Introduction to the calculation of phonons and of vibrational spectra

P. Giannozzi
Università di Udine and Democritos National Simulation Center, Italy

September 23, 2009
Vibrational Spectroscopy: experiments

- Observation 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 and of the chemical bonding and thus of the electronic structure

- Most frequently used experimental techniques:
  - Neutron scattering (technically difficult, the entire dispersion is observable)
  - Infrared (IR) spectroscopy (simple, only some modes are observable)
  - Raman spectroscopy (simple, a different subset of modes is observable)

Theoretical calculation of vibrational mode frequencies and intensities from first principles is very helpful in analyzing vibrational spectra
Basic theory: Born-Oppenheimer approximation

The behavior of a system of interacting electrons \( r \) and nuclei \( R \) is determined by the solutions of the *time-dependent Schrödinger equation*:

\[
i\hbar \frac{\partial \hat{\Phi}(r, R; t)}{\partial t} = \left( -\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial R_I^2} - \sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_i^2} + V(r, R) \right) \hat{\Phi}(r, R; t)
\]

where \( V(r, R) \) is the potential describing the coulombian interactions:

\[
V(r, R) = \sum_{I>J} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \sum_{i>j} \frac{e^2}{|r_i - r_j|}
\]

\[
\equiv V_{nn}(R) + V_{ne}(r, R) + V_{ee}(r)
\]

Born-Oppenheimer (or adiabatic) approximation (valid for \( M_I >> m \)):

\[
\hat{\Phi}(r, R; t) \simeq \Phi(R)\Psi(r|R) e^{-i\hat{E}t/\hbar}
\]

NB: \( r \equiv (r_1, \ldots, r_N) \), \( R \equiv (R_1, \ldots, R_n) \)
Basic theory: Potential Energy Surface

The Born-Oppenheimer approximation allows to split the problem into an electronic problem depending upon nuclear positions:

\[
\left(-\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_i^2} + V(r, R) \right) \Psi(r|R) = E(R)\Psi(r|R)
\]

and a nuclear problem under an effective interatomic potential determined by the electrons:

\[
\left(-\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial R_I^2} + E(R) \right) \Phi(R) = \hat{E}\Phi(R)
\]

\(E(R)\) determines the Potential Energy Surface and the equilibrium geometry. At equilibrium, forces \(F_I\) on nuclei vanish:

\[
F_I = -\frac{\partial E(R)}{\partial R_I} = 0
\]

NB: \(r \equiv (r_1, \ldots, r_N)\), \(R \equiv (R_1, \ldots, R_n)\)
Normal vibrational modes in molecules and crystals

**Harmonic approximation**: the interatomic potential energy is expanded to 2nd order. The resulting Hamiltonian transforms into a sum of independent oscillators.

**Normal mode** frequencies, $\omega$, and displacement patterns, $U_\alpha^I$ for cartesian component $\alpha$ of atom $I$, at atomic position $R_I$, are determined by the secular equation:

$$\sum_{J,\beta} \left( C_{IJ}^{\alpha\beta} - M_I \omega^2 \delta_{IJ} \delta_{\alpha\beta} \right) U_\beta^J = 0,$$

where $C_{IJ}^{\alpha\beta}$ is the matrix of *inter-atomic force constants*, i.e. second derivatives of the energy with respect to atomic positions:

$$C_{IJ}^{\alpha\beta} \equiv \frac{\partial^2 E(\{R\})}{\partial R_\alpha^I \partial R_\beta^J} = -\frac{\partial F_{\alpha I}(\{R\})}{\partial R_\beta^J}.$$

In crystals, normal modes are classified by a wave-vector $q$. **Phonon** frequencies, $\omega(q)$, and displacement patterns, $U_\alpha^s(q)$, are determined by the secular equations:

$$\sum_{t,\beta} \left( \tilde{C}_{st}^{\alpha\beta}(q) - M_s \omega^2(q) \delta_{st} \delta_{\alpha\beta} \right) U_\beta^t(q) = 0$$
Practical calculation of vibrational modes


- **Frozen-phonon** technique: finite differentiation of forces

- **Density-functional Perturbation Theory** (DFPT): direct calculation of second-order derivatives of the energy

Alternative method (not using Interatomic Force Constants):

- **Molecular Dynamics**: spectra can be extracted from Molecular Dynamics runs, via the Fourier Transform of the velocity-velocity autocorrelation function

\[
 f(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_I \frac{\langle \mathbf{v}_I(t) \cdot \mathbf{v}_I(0) \rangle}{\langle \mathbf{v}_I(0) \cdot \mathbf{v}_I(0) \rangle} \, dt,
\]  

Function \( f(\omega) \) has peaks at the vibrational frequencies.

Let us focus on the case of phonons in crystals.
Calculation of phonon spectra

Introduce monochromatic perturbation $u$ to atomic positions $R_I = R_l + \tau_s$ as

$$R_I[u_s(q)] = R_l + \tau_s + u_s(q)e^{iq\cdot R_l}.$$  

($R_l =$lattice vector, $\tau_s =$equilibrium position of the s-th atom in the unit cell).

Fourier transform of force constants at $q$ are second derivatives of the energy with respect to such monochromatic perturbations:

$$\tilde{C}_{s\ell}^{\alpha\beta}(q) \equiv \sum_R e^{-i\cdot R}C_{s\ell}^{\alpha\beta}(R) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^\alpha(q) \partial u_t^\beta(q)}$$

Quantum ESPRESSO calculates them from the knowledge of the linear response $\partial n(r)/\partial u_s^\alpha(q)$ and diagonalized to get phonon modes at $q$. Note that:

- the linear response has the same wave vector $q$ of the perturbation: this algorithm will work for any $q$ without any supercell involved

- in the spirit of adiabatic approximation, one can use static response.
**Frozen phonon**

*Frozen phonons* is an older and alternative way to calculate phonons. The monochromatic perturbation is *frozen in* with a finite amplitude in the system, Fourier transform of force constants at $\mathbf{q}$ are calculated from *finite differences of forces* induced on all the atoms of the supercell by the monochromatic perturbation.

**Advantages:**

- straightforward to implement

**Disadvantages:**

- limited to small supercells, i.e. $\mathbf{q} = \mathbf{G}/n$, where $\mathbf{G}$ is a reciprocal lattice vector of the original cell, $n = 2, 3, 4, \ldots$, but in any case a small number.

Note that this is *not* the algorithm used by Quantum ESPRESSO!

What if we want the entire dispersions for all $\mathbf{q}$-vectors in the Brillouin Zone?
Calculation of interatomic force constants

Inter-atomic force constants in real-space, $C_{st}^{\alpha\beta}(\mathbf{R})$, are obtained by

- calculating $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q})$ on a discrete $(n_1, n_2, n_3)$ grid of $\mathbf{q}$-vectors:

  $$\mathbf{q}_{ijk} = \frac{i - 1}{n_1} \mathbf{G}_1 + \frac{j - 1}{n_2} \mathbf{G}_2 + \frac{k - 1}{n_3} \mathbf{G}_3, \quad i = 1, \ldots, n_1, \text{and the like for } j, k;$$

- Fourier-transforming to the corresponding real-space grid:

  $$C(\mathbf{q}_{ijk}) \iff C(\mathbf{R}_{lmn}), \quad \mathbf{R}_{lmn} = l\mathbf{R}_1 + m\mathbf{R}_2 + n\mathbf{R}_3$$

  $$l = -n_1/2, \ldots, n_1/2 \text{ and the like for } m, n.$$

The denser the grid of $\mathbf{q}$-vectors, the larger the vectors $\mathbf{R}_{lmn}$ for which the inter-atomic force constants are calculated. Inter-atomic force constants are short-ranged and require a moderate number of calculations at different $\mathbf{q}$ (for polar systems, see later).
Density-Functional Perturbation Theory

Let us assume that the external potential depends on some parameter $\lambda$

$$V_\lambda(r) \simeq V(r) + \lambda \frac{\partial V(r)}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 V(r)}{\partial \lambda^2} + ...$$

(all derivatives calculated at $\lambda = 0$) and expand the charge density

$$n_\lambda(r) \simeq n(r) + \lambda \frac{\partial n(r)}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 n(r)}{\partial \lambda^2} + ...$$

and the energy functional into powers of $\lambda$:

$$E_\lambda \simeq E + \lambda \frac{\partial E}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 E}{\partial \lambda^2} + ...$$

The first-order derivative $\partial E / \partial \lambda$ does not depend on any derivative of $n(r)$ ($Hellmann-Feynman$ theorem):

$$\frac{\partial E}{\partial \lambda} = \int n(r) \frac{\partial V(r)}{\partial \lambda} d\mathbf{r}$$
Density-Functional Perturbation Theory II

The second-order derivative $\frac{\partial^2 E}{\partial \lambda^2}$ depends on the first-order derivative of the charge density, $\frac{\partial n(r)}{\partial \lambda}$:

$$\frac{\partial^2 E}{\partial \lambda^2} = \int \frac{\partial V(r)}{\partial \lambda} \frac{\partial n(r)}{\partial \lambda} dr + \int n(r) \frac{\partial^2 V(r)}{\partial \lambda^2} dr$$

The result can be generalized to mixed derivatives:

$$\frac{\partial^2 E}{\partial \lambda \partial \mu} = \int \frac{\partial V(r)}{\partial \lambda} \frac{\partial n(r)}{\partial \mu} dr + \int n(r) \frac{\partial^2 V(r)}{\partial \lambda \partial \mu} dr$$

(the order of derivatives can be exchanged)

In general, the $(2n + 1)$–th derivative of energy depends only on derivatives up to order $n$ of the charge density ($(2n + 1)$ theorem) due to its variational character.

$\frac{\partial n}{\partial \lambda}$ can be calculated either by a self-consistent procedure, or by direct minimization of the 2nd-order energy, written as a functional of $\frac{\partial n}{\partial \lambda}$.
Calculation of the Linear Response

The minimization of the second-order functional, or alternatively the linearization of Kohn-Sham equations, yields a set of equations:

\[
(H_{KS} - \epsilon_i) \frac{\partial \psi_i(\mathbf{r})}{\partial \lambda} + \sum_j K_{ij} \frac{\partial \psi_j}{\partial \lambda} = -P_c \frac{\partial V}{\partial \lambda} |\psi_i\rangle
\]

where \( P_c \) is the projector over unoccupied states, \( K_{ij} \) is a nonlocal operator:

\[
\left( K_{ij} \frac{\partial \psi_j}{\partial \lambda} \right)(\mathbf{r}) = 4 \int \psi_i(\mathbf{r}) \left( \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \right) \psi_j^{*}(\mathbf{r}') \frac{\partial \psi_j}{\partial \lambda}(\mathbf{r}') d\mathbf{r}'
\]

and the linear charge response:

\[
\frac{\partial n(\mathbf{r})}{\partial \lambda} = 2 \text{Re} \sum_i \psi_i^{*}(\mathbf{r}) \frac{\partial \psi_i(\mathbf{r})}{\partial \lambda}
\]

These equations can be solved as a linear system for all \( \frac{\partial \psi_i(\mathbf{r})}{\partial \lambda} \), or else as many linear systems for each \( \frac{\partial \psi_i(\mathbf{r})}{\partial \lambda} \) followed by self-consistency.
Phonons and macroscopic electric fields

Polar materials in the $\mathbf{q}=0$ limit: a macroscopic electric field appear as a consequence of long-rangeness of Coulomb interactions. Incompatible with Periodic Boundary Conditions! Macroscopic electric fields contribute a non-analytic term to the dynamical matrix:

$$n_{a\alpha} \tilde{C}_{st}^{\alpha\beta} = \frac{4\pi}{\Omega} \frac{(\mathbf{q} \cdot \mathbf{Z}^*_s)_{\alpha} (\mathbf{q} \cdot \mathbf{Z}^*_t)_{\beta}}{\mathbf{q} \cdot \epsilon_{\infty} \cdot \mathbf{q}}$$

Effective charges $\mathbf{Z}^*$ are related to polarization P induced by a lattice distortion:

$$\mathbf{Z}^*_{s\alpha\beta} = \Omega \frac{\partial P_\alpha}{\partial u_\beta^s(\mathbf{q} = 0)}$$

Dielectric tensor $\epsilon_{\infty}^{\alpha\beta}$ are related to polarization induced by an electric field E:

$$\epsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \left. \frac{\partial P_\alpha}{\partial E_\beta} \right|_{u_s(\mathbf{q}=0)=0}$$

All of the above can be calculated from (mixed) second derivatives of the energy.
Practical calculations for electric fields

We need the response to a macroscopic electric field $E$: $\partial V / \partial E_\alpha = -e r_\alpha$.
This is *ill-defined* in a crystal, because $r$ is not a lattice-periodic operator!
It can however be recast into a well-defined expression using the following trick:

$$\langle \psi_c | r | \psi_v \rangle = \frac{\langle \psi_c | [H_{KS}, r] | \psi_v \rangle}{\epsilon_c - \epsilon_v} \quad \text{for} \quad c \neq v.$$ 

We can rewrite $|\tilde{\psi}_v^\alpha\rangle = P_c r_\alpha |\psi_v\rangle$ as the solution of a linear system:

$$(H_{KS} - \epsilon_v)|\tilde{\psi}_v^\alpha\rangle = P_c [H_{KS}, r_\alpha] |\psi_v\rangle,$$

where the commutator can be calculated from the following expression:

$$[H_{KS}, r] = -\hbar^2 \frac{\partial}{\partial r} + \left[ \hat{V}_{NL}, r \right].$$

($V_{NL}$ is the nonlocal term of the potential if present).

*Alternative technique:* differentiation wrt Bloch vector (numerically performed)
Infrared spectroscopy (absorption/reflectivity, energy loss spectroscopy, FTIR): $\lambda >> a$, the electromagnetic field can be considered macroscopic. Selection rules:

- Only phonons close to the $\Gamma$-point ($\mathbf{q} = 0$) are involved, i.e. *IR-active*

- Only phonons that induce a nonzero dipole are IR-active

The IR intensity is proportional to the square of the dipole induced by the phonon that is excited by the IR radiation:

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

This is a trivial byproduct of a phonon calculation.

Alternative technique: effective charges are expressed via the *Berry’s phase*.
Calculation of Raman Cross Sections

Non-resonant, resonant, surface-enhanced Raman scattering: an inelastic process in which light is scattered and a phonon or normal mode is created or destroyed.

\[ \omega_S = \omega_L - \omega_k \]

Stokes process:

\[ \omega_S = \omega_L + \omega_k \]

Anti-Stokes process:

Resonant Raman: \( \omega_{L,S} \sim \omega_{el} = \) typical electronic excitation frequencies
Non-resonant Raman: \( \omega_{L,S} \ll \omega_{el} \). This is the simpler case.

Again, only phonons near \( \Gamma (k = 0) \) contribute.
Calculation of Raman Cross Sections (2)

Non-resonant Raman intensities in the Placzek approximation:

\[ I_{\text{Stokes}}(\nu) \propto \frac{(\omega_L - \omega_\nu)^4}{\omega_\nu} r_{\alpha\beta}(\nu), \quad r_{\alpha\beta}(\nu) = \left| \frac{\partial \chi_{\alpha\beta}}{\partial u^{(\nu)}} \right|^2 \]

\( \chi \) = electric polarizability, \( u^{(\nu)} \) = normal mode coordinate along mode \( \nu \). The Raman tensor \( r_{\alpha\beta}(\nu) \) is a third-order derivative of the energy that can be calculated using:

- DFPT for \( \chi + \) Frozen-phonon (finite differences)
- DFPT using the \((2n+1)\) theorem: the \((2n+1)\)–th derivative of energy depends only on derivatives up to order \( n \) of the charge density (not implemented).
- DFPT + Second-order response to electric field (implemented)
- Finite electric fields + Frozen phonon
Practical phonon calculation in Quantum ESPRESSO

First step: scf calculation at equilibrium positions (performed by pw.x)

- Single phonon calculation at finite wave-vector $q$
  - Generate $\psi_{k,v}$ and $\psi_{k+q,v}$ in the Irreducible Brillouin Zone relative to the
    small group of $q$; calculate $C(q)$, diagonalize, produce $\omega(q)$ and $U(q)$ (code ph.x)

- Single phonon calculation at $\Gamma$ wave-vector ($q=0$)
  - Calculate $C(q=0)$, diagonalize, produce $\omega(q=0)$ and $U(q=0)$ (ph.x)
    For polar materials: calculate non-analytical terms that are missing from $C(q=0)$ (LO-TO splitting are absent from $\omega(q=0)$): specify option epsil=.true. to ph.x (will calculate and store in output file $Z^*$ and $\epsilon^\infty$).
    For non resonant Raman: specify option lraman=.true.
    - Impose Acoustic Sum Rule (ASR), add the nonanalytic LO-TO splitting, calculate cross sections (if data available) (code dynmat.x)
First step as before: scf calculation \textit{at equilibrium positions} (performed by \texttt{pw.x})

- Perform many single-phonon calculations on a uniform grid of wave-vectors $q_i$, including $q = 0$ (if system is polar, calculate in the latter case $Z^*$ and $\epsilon^\infty$); save all $C'(q_1)$ (and $Z^*$, $\epsilon^\infty$) (code \texttt{ph.x} with option \texttt{ldisp=\.true.})

- Perform inverse FFT of the $C(q_i)$, obtain interatomic force constants in real space $C(R)$. For polar materials: a term having the same behaviour for $q \to 0$ as the non-analytic term is subtracted from $C(q_i)$ before the Fourier Transform and re-added to $C(R)$, so that no problem related to non-analytic behaviour and related long-rangeness arises in the Fourier Transform (code \texttt{q2r.x})

- Calculate phonons at any wave-vector using code \texttt{matdyn.x}
Fast algorithm for specific cases

If you sample the Brillouin Zone with only the Γ point (e.g. molecules, large unit cells) and you need phonon modes only at Γ, you can use a simplified and faster algorithm.

- scf calculation at equilibrium positions with Γ – point tricks: performed by pw.x with card
  K_POINTS gamma

- use specialized code phcg.x to find $C(q = 0)$; specify option epsil=.true. to calculate $Z^*$ and $\epsilon^\infty$.

- Impose Acoustic Sum Rule (ASR), add the nonanalytic LO-TO splitting, calculate IR cross sections with code dynmat.x

Restrictions: no Raman, no Ultrasoft Pseudopotentials