

This is a three-hour test.

Please answer all 7 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 ground-state electron ($n = 1$) in a box of width $L = 0.100$ nm.

a) Calculate: i) the energy of the electron

$$E_1 = \frac{(1)^2 h^2}{8 m_e L^2} = \frac{(6.626 \times 10^{-34})^2}{8 (9.110 \times 10^{-31}) (0.100 \times 10^{-9})^2}$$

$E_1 = 6.02 \times 10^{-18} \text{ J}$

(37.6 eV)
 ("all" kinetic energy)

ii) the speed of the electron

$$E_1 = \frac{1}{2} m_e v_e^2 \quad v_e = \sqrt{2E_1 / m_e}$$

$$v_e = \sqrt{2(6.02 \times 10^{-18}) / (9.110 \times 10^{-31})} = \boxed{3.64 \times 10^6 \frac{\text{m}}{\text{s}}}$$

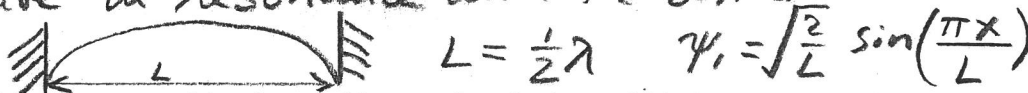
[7] iii) the de Broglie wavelength of the electron

$$\lambda = \frac{h}{p_x} = \frac{h}{m_e v_e} = \frac{6.626 \times 10^{-34}}{(9.110 \times 10^{-31})(3.64 \times 10^6)}$$

$\lambda = 2.00 \times 10^{-10} \text{ m} = 0.200 \text{ nm}$

d) The de Broglie wavelength of the electron is exactly twice the box width. Why? How does this help to explain the origins of discrete energy levels in quantum mechanics?

The electron with $\lambda = 0.200$ nm is a stable "standing wave" in resonance with the box dimension.



e) The uncertainty in the electron position is roughly equal to the box width ($\sigma_x \approx L$). Use the Uncertainty Principle to explain why the ground-state energy of the electron cannot be zero.

$\sigma_x \sigma_{p_x} \geq \frac{h}{2\pi}$
if $E_1 = \frac{1}{2} m_e v_e^2 = \frac{p_x^2}{2m_e} = 0$
then $p_x = 0$ (exactly) and $\sigma_{p_x} = 0$
then $\sigma_x \sigma_{p_x} \approx L(0) = 0$

violates the uncertainty principle \implies

Q2. This question refers to an electron in a box of width L extending from $x = -L/2$ to $x = +L/2$ described by the wave functions

$$[8] \quad \begin{aligned} \psi_n(x) &= (2/L)^{1/2} \cos(n\pi x/L) & n &= 1, 3, 5, 7, \dots \\ \psi_n(x) &= (2/L)^{1/2} \sin(n\pi x/L) & n &= 2, 4, 6, 8, \dots \end{aligned}$$

a) Show the wave functions satisfy the **boundary conditions** for the particle in the box.

odd n : $\psi_n(\pm \frac{L}{2}) = (2/L)^{1/2} \cos(\pm \frac{n\pi}{2}) = \cos(\pm \frac{\pi}{2}), \cos(\pm \frac{3\pi}{2}), \dots = 0$

even n : $\psi_n(\pm \frac{L}{2}) = (2/L)^{1/2} \sin(\pm \frac{n\pi}{2}) = \sin(\pm \pi), \sin(\pm 2\pi), \dots = 0$

b) The wave functions are **normalized**. What does this mean? Be specific.

$$\int_{-L/2}^{L/2} \psi_n^* \psi_n dx = \int_{-L/2}^{L/2} \psi_n^2 dx = 1 \quad \left(\begin{array}{l} \psi_n \text{ is real} \\ \text{so } \psi_n^* = \psi_n \end{array} \right)$$

c) The wave functions are **orthogonal**. What does this mean? Be specific.

$$\int_{-L/2}^{L/2} \psi_m^* \psi_n dx = 0 \quad (m \neq n)$$

d) Without using a table of integrals, show $\langle p_x \rangle = 0$.

$$\begin{aligned} \langle P_x \rangle &= \int_{-L/2}^{L/2} \psi_n^* \hat{P}_x \psi_n dx = \int_{-L/2}^{L/2} \psi_n (-i\hbar \frac{\partial}{\partial x}) \psi_n dx \\ &= \int_{-L/2}^{L/2} (\text{odd})(\text{even}) dx \quad \text{or} \quad \int_{-L/2}^{L/2} (\text{even})(\text{odd}) dx \quad \boxed{= 0} \end{aligned}$$

e) $\langle p_x \rangle = 0$, so the momentum of the electron is zero? Explain briefly.

No! The average momentum is zero, but negative momentum ($v_x < 0$) and positive momentum ($v_x > 0$) are equally probable

f) The dipole moment of the electron in the box is $-ex$. For the $n_i \rightarrow n_f$ transition, use the transition dipole moment $-e \int_{-L/2}^{L/2} \psi_{n_f}(x) x \psi_{n_i}(x) dx$ to derive the **spectroscopic selection rule**

that $\Delta n = n_f - n_i$ must be an odd integer.

(odd) must be odd for a non-zero transition dipole moment

$$-e \int x \psi_{n_f} \psi_{n_i}$$

$\psi_{n_f} \psi_{n_i}$ is odd only if n_f odd and n_i is even, or vice versa

(* $\int (\text{odd})(\text{odd}) dx \neq 0$)

- Q3. a) For motion in the x -direction, use the linear momentum operator $\hat{p}_x = -i\hbar \partial / \partial x$ to show the corresponding kinetic energy operator is $\hat{T}_x = -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2}$.
Hint: From classical mechanics, $E_x = p_x^2 / 2m$.

$$\begin{aligned}\hat{T}_x &= \frac{\hat{p}_x \cdot \hat{p}_x}{2m} = \frac{1}{2m} (-i\hbar \frac{\partial}{\partial x}) (-i\hbar \frac{\partial}{\partial x}) \\ &= \frac{1}{2m} i^2 \hbar^2 \frac{\partial^2}{\partial x^2} = \frac{1}{2m} (-1) \left(\frac{\hbar}{2\pi}\right)^2 \frac{\partial^2}{\partial x^2} \\ &= -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2}\end{aligned}$$

- b) A free particle is described by the wave function $\psi(x) = Ae^{-i\sqrt{2mE}x/\hbar}$.

- i) Give $\text{Re}[\psi(x)]$, the real part of the wave function.

$$\begin{aligned}\text{Re}[A \cos(-\sqrt{2mE}x/\hbar) + iA \sin(-\sqrt{2mE}x/\hbar)] &= A \cos(-\sqrt{2mE}x/\hbar) \\ &= A \cos(\sqrt{2mE}x/\hbar)\end{aligned}$$

- ii) Give $\text{Im}[\psi(x)]$, the imaginary part of the wave function.

$$[7] \quad \text{Im}[\psi(x)] = A \sin(-\sqrt{2mE}x/\hbar) = -A \sin(\sqrt{2mE}x/\hbar)$$

- iii) Is the particle moving in the positive x -direction? Justify your answer.

No!

$$\begin{aligned}\hat{p}_x \psi(x) &= -i\hbar \frac{\partial}{\partial x} A e^{-i\sqrt{2mE}x/\hbar} \\ &= (-i\hbar) A (-i\sqrt{2mE}/\hbar) e^{-i\sqrt{2mE}x/\hbar} = -\sqrt{2mE} \psi(x)\end{aligned}$$

eigenvalue $= p_x$

$$p_x = mv_x = -\sqrt{2mE} < 0 \quad v_x < 0$$

- iv) Show $\psi(x)$ is eigenfunction of the kinetic energy operator with eigenvalue E .

$$\begin{aligned}\hat{T}_x \psi(x) &= -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} A e^{-i\sqrt{2mE}x/\hbar} \\ &= -\frac{\hbar^2}{8\pi^2 m} A \left(\frac{-i\sqrt{2mE}}{\hbar}\right)^2 e^{-i\sqrt{2mE}x/\hbar} \\ &= \frac{\hbar^2}{8\pi^2 m} \frac{2mE}{\hbar^2} \psi(x) = \frac{\hbar^2}{8\pi^2 m} \frac{2mE}{\hbar^2/4\pi^2} \psi(x) = E \psi(x)\end{aligned}$$

- Q4. A free electron with kinetic energy $E = 6.00$ eV moving in the positive x -direction hits an infinitely-wide $V_0 = 10.00$ eV potential energy barrier starting at $x = 0$.

[7]



- a) Calculate the electron penetration depth (D_p) into the barrier using classical mechanics.

$E < V_0 \therefore D_p = 0$ classically (the electron doesn't have enough kinetic energy to penetrate the barrier)

- b) Calculate D_p using quantum mechanics.

$$D_p = \frac{h/2\pi}{\sqrt{2m_e(V_0 - E)}} = \frac{6.626 \times 10^{-34} / 2\pi}{\sqrt{(2)(9.110 \times 10^{-31})(10.00 - 6.00)(1.602 \times 10^{-19})}}$$

$$= 9.76 \times 10^{-11} \text{ m}$$

$$\boxed{D_p = 0.0976 \text{ nm}}$$

- c) Show the wave function $\psi_{II}(x) = C \exp(-x/D_p)$ in zone II ($x \geq 0$) is normalized by using $C = (2/D_p)^{1/2}$.

$$\left(\int_0^{\infty} e^{-ax} dx = \frac{1}{a} \right) \int_0^{\infty} \psi_{II}^*(x) \psi_{II}(x) dx = \int_0^{\infty} C e^{-x/D_p} C e^{-x/D_p} dx$$

$$= C^2 \int_0^{\infty} e^{-2x/D_p} dx = C^2 \frac{1}{\frac{2}{D_p}} = \frac{2}{D_p} \frac{1}{\frac{2}{D_p}} = 1$$

- d) Use the normalized wave function $\psi_{II}(x) = (2/D_p)^{1/2} \exp(-x/D_p)$ to calculate $\langle x \rangle$, the average electron penetration depth into zone II.

$$\left(\int_0^{\infty} x e^{-ax} dx = \frac{1}{a^2} \right) \langle x \rangle = \int_0^{\infty} \psi_{II}^* x \psi_{II} dx$$

$$\langle x \rangle = \int_0^{\infty} C e^{-x/D_p} x C e^{-x/D_p} dx = C^2 \int_0^{\infty} x e^{-2x/D_p} dx$$

$$= C^2 \frac{1}{\left(\frac{2}{D_p}\right)^2} = \frac{2}{D_p} \frac{D_p^2}{4} = \frac{D_p}{2} = \frac{9.76 \times 10^{-11} \text{ m}}{2}$$

$$\langle x \rangle = 4.88 \times 10^{-11} \text{ m} = \boxed{0.0488 \text{ nm}}$$

Q5. This question refers to a ground-state harmonic oscillator described by the wave function

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad (\alpha = \sqrt{4\pi^2 k\mu / h^2})$$

a) What is x ? Be specific.

x is the displacement of the reduced mass from its equilibrium position where $x=0$ and $V(0)=0$

b) Derive an expression for $P(x)$.

($\psi_0(x)$ is real, so $\psi^* = \psi$)

$$P(x) = \psi_0^*(x) \psi_0(x) = \psi_0(x) \psi_0(x) = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha x^2}$$

c) Use $P(x)$ to calculate the average value of x .

[7]
$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = \int_{-\infty}^{\infty} x \sqrt{\frac{\alpha}{\pi}} e^{-\alpha x^2} dx$$

$= \int_{-\infty}^{\infty} (\text{odd})(\text{even}) dx$

$= 0$

(odd) (even)

d) Give the most probable value of x .

max. $P(x)$ at $x=0$ where $\frac{dP(x)}{dx} = -\frac{2\alpha^{3/2}}{\sqrt{\pi}} x e^{-\alpha x^2} = 0$

e) Show that $P(x)$ has SI units m^{-1} .

$P(x)$ has the same units as $\sqrt{\alpha}$

$$\sqrt{\alpha} \sim \left(\frac{Nm}{h^2}\right)^{1/4} \sim \sqrt{\frac{N}{J^2} \frac{kg}{s^2}} \sim \sqrt{\frac{1 \frac{kg m}{s^2} kg}{\left(\frac{kg m^2}{s^2}\right)^2}} \sim \frac{1}{m}$$

f) Wait! Probabilities are dimensionless numbers between 0 and 1. Why does $P(x)$ have units?

$P(x)$ is not a probability!

$P(x)$ is the probability distribution function.

The probability x is between x_1 and x_2 is

$$\int_{x_1}^{x_2} P(x) dx \leftarrow m^{-1} \cdot m \sim \text{dimensionless probability}$$

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

- Q6. a) Calculate the energy required to raise a N_2 molecule from its ground vibrational state ($n = 0$) to the first excited state ($n = 1$). Use $\nu = 2360 \text{ cm}^{-1}$ for the fundamental vibration frequency.

$$E_1 - E_0 = h\nu$$

$$= (6.626 \times 10^{-34} \text{ Js})(2360 \text{ cm}^{-1})(2.998 \times 10^{10} \text{ cm s}^{-1})$$

$$= \boxed{4.688 \times 10^{-20} \text{ J}} \quad (0.293 \text{ eV})$$

[6]

- b) At temperature T , show the ratio of the number of N_2 molecules in energy level $n = 1$ to the number of N_2 molecules in energy level $n = 0$ is

$$P_i \propto e^{-E_i/KT}$$

$$P_1/P_0 = e^{-h\nu/KT}$$

$$\begin{aligned} \frac{P_1}{P_0} &= \frac{e^{-E_1/KT}}{e^{-E_0/KT}} = e^{E_0/KT} e^{-E_1/KT} \\ &= e^{-(E_1 - E_0)/KT} \end{aligned}$$

- c) Calculate P_1/P_0 for N_2 at 300 K.

$$\frac{P_1}{P_0} = e^{-\frac{(4.688 \times 10^{-20})}{(1.381 \times 10^{-23})(300)}} = e^{-11.3}$$

$$= \boxed{1.22 \times 10^{-5}}$$

- d) According to classical mechanics, the molar heat capacity $C_{V,m}$ of N_2 should be $7R/2$. Use the results from this question to explain the non-classical result that $C_{V,m}$ for N_2 is $5R/2$

at 300 K, virtually all N_2 molecules (99.999 % !)
are in the ground ($n = 0$) vibration state

add some heat, \approx all N_2 molecules are still in
the ground vibrational state \Rightarrow zero vibrational heat capacity

$$\begin{aligned} C_{V,m} &= 3 \frac{R}{2} \text{ (3 translations)} + 2 \frac{R}{2} \text{ (2 rotations)} \\ &= 5R/2 \end{aligned}$$

Q7. a) Solving the same Schrodinger equation $-\frac{\hbar^2}{8\pi^2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x)$ gives different wave functions for a particle in a box and a free particle! Why?

particle in a box
($0 \leq x \leq L$)

$$\psi(0) = \psi(L) = 0$$

different boundary conditions

free particle

no boundary conditions

b) The diagram below from the course notes gives the tunneling probability T for a particle of mass m with kinetic energy E hitting an energy barrier of height V_0 and width L . Use the diagram to show:

i) T increases with E

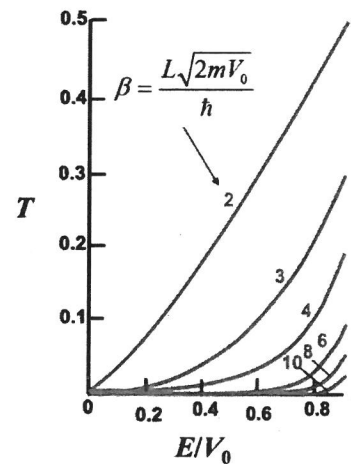
$$\frac{dT}{d\frac{E}{V_0}} > 0$$

ii) T decreases with m , and V_0 and L .

β increases with L, m, V_0

T decreases with β ,

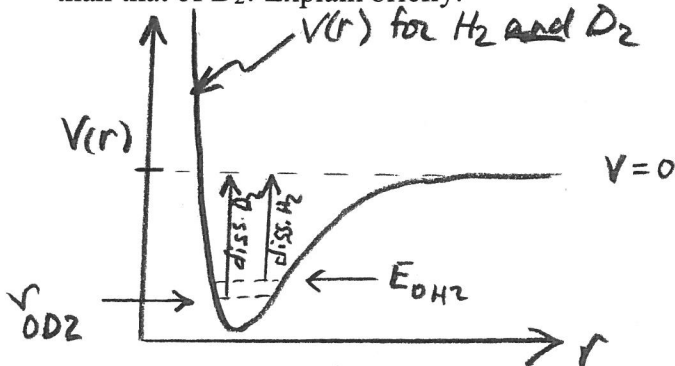
[8] as shown in the graph of T vs. E/V_0



c) What is a **scanning tunneling microscope**? What is doing the scanning? What is doing the tunneling? Tunneling through what?

- high-resolution (atomic scale) imaging device for surfaces
- a sharp metallic needle is scanned over a surface
- the tunneling current due to electrons jumping between the needle and the surface (the barrier) is measured

d) H_2 and D_2 molecules have nearly identical force constants, nearly identical bond lengths, and nearly identical electronic structures. But the dissociation energy of H_2 is significantly lower (by 8 kJ mol^{-1}) than that of D_2 ! Explain briefly.



H_2 and D_2 have different zero-point vibrational energies $E_0 = \hbar\nu/2$

$$\nu \propto \sqrt{\frac{1}{m}}$$

$$m_{D_2} \approx 2m_{H_2}$$

$$\nu_{D_2} \approx \frac{\nu_{H_2}}{\sqrt{2}}$$

$$E_{0D_2} \sim E_{0H_2}/\sqrt{2}$$

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