Electron localization in the insulating state: Application to crystalline semiconductors

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We measure electron localization in different materials by means of a “localization tensor”, based on Berry phases and related quantities. We analyze its properties, and we actually compute such tensor from first principles for several tetrahedrally coordinated semiconductors. We discuss the trends in our calculated quantity, and we relate our findings to recent work by other authors. We also address the “hermaphrodite orbitals”, which are localized (Wannier–like) in a given direction, and delocalized (Bloch–like) in the two orthogonal directions: our tensor is related to the optimal localization of these orbitals. We also prove numerically that the decay of the optimally localized hermaphrodite orbitals is exponential.

1. INTRODUCTION

A nonmetal is distinguished from a metal by its vanishing conductivity at low temperature and low frequency: we use here the term “insulator” to include any nonmetal, like the semiconducting materials which are the case studies actually addressed in this work.

Within classical physics, the qualitative difference between an insulator and a metal is attributed to the nature of the electronic charge: either “bound” (Lorentz model for insulators) or “free” (Drude model for metals). In other words, electrons are localized in insulators and delocalized in metals. In a milestone paper published in 1964, W. Kohn characterized the insulating state of matter in a way which is reminiscent of the classical picture: he gave evidence that the main feature determining the insulating behavior of matter is electron localization in the ground–state wavefunction. Although this work mainly addressed correlated many–electron systems, its message is very relevant even for materials where an independent–electron description is quite adequate, as the semiconductor crystals studied here. Recently a novel measure of electron localization—different from Kohn’s one—was proposed by Resta and Sorella, hereafter cited as RS. Their approach is deeply rooted into the modern theory of polarization.

Metals and insulators reveal their qualitative difference when static dielectric polarization is addressed. Suppose we expose a finite macroscopic sample to an electric field, say inserting it in a charged capacitor. In metals polarization is trivial: universal, material–independent, due to surface phenomena only (screening by free carriers). Therefore polarization in metals is not a bulk phenomenon. The opposite is true for insulators: macroscopic polarization is a nontrivial, material–dependent, bulk phenomenon. We can therefore phenomenologically characterize an insulator, in very general terms, as a material whose ground wavefunction sustains a nonzero bulk macroscopic polarization whenever the electronic Hamiltonian is non centrosymmetric. If the Hamiltonian is instead centrosymmetric, the polarization vanishes but remains a well defined bulk property, at variance with the metallic case. The phenomenological link between macroscopic polarization and insulating behavior was first pointed out and exploited—taking advantage of the modern theory of polarization—by RS in 1999. This approach is based on Berry phases and related concepts. Even the RS paper, like Kohn’s 1964 one, mostly concerns correlated systems. Furthermore, in order to keep the presentation simple and concise, most results are explicitly shown in one dimension, while the d–dimensional formulation is only sketched in the final paragraphs of RS. In the present paper we provide more details on how the RS theory of localization works in three dimensions, specializing to a system of noninteracting electrons, like the band insulators chosen as case studies here.

Some other important papers must be mentioned at this point. In 1997 Marzari and Vanderbilt hereafter cited as MV, while not addressing metals at all (and hence their difference from insulators), establish nonetheless some results which are relevant to the present viewpoint. In a very recent comprehensive paper, Souza, Wilkens, and Martin—hereafter cited as SWM—generalize and extend in various ways the main finding of RS: we adopt here some of their notations. Finally, after this work was completed, we became aware of Ref. 13, whose conclusions bear some implications for our results shown in Sect. VI.

The paper is organized as follows. In Sect. II we define the basic ingredients providing both polarization and localization, namely the expectation values of the many–body phase operators $z_N^{(α)}$ for the three Cartesian coordinates, Eq. (4). In Sect. III following RS, we show how the modulus of $z_N^{(α)}$ defines a very meaningful quantity, the localization tensor, for which we adopt the SWM notations: such tensor is finite in insulators and diverges in metals. In Sect. IV we discuss the main properties of the localization tensor, and in Sect. V we...
present first-principle calculations for several elemental and binary semiconductors: the main trends are analyzed. In Sect. [X] we calculate orbitals which are optimally localized in a given direction, and whose average quadratic spread coincides with the localization tensor. We also heuristically check the exponential localization of these orbitals, which we call “hermaphrodite orbitals”. In Sect. [XI] we draw our main conclusions. In the Appendix we consider a molecule or a cluster an we discuss our localization tensor therein, showing its relationship to some results of Boys localization theory,[3] well known in quantum chemistry.[3]

II. MANY-BODY PHASE OPERATORS

We are addressing here, as it is done by MV, a crystalline system of independent electrons, having in mind a Kohn–Sham scheme. The properties of interest, namely, macroscopic polarization and electron localization, are not properties of the individual KS orbitals: instead, they are global properties of the occupied KS manifold. As shown in Refs. [3,4,9] it proves formally convenient to deal with a many-body wavefunction $\Psi$, obtained as a Slater determinant of occupied orbitals. This determinant is uniquely determined by the manifold of the occupied orbitals and is invariant by unitary transformation of these orbitals among themselves: for instance, in insulating crystals, an important transformation of this class converts the occupied Bloch orbitals into Wannier orbitals:

$$\langle \psi_{n\mathbf{q}}, | \psi_{n'\mathbf{q}'} \rangle = \frac{1}{L^3} \int_{\text{BvK cell}} d\mathbf{r} \psi_{n\mathbf{q}}^*(\mathbf{r}) \psi_{n'\mathbf{q}'}(\mathbf{r}) = \delta_{nn'} \delta_{ss'},$$

(2)

If the system is insulating with $n_b$ doubly occupied bands, there are $N = 2n_b M^3$ independent spinorbitals, out of which we write a single-determinant many-body wavefunction for $N$ electrons:

$$\Psi = A \prod_{n,s} \frac{1}{L^3} \psi_{n\mathbf{q}_s} \bar{\psi}_{n\mathbf{q}_s},$$

(3)

where the product runs over all occupied bands and all mesh points, $A$ is the antisymmetrizer operator, and the factor ensures that the $N$-body wavefunction is normalized to one on the hypercube of side $L$. If, instead, the system is metallic, then the many-body wavefunction $\Psi$ can still be written in the form of Eq. (3), but where not all the Bloch vectors of a given band are included in the product.

According to Refs. [3,4] the key quantities to deal with both macroscopic polarization and electron localization are expectation values of “many-body phase operators”. For a three-dimensional system there are three such operators, one for each Cartesian direction. We indicate as $z^{(\alpha)}_N$, where $\alpha$ is a Cartesian index, their ground-state expectation values:

$$z^{(\alpha)}_N = \langle \Psi | e^{i\frac{\pi}{2} \sum_{i=1}^N x_i} | \Psi \rangle,$$

(4)

and analogously for $y$ and $z$ directions. This remarkably compact expression is very general and applies as it stands even to correlated and/or disordered systems: here we specialize to a crystalline system of independent electrons, whose wavefunction $\Psi$ assumes the form of Eq. (3), where the product indices have to be differently specified in the insulating and metallic cases.

We may conveniently recast $z^{(\alpha)}_N$ as an overlap

$$z^{(\alpha)}_N = \langle \bar{\Psi} | \Psi \rangle,$$

(5)

where $\bar{\Psi}$ is the Slater determinant of a different set of Bloch spinorbitals:

$$\tilde{\psi}_{n\mathbf{q}_s}(\mathbf{r}) = e^{i \frac{\pi}{2} \alpha} \psi_{n\mathbf{q}_s}(\mathbf{r}),$$

(6)

and analogously for the bar (spin-down) ones. According to a well known theorem, the overlap between two single-determinant wavefunctions is equal to the determinant of the $N \times N$ overlap matrix built out of the occupied spinorbitals. Since the overlaps between different-spin spinorbitals vanish, and those between equal-spin ones are identical in pairs, we can write

$$z^{(\alpha)}_N = (\det S)^2,$$

(7)

where $S$ is the overlap matrix between spatial orbitals, having size $N/2 = n_b M^3$. Its elements are:
enough to imply that it shows up already at finite \( N \). It is remarkable that, in the present case, such difference runs over the whole one dimension, and by a “localization tensor” in three dimensions. This tensor is an intensive quantity, has the dimensions of a squared length, and measures the localization of the many–electron system as a whole: in the present case, it is a global property of the occupied KS manifold. The localization tensor is finite for insulators and diverges for metals.

In the metallic case, instead, the \( z_N^{(a)} \)’s are identically zero. This is easily understood by looking at the simple case with only one band. Suppressing the band index the small overlap matrix becomes a \( c \)-number \( S(\mathbf{q}, \mathbf{q}') \), and Eq. (9) becomes a product of \( c \)-numbers, with no determinant to evaluate. In an insulator this product runs over the whole \( \mathbf{q}_s \) mesh, and all factors are nonzero; in a metal the analogous product runs only on the \( \mathbf{q}_s \)’s within the Fermi surface. Looking at the definition of \( S(\mathbf{q}, \mathbf{q}') \), Eqs. (6) and (5), it is clear that there exists at least one occupied \( \mathbf{q}_s \), adjacent to the Fermi surface, such that \( S(\mathbf{q}_s, \mathbf{q}_s') \) vanishes for all occupied \( s' \). This is enough to imply that \( z_N^{(a)} \) vanishes as well.

The complex numbers \( z_N^{(a)} \) are ground–state expectation values, and do not access any spectral information. Yet they qualitatively discriminate between insulators and metals: they are in fact nonvanishing in the former materials, and vanishing in the latter ones. This shows, according to RS, that there is a qualitative difference in the organization of the electrons in their ground state. It is remarkable that, in the present case, such difference shows up already at \( \textit{finite} N \), before the thermodynamic limit is taken.

### III. ELECTRON LOCALIZATION

In centrosymmetric materials the expectation values \( z_N^{(a)} \) are real (provided the origin is chosen at a centrosymmetric site), while in noncentrosymmetric materials they are in general complex: their phases define then the Cartesian components of the macroscopic polarization in suitable units. In the metallic case the \( z_N^{(a)} \)’s vanish and the polarization is ill defined, in agreement with the phenomenological viewpoint illustrated in Sect. 3. We address electron localization using the moduli of the same \( z_N^{(a)} \)’s. Following RS, electron localization is measured by a squared localization length in one dimension, and by a “localization tensor” in three dimensions. This tensor is an intensive quantity, has the dimensions of a squared length, and measures the localization of the many–electron system as a whole: in the present case, it is a global property of the occupied KS manifold. The localization tensor is finite for insulators and diverges for metals.

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The proof is relatively straightforward, starting from Eq. (10) and discretizing integrals and derivatives on the mesh defined in Eq. (1).

Expressions such as Eq. (10) and similar ones had appeared in the literature before MV in relationship to Wannier functions. By means of an expression of this kind, MV define a ground-state quantity $\Omega$ which sets a lower bound for the second (spherical) moments of the Wannier functions. More precisely, for an insulator with $n_b$ occupied bands (hence $n_b$ Wannier functions per cell) such second moment is no smaller in average than $\Omega/n_b$. It is worth mentioning at this point that the logic of the MV paper goes backwards with respect to the present approach: first they provide a continuum theory, and then they discretize for computational purposes. Their discretization is different from Eq. (13), which emerges naturally from the present formulation starting from the remarkably compact Eq. (13). Both discretizations obviously converge to the same $M \to \infty$ limit: their convergence properties are different, though.

Specializing MV to a cubic material, RS have found that electron gas, the density matrix is known exactly: $\Omega = 3n_b$ (for $|x^2|_c$ is intensive, while $\Omega$ is not such. Building upon MV’s work, we are now ready to generalize the localization tensor to materials of arbitrary symmetry:

$$\langle r_\alpha r_\beta \rangle_c = \frac{V_c}{n_b (2\pi)^3} \int d\mathbf{q} \left( \sum_n \langle \partial_{\mathbf{q}_\alpha} u_{n\mathbf{q}} | \partial_{\mathbf{q}_\beta} u_{n\mathbf{q}} \rangle - \sum_{n, n'} \langle u_{n\mathbf{q}} | \partial_{\mathbf{q}_\alpha} u_{n'\mathbf{q}} \rangle \langle \partial_{\mathbf{q}_\beta} u_{n'\mathbf{q}} | u_{n\mathbf{q}} \rangle \right),$$

where $V_c$ is the cell volume. Notice that the imaginary part of the integrand in Eq. (17), being antisymmetric in $\mathbf{q}$, cancels in the integral, such that the localization tensor is real. Even the off-diagonal elements, as defined in Eq. (16), are antisymmetric.

The localization tensor (in the thermodynamic limit) has been written as a Brillouin-zone integral in Eq. (17). This integral can be identically transformed into a particularly simple expression whose only ingredient is $P$:

$$\langle r_\alpha r_\beta \rangle_c = \frac{1}{2n_b} \int d\mathbf{r} \int d\mathbf{r}' (\mathbf{r} - \mathbf{r}')_\alpha (\mathbf{r} - \mathbf{r}')_\beta |P(\mathbf{r}, \mathbf{r}')|^2,$$

(19)

which is the second moment of the (squared) density matrix in the coordinate $\mathbf{r} - \mathbf{r}'$. The proof of the equivalence between Eq. (19) and Eq. (17) can be worked out using the same algebra appearing in Ref. [6] for a different argument proving the same result, see the Appendix.

We have arrived at Eq. (14) considering an insulating crystal for. In this case we know, under general arguments [3][4] that $P(\mathbf{r}, \mathbf{r}')$ is asymptotically exponential in the argument $|\mathbf{r} - \mathbf{r}'|$: this confirms that the integral over all space in Eq. (19) converges and the localization tensor is therefore finite. At this point, it is worthwhile to apply the general form of Eq. (19) to the metallic case. For the simplest metal of all, the free electron gas, the density matrix is known exactly [4]:

$$P(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \rho(\mathbf{r}, \mathbf{r}') = \frac{3n_b j_1(k_F|\mathbf{r} - \mathbf{r}'|)}{2k_F|\mathbf{r} - \mathbf{r}'|}.$$

(20)

Replacement of Eq. (20) into Eq. (19) results in a diverging integral, thus confirming that our localization tensor is formally infinite in this paradigmatic metal. Other, more realistic, metals feature this same divergence.

The fact that the density matrix $\rho(\mathbf{r}, \mathbf{r}')$ is short-range in the variable $\mathbf{r} - \mathbf{r}'$ has been named “nearsightedness” by W. Kohn [4]. The second moment expression in Eq. (19) shows that our localization tensor is indeed a meaningful quantitative measure of such nearsightedness. We are going to analyze below the major trends over an important class of materials: tetrahedral semiconductors. We mention at this point that a conceptually different measure of the nearsightedness of a given electronic ground state focuses instead on the exponent governing the exponential decay of $\rho(\mathbf{r}, \mathbf{r}')$ in insulators: some case studies have been recently investigated [12][13].

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IV. PROPERTIES OF THE LOCALIZATION TENSOR

We have already emphasized that the localization tensor is a property of the occupied KS manifold as a whole. The main quantity which defines such manifold is the (spin-integrated) single-particle density matrix $\rho$, which coincides with twice the projector $P$ over the occupied KS orbitals: this projector is invariant by unitary transformations of the orbitals. Using Bloch eigenfunctions the projector reads, for an insulator with $n_b$ occupied bands:

$$P(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \rho(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \sum_{n=1}^{n_b} \int d\mathbf{q} \psi_{n\mathbf{q}}(\mathbf{r}) \psi_{n\mathbf{q}}^*(\mathbf{r}').$$

(18)

The second moment expression in Eq. (17) in insulators:

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Wannier functions”, i.e. those localized orbitals which minimize the average spherical moment. They prove, among other things, that such moment is strictly larger than the trace of our localization tensor. Building on their results, it is straightforward to attribute a similar meaning to the tensor itself: for any transformation of the occupied orbitals into a set of unitarily equivalent ones, the second moment in a given direction can be no smaller than the localization tensor, projected on that direction.

Since we are going to apply our results to cubic materials only, we focus on those orbitals which minimize in average the quadratic spread (second moment) in the $x$ coordinate. The present formalism makes the definition of these orbitals particularly simple: they are in fact the eigenfunctions of the position operator $x$, projected over the occupied manifold. Calling $\Xi = P x P$ this operator, its expression in the Schrödinger representation is:

$$\Xi(r, r') = \int_{\text{all space}} d\mathbf{r}'' P(r, r'') x'' P(r'', r'). \quad (21)$$

Notice that $x$ is incompatible with BvK boundary conditions and its matrix elements over Bloch states are ill defined; nonetheless, $\Xi$ is—in insulators—a well defined operator, which maps any vector of the occupied manifold into another vector of the same manifold. This fact owes to the exponential localization of $P$ in Eq. (21).

The relationship between $\Xi$ and the orbitals optimally localized in the $x$ direction is easily proved borrowing some results from MV; for a different argument leading to the same proof, see the Appendix. We also notice an important difference with respect to the three–dimensional localization explicitly considered by MV. While the trace of the localization tensor provides a lower bound for three–dimensional localization, its element $\langle x^2 \rangle_c$ provides instead a genuine minimum for one–dimensional localization (in a cubic material). This qualitative difference owes to the fact that, while one can manifestly diagonalize $P x P$, one cannot simultaneously diagonalize $P x P$, $P y P$, and $P z P$.

We end this Section about the properties of the localization tensor with a most important issue: is $\langle r_\alpha r_\beta \rangle_c$ a measurable quantity? The answer, due to SWM, is “yes”. They prove the identity:

$$\langle r_\alpha r_\beta \rangle_c = \frac{\hbar V_c}{2\pi e^2 n_b} \int_0^\infty d\omega \frac{\omega}{\omega} \text{Re} \sigma_{\alpha\beta}(\omega), \quad (22)$$

where $\sigma_{\alpha\beta}$ is the conductivity tensor. Notice that the left hand side, as emphasized throughout the present work, is a property of the electronic ground state, while the right hand side is a measurable property related to electronic excitations: therefore Eq. (22) must be regarded as a sum rule. The frequency integral in Eq. (22) diverges in metals and is finite in insulators, as obviously expected. Since in the latter materials there is a gap for electronic excitations, Eq. (22) immediately leads to the inequality:

$$\langle r_\alpha r_\beta \rangle_c < \frac{\hbar V_c}{2\pi e^2 n_b} \int_0^\infty d\omega \text{Re} \sigma_{\alpha\beta}(\omega), \quad (23)$$

where $\varepsilon_g$ is the direct gap. Using then the oscillator–strength sum rule, Eq. (23) for a cubic material is cast as:

$$\langle x^2 \rangle_c < \frac{\hbar^2}{2m_e \varepsilon_g}. \quad (24)$$

Below, we investigate the trends in both members of this inequality for our test–case materials.

V. CALCULATED LOCALIZATION TENSORS

We have studied several tetrahedrally coordinated crystalline materials, from the group IV, III–V, and II–VI, having the diamond and zincblende structure. The first–principle calculations have been performed within density-functional theory in the local–density approximation, using pseudopotential[4] and plane waves. We implement a trivial extension of the formulas presented above, using a rectangular unit cell instead of a simple cubic one: we thus describe the diamond and zincblende structures by means of a tetragonal cell with a lattice constant $a$ in the basal plane and $c = \sqrt{2}a$. There are four atoms per unit cell, whose projections on the $c$ axis are equispaced; for the sake of consistency with the formal results, we take $x$ along the $c$ axis and $yz$ in the basal plane. We then use a BvK cell of sides $M_x a$, $M_y a$, and $M_z a$, corresponding to a mesh in reciprocal space with $M_x, M_y, M_z$ points: this allows an easier control of convergence.

We start evaluating at the mesh points the Hermitian matrices

$$A_s = S^\dagger(q_s, q_s + \Delta q^{(x)}) S(q_s, q_s + \Delta q^{(x)}); \quad (25)$$

then Eqs. (14) and (15) are written as

$$\langle x^2 \rangle_c = \frac{1}{M_y M_z} \sum_{s_2=1}^{M_y} \sum_{s_3=1}^{M_z} \left( -\frac{e^2 M_z}{4\pi^2 n_b} \sum_{s_1=1}^{M_x} \ln \det A_s \right). \quad (26)$$

In general convergence is fast in $M_y, M_z$, and slower in $M_x$. The expression in parenthesis in Eq. (26) is precisely the one–dimensional expression discussed in detail by RS, and the three dimensional one simply obtains from it as an average in the $(q_y, q_z)$ plane.

First we show in Fig. 1 the convergence of our expressions over a genuinely cubic grid, which coincides with the one used by MV in their evaluation of the quantity $\Omega_l = 3n_b \langle x^2 \rangle_c$. They use a different discretization of the same $k$ space integral: both calculations converge to the same localization tensor, although our discretization, based on Eqs. (14) and (15), converges faster. All the following results have been obtained using noncubic grids, as in Eq. (26), in order to achieve faster convergence.
We have systematically calculated well converged localization tensors for several elemental and binary semiconductors. In Fig. 3 we plot the localization tensors versus the right-hand member of the inequality in Eq. (24), where for the gap $\varepsilon_g$ we have used both (i) the theoretical and (ii) the experimental values. In case (i) the inequality owes to an exact sum rule and must be satisfied: we are therefore checking the internal consistency of the calculations. Also, it may be noticed that the inequality is very strongly verified. In case (ii) there is no a-priori guarantee that the inequality is verified, particularly given the fact that the experimental gap is systematically larger than the KS one. Nonetheless the localization tensor is obtained here as a pure ground state property, and it is well known that density-functional theory in the local-density approximation provides a good representation of the ground state, though not of the excitations. It is therefore interesting to verify that even for case (ii) the inequality in Eq. (24) is strongly verified for all the materials considered.

The localization tensor ranges roughly between 1 and 3 bohr$^2$ for all the materials considered, diamond being the most localized and germanium the most delocalized. The trend is qualitatively expected, in agreement with SWM’s statement that “the larger the gap, the more localized the electrons are”. However this is a trend more than a strict rule, and indeed a few materials show irregularities. Better trends are obtained when comparing families of materials: either isoelectronic series or isovalent series. In order to enhance such regularities, we have heuristically tried a few different laws. In Fig. 3 we plot our localization tensor versus $1/\varepsilon_g$, using the minimum gaps instead of the direct ones: here monotonical trends are very perspicuous.

### VI. MAXIMALLY LOCALIZED HERMAPHRODITE ORBITALS

We actually perform localizing transformations on the Bloch orbitals. At variance with the most standard approach, we focus on orbitals which are localized in one direction only, say $x$, while they are completely delocalized in the $yz$ directions. By analogy with the standard theory of Wannier functions, one obtains such orbitals by integration of the Bloch ones over one component only of the Bloch vector. The resulting orbitals are Wannier–like in one direction and Bloch–like in the other two: they can be therefore called “hermaphrodite orbitals”. Because of the same reasons as for ordinary Wannier functions, such hermaphrodite orbitals are nonunique: we focus here on those hermaphrodite orbitals which are optimally localized in the $x$ direction. It has been shown above that, in the thermodynamic limit, these orbitals are eigenfunctions of the operator $\Xi$, Eq. (23), and their centers are the corresponding eigenvalues. It is expedient to consider the modified operator

$$\Xi(r, r') = \int_\text{all space} \, \text{d}r'' \, P(r, r'') \exp\left(\frac{i\pi}{\varepsilon_g} x''^2\right) P(r'', r'),$$

which to leading order in $1/M_x$ has the same eigenfunctions as $\Xi$, and simply related eigenvalues.

When considering a finite sample with BvK boundary conditions—or equivalently a discrete grid in the reciprocal unit cell—the operator $\Xi$ as in Eq. (24) is useless because the operator $x$ therein becomes ill defined. Instead the operator $\Xi$ is well defined, provided the value of $M_x$ is consistent with the choice of the grid. The integral in Eq. (27) is now performed over the BvK cell and not over all space; the projector projects over the finite occupied manifold, having dimension $n_b M_y M_z$. Choosing the Bloch functions as the basis in the occupied manifold, the matrix elements of $\Xi$ are nothing else than the matrix $S$ defined in Eq. (8). Therefore in the discrete case the hermaphrodite orbitals which achieve optimal localization in the $x$ direction are simply obtained by diagonalizing the matrix $S$. Since, as already observed, the matrix is already diagonal in $s_2$ and $s_3$, the problem is reduced to $M_y M_z$ independent diagonalizations of submatrices of size $n_b M_x$. We characterize our orbitals as $|j, s_2, s_3\rangle$, where $(s_2, s_3)$ is a two–dimensional Bloch–index and $j$ is a one–dimensional Wannier–like index, with $1 \leq j \leq n_b M_x$. We are going to verify that these orbitals indeed minimize the average quadratic spread in one–dimension. If we define

$$z_{j, s_2, s_3} = \int_\text{BvK cell} \, \text{d}r \, |w_{j, s_2, s_3}(r)|^2 \exp\left(\frac{i\pi}{\varepsilon_g} x^2\right),$$

then according to RS the quadratic spread of one given hermaphrodite orbital is:

$$\langle w_{j, s_2, s_3}|x^2|w_{j, s_2, s_3}\rangle_c = -\frac{c^2 M_x^2}{4\varepsilon_g^2} \ln |z_{j, s_2, s_3}|^2.$$
the closer to unitarity the matrix becomes: we know that the modulus of its determinant differs by one for a term of the order $1/M_x$, hence the modulus of each eigenvalue differs by one for a term of the order $1/M_x^2$. We recover exact orthonormality in the thermodynamic limit; in our calculations already at $M_x \simeq 20$ deviations from orthogonality are hardly noticeable.

We have calculated the orbitals $w_{j,s_2,s_3}$ for several crystalline semiconductors: to the purpose of display, we call the $yz$ average of $|w_{j,s_2,s_3}|^2$ as $n_{loc}(x)$, where the indices remain implicit. At fixed $(s_2, s_3)$ we have, given our double cell, $8M_x$ orbitals centered on a BvK period of length $M xc$. There are however at most four different shapes, and one obtains all the functions upon translations in the $x$ direction (by multiples of $c/2$) of the four basic ones: this is not surprising, since the genuine unit cell is one half of our computational one. We find that the different shapes are actually always four, with the only exception of an elemental semiconductor at $s_2 = s_3 = 0$. In this very special case the different shapes are only two, the orbitals are centered at the bond center, and their densities are centrosymmetric; the corresponding functions $n_{loc}(x)$ are shown in Fig. 4 for the case of Si. The most general case is exemplified by Fig. 5: it shows the four different $n_{loc}(x)$ for the case of Ge and for two different $(s_2, s_3)$. It is seen that there is a wide region where the plots have an overall linear behavior, with superimposed oscillations having the crystal periodicity along the $x$ direction ($c/2$ in the present case). The slopes at different $(s_2, s_3)$ are very different, though; the $n_{loc}(x)$ with the slowest decay corresponds to $s_2 = s_3 = 0$ and therefore to the least localized, as we previously observed. Next, we filter the disturbing periodic oscillations using our favorite tool of the macroscopic average. We tried both ways: filtering $n_{loc}(x)$ first and then taking the logarithm, or filtering $\ln n_{loc}(x)$: the latter turns out to work best. The macroscopic filtering is also shown in Fig. 6 (thick solid lines): it is easily realized, especially looking at the magnified plot in the lower panel, that there is a sizeable region, spanning several cells, where the plotted function looks accurately linear with $x$, hence $n_{loc}(x) \propto \exp(\pm bx)$. We therefore demonstrate “experimentally” the exponential localization of our $w$ orbitals. After we became aware of Ref. 13, we checked that the power–law prefactor suggested therein does not improve the quality of our fits. It is hard to assess whether this is due to a basic difference between our case and a genuine one–dimensional one, or to the limited resolution achievable in our selfconsistent three-dimensional finite–size calculation. Finally, in Fig. 7 we display some correlations between the localization length and the exponential decay length $1/b$ averaged over the two–dimensional mesh $(s_2, s_3)$.

VII. CONCLUSIONS

In the present work we provide the three–dimensional formulation of the RS theory of electron localization, specializing it to the case of independent KS electrons; we discuss some of its relationships to the MV and SWM papers and also (in the Appendix) how it relates to Boys theory of localization in molecules. We then implement the theory to several materials in the class of tetrahedrally coordinated semiconductors. Among the results, we find that in general the calculated localization length is a monotonical function of the gap, although a few materials show irregularities. The trend is more regular within a given family (isoelectronic or isovalent). Finally, we heuristically show that the orbitals which are optimally localized in a given direction (“hermaphrodite orbitals”) show exponential localization.
ACKNOWLEDGMENTS

R.R. acknowledges partial support by ONR grant N00014-96-1-0689.

APPENDIX: RELATIONSHIP TO BOYS LOCALIZATION IN MOLECULES

We abandon here the BvK boundary conditions used throughout this work, and we consider an $N$–electron system which is bounded in space. Both the orbitals and the many–body wavefunction $\Psi$ are therefore exponentially vanishing at large distances. Supposing that $N$ is even and the state is a singlet, for independent particles the wavefunction is the Slater determinant:

$$
\Psi = \frac{1}{N!} \begin{vmatrix} \varphi_1 & \varphi_2 & \varphi_3 & \cdots & \varphi_N \end{vmatrix}.
$$  \hspace{1cm} (A1)

The orbitals enjoy no specific symmetry. Any unitary transformation of the orbitals produces the same many–body ground state (modulo an overall phase): a specific choice of the orbitals will be referred to as “choice of the gauge” in the following. Obviously all ground state properties are gauge–invariant. The density matrix is twice the projector over the occupied orbitals:

$$
\rho(r,r') = 2P(r,r') = 2 \sum_{i=1}^{N/2} \varphi_i(r)\varphi_i^*(r').
$$  \hspace{1cm} (A2)

We are interested in exploiting the gauge freedom in order to express the ground state in terms of localized orbitals. Here we recast this identically as:

$$
n \rho(r,r') = 2P(r,r') = 2 \sum_{i=1}^{N/2} \varphi_i(r)\varphi_i^*(r').
$$  \hspace{1cm} (A3)

We are interested instead in minimzing the spherical second moments, in general we cannot diagonalize simultaneously $P_xP$, $P_yP$, and $P_zP$. Therefore the spherical spread will be in general strictly larger than the Cartesian trace of the localization tensor. This is a key feature in the work of Boys and MV as well.

We have defined the localization tensor in Eq. (A6). With an obvious generalization of the previous arguments, this tensor provides in general the maximum localizability in any given direction. An equivalent expression for the localization tensor is:

$$
\langle r_\alpha r_\beta \rangle_c = \frac{2}{N} \int d\mathbf{r} \int d\mathbf{r}' (r - r')\langle r_\alpha r_\beta \rangle_c |P(r, r')|^2,
$$  \hspace{1cm} (A7)

which has the meaning of the second moment of the (squared) density matrix in the coordinate $r - r'$.

At this point, we may think of a crystalline solid as of a very large “molecule”, or a cluster, and take the thermodynamic limit. Since bulk properties must be independent of the choice of boundary conditions (either BvK or “free”), the density matrix and the localization tensor must be the same as the one previously found in this work. And indeed, a glance to Eq. (19) shows that it coincides with the thermodynamic limit of Eq. (A7) in the insulating case. As for the metallic case, our previous findings bear an important message concerning Boys localization. For a cluster of finite size, no matter how large, one can doubtless build localized Boys orbitals. But our results prove that, in the large $N$ limit, the quadratic spread of these Boys orbitals diverges whenever the cluster is metallic.

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FIG. 3. Trends of the squared localization length vs. the inverse experimental minimum gap. The lines connect the isoelectronic series MgS–AlP–Si and ZnSe–GaAs–Ge, and the isovalent one C–Si–Ge.

FIG. 4. Hermaphrodite orbitals for Si. The quantity displayed is $n_{\text{loc}}(x)$, defined as the $yz$ average of the square modulus of the orbital $w_{j, s_2, s_3}$, for $s_2 = s_3 = 0$, and for the four $j$ values localizing within the same cell.

FIG. 5. Hermaphrodite orbitals for GaAs. The quantity displayed is $n_{\text{loc}}(x)$, defined as the $yz$ average of the square modulus of the orbital $w_{j, s_2, s_3}$, for $s_2 = s_3 = 0$, and for the four $j$ values localizing within the same cell.
FIG. 6. Exponential decay of two hermaphrodite orbitals for Ge. Thin lines correspond to the logarithm of two different $n_{loc}(x)$, defined as the $yz$ average of the square modulus of the orbital $w_{j,s_2,s_3}$, for the same $j$ and two different points of the two-dimensional mesh($s_2,s_3$). The one with the slowest decay corresponds to $s_2 = s_3 = 0$. Thick lines are the macroscopic average (see text) of $\ln n_{loc}(x)$. The lower panel is a magnification of the region indicated in the upper panel in order to better appreciate the linear behavior of $\ln n_{loc}(x)$.

FIG. 7. Exponential decay length, averaged over the two-dimensional mesh ($s_2, s_3$), vs. our localization length (square root of the second cumulant moment). The straight-line segments are only a guide to the eye linking compounds of the same isoelectronic series. The vertical bars are an estimate of the accuracy of the interpolation scheme used to extract the $b$ value from the asymptotic macroscopic average of $n_{loc}(x)$. 