M.Sc. course in Chemistry
Teacher: Prof. Hannes Jónsson

# Ground State Energy in a Square Well Potential
## - Use of Approximate Methods –

The square well with bound states



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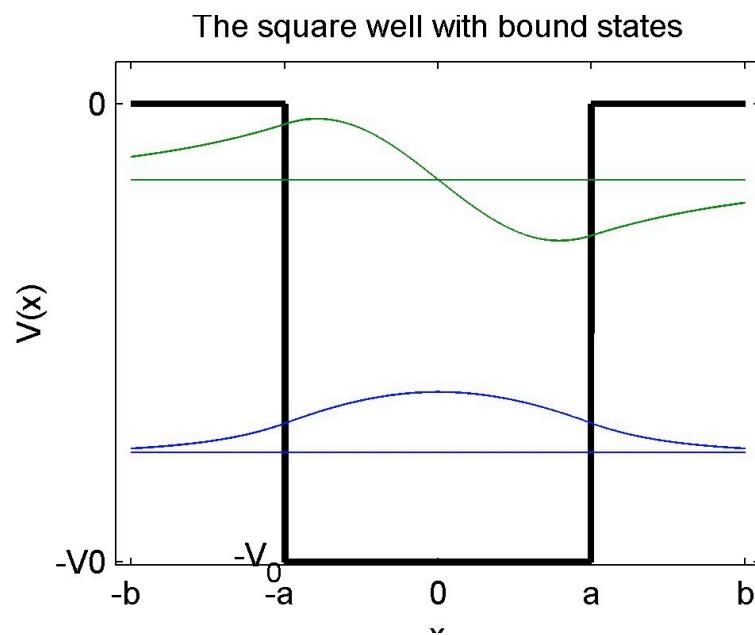
# 1 The Problem

We wish to use the variational method to calculate the ground state energy ($E_0$) of a Lithium atom which contains one valence electron. We make the assumption that the interaction between the valence electron and other core electrons and the nucleus can be described by a square well potential.

$$V(x) = \begin{cases} V_0 \text{ if } \text{-a} \leq x \leq a \\ 0 \text{ otherwise} \end{cases} \tag{1}$$
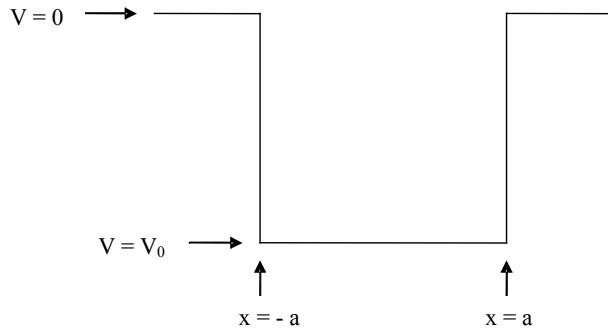


**Figure 1 – The square potential V(x)**

The ground state wave function, $\psi_0$, and energy $E_0$ satisfy the Schrödinger equation

$$H\psi_0 = E_0\psi_0$$
$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{2}$$

The exact solution is of the form

$$\psi_0(x) = \begin{cases} e^{\kappa x} \text{ if } x \leq -a \\ A\cos(kx) \text{ if } \text{-a} \leq x \leq a \\ e^{-\kappa x} \text{ if } x \geq a \end{cases} \tag{3}$$

By using atomic units and choosing

$$\begin{aligned} \hbar &= 1 \\ m &= 1 \\ a &= 2,93 \\ V_0 &= -0,276 \end{aligned} \tag{4}$$

the exact ground state energy becomes $E_0$ = -0,21 H = 5,7 eV. We wish to see how close we can get to the exact value by using the variational method with Gaussian trial functions.

## 2   The Variational Method

It is not possible to solve the Schrödinger equation exactly for any atom or molecule more complicated than the hydrogen atom. However there are approximate methods that can be used to solve the Schrödinger equation to almost any accuracy desired. One of the most widely used methods is the variational method. The variational method gives an upper bound on the ground state energy, $E_0$, by use of any trial function, $\phi$

$$E_\phi = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0 \qquad (5)$$

$\phi$ can be chosen such that it depends on some arbitrary parameters $\alpha$, $\beta$, $\gamma$, ... The energy $E_\phi$ will also depend on these parameters and Eq. (5) will read

$$E_\phi(\alpha, \beta, \gamma, ...) \geq E_0 \qquad (6)$$

$E_\phi$ can now be minimized with respect to each of these parameters and thus approach the exact ground state energy, $E_0$. The more parameters $\phi$ depends on, the better result one can expect.

If we use a trial function that is a linear combination of arbitrary known functions, $f_n$,

$$\phi = \sum_{n=1}^{N} c_n f_n \qquad (7)$$

where the $c_n$ are variational parameters, we end up with an N × N secular determinant after minimizing $E_\phi$ with respect to $c_1$, $c_2$, …

$$\begin{vmatrix} H_{11} - ES_{11} & H_{21} - ES_{21} & ... & H_{N1} - ES_{N1} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & ... & H_{N2} - ES_{N2} \\ \vdots & \vdots & & \vdots \\ H_{1N} - ES_{1N} & H_{2N} - ES_{2N} & ... & H_{NN} - ES_{NN} \end{vmatrix} = 0 \quad \ddot{} \qquad (8)$$

where

$$H_{ij} = \int f_i^* H f_j d\tau$$
$$S_{ij} = S_{ji} = \int f_i^* f_j d\tau \qquad (9)$$

and $H_{ij} = H_{ji}$ since H is hermitian.

The secular equation associated with this secular determinant is an Nth-order polynomial in E. The smallest root of the Nth-order secular equation approximates the ground-state energy.

## 3   Selection of the trial function

We use a Gaussian-basis for the trial function.

In order to determine how much the results depend on the number of parameters used in the trial function we tried three different functions.

The first trial function consists of a single Gaussian and depends only on one parameter,$\alpha$. The second trial function is a linear combination of two Gaussians and the third a linear combination of three Gaussians.

$$\phi_1(x,\alpha) = e^{-\alpha x^2/2}$$
$$\phi_2(x,c_1,c_2) = c_1 e^{-\alpha x^2/2} + c_2 e^{-\beta \alpha x^2/2} \tag{10}$$
$$\phi_3(x,c_1,c_2,c_3) = c_1 e^{-\alpha x^2/2} + c_2 e^{-\beta \alpha x^2/2} + c_3 e^{-\gamma \alpha x^2/2}$$

$\alpha$ is determined by minimizing $E_{\phi_1}$. $\beta$ and $\gamma$ are predetermined constants.

## 4   Solution of problem

Minimization of $E_{\phi_1}$ with respect to $\alpha$ gives the value of $\alpha$ that corresponds to the upper bound on $E_0$. This value was used in $\phi_2$ and $\phi_3$, but multiplied with the predetermined constants, $\beta$ and $\gamma$.

Appendix A contains the mathematical solution of the problem contains and Appendix B a Matlab code that was written in order to solve the problem numerically.

## 5   Results

Minimization of $E_{\phi_1}$ gives $\alpha = 0,0256$ and $E_0 = -0,13$ H = -3,53 eV. Comparison with the exact value given above shows that this value is approximately 38% too high.

By choosing $\beta = 10$ and $\gamma = 20$ we get the following results for the second and third trial functions:

$\phi_2$:
$$\phi_2(x) = 0,1352 \cdot e^{-0,0128x^2} + 0,9908 \cdot e^{-0,006x^2}$$
$E_0 = -0,21$ H = -5,6 eV
error is 1%

$\phi_3$:
$$\phi_3(x) = 0,0256 \cdot e^{-0,0128x^2} + 0,9839 \cdot e^{-0,006x^2} - 0,1770 \cdot e^{-0,026x^2}$$
$E_0 = -0,21$ H = -5,7 eV
error is 0%, have reached the correct value
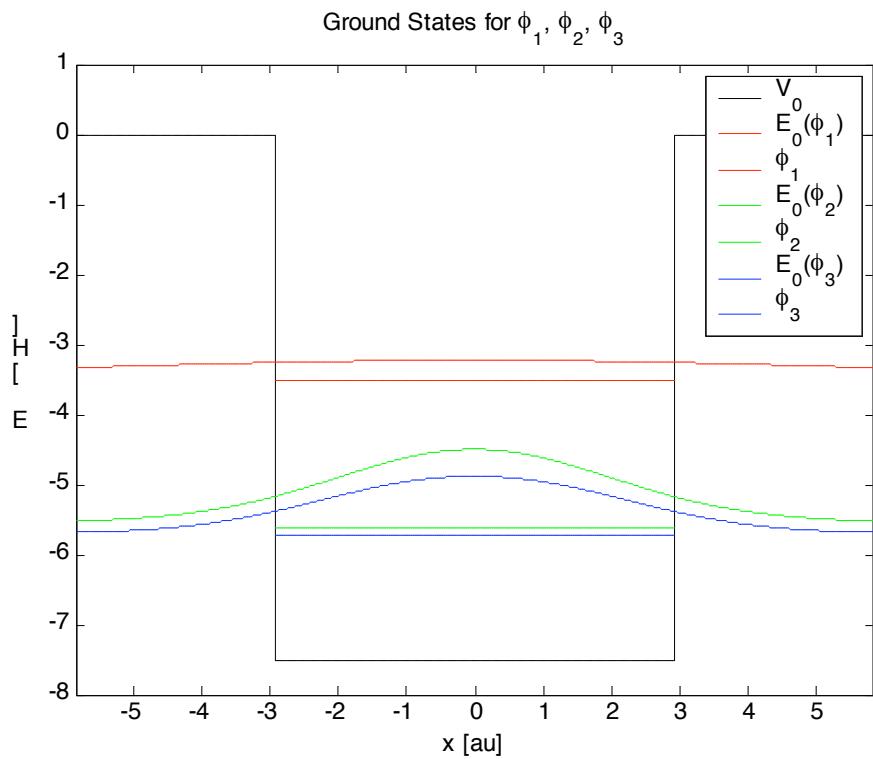
**Figure 2 – Ground State Energies and Wave Functions for $\phi_1$, $\phi_2$ and $\phi_3$**

**($\beta = 10$ and $\gamma = 20$)**
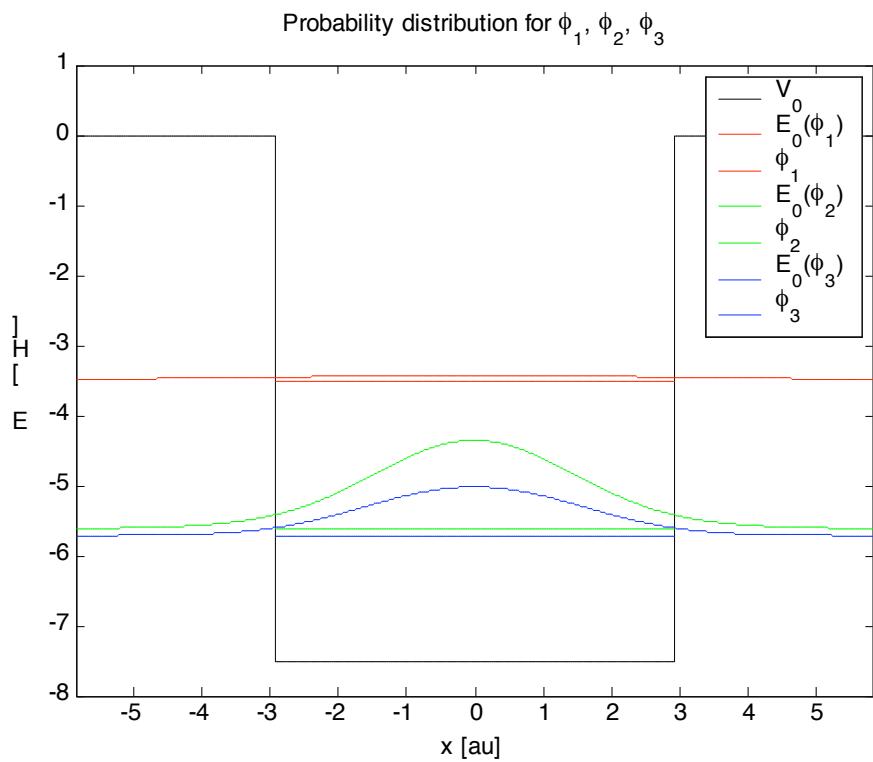


**Figure 3 – Ground State Energies and Probability Distributions for $\phi_1$, $\phi_2$ and $\phi_3$**

**($\beta = 10$ and $\gamma = 20$)**

These results therefore show that approximate ground energies can be improved by using a trial function that is a sum of Gaussians rather than a single one.

## 5.1 The convergence of $E_0$ depends highly on $\beta$ and $\gamma$

Although the values $\beta = 10$ and $\gamma = 20$ give rapid convergence toward the exact result that is not the case with all values of $\beta$ and $\gamma$.

If we e.g. choose $\beta = 0.5$ and $\gamma = 2$ the convergence is very poor

$\phi_2$:

$$\phi_2(x) = 0,8808 \cdot e^{-0,0128x^2} - 0,4735 \cdot e^{-0,006x^2}$$

$E_0$= -0,15 H = -4,15 eV
error is 27%

$\phi_3$:

$$\phi_3(x) = 0,0286 \cdot e^{-0,0128x^2} + 0,9991 \cdot e^{-0,006x^2} - 0,0311 \cdot e^{-0,026x^2}$$

$E_0$= -0,19 H = -5,21 eV
error is 9%
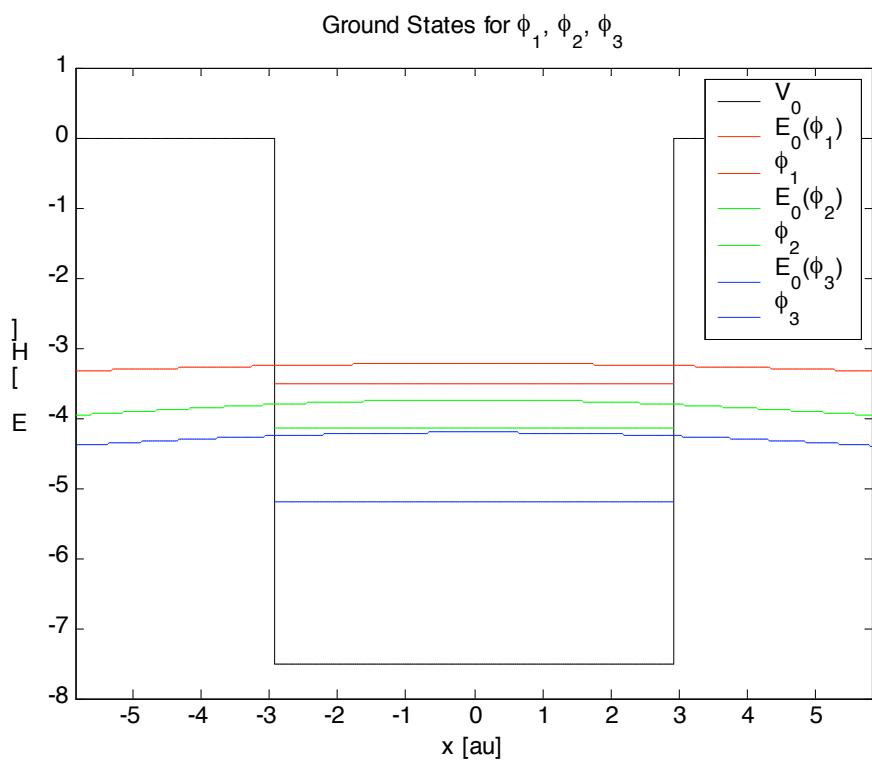


**Figure 4 - Figure 5 – Ground State Energies and Wave Functions for $\phi_1$, $\phi_2$ and $\phi_3$**

**($\beta = 0,5$ and $\gamma = 2$)**

Probability distribution for $\phi_1$, $\phi_2$, $\phi_3$
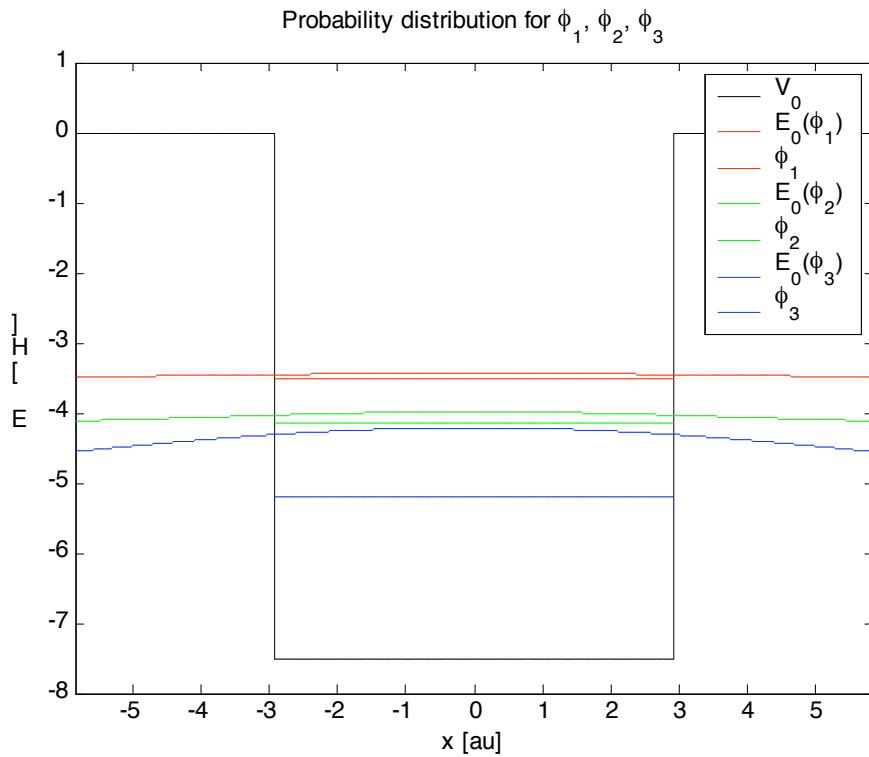
**Figure 6 - Ground State Energies and Probability Distributions for $\phi_1$, $\phi_2$ and $\phi_3$**

**($\beta = 0{,}5$ and $\gamma = 2$)**

For these values of $\alpha$ and $\beta$ one therefore needs more than three gaussian terms in the trial function to get convergence to the exact result.

The reason for this is quite obvious when one looks at the graphs of the gaussian terms involved in the trial functions and compares them with the exact wave function.

$\phi_1$ is obviously very different from the exact function – is much more flat. Therefore one must select more peaked functions in $\phi_2$ and $\phi_3$ in order to get closer to the exact solution, i.e. increase the values of $\beta$ and $\gamma$.



x = -20       x = 20       x = -2       x = 2       x = -3       x = 3
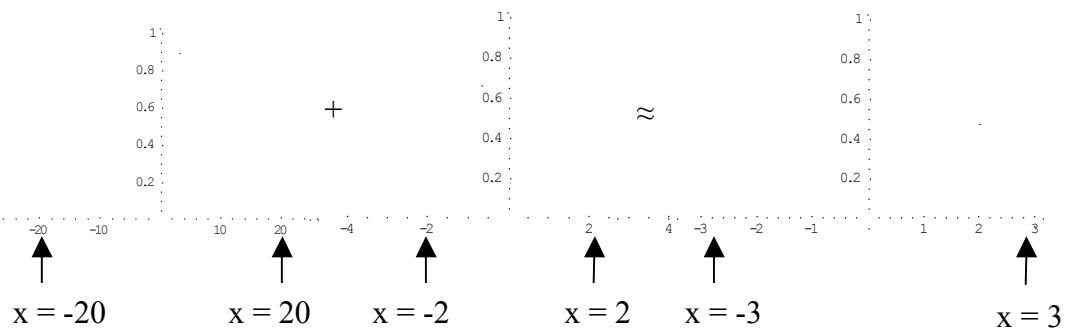
**Figure 7 – Different Gaussian functions can approximate a cosine**

# 6 Conclusion

The variational method with Gaussian trial functions can be used to approximate the ground state energy of a Li atom which interactions are approximated by a square well potential. The approximated ground state energy appraches the exact result as more Gaussian terms are added to the trial function.

By summing together approprately flat and peaked Gaussians one can get the exact ground state energy for the Li atom.

# Appendix A
# Mathematical Solution

## 1. $\phi_1$

We start out with the trial function

$$\phi_1(x,\alpha) = e^{-\alpha x^2/2} \tag{A1}$$

The energy corresponding to $\phi_1$ is

$$E_\phi(\alpha) = \frac{\int \phi^* H\phi\, d\tau}{\int \phi^* \phi\, d\tau} = \frac{\dfrac{\hbar^2}{4m}\sqrt{\alpha\pi} + V_0\left(\dfrac{\pi}{\alpha}\right)^{1/2} erf(\alpha^{1/2}a)}{\sqrt{\alpha\pi}}$$

$$= \frac{\hbar^2}{4m}\alpha + V_0\frac{2}{\pi^{1/2}}erf\left(\alpha^{1/2}a\right) \tag{A2}$$

Minimization of (A2) with respect to $\alpha$ gives

$$\frac{dE_\phi}{d\alpha} = \frac{\hbar^2}{4m} + \frac{2V_0}{\pi^{1/2}}e^{-\alpha a^2} = 0$$

$$\Rightarrow \quad \alpha = -\left(\frac{1}{a^2}\right)\ln\left(\frac{-\hbar^2\pi^{1/2}}{8V_0 m}\right) \tag{A3}$$

One gets the approximated ground state energy, $E_0$, by inserting this value of $\alpha$ into (A2).

The corresponding normalized wave function is of the form

$$\phi_1(x,\alpha) = \left(\frac{\pi}{\alpha}\right)^{1/4} e^{-\alpha x^2/2} \tag{A4}$$

## 2. $\phi_2$

We start out with the trial function

$$\phi_2(x,c_1,c_2) = c_1 e^{-\alpha x^2/2} + c_2 e^{-\beta\alpha x^2/2} \tag{A5}$$

The energy corresponding to $\phi_2$ is

$$E_{\phi_2}(c_1,c_2) = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}} \tag{A6}$$

where

$$H_{ij} = \int \phi_i * H \phi_j dx$$
$$S_{ij} = S_{ji} = \int \phi_i * \phi_j dx \tag{A7}$$

and $H_{ij} = H_{ji}$ since H is hermitian.

After rather cumbersome calculations, one gets

$$H_{11} = \frac{\hbar^2}{4m}\sqrt{\alpha\pi} + V_0 \left(\frac{\pi}{\alpha}\right)^{1/2} erf\left(\alpha^{1/2}a\right)$$

$$H_{12} = \frac{\hbar^2}{2m}\sqrt{\alpha\pi}\left(\left(\frac{2}{1+\beta}\right)^{1/2} - \frac{1}{2}\left(\frac{2}{1+\beta}\right)^{3/2}\right)$$

$$+ V_0\left(\frac{2\pi}{(\beta+1)\alpha}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2} erf\left(\left(\frac{(\beta+1)\alpha}{2}\right)^{1/2}a\right) \tag{A8}$$

$$H_{22} = \frac{\hbar^2}{4m}\sqrt{\beta\alpha\pi} + V_0\left(\frac{\pi}{\beta\alpha}\right)^{1/2} erf\left((\beta\alpha)^{1/2}a\right)$$

and

$$S_{11} = \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$S_{12} = \left(\frac{2\pi}{(1+\beta)\alpha}\right)^{1/2} \tag{A9}$$

$$S_{22} = \left(\frac{\pi}{\beta\alpha}\right)^{1/2}$$

Minimization of (A7) with respect to $c_1$ and $c_2$ gives a 2x2 secular determinant which can be expanded into a second order polynomial in E

$$0 = \begin{vmatrix} H_{11} - ES_{11} & H_{21} - ES_{21} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix}$$
$$= (S_{11}S_{22} - S_{12}^2)E^2 + (H_{11}S_{22} - H_{22}S_{11} + 2H_{12}S_{12})E + H_{11}H_{22} - H_{12}^2 \tag{A10}$$

The lower root of (A10) is the approximated ground state energy $E_0$.

The corresponding normalized wave function is of the form (A5) with $c_1$ and $c_2$ caluclated from

$$c_1' = 1$$

$$c_2' = \frac{-H_{11} + E_0 S_{11}}{H_{12} + E_0 S_{12}}$$

$$N = \left(\frac{1}{(c_1')^2 + (c_2')^2}\right)^{1/2} \tag{A11}$$

$$c_1 = N c_1'$$

$$c_2 = N c_2'$$

## 3. $\phi_3$

We start out with the trial function

$$\phi_3(x, c_1, c_2, c_3) = c_1 e^{-\alpha x^2/2} + c_2 e^{-\beta \alpha x^2/2} + c_3 e^{-\gamma \alpha x^2/2} \tag{A12}$$

The energy corresponding to $\phi_3$ is

$$E_{\phi_2}(c_1, c_2, c_3) = \frac{c_1^2 H_{11} + c_2^2 H_{22} + c_3^2 H_{33} + 2c_1 c_2 H_{12} + 2c_1 c_3 H_{13} + 2c_2 c_3 H_{23}}{c_1^2 S_{11} + c_2^2 S_{22} + + c_3^2 S_{33} + 2c_1 c_2 S_{12} + 2c_1 c_3 S_{13} + 2c_2 c_3 S_{23}} \tag{A13}$$

Expression (A7) is still valid and $H_{11}$, $H_{22}$, $H_{12}$, $S_{11}$, $S_{22}$ and $S_{12}$ are given by expression (A8).

Other terms in (A13) are given by

$$H_{33} = \frac{\hbar^2}{4m}\sqrt{\gamma \alpha \pi} + V_0 \left(\frac{\pi}{\gamma \alpha}\right)^{1/2} erf\left((\gamma \alpha)^{1/2} a\right)$$

$$H_{13} = \frac{\hbar^2}{2m}\sqrt{\alpha \pi}\left(\gamma\left(\frac{2}{1+\gamma}\right)^{1/2} - \frac{\gamma^2}{2}\left(\frac{2}{1+\gamma}\right)^{3/2}\right)$$

$$+ V_0 \left(\frac{2\pi}{(1+\gamma)\alpha}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2} erf\left(\left(\frac{(1+\gamma)\alpha}{2}\right)^{1/2} a\right) \tag{A14}$$

$$H_{23} = \frac{\hbar^2}{2m}\sqrt{\alpha \pi}\left(\gamma\left(\frac{2}{\beta+\gamma}\right)^{1/2} - \frac{\gamma^2}{2}\left(\frac{2}{\beta+\gamma}\right)^{3/2}\right)$$

$$+ V_0 \left(\frac{2\pi}{(\beta+\gamma)\alpha}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2} erf\left(\left(\frac{(\beta+\gamma)\alpha}{2}\right)^{1/2} a\right)$$

and

$$S_{33} = \left(\frac{\pi}{\gamma\alpha}\right)^{1/2}$$

$$S_{13} = \left(\frac{2\pi}{(1+\gamma)\alpha}\right)^{1/2} \tag{A15}$$

$$S_{23} = \left(\frac{\pi}{(\beta+\gamma)\alpha}\right)^{1/2}$$

Minimization of (A13) with respect to $c_1$, $c_2$ and $c_2$ gives a 3x3 secular determinant which can be expanded into a third order polynomial in E

$$0 = \begin{vmatrix} H_{11}-ES_{11} & H_{21}-ES_{21} & H_{31}-ES_{31} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{32}-ES_{32} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} \end{vmatrix} = AE^3 + BE^2 + CE + D \tag{A16}$$

where the constants A, B, C and D are given by

$$A = S_{13}^2 S_{22} - 2S_{12}S_{13}S_{23} + S_{11}S_{23}^2 + S_{12}^2 S_{33} - S_{11}S_{22}S_{33}$$

$$B = -H_{33}S_{12}^2 + 2H_{23}S_{12}S_{13} - H_{22}S_{13}^2 + H_{33}S_{11}S_{22} - 2H_{13}S_{13}S_{22} - 2H_{23}S_{11}S_{23}$$
$$\quad + 2H_{13}S_{12}S_{23} + 2H_{12}S_{13}S_{23} - H_{11}S_{23}^2 + H_{22}S_{11}S_{33} - 2H_{12}S_{12}S_{33} + H_{11}S_{22}S_{33}$$

$$C = H_{23}^2 S_{11} - H_{22}H_{33}S_{11} - 2H_{13}H_{23}S_{12} + 2H_{12}H_{33}S_{12} + 2H_{13}H_{22}S_{13} - 2H_{12}H_{23}S_{13} \tag{A17}$$
$$\quad + H_{13}^2 S_{22} - H_{11}H_{33}S_{22} - 2H_{12}H_{13}S_{23} + 2H_{11}H_{23}S_{23} + H_{12}^2 S_{33} - H_{11}H_{22}S_{33}$$

$$D = -H_{13}^2 H_{22} + 2H_{12}H_{13}H_{23} - H_{11}H_{23}^2 - H_{12}^2 H_{33} + H_{11}H_{22}H_{33}$$

The lowest root of (A16) is the approximated ground state energy $E_0$.

The corresponding normalized wave function is of the form (A13) with $c_1$, $c_2$ and $c_3$ caluclated from

$$c_1' = 1$$

$$c_2' = \frac{-\left(-H_{12}H_{13} + H_{11}H_{23} - E_0 H_{23}S_{11} + E_0 H_{13}S_{12} + E_0 H_{12}S_{13} - E_0^2 S_{12}S_{13} - E_0 H_{11}S_{23} + E_0 S_{11}S_{23}\right)}{\left(-H_{13}H_{22} + H_{12}H_{23} - E_0 H_{23}S_{23} + E_0 H_{22}S_{13} + E_0 H_{13}S_{22} - E_0^2 S_{13}S_{22} - E_0 H_{12}S_{23} + E_0^2 S_{12}S_{23}\right)}$$

$$c_3' = \frac{-\left((H_{12} - E_0 S_{12})^2 - (H_{11} - E_0 S_{11})(H_{22} - E_0 S_{22})\right)}{\left(-(H_{13} - E_0 S_{13})(H_{22} - E_0 S_{22}) + (H_{12} - E_0 S_{12})(H_{23} - E_0 S_{23})\right)}$$

$$N = \left(\frac{1}{(c_1')^2 + (c_2')^2 + (c_3')^2}\right)^{1/2}$$

$$c_1 = Nc_1'$$

$$c_2 = Nc_2'$$

$$c_3 = Nc_3'$$

$$\tag{A18}$$

# Appendix B
# Matlab Code

```matlab
clear all;
close all;

a=2.93;
b=2*a;
hbar=1;
m=1;
V0=-0.276;
c=hbar^2/(4*m);
N=10001;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
% We begin with a trial function consisting of one Gaussian
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%

alpha1=-(1/a^2)*log(-(hbar^2*sqrt(pi))/(8*V0*m));
E10=c*alpha1+V0*erf(sqrt(alpha1)*a);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
% Now we use a linear combination of two Gaussians as trial function
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%

beta=10;
alpha2=beta*alpha1;

H11=c*sqrt(alpha1*pi)+V0*sqrt(pi/alpha1)*erf(a*alpha1^0.5);
H22=c*sqrt(alpha2*pi)+V0*sqrt(pi/alpha2)*erf(a*alpha2^0.5);
H12=2*c*sqrt(alpha1*pi)*((2/(1+beta))^0.5-
0.5*(2/(1+beta))^1.5)+V0*(2*pi/(alpha2+alpha1))^0.5*erf(a*((alpha2+alpha1)/2)^0.5);

S11=(pi/alpha1)^0.5;
S22=(pi/alpha2)^0.5;
S12=(2*pi/(alpha1+alpha2))^0.5;

A2=S11*S22-S12^2;
B2=-H11*S22-H22*S11+2*H12*S12;
C2=H11*H22-H12^2;

p2=[A2 B2 C2];
r2=roots(p2);
r2=sort(r2);

E20=r2(1);
E21=r2(2);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
% Now we use a linear combination of three Gaussians as trial function
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%

gamma=20;
```

```
alpha3=gamma*alpha1;

H33=c*sqrt(alpha3*pi)+V0*(pi/alpha3)^0.5*erf(a*alpha3^0.5);
H13=2*c*sqrt(alpha1*pi)*(gamma*(2/(1+gamma))^0.5-
0.5*gamma^2*(2/(1+gamma))^1.5)+V0*((2*pi/(alpha1+alpha3))^0.5*erf(a*((alpha1+alpha3)/2)^0.5));
H23=2*c*sqrt(alpha1*pi)*(gamma*(2/(beta+gamma))^0.5-
0.5*gamma^2*(2/(beta+gamma))^1.5)+V0*(2*pi/(alpha2+alpha3))^0.5*erf(a*((alpha2+alpha3)/2)^0.5
);

S33=(pi/alpha3)^0.5;
S13=(2*pi/(alpha1+alpha3))^0.5;
S23=(2*pi/(alpha2+alpha3))^0.5;

D3=-H13^2*H22+2*H12*H13*H23-H11*H23^2-H12^2*H33+H11*H22*H33;
C3=H23^2*S11-H22*H33*S11-2*H13*H23*S12+2*H12*H33*S12+2*H13*H22*S13-
2*H12*H23*S13+H13^2*S22-H11*H33*S22-2*H12*H13*S23+2*H11*H23*S23+H12^2*S33-
H11*H22*S33;
B3=-H33*S12^2+2*H23*S12*S13-H22*S13^2+H33*S11*S22-2*H13*S13*S22-
2*H23*S11*S23+2*H13*S12*S23+2*H12*S13*S23-H11*S23^2+H22*S11*S33-
2*H12*S12*S33+H11*S22*S33;
A3=S13^2*S22-2*S12*S13*S23+S11*S23^2+S12^2*S33-S11*S22*S33;

p3=[A3 B3 C3 D3];
r3=roots(p3);
r3=sort(r3);

E30=r3(1);
E31=r3(2);
E32=r3(3);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
% Calculate the normalised c-constants for the three trial functions
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%

c101=(alpha1/pi)^0.25;

c201=1;
c202=(-H11+E20*S11)/(H12-E20*S12);
norm20=sqrt(1/(c201^2+c202^2));
c201=norm20*c201;
c202=norm20*c202;
norm20=sqrt(1/(c201^2+c202^2));

c211=1;
c212=(-H11+E21*S11)/(H12-E21*S12);
norm21=sqrt(1/(c211^2+c212^2));
c211=norm21*c211;
c212=norm21*c212;
norm21=c211^2+c212^2;

c301=1;
c302=-(-H12*H13+H11*H23-E30*H23*S11+E30*H13*S12+E30*H12*S13-E30^2*S12*S13-
E30*H11*S23+E30*S11*S23)/(-H13*H22+H12*H23-E30*H23*S23+E30*H22*S13+E30*H13*S22-
E30^2*S13*S22-E30*H12*S23+E30^2*S12*S23);
c303=-((H12-E30*S12)^2-(H11-E30*S11)*(H22-E30*S22))/(-(H13-E30*S13)*(H22-
E30*S22)+(H12-E30*S12)*(H23-E30*S23));
norm30=sqrt(1/(c301^2+c302^2+c303^2));
c301=norm30*c301;
```

```
c302=norm30*c302;
c303=norm30*c303;

c311=1;
c312=-(-H12*H13+H11*H23-E31*H23*S11+E31*H13*S12+E31*H12*S13-E31^2*S12*S13-
E31*H11*S23+E31*S11*S23)/(-H13*H22+H12*H23-E31*H23*S23+E31*H22*S13+E31*H13*S22-
E31^2*S13*S22-E31*H12*S23+E31^2*S12*S23);
c313=-((H12-E31*S12)^2-(H11-E31*S11)*(H22-E31*S22))/(-(H13-E31*S13)*(H22-
E31*S22)+(H12-E31*S12)*(H23-E31*S23));
norm31=sqrt(1/(c311^2+c312^2+c313^2));
c311=norm31*c311;
c312=norm31*c312;
c313=norm31*c313;
norm31=sqrt(1/(c311^2+c312^2+c313^2));

c321=1;
c322=-(-H12*H13+H11*H23-E32*H23*S11+E32*H13*S12+E32*H12*S13-E32^2*S12*S13-
E32*H11*S23+E32*S11*S23)/(-H13*H22+H12*H23-E32*H23*S23+E32*H22*S13+E32*H13*S22-
E32^2*S13*S22-E32*H12*S23+E32^2*S12*S23);
c323=-((H12-E32*S12)^2-(H11-E32*S11)*(H22-E32*S22))/(-(H13-E32*S13)*(H22-
E32*S22)+(H12-E32*S12)*(H23-E32*S23));
norm32=sqrt(1/(c321^2+c322^2+c323^2));
c321=norm32*c321;
c322=norm32*c322;
c323=norm32*c323;
norm32=sqrt(1/(c321^2+c322^2+c323^2));

x1=-b:2*b/(N-1):b;
x2=-a:2*a/(N-1):a;
Well=zeros(length(x1),1);
Ener10=zeros(length(x2),1);
Ener20=zeros(length(x2),1);
Ener21=zeros(length(x2),1);
Ener30=zeros(length(x2),1);
Ener31=zeros(length(x2),1);
Ener32=zeros(length(x2),1);
Psi10=zeros(length(x1),1);
Psi20=zeros(length(x1),1);
Psi21=zeros(length(x1),1);
Psi30=zeros(length(x1),1);
Psi31=zeros(length(x1),1);
Psi32=zeros(length(x1),1);
Psi10sq=zeros(length(x1),1);
Psi20sq=zeros(length(x1),1);
Psi21sq=zeros(length(x1),1);
Psi30sq=zeros(length(x1),1);
Psi31sq=zeros(length(x1),1);
Psi32sq=zeros(length(x1),1);

%Change energy units to eV
V0=V0*27.21;
E10=E10*27.21;
E20=E20*27.21;
E21=E21*27.21;
E30=E30*27.21;
E31=E31*27.21;
E32=E32*27.21;


for i=1:1:N
```

```
  if x1(i)<=-a
    Well(i)=0;
  end
  if x1(i)>-a
    Well(i)=V0;
  end
  if x1(i)>=a
    Well(i)=0;
  end
end

for i=1:1:N
  Ener10(i)=E10;
  Ener20(i)=E20;
  Ener21(i)=E21;
  Ener30(i)=E30;
  Ener31(i)=E31;
  Ener32(i)=E32;
  Psi10(i)=Psi1(x1(i),alpha1,c101)+E10;
  Psi20(i)=Psi2(x1(i),alpha1,alpha2,c201,c202)+E20;
  Psi21(i)=Psi2(x1(i),alpha1,alpha2,c211,c212)+E21;
  Psi30(i)=Psi3(x1(i),alpha1,alpha2,alpha3,c301,c302,c303)+E30;
  Psi31(i)=Psi3(x1(i),alpha1,alpha2,alpha3,c311,c312,c313)+E31;
  Psi32(i)=Psi3(x1(i),alpha1,alpha2,alpha3,c321,c322,c323)+E32;
  Psi10sq(i)=(Psi1(x1(i),alpha1,c101))^2+E10;
  Psi20sq(i)=(Psi2(x1(i),alpha1,alpha2,c201,c202))^2+E20;
  Psi21sq(i)=(Psi2(x1(i),alpha1,alpha2,c211,c212))^2+E21;
  Psi30sq(i)=(Psi3(x1(i),alpha1,alpha2,alpha3,c301,c302,c303))^2+E30;
  Psi31sq(i)=(Psi3(x1(i),alpha1,alpha2,alpha3,c311,c312,c313))^2+E31;
  Psi32sq(i)=(Psi3(x1(i),alpha1,alpha2,alpha3,c321,c322,c323))^2+E32;
end

figure(1)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
ylabel('E [eV]');
title('Ground State for \phi_1');
hold on
plot(x2,Ener10,'r');
hold on
plot(x1,Psi10,'r');
hold off

figure(2)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
ylabel('E [H]');
title('Ground State for \phi_2');
hold on
plot(x2,Ener20,'g');
hold on
plot(x1,Psi20,'g');
hold off

figure(3)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
```

```
ylabel('E [H]');
title('Ground State for \phi_3');
hold on
plot(x2,Ener30,'b');
hold on
plot(x1,Psi30,'b');
hold off

figure(4)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
ylabel('E [H]');
title('Ground States for \phi_1, \phi_2, \phi_3');
hold on
plot(x2,Ener10,'r');
hold on
plot(x1,Psi10,'r');
hold on
plot(x2,Ener20,'g');
hold on
plot(x1,Psi20,'g')
hold on
plot(x2,Ener30,'b');
hold on
plot(x1,Psi30,'b')
legend('V_0','E_0(\phi_1)','\phi_1','E_0(\phi_2)','\phi_2','E_0(\phi_3)','\phi_3');
hold off

figure(5)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
ylabel('E [H]');
title('Probability distribution for \phi_1');
hold on
plot(x2,Ener10,'r');
hold on
plot(x1,Psi10sq,'r');
hold off

figure(6)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
ylabel('E [H]');
title('Probability distribution for \phi_2');
hold on
plot(x2,Ener20,'g');
hold on
plot(x1,Psi20sq,'g');
hold off

figure(7)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
ylabel('E [H]');
title('Probability distribution for \phi_3');
hold on
```

```
plot(x2,Ener30,'b');
hold on
plot(x1,Psi30sq,'b');
hold off

figure(8)
plot(x1,Well,'k');
axis([-b b -8 1]);
xlabel('x [au]');
ylabel('E [H]');
title('Probability distribution for \phi_1, \phi_2, \phi_3');
hold on
plot(x2,Ener10,'r');
hold on
plot(x1,Psi10sq,'r');
hold on
plot(x2,Ener20,'g');
hold on
plot(x1,Psi20sq,'g')
hold on
plot(x2,Ener30,'b');
hold on
plot(x1,Psi30sq,'b')
legend('V_0','E_0(\phi_1)','\phi_1','E_0(\phi_2)','\phi_2','E_0(\phi_3)','\phi_3');
hold off
```