QUANTUM THEORY

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(1) Using the de Broglie relation, $\lambda = h/p = h/mv$:

(a) $m = 1.67\times10^{-27}$ kg

$mv = 1.67\times10^{-27}\times275 = 4.6\times10^{-25}$ kgms^{-1}; $\lambda = \dfrac{6.63\times10^{-34}}{4.6\times10^{-25}} = \underline{1.4\times10^{-9}\text{ m}}$.

(b) $m = 50\text{ kg}/N_\text{A} = 8.3\times10^{-23}$ kg

$mv = 8.3\times10^{-23}\times12 = 1.0\times10^{-21}$ kgms^{-1}; $\lambda = \dfrac{6.63\times10^{-34}}{1.0\times10^{-21}} = \underline{6.6\times10^{-13}\text{ m}}$.

(c) $mv = 0.024\times20 = 0.48$ kgms^{-1}; $\lambda = \dfrac{6.63\times10^{-34}}{0.48} = \underline{1.4\times10^{-33}\text{ m}}$.

The larger the mass, the larger the momentum, the shorter the de Broglie wavelength. For classical objects, e.g., squash balls, the de Broglie wavelength is immeasurably small, and is utterly negligible compared to the dimensions of the objects.

(2) Heisenberg's Uncertainty Relation: $\Delta x\Delta p = m\Delta x\Delta v \geq \frac{1}{2}\hbar = h/4\pi$.

(a) $\Delta v \geq \dfrac{h}{4\pi\times m_\text{e}\times10^{-10}} = \underline{5.8\times10^{5}\text{ ms}^{-1}}$.

(b) $\Delta v \geq \dfrac{h}{4\pi\times8.3\times10^{-23}\times10^{-6}} = \underline{6.4\times10^{-7}\text{ ms}^{-1}}$.

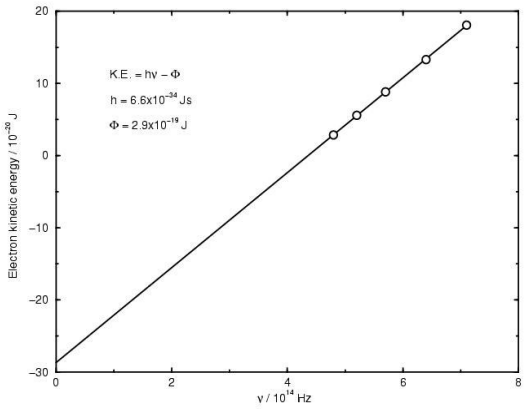
(c) $\Delta v \geq \dfrac{h}{4\pi\times0.024\times10} = \underline{2.2\times10^{-34}\text{ ms}^{-1}}$.

For small particles ($m \approx 10^{-27}$ kg) in small spaces ($L \approx 10^{-10}$ m), quantum mechanical effects are pronounced. For larger and more massive objects, quantum effects become negligible; for (b) and (c), compare the uncertainties in the velocities with the corresponding velocities in Question (1).

(3) The electron kinetic energy is equal to $\frac{1}{2}m_\text{e}v_\text{e}^2$:

ν (Hz)	4.8×10^{14} (orange)	5.2×10^{14} (yellow)	5.7×10^{14} (green)	6.4×10^{14} (blue)	7.1×10^{14} (violet)
v_e (ms^{-1})	2.5×10^{5}	3.5×10^{5}	4.4×10^{5}	5.4×10^{5}	6.3×10^{5}
$\frac{1}{2}m_\text{e}v_\text{e}^2$ (J)	2.8×10^{-20}	5.6×10^{-20}	8.8×10^{-20}	1.3×10^{-19}	1.8×10^{-19}

(a) A plot of $\frac{1}{2}m_e v_e^2$ as a function of ν looks like this:



From the slope of the plot: $h = \underline{6.6\times10^{-34}\ \text{Js}}$.

From the intercept of the plot: $\Phi = \underline{2.9\times10^{-19}\ \text{J} = 1.81\,\text{eV}}$.

(b) Threshold: $\nu_{\min} = \dfrac{\Phi}{h} = \dfrac{2.9\times10^{-19}}{6.6\times10^{-34}} = \underline{4.4\times10^{14}\ \text{Hz}}$, or $\lambda_{\max} = \dfrac{c}{\nu_{\min}} = \underline{682\ \text{nm}}$.

(4) (a) $\hat{\Omega}_1 f = a\cos ax$ (not an eigenfunction).

$\hat{\Omega}_2 f = -a^2 \sin ax = -a^2 f$ (is an eigenfunction; eigenvalue is $-a^2$).

$\hat{\Omega}_3 f = (a^2 + 4a^2x^2)\sin ax$ (not an eigenfunction).

(b) $\hat{\Omega}_1 f = -ae^{-ax} = -af$ (is an eigenfunction; eigenvalue is $-a$).

$\hat{\Omega}_2 f = a^2 e^{-ax} = a^2 f$ (is an eigenfunction; eigenvalue is a^2).

$\hat{\Omega}_3 f = (-a^2 + 4a^2x^2)e^{-ax}$ (not an eigenfunction).

(c) $\hat{\Omega}_1 f = -2axe^{-ax^2}$ (not an eigenfunction).

$\hat{\Omega}_2 f = -2ae^{-ax^2} + 4a^2x^2e^{-ax^2}$ (not an eigenfunction).

$\hat{\Omega}_3 f = -\left(-2ae^{-ax^2} + 4a^2x^2e^{-ax^2}\right) + 4a^2x^2e^{-ax^2} = 2af$ (is an eigenfunction; eigenvalue is $2a$).

(5) (a) $\hat{H}\psi_n = -\dfrac{\hbar^2}{2m}\times\left(-\dfrac{n^2\pi^2}{L^2}\right)\times\sqrt{\frac{2}{L}}\sin(n\pi x/L) = \dfrac{n^2h^2}{8mL^2}\psi_n = E_n\psi_n$.

$E_n = \dfrac{n^2h^2}{8mL^2}$.

(b) *See lecture notes for energy-level diagram.*

(c) $\Delta E = E_{n+1} - E_n = \dfrac{h^2}{8mL^2}\left[(n+1)^2 - n^2\right] = \dfrac{h^2}{8mL^2}\left(n^2 + 2n + 1 - n^2\right) = \dfrac{(2n+1)h^2}{8mL^2}$

(d) *See lecture notes for plots of* $\psi_n(x)$.

Why *n* can't equal zero -

Mathematical reason: if *n* were zero, then $\psi_n(x)$ would be zero everywhere, which implies that the particle doesn't exist!

'Physical' reason: the **maximum** uncertainty in the position of the particle is of order *L* (we know the particle is in the box); therefore, the **minimum** uncertainty in the momentum is finite (Heisenberg's Uncertainty Principle). If *n* were zero, the energy, momentum, and hence the uncertainty in the momentum, would all be precisely zero, thus violating HUP.

(e) *See lecture notes for plots of* $P_n(x) = \left[\psi_n(x)\right]^2$.

The average location, or expectation value $\langle x \rangle = L/2$.

(f) The $n = 1 \rightarrow n = 2$ transition requires the absorption of a photon with energy $\Delta E = 3h^2/8m_e L^2$ [from part (d)]. The energy of a 'blue' photon is,

$$h\nu = 6.63\times10^{-34} \times 6.4\times10^{14} = 4.2\times10^{-19}\ \text{J}.$$

Hence,

$$L = \sqrt{\frac{3h^2}{8m_e \times 4.2\times10^{-19}}} = \underline{6.6\times10^{-10}\ \text{m}}.$$

(6) (a) Non-degenerate: (1,1,1)

(b) Three-fold degenerate: (1,1,2), (1,2,1), (2,1,1)

(c) Six-fold degenerate: (1,2,3), (2,3,1), (3,1,2), (2,1,3), (1,3,2), (3,2,1).

(7) (a) Schrödinger equation: $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}kx^2\psi = E\psi$.

(b) Insert $\psi_0(x)$ into Schrödinger equation from part (a):

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}kx^2\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right) = -\frac{\hbar^2}{2m}\left(-\frac{m\omega}{\hbar} + \frac{m^2\omega^2x^2}{\hbar^2}\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$
$$+ \tfrac{1}{2}kx^2\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$
$$= \left(\tfrac{1}{2}\hbar\omega - \tfrac{1}{2}m\omega^2x^2 + \tfrac{1}{2}kx^2\right)\psi_0$$
$$= \tfrac{1}{2}\hbar\omega\psi_0.$$

(c) Minimum energy = $\frac{1}{2}\hbar\omega$. Zero-point energy due to Heisenberg's Uncertainty Principle; the argument is along the same lines as in Question (5) part (d), but this time the particle is confined to a parabolic (harmonic) potential well.

(d) *See lecture notes for energy-level diagram.*

The spacing between neighbouring energy levels is constant, and equal to $\hbar\omega$.

(e) *See lecture notes for plots of* $\psi_0(x)$ and $P_0(x) = \left[\psi_0(x)\right]^2$.

The most probable location of the particle is at $x = 0$.

(f) $h\nu = \hbar\omega = \hbar\sqrt{\frac{k}{m}}$. (For the moment, note that the carbon atom is much heavier than the hydrogen, and so the **reduced mass** $\mu \approx m_{\mathrm{H}}$.)

$$k = 4\pi^2\nu^2 m_{\mathrm{H}} = 4\pi^2 \times 7.6\times10^{27} \times 1.67\times10^{-27} = \underline{500\ \mathrm{Nm^{-1}}}\ .$$

(8) (a) *See lecture notes for energy-level diagram.* Quantum numbers: 1s orbital, n=1, l=0, m_l=0; 2p orbitals, n=2, l=1, m_l=-1,0,1; 3d orbitals, n=3, l=2, m_l=-2,-1,0,1,2; etc.

(b) Orbitals are related to electron wavefunctions. The well-known shapes of orbitals correspond to the bounding surfaces, the surfaces of constant probability (proportional to $|\psi|^2$) within which there is a high probability (say, 90%) of finding the electron.

(c) $E_{1\mathrm{s}} = -R_{\mathrm{H}}$; $E_{2\mathrm{s}} = E_{2\mathrm{p}} = -\frac{1}{4}R_{\mathrm{H}}$; $E_{3\mathrm{d}} = -\frac{1}{9}R_{\mathrm{H}}$. Note that the energy levels are determined solely by the principal quantum number, n; the n^{th} energy level is n^2-fold degenerate.

(d) The ionisation energy of a hydrogen atom in its ground state is simply the amount of energy required to promote the electron from the $n=1$ quantum state, to a state where $E=0$, i.e., $n=\infty$. Hence, the ionisation energy is simply equal to $IP = -R_{\mathrm{H}}\left(\frac{1}{\infty^2} - \frac{1}{1^2}\right) = R_{\mathrm{H}} = 13.60\,\mathrm{eV}$.

(e) *See lecture notes for plots of* $\psi_{1\mathrm{s}}(r)$ and $\rho_{1\mathrm{s}}(r) = 4\pi r^2[\psi_{1\mathrm{s}}(r)]^2$.

The particle is most likely to be found at a distance $r = a_0$ from the proton. This is the position of the maximum in $\rho_{1\mathrm{s}}(r)$ (just differentiate $r^2 e^{-2r/a_0}$, and set equal to zero). Note that this distance corresponds to the hydrogen atom having a 'diameter' of about $100\ \mathrm{pm} = 1\ \mathrm{\AA}$ [see Question (2) part (a)].