

C 2 Density Functional Perturbation Theory¹

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1 Introduction

Density Functional Theory has emerged as a very successful technique to calculate the ground state properties of electronic systems, whether in bulk, nanostructures, or molecules. Formally DFT only provides the ground state density and total energy, and there are well known failures in the representation of electronic excited states. If however the ground state is perturbed very lightly, typically in such a manner as to leave the system close to its electronic ground state, one can easily apply the traditional quantum formalism for perturbation theory, giving density functional perturbation theory (DFPT). This approach was invented at the end of the 1980s, and has been particularly successful in predicting many experimentally observable quantities: experiment always probes excitations of a system, but for low energy “slow” excitations DFPT builds on the very good representation of the ground state in DFT to give accurate excitations as well. Higher energies imply more electronic transitions, in which the intrinsic DFT is a much worse approximation. The cures to these woes (TDDFT, GW etc...) are presented in several other chapters of these proceedings.

The first development of DFPT came from Baroni, Giannozzi, and Testa in Trieste [1]. Several groups followed suite in the 1990s, in particular those of Xavier Gonze, Serguei Savrasov, Amy Liu, and then many others. A large number of electronic structure simulation packages now implement and use DFPT. The historic ones are Quantum Espresso [2] and ABINIT [3], but also VASP [4], octopus [5], CASTEP [6] and many others. DFPT has become a popular tool for the analysis of the vibrational and spectroscopic properties of materials, routinely providing phonon frequencies and dielectric properties with just a few percent of error with respect to experiment.

In the following sections we will give basic definitions and review the important concepts of DFPT. Some derivations will be followed through, but the details will be left buried in the appropriate literature. The aim is to provide a framework and support for the lectures in the FZJ Spring School 2014, and to showcase a variety of representative and interesting applications which have links to other Lectures from the school. By the end of this Lecture students should have an accurate idea of what they can calculate with DFPT, how the calculation is carried out, and which experimentally observable quantities can be extracted. A number of review articles have been published over the past 25 years (e.g. Ref. [7] which we referred to frequently), in particular the Review of Modern Physics by Baroni et al. [8].

This chapter is dedicated to the memory of Professor Jean-Pol Vigneron (1950-2013).

2 Density Functional Perturbation Theory

2.1 Response functions

Many interesting physical properties (*response functions*) are the result of the application of an external perturbation to the system under investigation. Response functions are second, third, or higher order derivatives of the total energy with respect to applied perturbation(s). Typical perturbations can be atomic displacements, homogeneous external electric or magnetic fields, strain, alchemical change, etc... The physical properties related to the derivatives of the total (electronic plus ionic) energy are

1^{st} **order:** forces, stress, dipole moment, ...

2^{nd} **order:** phonon dynamical matrix, elastic constants, dielectric susceptibility, Born effective charges, piezoelectricity, internal strain

3^{rd} **order:** non-linear dielectric susceptibility, phonon-phonon interaction, Grüneisen parameters, anharmonic elastic constants, ...

Further physical properties - such as entropy or thermal expansion - can be obtained integrating the total energy (or a thermodynamic potential) over phononic degrees of freedom.

Total energy derivatives can be computed using either direct approaches (e.g., finite differences, molecular-dynamics spectral analysis) or perturbative techniques. The former suffer from various limitations such as size effects, ergodicity constraints, commensurability problems or the difficulty to decouple the responses to perturbations of different wavelength. The perturbative theory applied to DFT, instead, allows one to treat not only periodic perturbations but also perturbations characterized by a non-zero, commensurate or incommensurate, wavevector [9]. In addition, the computation of 1^{st} order corrections to wavefunctions within perturbation theory can be done using a variational approach (Section 2.3) and algorithms similar to those used for ground-state (i.e. unperturbed) calculations. Hence, the perturbative technique can be naturally included in the usual DFT framework. In the following, unless otherwise specified, we will use Hartree atomic units $\hbar = m_e = e = 1/4\pi\epsilon_0 = 1$

2.2 Perturbation theory

Any perturbation theory starts by the identification of a small parameter, $\lambda \ll 1$, characterizing the change in the unperturbed Hamiltonian of the system $H^{(0)}$ due to an external potential $V_{ext}(\lambda)$:

$$H(\lambda) = H^{(0)} + V_{ext}(\lambda) \quad (1)$$

We assume that the unperturbed Schrödinger equation

$$H^{(0)} |\psi_i^{(0)}\rangle = \epsilon_i^{(0)} |\psi_i^{(0)}\rangle \quad (2)$$

can be solved exactly and the normalization condition on the unperturbed wavefunctions is satisfied

$$\langle \psi_i^{(0)} | \psi_i^{(0)} \rangle = 1 \quad (3)$$

where i labels eigenvalues and eigenvectors of $H^{(0)}$. Our goal is to solve the perturbed Schrödinger equation

$$H(\lambda) |\psi_i(\lambda)\rangle = \epsilon_i(\lambda) |\psi_i(\lambda)\rangle \quad (4)$$

with the normalization condition on wavefunctions

$$\langle \psi_i(\lambda) | \psi_i(\lambda) \rangle = 1 \quad (5)$$

The next section will describe the specific types of perturbations usually examined. The fundamental hypothesis is that all of the observables and physical quantities can be expanded in Taylor series with respect to λ , and that these series are well defined and will converge. This constraint is not trivial formally, but in practice is usually verified. A perturbation of the Hamiltonian will change the resulting eigenstates and eigenvalues, generically to arbitrary order in λ . Let

$$H(\lambda) = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \quad (6)$$

Then the resulting eigensolutions for the full H are:

$$\psi_i(\lambda) = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + \dots \quad (7)$$

and eigenvalues

$$\epsilon_i(\lambda) = \epsilon_i^{(0)} + \lambda \epsilon_i^{(1)} + \lambda^2 \epsilon_i^{(2)} + \dots \quad (8)$$

The n^{th} order correction to the eigenvalues (respectively, eigenvectors) is n^{th} -derivative of the eigenvalue (respectively, eigenvectors) computed at $\lambda = 0$. For instance

$$\epsilon_i^{(1)} = \left. \frac{d\epsilon_i(\lambda)}{d\lambda} \right|_{\lambda=0} \quad (9)$$

Hence the utility of perturbation theory to compute 1st, 2nd and 3rd order derivatives of the total energy with respect to small perturbations. For certain perturbations the zeroth or first order, or, e.g., all even order corrections can be 0, depending on symmetry. In Eq. 7 we will presume that the eigenstate starts from a Kohn Sham (KS) independent particle orbital, and that $H^{(0)}$ is the corresponding KS Hamiltonian (the same form would be true for the full Many Body wavefunction and hamiltonian, of course). The new state is again a stationary solution of the new Hamiltonian, and we restrict ourselves to static perturbations for the moment. Replacing the above in the eigenequation for ψ (Eq. 4) and identifying terms in powers of λ gives a hierarchical and constructive set of equations for progressively higher order solutions:

$$H^{(0)} |\psi_i^{(1)}\rangle + H^{(1)} |\psi_i^{(0)}\rangle = \epsilon_i^{(0)} |\psi_i^{(1)}\rangle + \epsilon_i^{(1)} |\psi_i^{(0)}\rangle \quad (10)$$

$$H^{(0)} |\psi_i^{(2)}\rangle + H^{(1)} |\psi_i^{(1)}\rangle + H^{(2)} |\psi_i^{(0)}\rangle = \epsilon_i^{(0)} |\psi_i^{(2)}\rangle + \epsilon_i^{(1)} |\psi_i^{(1)}\rangle + \epsilon_i^{(2)} |\psi_i^{(0)}\rangle \quad (11)$$

...

with the 0th order Schrödinger equation given by Eq. 2. Inserting the perturbative series of ψ (7) in the normalization condition (5) we obtain a condition on the orthonormality of wavefunctions at each order:

$$\langle \psi_i^{(0)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | \psi_i^{(0)} \rangle = 0 \quad (12)$$

$$\langle \psi_i^{(0)} | \psi_i^{(2)} \rangle + \langle \psi_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(2)} | \psi_i^{(0)} \rangle = 0 \quad (13)$$

...

where the 0th order normalization condition is given by Eq. 3. Left multiplying the 1st order Schrödinger equation (10) by $\langle \psi_i^{(0)} |$ and using the orthonormality conditions (3) and (12) we obtain the 1st order eigenvalues:

$$\epsilon_i^{(1)} = \langle \psi_i^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle \quad (14)$$

This result is equivalent to the Hellmann-Feynman theorem [10, 11], which states that the first derivative of the eigenvalues of the Hamiltonian $H(\lambda)$ is given by the expectation value of the derivative of the Hamiltonian with respect to the parameter λ . From Eq. 14 it follows that the first-order corrections to the energy can be computed from the unperturbed wavefunctions and from the first-order change in the external potential. Higher-order terms are not needed to compute $\epsilon_i^{(1)}$.

The first-order correction to the wavefunctions can be computed by solving the so-called Sternheimer equation [12]:

$$(H^{(0)} - \epsilon_i^{(0)}) |\psi_i^{(1)}\rangle = -(H^{(1)} - \epsilon_i^{(1)}) |\psi_i^{(0)}\rangle \quad (15)$$

which is obtained by rearranging the terms in the 1st order Schrödinger equation (10). Solving the Sternheimer equation for the $\psi_i^{(0)}$ requires the inversion of the $(H^{(0)} - \epsilon_i^{(0)})$ operator. However, the inversion cannot be done for arbitrary vectors since $\epsilon_i^{(0)}$ is an eigenvalue of $H^{(0)}$. The problem can be solved by expanding $|\psi_i^{(1)}\rangle$ in the basis of $|\psi_j^{(0)}\rangle$ (which is orthonormal and complete):

$$|\psi_i^{(1)}\rangle = \sum_j c_{ij}^{(1)} |\psi_j^{(0)}\rangle \quad (16)$$

This allows one to separate the 0th order wavefunctions in two subsets: the subset I of the wavefunction(s) corresponding to the eigenvector $\epsilon_i^{(0)}$ and the subset of the wavefunctions in the orthogonal subspace I^\perp . After some algebra, it is possible to determine the coefficient $c_{ij}^{(1)}$ with $j \in I^\perp$, which permits to write the 1st order correction to the wavefunctions in terms of a sum over the spectrum of the unperturbed Hamiltonian:

$$|\psi_i^{(1)}\rangle = \sum_{j \in I^\perp} |\psi_j^{(0)}\rangle \frac{\langle \psi_j^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \quad (17)$$

This sum runs over all the states (both occupied and empty) of the system except the specific eigenstate under consideration, for which the denominator would vanish. The coefficient $c_{ij}^{(1)}$ with $j \in I$ remains unknown in this approach, which gives us a gauge freedom. Imposing the normalization condition on the 1st order eigenvector results in $c_{ij}^{(1)} = 0$ when $j \in I$.

The Sternheimer equation can also be written in terms of the projector onto the I^\perp subspace $P_{I^\perp} = \sum_{j \in I^\perp} |\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|$ as

$$P_{I^\perp} \left(H^{(0)} - \epsilon_i^{(0)} \right) P_{I^\perp} |\psi_i^{(1)}\rangle = -P_{I^\perp} H^{(1)} |\psi_i^{(0)}\rangle \quad (18)$$

where a full identity $\mathbf{I} = P_{I^\perp} + P_I$ has been inserted in the left hand side, and applied to the left. The advantage of this expression is that the singularity has been removed and, hence, the Sternheimer equation can be solved for $\psi_i^{(1)}$. Defining the Green's function in the subspace I^\perp as

$$G_{I^\perp}(\epsilon) = [P_{I^\perp} (\epsilon - H^{(0)}) P_{I^\perp}]^{-1} \quad (19)$$

the equation to solve becomes

$$P_{I^\perp} |\psi_i^{(1)}\rangle = G_{I^\perp}(\epsilon_i^{(0)}) H^{(1)} |\psi_i^{(0)}\rangle \quad (20)$$

i.e. Green's function techniques can be used to solve the Sternheimer equation (15).

Several expressions exist for the second-order corrections to the energy. A simple expression can be obtained by left multiplying the 2^{nd} order Schrödinger equation (11) by $\langle \psi_i^{(0)} |$ and using the 0^{th} order equations (2) and (3):

$$\epsilon_i^{(2)} = \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(0)} | H^{(1)} - \epsilon_i^{(1)} | \psi_i^{(1)} \rangle \quad (21)$$

summing this expression to its Hermitian conjugate and using the 1^{st} order normalization condition (12) we obtain:

$$\epsilon_i^{(2)} = \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \frac{1}{2} \left(\langle \psi_i^{(0)} | H^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} | \psi_i^{(0)} \rangle \right) \quad (22)$$

The 2^{nd} order correction to the energy can also be obtained by minimizing with respect to $\psi_i^{(1)}$ the expression

$$\epsilon_i^{(2)} = \min_{\psi_i^{(1)}} \left\{ \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(0)} - \epsilon_i^{(0)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(0)} | H^{(1)} - \epsilon_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \epsilon_i^{(1)} | \psi_i^{(0)} \rangle \right\} \quad (23)$$

under the normalization constraint Eq. 12. The expression enclosed by curly brackets is usually referred to as the *variational expression* of the 2^{nd} order correction to the energy. Similar variational expressions exist for all even orders. The number of terms to be calculated is larger, and the non-variational expressions (which exist for all orders) are often used for simplicity in other cases. They can often obtain the full set of $\epsilon^{(2)}$ without needing the full set of $\psi^{(1)}$.

2.3 Density Functional Perturbation Theory

The DFT ground-state energy of the electronic system is obtained by minimizing the functional of the electronic density:

$$E_{el}[\rho(\lambda)] = \sum_{i=1}^{N_e} \langle \psi_i(\lambda) | (T + V_{ext}(\lambda)) | \psi_i(\lambda) \rangle + E_{Hxc}[\rho(\lambda)] \quad (24)$$

under the orthonormality constraint on the Kohn-Sham orbitals:

$$\langle \psi_i(\lambda) | \psi_j(\lambda) \rangle = \delta_{ij} \quad (25)$$

The sum in Eq. 24 is performed on all the occupied states, T is the kinetic energy operator, V_{ext} is the external potential (which includes the nuclear potential), E_{Hxc} is the Hartree and exchange-correlation energy functional. The electronic density is given by

$$\rho(\mathbf{r}; \lambda) = \sum_{i=1}^{N_e} \psi_i^*(\mathbf{r}; \lambda) \psi_i(\mathbf{r}; \lambda) = \rho^{(0)}(\mathbf{r}) + \lambda \rho^{(1)}(\mathbf{r}) + \lambda^2 \rho^{(2)}(\mathbf{r}) + \dots \quad (26)$$

and the minimization can be performed using the Lagrange multiplier method. The canonical Euler-Lagrange equations can be cast in the form of a Schrödinger equation (4) with the Hamiltonian

$$H = T + V_{ext}(\lambda) + V_{Hxc}(\lambda) \quad (27)$$

where

$$V_{Hxc}(\mathbf{r}; \lambda) = \frac{\partial E_{Hxc}[\rho(\lambda)]}{\partial \rho(\mathbf{r})} \quad (28)$$

Analogously to standard perturbation theory (Section 2.2), it is assumed that the unperturbed problem ($\lambda = 0$) can be solved exactly and the perturbing potential is known at all orders. As mentioned in the Introduction, the goal of Density Functional Perturbation Theory (DFPT) is to compute the derivatives of the DFT electronic energy with respect to different perturbations. The full derivation of the (many) DFPT equations can be found in [1, 13, 14, 15]. In order to describe the whole Born-Oppenheimer energy, the electrostatic repulsion between nuclei must be added to the electronic contribution. The nuclei-nuclei interaction energy can be obtained by treating the nuclei as classical point charges, so it does not present particular computational difficulties and hence we focus here on the electronic contribution only.

In standard perturbation theory it is shown that the first order correction to the electronic energy can be computed from the 0^{th} order wavefunctions and the perturbing potential at the 1^{st} order (14):

$$E_{el}^{(1)} = \sum_{i=1}^{N_e} \langle \psi_i^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle = \sum_{i=1}^{N_e} \langle \psi_i^{(0)} | (T + V_{ext})^{(1)} | \psi_i^{(0)} \rangle + \left. \frac{dE_{Hxc}[\rho^{(0)}]}{d\lambda} \right|_{\lambda=0} \quad (29)$$

which is the Hellmann-Feynman theorem for DFT.

The constraint on the wavefunctions at 1^{st} order is given by Eq. 12. The 1^{st} order change in the wavefunctions can be obtained by solving directly the Sternheimer equation (15) using iterative techniques or a self-consistent approach analogous to the self-consistent solution of the unperturbed problem where the Kohn-Sham equation is replaced by Eq. 15. Sternheimer gives a system of N_e linearly coupled equations: this is formally much simpler than standard DFT, where the $E_{xc}[\rho]$ dependency is non-linear. The $\psi_i^{(1)}$ - solution of Eq. 15 - can also be computed using the *sum over states* expression (Eq. 17) which only requires the knowledge of eigenvalues and eigenvectors of the unperturbed Hamiltonian, and the perturbing potential at 1^{st} order.

As discussed in Section 2.2 the Sternheimer equation can also be solved using Green's function techniques (Eq. 18). For semiconductors $P_{I\perp}$ becomes the projector upon the conduction states. For metals one should take explicitly into account that a finite density of states is present at the Fermi energy and hence the external perturbation can affect the occupation numbers. The linear response of metals has been treated by de Gironcoli [16]. The limits of validity of DFPT are dictated by the requirement that the external perturbation is small, i.e. $\lambda |\psi_i^{(1)}\rangle \ll |\psi_j^{(0)}\rangle$. Hence Eq. (17) implies $|\lambda \langle \psi_j^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle| \ll |\epsilon_i^{(0)} - \epsilon_j^{(0)}|$, which means that the external perturbation must be small with respect to electronic excitations.

Once the 1^{st} order change of wavefunctions $\psi_i^{(1)}$ is known, the first-order change of density can be obtained by inserting the expansion (7) in Eq. 26:

$$\rho^{(1)}(\mathbf{r}) = \sum_{i=1}^{N_e} \left[\psi_i^{*(1)}(\mathbf{r}) \psi_i^{(0)}(\mathbf{r}) + \psi_i^{*(0)}(\mathbf{r}) \psi_i^{(1)}(\mathbf{r}) \right] \quad (30)$$

and, hence, the computation of the first-order change in the Hamiltonian can be done using [1]

$$H^{(1)} = T^{(1)} + V_{ext}^{(1)} + V_{Hxc}^{(1)} = T^{(1)} + V_{ext}^{(1)} + \int \left. \frac{\partial^2 E_{Hxc}}{\partial \rho(\mathbf{r}) \partial \rho(\mathbf{r}')} \right|_{\rho^{(0)}} \rho^{(1)}(\mathbf{r}') d\mathbf{r}' \quad (31)$$

The 2^{nd} order derivative of the electronic energy can be given by a non-variational expression that follows from Eq. 22:

$$E_{el}^{(2)} = \sum_{i=1}^{N_e} \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \sum_{i=1}^{N_e} \langle \psi_i^{(0)} | H^{(1)} | \psi_i^{(1)} \rangle \quad (32)$$

A more accurate variational expression (analogous to Eq. 23 of standard perturbation theory) can be obtained by minimizing

$$\begin{aligned} E_{el}^{(2)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\} \right] &= \sum_{i=1}^{N_e} \left[\langle \psi_i^{(0)} | (T + V_{ext})^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | (H - \epsilon_i)^{(0)} | \psi_i^{(1)} \rangle + \right. \\ &\quad \left. \langle \psi_i^{(0)} | (T + V_{ext})^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | (T + V_{ext})^{(1)} | \psi_i^{(0)} \rangle \right] + \\ \frac{1}{2} \int \int \frac{\partial^2 E_{Hxc}[\rho^{(0)}]}{\partial \rho(\mathbf{r}) \partial \rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' &+ \int \frac{d}{d\lambda} \frac{\partial E_{Hxc}[\rho^{(0)}]}{\partial \rho(\mathbf{r})} \Big|_{\lambda=0} \rho^{(1)}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \frac{d^2 E_{Hxc}[\rho^{(0)}]}{d\lambda^2} \Big|_{\lambda=0} \end{aligned} \quad (33)$$

with respect to $\{\psi_i^{(1)}\}$ under the constraints $\langle \psi_i^{(0)} | \psi_j^{(1)} \rangle = 0$ for all occupied states i and all j .

Since $E_{el}^{(2)}$ is variational with respect to $\{\psi_i^{(1)}\}$, this leads to Euler-Lagrange equations which are equivalent to the self-consistent Sternheimer equation (Eq. 18).

Equations (32) and (33) explicitly show that the 2^{nd} order derivatives of the total energy are completely determined by the 1^{st} order derivatives of the wavefunctions. In both standard perturbation theory and DFPT it can be shown that the 3^{rd} order correction to the energies can be obtained by knowing the correction to the wavefunctions up to the 1^{st} order. These results are actually more general and are a consequence of the so-called “ $2n + 1$ ” theorem of quantum mechanics. This theorem states that the knowledge of the derivatives of the wavefunctions at order n^{th} permits the computation of the derivatives of the energy up to order $2n + 1$. The theorem follows from the variational principle and has been demonstrated in DFT by Gonze and Vigneron [13]. The practical importance of the “ $2n + 1$ ” theorem is that it allows one to access 3^{rd} order derivatives of the total energy, e.g. 3^{rd} order effects (such as anharmonic phonon line widths, Raman scattering cross sections, nonlinear optical response) at the same computational cost as harmonic properties.

As a final cherry on the cake, once certain first-order wavefunctions are known, the non-variational expressions produced from Eq. 32 can be used to obtain many more mixed perturbations, at no extra cost. As an example see the Born effective charges below, or the off-diagonal terms of the dielectric susceptibility. The same holds true for third order (“ $2n+1$ ”) quantities: normally only two of the three $\psi^{(1)}$ are explicitly needed to get all of the mixed $E^{(3)}$ derivatives.

3 The most common perturbations

3.1 Phonons

The quantum mechanical modeling of bulk, molecules and nanostructured materials is usually performed in the *adiabatic approximation* of Born and Oppenheimer [17]. This approximation relies on the much greater mass of nuclei with respect to electrons. From this it follows that the nuclear motion is much slower than the electrons motion. Hence, it is possible to decouple nuclear (i.e. vibrational) and electronic degrees of freedom in the Hamiltonian and perform the computation of the total energy of the system in two steps. At first, the kinetic energy of the nuclei is supposed to be constant and subtracted from the total Hamiltonian. The resulting Born-Oppenheimer Hamiltonian H_{BO} depends parametrically upon the nuclear positions τ and describes the problem of the interacting electrons moving in the electrostatic field of nuclei at fixed positions:

$$H_{BO}(\tau) = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i, \kappa} \frac{Z_\kappa}{|\mathbf{r}_i - \tau_\kappa|} + \frac{1}{2} \sum_{\kappa \neq \mu} \frac{Z_\kappa Z_\mu}{|\tau_\kappa - \tau_\mu|} \quad (34)$$

where \mathbf{r} are the electronic coordinates, latin (i, j) and greek (κ, μ) letters respectively label electron and nuclei, and Z is the nuclear charge. In H_{BO} the kinetic energy of the electrons and the various electrostatic interaction terms (the repulsive electron-electron, the attractive electron-nucleus, and the repulsive nucleus-nucleus) can easily be identified. Eq. 34 can be solved, for instance, using DFT techniques and gives the ground-state Born-Oppenheimer energy of the system $E_{BO}(\tau)$. Then the kinetic energy of the nuclei is added, resulting in a Schrödinger equation for the nuclear motion which determines the dynamics of the lattice of the system

$$\left(-\frac{1}{2} \sum_\kappa \frac{1}{M_\kappa} \frac{\partial^2}{\partial \tau_\kappa^2} + E_{BO}(\tau) \right) \Psi(\tau) = E \Psi(\tau) \quad (35)$$

where E is the total energy and M_κ are the masses of the atoms.

Let us suppose that the system under investigation is periodic and, hence, can be described by the periodic repetition of a unit cell. Let the vector \mathbf{R} identify the position of a periodic image of the unit cell with respect to the chosen origin, κ label a nucleus within the unit cell, and β label the cartesian directions. The nuclei are not fixed to their classical zero-temperature ideal positions but actually perform small displacements $u_{\mathbf{R}\kappa\beta}$ around their equilibrium positions $\tau_{\mathbf{R}\kappa\beta}$. Hence the Born-Oppenheimer energy of a crystal can be expanded in a Taylor series as a function of the nuclear displacements

$$E_{BO}(\mathbf{u}) = E_{BO}^0 + \frac{1}{2} \sum_{\mathbf{R}\kappa\beta} \sum_{\mathbf{R}'\kappa'\beta'} \frac{\partial^2 E_{BO}}{\partial \tau_{\mathbf{R}\kappa\beta} \partial \tau_{\mathbf{R}'\kappa'\beta'}} u_{\mathbf{R}\kappa\beta} u_{\mathbf{R}'\kappa'\beta'} + \dots \quad (36)$$

where E^0 is the minimum of the energy in the static approximation, when all the displacements are zero, and can be calculated within standard DFT. The 1st order term in the series represents the forces acting on each nucleus, which vanish at the equilibrium when E_{BO} reaches a minimum and $F_{\mathbf{R}\kappa\beta} = \partial E_{BO} / \partial \tau_{\mathbf{R}\kappa\beta} = 0$. Hence the linear contribution in the expansion (36) disappears. The term containing the 2nd derivative of the energy is called *harmonic* and the Taylor expansion truncated at the 2nd order is referred to as the *harmonic approximation*. Anharmonic effects are described by higher order terms in Eq. 36 and will be discussed in Section 4.1.

When a nucleus is displaced from its equilibrium position a force appears to bring the atom back, according to the principle of virtual work. In the harmonic approximation (36), the force acting on a nucleus presents a linear dependence on the displacement of that nucleus:

$$F(\mathbf{R}'\kappa'\beta') = \frac{\partial E_{BO}}{\partial u_{\mathbf{R}\kappa\beta}} = - \sum_{\mathbf{R}'\kappa'\beta'} \frac{\partial^2 E_{BO}}{\partial \tau_{\mathbf{R}\kappa\beta} \partial \tau_{\mathbf{R}'\kappa'\beta'}} u_{\mathbf{R}'\kappa'\beta'} = - \sum_{\mathbf{R}'\kappa'\beta'} \Phi^{(2)}(\mathbf{R}\kappa\beta; \mathbf{R}'\kappa'\beta') u_{\mathbf{R}'\kappa'\beta'} \quad (37)$$

Equation (37) defines the matrix of *interatomic force constants* (IFCs), which is used to describe the force acting on a specific nucleus κ due to the displacement of another nucleus κ' .

In classical mechanics the lattice dynamics is described by the Newton equations of motion whose solution (in the harmonic approximation) is a superposition of the *normal modes of vibration* of the system. Taking into account the periodicity of the lattice, the normal modes can be written as Bloch states, i.e. as the product of a plane wave (which depends on the cell \mathbf{R} in the direct lattice) and a lattice-periodic function

$$U_{\mathbf{R}m\mathbf{q}}(\kappa\beta) = e^{i\mathbf{q}\cdot\mathbf{R}} U_{m\mathbf{q}}(\kappa\beta) \quad (38)$$

where the wavevector \mathbf{q} is a vector in the first Brillouin zone and characterizes the normal modes of vibration. The harmonic ansatz also implies a simple phase dependency on time $\exp(-i\omega t)$ to be added to Eq. 38 before insertion in Newton's law. In quantum mechanics the nuclear displacements $U_{\mathbf{R}m\mathbf{q}}(\kappa\beta)$ are quantized and known as *phonons*. Phonon eigendisplacements and their frequencies $\omega_{m\mathbf{q}}$ can be obtained by solving a generalized eigenvalue equation for the periodic part of the Bloch state

$$\sum_{\kappa'\beta'} \tilde{\Phi}^{(2)}(\kappa\beta; \kappa'\beta'; \mathbf{q}) U_{m\mathbf{q}}(\kappa'\beta') = M_\kappa \omega_{m\mathbf{q}}^2 U_{m\mathbf{q}}(\kappa\beta) \quad (39)$$

where the *dynamical matrix* $\tilde{\Phi}^{(2)}(\kappa\beta; \kappa'\beta'; \mathbf{q})$ is the Fourier transform of the IFC matrix

$$\tilde{\Phi}^{(2)}(\kappa\beta; \kappa'\beta'; \mathbf{q}) = \sum_{\mathbf{R}'} \Phi^{(2)}(\mathbf{0}\kappa\beta; \mathbf{R}'\kappa'\beta') e^{i\mathbf{q}\cdot\mathbf{R}'} \quad (40)$$

and the eigendisplacements satisfy the normalization condition

$$\sum_{\kappa\beta} M_\kappa [U_{m\mathbf{q}}(\kappa\beta)]^* U_{m\mathbf{q}}(\kappa\beta) = 1 \quad (41)$$

If the system under investigation has N atoms in the unit cell, the dimension of the dynamical matrix is $3N \times 3N$ and the eigendisplacements are vectors of length $3N$ describing the displacements of the N nuclei along the 3 Cartesian directions. The resulting phonon band structure is not unbounded from above in energy, as is the case for electrons, but contains exactly $3N$ bands, with usual energies in the 1-10 meV range (up to several hundreds of meV for bonds involving Hydrogen).

The interatomic force constants and dynamical matrices are 2^{nd} -order derivatives of the Born Oppenheimer energy with respect to atomic displacements. Hence they can be accurately and efficiently computed using DFPT.

3.2 Periodic systems and incommensurate perturbations

The quantum mechanical modeling of systems under a periodic external potential can easily be accomplished thanks to the Bloch theorem. In this section we will discuss how to treat the case of a perturbation characterized by an incommensurate wavevector, which breaks the translational symmetry.

Bloch's theorem demonstrates that the wavefunction of a system subject to a potential with translational periodicity \mathbf{R} in the direct lattice

$$V_{ext}^{(0)}(\mathbf{r} + \mathbf{R}) = V_{ext}^{(0)}(\mathbf{r}) \quad (42)$$

can be expressed as the product of a plane wave characterized by a vector \mathbf{k} of the reciprocal lattice and a periodic function $u_{j\mathbf{k}}^{(0)}$ having the same periodicity as the external potential:

$$\psi_{j\mathbf{k}}^{(0)}(\mathbf{r}) = \frac{1}{N_{cell}\Omega_0} e^{i\mathbf{k}\cdot\mathbf{r}} u_{j\mathbf{k}}^{(0)}(\mathbf{r}) \quad (43)$$

where N_{cell} is the number of replicas of the unit cell included in the Born-von-Karman supercell, Ω_0 is the volume of the unit cell, and j is the electronic band index. The electron density has the same periodicity of the wavefunctions and is given by integrating the wavevectors \mathbf{k} in the first Brillouin zone and summing j on the occupied bands

$$n^{(0)}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int_{BZ} \sum_j^{occ} u_{j\mathbf{k}}^{(0)*}(\mathbf{r}) u_{j\mathbf{k}}^{(0)}(\mathbf{r}) d\mathbf{k} \quad (44)$$

Let us consider a perturbation to the periodic potential $V_{ext}^{(0)}$ which is characterized by an incommensurate wavevector \mathbf{q} [13, 15, 18]: such that

$$V_{ext,\mathbf{q}}^{(1)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}} V_{ext,\mathbf{q}}^{(1)}(\mathbf{r}) \quad (45)$$

As written, this perturbing potential is Hermitian only when \mathbf{q} is half of a vector of the reciprocal lattice. For generic \mathbf{q} , the sum of this potential and its Hermitian conjugate, $V_{ext,\mathbf{q}}^{(1)} + V_{ext,-\mathbf{q}}^{(1)}$, should be used instead, such that the Hamiltonian is Hermitian. With this potential we have:

$$V_{ext,\mathbf{q}}^{(1)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}} V_{ext,\mathbf{q}}^{(1)}(\mathbf{r}) + e^{-i\mathbf{q}\cdot\mathbf{R}} V_{ext,-\mathbf{q}}^{(1)}(\mathbf{r}) \quad (46)$$

If we apply a translation \mathbf{R} , the 1st order wavefunction can be obtained from Eq. (17) of perturbation theory:

$$\psi_{j\mathbf{k}\mathbf{q}}^{(1)}(\mathbf{r} + \mathbf{R}) = e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}} \psi_{j\mathbf{k}\mathbf{q}}^{(1)}(\mathbf{r}) \quad (47)$$

where the 0th order wavefunction Eq. (43) and the periodicity of $u_{j\mathbf{k}}^{(0)}(\mathbf{r})$ have been used. The 1st order density at $(\mathbf{r} + \mathbf{R})$ is given by Eq. (30)

$$n_{\mathbf{q}}^{(1)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}} n_{\mathbf{q}}^{(1)}(\mathbf{r}) \quad (48)$$

In order to restore the translational periodicity of the unperturbed system, we need to eliminate the phase factor $e^{i\mathbf{q}\cdot\mathbf{R}}$ in the 1st order wavefunction and density (as with ordinary applications of Bloch's theorem). To this end we define the following functions:

$$u_{j\mathbf{k}\mathbf{q}}^{(1)}(\mathbf{r}) = \sqrt{N_{cell}\Omega_0} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} \psi_{j\mathbf{k}\mathbf{q}}^{(1)}(\mathbf{r}) \quad (49)$$

$$\bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}) = e^{-i\mathbf{q}\cdot\mathbf{r}} n_{\mathbf{q}}^{(1)}(\mathbf{r}) \quad (50)$$

whose periodicity in \mathbf{R} can be easily tested using Eq. (47) and Eq. (48). The latter relationships allow one to write the 1st order change in the electron density as

$$\bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}) = \frac{2}{(2\pi)^3} \int_{BZ} \sum_j^{occ} s u_{j\mathbf{k}}^{(0)*}(\mathbf{r}) u_{j\mathbf{k}}^{(1)}(\mathbf{r}) d\mathbf{k} \quad (51)$$

In this manner, the 1st order problem can be addressed by solving equations which have the same translational symmetry as the unperturbed system.

Thermodynamical quantities

At usual temperatures for Humans, up to perhaps a thousand Kelvin, the main contributors to the variation of entropy and internal energy are the phonons. Electronic energies, of order eV, correspond to tens of thousands of degrees, and, whether in metals or high-T insulators, the number of thermally active electronic degrees of freedom (i.e. those close to the chemical potential) is quite low. Other degrees of freedom, e.g. magnetic ones or strong or weak nuclear forces, correspond to very small or very large energy scales, and are usually inactive at ambient conditions, either frozen out or saturated uniformly. The vibrational modes of a system thus give quantitative access to many thermodynamical observables. These are derived directly from the number of accessible states at a given energy, viz. the normalized density of phonon states

$$g(\omega) = \frac{(2\pi)^3}{3N\Omega_0} \sum_m \int_{BZ} \delta(\omega - \omega_{\mathbf{q}m}) d\mathbf{q} \quad (52)$$

The internal energy and entropy are expressed simply using Bose-Einstein statistics with a dimensionless argument $x = \hbar\omega/k_B T$:

$$\begin{aligned} E^{ph} &= (3N) \int_0^{\omega_{\max}} \left(\frac{e^x + 1}{e^x - 1} \right) \frac{\hbar\omega}{2} g(\omega) d\omega \\ S^{ph} &= (3N) k_B \int_0^{\omega_{\max}} \left(\frac{x e^x}{e^x - 1} - \ln(e^x - 1) \right) g(\omega) d\omega \end{aligned}$$

which combined give the free energy

$$F^{ph} = (3N) k_B T \int_0^{\omega_{\max}} \ln \left(2 \sinh \frac{x}{2} \right) g(\omega) d\omega$$

whose T derivative is the constant volume specific heat

$$C_V^{ph} = (3N) k_B \int_0^{\omega_{\max}} \left(\frac{x}{e^{x/2} - e^{-x/2}} \right)^2 g(\omega) d\omega$$

So far we have considered only constant volume quantities in the (N, V, T) ensemble. As we will see in Sec. 4.1 interatomic forces are not purely harmonic and this leads to variations of V with T - most experiments are performed at constant pressure. The simplest approach to this is the *quasi-harmonic* approximation: performing several calculations for different volumes, we can obtain both variations of F^{ph} with V and T and the full equation of state (EOS), presuming all anharmonic effects are in the volume expansion. Extracting the bulk modulus B and the volume thermal expansion coefficient α_V from the EOS, one can derive the constant pressure specific heat: $C_P^{ph} = C_V^{ph} + \alpha_V^2(T) B \Omega_0 T$

3.3 Macroscopic Electric Field

Overview and \mathbf{k} derivatives

After atomic displacements, the next most common perturbation is that by a macroscopic electric field \mathcal{E} . Its inclusion in DFPT is relatively simple, in that no term in the normal BO Hamiltonian depends explicitly on the electric field, only implicitly through induced changes in the wave functions and density. Thermodynamically an external electric field couples directly to the electrical dipole moment or polarization \mathcal{P} , and we must add a term $\mathcal{E} \cdot \mathcal{P} \sim \int d\mathbf{r} \mathcal{E} \cdot \hat{\mathbf{r}}$ to the Hamiltonian.

As is, this term is unbounded and ill defined in periodic boundary conditions. For the ground state it should be treated with the modern theory of polarization, see Ref. [19], Lecture A6, and comments below. This is possible and has other advantages, but makes the formalism more involved. Here for the description of linear responses it will be sufficient to start with a finite \mathbf{q} field, whose potential is bounded, and whose wavelength will later be taken to infinity ($\mathbf{q} \rightarrow 0$). The chosen dependency on \mathcal{E} limits us to longitudinal fields, but again this will be the response function we are interested in. Finally we will consider static fields and insulators - the response of metals is more complex (electrical transport is considered in Sect. 4.4).

In general one can relate the macroscopic electric field with an electrical polarization \mathcal{P} and the corresponding displacement $\mathcal{D} = \mathcal{E} + 4\pi\mathcal{P}$. The linear term in \mathcal{D} gives the (purely electronic part of the) dielectric permittivity tensor:

$$\varepsilon_{\alpha\beta}^{\infty} = \delta_{\alpha\beta} + 4\pi \frac{\partial \mathcal{P}_{\alpha}}{\partial \mathcal{E}_{\beta}} \quad (53)$$

which is measured experimentally at frequencies high enough to be ignored by the phonons but low enough not to excite electrons into the conduction band. As the first derivative of the total energy with respect to \mathcal{E} is just \mathcal{P} , we can relate ε^{∞} to the second derivative of E with respect to \mathcal{E} , which is also the dielectric susceptibility χ .

The photon has no mass, such that its (relativistic) momentum is almost negligible compared to that of the phonons. Short of going to hard X rays or gamma radiation, we can consider that $\Delta\mathbf{q}$ due to the photon is 0, and the macroscopic \mathcal{E} field considered here will be valid in general. The long wavelength limit is carried out [15] with a second Taylor expansion, with respect to the wavevector \mathbf{q} . The first non-zero term ($d\psi^{(1)}/dq_{\alpha}$) must be orthonormalized to $\psi^{(0)}$ but also to $d\psi^{(0)}/dk_{\alpha}$. This derivative with respect to wavevector (or momentum) should not surprise us: the position operator $\hat{\mathbf{r}}$ (present in the electric field term of the Hamiltonian) can be linked by Fourier transform to the operator $d/d\mathbf{k}$ operating on a plane wave. The wave-vector derivatives $d\psi^{(0)}/dk_{\alpha}$ must be pre-calculated, but at little extra cost: the only terms with a contribution (those which do not commute with $d/d\mathbf{k}$) are the kinetic energy and an eventual non-local pseudopotential. In reciprocal space the derivatives of these terms are straightforward. The external potential is local, and in DFT the xc potential is as well: locality in real space implies no dependency on \mathbf{k} and $d/d\mathbf{k} = 0$.

Once the $\psi^{\mathcal{E}\alpha}$ have been calculated through a stationary expression like Eq. 33, the full matrix of second derivatives with respect to macroscopic electric field can be calculated from a simple non-stationary expression:

$$E^{\mathcal{E}\alpha\mathcal{E}\beta} = \frac{\Omega_0}{8\pi^3} \int_{\text{BZ}} d\mathbf{k} \sum_j \langle i\psi_{\mathbf{k}j}^{(1)k_{\alpha}} | \psi_{\mathbf{k}j}^{(1)\mathcal{E}\alpha} \rangle \quad (54)$$

where the superscripts on the ψ indicate which derivative/perturbation is being taken.

Born effective charges

The Born effective charge is defined as the change in polarization when an atom is displaced, or equivalently the change in force induced on a given atom when an electric field is applied:

$$Z_{\kappa,\beta\alpha}^* = \Omega_0 \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa\alpha}(\mathbf{q} = \mathbf{0})} = \frac{\partial F_{\kappa\alpha}}{\partial \mathcal{E}_\beta} \quad (55)$$

These values are tensorial since the induced charge may potentially give polarization changes in any direction β for an atomic displacement along α , depending on symmetry. For cubic and hexagonal systems the Z^* are usually diagonal. With the $\psi^{(1)}$ obtained for atomic-displacement perturbations, one can use a non-stationary expression to calculate Z^* :

$$Z_{\kappa,\beta\alpha}^* = Z_\kappa \delta_{\beta\alpha} + 2 \frac{\Omega_0}{8\pi^3} \int_{\text{BZ}} d\mathbf{k} \sum_j \langle \psi_{\mathbf{k}j\mathbf{q}=\mathbf{0}}^{(1)\tau_{\kappa\alpha}} | i \psi_{\mathbf{k}j}^{(1)k_\beta} \rangle \quad (56)$$

where Z_κ is the (valence) ionic charge of atom κ .

Static dielectric response and LO/TO splitting

The Born effective charges are a univocal and quantitative way to assess charge associations in solids: if the second term in Eq. 56 is large something interesting is happening with bonding or electronic states in interaction with the phonons. The main use of Z^* is as an ingredient to describe the dielectric response in other quantities.

In the low frequency limit (photon energy comparable with the phonon ones) the dielectric response of solids includes the electronic part derived above but also the ionic part. We define $p_{m\gamma} = \sum_{\kappa\beta} Z_{\kappa\gamma\beta}^* \eta_{m\mathbf{q}=\mathbf{0}}(\kappa\beta)$ to be the mode polarity, i.e. the nominal variation of the polarization along the phonon displacement vector. The full response is then:

$$\varepsilon_{\alpha\beta}^0(\omega) = \varepsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{p_{m\alpha} p_{m\beta}}{\omega_{m\mathbf{q}=\mathbf{0}}^2 - \omega^2} = \varepsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m\alpha\beta}}{\omega_{m\mathbf{q}=\mathbf{0}}^2 - \omega^2} \quad (57)$$

where S_m is the mode-dependent oscillator strength. This also provides the infrared absorption intensity

$$I(\omega) = \sum_m \delta(\omega - \omega_m) \text{Tr}[S_m] = \sum_m \delta(\omega - \omega_m) \left| \sum_{\kappa\beta} p_{m\beta} \right|^2 \quad (58)$$

for an α polarized \mathcal{E} field.

The infrared reflectivity follows directly from the determination of ε^0 . One needs to project onto the direction of the (longitudinal) \mathcal{E} field for an EM wave normal to a surface

$$\varepsilon_{\hat{\mathbf{q}}}(\omega) = \sum_{\alpha\beta} \hat{q}_\alpha \varepsilon_{\alpha\beta}^0(\omega) \hat{q}_\beta \quad (59)$$

to yield the reflectivity

$$R(\omega) = \left| \frac{\varepsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) - 1}{\varepsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) + 1} \right|^2 \quad (60)$$

One final consequence of the dynamical behavior of charges around atoms is that the frequency of certain long wavelength ($\mathbf{q} \rightarrow 0$) phonons will be affected in ionic compounds: if atomic displacements are longitudinal (i.e. along the direction of \mathbf{q}), a macroscopic electrical polarization may develop. This will cost energy, pushing the phonon frequency up. The correction term to the dynamical matrix (resp. frequencies) is proportional to the Born effective charges, and is screened by the electronic dielectric permittivity:

$$\begin{aligned} \tilde{\Phi}^{(2)}(\kappa\alpha; \kappa'\beta; \mathbf{q} \rightarrow 0) &= \tilde{\Phi}^{(2)}(\kappa\alpha; \kappa'\beta; \mathbf{q} = 0) + \frac{4\pi}{\Omega_0} \frac{(\sum_{\gamma} q_{\gamma} Z_{\kappa\gamma\alpha}^*)(\sum_{\delta} q_{\delta} Z_{\kappa'\delta\beta}^*)}{\sum_{\gamma\delta} q_{\gamma} \varepsilon_{\gamma\delta}^{\infty} q_{\delta}} \\ \omega_m^{\text{LO}} &= \omega_m^{\text{TO}} + \frac{4\pi}{\Omega_0} \frac{(\mathbf{q} \cdot \mathbf{p}_m)^2}{\sum_{\gamma\delta} q_{\gamma} \varepsilon_{\gamma\delta}^{\infty} q_{\delta}} \end{aligned} \quad (61)$$

For acoustic modes all atoms move together, whether along \mathbf{q} or not, and no polarization develops in any event. The optical modes must be separated into two sets. For a given \mathbf{q} there will be two phonons which are transverse (labeled TO if $\mathbf{Z}^* \cdot \mathbf{q} = 0$), where nothing happens, and one mode which is longitudinal (LO). For ionic systems there will be a splitting between the LO and TO frequencies at Γ .

Care must be taken with limits coming from different directions in \mathbf{q} . Due to the tensorial nature of Z^* the correction term is not analytic, and its value *at* $\mathbf{q} = 0$ will depend on the direction $\hat{\mathbf{q}}$ (note the norm of \mathbf{q} simplifies in Eq. 61). This strange behavior is physical, and several sets of frequencies can be observed, e.g. by infrared spectroscopy, depending on the orientation of a crystal. The frequency of the observed phonons depends on the polarizability in the different directions, with respect to the propagation of the incoming electric field.

4 Other perturbations and developments

This section details a selection of extensions of DFPT to other perturbations: other external fields or other internal parameters of the DFT Hamiltonian. We also mention a few developments of the “normal” theory to include interesting electronic effects, in particular relativistic and spin effects for heavy and magnetic elements.

4.1 3rd order responses

Tensors of Raman intensities

Raman spectroscopy observes the shift in frequency of a laser passing through a material, usually in the infra-red or visible range [20]. As a chemical and structural analysis tool Raman is very widely used to characterize molecules, additives, biological complexes, minerals and many other materials, both experimentally and industrially. The shift in light frequency is due to the absorption or emission of a Γ -point phonon in the material (usually the only ones able to interact with photons), such that the distribution of Raman frequencies can be calculated from the harmonic phonon frequencies developed in the previous sections, choosing the irreducible representations which are active for the Raman interaction Hamiltonian. The symmetry of the specific phonon mode involved can be determined experimentally by polarizing the light coming in and out of the sample, giving selection rules for the full 3D tensor of Raman intensities $\aleph_{\alpha\beta}$ (see chapter 8 of Ref. [21]). The intensity of the absorption, however, is a more complex quantity, which includes the number of available phonon states (DOS) and the strength of the transition matrix element. Because of the quantum mechanics of harmonic oscillator creation and annihilation operators, the absorption is always favored (the shifts in frequencies are also known as Stokes and anti-Stokes). The transitions can be seen electromagnetically as a modulation of the dielectric constant of the medium by the phonons. We have detailed above that the (static) dielectric constant $\varepsilon_{\alpha\beta}$ can be calculated from the electronic response corrected by the ionic response given as a function of Z^* , the Born effective charges (i.e. harmonic or second order derivatives). For the Raman intensities we need the variation of these quantities with respect to a phonon mode, and is therefore a 3rd order derivative of the energy. Luckily, using the 2n+1 theorem, we can extract this derivative from the 1st order perturbed wavefunctions, which are already provided by the normal harmonic phonon calculation [22].

The dielectric constant can be obtained as the second order derivative of the total energy with respect to macroscopic external electric fields: the first derivative gives the polarization, and the linear term in the polarization is proportional to $\varepsilon_{\alpha\beta}$, or equivalently to the polarizability $\chi_{\alpha\beta}$. The Raman scattering cross section per unit solid angle is given by

$$\frac{dS}{d\Omega} = (n_m + 1) \frac{h}{2\omega_m} \frac{(\omega_0 - \omega_m)^4}{c^4} |\mathbf{e}_s \cdot \aleph^m \cdot \mathbf{e}_0|^2 \quad (62)$$

where ω_m is the phonon energy, ω_0 the photon energy, \mathbf{e}_s and \mathbf{e}_0 the outgoing and incoming polarizations, and n_m is the Bose-Einstein occupation factor for the phonon under consideration. The central DFPT quantity is the third order derivative of the energy with respect to two electric fields \mathcal{E} (i.e. the first order dielectric susceptibility) and one atomic position $\tau_{\kappa\beta}$ (atom κ and direction β).

$$\frac{\partial \chi_{\alpha\beta}^{\infty(1)}}{\partial \tau_{\kappa\beta}} = \left. \frac{\partial^3 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \tau_{\kappa\beta}} \right|_{\mathcal{E}=0} - \frac{8\pi}{\Omega_0} \frac{\sum_l Z_{\kappa\beta\gamma}^* q_\gamma}{\sum_{\gamma\gamma'} q_\gamma \varepsilon_{\gamma\gamma'}^\infty q_{\gamma'}} \sum_\gamma \chi_{\alpha\beta\gamma}^{\infty(2)} q_\gamma \quad (63)$$

where we have added the non-analytic contribution for polar crystals (the most common case) in which Z^* is the Born effective charge, \mathbf{q} the wavevector of the photon, which is only important by its direction, ε^∞ is the optical dielectric constant as above, and $\chi_{\alpha\beta\gamma}^{\infty(2)}$ is the non-linear optical susceptibility.

The Raman tensor is then given by

$$\aleph_{\alpha\beta}^m = \sqrt{\Omega_0} \sum_{\kappa\gamma} \frac{\partial \chi_{\alpha\beta}^{\infty(1)}}{\partial \tau_{\kappa\gamma}} \eta_m(\kappa\gamma) \quad (64)$$

where $\eta_m(\kappa\gamma)$ is the displacement vector for phonon mode m . In powder, polycrystalline, or disordered samples appropriate averages of \aleph must be taken to compare to experiment. The theory exposed so far has described non-resonant Raman, and presumed no electronic transitions are available at the same photon energies. In many materials, in particular metals, this is not true, as there is no energy gap in the electron spectrum. The generalization to resonant Raman is an active field of research, e.g. for DFPT in a recent paper by Gillet *et al.* [23].

Note finally that \aleph gives the intensity of the Raman peaks (in particular it tells you if for some Raman-allowed modes \aleph^m is small or 0) but does not give the broadening or line width. To this end one must explicitly consider the processes which limit phonon lifetimes, in particular the electron-phonon and phonon-phonon interactions, which will be described below.

Electro-optic coefficients

A closely related quantity is the electro-optic coefficient, which is the variation of dielectric constant ε under applied external electric field. The field will give a direct effect through $\chi^{\infty(2)}$ (the third partial derivative with respect to electric field) and an indirect effect when the atomic positions relax under the field. The latter can be estimated to first order from the phonon and electric field derivatives we already have. The variation of ε

$$\Delta(\varepsilon^{-1})_{\alpha\beta} = \sum_{\gamma=1}^3 r_{\alpha\beta\gamma} \mathcal{E}_\gamma \quad (65)$$

is given by the Pockels coefficient $r = r^{el} + r^{ion}$

$$r_{\alpha\beta\gamma}^{el} = \frac{-8\pi}{\mathbf{n}_\alpha^2 \mathbf{n}_\beta^2} \chi_{\alpha\beta\gamma}^{\infty(2)} \quad (66)$$

$$r_{\alpha\beta\gamma}^{ion} = -\frac{4\pi}{\sqrt{\Omega_0} \mathbf{n}_\alpha^2 \mathbf{n}_\beta^2} \sum_m \frac{\aleph_{\alpha\beta}^m p_{m\gamma}}{\omega_m^2} \quad (67)$$

where \mathbf{n} is the refractive index and $p_{m\gamma}$ is the mode polarity as in section 3.3.

If, further, the strain changes under applied field (which is generically always the case) a full set of linear equations must be solved for the so-called ‘‘unclamped’’ effect of the external field, including piezoelectric and strain perturbation effects. For finite electric fields within the Berry phase formulation of the modern theory of polarization [19] (see Lecture A6) it is not trivial whether to first discretize the calculation of the Berry phase then do the perturbation theory or the reverse. Veithen *et al.* [22] have shown the former (Perturbation Expansion After Discretization) is more efficient in terms of convergence, though both give the same numerical results.

Anharmonic inter-atomic force constants

The lattice dynamics of real crystals is never fully harmonic. Interatomic potential energies and the corresponding force constants are always anharmonic beyond a certain distance of stretching, and often beyond just a small fraction of an interatomic distance. The anharmonicity of these potentials leads to lower forces upon stretching bonds, and when a crystal is heated and more phonons are excited the distances expands. With respect to the ideal harmonic phonon picture, the presence of a non-harmonic potential gives rise to (quasi)-particles with a finite lifetime. Spectroscopic features (e.g. Raman) due to a phonon will no longer be infinitely sharp, but have a width in frequency/energy, which is linked to the inverse of the lifetime through a Heisenberg relation.

Thermal expansion is the first visible consequence of anharmonicity, but there are many others. The thermal conductivity of solids is determined mainly by phonon heat transfer, limited by phonon-phonon interactions (the “lattice” contribution). This is true both in insulators and, for intermediate temperatures, in metals - at very high T the electronic contribution dominates as there are often many more degrees of freedom in the electrons. The thermal variation of any experimental observable is a combination of a term due to thermal expansion, and additional terms due to direct interaction with phonons. Thermal motion guarantees that some of the anharmonic energy landscape will be sampled by atomic trajectories, and in many cases can dynamically stabilize or destabilize a crystal. One such case is Calcium under pressure, where a simple cubic phase is stabilized by anharmonic renormalizations of the phonon frequencies: a tetragonal phase with lower internal energy is rendered unstable at finite temperature [24] with full anharmonic renormalization (NB this is beyond DFPT), and may even be less stable in internal energy at low temperature, if full quantum effects are taken into account [25] (NB this builds on developments in the present section).

The full energy of a crystal can be written in a Taylor series (as Eq. 36 above) but with an extra term written explicitly),

$$\begin{aligned}
 E = E_0 &+ \sum_{\mathbf{R}\kappa\beta} \Phi^{(1)}(\mathbf{R}\kappa\beta) u_{\mathbf{R}\kappa\beta} + \frac{1}{2} \sum_{\mathbf{R}\kappa\beta\mathbf{R}'\kappa'\beta'} \Phi^{(2)}(\mathbf{R}\kappa\beta; \mathbf{R}'\kappa'\beta') u_{\mathbf{R}\kappa\beta} u_{\mathbf{R}'\kappa'\beta'} \\
 &+ \frac{1}{3!} \sum_{\mathbf{R}\kappa\beta\mathbf{R}'\kappa'\beta'\mathbf{R}''\kappa''\beta''} \Phi^{(3)}(\mathbf{R}\kappa\beta; \mathbf{R}'\kappa'\beta'; \mathbf{R}''\kappa''\beta'') u_{\mathbf{R}\kappa\beta} u_{\mathbf{R}'\kappa'\beta'} u_{\mathbf{R}''\kappa''\beta''} + \dots \quad (68)
 \end{aligned}$$

with the various orders of force constants Φ and displacements u of the atomic positions τ in the unit cell at \mathbf{R} , and κ runs over all atoms in the cell. If atoms start from their equilibrium positions the linear term (the force) is 0 and the second order (harmonic) force constants are those calculated in Section 3.1. For temperatures well below melting, the u can be considered small parameters and the series converges, each higher order term being smaller than the previous one. Near melting, or in ionic conductors, atoms can diffuse and the u are by no means small, or even bounded, and the series expansion is not well defined. With these limitations, DFPT can in principle calculate all of the $\Phi^{(n)}$, following the ladder of variational approximations and $2n+1$ theorems exposed above, but the increasing complexity of the formulae and the associated phase space (number of \mathbf{q} vectors) limit calculations to $\Phi^{(3)}$ for the moment - these are also the most important contributions in almost all cases. Combinations of DFPT with additional finite differentiation have yielded $\Phi^{(4)}$ for some simple systems, such as in Ref. [25].

The theory for the calculation of $\Phi^{(3)}$ was implemented by Alberto Debernardi [26, 27] for

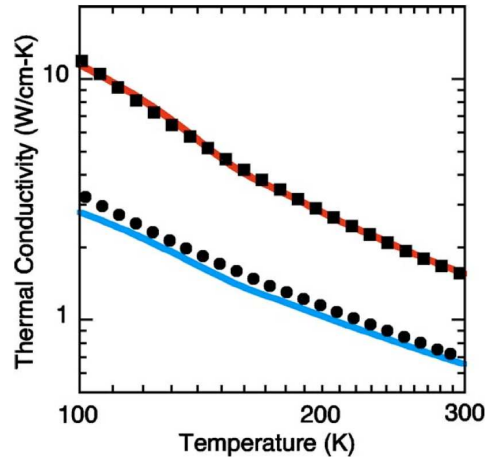


Fig. 1: Thermal conductivity of Silicon (top red curve) and Germanium (bottom blue curve), compared to experimental data. From Reference [30]. Excellent agreement is obtained with 3rd order phonon-phonon scattering, plus isotopic and defect contributions (both of which have much simpler forms).

Γ -point phonons, yielding directly the derivative

$$\Phi^{(3)}(\mathbf{R}\kappa\beta; \mathbf{R}'\kappa'\beta'; \mathbf{R}''\kappa''\beta'') = \frac{\partial^3 E}{\partial \tau_{\mathbf{R}\kappa\beta} \partial \tau_{\mathbf{R}'\kappa'\beta'} \partial \tau_{\mathbf{R}''\kappa''\beta''}} \quad (69)$$

(each atom κ is in unit cell \mathbf{R} and displaced in direction β) or more often its lattice Fourier transform:

$$\Phi_{\kappa\beta\kappa'\beta'\kappa''\beta''}^{(3)}(\mathbf{q}\mathbf{q}'\mathbf{q}'') = \frac{1}{N} \sum_{\mathbf{R}=\mathbf{0}\mathbf{R}'\mathbf{R}''} e^{i\mathbf{q}\cdot\mathbf{R}} e^{i\mathbf{q}'\cdot\mathbf{R}'} e^{i\mathbf{q}''\cdot\mathbf{R}''} \Phi^{(3)}(\mathbf{0}\kappa\beta; \mathbf{R}'\kappa'\beta'; \mathbf{R}''\kappa''\beta'') \quad (70)$$

with the variation of κ restricted to a single unit cell at the origin and the use of translational invariance. Note that this partial FT with respect to lattice vectors is very common, and yields a hybrid quantity in reciprocal (for \mathbf{q}) and real space (for $\tau_{\mathbf{0}\kappa}$). Both energy and momentum must be conserved in the 3 phonon interaction:

$$\mathbf{q} + \mathbf{q}' + \mathbf{q}'' = \mathbf{G} \quad (71)$$

$$\omega_{\mathbf{q}m} + \omega_{\mathbf{q}'m'} \pm \omega_{\mathbf{q}''m''} = 0 \quad (72)$$

where the sign determines phonon emission or absorption. For Γ point phonons a significant reduction of the phase space happens, as $\mathbf{q}' = -\mathbf{q}''$ to within a \mathbf{G} vector. This is the useful case for the Raman modes mentioned above. Extensions of the implementation to finite \mathbf{q} were carried out in the Regensburg group by Deinzer, Strauch et al. [28, 29].

From the $\Phi^{(3)}$ one can calculate the phonon linewidth as a function of temperature (here at Γ for simplicity):

$$\begin{aligned} \Gamma_{m\mathbf{q}=0} &= \frac{\pi}{2\hbar^2} \sum_{\mathbf{q}'m'm''} \left| \sum_{\kappa\beta} \Phi_{\kappa\beta\kappa'\beta'\kappa''\beta''}^{(3)}(\mathbf{0} \ \mathbf{q}' - \mathbf{q}'') \eta_{m0}(\kappa\beta) \eta_{m'\mathbf{q}'}(\kappa'\beta') \eta_{m''\mathbf{q}''}(\kappa''\beta'') \right|^2 \\ &\times [(1 + n_{\mathbf{q}'m'} + n_{-\mathbf{q}''m''}) \delta(\omega_{\mathbf{q}'m'} + \omega_{-\mathbf{q}''m''} - \omega_m) \\ &+ 2(n_{\mathbf{q}'m'} - n_{-\mathbf{q}''m''}) \delta(\omega_{\mathbf{q}'m'} - \omega_{-\mathbf{q}''m''} - \omega_m)] \end{aligned} \quad (73)$$

and other quantities such as Grüneisen parameters [31] through similar formulae:

$$\gamma_{m\mathbf{q}} = -\frac{1}{6\omega_{m\mathbf{q}}^2} \sum_{\kappa\beta; \mathbf{R}'; \kappa'\beta'; \mathbf{R}'' \kappa''\beta''} \Phi^{(3)}(\mathbf{0}\kappa\beta; \mathbf{R}'\kappa'\beta'; \mathbf{R}''\kappa''\beta'') \eta_{m\mathbf{q}}^*(\kappa\beta) \eta_{m\mathbf{q}}(\kappa'\beta') e^{i\mathbf{q}\cdot\mathbf{R}'} \tau_{\mathbf{R}''\kappa''\beta''}$$

The positions τ in the final factor will be renormalized by the thermal phonon displacements if the symmetry is low enough - see Ref. [31]. Finally, the thermal conductivity was first determined from DFPT by Broido et al. in Ref. [30] - see Fig. 1. In many systems $\Phi^{(3)}$ gives the bulk of the anharmonicity and very good agreement can be obtained, once isotopic and impurity scattering is added to the phonon contribution.

4.2 Spin and magnetic effects

Magnetic field and magnons

The second variation of the energy with respect to an external magnetic field gives the magnetic susceptibility χ_m . In non magnetic materials, paradoxically, the (dia)magnetic response is more complex to calculate. This response determines the nuclear magnetic resonance (NMR) or electron paramagnetic resonance (EPR) shifts, and is the subject of ongoing research [32, 33, 34]. In ferromagnetic or antiferromagnetic systems (in particular metals, but sometimes insulators as well) the χ_m presents poles for excitations of the magnetic system (waves of oscillating spins or magnons). These excitations are quite low in energy (meV or much less). Because the degree of freedom (the spin) being perturbed is intimately linked to the electron wave functions, one can not use a phonon-like separation of ionic and electronic coordinates to study “just” the effect of the \mathbf{B} field perturbatively. The correct formulation was developed by Savrasov [35] as a perturbation theory built on top of time dependent DFT [36] (see Lecture A7). The action is varied perturbatively, instead of the total energy, under an applied *time dependent* magnetic field

$$\delta B_{\text{ext}}(\mathbf{r}t) = \delta \mathbf{b} e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} e^{i\omega t} \quad (74)$$

The first order change in wave functions induces changes in density *and* magnetization:

$$\delta \mathbf{m} = \mu_B \sum_{iss'} \psi_{is}^{(1)} \sigma_{ss'} \psi_{is'}^{(0)} + \text{c.c.} \quad (75)$$

summing over bands i and spins s , where μ_B is the Bohr magneton and σ are the Pauli matrices. The change $\delta \mathbf{m}$ for a given field yields χ_m . The 2n+1 and variational principles are extended, giving the time dependent Sternheimer equation, conveniently written in frequency space:

$$(H - \epsilon_i \pm \omega) \psi_i^{(1)} + (V_{\text{eff}}^{(1)} I - \mu_B \sigma \delta B_{xc}) \psi_i^{(1)} = 0 \quad (76)$$

where I is the 2×2 spin identity matrix. There is a further feedback effect through the exchange-correlation magnetic field δB_{xc} , which is induced by the DFT electrons themselves.

Magnon bands are seen as peaks or divergencies of χ_m at specific energies, but $\chi_m(\omega)$ is a continuous function giving the full response at all frequencies. The equations must be solved for the full $\mathbf{q} \omega$ space, which makes things quite heavy numerically. Few systems with more than 1 atom per unit cell have been calculated in this way. Other approaches such as the Korringa Kohn Rostoker [37] Green’s function approach are more widely used for magnon dispersions.

Spin-orbit coupling

In heavy atoms the Coulomb potential is extremely strong near the nucleus. Core electrons see a very large electric field, and feel a very strong potential. This quantum confinement implies a correspondingly high kinetic energy, and core electrons can quickly attain relativistic speeds, obeying the Dirac 4-component spinor equation instead of the “classical” Schrödinger one (see Ref. [38] and Lecture A10). In the frame of reference of the electrons, the electric field is equivalent to a magnetic one, which affects the spin angular momentum of the electron. Depending on the orbital angular momentum L of the electrons, they will have an angular speed, and a Taylor expansion of the Dirac equation leads to scalar corrections and then the famous spin-orbit coupling (SOC) term, proportional to $\mathbf{L} \cdot \mathbf{s}$ with a prefactor proportional to ∇v_{ext} (i.e. the electric field).

The coupling between spin and angular orbital moments is almost always treated in DFT through a reduced equation for 2-component Pauli spinors [39] with spin up and spin down components, instead of the full Dirac equation. In this case the scalar and spin-orbit relativistic terms are simply additive in the normal Kohn-Sham Hamiltonian, and the extension of DFPT is quite straightforward. Only the spin-orbit term is not spin-component diagonal. In norm-conserving pseudopotential [40] and projector augmented wave [41] formalisms the effect on the active valence electrons is treated in a perturbative way: the valence electron wave functions are projected on an atomic basis, in which the matrix element of the SOC is evaluated. The effect can be wrapped into non-local pseudopotential like projectors, in a sphere around each atom. In this way, for phonon perturbations, the dependency on atomic positions is simple: the projector is rigidly shifted with the atom. In reciprocal space the phase factor corresponding to the non-local projection operators are simple to derive with respect to ionic positions. We consider a SOC pseudopotential term of the form:

$$V_l^{SO}(\mathbf{G}s, \mathbf{G}'s') = -i \frac{4\pi}{\Omega_0} (2l+1) \sum_{\kappa} E_{\kappa l}^{KB,SO} P_l'(\hat{G} \cdot \hat{G}') \zeta_{\kappa l}^{SO}(\mathbf{G}) \zeta_{\kappa l}^{SO}(\mathbf{G}') \left(\langle s|\sigma|s' \rangle \cdot \frac{\mathbf{G} \times \mathbf{G}'}{GG'} \right) e^{i(\mathbf{G}'-\mathbf{G})\tau_{\kappa}} \quad (77)$$

in reciprocal space \mathbf{G} , where $\zeta_{\kappa l}^{SO}(\mathbf{G})$ is the spherical Fourier transform of the radial part of the potential, and with Kleinman Bylander energies E_l^{KB} and Legendre polynomials P_l for each angular momentum channel l . It becomes clear that the atomic position dependency is simple. The second derivative of the energy term becomes:

$$\frac{\partial^2 E^{SO}}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa\alpha}} = i \frac{4\pi}{\Omega_0} \sum_{nl} f_n (2l+1) E_{\kappa l}^{KB,SO} \sum_{\mathbf{G}s\mathbf{G}'s'} P_l'(\hat{G} \cdot \hat{G}') \zeta_{\kappa l}^{SO}(\mathbf{G}) \zeta_{\kappa l}^{SO}(\mathbf{G}') \left(\langle s|\sigma|s' \rangle \cdot \frac{\mathbf{G} \times \mathbf{G}'}{GG'} \right) \times 2\Re \mathfrak{e}[(G'_{\alpha} - G_{\alpha})G'_{\beta} \cdot c_{ns}^{(0)*}(\mathbf{G}) c_{ns'}^{(0)}(\mathbf{G}') \cdot e^{i(\mathbf{G}'-\mathbf{G})\tau_{\kappa}}] \quad (78)$$

where f_n is the Fermi Dirac occupation and $c_{ns}(\mathbf{G})$ are the plane wave coefficients for $\psi_n^{(0)}$. The formalism has been developed for norm-conserving pseudopotentials in Verstraete *et al.* [42] and for PAW by Dal Corso [43]. For Pb the effect of spin orbit coupling on the phonons is particularly strong at the X point. The SOC produces a shift of the Fermi surface, part of which moves to half of the distance between X and the zone center. The resulting nesting emphasizes a Kohn anomaly [44] at X and softens the phonon frequency - see Fig. 2.

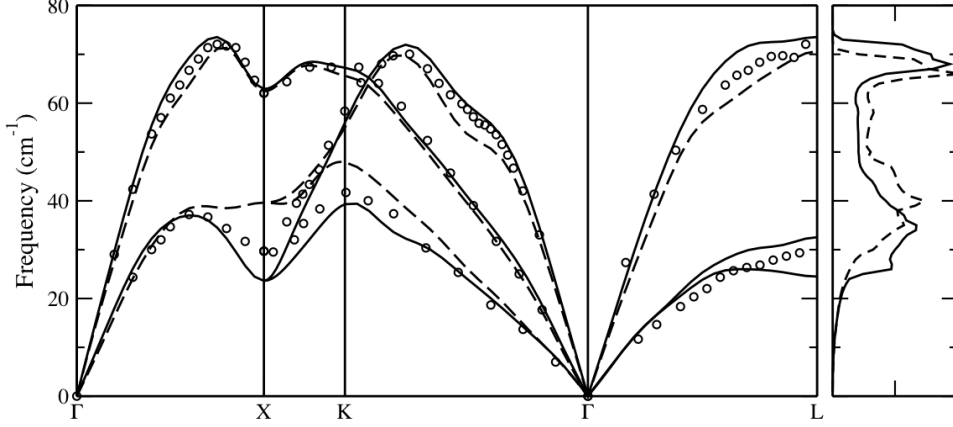


Fig. 2: Phonon band structure and DOS of lead, with (solid) and without (dashed) spin-orbit coupling, compared to experiment (symbols). A huge softening at X results from changes in the Fermi surface due to SOC and a resulting Kohn anomaly. From Reference [42]

4.3 Elastic constants

Another important physical response function is the elastic constant tensor, the second derivatives of the total energy (or rather the Helmholtz free energy) with respect to applied strain ς . As with all second derivatives they can be calculated from the first order perturbed wave functions, but the derivatives are much more involved for reasons we will see. A DFPT formalism was first written down by Baroni, Giannozzi and Testa [45] for isotropic stress and local pseudopotentials, and generalized more recently by Hamann *et al.* [46] (we will follow the latter). Because the strain can change the unit cell angles as well as the cell parameters, the basis set itself will be affected, and all of the terms of the energy will vary. The formalism is expressed as a function of the reduced atomic coordinates and the metric tensors:

$$\Xi_{ij} = \sum_{\alpha} R_{\alpha i} R_{\alpha j} \quad (79)$$

$$\Upsilon_{ij} = \sum_{\alpha} G_{\alpha i} G_{\alpha j} \quad (80)$$

in real and reciprocal space, with α here a cartesian coordinate, i, j reduced coordinates (we use roman letters to denote reduced coordinates in this section for clarity), and R and G the real and reciprocal space lattice vectors. The main advantage is that in reduced coordinates the boundary conditions do not change, which is not the case in cartesian coordinates: any finite strain produces arbitrarily large shifts for atoms far enough away from the origin. The derivatives of Υ (idem for Ξ) with respect to strain are apparently simple:

$$\Upsilon_{ij}^{(\alpha\beta)} = \frac{\partial \Upsilon_{ij}}{\partial \varsigma_{\alpha\beta}} = -G_{\alpha i} G_{\beta j} - G_{\beta i} G_{\alpha j} \quad (81)$$

$$\begin{aligned} \Upsilon_{ij}^{(\alpha\beta\gamma\delta)} = \frac{\partial^2 \Upsilon_{ij}}{\partial \varsigma_{\alpha\beta} \partial \varsigma_{\gamma\delta}} &= \delta_{\alpha\gamma} (G_{\beta i} G_{\delta j} + G_{\delta i} G_{\beta j}) + \delta_{\beta\gamma} (G_{\alpha i} G_{\delta j} + G_{\delta i} G_{\alpha j}) \\ &+ \delta_{\alpha\delta} (G_{\beta i} G_{\gamma j} + G_{\gamma i} G_{\beta j}) + \delta_{\beta\delta} (G_{\alpha i} G_{\gamma j} + G_{\gamma i} G_{\alpha j}) \end{aligned} \quad (82)$$

The dependency on Ξ and Υ can be made explicit in each of the energy terms, as well as the wave function normalization expressions. We will not go through all of the derivatives, but

show as an example the effect on the kinetic energy T , which is not directly affected by *any* other perturbation (only indirectly through variations of the wave functions). The contribution of individual plane waves to T is:

$$\langle \tilde{\mathbf{K}}' | T | \tilde{\mathbf{K}} \rangle = \frac{1}{2} \delta_{\tilde{\mathbf{K}}\tilde{\mathbf{K}}'} \sum_{ij} \Upsilon_{ij} \tilde{K}_i \tilde{K}_j \quad (83)$$

where the tilde denotes reduced vectors. The first derivatives (stress contributions) are then:

$$\langle \tilde{\mathbf{K}}' | \frac{\partial T}{\partial \varsigma_{\alpha\beta}} | \tilde{\mathbf{K}} \rangle = \frac{1}{2} \delta_{\tilde{\mathbf{K}}\tilde{\mathbf{K}}'} \sum_{ij} \Upsilon_{ij}^{(\alpha\beta)} \tilde{K}_i \tilde{K}_j \quad (84)$$

The second derivatives (elastic constant contributions) are:

$$\langle \tilde{\mathbf{K}}' | \frac{\partial^2 T}{\partial \varsigma_{\alpha\beta} \partial \varsigma_{\gamma\delta}} | \tilde{\mathbf{K}} \rangle = \frac{1}{2} \delta_{\tilde{\mathbf{K}}\tilde{\mathbf{K}}'} \sum_{ij} \Upsilon_{ij}^{(\alpha\beta\gamma\delta)} \tilde{K}_i \tilde{K}_j \quad (85)$$

As can be seen the diagonal character of the kinetic energy and its simple form are preserved in reduced coordinates. Corresponding terms can be written for the Hartree, exchange-correlation, and pseudopotential energies, and a variational second order expression found which can be minimized to give $\psi^{(1)}$, then the elastic constants (supposing you start from an unstressed equilibrium state) are:

$$\bar{C}_{\alpha\beta;\gamma\delta} = \frac{1}{\Omega_0} \frac{\partial^2 E}{\partial \varsigma_{\alpha\beta} \partial \varsigma_{\gamma\delta}} \quad (86)$$

Combining the strain derivatives with electric field derivatives, one can access the piezoelectric coefficients (specifically the frozen ion piezoelectric tensor) through the mixed second derivative:

$$\bar{e}_{\gamma;\alpha\beta} = -\frac{\partial^2 E}{\partial \tilde{\mathcal{E}}_\gamma \partial \varsigma_{\alpha\beta}} = -2 \frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_m^{occ} \langle \psi_{\mathbf{km}}^{(\tilde{k}_\gamma)} | \psi_{\mathbf{km}}^{(\varsigma_{\alpha\beta})} \rangle d\mathbf{k} \quad (87)$$

in which the first perturbed wave function is derived with respect to the k-point coordinates (reduced), as above for other \mathcal{E} field derivatives, and the second with respect to strain.

Under applied strain all of the cartesian atomic positions will change as well. The reduced coordinates can often stay the same (e.g. a centered atom in a BCC unit cell under isotropic dilation), but, even if the system is very highly symmetric, a shear strain will usually break enough symmetries to allow additional internal degrees of freedom. In this case one must couple the strain derivatives to phonon derivatives to calculate the *relaxed ion* elastic tensor. The systematic treatment of phonon, electric field, and strain perturbation combinations is given in Ref. [47]. Quantities calculated with frozen ions are denoted with a bar. The internal strain tensor is defined as

$$\Lambda_{m;\alpha\beta} = -\Omega_0 \sum_{\kappa\gamma} \eta_{\mathbf{q}=0m}(\kappa\gamma) \frac{\partial^2 E}{\partial \tau_{\kappa\gamma} \partial \varsigma_{\alpha\beta}} \quad (88)$$

and the resulting relaxed ion elastic and piezoelectric tensors are:

$$C_{\alpha\beta;\gamma\delta} = \bar{C}_{\alpha\beta;\gamma\delta} - \Omega_0^{-1} \Lambda_{m;\alpha\beta} ((\Phi^{(2)})^{-1})_{mm'} \Lambda_{m';\gamma\delta} \quad (89)$$

$$e_{\gamma;\alpha\beta} = \bar{e}_{\gamma;\alpha\beta} + \Omega_0^{-1} Z_{m\gamma}^* ((\Phi^{(2)})^{-1})_{mm'} \Lambda_{m';\alpha\beta} \quad (90)$$

using the Born effective charges and the inverse of the harmonic force constants.

4.4 Electron-Phonon coupling

Framework theory

The response functions described up to this point determine the reaction of a system to perturbations, either of electrons or ions to external fields, or of electrons to the movement of the ions. We have supposed that the independent particle Kohn Sham picture is a good starting point, and that the corresponding single particle orbitals are good representations of the electronic states and excitations. Similarly we have supposed (except in Sect. 4.1) that the phonons are *also* ideal quasiparticles, with infinite lifetimes at a given volume and temperature. In reality, neither phonons nor electrons are ideal, and their main interaction is usually with each other - the presence of phonons (and many other scattering centers) limits the lifetime and free path of electrons, and vice versa. The electron phonon coupling (EPC) is central to “ordinary” BCS superconductivity, normal phase electron resistivity, and many other phenomena. The theory of EPC has been reviewed extensively by Allen and Mitrovic [48] and in a book by Grimvall [49]. The first DFT calculations in this framework were carried out by Marvin Cohen and coworkers in the 1980s [50]. The extension to DFPT is due to Savrasov [51]. Within the phonon perturbation theory exposed in the preceding sections we already have access to the necessary matrix element, which is

$$g_{\mathbf{k}+\mathbf{q}i'\mathbf{k}i}^{\mathbf{q}m} = \langle \psi_{\mathbf{k}+\mathbf{q}i'}^{(0)} | \delta^{\mathbf{q}m} V_{eff} | \psi_{\mathbf{k}i}^{(0)} \rangle \quad (91)$$

$$= \frac{1}{\sqrt{\omega_{\mathbf{q}m}}} \sum_{\kappa\alpha} \eta_{\mathbf{q}m}(\kappa\alpha) \frac{\partial V_{eff}}{\partial \tau_{\kappa\alpha}} \quad (92)$$

$$= \frac{1}{\sqrt{\omega_{\mathbf{q}m}}} \sum_{\kappa\alpha} \eta_{\mathbf{q}m}(\kappa\alpha) \langle \psi_{\mathbf{k}+\mathbf{q}i'}^{(0)} | H_{\mathbf{q}\kappa\alpha}^{(1)} | \psi_{\mathbf{k}i}^{(0)} \rangle \quad (93)$$

for phonon mode m at wave vector \mathbf{q} , and momentum conservation imposes $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ (we will impose energy conservation later). The phonon displacement vector $\eta_{\mathbf{q}m}(\kappa\alpha)$ is in units of meters (i.e. it is normalized with the square roots of atomic masses). The matrix element is nothing but $\epsilon^{(1)\mathbf{q}\kappa\alpha}$ from the Sternheimer equation. It contains the self consistent induced change in the effective KS potential. Within the Migdal approximation the self-interaction terms for EPC are only considered with one phonon propagator [52], so this matrix element is all we need. Through Fermi's Golden Rule, the interaction will determine an inverse lifetime for phonons (by interaction with electrons with Fermi level ϵ_F):

$$\gamma_{\mathbf{q}m}^{ph} = 2\pi\omega_{\mathbf{q}m} \sum_{\mathbf{k}i i'} |g_{\mathbf{k}+\mathbf{q}i'\mathbf{k}i}^{\mathbf{q}m}|^2 \delta(\epsilon_{\mathbf{k}i} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q}i'} - \epsilon_F) \quad (94)$$

and for electrons (by interactions with phonons - see e.g. Ref. [53, 49]):

$$\begin{aligned} \gamma_{\mathbf{k}i}^{el} &= 2\pi \sum_{\mathbf{q}m i'} |g_{i'\mathbf{k}+\mathbf{q}i\mathbf{k}}^{\mathbf{q}m}|^2 \times \{ [f(\epsilon_{\mathbf{k}+\mathbf{q}i'}) + n(\omega_{\mathbf{q}m})] \delta(\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}+\mathbf{q}i'} + \omega_{\mathbf{q}m}) \\ &+ [1 - f(\epsilon_{\mathbf{k}+\mathbf{q}i'}) + n(\omega_{\mathbf{q}m})] \delta(\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}+\mathbf{q}i'} + \omega_{\mathbf{q}m}) \} \end{aligned} \quad (95)$$

In the former we have made an additional approximation of elastic interaction, neglecting the phonon energy before the electron one, and restricting both initial and final states to be on the Fermi surface. In the latter one sees explicitly the terms for phonon emission and absorption, respectively.

Superconductivity

The full theory of phonon driven superconductivity is due to Eliashberg, who wrote a full microscopic and Green's function theory for the BCS interaction. The single term self-energy gives a spectral function analogous to a density of states, weighted by the EPC, known as the Eliashberg function:

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(\epsilon_F)} \sum_{\mathbf{q}m} \frac{\gamma_{\mathbf{q}m}}{\omega_{\mathbf{q}m}} \delta(\omega - \omega_{\mathbf{q}m}) \quad (96)$$

whose first inverse moment is the EPC coupling strength λ , which can be injected in your favorite formula for predicting superconducting critical temperatures (McMillan [54], Allen Dynes [55] ...).

The historical shortcoming of such formulae, and Eliashberg's final formulation as well, is the need for an empirical parameter characterizing the Coulomb repulsion between the Cooper-paired electrons in the system. The repulsion is well beyond the DFT interaction as it concerns two explicit electrons, and no mean field can provide a useful value. This problem has been addressed by the group of Hardy Gross [56, 57] using diagrammatic techniques on top of an explicit density functional theory for superconductors. Two density components are considered, for normal and superconducting electrons, and the coupling between the normal and "anomalous" densities are included. Very good agreement has been found in a number of systems (e.g. [58]).

Electron transport

The EPC matrix element also provides the main ingredient for theories studying electron transport. Phonon limitation of electrical conductivity can be included in any perturbational technique, but usually [59] starts from the semiclassical/mesoscopic Boltzmann transport equations (BTE). A number of seminal papers on EPC and BTE expressions were written by P.B. Allen since the 1970s [60, 61] and implemented in the work by Savrasov [51]. With a variational ansatz for the way the electron distribution is pushed out of equilibrium (away from Fermi Dirac) one can find a closed form for the transport coefficients. Allen introduces a generalized spectral function for transport, analogous to $\alpha^2 F$ but including Fermi velocity factors:

$$\alpha_{\text{tr}}^2 F(\alpha, \beta, \omega) = \frac{1}{2N(\epsilon_F)} \sum_{m; \mathbf{k}; \mathbf{k}'; i'} |g_{\mathbf{k}i\mathbf{k}'i'}^{\mathbf{q}m}|^2 \frac{[v_\alpha(\mathbf{k}) - v_\alpha(\mathbf{k}')] [v_\beta(\mathbf{k}) - v_\beta(\mathbf{k}')] }{\langle v_\alpha \rangle \langle v_\beta \rangle} \delta(\epsilon_{\mathbf{k}i}) \delta(\epsilon_{\mathbf{k}'i'}) \delta(\omega_{\mathbf{q}m} - \omega)$$

where N is the density of states, and $\mathbf{v}(\mathbf{k})$ is the Fermi velocity at \mathbf{k} , $\langle v_\beta \rangle$ the FS average of \mathbf{v} and ϵ_F has been set to 0. In the elastic approximation mentioned above, and to lowest order, the electrical resistivity is:

$$\rho_{\alpha\beta} = \frac{2\pi\Omega_0 k_B T}{N(\epsilon_F) \langle v_\alpha(\epsilon_F) \rangle \langle v_\beta(\epsilon_F) \rangle} \times \int_0^\infty \frac{d\omega}{\omega} \frac{x^2}{\sinh^2 x} \alpha_{\text{tr}}^2 F(\alpha, \beta, \omega) \quad (97)$$

where $x = \omega/2k_B T$. The electronic thermal resistivity (without the lattice contribution) has a similar form.

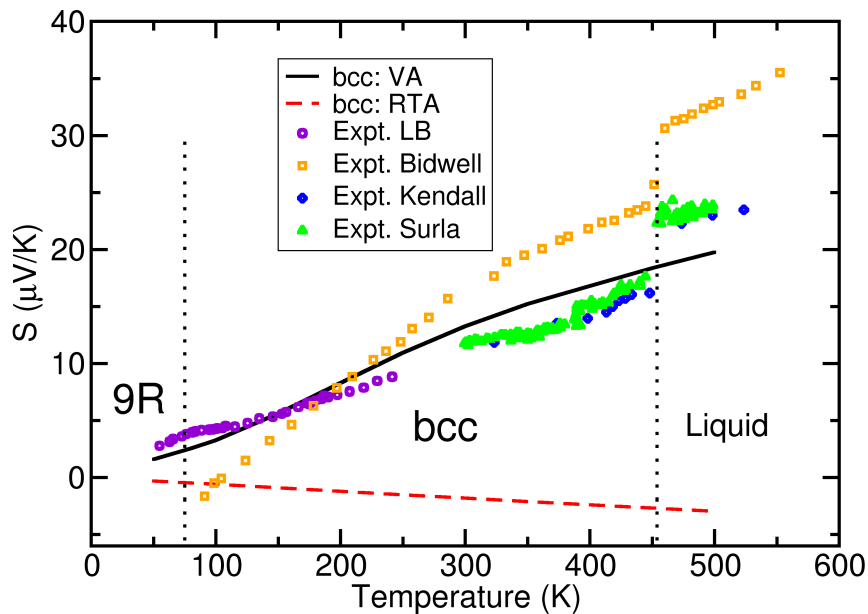


Fig. 3: Seebeck coefficient of BCC lithium within DFPT (black) compared to experimental data (symbols) and constant relaxation time (red dashed). The values are positive, despite the negative sign of the charge carriers in this simple metal, due to a complex energy dependency of the electron lifetime. From Reference [62]

Seebeck coefficients

Within the elastic approximation the Seebeck coefficient is identically zero, as electrons and holes will diffuse in exactly the same way at ϵ_F . Fermi smearing effects must be included, and the full expressions derived by Allen employed [61]. This was done recently [62] for BCC Li which presents an anomalous sign of the Seebeck coefficient. Standard approximations such as the constant relaxation time fail qualitatively (see Fig. 3).

Band gap renormalization

The interaction with phonons also has a more direct effect on the electronic energies, renormalizing them both through thermal expansion and through ionic screening and polarization effects. These are beyond the first order EPC described above, and were first codified by Allen, Heine and Cardona [63, 64] for empirical potentials. In the past few years several teams [65, 66] have implemented the DFPT calculation of the necessary terms and published results for diamond. There is some debate about the completeness of the AHC formalism and how close the DFT values should be to experiment.

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