

Mike Johnston, "Spaceman with Floating Pizza"

School on Electron-Phonon Physics, Many-Body Perturbation Theory, and Computational Workflows

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Lecture Mon.2

Density-functional perturbation theory

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- Very short reminder of density-functional theory (DFT)
- Basic density-functional perturbation theory (DFPT)
- Phonon calculations with DFPT
- Macroscopic electric fields and LO-TO splitting

Density-Functional Theory

Transforms the many-electron problem into an equivalent problem of (fictitious) non-interacting electrons, the *Kohn-Sham equations*:

$$H_{KS}\psi_v \equiv \left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r}) \right) \psi_v(\mathbf{r}) = \epsilon_v\psi_v(\mathbf{r})$$

The effective potential is a *functional* of the charge density:

$$V_{KS}(\mathbf{r}) = V(\mathbf{r}) + v[n(\mathbf{r})], \quad n(\mathbf{r}) = \sum_v |\psi_v(\mathbf{r})|^2$$

(Hohenberg-Kohn 1964, Kohn-Sham 1965). The sum is over occupied states only. $V(\mathbf{r})$ is the external potential on the system (the bare potential of the nuclei).

The exact form of $v[n(\mathbf{r})]$ is unknown, but approximate functionals yielding good results for the *ground state* of many materials are known. Less simple “advanced” functionals allow to obtain even better results and to deal with difficult cases

Density-Functional Theory (2)

The electronic energy is a functional of the charge density and is written as:

$$E[\{\psi\}] = -\frac{\hbar^2}{2m} \sum_v \int \psi_v^*(\mathbf{r}) \nabla^2 \psi_v(\mathbf{r}) d\mathbf{r} + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

Kohn-Sham equations arise from the minimization of the energy functional:

$$E = \min_{\psi} E[\{\psi\}], \quad \int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}$$

The functional $v[n(\mathbf{r})]$ can thus be written as

$$v(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \equiv V_H(\mathbf{r}) + V_{xc}(\mathbf{r}).$$

The second term above is called *exchange-correlation potential*.

Practical DFT: plane waves and pseudopotentials

- Expanding the Kohn-Sham orbitals into a suitable *basis* set turns Density-Functional Theory into a multi-variate minimization problem, and the Kohn-Sham equations into a *non-linear matrix eigenvalue problem*
- *Pseudopotentials* allows one to ignore chemically inert core states and to use a *plane-wave* basis set
- Plane waves are an *unbiased* basis set, imposed by periodicity (but a suitable *supercell* must be introduced for non-periodic systems)
- Plane waves are *orthogonal* and the *completeness* of the basis is easy to check
- Plane waves are simple to use, allow to efficiently solve the diagonalization problem and to solve the Poisson equation using iterative techniques, linear algebra (e.g. matrix-matrix products), Fast Fourier Transforms (FFTs)

(Note that other approaches based on different basis sets or all-electron atoms exist)

Energy functional expansion

Let us assume that the external (bare) potential in DFT depends on some parameter λ (typically, an atomic position, or an electric field) and let us consider the expansion into powers of λ for V_λ :

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

What are the equivalent expansion terms for the charge density:

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

and for the DFT energy functional:

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

? (all derivatives are calculated at $\lambda = 0$)

Energy functional expansion, first order

The first-order derivative, $\partial E/\partial\lambda$, is simply

$$\frac{\partial E}{\partial\lambda} = \int n(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial\lambda} d\mathbf{r}$$

and does not depend upon any derivative of $n(\mathbf{r})$, because the energy functional is *minimized* by the charge density $n(\mathbf{r})$ of the ground state. This is the DFT analogue of the *Hellmann-Feynman theorem* for many-body hamiltonians and wave functions:

$$\frac{\partial E}{\partial\lambda} = \langle \Psi | \frac{\partial H}{\partial\lambda} | \Psi \rangle$$

Such result is used in DFT calculations to compute forces on atoms.

In general, the $(2n + 1)$ *theorem* holds: the $(2n + 1)$ -th derivative of the energy depends only on derivatives up to order n of the charge density. Again, this is a consequence of the variational character of the energy functional.

Energy functional expansion, second order

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

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

The result can be generalized to mixed derivatives:

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

(note something far from evident in the r.h.s: the order of derivatives can be exchanged).

We now need to know the *linear response*, $\partial n / \partial \lambda$, in order to proceed.

This could be computed by writing $\partial^2 E / \partial \lambda^2$ as a quadratic functional of $\partial n / \partial \lambda$ and directly minimizing it; or with the equivalent, more traditional self-consistent procedure shown in the next slides.

Self-Consistent Linear Response

The basic DFT equations for the linear response to a perturbation $\partial V/\partial\lambda$ are:

$$\frac{\partial n(\mathbf{r})}{\partial\lambda} = 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) \frac{\partial\psi_v(\mathbf{r})}{\partial\lambda} \quad (1)$$

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial\lambda} = \frac{\partial V(\mathbf{r})}{\partial\lambda} + e^2 \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial n(\mathbf{r}')}{\partial\lambda} d\mathbf{r}' + \int \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \frac{\partial n(\mathbf{r}')}{\partial\lambda} d\mathbf{r}' \quad (2)$$

where v labels occupied (valence) states (we assume a nonmagnetic insulator). The linear variation of Kohn-Sham orbitals $\partial\psi_v/\partial\lambda$ can be obtained from perturbation theory:

$$\frac{\partial\psi_v}{\partial\lambda} = P_c \frac{1}{\epsilon_v - H_{KS}} P_c \frac{\partial V_{KS}}{\partial\lambda} \psi_v$$

where P_c is the projector over the empty-state manifold. Using the Sternheimer approach, the above equations can be recast into a set of linear systems:

$$(\epsilon_v - H_{KS}) P_c \frac{\partial\psi_v}{\partial\lambda} = P_c \frac{\partial V_{KS}}{\partial\lambda} \psi_v. \quad (3)$$

Self-Consistent Linear Response (2)

Equations (1-3) in the previous slide define a self-consistent procedure that can be solved by iteration, much in the same way as in the solution of Kohn-Sham equations.

Note that:

- The projector P_c is needed for numerical stability: there is no net contribution to $\partial n / \partial \lambda$ from inside the valence manifold.
- There is no need to perform *sums* over conduction bands. Conduction bands are actually *not needed at all*: in fact, $P_c = 1 - P_v$.
- Any “simple” (LDA, GGA) functional works as long as $\frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')}$ is implemented.

For plane-wave pseudopotential (PP) calculations in crystals:

- The procedure can be easily generalized to *non-local* norm-conserving PPs (*ultrasoft* PPs require additional terms, though).
- The procedure works for any *monochromatic* perturbation (periodic times $e^{i\mathbf{q}\cdot\mathbf{r}}$): the linear response contains only terms with the same wave-vector \mathbf{q} . There is no need to resort to supercells even for $\mathbf{q} \neq 0$.

Normal vibrational modes in molecules

Harmonic approximation: the potential energy surface – electronic plus nuclear-nuclear repulsion energy – is expanded to 2nd order. The resulting Hamiltonian transforms into a sum of independent oscillators.

Normal mode frequencies, ω , and displacement patterns, u_I^α for cartesian component α of atom I , at atomic position \mathbf{R}_I , are determined by the secular equation:

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

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

$$C_{IJ}^{\alpha\beta} \equiv \frac{\partial^2 E(\{\mathbf{R}\})}{\partial R_I^\alpha \partial R_J^\beta}.$$

Phonons in crystal

In crystals, Kohn-Sham orbitals are classified by a Bloch vector \mathbf{k} and a band index i : $\psi_v \equiv \psi_{i,\mathbf{k}}$. Atomic positions are identified via a position in the cell, $\boldsymbol{\tau}_s$, and a lattice vector \mathbf{R}_l : $\mathbf{R}_I = \mathbf{R}_l + \boldsymbol{\tau}_s$.

Normal modes are also classified by a Bloch vector (and a mode index). At a given wave-vector \mathbf{q} , phonon frequencies $\omega(\mathbf{q})$ and displacement patterns $u_s^\alpha(\mathbf{q})$ are determined by the secular equation:

$$\sum_{t,\beta} \left(\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) - M_s \omega^2(\mathbf{q}) \delta_{st} \delta_{\alpha\beta} \right) u_t^\beta(\mathbf{q}) = 0$$

where the $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q})$ are Fourier transforms:

$$\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) = \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R})$$

How can one compute the force constants?

Calculation of phonon spectra

Introduce monochromatic perturbation \mathbf{u} to atomic positions $\mathbf{R}_I = \mathbf{R}_l + \boldsymbol{\tau}_s$ as

$$\mathbf{R}_I[\mathbf{u}_s(\mathbf{q})] = \mathbf{R}_l + \boldsymbol{\tau}_s + \mathbf{u}_s(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_l}.$$

(\mathbf{R}_l =lattice vector, $\boldsymbol{\tau}_s$ =equilibrium position of the s -th atom in the unit cell).

Fourier transforms of force constants at \mathbf{q} are second derivatives of the energy with respect to such monochromatic perturbations:

$$\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^{*\alpha}(\mathbf{q}) \partial u_t^\beta(\mathbf{q})}$$

(N_c number of cells in crystal). These can be computed knowing the linear response $\partial n(\mathbf{r})/\partial u_s^\alpha(\mathbf{q})$ and diagonalized to get phonon modes at \mathbf{q} . Note that:

- one needs $3N_{at}$ linear-response calculations for a cell of N_{at} atoms
- no supercells are needed, unlike in the finite-difference (aka frozen phonon) method
- in the spirit of adiabatic approximation, one can use *static* response.

Inter-atomic force constants in real space

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 wave vectors:

$$\mathbf{q}_{ijk} = \frac{i-1}{n_1} \mathbf{G}_1 + \frac{j-1}{n_2} \mathbf{G}_2 + \frac{k-1}{n_3} \mathbf{G}_3, \quad i = 1, \dots, n_1,$$

and the like for j, k ($\mathbf{G}_{1,2,3}$ = vectors generating the reciprocal lattice)

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

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

$l = -n_1/2, \dots, n_1/2$ and the like for m, n ($\mathbf{R}_{1,2,3}$ = vectors generating the lattice).

The denser the grid of \mathbf{q} -vectors, the larger the vectors \mathbf{R}_{lmn} for which the inter-atomic force constants are calculated.

For simple semiconductors like Si and Ge, inter-atomic force constants have a short range, effectively vanishing for $|\mathbf{R}_{lmn}| > R_c$, for relatively small values of R_c . A small wave vector grid like $n_1 = n_2 = n_3 = 4$ is already quite good.

Inter-atomic force constants in real space (2)

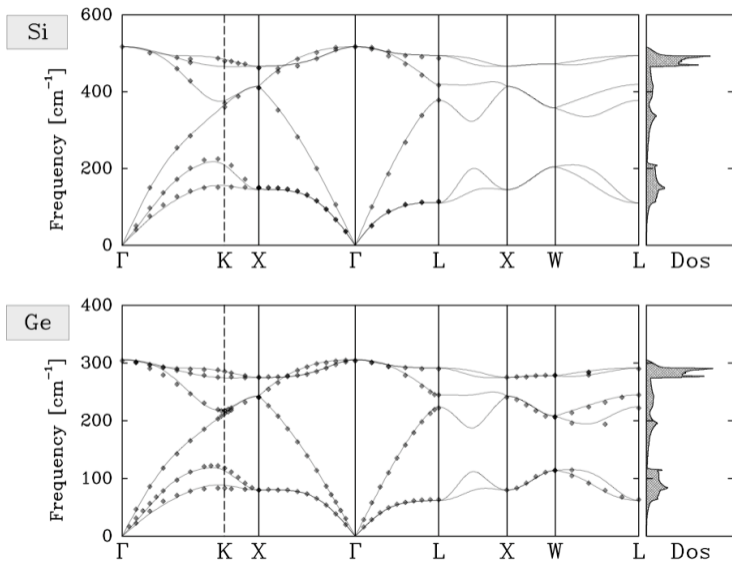
Symmetry can be used to reduce the number of needed linear-response calculations:

- Compute response only for wave vectors \mathbf{q} in the Irreducible Brillouin Zone (IBZ)
- Split displacement patterns into irreducible representations of the small group of \mathbf{q} (the subset of crystal symmetry leaving \mathbf{q} unchanged)
- Perform sums over Bloch \mathbf{k} vectors in the IBZ *of the small group of \mathbf{q}* , symmetrize them using the same group.

Each linear-response calculation has a computational cost at most a few times that of the corresponding ground-state calculation.

Once inter-atomic force constants are known, the entire phonon dispersion at any wave vector can be straightforwardly calculated.

An example: phonons in Si and Ge



Phonons and macroscopic electric fields

In many insulators a macroscopic (finite and constant) electric field is present in the $\mathbf{q}=0$ (long-wavelength) limit. Gives rise to observable *LO-TO splitting*. Macroscopic electric field are incompatible with periodic boundary conditions! Must be separately treated.

Phenomenological expression for the energy as a function of atomic displacements, \mathbf{u}_s , and of macroscopic electric field, \mathbf{E} (Born and Huang long-wavelength limit):

$$E(\{\mathbf{u}\}, \mathbf{E}) = \frac{1}{2} \sum_{st} \sum_{\alpha\beta} \mathbf{u}_s \cdot {}^{an}\tilde{\mathbf{C}}_{st} \cdot \mathbf{u}_t - \frac{\Omega}{8\pi} \mathbf{E} \cdot \boldsymbol{\epsilon}_\infty \cdot \mathbf{E} - e \sum_s \mathbf{u}_s \cdot \mathbf{Z}_s^* \cdot \mathbf{E},$$

(${}^{an}\tilde{\mathbf{C}}_{st}$ force constants, $\boldsymbol{\epsilon}_\infty$ dielectric tensor, \mathbf{Z}_s^* Born effective charge tensor; note that $\boldsymbol{\epsilon}_\infty$ is the electronic contribution only to the dielectric tensor).

Under which circumstances is an electric field \mathbf{E} generated by atomic displacements \mathbf{u} ? Which consequences does it have? The answer comes from electrostatics.

Phonons and macroscopic electric fields (2)

Let us consider *electric induction* $D = E + 4\pi P$ (where P is the induced polarization):

$$D = E + P_{el} + P_{ion} = \epsilon_{\infty} \cdot E + \frac{4\pi}{\Omega} e \sum_s \mathbf{u}_s \cdot \mathbf{Z}_s^*$$

Maxwell equations tell us $\mathbf{q} \cdot D = 0$ and $\mathbf{q} \times E = 0 \implies E = \mathbf{q}(\mathbf{q} \cdot E)$, hence

$$E = -\frac{4\pi e}{\Omega} \sum_s \frac{\mathbf{q}(\mathbf{q} \cdot \mathbf{Z}_s^* \mathbf{u}_s)}{\mathbf{q} \cdot \epsilon_{\infty} \cdot \mathbf{q}}$$

and

$$E(\{\mathbf{u}\}) = \frac{1}{2} \sum_{st} \sum_{\alpha\beta} \mathbf{u}_s \cdot \tilde{\mathbf{C}}_{st} \cdot \mathbf{u}_t, \quad \tilde{\mathbf{C}}_{st} = {}^{an}\tilde{\mathbf{C}}_{st} + {}^{na}\tilde{\mathbf{C}}_{st}$$

where

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

A *non-analytical* (in the $\mathbf{q}=0$ limit) term has appeared in the force constants!

Effective charges and dielectric tensor

Effective charges Z^* are related to polarization P induced by a lattice distortion:

$$Z_s^{*\alpha\beta} = \frac{\Omega}{e} \frac{\partial P_\alpha}{\partial u_s^\beta(\mathbf{q}=0)}.$$

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

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

One can observe that such quantities are second derivatives of the energy as well:

$$Z_s^{*\alpha\beta} = Z_s \delta_{\alpha\beta} - \frac{1}{N_c} \frac{\partial^2 E}{\partial E_\alpha \partial u_s^\beta(\mathbf{q}=0)},$$

$$\epsilon_\infty^{\alpha\beta} = \delta_{\alpha\beta} + \frac{1}{N_c} \frac{\partial^2 E}{\partial E_\alpha \partial E_\beta}.$$

Linear Response to an Electric Field

If the perturbing potential represents a macroscopic electric field $\delta\mathbf{E}$:

$$\delta V = -e\delta\mathbf{E} \cdot \mathbf{r}$$

it is ill-defined in a crystal, because \mathbf{r} is not a lattice-periodic operator! it can however be recast into a well-defined expression using the following trick:

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

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

$$(H_{KS} - \epsilon_v) |\bar{\psi}_v^\alpha\rangle = P_c [H_{KS}, \mathbf{r}_\alpha] |\psi_v\rangle,$$

where the commutator is well defined and can be easily computed:

$$[H_{KS}, \mathbf{r}] = -\frac{\hbar^2}{m} \frac{\partial}{\partial \mathbf{r}} + [\hat{V}_{NL}, \mathbf{r}] = -\frac{i\hbar \mathbf{p}}{m} + [\hat{V}_{NL}, \mathbf{r}].$$

Here \hat{V}_{NL} is the nonlocal part of the pseudopotential.

Calculation of effective charges

Polarization induced by an atomic displacement:

$$\frac{\partial P_\alpha}{\partial u_s^\beta(\mathbf{q} = 0)} = -\frac{e}{N_c \Omega} \int \mathbf{r} \frac{\partial n(\mathbf{r})}{\partial u_s(\mathbf{q} = 0)} d\mathbf{r} + \frac{e}{\Omega} Z_s \delta_{\alpha\beta}.$$

The integral is ill-defined for a crystal with periodic boundary conditions, but again we can use the trick just introduced. The effective charges can be written as:

$$Z_s^{*\alpha\beta} = Z_s + \frac{4}{N_c} \sum_{n=1}^{N/2} \left\langle \bar{\psi}_n^\alpha \left| \frac{\partial \psi_n}{\partial u_\beta(\mathbf{q} = 0)} \right. \right\rangle.$$

using the linear response to an atomic perturbation.

Remembering that the Z^* are mixed second derivatives of the energy, effective charges are alternatively computed as the force linearly induced on an atom by an electric field, using the linear response to an electric field:

$$Z_s^{*\alpha\beta} = Z_s + \frac{4}{N_c} \sum_{n=1}^{N/2} \left\langle \psi_n \left| \frac{\partial V}{\partial u_\beta(\mathbf{q} = 0)} \right| \frac{\partial \psi_n}{\partial \mathbf{E}_\alpha} \right\rangle$$

Calculation of dielectric tensor

The linear response to a macroscopic electric field can be calculated using the same trick as above. In fact, $V(\mathbf{r}) = e\mathbf{E} \cdot \mathbf{r}$ is incompatible with periodicity but we only need its non-diagonal matrix elements. The convenient way to solve the linear-response equations is to iterate over $V_{KS}(\mathbf{r})$ while keeping \mathbf{E} fixed:

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{E}} = \frac{\partial V(\mathbf{r})}{\partial \mathbf{E}} + \int \left(\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \right) \frac{\partial n(\mathbf{r}')}{\partial \mathbf{E}} d\mathbf{r}'.$$

Finally:

$$\epsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} - \frac{16\pi e}{N_c \Omega} \sum_{n=1}^{N/2} \left\langle \bar{\psi}_n^{\alpha} \left| \frac{\partial \psi_n}{\partial \mathbf{E}_{\beta}} \right. \right\rangle.$$

In the end, all we need to properly deal with LO-TO splitting in phonons are three additional linear-response calculations to an electric field

Final note: alternative techniques based on the *modern theory of polarizability* (Berry's phase) exist for the calculation of effective charges.

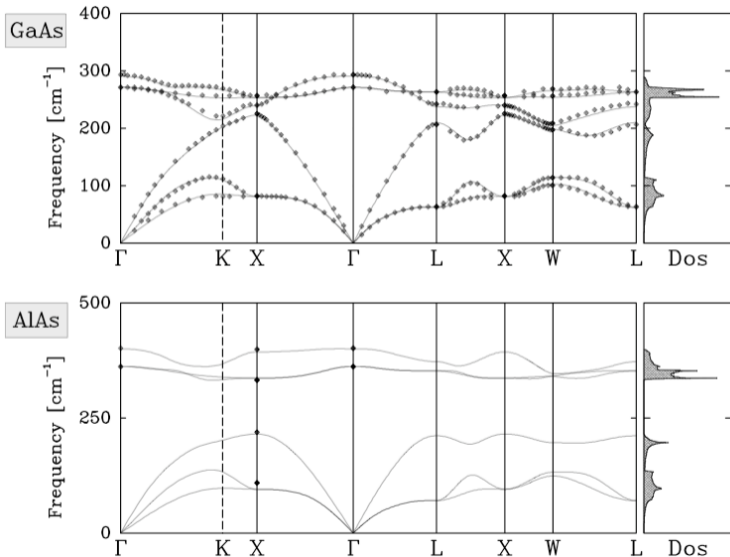
Inter-atomic force constants and LO-TO splitting

For materials having a LO-TO splitting (e.g.: polar semiconductors), the non-analytic term in the force constants makes inter-atomic force constants in real space *no longer short-range*. Fourier interpolation is no longer possible. Solution:

- Subtract from $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}_{ijk})$ a term that has the same $\mathbf{q} \rightarrow 0$ limit of the non-analytic term ${}^{na}\tilde{C}_{st}^{\alpha\beta}(\mathbf{q})$ and that is easy to compute at finite \mathbf{q}
- Fourier-transform from reciprocal to real space as for the non-polar case: force constants in real space are now short-range.
- When force constants at a general \mathbf{q} are re-calculated from those in real space, re-add the term removed before the Fourier transform.

Note: there is actually an additional *quadrupole* term that introduces a non-analyticity. See: M. Royo and M. Stengel, Phys. Rev **X** 9, 021050 (2019).

A polar example: phonons in GaAs and AlAs



Useful quantities one can compute

- *Infrared Intensities:*

$$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z_s^{\alpha\beta} u_s^{\beta}(\nu) \right|^2$$

can be directly calculated from effective charges and phonon displacement patterns $u_s^{\beta}(\nu)$ (displacement of atom s along the β direction for mode ν) at $\mathbf{q}=0$

- *Electron-phonon interactions coefficients* require as the basic quantity the matrix elements

$$g_{ij\nu}(\mathbf{k}, \mathbf{q}) = \left(\frac{\hbar}{2\omega_{\nu}(\mathbf{q})} \right)^{1/2} \langle \psi_{i,\mathbf{k}+\mathbf{q}} | \frac{\partial V_{SCF}}{\partial u(\nu, \mathbf{q})} | \psi_{j,\mathbf{k}} \rangle$$

where $u(\nu, \mathbf{q})$ is the displacement pattern for mode ν of wave-vector \mathbf{q} .
These are a natural by-product of a phonon calculation.

The concepts at the basis of DFPT can be extended to time-dependent DFT as well: see D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. **128**, 154105 (2008)

Superconducting transition temperatures

McMillan formula for the superconducting T_c :

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

where the Coulomb pseudopotential μ^* ranges from 0.11 to 0.13, Θ_D is the Debye temperature, and the electron-phonon interaction coefficient λ is

$$\lambda = \int d^3q \sum_{\nu} \frac{\gamma_{\nu}(\mathbf{q})}{\pi \hbar N(\epsilon_F) \omega_{\nu}^2(\mathbf{q})}$$

where $N(\epsilon_F)$ is the electronic DOS at the Fermi level,

$$\gamma_{\nu}(\mathbf{q}) = 2\pi\omega_{\nu}(\mathbf{q}) \sum_{ij} \int \frac{d^3k}{\Omega_{BZ}} |g_{ij\nu}(\mathbf{k}, \mathbf{q})|^2 \delta(\epsilon_i(\mathbf{k}) - \epsilon_F) \delta(\epsilon_j(\mathbf{k} + \mathbf{q}) - \epsilon_F),$$

Notice the double delta at the Fermi surface, making a precise calculation of such quantity problematic!

Very incomplete list of other things one can do

- Thermal properties in the quasi-harmonic approximation can be obtained from the calculation of the vibrational free energy:

$$F_{ph}(T, V) = -k_B T \int d^3q \sum_{\nu} \log (2 \sinh (\hbar \omega_{\nu}(\mathbf{q}) / 2 k_B T))$$

as a function of the volume V .

- Non-resonant Raman intensities (for $\mathbf{q} = 0$ phonons):

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

where χ is the electric polarizability of the system, are directly proportional to *third-order* derivatives of the energy. They can be computed as

- ▶ finite differences of the dielectric tensors, or
- ▶ using *second-order* response to an electric field: M.Lazzeri and F.Mauri, Phys. Rev. Lett. 90, 036401 (2003).

- *Phonons and related crystal properties from density-functional perturbation theory*, S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515-562 (2001). [\[link\]](#)
- *Density-Functional Perturbation Theory*, P. Giannozzi and S. Baroni, in *Handbook of Materials Modeling*, Vol.1: "Methods and Models", Editor S. Yip, Volume Editors: E. Kaxiras, N. Marzari, and B. Trout (Springer, 2005), p.195-214.
- *General invariance and equilibrium conditions for lattice dynamics in 1D, 2D, and 3D materials*, C. Lin, S. Poncé, and N. Marzari, *npj Comput. Mater.* **8**, 236 (2022), <https://doi.org/10.1038/s41524-022-00920-6>.
- *Density functional perturbation theory for gated two-dimensional heterostructures: Theoretical developments and application to flexural phonons in graphene*, T. Sohler, M. Calandra, and F. Mauri, *Phys. Rev.* **B 96**, 075448 (2017), <https://doi.org/10.1103/PhysRevB.96.075448>.