

This is a three-hour test.

Please answer all 8 questions in the spaces provided.

A calculator and the equation sheets provided can be used.

No books or notes are allowed. No marks for unreadable answers.

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Q1 This question refers to a **free particle** described by the wave function $\psi(x) = Be^{-i2\pi\sqrt{2mE}x/h}$.

a) What does "free" mean in this context?

No forces or potential energy - just unhindered motion.

b) $\psi(x)$ is a complex function. What does "complex" mean in this context?

Complex function: part real and part imaginary.

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$$e^{-i2\pi\sqrt{2mE}x/h} = \cos\left(\frac{2\pi\sqrt{2mE}x}{h}\right) - i \sin\left(\frac{2\pi\sqrt{2mE}x}{h}\right)$$

(real)
(imaginary)

c) Show $\psi(x)$ is an eigenfunction of the kinetic energy operator $-\frac{\hbar^2}{8\pi^2m} \frac{d^2}{dx^2}$ with eigenvalue E .

$$\begin{aligned}
 & -\frac{\hbar^2}{8\pi^2m} \frac{d}{dx} \frac{d}{dx} \left(Be^{-i2\pi\sqrt{2mE}x/h} \right) \\
 &= -\frac{\hbar^2}{8\pi^2m} \frac{d}{dx} \left(-i2\pi\sqrt{2mE}/h \right) Be^{-i2\pi\sqrt{2mE}x/h} \\
 &= -\frac{\hbar^2}{8\pi^2m} \left(-i2\pi\sqrt{2mE}/h \right)^2 Be^{-i2\pi\sqrt{2mE}x/h} = E\psi(x)
 \end{aligned}$$

d) Many scientists believe the energies of quantum particles are quantized (only discrete energy values are allowed). Use part c to show the energies of free particles are in fact *continuous*.

no quantization of E (as for particle in a box or the harmonic oscillator)

e) Use the expression for $\psi(x)$ to show negative energies are impossible for free particles.
Hint: Wave functions must be "well behaved".

if $E < 0$, then $\psi(x) = B \exp[-i2\pi\sqrt{2m(-1)|E|x/h}]$

$$= B \exp\left[\underbrace{2\pi\sqrt{2m|E|x/h}}_1 \right] \rightarrow \infty \text{ as } x \rightarrow \infty$$

(real)

Q2 An electron moving in the positive x -direction encountering an infinitely-wide potential energy barrier at $x = 0$ is described by the wave functions:

$$\begin{array}{lll} \psi_I(x) = A \exp(iK_I x) + B \exp(-iK_I x) & \text{zone I} & x < 0 & V(x) = 0 \\ \psi_{II}(x) = C \exp(iK_{II} x) & \text{zone II} & x \geq 0 & V(x) = V_0 \end{array}$$

with $K_I = 0.400 \text{ m}^{-1}$ and $K_{II} = 0.100 \text{ m}^{-1}$.

a) Show that the probability distribution $P_I(x) = \psi_I^*(x)\psi_I(x)$ in zone I is a real function.

$$\begin{aligned} P_I(x) &= \psi_I^*(x) \psi_I(x) = (Ae^{-iK_I x} + Be^{iK_I x})(Ae^{iK_I x} + Be^{-iK_I x}) \\ &= A^2 e^0 + AB e^{-2iK_I x} + AB e^{2iK_I x} + B^2 e^0 \\ &= A^2 + B^2 + AB [\cos(-2K_I x) + i \sin(-2K_I x) + \cos(2K_I x) + i \sin(2K_I x)] \end{aligned}$$

$$\begin{array}{l} \cos \theta = \cos(-\theta) \\ \sin \theta = -\sin(-\theta) \end{array}$$

[7]
$$= A^2 + B^2 + 2AB \cos(2K_I x) \quad (\text{all real})$$

b) Why does the electron probability distribution oscillate in zone I?

incoming electron $[Ae^{iK_I x}]$ with $v_x > 0$ interferes with reflected electron $[Be^{-iK_I x}]$ with $v_x < 0$

c) Show that the probability distribution $P_{II}(x) = \psi_{II}^*(x)\psi_{II}(x)$ in zone II is also a real function.

$$\begin{aligned} P_{II}(x) &= \psi_{II}^*(x) \psi_{II}(x) = C e^{-iK_{II} x} C e^{iK_{II} x} \\ &= C^2 e^0 \\ &= C^2 \end{aligned}$$

d) The electron probability distribution does not oscillate in zone II. Why?

electron in zone II has $v_x > 0$

(no reflection)

e) Does the electron show **barrier penetration**? If so, calculate the penetration depth. Or does the electron show **barrier transmission**? If so, calculate the transmission probability.

barrier transmission $P_{II}(x)$ is constant

$$\text{reflection coefficient } R = \left(\frac{K_I - K_{II}}{K_I + K_{II}} \right)^2 = \left(\frac{0.400 - 0.100}{0.400 + 0.100} \right)^2 = 0.36$$

barrier penetration
 $P_I(x) \rightarrow 0$
as $x \rightarrow \infty$

transmission coefficient $T = 1 - R = \boxed{0.64}$

Q3 A free electron with kinetic energy $E = 0.10$ eV moving in the positive x -direction encounters a $V_0 = 0.25$ eV energy barrier of width $L = 0.25$ nm extending from $x = 0$ to $x = 0.25$ nm.

$\psi_I(x) = A \exp(iK_I x) + B \exp(-iK_I x)$	zone I	$x < 0$	$V(x) = 0$
$\psi_{II}(x) = C \exp(iK_{II} x) + D \exp(-iK_{II} x)$	zone II	$0 \leq x \leq L$	$V(x) = V_0$
$\psi_{III}(x) = F \exp(iK_{III} x)$	zone III	$x > 0$	$V(x) = 0$

a) Why must $\psi_I(x)$ and $\psi_{II}(x)$ be identical at $x = 0$?

wave functions must be continuous and single-valued

b) Why must $d\psi_{II}(x)/dx$ and $d\psi_{III}(x)/dx$ be identical at $x = L$?

[6] *wave functions must be smooth and the electron can only have a single value of the momentum at $x = L$, so $-\frac{i\hbar}{2\pi} \frac{d\psi_{II}}{dx} = -\frac{i\hbar}{2\pi} \frac{d\psi_{III}}{dx}$ at $x = L$*

c) There is no term in $\exp(-iK_{III} x)$ for the wave function $\psi_{III}(x)$ in zone III. Why?

"tunneled" electron moves in the positive direction in zone III (no back-reflection here)

d) Give the probability the electron will tunnel through the energy barrier:

i) using classical mechanics

zero ($E < V_0$)

$$\left(\begin{array}{l} V_0 - E = 0.25 - 0.10 \text{ eV} \\ = 0.15 \text{ eV} \\ = 2.40 \times 10^{-20} \text{ J} \end{array} \right)$$

ii) using quantum mechanics

tunnelling parameter $\beta = \frac{L \sqrt{2m(V_0 - E)}}{\hbar/2\pi} = \frac{0.25 \times 10^{-9} \sqrt{2(9.110 \times 10^{-31})(2.40 \times 10^{-20})}}{6.626 \times 10^{-34} / 2\pi}$

$\beta = 0.496$

tunnelling probability $= \left[1 + \frac{V_0^2}{16E(V_0 - E)} (e^\beta - e^{-\beta})^2 \right]^{-1}$

$= \left[1 + \frac{0.25^2}{16(0.10)(0.15)} (e^{0.496} - e^{-0.496})^2 \right]^{-1} = 1.278^{-1}$

$T = 0.782$

$$\text{frequency } \nu = c\tilde{\nu} = \left(2.998 \times 10^{10} \frac{\text{cm}}{\text{s}}\right) (2360 \text{ cm}^{-1}) = 7.075 \times 10^{13} \text{ s}^{-1}$$

Q4 This question refers to the vibration of N_2 molecules (assumed to be harmonic). The fundamental frequency is 2360 cm^{-1} and the energy levels are $E_n = (n + \frac{1}{2})h\nu$ with $n = 0, 1, 2, 3, \dots$

$$E_n = h\nu \left(n + \frac{1}{2}\right)$$

a) Calculate the zero-point vibrational energy for one mole of N_2 .

$$E_0 = \frac{h\nu}{2} \text{ for one } \text{N}_2 \text{ molecule.}$$

$$\text{For one mole } \text{N}_2: E_{0m} = N_A \frac{h\nu}{2}$$

$$E_{0m} = (6.022 \times 10^{23} \text{ mol}^{-1}) \frac{(6.626 \times 10^{-34} \text{ J s})(7.075 \times 10^{13} \text{ s}^{-1})}{2} = \boxed{14.1 \frac{\text{kJ}}{\text{mol}}}$$

b) Why is the zero-point energy non-classical?

Classically, an oscillator can have zero energy.
(Not possible for a quantum oscillator (uncertainty principle))

c) The probability energy level E_n is occupied is proportional to $\exp(-E_n/kT)$. This gives

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$$\langle n \rangle = \frac{1}{e^{h\nu/kT} - 1}$$

for the average vibration quantum number. For N_2 at 300 K, show $\langle n \rangle = 0.000012$.

$$\begin{aligned} \langle n \rangle &= \frac{1}{\exp\left[\frac{(6.626 \times 10^{-34})(7.075 \times 10^{13})}{(1.381 \times 10^{-23}) 300}\right] - 1} \\ &= \frac{1}{e^{11.31} - 1} = 0.000012 \end{aligned}$$

d) Part c shows that almost all N_2 molecules are in the ground vibrational state ($n = 0$) at 300 K. Does this mean N_2 molecules are not vibrating at 300 K. Explain.

No.

They vibrate with the zero-point energy.

e) Classical mechanics predicts $C_{vm} = 7R/2$ for the molar heat capacity of N_2 , but the measured value is $5R/2$. Account for this discrepancy.

No vibrational heat capacity R .

All N_2 molecules are in the $n = 0$ energy level for vibration. No increase in vibrational energy as T increases $\rightarrow C_{vib} = 0$

$$\nu = c\tilde{\nu} = (2.998 \times 10^{10} \text{ cm s}^{-1}) (2990 \text{ cm}^{-1}) = 8.964 \times 10^{13} \text{ s}^{-1}$$

Q5 This question refers to the vibration of H^{35}Cl and D^{35}Cl molecules. Data:

$$m_{\text{H}} = 1.673 \times 10^{-27} \text{ kg} \quad m_{\text{D}} = 3.343 \times 10^{-27} \text{ kg} \quad m_{^{35}\text{Cl}} = 5.812 \times 10^{-26} \text{ kg}$$

a) IR absorption spectroscopy gives 2990 cm^{-1} for the fundamental vibration frequency of H^{35}Cl . Calculate the force constant k .

$$k = 4\pi^2 \nu^2 \mu$$

$$\mu = \frac{m_{\text{H}} m_{^{35}\text{Cl}}}{m_{\text{H}} + m_{^{35}\text{Cl}}} = \frac{(0.1673)5.812}{0.1673 + 5.812} \times 10^{-26} \text{ kg}$$

$$k = 4\pi^2 (8.964 \times 10^{13})^2 (1.626 \times 10^{-27})$$

$$\mu = 1.626 \times 10^{-27} \text{ kg} \quad (\text{H}^{35}\text{Cl})$$

$$k = 515.8 \text{ N m}^{-1}$$

b) A weak forbidden absorption in the IR spectrum of H^{35}Cl is observed at 5980 cm^{-1} . What does "forbidden" mean? Why is this transition weak?
 "forbidden" $n=0$ to $n=2$ ($\Delta n=2$) transition violating the selection rule $\Delta n = \pm 1$ for harmonic oscillators

c) H^{35}Cl and D^{35}Cl molecules have nearly identical electronic structures and therefore nearly identical force constants. Why? Explain briefly.

adding a neutron (no electric charge) to the H atom nucleus in H^{35}Cl has almost no effect on the charge distribution

d) Estimate the fundamental vibration frequency of D^{35}Cl molecules.

$$\mu_{\text{D}^{35}\text{Cl}} = \frac{(0.3343)5.812}{0.3343 + 5.812} \times 10^{-26} \text{ kg} = 3.161 \times 10^{-27} \text{ kg} \quad (\approx \text{twice } \mu_{\text{H}^{35}\text{Cl}})$$

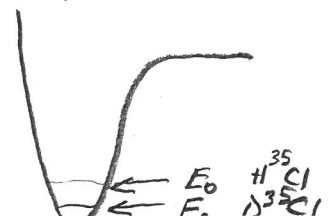
[7]

$$\frac{\nu_{\text{D}^{35}\text{Cl}}}{\nu_{\text{H}^{35}\text{Cl}}} = \frac{\frac{1}{2\pi} \sqrt{\frac{k_{\text{D}^{35}\text{Cl}}}{\mu_{\text{D}^{35}\text{Cl}}}}}{\frac{1}{2\pi} \sqrt{\frac{k_{\text{H}^{35}\text{Cl}}}{\mu_{\text{H}^{35}\text{Cl}}}}} \approx \sqrt{\frac{\mu_{\text{H}^{35}\text{Cl}}}{\mu_{\text{D}^{35}\text{Cl}}}} = \sqrt{\frac{1.626}{3.161}} = 0.717$$

$$\nu_{\text{D}^{35}\text{Cl}} = 0.717 (2990 \text{ cm}^{-1}) = 2144 \text{ cm}^{-1}$$

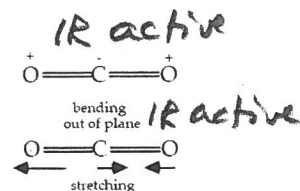
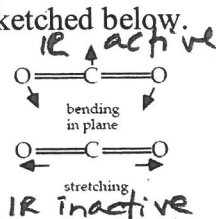
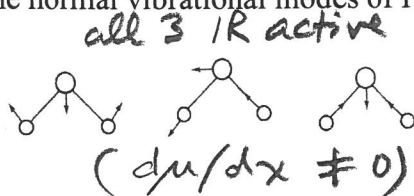
e) H^{35}Cl and D^{35}Cl have nearly identical electronic structures, but the dissociation energy of H^{35}Cl is 5.0 kJ mol^{-1} lower than the dissociation energy of D^{35}Cl . Why?

The zero-point energy (proportional to $1/\mu$) of H^{35}Cl is higher than that of D^{35}Cl



Q6

a) The normal vibrational modes of H₂O and CO₂ are sketched below.



i) H₂O and CO₂ are both triatomic molecules. But CO₂ has four normal modes and H₂O has three normal modes. Why?

CO₂ linear $3N-5 = 4$ vibrations (3 translations, 2 rotations)

H₂O nonlinear $3N-6 = 3$ vibrations (3 translations, 3 rotat.)

ii) H₂O has three IR absorption bands (1595, 3657 and 3756 cm⁻¹), but only two IR absorption bands (526 and 2565 cm⁻¹) are observed for CO₂. Explain briefly.

[6]

The symmetric stretch for CO₂ is inactive in the IR ($du/dx=0$) and the two bending vibrations have the same frequency. The second IR band for CO₂ is the asymmetric stretch.

b) CO₂ and O₂ are both nonpolar molecules. But CO₂ absorbs IR radiation and O₂ does not. Explain briefly.

O₂ is nonpolar and remains nonpolar during vibration.
CO₂ is nonpolar, but the asymmetric stretch and the bending vibrations produce an electric dipole moment, making CO₂ IR active.

c) O₂ does not have an IR spectrum. Does this mean O₂ molecules are not vibrating? Explain.

No. O₂ molecules are vibrating (even in the ground state ($n=0$))

But vibrating O₂ molecules do not interact with IR radiation.

d) The wave functions $\psi_0, \psi_1, \psi_2, \psi_3, \dots$ for the harmonic oscillator are orthogonal. What does "orthogonal" mean?

$$\int \psi_i^* \psi_k dx = 0 \quad \text{if } i \neq k$$

Q7 a) Classify each of the following functions $f(x)$ as odd (O), even (E) or neither odd nor even (N).

- | | | | |
|---------------|---------|-----------------------|---------|
| i) e^{-ix} | E O (N) | ii) $1 + 3x^2 + 5x^4$ | (E) O N |
| iii) e^{-x} | E O (N) | iv) $2x^3$ | E (O) N |
| v) e^{-2x} | E O (N) | vi) $\sin^2(x)$ | (E) O N |

b) Use the properties of even and odd functions to prove the average momentum of a harmonic oscillator is zero:
 here $\psi^*(x) = \psi(x)$ (real wavefunctions)

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi(x)^* \hat{p}_x \psi(x) dx = \int_{-\infty}^{\infty} \psi(x)^* \left(-\frac{i\hbar}{2\pi} \frac{d}{dx} \right) \psi(x) dx = 0$$

$$\langle p_x \rangle = -\frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} \psi(x) \frac{d}{dx} \psi(x) dx$$

$\psi(x)$ odd, then $\frac{d\psi(x)}{dx}$ even

$\psi(x)$ even, then $\frac{d\psi(x)}{dx}$ odd

$$= -\frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} \text{odd} \cdot \text{even} dx \quad \text{or} \quad -\frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} \text{even} \cdot \text{odd} dx = 0$$

[8]

c) The electrons in a high-resolution electron microscope have 400,000 eV kinetic energy.

i) Calculate speed of the electrons. $T = 400,000 \text{ eV}$

$$T = \frac{1}{2} m v_x^2 \quad v_x = \sqrt{2T/m}$$

$$v_x = \sqrt{\frac{2(400,000 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})}{9.110 \times 10^{-31} \text{ kg}}} = 3.75 \times 10^8 \text{ m s}^{-1}$$

ii) Calculate the de Broglie wavelength of the electrons.

$$\lambda = \frac{h}{p_x} = \frac{h}{m v_x} = \frac{6.626 \times 10^{-34}}{9.110 \times 10^{-31} (3.75 \times 10^8)} = 1.94 \times 10^{-12} \text{ m} = 0.00194 \text{ nm}$$

iii) Electron microscopes have higher resolution than optical microscopes. Why?

electrons at 10 to 400 keV shorter wavelength than visible light (~400 to 800 nm)

iv) Something is wrong with the electron speed calculated in part i! Explain.

$$v_x > c!$$

electron moving faster than the speed of light!

(should use relativistic equations)

Q8 This question refers to the harmonic vibration of a diatomic molecule:

$$E_n = (n + \frac{1}{2})h\nu \quad n = 0, 1, 2, 3, \dots \quad V(x) = \frac{1}{2} kx^2$$

$$\langle x \rangle = 0 \quad \langle x^2 \rangle = \frac{h}{2\pi\sqrt{\mu k}} \left(n + \frac{1}{2} \right) \quad \langle p_x \rangle = 0 \quad \langle p_x^2 \rangle = \frac{h\sqrt{\mu k}}{2\pi} \left(n + \frac{1}{2} \right)$$

Use the equations provided to show:

a) $\sigma_x = \sqrt{\frac{h}{2\pi\sqrt{\mu k}} \left(n + \frac{1}{2} \right)}$

$$\sigma_x = \sqrt{\sigma_x^2} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$= \sqrt{\frac{h}{2\pi\sqrt{\mu k}} \left(n + \frac{1}{2} \right) - 0}$$

b) $\sigma_{p_x} = \sqrt{\frac{h\sqrt{\mu k}}{2\pi} \left(n + \frac{1}{2} \right)}$

[4] $\sigma_{p_x} = \sqrt{\frac{h\sqrt{\mu k}}{2\pi} \left(n + \frac{1}{2} \right) - 0}$

c) the Heisenberg uncertainty principle $\sigma_x \sigma_{p_x} \geq h/4\pi$ is obeyed.

$$\sigma_x \sigma_{p_x} = \sqrt{\frac{h}{2\pi\sqrt{\mu k}} \left(n + \frac{1}{2} \right)} \sqrt{\frac{h\sqrt{\mu k}}{2\pi} \left(n + \frac{1}{2} \right)}$$

$$= \frac{h}{2\pi} \left(n + \frac{1}{2} \right) \quad n = 0, 1, 2, \dots$$

$$\geq \frac{h}{4\pi}$$

d) the average potential energy is one half of the total energy: $\langle V \rangle = E_n/2$.

$$V = \frac{1}{2} k x^2 \quad \langle V \rangle = \left\langle \frac{1}{2} k x^2 \right\rangle$$

$$= \frac{1}{2} k \langle x^2 \rangle$$

$$= \frac{1}{2} k \frac{h}{2\pi\sqrt{\mu k}} \left(n + \frac{1}{2} \right)$$

$$= \frac{1}{2} h \left(\frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \right) \left(n + \frac{1}{2} \right)$$

$$= \frac{1}{2} h \nu_0 \left(n + \frac{1}{2} \right) = \frac{E_n}{2}$$

Q1
Q2
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