Applications of Quantum Mechanics: Example Sheet 2

Nick Dorey, February 2023

1a. Using a non-Gaussian trial wavefunction of your choice, estimate the ground state energy of the quartic oscillator with Hamiltonian

\[ H = -\frac{d^2}{dx^2} + x^4 \]

and compare your result with that obtained with a Gaussian wavefunction. What motivated your choice?

[Suggestions: You could try \( \psi = \cos(\pi x/2\alpha) \) or \( \psi = (\alpha^2 - x^2) \) for \( |x| < \alpha \) and vanishing outside this interval.]

b. Use the Gaussian-type wavefunction \( \psi(x) = xe^{-\alpha x^2/2} \) to obtain an estimate of the energy of the first excited state of the quartic oscillator

[Hint: A handy way to do the integrals is to define \( I_n = \int_{-\infty}^{\infty} dx \, x^{2n}e^{-\alpha x^2} \) and to show that \( I_{n+1} = -\frac{d}{d\alpha} I_n \).]

2. A Hamiltonian takes the form \( H = T + V \), with \( T \) the kinetic energy and \( V \) the potential energy. Assuming a discrete energy spectrum, \( E_0 < E_1 < E_2 < ... \), show that the quantity \( \langle \psi | H | \psi \rangle \), where \( |\psi\rangle \) is normalized but otherwise arbitrary, is stationary whenever \( |\psi\rangle \) is an energy eigenstate of \( H \).

Suppose now that \( V \) is a homogeneous potential, satisfying \( V(\lambda x) = \lambda^n V(x) \). Show that the virial theorem \( 2\langle \psi | T | \psi \rangle = n\langle \psi | V | \psi \rangle \) holds for any energy eigenstate of \( H \).

Show that there can be no localised states for integer \( n \leq -3 \).

3a. The Hamiltonian for a single electron orbiting a nucleus of charge \( Z \) is

\[ H = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} \]

Use the variational method with the trial wavefunction \( \psi_\alpha(r) = e^{-\alpha r/a_0} \) where \( \alpha \) is a variational parameter and \( a_0 = 4\pi\epsilon_0\hbar^2/me^2 \) is the Bohr radius. Show that the minimum energy using this ansatz is

\[ E_0 = -\frac{\hbar^2}{2m} \frac{Z^2}{a_0^2} \]

Compare this to the true ground state energy.
b. The Hamiltonian for two electrons orbiting a nucleus of charge \( Z \) is

\[
H = \frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|}
\]

Use the variational method with ansatz \( \Psi(r_1, r_2) = \psi_\alpha(r_1)\psi_\alpha(r_2) \) to estimate the ground state energy. What physical effect underlies the new minimum value of \( \alpha \)?

**Hint:** You will need the following integral

\[
\int d^3r_1 d^3r_2 \frac{\psi_\alpha(r_1)^2\psi_\alpha(r_2)^2}{|r_1 - r_2|} = \frac{5\pi^2 a_0^5}{8\alpha^5}
\]

4*. A covalent bond forms because two ions can lower their energy by sharing an electron. The simplest example occurs for the hydrogen molecule \( H^- \). The Hamiltonian for a single electron, with position \( r \), orbiting two protons which are separated by distance \( R \) is given by

\[
H = \frac{p^2}{2m} + \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{R} - \frac{1}{r} - \frac{1}{|r - R|} \right]
\]

Use the un-normalised ansatz

\[
\Psi = \psi(r) + \psi(r - R) \quad \text{with} \quad \psi = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}
\]

and the integrals

\[
u(R) = \int d^3r \frac{\psi(r)\psi(r - R)}{r} = \frac{1}{a_0} \left( 1 + \frac{R}{a_0} \right) e^{-R/a_0}
\]

\[
v(R) = \int d^3r \frac{\psi(r)^2}{|r - R|} = \frac{1}{R} \left( 1 + \frac{R}{a_0} \right) e^{-2R/a_0}
\]

to show that the energy can be written as

\[
\langle E \rangle - E_0 = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} - \frac{v(R) + w(R)}{1 + u(R)} \right)
\]

where \( E_0 \) is the ground state energy of hydrogen. Sketch \( \langle E \rangle - E_0 \) as a function of \( R \) (you may need to do this numerically) and comment on the implications for the binding of two protons.
5a. A simple model of a crystal consists of an infinite linear array of equally spaced sites. The quantum amplitude to sit at the \textit{n}th site is \( \psi_n \), with \( n \in \mathbb{Z} \) and the time-independent Schrödinger equation is

\[
E \psi_n = E_0 \psi_n - t(\psi_{n-1} + \psi_{n+1})
\]

where \( E_0 \) and the hopping parameter \( t > 0 \) are both constant. Show that the energy \( E \) of the electron must lie in a band \( |E - E_0| \leq 2t \).

b. A defect is introduced into the crystal. As a result, the amplitude for jumping between sites \( n = 0 \) and \( n = 1 \) is changed from \( -t \) to \( -s \), with \( s > t \). Obtain the new Schrödinger equation for \( \psi_0 \) and \( \psi_1 \). By considering solutions of the form

\[
\psi_n = \begin{cases} 
\alpha c^{n-1} & n \geq 1 \\
\beta c^{-n} & n \leq 0
\end{cases}
\]

show that \( c = \pm t/s \) and hence that the electron may be trapped near the origin. Show that the energy of this localised electron is outside the original band.

6a. A quantized particle of mass \( m \) moves in one dimension in the presence of a delta-function potential

\[
V(x) = -\frac{\hbar^2 \lambda}{m} \delta(x)
\]

Show that there is a bound state with energy \(-\hbar^2 \lambda^2/2m\). The same particle now moves in the potential

\[
V(x) = -\frac{\hbar^2 \lambda}{m} \sum_{n=-\infty}^{\infty} \delta(x - na)
\]

Show that for \( \lambda a > 2 \), there is a negative band of energies with

\[
-\frac{\hbar^2 \mu^2}{2m} \leq E \leq -\frac{\hbar^2 \mu^2}{2m}
\]

where \( \mu \pm \) are determined by \( \cosh(\mu \pm a) - \frac{\lambda}{\mu \pm} \sinh(\mu \pm a) = \pm 1 \). Show that when \( a \to \infty \) the band narrows down to the bound state energy.

[\textit{Hint:} Use the obvious basis of negative energy solutions in the interval \(-a < x < 0\), and extend these to \( 0 < x < a \) to find the Floquet matrix.]
b. A defect is introduced into the crystal. The potential is now

\[
V(x) = -\frac{\hbar^2}{m} \lambda \sum_{n \neq 0} \delta(x - na) - \frac{\hbar^2}{m} \delta(x)
\]

Show that there exists a bound state satisfying \( \psi(x+a) = c\psi(x) \) with \(|c| < 1\) for \( x > 0 \), and \( \psi(-x) = \psi(x) \), if

\[
F \begin{pmatrix} \mu - \gamma \\ \mu + \gamma \end{pmatrix} = c \begin{pmatrix} \mu - \gamma \\ \mu + \gamma \end{pmatrix}
\]

where \( F \) is the Floquet matrix, defined with respect to the basis states \( e^{\pm \mu x} \) on the interval \( 0 < x < a \). Show that this state has energy outside the original negative band.

7. Explain how, for a general one-dimensional periodic potential,

\[
V(x) = \sum_{n=1}^{\infty} \alpha_n (e^{2\pi inx/a} + e^{-2\pi inx/a}),
\]

the nearly-free electron model leads to a band structure for the energy levels. Determine, in this approximation, the energy gap between adjacent energy bands.

8. Consider the scaled Schrödinger equation

\[
-\frac{d^2\psi}{dx^2} + \lambda \cos 2x \psi = E\psi
\]

where \(|\lambda|\) is small. Using the nearly-free electron approximation, determine the energies at the bottom and top of the lowest energy band, and also the Bloch states at these energies.