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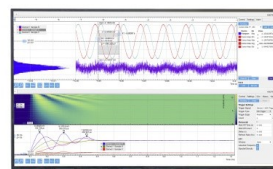
The localization spread and polarizability of rings and periodic chains

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ABSTRACT

The localization spread gives a criterion to decide between metallic and insulating behavior of a material. It is defined as the second moment cumulant of the many-body position operator, divided by the number of electrons. Different operators are used for systems treated with open or periodic boundary conditions. In particular, in the case of periodic systems, we use the complex position definition, which was already used in similar contexts for the treatment of both classical and quantum situations. In this study, we show that the localization spread evaluated on a finite ring system of radius R with open boundary conditions leads, in the large R limit, to the same formula derived by Resta and co-workers [C. Sgiarovello, M. Peressi, and R. Resta, Phys. Rev. B **64**, 115202 (2001)] for 1D systems with periodic Born–von Kármán boundary conditions. A second formula, alternative to Resta's, is also given based on the sum-over-state formalism, allowing for an interesting generalization to polarizability and other similar quantities.

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I. INTRODUCTION

The position operator $\hat{\mathbf{r}}$ plays a crucial role in quantum mechanics. Indeed, it is very often the key element to build the potential operator. Moreover, in a single-particle description, it is used to define multipole moments and polarizabilities. Finally, its spread is one of the key ingredients that enter the Heisenberg uncertainty principle. A similar crucial role occurs in many-particle systems. In this case, the one-body position operator $\hat{\mathbf{r}}_\mu$ of each particle μ can be combined in order to give the total-position operator

$$\hat{\mathbf{Q}} = \sum_\mu \hat{\mathbf{r}}_\mu. \tag{1}$$

This operator is, by definition, a quantity that refers to the entire system as a whole. In a series of papers, Resta and co-workers[1–4] and then Souza et al.,[5] after an original idea that goes back to Kohn more than 50 years ago,[6] showed that the spread of the total position, called by the authors *localization tensor* once it is divided by the number of identical particles, is able to discriminate between

systems that behave as insulators or conductors in the thermodynamic limit. Indeed, the *per electron* position spread (i.e., the localization tensor) diverges in the case of metals, while it remains finite for insulators. Some of us have recently used the localization tensor to study the Wigner localization.[7–9] However, it has been shown that in some cases, border effects can play a very important role and completely hide the behavior of the rest of the system.[10,11] For this reason, the extension of these ideas to periodic systems has attracted much attention.[12–15]

In quantum mechanics, the spread of any operator $\hat{A}$ is given by the standard expression

$$\bar{A} = \langle \Psi | \hat{A}^2 | \Psi \rangle - \langle \Psi | \hat{A} | \Psi \rangle^2. \tag{2}$$

When $\hat{A} = \hat{\mathbf{Q}}$, we get the total-position spread, denoted in the following as TPS. Indeed, this is the way the position spread is computed for finite systems. We systematically calculated the TPS for finite molecular systems, in which case, this quantity gives interesting information on the nature of bonds and the mechanism of bond

breaking.[16–21] If the size of the system is systematically increased, the thermodynamic limit can be computed by extrapolating finite calculations to the infinite-size limit.[7,22–31] However, for practical reasons, very large ("infinite") systems are often described within the framework of *periodic* or Born–von Kármán boundary conditions (in this context), and this poses a subtle theoretical problem. Indeed, in the Periodic Boundary Condition (PBC) formalism, the position operator is not a single-valued function because an infinite set of values of the periodic coordinates corresponds to the same point in the system. For this reason, the position spread for periodic systems must be defined in a different way.

The problem was addressed by Resta, in the context of the so-called modern theory of polarization.[4] The central quantity is $\hat{U}$, the exponential of the total position defined in Eq. (1), which is a N-body operator, and it is used to define the localization spread λ_R. In the case of a 1D system of N electrons and length L, one has the following:

$$\hat{U} = \exp\left(\frac{2\pi i}{L} \sum_{j=1}^{N} x_j\right),$$

$$\lambda_R = -\frac{L^2}{4\pi^2 N} \ln |\langle \Psi | \hat{U} | \Psi \rangle|^2. \quad (3)$$

Later, Sgiarovello *et al.* derived a formula for the computation of the thermodynamic limit of Eq. (3) for a determinantal wave function and applied it to some crystalline systems.[32]

We recently addressed this problem by adopting a different strategy.[33] We note that all functions of the position that have the same periodicity of the whole system are perfectly acceptable quantities. This is the case, for instance, for the periodic potentials defined for these types of systems. Our approach (see Refs. 9 and 33) is to redefine the one-particle position operator itself, essentially replacing the position by the imaginary exponent of the position. In doing that, one must assure two basic requirements:

1. The new operator must have the same periodicity as the PBC system.
2. The difference between two operators corresponding to fixed values of the coordinates must tend, in the limit of infinite system and up to a phase factor, to the corresponding difference obtained from the ordinary position operator.

The above conditions can be satisfied in different ways. In our previous work (Ref. 33), we defined a complex position operator as

$$\hat{q}_L(x) = \frac{L}{2\pi i}\left[e^{\frac{2\pi i}{L}x} - 1\right]. \quad (4)$$

This choice has the advantage that $\hat{q}_L(x)$ reduces to the standard position operator when $x/L \ll 1$, i.e., $\hat{q}_L(x) = x$. In the present context, we compute a cumulant of the square norm of the position. Because of this fact, the constant shift $-\frac{L}{2\pi}$ in Eq. (4) and the imaginary unit can be dropped. In the case of a 1D system of length L, we can simply use the following quantity:

$$\hat{q}_x = \frac{L}{2\pi} e^{\frac{i2\pi x}{L}}. \quad (5)$$

We note that this definition of the position is not restricted to the quantum-mechanics context. Indeed, it has been used in

classical physics in order to perform Madelung sums for ionic systems[34,35] and to compute the classical energy and harmonic and anharmonic corrections of Wigner crystals.[36] In Appendix C, a detailed discussion on the choice of the position operator for periodic systems is presented.

In this paper, we assume a slightly different starting point. We consider the localization spread of a ring system with the *open* boundary conditions (OBCs) where the definition of Eq. (2) holds, and we obtain the same results one gets with the *complex position operator* of Eq. (5) for a periodic system. Moreover, we also get the formula of Ref. 32, which was derived from the formalism of Resta. In detail, we can summarize the scheme of the present paper as follows, which is concerned with rings with OBC and 1D systems with PBC: we first derive formulas for the TPS and the polarizability of a one-determinant wave function of many electrons in a ring under a potential of C_n symmetry; then, thanks to the isomorphism of C_n and the translation in a 1D system with Born–von Kármán PBC, all the treatment extends to the latter; the formula for the TPS shows that a partially filled band leads to a per electron TPS diverging in the thermodynamic limit; the formula for the TPS is alternative but equivalent to the Sgiarovello–Peressi–Resta[32] one for a complete orbital basis; finally, we show applications to the Hückel wave function for dimerized annulene and cyclacene, where closed analytical solutions are found. This approach is called tight-binding (TB) in the physical literature.

For the sake of simplicity, as previously said, we will focus on one dimension in the whole of this paper and the generalization to higher dimensions will be addressed in forthcoming papers. Finally, we stress the fact that atomic units (bohr, hartree, etc.) will be used in the whole of the presentation.

II. PARTICLES IN A RING UNDER A PERIODIC POTENTIAL (C_n)

A. General considerations

Let us consider a system of non-interacting electrons moving in a ring of length L and radius $R = L/2\pi$ and subject to a non-constant potential U of C_n symmetry. Its wave function will be a Slater determinant of spin–orbitals that can be taken to be eigenfunctions of $\hat{C}_n$, the anticlockwise rotation of $2\pi/n$ around the center of the ring. The structure of such orbitals is that of Bloch orbitals for 1D periodic systems (see the supplementary material for details). This is due to the isomorphism of the C_n group generated by the in-plane rotation $\hat{C}_n$ of an angle $2\pi/n$ and the group T_n generated by the translation $\hat{t}_d$ of a displacement d when acting on the space of periodic functions of period $L = nd$, according to the Born–von Kármán boundary conditions. Actually, these two groups are both examples of finite cyclic groups, and this is the reason of the isomorphism.[37,38]

The eigenfunctions of $\hat{C}_n$ have the following Bloch structure:

$$\psi(s) = \psi_k(s) = e^{\frac{2\pi i k s}{L}} u_k(s) = e^{iKs} u(s, K), \quad (6)$$

where $u_k(s) = u_k(s + d)$ is a periodic function and k is an integer defined mod n. In order to conform to the solid-state literature, we introduced the (discrete) variable $K = \frac{2\pi k}{L}$ and the alternative notation $u(s, K)$ for $u_k(s)$. The structure of the function given in Eq. (6) can be described as a plane wave modulated by a periodic

factor $u(s, K)$. The discrete variable K becomes (quasi-)continuous for large n.

The proper definitions of the orbitals taking into account normalization are given in the following two notations:

$$\text{integer } k: \quad \psi_k(s) = \frac{1}{\sqrt{n}} e^{\frac{2\pi i k s}{nd}} u_k(s), \tag{7}$$

$$K = \frac{2\pi k}{nd}: \quad \psi(s, K) = \frac{1}{\sqrt{n}} e^{iKs} u(s, K). \tag{8}$$

B. Approximate wave functions

Exact solutions of the Schrödinger equation with a periodic Hamiltonian are known only in exceptional cases, and in practice, one resorts to variational treatments by expanding the orbitals in suitably chosen basis functions, such as in the well-known LCAO approximation. We place in each cell μ, a number n_c of basis functions $\chi_j(s)$, $j = 1, 2, \ldots, n_c$ centered in n_c points $s_{1\mu}, s_{2\mu}, \ldots, s_{n_c\mu}$, $s_{j\mu} = s_{j0} + \mu d$. We introduce the symmetry-adapted basis functions

$$b_{kj}(s) = \sum_{\mu=0}^{n-1} e^{\frac{2\pi i k \mu}{n}} \chi_j(s - s_{j\mu})$$

$$= e^{iKs} \sum_{\mu=0}^{n-1} e^{\frac{2\pi i k(\mu d - s)}{nd}} \chi_j(s - s_{j\mu}), \quad j = 1, 2, \ldots, n_c, \tag{9}$$

$$\hat{C}_n b_{kj}(s) = \sum_{\mu=0}^{n-1} e^{\frac{2\pi i k \mu}{n}} \chi_j(s - s_{j\mu+1}).$$

The total number of b_{kj}'s is $n \times n_c$.

The matrix elements of the overlap S and the Hamiltonian $\hat{H}$ in the symmetry-adapted basis are as follows:

$$\langle b_{kj} | b_{k'j'} \rangle = \delta_{kk'} \sum_{\mu\mu'} e^{\frac{2\pi i k(\mu' - \mu)}{n}} \langle \chi_{j\mu} | \chi_{j'\mu'} \rangle, \tag{10}$$

$$\langle b_{kj} | \hat{H} | b_{k'j'} \rangle = \delta_{kk'} \sum_{\mu\mu'} e^{\frac{2\pi i k(\mu' - \mu)}{n}} \langle \chi_{j\mu} | \hat{H} | \chi_{j'\mu'} \rangle. \tag{11}$$

Given that $[\hat{H}, \hat{C}_n] = 0$, the matrix of $\hat{H}$ assumes a block structure: there are n blocks $\mathbf{H}_k$ and $\mathbf{S}_k$ each of dimension $n_c \times n_c$ that can be diagonalized to get the variational solution. If $c_{1\gamma}, c_{2\gamma}, \ldots, c_{n_c\gamma}$ is the γth eigenvector of $\mathbf{H}_k$ in the metric $\mathbf{S}_k$, one has the variational solution

$$\psi_{\gamma k}(s) = \mathcal{N} \sum_{j=1}^{n_c} c_{j\gamma} b_{kj}(s) = \mathcal{N} \sum_{\mu=0}^{n-1} e^{\frac{2\pi i k \mu}{n}} \sum_{j=1}^{n_c} c_{j\gamma} \chi_j(s - s_{j\mu}), \tag{12}$$

where $\mathcal{N}$ is the normalization constant. The wave function in Eq. (12) can be rewritten in the form reported in Eq. (8) with its periodic factor defined as follows:

$$u_\gamma(s, K) = \sum_{\mu=0}^{n-1} e^{\frac{2\pi i k(\mu d - s)}{nd}} \sum_j c_{j\gamma}(K) \chi_j(s - s_{j\mu}). \tag{13}$$

From Eq. (11), one finds that the blocks $\mathbf{H}_k$ and $\mathbf{H}_{-k}$ are complex conjugated, but both are Hermitian matrices, so their

eigenvalues are the same. The corresponding eigenfunctions can be grouped in couples with the same energy and behave like degenerate eigenvectors belonging to a two-dimensional IR of a non-Abelian group. Besides the variational treatment, further approximations may be adopted to simplify the computation of the matrix elements of the Hamiltonian matrix. As a limit case of such an approach, we may consider the well-known Hückel model. The expansion basis contains site functions χ centered in a point $P_{j\mu}$ with which are supposed to be orthonormal eigenfunctions of the position operators. This is the common practice although these site functions are rather awkward mathematical objects; see, e.g., Ref. 39. Accordingly, χ's are everywhere vanishing but in P. As concerns the Hamiltonian matrix elements in this basis, they are treated as adjustable parameters assumed to be zero except for χ functions placed on nearest neighbor sites. In solid-state physics, such Hamiltonian parameters are known as *hopping integrals* and denoted by the symbol t, while in quantum chemistry, the name *resonance integral* and the symbol $\beta = -t$ are preferred. The advantage of the Hückel model is its exact solubility in a number of cases, combined with an ability to gain an insight into the electronic structure and properties.[40] This is the reason why the examples we provide are concerned with Hückel wave functions.

C. The TPS of *n* electrons in a ring

We now consider an n-electron determinantal wave function Φ constructed using the Bloch orbitals defined in Eq. (6) and the total position operators

$$\hat{X} = \sum_{j=1}^{n} x_j, \quad \hat{Y} = \sum_{j=1}^{n} y_j. \tag{14}$$

The TPS tensor $\boldsymbol{\Lambda}$ of a ring is diagonal, and its xx and yy components are equal;[41] for this reason, we may consider its trace

$$\begin{aligned} Tr(\boldsymbol{\Lambda}) &= \boldsymbol{\Lambda}_{xx} + \boldsymbol{\Lambda}_{yy} \\ &= \langle \Phi | \hat{X}\hat{X} + \hat{Y}\hat{Y} | \Phi \rangle - \langle \Phi | \hat{X} | \Phi \rangle^2 - \langle \Phi | \hat{Y} | \Phi \rangle^2 \\ &= \langle \Phi | (\hat{X} \pm i\hat{Y})(\hat{X} \mp i\hat{Y}) | \Phi \rangle. \end{aligned} \tag{15}$$

In Eq. (15), we introduced the operators $\hat{X} \pm i\hat{Y}$ in order to take advantage of the C_n symmetry of the system, which ensures that $\langle \Phi | \hat{X} | \Phi \rangle = \langle \Phi | \hat{Y} | \Phi \rangle = 0$ and $\langle \Phi | \hat{X}\hat{Y} | \Phi \rangle = 0$. One can show (see the supplementary material) that the operator $x \pm iy$ shifts by one unit the value of k associated with a Bloch orbital,

$$\begin{aligned} (x \pm iy)\psi_{k\gamma}(s) &= R\left[\cos\left(\frac{s}{R}\right) \pm i \sin\left(\frac{s}{R}\right)\right] e^{\frac{2\pi i k s}{L}} u_{k\gamma}(s) \\ &= R e^{\pm \frac{is}{R}} e^{\frac{2\pi i k s}{L}} u_{k\gamma}(s) \\ &= R e^{\frac{2\pi i (k \pm 1) s}{L}} u_{k\gamma}(s), \end{aligned} \tag{16}$$

where s is the arc length. More interesting, Eq. (16) shows that on a circle of length L, one has

$$x \pm iy = \frac{L}{2\pi} e^{\pm \frac{2\pi i s}{L}}. \tag{17}$$

This quantity is nothing but the complex position operator defined in Eq. (5) for a periodic system of period L, where s is the

ordinary position. Consequently, the results obtained in the sequel for a ring with OBC can be transferred to a 1D system with PBC. Equation (17) provides a new interpretation of the complex position operator defined in Eq. (5).

The function $\tilde{\psi}_{k\pm1,\gamma} = (x \pm iy)\psi_{k\gamma}$ will not be, in general, an eigenfunction of $\hat{H}$ because of the mismatch between the quantum number k of $u_{k\gamma}(s)$ and that of the associated plane wave. However, $\tilde{\psi}_{k\pm1,\gamma}$ is still an eigenfunction of $\hat{C}_n$ because it keeps the structure of Eq. (6). The one-electron matrix elements of $x \pm iy$ are given by

$$\langle\psi_{k\gamma}|x \pm iy|\psi_{k'\gamma'}\rangle = R\delta_{k,k'\mp1}\int_0^d u_{k,\gamma}(s)^* u_{k\mp1,\gamma'}ds. \tag{18}$$

The operators $\hat{X} \pm i\hat{Y}$ transform a Slater determinant Φ into a sum of single excitations by replacing each occupied spin orbital $\psi_{k\gamma\sigma}$ with $\tilde{\psi}_{k\pm1,\gamma\sigma}$. In order to simplify the notation, we introduce a multi-index $j = k\gamma\sigma$ to address the spin orbital $\psi_{k\gamma\sigma}$ and $\tilde{\jmath}$ for the spin orbital $(x \pm iy)\psi_{k\gamma\sigma}$,

$$(\hat{X} \pm i\hat{Y})\,\Phi \;=\; \sum_j \Phi_j^{\tilde{\jmath}}. \tag{19}$$

In Eq. (19), multi-indexes j, $\tilde{\jmath}$ span the occupied spin–orbitals and $\Phi_j^{\tilde{\jmath}}$ denotes the single excitation $\psi_j \to (x + iy)\psi_j$. By noting that $\langle\Phi|\Phi_j^{\tilde{\jmath}}\rangle = \langle\psi_{k\gamma}|x \pm iy|\psi_{k\gamma}\rangle = 0$ because of Eq. (18), one has

$$\langle\Phi|\hat{X} \pm i\hat{Y}|\Phi\rangle \;=\; 0. \tag{20}$$

Indeed, each determinant is an eigenfunction of $\hat{C}_n$, and its eigenvalue is the sum of the k quantum numbers of the occupied spin orbitals. Accordingly, all excitations in Eq. (19) differ by one unit in k from Φ and Eq. (20) follows.

By using the result of Eq. (20), Eq. (15) can be written as follows:

$$Tr(\mathbf{\Lambda}) = \langle\Phi|(\hat{X} \pm i\hat{Y})(\hat{X} \mp i\hat{Y})|\Phi\rangle \;=\; \left\langle\sum_j \Phi_j^{\tilde{\jmath}}\Big|\sum_{j'}\Phi_{j'}^{\tilde{\jmath}'}\right\rangle, \tag{21}$$

where j, j' span the occupied spin orbitals. To compute Eq. (21), we consider the following two possibilities:

1. We compute Eq. (21) directly involving only occupied orbitals.
2. Sum over states: we expand each $\sum_j \Phi_j^{\tilde{\jmath}}$ in the space spanned by the usual single excitation from occupied to virtual spin orbitals.

1. Direct computation

In order to compute Eq. (21), we use the following results:

$$\left\langle\Phi_j^{\tilde{\jmath}}\Big|\Phi_{j'}^{\tilde{\jmath}'}\right\rangle = \begin{cases} \langle\tilde{\psi}_j|\psi_j\rangle\langle\psi_{j'}|\tilde{\psi}_{j'}\rangle & \text{if } j \neq j', \\[2mm] \langle\tilde{\psi}_j|\tilde{\psi}_j\rangle - \sum_{m\neq j}\langle\tilde{\psi}_j|\psi_m\rangle\langle\psi_m|\tilde{\psi}_j\rangle & \text{if } j = j'. \end{cases} \tag{22}$$

By noting that $\langle\tilde{\psi}_j|\psi_j\rangle = 0$ because the two ψ's correspond to different eigenvalues of C_n, the double summation $\sum_{jj'}$ becomes $\sum_j$ and we find that

$$Tr(\mathbf{\Lambda}) = \sum_j\langle\tilde{\psi}_j|\tilde{\psi}_j\rangle - \sum_{jm}\langle\tilde{\psi}_j|\psi_m\rangle\langle\psi_m|\tilde{\psi}_j\rangle$$
$$= \sum_j\langle\tilde{\psi}_j|\tilde{\psi}_j\rangle - \sum_j\langle\tilde{\psi}_j|\hat{P}_{occ}|\tilde{\psi}_j\rangle, \tag{23}$$

where $\hat{P}_{occ} = \sum_m|\psi_m\rangle\langle\psi_m|$ is the projection onto the occupied orbital subspace because the multi-indexes j, m label the occupied spin orbitals. Equation (23) separates in contributions from each spin $\sigma = \alpha$ or β as follows:

$$Tr(\mathbf{\Lambda})_\sigma = \left[\sum_{\gamma k}\left(\langle\tilde{\psi}_{k\gamma}|\tilde{\psi}_{k\gamma}\rangle - \langle\tilde{\psi}_{k\gamma}|\hat{P}_{occ}|\tilde{\psi}_{k\gamma}\rangle\right)\right]_\sigma$$
$$= \sum_{\gamma k}Tr(\mathbf{\Lambda})_{\gamma k\sigma}, \tag{24}$$

where only occupied orbitals of the given spin are involved in the sums. Equation (24) shows the contribution $Tr(\mathbf{\Lambda})_{\gamma k\sigma}$ of each occupied spin orbital to $Tr(\mathbf{\Lambda})$, and we note that it cannot be negative because $1 - \hat{P}_{occ}$ is a projection. Then, we find that

$$\langle\tilde{\psi}_{k\gamma}|\tilde{\psi}_{k\gamma}\rangle = R^2\int_0^d u_{k\mp1,\gamma}(s)^* u_{k\mp1,\gamma}(s)\,ds$$
$$= R^2 \;=\; \left(\frac{nd}{2\pi}\right)^2. \tag{25}$$

As concerns the second term, $\langle\tilde{\psi}_{k\gamma}|\hat{P}_{occ}|\tilde{\psi}_{k\gamma}\rangle$, of Eq. (24), by taking into account Eq. (18), it can be rewritten as follows:

$$\langle\tilde{\psi}_{k\gamma}|1 - \hat{P}_{occ}|\tilde{\psi}_{k\gamma}\rangle = \langle\tilde{\psi}_{k\gamma}|\tilde{\psi}_{k\gamma}\rangle - \sum_{\gamma'}\langle\tilde{\psi}_{k\gamma}|\psi_{k\pm1\gamma'}\rangle\langle\psi_{k\pm1\gamma'}|\tilde{\psi}_{k\gamma}\rangle$$
$$= R^2\left(1 - \sum_{\gamma'}\left|\int_0^d u_{k\gamma}(s)\,u_{k\pm1\gamma'}(s)ds\right|^2\right), \tag{26}$$

where all indexes refer to *occupied orbitals* of the given spin. In this connection, we point out an essential difference between completely and partially filled bands. Consider a partially filled band up to a Fermi value k_F, the orbital $\tilde{\psi}_{k_F\gamma}$ will have zero projection in the occupied space of the band $\gamma' = \gamma$, while this is not the case in a completely filled band because k is defined mod n. Therefore, $Tr(\mathbf{\Lambda})_{\gamma k_F\sigma}$ diverges for $n \to \infty$ as $R^2 = O(n^2)$ and the localization per electron $Tr(\lambda)_\sigma = Tr(\mathbf{\Lambda})_\sigma/(n_c n)$ will diverge as $O(n)$ for $n \to \infty$.

Equation (26) can be used to compute numerically $Tr(\lambda)_\sigma$ for a finite system; in the case of a partly filled band, the sum $\sum_{\gamma'}$ is missing for some value of k and $\gamma' = \gamma$. As concerns the other values of k and γ', in order to compute the limit for $n \to \infty$, it is convenient to use the variable $K = 2\pi k/(nd)$ instead of k and consider $u_{k,\gamma}(s)$ as a function of the continuous variable K,

$$u_{k,\gamma}(s) \;\leftrightarrow\; u_\gamma(s, K),$$
$$u_{k\pm1,\gamma}(s) \;\leftrightarrow\; u_\gamma(s, K \pm \Delta K), \tag{27}$$

where $\Delta K = 2\pi/(nd)$. Now, for large n, we write

$$u_\gamma(s, K \pm \Delta K) = u_\gamma(s,K) \pm \frac{2\pi}{nd}\frac{\partial u_\gamma}{\partial K} + \frac{2\pi^2}{n^2 d^2}\frac{\partial^2 u_\gamma}{\partial K^2} + O(n^{-3}), \quad (28)$$

and therefrom,

$$
\begin{aligned}
\left|\langle u_{k,\gamma}|u_{k\pm 1,\eta}\rangle\right|^2 &= \delta_{\gamma\eta} \pm \delta_{\gamma\eta}\frac{2\pi}{nd}\left(\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right.\right\rangle + \left\langle\frac{\partial u_\eta}{\partial K}\left|u_\gamma\right.\right\rangle\right) \\
&\quad + \left(\frac{2\pi}{nd}\right)^2\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right.\right\rangle\left\langle\frac{\partial u_\eta}{\partial K}\left|u_\gamma\right.\right\rangle \\
&\quad + \frac{\delta_{\gamma\eta}}{2}\left(\frac{2\pi}{nd}\right)^2\left(\left\langle u_\gamma\left|\frac{\partial^2 u_\eta}{\partial K^2}\right.\right\rangle + \left\langle\frac{\partial^2 u_\eta}{\partial K^2}\left|u_\gamma\right.\right\rangle\right) + O(n^{-3}) \\
&= \delta_{\gamma\eta} + \left(\frac{2\pi}{nd}\right)^2\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right.\right\rangle\left\langle\frac{\partial u_\eta}{\partial K}\left|u_\gamma\right.\right\rangle \\
&\quad - \delta_{\gamma\eta}\left(\frac{2\pi}{nd}\right)^2\left\langle\frac{\partial u_\gamma}{\partial K}\left|\frac{\partial u_\gamma}{\partial K}\right.\right\rangle + O(n^{-3}),
\end{aligned}
\quad (29)
$$

where we used the relations $\frac{\partial}{\partial k}\langle u_{K\gamma}|u_{K'\gamma'}\rangle = 0$ and $\frac{\partial^2}{\partial k^2}\langle u_{K\gamma}|u_{K'\gamma'}\rangle = 0$. For each value of k such that $k \pm 1$ is occupied, Eq. (24) involves the integrals $\langle\psi_{k\mp 1\,\gamma}|\tilde\psi_{k\gamma'}\rangle$, and from Eq. (29),

$$
\begin{aligned}
Tr(\boldsymbol{\lambda})_{k\sigma} &= \frac{1}{n}\sum_\gamma\left\{R^2 - \sum_{\gamma'}\langle\psi_{k\mp 1\gamma}|\tilde\psi_{k\gamma'}\rangle\langle\tilde\psi_{k\gamma'}|\psi_{k\mp 1\,\gamma}\rangle\right\} \\
&= \frac{R^2}{n}\sum_\gamma\left\{1 - \sum_{\gamma'}\left[\delta_{\gamma\gamma'}\right.\right. \\
&\quad + \left(\frac{2\pi}{nd}\right)^2\left\langle u_\gamma\left|\frac{\partial u_{\gamma'}}{\partial K}\right.\right\rangle\left\langle\frac{\partial u_{\gamma'}}{\partial K}\left|u_\gamma\right.\right\rangle \\
&\quad - \left.\left.\delta_{\gamma\gamma'}\left(\frac{2\pi}{nd}\right)^2\left\langle\frac{\partial u_\gamma}{\partial K}\left|\frac{\partial u_\gamma}{\partial K}\right.\right\rangle + O(n^{-3})\right]\right\} \\
&= \frac{1}{n}\left\{\sum_\gamma\left\langle\frac{\partial u_\gamma}{\partial K}\left|\frac{\partial u_\gamma}{\partial K}\right.\right\rangle\right. \\
&\quad - \left.\sum_{\gamma\gamma'}\left\langle u_\gamma\left|\frac{\partial u_{\gamma'}}{\partial K}\right.\right\rangle\left\langle\frac{\partial u_{\gamma'}}{\partial K}\left|u_\gamma\right.\right\rangle + O(n^{-1})\right\}.
\end{aligned}
\quad (30)
$$

The quantity $O(n^{-1})/n$ in Eq. (30) when summed over all values of occupied k's [they are $O(n)$] gives a contribution $O(n^{-1})$ vanishing for $n \to \infty$. Therefore, if no partially filled bands are present, one derives the following formula for each spin:

$$\lim_{n\to\infty}\frac{Tr(\boldsymbol{\Lambda})_\sigma}{n} = \frac{d}{2\pi}\int_{K_1}^{K_2}\left(\sum_\gamma\left\langle\frac{\partial u_\gamma}{\partial K}\left|\frac{\partial u_\gamma}{\partial K}\right.\right\rangle\right.$$
$$\left. - \sum_{\gamma\gamma'}\left\langle u_\gamma\left|\frac{\partial u_{\gamma'}}{\partial K}\right.\right\rangle\left\langle\frac{\partial u_{\gamma'}}{\partial K}\left|u_\gamma\right.\right\rangle\right)dK, \quad (31)$$

where we replaced $\sum_k$ by $\frac{nd}{2\pi}\int_{K_1}^{K_2}\cdots dK$. In the case of n_b doubly occupied bands, we have $2n_b$ electrons per cell, but Eq. (31) should be multiplied by 2 to account for both spins. The final result is Eq. (31)

divided by n_b, which is nothing but Eq. (16) of the paper by Sgiarovello et al.[32] The latter was obtained by working out the formalism of Resta and Sorella[2] for a determinantal wave function with PBC.

2. Sum over states

By inserting a completeness of the virtual space in Eq. (21), it can be rewritten as follows:

$$Tr(\boldsymbol{\Lambda}) = \sum_{jl}\sum_{mv}\left\langle\Phi_j^{\tilde\jmath}|\Phi_m^v\right\rangle\left\langle\Phi_m^v|\Phi_l^{\tilde l}\right\rangle, \quad (32)$$

where multi-indexes j, l, m run over occupied spin orbitals and v over virtual ones, $v = \{k_v, \eta, \sigma\}$. Given that $\left\langle\Phi_m^v|\Phi_l^{\tilde l}\right\rangle = \langle\psi_v|\tilde\psi_l\rangle\delta_{lm}$ and using Eq. (18), we realize that the previous expression contains the factor $\delta_{kk'}\delta_{\gamma\gamma'}\delta_{k_v,k\mp 1}$. In this way, we get, for each spin α and β, the following contribution to $Tr(\boldsymbol{\Lambda})$:

$$
\begin{aligned}
Tr(\boldsymbol{\Lambda})_\sigma &= \sum_{k,\gamma,\eta}\left\langle(x\pm iy)\psi_{k\gamma}|\psi_{k\pm 1,\eta}\right\rangle\left\langle\psi_{k\pm 1,\eta}|(x\pm iy)\psi_{k\gamma}\right\rangle \\
&= \left(\frac{nd}{2\pi}\right)^2\sum_{k\gamma\eta}\left|\int_0^d[u_{k,\gamma}(s)]^* u_{k\pm 1,\eta}(s)ds\right|^2 \\
&= \sum_{k\gamma}\left[\sum_\eta\left(\frac{nd}{2\pi}\right)^2\left|\langle u_{k,\gamma}|u_{k\pm 1,\eta}\rangle\right|^2\right] \\
&= \sum_{\gamma k}Tr(\boldsymbol{\Lambda})_{\gamma k\sigma},
\end{aligned}
\quad (33)
$$

where k, γ run over occupied spin orbitals of the given spin σ and η over virtual ones. Equation (33) gives an alternative expression of the contribution of each spin orbital and can be used to numerically compute $Tr(\boldsymbol{\Lambda})$ for a given value of n. It should also be reminded that the sum over virtual orbitals is, in principle, infinite because the expansion of $\Phi_j^{\tilde\jmath}$ in single excitations is exact, in general, only when the orbital basis is complete. This condition is not, in general, fulfilled in actual calculations of LCAO type, and this amounts to an approximation. An exception is the Hückel method where Eqs. (33) and (24) or (26) are strictly equivalent as a result of particular assumptions about the orbital basis. In order to examine Eq. (33), we refer to Eq. (29) and point out the presence of $\delta_{\gamma\eta}$ in the right-hand side. Suppose that there is a band γ not completely filled: virtual band index η can assume the value γ and generates a diverging contribution $(nd/2\pi)^2 + O(1)$ for $n \to \infty$. In this way, we show again the equivalence of two criteria for establishing the metallic–insulating character of a system, namely, (1) fractionally filled band and (2) divergence for $n \to \infty$ of the TPS/number of electrons.

Let us now consider a system with completely filled bands (insulator), for which $\delta_{\gamma\eta} = 0$ always. We replace $\sum_k$ by $\frac{nd}{2\pi}\int_{K_1}^{K_2}dK$ with $K_2 - K_1 = 2\pi/d$ and obtain the final result for the contribution of each spin to $Tr(\boldsymbol{\Lambda})$,

$$Tr(\boldsymbol{\Lambda})_\sigma = \frac{nd}{2\pi}\sum_{\gamma\eta}\int_{K_1}^{K_2}\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right.\right\rangle\left\langle\frac{\partial u_\eta}{\partial K}\left|u_\gamma\right.\right\rangle dK. \quad (34)$$

It is clear from Eq. (34) that the TPS diverges for $n \to \infty$, as expected. The TPS per electron is obtained by dividing Eq. (34) by the number

of electrons n_e. The latter is proportional to n; it can be expressed as a function of the density ρ as $n_e = nd\rho = L\rho$ or the number of occupied bands n_b times their occupation number n_o (1 or 2) and the number of addends n_k in $\sum_k$. For a system with only doubly filled bands, one has $n_k = n$, $n_o = 2$, $n_e = 2n\,n_b$,

$$\frac{Tr(\boldsymbol{\Lambda})_\alpha + Tr(\boldsymbol{\Lambda})_\beta}{2nn_b} = \frac{d}{2\pi n_b}\sum_{\gamma\eta}\int_{-\pi/d}^{\pi/d}\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right\rangle\left\langle\frac{\partial u_\eta}{\partial K}\right|u_\gamma\right\rangle dK, \quad (35)$$

where n_b is the number of doubly occupied bands, γ runs over occupied, and η runs over virtual bands.

D. The polarizability

The static dipole polarizability tensor is given by[42]

$$\boldsymbol{\alpha}_{xy} = 2\langle\Phi_0|\mu_x(\mathbf{H}-E_0)_\perp^{-1}\mu_y|\Phi_0\rangle, \quad (36)$$

where $(\mathbf{H}-E_0)_\perp^{-1}$ is the reduced resolvent of the Hamiltonian in the orthogonal complement to Φ_0.

Let us consider the following quantity:

$$\begin{aligned}\boldsymbol{\alpha} &= \left\langle(\hat{X}\pm i\hat{Y})\Phi\big|(\mathbf{H}_K-E_0)_\perp^{-1}\big|(\hat{X}\pm i\hat{Y})\Phi\right\rangle \\ &= \left\langle\hat{X}\Phi\big|(\mathbf{H}_K-E_0)_\perp^{-1}\big|\hat{X}\Phi\right\rangle \\ &\quad+ \left\langle\hat{Y}\Phi\big|(\mathbf{H}_K-E_0)_\perp^{-1}\big|\hat{Y}\Phi\right\rangle \\ &\quad\pm i\left\langle\hat{X}\Phi\big|(\mathbf{H}_K-E_0)_\perp^{-1}\big|\hat{Y}\Phi\right\rangle \\ &\quad\mp i\left\langle\hat{Y}\Phi\big|(\mathbf{H}_K-E_0)_\perp^{-1}\big|\hat{X}\Phi\right\rangle. \end{aligned} \quad (37)$$

As shown in the Appendix A, the first two terms of Eq. (37) are equal, while the last two are vanishing; this allows us to write the following:

$$\boldsymbol{\alpha}_{xx} = \left\langle\sum_j\Phi_j^{\bar{j}}\bigg|(\mathbf{H}_K-E_0)_\perp^{-1}\bigg|\sum_{j'}\Phi_{j'}^{\bar{j}'}\right\rangle. \quad (38)$$

In the subspace of single excitations, one has the following:

$$(\mathbf{H}_K-E_0)^{-1} = \sum_{j,v}\frac{|\Phi_j^v\rangle\langle\Phi_j^v|}{\epsilon_v-\epsilon_j}, \quad (39)$$

and for finite n and a given spin σ,

$$\begin{aligned}\boldsymbol{\alpha}_{xx\sigma} &= \sum_{k,\gamma,\eta}\frac{\langle(x\pm iy)\psi_{k\gamma}|\psi_{k\pm1,\eta}\rangle\langle\psi_{k\pm1,\eta}|(x\pm iy)\psi_{k\gamma}\rangle}{\epsilon_{k\pm1,\eta}-\epsilon_{k,\gamma}} \\ &= \left(\frac{nd}{2\pi}\right)^2\sum_{k\gamma\eta}\frac{\left|\int_0^d[u_{k,\gamma}(s)]^*u_{k\pm1,\eta}(s)\,ds\right|^2}{\epsilon_{k\pm1,\eta}-\epsilon_{k,\gamma}} \\ &= \left(\frac{nd}{2\pi}\right)^2\sum_{k\gamma\eta}\frac{|\langle u_{k,\gamma}|u_{k\pm1,\eta}\rangle|^2}{\epsilon_{k\pm1,\eta}-\epsilon_{k,\gamma}}. \end{aligned} \quad (40)$$

For large n, we switch to the K variable also for ϵ [$\epsilon_{k,\eta}\leftrightarrow\epsilon_\eta(K)$; see Eq. (27)]. From Eq. (29) and provided that $\epsilon_{k,\eta}\neq\epsilon_{k,\gamma}$, one has the following:

$$\begin{aligned}(\epsilon_{k+1,\eta}-\epsilon_{k,\gamma})^{-1} &= (\epsilon_\eta(K)-\epsilon_\gamma(K))^{-1} \\ &\quad- \frac{2\pi}{nd}(\epsilon_\eta(K)-\epsilon_\gamma(K))^{-2}\frac{\partial\epsilon_\eta}{\partial K} + O(L^{-2}), \quad (41) \end{aligned}$$

and we get that

$$\begin{aligned}\frac{|\langle u_{k,\gamma}|u_{k\pm1,\eta}\rangle|^2}{\epsilon_{k\pm1,\eta}-\epsilon_{k,\gamma}} &= \frac{\delta_{\gamma\eta}}{\epsilon_\eta(K)-\epsilon_\gamma(K)} + \frac{2\pi}{nd}\frac{\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right\rangle\left\langle\frac{\partial u_\eta}{\partial K}\right|u_\gamma\right\rangle}{\epsilon_\eta(K)-\epsilon_\gamma(K)} \\ &\quad+ \delta_{\gamma\eta}\frac{2\pi}{nd}\frac{\partial\epsilon_\eta}{\partial K}\frac{1}{(\epsilon_\eta(K)-\epsilon_\gamma(K))^2} \\ &\quad+ \left(\frac{2\pi}{nd}\right)^2\frac{\partial\epsilon_\eta}{\partial K}\frac{\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right\rangle\left\langle\frac{\partial u_\eta}{\partial K}\right|u_\gamma\right\rangle}{(\epsilon_\eta(K)-\epsilon_\gamma(K))^2} \\ &\quad- \delta_{\gamma\eta}\left(\frac{2\pi}{nd}\right)^2\frac{\left\langle\frac{\partial u_\gamma}{\partial K}\left|\frac{\partial u_\eta}{\partial K}\right\rangle\right.}{\epsilon_\eta(K)-\epsilon_\gamma(K)} + O(L^{-3}). \quad (42) \end{aligned}$$

In the case of a band insulator with a gap separating the occupied band γ from the virtual one η, the polarizability per unit cell is given by

$$\alpha_{xx} = \frac{d}{\pi}\sum_{\gamma\eta}\int_{-\pi/d}^{\pi/d}\frac{\left\langle u_\gamma\left|\frac{\partial u_\eta}{\partial K}\right\rangle\left\langle\frac{\partial u_\eta}{\partial K}\right|u_\gamma\right\rangle}{\epsilon_\eta(K)-\epsilon_\gamma(K)}\,dK. \quad (43)$$

In the case of a partially filled band $\gamma = \eta$, the denominator vanishes at $k = k_F$ and the polarizability diverges.

III. EXAMPLES

Formulas (31) and (34) can be used for numerical computation, in general, but in the case of exactly solvable models, a symbolic evaluation is possible. Here, we consider two examples: the Hückel model of dimerized annulene and that of cyclacene. The orbitals ψ are linear combinations of site functions $\chi(P)$ centered in point P as previously pointed out in Sec. II B.

A. Dimerized annulene

The Hückel model for dimerized annulene of length $L = nd$ consists of n units or cells, each containing two sites and one-electron per site. The sites are assumed to be equally separated but connected by bonds of different strength described by two resonance integrals β_1, β_2. The dimerization is parameterized by δ in such a way that the non-dimerized case is recovered at $\delta = 0$, as detailed in the following. A schematic representation of a dimerized annulene with $n = 10$ is reported in Fig. 1.

The orbitals are given by

$$\psi_k(x,y) = \frac{1}{\sqrt{n}}\sum_{\mu=0}^{n-1}e^{\frac{2\pi ik\mu}{n}}[c_1\,\chi(P_{1\,\mu}) + c_2\,\chi(P_{2\,\mu})], \quad (44)$$
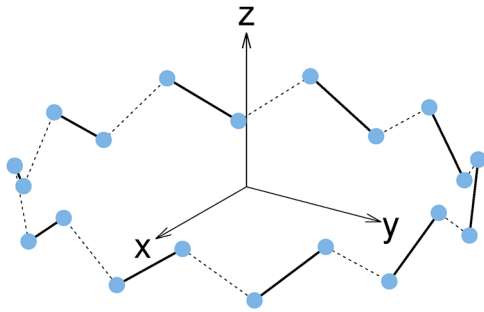
FIG. 1. Geometry of dimerized annulene for $n = 10$. The full lines and dashed lines connecting the C atoms indicate the two resonance integrals, β_1 and β_2, respectively.

where μ is the cell index and the coordinates of the centers are as follows:

	x	y
$P_{1\mu}$	$R\cos\frac{\mu d}{R}$	$R\sin\frac{\mu d}{R}$
$P_{2\mu}$	$R\cos\frac{(\mu+1/2)d}{R}$	$R\sin\frac{(\mu+1/2)d}{R}$

The coefficients c_1 and c_2 are obtained by diagonalizing the Hamiltonian matrix $\mathbf{H}_k$ defined in Eq. (11) and reported in Table I, where $\beta_1 = -t(1+\delta), \beta_2 = -t(1-\delta)$ and $t > 0$ is the hopping integral of the undimerized annulene. In Table II, we report eigenvalues ϵ and eigenvector components $\{c_1, c_2\}$ of the matrix reported in Table I for $\alpha = 0$.

We used the variable $\varkappa = 2\pi k/n$ related to K by $K = \varkappa/d$. According to Eqs. (7) and (8), the periodic part of the Hückel orbital is given in cell μ by

$$u_k(s) = c_1\chi(P_{1\ \mu}) + e^{-i\pi k/n}c_2\chi(P_{2\ \mu}), \qquad (45)$$

$$u(s, K) = c_1\chi(P_{1\ \mu}) + e^{-iKd/2}c_2\chi(P_{2\ \mu}), \qquad (46)$$

TABLE I. Effective Hamiltonian matrix for dimerized annulene.

$$\mathbf{H}_k = \begin{bmatrix} \alpha & \beta_1 e^{\frac{-2\pi ik}{n}} + \beta_2 \\ \beta_1 e^{\frac{2\pi ik}{n}} + \beta_2 & \alpha \end{bmatrix}$$

TABLE II. Eigenvalues and normalized eigenvectors of the matrix $\mathbf{H}_k$ of dimerized annulene.

ϵ	$-t\sqrt{2[1+\delta^2+(1-\delta^2)\cos\varkappa]}$	$t\sqrt{2[1+\delta^2+(1-\delta^2)\cos\varkappa]}$
c_1	$\frac{e^{i\varkappa}(\delta-1)-\delta-1}{\sqrt{2}(e^{i\varkappa}(\delta+1)-\delta+1)}$	$-\frac{e^{i\varkappa}(\delta-1)-\delta-1}{\sqrt{2}(e^{i\varkappa}(\delta+1)-\delta+1)}$
c_2	$\frac{e^{i\varkappa}(\delta-1)-\delta-1}{2\sqrt{1+\delta^2+(1-\delta^2)\cos\varkappa}}$	$\frac{e^{i\varkappa}(\delta-1)-\delta-1}{2\sqrt{1+\delta^2+(1-\delta^2)\cos\varkappa}}$

where it should be reminded that c_1 and c_2 are functions of k or K.

Equations (31) and (35) were both symbolically computed using MATHEMATICA 12.1[43] and gave the following identical results:

$$\frac{Tr(\Lambda)_\alpha + Tr(\Lambda)_\beta}{2n} = \frac{d^2(1+\delta^2)}{32|\delta|}. \qquad (47)$$

This result has also been reported in Ref. 33, where a factor of 16 at the denominator is reported instead of 32; therefore, the TPS per unit is given there instead of the TPS per electron. Equation (47) is reported in Fig. 2 for $d = 1$.

The limit $\delta \to 0$ is $+\infty$ as expected for a conductor, while for $\delta = \pm 1$, one gets $d^2/16$, which is the value of a molecule composed of two sites at the distance $d/2$. The TPS of such a system with one-electron sitting on each site is $(d/4)^2 + (-d/4)^2$ to be divided by two electrons.

As concerns the polarizability, we find that

$$\alpha_\| = \frac{2(1+\delta^2)E(1-\delta^2) - \delta^2K(1-\delta^2)}{48\pi\delta^2}\frac{d^2}{t}, \qquad (48)$$

where K and E are the complete elliptic integrals of the first and second kind, respectively,

$$K(x) = \int_0^{\pi/2}\left(1-x\sin^2\theta\right)^{-1/2}d\theta \qquad (49)$$

and

$$E(x) = \int_0^{\pi/2}\left(1-x\sin^2\theta\right)^{1/2}d\theta. \qquad (50)$$

In Fig. 3, we report $\alpha_\|$ as a function of δ for $d = t = 1$.

B. Cyclacene

The geometry of cyclacene is assumed to be a strip of n regular hexagons folded in a cylinder; see Fig. 4. The axis of the cyclacene ring is z. The length of the elementary cell is $d = b\sqrt{3}$, where b is the side of the hexagon. The coordinates of the sites are given in
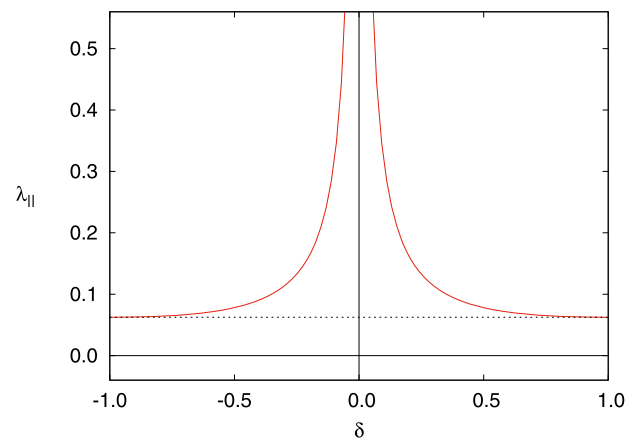

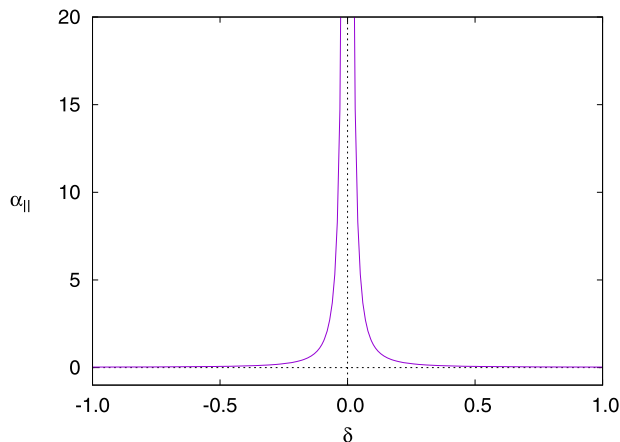**FIG. 2.** TPS per electron of dimerized annulene as a function of δ.

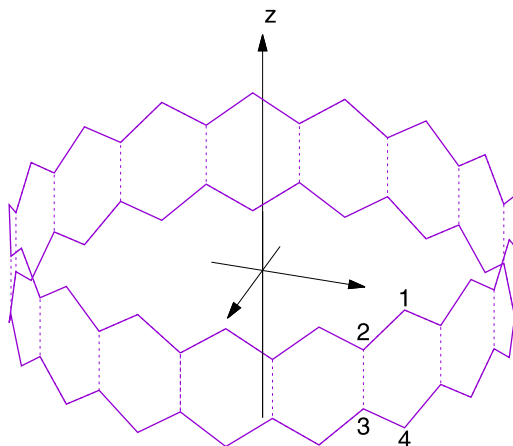**FIG. 3.** $\alpha_\parallel$ per cell of dimerized annulene as a function of δ.

FIG. 4. Geometry of cyclacene for $n = 17$. The full lines and dashed lines connecting the C atoms indicate the two different hopping integrals, t and ηt, respectively.

Table III. The cyclacene molecule is symmetric with respect to the x, y plane and can be viewed as two annulene rings, one above and one below this σ_h plane, connected by bonds parallel to the z axis, as shown in Fig. 4 by the dashed lines. The effective Hamiltonian matrix is given in Table IV, where we considered the possibility of a different strength for the vertical bonds connecting the two annulene rings by introducing a parameter $0 \le \eta \le 1$. The value $\eta = 1$ corresponds to the cyclacene molecule, while for $\eta = 0$, one gets two

TABLE III. Coordinates of the sites ($\mu = 0, \ldots, n - 1$) for the cyclacene molecule.

	x	y	z
$P_{1\mu}$	$R \cos \frac{(\mu+1/2)d}{R}$	$R \sin \frac{(\mu+1/2)d}{R}$	b
$P_{2\mu}$	$R \cos \frac{\mu d}{R}$	$R \sin \frac{\mu d}{R}$	$\frac{b}{2}$
$P_{3\mu}$	$R \cos \frac{\mu d}{R}$	$R \sin \frac{\mu d}{R}$	$-\frac{b}{2}$
$P_{4\mu}$	$R \cos \frac{(\mu+1/2)d}{R}$	$R \sin \frac{(\mu+1/2)d}{R}$	$-b$

TABLE IV. Effective Hamiltonian matrix for cyclacene; $t > 0$ is the hopping integral.

$$
\begin{bmatrix}
\alpha & -t\left(1+e^{\frac{2\pi ik}{n}}\right) & 0 & 0 \\
-t\left(1+e^{\frac{-2\pi ik}{n}}\right) & \alpha & -\eta t & 0 \\
0 & -\eta t & \alpha & -t\left(1+e^{\frac{-2\pi ik}{n}}\right) \\
0 & 0 & -t\left(1+e^{\frac{2\pi ik}{n}}\right) & \alpha
\end{bmatrix}
$$

TABLE V. Eigenvalues of cyclacene. $\Upsilon = 8 + \eta^2 + 8 \cos \frac{2\pi k}{n}$.

	ϵ_1	ϵ_2	ϵ_3	ϵ_4
σ_h	$+$	$-$	$+$	$-$
Energies	$-t\frac{\eta+\sqrt{\Upsilon}}{2}$	$t\frac{\eta-\sqrt{\Upsilon}}{2}$	$t\frac{\sqrt{\Upsilon}-\eta}{2}$	$t\frac{\sqrt{\Upsilon}+\eta}{2}$

non-interacting and undimerized annulenes. The eigenvalues are reported in Table V; the eigenvectors are not reported because they are exceedingly complicated, but they can be found in Appendix B.

In Eq. (51), we report the localization spread and polarizability per cell of cyclacene. The TPS per electron was computed using Eq. (31) or Eq. (35) and the polarizability per cell using Eq. (36), obtaining the following:

$$
\lambda_\parallel(\eta) = \frac{3}{2\eta\sqrt{16+\eta^2}} b^2,
$$

$$
\alpha_\parallel(\eta) = \frac{1}{8\pi\sqrt{16+\eta^2}} \left[\frac{32+\eta^2}{\eta^2} E\left(\frac{16}{16+\eta^2}\right) \right. \tag{51}
$$

$$
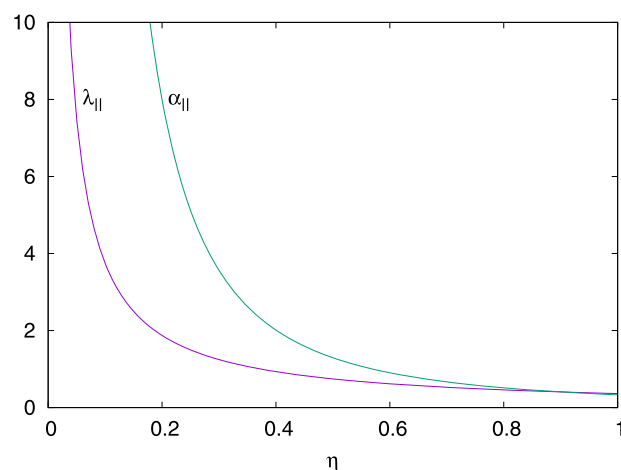\left. - K\left(\frac{16}{16+\eta^2}\right) \right] \frac{b^2}{t},
$$

FIG. 5. TPS per electron and polarizability of parameterized cyclacene as a function of η. The units are b^2 and b^2/t for $\lambda_\parallel$ and $\alpha_\parallel$, respectively.

where $K(x)$ and $E(x)$ are defined in Eqs. (49) and (50). In Fig. 5, we report the results given in Eq. (51).

Both $\lambda_\parallel$ and $\alpha_\parallel$ diverge for $\eta \to 0$ as expected for a couple of metallic annulenes. On the other hand, at $\eta = 1$, we obtain the following results for the cyclacene molecule:

$$\lambda_\parallel(1) = \frac{3}{2\sqrt{17}} b^2 \approx 0.363\,804\, b^2,$$

$$\alpha_\parallel(1) = \frac{33E\left(\frac{16}{17}\right) - K\left(\frac{16}{17}\right)}{8\pi\sqrt{17}} \frac{b^2}{t} \approx 0.313\,082 \frac{b^2}{t},$$

showing its insulating character in the xy plane and recovering the results found in a previous paper.[30]

IV. DISCUSSION AND CONCLUSIONS

In this paper, we exploit the isomorphism between the C_n group and the group of 1D translations with periodic Born–von Kármán boundary conditions. We consider a finite ring of radius R with open boundary conditions in the (x, y) plane and a segment of length $L = 2\pi R$ on a straight line with periodic boundary conditions. If we denote by ϕ the rotation angle around the center of the ring in the counterclockwise direction, the arc length $s = R\phi$ on the ring is mapped on the coordinate, say ζ, on the line segment counted from, e.g., its leftmost point: $0 \le \zeta < L$. This can be viewed as rolling the ring on the straight line, and in this sense, all the points of the line can be mapped on the ring, provided that the angle ϕ is allowed to assume any real value. In the plane, we can use a single complex coordinate $z = x + iy$ to describe any curve, and in this way, the equation of the ring is $z = R(\cos\phi + i\sin\phi) = R\exp(i\phi) = R\exp(is/R)$. The point $P(z)$ of the ring is mapped on the point $P(\zeta)$ on the line, and we recover the *complex position* operator introduced in Ref. 33. This mapping provides a new insight into the nature of the complex position operator.

As far as the TPS is concerned, we can easily derive formulas for the thermodynamic limit for systems treated at the non-correlated level, i.e., described by a Slater determinant. In particular, a formula of Sgiarovello *et al.* is obtained in a different way from the original derivation.[32] More interesting, a second formula, we called *sum over states*, for the TPS, equivalent to the Resta one in the limit of a complete basis, is also obtained. The latter allows for an interesting extension to the polarizability and to any quantity expressed as follows:

$$\langle \Phi_0 \mu_x (\mathbf{H} - E_0)_\perp^{K+1} \mu_x \Phi_0 \rangle = S_K. \tag{52}$$

The quantities S_K have been the object of much interest in the old days of perturbation theory[42] and are known as sum rules for oscillator strength. As already pointed out in Ref. 33, our approach using the complex position one-body operator can be applied to metallic systems, avoiding the awkward "ln 0" singularity. This allows us to compute λ for finite systems and study their behavior when approaching the thermodynamic limit. As discussed in Secs. II C 1 and II C 2, the divergence of λ is due to the partial filling of a band: this shows the equivalence of the two criteria for a non-correlated system to be a conductor.

Finally, we want to stress the fact that our approach is not confined to the treatment of periodic non-interacting systems, although

this was the subject of the present work. Indeed, once the ordinary position operator is replaced by the periodic complex position one, it is possible to proceed exactly as in the case of OBC. It is worth noting that the use of the periodic complex position operator does not introduce complications for the numerical evaluation of its mean value, given that it is the square of a one-electron operator, exactly as in the case of the ordinary position operator. In all the cases we have investigated so far, the large-system qualitative behavior of the real and complex position quantities is identical.

Concerning the treatment of correlated systems, we note that our approach does not present peculiar problems, given that one has to evaluate the mean value of the square of a one-electron operator and the machinery of quantum chemistry can be easily adapted to perform this task (paying attention to the fact that the operator is in this case complex). Actually, we have already treated correlated systems following the approach here reported.[33] The difficulty, which is general for any approach, is mainly a "technical" one since it is very hard to compute correlated wave functions for systems having more than a dozen identical units. In a similar way, it will be possible to treat disordered systems, exactly in the same way done by using the finite OBC formalism.[44]

Finally, we note that the extension of the formalism to 2D and 3D systems will be the subject of future work.

SUPPLEMENTARY MATERIAL

See the supplementary material for a detailed derivation of Bloch's theorem for ring systems.

APPENDIX A: MATRIX ELEMENTS IN THE C_n GROUP

In this appendix, we show the vanishing of some matrix elements for systems enjoying the symmetry of the C_n group. In particular, we consider the matrix elements of Eq. (37) and use group theory arguments. Let us first consider the functions defined by the Cartesian coordinates x, y of a point P follows:

$$x(P) = \frac{R}{2}\left(e^{\frac{2\pi i s}{L}} + e^{\frac{-2\pi i s}{L}}\right), \tag{A1}$$

$$y(P) = -i\frac{R}{2}\left(e^{\frac{2\pi i s}{L}} - e^{\frac{-2\pi i s}{L}}\right), \tag{A2}$$

and by comparison with Eq. (6), we realize that this couple of functions belong to the reducible representation E with $k = \pm 1$. Therefore, expectation values of the dipole operators in the ring wave functions are vanishing. As concerns the second moments, we have the following:

$$x^2(P) = \frac{R^2}{4}\left[e^{\frac{4\pi i s}{L}} + e^{\frac{-4\pi i s}{L}} + 2\right], \tag{A3}$$

$$y^2(P) = -\frac{R^2}{4}\left[e^{\frac{4\pi i s}{L}} + e^{\frac{-4\pi i s}{L}} - 2\right], \tag{A4}$$

$$xy(P) = -i\frac{R^2}{4}\left[e^{\frac{4\pi i s}{L}} + e^{\frac{-4\pi i s}{L}}\right]. \tag{A5}$$

Therefore, xy and $x^2 - y^2$ belong to the reducible representation $k = \pm 2$, while x^2 and y^2 contain the A representation ($x^2 + y^2$ belong to A).

TABLE VI. Eigenvalues and normalized eigenvectors of two weakly bonded annulenes forming cyclacene for $\eta = 1$. $\Upsilon = 8 + \eta^2 + 8 \cos \frac{2\pi k}{n}$.

	Eigenvector 1	Eigenvector 2
Energy	$-t(\eta + \sqrt{\Upsilon})/2$	$t(\eta - \sqrt{\Upsilon})/2$
σ_h	$+$	$-$
c_1	$\frac{(\Upsilon - \eta\sqrt{\Upsilon})\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$	$-\frac{(\Upsilon + \eta\sqrt{\Upsilon})\sqrt{\Upsilon - \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$
c_2	$\frac{\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}\sqrt{\Upsilon^2 - \eta^2\Upsilon}(1 - i \tan(k\pi/n))}{32\Upsilon \cos(k\pi/n)}$	$\frac{\sqrt{-\Upsilon + \eta\sqrt{\Upsilon}}\sqrt{\Upsilon^2 - \eta^2\Upsilon}(1 + i \tan(k\pi/n))}{32\Upsilon \cos(k\pi/n)}$
c_3	$\frac{\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}\sqrt{\Upsilon^2 - \eta^2\Upsilon}(1 - i \tan(k\pi/n))}{32\Upsilon \cos(k\pi/n)}$	$\frac{(\Upsilon + \eta\sqrt{\Upsilon})\sqrt{\Upsilon - \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$
c_4	$\frac{(\Upsilon - \eta\sqrt{\Upsilon})\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$	$\frac{(\Upsilon + \eta\sqrt{\Upsilon})\sqrt{\Upsilon - \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$
Energy	$t(\sqrt{\Upsilon} - \eta)/2$	$t(\sqrt{\Upsilon} + \eta)/2$
σ_h	$+$	$-$
c_1	$\frac{(\Upsilon + \eta\sqrt{\Upsilon})\sqrt{\Upsilon - \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$	$-\frac{(\Upsilon - \eta\sqrt{\Upsilon})\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$
c_2	$\frac{\sqrt{-\Upsilon + \eta\sqrt{\Upsilon}}\sqrt{\Upsilon^2 - \eta^2\Upsilon}(-1 + i \tan(k\pi/n))}{32\Upsilon \cos(k\pi/n)}$	$\frac{-\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}\sqrt{\Upsilon^2 - \eta^2\Upsilon}(1 - i \tan(k\pi/n))}{32\Upsilon \cos(k\pi/n)}$
c_3	$\frac{\sqrt{-\Upsilon + \eta\sqrt{\Upsilon}}\sqrt{\Upsilon^2 - \eta^2\Upsilon}(-1 + i \tan(k\pi/n))}{32\Upsilon \cos(k\pi/n)}$	$\frac{\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}\sqrt{\Upsilon^2 - \eta^2\Upsilon}(1 - i \tan(k\pi/n))}{32\Upsilon \cos(k\pi/n)}$
c_4	$\frac{(\Upsilon + \eta\sqrt{\Upsilon})\sqrt{\Upsilon - \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$	$\frac{(\Upsilon - \eta\sqrt{\Upsilon})\sqrt{\Upsilon + \eta\sqrt{\Upsilon}}}{8\Upsilon \cos(k\pi/n)}$

APPENDIX B: EIGENVALUES AND EIGENVECTORS FOR CYCLACENE

Here, we report the eigenvalues and eigenvectors of the system of two annulenes coupled to form a cyclacene molecule when the parameter η is equal to 1 (Table VI).

APPENDIX C: POSITION OPERATOR FOR PERIODIC SYSTEMS

We detail here the reasons that led us to the choice of the imaginary exponential function in order to generalize the position operator to periodic systems. We limit ourselves to the 1D case. These arguments had already been very schematically introduced in Ref. 33. Let us consider the periodic interval (the "supercell") $[0, L]$, and let x be the coordinate of a point belonging to the supercell: $x \in [0, L]$. Let us call $q(x)$ the periodic position associated with the point of coordinate x. We impose the three following general conditions to the periodic position:

1. The function $q(x)$ must be a continuous periodic function of period L,
$$q(x + L) = q(x), \quad \forall x. \tag{C1}$$
   In other words, $q(x)$ is translationally invariant in the supercell $[0, L]$.

2. The distance between two points, x and $x + d$, defined as the modulus of the difference between the corresponding complex positions, must be a function of d alone, independent of x,
$$|q(x + d) - q(x)|^2 = |q(d) - q(0)|^2. \tag{C2}$$

3. For large values of L and d fixed, we must obtain the ordinary distance between the two points,

$$\lim_{L \to \infty} |q(d) - q(0)|^2 = d^2. \tag{C3}$$

In the limit of an infinite supercell, one must recover the non-periodic result.

Condition 1 is manifestly satisfied choosing for $q(x)$ a function of the type

$$q(x) = \sum_{k=-\infty}^{\infty} a_k \exp\left(\frac{i2\pi k x}{L}\right), \tag{C4}$$

with k being an integer. In order to investigate condition 2, we compute the difference $q(x + d) - q(x)$ by using the previous equation. We obtain the following:

$$q(x + d) - q(x) = \sum_{k=-\infty}^{\infty} a_k \exp\left(\frac{i2\pi k x}{L}\right)\left[\exp\left(\frac{i2\pi k d}{L}\right) - 1\right]. \tag{C5}$$

We now compute the square of the distance between the points $x + d$ and x, given by the square modulus of this quantity, $|q(x + d) - q(x)|^2$. We get

$$|q(x + d) - q(x)|^2 = \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} a_k^* a_l \left[\exp\left(\frac{i2\pi(l - k)x}{L}\right)\right] \times \left[\exp\left(\frac{-i2\pi k d}{L}\right) - 1\right]\left[\exp\left(\frac{i2\pi l d}{L}\right) - 1\right]. \tag{C6}$$

Among the three terms within square brackets, the only one containing x is the first exponential factor. Therefore, in order to have a quantity not depending on x, a sufficient condition is that all terms having $l \neq k$ in this equation vanish. This happens if only one term in Eq. (C6) survives. Besides the trivial constant solution $q(x) = a_0$, which does not lead to any physically acceptable result, let us consider a term a_j different from zero. One can note that the corresponding a_{-j} term is vanishing. This fact rules out real solutions of the type $q(x) = a \sin\left(\frac{2\pi j x}{L}\right)$ or $q(x) = a \cos\left(\frac{2\pi j x}{L}\right)$. We note, moreover, that an exponential function is much easier to manipulate than a trigonometric one. Therefore, condition 2 suggests the choice, for instance (let us assume $j = 1$),

$$q(x) = a_1 \exp\left(\frac{i 2\pi x}{L}\right) + a_0. \tag{C7}$$

It is worth noting that the presence of the a_0 term does not invalidate the request that the quantity in Eq. (C6) does not depend on x, given that for $k = 0$ or $l = 0$, the second or the third term in square brackets is vanishing. Finally, a Taylor expansion of condition 3 implies that $a_1 = \frac{L}{2\pi}$. On the other hand, no physical constraints can be used to fix a value for a_0, which is an arbitrary parameter related to the zero of the periodic position.

The above reasons suggest the definition

$$q(x) = \frac{L}{2\pi} \exp\left(\frac{i 2\pi x}{L}\right), \tag{C8}$$

which is the one we use. The equivalent choice

$$q(x) = \frac{L}{2\pi} \exp\left(\frac{-i 2\pi x}{L}\right) \tag{C9}$$

is also possible, being simply obtained from the previous one by a parity operation. The constant term a_0 can be chosen equal to $-\frac{L}{2\pi i}$ in such a way to remove the constant term appearing in the exponential expansion.

Different non-equivalent choices are also possible for the integer k, for instance, by choosing different a_k ($k = \pm 2$ or $k = \pm 3, \ldots$) as the only non-zero term in Eq. (C6). In the limit of large boxes, all these choices lead to the same results and are therefore equivalent. However, the choices of a_1 (or equivalently, a_{-1}) are those that converge most quickly to the infinite-size limit and are therefore preferable. Note that, as far as we have been able to find, no real solution satisfies all the three conditions, 1–3. The characteristic of a complex nature is also shared by the operator $\hat{U}$ introduced in Resta's formalism. The periodic position seems to be intrinsically complex.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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