

Answer Key for Minor 1

Feb. 10, 2011

1 True/False with justification (4×5)

1. The amplitude of a wavefunction in regions where the potential energy is high.
This statement is in "general" true. The energy E is composed of the potential and kinetic energies and obeys the relation $E = T + V$. If V is high, T , that is the kinetic energy, is low. If the kinetic energy is low, the particle spends more time in this region or the probability of being in that region is high. The probability being $|\psi|^2$ which is reflected in a higher amplitude of the wavefunction. However, if we consider the harmonic oscillator ground state, which has highest amplitude at the point of minimum V , we will conclude that this statement is not true. SO BOTH TRUE OR FALSE ARE ACCEPTABLE AS ANSWERS DEPENDING ON THE ARGUMENT PROVIDED.
2. Wherever the potential energy is greater than the total energy, the exponential decay constant of the wavefunction with distance is greater for a larger value of $V - E$.
The wavefunction in such regions has the form $A \exp(-\alpha x) + B \exp(\alpha x)$, with $\alpha = \sqrt{\frac{2m(V-E)}{\hbar^2}}$. The α term is higher when $V - E$ is higher. Physically, this implies that if the potential energy is higher than the E then the wavefunction decays faster. So the statement is TRUE.
3. When a free particle of energy $E < V_0$ tunnels through a potential $V = V_0$ it loses energy. This statement is FALSE. Energy is conserved. It is the amplitude of the wavefunction that is decreased on tunneling.
4. A quantum mechanical oscillator in the ground state, like a classical oscillator, is most likely to be found at the classical turning points.
This statement is FALSE. The ground state wavefunction has highest amplitude where the potential is a minimum. Classically the oscillator is most likely to be found at the classical turning points because the kinetic energy is zero there and hence is likely to spend most of its time there.

2 Short answer

1. Consider a crude model representing a benzene molecule as a three-dimensional rectangular box with dimensions 350 pm by 350 pm by 125 pm ($1 \text{ pm} = 1.0 \times 10^{-12} \text{ m}$). Include only the six π electrons, which are assumed to move in the entire box.
 - (a) Identify the quantum numbers of the highest state that contains electrons. Is this state degenerate? If so, what is the degeneracy? [2+2]
The energy expression can be written as

$$E_{x,y,z} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right),$$

where $a = b = 350$ pm and $c = 125$ pm. We rewrite this expression as

$$E_{x,y,z} = \frac{h^2}{8ma^2} \left(n_x^2 + n_y^2 + n_z^2 \frac{a^2}{c^2} \right),$$

with $\frac{a}{c} = \frac{350}{125} = \frac{14}{5}$. The lowest three states have quantum numbers $(1, 1, 1)$, $(1, 2, 1)$, and $(2, 1, 1)$. The last two occupied states have quantum numbers $(1, 2, 1)$, and $(2, 1, 1)$ (**2 marks**) and are doubly degenerate (**2 marks**). Their energy is $12.84h^2/8ma^2$.

- (b) What is the uncertainty in the measurement of z -component of the angular momentum of an electron in the state in part (a)? [6]

We know that $\Delta p_z = \sqrt{\langle p_z^2 \rangle - \langle p_z \rangle^2}$ (**1 mark**). In addition we know that $\langle p_z \rangle = 0$ (**1 mark**) and $\langle p_z^2 \rangle = 2m \langle E_z \rangle$ (**1 mark**) so that $\Delta p_z = \sqrt{2mE_z}$. The energy $E_z = \frac{7.84h^2}{8ma^2}$ so that $\Delta p_z = \frac{14h}{10a} = 3.092 \times 10^{-24}$ kg m s⁻¹ (**3 marks**).

- (c) Find the wavelength of the photon absorbed when an electron makes a transition from the highest occupied state to the lowest unoccupied state. [10]

The energies of the highest occupied state and lowest unoccupied state are, in units of $\frac{h^2}{8ma^2}$, 12.84 (**2 marks**) and 15.84 (**2 marks**). Thus the energy difference is $\frac{3h^2}{8ma^2}$ (**2 marks**). Converting this into wavelength one gets $\lambda = \frac{8 \times 9.1 \times 10^{-31} \times (3.5 \times 10^{-10})^2 \times 3 \times 10^8}{3 \times 6.626 \times 10^{-34}} = 134$ nm (**4 marks**).

2. A beam of electrons that all have the same energy E are traveling from left ($x < 0$) to right through a conducting wire. At $x = 0$, the wire becomes a different kind of metal so that the potential energy of the electrons increases from zero to U_0 . Imagine that $E > U_0$.

- (a) Write the Schrödinger equation in the two regions. [5]

In region I, it is (**2 marks**)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_I}{\partial x^2} = E\psi_I,$$

while in region II, it would be (**3 marks**)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_{II}}{\partial x^2} + U_0\psi_{II} = E\psi_{II}.$$

- (b) Solve the Schrödinger equation in the two regions. Define all the symbols used. [10]
The wavefunctions in the two regions (**3 marks each**) are respectively

$$\psi_I = A \exp(ik_I x) + B \exp(-ik_I x)$$

and

$$\psi_{II} = C \exp(ik_{II} x) + D \exp(-ik_{II} x)$$

with (**2 marks**)

$$k_I = \sqrt{\frac{2mE}{\hbar^2}}$$

and (**2 marks**)

$$k_{II} = \sqrt{\frac{2m(E - U_0)}{\hbar^2}}$$

- (c) Derive the result by applying the boundary conditions on the wavefunctions? [10]

The boundary conditions are $\psi_I = \psi_{II}$ (**2 marks**) and $d\psi_I/dx = d\psi_{II}/dx$ (**2 marks**) at $x = 0$. This implies that

$$A + B = C + D$$

(2 marks) and

$$ik_I(A - B) = ik_{II}(C - D).$$

(2 marks)

- (d) Obtain the restriction that arises from imposing the normalization condition. [5]
The restriction imposed by normalization is that (2 marks)

$$A^2 + B^2 + C^2 + D^2 = 1$$

Note: In parts (b), (c), and (d), the D term is actually zero because there is no left moving wave in region II as there is no barrier for $x > 0$. Credit is given for both options.

3. The nitrogen atom in ammonia has two equilibrium positions - either above or below a plane containing the three hydrogen atoms. This motion of nitrogen between the two equilibrium positions is called umbrella inversion. The potential $V(x) = -ax^2 + bx^4$ ($a, b > 0$) is an approximation for this process.

- (a) Sketch this potential. [4]
The potential is a double minimum potential with a maximum at $x = 0$. The potential minima occur at $x = \pm\sqrt{\frac{a}{2b}}$. At $x = 0$ the potential is zero while at the minima it is $-\frac{a^2}{4b}$.
- (b) Sketch the ground state wavefunction in this potential. Explain its features. [4+8]
The ground state wavefunction will look "like" two harmonic oscillator ground state wavefunctions centred at the two minima (4 marks). The wavefunctions features are (a) it is symmetric, (b) it has no nodes, and (c) it is a decaying exponential in the classically forbidden region (4 marks each if any two of the features are explained correctly).
- (c) Evaluate the "spring constant" (in terms of the potential parameters a and b) in the simple harmonic approximation to the potential energy near the minimum. [4]
The spring constant is obtained by evaluating the second derivative of the potential at the potential minima because from Taylor's expansion we know that $V(x) = V(x = x_{min}) + \left(\frac{dV}{dx}\right)_{x=x_{min}}(x - x_{min}) + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_{x=x_{min}}(x - x_{min})^2 + \dots$. The second derivative of the potential is $-2a + 12bx^2$ (1 mark), which when evaluated at the minima works out to be $4a$ (1 mark) and hence $k = 4a$ (2 marks).
- (d) Imagine that the diatomic molecule $^{14}\text{N}^3\text{H}$ is a crude approximation for ammonia. If it has a "spring constant" of 640 N m^{-1} , evaluate the zero point energy of the vibrational motion and the frequency of a vibrational transition. [10]
We know that (2 marks)

$$\omega = \sqrt{\frac{k}{\mu}},$$

where $k = 640 \text{ N m}^{-1}$ and (2 marks)

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

with $m_1 = 14 \text{ amu}$ and $m_2 = 3 \text{ amu}$. The zero point energy is (3 marks)

$$\frac{\hbar\omega}{2} = \frac{6.626 \times 10^{-34}}{4\pi} \sqrt{\frac{640}{\frac{42}{17} \times 1.66 \times 10^{-27}}} = 2.08 \times 10^{-20} \text{ J.}$$

The frequency is (3 marks)

$$\nu = \frac{2.08 \times 10^{-20}}{6.626 \times 10^{-34}} = 3.14 \times 10^{13} \text{ Hz.}$$