

Magnetic Susceptibility of Insulators from First Principles

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We present an *ab initio* approach for the computation of the magnetic susceptibility χ of insulators. The approach is applied to compute χ in diamond and in solid neon using density functional theory in the local density approximation, obtaining good agreement with experimental data. In solid neon, we predict an observable dependence of χ upon pressure. [S0031-9007(96)00308-0]

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The response of an extended system to a uniform external magnetic field is a fundamental property. This response can be used as a sensitive probe to the structural and electronic properties of materials, such as in the case of nuclear magnetic resonance spectroscopy. However, to our knowledge, the orbital magnetic susceptibility χ of real solids has not been computed from first principles. In this Letter we discuss an *ab initio* approach for the evaluation of χ in insulators within density functional theory (DFT). We applied our formalism to diamond and solid neon using the local density approximation (LDA) for the exchange and correlation energy. The agreement of our results with experimental data indicates that DFT-LDA describes correctly the magnetic response of these systems.

The susceptibility χ has been evaluated in cubic semiconductors using empirical methods [1]. Exact expressions for χ of a periodic solid in terms of Bloch eigenstates and eigenvalues have already been derived in the 1960s [2–4]. However, these approaches are rather involved and have not been applied to real materials. A more compact expression for χ was recently given in Ref. [5], where it is applied to a model two-dimensional system. Our approach for the computation of χ in real systems is related to the one in Ref. [5].

This paper is organized as follows. First, we present the formalism for a generic single particle Hamiltonian. Then we justify the use of DFT in the LDA in the computation of χ , and we discuss the accuracy and the limits of the additional use of the pseudopotential approximation. Finally, we apply our formalism to diamond and solid neon, studying the behavior of χ as a function of the lattice constant.

The magnetic susceptibility is defined as the second derivative of the total energy per unit volume E with respect to the macroscopic magnetic field \mathbf{B} , i.e.,

$$\chi_{ij} = -\frac{d^2 E}{dB_i dB_j}, \quad (1)$$

where i and j are the Cartesian indexes. To simplify the notation in the following discussion, we consider a cubic system for which $\chi_{ij} = \delta_{ij}\chi$.

Perturbation theory can be used to compute χ . This is straightforward for a finite system. However, in an ex-

tended solid, the expectation values of the perturbative Hamiltonian on delocalized eigenstates are not well-defined quantities for a uniform field. To avoid this problem we consider the response of the system to a magnetic field with a finite wavelength $\mathbf{q} = (q, 0, 0)$, i.e., $\mathbf{B}(x) = b(0, 0, \sqrt{2} \cos(qx)) = \nabla \times \mathbf{A}$ with $\mathbf{A}(x) = b(0, \sqrt{2} \sin(qx)/q, 0)$. Defining

$$\chi(q) = -\frac{d^2 E}{db^2}, \quad (2)$$

in the limit of $q \rightarrow 0$, we obtain the macroscopic susceptibility χ [4].

Let us first consider a system described by a single particle Hamiltonian. If the coupling between \mathbf{B} and the spin of the electron can be neglected, the perturbation to the Hamiltonian can be written as $\Delta H = H^{(1)} + H^{(2)}$ with

$$H^{(1)} = \frac{1}{c} \mathbf{p} \cdot \mathbf{A} = \frac{\sqrt{2}}{c} \frac{\sin(qx)}{q} p_y b, \\ H^{(2)} = \frac{1}{2c^2} A^2 = \frac{1}{c^2} \frac{\sin^2(qx)}{q^2} b^2, \quad (3)$$

where atomic units are used, \mathbf{p} is the momentum operator, and c is the speed of light.

For a periodic insulator we have

$$\chi(q)b^2 = -4 \frac{\Omega}{c^2} \int \frac{d^3 \mathbf{k}}{8\pi^3} \int \frac{d^3 \mathbf{k}'}{8\pi^3} \\ \times \sum_{i \in \mathcal{O}, j \in \mathcal{E}} \frac{|\langle \psi_{\mathbf{k},i} | H^{(1)} | \psi_{\mathbf{k}',j} \rangle|^2}{\epsilon_{\mathbf{k},i} - \epsilon_{\mathbf{k}',j}} \\ - \frac{4}{c^2} \int \frac{d^3 \mathbf{k}}{8\pi^3} \sum_{i \in \mathcal{O}} \langle \psi_{\mathbf{k},i} | H^{(2)} | \psi_{\mathbf{k},i} \rangle, \quad (4)$$

where $\psi_{\mathbf{k},i}$ and $\epsilon_{\mathbf{k},i}$ are the Bloch eigenstates and eigenvalues of the unperturbed Hamiltonian, Ω is the volume of the unit cell, \mathcal{O} and \mathcal{E} are the sets of occupied and empty bands, and a factor of 2 for spin degeneracy is included. By inserting Eq. (3) into Eq. (4), we get

$$\chi(q) = -\frac{2}{c^2 q^2} \int \frac{d^3 \mathbf{k}}{8\pi^3} [g(\mathbf{k} + \mathbf{q}, \mathbf{k}) + g(\mathbf{k} - \mathbf{q}, \mathbf{k})] \\ - \frac{N}{\Omega c^2 q^2}, \quad (5)$$

where N is the number of electrons per unit cell,

$$g(\mathbf{k}', \mathbf{k}) = \sum_{i \in \mathcal{O}, j \in \mathcal{E}} \frac{|\langle u_{\mathbf{k}', i} | -i\nabla_y + (k'_y + k_y)/2 | u_{\mathbf{k}, j} \rangle|^2}{\epsilon_{\mathbf{k}', i} - \epsilon_{\mathbf{k}, j}}, \quad (6)$$

and $|u_{\mathbf{k}, i}\rangle$ is the periodic part of the Bloch eigenstate (normalized in the unit cell). For $q \rightarrow 0$, the two terms on the right-hand side (rhs) of Eq. (5) individually diverge, but $\chi(q)$ remains finite. To show this, we use the f -sum rule,

$$f_s = \frac{N}{\Omega} = -4 \int \frac{d^3\mathbf{k}}{8\pi^3} g(\mathbf{k}, \mathbf{k}). \quad (7)$$

By inserting Eq. (7) into Eq. (5) we obtain

$$\chi(q) = -\frac{2}{c^2} \int \frac{d^3\mathbf{k}}{8\pi^3} \times \frac{g(\mathbf{k} + \mathbf{q}, \mathbf{k}) - 2g(\mathbf{k}, \mathbf{k}) + g(\mathbf{k} - \mathbf{q}, \mathbf{k})}{q^2}. \quad (8)$$

Then

$$\chi = \lim_{q \rightarrow 0} \chi(q) = -\frac{2}{c^2} \int \frac{d^3\mathbf{k}}{8\pi^3} \frac{d^2}{dk_x^2} g(\mathbf{k}, \mathbf{k}')|_{\mathbf{k}'=\mathbf{k}}. \quad (9)$$

Similar conclusions have been obtained in Ref. [5].

In our numerical evaluation of the macroscopic χ we use Eq. (8) with a small but finite q . Note that Eq. (5) is not suitable to this approach. Indeed, in a practical application, both the integral in \mathbf{k} space and the sum over all empty bands are replaced by finite sums. Under these conditions the f -sum rule, Eq. (7), is no longer exactly satisfied. Then for $q \rightarrow 0$ the rhs of Eq. (5) will diverge as $\Delta f_s c^{-2} q^{-2}$, where Δf_s is the error in the f -sum rule. This numerical instability does not occur in Eq. (8), where every term is treated consistently.

We computed χ using DFT-LDA, i.e., we neglected any explicit dependence of the exchange-correlation functional on the current density. Reference [6] proposes an approximate functional for the exchange correlation energy E_{xc} which also depends on the current. The current term in E_{xc} influences the magnetic response in systems with a small electronic density. It is negligible in our case, since it yields a correction to χ smaller than 2% at the electronic densities typical of the systems we are studying [6,7]. We also do not consider magnetic local field effects, which are negligible in nonmagnetic materials [8]. Finally, we note that the DFT Hamiltonian depends in a self-consistent way upon the electronic charge density. Thus, in general, to compute the second order variation in the total energy with respect to an external perturbation, one should take into account the linear variation of the Hamiltonian induced by the linear variation of the charge $\delta\rho$ (see, e.g., Ref. [11]). However, if the perturbation is a magnetic field, $\delta\rho$ is zero by time reversal symmetry. Thus Eq. (8) is correct within DFT.

In our present practical calculation we used the pseudopotential approach, in which only the valence electrons are

considered. To discuss the validity of the pseudopotential approximation in the computation of χ , we divide the set of occupied bands \mathcal{O} into the sets of core bands \mathcal{C} and valence bands \mathcal{V} . Then we have

$$\chi = \chi_{\mathcal{C}, \mathcal{E}} + \chi_{\mathcal{V}, \mathcal{E}} = \chi_{\mathcal{C}} - \chi_{\mathcal{C}, \mathcal{V}} + \chi_{\mathcal{V}, \mathcal{E}}. \quad (10)$$

Here $\chi_{\mathcal{C}, \mathcal{E}}$ is given by Eqs. (6) and (9) with the sum over the i and j indexes in Eq. (6) running over the sets of core states, \mathcal{C} , and of empty states, \mathcal{E} , respectively. The other χ with two indices are defined in a similar way. $\chi_{\mathcal{C}}$ is the magnetic susceptibility of the core electrons, which is not sensitive on the chemical environment and thus can be computed considering the isolated atoms, i.e.,

$$\chi_{\mathcal{C}} = \chi_{\mathcal{C}, \mathcal{E}} + \chi_{\mathcal{C}, \mathcal{V}} \approx -\frac{1}{\Omega c^2} \sum_I \sum_{i \in \mathcal{C}} \langle \Psi_i^I | x^2 | \Psi_i^I \rangle, \quad (11)$$

where we sum over the atoms in the unit cell, and Ψ_i^I are the core atomic wave functions of the atom I . Among the three terms in the rhs of Eq. (10), $\chi_{\mathcal{V}, \mathcal{E}}$ is the only one accessible in a pseudopotential calculation; $\chi_{\mathcal{C}}$ can be computed using an atomic code, but the evaluation of $\chi_{\mathcal{C}, \mathcal{V}}$ requires the knowledge of both core and valence wave functions. Since $\chi_{\mathcal{C}, \mathcal{V}}$ and $\chi_{\mathcal{C}}$ are expected to be of the same order of magnitude, the pseudopotential approximation introduces an error of the order of $\chi_{\mathcal{C}}$ by neglecting $\chi_{\mathcal{C}, \mathcal{V}}$. This error is reasonably small only for elements in the first and second rows of the periodic table, for which $\chi_{\mathcal{C}} \ll \chi$. For application of the present theory to heavier elements, all-electron calculations are needed. Finally, in our pseudopotential calculation, we replaced the operator $-i\nabla + \mathbf{k}$ in Eq. (6) with the velocity operator $\mathbf{v}_{\mathbf{k}}^p = (d/d\mathbf{k})H_{\mathbf{k}}^p$ where $H_{\mathbf{k}}^p$ is the pseudo-Hamiltonian [12].

We computed χ for isolated carbon (C) and neon (Ne) atoms, for solid Ne in the fcc structure, and for solid C in the diamond structure. In the atomic phases we used the all-electron ground state wave functions to compute $\chi_{\mathcal{C}}$ using Eq. (11). In Ne we also computed the atomic χ using Eq. (11) with the sum over the index i running over all occupied states. In the solid phases, we evaluated $\chi_{\mathcal{V}, \mathcal{E}}$ using Eq. (8) with a $q = 0.03\pi/a$, where a is the lattice constant of the cubic cell. The pseudopotentials were generated using the prescription of Ref. [13]. In Ne we expanded the wave functions on a plane-wave basis set with a 120 Ry cutoff. We sampled the \mathbf{k} space integrals with 10 special \mathbf{k} points in the irreducible Brillouin zone, and considered 400 empty states. In diamond we used a 60 Ry cutoff, 60 special \mathbf{k} points, and 300 empty states. We verified that with the above parameters the convergence error in the value of χ is less than 0.2%.

The results for Ne are shown in Table I. The atomic calculation is in good agreement with the experimental data. For the solid fcc phase we report $\chi_{\mathcal{V}, \mathcal{E}}$ as a function of the lattice constant a . We note that $\chi_{\mathcal{V}, \mathcal{E}}$ reaches

TABLE I. Magnetic susceptibility of atomic and solid fcc Ne in units of 10^{-6} cm³/mole. In the solid, we considered different values of the lattice constant a . We indicate with a_0^e the experimental equilibrium lattice constant. The theoretical pressure P is also reported.

	$-\chi$	$-\chi_C$	$-\chi_{\mathcal{V},\mathcal{E}}$	P (GPa)
Atom (experiment)	7.2			
Atom (theory)	7.80	0.05		
Solid $a = 8.37$ a.u. = a_0^e			7.79	-2
Solid $a = 7.87$ a.u.			7.76	-2
Solid $a = 7.37$ a.u.			7.64	-1
Solid $a = 6.87$ a.u.			7.41	4
Solid $a = 6.37$ a.u.			7.14	15
Solid $a = 5.87$ a.u.			6.66	50
Solid $a = 5.37$ a.u.			6.04	151

a plateau for $a \sim a_0^e$, where a_0^e is the experimental equilibrium lattice constant. This indicates that for $a \geq a_0^e$ the interaction among Ne atoms is negligible. Moreover, $\chi_{\mathcal{V},\mathcal{E}}$ at $a = a_0$ is very close to the value of χ computed for the isolated atom. This establishes, in the atomic limit, the correctness of approach and the accuracy of the pseudopotential approximation. As a decreases, $-\chi_{\mathcal{V},\mathcal{E}}$ decreases. This can be understood by noting that for an isolated closed shell atom only a negative diamagnetic term contributes to χ , since the unperturbed Hamiltonian is spherically symmetric. As the Ne atoms get closer, spherical symmetry is broken and a positive paramagnetic term also contributes to χ . For the sake of comparison with future experiments, we also report the theoretical pressure P as a function of a . Solid Ne at zero P is bonded by a weak van der Waals interaction, which is incorrectly given by LDA [14]. Thus, for the larger a , we do not expect to obtain accurate values for P . However, we expect LDA to describe correctly the repulsive interaction between Ne atoms, which dominates P at smaller a . Note that at $P = 50$ GPa, $-\chi_{\mathcal{V},\mathcal{E}}$ is decreased by 16% with respect to its atomic value.

The results for C are shown in Table II. Since C is not a closed shell atom, in the atomic case only χ_C is reported. In the diamond phase we report $\chi_{\mathcal{V},\mathcal{E}}$ as a function of the lattice constant a . The computed pressure obtained from the LDA-DFT total energies is also shown. In the range of experimentally accessible pressures, $\chi_{\mathcal{V},\mathcal{E}}$ shows a negligible dependence upon a . Both the values of $\chi_{\mathcal{V},\mathcal{E}}$ at the experimental (a_0^e) and at the theoretical (a_0^t) equilibrium lattice constant are in very good agreement with the experimental data.

In conclusion, we have presented a method to compute the magnetic response of real solids from first principles. We have shown that DFT-LDA reproduces the magnetic susceptibility χ of diamond. In diamond, χ is found to be insensitive to the applied pressure, whereas we predict an observable pressure dependence of χ in solid Ne.

TABLE II. Magnetic susceptibility of atomic C and of diamond in units of 10^{-6} cm³/mole of C_2 . For the solid, we considered different values of the lattice constant a . We indicate with a_0^e and a_0^t the experimental and theoretical equilibrium lattice constants, respectively. The theoretical pressure P is also reported.

	$-\chi$	$-\chi_C$	$-\chi_{\mathcal{V},\mathcal{E}}$	P (GPa)
Atom (experiment)	11.8			
Atom (theory)		0.32		
Solid $a = 6.75$ a.u. = a_0^e			11.17	-17
Solid $a = 6.66$ a.u. = a_0^t			11.23	0
Solid $a = 6.55$ a.u.			11.26	25
Solid $a = 6.35$ a.u.			11.23	85
Solid $a = 6.15$ a.u.			11.26	168
Solid $a = 5.95$ a.u.			11.09	283

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