CML101: Tutorial 4 - Quantum Chemistry

UG Semester - I (2023-24)

Q1: The ground-state wave function of a quantum harmonic oscillator is given as,

$$\psi_0(x) = \left(\frac{b}{\pi}\right)^{1/4} e^{-bx^2/2}$$

Show that $\Delta p_x \Delta x = \frac{\hbar}{2}$. Where $\Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2}$ and $\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$ are the variances in p_x and x, respectively.

Ans:

$$\langle x^2\rangle = \left(\frac{b}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-bx^2/2} dx = 2\left(\frac{b}{\pi}\right)^{1/2} \frac{1}{4b}\left(\frac{\pi}{b}\right)^{1/2} = \frac{1}{2b}$$

$$\langle x\rangle = \left(\frac{b}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x e^{-bx^2/2} dx = 0$$

$$\begin{aligned}
\langle p_x^2\rangle &= \int_{-\infty}^{\infty} \psi_0(x)\left(\hbar^2 \frac{d^2}{dx^2}\right)\psi_0(x) dx \\
&= -\left(\frac{b}{\pi}\right)^{1/2} \hbar^2 \int_{-\infty}^{\infty} e^{-bx^2/2}\left(\frac{d^2}{dx^2}\right) e^{-bx^2/2} dx \\
&= -\left(\frac{b}{\pi}\right)^{1/2} \hbar^2 \int_{-\infty}^{\infty} e^{-bx^2/2}\left(\frac{d}{dx}\right)(-bxe^{-bx^2/2}) dx \\
&= -\left(\frac{b}{\pi}\right)^{1/2} \hbar^2 b \int_{-\infty}^{\infty} e^{-bx^2/2}(bx^2-1) dx \\
&= -\left(\frac{b}{\pi}\right)^{1/2} \hbar^2 b \left[\frac{1}{4}\left(\frac{\pi}{b}\right)^{1/2} - \frac{1}{2}\left(\frac{\pi}{b}\right)^{1/2}\right] \\
&= \hbar^2 b/2
\end{aligned}$$

$$\begin{aligned}
\langle p_x\rangle &= \int_{-\infty}^{\infty} \psi_0(x)\left(-i\hbar\frac{d}{dx}\right)\psi_0(x) dx \\
&= -\left(\frac{b}{\pi}\right)^{1/2} (-i\hbar)(-b) \int_{-\infty}^{\infty} x e^{-bx^2/2} dx \\
&= 0
\end{aligned}$$

$$\Delta p_x \Delta x = \left(\frac{\hbar^2 b}{2}\frac{1}{2b}\right)^{1/2} = \hbar/2$$

Q2: A strong absorption band of infrared radiation is observed for $^{1}H^{35}Cl$ at 2991 cm^{-1}. (a) Calculate the force constant, k, for this molecule. (b) By what factor do you expect the frequency to shift if H is replaced by D? Assume that the force constant does not get affected by this change.

Ans: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Evaluate $\mu_{HCl} = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$

$m_H = 1amu = 1.0078 \times 1.66053906660 \times 10^{-27} kg$

$m_{Cl} = 35.5amu = 35.5 \times 1.66053906660 \times 10^{-27}kg$

Evaluate μ_{DCl}

Q3: Derive the expression for the standard deviation of the bond length of a diatomic molecule when it is in its ground state. (b) What percentage of the equilibrium bond length is this standard deviation for CO in its ground state? For CO, $\tilde{\nu} = 2170$ cm^{-1} and Re = 113 pm.

Ans: (i) Heisenberg's uncertainty principle, $\Delta x \Delta p_x = \frac{\hbar}{2}$

$\Delta x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}$

where ω is the angular frequency, $\omega = 2\pi\tilde{\nu}$, and $\tilde{\nu} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Thus, $\Delta x = \left(\frac{\hbar}{4\pi c\tilde{\nu}\mu}\right)^{1/2}$

(ii) Evaluate $\mu_{CO} = \frac{m_H m_C}{m_C + m_O} = 1.139 \times 10^{-26}kg$

$\tilde{\nu} = 2170cm^{-1}$

% $\Delta x = 2.98$ %

Q4: The wave function of the ground state of H atom is given as, $\psi_{1s} = \frac{1}{2\pi}\left(\frac{Z}{a_0}\right) e^{-Zr/a_0}$.

(i) Find the average distance of 1s electron from the nucleus in the hydrogen atom.

(ii) Calculate the most probable distance (i.e., radius) at which the 1s electron of H-like atom with atomic number Z is to be found. Show that as Z increases, this most probable distance decreases.

Ans:

(i) $\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1s}.r.\psi_{1s} r^2 dr sin\theta d\theta d\phi = 3a_0/2$

(ii) P(r) = $|R_{10}(r)|^2 r^2$

$\frac{dP(r)}{dr} = \frac{a_0}{Z}$

Q5: Calculate the ground state energy of the hydrogen atom in SI units and convert the result to electronvolts (eV).

$$E_n = -\frac{Z^2}{n^2}\frac{e^2}{8\pi\epsilon_0 a} = \frac{Z^2 \mu e^4}{8\epsilon_0^2 n^2 h^2} \quad (1)$$

where $a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$

[Given m_e = 9.109 × 10−31 kg, e = 1.602 × 10−19 C, $\epsilon_0 = 8.854 \times 10^{-12}$ C^2/N-m^2, 1 eV = 1.602 $\times 10^{-19}$ J]

Q6: Calculate the wavelength and frequency for the spectral line that axis from n=5 to n=3 transition in the H-atom. [Rydberg constant (R_H) = 1.097373 $\times 10^7 m^{-1}$ and c=3$\times 10^8$ m/s]

Ans:

$$\frac{hc}{\lambda} = R_H \left[\frac{1}{n_I^2} - \frac{1}{n_I^2 I}\right]$$