Band-by-band decompositions of the Born effective charges

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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 analyze 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.

I. INTRODUCTION

The Born effective charge $\bar{Z}$ ($Z^*$) is the equivalent, for crystalline insulating solid, of the atomic polar tensor introduced for isolated molecules $Z$. 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 (LO) and transverse (TO) optic phonon modes.

In simple materials, like $A^N B^{8-N}$ binary crystals $Z$, the phonon eigenvectors are imposed by symmetry. Infra-red measurements of the splitting between LO and TO modes allows an accurate estimation of $|Z|^2/\varepsilon_\infty$ and offers therefore an unambiguous way to extract the amplitude of $Z^*$ from the experiment. However, in 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 $\bar{Z}$. 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 $\kappa$ is defined as the coefficient of proportionality relating, under the condition of zero macroscopic electric field, the change in macroscopic polarization $P_\beta$ along the direction $\beta$ and the collective nuclear displacements of atoms $\kappa$ along direction $\alpha$, times the unit cell volume $\Omega_0$:

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \frac{\partial P_\beta}{\partial \tau_{\kappa\alpha}} \bigg|_{\varepsilon=0} .$$

However, a thermodynamical equality relates the macroscopic polarization to a derivative of the electric enthalpy $\bar{E}$ and another relationship connects the forces $F_\kappa$ on the nuclei $\kappa$ to a derivative of the electric enthalpy so that $Z^*$ can be alternatively defined as follows:

$$Z^*_{\kappa,\alpha\beta} = -\frac{\partial^2 \bar{E}}{\partial \varepsilon_\beta \partial \tau_{\kappa\alpha}} = \frac{\partial F_\kappa}{\partial \varepsilon_\beta} \bigg|_{\tau_{\kappa\alpha}=0} .$$

From these relationships, $Z^*$ can therefore be thought either as (i) the change of polarization induced by the collective displacements of atoms $\kappa$, under zero field (ii) a mixed second derivative of the electric enthalpy or (iii) the derivative of the force induced on a nucleus $\kappa$ by an homogeneous effective electric field $\varepsilon_\beta$, at zero atomic displacements.

The three definitions are formally equivalent. However, each of them can lead to different algorithms for the computation of $Z^*$ from first-principles. Among the approaches which are the most widely used, a first powerful and systematic procedure was introduced by Baroni, Giannozzi and Testa $\bar{Z}$, who suggested to determine $Z^*$ 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 $\bar{Z}$, yielding a new alternative expression for $Z^*$. Thanks to progress in the theory of the macroscopic polarization, $Z^*$ is also directly accessible from finite difference of polarization $\bar{Z}$. The first two algorithms were exclusively implemented within the density functional formalism (DFT) while the last one also allowed calculations of changes in polarization within different other one-electron schemes (Hartree-Fock method $\bar{Z}$, model GW approximations to many-body theory $\bar{Z}$, Harrison tight-binding model $\bar{Z}$) and the Hubbard tight-binding model $\bar{Z}$. 

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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 appeared as a powerful tool to identify the microscopic mechanisms monitoring its amplitude. However, the physical interpretation of these decompositions was never explicitly discussed. Moreover, unlike 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 Eq. (1) and Eq. (2) differ, although independent approaches (linear response, Berry phase approach, electronic Wannier functions) to Eq. (2) are strictly equivalent provided the phase of the wavefunctions are correctly chosen.

The paper is organized as follows. In Section II, 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 notations of Ref. [18,19]. In Section III, we discuss how contributions from isolated sets of bands can be separated from each others. We identify different expressions and discuss their meaning in terms of electronic Wannier functions. In Section IV, we illustrate our results on a numerical example, emphasizing that independent decompositions yield in practice radically different values. Finally, in Section V, we conclude on the physically correct way of performing band-by-band decomposition of $Z^*$.

II. DIFFERENT FORMULATIONS OF $Z^*$

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

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

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

A. First derivative of the polarization

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

$$Z_{\kappa,\alpha\beta}^{el} = \Omega_o \lim_{\Delta \tau_{\kappa,\alpha} \to 0} \frac{\Delta P_{\beta}^{el}}{\Delta \tau_{\kappa,\alpha}} \quad (4)$$

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

$$P_{\beta}^{el} = -\frac{1}{(2\pi)^3} \sum_{n} s \int_{BZ} \langle u_{nk} | \frac{\partial}{\partial k_{\beta}} | u_{nk} \rangle \, dk \quad (5)$$

where $s$ is the occupation number of states in the valence bands ($s = 2$ in spin-degenerate system) and $u_{nk}$ is the periodic part 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 with the phases at neighbouring $k$ points. However, the integral of 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 fulfill the periodic gauge condition. This means that the periodic part of Bloch functions must satisfy

$$u_{nk}(r) = e^{i G \cdot r} \, u_{nk+G}(r), \quad (6)$$

This condition does not fix unambiguously the phase of the wavefunctions at a given $k$-point (even not at neighbouring $k$-points) but it imposes a constraint for wavefunctions at distant wavevectors. It defines a topology in $k$-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:

\[
H_k |u_{mk}\rangle = \sum_n^{occ} \Lambda_{mn,k} |u_{nk}\rangle
\]

This condition, associated with the minimisation 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 \(u_{nk}\) wavefunctions. We observe that a unitary transformation between the wavefunctions will leave that Hilbert space invariant, and Eq. (7) will remain satisfied provided the matrix of Lagrange multiplier \(\Lambda_{mn,k}\) is transformed accordingly. In order to build Kohn-Sham band structures, the unitary transform is implicitly chosen such as to guarantee

\[
\Lambda_{mn,k} = \delta_{mn} \epsilon_{m,k}
\]

in which case \(\epsilon_{m,k}\) correspond to the eigenvalues of the Kohn-Sham Hamiltonian and the associated functions \(u_{d,m,k}\) are the Kohn-Sham orbitals. This choice is called the diagonal gauge condition. All along this work, it will be emphasized by a “\(d\)” subscript.

We note that the periodic gauge condition connect wavefunctions at different \(k\)-points, while the diagonal gauge condition fixes wavefunctions at a given \(k\)-point. The choice defined by Eq. (8) is not mandatory, and the computation of the total energy, the density, or the Berry phase (Eq. (9)) will give the same value independently of the fulfillment of Eq. (8). The diagonal gauge is the natural choice for the ground-state wavefunctions while, as it will be discussed later, another choice is usually preferred for the change in wavefunctions in linear-response calculations.

Instead of approximating Eq. (1) from finite differences, it can be computed directly. The combination of Eqs. (1), (2) and (3) gives:

\[
Z_{\kappa,\alpha}^{el} = -\frac{\Omega}{(2\pi)^3} i \sum_n^{occ} \int_{BZ} \left[ \frac{\partial u_{\kappa,n,k}}{\partial \kappa_\alpha} + \langle u_{n,k} | \frac{\partial}{\partial k_\beta} | u_{n,k} \rangle \right] dk
\]

where the second expectation value can be worked out:

\[
\int_{BZ} \langle u_{n,k} | \frac{\partial}{\partial k_\beta} | u_{n,k} \rangle dk = \int_{BZ} \left[ \frac{\partial}{\partial k_\beta} \langle u_{n,k} | \frac{\partial u_{n,k}}{\partial \kappa_\alpha} \rangle - \langle u_{n,k} | \frac{\partial}{\partial k_\beta} | u_{n,k} \rangle \right] dk.
\]

In the last expression, the first term of 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:

\[
Z_{\kappa,\alpha}^{el} = -2 \frac{\Omega}{(2\pi)^3} i \sum_n^{occ} \int_{BZ} \langle u_{n,k} | \frac{\partial u_{n,k}}{\partial k_\beta} \rangle dk
\]

The first-derivatives of the wave functions, \(\partial u_{\kappa,n,k}/\partial \kappa_\alpha\) and \(\partial u_{n,k}/\partial k_\beta\), appearing in this expression, can be computed by linear-response techniques either by solving a first-order Sternheimer equation \(21\) or by the direct minimization of a variational expression as described in Ref. \(22\).

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

\[
\langle \frac{\partial u_{n,k}}{\partial \lambda} | u_{m,k} \rangle = 0
\]

for \(m\) and \(n\) labelling occupied states, and \(\lambda\) representing either the derivative with respect to the wavevector or to atomic displacements. As emphasized by the “\(p\)” subscript, this condition defines what is called the parallel gauge and insures 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 Eq. (8) at the first order of perturbation, as elaborated in Ref. \(22\).
B. 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 Eq. (41) of Ref. [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 \( \kappa \) and the first-order derivatives of the wavefunctions with respect to an electric field and to their wavevector \( \mathbf{k} \).

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

C. First derivative of the atomic force

By the same token as above, we can choose alternatively for \( \partial u_{nk}/\partial \mathbf{F}_\beta \) and the associated density derivative to vanish in Eq. (41) of Ref. [19], and we still obtain a valid expression for \( Z^* \):

\[
Z_{\kappa,\alpha,\beta}^{el} = 2 \left[ \frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_{n}^{occ} s \langle u_{nk} | \frac{\partial v_{ext,k}}{\partial \tau_{\kappa \alpha}} | u_{nk} \rangle d\mathbf{k} + \frac{1}{2} \int_{\Omega_0} \langle u_{nk} | \frac{\partial u_{nk}}{\partial \mathbf{F}_\beta} | u_{nk} \rangle^* d\mathbf{r} \right] \tag{13}
\]

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

\[
F_{\kappa,\alpha}^{el} = \frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_{n}^{occ} s \langle u_{nk} | \frac{\partial v_{ext,k}}{\partial \tau_{\kappa \alpha}} | u_{nk} \rangle d\mathbf{k} + \int_{\Omega_0} \langle u_{nk} | \frac{\partial u_{nk}}{\partial \mathbf{F}_\beta} | u_{nk} \rangle^* d\mathbf{r} \tag{14}
\]

Compared to Eq. (11) and Eq. (41) of Ref. [19], Eq. (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 Eq. (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).

III. BAND-BY-BAND DECOMPOSITIONS

A. Displacement of the center of gravity of Wannier functions

Inspired by a previous discussion by Zak [20], Vanderbilt and King-Smith [24] emphasized that the macroscopic electronic polarization acquires a particular meaning when expressed in terms of localized Wannier functions. The periodic part of Bloch functions \( u_{nk}(\mathbf{r}) \) are related to the Wannier functions \( W_n(\mathbf{r}) \) through the following transformations:

\[
u_{nk}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}.(\mathbf{r}-\mathbf{R})} W_n(\mathbf{r}-\mathbf{R}) \tag{15}
\]

\[
W_n(\mathbf{r}) = \sqrt{N} \frac{\Omega_0}{(2\pi)^3} \int_{BZ} e^{i\mathbf{k}.\mathbf{r}} u_{nk}(\mathbf{r}) \, d\mathbf{k} \tag{16}
\]

From this definition, we deduce that:

\[
\frac{\partial}{\partial \mathbf{k}_\beta} u_{nk}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \left[-i(\mathbf{r}_\beta - R_\beta)\right] e^{-i\mathbf{k}.(\mathbf{r}-\mathbf{R})} W_n(\mathbf{r}-\mathbf{R}) \tag{17}
\]
where \( \mathbf{R} \) runs over all real space lattice vectors. Introducing this result in Eq. (15), we obtain:

\[
\mathcal{P}^\text{el}_{\beta} = \frac{s}{\Omega_0} \sum_n^{occ} \int r_\beta d |W_n(\mathbf{r})|^2 \, d\mathbf{r}
\]  

(18)

From this equation, the electronic part of the polarization is simply deduced from the position of the center 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 centers of gravity associated with the occupied Wannier functions in each unit cell” [24].

We observe that Eqs. (13) and (14) establish a one-to-one correspondence between \( u_{nk} \) and \( W_n \). As previously emphasized in Section III, when working within the diagonal gauge, \( u_{nk} \) becomes identified with the Kohn-Sham orbitals so that the associated \( W_{d,n} \) will correspond to a single band Wannier function. Within this specific gauge, we can therefore isolate \( \mathcal{P}_{m,\beta} \), the contribution of band \( m \) to the \( \beta \) component of the polarization, by separating the different term in the sum appearing in Eq. (18):

\[
\mathcal{P}^\text{el}_{m,\beta} = \frac{s}{\Omega_0} \int r_\beta |W_{d,m}(\mathbf{r})|^2 \, d\mathbf{r}
\]

(19)

If we take the derivative of the polarization with respect to a collective atomic displacement, \( Z^\text{el}_{\kappa,\alpha\beta} \) can be written in terms of Wannier functions as:

\[
Z^\text{el}_{\kappa,\alpha\beta} = \sum_n^{occ} s \int r_\beta |(\frac{\partial W_n(\mathbf{r})}{\partial \tau_{\kappa,\alpha}}) |^* W_{d,n}(\mathbf{r}) + (W_{d,n}(\mathbf{r}))^* \frac{\partial W_n(\mathbf{r})}{\partial \tau_{\kappa,\alpha}} |d\mathbf{r}
\]

(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 center 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 all along the path of atomic displacements. In the previous expression, the contribution of band \( m \) to \( Z^\text{el}_{\kappa,\alpha\beta} \) can be isolated:

\[
[Z^\text{el}_{\kappa,\alpha\beta}]_m = s \int r_\beta |(\frac{\partial W_n(\mathbf{r})}{\partial \tau_{\kappa,\alpha}}) |^* W_{d,m}(\mathbf{r}) + (W_{d,m}(\mathbf{r}))^* \frac{\partial W_m(\mathbf{r})}{\partial \tau_{\kappa,\alpha}} |d\mathbf{r}
\]

(21)

This equation identifies the contribution from band \( m \) to the Born effective charge as \( \Omega_0 \) times the change of polarization corresponding to the displacement of a point charge \( s \) on a distance equal to the displacement of the Wannier center of this band. Eq. (21) can also be estimated from finite difference by combining Eq. (4) and (19), providing an easy way to decompose \( Z^\text{el}_{\kappa,\alpha\beta} \) as soon as the Wannier functions of the system are known [17].

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

\[
[Z^\text{el}_{\kappa,\alpha\beta}]_m = \Omega_0 \langle \frac{\Omega_0}{(2\pi)^3} |s \int_{BZ} (\frac{\partial u_{mk}}{\partial k_{\beta}}) |^* \frac{\partial u_{mk}}{\partial k_{\beta}} |dk\rangle
\]

(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 Eq. (22) keeps the same clear physical meaning as in Eq. (21):

\[
[Z^\text{el}_{\kappa,\alpha\beta}]_m = \Omega_0 \Delta \mathcal{P}^\text{el}_{m,\beta} = \Omega_0 s \Delta d_{\beta}
\]

(23)

where \( \Delta d_{\beta} \) is the displacement in direction \( \beta \) of the Wannier center of band \( m \) induced by the unitary displacement of the sublattice of atoms \( \kappa \) in direction \( \alpha \). This decomposition is strictly equivalent to what is obtained when computing \( \Delta \mathcal{P}^\text{el}_{m,\beta} \) from finite differences either in real space, using Wannier functions and Eq. (14), as reported by Marzari et al., or within the Berry phase approach when separating band by band contribution to Eq. (6), the reciprocal space equivalent of Eq. (14).

In practical calculations, where each band can be thought as a combination of well-known orbitals, the displacement of the Wannier center is associated to the admixture of a new orbital character to the band and must be attributed to dynamical changes of orbital hybridizations. As illustrated in some recent studies [13,14,16], the decomposition of \( Z^* \) appears therefore as a powerful tool for the microscopic characterisation 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 “d” subscript in Eq. (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 that the associated change in functions \( \hat{W}_{\kappa} \) defined from Eq. (10), will correspond to the change of a multi-band Wannier function. Evaluating Eq. (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 derivative of wavefunctions in the diagonal gauge \( \frac{du}{d\lambda} \) can be deduced from those in the parallel gauge \( \frac{du}{d\lambda} \) and the ground-state wavefunctions in the diagonal gauge \( u_{d,nk} \), by adding contributions from the subspace of the occupied bands:

\[
\frac{du_{m,k}}{d\lambda} = \frac{du_{m,k}}{d\lambda}_p - \sum_{n\neq m} \frac{(u_{d,nk} | \frac{\partial H}{\partial \lambda} | u_{d,m,k})}{(\epsilon_{nk} - \epsilon_{mk})} u_{d,nk}
\]

(24)

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

**B. Other band-by-band decompositions**

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

\[
n(r) = \frac{1}{(2\pi)^3} \int_{BZ} \sum_n^{occ} s \, n^*_n(r)u_{nk}(r)dk.
\]

(25)

It gives:

\[
Z_{\kappa,\alpha\beta}^{el} = 2 \frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_n^{occ} s \, \langle u_{nk} | \frac{\partial v_{\text{ext},k}'}{\partial \tau_{\kappa,\alpha}} + \frac{\partial v_{\text{xc}0}}{\partial \tau_{\kappa,\alpha}} | \frac{\partial u_{mk}}{\partial \beta} \rangle dk
\]

(26)

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

\[
\tilde{Z}_{\kappa,\alpha\beta}^{el}|_{m} = 2 \frac{\Omega_0}{(2\pi)^3} \int_{BZ} s \, \langle u_{d,m,k} | \frac{\partial v_{\text{ext},k}'}{\partial \tau_{\kappa,\alpha}} + \frac{\partial v_{\text{xc}0}}{\partial \tau_{\kappa,\alpha}} | \frac{\partial u_{m,k}}{\partial \beta} \rangle d_k
\]

(27)

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

\[
\left[ \langle u_{mk} | \frac{\partial v_{\text{ext},k}'}{\partial \tau_{\kappa,\alpha}} + \frac{\partial v_{\text{xc}0}}{\partial \tau_{\kappa,\alpha}} | \frac{\partial u_{m,k}}{\partial \beta} \rangle \right] - \left[ \langle \frac{\partial u_{mk}}{\partial \tau_{\kappa,\alpha}} - i \frac{\partial u_{mk}}{\partial \beta} \rangle \right] =
\]

\[
-\frac{1}{2} \int_{\Omega_0} K_{\text{xc}}(r, r') \left[ \frac{\partial n_{mk}}{\partial \tau_{\kappa,\alpha}}(r) \cdot \frac{\partial n_{mk}}{\partial \beta}(r') \right] dr d'r'
+ \frac{1}{2} \int_{\Omega_0} K_{\text{xc}}(r, r') \left[ \frac{\partial n_{mk}}{\partial \tau_{\kappa,\alpha}}(r) \right] \cdot \left[ \frac{\partial n_{mk}}{\partial \beta}(r') \right] dr d'r'
\]

(28)

where \( n_{mk}(r) \) is a short notation for \( u^*_m(r)u_{nk}(r) \). The summation of these differences on all the bands and integration on the Brillouin zone gives zero, as expected. However, the band-by-band difference, Eq. (28), does not vanish. This demonstrates that the quantity defined from Eq. (27) is independent from that of Eq. (21) and has therefore no specific meaning in terms of Wannier functions. Unlike Eq. (13), Eq. (41) of Ref. [19] is not naturally convertible in a sum of independent band contributions.
IV. NUMERICAL COMPARISON

The previous theoretical results can now be illustrated on 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 $Z^*$.

Our calculations have been performed within the density functional theory and the local density approximation. For the exchange-correlation energy, we used a polynomial parametrization of Ceperley-Alder homogeneous electron gas data. We adopted a planewave-pseudopotential approach. We choose highly transferable extended norm-conserving pseudopotentials as described in Ref. 28. The Ba 5s, Ba 5p, Ba 6s, Ti 3s, Ti 3p, Ti 3d, Ti 4p, O 2s, and O2p levels have been treated has valence states. The electronic wavefunction has been expanded in plane-waves up to a kinetic energy cutoff of 35 hartrees. Integrals over the Brillouin zone have been replaced by sums on 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 by linear response following the scheme described in Ref. 19.

In Table I, we summarize the results obtained from independent formulations for the titanium charge ($Z^*_{\text{Ti}}$). The decomposition of total $Z^*$ is provided, according to Eq. (22) and Eq. (27) in the diagonal gauge and to Eq. (22) in the parallel gauge. We also compare our results to those reported independently by Marzari et al. 17 from a direct computation of the displacement of the center of gravity of the electronic Wannier functions.

As expected in this class of compounds, the total charge on the Ti atom is anomalously large (+7.25) and comparable in amplitude to the value of +7.16 reported independently using the Berry phase approach. 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. Both 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. This was explicitly demonstrated for a parent compound (KNbO$_3$) by Posternak et al. 30.

We observe that the global charge is equivalent independently of the approach while it 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 mix the different bands. Second, the results deduced from Eq. (22) and Eq. (27) within the diagonal gauge are significantly different, demonstrating that the amplitude of the quantity defined in Eq. (28) is not negligible. Third, the results obtained from Eq. (22) within the diagonal gauge are comparable to those of Marzari et al. who explicitly computed the electronic Wannier functions and estimated Eq. (21) using a finite difference technique combining Eq. (4) and Eq. (19). This illustrates the physical interpretation of Eq. (22) in terms of localized Wannier functions: the contributions describe the displacement of the Wannier center of each given set of bands, induced in response to the displacement of the Ti atom.

V. 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 a 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 Eq. (22), when working within the diagonal gauge. The contribution $[Z^*_{\text{el},\alpha\beta}]_m$ is then directly related to the displacement in direction $\beta$ of the Wannier center of band $m$, when displacing the sublattice of atoms $\kappa$ in direction $\alpha$. The diagonal gauge condition is mandatory to identify single band contributions. The results obtained are conceptually and numerically different from those computed when using Eq. (27), independently of the gauge choice.

VI. ACKNOWLEDGMENTS

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Table I. Band-by-band decompositions of the Born effective charge of the Ti atom in the cubic phase of BaTiO$_3$. The first line refer to the pseudo-ion charge while the other contributions comes from the different valence electron levels. The nominal values expected in a purely ionic material are reported in the second column; band-by-band contributions presented in the three next columns were computed from linear response first-principles calculations. The last column refer to first-principles values deduced from the computation of Wannier functions \[17\].

|        | Reference nominal charges | Linear response | Wannier functions |
|--------|---------------------------|-----------------|------------------|
|        |                           | Diagonal gauge   | Parallel gauge   |
|        | from Eq. (22)             | from Eq. (27)    | from Eq. (24)    |
| $Z_{Ti}$ | +12.00                    | +12.00          | +12.00           |
| Ti 3s  | -2.00                     | -2.03           | -0.36            |
| Ti 3p  | -6.00                     | -6.22           | 5.50             |
| Ba 5s  | 0.00                      | +0.05           | 0.00             |
| O 2s   | 0.00                      | +0.23           | -0.41            |
| Ba 5p  | 0.00                      | +0.36           | +0.10            |
| O 2p   | 0.00                      | +2.86           | +3.01            |
| $Z_{Ti}$ | +4.00                    | +7.25           | +7.25            |

