Lecture 2: Phonons

1. Phenomenology
   → Finite systems (vibrational modes in a molecule)
   → Periodic systems (lattice waves)
2. Calculation of phonons & vibrational modes in DFT
   → Density-functional Perturbation Theory
   → Frozen phonon approach
   → Dielectric matrix method (if time permits)

Phenomenology: (Finite systems)

Under the B-O approx., we have seen that the nuclei move under a potential energy surface provided by the adiabatic electronic energy (usually the ground electronic energy)

In particular, for a system moving on the PES, we have:

$$\mathcal{H} = T_n + E(\vec{R}) \longrightarrow (1).$$

$\hookrightarrow$ ground state energy when $\vec{R} \equiv (\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_K)$

$$E(\vec{R}) = \frac{\langle \Psi_0(\vec{r};\vec{R}) | \hat{H}_{el}(\vec{R}) | \Psi_0(\vec{r};\vec{R}) \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \quad — (2).$$

$$\hat{H}_{el}(\vec{R}) = \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} + \frac{1}{2}\sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{I,i} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + E_{II}(\vec{R}) \quad — (3).$$

$\vec{F}_I = -\frac{\partial E}{\partial \vec{R}_I} = 0$ @ the equilibrium geometry/configuration $(\vec{R}^0)$

Dynamics of system in terms of small displacements about $\vec{R}^0$.

$$u_\alpha(k) = R_{k\alpha} - R^0_{k\alpha} \quad (4)$$

α^{th} Cartesian component of the k^{th} nuclear coordinate

$$E(\vec{R}) \simeq E(\vec{R}^0) + \underbrace{\sum_{k,\alpha} \left(\frac{\partial E}{\partial R_{k\alpha}}\right)_0 u_\alpha(k)}_{=0}$$

$$+ \frac{1}{2} \sum_{k,\alpha} \sum_{k',\beta} \left(\frac{\partial^2 E}{\partial R_{k\alpha} \partial R_{k'\beta}}\right)_0 u_\alpha(k) u_\beta(k') \quad (5)$$

upto 2nd order.

$$\tilde{E}(\vec{u}) = \frac{1}{2} \sum_{k,\alpha} \sum_{k',\beta} \Phi_{\alpha\beta}(k,k') \times u_\alpha(k)\, u_\beta(k') \quad \text{— (6)}$$

where $$\Phi_{\alpha\beta}(k,k') \equiv \left.\frac{\partial^2 E}{\partial u_\alpha(k)\, \partial u_\beta(k')}\right|_0 \quad \text{— (7)}$$

Hessian. Matrix

Let $W_\alpha(k) \equiv \sqrt{M_k}\; u_\alpha(k)$, $M_k \to$ mass of the k^{th} ion.

reduced displacements — (8)

Canonical momentum corresponding to $W_\alpha(k)$ is $P_\alpha(k) = p_\alpha(k)/\sqrt{M_k}$ — (9)

$$E(\vec{W}) = \frac{1}{2}\sum_{k\alpha}\sum_{k'\beta} D_{\alpha\beta}(k,k')\, W_\alpha(k)\, W_\beta(k') \quad \text{— (10)}$$

where $D_{\alpha\beta}(k,k') = \dfrac{1}{\sqrt{M_k M_{k'}}}\,\Phi_{\alpha\beta}(k,k')$ — (11)

Dynamical matrix:

$$\boxed{\mathcal{D}_{\alpha\beta}(k,k') \equiv \frac{1}{\sqrt{M_k M_{k'}}}\,\bar{\Phi}_{\alpha\beta}(k,k')} \quad (1)$$

$\vec{u}, \vec{w} \longrightarrow$ 3K-dimensional vectors

$$\vec{w} = \begin{pmatrix} w_{11} \\ w_{12} \\ w_{13} \\ \vdots \\ w_{K1} \\ w_{K2} \\ w_{K3} \end{pmatrix}$$

$\mathcal{D}, \bar{\Phi} \rightarrow 3K \times 3K$

$\underbrace{k\alpha}_{I}, \underbrace{k'\beta}_{J}$

I

$1, 3K$

$$D_{\alpha\beta}(k,k') = \frac{1}{\sqrt{M_k M_{k'}}} \left(\frac{\partial^2 E}{\partial u_\alpha(k)\, \partial u_\beta(k')}\right)_0$$

$$= \frac{1}{\sqrt{M_{k'} M_k}} \left(\frac{\partial^2 E}{\partial u_\beta(k')\, \partial u_\alpha(k)}\right)_0 = D_{\beta\alpha}(k',k)$$

$$D^T = D \Rightarrow D \text{ is a symmetric matrix} \qquad (12)$$

→ $\mathcal{D}$ has real eigenvalues.

→ $\mathcal{D}$ is diagonalizable & yields $3K$ eigenvectors upon diagonalization which are mutually orthogonal

→ The eigenvectors of $\mathcal{D}$ form a complete set in the $3K$-d space.

$$T_N = \sum_{k=1}^{K} \frac{p_k^2}{2M_k} = \sum_{k=1}^{K} \frac{P_k^2}{2} \quad -(13)$$

$$H = \sum_{k=1}^{K} \frac{P_k^2}{2} + \frac{1}{2} \sum_{k\alpha} \sum_{k'\beta} W_\alpha(k)\, D_{\alpha\beta}(k,k')\, W_\beta(k') \quad -(14)$$

The Hamiltonian is still in a quadratic form. $\longrightarrow$ 3K uncoupled oscillators

$$\sum_{k'\beta} D_{\alpha\beta}(k,k')\, e_\beta(k'|j) = \omega_j^2\, e_\alpha(k|j) \qquad (15)$$

We have defined above a set of vectors $\vec{e}(j)$ such that for each j we have (15) satisfied.

$$\vec{e}(j) \rightarrow 3K\text{-d vectors}$$

$$\downarrow$$

$$\{e_\alpha(k|j)\}$$

$$j = 1, 2, \cdots, 3K$$

$$\left(\vec{e}(j), \vec{e}(j')\right) = \delta_{j,j'}$$

$$\sum_k \sum_\alpha e_\alpha(k|j)\, e_\alpha(k|j') = \delta_{jj'} \quad \text{— (16)}$$

$$W_\alpha(k) = \sum_j e_\alpha(k|j)\, q_j \quad \text{— (17)}$$

$\therefore$ $\{\vec{e}(j)\}$ form a complete set.

Secular equation for $\mathcal{D}$:

$$\det \left| \mathcal{D}_{\alpha\beta}(k,k') - \omega^2 \delta_{kk'} \delta_{\alpha\beta} \right| = 0 \quad (18)$$

$\rightarrow$ solution for ω^2

$$A = \left| \vec{e}(1) \quad \vec{e}(2) \quad \cdots \quad \vec{e}(3K) \right|$$

$$A^T = \left(\vec{e}(1) \quad \vec{e}(2) \quad \cdots \quad \vec{e}(3K) \right)^T$$

$$A^T A = \mathbb{1} = A A^T \quad (19)$$

$$\Rightarrow \sum_j e_\alpha(k|j)\, e_\beta(k'|j) = \delta_{\alpha\beta}\,\delta_{kk'} \quad (20)$$

$$\tilde{E} = \frac{1}{2} \sum_{k\alpha} \sum_{k'\beta} W_\alpha(k)\, D_{\alpha\beta}(k,k')\, W_\beta(k')$$

$$= \frac{1}{2} \sum_{k\alpha} \sum_{k'\beta} \left(\sum_j q_j\, e_\alpha(k|j) \right) D_{\alpha\beta}(k,k') \times \left(\sum_{j'} q_{j'}\, e_\beta(k'|j') \right)$$

$$= \frac{1}{2} \sum_j \sum_{j'} q_j\, q_{j'} \times \left\{ \sum_{k\alpha} \sum_{k'\beta} e_\alpha(k|j)\, D_{\alpha\beta}(k,k')\, e_\beta(k'|j') \right\} \quad (21)$$

$$\left\{ \sum_{k\alpha} e_\alpha(k|j) \left(\sum_{k'\beta} D_{\alpha\beta}(k,k') e_\beta(k'|j') \right) \right\}$$

$$= \left\{ \sum_{k\alpha} e_\alpha(k|j) \times \omega_{j'}^2 e_\alpha(k'|j') \right\}$$

$$= \omega_{j'}^2 \left(\vec{e}(j), \vec{e}(j') \right) = \omega_{j'}^2 \delta_{jj'} \quad (22)$$

$$\Rightarrow \tilde{E} = \frac{1}{2} \sum_{j=1}^{3K} \omega_j^2 \, q_j^2 \quad \text{--- (23)}$$

$$T_N = \sum_{k=1}^{K} \frac{P_k^2}{2} = \sum_{j=1}^{3K} \pi_j^2/2 \quad \text{--- (24)}$$

where π_j is the canonical momentum conjugate to q_j.

$$H = \sum_{j=1}^{3K} \left\{ \frac{\pi_j^2}{2} + \omega_j^2 q_j^2 \right\} \quad \text{— } (25)$$

$\rightarrow q_j \rightarrow$ normal coordinate

$\rightarrow \omega_j \rightarrow$ angular frequency of oscillation of the j^{th} normal mode

$\rightarrow \vec{e}(j) \rightarrow$ normal modes

$$\mathcal{E}(\vec{n}) = \sum_{j=1}^{3K} \hbar\omega_j \left(n_j + 1/2\right) \quad \text{—(26)}$$

$$n_j = 0, 1, 2, \cdots$$

$$\vec{n} = (n_1, n_2, \cdots, n_{3K})$$

$\rightarrow$ QM energies

Classical equation of motion

$$\rightarrow \quad M_k \ddot{u}_\alpha(k) = -\left.\frac{\partial E}{\partial u_\alpha(k)}\right|_0 = -\sum_{k'\beta} \Phi_{\alpha\beta}(k,k') \times u_\beta(k')$$

$$\Rightarrow \quad \ddot{W}_\alpha(k) = -\sum_{k'\beta} D_{\alpha\beta}(k,k') W_\beta(k) \quad \text{—— (27)}$$

Using (17) then we get

$$\ddot{q}_j(t) = -\omega_j^2 q_j(t) \quad \text{—— (28)}$$

This gives the justification for ω_j as a frequency. We can write the general solution to be:

$$q_j(t) = Q_j \cos(\omega_j t) + Q_j' \sin(\omega_j t) \quad (29)$$

$$u_\alpha(k,t) = \frac{1}{\sqrt{M_k}} W_\alpha(k,t)$$

$$= \frac{1}{\sqrt{M_k}} \sum_{j=1}^{3K} q_j(t)\, e_\alpha(k|j) \quad (30)$$

$$u_\alpha(k,t) = \sum_{j=1}^{3K} q_j(t) \left\{ \frac{1}{\sqrt{M_k}} e_\alpha(k|j) \right\} \quad \text{—} (31)$$

Cartesian Displacements

$$\vec{e}^{\,c}(j) \equiv \underline{M}^{-1/2}\, \vec{e}(j) \quad \text{—} (32)$$

where $\left(\underline{M}^{-1/2}\right)_{k\alpha,k'\beta} = \frac{1}{\sqrt{M_k}} \delta_{kk'} \delta_{\alpha\beta}$ — (33)

$$\vec{e}^{\,c}(j)^T \, \vec{e}^{\,c}(j) = \vec{e}(j)^T \underline{(M^{-1/2})^T M^{-1/2}} \, \vec{e}(j)$$

Cartesian (eigen) displ.

$$\neq \hat{1}$$

$$\sum_{k,\alpha} e^c_\alpha(k|j) \, e^c_\alpha(k|j') = M_k \, \delta_{jj'} \quad (34)$$

$$\sum_{j=1}^{3K} e^c_\alpha(k|j) \, e^c_\beta(k'|j) = M_k \, \delta_{kk'} \, \delta_{\alpha\beta} \quad (35)$$

$$\Delta R_{k\alpha}(t) \equiv u_\alpha(k,t)$$

$$= \sum_{j=1}^{3K} Q_j \cos(\omega_j t)\, e_\alpha^c(k|j) \quad \text{— (36)}$$

$Q_j \rightarrow$ decided by initial conditions

<u>Note</u>:

→ 3 translation modes have $\omega = 0$

→ 2 (if linear) or 3 (non-linear) rotational modes have $\omega = 0$

→ $3N-5$ or $3N-6$ vibrational modes.

Because D is symmetric (Hermitian) the eigenvalues ω_j^2 have to be real.

$$\omega_j^2 = \begin{cases} \geq 0 & \text{i.e. } \omega_j \text{ is real} \\ < 0 & \text{i.e. } \omega_j \text{ is purely imaginary} \end{cases}$$

$\Rightarrow$ DYNAMIC STABILITY ANALYSIS

$$\frac{d^2 E}{d q_j^2} < 0 \Rightarrow E \text{ is a maximum in that direction!}$$

BFGS.

Periodic Systems :

Consider a crystal with a unit cell composed of 'n' basis atoms (labeled by $k = 1, 2, \ldots, n$)

Let $\vec{a}_1, \vec{a}_2, \vec{a}_3$ be the primitive translation vectors.

$$\vec{R}_l \equiv l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3 \quad \text{--- (37)}$$

$$l \equiv (l_1, l_2, l_3) \;\text{ ; }\; l_i \in \mathbb{Z}$$

$$\vec{X}^{(0)} \equiv \left\{ \vec{X}^{(0)}\begin{pmatrix} l \\ k \end{pmatrix} \right\}$$ position of the k^{th} atom in the l^{th} unit cell

$\rightarrow$ equilibrium structure

$$\vec{X}(t) \equiv \left\{ \vec{X}\begin{pmatrix} l \\ k \end{pmatrix} \right\}$$ instantaneous configuration of the crystal

$$\vec{u}\begin{pmatrix} l \\ k \end{pmatrix} \equiv \vec{X}\begin{pmatrix} l \\ k \end{pmatrix} - \vec{X}^{(0)}\begin{pmatrix} l \\ k \end{pmatrix} \quad \text{--- } (38)$$

instantaneous displacements

P.E. for small displacements

$$\tilde{E}(\vec{u}) \equiv \frac{1}{2} \sum_{l,k,\alpha} \sum_{l',k',\beta} \left(\frac{\partial^2 E}{\partial u_\alpha\binom{l}{k} \partial u_\beta\binom{l'}{k'}} \right)_0 \times u_\alpha\binom{l}{k} u_\beta\binom{l'}{k'} \quad \text{— (39)}$$

$$\Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \equiv \left(\frac{\partial^2 E}{\partial u_\alpha\binom{l}{k} \partial u_\beta\binom{l'}{k'}} \right)_0 \quad \text{— (40)}$$

$$\vec{R}_l - \vec{R}_{l'} = \vec{R}_{l-l'}$$

$$= \Phi_{\alpha\beta}\begin{pmatrix} l-l' \\ k \; k' \end{pmatrix} \quad \text{— (41)}$$

$$\tilde{E} = \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \tilde{\Phi}_{\alpha\beta}\begin{pmatrix} l-l' \\ k\,k' \end{pmatrix} u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} u_\beta\begin{pmatrix} l' \\ k' \end{pmatrix} \quad \text{— (42)}$$

We introduce:

a) $$\mathcal{D}_{\alpha\beta}\begin{pmatrix} l-l' \\ k\,k' \end{pmatrix} \equiv \frac{1}{\sqrt{M_k M_{k'}}} \tilde{\Phi}_{\alpha\beta}\begin{pmatrix} l-l' \\ k\,k' \end{pmatrix} \quad \text{— (43)}$$

Dynamical Matrix

b) $$W_\alpha\begin{pmatrix} l \\ k \end{pmatrix} \equiv \sqrt{M_k}\, u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} \quad \text{— (44)}$$

Reduced displacements

Thus, K.E. becomes:

$$\frac{1}{2}\sum_{lk\alpha} M_k \dot{u}_\alpha\begin{pmatrix} l \\ k \end{pmatrix}^2 = \frac{1}{2}\sum_{lk\alpha} \dot{W}_\alpha\begin{pmatrix} l \\ k \end{pmatrix}^2 \quad -(45)$$

<u>Lattice Fourier Series</u>

$$W_\alpha\begin{pmatrix} l \\ k \end{pmatrix} \equiv \frac{1}{\sqrt{N}} \sum_{\vec{q}\in B.Z.} W_\alpha(k|\vec{q})\, e^{i\vec{q}\cdot\vec{R}_l} \quad -(46)$$

$$N = N_1 \times N_2 \times N_3 \longrightarrow \text{total no. of unit cells in crystal.}$$

$$\vec{q} = h_1\vec{b}_1 + h_2\vec{b}_2 + h_3\vec{b}_3 \quad -(47)$$

where $\vec{b}_1, \vec{b}_2, \vec{b}_3 \longrightarrow$ reciprocal primitive lattice vectors

$$h_i = \frac{m_i}{N_i} \quad \text{where} \quad -\frac{N_i}{2} < m_i \leq \frac{N_i}{2} \qquad (48)$$

$$W_\alpha \begin{pmatrix} l + (N_1, 0, 0) \\ k \end{pmatrix} = W_\alpha \begin{pmatrix} l \\ k \end{pmatrix} \qquad (49)$$

$W_\alpha(k \mid \vec{q}) \longrightarrow$ wave amplitudes

$2\pi / |\vec{q}| = \lambda$ wavelength

Properties of wave amplitudes:

(i) $$W_\alpha^*(k|\vec{q}) = W_\alpha(k|-\vec{q})$$ — (50)

(ii) $$W_\alpha(k|\vec{q}) = \frac{1}{\sqrt{N}} \sum_l W_\alpha\begin{pmatrix} l \\ k \end{pmatrix} e^{-i\vec{q}\cdot\vec{R}_l}$$ — (51)

(iii) $$\Delta(\vec{q}) \equiv \frac{1}{N} \sum_l e^{i\vec{q}\cdot\vec{R}_l} = \begin{cases} 0 & \text{if } \vec{q} \neq 0 \\ 1 & \text{if } \vec{q} = 0. \end{cases}$$ — (52)

Lattice Kronecker delta

$$\tilde{E} = \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} D_{\alpha\beta}\begin{pmatrix} l-l' \\ kk' \end{pmatrix} w_\alpha\begin{pmatrix} l \\ k \end{pmatrix} w_\beta\begin{pmatrix} l' \\ k' \end{pmatrix}$$

$$= \frac{1}{2N} \sum_{lk\alpha} \sum_{l'k'\beta} D_{\alpha\beta}\begin{pmatrix} l-l' \\ kk' \end{pmatrix} \left(\sum_{\vec{q} \in BZ} W_\alpha(k|\vec{q}) e^{i\vec{q}\cdot\vec{R}_l} \right)$$

$$\times \left(\sum_{\vec{q}' \in BZ} W_\beta(k'|\vec{q}') e^{i\vec{q}'\cdot\vec{R}_{l'}} \right)$$

$$= \frac{1}{2N} \sum_{lk\alpha} \sum_{l'k'\beta} D_{\alpha\beta}\begin{pmatrix} l-l' \\ kk' \end{pmatrix} \sum_{\vec{q}} \sum_{\vec{q}'} \times$$

$$W_\alpha(k|\vec{q}) W_\beta(k'|\vec{q}') e^{i(\vec{q}+\vec{q}')\cdot\vec{R}_l} \times \underline{e^{i\vec{q}'\cdot(\vec{R}_{l'}-\vec{R}_l)}}$$

$$= \frac{1}{2N} \sum_{l k \alpha} \sum_{k' \beta} \sum_{\vec{q}} \sum_{\vec{q}\,'} W_\alpha(k|\vec{q}) \, W_\beta(k'|\vec{q}\,') \times e^{i(\vec{q}+\vec{q}\,')\cdot\vec{R}_l} \left\{ \sum_{l'} D_{\alpha\beta}\begin{pmatrix} l-l' \\ k\ k' \end{pmatrix} e^{i\vec{q}\,'\cdot(\vec{R}_{l'}-\vec{R}_l)} \right\} \quad (53)$$

$$= \frac{1}{2N} \sum_{l k \alpha} \sum_{k' \beta} \sum_{\vec{q}} \sum_{\vec{q}\,'} W_\alpha(k|\vec{q}) \, W_\beta(k'|\vec{q}\,') \times e^{i(\vec{q}+\vec{q}\,')\cdot\vec{R}_l} \cdot \left\{ \sum_{\tilde{l}} D_{\alpha\beta}\begin{pmatrix} \tilde{l} \\ k\ k' \end{pmatrix} e^{i\vec{q}\,'\cdot\vec{R}_{\tilde{l}}} \right\}. \quad (54)$$

$\swarrow_{l-l'}$

Let's define:

$$D_{\alpha\beta}\begin{pmatrix}\vec{q}\\ kk'\end{pmatrix} \equiv \sum_{\tilde{l}} D_{\alpha\beta}\begin{pmatrix}\tilde{l}\\ kk'\end{pmatrix} e^{i\vec{q}\cdot\vec{R}_{\tilde{l}}} \quad \text{--- (55)}$$

$$\tilde{E} = \frac{1}{2N}\sum_{lk\alpha}\sum_{k'\beta}\sum_{\vec{q}}\sum_{\vec{q}'} W_\alpha(k|\vec{q})\, W_\beta(k'|\vec{q}') \cdot \underbrace{e^{i(\vec{q}+\vec{q}')\cdot\vec{R}_l}}_{\Delta(\vec{q}+\vec{q}')} D_{\alpha\beta}\begin{pmatrix}\vec{q}'\\ kk'\end{pmatrix}$$

$$= \frac{1}{2} \sum_{k\alpha}{}' \sum_{k'\beta}{}' \sum_{\vec{q}}{}' \sum_{\vec{q}\,'}{}' W_\alpha(k|\vec{q})\, W_\beta(k'|\vec{q}\,') \times \Delta(\vec{q}+\vec{q}\,')\, D_{\alpha\beta}\begin{pmatrix} \vec{q}\,' \\ k\,k' \end{pmatrix}$$

$$= \frac{1}{2} \sum_{\vec{q}\,'}{}' \sum_{k\alpha}{}' \sum_{k'\beta}{}' \underline{W_\alpha(k|-\vec{q}\,')}\, D_{\alpha\beta}\begin{pmatrix} \vec{q}\,' \\ k\,k' \end{pmatrix} \times W_\beta(k'|\vec{q}\,')$$

$$= \frac{1}{2} \sum_{\vec{q}}{}' \underbrace{\sum_{k\alpha}{}' \sum_{k'\beta}{}' W_\alpha^{*}(k|\vec{q})\, D_{\alpha\beta}\begin{pmatrix} \vec{q} \\ k\,k' \end{pmatrix} W_\beta(k'|\vec{q})}_{56}$$

$$= \sum_{\vec{q} \in B.Z.} \frac{1}{2} \vec{W}(\vec{q})^{\dagger} D(\vec{q}) \vec{W}(\vec{q}) \qquad (57)$$

$$\vec{W}(\vec{q}) = \begin{pmatrix} w_1\binom{\vec{q}}{1} \\ w_2\binom{\vec{q}}{1} \\ w_3\binom{\vec{q}}{1} \\ \vdots \\ w_1\binom{\vec{q}}{n} \\ w_2\binom{\vec{q}}{n} \\ w_3\binom{\vec{q}}{n} \end{pmatrix} \qquad D_{\alpha\beta}\begin{pmatrix} \vec{q} \\ k\, k' \end{pmatrix}$$

3n - vector

$3n \times 3n$ matrix

$$\underline{\underline{D^*_{\alpha\beta}\begin{pmatrix} \vec{q} \\ k\,k' \end{pmatrix}}} = \left(\sum_l D_{\alpha\beta}\begin{pmatrix} l \\ k\,k' \end{pmatrix} e^{i\vec{q}\cdot\vec{R}_l} \right)^*$$

$$= \sum_l D^*_{\alpha\beta}\begin{pmatrix} l \\ k\,k' \end{pmatrix} e^{-i\vec{q}\cdot\vec{R}_l}$$

$$= \sum_l D_{\beta\alpha}\begin{pmatrix} l \\ k'\,k \end{pmatrix} e^{-i\vec{q}\cdot\vec{R}_l}$$

$l \to -l$

$$= \sum_l D_{\beta\alpha}\begin{pmatrix} l \\ k'\,k \end{pmatrix} e^{i\vec{q}\cdot\vec{R}_l} = \underline{\underline{D_{\beta\alpha}\begin{pmatrix} \vec{q} \\ k'\,k \end{pmatrix}}}$$

58

$\Rightarrow \mathcal{D}(\vec{q})$ is a Hermitian matrix.

→ Diagonalizable

→ $3n$ eigenvectors (for every $\vec{q}$) & eigenvalues

→ Eigenvalues are real $\Rightarrow$ $\omega_j^2(\vec{q})$

$j = 1, 2, \ldots, 3n$

→ Eigenvectors are orthogonal to each other & chosen to be normalized

$\longrightarrow \left\{ e_\alpha\left(k \,\middle|\, \begin{matrix}\vec{q} \\ j\end{matrix}\right) \right\}$ $\alpha = 1,3$; $k = 1, n$; $j = 1, 3n$; $\vec{q} \in BZ$.

→ eigenvectors form a complete set.

$$\sum_{k,\alpha} e_\alpha^*\left(k \middle| \begin{matrix}\vec{q}\\ j\end{matrix}\right) e_\alpha\left(k \middle| \begin{matrix}\vec{q}\\ j'\end{matrix}\right) = \delta_{jj'} \quad (59)$$

$$\sum_{j} e_\beta^*\left(k' \middle| \begin{matrix}\vec{q}\\ j\end{matrix}\right) e_\alpha\left(k \middle| \begin{matrix}\vec{q}\\ j\end{matrix}\right) = \delta_{kk'}\,\delta_{\alpha\beta} \quad (60)$$

$$W_\alpha\left(\vec{k} \middle| \vec{q}\right) = \sum_{j=1}^{3n} e_\alpha\left(k \middle| \begin{matrix}\vec{q}\\ j\end{matrix}\right) Q\left(\begin{matrix}\vec{q}\\ j\end{matrix}\right) \quad (61)$$

complex normal mode coordinates.

$$Q_j\begin{pmatrix}\vec{q}\\ j\end{pmatrix} = \sum_{k\alpha} e_\alpha^*\left(k\,\middle|\,\begin{matrix}\vec{q}\\ j\end{matrix}\right) w_\alpha\left(k\,\middle|\,\vec{q}\right) \qquad (62)$$

$$\tilde{E} = \frac{1}{2}\sum_{\vec{q}\in B.Z}\sum_{j=1}^{3n}\omega^2\begin{pmatrix}\vec{q}\\ j\end{pmatrix} Q^*\begin{pmatrix}\vec{q}\\ j\end{pmatrix} Q\begin{pmatrix}\vec{q}\\ j\end{pmatrix} \qquad (63)$$

$$K.E. = \frac{1}{2}\sum_{\vec{q}\in BZ.}\sum_{j=1}^{3n}\dot{Q}\begin{pmatrix}\vec{q}\\ j\end{pmatrix}^{*}\dot{Q}\begin{pmatrix}\vec{q}\\ j\end{pmatrix} \qquad (64)$$

eigenvalues are determined for each $\vec{q}$ from:

$$\det \left| D_{\alpha\beta}\begin{pmatrix} \vec{q} \\ k\,k' \end{pmatrix} - \omega^2 \delta_{\alpha\beta}\,\delta_{kk'} \right| = 0 \qquad (65)$$

↓ complex conjugate

$$\det \left| D_{\alpha\beta}\begin{pmatrix} -\vec{q} \\ k\,k' \end{pmatrix} - \omega^2 \delta_{\alpha\beta}\,\delta_{kk'} \right| = 0 \qquad (66)$$

$$\omega^2(\vec{q}) \equiv \omega^2(-\vec{q}) \qquad (67)$$

Also implies that,

$$e_\alpha^*\begin{pmatrix} k \bigg| \begin{matrix}\vec{q}\\ j\end{matrix}\end{pmatrix} = e_\alpha\begin{pmatrix} k \bigg| \begin{matrix}-\vec{q}\\ j\end{matrix}\end{pmatrix} \quad — (68)$$

Also,

$$Q^*\begin{pmatrix}\vec{q}\\ j\end{pmatrix} = Q\begin{pmatrix}-\vec{q}\\ j\end{pmatrix} \quad — (69)$$

(Show these as H.W.)

$$W_\alpha\begin{pmatrix} l \\ k \end{pmatrix} = \frac{1}{\sqrt{N}} \sum_{\vec{q} \in BZ} W_\alpha(k|\vec{q})\, e^{i\vec{q}\cdot\vec{R}_l}$$

$$= \frac{1}{\sqrt{N}} \sum_{\vec{q} \in BZ} \sum_{j=1}^{3n} e_\alpha\left(k\middle|\begin{matrix}\vec{q} \\ j\end{matrix}\right) Q\begin{pmatrix}\vec{q} \\ j\end{pmatrix} e^{i\vec{q}\cdot\vec{R}_l} \quad \text{— } 70$$

$$u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} = \frac{1}{\sqrt{N}} \sum_{\vec{q}} \sum_{j=1}^{3n} \left(\frac{e_\alpha\left(k\middle|\begin{matrix}\vec{q} \\ j\end{matrix}\right)}{\sqrt{M_k}}\right) Q\begin{pmatrix}\vec{q} \\ j\end{pmatrix} \underline{\underline{e^{i\vec{q}\cdot\vec{R}_l}}} \quad \text{— } 71$$

@ $\vec{q} = 0$

Γ point.

$$u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} = \frac{1}{\sqrt{N}} \sum_{j=1}^{3n} \left(\frac{e_\alpha\left(k\middle|\begin{matrix}0 \\ j\end{matrix}\right)}{\sqrt{M_k}}\right) Q\begin{pmatrix}0 \\ j\end{pmatrix} \quad \text{— } 72$$

Density-Functional Perturbation Theory

$$\Phi_{\alpha\beta}(k,k') = \left(\frac{\partial^2 E}{\partial u_\alpha(k)\,\partial u_\beta(k')}\right)_0$$

$$= \left.\frac{\partial F_\alpha(k)}{\partial u_\beta(k')}\right|_0 \qquad (73)$$

$$= \lim_{u_\beta(k')\to 0} \frac{F_\alpha(k)[u_\beta(k')] - F_\alpha(k)[0]}{u_\beta(k')}$$

$$F_\alpha(k) = \frac{\partial E[n]}{\partial u_\alpha(k)} \qquad \text{— } 74$$

$$= -\left\{ \int d^3r \; n(\vec{r}) \, \frac{\partial V_{ext}}{\partial u_\alpha(k)} + \frac{\partial E_{II}}{\partial u_\alpha(k)} \right\} \qquad \text{— } 75$$

By

Hellmann-Feynman Theorem

$$\left.\frac{\partial F_\alpha(k)}{\partial u_\beta(k')}\right|_0 = -\left\{\int d^3r\, n(\vec{r})\left(\frac{\partial^2 V_{ext}(\vec{r})}{\partial u_\alpha(k)\partial u_\beta(k')}\right)_0 + \int d^3r \left(\frac{\partial n(\vec{r})}{\partial u_\beta(k')}\right)_0 \left(\frac{\partial V_{ext}(\vec{r})}{\partial u_\alpha(k)}\right)_0 + \left(\frac{\partial^2 E_{II}}{\partial u_\alpha(k)\partial u_\beta(k')}\right)_0\right\} \quad - (76)$$

First-order Density response to the ionic displacement

The crucial quantity required for analytical evaluation of the Hessian is the (first-order) density response of the system:

$$\delta n(\vec{r}) = \left(\frac{\partial n}{\partial \vec{u}}\right)_0 \cdot \delta \vec{u} \quad - \; ??$$

$$V_{ext}(\vec{r}) = \sum_I \frac{-Z_I}{|\vec{r} - \vec{R}_I^{(0)}|} \quad \text{— (78)}$$

If $\vec{R}_I \longrightarrow \vec{R}_I + \lambda \vec{u}_I$ then let $0 < \lambda < 1$

$$V_{ext}(\vec{r}) \longrightarrow V_{ext}(\vec{r}) + \lambda\, \delta V_0(\vec{r}) \quad \text{— (79)}$$

$$\Downarrow$$

$$n(\vec{r}) \longrightarrow n(\vec{r}) + \delta n(\vec{r}) \quad \text{— (80)}$$

Recap of Perturbation Theory:

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle \quad \text{— (81)}$$

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}^{(1)} \quad \text{— (82)}$$

$$\hat{H} |\Psi_n\rangle = E_n |\Psi_n\rangle \quad \text{— (83)}$$

$$\left.\begin{aligned} |\Psi_{n,\lambda}\rangle &= |\Psi_n^{(0)}\rangle + \lambda |\Psi_n^{(1)}\rangle + \lambda^2 |\Psi_n^{(2)}\rangle + \cdots \\ E_{n,\lambda} &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \end{aligned}\right\} \quad (84)$$

$$\hat{H}_0 |\Psi_n^{(0)}\rangle = E_n^{(0)} |\Psi_n^{(0)}\rangle \quad \text{— } 85$$

$$E_n^{(0)} \longrightarrow \epsilon_n \quad (\text{as } \lambda \to 0)$$

$$(\hat{H}_0 - \epsilon_n)|\Psi_n^{(1)}\rangle = -(\hat{H}^{(1)} - E_n^{(1)})|\Psi_n^{(0)}\rangle \quad \text{— } 86$$

$$(\hat{H}_0 - \epsilon_n)|\Psi_n^{(2)}\rangle = -(\hat{H}^{(1)} - E_n^{(1)})|\Psi_n^{(1)}\rangle + (\hat{H}^{(2)} - E_n^{(2)})|\Psi_n^{(0)}\rangle \quad \text{— } 87$$

$$\vdots$$

$|\Psi_n^{(0)}\rangle \longrightarrow$ space of unperturbed eigenfunctions correspondin to E_n

e.g. $|\Psi_n^{(0)}\rangle = |\psi_n\rangle$ — (88)

$$E_n^{(1)} = \langle \psi_n | \hat{H}^{(1)} | \psi_n \rangle \quad \text{— (89)}$$

If $\langle \Psi_n | \Psi_n \rangle = 1$

then, $\langle \Psi_n^{(0)} | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(1)} | \Psi_n^{(0)} \rangle = 0$ — (90)

⋮

First order correction eqn.

$$\left(\hat{H}_0 - \epsilon_m\right)|\Psi_n^{(1)}\rangle = -\left(\hat{H}^{(1)} - E_n^{(1)}\right)|\Psi_n^{(0)}\rangle$$

$$|\Psi_n^{(1)}\rangle = \sum_{m \neq n} |\psi_m\rangle \frac{\langle \psi_m | \hat{H}^{(1)} | \psi_n \rangle}{(\epsilon_n - \epsilon_m)} \quad \text{--- } (91)$$

$$\Rightarrow \langle \Psi_n^{(0)} | \Psi_n^{(1)} \rangle = 0$$

$$\delta V_0 \longrightarrow \delta n(\vec{r}) \longrightarrow \delta V_s(\vec{r})$$

$$n(\vec{r}) \longleftrightarrow V_s(\vec{r}) = V_{ext}(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}[n](\vec{r}) \quad \text{— (92)}$$

$$n(\vec{r}) + \delta n(\vec{r}) \longleftrightarrow V_s(\vec{r}) + \delta V_s(\vec{r}) =$$

$$V_{ext}(\vec{r}) + \delta V_0(\vec{r}) + \int \frac{\left(n(\vec{r}') + \delta n(\vec{r}')\right)}{|\vec{r}-\vec{r}'|} d^3r' + v_{xc}[n+\delta n](\vec{r}) \quad \text{— (93)}$$

$$= \underbrace{V_{ext}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' + v_{xc}[n](\vec{r})}_{v_s(\vec{r})}$$

$$+ \lambda \delta V_{ext}(\vec{r}) + \int \frac{\delta n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' + \left(v_{xc}[n+\delta n](\vec{r}) - v_{xc}[n](\vec{r}) \right) \quad — (94)$$

$$\delta n(\vec{r}) = \lambda n^{(1)}(\vec{r}) + \lambda^2 n^{(2)}(\vec{r}) + \cdots \quad — (95)$$

$$v_{xc}[n+\delta n] - v_{xc}[n] = \int d^3r' \frac{\delta v_{xc}[n](\vec{r})}{\delta n(\vec{r}')} \delta n(\vec{r}'). \quad — (96)$$

$$\delta v_s(\vec{r}) = \lambda \left\{ \delta v_{ext}(\vec{r}) + \int \frac{n^{(1)}(\vec{r}\,')}{|\vec{r}\,' - \vec{r}\,'|} d^3r' + \int d^3r' \, \frac{\delta v_{xc}(\vec{r})}{\delta n(\vec{r}\,')} n^{(1)}(\vec{r}\,') \right\} + O(\lambda^2) \tag{97}$$

$$\left\{-\frac{\nabla^2}{2} + v_s(\vec{r})\right\}\psi_n(\vec{r}) = \epsilon_n \psi_n(\vec{r}) \quad \text{— (98)}$$

(assume a spin unpolarized system and an insulating ground state)

$$n(\vec{r}) = 2\sum_{m=1}^{N/2} |\psi_m(\vec{r})|^2 \quad \text{— (99)}$$

$$\Big[\underbrace{-\frac{\nabla^2}{2} + V_s(\vec r)}_{\hat h_0} + \underbrace{\delta V_s(\vec r)}_{\hat h^{(1)}}\Big]\tilde\psi_n(\vec r) = \tilde\epsilon_n \tilde\psi_n(\vec r) \qquad \text{— } (100)$$

To first order we have

$$(\hat h_0 - \epsilon_n)\,|\psi_n^{(1)}\rangle = -\left(\delta V_s(\vec r) - \epsilon_n^{(1)}\right)|\psi_n\rangle \qquad \text{— } (101)$$

$$\delta n(\vec{r}) = n^{(1)}(\vec{r}) + O(\lambda^2)$$

$$= 2\sum_{n=1}^{N/2} \left\{ \psi_n^*(\vec{r})\, \psi_n^{(1)}(\vec{r}) + c.c. \right\}$$

$$= 4\sum_{n=1}^{N/2} \mathrm{Re}\left\{ \psi_n^*(\vec{r})\, \psi_n^{(1)}(\vec{r}) \right\} \qquad (102)$$

$$\left|\psi_n^{(1)}\right\rangle = \sum_{\substack{m \neq n \\ m \in \underline{\text{unocc}}}} \left|\psi_m\right\rangle \frac{\left\langle \psi_m \middle| \delta V_s \middle| \psi_n \right\rangle}{(\epsilon_n - \epsilon_m)}$$

$\rightarrow$ sum-over-states

$\leftarrow$ 103

$$n^{(1)}(\vec{r}) = 2 \sum_{n=1}^{N/2} \sum_{m \neq n} \left\{ \psi_n^*(\vec{r})\, \psi_m(\vec{r}) \frac{\left\langle \psi_m \middle| \delta V_s \middle| \psi_n \right\rangle}{(\epsilon_n - \epsilon_m)} + \text{c.c.} \right\}$$

$$= 2 \sum_{n=1}^{N/2} \sum_{m \in \text{unocc.}} \left\{ \psi_n^*(\vec{r})\, \psi_m(\vec{r}) \frac{\left\langle \psi_m \middle| \delta V_s \middle| \psi_n \right\rangle}{\epsilon_n - \epsilon_m} + \text{c.c.} \right\}$$

104 $\rightarrow$

$$(\hat{h}_0 - \epsilon_n)|\psi_n^{(1)}\rangle = -(\delta V_s(\vec{r}) - \epsilon_n^{(1)})|\psi_n\rangle$$

$$|\psi_n^{(1)}\rangle = (\epsilon_n - \hat{h}_0)^{-1}\left[\delta V_s(\vec{r}) - \epsilon_n^{(1)}\right]|\psi_n\rangle \quad \text{— } (105)$$

But $(\epsilon_n - \hat{h}_0)$ is singular

$\Rightarrow$ non-invertible

Let

$$\hat{P}_v = \sum_{j \in occ} |\psi_j\rangle\langle\psi_j| \quad \text{— } (106)$$

$$\hat{P}_c = \sum_{j \in unocc} |\psi_j\rangle\langle\psi_j| \quad \text{— } (107)$$

$$\hat{P}_c + \hat{P}_v = \hat{\mathbb{1}} \quad \text{— } 107$$

$$\hat{P}_c \hat{P}_v = 0 \quad \text{— } 108$$

$$\overbrace{\left(\hat{h}_0 - \epsilon_n + \alpha \hat{P}_v\right) |\psi_n^{(1)}\rangle}$$

$$= - \hat{P}_c \, \delta U_s |\psi_n\rangle$$

(1) Applied $\hat{P}_c$ on both sides of 101 — 109

(2) added αP_v to LHS of 101

$$|\psi_n^{(1)}\rangle = \overbrace{\underbrace{\left(\epsilon_n - \hat{h}_0 - \alpha \hat{P}_v\right)^{-1}}_{\text{Green's function}} \hat{P}_c}^{} \, \delta v_s \, |\psi_n\rangle \quad \text{— (110)}$$

$$\hat{P}_c = \hat{\mathbb{1}} - \hat{P}_v = \hat{\mathbb{1}} - \sum_{j \in \text{core}} |\psi_j\rangle\langle\psi_j| \quad \text{— (111)}$$

(110) needs only the occupied manifold

→ $N/2$ coupled equation ($\because \delta v_s \equiv \delta v_s[\delta n]$)

→ solved by self-consistency

$$\delta v_s(\vec{r}) = \delta v_{ext}(\vec{r}) + \int d^3r' \, K(\vec{r},\vec{r}') \, n^{(1)}(\vec{r}') \quad (112)$$

$$K(\vec{r},\vec{r}') = \frac{1}{|\vec{r}-\vec{r}'|} + \frac{\delta v_{xc}(\vec{r})}{\delta n(\vec{r}')} \quad (113)$$

Sternheimer Eqn

$$\left[\hat{P}_c(\epsilon_n - \hat{h}_0)\hat{P}_c\right]|\psi_n^{(1)}\rangle = -\hat{P}_c \, \delta v_s |\psi_n\rangle \quad (114)$$

$$n^{(1)}(\vec{r}) = 4 \sum_{m=1}^{N_k} \mathrm{Re}\left\{\psi_m^*(\vec{r}) \, \psi_m^{(1)}(\vec{r})\right\} \quad (115)$$