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Density-operator theory of orbital magnetic susceptibility in periodic insulators

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The theoretical treatment of homogeneous static magnetic fields in periodic systems is challenging, as the corresponding vector potential breaks the translational invariance of the Hamiltonian. Based on density operators and perturbation theory, we propose for insulators a periodic framework for the treatment of magnetic fields up to arbitrary order of perturbation, similar to widely used schemes for electric fields. The second-order term delivers a new, remarkably simple formulation of the macroscopic orbital magnetic susceptibility for periodic insulators. We validate the latter expression using a tight-binding model, analytically from the present theory and numerically from the large-size limit of a finite cluster, with excellent numerical agreement.

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I. INTRODUCTION

The ability to compute the response of periodic systems to homogeneous electric fields, strain, and atomic displacements is a key ingredient in our current understanding of dielectric materials (also ferroelectrics, piezoelectrics): from first principles[1–3] one obtains easily the polarization, dielectric constants, piezoelectric coefficients, phonon band structure, etc. Compared to the treatment of such responses for molecules, the handling of periodic boundary conditions has raised numerous challenges: for instance, the linear potential associated with a static homogeneous electric field breaks the translational symmetry. While such problems have been successfully addressed for the above-mentioned perturbations, the treatment of *homogeneous magnetic fields* is not as mature. With the current interest in multiferroïc materials,[4] and the long-term interest in magnetic field-based spectroscopies, a unified framework for all these responses is highly desirable.

The first strategy followed to treat a periodicity breaking was to consider perturbations with specific commensurate wave vectors and corresponding supercells. For atomic displacements, this approach is known as the "frozen-phonon" method.[1] Homogeneous magnetic fields can be treated in this spirit, with an artificial modulation,[5] although (1) working with supercells is CPU time consuming, (2) the study of couplings is tedious in this approach. More powerful formalisms, based on perturbation theory that do not rely on supercells or long-wavelength limits, have been developed for atomic displacements and electric fields.[2,3,6–8] For phonons, the long-wavelength phases can be factorized, such that a purely periodic treatment is recovered. For the electric field, the position operator can be replaced by the differentiation with respect to the wave vector. The Berry phase approach to the electrical polarization is probably the most striking consequence of the latter link.[6] Owing to these advances, linear and nonlinear responses can be addressed, as well as couplings between different perturbations, in a purely periodic primitive cell framework.

For homogeneous magnetic fields in insulators the difficulties outlined above are more severe. We focus only on the orbital coupling; coupling to spin is not affected by periodicity issues. The presence of the magnetic field not only breaks the periodicity of the Hamiltonian but also induces a vector coupling to the electron dynamics. In a pioneering work, Mauri and Louie proposed a method to compute the orbital magnetic susceptibility (OMS) from the long wavelength limit of an oscillating perturbation.[9] The theory has been adapted to the computation of the chemical shielding tensor and related quantities.[10–12] Although relying on perturbation theory concepts to avoid the use of supercells, this formalism introduces auxiliary oscillating quantities that are not consistent with the periodicity of the lattice and that break the rotational invariance of the global system. Thus for example the tensorial structure of the expression of the OMS could not be recovered.[9] In a related alternative approach, by Sebastiani and Parrinello,[13] the position operator is replaced by localized sawtooth potentials, one for each orbital. In practice, the use of supercells needed to deal with the spatially localized Wannier functions is still necessary in this approach.

Recently, a theory of orbital magnetization has been proposed, in which only periodic Bloch wave functions and Hamiltonian are used,[14] bringing the understanding of this (bulk) quantity to the same formal level as the electric polarization. Based on this result, the orbital magnetoelectric coupling has been derived from density-matrix perturbation theory.[15] No use of a supercell or long-wavelength limit is needed in this approach.

In the present contribution we show how to apply the density operator approach of Ref. 15 to *arbitrary orders of perturbation* in the magnetic field. Focusing on the second order in this expansion, we obtain a new formula for the OMS, based on the first-order response of the density operator to magnetic field and wave vector, in a *purely periodic* framework. The present approach is compatible with the similar treatment of electric fields, of atomic displacements, and of their couplings to arbitrary orders. We then check the theory by considering a two-dimensional (2D) periodic tight-binding (TB) model, for which, thanks to the new approach, the OMS can be obtained as an integral over the Brillouin zone (BZ) of an analytical expression. Alternatively, we numerically solve this model for clusters of increasing size, considering explicitly the magnetic field. Essentially exact agreement is obtained between the two approaches.

Alternative OMS formulas were proposed already 50 years ago,[16] in the context of effective Hamiltonians or TB models. However, none of them seem compatible with the currently used formalisms for electric or atomic displacement responses. The present approach is actually considerably simpler. Furthermore, to our knowledge, no OMS formula for a periodic insulator has ever been validated by comparison with numerical results on a solvable cluster model in the large size limit.

II. THEORY

Let us recall the first steps in the approach of Ref. [15]. In atomic units, the Hamiltonian H for an electron in a vector potential $\mathbf{A}(\mathbf{r})$ is $H = \frac{1}{2}(-i\nabla - \frac{1}{c}\mathbf{A})^2 + V(\mathbf{r})$, where c is the speed of light, and the potential V is periodic for lattice vectors $\mathbf{R}$, that is, $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$. Choosing the gauge $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$, the Hamiltonian does not possess the translation symmetry of the lattice, but does have magnetic translation symmetry.[17] The kernel of operators O possessing this symmetry can be related to a periodic kernel $\bar{O}$:

$$O(\mathbf{r}_1,\mathbf{r}_2) = \bar{O}(\mathbf{r}_1,\mathbf{r}_2)e^{-i\mathbf{B}\cdot\mathbf{r}_1\times\mathbf{r}_2/2c}, \tag{1}$$

with $\bar{O}(\mathbf{R}_1 + \mathbf{r},\mathbf{r}_2 + \mathbf{R}) = \bar{O}(\mathbf{r}_1,\mathbf{r}_2)$. Crucially, the periodic counterpart of the Hamiltonian in this approach has no vector potential dependence (nor magnetic field dependence): $\bar{H} = -\frac{1}{2}\nabla^2 + V(\mathbf{r})$.

The density operator corresponding to an Hamiltonian, for an insulator at 0 K, can be obtained by the minimization of the expectation value of the energy of the system on the ensemble of idempotent density matrices (i.e., $\rho = \rho\rho$) with fixed electron number:

$$E(\mathbf{B}) = \min_{\rho \text{ idempotent}} \{\mathrm{Tr}[\rho H(\mathbf{B})]\}. \tag{2}$$

At the minimum, $[\rho,H] = 0$. The density operator also possesses magnetic translation symmetry, so that Eq. (2) can be recast in terms of $\bar{H}$ and $\bar{\rho}$ provided that the product of the two operators is transformed according to Eq. (1). In real space the product of two operators $\mathcal{T} = \mathcal{V}W$ becomes[15,17]

$$\bar{\mathcal{T}}(\mathbf{r}_1,\mathbf{r}_3) = \int d\mathbf{r}_2 \bar{\mathcal{V}}(\mathbf{r}_1,\mathbf{r}_2)\bar{\mathcal{W}}(\mathbf{r}_2,\mathbf{r}_3)e^{-i\phi_{123}/\phi_0}, \tag{3}$$

where

$$\phi_{123}/\phi_0 = \mathbf{B}(\mathbf{r}_1 \times \mathbf{r}_2 + \mathbf{r}_2 \times \mathbf{r}_3 + \mathbf{r}_3 \times \mathbf{r}_1)/2 \tag{4}$$

is proportional to the magnetic flux through triangle 123. Based on Eq. (3), $\bar{\rho}$ is no longer idempotent, due to the appearance of the $e^{-i\phi_{123}/\phi_0}$ phase factor. In Ref. [15], $\bar{\rho}$ is expanded to first order in $\mathbf{B}$, before considering the decomposition of the operators in the BZ, in order to obtain the orbital magnetoelectric coupling.

We find that the idempotency problem can be avoided by transforming Eq. (3) to a combined BZ and primitive cell integral, *before* any expansion in $\mathbf{B}$. To obtain this result, we decompose periodic operators $\bar{O}(\mathbf{r}_1,\mathbf{r}_2)$ into operators that are separately periodic in each argument and characterized by a wave vector:

$$\bar{O}(\mathbf{r}_1,\mathbf{r}_2) = \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}_1} \tilde{O}_\mathbf{k}(\mathbf{r}_1,\mathbf{r}_2)e^{-i\mathbf{k}\cdot\mathbf{r}_2}, \tag{5}$$

with $\tilde{O}_\mathbf{k}(\mathbf{r}_1 + \mathbf{r},\mathbf{r}_2) = \tilde{O}_\mathbf{k}(\mathbf{r}_1,\mathbf{r}_2 + \mathbf{r}) = \tilde{O}_\mathbf{k}(\mathbf{r}_1,\mathbf{r}_2)$, and $\tilde{O}_\mathbf{k}(\mathbf{r}_1,\mathbf{r}_2) = \tilde{O}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}_1,\mathbf{r}_2)$ for all reciprocal-lattice vectors $\mathbf{G}$. Under this decomposition, Eq. (3) becomes

$$\bar{\mathcal{T}}(\mathbf{r}_1,\mathbf{r}_3) = \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} \int_{\Omega_0} d\mathbf{r}_2 e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_3)}$$
$$\times \tilde{\mathcal{V}}_\mathbf{k}(\mathbf{r}_1,\mathbf{r}_2)\tilde{\mathcal{W}}_{\mathbf{k}+\Delta\mathbf{k}(\mathbf{B})}(\mathbf{r}_2,\mathbf{r}_3), \tag{6}$$

where Ω_0 is the primitive cell volume and $\Delta\mathbf{k} = (\mathbf{r}_3 - \mathbf{r}_1) \times \mathbf{B}/2c$ is a position- and magnetic field- dependent increment of the wave vector $\mathbf{k}$. Such an increment defines an $\mathbf{r}_1$-dependent kernel, and hence, an $\mathbf{r}_1$-dependent operator. Although unusual, these expressions are mathematically well defined. The transformation proceeds with the Taylor expansion of $\tilde{\mathcal{W}}$ with respect to $\mathbf{B}$, followed by multiple integrations by parts with respect to $\mathbf{k}$. This procedure yields the full expansion of $\tilde{\mathcal{T}}_\mathbf{k}$ to all orders in $\mathbf{B}$. For simplicity we denote the derivatives with respect to $\mathbf{k}$ in direction α by ∂_α, omit real-space arguments, and use the summation convention with ε the totally antisymmetric unit tensor. The expansion is then

$$\tilde{\mathcal{T}}_\mathbf{k} = \tilde{\mathcal{V}}_\mathbf{k}\tilde{\mathcal{W}}_\mathbf{k} + \sum_{m=1}^\infty \frac{1}{m!}\left(\frac{i}{2c}\right)^m \left(\prod_{n=1}^m \varepsilon_{\alpha_n\beta_n\gamma_n}B_{\alpha_n}\right)$$
$$\times \left(\partial_{\beta_1}\cdots\partial_{\beta_m}\tilde{\mathcal{V}}_\mathbf{k}\right)\left(\partial_{\gamma_1}\cdots\partial_{\gamma_m}\tilde{\mathcal{W}}_\mathbf{k}\right), \tag{7}$$

and explicitly to second order,

$$\tilde{\mathcal{T}}_\mathbf{k} = \tilde{\mathcal{V}}_\mathbf{k}\tilde{\mathcal{W}}_\mathbf{k} + (i/2c)(\varepsilon_{\alpha\beta\gamma}B_\alpha)(\partial_\beta\tilde{\mathcal{V}}_\mathbf{k})(\partial_\gamma\tilde{\mathcal{W}}_\mathbf{k})$$
$$- \frac{1}{8c^2}\left(\prod_{n=1}^2 \varepsilon_{\alpha_n\beta_n\gamma_n}B_{\alpha_n}\right)(\partial_{\beta_1}\partial_{\beta_2}\tilde{\mathcal{V}}_\mathbf{k})(\partial_{\gamma_1}\partial_{\gamma_2}\tilde{\mathcal{W}}_\mathbf{k}) + O(\mathbf{B}^3). \tag{8}$$

The density-matrix perturbation theory valid for arbitrary orders of perturbation, as developed in $\mathbf{k}$ space for homogeneous electric fields,[18] can now be generalized to magnetic fields. Defining perturbation orders by λ such that $\mathbf{B}(\lambda) = \lambda\mathbf{B}_{\lambda=1}$, we expand a generic quantity X as $X(\mathbf{B}) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \cdots$. The periodic counterpart of the Hamiltonian $\tilde{H}_\mathbf{k}$ has no magnetic field dependence, as outlined before, hence, $\tilde{H}_\mathbf{k} = \tilde{H}_\mathbf{k}^{(0)}$ while for $m \neq 0$, $\tilde{H}_\mathbf{k}^{(n)} = 0$. The density operator at any order can be decomposed into different blocks, acting inside the occupied subspace (denoted V for valence), or inside the unoccupied subspace (C for conduction), or coupling different subspaces CV/VC (we refer to the subspaces obtained at zero $\mathbf{B}$). As $\tilde{H}_\mathbf{k} = \tilde{H}_\mathbf{k}^{(0)}$ is block diagonal in these subspaces, the expansion of the energy yields

$$E^{(n)} = \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} \mathrm{Tr}\left[\left(\tilde{\rho}_{\mathbf{k}VV}^{(n)} + \tilde{\rho}_{\mathbf{k}CC}^{(n)}\right)\tilde{H}_\mathbf{k}\right]. \tag{9}$$

The first-order term is related to the magnetization $\mathbf{M}$, $E^{(1)} = \mathbf{B} \cdot \mathbf{M}$, while the second-order term is related to the OMS χ, $E^{(2)} = 2\sum_{ij} B_i\chi_{ij}B_j$.

The $\tilde{\rho}_\mathbf{k}^{(n)}$ can be found recursively from the $\tilde{\rho}_\mathbf{k}^{(i)}$, with $i < n$, by an adaptation of the density-matrix perturbation theory of

Ref. 18. The block-diagonal parts of density matrices are given by

$$\tilde{\rho}_{\mathbf{k}VV}^{(n)} = -\tilde{\rho}_{\mathbf{k}}^{(0)}\tilde{\rho}_{\mathbf{k}D}^{(n)}\tilde{\rho}_{\mathbf{k}}^{(0)}, \tag{10}$$

$$\tilde{\rho}_{\mathbf{k}CC}^{(n)} = \left(1 - \tilde{\rho}_{\mathbf{k}}^{(0)}\right)\tilde{\rho}_{\mathbf{k}D}^{(n)}\left(1 - \tilde{\rho}_{\mathbf{k}}^{(0)}\right), \tag{11}$$

where, for first and second orders,

$$\tilde{\rho}_{\mathbf{k}D}^{(1)} = \frac{i}{2c}\varepsilon_{\alpha\beta\gamma}B_\alpha\left(\partial_\beta\tilde{\rho}_{\mathbf{k}}^{(0)}\right)\left(\partial_\gamma\tilde{\rho}_{\mathbf{k}}^{(0)}\right), \tag{12}$$

$$\begin{aligned}
\tilde{\rho}_{\mathbf{k}D}^{(2)} &= \tilde{\rho}_{\mathbf{k}}^{(1)}\tilde{\rho}_{\mathbf{k}}^{(1)} + \frac{i}{2c}\varepsilon_{\alpha\beta\gamma}B_\alpha\Big[\left(\partial_\beta\tilde{\rho}_{\mathbf{k}}^{(0)}\right)\left(\partial_\gamma\tilde{\rho}_{\mathbf{k}}^{(1)}\right) \\
&+ \left(\partial_\beta\tilde{\rho}_{\mathbf{k}}^{(1)}\right)\left(\partial_\gamma\tilde{\rho}_{\mathbf{k}}^{(0)}\right)\Big] - \frac{1}{8c^2}\left(\prod_{n=1}^{2}\varepsilon_{\alpha_n\beta_n\gamma_n}B_{\alpha_n}\right) \\
&\times \partial_{\beta_1}\partial_{\beta_2}\tilde{\rho}_{\mathbf{k}}^{(0)}.\partial_{\gamma_1}\partial_{\gamma_2}\tilde{\rho}_{\mathbf{k}}^{(0)}.
\end{aligned} \tag{13}$$

For the full $\tilde{\rho}^{(1)}$, the off-diagonal CV blocks are needed in addition to the first-order CC and VV blocks, and are obtained by solving the equation

$$\begin{aligned}
\left[\tilde{H}_{\mathbf{k}},\tilde{\rho}_{\mathbf{k}CV}^{(1)}\right] &= \frac{i}{2c}\varepsilon_{\alpha\beta\gamma}B_\alpha\left(1 - \tilde{\rho}_{\mathbf{k}}^{(0)}\right) \\
&\times \left[\left(\partial_\beta\tilde{\rho}_{\mathbf{k}}^{(0)}\right)\left(\partial_\gamma\tilde{H}_{\mathbf{k}}\right) - \left(\partial_\beta\tilde{H}_{\mathbf{k}}\right)\left(\partial_\gamma\tilde{\rho}_{\mathbf{k}}^{(0)}\right)\right]\tilde{\rho}_{\mathbf{k}}^{(0)},
\end{aligned} \tag{14}$$

where the r.h.s expression is a CV projection of the angular-momentum operator times the magnetic field, in reciprocal space.[18]

For $n = 1$, these equations reduce to Eqs. (21), (23), and (28) of Ref. 15, where they have been further expressed in terms of Bloch wave functions for *occupied states* and their first k derivatives. When substituted into the first-order term of Eq. (9), the multiband formula derived in Ref. 14 for the magnetization is obtained (as $\mathbf{B} \cdot \mathbf{M}$). Likewise, the second-order equations can be expressed in terms of the Bloch wave functions for occupied states only, their first-order changes, and their first and second k derivatives, yielding an explicitly periodic formulation of the OMS. These rather lengthy expressions will be detailed elsewhere. The tensorial structure of Eqs. (9)–(14) is obvious, as the terms depend on n factors of B in different directions.

The OMS is seen from Eq. (9) to arise from both the valence and the conduction subspaces, like the magnetization. For both subspaces, from Eq. (13), there are three contributions: a term quadratic in the density-operator response $\tilde{\rho}_{\mathbf{k}}^{(1)}$, a term linear in this response, and a term that is independent of the response of the electrons. The quadratic and linear CV contributions can be linked to each other on the basis of Eq. (14). Their sum, being always negative and due to density matrix relaxation, yields the Van Vleck paramagnetic contribution in the present formalism.[19] Alternative decompositions of the OMS Eq. (13) exist, similarly to the different expressions for the dielectric susceptibility in density functional perturbation theory [see, e.g., Eqs. (37) and (38) of Ref. 3]. The expression for the OMS presented here can be shown to be variational, and delivers Eq. (14) from Euler-Lagrange conditions.
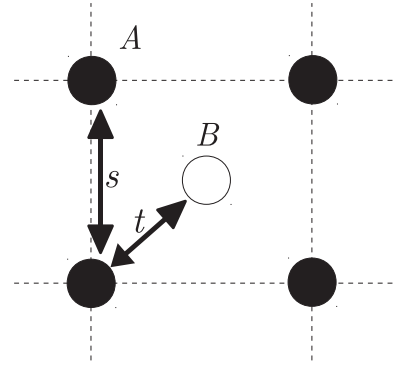

FIG. 1. Tight-binding model used to check the theory. A square lattice of A sites and B sites are coupled by energies t (A-B nearest neighbors) and s (A-A nearest neighbors).

III. VALIDATION OF THEORY

The predictions of the theory were checked using a tight-binding model (Fig. 1). This model consists of a 2D square lattice with A sites at the vertices and B sites at the center of each square, with on-site energies $E_A < E_B$. Nearest-neighbor A,B pairs are coupled by energy t, and nearest-neighbor A,A pairs by energy s (Fig. 1). The A sites are defined as initially occupied and the B sites empty. The two different types of couplings are necessary to exhibit nontrivial behavior from all three contributions to the susceptibility; with only the more obvious t couplings, only the frozen-density-operator contribution is nonzero. Following Ref. 15, the presence of a magnetic field perpendicular to the plane of the model is included by multiplying the Hamiltonian matrix elements by $e^{-iB(\mathbf{r}_a\times\mathbf{r}_b)/2}$, where $\mathbf{r}_a$ and $\mathbf{r}_b$ describe the locations of the coupled sites.

This model is simple enough for Eqs. (9)–(14) to lead to analytical expressions, apart for a global integral over the 2D BZ. The occupied (valence) band eigenenergies $E_{\mathbf{k}v}$ are given by

$$E_{\mathbf{k}v} = \bar{E}_{\mathbf{k}} - D_{\mathbf{k}}, \tag{15}$$

with

$$D_{\mathbf{k}} = \sqrt{(1 + \bar{E}_{\mathbf{k}})^2 + \Delta_{\mathbf{k}}^2}, \tag{16}$$

$$\bar{E}_{\mathbf{k}} = -s(\cos k_x + \cos k_y), \tag{17}$$

$$\Delta_{\mathbf{k}} = -4t\cos(k_x/2)\cos(k_y/2). \tag{18}$$

The periodic part of the Bloch eigenfunctions for the valence band are

$$|u_{\mathbf{k}v}\rangle = \cos\theta_{\mathbf{k}}|A\rangle + \sin\theta_{\mathbf{k}}|B\rangle, \tag{19}$$

where

$$\tan\theta_{\mathbf{k}} = (1 - \bar{E}_{\mathbf{k}} - D_{\mathbf{k}})/\Delta_{\mathbf{k}}. \tag{20}$$

With these definitions, the frozen, linear, and quadratic density operator contributions to χ are respectively,

$$\chi_{\text{froz}} = \int_{\text{BZ}}\frac{d\mathbf{k}}{4(2\pi)^3}D_{\mathbf{k}}\left[\left(\frac{\partial^2\theta_{\mathbf{k}}}{\partial k_x\partial k_y}\right)^2 - \frac{\partial^2\theta_{\mathbf{k}}}{\partial k_x^2}\frac{\partial^2\theta_{\mathbf{k}}}{\partial k_y^2}\right], \tag{21}$$

$$\chi_{\text{lin}} = -2\chi_{\text{quad}} = -2(2\pi)^{-3}\int_{\text{BZ}}d\mathbf{k}R_{\mathbf{k}}^2 D_{\mathbf{k}}^{-5},$$
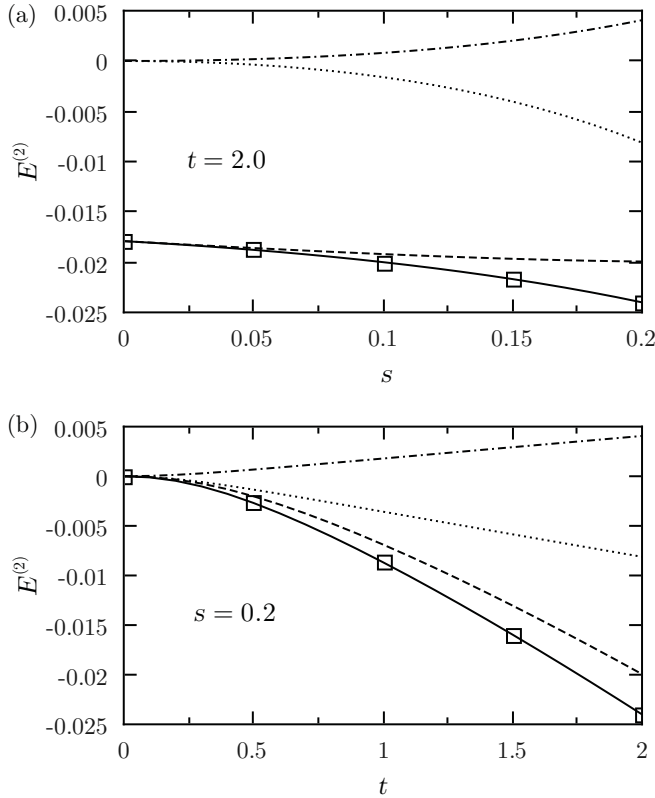
FIG. 2. Magnetic susceptibility for the tight-binding model with (a) $t = 2.0$ and a range of s values, and (b) $s = 0.2$ and a range of t values. In both cases, the full theory (solid line) is composed of three terms (dashed line: frozen wave function; dotted line: linear in $\tilde{\rho}^{(1)}$; dash-dot line: quadratic in $\tilde{\rho}^{(1)}$). Squares: exact diagonalization values.

with

$$R_{\mathbf{k}} = st(1 + \bar{E}_{\mathbf{k}}) \sin\left(\frac{k_x}{2}\right) \sin\left(\frac{k_y}{2}\right)$$
$$\times \left[\cos^2\left(\frac{k_y}{2}\right) - \cos^2\left(\frac{k_x}{2}\right)\right]. \tag{22}$$

These integrals were carried out numerically to 10^{-10} convergence.

The susceptibility of the model was also computed directly by diagonalization of the Hamiltonian matrix for finite size lattices. For an $N \times N$ grid the energy converged roughly like $1/N$. For a given parameter triple (t, s, B) the energy was computed for a range of lattice sizes ($N = 10 \cdots 100$), and the resulting values fit to a fourth order polynomial in $1/N$. This procedure yielded an estimate of the infinite-size limit accurate to about 1 part in 10^6. To compute the second-order energy change with magnetic field, energies as a function of mesh size were computed for parameter triples (s, t, B), where B was one of 0.00, 0.05, and 0.10, and s and t

were fixed. Then $E^{(2)}$ was estimated from a finite-difference formula, valid when $E(B) = E(-B)$: $E^{(2)} \approx [16E(B/2) - E(B) - 15E(0)]/(3B^2)$ for $B = 0.10$.

Figure 2 shows the agreement between the theoretical prediction of $E^{(2)}$ and that obtained by exact diagonalization. Note that at large s or t, $E^{(2)}$ has substantial contributions from the linear and quadratic components, in addition to the frozen term. In all cases agreement between theory and numerical diagonalization is on the order of a few parts in 10^4 or better.

Beyond the OMS, the knowledge of the first-order density matrix allows computation of *every* coupling between a magnetic field and other (regular) perturbations of the system, as well as the orbital current as needed for the nuclear magnetic resonance (NMR) shielding. Indeed, the mixed derivative of the energy with respect to the magnetic field (indexed by λ) and another perturbation (indexed by μ) is given by

$$\frac{\partial^2 E}{\partial\mu\,\partial\lambda} = \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} \text{Tr}\left[\tilde{\rho}_{\mathbf{k}}^{(1)} \frac{\partial \tilde{H}_{\mathbf{k}}}{\partial\mu}\right]. \tag{23}$$

where, crucially, the derivative of the first-order density matrix with respect to μ is not needed.

IV. CONCLUSIONS

The present approach to the OMS through expansion of the total energy [Eq. (9)] places it in a new framework, in which its link with the orbital magnetization (from the first-order term) is clear, and higher-order susceptibilities can be computed as well. Of course, the interest in higher-order derivatives of the total energy with respect to the magnetic field is purely academic. However, electric fields and vibrational effects can be treated on the same footing, at linear and nonlinear orders, so that the path is opened to a unified approach to coupled magnetic, electric, and thermodynamic effects in insulators, expected to help understanding multiferroïcs, materials for spintronics applications, as well as temperature-dependent responses to magnetic fields, as needed for NMR experiments.

Although we have focused on insulators at 0 K, a generalization to metals at finite temperatures likely exists, as in the case of the orbital magnetization (the $n = 1$ term in our expansion), as outlined in Ref. 20. Note, however, that the density matrix idempotency relationship $\rho = \rho\rho$ is not valid for such cases, so the density-matrix perturbation theory as developed in Ref. 18 cannot be applied straightforwardly.

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