Anharmonic effects in crystals

from

Density-Functional Perturbation Theory

Thesis submitted for the degree of

"Magister Philosophiæ"

CANDIDATE	SUPERVISOR
Alberto Debernardi	Prof. Stefano Baroni

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SISSA ISAS

SCUOLA INTERNAZIONALE SUPERIORE DI STUDI AVANZATI
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Introduction

Density Functional Perturbation Theory (DFPT) is a powerful tool to determine low-order derivatives of the ground-state electronic energy of materials with respect to some external parameters. The use of DFPT is twofold. On the one hand, it allows to calculate response functions—which are directly accessible to experiments—or other measurable properties which can be related to response functions—such as e.g. phonon frequencies in the adiabatic approximation. On the other hand, it can be used to calculate properties of specific, complex, materials which can viewed as small perturbations with respect to other, simpler, systems. Since DFPT was demonstrated to be a computationally viable technique [1], many applications have appeared belonging to either categories. The first group includes the calculation of elastic constants [2], dielectric and piezoelectric constants [3], and various lattice-dynamical properties [4,5]. Other applications belonging to the second group are based on the so called *computational alchemy* approach to semiconductor alloys [6] and superlattices [7] in which the disordered semiconductor is viewed as a small perturbation with respect to a reference, periodic system (the *virtual* crystal).

Third-Order Density-Functional Perturbation Theory

All the applications of DFPT appeared so far are limited to second order in the energy. It is a well known result of elementary quantum-mechanics that the knowledge of the wavefunction response of a system up to n-th order in the strength of an external perturbation is sufficient to determine the energy derivative up to order $2n + 1$ [8]. The validity of this '$2n + 1$ theorem' within self-consistent field (SCF) theories has been known since several years in the quantum-chemistry community [9], and recently it has been generalized to density-functional theory (DFT) by Gonze and Vigneron [10]. A first important conclusion we can draw from this 'theorem' is that the knowledge of the *linear* response of a system to an external perturbation allows to determine the *third* derivatives of the energy with respect to the strength of the perturbation and it gives therefore a practical way to link linear and quadratic generalized susceptibilities. The interest in doing so is evident: one can in principle obtain higher-order susceptibilities or gain in the accuracy achieved by perturbation theory essentially *for free*. In the following, we will concentrate on the formulation by Gonze and Vigneron and will restate it in a form which is free from some of its original drawbacks, and is well suited for practical implementations. As an example, we calculate the third-order anharmonic coupling coefficients in Silicon at some high-symmetry points of the Brillouin zone (BZ), and compare them with results obtained by the frozen-phonon method.

Analytical Results

Let us suppose that the *external* potential acting on the electrons of a given system depends *linearly* on some external parameter, λ:

$$v_{ext}(\mathbf{r}) \equiv v^0_{ext}(\mathbf{r}) + \lambda v^1_{ext}(\mathbf{r}). \tag{1}$$

The case where the dependence of v^λ_{ext} upon λ is non linear requires a straightforward generalization of the results obtained in the linear case and will be considered later. According to Gonze and Vigneron [10], the third-order derivative of the DFT ground-state energy with respect to λ reads:

$$\left.\frac{\partial^3 E^\lambda}{\partial \lambda^3}\right|_{\lambda=0} = 6\sum_v \langle \psi^1_v | H^1_{SCF} - \epsilon^1_v | \psi^1_v \rangle + \int K^3(\mathbf{r}, \mathbf{r}', \mathbf{r}'') n^1(\mathbf{r}) n^1(\mathbf{r}') n^1(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'', \tag{2}$$

where the sum runs over occupied (*valence*) Kohn-Sham (KS) orbitals, ψ^1 and ϵ^1 indicate the first derivatives of the KS orbitals and energy levels respectively, n^1 and H^1_{SCF} indicate the corresponding linear corrections to the electron ground-state density and KS one-electron hamiltonian, and K^3 is finally the third-order functional derivative of the exchange-correlation energy with respect to the electron density: $K^3(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \left.\frac{\delta^3 E_{XC}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')}\right|_{n=n^0}$. Eq. (2) clearly shows that the calculation of the third-order correction to the energy requires only the knowledge of such ingredients as ψ^1 and ϵ^1 which are directly accessible to first-order perturbation theory.

All the results of DFT must be invariant with respect to unitary transformations of the orbitals which do not mix the manifolds of occupied and empty (*conduction*) states. As it stands, Eq. (2) does not manifestly display this invariance. Furthermore, its implementation would require the knowledge of the components of the perturbed wavefunction, ψ^1_v, along all the valence wavefunctions different from

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ψ_v^0 itself: $\langle \psi_{v'}^0 | \psi_v^1 \rangle_{v' \neq v}$. Once again, this is innatural because in DFT the variation of any physical property must only depend on the variation of the one-electron density matrix which is not affected by components of the perturbed valence orbitals along the unperturbed valence manifold. This situation is particularly unpleasant when, due to the degeneracy or quasi-degeneracy of some unperturbed valence states, the actual implementation of Eq. (2) would require the use of degenerate-state perturbation theory. We will now show that Eq. (2) can be recast in a form which requires only the knowledge of the conduction-manifold projection of the ψ_v^1's, which is manifestly invariant with respect to unitary transformations within the valence manifold, and which can be straightforwardly and efficiently implemented using standard non-degenerate first-order perturbation theory.

The second term on the right-hand side (rhs) of Eq. (2) already displays the desired unitary invariance, and we concentrate on the first term. Our final result is:

$$\sum_v \langle \psi_v^1 | H_{SCF}^1 - \epsilon_v^1 | \psi_v^1 \rangle = \sum_v \langle \psi_v^1 | P_c H_{SCF}^1 P_c | \psi_v^1 \rangle - \sum_{vv'} \langle \psi_v^1 | P_c | \psi_{v'}^1 \rangle \langle \psi_{v'}^0 | H_{SCF}^1 | \psi_v^0 \rangle,$$

(3)

where $P_c \equiv \sum_c |\psi_c^0\rangle \langle \psi_c^0|$ is the projector over the unperturbed conduction-state manifold (from now on, 'c' will indicate an index running over conduction states, while 'v' indicates sums over valence states). Before demonstrating Eq. (3) we notice that it is manifestly invariant with respect to unitary transformations within the valence manifold. In fact, it is the sum of the trace of a matrix defined over that manifold (first term on the rhs) and of the product of two such matrices (second term). The desired invariance derives from the invariance property of the trace. The demonstration of Eq. (3) is tedious, but straightforward. Let us start from the definition of the first-order correction to the v-th unperturbed valence state,

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and consider its projections over the valence- and conduction-state manifolds:

$$|\psi_v^1\rangle = P_c|\psi_v^1\rangle + P_v|\psi_v^1\rangle, \tag{4a}$$

$$P_c|\psi_v^1\rangle = \sum_c |\psi_c^0\rangle \frac{\langle\psi_c^0|H_{SCF}^1|\psi_v^0\rangle}{\epsilon_v^0 - \epsilon_c^0}, \tag{4b}$$

$$P_v|\psi_v^1\rangle = \sum_{v'\neq v} |\psi_{v'}^0\rangle \frac{\langle\psi_{v'}^0|H_{SCF}^1|\psi_v^0\rangle}{\epsilon_v^0 - \epsilon_{v'}^0}, \tag{4c}$$

where $P_v \equiv 1 - P_c$ is the projector over the valence manifold. Substituting Eq. (4a) into the left-hand size of Eq. (3), one obtains the sum of four terms, which will be denoted by cc, cv, vc, and vv, according to the couple of projectors appearing inside the matrix elements. Inserting Eq. (4c) into the expression of the vv term and separating out terms with $v' = v''$ from those with $v' \neq v''$, one obtains:

$$\sum_v \langle\psi_v^1|P_v(H_{SCF}^1 - \epsilon_v^1)P_v|\psi_v^1\rangle = \sum_{v\neq v'} \frac{\langle\psi_v^0|H_{SCF}^1|\psi_{v'}^0\rangle(\epsilon_{v'}^1 - \epsilon_v^1)\langle\psi_{v'}^0|H_{SCF}^1|\psi_v^0\rangle}{(\epsilon_v^0 - \epsilon_{v'}^0)^2} +$$

$$+ \sum_{v\neq v'\neq v''} \frac{\langle\psi_v^0|H_{SCF}^1|\psi_{v'}^0\rangle\langle\psi_{v'}^0|H_{SCF}^1|\psi_{v''}^0\rangle\langle\psi_{v''}^0|H_{SCF}^1|\psi_v^0\rangle}{(\epsilon_v^0 - \epsilon_{v'}^0)(\epsilon_v^0 - \epsilon_{v''}^0)}. \tag{5}$$

Both the terms on the rhs of Eq. (5) vanish because the parities of the numerators and those of the denominators with respect to the exchanges $v \rightleftharpoons v'$ $v \rightleftharpoons v''$ are different. Let us come now to the cv and vc terms. Using Eqs. (4b) and (4c) and a few algebraic manipulations, one obtains:

$$\sum_v \Big(\langle\psi_v^1|P_c(H_{SCF}^1 - \epsilon_v^1)P_v|\psi_v^1\rangle + \langle\psi_v^1|P_v(H_{SCF}^1 - \epsilon_v^1)P_c|\psi_v^1\rangle \Big) =$$

$$\sum_{c,v\neq v'} \frac{\langle\psi_v^0|H_{SCF}^1|\psi_c^0\rangle\langle\psi_c^0|H_{SCF}^1|\psi_{v'}^0\rangle\langle\psi_{v'}^0|H_{SCF}^1|\psi_v^0\rangle}{(\epsilon_v^0 - \epsilon_{v'}^0)} \left(\frac{1}{\epsilon_v^0 - \epsilon_c^0} - \frac{1}{\epsilon_{v'}^0 - \epsilon_c^0} \right) =$$

$$- \sum_{c,v\neq v'} \frac{\langle\psi_v^0|H_{SCF}^1|\psi_c^0\rangle\langle\psi_c^0|H_{SCF}^1|\psi_{v'}^0\rangle\langle\psi_{v'}^0|H_{SCF}^1|\psi_v^0\rangle}{(\epsilon_v^0 - \epsilon_c^0)(\epsilon_{v'}^0 - \epsilon_c^0)}. \tag{6}$$

The cc term reads:

$$\sum_v \langle\psi_v^1|P_c(H_{SCF}^1 - \epsilon_v^1)P_c|\psi_v^1\rangle =$$

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$$\sum_v \langle \psi_v^1 | P_c H_{SCF}^1 P_c | \psi_v^1 \rangle - \sum_{c,v} \frac{\langle \psi_v^0 | H_{SCF}^1 | \psi_c^0 \rangle \langle \psi_c^0 | H_{SCF}^1 | \psi_v^0 \rangle \langle \psi_v^0 | H_{SCF}^1 | \psi_v^0 \rangle}{(\epsilon_v^0 - \epsilon_c^0)(\epsilon_v^0 - \epsilon_c^0)}. \quad (7)$$

The first term on the rhs of Eq. (7) coincides with the first term on the rhs of Eq. (3). The second term has the same form as the rhs of Eq. (6), just providing the $v = v'$ terms which were missing therein. By combining these terms, we finally obtain:

$$\sum_v \langle \psi_v^1 | H_{SCF}^1 - \epsilon_v^1 | \psi_v^1 \rangle = \sum_v \langle \psi_v^1 | P_c H_{SCF}^1 P_c | \psi_v^1 \rangle -$$

$$- \sum_{c,v} \frac{\langle \psi_v^0 | H_{SCF}^1 | \psi_c^0 \rangle \langle \psi_c^0 | H_{SCF}^1 | \psi_{v'}^0 \rangle \langle \psi_{v'}^0 | H_{SCF}^1 | \psi_v^0 \rangle}{(\epsilon_v^0 - \epsilon_c^0)(\epsilon_{v'}^0 - \epsilon_c^0)}. \quad (8)$$

By using Eq. (4b) and the condition that different conduction state are orthogonal to each other, we finally arrive at Eq. (3).

Eq. (3) can be easily generalized to the case where the perturbation depends nonlinearly on more than one parameter (as it is actually the case, e.g., in lattice dynamics if λ is identified with a nuclear displacement). Suppose there are three different such parameters, $\{\lambda_1, \lambda_2, \lambda_3\}$. Following the notation and the line of reasoning of Ref. [10], we easily arrive at the final result:

$$\frac{\partial^3 E}{\partial \lambda_1 \partial \lambda_2 \partial \lambda_3} = \widetilde{E}^{\lambda_1 \lambda_2 \lambda_3} + \widetilde{E}^{\lambda_2 \lambda_1 \lambda_3} + \widetilde{E}^{\lambda_1 \lambda_3 \lambda_2} + \widetilde{E}^{\lambda_3 \lambda_1 \lambda_2} + \widetilde{E}^{\lambda_3 \lambda_2 \lambda_1} + \widetilde{E}^{\lambda_2 \lambda_3 \lambda_1}, \quad (9)$$

where

$$\widetilde{E}^{\lambda_1 \lambda_2 \lambda_3} =$$

$$\sum_v \left(\langle \psi_v^{\lambda_1} | P_c H_{SCF}^{\lambda_2} P_c | \psi_v^{\lambda_3} \rangle + \langle \psi_v^{\lambda_1} | P_c v^{\lambda_2 \lambda_3} | \psi_v^0 \rangle + \langle \psi_v^0 | v^{\lambda_1 \lambda_2} P_c | \psi_v^{\lambda_3} \rangle + \langle \psi_v^0 | v^{\lambda_1 \lambda_2 \lambda_3} | \psi_v^0 \rangle \right)$$

$$- \sum_{vv'} \langle \psi_v^{\lambda_1} | P_c | \psi_{v'}^{\lambda_2} \rangle \langle \psi_{v'}^0 | H_{SCF}^{\lambda_3} | \psi_v^0 \rangle + \frac{1}{6} \int K^3(\mathbf{r}, \mathbf{r}', \mathbf{r}'') n^{\lambda_1}(\mathbf{r}) n^{\lambda_2}(\mathbf{r}') n^{\lambda_3}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'', (10)$$

where the λ_i superscript indicates the derivative with respect to λ_i. One sees that when the external potential depends lineary on just one parameter, λ, Eq.

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(2) is recovered. In the general case where the positions of the nuclei also depend on the λ's, one must of course add to Eq. (9) the derivative of the ionic contribution to the energy which is usually expressed as an Ewald sum. All the ingredients necessary to implement Eq. (10) are naturally provided by any computer code aimed at standard second-order DFPT, such as the one we routinely use for lattice-dynamical calculations. In the following, we present some tests of the above formulation which we have made on the anharmonic coupling between lattice distortions of Silicon at selected high-simmetry points of the BZ.

Numerical Tests

The equilibrium and lattice-dynamical properties of Silicon have been calculated within the local-density approximation, using the plane-wave pseudopotential method. We have used the same pseudopotential as in Ref. [4], plane waves up to a kinetic-energy cutoff of 14 Ry, and the (444) Monkhorst-Pack mesh for BZ integrations [11]. Calculations have been done at the Γ and X points of the BZ both within DFPT and, for comparison, by the frozen-phonon method. In the latter case, the unit cell has a lower (rotational and/or translational) symmetry, and the set of k-point used for sampling the BZ has been modified accordingly. We stress that, as it is the case for the harmonic dynamical matrix [4], the calculation of anharmonic coefficients at arbitrary points of the BZ within DFPT does *not* require the use of any supercells, but it only uses wavefunctions and band energies calculated for the unperturbed system. There are four independent parameters describing the harmonic properties of the crystal within the set of distortions corresponding to Γ and X phonons (the Γ_{LTO}, X_{LAO}, X_{TA}, and X_{TO} frequencies), whereas there are six anharmonic constants: one describing the coupling between

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three Γ-like phonons, and five describing the coupling between one Γ- and two X-like phonons. We refer to Ref. [12] for a full group-theoretical analysis of the independent coupling coefficients and for an explanation of the notations we borrow from it. In Table I we compare the third-order coupling coefficients calculated in the present work with DFPT and the frozen-phonon method. The values obtained with the latter method have been obtained using a procedure analogous to the one used in Ref. [12]. As one can see, DFPT give results which are in perfect agreement with those obtained by the frozen-phonon method. Actually, they are in principle more accurate because DFPT directly provides the energy derivatives without the need of any numerical differentiations.

TABLE I. Comparison of the third-order anharmonic coupling constants between phonons at the Γ and X points of the Brillouin zone in Silicon, as obtained by density-functional perturbation theory (DFPT) and the frozen-phonon (FP) method. The notations are the same as in Ref. [12]. Units are eV/$\overset{\circ}{A}^3$.

	B_{xyz}	$I_{z\overline{aa}}$	$I_{z\overline{bb}}$	$I_{z\overline{cc}}$	$I_{\overline{xac}}$	$I_{\overline{ybc}}$
DFPT	-295.06	232.41	-35.27	55.92	447.64	-64.74
FP	-295.27	232.11	-35.23	55.44	447.19	-64.84

We conclude that DFPT provides an accurate and computationally convenient tool for calculating the anharmonic coupling of phonons at arbitrary points of the BZ, with a numerical effort which essentially does not depend on the position in the BZ. This opens the way to a systematic investigation of such effects in real materials. A calculation of the anharmonic-decay phonon lifetimes in semiconductors along the lines presented in this paper is presently under way [13].

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