Quantum-Mechanical Position Operator in Extended Systems

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The position operator (defined within the Schrödinger representation in the standard way) becomes meaningless when periodic boundary conditions are adopted for the wave function, as usual in condensed matter physics. I show how to define the position expectation value by means of a simple many-body operator acting on the wave function of the extended system. The relationships of the present findings to the Berry-phase theory of polarization are discussed. [S0031-9007(98)05419-2]

The position operator within the Schrödinger representation acts multiplying the wave function by the space coordinate. This is trivial, but applies only to the bound eigenstates of a finite system, which belong to the class of square-integrable wave functions. This is not the way condensed matter theory works: almost invariably, one considers a large system within periodic boundary conditions (PBC), and the position operator (defined as usual) becomes then meaningless. For the sake of simplicity, most of this Letter will deal with the one-dimensional case. The Hilbert space of the single-particle wave functions is defined by the condition $\psi(x + L) = \psi(x)$, where L is the imposed periodicity, chosen to be large with respect to atomic dimensions. An operator maps any vector of the given space into another vector belonging to the same space: the multiplicative position operator x is *not* a legitimate operator when PBC are adopted for the state vectors, since $x\psi(x)$ is not a periodic function whenever $\psi(x)$ is such. Of course, any periodic function of x is a legitimate multiplicative operator: this is the case, e.g., of the nuclear potential acting on the electrons. Since the position operator is ill defined, so is its expectation value, whose observable effects in condensed matter are related to macroscopic polarization. For the crystalline case, the long-standing problem of dielectric polarization has been solved a few years ago [1–3]: polarization is a manifestation of the Berry phase [4,5], i.e., it is an observable which cannot be cast as the expectation value of *any* operator, being instead a gauge-invariant phase of the wave function. Here we find a different, and more fundamental, solution: we arrive indeed at defining the expectation value of the position in an extended quantum system within PBC, where the operator entering this definition is simple but rather peculiar. Among the most relevant features, the expectation value is defined modulo L, and the operator is no longer one body: it acts as a genuine many-body operator on the periodic wave function of N electrons.

The present result can be related to a discretized Berry phase, and sheds new light into the physical meaning of the latter. Our compact and general expression for the macroscopic polarization, Eq. (4) below, applies on the same footing to correlated systems and to independent-electron systems, as well as to crystalline and to disordered systems. At variance with present understanding [1–3], lattice periodicity and integration in reciprocal space are not needed in order to *define* what polarization is. In the case of a correlated electron system, polarization was previously defined by means of a peculiar kind of "ensemble average," integrating over a set of many-body wave functions [3,5]: this is correct, but unnecessary. The present advance allows defining polarization by means of a "pure state" expectation value.

We study a system of N electrons in a segment of length L, and eventually the thermodynamic limit is taken: $L \to \infty$, $N \to \infty$, and $N/L = n_0$ constant. At any finite L the ground eigenfunction obeys PBC in each electronic variable separately:

$$\Psi_0(x_1, \ldots, x_i, \ldots, x_N) = \Psi_0(x_1, \ldots, x_i + L, \ldots, x_N).$$
(1)

We assume the ground state nondegenerate, and we deal with insulating systems only: This means that the gap between the ground eigenvalue and the excited ones remains finite for $L \to \infty$. Since the spin variable is irrelevant to this problem, we omit it altogether, and we deal with a system of spinless electrons. Our major goal is defining the expectation value of the electronic position $\langle X \rangle$, and to prove that our definition provides in the thermodynamic limit the physical macroscopic polarization of the sample.

Before attacking the main problem, let us discuss the much simpler case where PBC are *not* chosen, and the N-particle wave function (called Φ_0 in this case) goes to zero exponentially outside a bounded region of space. We may safely use the operator $\hat{X} = \sum_{i=1}^{N} x_i$, and define the position expectation value as usual:

$$\langle X \rangle = \langle \Phi_0 | \hat{X} | \Phi_0 \rangle = \int dx \, x \, n(x),$$
(2)

where $n(x)$ is the one-particle density. The value of $\langle X \rangle$ scales with the system size, and the quantity of interest is indeed the dipole per unit length, which coincides

with macroscopic polarization. The expectation value of this same operator cannot be evaluated if the wave function obeys PBC: In fact $\hat{X}$ does not commute with a translation by L, and therefore is not a legitimate operator in the Hilbert space defined by Eq. (1).

We are now ready to state our main result, demonstrated in the following. When PBC are adopted, the position expectation value can be defined through

$$\langle X \rangle = \frac{L}{2\pi} \, \mathrm{Im} \ln \langle \Psi_0 | e^{i \frac{2\pi}{L} \hat{X}} | \Psi_0 \rangle . \qquad (3)$$

The expectation value $\langle X \rangle$ is thus defined only modulo L, hardly a surprising finding since the wave function is periodical. The right-hand side of Eq. (3) is not simply the expectation value of an operator: the given form, as the imaginary part of a logarithm, is indeed essential. Furthermore, its main ingredient is the expectation value of the multiplicative operator $e^{1(2\pi/L)\hat{X}}$: It is important to realize that this is a genuine *many-body* operator. In general, one defines an operator to be one body whenever it is the *sum* of N identical operators, acting on each electronic coordinate separately: for instance, the $\hat{X}$ operator in Eq. (2). In order to express the expectation value of a one-body operator the full many-body wave function is not needed: knowledge of the reduced one-body reduced density matrix $\rho(x, x')$ is enough. This is, e.g., the case in Eq. (2), where $n(x) = \rho(x, x)$. I stress that, instead, the expectation value of $e^{i(2\pi/L)\hat{X}}$ over a correlated wave function *cannot* be expressed in terms of ρ, and knowledge of the N-electron wave function is explicitly needed.

What remains to be done is to prove that our definition of $\langle X \rangle$ provides the relevant physical observable in the thermodynamic limit. Notice that $L \to \infty$ is a tricky limit, since the exponential operator in Eq. (3) goes formally to the identity, but the size of the system and the number of electrons in the wave function increase with L [6]. We will show that the electronic polarization (dipole per unit length) is

$$P_{\mathrm{el}} = \lim_{L \to \infty} \frac{e}{2\pi} \, \mathrm{Im} \ln \langle \Psi_0 | e^{i \frac{2\pi}{L} \hat{X}} | \Psi_0 \rangle , \qquad (4)$$

where e is the electron charge. It is expedient to introduce the family of Hamiltonians:

$$\hat{H}(\alpha) = \frac{1}{2m} \sum_{i=1}^{N} (p_i - \hbar\alpha)^2 + \hat{V} , \qquad (5)$$

where α is a real constant, and $\hat{V}$ is the many-body potential. A parametric Hamiltonian of this kind was first introduced by Kohn many years ago [7], and subsequently used by different authors [3,8]. The ground eigenstate of $\hat{H}(0)$ is precisely $|\Psi_0\rangle$; more generally, the state vector $e^{i\alpha\hat{X}}|\Psi_0\rangle$ fulfills the equation

$$\hat{H}(\alpha)e^{i\alpha\hat{X}}|\Psi_0\rangle = E_0 e^{i\alpha\hat{X}}|\Psi_0\rangle , \qquad (6)$$

with an α-independent E_0. This does not warrant that it is an eigenstate since PBC, Eq. (1), are *not* fulfilled,

except in the special cases where α is a multiple of $2\pi/L$. Since by hypothesis E_0 is nondegenerate, $e^{i(2\pi/L)\hat{X}}|\Psi_0\rangle$ is the ground eigenstate of $\hat{H}(2\pi/L)$: we may then use perturbation theory to expand it to leading order in $1/L$ in terms of the eigenstates $|\Psi_j\rangle$ of $\hat{H}(0)$. However, the standard formulas perform an arbitrary choice for the phase of the perturbed eigenstate; in the most general case we write instead:

$$e^{i \frac{2\pi}{L} \hat{X}}|\Psi_0\rangle \simeq e^{i\gamma_L}\left(|\Psi_0\rangle - \frac{2\pi\hbar}{mL} \sum_{j \neq 0} |\Psi_j\rangle \frac{\langle \Psi_j | \hat{P} | \Psi_0 \rangle}{E_0 - E_j} \right), \qquad (7)$$

where $\hat{P} = \sum_{i=1}^{N} p_i$ is the momentum operator. It is important to realize that the perturbative expansion is a good approximation whenever L is much larger than a typical atomic dimension, while the number of electrons in the wave function and the system size are irrelevant.

Replacement of Eq. (7) into Eq. (3) shows that the phase γ_L is a most fundamental quantity and cannot be forgotten, since

$$\langle X \rangle \simeq \frac{L\gamma_L}{2\pi} . \qquad (8)$$

But perturbation theory is unable to provide γ_L, and a different path must be chosen for relating Eq. (3) to a physical observable. In order to prove that $e\langle X \rangle/L$ for large L is indeed the electronic polarization—as anticipated in Eq. (4)—it will be enough to show that its time derivative coincides with the adiabatic electrical current flowing through the system whenever the Hamiltonian contains a slowly varying time-dependent term. We start from

$$\frac{d}{dt}\langle X \rangle = \frac{L}{2\pi} \, \mathrm{Im}\left(\frac{\langle \dot{\Psi}_0 | e^{i \frac{2\pi}{L} \hat{X}} | \Psi_0 \rangle}{\langle \Psi_0 | e^{i \frac{2\pi}{L} \hat{X}} | \Psi_0 \rangle} + \frac{\langle \Psi_0 | e^{i \frac{2\pi}{L} \hat{X}} | \dot{\Psi}_0 \rangle}{\langle \Psi_0 | e^{i \frac{2\pi}{L} \hat{X}} | \Psi_0 \rangle} \right), \qquad (9)$$

where $|\dot{\Psi}_0\rangle$ is the time derivative of the instantaneous adiabatic eigenstate. Substituting now Eq. (7) into Eq. (9) the (undetermined) phase factor cancels out; to lowest order in $1/L$ we get

$$\frac{e}{L}\frac{d}{dt}\langle X \rangle \simeq \frac{ie\hbar}{mL} \sum_{j \neq 0} \langle \dot{\Psi}_0 | \Psi_j \rangle \frac{\langle \Psi_j | \hat{P} | \Psi_0 \rangle}{E_0 - E_j} + \text{ c.c.}, \qquad (10)$$

where c.c. indicates the complex conjugate. In Eq. (10) the $j = 0$ term is omitted from the sum, since $\langle \dot{\Psi}_0 | \Psi_0 \rangle + \langle \Psi_0 | \dot{\Psi}_0 \rangle$ is real; furthermore we have exploited time-reversal symmetry, owing to which all the adiabatic instantaneous eigenstates Ψ_j can be taken as real.

This concludes our proof. In fact the right-hand member of Eq. (10) is the electronic current flowing through the system when the potential $\hat{V}$ is adiabatically varied, a well-known expression previously used by Niu and Thouless [8] in demonstrating the quantization of particle transport [9]. The rest of this Letter is devoted to an analysis of our major result, Eqs. (3) and (4), and of its relationship to previous work.

The special case of $N = 1$ corresponds to a lone quantum electron diluted in a large sample. The position expectation value, Eq. (3), can then be expressed in terms of the periodic density as

$$\langle X \rangle = \frac{L}{2\pi} \, \text{Im} \ln \int_0^L dx \, e^{1\frac{2\pi}{L}\hat{X}} n(x). \quad (11)$$

A similar expression has been previously used by a few authors [10] in order to heuristically follow the adiabatic time evolution of a single quantum particle in a disordered condensed system within PBC. The case $N > 1$ is *qualitatively* different, in that—as stressed above—the operator used in Eq. (3) to define $\langle X \rangle$ is a genuine many-body one. This is particularly remarkable in view of the fact that the physical observable is an integrated current: the current is a typical one-body operator, as in fact is the operator $\hat{P}$ in the right-hand member of Eq. (10). The case of independent electrons is also worth commenting on. In this special case the N-particle wave function is uniquely determined by the one-body reduced density matrix $\rho(x, x')$ (which is the projector over the set of the occupied one-particle orbitals): therefore the expectation value $\langle X \rangle$ is uniquely determined by ρ.

For the crystalline case, macroscopic polarization is presently understood as a manifestation of the Berry phase [4], both for independent electrons [1,2] and for correlated electrons [3,5]. The definition of Eq. (4) reduces to the well established ones in the crystalline case: for finite L the present findings can be shown to be equivalent to a discretization of the line integral defining the Berry phase. In this Letter I provide an explicit proof for the independent-electrons case only: the algebra for the correlated case is not much different, although the present finding leads to a novel—and more fundamental—physical interpretation.

Suppose we have a crystalline system of lattice constant a, where we impose PBC over M linear cells: there are then M equally spaced Bloch vectors in the reciprocal cell $[0, 2\pi/a)$:

$$q_s = \frac{2\pi}{Ma} s, \qquad s = 0, 1, \ldots, M - 1. \quad (12)$$

The size of the periodically repeated system is $L = Ma$. The one-body orbitals can be chosen to have the Bloch form

$$\psi_{q_s,m}(x + \tau) = e^{iq_s\tau}\psi_{q_s,m}(x), \quad (13)$$

where $\tau = la$ is a lattice translation, and m is a band index. There are N/M occupied bands in the Slater determinant wave function, which we write as

$$|\Psi_0\rangle = \text{A} \prod_{m=1}^{N/M} \prod_{s=0}^{M-1} \psi_{q_s,m}, \quad (14)$$

where A is the antisymmetrizer. It is now expedient to define a new set of Bloch orbitals:

$$\tilde{\psi}_{q_s,m}(x) = e^{-i\frac{2\pi}{L}x}\psi_{q_s,m}(x). \quad (15)$$

We then recast the expectation value of Eq. (3), after a double change of sign, as

$$\langle X \rangle = -\frac{L}{2\pi} \, \text{Im} \ln \langle \Psi_0 | \tilde{\Psi}_0 \rangle, \quad (16)$$

where $|\tilde{\Psi}_0\rangle$ is the Slater determinant of the $\tilde{\psi}$'s. According to a well-known theorem, the overlap among two determinants is equal to the determinant of the overlap matrix among the orbitals:

$$\langle X \rangle = -\frac{L}{2\pi} \, \text{Im} \ln \det S, \quad (17)$$

where

$$S_{sm,s'm'} = \int_0^L dx \, \psi^*_{q_s,m}(x) e^{-i\frac{2\pi}{L}x}\psi_{q_{s'},m'}(x). \quad (18)$$

Owing to the orthogonality properties of the Bloch functions, the overlap matrix elements vanish except when $q_{s'} = q_s + 2\pi/L$, that is $s' = s + 1$. The $N \times N$ determinant can then be factorized into M small determinants:

$$\det S = \prod_{s=0}^{M-1} \det S(q_s, q_{s+1}), \quad (19)$$

where—in order to make contact with previous literature [2]—for the small overlap matrix we use the notation

$$S_{m,m'}(q_s, q_{s+1}) = \int_0^L dx \, \psi^*_{q_s,m}(x) e^{-i\frac{2\pi}{L}x}\psi_{q_{s+1},m'}(x), \quad (20)$$

and $\psi_{q_M,m}(x) \equiv \psi_{q_0,m}(x)$ is implicitly understood (so-called periodic gauge). Replacing Eq. (7) into Eq. (4) we get

$$P_{\text{el}} = -\frac{e}{2\pi} \lim_{L\to\infty} \text{Im} \ln \prod_{s=0}^{M-1} \det S(q_s, q_{s+1}), \quad (21)$$

which concludes our equivalence proof. Equation (21) coincides in fact with the well-known expression of the modern theory of polarization [1,2], obtained by King-Smith and Vanderbilt by defining a (continuum) Berry phase as a line integral, and then discretizing it.

The discretization of the Berry phase was originally introduced for purely computational purposes, and is in fact routinely used in first-principles calculations [2]. The alternate path followed here to arrive at the same result shows that the discretization has instead a very basic meaning of its own. Macroscopic polarization can be cast as the thermodynamic limit of an expression involving the expectation value of a relatively simple and physically meaningful many-body operator as in Eq. (4). This operator "extracts" the Berry phase from the *square modulus* of the many-body wave function, which embeds the relevant information about the *relative phases* of the one-particle orbitals.

Several previous findings about macroscopic polarization [1–3] apply to the present formulation as well: we report here a few of them for the sake of completeness.

One is not interested in defining an "absolute" polarization: the measured bulk quantity is always the difference ΔP between two states of the given solid, connected by an adiabatic transformation of the Hamiltonian:

$$\Delta P = \Delta P_{\text{nucl}} + \Delta P_{\text{el}} = \int_0^{\Delta t} dt\, J(t), \qquad (22)$$

where $J(t)$ is the total (nuclear + electronic) current flowing through the sample while the potential $\hat{V}$ is adiabatically varied. Notice that in the adiabatic limit Δt goes to infinity and $J(t)$ goes to zero. The quantity of interest ΔP can be evaluated as a two-point formula, using the initial and final states only: for the electronic term, one evaluates Eq. (4) with both the final and the initial wave functions, and takes the difference. The result is only defined modulo e; a similar indeterminacy applies to the nuclear term ΔP_{nucl}. Nothing can be done about this ambiguity of the two-point formula, which ultimately stems from Niu-Thouless quantization of particle transport [8,11]. There is, of course, no indeterminacy if one trades away the two-point formula and performs instead the time integral in Eq. (22), using for the electronic current the right-hand term of Eq. (10).

Generalization of Eqs. (3) and (4) to the three-dimensional case requires some care. Since $\langle X \rangle$ is extensive, within a naïf approach the x component of $\Delta \mathbf{P}_{\text{el}}$ would be defined only modulo e/L^2, which becomes vanishingly small in the thermodynamic limit. Fortunately, the problem is less serious than this, and the drawback is easily eliminated by adapting to the present formulation a major finding from Ref. [3]. Suppose the system is crystalline with a simple cubic lattice of constant a. Then—upon exploiting the lattice periodicity of the one-particle density—it can be shown that the two-point formula provides each component of $\Delta \mathbf{P}_{\text{el}}$ with an indeterminacy of e/a^2, which is no serious drawback. Such indeterminacy has nothing to do with electron correlation, and not even with quantum mechanics: a similar indeterminacy is also present in the classical nuclear term $\Delta \mathbf{P}_{\text{nucl}}$ whenever this term is evaluated as a two-point formula [12]. If the system is noncrystalline, then a large "supercell" is needed to reproduce the disorder, and only small polarization differences are accessible via the two-point formula. Again, this looks like a fundamental consequence of Niu-Thouless quantization of particle transport [8,11].

The modern viewpoint about macroscopic polarization [1–3] has even spawned a critical rethinking of density-functional theory in extended systems. The debate started in 1995 with a paper by Gonze, Ghosez, and Godby [13], and continues these days [14]. When mapping the interacting system into the noninteracting Kohn-Sham one, the awkward quantity to deal with is precisely macroscopic polarization. The polarization of an interacting extended system, in fact, could be defined only as a peculiar kind of ensemble average and not as a pure state property [3,5]. The present main achievement—namely, defining the polarization of a many-electron system by means of a simple expectation value—removes this drawback and could possibly help in further clarifying the matter.

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