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2000 J. Phys.: Condens. Matter 12 9179

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Band-by-band decompositions of the Born effective charges

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Received 3 July 2000, in final form 12 September 2000

Abstract. The Born effective charge, Z^* , that describes the polarization created by collective atomic displacements, can be computed from first principles following different techniques. We establish the connections existing between these different formulations, and analyse the related band-by-band decompositions. We show that unlike for the full Z^* , the different band-by-band values are not equal, and emphasize that one of them has a natural physical meaning in terms of Wannier functions.

1. Introduction

The Born effective charge [1] (Z^*) is the equivalent, for crystalline insulating solid, of the atomic polar tensor introduced for isolated molecules [2]. It is a dynamical charge related to the macroscopic polarization induced by the collective displacements of nuclei belonging to a given sublattice. In the study of the lattice dynamics of insulating crystals, it is considered as a fundamental quantity, because it governs the amplitude of the long-range Coulomb interaction between nuclei, and the splitting between longitudinal optic (LO) and transverse optic (TO) phonon modes.

In simple materials, like $A^N B^{8-N}$ binary crystals [3], the phonon eigenvectors are imposed by symmetry. Infra-red measurements of the splitting between LO and TO modes allow an accurate estimation of $|Z^*|^2/\epsilon_\infty$ and offer therefore an unambiguous way to extract the amplitude of Z^* from the experiment. However, for more complex materials like ABO_3 compounds, LO and TO mode eigenvectors are not necessarily equivalent. The determination of Z^* from the experimental data is consequently not straightforward and requires the use of some approximations [4]. For such compounds, the development of theoretical methods giving direct access to Z^* acquires therefore a specific interest.

Conventionally, the Born effective charge tensor $Z_{\kappa,\alpha\beta}^*$ of nuclei belonging to the sublattice κ is defined as the coefficient of proportionality relating, under the condition of zero macroscopic electric field, the change in macroscopic polarization \mathcal{P}_β along the direction β and the collective nuclear displacements of atoms κ along direction α , times the unit-cell volume Ω_0 :

$$Z_{\kappa,\alpha\beta}^* = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa\alpha}} \right|_{\mathcal{E}=0}. \quad (1)$$

However, a thermodynamical equality relates the macroscopic polarization to a derivative of the electric enthalpy \tilde{E} and another relationship connects the forces F_κ on the nuclei κ to a

derivative of the electric enthalpy, so Z^* can be alternatively defined as follows:

$$Z_{\kappa,\alpha\beta}^* = -\frac{\partial^2 \tilde{E}}{\partial \mathcal{E}_\beta \partial \tau_{\kappa\alpha}} = \left. \frac{\partial F_{\kappa,\alpha}}{\partial \mathcal{E}_\beta} \right|_{\tau_{\kappa\alpha}=0}. \quad (2)$$

From these relationships, Z^* can therefore be thought either as (i) the change of polarization induced by the collective displacements of atoms κ , under zero field, (ii) a mixed second derivative of the electric enthalpy or (iii) the derivative of the force induced on a nucleus κ by a homogeneous effective electric field \mathcal{E}_β , at zero atomic displacement.

The three definitions are formally equivalent. However, they can lead to different algorithms for the computation of Z^* from first principles. Among the approaches which are the most widely used, the first powerful and systematic procedure was introduced by Baroni, Giannozzi and Testa [5], who suggested determining Z^* from a linear response formalism grounded on a Sternheimer equation. A different algorithm, based on a variational principle, was later reported by Gonze, Allan and Teter [6], yielding a new alternative expression for Z^* . Thanks to progress in the theory of the macroscopic polarization, Z^* is also directly accessible from the finite difference in polarization [7]. The first two algorithms were exclusively implemented within the density functional theory (DFT) formalism while the last one also allowed calculations of changes in polarization within other different one-electron schemes (the Hartree–Fock method [8], model GW -approximations to many-body theory [9, 10], the Harrison tight-binding model [11]) and the Hubbard tight-binding model [12].

Accurate predictions of the Born effective charges have been reported for a large variety of materials. In some of these studies [9, 13–17], the decomposition of Z^* into individual contributions from separate groups of occupied bands emerged as a powerful tool for identifying the microscopic mechanisms monitoring its amplitude. However, the physical interpretation of these decompositions was never explicitly discussed. Moreover, unlike the case for the total Z^* , contributions from individual groups of bands are not uniquely defined.

In the present paper, we aim at presenting the links between the theoretical frameworks used nowadays to compute Z^* , and at deducing from this comparison the correct way to develop a band-by-band analysis. We demonstrate that the natural decompositions arising from equation (1) and equation (2) *differ*, although independent approaches (linear response, Berry phase, electronic Wannier functions) to equation (2) are strictly *equivalent* provided that the phases of the wavefunctions are correctly chosen.

The paper is organized as follows. In section 2, we describe the mathematical links existing between the different expressions that can be used to determine the global value of $Z_{\kappa,\alpha\beta}$ within the density functional formalism without yet referring to band-by-band decompositions. We adopt the notation of references [18, 19]. In section 3, we discuss how contributions from isolated sets of bands can be separated from each other. We identify different expressions and discuss their meaning in terms of electronic Wannier functions. In section 4, we illustrate our results using a numerical example, emphasizing that independent decompositions yield in practice radically different values. Finally, in section 5, we reach a conclusion as to the physically correct way of performing band-by-band decomposition of Z^* .

2. Different formulations of Z^*

For practical purposes, in what follows, the Born effective charge will be decomposed into two contributions:

$$Z_{\kappa,\alpha\beta}^* = Z_\kappa \delta_{\alpha\beta} + Z_{\kappa,\alpha\beta}^{el}. \quad (3)$$

The first term, Z_κ , is the charge of the nuclei (or pseudo-ion, in the case of pseudopotential calculations), and can be trivially assigned. The second, $Z_{\kappa,\alpha\beta}^{el}$, is the contribution due to the electrons.

2.1. The first derivative of the polarization

A first straightforward approach for the determination of Z_κ^* consists in computing the difference in macroscopic polarization between a reference state and a state where the atoms belonging to the sublattice κ have been displaced by a small but finite distance $\Delta\tau_{\kappa,\alpha}$. The electronic contribution to Z^* can be obtained as

$$Z_{\kappa,\alpha\beta}^{el} = \Omega_0 \lim_{\Delta\tau_{\kappa,\alpha} \rightarrow 0} \frac{\Delta\mathcal{P}_\beta^{el}}{\Delta\tau_{\kappa,\alpha}}. \quad (4)$$

In periodic systems, the change in electronic polarization in zero field can be computed from the King-Smith and Vanderbilt formula [7]:

$$\mathcal{P}_\beta^{el} = -\frac{1}{(2\pi)^3} i \sum_n^{\text{occ}} s \int_{BZ} \langle u_{nk} | \partial/\partial k_\beta | u_{nk} \rangle d\mathbf{k} \quad (5)$$

where s is the occupation number of states in the valence bands ($s = 2$ in a spin-degenerate system) and u_{nk} are the periodic parts of the Bloch functions. Taken independently, the matrix elements of the previous equation are ill-defined, because the phase of the wavefunctions at a given wavevector of the Brillouin zone is arbitrary, and thus unrelated to the phases at neighbouring \mathbf{k} -points. However, the *integral* on the right-hand side is a well-defined quantity, which takes the form of a Berry phase of band n , as discussed by Zak [20].

The King-Smith and Vanderbilt definition is valid *only* under the constraint that the wavefunctions fulfil the *periodic gauge* condition. This means that the periodic parts of the Bloch functions must satisfy

$$u_{nk}(\mathbf{r}) = e^{i\mathbf{G}\cdot\mathbf{r}} u_{n\mathbf{k}+\mathbf{G}}(\mathbf{r}). \quad (6)$$

This condition does not unambiguously fix the phase of the wavefunctions at a given \mathbf{k} -point (not even at neighbouring \mathbf{k} -points) but it imposes a constraint for wavefunctions at distant wavevectors. It defines a topology in \mathbf{k} -space, within which the polarization takes the convenient form of a Berry phase.

When working within one-electron schemes (DFT, Hartree–Fock, ...), a second choice of phase is present at *another* level. For the ground state, the Lagrange multiplier method, applied to the minimization of the Hohenberg and Kohn functional under orthonormalization conditions on the wavefunctions [22], gives the following equations:

$$H_{\mathbf{k}} |u_{m\mathbf{k}}\rangle = \sum_n^{\text{occ}} \Lambda_{mn,\mathbf{k}} |u_{n\mathbf{k}}\rangle. \quad (7)$$

This condition, associated with the minimization of the Hohenberg and Kohn energy functional, means that the application of the Hamiltonian to a given wavefunction generates a vector which must stay within the Hilbert space defined by the set of $u_{n\mathbf{k}}$ -wavefunctions. We observe that a unitary transformation between the wavefunctions will leave that Hilbert space invariant, and equation (7) will remain satisfied provided that the matrix of Lagrange multipliers $\Lambda_{mn,\mathbf{k}}$ is transformed accordingly. In order to build Kohn–Sham band structures, the unitary transform is implicitly chosen so as to guarantee that

$$\Lambda_{mn,\mathbf{k}} = \delta_{mn} \epsilon_{m,\mathbf{k}} \quad (8)$$

in which case the $\epsilon_{m,\mathbf{k}}$ correspond to the eigenvalues of the Kohn–Sham Hamiltonian and the associated functions $u_{d,m\mathbf{k}}$ are the Kohn–Sham orbitals. This choice is called the *diagonal gauge* condition. Throughout this work, it will be emphasized by a subscript ‘*d*’.

We note that the periodic gauge condition connects wavefunctions at different \mathbf{k} -points, while the diagonal gauge condition fixes wavefunctions at a given \mathbf{k} -point. The choice defined by equation (8) is *not* mandatory, and the computation of the total energy, the density or the Berry phase (equation (5)) will give the *same* value independently of the fulfilment of equation (8). The diagonal gauge is the natural choice for the ground-state wavefunctions while, as will be discussed later, another choice is usually preferred for the change in wavefunctions in linear response calculations.

Instead of approximating equation (1) from finite differences, it can be computed directly. The combination of equations (1), (3) and (5) gives

$$Z_{\kappa,\alpha\beta}^{el} = -\frac{\Omega_0}{(2\pi)^3} i \sum_m^{\text{occ}} s \int_{BZ} \left[\left\langle \frac{\partial u_{n\mathbf{k}}}{\partial \tau_{\kappa,\alpha}} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_\beta} \right\rangle + \langle u_{n\mathbf{k}} | \partial / \partial k_\beta | \partial u_{n\mathbf{k}} / \partial \tau_{\kappa,\alpha} \rangle \right] d\mathbf{k} \quad (9)$$

where the second expectation value can be worked out:

$$\int_{BZ} \langle u_{n\mathbf{k}} | \partial / \partial k_\beta | \partial u_{n\mathbf{k}} / \partial \tau_{\kappa,\alpha} \rangle d\mathbf{k} = \int_{BZ} \left[\frac{\partial}{\partial k_\beta} \langle u_{n\mathbf{k}} | \partial u_{n\mathbf{k}} / \partial \tau_{\kappa,\alpha} \rangle - \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_\beta} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial \tau_{\kappa,\alpha}} \right\rangle \right] d\mathbf{k}. \quad (10)$$

In the last expression, the first term on the right-hand side is the gradient of a periodic quantity integrated over the Brillouin zone. Within any periodic gauge, its contribution will be zero. Using the time-reversal symmetry, we arrive therefore at the final expression:

$$Z_{\kappa,\alpha\beta}^{el} = -2 \frac{\Omega_0}{(2\pi)^3} i \sum_n^{\text{occ}} s \int_{BZ} \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial \tau_{\kappa,\alpha}} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_\beta} \right\rangle d\mathbf{k}. \quad (11)$$

The first derivatives of the wavefunctions, $\partial u_{n\mathbf{k}} / \partial \tau_{\kappa,\alpha}$ and $\partial u_{n\mathbf{k}} / \partial k_\beta$, appearing in this expression, can be computed by linear response techniques either by solving a first-order Sternheimer equation [5, 21] or by the direct minimization of a variational expression as described in references [6, 18].

We note that the choice of gauge will influence the value of the first derivative of $u_{n\mathbf{k}}$, although the integrated quantity $Z_{\kappa,\alpha\beta}^{el}$ must remain independent of this choice (in any periodic gauge). Usually, the following choice is preferred in linear response calculations:

$$\left\langle \frac{\partial u_{n\mathbf{k}}}{\partial \lambda} \middle| \right|_p u_{m\mathbf{k}} \rangle = 0 \quad (12)$$

for m and n labelling occupied states, and λ representing either the derivative with respect to the wavevector or that with respect to atomic displacements. As emphasized by the subscript ‘*p*’, this condition defines what is called the *parallel gauge* and ensures that the changes in the occupied wavefunctions are orthogonal to the space of the ground-state occupied wavefunctions. This projection on the conduction bands is not reproduced within the diagonal gauge defined by the generalization of equations (7), (8) at the first order of perturbation, as elaborated on in reference [22].

2.2. The mixed second derivative of the electric enthalpy

The Born effective charge also appears as a mixed second derivative of the electric enthalpy. Therefore, as reported in equation (41) of reference [19], $Z_{\kappa,\alpha\beta}^{el}$ can be alternatively formulated in terms of a *stationary* expression, involving the first-order derivative of the wavefunctions

with respect to a collective displacement of atoms of the sublattice κ and the first-order derivatives of the wavefunctions with respect to an electric field and to their wavevector[†].

The mathematical equivalence of equation (11) and equation (41) of reference [19] is a consequence of the interchange theorem but can be directly established from the stationary character of the latter. Indeed, as the error on Z^* is proportional to the product of the errors on the first-order change in wavefunctions, if $\partial u_{nk}/\partial \tau_{\kappa,\alpha}$ was known exactly, a correct estimation of $Z_{\kappa,\alpha\beta}^{el}$ could be obtained independently of the knowledge of $\partial u_{nk}/\partial \mathcal{E}_\beta$. Putting therefore $\partial u_{nk}/\partial \mathcal{E}_\beta$ and the corresponding density changes in equation (41) of reference [19] to zero, most of the terms cancel out and we recover equation (11), which when evaluated for the exact $\partial u_{nk}/\partial \tau_{\kappa,\alpha}$ must still correspond to a valid expression for Z^* .

2.3. The first derivative of the atomic force

By the same token as above, we can choose alternatively for $\partial u_{nk}/\partial \tau_{\kappa,\alpha}$ and the associated density derivative to vanish in equation (41) of reference [19], and we still obtain a valid expression for Z^* :

$$Z_{\kappa,\alpha\beta}^{el} = 2 \left[\frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_n^{\text{occ}} s \langle u_{nk} | \partial v'_{\text{ext},k} / \partial \tau_{\kappa\alpha} | \partial u_{nk} / \partial \mathcal{E}_\beta \rangle d\mathbf{k} + \frac{1}{2} \int_{\Omega_0} \left[\frac{\partial v_{\text{xc}0}}{\partial \tau_{\kappa\alpha}}(\mathbf{r}) \right] \left[\frac{\partial n}{\partial \mathcal{E}_\beta}(\mathbf{r}) \right]^* d\mathbf{r} \right]. \quad (13)$$

This equation corresponds to the third formulation of Z^* in which it appears as the first derivative of the force on the atoms κ with respect to an electric field (equation (2)). Indeed, it is directly connected to the following expression of the force, deduced from the Hellmann–Feynman theorem:

$$F_{\kappa,\alpha}^{el} = \frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_n^{\text{occ}} s \langle u_{nk} | \partial v'_{\text{ext},k} / \partial \tau_{\kappa\alpha} | u_{nk} \rangle d\mathbf{k} + \int_{\Omega_0} \left[\frac{\partial v_{\text{xc}0}}{\partial \tau_{\kappa\alpha}}(\mathbf{r}) \right] [n(\mathbf{r})]^* d\mathbf{r}. \quad (14)$$

Compared to equation (11) and equation (41) of reference [19], equation (13) has the advantage that the computation of the first-order wavefunction derivative with respect to the electric field perturbation is the *only* computationally intensive step needed to deduce the *full* set of effective charges. We note however that the implementation of equation (13), rather easy within a plane-wave–pseudopotential approach, is not so straightforward when the basis set is dependent on the atomic positions, as in LAPW methods (additional Pulay terms must be introduced).

3. Band-by-band decompositions

3.1. Displacement of the centres of gravity of Wannier functions

Inspired by a previous discussion by Zak [20], Vanderbilt and King-Smith [23] emphasized that the macroscopic electronic polarization acquires a particular meaning when expressed in terms of localized Wannier functions. The periodic parts of the Bloch functions $u_{nk}(\mathbf{r})$ are related to the Wannier functions $W_n(\mathbf{r})$ through the following transformations:

$$u_{nk}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} W_n(\mathbf{r} - \mathbf{R}) \quad (15)$$

$$W_n(\mathbf{r}) = \frac{\sqrt{N}\Omega_0}{(2\pi)^3} \int_{BZ} e^{i\mathbf{k}\cdot\mathbf{r}} u_{nk}(\mathbf{r}) d\mathbf{k}. \quad (16)$$

[†] This lengthy expression will not be reproduced here.

From this definition, we deduce that

$$\frac{\partial}{\partial \mathbf{k}_\beta} u_{nk}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} [-i(r_\beta - R_\beta)] e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} W_n(\mathbf{r} - \mathbf{R}) \quad (17)$$

where \mathbf{R} runs over all real-space lattice vectors. Introducing this result in equation (5), we obtain

$$\mathcal{P}_\beta^{el} = \frac{s}{\Omega_0} \sum_n^{\text{occ}} \int r_\beta |W_n(\mathbf{r})|^2 d\mathbf{r}. \quad (18)$$

From this equation, the electronic part of the polarization is simply deduced from the position of the centre of gravity of the electronic charge distribution, as expressed in terms of localized Wannier functions. In other words, for the purpose of determining the polarization, *'the true quantum mechanical electronic system can be considered as an effective classical system of quantized point charges, located at the centres of gravity associated with the occupied Wannier functions in each unit cell'* [23].

We observe that equations (15) and (16) establish a one-to-one correspondence between u_{nk} and W_n . As previously emphasized in section 3, when working within the *diagonal* gauge, $u_{d,nk}$ becomes identified with the Kohn–Sham orbitals, so the associated $W_{d,n}$ will correspond to a single-band Wannier function. Within this specific gauge, we can therefore isolate $P_{m,\beta}$, the contribution of band m to the β -component of the polarization, by separating the different terms in the sum appearing in equation (18):

$$\mathcal{P}_{m,\beta}^{el} = \frac{s}{\Omega_0} \int r_\beta |W_{d,m}(\mathbf{r})|^2 d\mathbf{r}. \quad (19)$$

If we take the derivative of the polarization with respect to a collective atomic displacement, $Z_{\kappa,\alpha\beta}^{el}$ can be written in terms of Wannier functions as

$$Z_{\kappa,\alpha\beta}^{el} = \sum_n^{\text{occ}} s \int r_\beta \left[\left(\frac{\partial W_n(\mathbf{r})}{\partial \tau_{\kappa,\alpha}} \Big|_d \right)^* W_{d,n}(\mathbf{r}) + (W_{d,n}(\mathbf{r}))^* \frac{\partial W_n(\mathbf{r})}{\partial \tau_{\kappa,\alpha}} \Big|_d \right] d\mathbf{r}. \quad (20)$$

As for the polarization, this equation has a simple physical meaning. In response to an atomic displacement, the electronic distribution is modified and the electronic contribution to Z^* can be identified from the displacement of the centres of gravity of the occupied Wannier functions. Working within the diagonal gauge at any order of perturbation, we will be able to follow the change of single-band Wannier functions along the entire path of atomic displacements. In the previous expression, the contribution of band m to $Z_{\kappa,\alpha\beta}^{el}$ can be isolated:

$$[Z_{\kappa,\alpha\beta}^{el}]_m = s \int r_\beta \left[\left(\frac{\partial W_m(\mathbf{r})}{\partial \tau_{\kappa,\alpha}} \Big|_d \right)^* W_{d,m}(\mathbf{r}) + (W_{d,m}(\mathbf{r}))^* \frac{\partial W_m(\mathbf{r})}{\partial \tau_{\kappa,\alpha}} \Big|_d \right] d\mathbf{r}. \quad (21)$$

This equation identifies the contribution from band m to the Born effective charge as Ω_0 times the *change of polarization corresponding to the displacement of a point charge s by a distance equal to the displacement of the Wannier centre of this band*. Equation (21) can also be estimated from a finite-difference method by combining equations (4) and (19), providing an easy way to decompose $Z_{\kappa,\alpha\beta}^{el}$ as soon as the Wannier functions of the system are known [17].

Alternatively, equation (21) can also easily be evaluated in reciprocal space:

$$[Z_{\kappa,\alpha\beta}^{el}]_m = -2 \frac{\Omega_0}{(2\pi)^3} i s \int_{BZ} \left\langle \frac{\partial u_{mk}}{\partial \tau_{\kappa,\alpha}} \Big|_d \Big| \frac{\partial u_{mk}}{\partial k_\beta} \Big|_d \right\rangle d\mathbf{k}. \quad (22)$$

As Bloch and Wannier functions are related through a band-by-band transformation, the contribution from band m to $Z_{\kappa,\alpha\beta}^*$ in equation (22) keeps the same clear physical meaning as in equation (21):

$$[Z_{\kappa,\alpha\beta}^{el}]_m = \Omega_0 \Delta \mathcal{P}_{m,\beta}^{el} = \Omega_0 s \Delta d_\beta \quad (23)$$

where Δd_β is the displacement in direction β of the Wannier centre of band m induced by the unitary displacement of the sublattice of atoms κ in direction α . This decomposition is strictly equivalent to what is obtained when computing $\Delta \mathcal{P}_{m,\beta}^{el}$ from finite differences either in real space, using Wannier functions and equation (19), as reported by Marzari and Vanderbilt [17], or within the Berry phase approach when separating band-by-band contributions to equation (5), the reciprocal-space equivalent of equation (19).

In practical calculations, where each band can be thought of as a combination of well-known orbitals, the displacement of the Wannier centre is associated with the admixture of a new orbital character with the band and must be attributed to dynamical changes of orbital hybridizations. As illustrated in some recent studies [9, 13–16], the decomposition of Z^* appears therefore as a powerful tool for microscopic characterization of the bonding in solids.

Let us emphasize again that the previous decomposition in terms of a single band is valid only if the *diagonal* gauge was used to define the Kohn–Sham wavefunctions, hence the subscript ‘ d ’ in equations (19), (21) and (22). The ground-state wavefunctions are conventionally computed within the diagonal gauge. However, in most calculations, the first derivatives of these wavefunctions are computed within the *parallel* gauge. Within this choice, the change in each Bloch function will be a mixing of different Kohn–Sham orbitals when the perturbation is applied, so the associated change in the functions W_n , defined on the basis of equation (16), will correspond to the change of a multi-band Wannier function. Evaluating equation (21) or (22) within such a gauge, we will identify the displacement of a complex of bands rather than that of a single band. In practice, the first-order derivatives of wavefunctions in the diagonal gauge $(du_{nk}/d\lambda)|_d$ can be deduced from those in the parallel gauge $(du_{nk}/d\lambda)|_p$ and the ground-state wavefunctions in the diagonal gauge $u_{d,nk}$, by adding contributions from the subspace of the occupied bands:

$$\left. \frac{du_{mk}}{d\lambda} \right|_d = \left. \frac{du_{mk}}{d\lambda} \right|_p - \sum_{n \neq m}^{\text{occ}} \frac{\langle u_{d,nk} | \partial H / \partial \lambda | u_{d,mk} \rangle}{(\epsilon_{nk} - \epsilon_{mk})} u_{d,nk}. \quad (24)$$

We note that this transformation (equation (24)) can present some problems when the denominator vanishes: this happens when the valence energies are degenerate. The problem can be partly bypassed by keeping a parallel transport gauge within the space of degenerate wavefunctions. Practically, this means that we will only be able to separate the contributions of disconnected sets of bands.

3.2. Other band-by-band decompositions

After focusing on equation (11), we now investigate the possible band-by-band decompositions of equation (41) of reference [19] and equation (13). These expressions, unlike equation (11), are not written as simple sums of matrix elements, each related to a single band. However, individual contributions to equation (13) can be identified using the following decomposition of the density:

$$n(\mathbf{r}) = \frac{1}{(2\pi)^3} \int_{BZ} \sum_n^{\text{occ}} s u_{nk}^*(\mathbf{r}) u_{nk}(\mathbf{r}) \, d\mathbf{k}. \quad (25)$$

It gives

$$Z_{\kappa,\alpha\beta}^{el} = 2 \frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_n^{\text{occ}} s \langle u_{nk} | \partial v'_{\text{ext},k} / \partial \tau_{\kappa\alpha} + \partial v_{\text{xc}0} / \partial \tau_{\kappa\alpha} | \partial u_{nk} / \partial \mathcal{E}_\beta \rangle \, d\mathbf{k} \quad (26)$$

for which the following decomposition is obtained, using the diagonal gauge wavefunctions:

$$[\tilde{Z}_{\kappa,\alpha\beta}^{el}]_m = 2 \frac{\Omega_0}{(2\pi)^3} \int_{BZ} s \langle u_{d,mk} | \partial v'_{\text{ext},k} / \partial \tau_{\kappa\alpha} + \partial v_{\text{xc}0} / \partial \tau_{\kappa\alpha} | (\partial u_{mk} / \partial \mathcal{E}_\beta)|_d \rangle \, d\mathbf{k}. \quad (27)$$

This expression corresponds to the contribution of the electrons of band m to the force induced on atom κ by a macroscopic field \mathcal{E}_β . However, it is not equivalent to equation (21) or (22). Indeed, for a particular band m , the difference between matrix elements present in equations (22) and (27) is (within a given gauge)

$$\begin{aligned} & [\langle u_{mk} | \partial v'_{\text{ext},k} / \partial \tau_{\kappa\alpha} + \partial v_{\text{xc}0} / \partial \tau_{\kappa\alpha} | \partial u_{mk} / \partial \mathcal{E}_\beta \rangle] - [\langle \partial u_{mk} / \partial \tau_{\kappa,\alpha} | -i \partial u_{mk} / \partial k_\beta \rangle] \\ &= -\frac{1}{2} \int_{\Omega_0} K_{\text{xc}}(\mathbf{r}, \mathbf{r}') \left[\frac{\partial n}{\partial \tau_{\kappa\alpha}}(\mathbf{r}) \right]^* \frac{\partial n_{mk}}{\partial \mathcal{E}_\beta}(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \\ &+ \frac{1}{2} \int_{\Omega_0} K_{\text{xc}}(\mathbf{r}, \mathbf{r}') \left[\frac{\partial n_{mk}}{\partial \tau_{\kappa\alpha}}(\mathbf{r}) \right]^* \frac{\partial n}{\partial \mathcal{E}_\beta}(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \end{aligned} \quad (28)$$

where $n_{mk}(\mathbf{r})$ is shorthand notation for $u_{mk}^*(\mathbf{r})u_{mk}(\mathbf{r})$. The summation of these differences over all the bands and integration over the Brillouin zone gives zero, as expected. However, the band-by-band difference, equation (28), does not vanish. This demonstrates that the quantity defined on the basis of equation (27) is independent of that of equation (21) and has therefore no specific meaning in terms of Wannier functions. Unlike equation (13), equation (41) of reference [19] is not naturally convertible into a sum of independent band contributions.

4. Numerical comparison

The previous theoretical results can now be illustrated using a numerical example. In what follows, we will consider the case of barium titanate (BaTiO_3), a well-known ferroelectric material which is stable at high temperature in a cubic perovskite structure and exhibits non-trivial values of Z^* [16].

Our calculations have been performed within the density functional theory and the local density approximation [24]. For the exchange–correlation energy, we used a polynomial parametrization [25] of Ceperley–Alder [26] homogeneous electron gas data. We adopted a plane-wave–pseudopotential approach. We chose highly transferable extended norm-conserving pseudopotentials as described in reference [27]. The Ba 5s, Ba 5p, Ba 6s, Ti 3s, Ti 3p, Ti 3d, Ti 4p, O 2s and O 2p levels have been treated as valence states. The electronic wavefunction has been expanded in plane waves up to a kinetic energy cut-off of 35 hartrees. Integrals over the Brillouin zone have been replaced by sums over a $6 \times 6 \times 6$ mesh of special k -points. The Born effective charges have been computed in the cubic phase at the optimized lattice parameter of 3.94 Å. They have been obtained from linear responses following the scheme described in reference [19].

In table 1, we summarize the results obtained from independent formulations for the titanium charge (Z_{Ti}^*). The decomposition of the total Z^* is provided, according to equation (22) and equation (27), in the diagonal gauge and, according to equation (22), in the parallel gauge. We also compare our results to those reported independently by Marzari and Vanderbilt [17], obtained from a direct computation of the displacements of the centres of gravity of the electronic Wannier functions.

As expected for this class of compounds [16], the total charge on the Ti atom is anomalously large (+7.25) and comparable in amplitude to the value of +7.16 obtained independently using the Berry phase approach [28]. The main anomalous contribution (deviation from the nominal value of the second column) is located in the O 2p bands. Similarly, the oxygen charge along the Ti–O bond is anomalously large and equal to –5.71. The Ti and O anomalous charge contributions are related to each other and can be assigned to dynamical changes of hybridization between O 2p and Ti 3d orbitals [16]. This was explicitly demonstrated for a parent compound (KNbO_3) by Posternak *et al* [29].

Table 1. Band-by-band decompositions of the Born effective charge of the Ti atom in the cubic phase of BaTiO₃. The first line refers to the pseudo-ion charge while the other contributions come from the different valence electron levels. The nominal values expected for a purely ionic material are reported in the second column; band-by-band contributions presented in the next three columns were computed from linear response first-principles calculations. The last column refers to first-principles values deduced from the computation of Wannier functions [17].

	Reference nominal charges	Linear response			Wannier functions
		Diagonal gauge		Parallel gauge	Diagonal gauge
		From (22)	From (27)	From (22)	From (21)
Z _{Ti}	+ 12.00	+ 12.00	+ 12.00	+ 12.00	+ 12.00
Ti 3s	−2.00	−2.03	+ 1.56	−0.36	−2.04
Ti 3p	−6.00	−6.22	−9.54	−5.50	−6.19
Ba 5s	0.00	+ 0.05	−0.36	0.00	+ 0.04
O 2s	0.00	+ 0.23	−1.56	−0.41	+ 0.20
Ba 5p	0.00	+ 0.36	+ 1.47	+ 0.10	+ 0.31
O 2p	0.00	+ 2.86	+ 3.68	+ 1.42	+ 3.01
Z _{Ti} [*]	+ 4.00	+ 7.25	+ 7.25	+ 7.25	+ 7.33

We observe that the global charge is equivalent independently of the approach, while this is not the case for partial contributions coming from different isolated sets of bands. First, the band-by-band decompositions obtained within the diagonal and parallel gauges are not similar. This means that the unitary transform performed when changing the gauge strongly mixes the different bands. Second, the results deduced from equations (22) and (27) within the diagonal gauge are *significantly* different, demonstrating that the amplitude of the quantity defined in equation (28) is not negligible. Third, the results obtained from equation (22) within the diagonal gauge are comparable to those of Marzari and Vanderbilt [17] who explicitly computed the electronic Wannier functions and estimated equation (21) using a finite-difference technique combining equation (4) and equation (19). This illustrates the physical interpretation of equation (22) in terms of localized Wannier functions: the contributions describe the displacement of the Wannier centre of each given set of bands, induced in response to the displacement of the Ti atom.

5. Conclusions

In conclusion, the Born effective charges can be computed from first principles using different techniques and algorithms. The global charge is a gauge-invariant quantity and is obtained independently of the approach, while special care is needed to separate individual contributions from separate groups of occupied bands. When using linear response techniques, the identification of band-by-band contributions, equivalent to those obtained within the Berry phase approach, requires the use of equation (22), when working within the diagonal gauge. The contribution $[Z_{\kappa,\alpha\beta}^{el}]_m$ is then directly related to the displacement in direction β of the Wannier centre of band m , when displacing the sublattice of atoms κ in direction α . The diagonal gauge condition is mandatory for identifying single-band contributions. The results obtained are conceptually and numerically different from those computed when using equation (27), independently of the choice of gauge.

Acknowledgments

We thank N Marzari for interesting discussions. XG acknowledges financial support from the FNRS (Belgium), from the programme 'Pole d'attraction interuniversitaire' P4/10 of the Belgian SSTC and from the FNRS-FRFC project 2.4556.99.

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