Linear Response Calculations of Spin Fluctuations

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A variational formulation of the time-dependent linear response based on the Sternheimer method is developed in order to make practical *ab initio* calculations of dynamical spin susceptibilities of solids. Using gradient density functional and a muffin-tin-orbital representation, the efficiency of the approach is demonstrated by applications to selected magnetic and strongly paramagnetic metals. The results are found to be consistent with experiment and are compared with previous theoretical calculations. [S0031-9007(98)07119-1]

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Full wave-vector and frequency dependent spin susceptibility χ is a central quantity in understanding spin fluctuational spectra of solids. Its knowledge accessible directly via neutron-scattering measurements is important due to significant influence of spin fluctuations to many physical properties and phenomena [1], such as, e.g., the electronic specific heat, electrical and thermal resistivity, suppression of superconductivity for singlet spin pairing, etc. In magnetically ordered materials, transverse spin fluctuations are spin waves whose energies and lifetimes are seen in the structure of transverse susceptibility. High-temperature superconductivity, a highly exciting phenomenon, whose origin is still not recognized, can be due to a spin fluctuational mechanism [2].

Despite large past efforts put on the development of methods for *ab initio* calculations of the dynamical spin susceptibility based either on the random-phase approximation (RPA) decoupling of the Bethe-Salpeter equation [3], or within density functional formalism [4,5], quantitative estimates of χ with realistic energy bands, wave functions, and self-consistently screened electron-electron matrix elements are scarce in the literature [6–9]. This is not only because of the absence of complete theory for the proper description of exchange-correlation effects which is a true many-body problem, but also because standard perturbative treatment of the electronic response has serious problems connected with the summation over high-energy states and matrix inversion.

This paper proposes a method which avoids the latter two problems. The method is a time-dependent generalization of an all-electron Sternheimer approach [10] which has proven to be very efficient in *ab initio* calculations of phonon dispersions, electron-phonon interactions, and transport properties of transition-metal materials including high-T_c superconductors [11]. The method employs a muffin-tin-orbital representation [12] which allows one to greatly facilitate the treatment of localized states such as, e.g., d and f electrons of strongly paramagnetic and magnetic materials whose studying is the main purpose of this work.

Applications to transverse spin fluctuations in Fe and Ni as well as calculations of paramagnetic response in Cr and Pd demonstrate an efficiency of the approach and resolve some discrepancies found in previous theoretical studies. In particular, experimental evidence of an "optical" spin-wave branch for Ni [13] and its absence for Fe [14] is correctly described by the present calculation which was not done in either early semiempirical approaches [7,8] or within a recent frozen-magnon scheme [15]. For the first time, the dynamical susceptibility is calculated *ab initio* for paramagnetic Cr, a highly interesting material due to its incommensurate antiferromagnetism [16]. The calculation predicts a wave vector of the spin density wave (SDW), and clarifies the role of Fermi-surface nesting. Strong long-wavelength spin fluctuations of Pd are evident from the present and earlier [9] theoretical studies.

The description of the method starts by considering a small external magnetic field

$$\delta \mathbf{B}_{\mathrm{ext}}(\mathbf{r}t) = \delta \mathbf{b} e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} e^{i\omega t} e^{-\eta|t|} + \text{c.c.} \qquad (1)$$

applied to a solid. Here $\delta \mathbf{b} = \sum_\mu \delta b^\mu \mathbf{e}_\mu$ shows a polarization of the field (μ runs over x, y, z or over $-1, 0, 1$), wave vector $\mathbf{q}$ lies in the first Brillouin zone, $\mathbf{G}$ is a reciprocal lattice vector, and η is an infinitesimal positive quantity. If the unperturbed system is described by charge density $\rho(\mathbf{r})$ and, in general, by magnetization $\mathbf{m}(\mathbf{r})$, the main problem is to find self-consistently first-order changes $\delta\rho(\mathbf{r}t)$ and $\delta\mathbf{m}(\mathbf{r}t) = \sum_\nu \delta m_\nu(\mathbf{r}t)\mathbf{e}^\nu$ induced by the field $\delta\mathbf{B}_{\mathrm{ext}}(\mathbf{r}t)$. If the polarization $\delta\mathbf{b}$ in (1) is fixed to a particular μth direction, and $\delta\mathbf{m}(\mathbf{r}t)$ is calculated afterwards, a μth column of the spin susceptibility matrix $\chi_{\nu\mu}(\mathbf{r}, \mathbf{q} + \mathbf{G}, \omega)$ will be found [17]. This essentially solves the problem.

A central issue of employing *time-dependent* (TD) density functional theory (DFT) [18] to find the quantities $\delta\rho(\mathbf{r}t)$ and $\delta\mathbf{m}(\mathbf{r}t)$ is now discussed. The unperturbed density and magnetization are described accurately by the static DFT and are expressed via occupied Kohn-Sham states. This is by now a well established method in practical *ab initio* calculations. In order to find the dynamical response within TD DFT, only the knowledge of these unperturbed Kohn-Sham states (both occupied and unoccupied) is required; no knowledge of real excitation spectra (both energies and lifetimes) is necessary. This is the main

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advantage of such an approach. Unfortunately, within TD DFT, an accurate approximation to the kernel $I_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ describing dynamical exchange-correlation effects is unknown while some progress is currently being made [19]. In the following, the so-called adiabatic local density approximation (ALDA) [18] and a generalized gradient approximation (GGA) [20] are adopted to treat $I_{xc}(\mathbf{r}, \mathbf{r}', \omega)$. To date, these are the most popular tools for practical *ab initio* calculations, which are known to produce static response functions as well as other ground-state, optical [21], plus, recently [11], superconducting and transport properties for a large variety of solids in good agreement with experiments. The use of other approximations to $I_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ will be addressed in future work.

An important issue of *variational* linear-response formulation is now discussed. The advantage of variational principles for the calculation of physical quantities is that if one makes a first-order error in the trial function, the error in the variational quantity is of the second order. *Static* charge and spin susceptibilities appeared as second-order changes in the total energy due to applied external fields can be calculated in a variational way. This was demonstrated a long time ago [22] on the example of magnetic response, and, recently [10,23], in the problem of lattice dynamics which is an example of charge response. The proof is directly related to a powerful "$2n + 1$" theorem of perturbation theory and stationarity property for the total energy itself [24]. Any $(2n + 1)$th change in the total energy E_{tot} involves finding only nth order changes in one-electron wave functions ψ_i, and corresponding changes in the charge density as well as in the magnetization. Any $2n$th change in E_{tot} is then variational with respect to the nth-order changes in ψ_i.

A time-dependent generalization of these results is now required. For TD external fields, the action S as a functional of $\rho(\mathbf{r}t)$ and $\mathbf{m}(\mathbf{r}t)$ is considered within TD DFT [18,25]. These functions are expressed via Kohn-Sham spinor orbitals $\vec{\psi}_i(\mathbf{r}t)$ satisfying TD Schrödinger's equation [26]. Therefore, S as the stationary functional of $\vec{\psi}_i(\mathbf{r}t)$ is considered in practice. When the external field is small, the perturbed wave function is represented as $\vec{\psi}_i(\mathbf{r})e^{-i\epsilon_i t} + \delta\vec{\psi}_i(\mathbf{r}t)$ and the first-order changes $\delta\vec{\psi}_i(\mathbf{r}t)$ define the induced charge density as well as the magnetization:

$$\delta\rho = \sum_i (\{\delta\vec{\psi}_i|I|\vec{\psi}_i\} + \{\vec{\psi}_i|I|\delta\vec{\psi}_i\}), \tag{2}$$

$$\delta\mathbf{m} = \mu_B \sum_i (\{\delta\vec{\psi}_i|\sigma|\vec{\psi}_i\} + \{\vec{\psi}_i|\sigma|\delta\vec{\psi}\}). \tag{3}$$

Here $\{|\,|\}$ denotes averaging over spin degrees of freedom only, I is the unit 2×2 matrix, and σ is the Pauli matrix. It is now seen that the knowledge of $\delta\vec{\psi}_i(\mathbf{r}t)$ will solve the problem.

In order to find $\delta\vec{\psi}_i(\mathbf{r}t)$, a time-dependent analog of the $2n + 1$ theorem is now introduced. Any $(2n + 1)$th change in the action functional S involves finding only nth order changes in the TD functions $\vec{\psi}_i(\mathbf{r}t)$, and corresponding changes in charge density as well as in the magnetization. Any $2n$th change in S is then variational with respect to the nth-order changes in $\vec{\psi}_i(\mathbf{r}t)$. The proof is the same as for the static case [24] if the stationarity property of S and the standard TD perturbation theory are exploited. For important case $n = 2$, this theorem makes the second-order change $S^{(2)}$ in the action *variational* with respect to the first-order changes $\delta\vec{\psi}_i(\mathbf{r}t)$. If the perturbation has the form (1), $S^{(2)}$ is directly related to the real diagonal part of the dynamical spin susceptibility $\text{Re}[\chi_{\nu\mu}(\mathbf{q} + \mathbf{G}', \mathbf{q} + \mathbf{G}, \omega)]_{\mathbf{G}'=\mathbf{G}}$, thus allowing its variational estimate [25].

The problem is now reduced to find $S^{(2)}$ as a functional of $\delta\vec{\psi}_i(\mathbf{r}t)$ and to minimize it. This will bring an equation for $\delta\vec{\psi}_i(\mathbf{r}t)$. Any change in the action functional can be established by straightforward varying S of TD DFT [18,25] with respect to the perturbation (1). This is analogous to what is done in the static DFT to derive, for example, the dynamical matrix [10]. $S^{(2)}$ is found to be

$$S^{(2)}[\delta\vec{\psi}_i] = \sum_i 2\langle\delta\vec{\psi}_i|H - i\partial_t I|\delta\vec{\psi}_i\rangle + \int \delta\rho\,\delta V_{\text{eff}} - \int \delta\mathbf{m}(\delta\mathbf{B}_{\text{eff}} + \delta\mathbf{B}_{\text{ext}}), \tag{4}$$

where the unperturbed 2×2 Hamiltonian matrix $H = (-\nabla^2 + V_{\text{eff}})I - \mu_B\sigma\mathbf{B}_{\text{eff}}$. V_{eff} and $\mathbf{B}_{\text{eff}}$ are the ground-state potential and magnetic field of the DFT. δV_{eff} and $\delta\mathbf{B}_{\text{eff}}$ are their first-order changes induced by the perturbation (1) which involve the Hartree (for δV_{eff}) and the exchange-correlation contributions expressed via $\delta\rho$ and $\delta\mathbf{m}$ in the standard manner [4].

The differential equation for $\delta\vec{\psi}_i(\mathbf{r}t)$ is now derived from the stationarity condition of (4). It is given by

$$(H - i\partial_t I)\delta\vec{\psi}_i + (\delta V_{\text{eff}} I - \mu_B\sigma\delta\mathbf{B}_{\text{eff}})\vec{\psi}_i = 0. \tag{5}$$

This is a time-dependent version of the so-called Sternheimer equation which is the Schrödinger equation to linear order. It can be solved easily on the frequency axis which substitutes $-i\partial_t$ by $\epsilon_i \pm \omega$ in (5). The solution of the whole problem assumes self-consistency: First, Eq. (5) is solved with the external field (1). Second, $\delta\rho(\mathbf{r}\omega)$ and $\delta\mathbf{m}(\mathbf{r}\omega)$ are found according to (2) and (3). Third, screened potential $\delta V_{\text{eff}}(\mathbf{r}\omega)$ and magnetic field $\delta\mathbf{B}_{\text{eff}}(\mathbf{r}\omega)$ are constructed. The cycle is repeated again by solving (5). Evaluating $S^{(2)}$ after (4) brings the variational estimate of the real diagonal susceptibility at the iteration.

In order to access the whole susceptibility matrix $\chi(\mathbf{q} + \mathbf{G}', \mathbf{q} + \mathbf{G}, \omega)$ one has to perform the self-consistency for every $\mathbf{q} + \mathbf{G}$ and ω appearing in (1) with the subsequent Fourier transform of the function $\delta\mathbf{m}(\mathbf{r}\omega)$. The self-consistency takes into account all local-field effects in each $\mathbf{q} + \mathbf{G}$ channel. This means

that in practice for every particular $\mathbf{q} + \mathbf{G}$, a whole row of $\chi(\mathbf{q} + \mathbf{G}', \mathbf{q} + \mathbf{G}, \omega)$ is accessed. As an example, the acoustic spin waves can be found, first, by selecting some $\mathbf{q}$ and $\mathbf{G} = 0$ in (1), second, by self-consistent finding of $\chi(\mathbf{q} + \mathbf{G}', \mathbf{q}, \omega)$, and, third, by tracing for frequency peaks in $\mathrm{Im}[\chi(\mathbf{q}, \mathbf{q}, \omega)]$.

The advantages of this method are now seen: First, Eq. (5) does not require an expansion of $\delta\vec{\psi}_i$ over a complete set of unperturbed wave functions $\vec{\psi}_j$ as it is done in the standard perturbation theory. Only the knowledge of occupied and those unoccupied states which are below $E_F + \omega$ is necessary. Second, the inversion problem is substituted by the self-consistent finding of δV_{eff} and $\delta \mathbf{B}_{\mathrm{eff}}$ which allows alternative treatment of the local field effects. Normally 10 iterations is sufficient to reach the convergency. Third, the computational scheme is the same for both longitudinal and transverse spin fluctuations which is achieved by choosing the polarization $\delta\mathbf{b}$ in (1) along or perpendicular to the magnetization axe. The method also accesses *charge*-spin fluctuations via the knowledge of $\delta\rho(\mathbf{r}\omega)$, and it can be used to study dynamical charge fluctuations, if a TD *scalar* filed of the type (1) is considered as the perturbation.

An implementation of the method using linear muffin-tin orbital (LMTO) representation is now discussed. As the original wave function $\vec{\psi}_i$ is expanded in terms of the LMTOs χ_α with the coefficients $\vec{A}_i^\alpha$, the first-order change $\delta\vec{\psi}_i$ generally involves both changes $\delta\vec{A}_i^\alpha$ in the expansion coefficients and changes $\delta\chi_\alpha$ in the LMTO basis set [10]. Changes $\delta\vec{A}_i^\alpha$ are now new variational parameters instead of $\delta\vec{\psi}_i$. They must be found by minimizing the functional (4). Changes $\delta\chi_\alpha$ are, on the other hand, an auxiliary set of functions which is constructed to make the expansion of $\delta\vec{\psi}_i$ fast convergent. Basis $\{\delta\chi_\alpha\}$ is normally adjusted to the perturbation in the same way the original basis $\{\chi_\alpha\}$ is tailored to the unperturbed one-electron potential. Such perturbative technique was found to be extremely efficient in the problem of lattice dynamics [10]. In the magnetic response calculation introducing $\delta\chi_\alpha$ is important for the fields exhibiting strong short-wavelength oscillations. On the other hand, in the calculations with $\mathbf{G} = 0$ in (1) the contributions originating from $\delta\chi_\alpha$ are found to be small.

Numerical efficiency of the method is now demonstrated by calculating spin susceptibilities at zero temperature for a number of metals. No shape approximations are made either for the charge densities and the potentials or for the dynamical response functions. All the relevant quantities are expanded in spherical harmonics inside muffin-tin spheres and in plane waves in the interstitial region similar to the static linear-response LMTO method [10]. The use of GGA gives practically coinciding theoretical and experimental lattice constants. Necessary Brillouin zone (BZ) integrals are carried out using a multigrid tetrahedron technique [10] with 1000 $\mathbf{k}$ points per $\frac{1}{48}$ BZ.

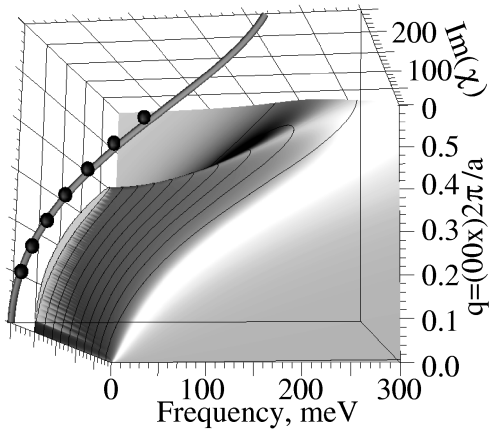

FIG. 1. Calculated $\mathrm{Im}[\chi_{+-}(\mathbf{q}, \omega)]$ (arb. units) for Fe. The experimental data are indicated by balls [14].

The *ab initio* results obtained for bcc Fe are now reported. Figure 1 shows calculated transverse spin susceptibility $\mathrm{Im}[\chi_{+-}(\mathbf{q}, \omega)]$ ($\mathbf{G}' = \mathbf{G} = 0$) for $\mathbf{q} = (00x)2\pi/a$. At small $\mathbf{q}$ the nondecaying spin waves are seen to persist in the structure of $\mathrm{Im}[\chi]$ exhibiting a standard dispersion law $\omega(q) = Dq^2$, where D is the spin stiffness of the material. The spin waves rapidly decay when $\mathbf{q}$ approaches approximately one-half of the BZ. A similar picture has been found for the $\mathbf{q}$'s along the (111) direction. The deduced magnon spectrum (line) is shown on the top of Fig. 1. It agrees well with the experiment [14] (balls) as well as with the recent frozen-magnon calculations [15]. Also, in agreement with experiment any additional structure which can be attributed to the appearance of optical spin-wave branches is not predicted. This advances the early RPA calculation [7].

$\mathrm{Im}[\chi_{+-}(\mathbf{q}, \omega)]$ obtained for fcc Ni is shown on Fig. 2. The unusual structure for the energies near 100 meV and for the $\mathbf{q}$'s $(0, 0, 0.2-0.4)2\pi/a$ due to interband transitions is clearly distinguishable. This was attributed to the

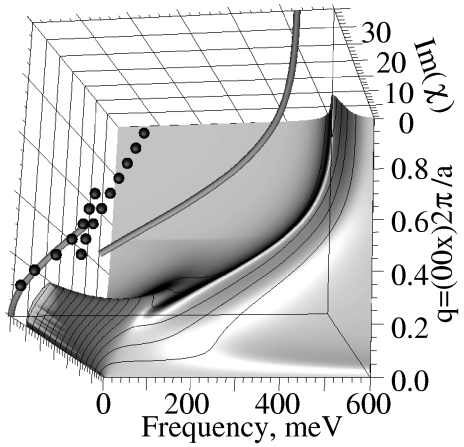

FIG. 2. Calculated $\mathrm{Im}[\chi_{+-}(\mathbf{q}, \omega)]$ (arb. units) for Ni. The experimental data are indicated by balls [13].

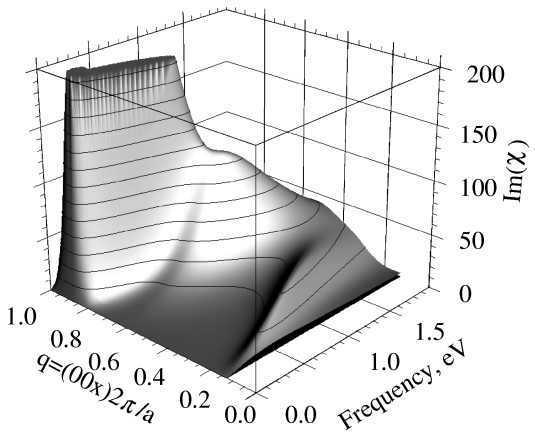

FIG. 3. Calculated $\mathrm{Im}[\chi(\mathbf{q},\omega)]$ (Ry^{-1}) for Cr.

appearance of the optical branch in the spin-wave spectrum [7,13]. However, since this structure is seen to be localized only in a certain region of $\mathbf{q}$ space, its interpreting [7] as a well-defined branch persisting to the BZ boundary might not be completely correct. The computations along the (111) direction do not show such unusual behavior. The obtained magnon spectrum (line on top of Fig. 2) is in agreement with the measured one (balls) [13] in the low-frequency interval while it is overestimated for higher ω. The latter is found in both (001) and (111) directions and is attributed to the poor treatment of dynamical exchange and correlation due to GGA.

Two examples of calculating paramagnetic spin fluctuations are now considered. Figure 3 shows calculated $\mathrm{Im}[\chi(\mathbf{q},\omega)]$ for paramagnetic bcc Cr. A remarkable structure is clearly seen for the $\mathbf{q}$'s near $(0,0,x_{\mathrm{SDW}} \sim 0.92)2\pi/a$, where the susceptibility is mostly enhanced at low frequencies. This predicts Cr to be an incommensurate antiferromagnet (experimentally, $x_{\mathrm{SDW}} = 0.95$). To clarify the role of the Fermi-surface nesting in the origin of such behavior [16], the *noninteracting* susceptibility $\chi_0(\mathbf{q},\omega)$ can be analyzed. $\mathrm{Im}[\chi_0(\mathbf{q},\omega)]$ *does not* show up as a structure peaked at $x_{\mathrm{SDW}} \sim 0.9$ and is a monotonically varying function. Static $\mathrm{Re}[\chi_0(\mathbf{q})]$ slowly increases when x increases from 0 to 1 and exhibits a small maximum at x_{SDW}. This means that the generalized Stoner criterion $1 = I_{xc}\chi_0(\mathbf{q})$ does not necessarily assume a large peak in $\chi_0(\mathbf{q}_{\mathrm{SDW}})$ for Cr; $\chi(\mathbf{q})$ is strongly enhanced for all large $\mathbf{q}$ along ΓX. At the absence of nesting, $\chi_0(\mathbf{q})$ is largest at $x = 1$, and this would predict Cr to be *commensurate* antiferromagnet. Nesting brings a small feature in $\chi_0(\mathbf{q})$ and shifts x_{SDW} from 1 to a slightly smaller value.

$\mathrm{Im}[\chi(\mathbf{q},\omega)]$ in Pd is found to be strongly enhanced at small $\mathbf{q}$'s in complete agreement with the early studies [9]. Therefore, the method also confirms a closeness of Pd to the ferromagnetic instability.

In conclusion, the developed approach is able to describe known spin-fluctuational spectra of real materials which demonstrates its efficiency for practical *ab initio* calculations. Also, more elaborate approximations to the dynamical exchange and correlation are clearly required in order to account for the observed discrepancies.

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