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Time-resolved Dyson equations in the context of time-dependent density-functional theory: Extension to solid systems

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It is shown that under certain conditions an instantaneous resolvent $G(z;t)$ of a time-dependent Kohn-Sham or Kohn-Sham-Dirac operator $\mathcal{H}(t)$ can be defined from which the particle and the magnetization density can be evaluated directly using contour integrations. The corresponding Green's function can be evaluated within a multiple-scattering scheme by solving at each given time t coupled radial differential equations for the single-site problem. This scheme is in particular intriguing since within the adiabatic time-dependent density functional the configurational part of a time-dependent perturbation can be viewed as a contribution to an effective (full) potential. First applications are shown for an Fe atom excited by a femtosecond laser pulse.

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I. INTRODUCTION

Although the concept of time-dependent density functional (TDDFT) was introduced already about 20 years ago (see, e.g., the review article by Marques and Gross[1]) no practicable schemes for magnetic solid systems that can be generalized fully relativistically—not even in the so-called adiabatic local density approximation (ALDA)—was designed up to now. The reason for this regrettable fact, however, is very easy to see: most formulations up to now were based on either derivations from (*nonrelativistic*) exact many-body wave functions for a limited number of particles permitting one, e.g., the use of Slater determinants[2] in order to arrive eventually at time-dependent Kohn-Sham-type (TDKS) equations, or such formulations made use in other ways of discrete spectral properties of the initial (ground) state Hamiltonian (evolution operator techniques). It is of course prohibitive to even think about the use of Slater determinants for solid systems. Even for an initial state Hamiltonian with a three-dimensional Bloch periodic spectrum such an attempt would be extremely clumsy when trying to follow spin-polarized Kohn-Sham orbitals for quite a few $\vec{k}$ vectors and a limited number of bands. Of course there had been attempts to apply TDDFT to three-dimensional periodic solids in particular by making use of the GW scheme. Botti *et al.*[3] for example calculated the real and the imaginary parts of the dielectric function for a few semiconducting systems such as Si or Ge for which the use of pseudopotential schemes is most suited. Other attempts were mainly concerned about analytically solvable models by comparing TDDFT to approaches based on the Bethe-Salpeter equation[4] or discussing particular aspects of the GW approach in terms of simple models.[5] However, once it comes to consider semi-infinite systems with only two-dimensional Bloch periodicity, i.e., solids with surfaces or interfaces, most up-to-now-introduced techniques[6] are no longer useful or well defined.

In the present paper an approach is introduced that facilitates not only the description of solid systems with surfaces, but that also can be generalized (fully) relativistically. This approach is in particular designed to evaluate directly spin currents and spin transfer torques defined in relativistic quantum mechanics when considering the time-dependent Dirac equation in the presence of an external electromagnetic field.[7] Although this sounds a bit academic, it is not: having in mind current-induced magnetization switching or domain wall motions, a field of enormous technological interest is addressed in which only phenomenological methods or *ad hoc* approaches are presently customary. Considering that relevant switching times are of the order of picoseconds to nanoseconds and that already very short (nearly rectangular) electric-field pulses can move domain walls with macroscopic speeds at least attempts have to be made to cope with all these new experimental findings.

Clearly enough the formal basis of TDDFT (still) relies on the so-called Runge-Gross theorem,[8] which makes use of the stationary properties of the action integral

$$A(t_1) = \int_{t_0}^{t_1} \Phi(t)dt, \quad \Phi(t) = \langle \psi(t) | i\hbar \frac{\partial}{\partial t} - \mathcal{H}(t) | \psi(t) \rangle, \quad (1)$$

with t_0 referring to the initial state and $\Phi(t)$ being a functional of $\psi(t)$. This theorem states that "the exact time-dependent density of a system" can be obtained as

$$n(\mathbf{r},t) = \sum_{i=1}^{N} \varphi_i^*(\mathbf{r},t)\varphi_i(\mathbf{r},t), \quad (2)$$

where the "single-particle orbitals" fulfill (in the nonmagnetic case) a time-dependent Schrödinger equation of the type

$$\left(i\hbar\frac{\partial}{\partial t}-\mathcal{H}_{\text{eff}}(\mathbf{r},t)\right)\varphi_i(\mathbf{r},t)=0, \tag{3}$$

$$\mathcal{H}_{\text{eff}}(\mathbf{r},t)=T+V_{\text{eff}}\{\mathbf{r},t;[n(\mathbf{r},t)]\} \tag{4}$$

for an effective potential $V_{\text{eff}}\{\mathbf{r},t;[n(\mathbf{r},t)]\}=V_{\text{ext}}(\mathbf{r},t)+V_H\{\mathbf{r},t;[n(\mathbf{r},t)]\}+V_{\text{xc}}\{\mathbf{r},t;[n(\mathbf{r},t)]\}$ and with T being the (single-particle) kinetic-energy operator. Later on the action integral in Eq. (1) was generalized by van Leeuwen[9] by introducing a Keldysh[10] pseudotime and making use of contour integrations over the time variable. Both descriptions require solving a time-dependent Schrödinger equation repeatedly for each orbital in turn and, furthermore, require the number of orbitals N in Eq. (2) to be finite.

Since the aim of this paper is to partially use the concepts of TDDFT to solid systems and in particular to consider relativistic initial state Hamiltonians with a discrete and a continuous spectrum rather than indulging in the subtleties of Green's functions in space and time, in the following the simplest possible approximation for the exchange-correlation potential $V_{\text{xc}}\{\mathbf{r},t;[n(\mathbf{r},t),\mathbf{m}(\mathbf{r};t)]\}$ and effective exchange field $\mathbf{B}\{\mathbf{r},t;[n(\mathbf{r},t),\mathbf{m}(\mathbf{r};t)]\}$, $\mathbf{m}(\mathbf{r};t)$ being the magnetization density, of an in-general magnetic system, namely, ALDA,

$$V_{\text{xc}}\{\mathbf{r},t;[n(\mathbf{r},t),\mathbf{m}(\mathbf{r};t)]\}=\frac{\delta E_{\text{xc}}[n(\mathbf{r};t),\mathbf{m}(\mathbf{r};t)]}{\delta n(\mathbf{r};t)}, \tag{5}$$

$$\mathbf{B}\{\mathbf{r},t;[n(\mathbf{r},t),\mathbf{m}(\mathbf{r};t)]\}=\frac{e\hbar}{2mc}\frac{\delta E_{\text{xc}}[n(\mathbf{r};t),\mathbf{m}(\mathbf{r};t)]}{\delta\mathbf{m}(\mathbf{r};t)}, \tag{6}$$

will be assumed, which is local both in space and time.[6] Furthermore, we will require that the system returns to the ground state after a certain period of time. Such a requirement has to be taken into account for a time-dependent process such as current-induced switching or current-driven domain wall motions in order to be turned eventually into technologically useful phenomena.

In the following sections first the concepts of time-dependent resolvents and Dyson equations and corresponding expressions for the particle and magnetization density are given. Only after these more formal sections a numerical concept, namely, instantaneous multiple-scattering theory, is presented in order to evaluate directly $n(\mathbf{r},t)$ and $\mathbf{m}(\mathbf{r};t)$ for a given time-dependent process starting from a well-defined ground state. Finally, in order to test and illustrate the proposed scheme for the evaluation of instantaneous single-site t matrices occurring in the expression for the Green's function, the simplest possible case, namely, a magnetic atom, is considered for which a direct comparison with Schrödinger's first-order time-dependent perturbation theory can readily be made. As will be shown even this simple example carries somewhat new features, not only because the description is based on a Kohn-Sham-Dirac Hamiltonian, but also since almost textbook-like illustrations can be generated.

II. TIME-DEPENDENT RESOLVENT

Suppose that in Eqs. (3) and (4) $\mathcal{H}(t)\equiv\mathcal{H}_{\text{eff}}(\mathbf{r},t)$ is defined as

$$\mathcal{H}(t)=\begin{cases}\mathcal{H}_0+\mathcal{W}(t), & t\geq t_0\\ \mathcal{H}_0, & t<t_0\end{cases}, \tag{7}$$

and that the following (time-independent) initial eigenvalue equation applies

$$\mathcal{H}(t_0)\psi(t_0)=\mathcal{H}_0\psi(t_0)=E(t_0)\psi(t_0). \tag{8}$$

By introducing the resolvent of $\mathcal{H}(t)$ with t as a parameter,

$$G(z;t)=[z-\mathcal{H}(t)]^{-1}, \tag{9}$$

into the expression for the evolution operator corresponding to infinitesimal time steps (for details, see Appendix),

$$U(t,t_0)=\frac{1}{2\pi i}\oint_{C_-\cup C_+}dz\,\exp\left[-\frac{i}{\hbar}z(t-t_0)\right]G(z;t_0), \tag{10}$$

from Cauchy's residue theorem immediately follows that

$$U(t,t_0)=\exp\left[-\frac{i}{\hbar}\mathcal{H}(t_0)(t-t_0)\right], \tag{11}$$

which in turn is identical to

$$U(t,t_0)=\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t}dt'\mathcal{H}(t')\right], \tag{12}$$

if and only if

$$\int_{t_0}^{t}dt'\mathcal{W}(t')\simeq\mathcal{W}(t_0)(t-t_0). \tag{13}$$

In particular from Eq. (11) follows that $U(t_0,t_0)=1$ and that for an infinitesimal time step dt the evolution operator is of the form

$$U(t,t_0)\equiv U(t_0+dt,t_0)=1-\frac{i}{\hbar}\mathcal{H}(t_0)dt. \tag{14}$$

Clearly enough for practical use of Eq. (13) the infinitesimal time step dt has to be replaced by a finite difference δt, i.e., in the following time derivatives will be defined over a set of sufficiently dense points.

III. TIME-EVOLUTION OF DENSITIES

The use of resolvents [see Eq. (9)] is in particular useful since they are analytic in the complex plane and, therefore, so-called contour integrations can be applied instead of cumbersome summations over states as used in Eq. (2). Usually only about 12–16 complex energy points are sufficient along a suitable contour to ensure sufficient accuracy.

As is well known in terms of Green's functions the valence-band particle density of a solid system, at $t=t_0$, is simply given for the initial state by[11]

$$n(\mathbf{r};t_0)=-\pi^{-1}\,\text{Im Tr}\int_{E_b}^{E_F(t_0)}\langle\mathbf{r}|G(z;t_0)|\mathbf{r}\rangle dz, \tag{15}$$

where E_b denotes the band bottom[12] and $E_F(t_0)$ is the Fermi energy of the equilibrium system. Similarly, assuming that the time evolution of the system can be described by the instantaneous eigenvalue problem,

$$\mathcal{H}(t)\psi(t) = E(t)\psi(t), \tag{16}$$

by using $G(z;t)$ [see Eq. (9)] the density $n(\mathbf{r};t)$ at a given time t can be defined in terms of the following (contour) integration:

$$n(\mathbf{r};t) = -\pi^{-1}\,\mathrm{Im\,Tr}\int_{E_b}^{E_F(t)} \langle \mathbf{r}|G(z;t)|\mathbf{r}\rangle dz, \tag{17}$$

where $E_F(t)$ is now a "fictitious" Fermi energy at t determined such that the below condition for a constant number of particles applies.

Suppose that at t_0 (well-defined initial state) the number of particles is N_0. The condition for a constant number of particles (one of the requirements of density-functional theory) then implies that

$$N(t) = N_0, \qquad \forall\, t, \tag{18}$$

with $N(t)$ being defined in terms of $n(\mathbf{r};t)$ [see Eq. (17)] as

$$N(t) = \int_\Omega n(\mathbf{r};t)d\mathbf{r}. \tag{19}$$

Suppose further that at a particular t this condition was already fulfilled by closing the contour at a properly adjusted upper integral boundary $E_F(t)$, then correspondingly at $t' = t + \Delta t$ the contour has to be closed at $E_F(t')$,

$$N(t') = -\pi^{-1}\int_\Omega \mathrm{Im\,Tr}\int_{E_b}^{E_F(t')} \langle \mathbf{r}|G(z;t')|\mathbf{r}\rangle dz d\mathbf{r}, \tag{20}$$

such that Eq. (18) is met, i.e., $N(t') - N(t) = 0$. From fulfilling the condition in Eq. (18) it follows immediately that the time evolution of the particle density maintaining a constant number of particles is given by

$$\frac{\delta n(\mathbf{r};t)}{\delta t} \simeq -\pi^{-1}\left\{\mathrm{Im\,Tr}\int_{E_b}^{E_F(t)} \langle \mathbf{r}|\frac{\delta G(z;t)}{\delta t}|\mathbf{r}\rangle dz + \frac{\delta E_F(t)}{\delta t}\mathrm{Im\,Tr}\langle \mathbf{r}|G(E_F(t);t)|\mathbf{r}\rangle\right\}. \tag{21}$$

The time evolution of the magnetization density can easily be obtained from the below definition,

$$\mathbf{m}(\mathbf{r};t) = -\pi^{-1}\,\mathrm{Im\,Tr}\int_{E_b}^{E_F(t)} \langle \mathbf{r}|\mathbf{S}G(z;t)|\mathbf{r}\rangle dz, \tag{22}$$

where $\mathbf{S} = \boldsymbol{\sigma}$ in the nonrelativistic case and $\beta\boldsymbol{\Sigma}$ in the case of a relativistic description,

$$\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z), \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \quad \boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}, \tag{23}$$

with I_n being a n-dimensional unit matrix and Tr denoting the trace in spin space. Imposing particle conservation, this implies

$$\frac{\delta \mathbf{m}(\mathbf{r};t)}{\delta t} \simeq -\pi^{-1}\left\{\mathrm{Im\,Tr}\int_{E_b}^{E_F(t)} \langle \mathbf{r}|\mathbf{S}\frac{\delta G(z;t)}{\delta t}|\mathbf{r}\rangle dz + \frac{\delta E_F(t)}{\delta t}\mathrm{Im\,Tr}\langle \mathbf{r}|\mathbf{S}G(E_F(t);t)|\mathbf{r}\rangle\right\}. \tag{24}$$

From Eqs. (21) and (24) it is obvious that the time evolution of any other density such as of the polarization and the spin density[7] can be evaluated in the same manner. It should be noted that by making use of Eqs. (17) and (22) directly the particle and magnetization density is available.

As easily can be shown from Eq. (13) also a time-dependent (instantaneous) multiple-scattering theory can be formulated starting from a time-independent resolvent $G^{(0)}(z)$ that corresponds to a given (time-independent) reference Hamiltonian H_0,

$$\mathcal{H}(t) = \mathcal{H}_0 + V + \mathcal{W}(t), \quad G_0(z) = (z - \mathcal{H}_0)^{-1}. \tag{25}$$

The realization of such an approach in terms of the Korringa-Kohn-Rostoker (KKR) method shall be sketched in the following section.

IV. TIME-DEPENDENT KORRINGA-KOHN-ROSTOKER SCHEME

Let a time-dependent Kohn-Sham-Hamiltonian be defined as

$$\mathcal{H}(\mathbf{r};t) = \mathcal{H}^{(0)}(\mathbf{r}) + \mathcal{W}(\mathbf{r};t), \tag{26}$$

where for matters of generality $\mathcal{H}^{(0)}(\mathbf{r})$ is of Dirac-type,

$$\mathcal{H}^{(0)}(\mathbf{r}) = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 + V(\mathbf{r})I_4 + \beta\boldsymbol{\Sigma}\cdot\mathbf{B}(\mathbf{r}), \tag{27}$$

and $\mathcal{W}(\mathbf{r};t)$ is of the form

$$\mathcal{W}(\mathbf{r};t) = \sum_{\Lambda>0} W_\Lambda(r;t)Y_\Lambda(\hat{\mathbf{r}}), \quad \Lambda = (l,m), \tag{28}$$

such as, e.g., for an interaction with a laser pulse in the dipole approximation, see also Appendix and in there in particular Eq. (64),

$$\mathcal{W}(\mathbf{r};t) = e\mathcal{E}_0\mathcal{E}(t)\cos(\omega_0 t)(\mathbf{r}\cdot\mathbf{e}) = eE(t)|\mathbf{r}|[Y_{11}(\hat{\mathbf{r}})e_x + Y_{1-1}(\hat{\mathbf{r}})e_y + Y_{10}(\hat{\mathbf{r}})e_z], \tag{29}$$

with e being the elementary charge, $\mathcal{E}_0$ being a real amplitude, $\mathcal{E}(t)$ being a real envelope function, ω_0 being the carrier frequency, and $\mathbf{e}$ being the polarization unit vector. In viewing the last equation it is obvious that at a given time t the term $E(t) = \mathcal{E}_0\mathcal{E}(t)\cos(\omega t)$ is a real scalar quantity that multiplies $(\mathbf{r}\cdot\mathbf{e})$. Assuming now that integrations in configurational space can be split up into integrations over nonoverlapping cells Ω_n

$$\Omega = \sum_n \Omega_n, \qquad \int_\Omega d\mathbf{r} = \sum_n \int_{\Omega_n} d\mathbf{r}_n, \tag{30}$$

then the previously introduced concept of multiple scattering can be straightforwardly applied. It should be noted in particular that the Hamiltonian in Eq. (26) is structurally of the same form as the one treated in the so-called full potential KKR method, however, with the time t appearing now as a parameter: technically $W(r;t)$ can be absorbed into the $l=1$ terms of the potential $V(r)$ in Eq. (27). In effect all that is needed therefore is to reconsider the construction of the so-called single-site t matrices appearing in multiple scattering.

A. Multiple scattering

At a particular time t the instantaneous single-particle Green's function $G(r,r',z;t)$,

$$\begin{aligned} G(\mathbf{r},\mathbf{r}',z;t) &= G(\mathbf{r}_n+\mathbf{R}_n,\mathbf{r}'_m+\mathbf{R}_m,z;t) \\ &= \mathbf{Z}^n(\mathbf{r}_n,z;t)\tau_{nm}(z;t)\mathbf{Z}(;\mathbf{r}'_m,z;t)^{\times} \\ &\quad - \delta_{nm}\{\mathbf{J}^n(\mathbf{r}_n,z;t)\mathbf{Z}^n(\mathbf{r}'_n,z;t)^{\times}\Theta((r_n-r'_n) \\ &\quad + \mathbf{Z}^n(\mathbf{r}_n,z;t)\mathbf{J}^n(\mathbf{r}'_n,z;t)^{\times}\Theta((r'_n-r_n)\ \}, \end{aligned} \tag{31}$$

where the R_n denote sites, is defined in terms of the so-called scattering path operator $\tau(z;t)=\{\tau_{nm}(z;t)\}$,[13] which essentially consists of two parts, namely, of time-dependent single-site t matrices and time-independent structure constants,[14]

$$\tau(z;t) = [\mathbf{t}^{-1}(z;t) - \mathbf{G}_0(z)]^{-1}. \tag{32}$$

Note that the structure constants $G_0(z)$ refer to the Green's function for a constant (zero) reference potential, i.e., remain constant in time. In Eq. (31) the $Z^n(r_n,z;t)$ and $J^n(r_n,z;t)$ refer to the so-called regular and irregular scattering solutions to be obtained from solving the single-site problem.

B. Single-site scattering

According to Eq. (26) the Kohn-Sham-Dirac Hamiltonian corresponding to a particular cell (site) of an ensemble of atoms can in principle be rewritten as

$$\mathcal{H}(\mathbf{r};t) = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 + \mathcal{U}(\mathbf{r};t), \tag{33}$$

with

$$\mathcal{U}(\mathbf{r};t) = \begin{pmatrix} \mathcal{U}^{+}(\mathbf{r};t) & 0 \\ 0 & \mathcal{U}^{-}(\mathbf{r};t) \end{pmatrix}, \tag{34}$$

$$\mathcal{U}^{+}(\mathbf{r};t) = \mathcal{V}(\mathbf{r};t) + \sigma_z\mathcal{B}(r;t), \tag{35}$$

$$\mathcal{U}^{-}(\mathbf{r};t) = \mathcal{V}(\mathbf{r};t) - \sigma_z\mathcal{B}(r;t) \tag{36}$$

since initially — because of the properties of the local spin-density functional — only the z component of the spin operator $\boldsymbol{\Sigma}$ appears.[15] The potential $\mathcal{V}(\mathbf{r};t)$ can now be expanded as follows:

$$\mathcal{V}(\mathbf{r};t) = V(\mathbf{r};t)\sigma^{(s)}(\mathbf{r}) = \sum_{\Lambda\Lambda'\Lambda'',\ell'\leq 1} C^{\Lambda}_{\Lambda'\Lambda''}V_{\Lambda'}(r;t)\sigma^{(s)}_{\Lambda''}(r)Y_{\Lambda}(\hat{\mathbf{r}}), \tag{37}$$

with

$$V(\mathbf{r};t) = V(\mathbf{r}) + \mathcal{W}(\mathbf{r};t) = \sum_{\Lambda} V_{\Lambda}(r;t)Y_{\Lambda}(\hat{\mathbf{r}}), \tag{38}$$

where

$$V_{\Lambda}(r;t) = \begin{cases} \sqrt{4\pi}V(r), & \Lambda = (0,0) \\ W_{\Lambda}(r;t), & \Lambda \neq (0,0) \end{cases}. \tag{39}$$

The functions $\sigma^{(s)}(\mathbf{r})$ are so-called shape functions[16] that ensure that according to the conditions of multiple scattering the individual potentials $\mathcal{V}(\mathbf{r};t)$ are restricted to nonoverlapping cells. Adopting for matters of simplicity the so-called atomic sphere approximation (ASA) and assuming the polarization e to point along the z axis, Eq. (38), Eq. (29) simply reduces to

$$V_{00}(r;t) = \sqrt{4\pi}V(r),$$

$$V_{10}(r;t) = \mathcal{E}_0\mathcal{E}(t)\cos(\omega t)|\mathbf{r}|Y_{10}(\hat{\mathbf{r}}). \tag{40}$$

Making the ansatz for the wave functions

$$\psi_Q(\mathbf{r};t) = \sum_{Q'} \begin{pmatrix} g_{Q'Q}(r;t)\chi_{Q'}(\hat{\mathbf{r}}) \\ if_{Q'Q}(r;t)\chi_{\bar{Q}'}(\hat{\mathbf{r}}) \end{pmatrix}, \tag{41}$$

where $Q=(\kappa,\mu)$ and $\bar{Q}=(-\kappa,\mu)$, κ and μ being the relativistic angular momentum quantum numbers, one arrives at a system of coupled radial equations, which as described in Ref. 17 can be used to obtain the single-site t matrices $t(z;t)$ and the regular and irregular scattering solutions $Z_Q(\mathbf{r},z;t)$, $J_Q(\mathbf{r},z;t)$, and $z=\epsilon+i\delta$. Clearly enough instead of Eqs. (27) and (33) also a nonrelativistic description can be given. In this case simply the methods described in Ref. 18 have to be applied. However, having in mind for example current-induced magnetization switching and domain wall motions, a relativistic approach definitely is required.

C. Particle and magnetization densities

From the Green's function in Eq. (31) the time-dependent particle and magnetization densities can now easily be evaluated,[19] according to the requirements of the full potential KKR method, see Eqs. (37)–(39)

$$n(\mathbf{r};t) = \sum_n n(\mathbf{r}_n;t), \quad m(\mathbf{r};t) = \sum_n m(\mathbf{r}_n;t), \tag{42}$$

$$\begin{aligned} n(\mathbf{r}_n;t) = -\pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}\int_{E_b}^{E_F(t)} &\{\mathbf{Z}^n(\mathbf{r}_n,z;t)\tau_{nn}(z;t) \\ &\times \mathbf{Z}(;\mathbf{r}_n,z;t)^{\times} - \mathbf{J}^n(\mathbf{r}_n,z;t)\mathbf{Z}^n(\mathbf{r}_n,z;t)^{\times}\}dz, \end{aligned} \tag{43}$$

$$\begin{aligned} \mathbf{m}(\mathbf{r};t) = -\pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}\int_{E_b}^{E_F(t)} &\beta\boldsymbol{\Sigma}\{\mathbf{Z}^n(\mathbf{r}_n,z;t)\tau_{nn}(z;t) \\ &\times \mathbf{Z}(;\mathbf{r}_n,z;t)^{\times} - \mathbf{J}^n(\mathbf{r}_n,z;t)\mathbf{Z}^n(\mathbf{r}_n,z;t)^{\times}\}dz, \end{aligned} \tag{44}$$

where $E_F(t)$ refers to that energy on the real axis at which the contour must be closed such that the number of particles remains constant.

From Eq. (32) it is obvious that the first main task to apply the above proposed scheme to generate time-

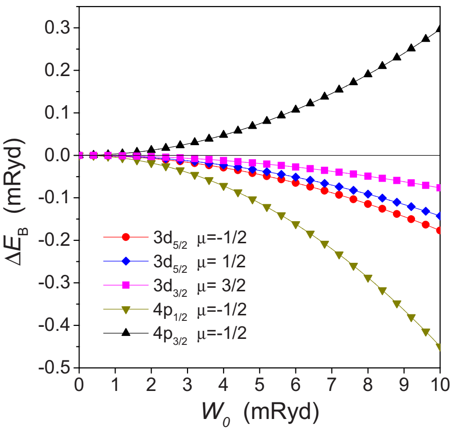

FIG. 1. (Color online) Variation in ΔE_B with respect to W_0 for selected $3d$ and $4p$ states of an Fe atom. The labeling is according to the angular momentum component of the given state that mostly contributes.

dependent densities is to prove that the system of coupled differential equations mentioned in connection with Eq. (41) can be solved accurately enough.

V. APPLICATION TO AN ATOM

Because of the lack of any available comparisons, in this section the numerical procedure for solving the instantaneous problem for a magnetic atom [see in particular Eq. (41)] is illustrated. For illustrative purposes calculations neglecting the time evolution of the charge and magnetization densities were performed for an Fe atom, corresponding to a spherically symmetric effective potential and effective exchange field pointing also along the z axis. In order to determine the bound states of this system when for matters of simplicity the polarization of the laser pulse e is parallel to the z axis [see Eq. (29)] the Newton-Raphson scheme of Ref. 20 was generalized. Note that the very same numerical procedures for solving the corresponding differential equation have to be applied for the single-site t matrices and scattering solutions for different boundary conditions (at a sphere circumscribing the Wigner-Seitz cells), which, however, does not pose any further formal or numerical difficulties. Furthermore, the present procedures already take care of evaluating the so-called core charge densities needed in a self-consistent treatment.[11]

Figure 1 clearly shows that the difference in orbital energies, $\Delta E_B = E(W_0) - E(W_0=0)$, varies quadratically with the magnitude of the electric field, $W_0 = ea_0\mathcal{E}_0$, a_0 being the Bohr radius. Such a behavior is well known as the second-order Stark effect. Apparently the $4p$ states of an Fe atom are stronger affected by the external electric field than the more localized $3d$ states.

In Fig. 2 the time dependence of the electric field is depicted for a laser pulse similar to that one used in experiments to study magnetization dynamics.[21] In the following the instantaneous time evolution of bound states is studied for an interaction of the electrons in an Fe atom with a double-exponential laser pulse,

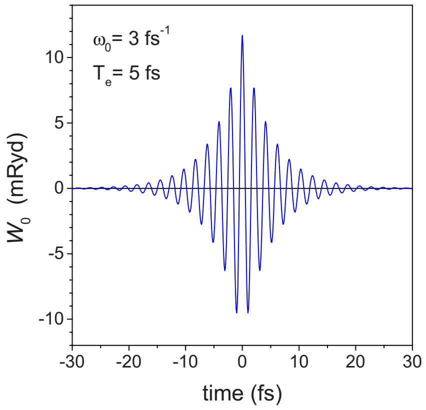

FIG. 2. (Color online) Electric field in units of the interaction strength W_0 for a double-exponential laser pulse of intensity $I = 6\ \mathrm{mJ/cm^2}$.

$$\mathcal{E}(t) = \exp\left(-\frac{|t|}{T_e}\right), \tag{45}$$

where T_e is a time constant characterizing the decay of the laser pulse. The width of the laser pulse is usually defined in experiments by $\Delta t = T_e \ln 2$, while the intensity (power density) is given by $I = \epsilon_0 c T_e \mathcal{E}_0^2$ with ϵ_0 being the vacuum permittivity and c the light velocity.

In order to demonstrate the accuracy of the solutions in Eq. (41) in the following a comparison between the results of (first-order) time-dependent perturbation theory and the present approach is shown. As is well known from time-dependent perturbation theory, the first-order transition probabilities (TP) are given by

$$P_{if}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt' \langle \psi_i^0 | \mathcal{W}(t') | \psi_f^0 \rangle \exp(i\omega_{if} t')\right|^2, \tag{46}$$

where $\mathcal{W}(t)$ starts at $t = t_0$, ψ_i^0 and ψ_f^0 are the initial and the final state wave functions of the unperturbed system corresponding to the eigenvalues E_i^0 and E_f^0, respectively, and $\omega_{if} = (E_i^0 - E_f^0)/\hbar$. Clearly first-order TPs can also be defined (beyond the adiabatic approximation) as[22]

$$P_{if}(t) = \left|\int_{t_0}^{t} dt' \left\langle \psi_i(t') \left| \frac{d}{dt'} \psi_f(t') \right.\right\rangle \exp\left[i \int_{t_0}^{t'} dt'' \omega_{if}(t'')\right]\right|^2, \tag{47}$$

where $\psi_i(t)$ and $\psi_f(t)$ are the solutions of the instantaneous equation,[23]

$$\mathcal{H}(t)\psi_j(t) = E_j(t)\psi_j(t), \quad (j = i, f), \tag{48}$$

and $\omega_{if}(t) = [E_i(t) - E_f(t)]/\hbar$. Note that in terms of Eq. (48) the expression in Eq. (47) can be reformulated as

$$P_{if}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt' \frac{\langle \psi_i(t') | (d\mathcal{W}(t')/dt') | \psi_f(t') \rangle}{\omega_{if}(t')} \times \exp\left[i \int_{t_0}^{t'} dt'' \omega_{if}(t'')\right]\right|^2. \tag{49}$$

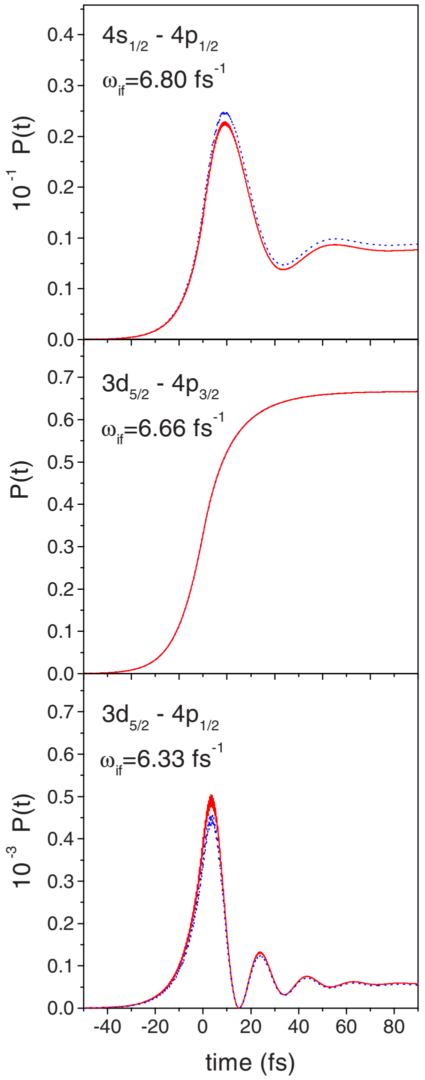

FIG. 3. (Color online) Calculated first-order transition probabilities [solid line: Eq. (49), dotted line: Eq. (46)] for selected transitions in an Fe atom due to a double-exponential laser pulse with $I=6$ mJ/cm^2, $\omega_0=6.66$ fs^{-1}, and $T_e=15$ fs.

The results shown in Figs. 3 and 4 refer to a double-exponential laser pulse [see Eq. (45)] with $I=6$ mJ/cm^2 and $T_e=15$ fs. As a carrier frequency the transition frequency corresponding to the transition $3d_{5/2}-4p_{3/2}$ $(\mu=-1/2)$, namely, $\omega_0=6.66$ fs^{-1}, has been selected. The initial time, t_0, was taken to be at $-6T_e$, i.e., when the amplitude of the electric field is about 400 times smaller than at the center of the laser pulse. It turned out that a time step of 0.1 fs was sufficient to accurately perform the integrations in Eq. (49).

In Fig. 3 TPs as calculated by using Eqs. (46) and (49) are shown for three different transitions. Note that, as in Fig. 2, the zero of the time scale refers to the center of the laser pulse.

As can be seen in particular from the resonant transition (middle panel Fig. 3), the two applied schemes to evaluate TPs compare fairly well with each other over the entire range of times, indicating in turn that the numerical procedure to calculate the instantaneous eigenstates of $\mathcal{H}(t)$ *works very accurately*.

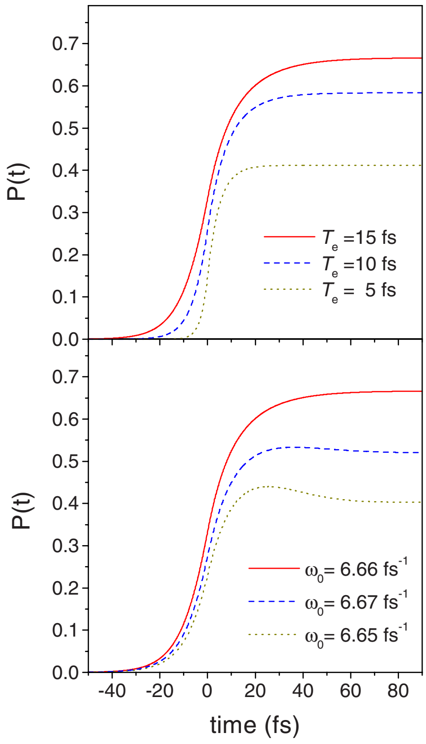

FIG. 4. (Color online) Variation in the calculated transition probabilities with respect to the characteristics of a double-exponential laser pulse [see Eqs. (29) and (45)] for a transition $3d_{5/2}-4p_{3/2}$ $(\mu=-1/2)$ in an Fe atom. The upper panel refers to $\omega_0=6.66$ fs^{-1}, the lower one to $T_e=15$ fs. In all cases the intensity of the laser pulse was fixed to $I=6$ mJ/cm^2.

Finally, Fig. 4 illustrates the sensitivity of TPs with respect to the characteristics of double-exponential laser pulse. In this figure only the $3d_{5/2}-4p_{3/2}$ $(\mu=-1/2)$ transition in the vicinity of the resonance was considered, keeping the intensity of the pulse at $I=6$ mJ/cm^2. Since in this particular case it easily can be shown that in the limit of $t\rightarrow\infty$, $\omega\rightarrow\omega_0$, and $\omega_0 T_e \gg 1$ the TP is proportional to T_e, it is not surprising at all that the calculated TPs monotonously decrease with decreasing duration time of the pulse (upper panel of Fig. 4). As to be expected the TPs are extremely sensitive to the carrier frequency: a relative change in ω_0 of only about 0.1% can decrease the magnitude of the corresponding TP by about 20%–40% (see the lower panel of Fig. 4).

It should be noted that because the polarization was chosen to point along the z axis, the well-known atomic selection rules $\Delta\ell=\pm 1$ and $\Delta m=0$ apply, which in a relativistic description allow transitions for $\Delta j=\pm 2$, since $(\ell=2, j=5/2)\rightarrow(\ell'=1, j'=1/2)$ (see lowest panel of Fig. 4). Furthermore, since the external potential is spin-independent, the selection rule $\Delta m=0$ immediately implies $\Delta\mu=0$.

VI. DISCUSSION AND SUMMARY

Clearly enough the proposed time-dependent scheme can also be applied in any other "band structure" approach than KKR that can deal with "full potentials" such as the augmented plane waves FLAPW or the muffin-tin orbitals FP-LMTO method, at least as long as the obtained instantaneous wave functions are only used to evaluate the particle and the magnetization density, i.e., as long as only quadratic forms are considered. The proposed scheme is not necessarily restricted to a Green's function approach, although such an approach is desirable in order to evaluate time-dependent transport properties.

It is very important to note that Eq. (2), which looks so familiar from time-independent density-functional theory, does use a finite upper index N. In the present description N is replaced by a fictitious "time-dependent Fermi energy" as upper boundary in the contour integrals.

In comparing with other schemes dealing with time-dependent phenomena such as the use of evolution operator techniques in order to solve the time-dependent Schrödinger equation directly, it should be recalled that to follow the time evolution of all occupied orbitals corresponding to a given initial state in the case of semi-infinite solids is almost impossible for solid systems with a surface. Like in the case of time-independent ("traditional") local density approximation (LDA) calculations a suitable parametrization has to be applied, which of course in principle is only valid for the initial (ground) state. It might turn out that perhaps in certain cases one can assume time independence of the local exchange-correlation potential and exchange field in order to describe the main features of time-dependent phenomena. As already said the main emphasis of the proposed scheme is not directed toward many-body theory as such, but to descriptions of excitations in realistic solid systems, namely, to those with a surface as for example by applying picosecond to nanosecond electric-field pulses as used currently for current-driven switching or domain wall motions.[24] Since very often in modern magnetic devices anisotropy effects are crucial, but also since frequently noncollinearly aligned, disordered substitutional magnetic alloys such as permalloy are in use experimentally, there is a definite need for a scheme that is suitable to describe most of these aspects sufficiently well.

APPENDIX: GREEN'S FUNCTIONS AND EVOLUTION OPERATORS

By assuming that the time-dependent Hamiltonian can be written as

$$\mathcal{H}(t) = \mathcal{H}^{(0)}(t) + \mathcal{W}(t), \tag{50}$$

and that for $\mathcal{H}^{(0)}(t)$ the corresponding evolution operator $U^{(0)}(t,t_0)$ is known, the evolution operator $U(t,t_0)$ of a system described by $\mathcal{H}(t)$ is given by

$$\begin{aligned} U(t,t_0)\Theta(t-t_0) = U^{(0)}(t,t_0)\Theta(t-t_0)\frac{i}{\hbar}\int_{t_0}^{t} dt' U^{(0)}(t,t') \\ \times \mathcal{W}(t')U(t',t_0)\Theta(t-t_0), \end{aligned} \tag{51}$$

where $\Theta(x)$ is the Heaviside function. By replacing on the right-hand side of Eq. (51) $\Theta(t-t_0)$ by $\Theta(t-t')\Theta(t'-t_0)$ and extending the integration limits to $\pm\infty$, one obtains

$$K_+(t,t_0) = K_+^{(0)}(t,t_0) - \frac{i}{\hbar}\int_{-\infty}^{+\infty} dt' K_+^{(0)}(t,t')\mathcal{W}(t')K_+(t',t_0), \tag{52}$$

where for $t \geq t_0$ the retarded Green's functions

$$K_+(t,t_0) = U(t,t_0)\Theta(t-t_0), \tag{53}$$

$$K_+^{(0)}(t,t_0) = U^{(0)}(t,t_0)\Theta(t-t_0) \tag{54}$$

obey the below equation of motion,

$$\begin{aligned} \left[i\hbar\frac{\partial}{\partial t} - \mathcal{H}(t)\right]K_+(t,t_0) = \left[i\hbar\frac{\partial}{\partial t} - \mathcal{H}_0(t)\right]K_+^{(0)}(t,t_0) \\ = i\hbar\delta(t-t_0), \end{aligned} \tag{55}$$

and vanish for $t < t_0$, i.e., $K_+(t,t_0) = K_+^{(0)}(t,t_0) = 0$. In analogy to Eq. (52), the advanced Green's functions are defined as

$$K_-(t,t_0) = -U(t,t_0)\Theta(t_0-t), \tag{56}$$

$$K_-^{(0)}(t,t_0) = -U^{(0)}(t,t_0)\Theta(t_0-t), \tag{57}$$

and for $t \leq t_0$ satisfy a similar equation of motion as in Eq. (55), however, for different boundary conditions.[25]

Taking the partial Fourier transform with respect to t of both the retarded and advanced Green's functions, one in fact considers the following propagators:

$$\left\{\begin{aligned} \mathrm{G}_\pm(\varepsilon;t_0) &= -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt\,\exp\left(+\frac{i}{\hbar}\varepsilon t\right)K_\pm(t,t_0) \\ \mathrm{G}_\pm^{(0)}(\varepsilon;t_0) &= -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt\,\exp\left(+\frac{i}{\hbar}\varepsilon t\right)K_\pm^{(0)}(t,t_0) \end{aligned}\right., \tag{58}$$

$\varepsilon \in \mathbb{R}$, in terms of which, i.e., by using the inverse Fourier transform, then

$$\left\{\begin{aligned} K_\pm(t,t_0) &= -\frac{1}{2\pi i}\int_{-\infty}^{+\infty} d\varepsilon\,\exp\left(-\frac{i}{\hbar}\varepsilon t\right)\mathrm{G}_\pm(\varepsilon;t_0) \\ K_\pm^{(0)}(t,t_0) &= -\frac{1}{2\pi i}\int_{-\infty}^{+\infty} d\varepsilon\,\exp\left(-\frac{i}{\hbar}\varepsilon t\right)\mathrm{G}_\pm^{(0)}(\varepsilon;t_0) \end{aligned}\right., \tag{59}$$

where

$$\begin{aligned} \mathrm{G}_\pm(\varepsilon;t_0) = \mp\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt\,\exp\left(+\frac{i}{\hbar}\varepsilon t\right) \\ \times\left\{\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt'\mathcal{H}(t')\right]\right\}_+\Theta[\pm(t-t_0)], \end{aligned} \tag{60}$$

$$\begin{aligned} \mathrm{G}_\pm^{(0)}(\varepsilon;t_0) = \mp\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt\,\exp\left(+\frac{i}{\hbar}\varepsilon t\right) \\ \times\left\{\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt'\mathcal{H}^{(0)}(t')\right]\right\}_+\Theta[\pm(t-t_0)], \end{aligned} \tag{61}$$

with $(\ldots)_+$ denoting the time ordering. Having determined $\mathrm{G}_\pm(\varepsilon;t_0)$ in Eq. (60) in terms of Eqs. (53) and (56), the evolution operator $U(t,t_0)$ is immediately obtained as

$$U(t,t_0) = K_+(t,t_0) - K_-(t,t_0) = -\frac{1}{2\pi i}\int_{-\infty}^{+\infty} d\varepsilon \exp\left(-\frac{i}{\hbar}\varepsilon t\right)[\mathrm{G}_+(\varepsilon;t_0) - \mathrm{G}_-(\varepsilon;t_0)] \tag{62}$$

since

$$\Theta(\tau) + \Theta(-\tau) \equiv 1, \quad \text{for} \quad \forall\, \tau \in \mathbb{R}.$$

In the following it will be assumed that in Eq. (50)

$$\mathcal{H}^{(0)}(t) = \mathcal{H}^{(0)} = \mathcal{H}_0 + V, \quad \text{for} \quad \forall\, t \geq t_0, \tag{63}$$

i.e., only $\mathcal{W}(t)$ is time dependent. If interaction Hamiltonians at different times commute with each other, which in fact is always the case whenever one uses the semiclassical approximation, namely,

$$[\mathcal{W}(t'),\mathcal{W}(t'')] = 0, \quad t_0 < t',t'' < t, \tag{64}$$

then the retarded (advanced) propagator can be approximated to order $O[(t-t_0)^2]$ by

$$\mathrm{G}_\pm(\varepsilon;t_0) \simeq \mp\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt \exp\left(+\frac{i}{\hbar}\varepsilon t\right)\exp\left[-\frac{i}{\hbar}\mathcal{H}^{(0)}(t-t_0)\right] \times \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt'\mathcal{W}(t')\right]\Theta[\pm(t-t_0)] \tag{65}$$

because in this case the ordered exponential in Eqs. (60) and (61) turns into an ordinary one.[26]

Finally, by making use of Eq. (62) the evolution operator for an infinitesimal small time step can be written as

$$U(t,t_0) = -\frac{1}{2\pi i}\int_{-\infty}^{+\infty} d\varepsilon \exp\left[-\frac{i}{\hbar}\varepsilon(t-t_0)\right] \times [G_+(\varepsilon;t_0) - G_-(\varepsilon;t_0)] = \frac{1}{2\pi i}\oint_{C_-\cup C_+} dz \exp\left[-\frac{i}{\hbar}z(t-t_0)\right]G(z;t_0), \tag{66}$$

with the resolvent $G(z;t)$ of the Hamiltonian $\mathcal{H}(t)$,

$$G(z;t) = \frac{1}{z - \mathcal{H}(t)}, \tag{67}$$

when $t = t_0$ and $z = \varepsilon \pm i\eta$ tends to ε on the real axis. In Eq. (66) C_+ (C_-) is a contour immediately above (below) the real axis followed from right (left) to left (right) such that for $t - t_0 > 0$ the contour C_- and for $t - t_0 < 0$ the contour C_+ yields vanishing contributions.

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[1] M. A. L. Marques and E. K. U. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).

[2] K. Capelle, G. Vignale, and B. L. Györffy, Phys. Rev. Lett. **87**, 206403 (2001).

[3] S. Botti, F. Sottile, N. Vast, V. Olevano, L. Reining, H. C. Weissker, A. Rubio, G. Onida, R. Del Sole, and R. W. Godby, Phys. Rev. B **69**, 155112 (2004).

[4] R. Stubner, I. V. Tokatly, and O. Pankratov, Phys. Rev. B **70**, 245119 (2004).

[5] J. Toulouse, Phys. Rev. B **72**, 035117 (2005).

[6] H. Appel and E. K. U. Gross, in *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, NIC Series Vol. 10, edited by J. Grotendorst, D. Marx, and A. Muramatsu (John von Neumann Institute for Computing, Jülich, 2002), p. 255.

[7] A. Vernes, B. L. Györffy, and P. Weinberger, Phys. Rev. B **76**, 012408 (2007).

[8] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[9] R. van Leeuwen, Phys. Rev. Lett. **80**, 1280 (1998).

[10] L. V. Keldysh, Sov. Phys. JETP **20**, 1018 (1965).

[11] P. Lloyd and P. V. Smith, Adv. Phys. **21**, 69 (1972).

[12] In principle of course the lower integration boundary can be extended to $-\infty$ in order to include all electrons.

[13] Chapters 3 and 16 of Ref. 27.

[14] Chapter 15 of Ref. 27.

[15] Since all usual parametrizations in LDA are nonrelativistic the corresponding Kohn-Sham Hamiltonians are SU2 invariant, i.e., are only defined with respect to an artificial z axis in spin space. Only by including a spin-orbit term spin and configuration space coordinates become coupled.

[16] Chapter 4 of Ref. 27.

[17] Chapter 11 of Ref. 27.

[18] Chapter 6 of Ref. 27.

[19] Chapter 18 of Ref. 27.

[20] H. Ebert, J. Phys.: Condens. Matter **1**, 9111 (1989).

[21] C. Rulliere, T. Amand, and X. Marie, in *Femtosecond Laser Pulses*, edited by C. Rulliere (Springer-Verlag, Berlin, 1998), Chap. 8, p. 203.

[22] A. Galindo and P. Pascual, *Quantum Mechanics* (Springer-Verlag, Berlin, 1990).

[23] F. Hansteen, A. Kimel, A. Kirilyuk, and T. Rasing, Phys. Rev. Lett. **95**, 047402 (2005).

[24] M. Hayashi, L. Thomas, C. Rettner, R. Moriya, Y. B. Bazaliy, and S. S. P. Parkin, Phys. Rev. Lett. **98**, 037204 (2007).

[25] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions: Basic Processes and Applications* (Wiley, Weinheim, 2004).

[26] H. M. Fried, *Green's Functions and Ordered Exponentials* (Cambridge University Press, Cambridge, 2002).

[27] J. Zabloudil, R. Hammerling, L. Szunyogh, and P. Weinberger, *Electron Scattering in Solid Matter: A Theoretical and Computational Treatise* (Springer-Verlag, Berlin, 2005).