CML101: Tutorial 3 - Quantum Chemistry

UG Semester - I (2023-24)

Q1: Consider a particle of mass 100 g can be located within a distance range 10^{-8} cm. What is the uncertainty in its velocity measurement? Do the same exercise for an electron with mass $\sim 10^{-27}$ g. Compare and rationalize the uncertainty values.

Ans: Uncertainty principle, apply $\Delta x.\Delta p_x = \Delta x.(m\Delta v_x) = h/4\pi$

Q2: Photochemical studies with a sodium surface resulted the following data,

Wavelength (Å):	3125	3650	4047	4339	5461
Retarding potential (Volts):	- 0.382	-0.915	-1.295	-1.485	-2.043

Calculate the work function and the Planck's constant. You can take the help of a graphical method.

Ans: Photoelectric effect: $KE_{max} = eV_{stop} = E_{photon} - \phi$;
$E_{photon} = hc/\lambda$

Q3: The work function (ϕ) for Cesium is 3.43×10^{-19} J. What is the kinetic energy of an electron released by radiation of 550 nm? What is the stopping voltage (V)? How many photons are absorbed if the total energy supplied to the surface at the same wavelength is 1.00×10^{-19} J?
[V = $\frac{KE_{max}}{e}$, Charge of an electron (e) is 1.602×10^{-19}C]

Ans: Photoelectric effect: $KE_{max} = eV_{stop} = E_{photon} - \phi$
$V_{stop} = KE_{max}/e = 0.115$ V
$E_{photon} = Nh\nu$
$N = 2.767 \times 10^{15}$

Q4: Calculate the wavelength of (i) a 65 g tennis ball served at a velocity of 100 mph, and (ii) an electron ejected from an atom with kinetic energy 2.5 eV. What inference you draw from the calculated wavelengths of the two objects?
[100 mph $\approx$ 45 m s^{-1} and 1 eV = 1.6×10^{-19} J]

Ans: Wave-particle duality, de Broglie:
$\lambda = \frac{h}{mv} = 2.3 \times 10^{-34}$m for the tennis ball and 0.77 nm for the electron

Q5: Assume a wave function has the following form,
$\psi(x) = N(a^2 - x^2)$ Find out it's normalization constant N if the function is bound between -a to +a.

Ans: Normalization

$$\int_{-a}^{a} \psi^*\psi dx = 1$$
$$\int_{-a}^{a} N^2(a^2 - x^2)^2 dx = 1$$
$$N^2\left(\frac{16a^5}{15}\right) = 1$$
$$N = \sqrt{\frac{15}{16a^5}}$$

Q6: Which of the functions (i) sinkx, (ii) $5x^2$, (iii) 1/x, and (iv) $5e^{-5x}$ are eigenfunctions of $\frac{d^2}{dx^2}$? Find out the eignevalues.

Ans: Operators, Eigenvalue equations:

$$\frac{d^2}{dx^2}\ \text{sin(kx)} = \text{-k sin(kx)}$$

Q7: Evaluate the commutators

$$\left[x, \frac{d}{dx}\right], \left[\frac{d}{dx}, \frac{d^2}{dx^2}\right], \left[3x^2, \frac{d}{dx}\right], \left[\frac{d}{dx} - x, \frac{d}{dx} + x\right]$$

Ans: Operators and commutators:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$$
$$\left[x, \frac{d}{dx}\right]\psi = x\frac{d\psi}{dx} - \frac{d(x\psi)}{dx} = -\psi$$
$$\left[x, \frac{d}{dx}\right] = \text{-1}$$

Similarly,

$$\left[\frac{d}{dx}, \frac{d^2}{dx^2}\right] = 0$$
$$\left[3x^2, \frac{d}{dx}\right] = \text{-6x}$$
$$\left[\frac{d}{dx} - x, \frac{d}{dx} + x\right] = -2x^2$$

Q8: Show that, $\left[\hat{x}, \hat{p}_x\right] = ih/2\pi$

What is the significance of this outcome?

Ans: Operators and commutators: x and p_x do not commute, they cannot be measured simultaneously.

Q9: Consider a function ψ = Nx(l-x) confined in a box of length (0,l), where N is the normalization constant. Find the average kinetic energy of the particle.

Ans: Normalization

$$\int_{-a}^{a} \psi^* \psi dx = 1$$
$$\int_0^l N^2 x^2 (l-x)^2 dx = 1$$

Evaluate: $N = \sqrt{20/l^5}$

$$\langle KE \rangle = \int_0^l Nx(l-x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)Nx(l-x)dx$$
$$\langle KE \rangle = \frac{5\hbar^2}{ml^2}$$

Q10: A wavefunction of a particle in a 1D box is given as,

$$\psi(x) = \sqrt{\frac{2}{L}} sin\left(\frac{\pi x}{L}\right)$$

(i) Find $< x >$ and $< x^2 >$ for a particle of mass m in the ground state of a box of length L.

(ii) The technical definition of uncertainty is

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

What is Δx for the ground state in a box?

Ans: (i) Expectation value:

$$\begin{aligned}\langle x \rangle &= \int_0^L \psi^* x \psi dx \\ &= \int_0^L \sqrt{\frac{2}{L}} sin\left(\frac{\pi x}{L}\right) x \sqrt{\frac{2}{L}} sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2}{L}\int_0^L x sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{1}{L}\int_0^L x\left[1 - cos\left(\frac{2\pi x}{L}\right)\right] dx \\ &= L/2\end{aligned}$$

Similarly,

$$\begin{aligned}\langle x^2 \rangle &= \int_0^L \psi^* x^2 \psi dx \\ &= \frac{2}{L}\int_0^L x^2 sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{1}{L}\int_0^L x^2\left[1 - cos\left(\frac{2\pi x}{L}\right)\right] dx \\ &= \frac{L^2}{3} + \frac{L^2}{2\pi^2}\end{aligned}$$

(ii) Calcualte Δx from the above data.

Q11: For an electron in a 1-D box of length 2.0 Å

(i) Calculate the energy difference between n=2 and n=3 levels.

(ii) Calculate the wavelength of the photon corresponding to a transition between these two energy levels.

(iii) In what part of the electromagnetic spectrum will this wavelength be?

Ans: (i) Particle in 1-D box:

$$\Delta E = \frac{(n_3^2 - n_2^2)h^2}{8mL^2} = 0.75 \times 10^{-19}\text{J}$$
$$\lambda = hc/\Delta E = 265nm(UV)$$

Q12: The generalized wavefunction of a particle in a 1D box is given as,

$$\psi(x) = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right)$$

Show that the wavefunctions $\psi_{n=1}$ and $\psi_{n=2}$ are orthogonal to each other.

Ans: Orthogonality: $\int \psi_{n=1}\psi_{n=2}\text{dx} = 0$

Q13: Consider a particle in its ground state confined to a 1-D box in the interval (0,8). What is the probability of finding the particle in between [4 - d/2 to 4 + d/2] where d is very small so that function can be taken as constant?

Ans: The wave function for a particle in a 1-dimensional box in its ground state:

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

Probability can be calculated as,
p = $\psi^*\psi dx$
And the interval of interest: $[4 - \frac{d}{2}, 4 + \frac{d}{2}]$
The correct value of $\psi(4)$ is:

$$\psi(4) = \sqrt{\frac{2}{8}} \sin\left(\frac{\pi \cdot 4}{8}\right) = \frac{1}{2} \cdot \sin\left(\frac{\pi}{2}\right) = \frac{1}{2}$$

So, the probability of finding the particle in the interval $[4 - \frac{d}{2}, 4 + \frac{d}{2}]$ is:

$$p(4 - \frac{d}{2} \leq x \leq 4 + \frac{d}{2}) \approx |\psi(4)|^2 \cdot d = \left(\frac{1}{2}\right)^2 \cdot d = \frac{1}{4} \cdot d = \frac{d}{4}$$

Q14: What is the degeneracy of the energy level which has three times energy than that of the lowest energy level in 3-D box?

Ans: The lowest energy level is $3h^2/8mL^2$
For a level having energy three times, $n^2 = (n_x^2 + n_x^2 + n_x^2) = 9$ with degeneracy = 3, (1,2,2), (2,1,2), (2,2,1)