Lifetimes of Excited Electrons In Fe And Ni: First-Principles GW and the *T*-Matrix Theory

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We present the results of an *ab initio* calculation of excited electron lifetimes in ferromagnetic materials which incorporates non-spin-flip and spin-flip processes within GW and *T*-matrix approaches. The method we develop is applied to low-energy electron excitations in Fe and Ni. It is found that the spin-wave generation in Fe essentially reduces the lifetimes of the spin-minority *d* states whereas the free-electron-like spin-minority states and all the spin-majority states are affected much less. The influence of spin-flip scattering on the lifetimes in Ni appears to be weak. The *T*-matrix non-spin-flip processes are important for the lifetimes of excited spin-minority states.

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In spite of many studies [1–3] our present understanding of electron dynamics in ferromagnetic materials is far from being perfect. The relaxation times of excited electrons can be measured by inverse photoemission, two-photon photoemission, and by scanning tunneling techniques [4–7]. They are influenced by many processes, such as defect scattering, cascade electrons generation, transport effects, etc. [7], which are not sufficiently well studied. It is well understood that the most important contribution to the relaxation times, the so-called lifetime, is provided by inelastic electron-electron scattering. In ferromagnetic materials the lifetime, being spin dependent [2,7], characterizes the ability of electrons to transfer the spin and is important for transport and spin accumulation phenomena [8–10].

On the theoretical side, a number of methods to evaluate lifetimes has been proposed. Some of these methods employ model Hamiltonians with adjustable parameters [11]. *Ab initio* calculations of lifetimes have been performed mainly within the GW approximation (GWA) [12]. The GWA is fairly good for systems with long-range screening, whereas it fails to describe short-range interactions in strongly correlated systems. In order to improve the description of optical spectra in strongly correlated systems, several model and *ab initio* approaches based on the *T*-matrix theory have been developed [13,14]. In Ref. [15] a formalism for calculating *ab initio* magnetic response functions has been developed and successfully applied to the study of spin-wave spectra in Fe and Ni.

In this Letter we extend the formalism of Aryasetiawan and Karlsson in order to evaluate electron lifetimes in ferromagnetic materials. Our calculations take into account spin-flip scattering processes neglected in the GWA. The results for Fe and Ni show that Stoner's excitations and spin waves are important channels in the decay processes.

In the framework of many-body theory [16], electron lifetimes are obtained from the imaginary part of the electron self-energy. Within the GWA the self-energy Σ is calculated retaining the first term in the series expansion of Σ in terms of the spin-independent screened Coulomb potential W,

$$\Sigma_\sigma(1,2) = iG_\sigma(1,2)W(1,2), \tag{1}$$

where G_σ is a one-electron Green function with spin σ and $1 \equiv (\mathbf{r}_1, t_1)$. So the self-energy of an excited electron with spin σ is determined by the Green function with the same spin and therefore does not include spin-flip processes. *T*-matrix theory [16] permits us to perform a summation of the higher order self-energy terms shown in Fig. 1. In its complete form it includes direct terms of multiple electron-electron interactions (B), direct terms of electron-hole interactions (C), and exchange terms (D).

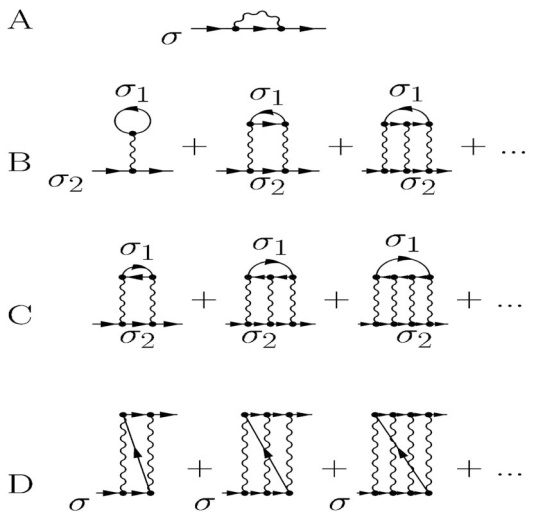

FIG. 1. Feynman diagrams for GW and *T*-matrix self-energy terms of perturbation theory. A: GW term; B: *T*-matrix direct terms for electron-electron interactions; C: *T*-matrix direct terms for electron-hole interactions; D: *T*-matrix exchange terms. The wiggly line represents the screened potential W, and the line with the arrow is the Green function G.

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Green functions of the polarization bubbles may have a spin equal or opposite to the one of an excited electron and thus the T-matrix theory incorporates spin-flip processes.

The terms B with $\sigma_1 = -\sigma_2$ are determined by the convolution of the spin-up and spin-down empty states. In Fe and Ni this convolution is much smaller than the convolution of empty and occupied states that determines the terms C. It is plausible therefore to omit the smaller B terms with $\sigma_1 = -\sigma_2$. One can also show that within the approximations discussed below the contribution of diagrams B with $\sigma_1 = \sigma_2$ cancels the exchange terms D. Thus we treat only direct terms C with multiple electron-hole interactions. In this case the T-matrix operator is defined as the solution of the Bethe-Salpeter equation

$$T_{\sigma_1,\sigma_2}(1,2|3,4) = W(1,2)\delta(1-3)\delta(2-4) + W(1,2)\int d1'd2' K_{\sigma_1,\sigma_2}(1,2 \mid 1',2') \times T_{\sigma_1,\sigma_2}(1',2' \mid 3,4). \quad (2)$$

Here kernel K is a product of particle and hole Green functions

$$K_{\sigma_1,\sigma_2}(1,2 \mid 1',2') = iG^h_{\sigma_1}(1,1')G^e_{\sigma_2}(2',2). \quad (3)$$

The sum of direct self-energy terms is expressed as

$$\Sigma^d_{\sigma_2}(4,2) = -i\sum_{\sigma_1}\int d1d3 G^e_{\sigma_1}(3,1)T_{\sigma_2,\sigma_1}(1,2|3,4). \quad (4)$$

In order to make computations feasible we use the static approximation $W(1,2) = W(\mathbf{r}_1,\mathbf{r}_2)\delta(t_1 - t_2)$ for the screened potential as well as the static and local approximation, $1 = 2, 3 = 4$, for the T-matrix operator. The validity of such approximations is confirmed by successful calculations of spin-wave energies in Fe and Ni [14]. We calculate first the spectral function of the kernel

$$S_{\sigma_1,\sigma_2}(1,2,\omega) = \sum_{\mathbf{k}n}^{\text{occ}}\sum_{\mathbf{k}'n'}^{\text{unocc}} \{\psi_{\mathbf{k}'n'\sigma_1}(1)\psi^*_{\mathbf{k}'n'\sigma_1}(2)\psi_{\mathbf{k}n\sigma_2}(2) \times \psi^*_{\mathbf{k}n\sigma_2}(1)\delta(\omega + \epsilon_{\mathbf{k}n\sigma_2} - \epsilon_{\mathbf{k}'n'\sigma_1}) - \psi_{\mathbf{k}n\sigma_1}(1)\psi^*_{\mathbf{k}n\sigma_1}(2)\psi_{\mathbf{k}'n'\sigma_2}(2)\psi^*_{\mathbf{k}'n'\sigma_2}(1) \times \delta(\omega + \epsilon_{\mathbf{k}'n'\sigma_2} - \epsilon_{\mathbf{k}n\sigma_1})\} \quad (5)$$

by using eigenfunctions and eigenvalues obtained from linear muffin-tin orbital (LMTO) band-structure calculations [17]. The whole kernel is then derived through the Hilbert transform

$$-K_{\sigma_1,\sigma_2}(1,2,\omega) = \mathcal{P}\int d\omega' \frac{S_{\sigma_1,\sigma_2}(1,2,\omega')}{(\omega - \omega')} - i\pi S_{\sigma_1,\sigma_2}(1,2,\omega)\text{sgn}(\omega). \quad (6)$$

Using the frequency representation for G and T the imaginary part of the direct T-matrix self-energy term can be written as

$$\text{Im}\Sigma^d_{\sigma_2}(4,2,\omega > \mu) = -\sum_{\sigma_1}\sum_{\mathbf{k}}\sum_{n'}^{\text{unocc}}\int d^3r_1 d^3r_3 \psi_{\mathbf{k}n'\sigma_1}(3) \times \psi^*_{\mathbf{k}n'\sigma_1}(1) \times \text{Im}T_{\sigma_2,\sigma_1}(1,2 \mid 3,4,\omega - \epsilon_{\mathbf{k}n'\sigma_1}) \times \theta(\omega - \epsilon_{\mathbf{k}n'\sigma_1}) \quad (7)$$

and

$$\text{Im}\Sigma^d_{\sigma_2}(4,2,\omega < \mu) = \sum_{\sigma_1}\sum_{\mathbf{k}}\sum_{n}^{\text{occ}}\int d^3r_1 d^3r_3 \psi_{\mathbf{k}n\sigma_1}(3) \times \psi^*_{\mathbf{k}n\sigma_1}(1) \times \text{Im}T_{\sigma_2,\sigma_1}(1,2 \mid 3,4,\omega - \epsilon_{\mathbf{k}n\sigma_1}) \times \theta(\epsilon_{\mathbf{k}n\sigma_1} - \omega). \quad (8)$$

The real part of Σ^d is also calculated through the Hilbert transform. We add together the GWA and T-matrix components of self-energy (GW + T) and solve the Dyson equation for the complex quasiparticle energy $E_{\mathbf{q}n\sigma}(\omega)$,

$$E_{\mathbf{q}n\sigma}(\omega) = \epsilon_{\mathbf{q}n\sigma} + \langle\psi_{\mathbf{q}n\sigma} \mid \Delta\Sigma_\sigma(\omega) \mid \psi_{\mathbf{q}n\sigma}\rangle. \quad (9)$$

Here $\Delta\Sigma_\sigma(\omega) = \Sigma_\sigma(\omega) - V^{xc}_\sigma(\text{LSDA})$, with $V^{xc}_\sigma(\text{LSDA})$ being the local spin density approximation (LSDA) exchange-correlation potential, provides many-body corrections to the LSDA eigenvalues $\Delta\epsilon_{\mathbf{q}n\sigma} = E_{\mathbf{q}n\sigma} - \epsilon_{\mathbf{q}n\sigma}$. We solve the equation by employing the renormalization factor Z [16]. Finally, the inverse of the quasiparticle lifetime, $\tau^{-1}_{\mathbf{q}n\sigma}$, (linewidth, Γ) is given by

$$\tau^{-1}_{\mathbf{q}n\sigma} = \Gamma = 2 \times |\text{Im}\Delta\epsilon_{\mathbf{q}n\sigma}|. \quad (10)$$

As discussed in Ref. [14], in the case of electron-electron multiple scattering the direct second-order term of the T-matrix self-energy (the so-called "double-counting term") has to be removed, because it has already been included in GWA; however, it is small and can be neglected. We find that in the case of electron-hole multiple scattering the calculated double-counting term is also small; therefore, in the present discussions we omit it, too. We perform the many-body calculations by using LMTO product orbitals [17]. The screened potential W is evaluated within the random phase approximation; for details, see Ref. [18].

Within the adopted approach the contribution of non-spin-flip processes to the inverse lifetimes is described by the GW term and by the T-matrix term with $\sigma_1 = \sigma_2$, whereas the spin-flip contributions follow from the T-matrix term with $\sigma_1 \neq \sigma_2$. The spin-flip part of the inverse lifetime for an excited electron in the state $\psi_{\mathbf{q}i\sigma}$ is determined by the unoccupied states $\psi_{\mathbf{k}n'-\sigma}$ with lower energy and opposite spin and by the transition probabilities between the $\psi_{\mathbf{q}i\sigma}$ and the $\psi_{\mathbf{k}n'-\sigma}$ states weighted by

$\mathrm{Im}T_{\sigma,-\sigma}(\omega)$ at energy $\omega = \epsilon_{\mathbf{q}i\sigma} - \epsilon_{\mathbf{k}n'-\sigma}$. Schematically, the decay of electrons with a spin σ is determined by

$$\mathrm{Im}T_{\sigma,-\sigma}(\omega) = \mathrm{Im}[1 - WK_{\sigma,-\sigma}(\omega)]^{-1} \times W. \quad (11)$$

If we use the transverse susceptibility

$$R_{\sigma,-\sigma}(\omega) = K_{\sigma,-\sigma}(\omega)[1 - WK_{\sigma,-\sigma}(\omega)]^{-1}, \quad (12)$$

then

$$\mathrm{Im}T_{\sigma,-\sigma}(\omega) = W \times \mathrm{Im}R_{\sigma,-\sigma}(\omega) \times W, \quad (13)$$

where

$$\mathrm{Im}R_{\sigma,-\sigma}(\omega) = \mathrm{Im}K_{\sigma,-\sigma}(\omega)1/\{[1 - W\mathrm{Re}K_{\sigma,-\sigma}(\omega)]^2 + [W\mathrm{Im}K_{-\sigma,\sigma}(\omega)]^2\} \quad (14)$$

is the spin-wave excitation spectra. Here, instead of a frequency-dependent potential W used in the GWA self-energy, in the T-matrix theory we use a static potential scaled with the energy distribution of magnon states.

In Fig. 2 we show the calculated spin-projected densities of states as well as the GWA and GW + T momentum-averaged inverse lifetimes Γ for Fe. For the spin-majority excited electrons in Fe the contributions of both-spin-flip and non-spin-flip terms of the T matrix to inverse lifetimes appear to be small. In this case $\mathrm{Im}K_{1/2,-1/2}$ results mostly from $3d(\sigma = -1/2) \rightarrow 4p(\sigma = 1/2)$ transitions which accompany the deexcitations of spin-majority electrons. Because of the small density of $4p_{1/2}$ states this value is small at all energies. The corresponding $\mathrm{Re}K$ is also small, and $1 - W\mathrm{Re}K$ is far from zero that results in small values of the $\mathrm{Im}R_{1/2,-1/2}$ function and in small contributions of spin-flip processes to the lifetimes. Small contributions from the T-matrix non-spin-flip term are explained in a similar way, by small values of the $\mathrm{Im}K_{1/2,1/2}$ function.

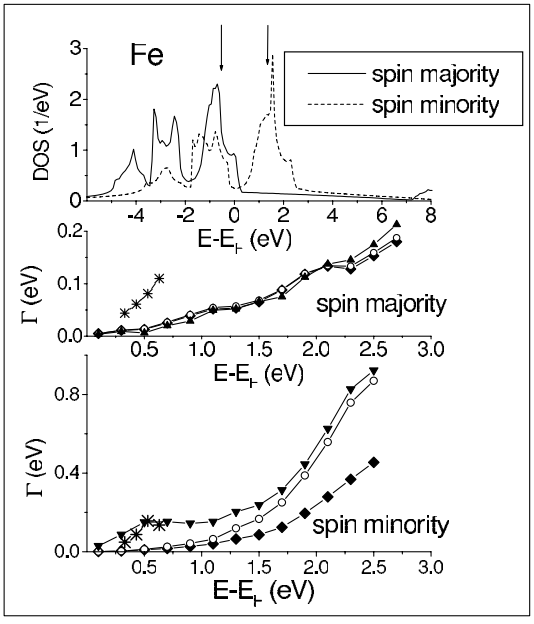

FIG. 2. The calculated and experimental inverse lifetimes of excited electrons in Fe. The solid diamonds show the GW contribution to Γ, the open circles show GW + T non-spin-flip contribution, and the black triangles show complete GW + T (non-spin-flip + spin-flip) Γ values. The stars show the experimental inverse lifetimes of Ref. [11].

For the spin-minority electrons both the spin-flip and non-spin-flip contributions of the T matrix to $\mathrm{Im}\Sigma$ are important. The function $\mathrm{Im}K_{-1/2,1/2}$ of the spin-flip processes has a peak at a frequency about 2 eV which results from the $3d(\sigma = 1/2) \rightarrow 3d(\sigma = -1/2)$ transitions between the exchange-split bands marked by arrows in Fig. 2. So $\mathrm{Re}K_{-1/2,1/2}$, is sufficiently large to make the value $1 - WK$ close to zero for frequencies between 0 and 0.6 eV. Therefore $\mathrm{Im}R_{-1/2,1/2}$ contains in this energy range peaks related to spin-wave excitations. At higher energy it has shoulders related to Stoner's transitions which extend up to an energy of about 3 eV. So at excitation energies from 0 up to 0.6 eV the spin-flip T-matrix term essentially contributes to $\mathrm{Im}\Sigma_{-1/2}$; then its contribution decreases and becomes small at energies ≥ 3 eV. Non-spin-flip processes become important for electron energies ≥ 1.5 eV. For smaller energies the spectral function $\mathrm{Im}K_{-1/2,-1/2}$ is small because of the very low density of minority states at E_F.

In Ni (Fig. 3), similar effects as in Fe prevent any essential T-matrix contribution to the self-energy for spin-majority excited states. For spin-minority states, the energy dependence of $\mathrm{Im}R_{-1/2,1/2}$ has also peaks related to spin-wave generation. However, due to a small

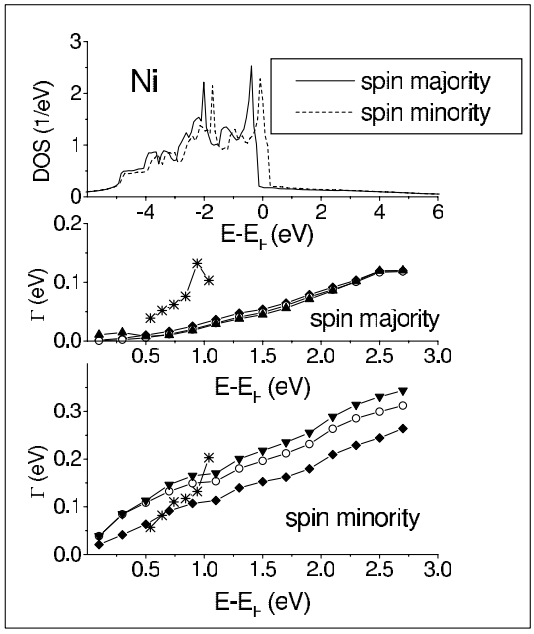

FIG. 3. The calculated and experimental [11] inverse lifetimes of excited electrons in Ni. Notations are as in Fig. 2.

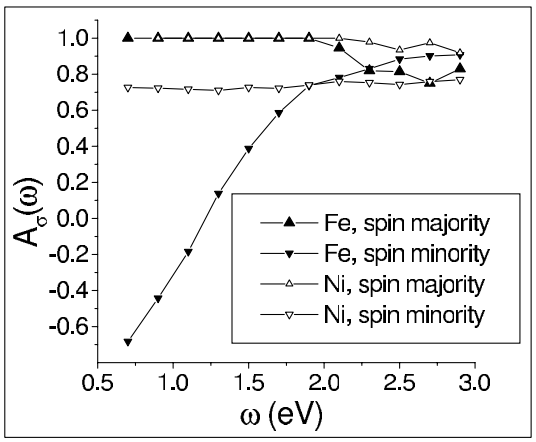

FIG. 4. The calculated spin asymmetry of excited electron decay in Fe and Ni.

exchange splitting, $\simeq 0.3$ eV, ImK and consequently ImR is about 1 order of magnitude smaller than in Fe, so the spin-flip contribution is insignificant. The non-spin-flip contributions to $\mathrm{Im}\Sigma_{-1/2}$ are larger by factor of 2 than the spin-flip ones.

The role of spin-flip and non-spin-flip channels in the electron decay processes can be clearly seen from an asymmetry function which we define as

$$A_\sigma(\omega) = \frac{|\mathrm{Im}\Delta\Sigma_\sigma^{\mathrm{nsf}}(\omega)| - |\mathrm{Im}\Delta\Sigma_\sigma^{\mathrm{sf}}(\omega)|}{|\mathrm{Im}\Delta\Sigma_\sigma^{\mathrm{nsf}}(\omega)| + |\mathrm{Im}\Delta\Sigma_\sigma^{\mathrm{sf}}(\omega)|}. \qquad (15)$$

Here we write nsf and sf for the non-spin-flip and spin-flip contributions, respectively. As follows from Fig. 4, both spin-majority and spin-minority excited states in Ni and spin-majority excited states in Fe decay preferably without change of a spin. With the decrease of the excitation energy the probability of spin-flip decay of excited spin-minority states in Fe strongly increases. At energy around 1.2 eV, when $A = 0$, the probability of decay into both spin channels is equal, and at energies below 0.7 eV, due to spin-wave generations, more than 80% of the decay occurs with change of a spin.

Our conclusion regarding a very small contribution of the spin-flip processes to the self-energy of spin-majority states in Fe and Ni is in agreement with previous estimations based on a Hubbard model [19]. However, in Ref. [19] the spin-flip contribution to ImΣ for spin-minority states in Fe permanently increases with the increase of excitation energy. This result agrees neither with the frequency change of ImR nor with our results on ImΣ. We also find that the evaluations of Ref. [19] overestimate the spin-flip contributions to the self-energy of spin-minority states in Ni. So the decay of quasiparticles in Fe and Ni seems to be a case where first-principle calculations with the inclusion of all the necessary transition probabilities in the GW and T-matrix terms are important.

Comparing our calculated Γ values with the experimental data of Ref. [7] we see that for the spin-minority states in Fe the inclusion of spin-flip processes improves the agreement between theory and experiment. The theoretical Γ values for spin-majority states in Fe and Ni still remain lower than the experimental data. This is consistent with the fact that the experimental data of Ref. [11] include the effects of transport, electron-impurity, and electron-phonon scattering. Similarly, our calculated inverse lifetimes are smaller than those obtained from inverse photoemission experiments [1] (0.9 eV for the state P_3, 1.0 eV for Γ_{12} and 0.9 eV for H'_{25} at the excitation energy about 2eV). This can also be attributed to electron-phonon and electron-impurity scattering which is intrinsically included in the experimental data [1]. Further experimental work is necessary to throw light on this issue.

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