1 Variational Principle for Hydrogen

1.1

We wish to make the replacement:

\[ E = \mathcal{E} E_0, \quad r = y r_0, \quad (1) \]

giving:

\[ E_0 \mathcal{E} \psi(s) = -\frac{\hbar^2}{2 m r_0^2} \partial^2_s \psi(s) - \frac{e^2}{4 \pi \epsilon_0 r_0} \frac{1}{s} \psi(s). \quad (2) \]

We have assumed that the ground state is spherically symmetric, such that \( \nabla^2 = \partial^2_s \). This equation is greatly simplified with the choice:

\[ E_0 = \frac{\hbar^2}{2 m r_0^2} = \frac{e^2}{4 \pi \epsilon_0 r_0}, \quad (3) \]

which allows to divide out the common factor to arrive at the adimensional Schrödinger equation:

\[ \mathcal{E} \psi(s) = -\partial^2_s \psi(s) - \frac{1}{s} \psi(s). \quad (4) \]

Eq. (3) is solved by:

\[ r_0 = \frac{2 \pi \epsilon_0 \hbar^2}{e^2 m}, \quad E_0 = \frac{2 e^4 m}{(4 \pi \epsilon_0)^2 \hbar^2}. \quad (5) \]

1.2

Multiplying Eq. (4) by \( \psi(s)^* \) gives:

\[ \mathcal{E} |\psi(s)|^2 = - (\partial^2_s \psi(s)) \psi(s)^* - \frac{1}{s} |\psi(s)|^2, \quad (6) \]

which we can integrate on both sides over all space, and integrate the first term on the RHS by parts (assuming the boundary terms go to zero):

\[ \mathcal{E} \int d^3 s |\psi(s)|^2 = - \int d^3 s (\partial^2_s \psi(s)) \psi(s)^* - \int d^3 s \frac{|\psi(s)|^2}{s}, \quad (7) \]

\[ \mathcal{E} = \int d^3 s |\partial_s \psi(s)|^2 - \int d^3 s \frac{1}{s} |\psi(s)|^2. \quad (8) \]

We find that \( A = 1 \) and \( B = -1 \).
1.3

Performing the integral gives:

\[
\frac{E}{E_0} = A \left(\frac{-1}{2\lambda} \right)^2 \int d^3 s |\psi(s)|^2 + B \frac{1}{8\pi \lambda^3} \int d^3 s \frac{e^{-s/\lambda}}{s},
\]

(9)

\[
\frac{E}{E_0} = A \frac{1}{4\lambda^2} + B \frac{1}{2\lambda^3} \int ds se^{-s/\lambda},
\]

(10)

\[
\frac{E}{E_0} = A \frac{1}{4\lambda^2} + B \frac{1}{2\lambda^3} \left[ (-\lambda)[se^{-s/\lambda}]_0^\infty - \int_0^\infty ds (-\lambda)e^{-s/\lambda} \right],
\]

(11)

\[
\frac{E}{E_0} = A \frac{1}{4\lambda^2} + B \frac{1}{2\lambda}.
\]

(12)

Therefore:

\[
E(\lambda) = E_0 \left( A \frac{1}{4\lambda^2} + B \frac{1}{2\lambda} \right).
\]

(13)

1.4

To find the minimum energy, we wish to solve \( \partial_{\lambda} E(\lambda) = 0 \), ensuring also that it is a minimum:

\[
\partial_{\lambda} E(\lambda)|_{\lambda_0} = 0 = E_0 \left( -A \frac{1}{2\lambda_0^3} - B \frac{1}{2\lambda_0^2} \right),
\]

(14)

\[
\implies \lambda_0 = \frac{A}{B} \quad (\text{or } \lambda \to \infty).
\]

(15)

To check that the first solution is indeed a minimum, note that the function goes to +ive infinity at \( \lambda = 0 \), is negative at \( \lambda_0 \), and goes to 0 as \( \lambda \to \infty \).

1.5

Performing the substitution gives:

\[
E(\lambda_0) = -\frac{E_0 B^2}{4 A}.
\]

(16)

In order to get a number out of this, note that:

\[
E_0 = 2 \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{\hbar} = 2 \left( \frac{1}{137} \right)^2 (0.51 \times 10^6 \text{ eV})
\]

(17)

\[
= 54.3 \text{ eV},
\]

(18)

where I have used that the fine structure constant \( \alpha = e^2/4\pi\epsilon_0\hbar c \simeq 137^{-1} \). Plugging this in gives:

\[
E_{\text{bound}} = 13.6 \text{ eV},
\]

(19)

which happens to be right on, due to a fortuitous choice of variational function.
2 Angular Momentum Operator

2.1
We have the relations (in physicist spherical polar coordinates):

\[ x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi. \]  

(20)

The chain rule tells us:

\[ \partial_\phi = \frac{\partial x}{\partial \phi} \partial_x + \frac{\partial y}{\partial \phi} \partial_y, \]  

\[ = -r \sin \theta \sin \phi \partial_x + r \sin \theta \cos \phi \partial_y, \]  

\[ = -y \partial_x + x \partial_y. \]  

(21)

Therefore:

\[ L_z \psi = -i \hbar (x \partial_y - y \partial_x) \psi = -i \hbar \partial_\phi \psi. \]  

(24)

3 Degeneracies of the 2D Harmonic Oscillator

3.1
The energy levels of the 2D harmonic oscillator are the same as those of two independent 1D harmonic oscillators. I.e.

\[ E = \hbar \omega (1/2 + n_x) + \hbar \omega (1/2 + n_y) = \hbar \omega (1 + n_x + n_y), \]  

(25)

assuming that the spring constant is the same in both directions.

3.2

\[
\begin{array}{|c|c|c|}
\hline
E/(\hbar \omega) & (n_x, n_y) & \text{Degeneracy} \\
\hline
1 & (0, 0) & 1 \\
2 & (1, 0), (0, 1) & 2 \\
3 & (2, 0), (1, 1), (0, 2) & 3 \\
4 & (3, 0), (2, 1), (1, 2), (0, 3) & 4 \\
\hline
\end{array}
\]  

(26)

3.3
Calling the \( E = n \hbar \omega \) energy level the \( n \)'th one, then the degeneracy is \( n \).

3.4
I spent 30 minutes on this part of the problem, and could not complete it
is one solution to the problem. The more complete solutions is as follows. Starting with:

\[ [\mathcal{L}_+, \mathcal{L}_z] = \frac{1}{2} \left( [a^+_x a_y, a^+_x a_x] - [a^+_y a_y, a^+_y a_y] \right), \quad (27) \]

we use the identities and pick out only those terms that are non-zero:

\[ [\mathcal{L}_+, \mathcal{L}_z] = \frac{1}{2} \left( a^+_x [a^+_x, a_x] a_y - a^+_x [a_y, a^+_y a_y] \right), \quad (28) \]

\[ = -a^+_x a_y = -\mathcal{L}_+. \quad (29) \]

Similarly:

\[ [\mathcal{L}_+, \mathcal{L}_z] = \frac{1}{2} \left( [a^+_y a_x, a^+_x a_x] - [a^+_y a_y, a^+_y a_y] \right), \quad (30) \]

\[ = \frac{1}{2} \left( a^+_y [a_x, a^+_x] a_y - a^+_y [a_y, a^+_y] a_x \right), \quad (31) \]

\[ = -a^+_y a_y = +\mathcal{L}_-. \quad (32) \]

Finally,

\[ [\mathcal{L}_+, \mathcal{L}_-] = [a^+_x a_y, a^+_y a_x] \quad (33) \]

\[ = \frac{1}{2} \left( a^+_y [a^+_x, a_x] a_y + a^+_x [a^+_y, a_x] a_y \right), \quad (34) \]

\[ = -a^+_y a_y + a^+_x a_x = 2\mathcal{L}_z. \quad (35) \]

**3.5**

The Hamiltonian is given by:

\[ H = \hbar \omega \left( 1 + a^+_x a_x + a^+_y a_y \right). \quad (36) \]

Therefore:

\[ [\mathcal{L}_+, H] = \hbar \omega \left( a^+_x a_y, a^+_x a_x \right) + \left[ a^+_y a_y, a^+_y a_y \right] \quad (37) \]

\[ = \hbar \omega \left( a^+_x [a^+_x, a_x] a_y + a^+_x [a_x, a^+_y a_y] \right) \quad (38) \]

\[ = 0 \quad (39) \]

and similarly for \( \mathcal{L}_- \). For \( \mathcal{L}_z \):

\[ [\mathcal{L}_z, H] = \frac{\hbar \omega}{2} \left( [a_x a_x, a^+_x a_x] + [a_y a_y, a^+_y a_y] \right) \quad (40) \]

\[ = \frac{\hbar \omega}{2} \left( [n_x, n_x] + [n_y, n_y] \right) \quad (41) \]

\[ = 0, \quad (42) \]

where, taking a break from repeated use of commutation identities, we have simply used our physical intuition/knowledge that number operators commute with themselves.
3.6

Looking at Fig. 1, we can see that the anisotropy completely breaks the degeneracies of the 2D harmonic oscillator, splitting each originally degenerate multiplet into sets of states with evenly spaced energies proportional to $\delta$.

![Figure 1: Energy splitting of anisotropic 2D harmonic oscillator](image)

4 Rydberg Atoms

4.1

In the $n$’th energy level, there are states with orbital angular momentum quantum number $l$ running over the integers from 0 to $n - 1$. For each $l$ there are $2l + 1$ states $m = -l, -l + 1, \ldots, +l$. Therefore, the total number of orbital states is:

$$
\sum_{l=0}^{n-1} (2l + 1) = \sum_{l=1}^{n} (2l - 1) = n(n + 1) - n = n^2. \quad (43)
$$

On top of this there are two electron spin states, meaning that the degeneracy is given by:

$$
\text{Degeneracy} = 2n^2 = 37538 \quad (44)
$$

4.2

The energy of the $n$’th level of a Hydrogen atom is given by

$$
E_n = -\frac{1}{n^2} \text{Ry}, \quad (45)
$$

where 1 Ry = 13.6 eV is the ionization energy of Hydrogen. Therefore, for $n = 137$,

$$
E_{137} = -7.2 \times 10^{-4} \text{eV}. \quad (46)
$$
4.3

The usual thing is that KE + PE = PE/2. Let’s check this.

\[ \partial_r V(r) = F_{\text{centrip}} = \frac{mv^2}{r} = \frac{2KE}{r} \]

\[ \Rightarrow \quad KE = \frac{r}{2} \partial_r V(r) = \frac{e^2}{8\pi\epsilon_0 r} \]

\[ = -\frac{PE}{2}. \]

Therefore

\[ E = -\frac{e^2}{8\pi\epsilon_0 r} \]

4.4

Combining Eqs. (46) with (50), we get

\[ r = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0\hbar c} \frac{1}{7.2 \times 10^{-4} \text{ eV}} \]

\[ = \frac{1}{2} \frac{1}{2137} \frac{1}{7.2 \times 10^{-4}} \times 1.97 \times 10^{-7} \text{ m} \]

\[ = 10^{-6} \text{ m} = 10^4 \text{ Å}. \]

4.5

With \( n = 1 \) we get:

\[ r = \frac{1}{2} \frac{1}{2137} \frac{1}{13.6} \times 1.97 \times 10^{-7} \text{ m} \]

\[ = 0.5 \text{ Å}, \]

which is surprisingly good!
5 Double Well Potential

5.1

5.2

Figure 2: The double well potential.

Figure 3: Time-varying probability density of a particle in a double potential well. Thanks to Wee Hao for this plot.
5.3

The particle tunnels back and forth between the two minima. It is always measured to be in one minimum or the other, never somewhere in the middle. This result is consistent with modelling Ammonia as a two-level system - it is well approximated by linear combinations of the states with the particle in one or the other minimum. This is because the potential barrier is high compared to the energies associated with small fluctuations about the minimum. Only if we added enough energy to the system such that it could go over the barrier would the intermediate states become important. You might also be able to see some small fast oscillations within each well, which correspond to the normal fluctuations of a simple harmonic oscillator.