Linear-response calculations of spin–fluctuations

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Spin–fluctuations influence many physical properties of solids, for instance the electronic specific heat and the electrical and thermal resistivities. Even for high–$\mathrm{T_c}$ superconductivity, spin–fluctuations seem to be the most important for the pairing. Central for the description of spin–fluctuations is the wavevector and frequency dependent linear spin–susceptibility, $\chi\left(\mathrm{q},\omega\right)$. Despite past efforts to develop methods for *ab initio* calculation of $\chi\left(\mathrm{q},\omega\right)$, quantitative estimates, employing realistic electronic energy bands and wavefunctions, as well as matrix elements of the self–consistently screened electron–electron interaction, have been rare. The major obstacle is undoubtedly the lack of a proper description of exchange–correlation effects. But the poor convergence of the standard perturbative treatment, which involves summation over high–energy states and matrix inversion, also poses a real hindrance.

I have developed and applied a method which circumvents the latter problem. This method is a time–dependent generalization of the Sternheimer approach that has been applied to static linear–response, density functional (DF) calculations for insulators and semiconductors by Baroni *et al.* [Phys. Rev. Lett. **58**, 1861 (1987)] and for metals, by myself. In the past, this static scheme was proven to be very efficient for *ab initio* calculations of phonon dispersions, electron–phonon interactions and phonon–related transport properties of crystals. The scheme presented here employs a basis set of muffin–tin orbitals and is therefore efficient also for systems containing *d* and *f* electrons.

Consider the situation in which a small, external, time–dependent magnetic field $\delta\mathbf{B}_{\mathrm{ext}}(\mathbf{r},\mathrm{t})$ is applied to the crystal. The response is the change of spin–density,

$$\delta\mathbf{m}(\mathbf{r},\mathrm{t}) \equiv \int \mathrm{d}^3\mathrm{r}' \int_{-\infty}^{\mathrm{t}} \mathrm{dt}'\chi\left(\mathbf{r},\mathbf{r}',\mathrm{t}-\mathrm{t}'\right)\,\delta\mathbf{B}_{\mathrm{ext}}(\mathbf{r}',\mathrm{t}'),$$

with $\chi(\mathbf{r},\mathbf{r}',\mathrm{t})$ being a tensor. In order to find $\delta\mathbf{m}(\mathbf{r},\mathrm{t})$, *time–dependent* density functional theory is used. The *un*perturbed charge and spin–densities, $\rho\left(\mathbf{r}\right)$ and $\mathbf{m}\left(\mathbf{r}\right)$, are described accurately by the conventional, static density functional theory and are expressed in terms of occupied Kohn–Sham orbitals, $\psi_{\mathrm{i}}\left(\mathbf{r}\right)$. With the time–dependent density functional Sternheimer approach, *no* knowledge of the real electronic excitations (energies and lifetimes) is required, but only the kernel $\mathrm{I_{xc}}(\mathbf{r},\mathbf{r}',\omega)$ describing dynamical exchange–correlation effects. Unfortunately, this is unknown and I have adopted the so–called adiabatic local density approximation (ALDA) and a generalized gradient approximation (GGA).

For time–dependent external fields the action, S, is considered a functional of $\rho(\mathbf{r},\mathrm{t})$ and $\mathrm{m}(\mathbf{r},\mathrm{t})$, and these functions are expressed in terms of the occupied Kohn–Sham spinors, $\vec{\psi}_{\mathrm{i}}\left(\mathbf{r},\mathrm{t}\right)$, which are solutions of the time–dependent Schrödinger equation. If the external field is small, the perturbed wavefunctions can be written as: $\vec{\psi}_{\mathrm{i}}\left(\mathbf{r}\right)\exp\left(-\varepsilon_{\mathrm{i}}\mathrm{t}\right)+\delta\vec{\psi}_{\mathrm{i}}\left(\mathbf{r},\mathrm{t}\right)$, where the first–order changes $\delta\vec{\psi}_{\mathrm{i}}\left(\mathbf{r},\mathrm{t}\right)$ define the induced charge and spin–densities:

$$\delta\rho = \sum_{\mathrm{i}} \{\delta\vec{\psi}_{\mathrm{i}}|\bar{\bar{1}}|\vec{\psi}_{\mathrm{i}}\} + \{\vec{\psi}_{\mathrm{i}}|\bar{\bar{1}}|\delta\vec{\psi}_{\mathrm{i}}\} \quad (1)$$

$$\delta\mathbf{m} = \mu_{\mathrm{B}} \sum_{\mathrm{i}} \{\delta\vec{\psi}_{\mathrm{i}}|\vec{\sigma}|\vec{\psi}_{\mathrm{i}}\} + \{\psi_{\mathrm{i}}|\vec{\sigma}|\delta\vec{\psi}_{\mathrm{i}}\}. \quad (2)$$

Here, $\{||\}$ denotes averaging over the spin–degrees of freedom only, $\bar{\bar{1}}$ is the unit 2×2 matrix and $\vec{\sigma}$ is the Pauli matrix. Since the ψ_{i} are known, computing $\delta\vec{\psi}_{\mathrm{i}}\,(\mathbf{r},\mathrm{t})$ solves the problem of determining $\delta\rho$ and $\delta\mathrm{m}$.

In order to do that, a *variational* linear response formulation is used. First, I derive a so–called 'time-dependent 2n + 1 theorem' which states that any (2n + 1)th–order change in the action functional involves only (n)th–order changes in $\vec{\psi}_{\mathrm{i}}\,(\mathbf{r},\mathrm{t})$ and the corresponding changes in the charge and spin–densities. Any $(2\mathrm{n})\mathrm{th}$–order change in S is therefore variational with respect to the nth–order changes in $\vec{\psi}_{\mathrm{i}}\,(\mathbf{r},\mathrm{t})$. The proof involves exploiting the stationarity property of S and standard time–dependent perturbation theory. Specifically, for n = 2 this theorem states that the second–order change, $\mathrm{S}^{(2)}$, of the action is *variational* with respect to the first–order changes $\delta\vec{\psi}_{\mathrm{i}}\,(\mathbf{r},\mathrm{t})$. Finally, $\mathrm{S}^{(2)}$ is directly related to $\mathrm{Re}\,\chi(\mathbf{q}+\mathbf{G}',\mathbf{q}+\mathbf{G},\omega)_{\mathbf{G}'=\mathbf{G}}$, and this allows a variational estimate of the latter.

The differential equation for $\delta\vec{\psi}_{\mathrm{i}}\,(\mathbf{r},\mathrm{t})$ is derived from the stationary property of $\mathrm{S}^{(2)}$ and is given by:

$$(\mathrm{H} - \mathrm{i}\frac{\partial}{\partial\mathrm{t}}\bar{\bar{1}})\,\delta\vec{\psi}_{\mathrm{i}} + (\delta\mathrm{V}_{\mathrm{eff}}\,\bar{\bar{1}} - \mu_{\mathrm{B}}\sigma\,\delta\mathbf{B}_{\mathrm{eff}})\,\vec{\psi}_{\mathrm{i}} = 0 \quad (3)$$

This is the time–dependent version of Sternheimer's equation, which itself is Schrödinger's equation to linear order in the perturbation. Equation (3) can easily be solved on the frequency axis, which substitutes $-\mathrm{i}\partial/\partial\mathrm{t}$ by $\epsilon_{\mathrm{i}} \pm \omega$. The solution of the whole problem assumes self–consistency: In the first iteration Eq. (3) is solved with $\delta\mathbf{B}_{\mathrm{eff}}$ being the external field $\delta\mathbf{B}_{\mathrm{ext}}$, and $\delta\rho(\mathbf{r},\omega)$ and $\delta\mathbf{m}(\mathbf{r},\omega)$ are found according to Eqs. (1) and (2). Then the screened fields, $\delta\mathrm{V}_{\mathrm{eff}}(\mathbf{r},\omega)$ and $\delta\mathbf{B}_{\mathrm{eff}}\,(\mathbf{r},\omega)$, are found. This cycle is finally repeated until self–consistency is reached. Finally, evaluation of $\mathrm{S}^{(2)}$ yields the variational estimate of the susceptibility.

The advantages of this method are: First, Eq. (3) does not require expansion of $\delta\vec{\psi}_{\mathrm{i}}$ over a complete set of unperturbed wavefunctions, $\vec{\psi}_{\mathrm{j}}$, as in standard perturbation theory, but only knowledge of the occupied and unoccupied states with energy below $\varepsilon_{\mathrm{F}} + \omega$. Second, the inversion is substituted by self–consistency iterations for $\delta\mathrm{V}_{\mathrm{eff}}$ and $\delta\mathbf{B}_{\mathrm{eff}}$.

Finally, to demonstrate the numerical efficiency of the method, spin–susceptibilities were calculated at zero temperature for the transition metal Fe. Figure 1 shows for ferromagnetic bcc Fe the calculated transverse spin–susceptibility, $\mathrm{Im}\,\chi_{+-}(\mathbf{q},\omega)_{\,\mathbf{G}'=\mathbf{G}=0}$, for $\mathbf{q} = (0,0,\mathrm{x})\,\frac{2\pi}{\mathrm{a}}$. At small $\mathbf{q}$,

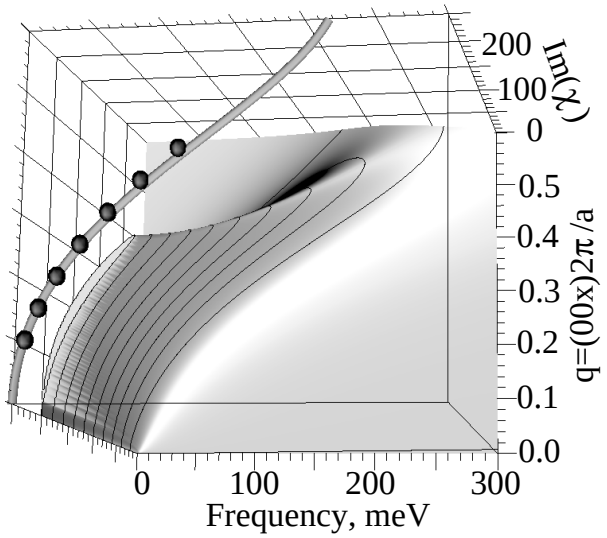

Figure 1: *Calculated $Im\,\chi_{+-}(\mathbf{q},\omega)$ (arb. units) for ferromagnetic bcc Fe at zero temperature. The experimental data are indicated by balls, the calculated magnon spectrum by the grey curve.*

the nondecaying spin–waves are seen to persist in the structure of $\mathrm{Im}\,\chi$ exhibiting a standard dispersion law: $\omega(\mathrm{q}) = \mathrm{Dq}^2$, where D is the spin–wave stiffness. The spin–waves rapidly decay when q exceeds approximately $\frac{\pi}{\mathrm{a}}$. A similar picture has been found for **q** along the (111)–direction. The deduced magnon spectrum (line) is shown at the top of the figure. It agrees well with experiment. Moreover, in contrast with earlier model calculations [J.F. Cooke, Phys. Rev. **B7**, 1108 (1973)] based on the random phase approximation, no structure is found ressembling optical spin–wave branches, in agreement with current experiments [L.W. Lynn, Phys. Rev. **B11**, 2624 (1975); C.-K. Loong *et al.*, J. Appl. Phys. **55**, 1895 (1984)].