Lecture 13: Vibrational Molecular Ground State

The ω-vibrational state of a molecular 1D-system is described by the Hamiltonian:

$$\hat{H}_{\omega} = -\frac{\hbar^2}{2m_0}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$$

while the stationary appropriate wave-function may be described by the two-parameters function:

$$\psi_{\omega}(c_1, c_2, x) = c_1 \exp\left(-c_2 x^2\right),\ c_1, c_2 (>0) \in \mathbf{R}$$

so that carrying the geometry of the parabolic potential that determines it, with the two constants to be determined by the two quantum constrains of the direct normalization of the trial wave-function followed by application of the variational principle for the eigen-energy.

Starting with fulfilling the normalization condition for the trial wave-function, we have:

$$1 = \int_{-\infty}^{+\infty} \psi_{\omega}^{*}\psi_{\omega} dx = c_1^2 \int_{0}^{\infty} e^{-2c_2 x^2} dx = c_1^2 \sqrt{\frac{\pi}{2c_2}}$$

$$\Rightarrow c_1 = \left(\frac{2c_2}{\pi}\right)^{1/4},$$

where we have considered the 0th order Poisson integral (see Appendix A.2.2).

Going now to compute the trial vibrational energy, we calculate successively:

$$\hat{H}_{\omega}\psi_{\omega} = -\frac{\hbar^2}{2m_0}\partial_x^2\left(c_1 e^{-c_2 x^2}\right) + \frac{c_1}{2}m\omega^2 x^2 e^{-c_2 x^2}$$

$$= c_1 c_2 \frac{\hbar^2}{m_0}\left(e^{-c_2 x^2} - 2c_2 x^2 e^{-c_2 x^2}\right) + \frac{c_1}{2}m\omega^2 x^2 e^{-c_2 x^2},$$

$$\psi_{\omega}^{*}\hat{H}_{\omega}\psi_{\omega} = c_1^2 c_2 \frac{\hbar^2}{m_0}\left(e^{-2c_2 x^2} - 2c_2 x^2 e^{-2c_2 x^2}\right) + \frac{c_1^2}{2}m\omega^2 x^2 e^{-2c_2 x^2}$$

$$= c_1^2 c_2 \frac{\hbar^2}{m_0} e^{-2c_2 x^2} + \left(\frac{c_1^2}{2}m\omega^2 - 2c_1^2 c_2^2 \frac{\hbar^2}{m_0}\right) x^2 e^{-2c_2 x^2},$$

$$E_\omega = \int_{-\infty}^{+\infty} \psi_\omega^* \hat{H}_\omega \psi_\omega dx$$

$$= c_1^2 c_2 \frac{\hbar^2}{m_0}\sqrt{\frac{\pi}{2c_2}} + \left(\frac{c_1^2}{2} m\omega^2 - 2c_1^2 c_2^2 \frac{\hbar^2}{m_0}\right)\frac{1}{4c_2}\sqrt{\frac{\pi}{2c_2}}$$

$$= c_2 \frac{\hbar^2}{2m_0} + \frac{1}{c_2}\frac{m\omega^2}{8}$$

where the 0th and 2nd order Poisson integrals were used (Appendix A.2.2) along the replacement of the above expression for c_1. Now, the variational principle on this energy leads with the c_2 result as well:

$$0 = \partial_{c_2} E_\omega(c_2) = \frac{\hbar^2}{2m_0} - \frac{1}{c_2^2}\frac{m\omega^2}{8},$$

$$\Rightarrow c_2 = \frac{m_0\omega}{2\hbar}, \Rightarrow c_1 = \left(\frac{2c_2}{\pi}\right)^{1/4} = \left(\frac{m_0\omega}{\hbar\pi}\right)^{1/4}$$

so that the fundamental (ground state) energy

$$E_0(\omega) = \frac{1}{2}\hbar\omega$$

together with the associate eigen-function

$$\psi_0(\omega, x) = \left(\frac{m_0\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{m_0\omega}{2\hbar}x^2\right)$$

are furnished in fully agreement with the previous general quantum eigen -energies and -functions determinations for harmonic oscillator; thus proving also by this example the reliability of variational principle to provide both fundamental or ground state energy and its wave-function, in a consistent quantum mechanically manner.

Appendix

- $I_0(a) = \int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$ … the 0th order Poisson integral

$$\textit{Proof}:\ I_0^2(a) = \left(\int_{-\infty}^{+\infty} e^{-ax^2} dx\right)\left(\int_{-\infty}^{+\infty} e^{-ay^2} dy\right) = \iint_{-\infty}^{+\infty} e^{-a\left(x^2+y^2\right)} dxdy$$

$$= \int_0^{\infty}\int_0^{2\pi} e^{-ar^2} r dr d\varphi = \left(\int_0^{\infty} e^{-ar^2} r dr\right)\left(\int_0^{2\pi} d\varphi\right)$$

$$= -\frac{2\pi}{2a}\int_0^{\infty} d\left(e^{-ar^2}\right) = -\frac{\pi}{a}\left(e^{-ar^2}\right)_0^{\infty} = \frac{\pi}{a}$$

- $I_1(a) = \int_{-\infty}^{+\infty} x e^{-ax^2} dx = 0$ … the 1st order Poisson integral

$$\textit{Proof}:\ I_1(a) = \int_{-\infty}^{+\infty} x e^{-ax^2} dx = -\frac{1}{2a}\int_{-\infty}^{+\infty} d\left(e^{-ax^2}\right) = -\frac{1}{2a}\left(e^{-ax^2}\right)_{-\infty}^{+\infty} = 0$$

- $I_2(a) = \int_{-\infty}^{+\infty} x^2 e^{-ax^2} dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$ … the 2nd Poisson integral

$$\textit{Proof}:\ I_2(a) = \int_{-\infty}^{+\infty} x^2 e^{-ax^2} dx = \int_{-\infty}^{+\infty} x\left(x e^{-ax^2}\right) dx = -\frac{1}{2a}\int_{-\infty}^{+\infty} x \frac{d}{dx}\left(e^{-ax^2}\right) dx$$

$$= -\frac{1}{2a}\left[\int_{-\infty}^{+\infty} \frac{d}{dx}\left(x e^{-ax^2}\right) dx - \int_{-\infty}^{+\infty} e^{-ax^2} dx\right] = -\frac{1}{2a}\int_{-\infty}^{+\infty} d\left(x e^{-ax^2}\right) + \frac{1}{2a}\sqrt{\frac{\pi}{a}}$$

$$= -\frac{1}{2a}\underbrace{\left(x e^{-ax^2}\right)_{-\infty}^{+\infty}}_{(l'Hospital)\to 0} + \frac{1}{2a}\sqrt{\frac{\pi}{a}} = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$$