

## PHY 304, II-Semester 2023/24, Assignment 4 solution

(1) **Variational Hydrogen atom:** [8 pts] Apply the variational method to the Hydrogen atom, with the Hamiltonian from Eq. (4.72) QM-I ( $\hat{H}_{rel}$  only).

(a) Use the trial wavefunction  $\phi(r) = \mathcal{N}e^{-\beta r^2}$ , with  $r = \sqrt{x^2 + y^2 + z^2}$ , to find an approximation for the ground-state energy and ground-state wavefunction [3pts]

*Solution: The Hamiltonian from Eq. (4.72) is:*

$$\hat{H}_{rel} = -\frac{\hbar^2}{2\mu}\Delta_{\mathbf{r}} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}|} \quad (1)$$

Before we minimize the energy functional  $\langle \phi(\mathbf{r}) | \hat{H}_{rel} | \phi(\mathbf{r}) \rangle$ , we first need to normalize the wavefunction. For that we require,

$$\int d^3\mathbf{r} |\phi(\mathbf{r})|^2 = 4\pi \int_0^\infty r^2 |\phi(r)|^2 dr = 1, \quad (2)$$

since nothing depends on angles and hence the angular integrations just give  $4\pi$ . Inserting the trial wavefunction we have

$$4\pi|\mathcal{N}|^2 \int_0^\infty r^2 e^{-2\beta r^2} dr = 2\pi|\mathcal{N}|^2 \sqrt{\frac{\pi}{2^5\beta^3}} = 1$$

$$\mathcal{N} = \left(\frac{2\beta}{\pi}\right)^{\frac{3}{4}}. \quad (3)$$

The energy functional is,

$$\langle \hat{H}_{rel} \rangle = \langle \hat{T} \rangle + \langle \hat{V} \rangle \quad (4)$$

We evaluate the expectation value of the kinetic term and the potential term separately.

$$\langle \hat{T} \rangle = -\frac{\hbar^2}{2\mu}|\mathcal{N}|^2 \int e^{-\beta r^2} (\nabla_{\mathbf{r}}^2 e^{-\beta r^2}) r^2 \sin\theta dr d\theta d\phi \quad (5)$$

We only need the radial part of the 3D Laplacian operator in spherical coordinates, since the trial wavefunction does not depend on angles and hence all the angular derivatives vanish. Thus:

$$(\nabla_{\mathbf{r}}^2 e^{-\beta r^2}) = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} e^{-\beta r^2} \right) = \frac{1}{r^2} \frac{d}{dr} \left( -2\beta r^3 e^{-\beta r^2} \right) = -2\beta(3r^2 - 2\beta r^4) e^{-\beta r^2}. \quad (6)$$

Inserting Eq. (6) into Eq. (5) we get

$$\begin{aligned} \langle \hat{T} \rangle &= -\frac{\hbar^2}{2\mu} \left(\frac{2\beta}{\pi}\right)^{3/2} (4\pi) \int_0^\infty (3r^2 - 2\beta r^4) e^{-2\beta r^2} dr \\ &= -\frac{\hbar^2}{\mu} \pi \beta^4 \left(\frac{2\beta}{\pi}\right)^{3/2} \left[ \frac{3}{8\beta} - \frac{\pi}{2\beta} - \frac{3}{32\beta^2} \right] \\ &= \frac{3\hbar^2\beta}{2\mu}. \end{aligned} \quad (7)$$

Evaluating the expectation value of the potential is easier

$$\langle \hat{V} \rangle = -\frac{e^2}{4\pi\epsilon_0} |\mathcal{N}|^2 4\pi \int_0^\infty e^{-2\beta r^2} \frac{1}{r} r^2 dr = -\frac{e^2}{2\pi\epsilon_0} \sqrt{\frac{2\beta}{\pi}}. \quad (8)$$

Combining both into Eq. (15) gives the complete energy expectation value

$$\langle \hat{H} \rangle = \frac{3\hbar^2\beta}{2\mu} - \frac{e^2}{2\pi\epsilon_0} \left( \frac{2\beta}{\pi} \right)^{1/2}. \quad (9)$$

Minimizing with respect to  $\beta$  and approximating  $\mu \approx m$  (since the mass of the proton is much larger than that of the electron),

$$\frac{\partial \langle \hat{H} \rangle}{\partial \beta} = \frac{3\hbar^2}{2m} - \frac{e^2}{2\pi\epsilon_0} \sqrt{\frac{2}{\pi\beta}} \stackrel{!}{=} 0 \Rightarrow \beta = \frac{2}{\pi} \left( \frac{me^2}{6\pi\epsilon_0\hbar} \right)^2 = \frac{8}{9\pi a_0^2} \quad (10)$$

Substituting the above parameter for the width of the Gaussian trial wavefunction into the upper bound on the minimum value of the energy in Eq. (9) gives us:

$$\langle H \rangle_{\min} = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{8}{3\pi} = \frac{8}{3\pi} E_1 = -11.5 \text{ eV}, \quad (11)$$

which is reasonably close to the true ground state energy of  $-13.6 \text{ eV}$ .

The Ansatz now with the value of the parameter  $\beta$  inserted, reads:

$$\phi(r) = \left( \frac{4}{3\pi a_0} \right)^{3/2} e^{-\frac{8r^2}{9\pi a_0^2}} \quad (12)$$

and correctly captures the scaling of the spatial delocalisation radius of the electron with  $a_0$ .

(b) Do the same, using the trial wavefunction  $\phi(r) = \mathcal{N}e^{-\alpha r}$  instead. [3pt]

*Solution:* We need to essentially follow the same steps as above. For the normalization we have,

$$\int_0^\infty 4\pi r^2 |\phi(r)|^2 dr = 1 \quad (13)$$

which gives,

$$4\pi |\mathcal{N}|^2 \int_0^\infty r^2 e^{-2\alpha r} dr = 4\pi |\mathcal{N}|^2 \frac{1}{4\alpha^3} = 1$$

$$\mathcal{N} = \sqrt{\frac{\alpha^3}{\pi}} \quad (14)$$

The energy functional as before can be broken as,

$$\langle \hat{H}_{rel} \rangle = \langle T \rangle + \langle V \rangle \quad (15)$$

The kinetic term is :

$$\langle T \rangle = -\frac{\hbar^2}{2\mu} |\mathcal{N}|^2 \int e^{-\alpha r} (\nabla_r^2 e^{-\alpha r}) r^2 \sin \theta dr d\theta d\phi \quad (16)$$

The radial part of the 3D Laplacian operator in spherical coordinates gives,

$$(\nabla_r^2 e^{-\alpha r}) = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} e^{-\alpha r} \right) = \frac{1}{r^2} \frac{d}{dr} (-\alpha r^2 e^{-\alpha r}) = \left( \alpha - \frac{2}{r} \right) \alpha e^{-\alpha r} \quad (17)$$

Plugging value from Eq. (17) to Eq. (16) we get,

$$\begin{aligned} \langle \hat{T} \rangle &= -\frac{\hbar^2}{2\mu} \mathcal{N}^2 (4\pi) \int_0^\infty \left( \alpha - \frac{2}{r} \right) \alpha e^{-2\alpha r} r^2 dr \\ &= -\frac{\hbar^2}{2\mu} \frac{\alpha^3}{\pi} 4\pi \left( \frac{-1}{4\alpha} \right) \\ &= \frac{\hbar^2 \alpha^2}{2\mu}. \end{aligned} \quad (18)$$

Similarly the potential energy term is:

$$\begin{aligned} \langle \hat{V} \rangle &= -\frac{e^2}{4\pi\epsilon_0} |\mathcal{N}|^2 4\pi \int_0^\infty e^{-2\alpha r} \frac{1}{r} r^2 dr \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{\alpha^3}{\pi} 4\pi \int_0^\infty r e^{-2\alpha r} dr \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{\alpha^3}{\pi} 4\pi \left( \frac{1}{4\alpha^2} \right) = -\frac{e^2}{4\pi\epsilon_0} \alpha \end{aligned} \quad (19)$$

Thus, the expectation value of the Hamiltonian is:

$$\langle \hat{H} \rangle = \frac{\hbar^2 \alpha^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0} \alpha \quad (20)$$

Minimizing with respect of  $\alpha$ , we obtain:

$$\begin{aligned} \frac{\hbar^2 \alpha}{\mu} - \frac{e^2}{4\pi\epsilon_0} &= 0 \text{ giving,} \\ \alpha &= \frac{\mu e^2}{4\pi\epsilon_0 \hbar^2} \end{aligned} \quad (21)$$

With this value of the parameter the upper bound on the energy is found to be:

$$\langle \hat{H} \rangle_{min} = -\frac{\mu e^4}{2\hbar^2 (4\pi\epsilon_0)^2} = -13.6 \text{ eV} \quad (22)$$

As can be seen, we get an exact answer with this ansatz, since it provided the correct functional form! The wavefunction after having plugged in the parameter is:

$$\phi(r) = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}, \quad (23)$$

which also is the exact solution.

- (c) Compare both results for wavefunction and energy with the known true solution and discuss. [2pts]

*Solution:* We plot the wavefunction found in (a) and (b) and compare it with the hydrogen wavefunction below:

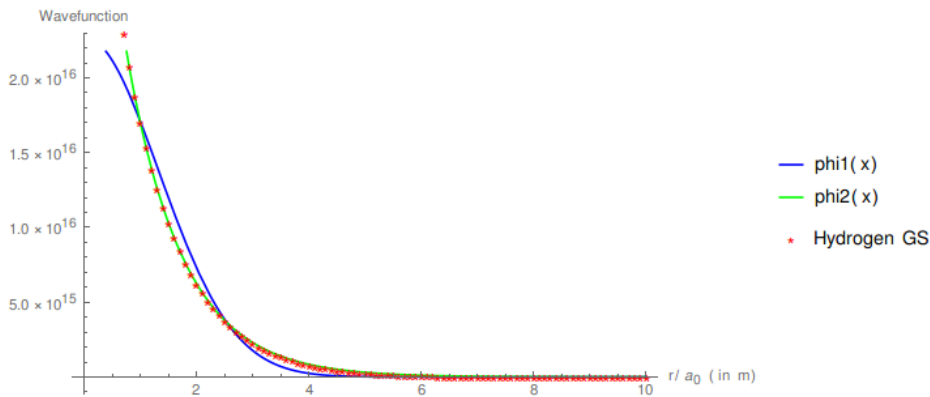


Figure 1: Here,  $\phi_1(x) = \left( \frac{4}{3\pi a_0} \right)^{3/2} e^{-\frac{8r^2}{9\pi a_0^2}}$  and  $\phi_2(x) = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-x/a_0}$ . We see that since our trial ansatz of (b) had the same functional form as the Hydrogen GS wavefunction, the variational method gives us the exact ground state energy. We also see that even the “wrongly shaped” Gaussian Ansatz has been matched onto the true solution as closely as possible, through the variational approach.

**(2) Negative Hydrogen ion: [6 pts]** In the lecture, we discussed the application of a variational Ansatz, Eq. (7.101) to approximate the ground-state of Helium, in which two electrons are bound to the Helium nucleus through the Coulomb potential. Instead we could attempt the same Ansatz and calculation for two electrons attached to a single proton, which would form  $H^-$ , a negatively charged Hydrogen ion.

- (a) Do that for the same trial wavefunction that we had used for Helium in the lecture and discuss the implications of your result for the ground-state energy [2pts].

*Solution:* Trial wavefunction is given by

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z_{eff}^3}{\pi a_0^3} e^{-Z_{eff}(r_1+r_2)/a_0} \quad (24)$$

The Hamiltonian is ( from Sec. (7.5))

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (25)$$

We can split the Hamiltonian (similar to Eq. (7.102))

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z_{eff}}{r_1} + \frac{Z_{eff}}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z_{eff} - 1}{r_1} + \frac{Z_{eff} - 1}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (26)$$

From Sec. (7.5.1) we can write the expectation value of  $\hat{H}$ ,

$$\begin{aligned} \langle \hat{H} \rangle &= 2Z_{eff}^2 E_{100} + 2(Z_{eff} - 1) \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle \\ &= 2Z_{eff}^2 E_{100} + 2(Z_{eff} - 1) \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{Z_{eff}}{a_0} \right) \\ &= 2Z_{eff}^2 E_{100} - 4(Z_{eff} - 1)Z_{eff} E_{100} - \frac{5Z_{eff}}{4} E_{100} \\ &= -2Z_{eff}^2 + \frac{11}{4} Z_{eff} E_{100} \end{aligned} \quad (27)$$

We now minimize  $\langle \hat{H} \rangle$ :

$$\frac{\partial \langle \hat{H} \rangle}{\partial Z_{eff}} = -4Z_{eff} E_{100} + \frac{11}{4} E_{100} \quad (28)$$

To get,

$$Z_{eff} = \frac{11}{16} \quad (29)$$

Inserting the value of  $Z_{eff}$  to find the energy in Eq. 27, we get

$$\langle \hat{H} \rangle_{min} = \frac{121}{128} E_{100} = -12.9 eV \quad (30)$$

In this case, we can see that  $\langle \hat{H} \rangle_{min} > -13.6 eV$ . Using this trial wavefunction, we would thus conclude that there is no stable negative ion bound state, since it is energetically favorable for one electron to fly off, leaving behind a neutral hydrogen atom.

(b) Now do the same for the more sophisticated two-electron trial wavefunction

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2) &= \mathcal{N} [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)], \quad \text{with} \\ \phi_1(\mathbf{r}) &= \sqrt{\frac{Z_1^3}{\pi a_0^3}} e^{-Z_1 r/a_0}, \quad \phi_2(\mathbf{r}) = \sqrt{\frac{Z_2^3}{\pi a_0^3}} e^{-Z_2 r/a_0}, \end{aligned} \quad (31)$$

for  $Z_1, Z_2 > 0$  real and adjustable,  $a_0$  the Bohr radius, and  $\mathcal{N}$  a normalisation factor. Which ground state energy do you find now, how does this change your conclusions and what would have to be the spin state of the two electrons? [4pts].

*Solution:*

*We begin with the normalization condition:*

$$\begin{aligned}
1 &= \int |\psi|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
&= |\mathcal{N}|^2 \left( \int \phi_1^2 d^3\mathbf{r}_1 \int \phi_2^2 d^3\mathbf{r}_2 + 2 \int \phi_1 \phi_2 d^3\mathbf{r}_1 \int \phi_1 \phi_2 d^3\mathbf{r}_2 + \int \phi_2^2 d^3\mathbf{r}_1 \int \phi_1^2 d^3\mathbf{r}_2 \right) \\
&= |\mathcal{N}|^2 (1 + 2S^2 + 1), \tag{32}
\end{aligned}$$

where

$$\begin{aligned}
S &= \int \phi_1(r) \phi_2(r) d^3\mathbf{r} \\
&= \frac{\sqrt{(Z_1 Z_2)^3}}{\pi a_0^3} \int e^{-(Z_1+Z_2)r/a_0} 4\pi r^2 dr = \frac{4}{a_0^3} \left(\frac{y}{3}\right)^3 \left[ \frac{2a_0^3}{(Z_1 + Z_2)^3} \right] = \left(\frac{y}{x}\right)^3. \tag{33}
\end{aligned}$$

The normalization constant  $A$  is therefore given by:

$$\mathcal{N}^2 = \frac{1}{2[1 + (y/x)^6]}. \tag{34}$$

For the Hamiltonian operator  $H$ , we have:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{35}$$

$$\begin{aligned}
H\psi &= \mathcal{N} \left\{ \left[ -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) \right] \phi_1(r_1) \phi_2(r_2) \right. \\
&\quad \left. + \left[ -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) \right] \phi_2(r_1) \phi_1(r_2) \right\} \\
&\quad + \mathcal{N} \frac{e^2}{4\pi\epsilon_0} \left\{ \left[ \frac{Z_1 - 1}{r_1} + \frac{Z_2 - 1}{r_2} \right] \phi_1(r_1) \phi_2(r_2) + \left[ \frac{Z_1 - 1}{r_1} + \frac{Z_2 - 1}{r_2} \right] \phi_2(r_1) \phi_1(r_2) \right\} + V_{ee} \psi \tag{36}
\end{aligned}$$

where  $V_{ee}$  is defined as:

$$V_{ee} \equiv \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{37}$$

The term in first curly brackets is  $(Z_1^2 + Z_2^2)E_1 \phi_1(r_1) \phi_2(r_2) + (Z_2^2 + Z_1^2)E_1 \phi_2(r_1) \phi_1(r_2)$ , so

$$\begin{aligned}
H\psi &= (Z_1^2 + Z_2^2)E_1\psi \\
&+ \mathcal{N} \frac{e^2}{4\pi\epsilon_0} \left\{ \left[ \frac{Z_1 - 1}{r_1} + \frac{Z_2 - 1}{r_2} \right] \phi_1(r_1)\phi_2(r_2) + \left[ \frac{Z_2 - 1}{r_1} + \frac{Z_1 - 1}{r_2} \right] \phi_2(r_1)\phi_1(r_2) \right\} + V_{ee}\psi,
\end{aligned} \tag{38}$$

The expectation value of  $\hat{H}$  in the state corresponding to the given trial wavefunction is,

$$\begin{aligned}
\langle H \rangle &= (Z_1^2 + Z_2^2)E_1 + \langle V_{ee} \rangle \\
&+ \mathcal{N}^2 \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\{ \langle \phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2) \left| \left( \frac{Z_1 - 1}{r_1} + \frac{Z_2 - 1}{r_2} \right) \right| \phi_1(r_1)\phi_2(r_2) \rangle \right. \\
&\left. + \langle \phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2) \left| \left( \frac{Z_1 - 1}{r_1} + \frac{Z_2 - 1}{r_2} \right) \right| \phi_2(r_1)\phi_1(r_2) \rangle \right\}
\end{aligned} \tag{39}$$

The term within the curly bracket can be simplified as,

$$\begin{aligned}
\left\{ \right\} &= (Z_1 - 1) \langle \phi_1(r_1) \left| \frac{1}{r_1} \right| \phi_1(r_1) \rangle + (Z_2 - 1) \langle \phi_2(r_2) \left| \frac{1}{r_2} \right| \phi_2(r_2) \rangle \\
&+ (Z_2 - 1) \langle \phi_1(r_1) \left| \frac{1}{r_1} \right| \phi_2(r_1) \rangle \langle \phi_2(r_2) \left| \frac{1}{r_2} \right| \phi_1(r_2) \rangle \\
&+ (Z_1 - 1) \langle \phi_1(r_1) \left| \frac{1}{r_1} \right| \phi_2(r_1) \rangle \langle \phi_2(r_2) \left| \frac{1}{r_2} \right| \phi_1(r_2) \rangle + (Z_1 - 1) \langle \phi_2(r_1) \left| \frac{1}{r_1} \right| \phi_1(r_1) \rangle \langle \phi_1(r_2) \left| \frac{1}{r_2} \right| \phi_2(r_2) \rangle \\
&+ (Z_2 - 1) \langle \phi_2(r_1) \left| \frac{1}{r_1} \right| \phi_1(r_1) \rangle \langle \phi_1(r_2) \left| \frac{1}{r_2} \right| \phi_2(r_2) \rangle + (Z_2 - 1) \langle \phi_2(r_1) \left| \frac{1}{r_1} \right| \phi_2(r_1) \rangle \\
&+ (Z_1 - 1) \langle \phi_1(r_2) \left| \frac{1}{r_2} \right| \phi_1(r_2) \rangle \\
&= 2(Z_1 - 1) \left\langle \frac{1}{r} \right\rangle_1 + 2(Z_1 - 1) \left\langle \frac{1}{r} \right\rangle_2 + 2(Z_1 - 1) \langle \phi_1 | \phi_2 \rangle \langle \phi_1 \left| \frac{1}{r} \right| \phi_2 \rangle \\
&+ 2(Z_2 - 1) \langle \phi_1 | \phi_2 \rangle \langle \phi_1 \left| \frac{1}{r} \right| \phi_2 \rangle
\end{aligned} \tag{40}$$

Where,  $\left\langle \frac{1}{r} \right\rangle_1 = \frac{Z_1}{a_0}$ ; and  $\left\langle \frac{1}{r} \right\rangle_2 = \frac{Z_2}{a_0}$ .

$$\begin{aligned}
\langle \phi_1 | \phi_2 \rangle &= \frac{\sqrt{Z_1^3 Z_2^3}}{\pi a_0^3} \times 4\pi \int_0^\infty r^2 dr e^{-(Z_1 + Z_2)r/a_0} \\
&= \frac{8\sqrt{Z_1^3 Z_2^3}}{a_0(Z_1 + Z_2)^2} \\
&= S = \left( \frac{y}{x} \right)^3
\end{aligned} \tag{41}$$

$$\begin{aligned}
\langle \phi_1 \left| \frac{1}{r} \right| \phi_2 \rangle &= \frac{\sqrt{(Z_1 Z_2)^3}}{\pi a_0^3} \times 4\pi \int_0^\infty e^{-(Z_1+Z_2)r/a_0} r dr \\
&= \frac{y^3}{2a_0^3} \left[ \frac{a_0}{Z_1 + Z_2} \right]^2 = \frac{y^3}{2a_0 x^2}
\end{aligned} \tag{42}$$

So, the expectation value as a function of  $x$  and  $y$  can be written as,

$$\begin{aligned}
\langle H \rangle &= (x^2 - \frac{1}{2}y^2)E_1 + \mathcal{N}^2 \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{2}{a_0} \left\{ [Z_1^2 + Z_2^2 - (Z_1 + Z_2)] + (x-2) \left( \frac{y}{x} \right)^3 \frac{y^3}{2x^2} \right\} + \langle V_{ee} \rangle \\
&= (x^2 - \frac{1}{2}y^2)E_1 + 4E_1 \mathcal{N}^2 \left[ x^2 - \frac{1}{2}y^2 - x + \frac{1}{2}(x-2) \frac{y^6}{x^5} \right] + \langle V_{ee} \rangle
\end{aligned} \tag{43}$$

Computing  $\langle V_{ee} \rangle$ :

$$\begin{aligned}
V_{ee} &= \frac{e^2}{4\pi\epsilon_0} \langle \psi \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi \rangle \\
&= \frac{e^2}{4\pi\epsilon_0} \mathcal{N}^2 \langle \phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2) \rangle \\
&= \frac{e^2}{4\pi\epsilon_0} \mathcal{N}^2 \left[ 2 \langle \phi_1(r_1)\phi_2(r_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_1(r_1)\phi_2(r_2) \rangle + 2 \langle \phi_1(r_1)\phi_2(r_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_2(r_1)\phi_1(r_2) \rangle \right] \\
&= 2 \frac{e^2}{4\pi\epsilon_0} \mathcal{N}^2 (B + C)
\end{aligned} \tag{44}$$

Where

$$B = \langle \phi_1(r_1)\phi_2(r_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_1(r_1)\phi_2(r_2) \rangle; \quad C = \langle \phi_1(r_1)\phi_2(r_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_2(r_1)\phi_1(r_2) \rangle. \tag{45}$$

$$B = \left( \frac{Z_1^3 Z_2^3}{(\pi a_0^3)^2} \right) \int \frac{e^{-2Z_1 r_1/a_0 - 2Z_2 r_2/a_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3 r_1 d^3 r_2. \tag{46}$$

As on Sec. (7.5.1), the  $r_2$  integral is

$$\int \frac{e^{-2Z_2 r_2/a_0}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}} d^3 r_2 = \frac{\pi a_0^3}{Z_2^3 r_1} \left[ 1 - \left( 1 + \frac{2Z_2 r_1}{a_0} \right) e^{-2Z_2 r_1/a_0} \right] \tag{47}$$

Continuing, we have

$$B = \left( \frac{Z_1^3 Z_2^3}{(\pi a_0^3)^2} \right) \left( \frac{\pi a_0^3}{Z_2^3} \right) \int_0^\infty e^{-2Z_1 r_1/a_0} \left[ 1 - \left( 1 + \frac{2Z_2 r_1}{a_0} \right) e^{-2Z_2 r_1/a_0} \right] r_1^2 dr_1 \tag{48}$$

$$= \frac{4Z_1^3}{a_0^3} \int_0^\infty r_1^2 e^{-2Z_1 r_1/a_0} - r_1^2 e^{-2(Z_1+Z_2)r_1/a_0} - \frac{2Z_2}{a_0} r_1^3 e^{-2(Z_1+Z_2)r_1/a_0} dr_1 \tag{49}$$

$$= \frac{4Z_1^3}{a_0^3} \left[ \frac{a_0^2}{(2Z_1)^2} - \frac{a_0^2}{(2(Z_1 + Z_2))^2} - \frac{2Z_2 a_0^3}{(2(Z_1 + Z_2))^3} \right] \tag{50}$$

$$= \frac{Z_1 Z_2}{a_0(Z_1 + Z_2)} \left[ 1 + \frac{Z_1 Z_2}{(Z_1 + Z_2)^2} \right] \frac{y^2}{4a_0^2} \left( 1 + \frac{y^2}{4a_0^2} \right). \tag{51}$$



and

$$\begin{aligned}
C &= \left( \frac{Z_1^3 Z_2^3}{(\pi a_0^3)^2} \right) \int e^{-Z_1 r_1/a_0 - Z_2 r_2/a_0 - Z_2 r_1/a_0 - Z_1 r_2/a_0} \frac{1}{|r_1 - r_2|} d^3 r_1 d^3 r_2 \\
&= \left( \frac{Z_1 Z_2}{a_0} \right)^3 \frac{5}{4a_0} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{y^2}{16a_0^5} \\
&= \frac{6}{16a_0} \frac{y^6}{x^5}.
\end{aligned} \tag{52}$$

So we have

$$\langle V_{ee} \rangle = 2 \left( \frac{e^2}{4\pi\epsilon_0} \right) \mathcal{N}^2 \left[ \frac{y^2}{4a_0 x} \left( 1 + \frac{y^2}{4a_0^2} \right) + \frac{5y^4}{16a_0 x^3} \right], \tag{53}$$

$$\begin{aligned}
\langle H \rangle &= E_1 \left\{ x^2 - \frac{1}{2}y^2 - \frac{2}{[1 + (y/x)^6]} \left[ x^2 - \frac{1}{2}y^2 - x + \frac{1}{2}(x-2)\frac{y^6}{x^5} \right] \right. \\
&\quad \left. - \frac{2}{[1 + (y/x)^6]} \frac{y^2}{4x} \left( 1 + \frac{y^2}{4x^2} + \frac{5y^4}{4x^4} \right) \right\} \\
&= \frac{E_1}{(x^6 + y^6)} \left\{ x^8 + x^2 y^6 - \frac{1}{2}x^6 y^2 - \frac{1}{2}y^8 - 2x^8 + x^6 y^2 \right. \\
&\quad \left. + 2x^7 - x^2 y^6 + 2xy^6 - \frac{1}{2}x^5 y^2 - \frac{1}{2}x^3 y^4 - \frac{5}{2}xy^6 \right\} \\
&= \frac{E_1}{(x^6 + y^6)} \left\{ -x^8 + 2x^7 + \frac{11}{2}x^6 y^2 - \frac{1}{2}x^5 y^2 - \frac{1}{2}x^3 y^4 + \frac{11}{8}xy^6 - \frac{1}{2}y^8 \right\}. \tag{54}
\end{aligned}$$

We can find the extrema of  $\langle H \rangle$  by solving:

$$\frac{\partial}{\partial x} \langle H \rangle = 0 = \frac{\partial}{\partial y} \langle H \rangle \tag{55}$$

By solving these equations using Mathematica we get the minimum of  $\langle H \rangle$  at  $x = 1.32245$ ,  $y = 1.08505$ , corresponding to  $Z_1 = 1.0392$ ,  $Z_2 = 0.2832$ .

Now, the calculated ground state energy for this case is,

$$\langle \hat{H} \rangle_{min} = 1.0266 E_{100} = -13.962 \text{ev}. \tag{56}$$

Here, we are using two different shielding factors, suggesting that one electron is relatively close to the nucleus and the other is further out. Now,  $\langle \hat{H} \rangle_{min} < -13.6 \text{ev}$  (but not by very much), which suggests that a bound state does exist for  $H^-$ . It's only barely bound. The spin state of two electrons should be anti-symmetric because electrons are identical particles, spatial wavefunction should be symmetric to interchange.

**(3) WKB approximation: [8 pts]** Using the WKB method, calculate the transmission coefficient for the potential barrier ( $V_0, a > 0$ )

$$V(x) = \begin{cases} V_0 \left(1 - \frac{|x|}{a}\right) & \text{if } |x| \leq a \\ 0 & \text{if } |x| > a, \end{cases} \quad (57)$$

for all values of  $E$ .

*Solution:*

From Sec 7.8, the transmission coefficient is

$$T = e^{-2 \int_{x_1}^{x_2} \gamma dx} \quad (58)$$

with  $\gamma^2 = \frac{2m}{\hbar^2}[V(x) - E]$  and  $x_1$  and  $x_2$  are the turning points. At the turning points,

$$E = V(x) = V_0 \left(1 - \frac{|x|}{a}\right) \text{ or } \frac{E}{V_0} = 1 - \frac{|x|}{a}$$

$$|x| = a \left(\frac{V_0 - E}{V_0}\right) \text{ or } x = \pm a \left(\frac{V_0 - E}{V_0}\right)$$

Now,

$$\begin{aligned} -2 \int_{x_1}^{x_2} \gamma dx &= -2 \sqrt{\frac{2m}{\hbar^2}} \int_{x_1}^{x_2} \left(V_0 - \frac{V_0 x}{a} - E\right)^{1/2} dx \\ &= -\frac{2\sqrt{2m}}{\hbar} \frac{2}{3} \left(-\frac{a}{V_0}\right) \left[ \left(V_0 - E - \frac{V_0 x}{a}\right)^{3/2} \right]_{x_1}^{x_2} \\ &= -\frac{16\sqrt{m}}{3\hbar} \frac{a}{V_0} (V_0 - E)^{3/2} \end{aligned} \quad (59)$$

Hence the transmission coefficient as a function of energy is

$$T = \exp \left[ -\frac{16\sqrt{m}}{3\hbar} \frac{a}{V_0} (V_0 - E)^{3/2} \right]. \quad (60)$$

**(4) WKB approximation in complex potential landscape: [8 pts]** The matlab script `Assignment4_program_draft_v3.nb` solves the TISE numerically as seen in e.g. Assignment 3 QM-I for the exact same potential as the movie frames in Example 1 QM-1. Run the script once, to generate the eigenstates and energies.

- (a) By changing `statepick` you can choose which eigenvector is shown (in the usual style where we change the baseline of the eigenfunction to sit on the energy). Make a few plots of qualitatively different states, and discuss, based on your insight of the WKB approximation, why they take the form shown. In particular focus on the states where the eigenenergy is close to (below and above) that local maximum (hump) in the potential. [3pts] *Note that solutions must use the mathematica code and plotting tools.*
- (b) Now upgrade `Assignment4_program_draft_v3.nb` at the bottom such that it can also calculate, tabulate, and plot the WKB approximation of the eigenstates that you implement, based on the classical momentum  $p(x)$  and the energy  $E_n$  (taken as known, from the numerical solution of the TISE). Plot those directly on top of the numerically found states, and discuss for a few examples. Plot the true and the WKB solution for a couple of cases where it works well or not so well, and discuss why either is the case. [5pts]

*Solution:*

*We show two states which have eigenenergies close to the local hump (one above and one below).*

*(i) For `statepick = 75` with energy = -1.9172*

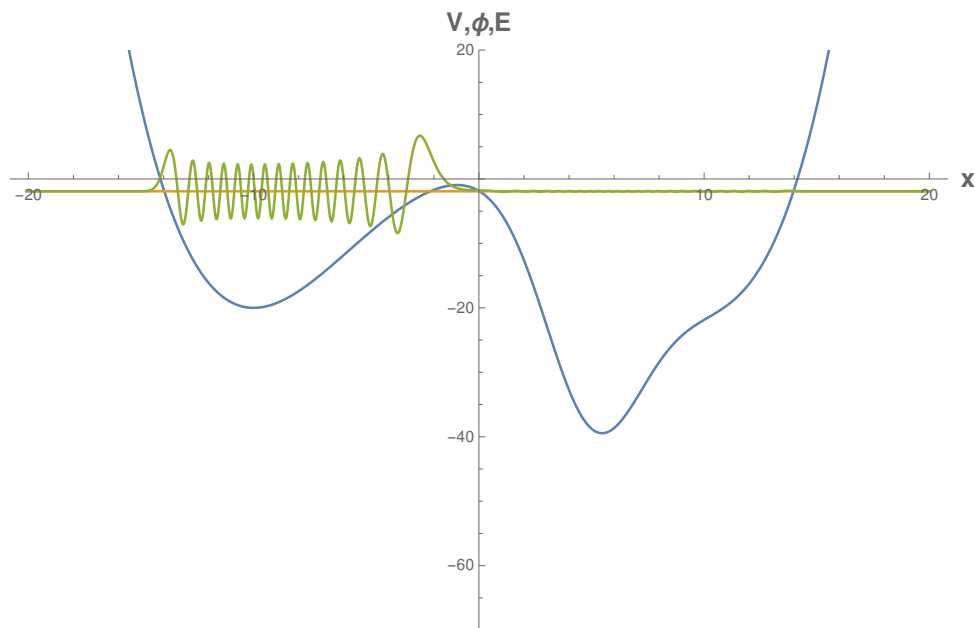


Figure 2: Plotted for `statepick = 75` on top of the energy eigenvalue line = -1.9172

*Discussion: From the WKB approximation we expect high frequency oscillations near the local minima and an increase in wavelength and amplitude near the hump. We see these features in the plot too. Since the wavefunction decays exponentially after the classical turning point, the oscillations have small magnitude after the hump for this case.*

*(ii) For `statepick = 82` with energy = -0.368868*

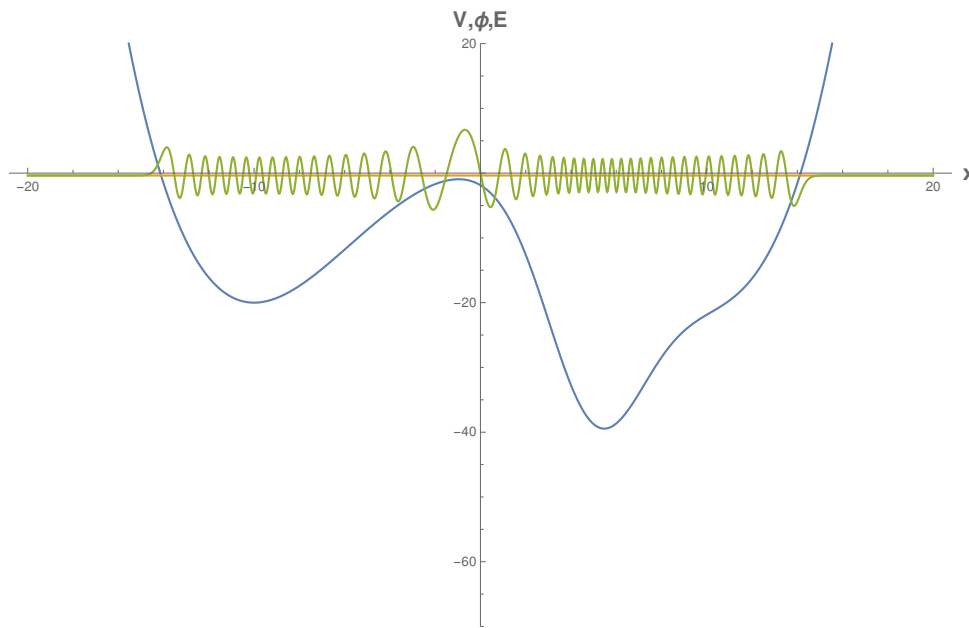


Figure 3: Plotted for `statepick = 82` on top of the energy eigenvalue line = -0.368868

*Discussion: In this case where the energy is slightly above the potential value at the hump we see high frequency oscillations with non-negligible amplitude at both (to the left and right of the hump) the minima regions with the wavefunction decaying after the edges of the plot where the potential becomes larger than the energy value. We also see the expected increase in the amplitude and wavelength at the bump indicating that the particle spends less time there on an average.*

*(b) See `Assignment4_program_solution_v2.nb` for the WKB implementation that generates the figures and read the descriptions in the caption for discussion.*

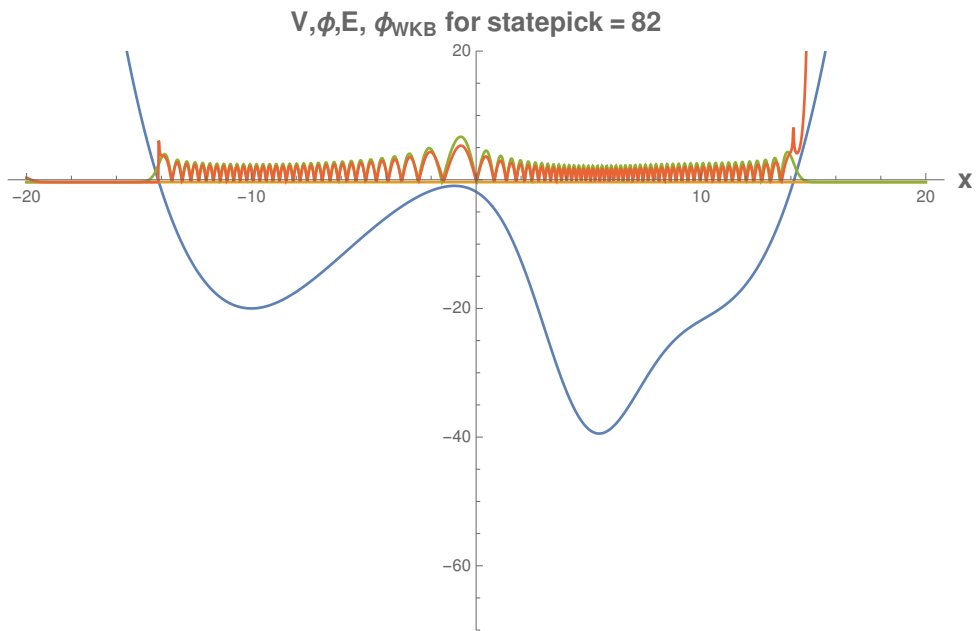


Figure 4: True density (green) and WKB density (red) for a high lying state. WKB breaks down near the classical turning point on the left, and then completely breaks down near the classical turning point (CTP) on the right (because the script does not address that one properly). Overall, WKB does quite good for this high lying states. Ignoring the expected failure at the right CTP, it nicely captures the probability density until we hit the left CTP coming from the right. We could do better here, by switching back to the WKB solution pertaining to the classically forbidden region, which was too clumsy to implement in the script, but could be done if need be.

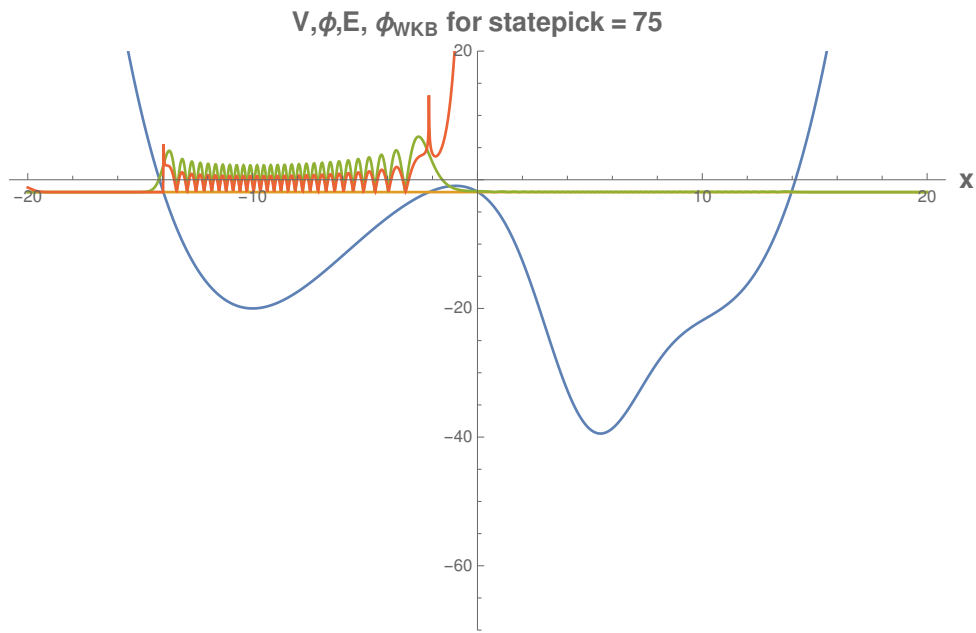


Figure 5: True density (green) and WKB density (red) for statepick = 75. Here we see the same features as for statepick = 82 except now the agreement the WKB and the true density becomes a little worse. Overall, the WKB still captures most of the true solution behaviour.

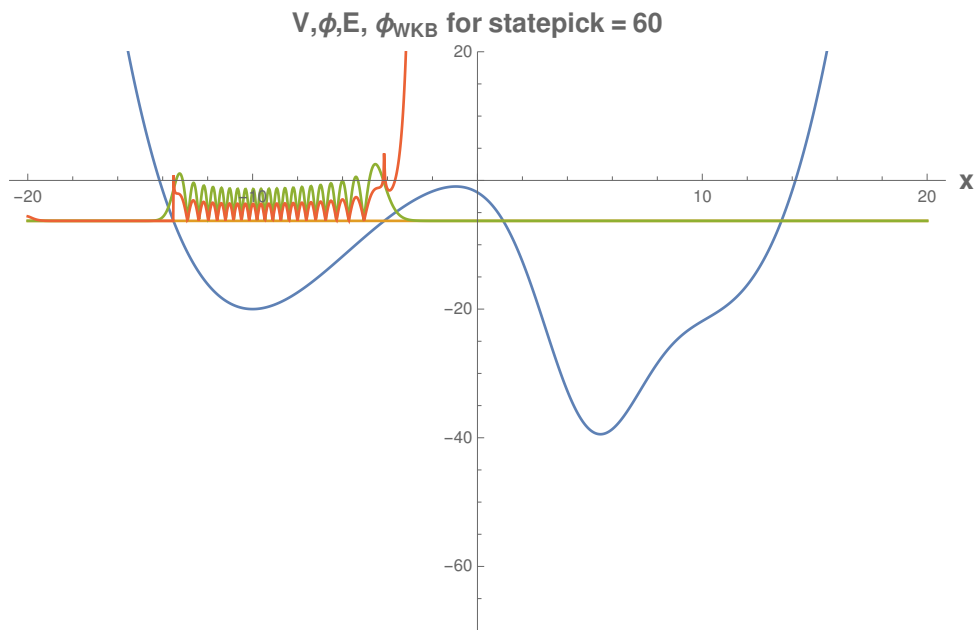


Figure 6: Overall WKB is still not that bad, though as expected we see that the WKB solution for statepick = 60 has even lesser agreement compared to statepick = 75 and statepick = 80. The WKB here still nicely captures the lengthening of the de-Broglie wavelength as potential increases and high frequencies at the minima