Applications of Quantum Mechanics: Example Sheet 2

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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 $V(\lambda\mathbf{x}) = \lambda^n V(\mathbf{x})$. 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

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

Use the variational method with the trial wavefunction $\psi_\alpha(\mathbf{r}) = e^{-\alpha r/a_0}$ where α 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

$$H = \frac{\mathbf{p}_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_1} + \frac{\mathbf{p}_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Use the variational method with ansatz $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_\alpha(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_2)$ to estimate the ground state energy. What physical effect underlies the new minimum value of α?

Hint: You will need the following integral

$$\int d^3r_1 d^3r_2 \; \frac{|\psi_\alpha(\mathbf{r}_1)|^2 |\psi_\alpha(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{5\pi^2}{8}\frac{a_0^5}{\alpha^5}$$

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_2^-. The Hamiltonian for a single electron, with position $\mathbf{r}$, orbiting two protons which are separated by distance $\mathbf{R}$ is given by

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

Use the un-normalised ansatz

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

and the integrals

$$\begin{aligned}
u(R) &= \int d^3r \; \psi(\mathbf{r})\psi(\mathbf{r} - \mathbf{R}) = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right) e^{-R/a_0} \\
v(R) &= \int d^3r \; \frac{\psi(\mathbf{r})\psi(\mathbf{r} - \mathbf{R})}{r} = \frac{1}{a_0}\left(1 + \frac{R}{a_0}\right) e^{-R/a_0} \\
w(R) &= \int d^3r \; \frac{\psi(\mathbf{r})^2}{|\mathbf{r} - \mathbf{R}|} = \frac{1}{R} - \frac{1}{R}\left(1 + \frac{R}{a_0}\right) e^{-2R/a_0}
\end{aligned}$$

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 n^{th} site is ψ_n, with $n \in \mathbf{Z}$ 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 ψ_0 and ψ_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.

[*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.