^2\partial_{r_1}\right) \tag{34}$$

Using (18) we thus have, (35)

$$\langle\psi_\pm|\hat{K}|\psi_\pm\rangle=$$

$$-\frac{\hbar^2}{2m}\iint(\psi_1(r_1)\psi_2(r_2)\pm\psi_1(r_2)\psi_2(r_1))\left(\left[\frac{1}{r_1^2}\partial_{r_1}\left(r_1^2\partial_{r_1}\right)\psi_1(r_1)\right]\psi_2(r_2)\pm\psi_1(r_2)\left[\frac{1}{r_1^2}\partial_{r_1}\left(r_1^2\partial_{r_1}\right)\psi_2(r_1)\right]\right)d^3r_1d^3r_2$$

If $Z_1/a_1=Z_2/a_2$, then we would have $\int\psi_1(r)\cdot\psi_2(r)d^3r=0$. But we do not wish to assume this because it limits our freedom to vary these parameters to optimise the minimum. In fact, in the case of the singlet state, because we require $Z_2/a_2=Z_0/a_0$, there would be no free parameter left and the method would fail. So we assume that $Z_1/a_1\neq Z_2/a_2$ in which case $\int\psi_1(r)\cdot\psi_2(r)d^3r\neq0$.

Leaving out the integration variables and integration measure, in an obvious shorthand, and writing $\hat{R}=\frac{1}{r_1^2}\partial_{r_1}\left(r_1^2\partial_{r_1}\right)$, (35) becomes,

$$\langle K\rangle_\pm = -\frac{\hbar^2}{2m}\left\{\int\psi_1\hat{R}\psi_1 + \int\psi_2\hat{R}\psi_2 \pm \left(\int\psi_1\psi_2\right)\left[\int\psi_2\hat{R}\psi_1 + \int\psi_1\hat{R}\psi_2\right]\right\} \tag{36}$$

where we have used the normalisation conditions, $\int\psi_1\psi_1 = \int\psi_2\psi_2 = 1$. Carrying out the differentiations on the explicit expressions (12) and (14) gives,

$$\hat{R}\psi_1(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z_1}{a_1}\right)^{3/2}\left[\left(\frac{Z_1}{a_1}\right)^2 - \frac{2}{r}\cdot\frac{Z_1}{a_1}\right]e^{-Z_1 r/a_1} \tag{37}$$

$$\hat{R}\psi_2(r) = \frac{1}{\sqrt{4\pi}}\left(\frac{Z_2}{2a_2}\right)^{3/2}\left[-\left(\frac{Z_2}{a_2}\right)^3\frac{r}{4} + \frac{5}{2}\left(\frac{Z_2}{a_2}\right)^2 - \frac{4}{r}\left(\frac{Z_2}{a_2}\right)\right]e^{-Z_2 r/2a_2} \tag{38}$$

All the integrals in (36) may then be evaluated using the standard integrals given in §4.3. We find,

$$\int\psi_1\psi_2 = 8\left(\frac{Z_1 Z_2}{2a_1 a_2}\right)^{3/2}\left(\frac{Z_1}{a_1} + \frac{Z_2}{2a_2}\right)^{-4}\left[\frac{Z_1}{a_1} - \frac{Z_2}{a_2}\right] \tag{39}$$

$$\int\psi_1\hat{R}\psi_1 = -\left(\frac{Z_1}{a_1}\right)^2 \tag{40}$$

$$\int\psi_2\hat{R}\psi_2 = -\left(\frac{Z_2}{2a_2}\right)^2 \tag{41}$$

$$\int\psi_2\hat{R}\psi_1 = -8\left(\frac{Z_1 Z_2}{2a_1 a_2}\right)^{3/2}\left(\frac{Z_1}{a_1}\right)^2\left(\frac{Z_1}{a_1} + \frac{Z_2}{2a_2}\right)^{-4}\left[\frac{Z_1}{a_1} + 2\frac{Z_2}{a_2}\right] \tag{42}$$

$$\int\psi_1\hat{R}\psi_2 = -2\left(\frac{Z_1 Z_2}{2a_1 a_2}\right)^{3/2}\left(\frac{Z_1 Z_2}{a_1 a_2}\right)\left(\frac{Z_1}{a_1} + \frac{Z_2}{2a_2}\right)^{-4}\left[4\frac{Z_1}{a_1} - \frac{Z_2}{a_2}\right] \tag{43}$$

Each of (39-43) is a volume integral. Substitution of (39-43) into (36) gives,

$$\langle K\rangle_\pm = \frac{\hbar^2}{2m}\left[\left(\frac{Z_1}{a_1}\right)^2 + \frac{1}{4}\left(\frac{Z_2}{a_2}\right)^2 \pm X\right] \tag{44}$$

where,

$$X = 2\left(\frac{Z_1 Z_2}{a_1 a_2}\right)^3\left(\frac{Z_1}{a_1}\right)\left(\frac{Z_1}{a_1} - \frac{Z_2}{a_2}\right)\left(\frac{Z_1}{a_1} + \frac{Z_2}{2a_2}\right)^{-8}\left[4\left(\frac{Z_1}{a_1}\right)^2 - \left(\frac{Z_2}{a_2}\right)^2 + 12\left(\frac{Z_1 Z_2}{a_1 a_2}\right)\right]$$

(45)

4.5 Evaluation of the Attractive Potential Energy

The negative potential energy due to the attraction of the electrons to the nucleus is,

$$\langle P_{nuc}\rangle_\pm = -2e^2\iint\psi_\pm(r_1,r_2)\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi_\pm(r_1,r_2)d^2r_1 d^3r_2 = -4e^2\iint\frac{(\psi_\pm(r_1,r_2))^2}{r_1}d^2r_1 d^3r_2 \tag{46}$$

Substituting (18) into (46) we get, using shorthand for the volume integrals again,

$$\left\langle P_{nuc} \right\rangle_{\pm} = -2e^2 \left\{ \int \frac{\psi_1^2}{r} + \int \frac{\psi_2^2}{r} \pm 2\left(\int \psi_1 \psi_2 \right) \left(\int \frac{\psi_1 \psi_2}{r} \right) \right\} \tag{47}$$

The integral $\int \psi_1 \psi_2$ is given by (39). The rest evaluate using §4.3 to,

$$\int \frac{\psi_1^2}{r} = \frac{Z_1}{a_1} \qquad \int \frac{\psi_2^2}{r} = \frac{Z_2}{4a_2} \tag{48}$$

$$\frac{\int \psi_1 \psi_2}{r} = 4\left(\frac{Z_1 Z_2}{2a_1 a_2} \right)^{3/2} \left(\frac{Z_1}{a_1} + \frac{Z_2}{2a_2} \right)^{-3} \left[\frac{Z_1}{a_1} - \frac{Z_2}{2a_2} \right] \tag{49}$$

So we get,

$$\left\langle P_{nuc} \right\rangle_{\pm} = -2e^2 \left\{ \frac{Z_1}{a_1} + \frac{Z_2}{4a_2} \pm Y \right\} \tag{50}$$

where, $$Y = 8\left(\frac{Z_1 Z_2}{a_1 a_2} \right)^3 \left(\frac{Z_1}{a_1} + \frac{Z_2}{2a_2} \right)^{-7} \left(\frac{Z_1}{a_1} - \frac{Z_2}{a_2} \right) \left[\frac{Z_1}{a_1} - \frac{Z_2}{2a_2} \right] \tag{51}$$

4.6 Evaluation of the Electron-Electron Interaction Energy

The positive energy due to the electrostatic repulsion between the two electrons is,

$$\begin{aligned} \left\langle P_{ee} \right\rangle_{\pm} &= e^2 \iint \frac{(\psi_{\pm}(r_1, r_2))^2}{r_{12}} d^2 r_1 d^3 r_2 = e^2 \iint \frac{(\psi_1(r_1)\psi_2(r_2) \pm \psi_1(r_2)\psi_2(r_1))^2}{r_{12}} d^2 r_1 d^3 r_2 \\ &= e^2 \iint \frac{\left((\psi_1(r_1)\psi_2(r_2))^2 + (\psi_1(r_2)\psi_2(r_1))^2 \pm 2\psi_1(r_1)\psi_2(r_1)\psi_1(r_2)\psi_2(r_2) \right)}{r_{12}} d^2 r_1 d^3 r_2 \\ &= \left\langle P_{ee} \right\rangle_1 \pm \left\langle P_{ee} \right\rangle_2 \end{aligned} \tag{52}$$

where,

$$\left\langle P_{ee} \right\rangle_1 = 2e^2 \iint \frac{\psi_1^2(r_1)\psi_2^2(r_2)}{r_{12}} d^3 r_1 d^3 r_2 \tag{53}$$

$$\left\langle P_{ee} \right\rangle_2 = 2e^2 \iint \frac{\psi_1(r_1)\psi_2(r_1)\psi_1(r_2)\psi_2(r_2)}{r_{12}} d^3 r_1 d^3 r_2 \tag{54}$$

Substituting (12) and (14) and carrying out the integrals gives,

$$\left\langle P_{ee} \right\rangle_1 = \frac{e^2 \alpha_2^3}{2} \left[\frac{1}{\alpha_2^2} - \frac{4\alpha_1^3 + 3\alpha_1 \alpha_2^2 + \alpha_2^3}{(\alpha_1 + \alpha_2)^5} \right] \tag{55}$$

$$\left\langle P_{ee} \right\rangle_2 = \frac{e^2}{\alpha_3^5} \left(\frac{\alpha_1 \alpha_2}{2} \right)^3 \left[5 - \frac{25}{2} \cdot \frac{\alpha_2}{\alpha_3} + \frac{33}{4} \cdot \left(\frac{\alpha_2}{\alpha_3} \right)^2 \right] \tag{56}$$

where, $$\alpha_1 = \frac{2Z_1}{a_1} \text{ and } \alpha_2 = \frac{Z_2}{a_2} \text{ and } \alpha_3 = \frac{\alpha_1 + \alpha_2}{2} \tag{57}$$

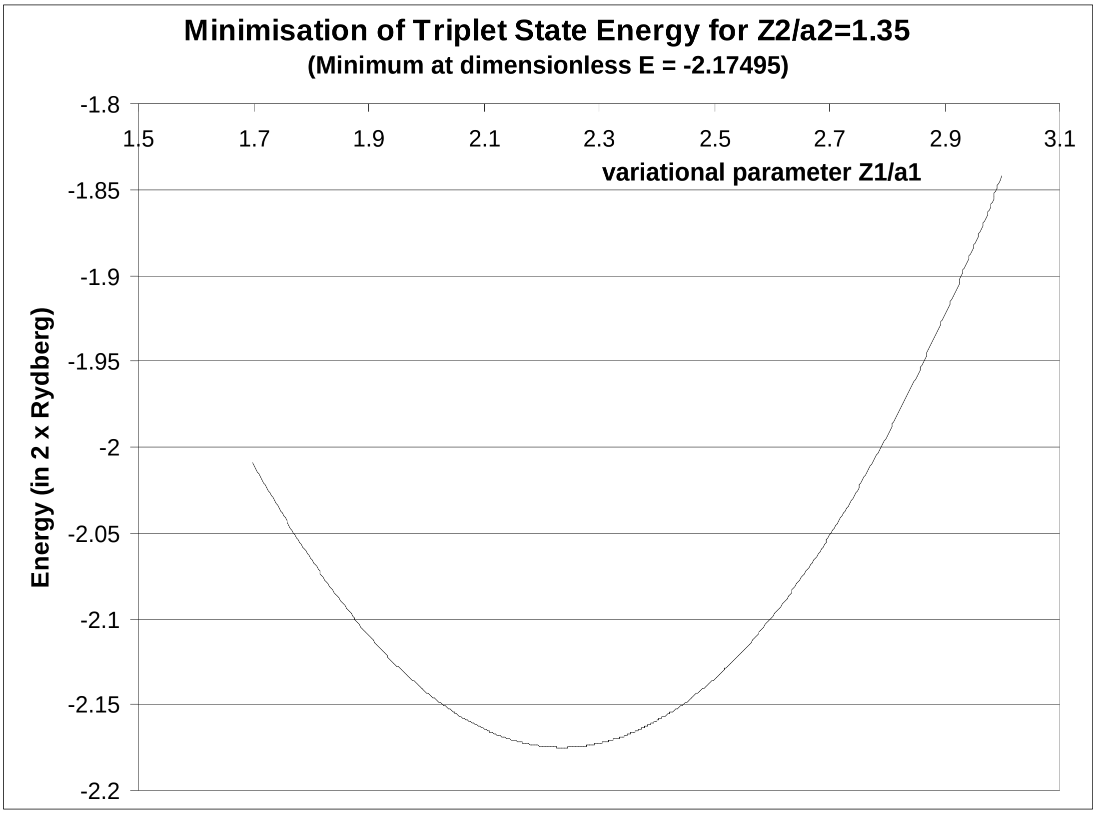
4.7 Minimisation of the Total Energy

Combining together (44,45,50,51,55,56,57) we get the total energy to be,

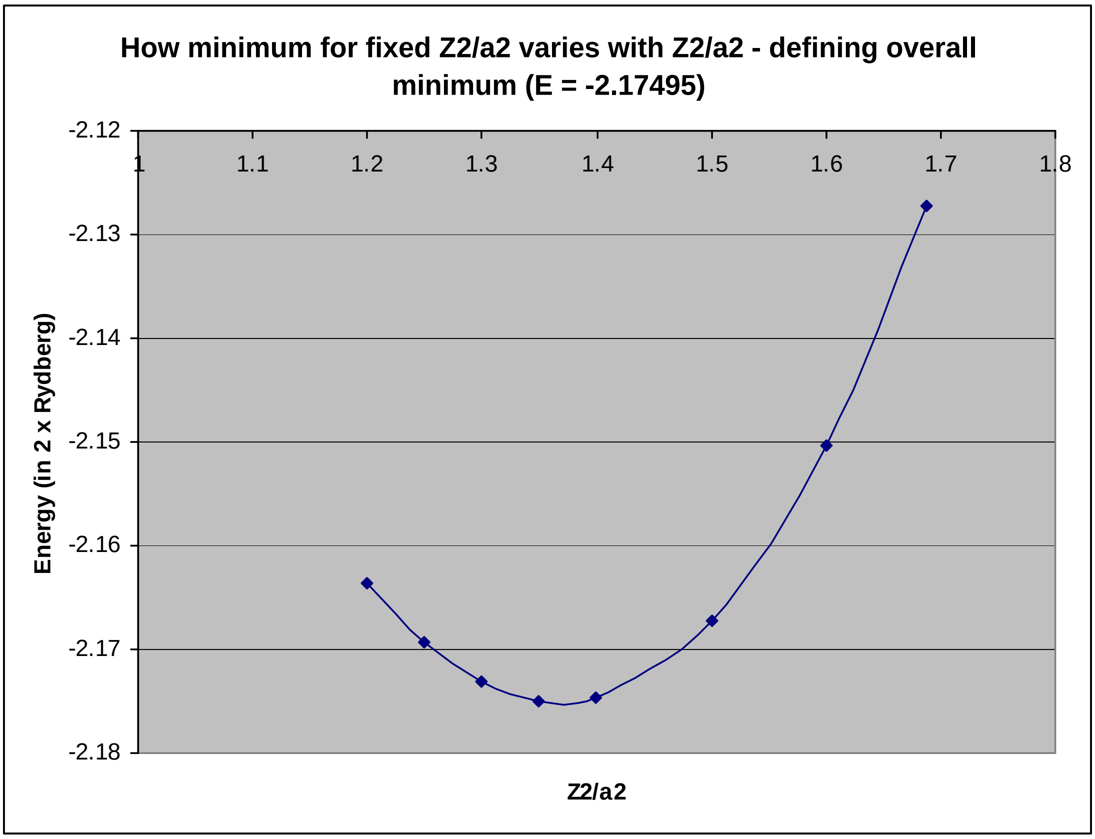
$$\begin{aligned}\langle E\rangle_{\pm} &= \frac{a_0 e^2}{8}\left[\alpha_1^2+\alpha_2^2\pm 2^6(\alpha_1\alpha_2)^3(\alpha\ \ )(\alpha_1-2\alpha_2)(\alpha_1+\alpha_2)^{-8}\left[\alpha_1^2-\alpha_2^2+6\alpha_1\alpha_2\right]\right]\\ &-e^2\left\{\alpha_1+\frac{\alpha_2}{2}\pm 2^6(\alpha_1\alpha_2)^3(\alpha_1+\alpha_2)^{-7}(\alpha_1-2\alpha_2)[\alpha_1-\alpha_2]\right\} \qquad (58)\\ &+\frac{e^2\alpha_2^3}{2}\left[\frac{1}{\alpha_2^2}-\frac{4\alpha_1^3+3\alpha_1\alpha_2^2+\alpha_2^3}{(\alpha_1+\alpha_2)^5}\right]\pm\frac{e^2}{\alpha_3^5}\left(\frac{\alpha_1\alpha_2}{2}\right)^3\left[5-\frac{25}{2}\cdot\frac{\alpha_2}{\alpha_3}+\frac{33}{4}\cdot\left(\frac{\alpha_2}{\alpha_3}\right)^2\right]\end{aligned}$$

Firstly we attempt to find a sensible solution for the singlet state, i.e., using the + sign in (58). In this case we are obliged to keep α_2 fixed at 27/16 [see (22)]. The result is a minimum energy of -1.71534 in units of $e^2/a_0=\alpha^2 mc^2=27.23eV$, i.e. an energy of -46.71eV. But the ground state energy of helium is -2.904 in units of $\alpha^2 mc^2$, i.e., an energy of -79.08eV. So this 'solution' would be 79.08 – 46.71 = 32.37eV above the ground state. But the first ionisation potential of helium is only 24.6eV, so this is drastically wrong. We conclude that the triplet state must be the better bet, i.e., it must be the triplet state which has the lower energy.

Hence we now take the – sign in (58), and we can now minimise with respect to both α_1 and α_2 as free parameters [though α_3 is then fixed by virtue of (57)]. The minimum has been found numerically. Firstly α_2 is kept fixed at a guessed value, and the minimum with respect to α_1 is found, plotting a graph like…



The minimum with respect to α_1 is found for a range of α_2 values, plotting the results against α_2 as follows,



Thus, the overall minimum is seen to be E = -2.17495 in $\alpha^2 mc^2 = 27.23eV$ units, i.e., -59.224eV. With respect to the ground state energy of helium, -79.08eV, this is an excitation energy of 79.08 – 59.224 = **19.856eV**.

The spectrum of helium gives the first transition line at a wavenumber of 159,855.9745 cm^{-1}. Translating to energy units this is **19.850eV**. Hence our estimate really is remarkably accurate – which is extremely gratifying after the rather heavy algebra.

Since the first ionisation potential of helium is 24.6eV (though we have not demonstrated this) the excited electron can be regarded as 24.6 – 19.85 = 4.75eV below being free, i.e., at an energy of -4.75eV. Interpreted in this manner it implies that the 1S electron must have an energy of -59.224 – (-4.75) = -54.47eV, which, of course, is just the second ionisation potential.

Our solution for the 2S triplet states achieves its minimum energy for $\frac{Z_1}{a_1} = 2.2356$ and $\frac{Z_2}{a_2} = 1.35$. Thus, the 'outer' (2S) electron is shielded even more from the nucleus than it was in the ground state, for which $\frac{Z_0}{a_0} = 1.6875$. This is, of course, what we would expect. On the other hand, the inner electron is shielded less, since $\frac{Z_1}{a_1} > \frac{Z_0}{a_0}$. In fact, the value of $\frac{Z_1}{a_1}$ is greater than 2. This suggests that $Z_1 \approx 2$ (little shielding) and that

$a_1 < a_0$. The latter condition merely means that the inner electron is held closer to the doubly charged helium nucleus than a single electron would be to the singly charged hydrogen nucleus. Again, not at all surprising.

Note that we have not found the next highest state, which would turn out to be the 2S singlet state. To do so we would need to contrive a trial state orthogonal to both the lower two states and with free parameters to vary. The form of state we have used so far will not do, because our solution for the 2S triplet states imposes a value for α_2 which contradict the requirement that the singlet state be orthogonal to the ground state. So, we would have to start again with a new functional form. This is left as an exercise for the reader.