Accurate polarization within a unified Wannier function formalism

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We present an alternative formalism for calculating the maximally localized Wannier functions in crystalline solids, obtaining an expression which is extremely simple and general. In particular, our scheme is exactly invariant under Brillouin zone folding, and therefore it extends trivially to the Γ-point case. We study the convergence properties of the Wannier functions, their quadratic spread and centers as obtained by our simplified technique. We show how this convergence can be drastically improved by a simple and inexpensive "refinement" step, which allows for very efficient and accurate calculations of the polarization in zero external field.

I. INTRODUCTION

The representation of the one-particle electronic structure of molecules and solids in terms of localized Wannier[1] orbitals is nowadays "enjoying a revival"[2] as a useful tool for many applications.[3–13] The main impetus for this renewal of interest was given by the establishment, by King-Smith and Vanderbilt (KSV), of a formally exact relationship between the sum of the Wannier function (WF) centers and a gauge-invariant Berry phase, in the context of the modern theory of polarization.[14] However, the intrinsic nonuniqueness in the Wannier function definition, and the difficulty in defining their centers within a periodic cell calculation, limited their practical use until a particularly elegant method due to Marzari and Vanderbilt[3] (MV) became available some years ago. Their scheme allows one to obtain, in a given isolated or extended system, a unique set of maximally localized Wannier functions that minimizes a well-defined spread functional. Moreover, the MV formalism provides as an important by-product the positions of the WF centers, whose sum gives direct access to the macroscopic polarization of the physical system. The MV scheme, which became instantly popular, presents nevertheless an inconvenience, in that crystalline solids are treated on a different footing compared with the case of, e.g., large disordered systems simulated at the Γ point only. The two prescriptions are indeed equivalent in the thermodynamic limit, but they formally differ when discrete Brillouin zone (BZ) samplings (or finite supercells for isolated objects) are used, which is necessarily the case in any practical calculation. In the first part of this work we show that there is nothing fundamental in this discrimination, i.e., that a given choice for a spread functional in Γ-sampled cells dictates unambiguously the mathematical expression in *discrete k*-point space, and that invariance under "BZ folding" is the guideline which estabilishes the link. The resulting formalism is completely general and, while being similar in spirit to the original (MV) one, presents a much simpler algebra.

A more relevant issue affects directly the modern theory of polarization and concerns the asymptotic convergence with respect to BZ sampling. It was already shown formally and numerically[3,15] that both methods (KSV and MV) for calculating the polarization of a molecule or a crystal in periodic boundary conditions (PBC) are plagued by a slow $\mathcal{O}(L^{-2})$ convergence, where L is the linear dimension of the supercell containing the isolated molecule, or alternatively the resolution of the k-point mesh. The problem is usually addressed, in the context of the Berry-phase KSV approach, by refining the k-point grid along "stripes" in the Brillouin zone within a separate, non-self-consistent calculation.[14] For finite systems, an extrapolation technique was recently proposed[16] in which the $\mathcal{O}(L^{-2})$ error is removed from the Wannier multipoles by performing a series of calculations in cubic supercells of increasing size.[17] Both solutions are somewhat unsatisfactory, in that they require many calculations to be performed on the same system, with a cost that is higher than that normally needed to converge total energies and densities. In the second part of this work we propose a simple "refining" procedure, which is able to provide an extremely accurate value for the center and spread once a well-localized set of maximally localized Wannier functions is available. We show first formally and then by numerical examples that this technique, while requiring a very minor computational effort, is able to outperform in terms of accuracy both the standard KSV Berry-phase approach and the alternative formula based on "unrefined" WF centers.[19] Finally, our derivation also provides an intuitive interpretation of the position/localization operator in periodic boundary conditions and of its relationship to the corresponding well-known free-space operators.

II. METHOD

The theoretical basis for the MV approach rests on a continuum formulation, in which the space is infinitely extended in all directions; this translates to an infinitely dense Brillouin zone sampling in the case of crystalline solids. For practical calculations a finite sampling (or finite simulation supercell) is necessary, and MV give detailed prescriptions for the "discretization" of the relevant mathematical objects (gradients and Laplacians in k-space). We start here our alternative derivation from a slightly different viewpoint, that is we "discretize" the problem from the very beginning by choosing an appropriate formulation in the Γ-point case, and then work out the formulas in k-space without making any

further approximation. This approach leads automatically to a general and size-consistent formalism that is invariant under BZ unfolding.

A. Definitions

First, we introduce some definitions and conventions that will be helpful in the remainder of the paper. We assume a Born-von Kármán (BvK) supercell of volume V_{BvK}, which is a multiple of the primitive (P) unit cell of the crystal (of volume V_P) under study. In this system with periodic boundary conditions (PBC) there are N allowed Bloch vectors, where N is given by the ratio between the volumes:

$$N = \frac{V_{BvK}}{V_P}.$$

The generalized Bloch orbitals (which are not necessarily eigenstates of the Hamiltonian) are orthonormal on the primitive cell (m and n are band indices and $\mathbf{k}$ is the crystal momentum):

$$\int_P \psi_{m\mathbf{k}}^*(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r} = \delta_{mn}$$

and can be written as usual:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}),$$

where the $u_{n\mathbf{k}}$ are periodic functions and can be represented on the reciprocal lattice of the P cell:

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_P}} \sum_{|\mathbf{G}+\mathbf{k}|^2 < E_{cut}} e^{i\mathbf{G}\cdot\mathbf{r}} \tilde{u}_{n\mathbf{k}}(\mathbf{G}).$$

E_{cut} represents the energy cutoff of the plane-wave basis set, $\mathbf{G}$ are reciprocal lattice vectors, and $\tilde{u}_{n\mathbf{k}}(\mathbf{G})$ is the Fourier coefficient of the lattice-periodic part of the Bloch function:

$$\tilde{u}_{n\mathbf{k}}(\mathbf{G}) = \frac{1}{\sqrt{V_P}} \int_P e^{-i\mathbf{G}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}.$$

We will use the BvK supercell for representing our Wannier functions:

$$w_n(\mathbf{r}-\mathbf{R}) = \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}),$$

where the normalization constant $N = V_{BvK}/V_P$ ensures that these w_n are orthonormal on the BvK supercell. At constant n, the lattice quantum number $\mathbf{R}$ identifies Wannier functions that are equivalent with respect to translation by a primitive lattice vector; we will set $\mathbf{R}=0$ in the remainder of the paper, and thus focus on the minimal set which is necessary to describe the solid.

A particularly simple expression relates the Fourier coefficients $\tilde{w}_n(\mathbf{q})$ of the Wannier functions to the reciprocal space representation of the Bloch vectors:

$$\tilde{w}_n(\mathbf{G}+\mathbf{k}) = \frac{1}{\sqrt{N}} \tilde{u}_{n\mathbf{k}}(\mathbf{G}). \tag{1}$$

We remind the reader that the reciprocal lattice of the BvK cell is spanned by all vectors of type $\mathbf{q}=\mathbf{G}+\mathbf{k}$, which we will call $\mathbf{q}$ in the following to distinguish them from the $\mathbf{G}$ vectors of the primitive reciprocal lattice.

B. Spread functional

Equation (1) does not define a unique set of Wannier functions because of the gauge arbitrariness in the choice of the unitary representation of the Bloch vectors. This indeterminacy can be solved by defining a spread functional Ω which depends explicitly on the gauge, so that the minimization of Ω leads to a well-defined set of localized orbitals with the desired properties. Resta[22] showed that the quadratic spread of a one-particle orbital in a periodic lattice sampled at the Γ point can be defined in several ways, that are all equivalent in the thermodynamic limit. Three possible alternatives have been reviewed and compared by Berghold and co-workers;[23] the authors found negligible differences between these expressions that are valid for Γ-only BZ sampling in a lattice of general symmetry, and therefore appropriate for the BvK supercell in which we are representing our Wannier functions. The following derivation is based on what we consider the most advantageous choice for Ω and the related Wannier centers $\bar{\mathbf{r}}_n$ (the other two possibilities, which are closer to the MV and Resta and Sorella[24] works, respectively, are discussed in Appendix A), that in our notations read:

$$\bar{\mathbf{r}}_{\mathbf{n}} = \sum_i \bar{w}_i \mathbf{b}_i \, \text{Im} \ln z_n^{(i)}, \tag{2a}$$

$$\Omega = \sum_n \sum_i \bar{w}_i 2(1 - |z_n^{(i)}|). \tag{2b}$$

Here $z_n^{(i)}$ are dimensionless complex numbers given by

$$z_n^{(i)} = \langle w_n | e^{i\mathbf{b}_i\cdot\mathbf{r}} | w_n \rangle = |z_n^{(i)}| e^{i\phi_n^{(i)}},$$

and $\mathbf{b}_i$ represents a small set of reciprocal space vectors $\mathbf{q}$ with associated weights $\bar{w}_i$ that must be chosen so that:[3]

$$\sum_i \bar{w}_i b_{i\alpha} b_{i\beta} = \delta_{\alpha\beta}.$$

In the case of a cubic BvK supercell of edge L these quantities reduce to the $i=1,\dots,3$ primitive reciprocal-space vectors of the BvK cell and the weights are all equal:

$$\mathbf{b}_i = \frac{2\pi}{L}\hat{\mathbf{i}}, \quad \bar{w}_i = \left(\frac{L}{2\pi}\right)^2,$$

while in the most general case of a triclinic cell a maximum number of six independent vectors and weights must be used, according to the prescriptions given in Refs. 3 and 25.

With these notations and conventions in hand, we are now ready to write down a k-space expression for $\bar{\mathbf{r}}_n$ and Ω. Both quantities depend directly on $z_n^{(i)}$, and the key part of the derivation is then the "Brillouin-zone unfolding" of this latter quantity. Using the same notation as MV:

$$M_{mn}^{(\mathbf{k},\mathbf{b}_i)} = \langle u_{m\mathbf{k}} | u_{n\mathbf{k}+\mathbf{b}_i} \rangle,$$

it is straightforward to derive a very simple expression for $z_n^{(i)}$:

$$z_n^{(i)} = \frac{1}{N} \sum_{\mathbf{k}} M_{nn}^{(\mathbf{k}, -\mathbf{b}_i)}.$$

With this formula we can write our operational definitions of position and quadratic spread in k-space:

$$\bar{\mathbf{r}}_{\mathbf{n}} = -\sum_i \bar{w}_i \mathbf{b}_i \, \mathrm{Im} \ln \left[\frac{1}{N} \sum_{\mathbf{k}} M_{nn}^{(\mathbf{k}, \mathbf{b}_i)} \right], \tag{3a}$$

$$\Omega = \sum_n \sum_i \bar{w}_i 2 \left(1 - \left| \frac{1}{N} \sum_{\mathbf{k}} M_{nn}^{(\mathbf{k}, \mathbf{b}_i)} \right| \right). \tag{3b}$$

It is interesting to note the close similarity between our expression for the centers [Eq. (3a)] and Eq. (31) of MV, the only difference being the order in which the complex logarithm and the average over k-points is taken.[26] We argue that the one proposed here is a more natural choice, since it retains the correct translational properties of the MV formula, while strictly enforcing size consistency. Size consistency means that the formalism gives mathematically identical answers for the k-point representation and for the equivalent BvK real-space Γ-point representation. Our formula is correct by construction, and extends exactly to the case of isolated systems with Γ-point sampling without any further algebra. Interestingly, during our numerical tests we observed that the values of the centers defined by Eq. (3a) and Eq. (23) of MV are very similar. This can be explained by noticing that the maximal localization requirement on the Wannier functions enforces the smoothest possible representation for the Bloch orbitals across the BZ; as a consequence, the matrix elements $M_{nn}^{(\mathbf{k}, \mathbf{b}_i)}$ exhibit only a weak dependence on $\mathbf{k}$, and by moving the average outside the logarithm the result is not significantly affected.

Another appealing feature of our unified formulation is that, in one-dimensional problems, the minimum spread solution coincides exactly with the one provided by the parallel transport algorithm.[3] We note that only the expression in Eq. (2b) has this property, in contrast to the alternative spread functionals discussed in Appendix A; a more in-depth discussion of this point is provided in Appendix B.

C. Gradients and optimization algorithm

For the optimization of the spread functional, its gradients with respect to an infinitesimal unitary rotation in a given $\mathbf{k}$ subspace must be computed. Thus we consider the transformation:

$$u'_{n\mathbf{k}}(\mathbf{r}) = \sum_m u_{m\mathbf{k}}(\mathbf{r}) U_{mn}^{(\mathbf{k})},$$

where the rotation matrices $U^{(\mathbf{k})}$ are obtained by adding an infinitesimal anti-Hermitian matrix dW to the identity:

$$U^{(\mathbf{k})} \sim 1 + dW^{(\mathbf{k})}.$$

The variation of the total spread with respect to this transformation leads to a particularly simple expression, which can be written in terms of the $M^{(\mathbf{k}, \mathbf{b}_i)}$ matrices and the *phases* of the $z_n^{(i)}$ complex numbers:

$$\left(\frac{d\Omega}{dW^{(\mathbf{k})}} \right)_{mn} = \frac{1}{N} \sum_i \bar{w}_i (M_{mn}^{(\mathbf{k}, \mathbf{b}_i)} C_n^{(i)*} + M_{nm}^{(\mathbf{k} - \mathbf{b}_i, \mathbf{b}_i)*} C_n^{(i)}) - \mathrm{H.c.}, \tag{4}$$

where H.c. stands for Hermitian conjugate, and $C_n^{(i)}$ is the phase:

$$C_n^{(i)} = e^{i\phi_n^{(i)}} = \frac{z_n^{(i)}}{|z_n^{(i)}|}.$$

This expression for the gradient can easily be obtained by observing that, in Eq. (2b), one can write $|z| = z e^{-i\phi}$.

We note that several possibilities exist for the spread functional [Eq. (2b)], which are all equivalent in the thermodynamic limit.[23] In Appendix A we briefly consider these alternatives and we provide a formal derivation of the gauge-invariant part of the spread,[3] which provides further evidence for the close relationship of our approach to the original MV scheme. Because of the exact mapping between the BvK supercell and the primitive one, we find it particularly natural to choose our Wannier functions to be real. Even if there is no formal proof that at the global minimum of Ω the Wannier functions are real, this is nevertheless a very reasonable assumption[3] and allows one to fully take advantage of the time-reversal symmetry, with significant gain in computational efficiency.

For the minimization of Ω with respect to the $U_{nn}^{(\mathbf{k})}$ degrees of freedom many efficient schemes are available.[23] We decided in this work to implement a damped dynamics algorithm, which allows for good control over the process, at the expense of requiring more human input for the optimal tuning of the two independent parameters (integration step and damping coefficient). In antiferromagnetic MnO, a case that is known[8] to be difficult to converge, we were able to obtain this way a very accurate and symmetrical minimum (to machine precision) in a couple of thousand time steps, which required only a few minutes on a modern workstation. An even more appealing feature of the dynamical scheme is the availability of a mathematically conserved constant of motion, which provides a very stringent test of the accuracy of the implementation.

III. CONVERGENCE PROPERTIES

Since the Wannier functions in an insulator are known to be *exponentially* localized in space,[27] similar convergence properties can be expected for any physical quantity that is extracted from this particular representation of the electronic structure. Instead, as we pointed out at the beginning, both the sum of Wannier centers and the Berry phase (which is formally related to the Wannier centers by the derivation in KSV) converge only as $\mathcal{O}(L^{-2})$, and need special treatment whenever accurate values are needed.

We will show in this section that this slow convergence is indeed not an *intrinsic* feature of the ground state electronic structure of an extended system and can be dramatically improved by a simple, inexpensive, and very general procedure. Before explaining our correction in detail, we will first provide an intuitive picture of the position operator in PBC,

which, as Resta showed,[28] is the "kernel" of both Berry phase and maximally localized Wannier function calculations.

Let us consider a one-dimensional system of a single electronic state $|\psi\rangle$, which we will assume to be well-localized within a periodic cell of length L.[29] The expression for the fundamental, dimensionless complex number z is very similar to the 3D expression:

$$z = \langle\psi|e^{i(2\pi/L)x}|\psi\rangle = |z|e^{i\phi}. \tag{5}$$

The average value of the position operator [Eq. (2a)] becomes

$$\bar{x} = \frac{L}{2\pi}\,\mathrm{Im}\,\ln z = \frac{L}{2\pi}\phi, \tag{6}$$

while the quadratic spread [Eq. (2b)] reduces to

$$\Omega = \left(\frac{L}{2\pi}\right)^2 2(1-|z|). $$

By defining the charge density $\rho(x)=|\psi(x)|^2$, it is easy to see that the following is true:[30]

$$\int_0^L \rho(x)\sin\left[\frac{2\pi}{L}(x-\bar{x})\right]dx = 0, \tag{7a}$$

$$\Omega = \left(\frac{L}{2\pi}\right)^2 \int_0^L \rho(x)\left\{2 - 2\cos\left[\frac{2\pi}{L}(x-\bar{x})\right]\right\}dx. \tag{7b}$$

These equations can be directly compared to the elementary textbook definitions of the position and quadratic spread for a square-integrable electronic state in one dimension (i.e., without PBC, the superscript F stands for "free-space"):

$$\int_{-\infty}^{\infty} \rho(x)(x-\bar{x}^F)dx = 0, \tag{8a}$$

$$\Omega^F = \int_{-\infty}^{\infty} \rho(x)(x-\bar{x}^F)^2 dx. \tag{8b}$$

The resemblance is apparent, the only difference being the replacement of the x and x^2 operators with trigonometric functions that are periodic on the cell. This relationship between the (polynomial) free-space operators and the (trigonometric) PBC ones is made evident in Fig. 1, where they are plotted together in order to show their close matching in a region surrounding the localized state. Indeed, by a Taylor expansion one obtains:

$$\left(\frac{L}{2\pi}\right)\sin\left(\frac{2\pi}{L}x\right) \sim x - \left(\frac{2\pi}{L}\right)^2\frac{x^3}{3!} + \cdots,$$

$$\left(\frac{L}{2\pi}\right)^2\left[2 - 2\cos\left(\frac{2\pi}{L}x\right)\right] \sim x^2 - 2\left(\frac{2\pi}{L}\right)^2\frac{x^4}{4!} + \cdots.$$

Thus we arrived from a different starting point at the same $\mathcal{O}(L^{-2})$ convergence of the position and spread, which has already been discussed in the literature.[3,15] It is particularly clear from this derivation that the intrinsic property of the
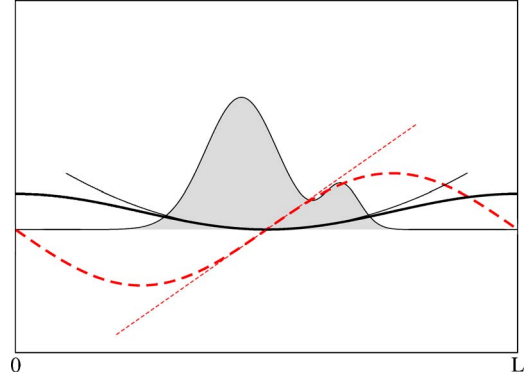

FIG. 1. (Color online) Pictorial representation of the position (red, broken lines) and spread (black, solid lines) operators as they are approximated by the Berry-phase formalism when working in periodic boundary conditions; the free-space operators $(x-x_0)$ and $(x-x_0)^2$ (thin lines) are replaced by the lattice-periodic trigonometric functions (thick lines) which reproduce them best in a neighborhood of the center of the Wannier charge distribution (shaded area).

periodic lattice and the localized state are by no means responsible for the slow convergence, which is instead determined exclusively by the mathematical form of the PBC position operator.

To end this section, we note that Eq. (7a) alone is not sufficient to *define* the center $\bar{x}$, since also $\bar{x}+L/2$ satisfies the same requirement. In the context of Eqs. (7a) and (7b), a correct definition of $\bar{x}$ can be given as the points in the lattice which minimize Eq. (7b) [it is easy to show that this definition is identical to the standard one in Eq. (6)]. Interestingly, from this point of view the position $\bar{x}$ can be thought of as an *internal* parameter of the formalism, which is implicit in the definition of the spread.

IV. CORRECTION SCHEME

Since we are working with Wannier functions which are expected to be well-localized in space (as the 1D state depicted in Fig. 1), there is actually no need to insist on using the PBC formulas for calculating Wannier centers. One could argue here that our "Wannier functions" are formally still periodic (although represented on a large BvK supercell), and since their Hilbert space is defined within PBC, only the action of PBC-allowed operators is justified on them. Actually, another point of view can be used. We recall that *true* Wannier functions are continuous functions in the full 3D (reciprocal) q-space. The mean value of a local operator $V(\mathbf{r})$ in real space can be written

$$\langle w_n|V|w_n\rangle = \int_{All\text{-}space} |w_n(\mathbf{r})|^2 V(\mathbf{r})d\mathbf{r} \tag{9}$$

or, equivalently in q-space [$\tilde{\rho}_n(\mathbf{q})$ is the continuous Fourier transform of the Wannier density $\rho_n(\mathbf{r})=|w_n(\mathbf{r})|^2$]:

$$\langle w_n|V|w_n\rangle = \int_{|\mathbf{q}|<E_{cut}} \widetilde{V}(\mathbf{q})^* \widetilde{\rho}_n(\mathbf{q}) d\mathbf{q}. \qquad (10)$$

If the Wannier function is localized (i.e., practically zero beyond a given distance from its center), the integral in Eq. (9) can be limited to a finite region of space, for example, a cubic box centered around the region where the Wannier density is nonzero. The q-space integral in Eq. (10) can then be recast to a sum over a *discrete* set of reciprocal space vectors, which is also *finite* because of the plane-wave cutoff.

If the integration box is chosen to be smaller than the region where the Wannier density is nonzero, then the reciprocal-space sum carries an error which is due to the overlap between the tails of the Wannier functions and their (artificially) repeated images. This overlap depends on the decay properties of the localized state, and in particular it goes *exponentially* to zero for increasing integration box size whenever $|w_n\rangle$ is exponentially localized.

In a standard DFT simulation of a periodic crystal, the discrete set of reciprocal-space Wannier function coefficients are defined by Eq. (1) and converge to their thermodynamic limit as soon as the total charge density is converged. Then, the only effect of a further refinement of the k-points mesh is an increase in the BvK cell volume, which leads to the progressive reduction of the overlap term discussed above. Therefore, assuming exponential decay for the Wannier functions, by performing q-space integrals over the BvK cell we can achieve *exponential* convergence of the calculated expectation value of any free-space operator with appropriate asymptotic behavior. The natural "bounding box" for the integration domain in real space is, for a general lattice, a Wigner-Seitz BvK cell aligned on the Wannier center. With this choice, the discrete Fourier representation of a given local free-space operator (we use here again the standard conventions for normalizations and Fourier transforms) is

$$\widetilde{V}(\mathbf{b}) = \frac{1}{V_{BvK}} \int_{Wigner\text{-}Seitz} e^{-i\mathbf{b}\cdot\mathbf{r}} V(\mathbf{r}) d\mathbf{r},$$

and the expectation value is simply given as

$$\langle w_n|V|w_n\rangle = V_{BvK} \sum_{\mathbf{b}} \widetilde{V}^*(\mathbf{b}) \widetilde{\rho}_n(\mathbf{b}).$$

Starting from a well-localized set of Wannier functions (obtained through the procedure described in the first part of this work) we can now define a "refined" spread operator Ω' $=\Sigma_n\Omega'_n$, where the contribution from the individual WF is

$$\Omega'_n = \int_{Wigner\text{-}Seitz} |\mathbf{r}-\bar{\mathbf{r}}'_n|^2 \rho_n(\mathbf{r}) d\mathbf{r}.$$

The q-space expression for this formula can be derived starting from the Fourier series of a parabola in a one-dimensional box:

$$\frac{1}{L}\int_{-L/2}^{L/2} \cos\left(\frac{2\pi k}{L}x\right) x^2 dx = \left(\frac{L}{2\pi}\right)^2 \frac{2(-1)^k}{k^2} \quad (k>0),$$

$$\frac{1}{L}\int_{-L/2}^{L/2} x^2 dx = \frac{L^2}{4},$$

and is readily generalized to three dimensions using the same set of vectors and weights $\{\mathbf{b}_i, \bar{w}_i\}$ introduced in Sec. II:

$$\Omega'_n = 2V_{BvK} \sum_{i,k>0} \bar{w}_i \, \text{Re}\left[\frac{2(-1)^k}{k^2} e^{ik\mathbf{b}_i\cdot\bar{\mathbf{r}}'_n} \widetilde{\rho}_n(k\mathbf{b}_i)\right] + \frac{\pi^2}{3}\sum_i \bar{w}_i. \tag{11}$$

The "refined" position $\bar{\mathbf{r}}'_n$ which appears in Eq. (11) is then again an *internal parameter*, which is defined by the minimum of Ω'_n for a given $\widetilde{\rho}_n$ (see the discussion at the end of Sec. III). By taking the gradient of Ω'_n with respect to $\bar{\mathbf{r}}'_n$ one obtains that, at the minimum, the integral

$$\Delta\mathbf{r}_n = \int_{Wigner\text{-}Seitz} (\mathbf{r}-\bar{\mathbf{r}}'_n)\rho_n(\mathbf{r})d\mathbf{r}$$

vanishes. Consistently with the definition of the spread, this condition has to be enforced in reciprocal space, where this integral becomes

$$\Delta\mathbf{r}_n = -2V_{BvK} \sum_{i,k>0} \bar{w}_i\mathbf{b}_i \, \text{Re}\left[i\frac{(-1)^k}{k} e^{ik\mathbf{b}_i\cdot\bar{\mathbf{r}}'_n} \widetilde{\rho}_n(k\mathbf{b}_i)\right]; \tag{12}$$

one can recognize at the right-hand side the Fourier expansion of a periodic sawtooth function. The stationary point can be obtained iteratively starting from a set of unrefined centers (the Wannier functions themselves are kept fixed), by updating at every iteration $\bar{\mathbf{r}}'_n$ through the addition of $\Delta\mathbf{r}_n$ as calculated in Eq. (12) until convergence is reached. If the Wannier function is exactly zero in a region surrounding the boundary of the Wigner-Seitz cell, one iteration is sufficient to provide the exact value of the center, while for less converged cases up to ten iterations may be necessary to achieve machine precision. These iterations have anyway negligible cost, since the Fourier transform of the Wannier function on the BvK cell has to be evaluated only at the beginning (twice for each Wannier function to get the density in reciprocal space).

Both expressions Ω and Ω' are in fact particular cases of a class of localization criteria which rely on individual Wannier densities only, through some generalized spread functional S:

$$\Omega = \sum_n S[\rho_n].$$

A similar generalized, density-dependent spread can be used in practice to explore alternative localization criteria, such as the maximal Coulomb self-repulsion of Edmiston and Ruedenberg,[31] or the orbital self-interaction as defined by Perdew and Zunger.[32] An article comparing such alternatives is under preparation.[33]

Since the present free-space-like expressions for position and spread are more accurate than those derived in the first part of this work, one could wonder why we did not use them from the beginning. The reason is exclusively related to com-

putational efficiency. In Eqs. (3) the localization algorithm involves operations on small $J \times J$ matrices only, where J is the number of bands in the primitive cell (the computationally intensive calculation of the $M^{(\mathbf{k}, \mathbf{b}_i)}$ matrices has to be performed only once at the beginning of the iterative minimization). If, instead, the refined spread (or one of the alternative localization criteria discussed above) is used directly for localizing the Wannier functions, several Fourier transforms on the full Wannier (BvK) grid are required for each iteration, at a substantially higher cost. This expensive procedure is anyway not necessary for the scope of the present work, since the actual set of Wannier wave functions obtained from one localization method or the other coincide in practice to a high degree of accuracy[4] (in particular, the decay properties are expected to be very similar). Therefore we find it most convenient to use this refinement step in a one-shot fashion once a set of maximally localized Wannier functions is obtained within the more efficient localization functional [Eqs. (3)].

V. NUMERICAL TESTS

To demonstrate the effectiveness of our method we have chosen two examples which have been extensively studied in the literature: (i) the dynamical Born effective charge of oxygen atoms in rock salt MgO, and (ii) the spontaneous polarization of the ferroelectric, tetragonally distorted phase of $KNbO_3$. Our calculations were performed within the local density approximation[32] by using norm-conserving Troullier and Martins[34] pseudopotentials in the Kleinman and Bylander[35] form. A nonlinear core correction[36] was adopted for the Mg pseudopotential, while the K pseudopotential was generated in the $4s^0$ ionized configuration with the semicore $3s, 3p$ orbitals included in the valence. We used the experimental lattice constants and atomic positions ($a_0 = 7.96$ a.u. for MgO,[37] and the structural data for $KNbO_3$ from Ref. 38). We expanded the electronic ground state on a plane-wave basis up to a cutoff of 70 Ry. The BZ sampling was performed with Γ-centered simple cubic (tetragonal) grids in reciprocal space for MgO ($KNbO_3$) of the type $N_k \times N_k \times N_k$, by taking into account the time-reversal symmetry only; the k-mesh resolution is defined by the number of k-points N_k along each direction.

We will compare the results as a function of N_k for three different methods for calculating the polarization: (i) the sum of Wannier centers as obtained by Eq. (3a); (ii) the sum of *refined* Wannier centers as described in the previous section; and (iii) the Berry-phase approach. We note that the Berry-phase result can be readily obtained from the quantities that are already available in the localization formalism:

$$\mathbf{r}_{Berry} = -\frac{1}{N} \sum_i \bar{w}_i \mathbf{b}_i \sum_{\mathbf{k}} \text{Im} \ln \det M^{(\mathbf{k}, \mathbf{b}_i)}. \quad (13)$$

We note that the Berry-phase technique is traditionally implemented by using a different k-point sampling ("stripes") with respect to the ground state calculation. However, Resta showed the formal identity between the Berry-phase formalism and the many-body position operator in pe-
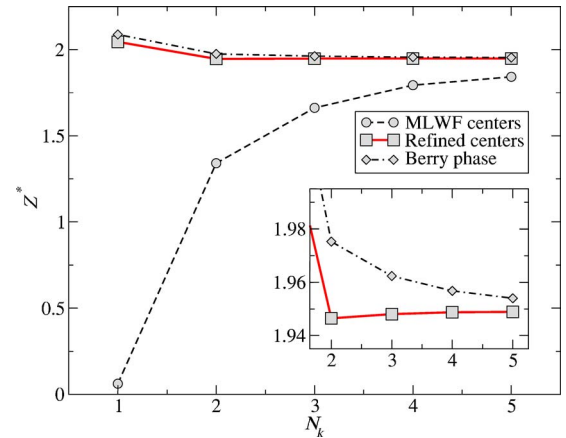

FIG. 2. (Color online) Absolute value of the Born effective charge Z^* of oxygen in MgO as a function of the k-mesh resolution (simple cubic $N_k \times N_k \times N_k$ regular grids in the first Brillouin zone are assumed). The values are computed by using the sum of unrefined Wannier centers [Eq. (3a), dashed line and circles], the Berry-phase approach [Eq. (13), dash-dotted line and diamonds], and our scheme [Eq. (11), red solid line and squares]. The blowup in the inset shows the improvement of our method with respect to the Berry-phase approach.

riodic systems, so it is also reasonable to use uniform Monkhorst-Pack meshes to calculate the polarization; Eq. (13) can be considered the extension to general lattices of the BZ folding procedure demonstrated in Ref. 39.

A. MgO

The dynamical Born effective charge (Z^*) of oxygen was calculated by the finite-difference method, i.e., by considering the difference in total polarization between the ideal centrosymmetric ground state and an atomic configuration where the oxygen sublattice was displaced by 1% of the cubic lattice constant along the x direction. The atomic coordinates were prepared in such a way that, in the ideal lattice, the O atom sits at the origin, and in this case the electronic contribution to the polarization is exactly zero modulo a polarization quantum (all four Wannier functions are symmetrical about the O in this case). We compare in Fig. 2 the resulting value for Z^* as calculated by the three different methods (i)–(iii). The results clearly show that the sum of the *unrefined* Wannier centers can be very inaccurate, and even for the finest mesh the error is still large. MgO is probably a very unfortunate case in that each sp^3-like Wannier function has a strong asymmetric shape, and the errors in the individual centers do not cancel out efficiently in the strained configuration, so that the total polarization carries an important deviation from the exact value.[40] The Berry-phase calculation is a much better estimate, but in the inset it can be seen that the convergence is still relatively slow. As we explained in the preceding sections, it was already shown that the Berry-phase result converges only as $\mathcal{O}(L^{-2})$, i.e., it shares the same asymptotic behavior as the sum of the unrefined Wannier centers (*albeit* with a quite different prefactor in this particular case). The sum of the *refined* Wannier cen-
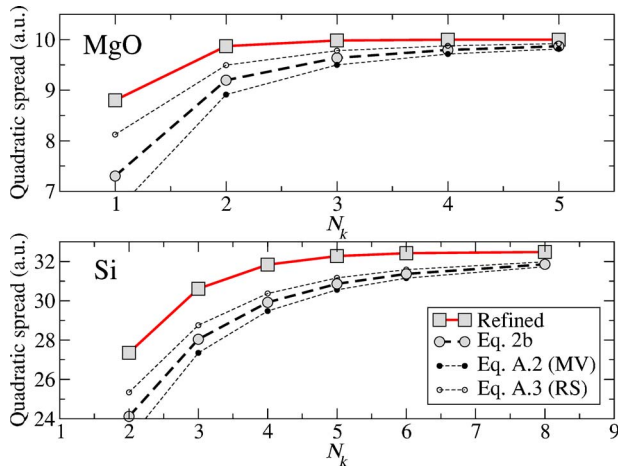
FIG. 3. (Color online) Convergence of the total spread as a function of the k-mesh resolution N_k (see text for explanation) in the case of MgO and Si. The improvement provided by the refined value [Eq. (11), red line and squares] with respect to the standard "trigonometric" spread [Eq. (3b), thick black line and circles] is apparent. We provide for comparison the alternative spreads discussed in Appendix A, which are also based on the same trigonometric kernel and show similar, slow convergence properties.

ters instead shows an extremely fast convergence and gives a very accurate result already for a $2 \times 2 \times 2$ mesh. The value of Z^* we obtain is -1.95, which is in excellent agreement with previous experimental and theoretical investigations.[41,42] The small difference with respect to the all-electron ($Z^* = 1.98$) value reported in Ref. 41 can be ascribed to the pseudopotentials adopted in our work; this is a particularly delicate issue for the Mg cation. To clarify this point, we repeated the calculation by using a substantially harder Mg pseudopotential with the $2s$ and $2p$ states kept in valence and we obtained $Z^* = 1.99$. The convergence properties we demonstrated in our analysis are not affected by the specific choice of the pseudopotentials.

To complement our methodological test, we calculated also the refined value for the total quadratic spread as a function of k-mesh resolution, and the results are reported in Fig. 3. It is clear that this quantity shares the same, excellent, convergence properties as the position operator (upper panel). In the lower panel of the same figure we report for comparison the results of an analogous calculation of the total spread in bulk silicon. The convergence is slower than in MgO, as can be expected from the different character of this covalent compound as compared to the highly ionic magnesium oxide, but the benefit that can be obtained through the use of the more accurate free-space definition of the spread is still apparent. The "unrefined" value of the spread is also compared to the alternative, similar prescriptions discussed in Appendix A.

B. KNbO$_3$

We present in Fig. 4 our results for the spontaneous polarization of KNbO$_3$. The sum of the unrefined Wannier centers is less inaccurate in this case and is fairly close to the
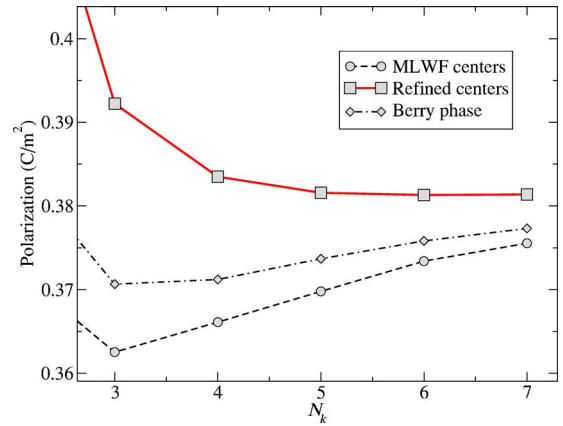

FIG. 4. (Color online) Convergence of the spontaneous polarization of the (tetragonal) ferroelectric phase of KNbO$_3$ as a function of the k-mesh resolution. The values are computed using the sum of unrefined Wannier centers [Eq. (3a), dashed line and circles], the Berry-phase approach [Eq. (13), dash-dotted line and diamonds], and our scheme [Eq. (11), red solid line and squares].

values obtained within the Berry phase formalism. The sum of the refined centers has, again, much better convergence properties than the two traditional methods. By increasing the mesh from $6 \times 6 \times 6$ to $7 \times 7 \times 7$ the value of the spontaneous polarization increases by 0.02%, while within the same $7 \times 7 \times 7$ mesh the traditional techniques carry an error which is two orders of magnitude higher. Extrapolating the $\mathcal{O}(L^{-2})$ trend one can guess that ~ 70 k-points along the reciprocal space stripes[14] would be needed to achieve similar accuracy within the Berry-phase formalism. The final value we obtain, 0.38 C/m^2, compares very well with experimental data and previous theoretical investigations.[21,38,43,44]

VI. CONCLUSIONS

In conclusion, we have derived a simple and general formalism for the computation of maximally localized Wannier functions. We provide an intuitive picture of the convergence properties of this scheme and similar ones, relating them to the Taylor expansion of elementary trigonometric functions. We show that the convergence can be dramatically improved by a simple strategy based on the exponential localization of the Wannier functions in insulating materials. We expect our scheme to open the way to both accurate and efficient calculations of polarization properties in a wide range of physical systems, making the expensive linear-response approach or the relatively cumbersome non-self-consistent calculation of "stripes" in reciprocal space unnecessary.

As a final remark, we note that the Wannier function-based theory of polarization is becoming increasingly important especially in disordered systems, where not only the global polarization but also the *local* bonding properties and dipole moments may be interesting to follow during, e.g., a molecular dynamics simulation.[5] In these applications the improved accuracy provided by our method could be an extremely valuable tool.

APPENDIX A: DECOMPOSITION INTO INVARIANT, OFF-DIAGONAL, AND DIAGONAL PARTS

The form 2b for the spread functional was chosen mainly because of its simplicity, and because it allows for a direct interpretation as the integral of the Wannier density multiplied by a real function on the BvK cell (see the discussion in Sec. III). Unfortunately this expression does not lead to an elegant separation into invariant and noninvariant parts. However, this issue is readily solved by choosing an alternative definition of the spread:

$$\Omega_{MV} = \left(\frac{L}{2\pi}\right)^2 (1 - |z|^2), \qquad (A1)$$

which coincides with the Γ-point prescription of MV and which *does* allow for an exact separation of the invariant part. This choice still allows for the simple interpretation based on cosinelike functions. If we define a function of x_0

$$f(x_0) = \int_0^L \rho(x) \cos\left[\frac{2\pi}{L}(x - x_0)\right] dx \qquad (A2)$$

it is clear that when x_0 maximizes f, x_0 is automatically the Wannier center of Eq. (2a). Both expressions for the spread [Ω as in Eq. (2b) and Ω_{MV} discussed here] are consistent with the same value of x_0 at the minimum:

$$\Omega = \left(\frac{L}{2\pi}\right)^2 \min_{x_0} 2[1 - f(x_0)],$$

$$\Omega_{MV} = \left(\frac{L}{2\pi}\right)^2 \min_{x_0} [1 - f^2(x_0)].$$

Moving on to 3D, the operational definition of the spread becomes

$$\Omega_{MV} = \sum_n \sum_i \bar{w}_i (1 - |z_n^{(i)}|^2),$$

where it is easy to see that $z_n^{(i)}$ are nothing other than the matrix elements indicated as X_{nn}, Y_{nn}, Z_{nn} in MV.

Now, "folding" this expression in k-space leads to a formula which is similar to Eq. (3b):

$$\Omega = \sum_n \sum_i \bar{w}_i \left(1 - \left|\frac{1}{N}\sum_\mathbf{k} M_{nn}^{(\mathbf{k}, \mathbf{b}_i)}\right|^2\right).$$

Thinking in terms of the big BvK cell, this can be written equivalently as

$$\Omega = \frac{1}{N}\sum_i \bar{w}_i \left(NJ - \sum_{\mathbf{R},n} |\langle \mathbf{R}n|e^{-i\mathbf{b}_i \cdot \mathbf{r}}|\mathbf{R}n\rangle|^2\right),$$

where the leading factor $1/N$ gives the spread per *primitive*

cell, and the same notation as MV for the nth Wannier function at the $\mathbf{R}$ site, $|\mathbf{R}n\rangle$ is used. From this expression it is clear how to construct an obvious invariant quantity, Ω_I (J is the number of bands in the primitive cell):

$$\Omega_I = \frac{1}{N}\sum_i \bar{w}_i \left(NJ - \sum_{\mathbf{R}\mathbf{R}',nm} |\langle \mathbf{R}n|e^{-i\mathbf{b}_i \cdot \mathbf{r}}|\mathbf{R}'m\rangle|^2\right),$$

and what remains to do is to "unfold" this formula in k-space. A first simplification is trivial:

$$\Omega_I = \sum_i \bar{w}_i \left(J - \sum_{\mathbf{R},nm} |\langle \mathbf{R}n|e^{-i\mathbf{b}_i \cdot \mathbf{r}}|\mathbf{0}m\rangle|^2\right).$$

A second simplification is obtained by reversing the formula between Eqs. (5) and (6) of MV, leading to

$$\Omega_I = \sum_i \bar{w}_i \left(J - \sum_{\mathbf{R},nm} \left|\frac{1}{N}\sum_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{R}}\langle u_{n\mathbf{k}}|e^{-i\mathbf{b}_i \cdot \mathbf{r}}|u_{m\mathbf{k}+\mathbf{b}}\rangle\right|^2\right).$$

By writing explicitly $|z|^2 = z^* z$ and noticing that

$$\sum_\mathbf{R} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = N\delta_{\mathbf{k},\mathbf{k}'},$$

we obtain the final expression in k-space:

$$\Omega_I = \sum_i \bar{w}_i \left(J - \sum_{mn}\frac{1}{N}\sum_\mathbf{k} |M_{nm}^{(\mathbf{k}, \mathbf{b}_i)}|^2\right), \qquad (A3)$$

which is exactly Eq. (34) of the MV paper.

It is interesting to work out the remaining terms, Ω_D and Ω_{OD}, which are indicated as "diagonal" and "off-diagonal" parts in MV (we recall that Ω_D vanishes for a centrosymmetric system[3]). The easiest way is to first solve the expression for

$$\Omega_{MV} - \Omega_D = \sum_i \bar{w}_i \left(J - \sum_{\mathbf{R},n} |\langle \mathbf{R}n|e^{-i\mathbf{b}_i \cdot \mathbf{r}}|\mathbf{0}n\rangle|^2\right).$$

By using an analogous algebra we readily arrive at the formula in k-space:

$$\Omega_{MV} - \Omega_D = \sum_i \bar{w}_i \left(J - \sum_n \frac{1}{N}\sum_\mathbf{k} |M_{nn}^{(\mathbf{k}, \mathbf{b}_i)}|^2\right),$$

from which it is very easy to evaluate Ω_{OD}:

$$\Omega_{OD} = \sum_i \bar{w}_i \sum_{m\neq n}\frac{1}{N}\sum_\mathbf{k} |M_{mn}^{(\mathbf{k}, \mathbf{b}_i)}|^2.$$

This means that Ω_D is given by the following difference:

$$\Omega_D = \sum_{i,n} \bar{w}_i \left(\left|\frac{1}{N}\sum_\mathbf{k} M_{nn}^{(\mathbf{k}, \mathbf{b}_i)}\right|^2 - \frac{1}{N}\sum_\mathbf{k} |M_{nn}^{(\mathbf{k}, \mathbf{b}_i)}|^2\right).$$

Comparing this formalism with the MV one, it is clear that Ω_I and Ω_{OD} are identical, while the terms Ω and Ω_D differ. This derivation provides in a certain sense a "unification" of the two, formerly distinct, MV prescriptions for the Γ-point case and in k-space. The gradients with respect to unitary rotations of the Bloch orbitals are simply given by setting $C = z$ (instead of $C = z/|z|$) in Eq. (4).

To complete our discussion, we note that a third form of the one-particle quadratic spread was proposed by Resta and

Sorella,[24] which leads to yet another operational definition for the localization criterion:

$$\Omega_{RS} = -\sum_n \sum_i \bar{w}_i \ln |z_n^{(i)}|^2.$$

The k-space folding of this formula is straightforward, while the gradient is again given by Eq. (4), with $C = z/|z|^2$. All functionals Ω, Ω_{MV}, and Ω_{RS} are identical in the thermodynamic limit. For finite BvK cells they all share the same definition of the Wannier center. The resulting maximally localized Wannier functions themselves are identical in cases where $|z_n|$ are equal for all $n = 1, \dots, J$ bands (e.g., bulk Si, centrosymmetric MgO crystal). The numerical value of the spread can differ slightly because the higher orders in the Taylor expansion are different. Some examples concerning this discrepancy are reported in the main text (see, e.g., Fig. 3).

APPENDIX B: ONE DIMENSION

We show in this appendix that in one-dimensional problems the minimization of the spread functional Eq. (3b) leads exactly to the same solution as the parallel transport algorithm.

We assume a set of J Wannier functions w_n, with $n = 1, \dots, J$ in a 1D cell of length L sampled at the Γ point only (given the BZ-folding invariance of our scheme this assumption does not affect the generality of the following discussion), and we consider the matrix:

$$M_{mn} = \langle w_m | e^{i(2\pi/L)x} | w_n \rangle.$$

The parallel transport solution corresponds to the particular representation where

$$M_{mn} = K_{mn} \gamma_n, \qquad (B1)$$

with K Hermitian; the complex numbers γ_n are *phases* and are directly related to the Wannier centers by

$$\gamma_n = e^{i(2\pi/L)x_n}.$$

It is easy to show that the sum of the centers x_n gives a value for the macroscopic polarization which is formally identical to the Berry-phase result; we want to show now that Eq. (B1) is also true for the "maximally localized Wannier functions" obtained minimizing Eq. (3b). Since the Wannier functions w_n minimize Ω, it is easy to see that the following condition is true:

$$\langle w_m | [C(x-x_m) - C(x-x_n)] | w_n \rangle = 0,$$

where $C(y) = \cos(2\pi/Ly)$. Elementary algebra leads to

$$\langle w_m | [S(x-x_m) + S(x-x_n)] | w_n \rangle = 0,$$

where $S(y) = \sin(2\pi/Ly)$, and therefore to

$$\langle w_m | (e^{i(2\pi/L)(x-x_m)} - e^{-i(2\pi/L)(x-x_n)} | w_n \rangle = 0.$$

This means that the matrix $A_{mn} = \langle w_m | e^{i(2\pi/L)(x-x_n)} | w_n \rangle$ is Hermitian, and the equivalence with the parallel transport solution follows immediately (it is easy to see that $A = K$).

If one is interested in only one component of the macroscopic polarization vector (e.g., when coupling the system to a uniform field[45] or in most ferroelectric materials where the distortion axis is obvious), one can use the parallel transport algorithm to localize the wave functions along one direction while retaining a Bloch-like character in the normal plane; the resulting "hermaphrodite"[39] orbitals have faster asymptotic decay than standard Wannier functions. The resulting set of centers can be then "refined" along the same lines already discussed in the main part of the text; this way it is possible to obtain even faster convergence with respect to the k-point sampling, with the further advantage of a very practical algorithm (the iterative minimization of the spread functional in three dimensions is replaced by a singular value decomposition problem, which is available in most numerical libraries; a substantial gain in efficiency can be further obtained by taking advantage of point symmetries). We believe that the simplicity, accuracy, and reduced cost of this strategy could motivate its use as an alternative to the traditional Berry-phase technique.

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