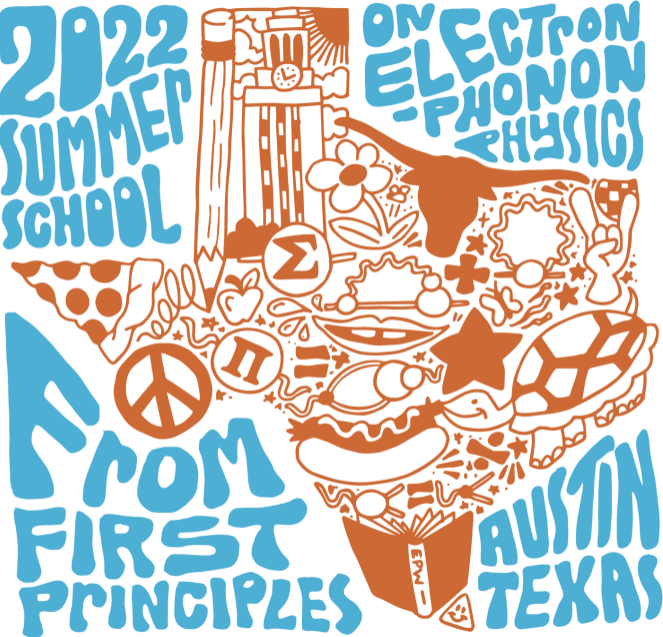


2022
SUMMER
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ON ELECTRON
ELECTRON
-PHONON
PHYSICS



U.S. DEPARTMENT OF
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Lecture Mon.2

Density-functional perturbation theory

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- A reminder of density-functional theory ...
- ... and of density-functional perturbation theory
- 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*.

Exchange-correlation functionals: simple approximations

What is $E_{xc}[n(\mathbf{r})]$? Viable approximations are at the heart of the success of DFT

- *Local Density Approximation* (LDA): First, "historical" approach (1965). Replace the energy functional with a *function* of the local density $n(\mathbf{r})$:

$$E_{xc} = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad V_{xc}(\mathbf{r}) = \epsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r}) \left. \frac{d\epsilon_{xc}(n)}{dn} \right|_{n=n(\mathbf{r})}$$

where $\epsilon_{xc}(n)$ is calculated for the homogeneous electron gas of density n (using Quantum Monte Carlo techniques) and fitted to some analytic form

- *Generalized Gradient Approximation* (GGA). The next step: a class of functionals depending upon the local density and the *local gradient* $|\nabla n(\mathbf{r})|$ of the density:

$$E_{xc} = \int n(\mathbf{r}) \epsilon_{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r}$$

There are many flavors of GGA, yielding similar (but slightly different) results. These are by now the "basic" functionals in most present-day calculations, with excellent price-to-performance ratio, but some noticeable shortcomings.

Basic DFT: advantages and shortcomings

- + *Computationally convenient*: calculations in relatively complex condensed-matter systems become affordable (GGA marginally more expensive than LDA)
- + *Excellent results* in terms of prediction of atomic structures, bond lengths, lattice parameters (within 1 ÷ 2%), binding and cohesive energies (5 to 10% GGA; LDA much worse, strongly overestimates), vibrational properties. Especially good for *sp*-bonded materials, may work well also in more "difficult" materials, such as transition metal compounds
- The infamous *band gap problem*: $\epsilon_c - \epsilon_v$ (or HOMO-LUMO in quantum chemistry parlance) wildly underestimates the true band gap, $\Delta = I - A$, where $I = E(N) - E(N - 1)$, ionization potential, $A = E(N + 1) - E(N)$, electron affinity
- Serious trouble in dealing with *strongly correlated materials*, such as e.g. magnetic materials (trouble mostly arising from spurious self-interaction)
- *No van der Waals interactions* in any functional based on the local density and gradients: van der Waals is nonlocal, cannot depend upon charge overlap

Density-Functional Theory, in practice

- 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, *matrix-vector products*, *Fast Fourier Transforms* (FFTs)

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

Density-Functional Perturbation Theory

Let us assume that the external potential depends on some parameter λ

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

(all derivatives calculated at $\lambda = 0$) and expand 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 the energy functional into powers of λ :

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

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

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

Energy functional expansion

The second-order derivative $\partial^2 E / \partial \lambda^2$ depends on 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:

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

(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 the variational character of the energy.

$\partial n / \partial \lambda$ can be calculated either by a self-consistent procedure (next slides), or by direct minimization of the 2nd-order energy, written as a functional of $\partial n / \partial \lambda$.

Self-Consistent Linear Response

The basic DFT equations for the linear response to a perturbation δV are:

$$\begin{aligned}\delta V_{KS}(\mathbf{r}) &= \delta V(\mathbf{r}) + e^2 \int \frac{\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \delta n(\mathbf{r}') d\mathbf{r}' \\ \delta n(\mathbf{r}) &= 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) P_c \frac{1}{\epsilon_v - H_{KS}} P_c \delta V_{KS} \psi_v,\end{aligned}$$

where v labels occupied states, P_c is the projector over the empty-state manifold. The linear variation of the charge density can be recast into the form

$$\delta n(\mathbf{r}) = 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) \delta \psi_v(\mathbf{r}), \quad \text{where} \quad \delta \psi_v = P_c \frac{1}{\epsilon_v - H_{KS}} P_c \delta V_{KS} \psi_v$$

$\delta \psi_v$ can be obtained from the solution of a linear equation:

$$(\epsilon_v - H_{KS}) P_c \delta \psi_v = P_c \delta V_{KS} \psi_v.$$

The above equations define a self-consistent procedure that can be solved by iteration, much in the same way as in the solution of KS equations.

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 mode index and a Bloch vector. At a given wave-vector \mathbf{q} phonon frequencies, $\omega(\mathbf{q})$, and displacement patterns \mathbf{q} , $U_s^\alpha(\mathbf{q})$, 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 these quantities?

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:

- the linear response has the same wave vector \mathbf{q} of the perturbation: this algorithm will work for *any* \mathbf{q} without any supercell involved, unlike 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)

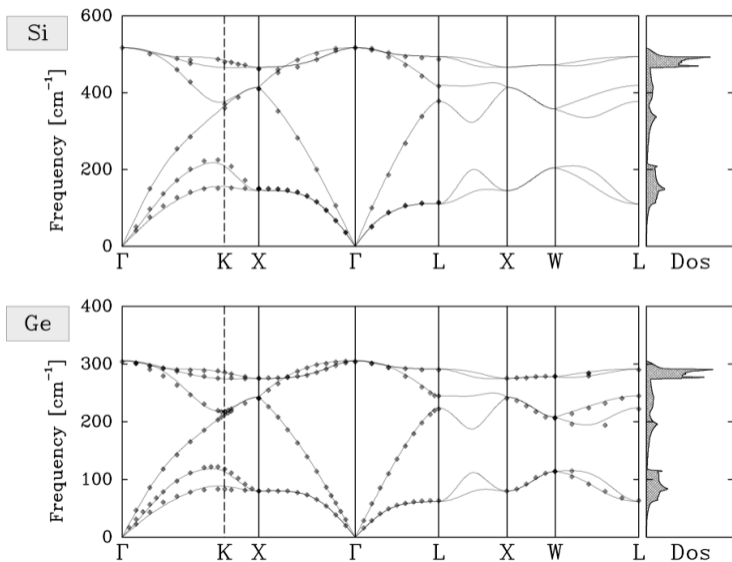
Symmetry can be used to reduce the number of needed linear-response calculations:

- 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 vectors in the IBZ for 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:

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

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

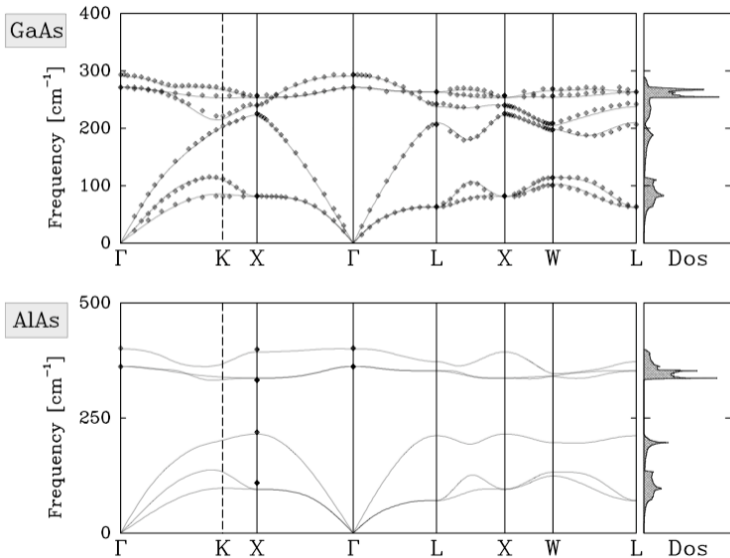
Final note: alternative techniques based on the *modern theory of polarizability* (Berry's phase) exist for the calculation of effective charges.

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.

A polar example: phonons in GaAs and AlAs



Infrared and Raman cross sections

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 at $\mathbf{q}=0$: $U_s^{\beta}(\nu)$ is the displacement of atom s along the β direction for mode ν .

Non-resonant Raman intensities:

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

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).

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:

$$F_{ph}(T, V) = -k_B T \sum_{\mathbf{q}, \nu} \log (2 \sinh (\hbar \omega(\mathbf{q}, \nu) / 2 k_B T))$$

as a function of the volume V .

- *Properties depending upon the electron-phonon interactions* require as the basic quantities the matrix elements

$$g_{ij\nu}(\mathbf{k}, \mathbf{q}) = \langle \psi_{i, \mathbf{k}+\mathbf{q}} | \frac{\partial V_{SCF}}{\partial U_{\mathbf{q}}(\nu)} | \psi_{j, \mathbf{k}} \rangle$$

that are a natural by-product of phonon calculations.

- *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.
- *Thermal Properties of Materials from ab-initio Quasi-Harmonic Phonons*, S. Baroni, P. Giannozzi, and E. Isaev, *Rev. Mineral. Geochem.* **71**, 39-57 (2010).