Phonons and related quantities from first principles

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Acknowledgments

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Vibrational spectroscopy

- Study of vibrational modes (*phonons* in crystals, *normal modes* in molecules) is a powerful tool in materials characterization.

- Vibrational spectroscopy is a sensitive probe of the atomic structure, of the chemical bonding and thus of the electronic structure.

- Most frequently used techniques:
  - *Neutron scattering* (difficult; the entire Brillouin zone is accessible)
  - *Infrared (IR) spectroscopy* (simple; only some modes are observable)
  - *Raman spectroscopy* (simple; only some modes are observable)

- Theoretical calculation of vibrational properties from first-principles is very useful to analyze the experimental spectra and investigate thermo-mechanical and transport properties.
Normal mode frequencies, $\omega$, and eigenvectors, $v$, are determined by the secular equation

$$\sum_{j \beta} D_{i \alpha, j \beta}(q) \ v_{j \beta}(q) = \omega^2(q) \ v_{j \beta}(q)$$

where

$$D_{i \alpha, j \beta}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_L \frac{\partial^2 E_{tot}}{\partial u_{i \alpha}(M) \partial u_{j \beta}(L)} e^{i q \cdot (R_L - R_M)}$$

$$= \frac{1}{\sqrt{M_i M_j}} \frac{1}{N_c} \frac{\partial^2 E_{tot}}{\partial u_{i \alpha}^*(q) \partial u_{j \beta}(q)}$$

$$u_{i \alpha}(L) = \text{displacement of the } i^{th} \text{ atom in the } L^{th} \text{ unit cell in the } \alpha \text{ direction} \ (\alpha=x,y,z)$$

$$u_{i \alpha}(L) = u_{i \alpha}(q) e^{i q \cdot R_L}$$

This matrix $\tilde{C}_{i \alpha, j \beta}(q)$ can be calculated from the linear response and diagonalized to get phonons at $q$. 

**Phonons**
Phonons

\( e^{i q R} \)

\( q = 0 \)

\( q = \frac{2\pi}{a} \frac{1}{2} \)

\( q = \frac{2\pi \sqrt{2}}{a} \frac{3}{4} \)
Real-space interatomic force constants

\[
C_{i\alpha,j\beta}(R_L) = \frac{\partial^2 E_{tot}}{\partial u_{i\alpha}(0) \partial u_{j\beta}(L)} = \frac{(2\pi)^3}{\Omega} \int_{BZ} \tilde{C}_{i\alpha,j\beta}(q)e^{-i\mathbf{q} \cdot R_L} \, dq
\]

\[
\approx \frac{1}{N_q} \sum_{q_s \in \text{grid}(l \times m \times n)} \tilde{C}_{i\alpha,j\beta}(q_s)e^{-i\mathbf{q_s} \cdot R_L}
\]

(sum on a uniform grid of q-points)
Fourier interpolation

Discrete Fourier transform

\[
\tilde{C}_{i\alpha, j\beta}(q_s) \quad \text{on a uniform grid (l x m x n)}
\]

\[
\frac{1}{N_q} \sum_n \tilde{C}_{i\alpha, j\beta}(q_n) e^{-i q_n \cdot R_L}
\]

\[
C_{i\alpha, j\beta}(R_L) \quad \text{on a supercell (l x m x n)}
\]

Fourier interpolation

\[
C_{i\alpha, j\beta}(R_L) \quad \text{on a supercell (l x m x n)}
\]

\[
\sum_L C_{i\alpha, j\beta}(R_L) e^{i q \cdot R_L}
\]

\[
\tilde{C}_{i\alpha, j\beta}(q) \quad \text{any given q (not necessarily belonging to the original grid in reciprocal space)}
\]
Kohn anomalies in metals

Sudden softening of the frequencies of certain phonons with a wavevector connecting two points of the Fermi surface as a result of abrupt change of the electronic screening of the atomic vibrations.

Polar materials

In the long-wavelength limit the long-range character of the Coulomb forces give rise to macroscopic electric fields that must be treated with care:

\[ V(r) = e \mathbf{E} \cdot \mathbf{r} \]

(not lattice periodic)

Phonons in cubic diatomic crystals
Polar materials

Consider a cubic polar material with two atoms per unit cell. The total energy of the system as a function of the optical phonon displacement and the electric field is (see, e.g., Born and Huang 1954):

\[
E(u, E) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \epsilon_\infty E^2 - eZ^* u \cdot E
\]

\[
\begin{align*}
\epsilon_\infty &= \text{Electronic (i.e. clamped nuclei) dielectric constant} \\
Z^* &= \text{Born effective charge} \\
M &= \text{Reduced mass}
\end{align*}
\]

\[
F = - \frac{\partial E}{\partial u} = - M \omega_0^2 u + eZ^* E
\]

\[
D = - \frac{4\pi}{\Omega} \frac{\partial E}{\partial E} = - \frac{4\pi}{\Omega} eZ^* u + \epsilon_\infty E
\]

In absence of external charges:

\[
\nabla \times E \sim iq \times E = 0
\]

\[
\nabla \cdot D \sim iq \cdot (E + 4\pi P) = 0
\]

\[
E = -4\pi \hat{q} \cdot (\hat{q} \cdot P)
\]
Polar materials

• Transverse modes:

\[ u \perp q \quad \rightarrow \quad E = 0 \]

\[ F = -\frac{\partial E}{\partial u} = -M\omega_0^2 u + eZ^*E \]

\[ \omega_{TO} = \omega_0 \]

• Longitudinal modes:

\[ u \parallel q \quad \rightarrow \quad D = 0 \]

\[ D = -\frac{4\pi}{\Omega} eZ^*u + \varepsilon_{\infty}E = 0 \]

\[ F = -\frac{\partial E}{\partial u} = -M\omega_0^2 u + eZ^*E \]

\[ \omega_{LO} = \sqrt{\omega_0^2 + \frac{4\pi e^2 Z^*2}{\Omega\varepsilon_{\infty}M}} \]

This result can be generalized to crystals of arbitrary symmetry
Polar materials

From the previous equations, the macroscopic electric polarization:

\[
P = - \frac{1}{\Omega} \sum_s e Z_s^* u_s + \frac{\epsilon_\infty - 1}{4\pi} E
\]

\[
e Z_{s\alpha\beta}^* = \Omega \frac{\partial P_\alpha}{\partial u_{s\beta}(q = 0)} \bigg|_{E=0} = -\frac{\partial^2 E_{tot}}{\partial E_\alpha \partial u_{s\beta}} = \frac{\partial F_{s\beta}}{\partial E_\alpha}
\]

\[
\epsilon_\infty^{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \frac{\partial P_\alpha}{\partial E_\beta} \bigg|_{u(q=0)=0} = \delta_{\alpha\beta} - \frac{4\pi}{\Omega} \frac{\partial^2 E_{tot}}{\partial E_\alpha \partial E_\beta}
\]

In the long-wavelength limit the dynamical matrix is the sum of an analytic and a non-analytic contributions:

\[
\tilde{C}_{i\alpha,j\beta} = \tilde{C}_{i\alpha,j\beta}^{an} + \tilde{C}_{i\alpha,j\beta}^{ma}
\]

\[
\tilde{C}_{i\alpha,j\beta}^{ma} = \frac{4\pi}{\Omega} \epsilon^2 \frac{(q \cdot Z_i^*)_\alpha (q \cdot Z_j^*)_\beta}{q \cdot \epsilon_\infty \cdot q}
\]
Acoustic sum rules

The interatomic force constants and the Born effective charges must satisfy sum rules related to the translational invariance of the system:

\[
\sum_{jL} C_{i\alpha,j\beta}(R_L) = 0
\]

\[
\sum_i Z_{i\alpha\beta}^* = 0
\]

Because of numerical inaccuracies related to

- Insufficiently accurate scf thresholds.
- XC energy computed in real space (more problematic for GGA than in LDA. For US pseudopotentials it could require large \textit{ecutrho}).
- k point sampling not accurate enough (in particular \(Z^*\) and \(\epsilon\) require a very dense k-point sampling).

these rules are not exactly satisfied and must be imposed.
The frequency of infrared radiation is of the same order as the vibrational frequencies of crystal lattices. This radiation can couple with the oscillating dipole moments in the crystal and transfer energy. The infrared intensity of a mode $\nu$ is:

$$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z_{s\alpha\beta}^{*} v_{s\beta}(\nu) \right|^2$$

- Born effective charges
- Phonon displacement
Raman intensities

Raman scattering (Stokes process):

\[ \omega_i, e_i \rightarrow \omega_s, e_s \rightarrow \omega_{ph} \quad \text{(optical phonon near } q=0) \]

Non resonant Raman intensity:

\[ I_{Stokes}(\nu) \propto \left| e_i \cdot A^\nu \cdot e_s \right|^2 \frac{1}{\omega_\nu} (n_\nu + 1) \]

\[ A^\nu_{lm} = \sum_{i\gamma} \frac{\partial^3 E}{\partial E_\alpha \partial E_\beta \partial u_{i\gamma}} \frac{v^\nu_{i\gamma}}{\sqrt{M_i}} \]

Raman susceptibility can be computed using second order response to an electric field [see M. Lazzeri and F. Mauri, PRL 90, 36401 (2003)]
Other methods

Common methods, based on density-functional theory, to calculate vibrational modes (via interatomic force constants).

- *Density-functional perturbation theory* (DFPT): direct calculation of second order derivatives of the energy (unit cell calculation)

- *Frozen phonon* technique: finite differentiation of the forces (supercell calculation)

Alternative method (not using interatomic force constants):

- *Molecular dynamics*: spectra can be extracted from molecular dynamics runs, via Fourier transform of the velocity-velocity autocorrelation function.
Thermo-mechanical properties

Within the quasiharmonic the free energy is:

\[ F(\{a_i\}, T) = E(\{a_i\}) + F_{vibr}(\{a_i\}, T) \]

\[ = E(\{a_i\}) + \sum_{qj} \frac{1}{2} \hbar \omega_{q,j}(\{a_i\}) + k_B T \sum_{qj} \ln \left( 1 - e^{-\frac{\hbar \omega_{q,j}(\{a_i\})}{k_B T}} \right) \]

Thermal expansion coefficient

Heat capacity

N. Mounet and N. Marzari, PRB 71, 205214 (2005)
Spectroscopy and transport

Carrier-carrier interaction from perturbation theory:

Phonon-phonon

\[ V_{123} = \frac{\partial^3 E}{\partial u_1 \partial u_2 \partial u_3} \]

Electron-phonon

\[ g_{(k+q), j, k i} = \langle k + q, j \mid \Delta V_{q, \lambda}^{KS} \mid k, i \rangle \sqrt{\frac{\hbar}{2M\omega}} \]

For example, phonon scattering rates (linewidths):

Phonon-phonon contribution

\[ \frac{1}{\tau_{PP}^{1}} = \frac{\pi}{\hbar^2} \sum_{23} \left| V_{123} \right|^2 \left[ (n_2 + n_3 + 1) \delta (\omega_1 - \omega_2 - \omega_3) + 2(n_2 - n_3) \delta (\omega_1 + \omega_2 - \omega_3) \right] \]

Electron-phonon contribution

\[ \frac{1}{\tau_{EP}^{q\eta}} = \frac{4\pi}{N_k} \sum_{k, ij} \left| g_{(k+q), j, k i} \right|^2 \left[ f_{ki} - f_{(k+q)j} \right] \delta (\epsilon_{ki} - \epsilon_{(k+q)j} + \hbar \omega_{q\eta}) \]
Spectroscopy and transport

**$E_{2g}$ phonon linewidth in graphene**

N. Bonini et al., PRL. 99, 176802 (2007)

**Thermal conductivity in Si and Ge**

$$k_\alpha = \frac{1}{\Omega} \sum_{q_s} C_{q_s} v_{q_s,\alpha}^2 \tau_{q_s}$$

- Specific heat
- Phonon group velocity
- Phonon lifetime
Phonon linewidth (electron-phonon contribution):

\[
\gamma_{q\nu} = 2\pi \omega_{q\nu} \sum_{mn} \sum_{k} |g_{k+q,k}^{q\nu,mn}|^2 \times \delta(\epsilon_{k+q,m} - \epsilon_F)\delta(\epsilon_k,n - \epsilon_F)
\]

\[
\alpha^2 F(\omega) = \frac{1}{2\pi N(\epsilon_F)} \sum_{q\nu} \frac{\gamma_{q\nu}}{\omega_{q\nu}} \delta(\omega - \omega_{q\nu})
\]

\[
\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega
\]

\[
T_c = \frac{\Theta_D}{1.45} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda(1 - 0.62\mu^*) - \mu^*} \right]
\]

(Eliashberg function)

(McMillan formula for the superconducting temperature)

Converged results require summations over several millions of \(k\)-points

Wannier-functions interpolation techniques

References

• M. Born and K. Huang, *Dynamical theory of crystal lattices*, Oxford University Press.

• G. Venkataraman et al., *Dynamics of perfect crystals*, MIT Press.

Questions?