Density-functional perturbation theory

forces, response functions, phonons, and all that

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Energy derivatives

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

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- (static) response functions

  elastic constants

  dielectric tensor

  piezoelectric tensor

  Born effective charges

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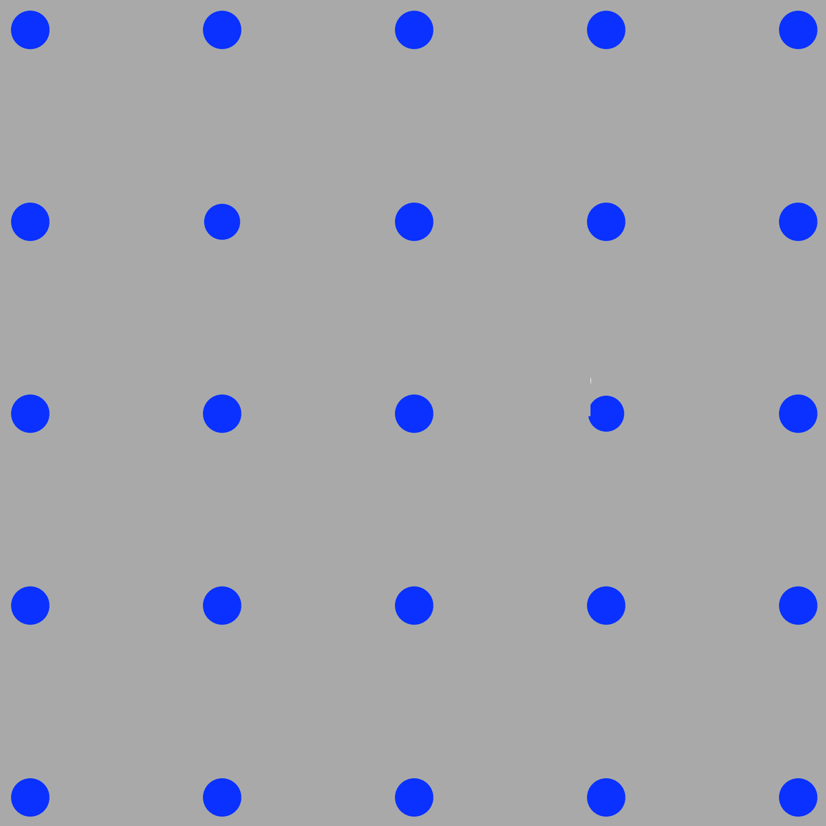
- vibrational modes in the adiabatic approximaton

Lattice dynamics



$$\begin{aligned} V(\mathbf{r}) &= V_0(\mathbf{r}) \\ &= \sum_{\mathbf{R}} v(\mathbf{r}-\mathbf{R}) \\ E &= E_0 \end{aligned}$$

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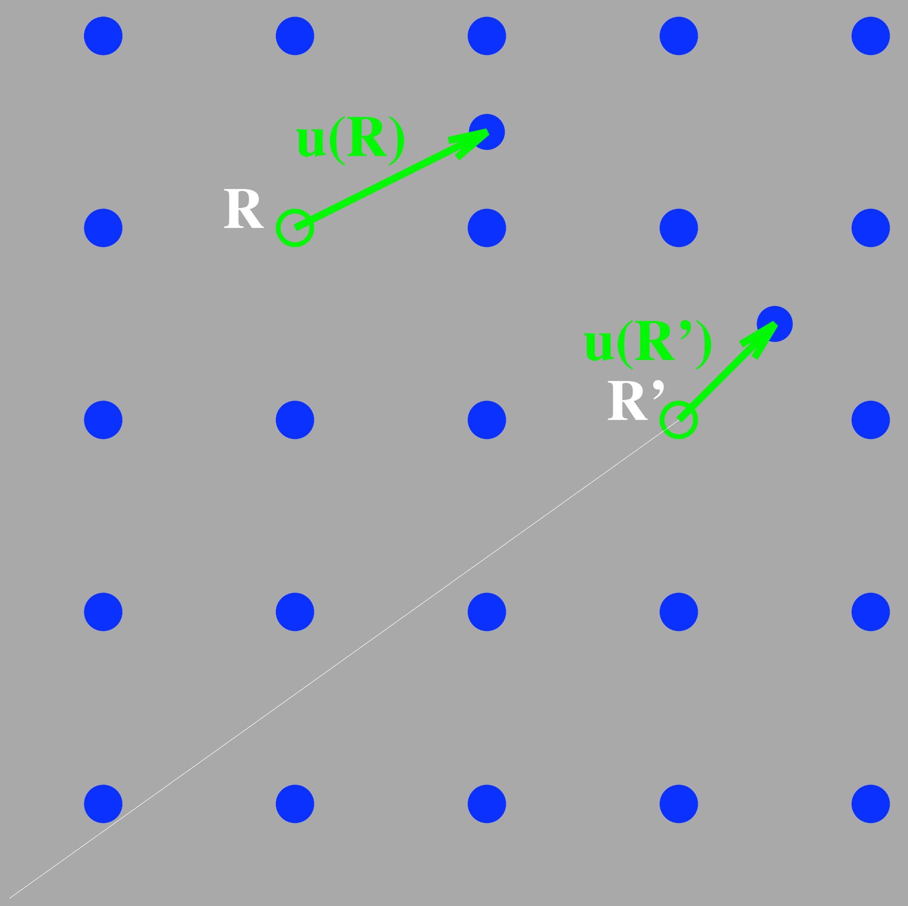

$$
\begin{aligned}
V(\mathbf{r}) &= V_0(\mathbf{r}) \\
&\quad + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} \\
E &= E_0 \\
&\quad + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}') \\
&\quad + \cdots
\end{aligned}
$$

Energy derivatives & perturbation theory

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The Hellmann-Feynman theorem

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

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

DFPT II: the equations

DFT

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

More about perturbation theory

$$H = H_0 + V'$$

$$\begin{cases} \phi_v^0 \longrightarrow \phi_v^0 + \phi_v' \\ \epsilon_v^0 \longrightarrow \epsilon_v^0 + \epsilon_v' \end{cases}$$

More about perturbation theory

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$$\phi_v' = \sum_{u \neq v} \phi_u^0 \frac{\langle \phi_u^0 | V' | \phi_v^0 \rangle}{\epsilon_v^0 - \epsilon_u^0}$$

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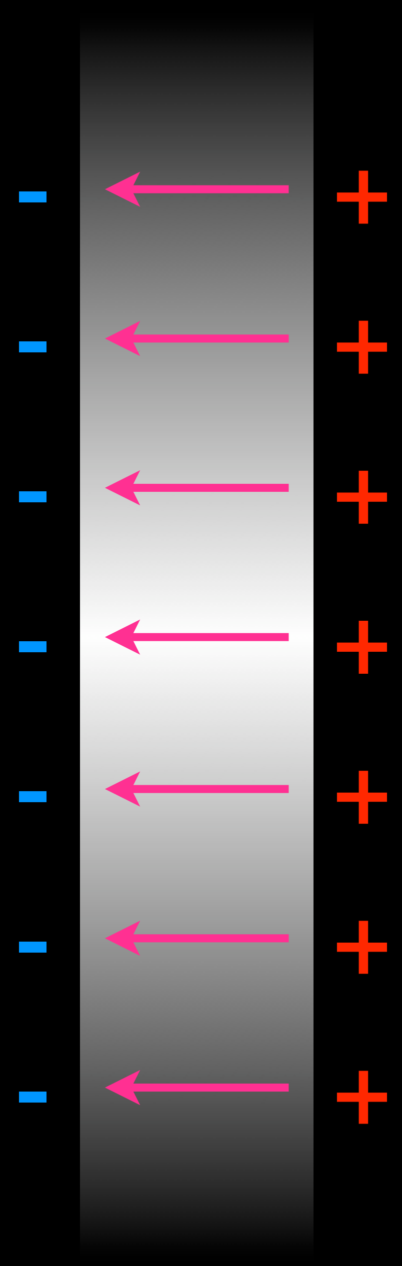
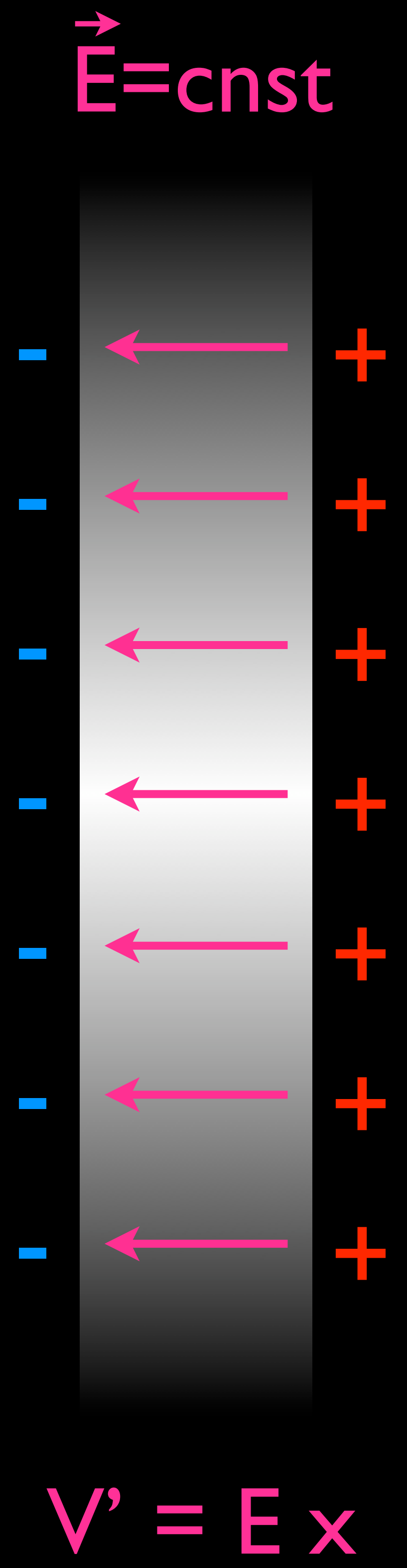
Macroscopic electric fields

$\vec{E}$=cnst



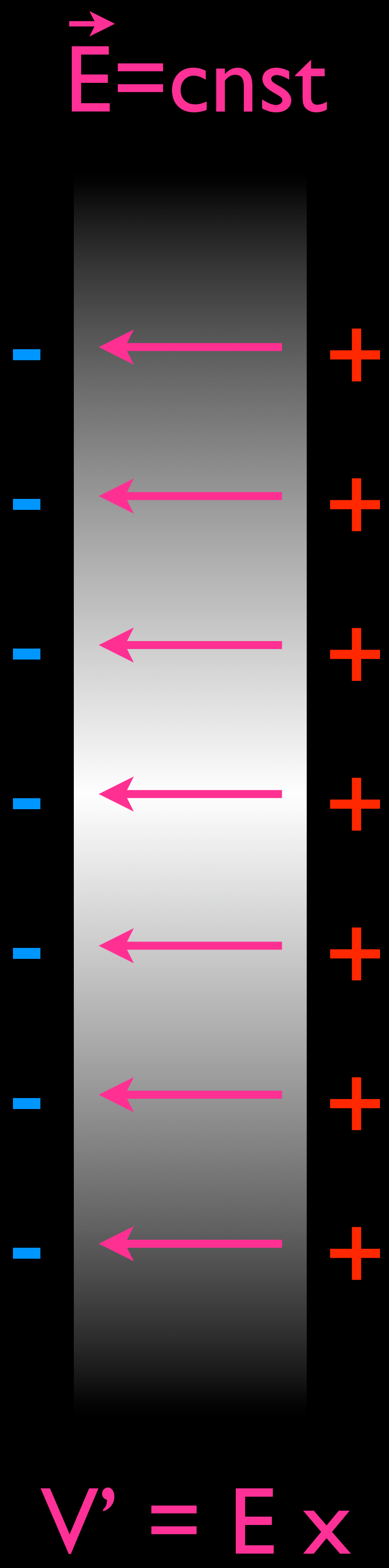
$V' = E\,x$

Macroscopic electric fields



$$\phi_v^0(\mathbf{r}) \quad = \quad \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r})$$

Macroscopic electric fields



$$
\begin{aligned}
\phi_v^0(\mathbf{r}) &= \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r}) \\
V'(\mathbf{r})\phi_v^0(\mathbf{r}) &= ??
\end{aligned}
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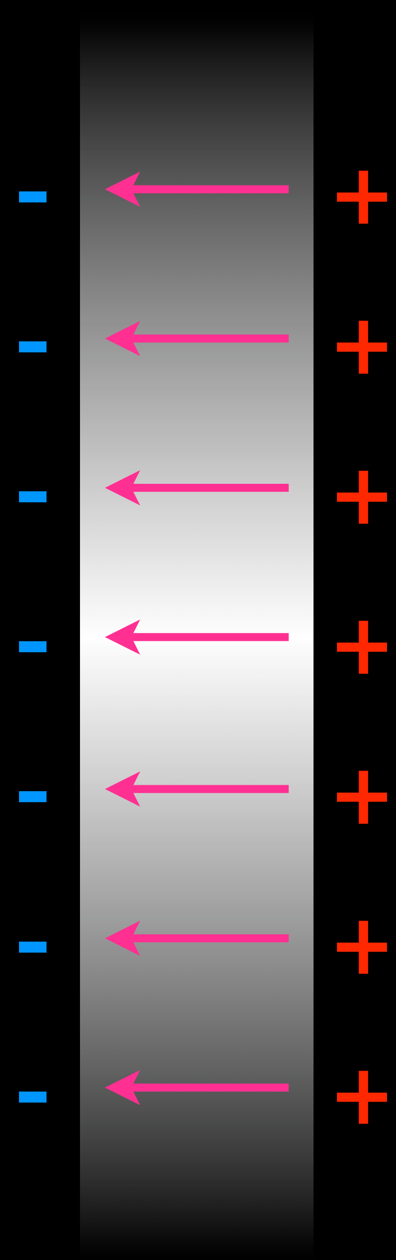

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$$\langle \phi_v^0 | x | \phi_u^0 \rangle = \frac{\langle \phi_v^0 | [H, x] | \phi_u^0 \rangle}{\epsilon_v^0 - \epsilon_u^0} \qquad [H, x] = -\frac{\hbar^2}{m}\frac{\partial}{\partial x}$$

Macroscopic electric fields

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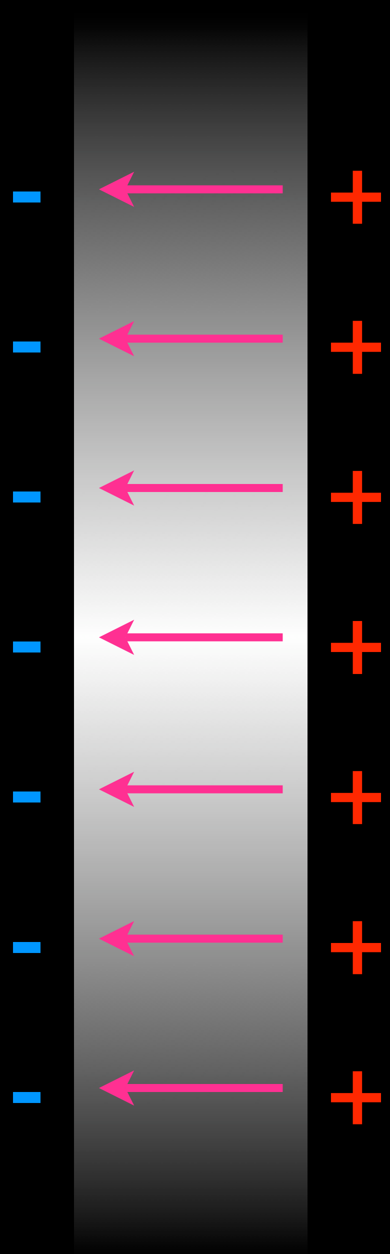

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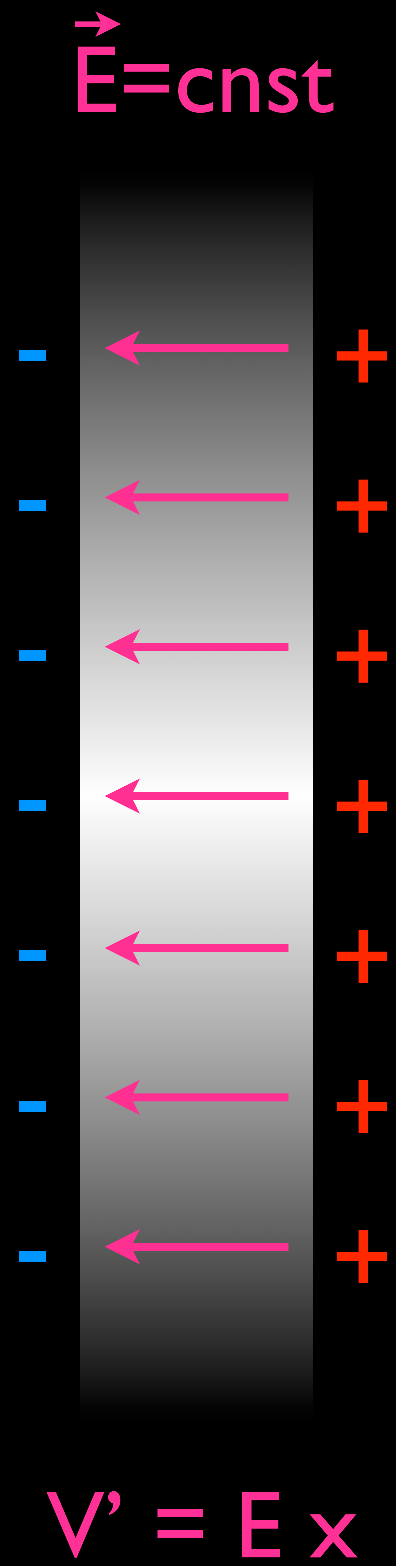
$$-P_c V' \phi_v^0 = -E \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle$$

Macroscopic electric fields



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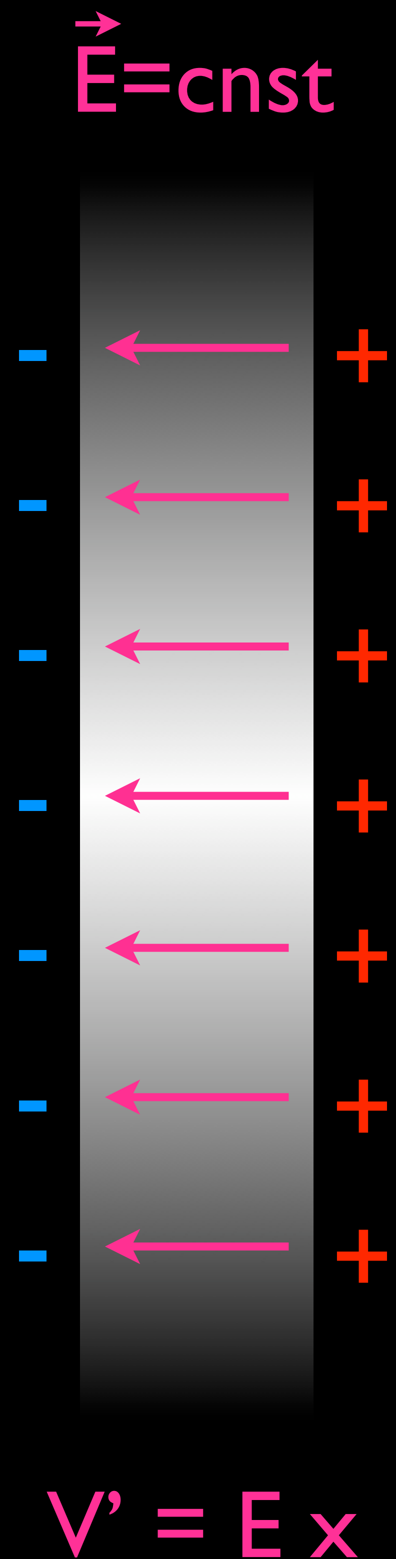
$$\begin{aligned} -P_c V' \phi_v^0 &= -E \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle \\ &= -E \sum_c \phi_c^0 \frac{\langle \phi_c^0 | [H_0, x] | \phi_v^0 \rangle}{\epsilon_c^0 - \epsilon_v^0} \equiv \psi_v' \end{aligned}$$

Macroscopic electric fields



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$$

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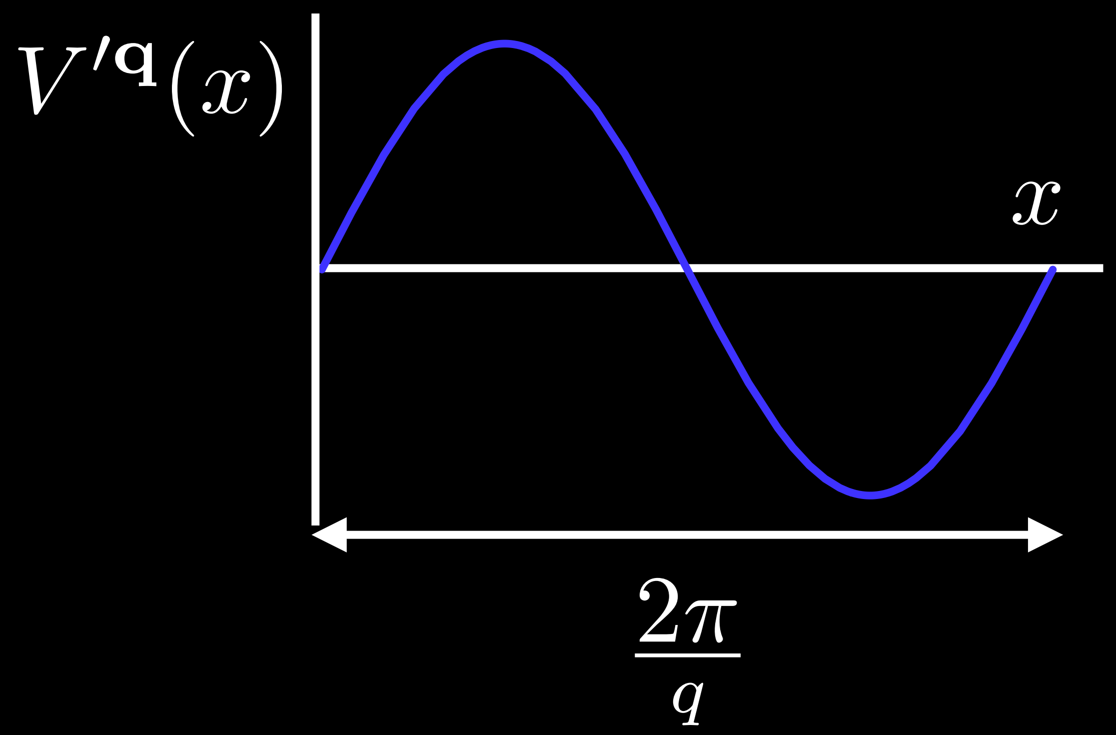
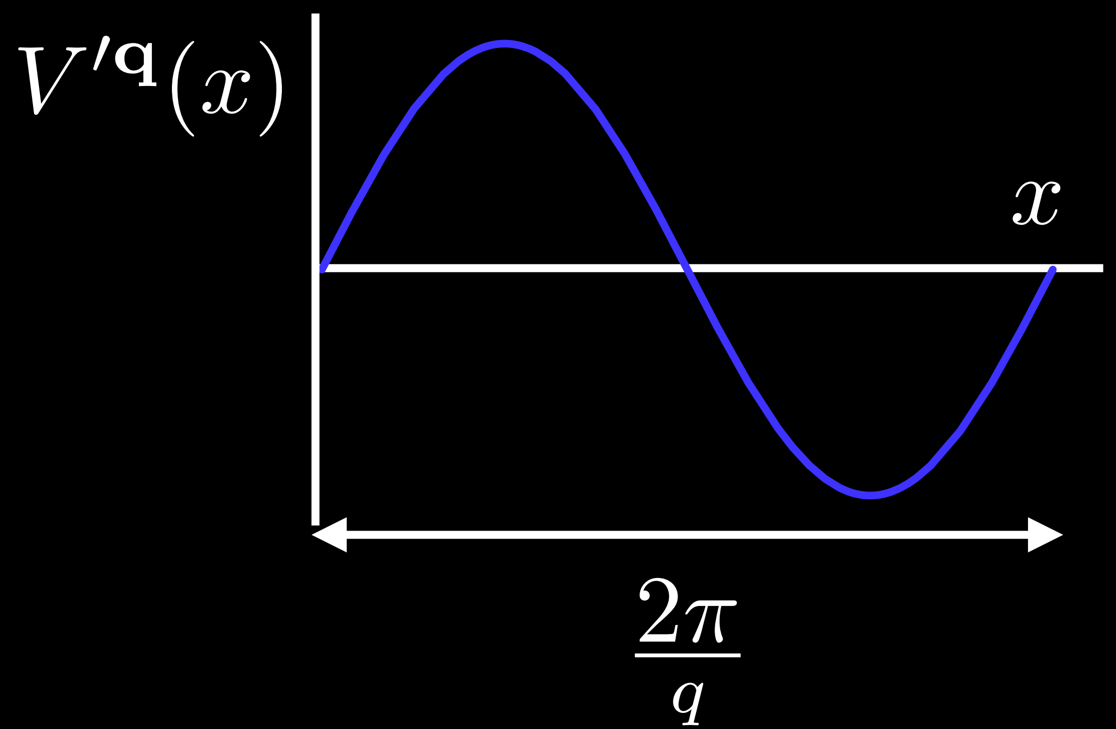
DFPT RHS

Monochromatic perturbations

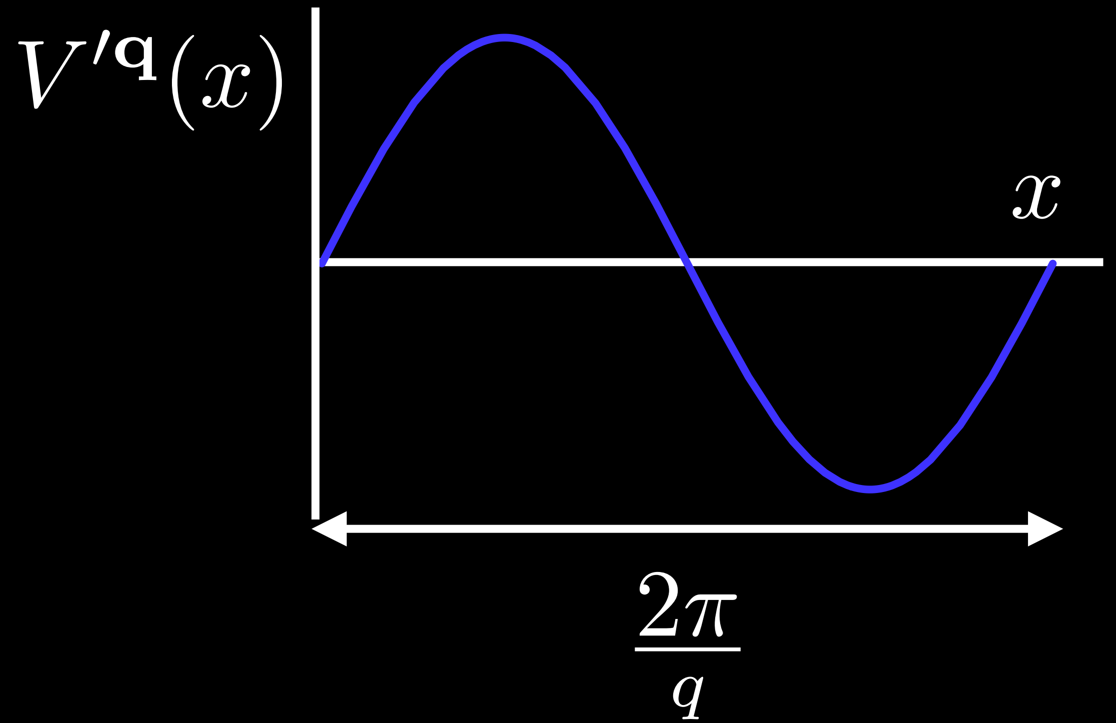


Monochromatic perturbations



$$\left(H_0 + \alpha P_v^{\mathbf{k}+\mathbf{q}} - \epsilon_v^{\mathbf{k}}\right)\phi_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r}) = -P_c V'^{\mathbf{q}} \phi_v^{\mathbf{k}}(\mathbf{r})$$

Monochromatic perturbations



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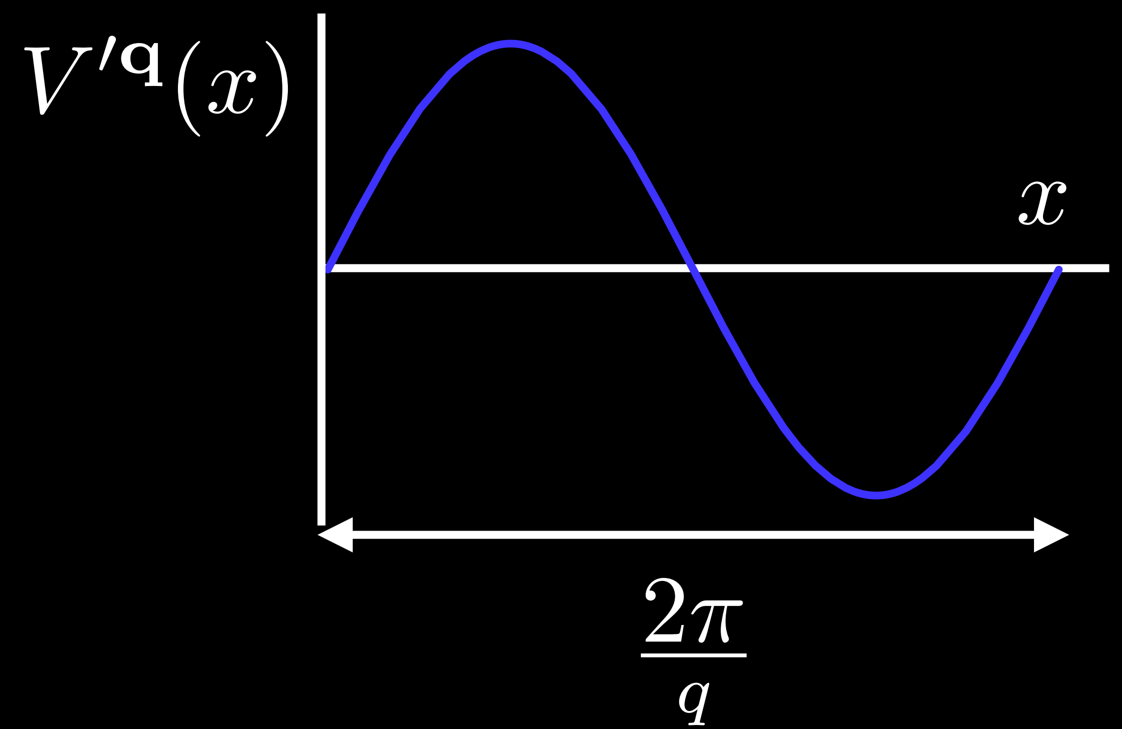

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Phonons in polar materials

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

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

Interatomic force constants

$$\Phi(\mathbf{R}-\mathbf{R}') = -\frac{\partial^2 E}{\partial \mathbf{u}_{\mathbf{R}} \partial \mathbf{u}_{\mathbf{R}'}}$$

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Short ranged + dipole-dipole

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  # **q**'s = # **R**'s

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Short ranged +
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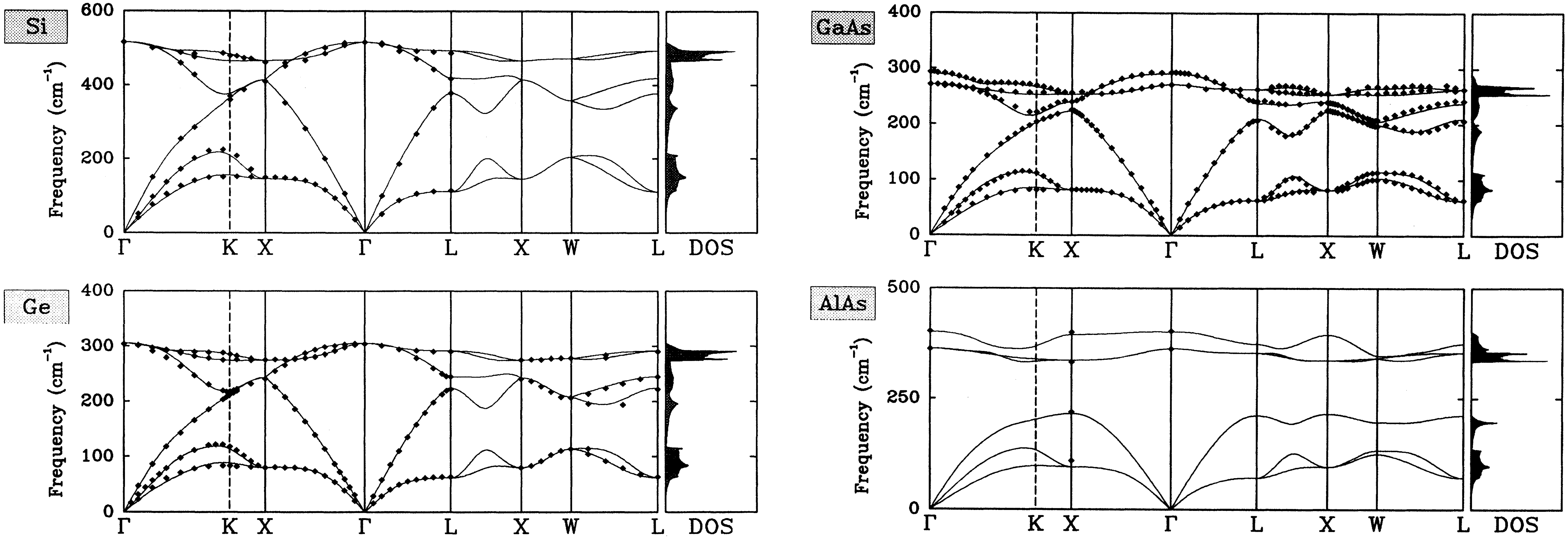
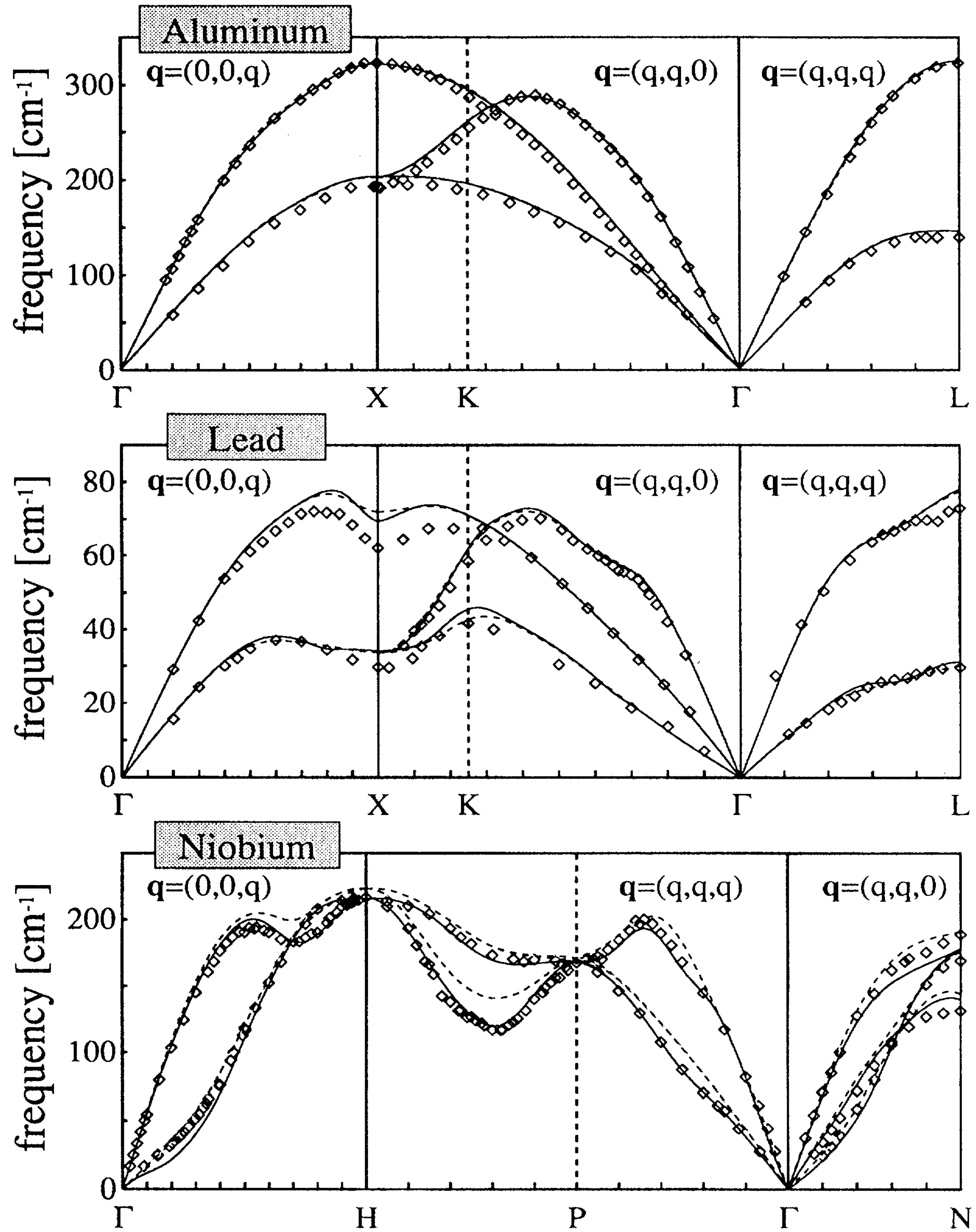
- Store information
- Interpolate phonon bands

Phonons from DFPT



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

Phonons from DFPT



S. 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
- …

S. Baroni, 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)

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