

## 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,  $E_0 < E_1 < E_2 < \dots$ , 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  $\alpha$  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

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

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  $\alpha$ ?

*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

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

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  $n^{\text{th}}$  site is  $\psi_n$ , 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  $\psi_0$  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  $a \rightarrow \infty$  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,

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

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.