Applications of Quantum Mechanics: Example Sheet 2

David Tong, February 2018

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 \( n < -3 \).

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

$$H = \frac{\mathbf{p}^2_1}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \frac{\mathbf{p}^2_2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|}$$

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

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

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

$$H = \frac{\mathbf{p}^2}{2m} + \frac{e^2}{4\pi\varepsilon_0 \left[ \frac{1}{R} - \frac{1}{r} - \frac{1}{|r - R|} \right]}$$

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

$$u(R) = \int d^3r \psi(r)\psi(r - R) = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right) e^{-R/a_0}$$

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

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

to show that the energy can be written as

$$\langle E \rangle - E_0 = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{R} - \frac{v(R) + w(R)}{1 + u(R)} \right)$$

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 probability to sit at the $n^{\text{th}}$ 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

$$V(x) = -\hbar^2\lambda \delta(x)$$

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

$$V(x) = -\hbar^2\lambda \sum_{n=-\infty}^{\infty} \delta(x - na)$$

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.

[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

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

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.