Quantum Physics 2011/12

Solutions to Tutorial Sheet 5: Variational Method, Molecules

1. *Estimate the ground-state energy of a 1-dimensional simple harmonic oscillator using as trial function*

    (a) $\psi_a(x) = \cos \alpha x$ for $|\alpha x| < \pi/2$, zero elsewhere,

    (b) $\psi_b(x) = \alpha^2 - x^2$ for $|x| < \alpha$, zero elsewhere,

    (c) $\psi_c(x) = C \exp(-\alpha x^2)$

    (d) $\psi_d(x) = C(\alpha - |x|)$ (for $|x| < \alpha$, zero elsewhere)

    (e) $\psi_e(x) = C \sin \alpha x$ (for $|\alpha x| < \pi$, zero elsewhere)

    In each case, α is the variational parameter. Don't forget the normalisation. Sketch the wavefunctions and compare them with the actual ground-state wavefunction.

    You may use the results

    $$\int_{-\infty}^{\infty} \exp(-\alpha x^2) \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}} \qquad \text{and} \qquad \int_{-\pi/2\alpha}^{\pi/2\alpha} x^2 \cos^2 \alpha x \, \mathrm{d}x = \pi(\pi^2 - 6)/24\alpha^3$$

    (a) The function is not normalised, so we need to calculate $\langle \psi_T | \psi_T \rangle$:

    $$\langle \psi_T | \psi_T \rangle = \int_{-\pi/2\alpha}^{\pi/2\alpha} \cos^2 \alpha x \, \mathrm{d}x = \frac{1}{2} \int_{-\pi/2\alpha}^{\pi/2\alpha} [1 + \cos 2\alpha x] \, \mathrm{d}x = \frac{1}{2} \left[x + \frac{1}{2\alpha} \sin 2\alpha x \right]_{-\pi/2\alpha}^{\pi/2\alpha} = \frac{\pi}{2\alpha}$$

    Noting that

    $$\frac{\mathrm{d}^2}{\mathrm{d}x^2} \cos \alpha x = -\alpha^2 \cos \alpha x$$

    we see that

    $$\langle \psi_T | - \frac{\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} | \psi_T \rangle = \frac{\hbar^2 \alpha^2}{2m} \frac{\pi}{2\alpha}$$

    The integral needed for the potential energy

    $$\frac{1}{2} m\omega^2 \langle \psi_T | x^2 | \psi_T \rangle = \frac{1}{2} m\omega^2 \int_{-\pi/2\alpha}^{\pi/2\alpha} x^2 \cos^2 \alpha x \, \mathrm{d}x = \frac{1}{2} m\omega^2 \pi(\pi^2 - 6)/24\alpha^3$$

    So now the quantity we need for the energy, with the normalisation, is:

    $$E(\alpha) = \frac{\langle \psi_T | \hat{H} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} = \frac{\hbar^2 \alpha^2}{2m} + m\omega^2 (\pi^2 - 6)/24\alpha^2$$

    Minimising with respect to α gives

    $$\frac{\mathrm{d}E(\alpha)}{\mathrm{d}\alpha} = \frac{\hbar^2 \alpha}{m} - m\omega^2 (\pi^2 - 6)/12\alpha^3 = 0$$

with solution

$$\alpha_{\min}^2 = \sqrt{\frac{\pi^2 - 6}{12}}\frac{m\omega}{\hbar}$$

Substituting this value into the expression for E gives as an upper bound on the ground-state energy

$$E(\alpha_{\min}) = \sqrt{\frac{\pi^2 - 6}{12}}\,\hbar\omega = 0.568\hbar\omega$$

(b) As before, we first calculate $\langle \psi_T | \psi_T \rangle$:

$$\langle \psi_T | \psi_T \rangle = \int_{-\alpha}^{\alpha} (\alpha^2 - x^2)^2 \, \mathrm{d}x = \frac{16}{15}\alpha^5$$

Noting that

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}(\alpha^2 - x^2) = -2$$

we see that the kinetic energy term is

$$\langle \psi_T | -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} | \psi_T \rangle = \frac{\hbar^2}{m} \int_{-\alpha}^{\alpha} (\alpha^2 - x^2)\, \mathrm{d}x = \frac{4\hbar^2\alpha^3}{3m}$$

whilst the potential energy term is

$$\langle \psi_T | \frac{1}{2}m\omega^2 x^2 | \psi_T \rangle = \frac{1}{2}m\omega^2 \int_{-\alpha}^{\alpha} x^2(\alpha^2 - x^2)^2\, \mathrm{d}x = \frac{8m\omega^2\alpha^7}{105}$$

Combining these results gives

$$E(\alpha) = \frac{5}{4}\frac{\hbar^2}{m\alpha^2} + \frac{1}{14}m\omega^2\alpha^2$$

The minimisation condition is

$$\frac{\mathrm{d}E(\alpha)}{\mathrm{d}\alpha} = -\frac{5}{2}\frac{\hbar^2}{m\alpha^3} + \frac{1}{7}m\omega^2\alpha = 0$$

so that

$$\alpha_{\min}^2 = \sqrt{\frac{35}{2}}\frac{\hbar}{m\omega}$$

giving for the upper bound on the ground-state energy

$$E(\alpha_{\min}) = \frac{5}{4}\sqrt{\frac{2}{35}}\,\hbar\omega + \frac{1}{14}\sqrt{\frac{35}{2}}\,\hbar\omega = 0.598\hbar\omega$$

(c) First we determine the normalisation constant, C:

$$|C|^2 \int_{-\infty}^{\infty} \exp(-2\alpha x^2)\, \mathrm{d}x = 1$$

Using the given Gaussian integral

$$\langle \psi_T | \psi_T \rangle = |C|^2 \sqrt{\frac{\pi}{2\alpha}} = 1 \quad \Rightarrow \quad C = \left(\frac{2\alpha}{\pi}\right)^{1/4}$$

To evaluate the kinetic energy term in the expectation value we can make use of the trick described in lectures:

$$\langle \psi_T | -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}|\psi_T\rangle = \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left|\frac{\mathrm{d}\psi_T}{\mathrm{d}x}\right|^2\,\mathrm{d}x = \frac{2\hbar^2\alpha^2|C|^2}{m}\int_{-\infty}^{\infty}x^2\exp(-2\alpha x^2)\,\mathrm{d}x$$

$$\frac{\mathrm{d}}{\mathrm{d}\alpha}\int_{-\infty}^{\infty}\exp(-2\alpha x^2)\,\mathrm{d}x = -2\int_{-\infty}^{\infty}x^2\exp(-2\alpha x^2)\,\mathrm{d}x = \frac{\mathrm{d}}{\mathrm{d}\alpha}\sqrt{\frac{\pi}{2\alpha}} = -\sqrt{\frac{\pi}{2}}\frac{1}{2}\alpha^{-3/2}$$

Thus the desired integral is

$$\int_{-\infty}^{\infty}x^2\exp(-2\alpha x^2)\,\mathrm{d}x = \frac{1}{4}\sqrt{\frac{\pi}{2\alpha}}\cdot\frac{1}{\alpha}$$

giving

$$\langle \psi_T | -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}|\psi_T\rangle = \frac{\hbar^2\alpha}{2m}$$

Likewise the potential energy term is

$$\langle \psi_T | \frac{1}{2}m\omega^2 x^2 |\psi_T\rangle = \frac{|C|^2 m\omega^2}{2}\int_{-\infty}^{\infty}x^2\exp(-2\alpha x^2)\,\mathrm{d}x = \frac{m\omega^2}{8\alpha}$$

The minimisation condition is

$$\frac{\mathrm{d}E(\alpha)}{\mathrm{d}\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0$$

giving

$$\alpha_{\min} = \frac{m\omega}{2\hbar}$$

and hence a bound

$$E(\alpha_{\min}) = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = 0.5\,\hbar\omega$$

This is, of course, the exact result because our trial function is the correct ground-state wavefunction for the 1-d oscillator.

(d) First, calculate the normalization constant

$$C^2\int_{-\alpha}^{\alpha}(\alpha - |x|)^2 = 2C^2\int_0^{\alpha}(\alpha - x)^2 = 1$$

Which gives

$$C = \sqrt{3/2\alpha^3}$$

Now, we calculate the potential energy

$$< V >= \frac{1}{2} m\omega^2 C^2 \int_{-\alpha}^{\alpha} x^2 (\alpha - |x|)^2$$

$$= m\omega^2 C^2 [\alpha^2 x^3/3 - 2\alpha x^4/4 + x^5/5]_0^\alpha$$

$$= m\omega^2 \alpha^2 / 20$$

The kinetic energy comes from the discontinuity at $x = 0$. One way to treat this is to redefine the function as having a form $\psi = C(\alpha' - bx^2)$ in a narrow region of half-width δ about the origin, and then the real wavefunction ψ_T is the limit as $\delta \to 0$. To avoid further discontiuities, we require the derivative to be continuous across the join. This determines α' and sets $2b\delta C = C$ The kinetic energy is then

$$< T >= -\hbar^2 C^2 / 2m \int_{-\delta}^{\delta} (\alpha' - bx^2)(-2b)dx$$

$$= \frac{3\hbar}{4m\alpha^2} [2\alpha' bx - 2b^2 x^3/3]_{-\delta}^{\delta}$$

$$= 3\hbar^2 / 2m\alpha^3 (\alpha' b\delta - b^2 \delta^3 / 3)$$

As $\delta \to 0$, $\alpha' \to \alpha$ whence $< T >= 3\hbar^2 / 2m\alpha^2$. Now we must minimise the total energy with respect to α, i.e.

$$\frac{d}{d\alpha} [3\hbar^2 / 2m\alpha^2 + m\omega^2 \alpha^2 / 20] = 0$$

which gives:

$$\alpha^4 = \frac{30\hbar^2}{m^2 \omega^2}$$

substituting for the energy:

$$U = \hbar\omega(\sqrt{9/60} + \sqrt{3/20}) = \hbar\omega(\sqrt{3/10}) = 0.5477\hbar\omega$$

e) $\psi_e(x) = C \sin \alpha x$ *(for $|\alpha x| < \pi$, zero elsewhere)*

Normalisation $\langle \psi_T | \psi_T \rangle$:

$$\langle \psi_T | \psi_T \rangle = \int_{-\pi/\alpha}^{\pi/\alpha} \sin^2 \alpha x \; dx = \frac{1}{2} \int_{-\pi/\alpha}^{\pi/\alpha} [1 - \cos 2\alpha x] \; dx = \frac{1}{2} \left[x - \frac{1}{2\alpha} \sin 2\alpha x \right]_{-\pi/\alpha}^{\pi/\alpha} = \frac{\pi}{\alpha}$$

So $C = \sqrt{\frac{\alpha}{\pi}}$.

As in section (a), we notice that

$$\frac{d^2}{dx^2} \sin \alpha x = -\alpha^2 \sin \alpha x$$

so that the kinetic energy

$$\langle T \rangle = \langle \psi_T | -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}|\psi_T\rangle = \frac{\hbar^2\alpha^2}{2m}$$

Now the potential energy is

$$\frac{1}{2}m\omega^2\langle \psi_T|x^2|\psi_T\rangle = \frac{1}{2}m\omega^2\frac{\pi}{\alpha}\int_{-\pi/\alpha}^{\pi/\alpha} x^2\sin^2\alpha x \,\mathrm{d}x = \frac{1}{2}m\omega^2\pi(\pi^2-6)/24\alpha^3$$

which we get by either integrating by parts, using maple or using the standard integral.

$$\int_{-\pi/a}^{\pi/a} x^2\sin^2 nax \,\mathrm{d}x = \frac{\pi(2n^2\pi^2-3)}{6n^2a^3}$$

Solving for the parameter α gives:

$$\alpha^2 = \sqrt{\frac{2\pi^2-3}{6}}$$

and substituting this back into the energy expression gives

$$E = \langle T \rangle + \langle V \rangle = \sqrt{\frac{2\pi^2-3}{6}}\hbar\omega = 1.67\hbar\omega$$

By inspection, the overlap integral between (e) and the others is zero, because (e) is an odd function and (a-d) are even functions. Since (a-d) are bounds for the ground state, and (e) is orthogonal to the ground state, it must represent an estimate for the first excited state. Moreover, since the exact ground state of an even potential is an even function, (e) is orthogonal to the exact ground state. Thus it provides an upper bound to the energy of the first excited state.

2. * *A particle moves in one dimension in the potential*

$$V(x) = \infty, \quad |x| > a, \qquad V(x) = 0, \quad |x| \le a$$

Use a trial function of the form

$$\psi_T(x) = \begin{cases} (a^2-x^2)(1+cx^2), & |x| \le a \\ 0, & |x| > a \end{cases}$$

where c is a variational parameter, to obtain an upper bound on the ground-state energy. You are advised to use Maple to solve the minimisation problem. How does your bound compare with the exact ground-state energy?

Despite the number of integrals in these exercises, almost all modern quantum mechanics is done using computers. Once you have a maple script to solve the variational problem, its simply a case of altering the potentials and trial wavefunction to use it for other cases.

Firstly we compute the normalisation factor

$$\langle \psi_T | \psi_T \rangle = \int_{-a}^{a} (a^2 - x^2)^2 (1 + cx^2)^2 \, dx$$

noting that the trial function vanishes for $|x| > a$. The Maple command is:

```
trial := (a^2-x^2)*(1+c*x^2);
i1 := int(trial*trial,x=-a..a);
```

Noting that in the potential well, there is no potential energy term, we just have to calculate the kinetic energy term. We use the trick employed in the previous question:

$$\langle \psi_T | -\frac{\hbar^2}{2m} \nabla^2 | \psi_T \rangle = \frac{\hbar^2}{2m} \int_{-a}^{a} \left| \frac{d\psi_T}{dx} \right|^2 \, dx$$

We can evaluate the integral with Maple as follows:

```
d1 := diff(trial,x);
i2 := int(d1*d1,x=-a..a);
```

We then obtain

$$E(c) = \frac{\langle \psi_T | -\dfrac{\hbar^2}{2m} \nabla^2 | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle}$$

by taking the ratio of the previously evaluated integrals:

```
ratio := (hbar^2/(2*m)*i2/i1);
simplify(%);
```

to obtain

$$E(c) = \left(\frac{3\hbar^2}{4ma^2} \right) \frac{11a^4c^2 + 14a^2c + 35}{a^4c^2 + 6a^2c + 21}$$

We then carry out the minimisation:

```
quad := diff(ratio,c);
solve(quad=0,c);
evalf(%);
```

giving two roots for c:

$$c^{(1)} = -0.22075a^{-2}, \qquad c^{(2)} = -7.31771a^{-2}$$

Substituting these values in the expression for $E(c)$

```
sols := %;
bound1 := subs(c=sols[1],ratio);
bound2 := subs(c=sols[2],ratio);
```

gives

$$E(c^{(1)}) = 1.23372 \frac{\hbar^2}{ma^2}, \qquad E(c^{(2)}) = 12.7663 \frac{\hbar^2}{ma^2}$$

so the minimum is reached for $c = c^{(1)}$, to be compared with the exact result for the ground-state energy:

$$E_1 = \frac{\hbar^2 \pi^2}{8ma^2} = 1.23370 \frac{\hbar^2}{ma^2}$$

So our variational estimate is an excellent approximation!

3. * *Repeat the previous problem taking*

$$\psi_T(x) = \begin{cases} (a^2 - x^2)(x + cx^3), & |x| \le a \\ 0, & |x| > a \end{cases}$$

as the trial function. Why does this give an upper bound for the first excited energy level? Compare your variational result with the exact eigenvalue of the $n = 2$ level.

The trial function has odd parity and is therefore orthogonal to the exact ground-state wavefunction, which has even parity. Thus it will give an upper bound on the energy of the lowest odd-parity state, which is the first excited state of the symmetric square well.

A similar exercise to the previous question, greatly simplified by using Maple:

```
trial := (a^2-x^2)*x*(1+c*x^2);
i1 := int(trial*trial,x=-a..a);
d1 := diff(trial,x);
i2 := int(d1*d1,x=-a..a);
ratio := (hbar^2/(2*m)*i2/i1);
simplify(%);
quad := diff(ratio,c);
solve(quad=0,{c});
evalf(%);
```

which gives

$$E(c) = \left(\frac{11\hbar^2}{4ma^2} \right) \frac{23a^4 c^2 + 54a^2 c + 63}{5a^4 c^2 + 22a^2 c + 33}$$

and two roots for c:

$$c^{(1)} = -.0516975a^{-2}, \qquad c^{(2)} = -3.24574a^{-2}$$

Substituting these values in $E(c)$ gives:

$$E(c^{(1)}) = 4.9377 \frac{\hbar^2}{ma^2}, \qquad E(c^{(2)}) = 25.0623 \frac{\hbar^2}{ma^2}$$

so the minimum is reached for $c = c^{(1)}$, to be compared with the exact result for the first excited-state energy:

$$E_2 = \frac{\hbar^2 \pi^2}{2ma^2} = 4.9348 \frac{\hbar^2}{ma^2}$$

4. A "1d atom" has ground state wavefunction $u_1(x) = \exp-\alpha|x|$. Consider a ring of N such atoms, one centred on $x = 0$ separated by a distance d. Using the single site wavefunctions $u_{1j}(x+jd)$ as LCAO basis functions, what are the LCAO wavefunctions according to Bloch's theorum in 1D?

If a Hamiltonian has a periodic potential, then the operator $\hat{D}f(x) = f(x-d)$ commutes with the Hamiltonian and eigenstates of the Hamiltonian must also be eigenstates of $\hat{D}$. The wavefunction must be single valued, hence $\phi(x) = \phi(x + Nd)$, this means that

$\phi(x) = \exp(2\pi nix/Nd)u(x)$

where $u(x)$ must have the same periodicity as the lattice. Assuming LCAO

$$u(x) = \sum_{j=1}^{N} u_1(x + jd)$$

Using the single site wavefunctions $u_{1j}(x + jd)$ as LCAO basis functions, write down the ground state wavefunction for ring of N such atoms separated by a distance d, which is an eigenstate of the displacement operator assuming that $< u_1(x)|u_1(x+d) >\ll 1$.

The ground state wavefunction must obey rules for translational symmetry, and will correspond to the least oscillatory wave, so it must be an eigenstate of the translation operator defined by $\hat{D}f(x) = f(x-d)$. :

In matrix representation with the single-site basis, this operator is

$$\begin{pmatrix} 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 1 & 0 & \dots \\ 0 & 0 & 0 & 1 & \dots \\ 0 & 0 & 0 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \\ 1 & 0 & 0 & 0 & \dots \end{pmatrix}$$

Where the final line represents the periodic boundaries.

The least oscillatory eigenvector solution to this is:

$$\Phi = (1, 1, 1, 1....) \equiv \sum_j u_1(x - jd)$$

What is the normalisation for this wavefunction? This represents one (delocalised) electron. The normalisation constant c is then given by

$$c^2 \sum_{jk} \langle u_1(x - jd)|u_1(x - kd)\rangle = 1$$

Neglecting off diagonal terms $\langle u_1(x - jd)|u_{100}(x - kd)\rangle = \delta_{jk}$ gives $c = \sqrt{1/N}$.

A computational physicist solves for this wavefunction using the variational method, with a trial wavefunction $\psi_T(r)$ and a set of variational parameters c_k, $k = 2\pi/Nd$

$$\psi_T(r) = \sum_k c_k \cos kx$$

Using your knowledge of the exact atomic solution u_1, what can you say about the coefficients c_k, and allowed values of k?

This trial wavefunction is simply a Fourier Series, with only even (cosine) terms. Thus the coefficients are the Fourier coefficients of the expansion of the wavefunction. Since the wavefunction is periodic with period d, we require the sum to be over $k = 2\pi n/d$ for integer n. Also, because u_1 has discontinuous slope at $x = 0$, there is a delta function in the kinetic energy, and many Fourier components are likely to be needed to describe the wavefunction well.

Remark: This is convenient for computation, because the trial wavefunction can be stored as an array of c_k coefficients, and moreover the contribution to the kinetic energy from each term is simply $|c_k|^2\hbar^2 k^2/2m$.

What would you get from a trial wavefunction of the form

$$\psi_T(x) = \sum_k c_k \sin kx$$

This is an odd function, orthogonal to the ground state and will give an upper bound to the first excited state. In fact, it gives an odd function at each atomic site, so it corresponds to the lowest state in the second *band* of states with $n = 2$: there are many lower lying states in the u_1 *band*.

5. *Obtain a variational estimate of the ground-state energy of the hydrogen atom by taking as trial function*

$$\psi_T(r) = \exp(-\alpha r^2)$$

How does your result compare with the exact result?

Now

$$\langle \psi_T | \psi_T \rangle = \int \exp(-2\alpha r^2)\, \mathrm{d}^3 r = 4\pi \int_0^\infty r^2 \exp(-2\alpha r^2)\, \mathrm{d}r = \frac{1}{2\sqrt{2}}\left(\frac{\pi}{\alpha}\right)^{3/2}$$

where we have used the Gaussian integral which appears in the last part of Question 1, noting the different limits.

In 3D, the kinetic energy term can be evaluated by the integration by parts trick, which is easier, but for interest here we will take the longer route. It is mathematically quite interesting to show that the same result is obtained by both methods.

$$\langle \psi_T | -\frac{\hbar^2}{2m}\nabla^2 |\psi_T \rangle = \langle \psi_T | -\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}^2}{\mathrm{d}r}r^2\frac{\mathrm{d}^2}{\mathrm{d}r}|\psi_T \rangle \tag{1}$$

$$= -\frac{\hbar^2}{2m}\int e^{-\alpha r^2}(4\alpha^2 r^2 - 6\alpha)e^{-\alpha r^2}4\pi r^2 dr \tag{2}$$

$$= \frac{3\hbar^2}{32m}\sqrt{\frac{2\pi}{a}} \tag{3}$$

Where the given Gaussian integral could be evaluated by parametric differentiation or by using Maple, to give

$$\langle \psi_T | -\frac{\hbar^2}{2m}\nabla^2 |\psi_T \rangle = \frac{\hbar^2\alpha}{2m}\frac{3}{2\sqrt{2}}\left(\frac{\pi}{\alpha}\right)^{3/2}$$

The potential energy term involves a simple integral and is

$$\langle \psi_T | - \frac{e^2}{(4\pi\epsilon_0)r} | \psi_T \rangle = -\frac{e^2}{(4\pi\epsilon_0)} 4\pi \int\limits_{0}^{\infty} r \exp(-2\alpha r^2) \, \mathrm{d}r = -\frac{e^2}{(4\pi\epsilon_0)} \frac{\pi}{\alpha}$$

Thus we obtain

$$\frac{\langle \psi_T | \hat{H} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} = E(\alpha) = \frac{3\hbar^2 \alpha}{2m} - \frac{e^2}{(4\pi\epsilon_0)} 2 \left(\frac{2}{\pi} \right)^{1/2} \alpha^{1/2}$$

Minimising gives

$$\frac{\mathrm{d}E(\alpha)}{\mathrm{d}\alpha} = \frac{3\hbar^2}{2m} - \frac{e^2}{(4\pi\epsilon_0)} \left(\frac{2}{\pi} \right)^{1/2} \alpha^{-1/2} = 0$$

yielding

$$\alpha_{\min}^{1/2} = \frac{e^2}{(4\pi\epsilon_0)} \left(\frac{2}{\pi} \right)^{1/2} \frac{2m}{3\hbar^2}$$

and substituting back into the expression for E yields the upper bound on the energy:

$$E(\alpha_{\min}) = -\frac{8}{3\pi} \left(\frac{e^2}{(4\pi\epsilon_0)} \right)^2 \frac{m}{2\hbar^2} = -\frac{8}{3\pi} \, \mathrm{Ry} = -11.54 \text{ eV}$$

How does your result compare with the exact result? Sketch the trial wavefunction and the actual wavefunction on the same graph.

The exact answer is the Rydberg constant, -13.6eV. The wavefunction is an exponential $\Psi_{exact} \equiv \exp(-ar)$.

The exponential (red, exact solution) and gaussian (green, trial solution) should each be normalised such that $\int \Psi^*\Psi 4\pi r^2 dr = 1$, thus setting a=1 we get the graph opposite. Note that although the trial wavefunction is a pretty poor estimate of the exact one, yet the energy is still only 15% wrong