Teoria de Perturbação

$$\hat{H}\psi = E\psi$$

Ordem zero,
problema com solução conhecida:

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

Sistema com perturbação:

$$\hat{H} = \hat{H}^{(0)} + \underbrace{\hat{H}'}_{\text{operador da perturbação}}$$

Solução do problema com perturbação:

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots$$

Exemplos:

Oscilador anarmônico: $$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \cdots$$

Átomo de hélio: $$\left\{\hat{H}_{\mathrm{H}}(1) + \hat{H}_{\mathrm{H}}(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right\}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

Teoria de Perturbação

$$\hat{H}\psi = E\psi$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \qquad \psi = \psi^{(0)} + \psi^{(1)} \qquad E = E^{(0)} + E^{(1)}$$

$$\left(\hat{H}^{(0)} + \hat{H}'\right)\left(\psi^{(0)} + \psi^{(1)}\right) = \left(E^{(0)} + E^{(1)}\right)\left(\psi^{(0)} + \psi^{(1)}\right)$$

$$\cancel{\hat{H}^{(0)}\psi^{(0)}} + \boxed{\hat{H}'\psi^{(0)}} + \boxed{\hat{H}^{(0)}\psi^{(1)}} + \underbrace{\cancel{\hat{H}'\psi^{(1)}}}_{\approx 0} = \cancel{E^{(0)}\psi^{(0)}} + \boxed{E^{(1)}\psi^{(0)}} + \boxed{E^{(0)}\psi^{(1)}} + \underbrace{\cancel{E^{(1)}\psi^{(1)}}}_{\approx 0}$$

$$\boxed{\left(\hat{H}^{(0)} - E^{(0)}\right)\psi^{(1)}} = \boxed{\left(E^{(1)} - \hat{H}'\right)\psi^{(0)}}$$

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right)\psi_n^{(1)} = (E_n^{(1)} - \hat{H}')\psi_n^{(0)}$$

Correção de primeira ordem do estado *n* como combinação linear das funções de ordem zero:

$$\psi_n^{(1)} = \sum_j c_j \psi_j^{(0)}$$

$$\int \sum_j c_j \ \psi_m^{(0)*}\left(\hat{H}^{(0)} - E_n^{(0)}\right)\psi_j^{(0)} d\tau = \int \psi_m^{(0)*}(E_n^{(1)} - \hat{H}')E\psi_n^{(0)} d\tau$$

$$\sum_j c_j \left[\int \psi_m^{(0)*}\hat{H}^{(0)}\psi_j^{(0)} d\tau - E_n^{(0)}\int \psi_m^{(0)*}\psi_j^{(0)} d\tau\right] = E_n^{(1)}\int \psi_m^{(0)*}\psi_n^{(0)} d\tau - \int \psi_m^{(0)*}\hat{H}'\psi_n^{(0)} d\tau$$

$$= E_j^{(0)}\psi_j^{(0)}$$

$$\delta_{mn} = \begin{cases} 1 \text{ se } m = n \\ 0 \text{ se } m \neq n \end{cases}$$

$$\sum_j c_j \left[E_j^{(0)}\int \psi_m^{(0)*}\psi_j^{(0)} d\tau - E_n^{(0)}\int \psi_m^{(0)*}\psi_j^{(0)} d\tau\right] = E_n^{(1)}\delta_{mn} - \int \psi_m^{(0)*}\hat{H}'\psi_n^{(0)} d\tau$$

$$\boldsymbol{c_m} \quad \boldsymbol{E_m} \quad \boldsymbol{\delta_{mj}}$$

$$c_m\left[E_m^{(0)}-E_n^{(0)}\right]=E_n^{(1)}\delta_{mn}-\int \psi_m^{(0)*}\,\hat{H}'\psi_n^{(0)}d\tau$$

$$H'_{mn}\equiv\int \psi_m^{(0)*}\,\hat{H}'\psi_n^{(0)}d\tau$$

$$c_m\left[E_m^{(0)}-E_n^{(0)}\right]=E_n^{(1)}\delta_{mn}-H'_{mn}$$

Se $m=n$ 0 $E_n^{(1)}$ H_{nn}'

Se $m\neq n$ 0 H_{mn}'

$$\boxed{E_n^{(1)}=\int \psi_n^{(0)*}\,\hat{H}'\psi_n^{(0)}d\tau}$$

$$\boxed{c_m=\frac{H'_{mn}}{E_n^{(0)}-E_m^{(0)}}}$$

Teoria de Perturbação

$$\hat{H}\psi = E\psi \qquad \hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

$$\downarrow$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \qquad \psi = \psi^{(0)} + \psi^{(1)} + \cdots \qquad E = E^{(0)} + E^{(1)} + \ldots$$

$$\downarrow$$

$$\psi_n^{(1)} = \sum_j c_j \psi_j^{(0)}$$

$$\boxed{\psi_n \approx \psi_n^{(0)} + \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} + \cdots}$$

$$H'_{mn} \equiv \int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$$

$$\boxed{E_n \approx E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \cdots}$$

Exemplo,

átomo de hélio:

$$\left\{\hat{H}_{\mathrm{H}}(1) + \hat{H}_{\mathrm{H}}(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right\}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$\hat{H}^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$E^{(0)} = -Z^2\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)\frac{e^2}{8\pi\varepsilon_0 a_0}, \qquad \begin{aligned} n_1 &= 1, 2, 3, \ldots \\ n_2 &= 1, 2, 3, \ldots \end{aligned}$$

$$E^{(0)}_{1s^2} = -108.83\ \mathrm{eV}$$

$$\psi^{(0)}_{1s^2} = 1s(1)1s(2) = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_1/a_0} \cdot \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_2/a_0}$$

1 eV = 96 kJ/mol = 8100 cm^{-1}

Correção da energia em primeira ordem: $$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$$

$$E^{(1)} = \frac{Z^6 e^2}{(4\pi\varepsilon_0)\pi^2 a_0^6} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \int_0^{\infty} \int_0^{\infty} e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} \frac{1}{r_{12}} r_1^2 \sin\theta_1 \, r_2^2 \sin\theta_2 \, dr_1 \, dr_2 \, d\theta_1 \, d\theta_2 \, d\phi_1 \, d\phi_2$$

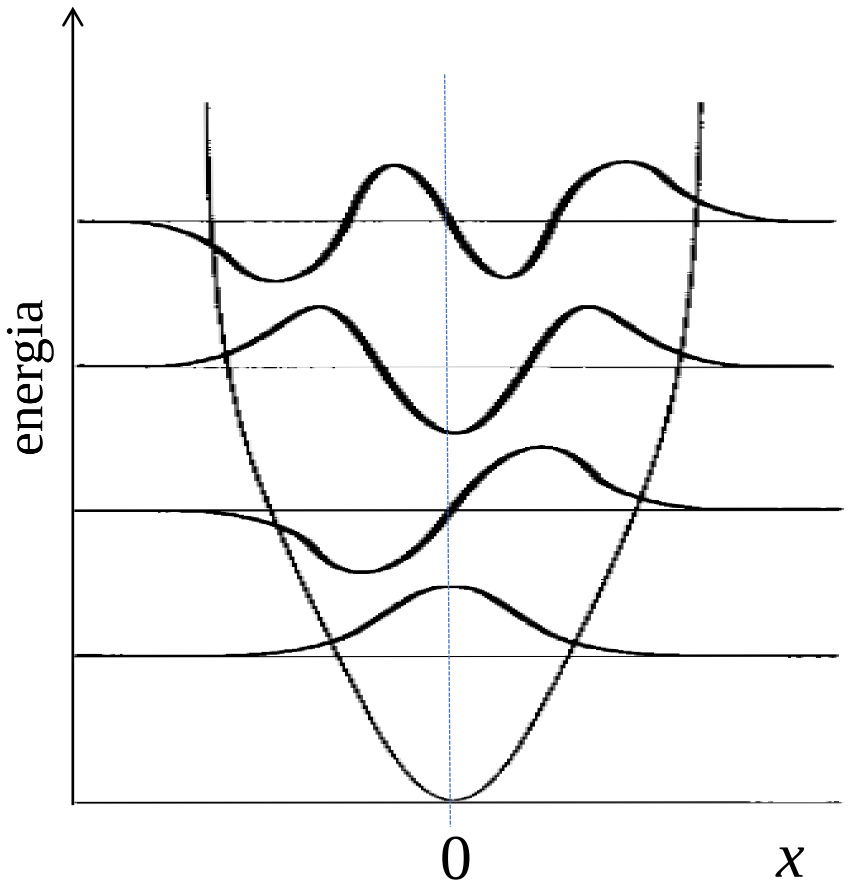
$$E^{(1)} = \frac{5Z}{8}\left(\frac{e^2}{4\pi\varepsilon_0 a_0}\right)$$

$$E^{(0)} + E^{(1)} = -108.83 \text{ eV} + 34.01 \text{ eV} = -74.82 \text{ eV}$$

(experimental, E = -79,00 eV)

Exemplo,
oscilador anarmônico:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2}_{\hat{H}^{(0)}} + \underbrace{\frac{1}{6}\gamma x^3 + \frac{b}{24}x^4}_{\hat{H}'}$$



$$E_v^{(0)} = \left(v + \frac{1}{2}\right)h\nu \qquad v = 0,\ 1,\ 2,\ \ldots$$

$$\psi^{(0)}(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$E^{(1)} = \int_{-\infty}^{\infty} \psi^{(0)}(x)^* \hat{H}^{(1)} \psi^{(0)}(x)dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \left[\frac{\gamma}{6}\cancel{\int_{-\infty}^{\infty} x^3 e^{-\alpha x^2}dx} + \frac{b}{24}\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2}dx\right]$$

oscilador anarmônico: $$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{b}{24}x^4$$

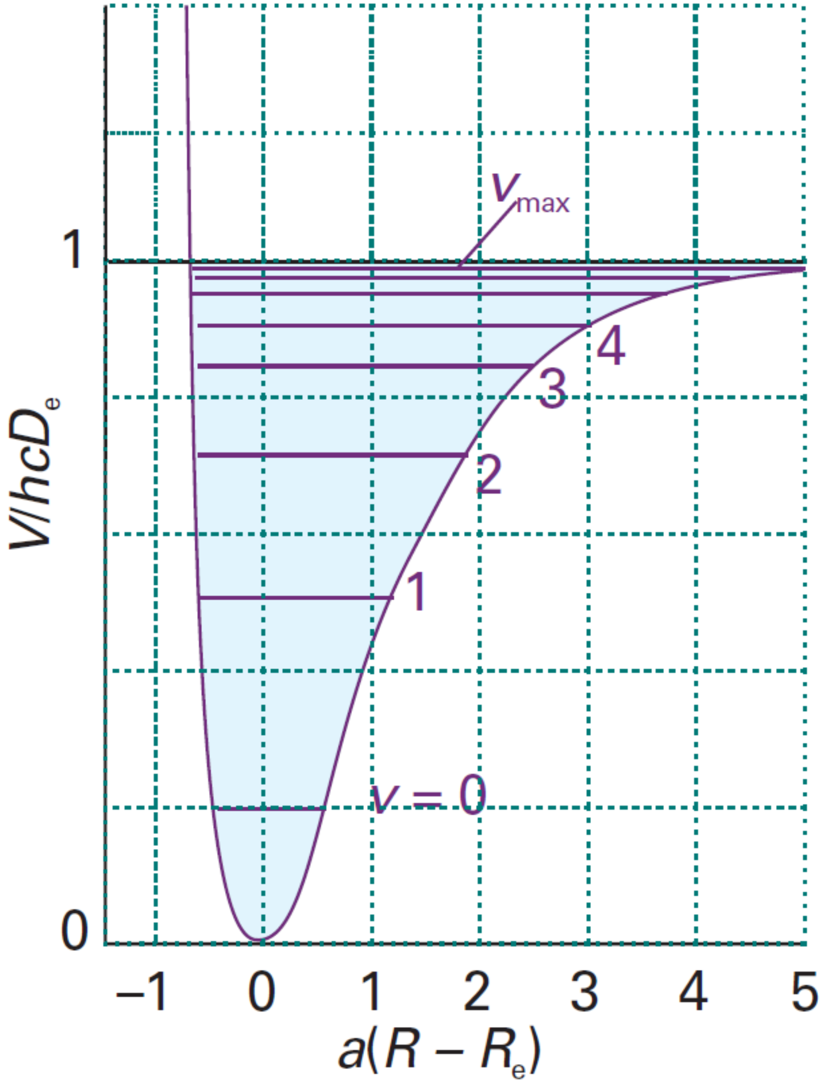
$$E^{(1)} = \int_{-\infty}^{\infty} \psi^{(0)}(x)^* \hat{H}^{(1)} \psi^{(0)}(x) dx$$

$$= \frac{b}{12}\left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} x^4 e^{-\alpha x^2} dx$$

Energia do estado fundamental: $E = E^{(0)} + E^{(1)} = \frac{h\nu}{2} + \frac{\hbar^2 b}{32k\mu}$

$$E_n \approx E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \cdots$$

Oscilador Anarmônico



harmônico

$$E_v = h\nu\left(v + \tfrac{1}{2}\right) \qquad \nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

$$v = 0,\ 1,\ 2,\ \ldots$$

Termo vibracional $G(v) = E_v/hc$ $\qquad \tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$

unidade: cm^{-1}

anarmônico:

$$G(v) = \tilde{\nu}_e(v + \tfrac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v + \tfrac{1}{2})^2 + \cdots$$

constante de anarmonicidade

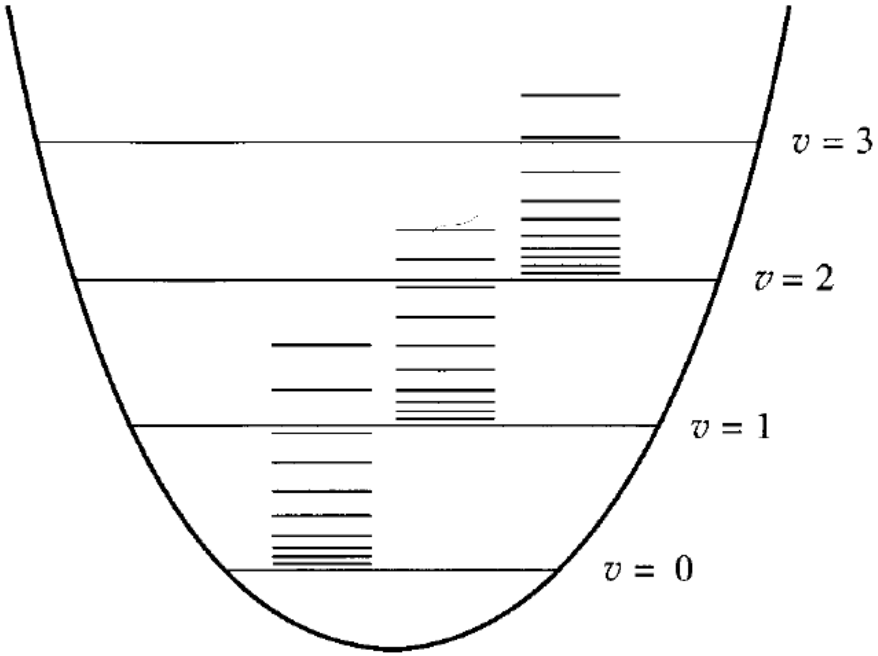
Vibração e rotação de molécula diatômica

$$E_v = (v + \tfrac{1}{2})h\nu \qquad v = 0,\ 1,\ 2,\ \ldots$$

$$E_J = \frac{\hbar^2}{2I}J(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots$$

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \tfrac{1}{2}) + \tilde{B}J(J+1)$$

$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \qquad \tilde{B} = h/8\pi^2 c\mu R_e^2$$



Regras de seleção
para absorção de radiação:

$$\Delta v = +1$$
$$\Delta J = \pm 1$$

$$\tilde{E}_{v+1,J+1} - \tilde{E}_{v,J} = \tilde{\nu} + 2\tilde{B}(J+1)$$

$$\tilde{E}_{v+1,J-1} - \tilde{E}_{v,J} = \tilde{\nu} - 2\tilde{B}J$$

Rotor não-rígido e acoplamento rotação-vibração

$$\tilde{E}_{v,J} = \tilde{\nu}(v + \tfrac{1}{2}) + \tilde{B}_v J(J+1)$$

$$\tilde{\nu}_R(\Delta J = +1) = E_{1,J+1} - E_{0,J}$$

$$= \tfrac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \tfrac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

$$\tilde{\nu}_P(\Delta J = -1) = E_{1,J-1} - E_{0,J}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$