MaX School on Advanced Materials and Molecular Modelling
with Quantum ESPRESSO

density-functional perturbation theory

response functions, phonons, and all that

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warning/disclaimer

the material in this lecture is advanced and its proper understanding requires a background in quantum mechanics that not all you may necessarily have

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at the very least, try to memorise the general concepts and terminology; all the technical details can be found in:

SB, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001)

response functions

$$\text{property} = \frac{\partial(\text{variable})}{\partial(\text{strength})}$$

response functions

$$\text{property} = \frac{\partial(\text{variable})}{\partial(\text{strength})}$$

☛ polarizability, dielectric constant	$\frac{\partial \mathsf{P}_i}{\partial \mathsf{E}_j}$
☛ elastic constants	$\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}$
☛ piezoelectric constants	$\frac{\partial \mathsf{P}_i}{\partial \epsilon_{kl}}$
☛ interatomic force constants	$\frac{\partial f_i^s}{\partial u_j^t}$
☛ Born effective charges	$\frac{\partial d_i^s}{\partial u_j^s}$
☛ …	…

the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda$$

the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \qquad E'_\lambda = \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle$$

the Hellmann-Feynman theorem

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$$\begin{aligned} E'_\lambda &= \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle \\ &= \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle + \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle + \langle \Psi_\lambda | \hat{H}_\lambda | \Psi'_\lambda \rangle \end{aligned}$$

the Hellmann-Feynman theorem

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the Hellmann-Feynman theorem

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the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \qquad E'_\lambda = \frac{\partial}{\partial\lambda}\langle\Psi_\lambda|\hat{H}_\lambda|\Psi_\lambda\rangle$$

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$$E_\lambda = \min_{\{\Psi:\ \langle\Psi|\Psi\rangle=1\}} \langle\Psi|\hat{H}_\lambda|\Psi\rangle$$

the Hellmann-Feynman theorem

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$$g(\lambda) = \min_x G[x,\lambda]$$

the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \qquad \begin{aligned} E'_\lambda &= \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle \\ &= \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle + \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle + \langle \Psi_\lambda | \hat{H}_\lambda | \Psi'_\lambda \rangle \\ &= \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle + \xcancel{E_\lambda \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \Psi_\lambda \rangle} \end{aligned}$$

$$E_\lambda = \min_{\{\Psi:\ \langle \Psi | \Psi \rangle = 1\}} \langle \Psi | \hat{H}_\lambda | \Psi \rangle$$

$$g(\lambda) = \min_x G[x, \lambda] \qquad \longrightarrow \qquad \left. \frac{\partial G}{\partial x} \right|_{x = x(\lambda)} = 0$$

the Hellmann-Feynman theorem

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$$\begin{tikzcd} g(\lambda) = \min\limits_x G[x,\lambda] \arrow[r] & \left.\dfrac{\partial G}{\partial x}\right|_{x=x(\lambda)} = 0 \arrow[dl] \\ g(\lambda) = G[x(\lambda),\lambda] & \end{tikzcd}$$

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g(\lambda) = G[x(\lambda),\lambda] \arrow[r] & g'(\lambda) = x'(\lambda)\left.\dfrac{\partial G}{\partial x}\right|_{x=x(\lambda)} + \dfrac{\partial G}{\partial\lambda}
\end{tikzcd}$$

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g(\lambda) = \min\limits_x G[x,\lambda] \arrow[r] & \boxed{\left.\dfrac{\partial G}{\partial x}\right|_{x=x(\lambda)} = 0} \arrow[dl] \arrow[d] \\
g(\lambda) = G[x(\lambda),\lambda] \arrow[r] & g'(\lambda) = \xcancel{x'(\lambda)\left.\dfrac{\partial G}{\partial x}\right|_{x=x(\lambda)}} + \dfrac{\partial G}{\partial\lambda}
\end{tikzcd}$$

the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda$$

$$E'_\lambda = \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle$$

$$\frac{\partial}{\partial \lambda} \min_x G(x, \lambda) = \left. \frac{\partial G(x, \lambda)}{\partial \lambda} \right|_{x = x(\lambda)}$$

susceptibilities as energy derivatives

$$\hat{H}_\alpha = \hat{H}^\circ + \alpha \hat{A}$$

$$\chi_{BA} = \frac{\partial \langle \hat{B} \rangle_\alpha}{\partial \alpha}$$

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$$\langle \hat{B} \rangle = \frac{\partial E_\beta}{\partial \beta}$$

(Hellmann & Feynman)

$$\hat{H}_\beta = \hat{H}^\circ + \beta \hat{B}$$

susceptibilities as energy derivatives

$$\hat{H}_\alpha = \hat{H}^\circ + \alpha \hat{A}$$

$$\chi_{BA} = \frac{\partial \langle \hat{B} \rangle_\alpha}{\partial \alpha}$$

$$\langle \hat{B} \rangle = \frac{\partial E_\beta}{\partial \beta}$$

(Hellmann & Feynman)

$$\hat{H}_\beta = \hat{H}^\circ + \beta \hat{B}$$

$$\boxed{\chi_{BA} = \frac{\partial^2 E_{\alpha\beta}}{\partial \alpha \partial \beta}}$$

$$\hat{H}_{\alpha\beta} = \hat{H}^\circ + \alpha \hat{A} + \beta \hat{B}$$

energy derivatives

$$H = H_0 + \sum_i \lambda_i v_i$$

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$$E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \cdots$$

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☛ structural optimization & molecular dynamics

energy derivatives

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☛ structural optimization & molecular dynamics

☛ (static) response functions
    elastic constants
    dielectric tensor
    piezoelectric tensor
    ...

☛ vibrational modes in the adiabatic approximation
    interatomic force constants
    Born effective charges
    ...

energy derivatives from perturbation

$$H = H_0 + \sum_i \lambda_i v_i \qquad E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \cdots$$

energy derivatives from perturbation

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$$f_i = - \left. \frac{\partial E}{\partial \lambda_i} \right|_{\lambda=0} = -\langle \Psi_0 | v_i | \Psi_0 \rangle = \int v_i(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r}$$

energy derivatives from perturbation

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$$h_{ij} = \left.\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j}\right|_{\lambda=0} \quad = \quad 2 \sum_n \frac{\langle \Psi_0 | v_i | \Psi_n \rangle \langle \Psi_n | v_j | \Psi_0 \rangle}{\epsilon_0 - \epsilon_n}$$

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energy derivatives from perturbation

$$H = H_0 + \sum_i \lambda_i v_i \qquad E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \cdots$$

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energy derivatives from perturbation

$$H = H_0 + \sum_i \lambda_i v_i \qquad\qquad E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \cdots$$

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$$H = H_0 + \sum_i \lambda_i v_i \qquad\qquad E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \cdots$$

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$$\begin{aligned} h_{ij} = \left. \frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} \right|_{\lambda=0} &= 2 \sum_n \frac{\langle \Psi_0 | v_i | \Psi_n \rangle \langle \Psi_n | v_j | \Psi_0 \rangle}{\epsilon_0 - \epsilon_n} \\ &= 2 \langle \Psi_0 | v_i | \Psi'_j \rangle &&= \int v_i(\mathbf{r}) \rho'_j(\mathbf{r}) d\mathbf{r} \\ &= 2 \langle \Psi'_i | v_j | \Psi_0 \rangle &&= \int v_j(\mathbf{r}) \rho'_i(\mathbf{r}) d\mathbf{r} \end{aligned}$$

the “2n+1” theorem

$$\Phi = \Phi_0 + \mathcal{O}(\epsilon) \Rightarrow E = E_0 + \mathcal{O}(\epsilon^2)$$

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the “2n+1” theorem

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$$E = \frac{\langle \Phi_0 + \Phi' | (H_0 + V') | \Phi_0 + \Phi' \rangle}{\langle \Phi_0 + \Phi' | \Phi_0 + \Phi' \rangle} + \mathcal{O}(V'^4)$$

the “2n+1” theorem

$$\Phi = \Phi_0 + \mathcal{O}(\epsilon) \Rightarrow E = E_0 + \mathcal{O}(\epsilon^2)$$

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$$E = \frac{\langle \Phi_0 + \Phi' | (H_0 + V') | \Phi_0 + \Phi' \rangle}{\langle \Phi_0 + \Phi' | \Phi_0 + \Phi' \rangle} + \mathcal{O}(V'^4)$$

$$\boxed{E^{(3)} = \langle \Phi' | V' | \Phi' \rangle - \langle \Phi' | \Phi' \rangle \langle \Phi_0 | V' | \Phi_0 \rangle}$$

density-functional perturbation theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i v_i(\mathbf{r})$$

density-functional perturbation theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i v_i(\mathbf{r})$$

$$E(\lambda) = \min_n \left(F[n] + \int V_\lambda(\mathbf{r}) n(\mathbf{r}) \right) \quad \int n(\mathbf{r}) d\mathbf{r} = N$$

DFT

density-functional perturbation theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i v_i(\mathbf{r})$$

$$E(\lambda) = \min_n \left(F[n] + \int V_\lambda(\mathbf{r}) n(\mathbf{r}) \right) \quad \int n(\mathbf{r}) d\mathbf{r} = N$$

DFT

$$\frac{\partial E(\lambda)}{\partial \lambda_i} = \int n_\lambda(\mathbf{r}) v_i(\mathbf{r}) d\mathbf{r}$$

HF

density-functional perturbation theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i v_i(\mathbf{r})$$

$$E(\lambda) = \min_n \left(F[n] + \int V_\lambda(\mathbf{r}) n(\mathbf{r}) \right) \quad \int n(\mathbf{r}) d\mathbf{r} = N$$ DFT

$$\frac{\partial E(\lambda)}{\partial \lambda_i} = \int n_\lambda(\mathbf{r}) v_i(\mathbf{r}) d\mathbf{r}$$ HF

$$\boxed{\frac{\partial^2 E(\lambda)}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_j} v_i(\mathbf{r}) d\mathbf{r}}$$ DFPT

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$n'(\mathbf{r}) = 2\mathrm{Re} \sum_v \phi_v^{\circ *}(\mathbf{r}) \phi'_v(\mathbf{r})$$

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$\begin{aligned} n'(\mathbf{r}) &= 2\mathrm{Re} \sum_v \phi_v^{\circ *}(\mathbf{r}) \phi_v'(\mathbf{r}) \\ &= 2\mathrm{Re} \sum_{cv} \rho_{vc}' \phi_v^{\circ *}(\mathbf{r}) \phi_c^{\circ}(\mathbf{r}) \end{aligned}$$

$$\phi_v' = \sum_c \phi_c^{\circ} \frac{\langle \phi_c^{\circ} | V' | \phi_v^{\circ} \rangle}{\epsilon_v^{\circ} - \epsilon_c^{\circ}}$$

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$\begin{aligned} n'(\mathbf{r}) &= 2\mathrm{Re} \sum_v \phi_v^{\circ *}(\mathbf{r}) \phi'_v(\mathbf{r}) \\ &= 2\mathrm{Re} \sum_{cv} \rho'_{vc} \phi_v^{\circ *}(\mathbf{r}) \phi_c^{\circ}(\mathbf{r}) \end{aligned}$$

$$\phi'_v = \sum_c \phi_c^{\circ} \frac{\langle \phi_c^{\circ} | V' | \phi_v^{\circ} \rangle}{\epsilon_v^{\circ} - \epsilon_c^{\circ}}$$

$$\boxed{(H^{\circ} - \epsilon_v^{\circ}) \phi'_v = -P_c V' \phi_v^{\circ}}$$

calculating the response

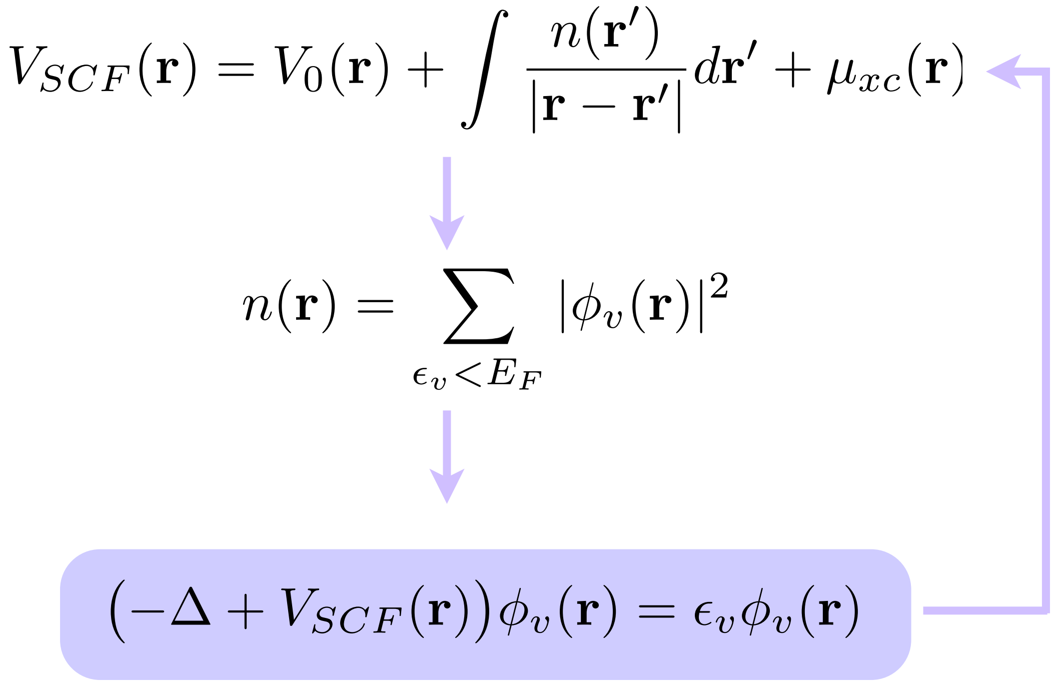
$$n'(\mathbf{r}) = 2\mathrm{Re}\sum_v \phi_v^{\circ *}(\mathbf{r})\phi_v'(\mathbf{r})$$

$$(H^\circ - \epsilon_v^\circ)\phi_v' = -P_c V' \phi_v^\circ$$

DFPT: the equations

DFT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$



$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$(-\Delta + V_{SCF}(\mathbf{r}))\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})$$

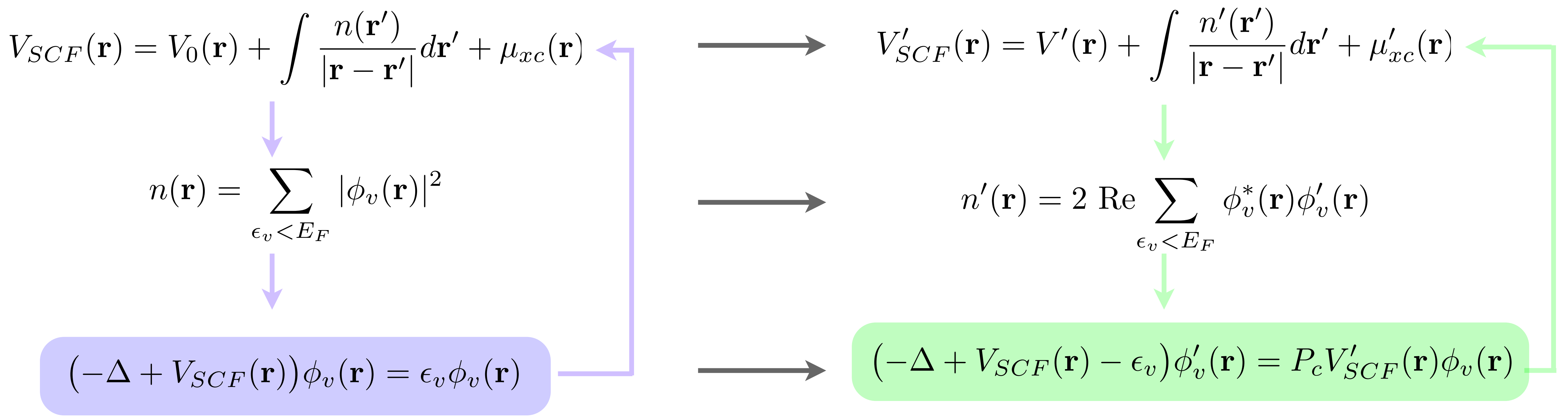
DFPT: the equations

DFT

DFPT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$V'(\mathbf{r}) \leftrightarrows n'(\mathbf{r})$$



$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$(-\Delta + V_{SCF}(\mathbf{r}))\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})$$

$$V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r})$$

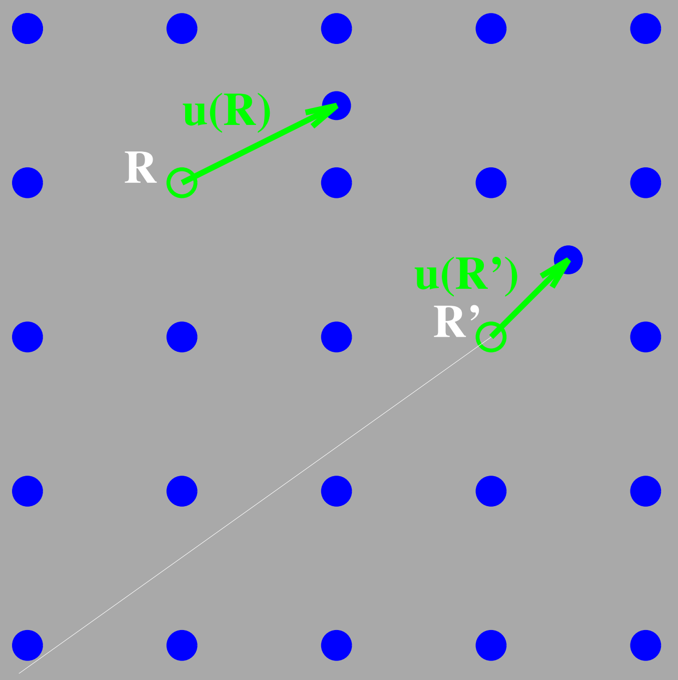
$$n'(\mathbf{r}) = 2 \ \mathrm{Re} \sum_{\epsilon_v < E_F} \phi_v^*(\mathbf{r})\phi'_v(\mathbf{r})$$

$$(-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v)\phi'_v(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r})\phi_v(\mathbf{r})$$

SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

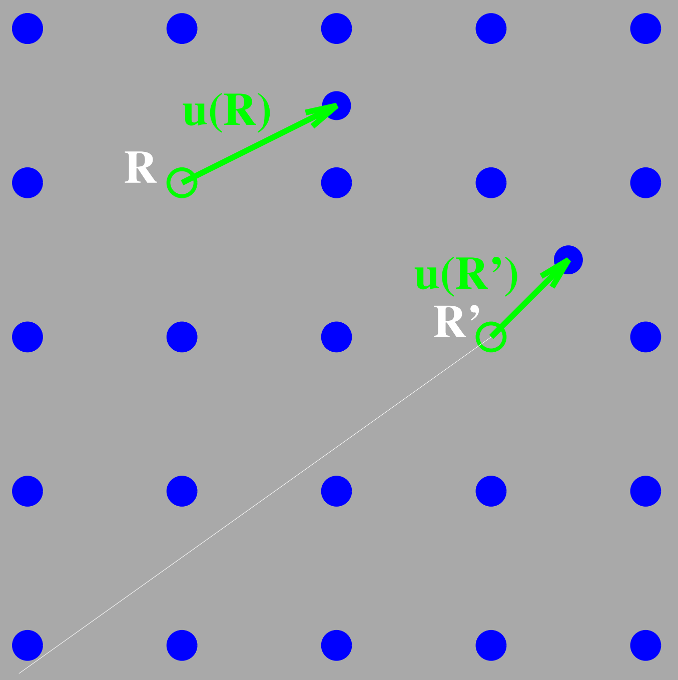
simulating atomic vibrations ...

lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

lattice dynamics

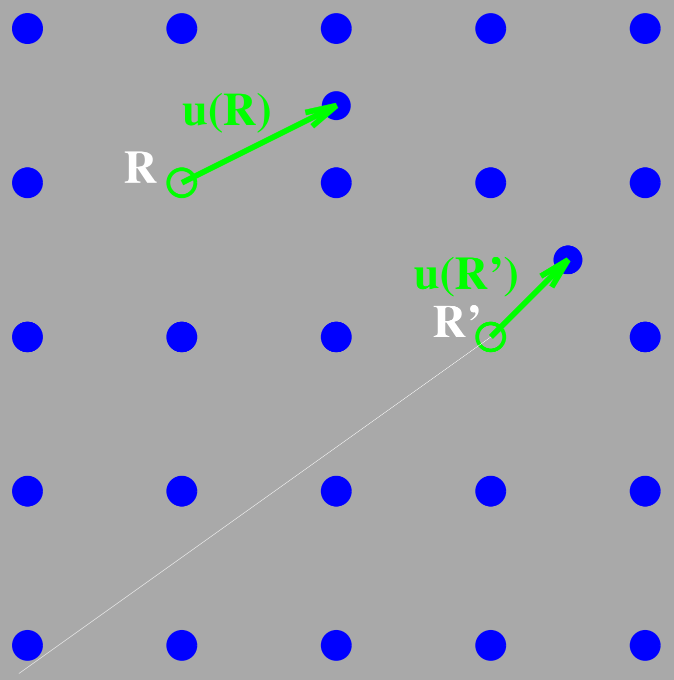


$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

$$+ \cdots$$

lattice dynamics



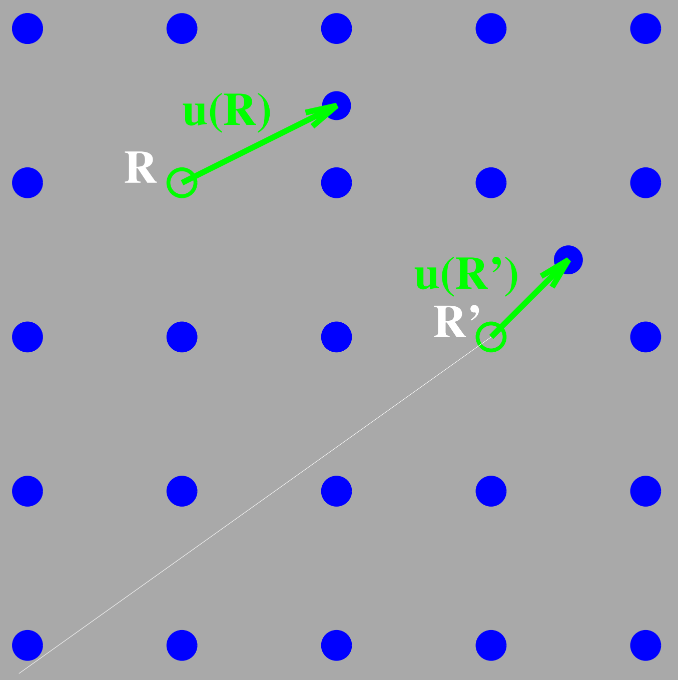
$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

$$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$$

$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

$$+ \cdots$$

lattice dynamics



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DFT

DPFT

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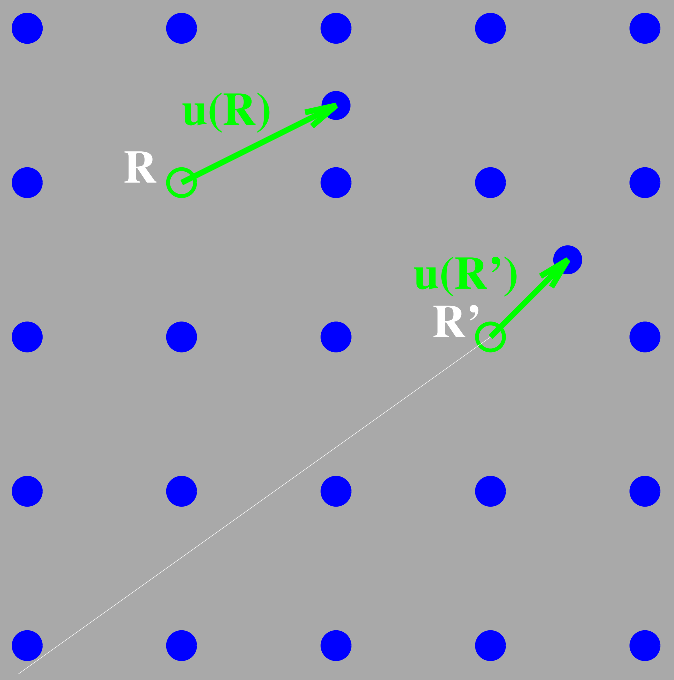

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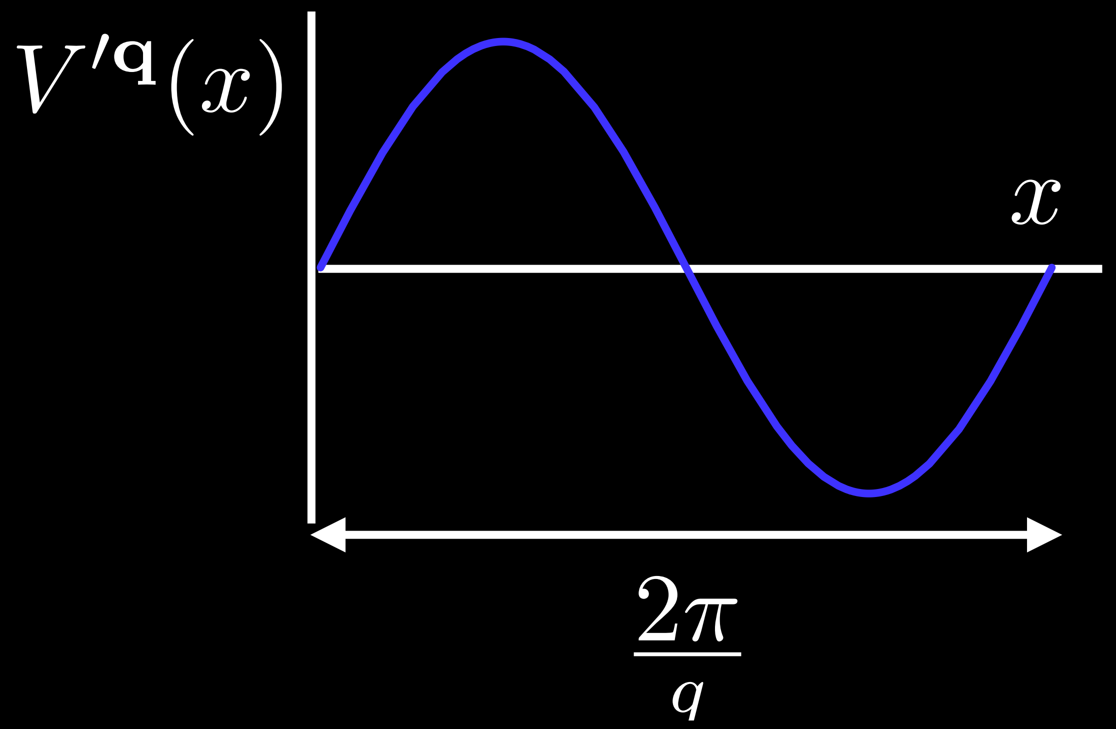
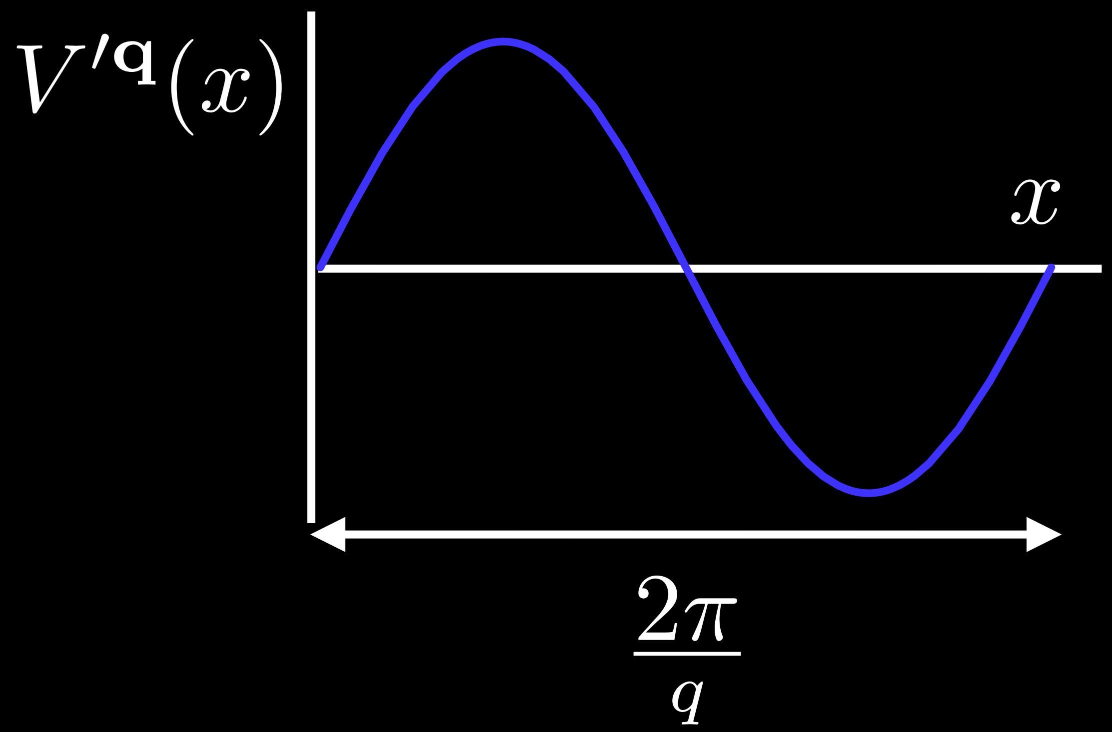
$$\det \left[\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} - \omega^2 M(\mathbf{R}) \delta_{\mathbf{R},\mathbf{R}'} \right] = 0$$

monochromatic perturbations



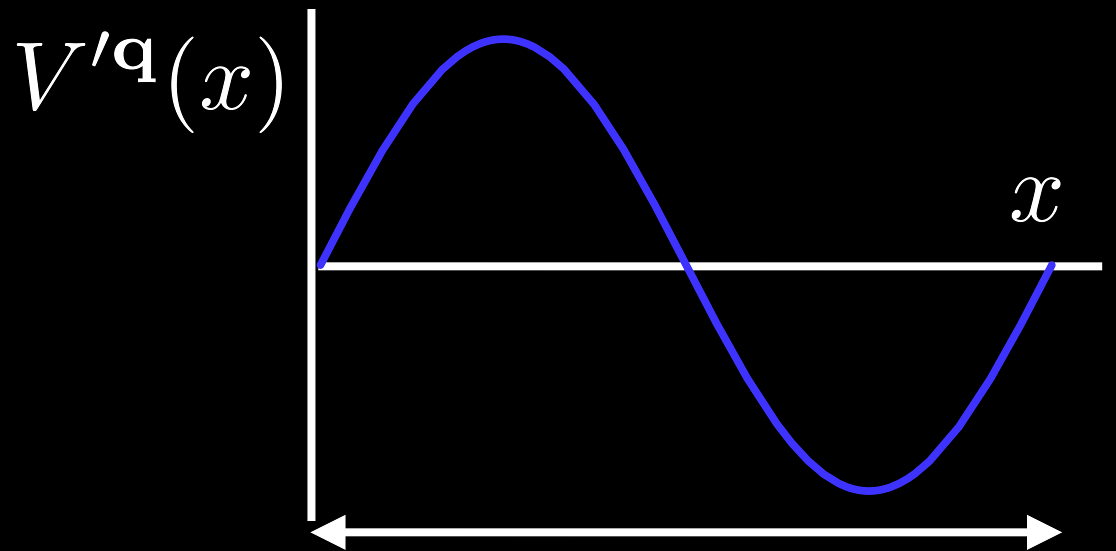
DFPT rhs: $-P_c V'^{\mathbf{q}}_{SCF} \phi^{\mathbf{k}}_v(\mathbf{r})$

monochromatic perturbations



$$\left(H_0-\epsilon_v^{\mathbf{k}}\right)\phi_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r})=-P_cV_{SCF}'^{\mathbf{q}}\phi_v^{\mathbf{k}}(\mathbf{r})$$

monochromatic perturbations



$\mathrm{e}^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} u'^{\mathbf{k}+\mathbf{q}}_v(\mathbf{r})$

$\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u^{\circ\mathbf{k}}_v(\mathbf{r})$

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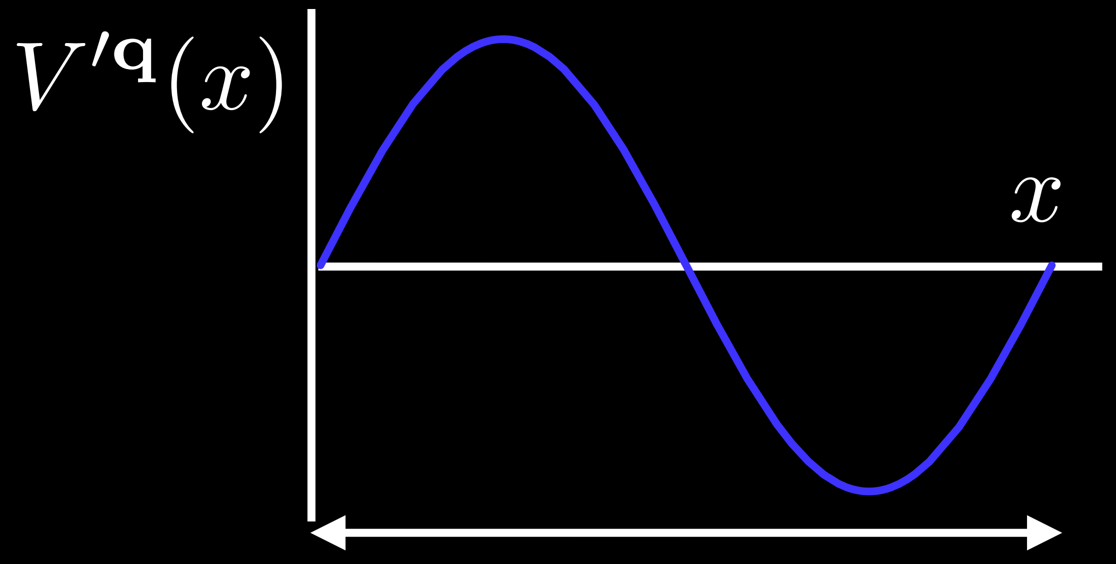

$\mathrm{e}^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}u'^{\mathbf{k}+\mathbf{q}}_v(\mathbf{r})$

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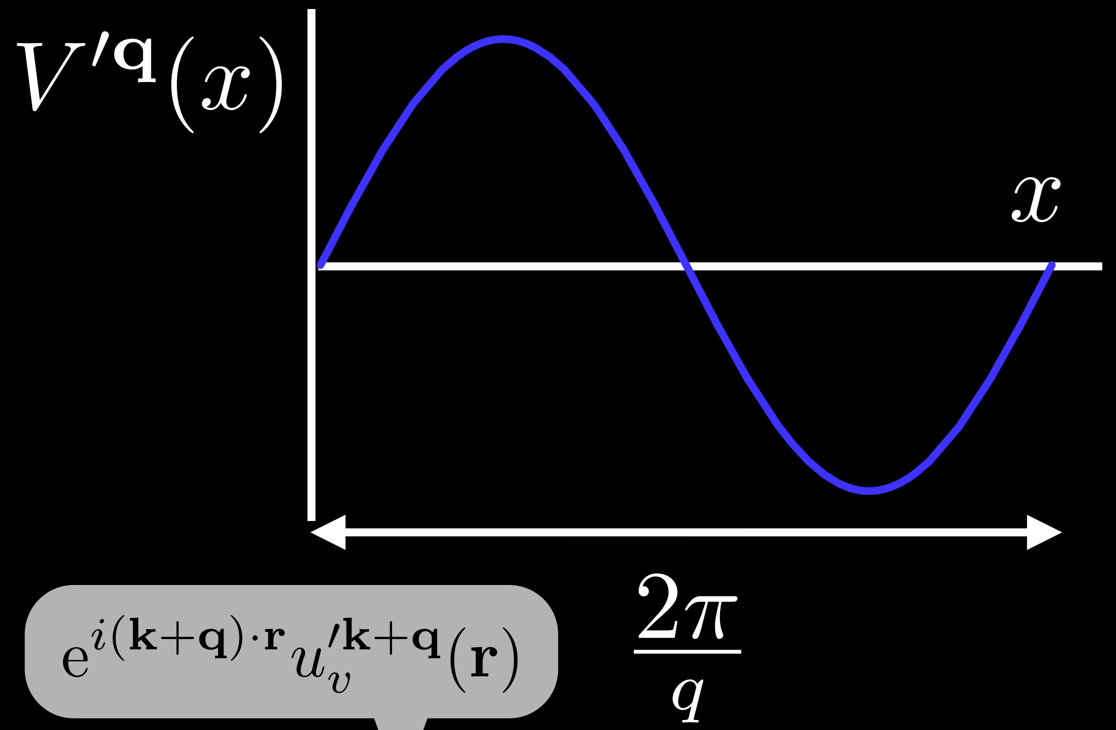
$$\left(H_0-\epsilon^{\mathbf{k}}_v\right)\phi'^{\mathbf{k}+\mathbf{q}}_v(\mathbf{r})=-P_cV'^{\mathbf{q}}_{SCF}\phi^{\mathbf{k}}_v(\mathbf{r})$$

$$n'^{\mathbf{q}}(\mathbf{r})=\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}}\sum_{v,\mathbf{k}}u^{\circ\mathbf{k}*}_v(\mathbf{r})u'^{\mathbf{k}+\mathbf{q}}_v(\mathbf{r})$$

monochromatic perturbations



$\mathrm{e}^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}u_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r})$

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$$V'^{\mathbf{q}}(\mathbf{r}) = V'^{\mathbf{q}}_{ext}(\mathbf{r}) + \int\left(\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}+\kappa_{xc}(\mathbf{r},\mathbf{r}')\right)n'^{\mathbf{q}}(\mathbf{r}')d\mathbf{r}'$$

phonons in polar materials

$$E(\mathbf{u} \quad) = \frac{1}{2} M \omega_0^2 u^2$$

phonons in polar materials

$$E(\mathbf{u}, \boldsymbol{\mathsf{E}}) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \epsilon_\infty \mathsf{E}^2 - e Z^* \mathbf{u} \cdot \boldsymbol{\mathsf{E}}$$

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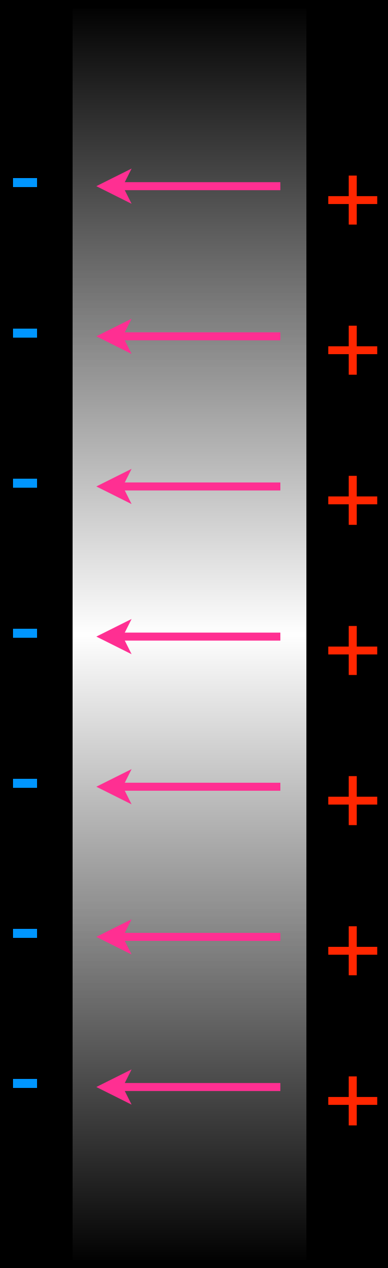
$$\mathbf{F}_T = -M\omega_0^2\mathbf{u} \qquad \mathbf{F}_L = -M\left(\omega_0^2 + \frac{4\pi Z^*}{M\Omega\epsilon_\infty}\right)\mathbf{u}$$

macroscopic electric fields

$$\mathbf{E} = \mathrm{const}$$



$$V'(\mathbf{r}) = \mathbf{E}\cdot\mathbf{r}$$

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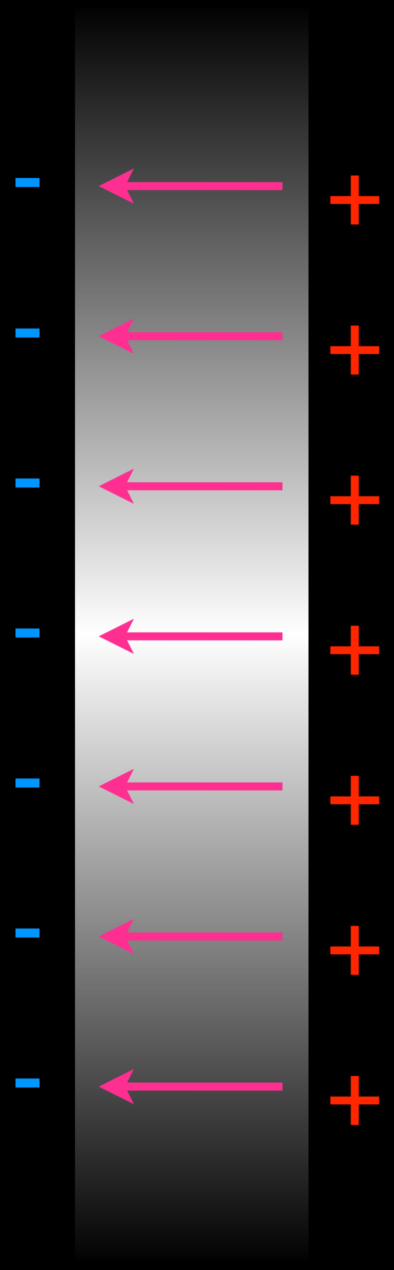

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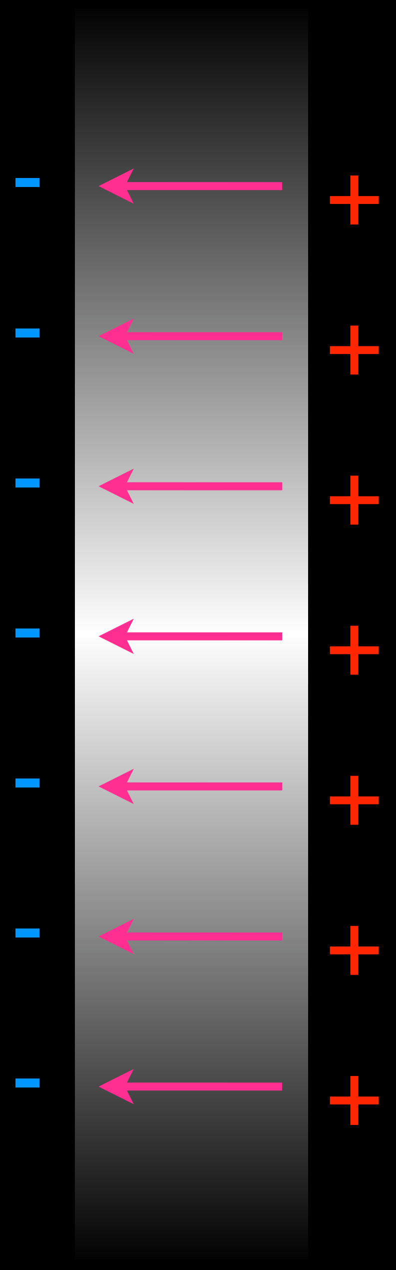

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$$
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V'(\mathbf{r})\phi_v^0(\mathbf{r}) &= ??
\end{aligned}
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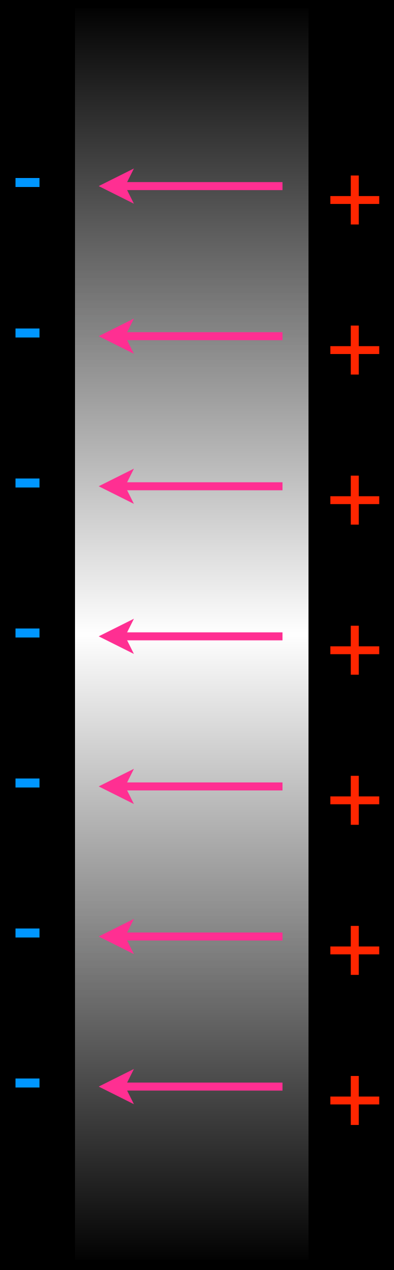

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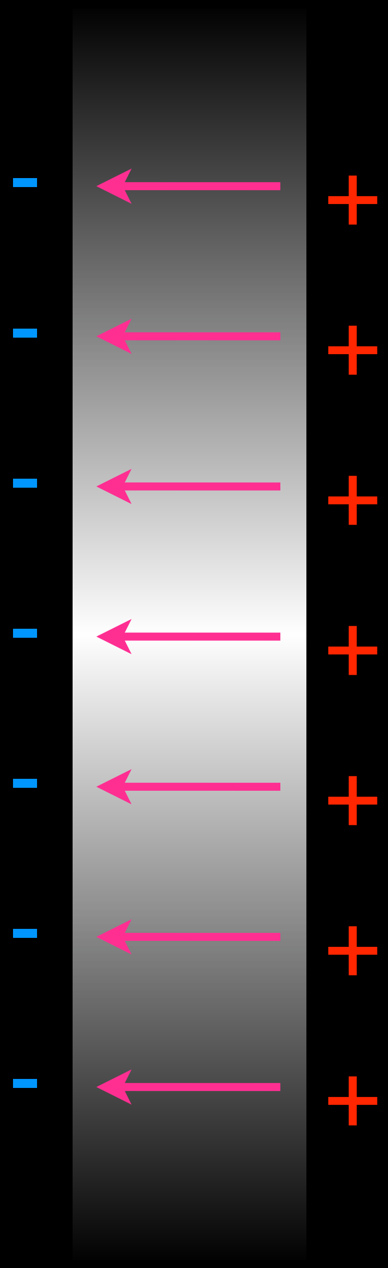

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$$\langle \phi_v^0 | x | \phi_u^0 \rangle = \frac{\langle \phi_v^0 | [H, x] | \phi_u^0 \rangle}{\epsilon_v^0 - \epsilon_u^0} \qquad [H, x] = -\frac{\hbar^2}{m}\frac{\partial}{\partial x} + [V_{nl}, x]$$

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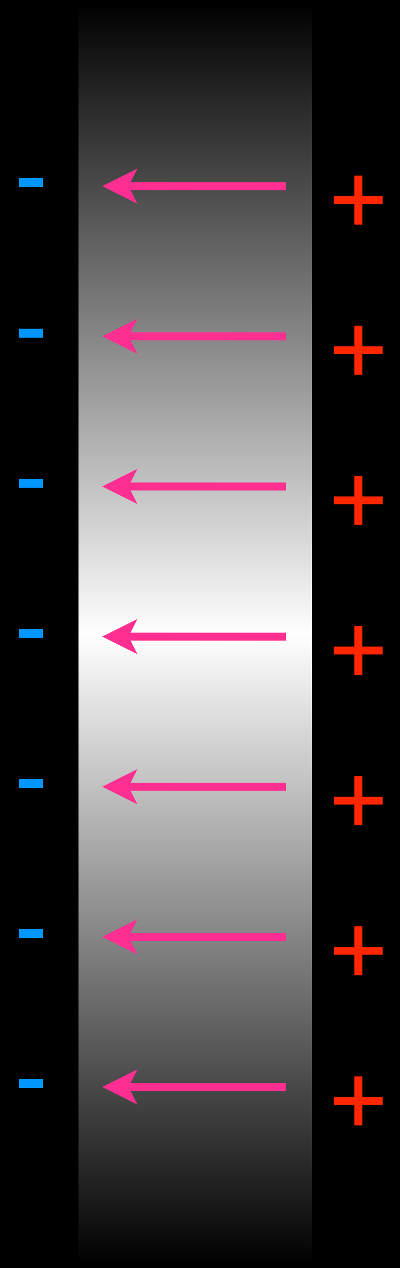
MA PER SEGUIR VIRTUTE E CANOSCENZA

macroscopic electric fields

$\mathsf{E} = \mathrm{const}$



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$$\begin{aligned} -P_c V' \phi_v^0 &= -\mathsf{E} \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle \\ &= -\mathsf{E} \sum_c \phi_c^0 \frac{\langle \phi_c^0 | [H_0, x] | \phi_v^0 \rangle}{\epsilon_c^0 - \epsilon_v^0} \equiv \psi_v' \end{aligned}$$

macroscopic electric fields

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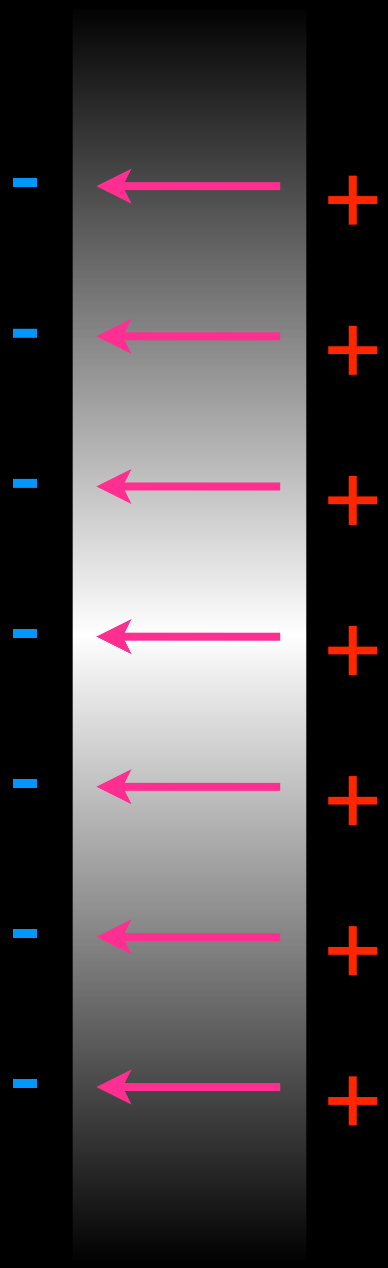

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$$\boxed{(H_0-\epsilon_v^0)\psi_v' = -\mathsf{E}P_c[H_0,x]\phi_v^0}$$

DFPT rhs

interatomic force constants

$$\Phi_{st}^{\alpha\beta}(\mathbf{R}-\mathbf{R}') \quad = \quad -\frac{\partial^2 E}{\partial u_s^\alpha(\mathbf{R})\partial u_t^\beta(\mathbf{R}')}$$

interatomic force constants

$$\begin{aligned}\Phi_{st}^{\alpha\beta}(\mathbf{R}-\mathbf{R}') &= -\frac{\partial^2 E}{\partial u_s^\alpha(\mathbf{R})\partial u_t^\beta(\mathbf{R}')} \\ &= \frac{\Omega}{(2\pi)^3}\int \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} D_{st}^{\alpha\beta}(\mathbf{q}) d\mathbf{q}\end{aligned}$$

interatomic force constants

$$
\begin{aligned}
\Phi^{\alpha\beta}_{st}(\mathbf{R}-\mathbf{R}') &= -\frac{\partial^2 E}{\partial u^\alpha_s(\mathbf{R})\partial u^\beta_t(\mathbf{R}')} \\
&= \frac{\Omega}{(2\pi)^3}\int \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} D^{\alpha\beta}_{st}(\mathbf{q})d\mathbf{q} \\
D^{\alpha\beta}_{st}(\mathbf{q}) &= \bar{D}^{\alpha\beta}_{st}(\mathbf{q}) + \frac{4\pi e^2}{\Omega\epsilon_\infty} Z^\star_s Z^\star_t \frac{q^\alpha q^\beta}{q^2}
\end{aligned}
$$

short ranged +
dipole-dipole

interatomic force constants

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short ranged +
dipole-dipole

- remove the singularities in D(q)
- do FFT’s (# R’s = # q’s - the shorter the range, the coarser the grid)
- store information
- interpolate D(q) on any finer mesh you may need for practical purposes (pad Φ with 0’s and do FFT^{-1}: # q’s = # R’s)
- calculate phonon bands

DFPT: the main features

- response functions calculated in terms of response orbitals, $\{\phi'_v\}$

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- non-periodic perturbations: OK

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- calculate the response to the perturbation you want, only
- non-local perturbations: OK
- non-periodic perturbations: OK
- macroscopic electric fields: OK

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Piezoelectric Properties of III-V Semiconductors from First-Principles Linear-Response Theory

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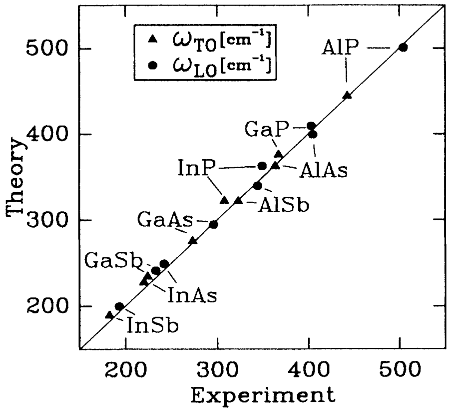
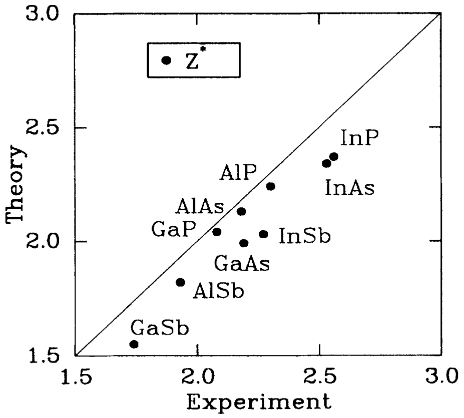
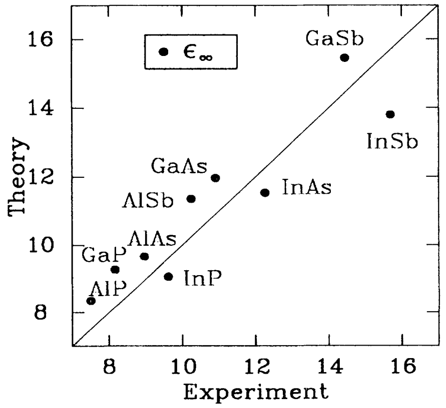
(Received 7 November 1988)

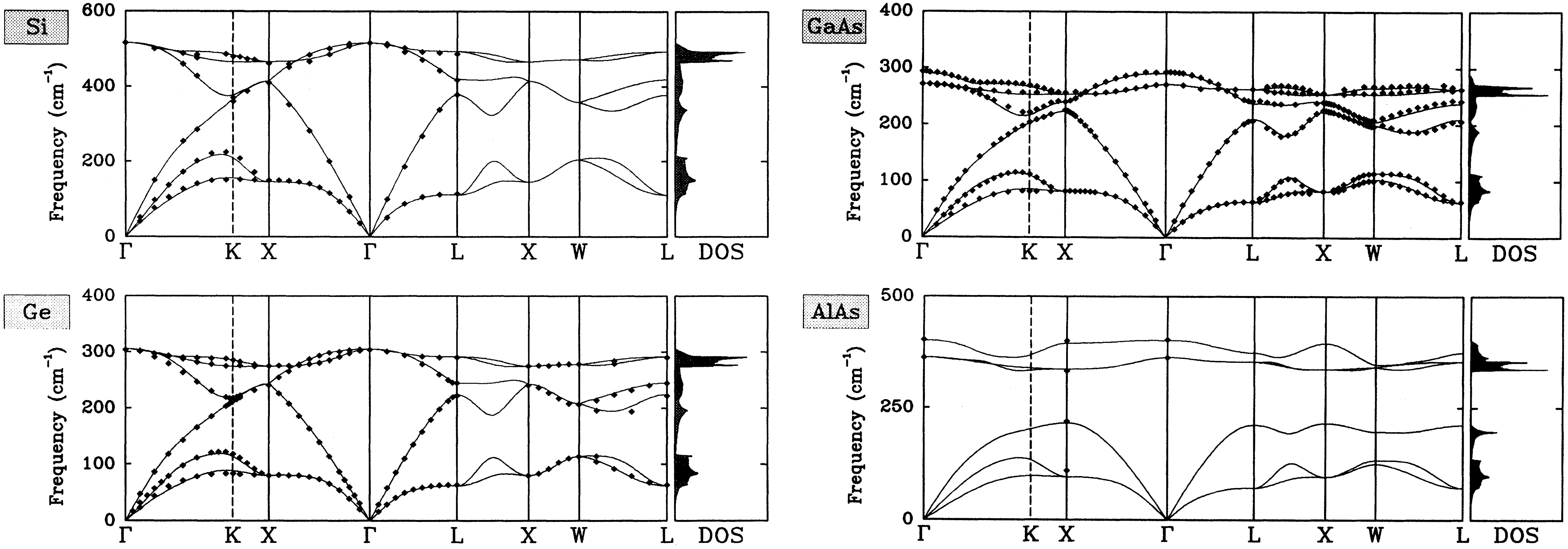






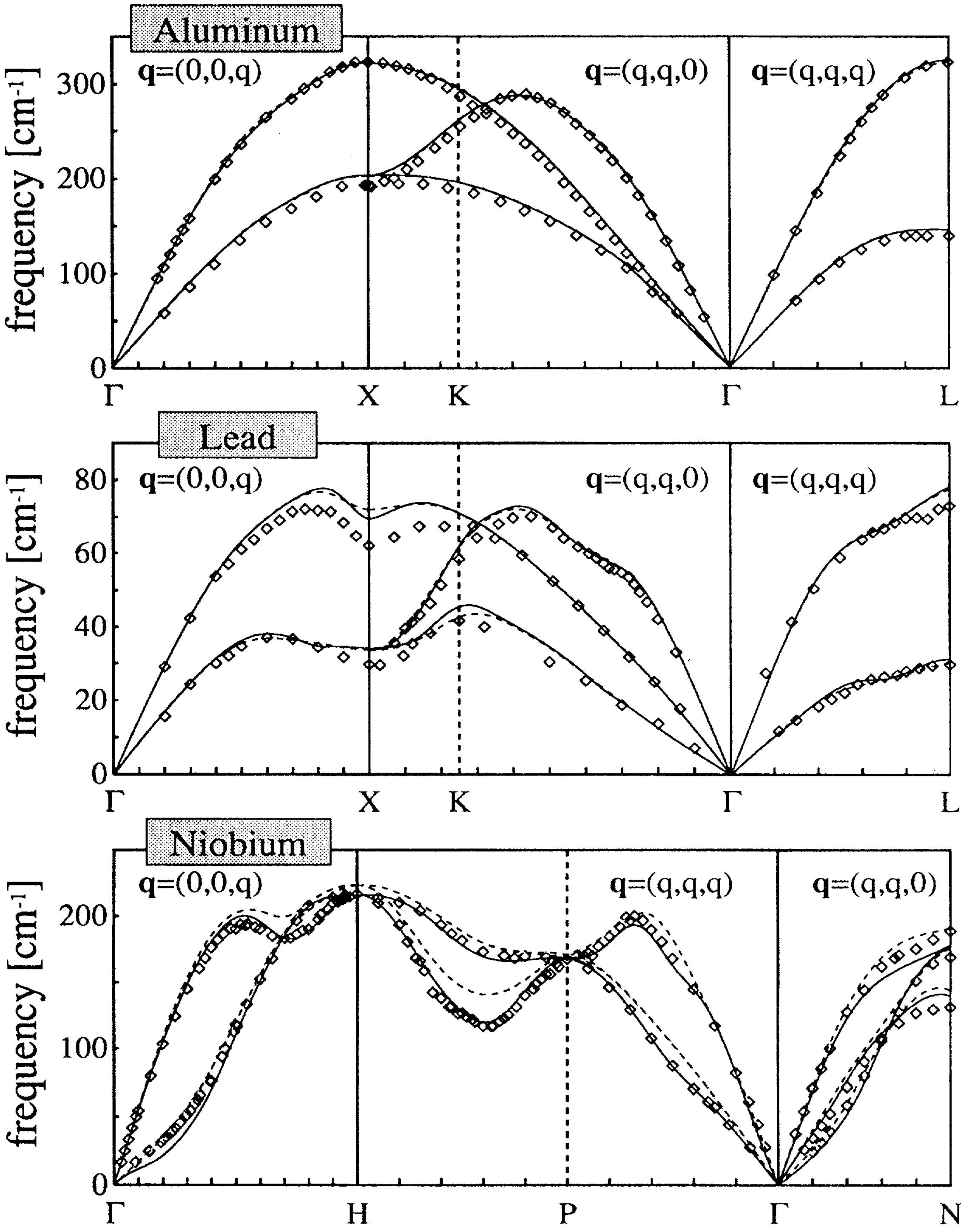
$\bar{\gamma}_{14}$	P	As	Sb
Al	0.11 (· · ·)	−0.03 (· · ·)	−0.13 (−0.16)
Ga	−0.18 (−0.18)	−0.35 (−0.32)	−0.40 (−0.39)
In	0.12 (|0.09|)	−0.08 (−0.10)	−0.20 (−0.18)

phonons from DFPT



P. Giannozzi, S. de Gironcoli, P. Pavone, and SB, Phys. Rev. B **43**, 7231 (1991)

DFPT phonons in metals



Stefano de Gironcoli,
Phys. Rev. B **51**, 6773 (1995)

applications done so far

- Dielectric properties
- Piezoelectric properties
- Elastic properties
- Phonon in crystals and alloys
- Phonon at surfaces, interfaces, super-lattices, and nano-structures
- Raman and infrared activities
- Anharmonic couplings and vibrational line widths

- Mode softening and structural transitions
- Electron-phonon interaction and superconductivity
- Thermal expansion
- Isotopic effects on structural and dynamical properties
- Thermo-elasticity and other thermal properties of minerals
- …

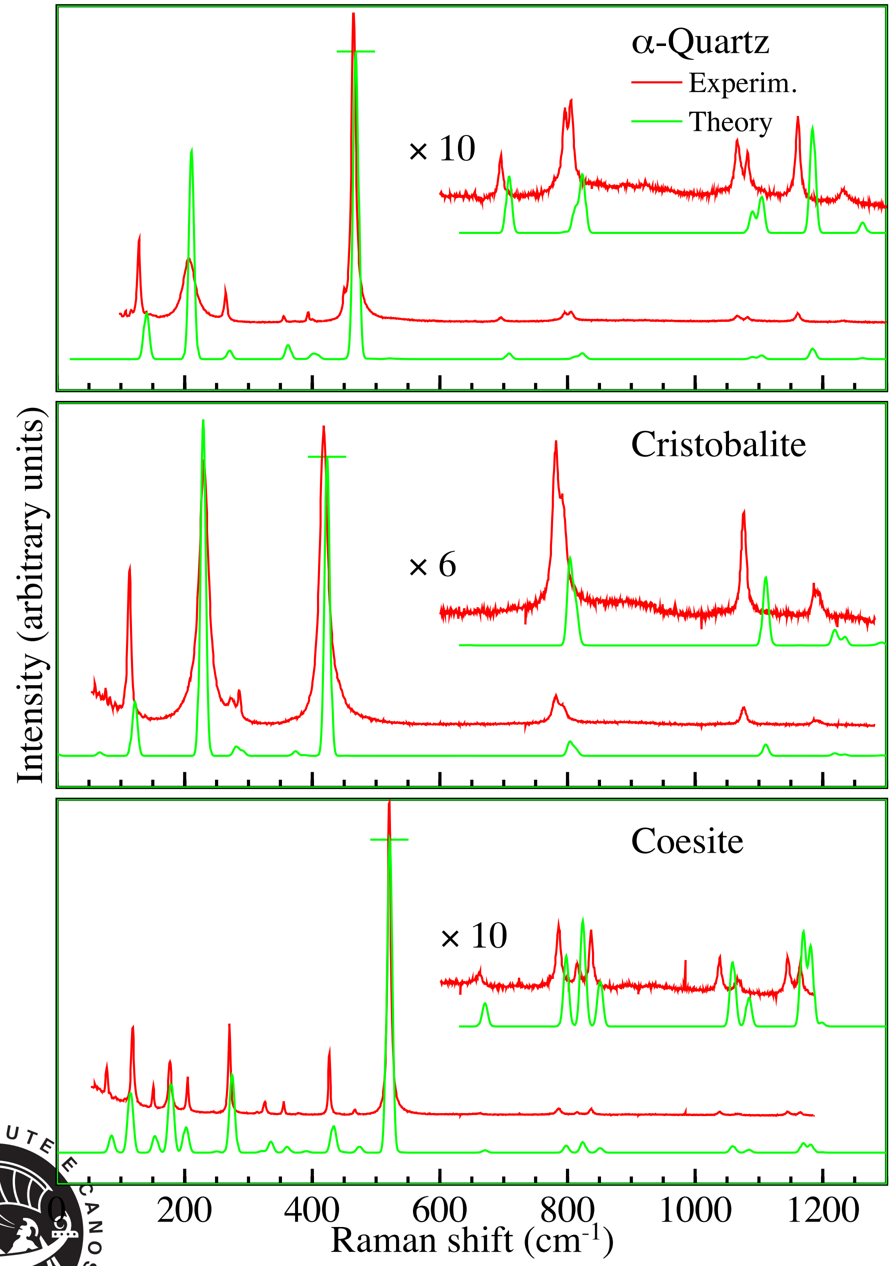
SB, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, *Phonons and related crystal properties from density-functional perturbation theory*, Rev. Mod. Phys. **73**, 515 (2001)

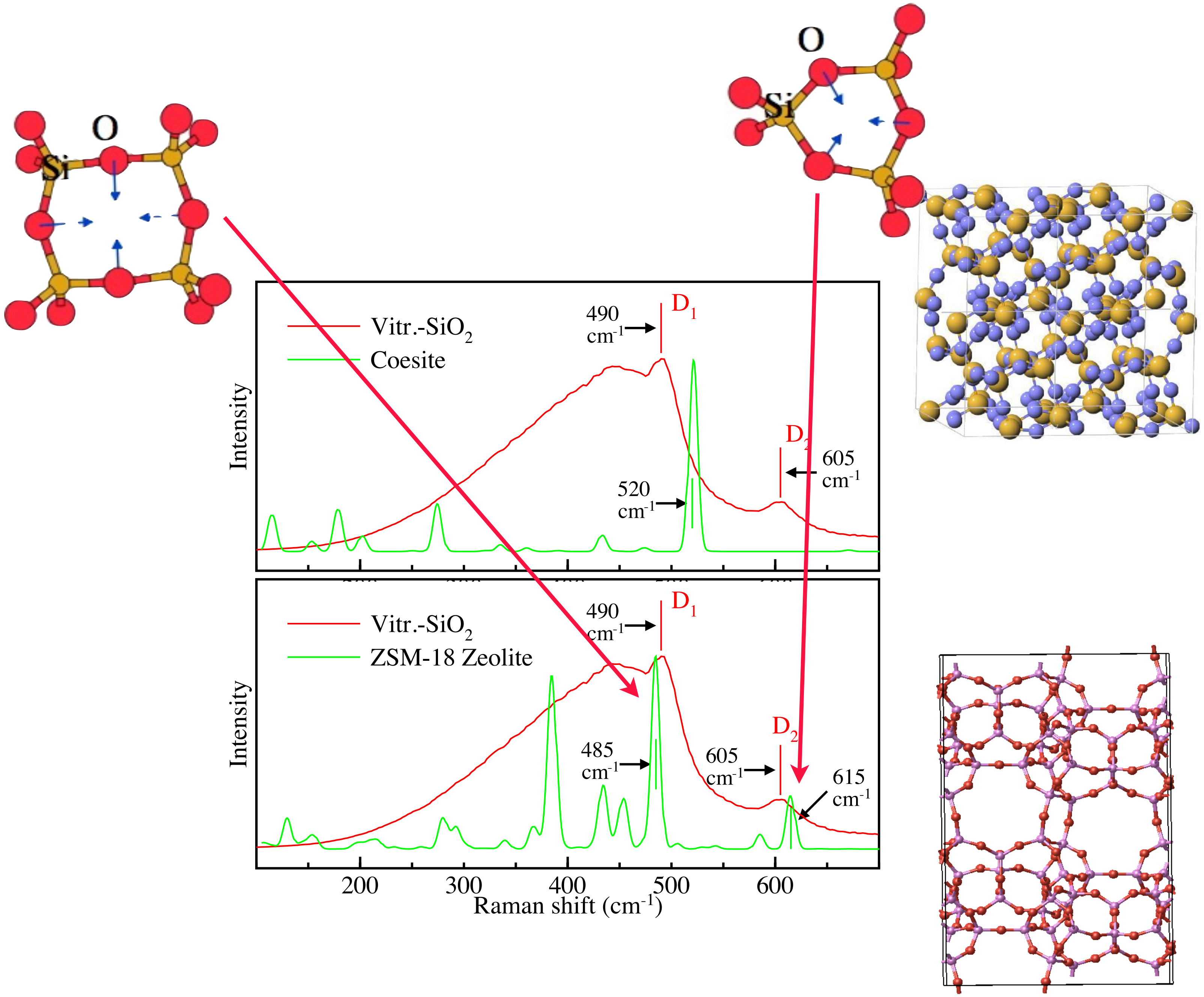
a sampler of more recent applications

VOLUME 90, NUMBER 3 PHYSICAL REVIEW LETTERS week ending 24 JANUARY 2003

First-Principles Calculation of Vibrational Raman Spectra in Large Systems: Signature of Small Rings in Crystalline SiO$_2$

Michele Lazzeri and Francesco Mauri





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J|A|C|S

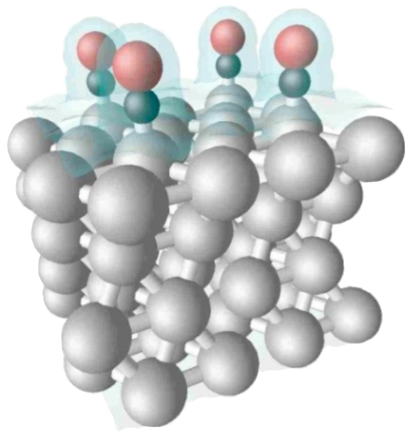
ARTICLES

Published on Web 08/17/2007

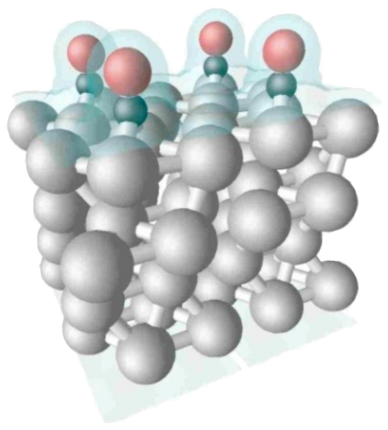
Vibrational Recognition of Adsorption Sites for CO on Platinum and Platinum−Ruthenium Surfaces

Ismaila Dabo,*,† Andrzej Wieckowski,‡ and Nicola Marzari†

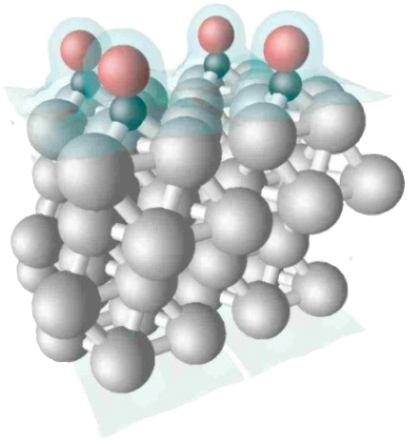
11046 J. AM. CHEM. SOC. ■ VOL. 129, NO. 36, 2007



atop (CO@Pt_1)
E_{DFT} = +0.10 eV
ν_{DFT} = 2050 cm^{-1}
ν_{exp} = 2070 cm^{-1}



bridge (CO@Pt_2)
E_{DFT} = +0.03 eV
ν_{DFT} = 1845 cm^{-1}
ν_{exp} = 1830 cm^{-1}



fcc (CO@Pt_3)
E_{DFT} = 0 eV
ν_{DFT} = 1743 cm^{-1}
ν_{exp} = 1780 cm^{-1}

↑ expt

DFT ↑

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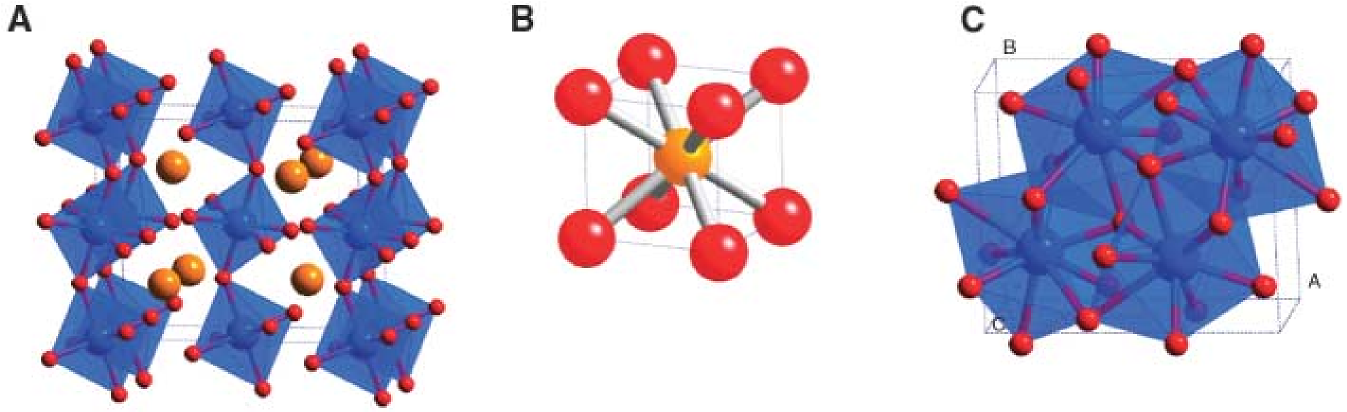
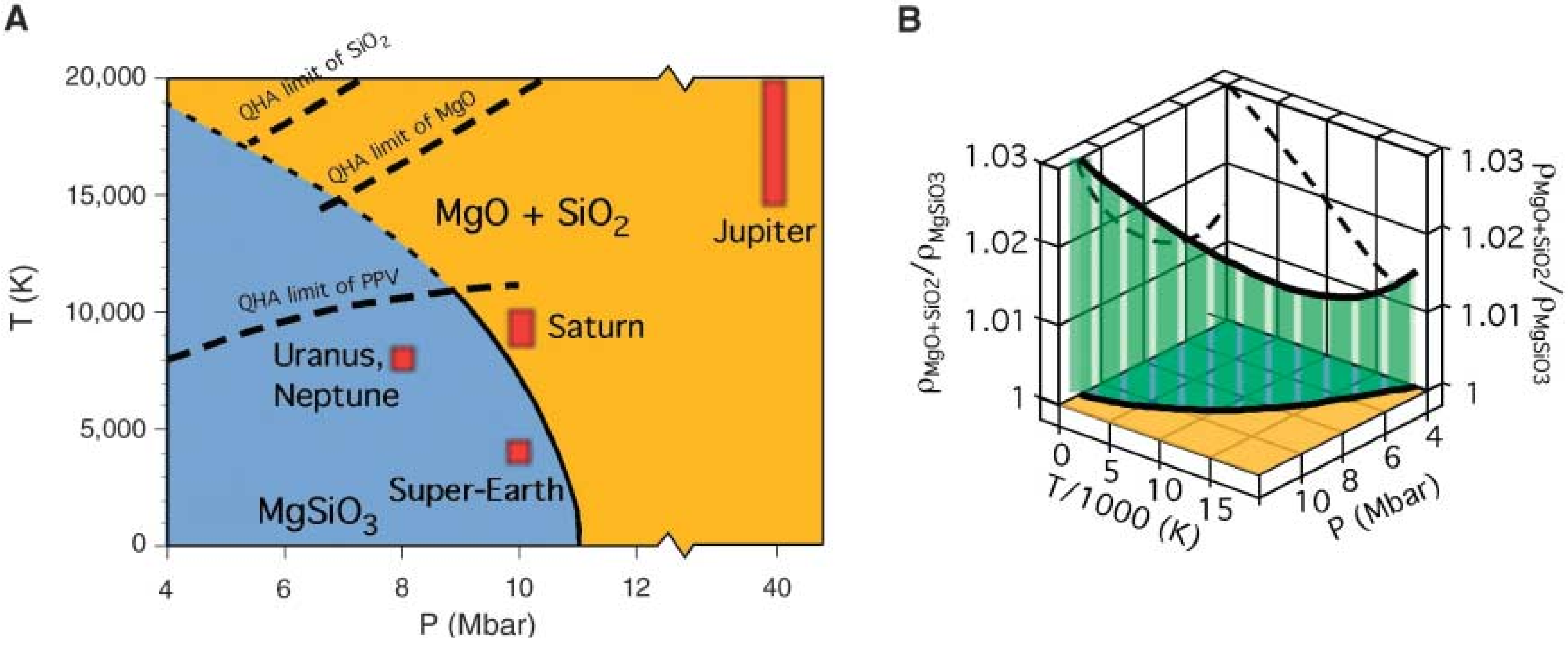
Dissociation of $MgSiO_3$ in the Cores of Gas Giants and Terrestrial Exoplanets

Koichiro Umemoto,[1] Renata M. Wentzcovitch,[1]* Philip B. Allen[2]

www.sciencemag.org SCIENCE VOL 311 17 FEBRUARY 2006 983





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PRL **100,** 257001 (2008) PHYSICAL REVIEW LETTERS week ending 27 JUNE 2008

Ab Initio Description of High-Temperature Superconductivity in Dense Molecular Hydrogen

P. Cudazzo,[1] G. Profeta,[1] A. Sanna,[2,3] A. Floris,[3] A. Continenza,[1] S. Massidda,[2] and E. K. U. Gross[3]

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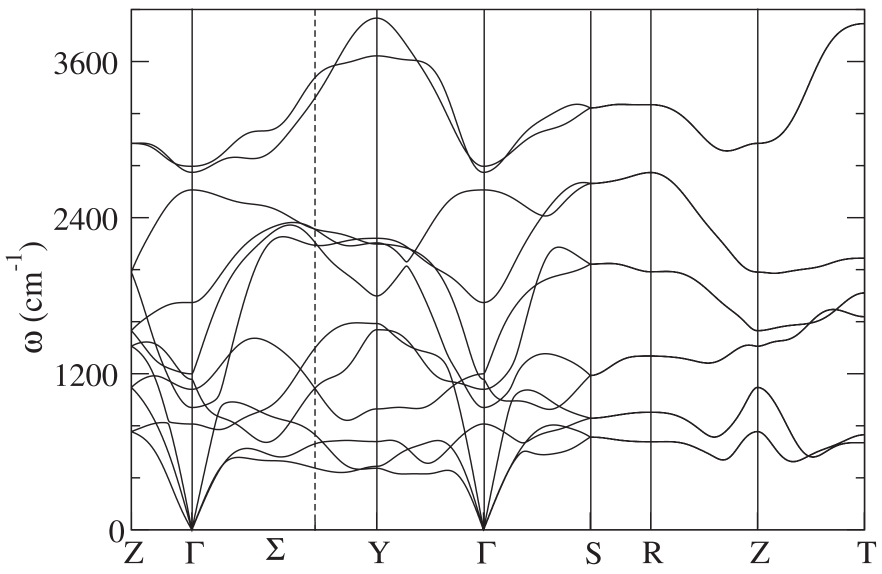
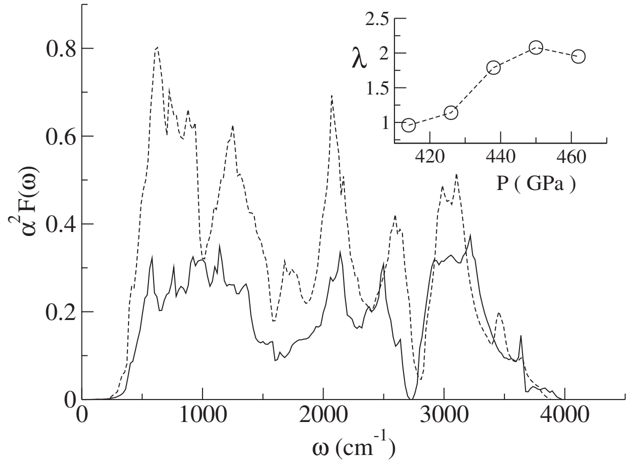
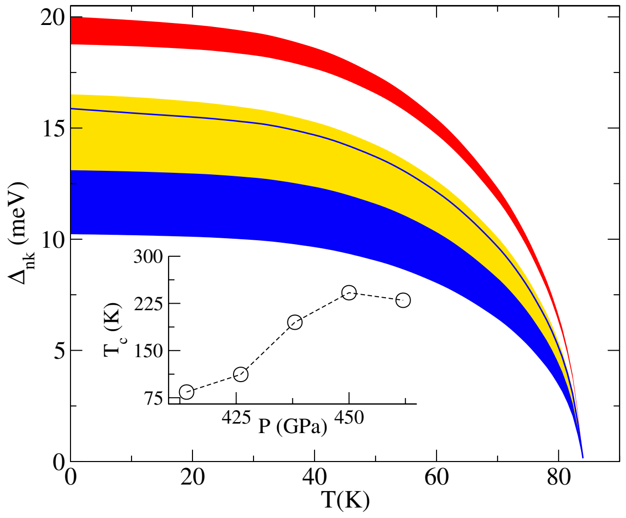
[2]*SLACS-INFM/CNR—Dipartimento di Fisica, Università degli Studi di Cagliari, I-09124 Monserrato (CA), Italy*
[3]*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*

(Received 7 December 2007; published 23 June 2008; corrected 27 June 2008)

414 GPa







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PRL **100,** 257001 (2008) PHYSICAL REVIEW LETTERS week ending 27 JUNE 2008

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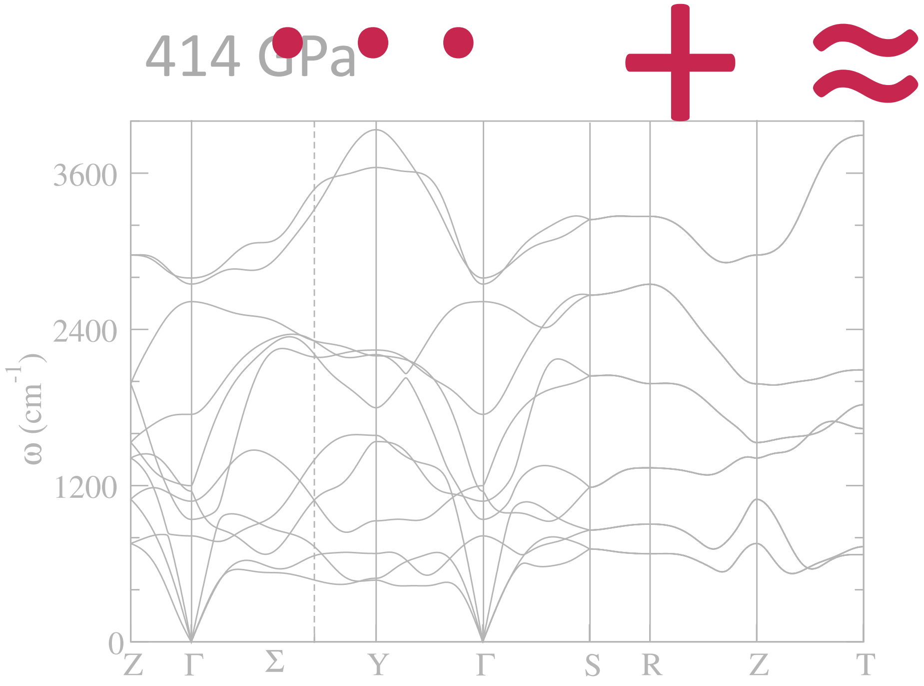
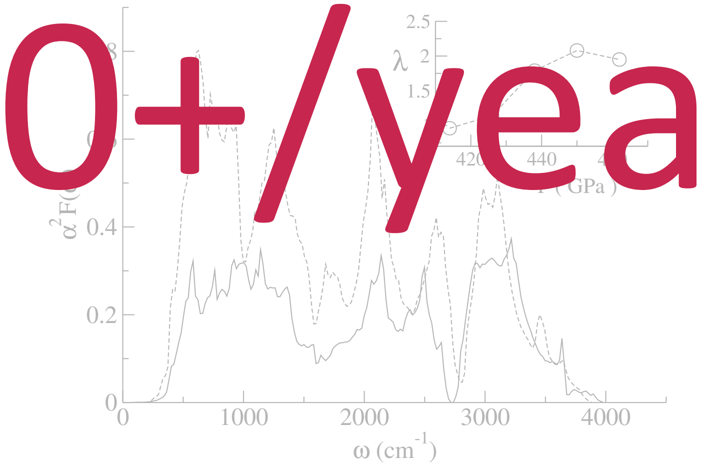
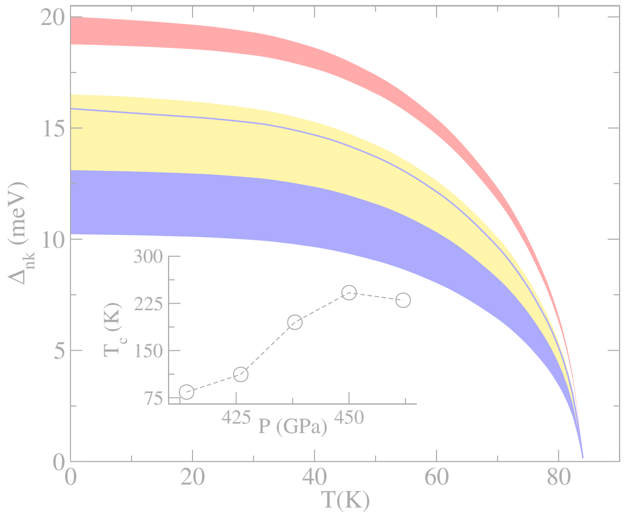
• • • + ≈500+/year







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