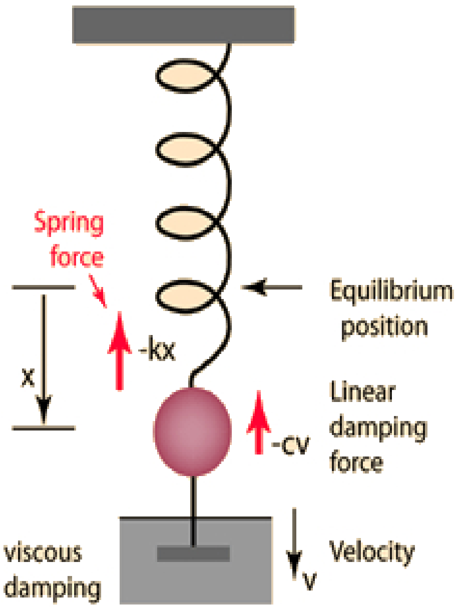
Harmonic oscillator



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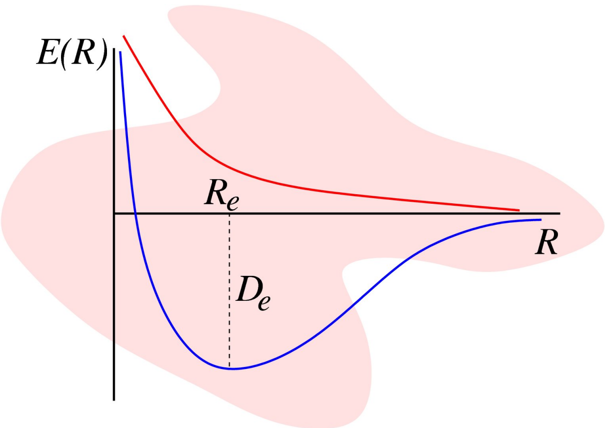
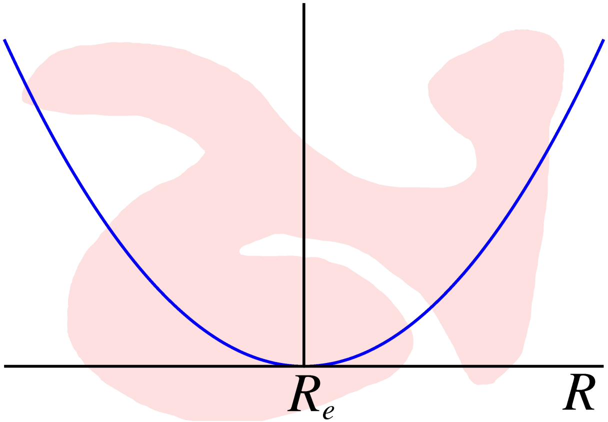
I.A. Parabolic approximation



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

- Potential energy curve

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



- Harmonic potential energy

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

- $\lim_{R\to\infty} V_{\text{h}}(R) = \infty \neq D_e$
- Minimum at $R = R_e$
- $\lim_{R\to 0} V_{\text{h}}(R) = \frac{1}{2}kR_e^2 < \infty$

Hooke's law

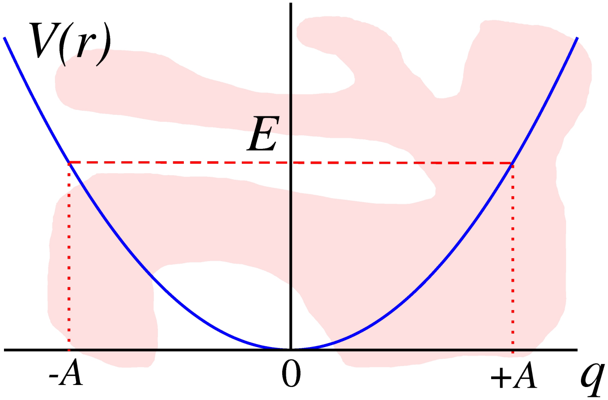
$$F = -\frac{dV_{\text{har}}}{dq} = -k\,q$$

II.A. Position

- Classical energy

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

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

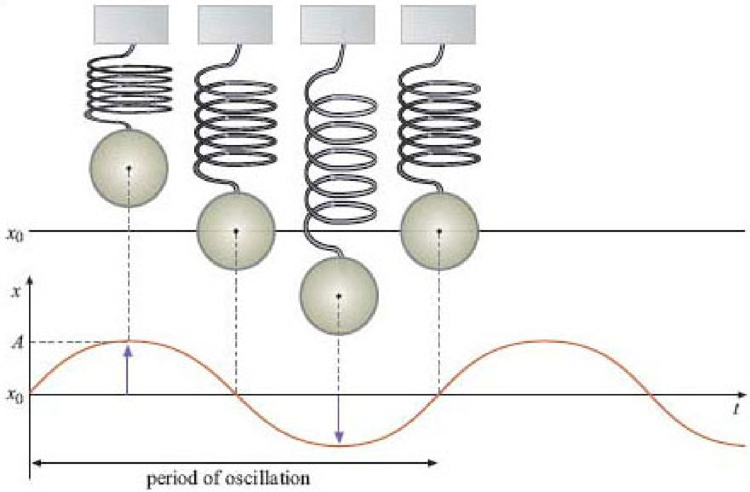


$$F = -kq = \mu a \rightarrow -kq = \mu \frac{d^2q}{dt^2}$$

$$\downarrow \; q(0)=0$$

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

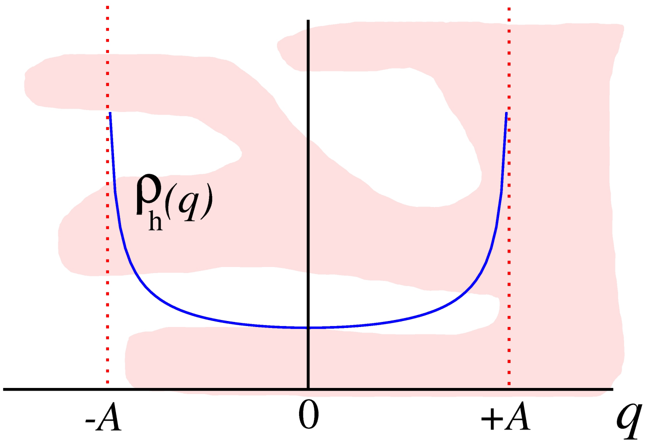
II.A. Position



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

II.B. Linear momentum

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



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

$$\downarrow$$

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

$$\rho(p) = \frac{1}{\pi\sqrt{p^2_{\text{máx}} - p^2(t)}}$$

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

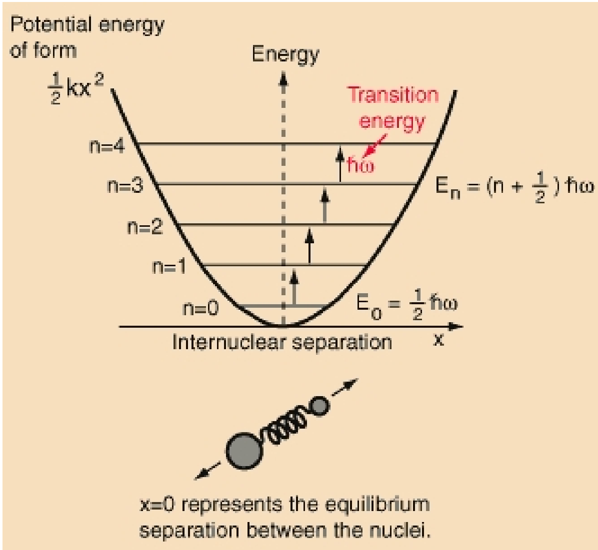
III.A. Energy

- Hamiltonian

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

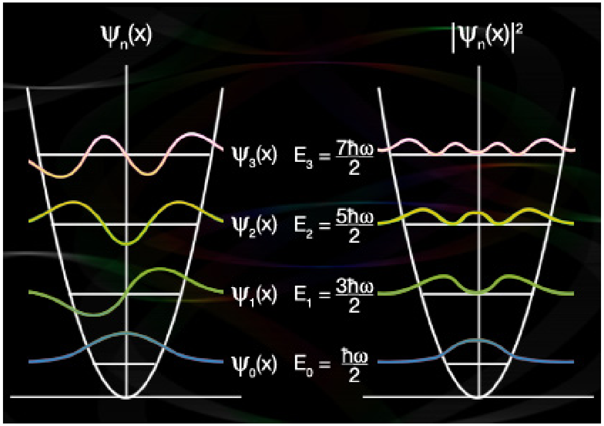
$\Rightarrow$ Eigenvalues

- $E_n = (n+\frac{1}{2})\underbrace{h\nu}_{\hbar\omega},\ n = 0, 1, 2, \ldots$
- 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



III.B. Eigenfunctions

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



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

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

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

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

- Nodes $\Rightarrow n$

III.C. Parity

- Parity

$$n = 0, 2, 4, \ldots \Rightarrow \phi_v(q) = \phi_v(-q) \rightarrow \text{ even functions}$$

$$n = 1, 3, 5, \ldots \Rightarrow \phi_v(q) = -\phi_v(-q) \rightarrow \text{ odd functions}$$

Parity
even · even = even
even · odd = odd
odd · even = odd
odd · odd = even

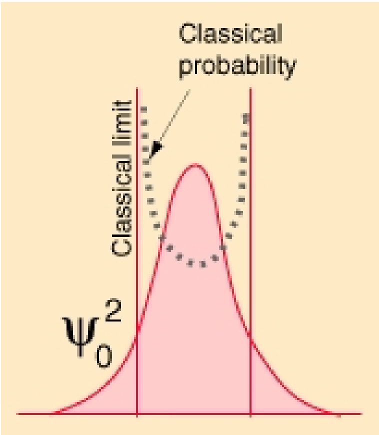
▷ $\int_{-\infty}^{+\infty} f_{\mathrm{odd}}(q)\, dq = 0$

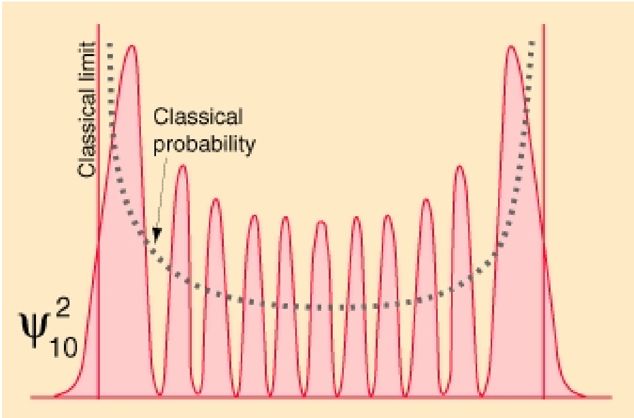
▷ $\int_{-\infty}^{+\infty} f_{\mathrm{even}}(q) dq = 2 \int_{0}^{+\infty} f_{\mathrm{even}}(q) dq$

III.D. Classical *vs* quantum distributions

- Classical allowed and forbidden regions

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





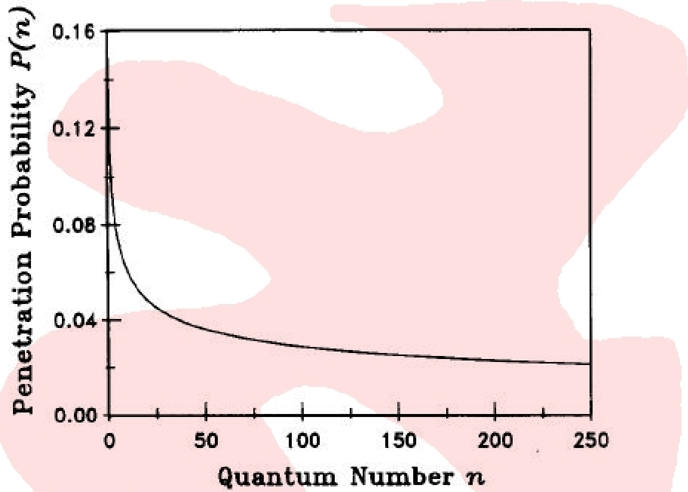


Fig. 1. The graph of the penetration probability $P(n)$ vs quantum number n for values of n ranging from $n=0$ to $n=250$.

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

- Problems
  - No dissocation limit $(\uparrow n)$
  - Anharmonicites $\Rightarrow k_3 q^3 + k_4 q^4 + \ldots \rightarrow \Delta E \neq$ constant