Density Functional Perturbation Theory (DFPT)

PRL 58 1861 (1987)

KS equations: $[\hat{t} + \hat{G}(r)]\varphi_\lambda = \varepsilon_\lambda \varphi_\lambda$,

$$\hat{G}(r) = -eV_H(r) + \underbrace{V(r)}_{e-n} + V_{xc}(r) = \frac{\delta}{\delta\rho(r)}\left[E_H + E_{xc} + E_{e-n}\right]$$

Total energy: $E = \sum_\lambda \langle\varphi_\lambda|\hat{t}|\varphi_\lambda\rangle + E_H + E_{xc} + E_{e-n} + E_{nn}$

Electron density: $\rho(r) = \sum_\lambda^{occ} \varphi_\lambda^*(r)\varphi_\lambda(r)$

Hellmann-Feynman theorem (the 1st energy derivative):

$$\frac{\partial E}{\partial R_{A\alpha}} = \sum_\lambda \langle\varphi_\lambda|\frac{\partial V}{\partial R_{A\alpha}}|\varphi_\lambda\rangle + \frac{\partial E_{nn}}{\partial R_{A\alpha}} = \int \rho(r)\frac{\partial V}{\partial R_{A\alpha}}dr + \frac{\partial E_{nn}}{\partial R_{A\alpha}}$$

2nd energy derivative (Hessian) $[\xi \equiv R_{A\alpha}]$:

$$\frac{\partial^2 E}{\partial\xi\partial\xi'} = \frac{\partial^2 E_{nn}}{\partial\xi\partial\xi'} + \int\rho(r)\frac{\partial^2 V}{\partial\xi\partial\xi'}dr + \int\frac{\partial V}{\partial\xi}\frac{\partial\rho(r)}{\partial\xi'}dr$$

Consider $\Delta\hat{G}(r)$ caused by a change $\xi \to \xi + \Delta\xi$ of ξ:

$$\Delta\hat{G}(r) = \Delta V(r) + \int dr' \frac{\delta}{\delta\rho(r')}\left[-eV_H(r) + V_{xc}(r)\right]\Delta\rho(r') = \Delta V(r) + \int dr'\left[\frac{-e}{|r-r'|} + \underbrace{\frac{\delta V_{xc}(r)}{\delta\rho(r')}}_{\delta(r-r')\left(\frac{dV_{xc}}{d\rho}\right)(r)}\right]\Delta\rho(r')$$

(LDA)

$$\frac{\partial\hat{G}(r)}{\partial\xi'} = \frac{\partial V}{\partial\xi'} + \int\frac{-e}{|r-r'|}\frac{\partial\rho(r')}{\partial\xi'}dr' + \left(\frac{dV_{xc}}{d\rho}\right)(r)\frac{\partial\rho(r)}{\partial\xi'}$$

On the other hand, $\rho(r) = \sum_{\lambda}^{occ} \varphi_\lambda^*(r)\,\varphi_\lambda(r)$

$$\Delta\rho(r) = \sum_{\lambda}^{occ}\left[\varphi_\lambda^*(r)\,\Delta\varphi_\lambda(r) + \Delta\varphi_\lambda^*(r)\,\varphi_\lambda(r)\right]$$

where, to the 1st order of perturbation theory:

$$\Delta\varphi_\lambda(r) = \underbrace{\sum_{\lambda'}^{all}{}'}_{v+c\ (\text{all}!)} \frac{\langle\varphi_{\lambda'}|\Delta\hat{G}|\varphi_\lambda\rangle}{\varepsilon_\lambda - \varepsilon_{\lambda'}}\,\varphi_{\lambda'}\,, \quad (\hat{t}+\hat{G})\,\varphi_\lambda = \varepsilon_\lambda\varphi_\lambda$$

v – occ
c – unocc

We finally obtain a <u>self-consistent scheme</u>:

$$\begin{cases} \dfrac{\partial\rho(r)}{\partial\xi'} = \displaystyle\sum_c\sum_v \frac{1}{\varepsilon_v-\varepsilon_c}\left[\langle\varphi_c|\frac{\partial\hat{G}(r)}{\partial\xi'}|\varphi_v\rangle\,\varphi_v^*(r)\,\varphi_c(r) + c.c.\right] \\[2ex] \dfrac{\partial\hat{G}(r)}{\partial\xi'} = \dfrac{\partial V}{\partial\xi'} + \displaystyle\int\frac{-e}{|r-r'|}\frac{\partial\rho(r')}{\partial\xi'}\,dr' + \left(\frac{dV_{xc}}{d\rho}\right)(r)\,\frac{\partial\rho(r)}{\partial\xi'} \end{cases}$$

v-v' terms cancel out!

$\Rightarrow$ $\boxed{\text{SCF}}$

<u>Advantages</u>

- Primitive unit cell $\Rightarrow$ any $\vec{k}$-point accessible
- Symmetry can be used
- Efficient implementations exist in many codes (QE, VASP, etc.)

Diagonalisation of the Hamiltonian

$$H = \sum_i \frac{p_i^2}{2M_i} + \frac{1}{2}\sum_{ij} \Phi_{ij} u_i u_j \quad , \quad \mathcal{L} = \sum_i \frac{M_i \dot{u}_i^2}{2} - \frac{1}{2}\sum_{ij}\Phi_{ij} u_i u_j$$

$$PE = \frac{1}{2} u^T \Phi u = \sum_\lambda \frac{1}{2}\omega_\lambda^2 y_\lambda^2(t),$$

$$\boxed{D\Upsilon_\lambda = \omega_\lambda^2 \Upsilon_\lambda}$$

where $y_\lambda(t) = M^{1/2}\Upsilon_\lambda^T u = \sum_i \sqrt{M_i}\,\Upsilon_{\lambda i} u_i$

Hence, $\dot{y}_\lambda = \sum_i \sqrt{M_i}\,\Upsilon_{\lambda i}\dot{u}_i \quad \Big| \times \sum_\lambda \Upsilon_{\lambda j}$

$$\Rightarrow \sum_\lambda \Upsilon_{\lambda j}\dot{y}_\lambda = \sum_i \sqrt{M_i}\underbrace{\left(\sum_\lambda \Upsilon_{\lambda j}\Upsilon_{\lambda i}\right)}_{\delta_{ij}}\dot{u}_i = \sqrt{M_j}\,\dot{u}_j \Rightarrow \dot{u}_j = \frac{1}{\sqrt{M_j}}\sum_\lambda \Upsilon_{\lambda j}\dot{y}_\lambda$$

Substitute into the KE:

$$KE = \frac{1}{2}\sum_j M_j \dot{u}_j^2 = \frac{1}{2}\sum_{\lambda\lambda'}\underbrace{\left(\sum_j \Upsilon_{\lambda j}\Upsilon_{\lambda' j}\right)}_{\delta_{\lambda\lambda'}}\dot{y}_\lambda \dot{y}_{\lambda'} = \frac{1}{2}\sum_\lambda \dot{y}_\lambda^2$$

The conjugate momentum:

$$p_\lambda = \frac{\partial \mathcal{L}}{\partial \dot{q}_\lambda} = \frac{\partial}{\partial \dot{q}_\lambda}(KE) = \dot{y}_\lambda = \sum_i \sqrt{M_i}\,\Upsilon_{\lambda i}\dot{u}_i \Rightarrow \boxed{p_\lambda = \sum_i \frac{1}{\sqrt{M_i}}\Upsilon_{\lambda i} p_i}$$

Hence, $KE = \frac{1}{2}\sum_\lambda p_\lambda^2$ and

$$\boxed{H = \sum_\lambda \left[\frac{1}{2}p_\lambda^2 + \frac{1}{2}\omega_\lambda^2 y_\lambda^2\right] = \sum_\lambda h_\lambda}$$

Dynamic properties via MD: vibrational spectrum

- $$H = \sum_i \frac{p_i^2}{2M} + \frac{1}{2}\sum_{ij} \Phi_{ij} u_i u_j \equiv \sum_\lambda \left(\frac{p_\lambda^2}{2} + \frac{\omega_\lambda^2 y_\lambda^2}{2} \right)$$

$$y_\lambda = \sum_i \sqrt{M_i}\, Y_{\lambda i} u_i \leftarrow \text{normal coordinates}$$
$$p_\lambda = \sum_i \frac{1}{\sqrt{M_i}} Y_{\lambda i} p_i \leftarrow \text{normal momenta}$$

$$\mathcal{D} = M^{-1/2} \Phi M^{-1/2}$$
$$\mathcal{D} Y_\lambda = \omega_\lambda^2 Y_\lambda$$

EoM: $\ddot{y}_\lambda + \omega_\lambda^2 y_\lambda = 0 \Rightarrow y_\lambda(t) = A_\lambda e^{i\omega_\lambda t} + c.c.$

$$u_i(t) = \sum_\lambda \frac{1}{\sqrt{M_i}} Y_{\lambda i} y_\lambda = \sum_\lambda \frac{1}{\sqrt{M_i}} Y_{\lambda i} \left(A_\lambda e^{i\omega_\lambda t} + c.c.\right), \quad p_i(t) = i \sum_\lambda \sqrt{M_i}\, Y_{\lambda i} \omega_\lambda A_\lambda e^{i\omega_\lambda t} + c.c.$$

A_λ, A_λ^* can be found from initial positions & momenta:

$$\sqrt{M_i}\, u_i^0 = \sum_\lambda Y_{\lambda i}(A_\lambda + A_\lambda^*) \text{ and } \frac{1}{\sqrt{M_i}} p_i^0 = i \sum_\lambda Y_{\lambda i}(A_\lambda - A_\lambda^*)$$

$$\Rightarrow A_\lambda = \sum_i Y_{\lambda i} \left[\sqrt{M_i}\, u_i^0 + \frac{1}{i\omega_\lambda \sqrt{M_i}} p_i^0 \right] \frac{1}{2}.$$

This yields:

$$\boxed{\begin{cases} u_i(t) = \sum_{j\lambda} Y_{i\lambda} Y_{j\lambda} e^{i\omega_\lambda t} \left[u_j^0 \left(\frac{1}{2}\sqrt{\frac{M_j}{M_i}} \right) + p_j^0 \left(\frac{1}{2i\sqrt{M_i M_j}\,\omega_\lambda} \right) \right] + c.c. \\[2ex] p_i(t) = \sum_{j\lambda} Y_{i\lambda} Y_{j\lambda} e^{i\omega_\lambda t} \left[u_j^0 \left(\frac{i}{2}\sqrt{M_i M_j}\,\omega_\lambda \right) + p_j^0 \left(\frac{1}{2}\sqrt{\frac{M_i}{M_j}} \right) \right] + c.c. \end{cases}}$$

- Statistical averages: $H = \sum_\lambda h_\lambda$, $h_\lambda = (p_\lambda^2 + \omega_\lambda^2 y_\lambda^2)/2$ $\boxed{\langle p_i(t)\, p_i(t')\rangle = ?}$

Jacobian: $\underbrace{\prod_i du_i dp_i}_{d\Gamma} = J \prod_\lambda dy_\lambda dp_\lambda$, $J = \left|\frac{\partial(u_i p_j)}{\partial(y_\lambda p_{\lambda'})}\right| = \left|\frac{\partial u_i}{\partial y_\lambda}\right| \cdot \left|\frac{\partial p_j}{\partial p_{\lambda'}}\right| = |M^{-\frac{1}{2}} e| \cdot |M^{1/2} e| = 1$

$$\langle F_\lambda \rangle = \frac{1}{Z}\int e^{-\beta H} F_\lambda \, d\Gamma = \prod_{\lambda'} \frac{1}{Z_{\lambda'}} \int dy_{\lambda'} dp_{\lambda'}\, e^{-\beta h_{\lambda'}} F_\lambda = \frac{1}{Z_\lambda}\int dy_\lambda dp_\lambda\, e^{-\beta h_\lambda} F_\lambda \,, \quad Z_\lambda = \frac{2\pi}{\beta \omega_\lambda}$$

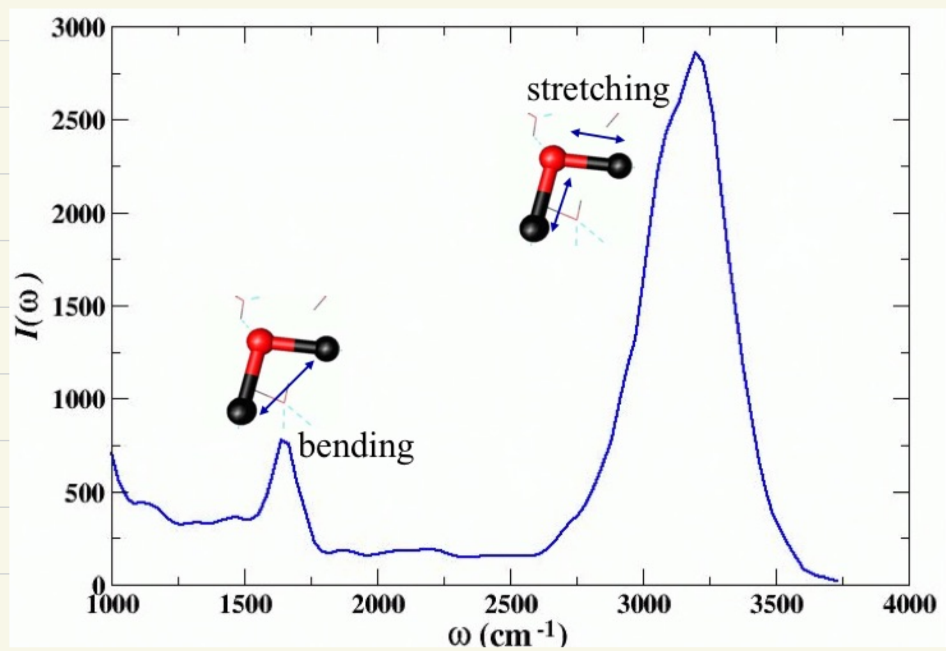
$$\langle y_\lambda^0 \rangle = \langle p_\lambda^0 \rangle = \langle y_\lambda^0 p_{\lambda'}^0 \rangle = 0 \,, \quad \langle y_\lambda^0 y_{\lambda'}^0 \rangle = \delta_{\lambda\lambda'} \frac{1}{\beta \omega_\lambda^2} \,, \quad \langle p_\lambda^0 p_{\lambda'}^0 \rangle = \delta_{\lambda\lambda'} \frac{1}{\beta}$$

$$\Rightarrow \begin{cases} \langle u_i^0 u_j^0 \rangle = \frac{1}{\sqrt{M_i M_j}} \sum_{\lambda\lambda'} Y_{\lambda i} Y_{\lambda' j} \langle y_\lambda^0 y_{\lambda'}^0 \rangle = \frac{1}{\beta} \frac{1}{\sqrt{M_i M_j}} \sum_\lambda \frac{Y_{\lambda i} Y_{\lambda j}}{\omega_\lambda} \\ \langle p_i^0 p_j^0 \rangle = \sqrt{M_i M_j} \sum_{\lambda\lambda'} Y_{\lambda i} Y_{\lambda' j} \langle p_\lambda^0 p_{\lambda'}^0 \rangle = \frac{1}{\beta} M_i \delta_{ij} \end{cases} \Bigg\| \quad \langle u_i^0 p_j^0 \rangle = 0$$

Consider now the correlation function:

$$\Rightarrow \sum_i \frac{1}{M_i} \langle p_i(t)\, p_i(t') \rangle = \frac{1}{\beta} \sum_\lambda \cos \omega_\lambda (t - t')$$ (after some (!) algebra)

since $\sum_j Y_{\lambda j} Y_{\lambda' j} = \delta_{\lambda\lambda'}$ and $\sum_\lambda Y_{\lambda i} Y_{\lambda j} = \delta_{ij}$.



Take the FT:

$$\mathcal{F}[\dots] = \frac{1}{\beta} \sum_\lambda \int_{-\infty}^{\infty} e^{i\omega\tau} \cos \omega_\lambda \tau \, d\tau$$

$$= \frac{2\pi}{\beta} \sum_\lambda \delta(\omega^2 - \omega_\lambda^2)$$

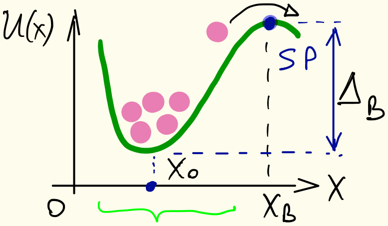
$\boxed{\text{phonon DOS}}$

Calculation of rates (an elementary event)

Transition State Theory $\boxed{TST}$

(75)

- **1D model** $\quad H = \frac{mv^2}{2} + \mathcal{U}(x)$



thermal equilibrium region

- Probability to find the particle in the ground state basin:

$$\rho(x,v) = \rho(x)\underbrace{\rho(v)}_{\text{Maxwell (probability density)}}, \quad \rho(x) = \frac{1}{Z_X} e^{-\beta\mathcal{U}(x)}, \quad Z_X = \int_0^{x_B} dx\, e^{-\beta\mathcal{U}(x)}$$

- Probability to find it at the saddle point: $\rho(x_B, v)$

- The total flux over the barrier to the right ($\dot{x} = v > 0$):

$$K_{TST} = \int_0^\infty v\,\rho(v)\,\rho(x_B)\,dv = \rho(x_B)\,\bar{v}_{\to}, \quad \bar{v}_{\to} = \int_0^\infty v\,\frac{1}{Z_V}\,e^{-\frac{mv^2}{2k_BT}}dv$$

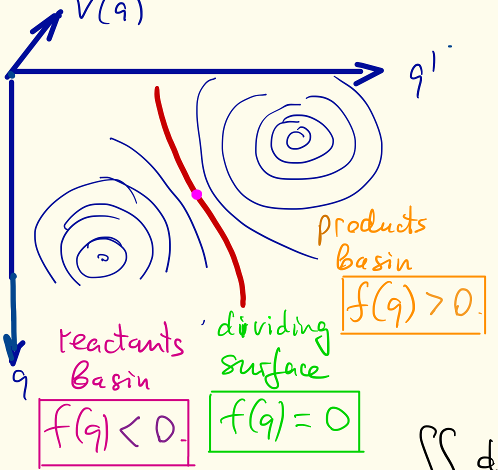
$$Z_V = \int_{-\infty}^{\infty} e^{-\beta\frac{mv^2}{2}}dv = \sqrt{\frac{2\pi}{\beta m}}, \quad \text{so } \bar{v}_{\to} = \frac{1}{\sqrt{2\pi m\beta}}$$

- In the harmonic model: $\mathcal{U}(x) = \mathcal{U}(x_0) + \frac{1}{2}m\omega_0^2 x^2$, $\quad \mathcal{U}(x_B) = \mathcal{U}(x_0) + \underbrace{\Delta_B}_{\text{barrier}}$

$$Z_X = \int_0^{x_B} dx\, e^{-\beta\mathcal{U}(x_0)} e^{-\beta\frac{1}{2}m\omega_0^2 x^2} \simeq \int_{-\infty}^{+\infty} dx \ldots = e^{-\beta\mathcal{U}(x_0)}\sqrt{\frac{2\pi}{\beta m\omega_0^2}}$$

$$\Rightarrow K_{TST} = \frac{1}{\sqrt{2\pi m\beta}}\sqrt{\frac{\beta m\omega_0^2}{2\pi}}\, e^{-\beta\mathcal{U}(x_B)}\, e^{+\beta\mathcal{U}(x_0)} \Rightarrow \boxed{K_{TST} = \frac{\omega_0}{2\pi} e^{-\beta\Delta_B}}$$

- **3N-D model**



- Flux through dS on the dividing surface:

$$dJ = dS(v\cdot\hat{n})\,dt\ , \quad \hat{n} = \nabla f(q) \quad (|\hat{n}|=1) \tag{83}$$

- The total flux to the right ($\rightarrow$ products):

$$dJ = dt\int dv \iint_S dS\ v\cdot\nabla f(q)\ P(q_s,v)\ \theta(v\cdot\nabla f(q_s)) \tag{84}$$

- Probability to be on the dividing surface:

$$P(q_s,v) = \frac{1}{Z_R} e^{-\beta H(q_s,v)}\ , \quad Z_R = \int dv\int dq\ \theta(-f(q))\ e^{-\beta H} \tag{85}$$

- The surface integral can be worked into the volume:

$$\iint_S dS \ldots = \int dq\ \delta(f(q))\ldots \quad \text{as } \delta(f(q)) \neq 0 \text{ only when } q\in S \tag{86}$$

- This allows writing the transition rate as:

$$\boxed{k_{TST} = \frac{dJ}{dt} = \frac{\int dv\int dq\ \delta(f(q))\,[v\cdot\nabla f(q)]\,e^{-\beta H}\,\theta(v\cdot\nabla f(q))}{\int dv\int dq\ \theta(-f(q))\,e^{-\beta H}}} \tag{87}$$

TST

- Bennett-Chandler correction In TST trajectories going over the S always fall into the products, never return. It is an approximation. A correction is needed.

- Velocities can be integrated out.

$$f(q) \simeq \underbrace{f(q^{SP})}_{0} + \underbrace{\left(\nabla f(q^{SP})\right)}_{\hat{n}}(q-q^{SP})$$ as SP is the crucial one.

Use normal coordinates: $y_\lambda = \sum_i \sqrt{m_i}\, e^{SP}_{i\lambda}(q_i - q_i^{SP})$

$$\frac{\partial f}{\partial q_i} = \sum_\lambda \underbrace{\frac{\partial f}{\partial y_\lambda}}_{\lambda=\lambda_r \text{ only}} \frac{\partial y_\lambda}{\partial q_i} = \underbrace{\frac{\partial f}{\partial y_{\lambda_r}}}_{\varkappa} \sqrt{m_i}\, e^{SP}_{i\lambda_r}$$

$$\boxed{\begin{array}{l} y_{\lambda_r} \to \text{across } S \\ y_\lambda (\lambda \neq \lambda_r) \to \text{within } S \end{array}}$$

$$v\cdot\hat{n} = \sum_i v_i \frac{\partial f}{\partial q_i} = \varkappa\left(\tilde{v}\cdot e^{SP}_{\lambda_r}\right),\quad \tilde{v} = \sqrt{M}\, v \leftarrow \text{rescaled velocities}$$

$K(v) = \sum_i \frac{1}{2}\tilde{v}_i^2$ is invariant under rotation in $\tilde{v}$ space.

Consider the numerator

$$N_r = \int dv\, (v\cdot\hat{n})\,\theta(v\cdot\hat{n})\, e^{-\beta K(v)} \leftarrow \text{rotate } \tilde{v} \to \bar{v} \text{ such that } \bar{v}_1 \parallel e^{SP}_{\lambda_r}$$

$$= \frac{\varkappa}{\sqrt{\det M}} \int d\bar{v}\; \bar{v}_1\, \theta(\bar{v}_1)\, e^{-\beta K(\bar{v})} = \frac{\varkappa}{\sqrt{\det M}} \int_0^\infty \bar{v}_1 e^{-\beta\frac{1}{2}\bar{v}_1^2} dv_1 \prod_{i=2}^{3N} \int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}\bar{v}_i^2} d\bar{v}_i$$

$$= \frac{\varkappa}{\sqrt{\det M}} \left(\frac{2\pi}{\beta}\right)^{3N/2} \frac{1}{\sqrt{2\pi\beta}}$$

Consider the q-integral now:

$$N_q = \int dq\, \delta(f(q))\, e^{-\beta U(q)}$$

where, $U(q) = U(q^{sp}) + \sum_{\lambda \neq \lambda_r} \frac{1}{2}\omega_\lambda^2 y_\lambda^2 - \frac{1}{2}\omega_{\lambda_r}^2 y_{\lambda_r}^2$

and

$$f(q) \simeq \sum_i \frac{\partial f}{\partial q_i}(q_i - q_i^{sp}) = \varkappa \sum_i \sqrt{m_i}\, e_{i\lambda_r}^{sp}(q_i - q_i^{sp}) \equiv \varkappa y_{\lambda_r}$$

$\delta(f(q)) = \frac{1}{\varkappa}\delta(y_{\lambda_r})$ and the Jacobian for $q \to y$ is $J = \frac{1}{\sqrt{\det M}}$

$$N_q = \frac{1}{\varkappa\sqrt{\det M}} \int dy\, \delta(y_{\lambda_r})\, e^{-\beta U} = \frac{1}{\varkappa\sqrt{\det M}} \left(\prod_{\lambda \neq \lambda_r} \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}\omega_\lambda^2 y_\lambda^2} dy_\lambda \right) e^{-\beta U(q^{sp})}$$

$$= \frac{1}{\varkappa\sqrt{\det M}}\, e^{-\beta U(q^{sp})} \left(\frac{2\pi}{\beta}\right)^{\frac{3N-1}{2}} \prod_{\lambda \neq \lambda_r} \frac{1}{\omega_\lambda^{sp}}$$

So, the numerator of K is:

$$N = N_v N_q = \frac{1}{\det M}\, e^{-\beta U(q^{sp})} \left(\frac{2\pi}{\beta}\right)^{3N-\frac{1}{2}} \frac{1}{\sqrt{2\pi\beta}} \prod_{\lambda \neq \lambda_r} \frac{1}{\omega_\lambda^{sp}}$$

- Similarly we consider the denominator of K using the normal coordinates $y_\lambda = \sum_i \sqrt{m_i}\, e_{i\lambda}(q_i - q_i^R)$

q^R – reactant basin minimum

$$U(q) = U(q^R) + \sum_\lambda^{M} \frac{1}{2}\omega_\lambda^2 y_\lambda^2 \quad (\omega_\lambda \equiv \omega_\lambda^R)$$

$$\Delta = \frac{1}{\det M} e^{-\beta U(q^R)} \left(\prod_{\lambda=1}^{3N} \int_{-\infty}^{\infty} dy_\lambda\, e^{-\beta \frac{1}{2}\omega_\lambda^2 y_\lambda^2} \right) \left(\prod_{i=1}^{3N} \int_{-\infty}^{\infty} d\tilde{v}_i\, e^{-\beta \frac{1}{2}\tilde{v}_i^2} \right)$$

$$= \frac{1}{\det M} e^{-\beta U(q^R)} \left(\frac{2\pi}{\beta}\right)^{3N} \prod_{\lambda=1}^{3N} \frac{1}{\omega_\lambda^R}$$

The rate

$$\boxed{K = \frac{N}{\Delta} = \frac{1}{2\pi} \frac{\prod_{\lambda=1}^{3N} \omega_\lambda^R}{\prod_{\lambda=1}^{3N-1} \omega_\lambda^{SP}} e^{-\beta \underbrace{(U(q^{SP}) - U(q^R))}_{\Delta E}}}$$

(Vineyard 1957)