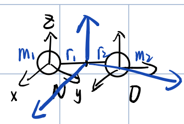
Rotation




$3 \times 2 = 6.$

translational Dof 3

vibrational Dof 1

rotional 2.

$m_1 r_1 = m_2 r_2.$

$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_e^2$ moment of inertion

$$\frac{r_1}{m_2} = \frac{r_2}{m_1} = \frac{r_1+r_2}{m_1+m_2} = \frac{r_e}{m_1+m_2}$$

$m_1 r_1 = m_2 r_2 = \mu r_e$

$\mathcal{H} = \frac{L^2}{2I}$. Hamiltoniam for rotational Degrees of freedom.

$\mathcal{H}|l,m\rangle = \frac{l(l+1)}{2I}\hbar^2 |l,m\rangle = l(l+1) B_h |l,m\rangle$

$m = -l, -l+1, \cdots, l-1, l.$ $2l+1$ Degeneracy

$$\begin{array}{l} \text{—— } l=3 \\ \quad\quad\quad\} \ 6B_h \\ \text{—— } l=2 \\ \quad\quad\quad\} \ 4B_h \\ \text{—— } l=1 \\ \quad\quad\quad\} \ 2B_h \\ \text{—— } l=0 \end{array}$$

$l(l+1) - l(l-1) = 2l.$

$E = \frac{L^2}{2I}$

$l \Rightarrow \infty$

$l(l+1)\hbar^2 \rightarrow L^2$

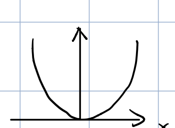
$l\hbar = L$

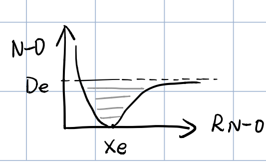
L is an interger, $\langle \theta, \varphi | l, m\rangle = Y_l^m(\theta, \varphi)$

$Y_l^m(\theta, \varphi + 2\pi) = Y_l^m(\theta, \varphi)$ periodic boundry condition (PBC) 周期性边界条件

$e^{i \cdot 2\pi m} = 1.$ m is interger 整数.

Morse Potential



$$V(r) = D_e(1 - e^{-a(x-x_e)})^2$$

$$E_n = h\nu_0(n+\tfrac{1}{2}) - \frac{[\hbar\nu_0(n+\frac{1}{2})]^2}{4D_e}$$

$$\nu_0 = \frac{a}{2\pi}\sqrt{2D_e/m}$$

## Ehrenfest Dynamics

$$O(t) = e^{\frac{iHt}{\hbar}} O e^{-\frac{iHt}{\hbar}}$$ Heisenberger Picture

$$\dot{O}(t) = \frac{i}{\hbar}[H, O]$$

$$H = \frac{P^2}{2m} + V(x)$$

$$\dot{x} = \frac{i}{\hbar}[H, x] = \frac{p}{m}.$$

$$\dot{p} = \frac{i}{\hbar}[H, p] = -\frac{\partial V}{\partial x}$$

$$[x, f(p)] = i\hbar\frac{\partial f}{\partial p}$$

$$[x, p] = i\hbar$$

$$[f(x), p] = i\hbar\frac{\partial f}{\partial x}.$$

$$\langle\dot{x}\rangle = \frac{\langle p\rangle}{m}$$

$$\langle\dot{p}\rangle = \langle -\frac{\partial V}{\partial x}\rangle$$

Ehrenfest Dynamics.

$$\langle\psi|x(t)|\psi\rangle = \langle x\rangle$$

$$\langle\psi|\frac{\partial H}{\partial t}|\psi\rangle = \frac{\partial E}{\partial x}$$ Hellmann-Feynmann Theorem.

$$V(x) = \frac{1}{2}m\omega^2x^2$$

$$\dot{x} = \frac{p}{m}. \quad \dot{p} = -m\omega^2x.$$

$$\ddot{x} = -\omega^2x.$$

$$x = x_0\cos(\omega t) + \frac{p_0}{\omega m}\sin(\omega t).$$ 解微分方程.

$$\frac{\partial}{\partial t}\langle\psi|\hat{O}|\psi\rangle$$ Schrödinger Picture.

$$\frac{\partial\hat{O}}{\partial t} = 0. \quad \frac{\partial}{\partial t}|\psi\rangle = \frac{\hat{H}}{i\hbar}|\psi\rangle$$

$$\langle\psi|\frac{\partial}{\partial t} = \langle\psi|\frac{\hat{H}}{-i\hbar}$$

$$= \frac{\partial}{\partial t}\langle\psi|\hat{O}|\psi\rangle + \underbrace{\langle\psi|\frac{\partial}{\partial t}\hat{O}|\psi\rangle}_{=0} + \langle\psi|\hat{O}\frac{\partial}{\partial t}|\psi\rangle$$

$$= \frac{i}{\hbar} \langle \varphi | [\hat{H}, \hat{O}] | \varphi \rangle$$

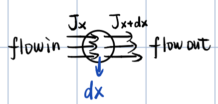
$\rho = |\varphi\rangle\langle\varphi|$ quantum Density Operator

$\rho(x) = \langle x|\varphi\rangle\langle\varphi|x\rangle$

- charge number is consentive.

$\int \rho(x)dx = 1.$

$\frac{\partial \rho}{\partial x} + \frac{\partial}{\partial x} J = 0.$ continuity equation.




1D.

$$\frac{\partial \rho \cdot dx}{\partial t} = J(x) - J(x+dx)$$

$$\frac{\partial \rho}{\partial t} = \frac{J(x) - J(x+dx)}{dx}$$

$$\frac{\partial \rho}{\partial t}(\vec{r}) + \nabla \cdot J(\vec{r}) = 0 \qquad 3D.$$

$$\frac{\partial \rho}{\partial t}(\vec{r}, t) = \frac{\partial}{\partial t}\varphi^*(\vec{r}) \cdot \varphi(\vec{r}) + \varphi^*(\vec{r})\frac{\partial}{\partial t}\varphi(\vec{r})$$

$$= \frac{i}{\hbar}\left[-\frac{\hbar^2}{2m}\nabla^2\varphi^*(\vec{r}) + V\varphi^*(\vec{r})\right]\varphi(\vec{r}) - \frac{i}{\hbar}\varphi^*(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2\varphi(\vec{r}) + V\varphi(\vec{r})\right]$$

$$= \frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\right)\left(\varphi(\vec{r})\nabla^2\varphi^*(\vec{r}) - \varphi^*(\vec{r})\nabla^2\varphi(\vec{r})\right)$$

$$= -\frac{i\hbar}{2m} \cdot \nabla \cdot (\varphi\nabla\varphi^* - \varphi^*\nabla\varphi)$$

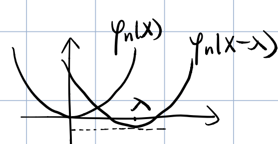
$J(\vec{r}) = \frac{\hbar}{2mi}(\varphi^*\nabla\varphi - \varphi\nabla\varphi^*)$ quantum current

electron transfer rate : Marcus theory

Shifted Homonic Oscillator

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 - q\varepsilon x.$$

$$= \frac{p^2}{2m} + \frac{1}{2}m\omega^2\left(x - \frac{q\varepsilon}{m\omega^2}\right)^2 - \frac{q^2\varepsilon^2}{2m\omega^2}.$$



$\lambda = \frac{q\varepsilon}{m\omega^2}$.

$\varphi_n(x-\lambda) = e^{-\lambda\frac{\partial}{\partial x}}\varphi_n(x)$ 泰勒展开. 系数项用e指数表示.

$U(\lambda) = e^{-\lambda\frac{\partial}{\partial x}} = e^{\bar{\lambda}(a^+-a)}$. $\bar{\lambda} = \lambda\sqrt{\frac{m\omega}{2\hbar}}$.

$V_1 = \frac{1}{2}m\omega^2x^2$

$V_2 = \frac{1}{2}m\omega^2(x-\lambda)^2$


$\mu_{nv,n'v'} = \langle \phi_n(r,R)\chi_v^{(n)}(R) | \hat{\mu}(r) | \phi_{n'}(r,R)\chi_{v'}^{(n')}(R) \rangle$

$= \langle \phi_n(r,R) | \mu(r) | \phi_{n'}(r,R) \rangle \underbrace{\langle \chi_v^{(n)}(R) | \chi_{v'}^{(n')}(R) \rangle}_{FC}$

$= \mu_{nn'}(R) \cdot FC$.  Frank-Cordon

$FC = \int \chi_v^1(x)\chi_v^2(x)$

$= \int \chi_v(x)\chi_{v'}(x-\lambda)dx$

$= \int \chi_v(x)U(\lambda)\chi_{v'}(x)dx$

$= \langle v | e^{\bar{\lambda}(a^+-a)} | v' \rangle$

Baker-Campell-Hausdroff formule

$e^Ae^B = e^{A+B+\frac{[A,B]}{2}}$.  $[A,B] = const$.

$e^{\bar{\lambda}(a^+-a)} = e^{\bar{\lambda}a^+}e^{-\bar{\lambda}a}e^{-\frac{\bar{\lambda}^2}{2}}$

$FC = \langle v | U(\lambda) | 0 \rangle = e^{-\frac{\bar{\lambda}^2}{2}}\langle v | e^{\bar{\lambda}a^+}e^{-\bar{\lambda}a} | 0 \rangle$

$= e^{-\frac{\bar{\lambda}^2}{2}}\langle v | e^{\bar{\lambda}a^+} | 0 \rangle$

$= e^{-\frac{\bar{\lambda}^2}{2}} \cdot \frac{\bar{\lambda}^v}{\sqrt{v!}}$

$K_{1\to2} = \frac{2\pi}{\hbar}\sum_v |\langle 2v | \mu | 10 \rangle|^2 \delta(E_{2v}-E_{10})$

$= \frac{2\pi}{\hbar}\sum_v |\mu_{12}|^2 \frac{e^{-\bar{\lambda}^2}}{v!}\lambda^{2v}\delta(E_2-E_1+\hbar v\omega)$

$K_{1\to2,\,v'} = \frac{2\pi}{\hbar}\sum_{vv'} P_{v'}|\langle 2v | \mu | 1v' \rangle|^2 \delta(E_{2v}-E_{1v'})$

$P_{v'} = \frac{1}{Z}e^{-\hbar v'\omega/kT}$  玻尔兹曼分布.

High Temperaturer

$$= \frac{|\mu_{12}|^2}{\hbar}\sqrt{\frac{\pi}{k_B T E_r}}\, e^{-(E_2-E_1-E_r)^2/4k_B T E_r}, \quad E_r = \frac{1}{2} m\omega^2 x^2.$$