

Harmonic oscillator

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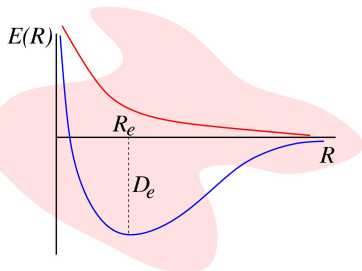


PHYSICAL CHEMISTRY I

- 1 Potential energy curve
 - Parabolic approximation
- 2 Classical treatment
 - Position
 - Linear momentum
- 3 Quantum treatment
 - Energy
 - Eigenfunctions
 - Parity
 - Classical vs quantum distributions



Parabolic approximation



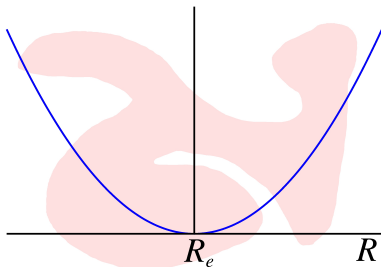
- **Unbound** states.
- **Bound** states.
 - Dissociation energy $\Rightarrow D_e$
 - Equilibrium internuclear distance $\Rightarrow R_e$ (bond distance)

- Potential energy curve

$$V(R) = \underbrace{V(R_e)}_{\text{energy origin}} + \underbrace{\left(\frac{\partial V}{\partial R}\right)_{R_e}}_{\text{minimum}}(R-R_e) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial R^2}\right)_{R_e}(R-R_e)^2 + \frac{1}{6}\left(\frac{\partial^3 V}{\partial R^3}\right)_{R_e}(R-R_e)^3 + \dots$$



Parabolic approximation



- $\lim_{R \rightarrow \infty} V_h(R) = \infty \neq D_e$
- Minimum at $R = R_e$
- $\lim_{R \rightarrow 0} V_h(R) = \frac{1}{2} k R_e^2 < \infty$

- Harmonic potential energy

$$V_{\text{har}}(R) = \frac{1}{2} \underbrace{\left(\frac{\partial^2 V}{\partial R^2} \right)_{R_e}}_{k \rightarrow \text{force constant}} \underbrace{(R - R_e)^2}_q$$



Hooke's law

$$F = - \frac{dV_{\text{har}}}{dq} = -k q$$



Position

- Classical energy

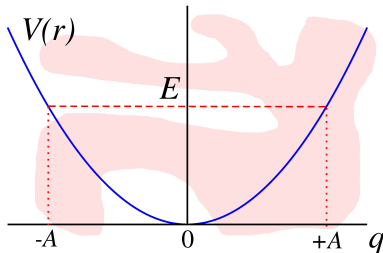
$$E = \frac{p^2}{2\mu} + \frac{1}{2}kq^2 = \frac{1}{2}kA^2$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$F = -k q = \mu a \rightarrow -k q = \mu \frac{d^2 q}{dt^2}$$

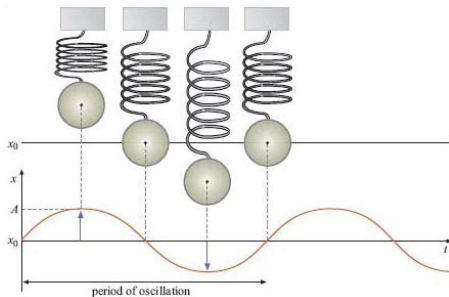
↓ $q(0)=0$

$$q(t) = A \sin(\omega t) \rightarrow \omega = 2\pi\nu = \sqrt{k/\mu}$$





Position

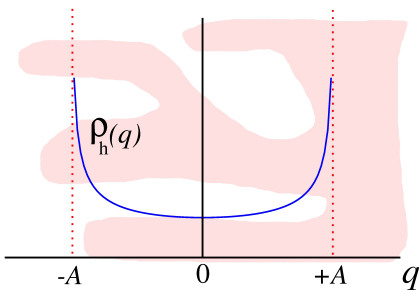


- $\nu = \frac{1}{2\pi} \sqrt{k/\mu} \Rightarrow \text{Frequency (s}^{-1}\text{)}$
- $\omega = 2\pi\nu \Rightarrow \text{Angular frequency (s}^{-1}\text{)}$
- $T = 1/\nu \Rightarrow \text{Period (s)}$



Linear momentum

$$p(t) = \mu \dot{q}(t) = \mu A \omega \cos(\omega t) = \mu \omega \sqrt{A^2 - q^2(t)}$$



$$\rho(q) \propto \frac{1}{p(t)}$$

↓

$$\rho(q) = \frac{1}{\pi \sqrt{A^2 - q^2(t)}}$$

$$\rho(p) = \frac{1}{\pi \sqrt{p_{\max}^2 - p^2(t)}}$$

R.W. Roninette, Am. J. Phys. **63**, 823 (1995)



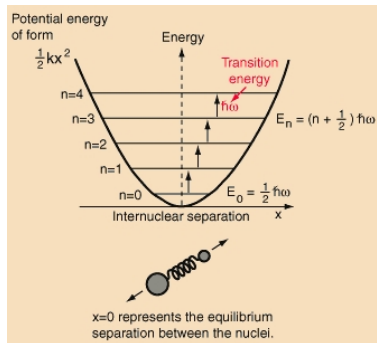
Energy

• Hamiltonian

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu} \frac{d^2}{dq^2} + \frac{1}{2}kq^2 \rightarrow \hat{H}(q)\phi_n(q) = E_n\phi_n(q)$$

⇒ Eigenvalues

- $E_n = (n + \frac{1}{2}) \underbrace{h\nu}_{\hbar\omega}, \quad n = 0, 1, 2, \dots$
- Minimal energy $\rightarrow E_0 = \frac{1}{2} h\nu \rightarrow$ Zero point energy
- $\Delta E = E_{n+1} - E_n = h\nu \rightarrow$ vibrational quantum

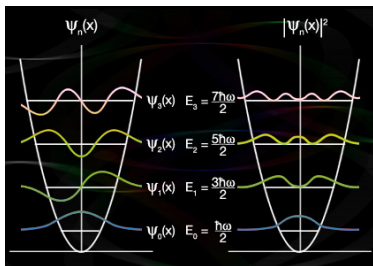




Energy

- Eigenfunctions $\Rightarrow$

$$\begin{cases} \phi_n(q) = (2^n n!)^{-1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} H_n(\sqrt{\alpha}x) \\ \text{Hermite's polynomials} \Rightarrow H_n(z) = (-1)^n e^{z^2} \frac{d^n e^{-x^2}}{dz^n} \\ \text{Parity} \Rightarrow n \text{ even, } n \text{ odd} \end{cases}$$



Nodes $\Rightarrow n$

$$\phi_0(q) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha q^2/2}$$

$$\phi_1(q) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} q e^{-\alpha q^2/2}$$

$$\phi_2(q) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (1 - 2\alpha q^2) e^{-\alpha q^2/2}$$

$$\alpha = \frac{2\pi\nu\mu}{\hbar}$$



Parity

○ Parity

$n = 0, 2, 4, \dots \Rightarrow \phi_v(q) = \phi_v(-q) \rightarrow$ even functions

$n = 1, 3, 5, \dots \Rightarrow \phi_v(q) = -\phi_v(-q) \rightarrow$ odd functions

Parity

even · even = even

even · odd = odd

odd · even = odd

odd · odd = even

$$\triangleright \int_{-\infty}^{+\infty} f_{\text{odd}}(q) dq = 0$$

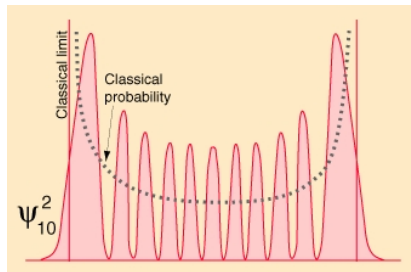
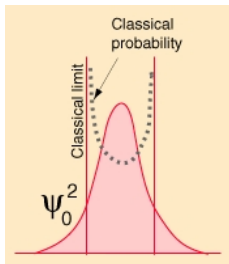
$$\triangleright \int_{-\infty}^{+\infty} f_{\text{even}}(q) dq = 2 \int_0^{+\infty} f_{\text{even}}(q) dq$$



Classical vs quantum distributions

- Classical allowed and forbidden regions

$$E = T + V \xrightarrow{T \geq 0} E \geq V \rightarrow -A \leq q_{\text{cl}} \leq +A$$





Classical vs quantum distributions

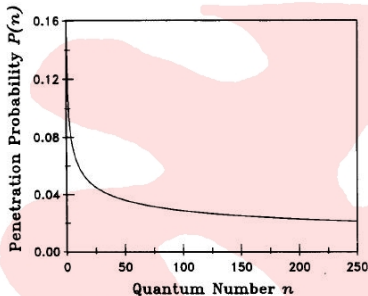


Fig. 1. The graph of the penetration probability $P(n)$ vs quantum number n for values of n ranging from $n=0$ to $n=250$.

▷ J.J. Diamond, Am. J. Phys. **60**, 912 (1992)

• Problems

- No dissociation limit ($\uparrow n$)
- Anharmonicities $\Rightarrow k_3 q^3 + k_4 q^4 + \dots \rightarrow \Delta E \neq \text{constant}$