Quantum Mechanics and Spectroscopy
CHEM 3PA3
Tutorial 3

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1. The energy eigenvalues of the harmonic oscillator are $E_n = \hbar\left(n+\frac{1}{2}\right)\sqrt{\frac{\kappa}{m}}$ with $n = 0, 1, 2, \cdots$. For the CN molecule, we have $m = 1.07 \times 10^{-26}$ kg, $\kappa = 1630$ Nm^{-1}. For vibrations, usually the absorptions/emissions are reported in wavenumbers. What is the wavenumber corresponding to the lowest-energy excitation from the ground state, $(n = 0) \to (n = 1)$, in this system?

   The ground state energy is given by the sum of two electron occupying the $(1, 1, 1)$ state and two electron occupying any of the three possible orbitals $(2, 1, 1), (1, 2, 1)$, and $(1, 1, 2)$.

$$E_1 - E_0 = \hbar\left(1+\frac{1}{2}\right)\sqrt{\frac{\kappa}{m}} - \hbar\left(0+\frac{1}{2}\right)\sqrt{\frac{\kappa}{m}} = \hbar\sqrt{\frac{\kappa}{m}} = \frac{hc}{\lambda} = \hbar c k$$

$$k = \frac{\sqrt{\frac{\kappa}{m}}}{c} = 1.301 \times 10^{6}\ \mathrm{m}^{-1}$$

2. What is the first order perturbation energy of the ground state of the anharmonic oscillator, given that the potential is:

$$V(x) = \frac{1}{2}\kappa x^2 + \frac{1}{6}\gamma_3 x^3 + \frac{1}{24}\gamma_4 x^4.$$

   A dummy parameter is introduced, so that the system can be solved by perturbation theory. The total Hamiltonian can then be expressed as:

$$H_T = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}\kappa x^2 + \lambda\left[\frac{1}{6}\gamma_3 x^3 + \frac{1}{24}\gamma_4 x^4\right].$$

   The total energy is given by $E(\lambda) = E(0) + \lambda \left.\frac{dE}{d\lambda}\right|_{\lambda=0}$. The first order perturbation of the energy is given by $\left.\frac{dE}{d\lambda}\right|_{\lambda=0}$, which can be evaluated using the Hellman-Feynmann theorem,

$$\begin{aligned}
\left.\frac{dE}{d\lambda}\right|_{\lambda=0} &= \int_{-\infty}^{\infty} \Psi_0^{\star}(0,x) \left.\frac{\partial H_T}{\partial \lambda}\right|_{\lambda=0} \Psi_0(o,x)dx \\
&= \int_{-\infty}^{\infty} \left(\frac{\sqrt{\kappa m}}{\pi\hbar}\right)^{1/2} \exp\left(-\frac{\sqrt{\kappa m}}{2\hbar}x^2\right)\left[\frac{1}{6}\gamma_3 x^3 + \frac{1}{24}\gamma_4 x^4\right]\exp\left(-\frac{\sqrt{\kappa m}}{2\hbar}x^2\right)dx \\
&= \int_{-\infty}^{\infty} \left(\frac{\sqrt{\kappa m}}{\pi\hbar}\right)^{1/2} \left[\frac{1}{24}\gamma_4 x^4\right]\exp\left(-\frac{\sqrt{\kappa m}}{\hbar}x^2\right)dx \\
&= \frac{\gamma_4\hbar^2}{64\kappa m}
\end{aligned}$$

3. Calculate the expectation value of the kinetic energy for the harmonic oscillator.

   The Hellman-Feynmann theorem can be used to avoid a long integral evaluation by finding how the Hamiltonian can be derived with respect to a parameter and obtaining the desired integral expression.

$$
\begin{aligned}
\frac{\partial E_0}{\partial \hbar} &= \int_{-\infty}^{\infty} \Psi_0^\star(x) \frac{\partial \hat{H}}{\partial \hbar} \Psi_0(x) dx \\
\frac{\partial}{\partial \hbar}\left[\frac{\hbar}{2}\sqrt{\frac{\kappa}{m}}\right] &= \int_{-\infty}^{\infty} \Psi_0^\star(x) \left[-\frac{\hbar}{m}\frac{d^2}{dx^2}\right] \Psi_0(x) dx \\
\left[\frac{1}{2}\sqrt{\frac{\kappa}{m}}\right] &= \int_{-\infty}^{\infty} \Psi_0^\star(x) \left[-\frac{\hbar}{m}\frac{d^2}{dx^2}\right] \Psi_0(x) dx \\
\left[\frac{\hbar}{4}\sqrt{\frac{\kappa}{m}}\right] &= \int_{-\infty}^{\infty} \Psi_0^\star(x) \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right] \Psi_0(x) dx \\
\left[\frac{\hbar}{4}\sqrt{\frac{\kappa}{m}}\right] &= \int_{-\infty}^{\infty} \Psi_0^\star(x) \hat{T} \Psi_0(x) dx
\end{aligned}
$$

4. Consider a particle on a ring on the xy-plane. The Hamiltonian in two dimensions in polar coordinates is

$$
\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)
$$

   (a) The motion is fixed on a ring, so r is constant, show that $\Phi(\phi) = Ae^{im\phi} + Be^{-im\phi}$ is an eigenfunction of the Hamiltonian.

$$
\begin{aligned}
\hat{H}\Phi(\phi) &= -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\left[Ae^{im\phi} + Be^{-im\phi}\right] \\
&= -\frac{\hbar^2 m^2}{2m_e r^2}\left[Ae^{im\phi} + Be^{-im\phi}\right]
\end{aligned}
$$

   (b) The particle's motion on the ring is cyclic, meaning that $\Phi(\phi + 2\pi) = \Phi(\phi)$. From this boundary condition, show that the values of m are now limited to $m = 0, \pm 1, \pm 2, \ldots$

$$
\begin{aligned}
\Phi(\phi + 2\pi) &= \Phi(\phi) \\
Ae^{im(\phi+2\pi)} + Be^{-im(\phi+2\pi)} &= Ae^{im\phi} + Be^{-im\phi} \\
Ae^{im(\phi}e^{i2m\pi} + Be^{-im(\phi)}e^{-i2m\pi} &= Ae^{im\phi} + Be^{-im\phi}
\end{aligned}
$$

Here, $e^{\pm i2m\pi} = 1$, so $\cos 2m\pi \pm i \sin 2m\pi = 1 + 0i$. In order to meet this equality, $m = 0, \pm 1, \pm 2, \cdots$.