CHM 421/621 Statistical Mechanics

Lecture 5 Energies in a QM system

Introduction and Review

Lecture Plan

Quantum Systems

- Particle in a box
- Harmonic oscillator
- Rigid rotor
- Many-particle quantum systems

Quantum Systems

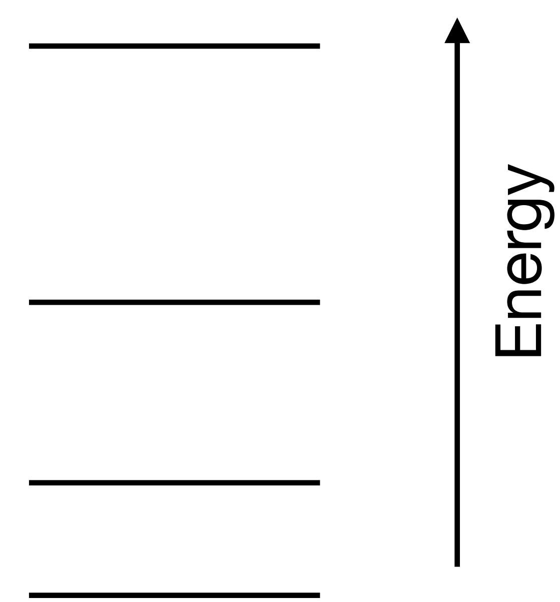
Particle in a box

Consider a quantum particle trapped in a cubic box of volume $V=L^3$

Eigenvalues are given by three quantum numbers

$$\epsilon_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

where allowed values for each $n=1,2,3,\ldots$



Spectrum in 1-d case

E.g., for H atom in V=1 cm^3.

$$\frac{\hbar^2\pi^2}{2mL^2} = 3.31 \times 10^{-37}\ J$$

Quantum Systems

Particle in a box

Typical energy in systems ~ $k_B T = 4.14 \times 10^{-21}$ *J* (@ *T* = *300 K*)

=> $n \sim 1 \times 10^8$

Minimum energy gap

$$\Delta\epsilon = \epsilon_{n_x,n_y,n_z} - \epsilon_{n_x+1,n_y,n_z} = 2(n_x+1)\frac{\hbar^2\pi^2}{2mL^2}$$

$$\approx 2n_x\frac{\hbar^2\pi^2}{2mL^2} = 10^{-8} \times \epsilon_{n_x,n_y,n_z}$$

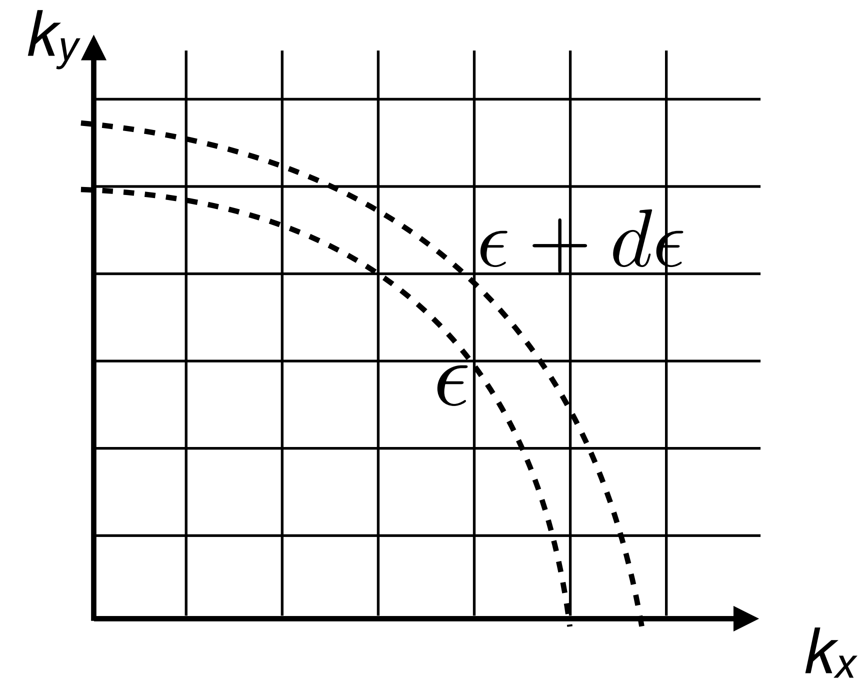
The gap is very small fraction of the level energy. Hence we can essentially treat the energies as continuously varying.

Quantum Systems

Particle in a box

Define $$\vec{k} = \frac{\pi}{L}\left(n_x, n_y, n_z\right)$$

Eigenvalues are then $$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$



$$\Omega = \left(\frac{\pi}{L}\right)^3$$

$$N(\epsilon) = \frac{\frac{1}{8} \times \frac{4}{3}\pi k^3}{\Omega} = \frac{\frac{1}{8} \times \frac{4}{3}\pi\left(\frac{2m\epsilon}{\hbar^2}\right)^{\frac{3}{2}}}{\left(\frac{\pi}{L}\right)^3}$$

$$= \frac{\sqrt{2}m^{\frac{3}{2}}}{3\pi^2\hbar^3} \times V \times \epsilon^{\frac{3}{2}}$$

Density of states:
No. of states in the shell (above) per unit volume

$$g(\epsilon) = \frac{1}{V}\frac{dN}{d\epsilon} = \frac{m^{\frac{3}{2}}}{\sqrt{2}\pi^2\hbar^3} \times \epsilon^{\frac{1}{2}}$$

Quantum Systems

Particle in a box

Example, canonical partition function

$$Q(N,V,T) = \sum_{\mathbf{n}} \exp(-\beta\epsilon(\mathbf{n})) = \sum_{n_x,n_y,n_z} \exp(-\beta\frac{\hbar^2}{2mL^2}(n_x^2+n_y^2+n_z^2))$$

$$= \sum_{k_x,k_y,k_z} \exp\left(-\beta\frac{\hbar^2 k^2}{2m}\right) \longrightarrow \frac{V}{\pi^3}\int d^3k\, \exp\left(-\beta\frac{\hbar^2 k^2}{2m}\right)$$

$$Q(N,V,T) = V\int_0^\infty d\epsilon\; g(\epsilon)\,\exp\left(-\beta\epsilon\right)$$

$$= \frac{V\; m^{\frac{3}{2}}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty d\epsilon\;\epsilon^{\frac{1}{2}}\,\exp\left(-\beta\epsilon\right) \qquad = \frac{V}{\Lambda^3}$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Quantum Systems

Rigid Rotor

Eigenvalues

$$\epsilon_J = J(J+1)\frac{\hbar^2}{2I}$$

J=0,1,2,...

$$I = \mu R^2$$

Degeneracy of each level is *2J+1*

$$\Delta\epsilon = \epsilon_1 - \epsilon_0 = 2\frac{\hbar^2}{2\mu R^2}$$

$$\approx 4.2 \times 10^{-22} J$$

For HCl with $I = 2.65 \times 10^{-47}\ kg/m^3$

Compared to the energy of first excitation in particle-in-a-box, this is much larger.

Hence, quantisation of levels is more important in this case.

Quantum Systems

Harmonic oscillator

Eigenvalues

$$\epsilon_v = (v + \frac{1}{2})h\nu$$ *v=0,1,2,...*

$$\Delta\epsilon = \epsilon_1 - \epsilon_0 = h\nu$$
$$\approx 5.7 \times 10^{-20} J$$
$$\gg \Delta\epsilon_{rot}$$

For HCl with $\nu = 8.65 \times 10^{13} Hz$

Hence, quantisation of levels is more important in this case too.

Quantum Systems

Electrons

Consider a H atom as example

$$\epsilon_n = -\frac{13.6}{n^2} eV$$

n=1,2,3,...

$$\Delta\epsilon = \epsilon_2 - \epsilon_1 = \frac{13.6 \times 3}{4}\ eV$$

$$\approx 1.63 \times 10^{-18} J$$

$$\nu = 8.65 \times 10^{13} Hz$$

$$\gg \Delta\epsilon_{vib}$$

The electronic energies and populations essentially remain constant due to this large gap. Thus, their contribution can be mostly ignored.

Quantum Systems

Many-electron systems

Consider a system of independent particles

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + ...$$

Separable Hamiltonian implies

$$E(n_1, n_2, n_3, ...) = \epsilon_{n_1} + \epsilon_{n_2} + \epsilon_{n_3} + ...$$

Where *n*'s are quantum numbers. In the present case, each quantum number corresponds to the level occupied by one of the *N* particles.

Thus, the microstate for a quantum system can be specified by specifying these quantum numbers (n_1, n_2, n_3, …).