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One-step theory of pump-probe photoemission

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A theoretical framework for pump-probe photoemission is presented. The approach is based on a general formulation using the Keldysh formalism for the lesser Green's function to describe the real-time evolution of the electronic degrees of freedom in the initial state after a strong pump pulse that drives the system out of equilibrium. The final state is represented by a time-reversed low-energy electron-diffraction state. Our one-step description is related as close as possible to Pendry's original formulation of the photoemission process. The formalism allows for a quantitative calculation of time-dependent photocurrent for simple metals where a picture of effectively independent electrons is assumed to be reliable. The theory is worked out for valence- and core-electron excitations. It comprises the study of different relativistic effects as a function of the pump-probe delay.

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I. INTRODUCTION

Angle-resolved photoemission has developed over several decades into a technique of choice for determining the electronic structure of new crystalline materials and represents a mature tool in materials physics [1]. Particularly, time-resolved photoemission spectroscopy (TR-PES) has been advanced on the experimental side in recent years. To study the nonequilibrium dynamics of electronic degrees of freedom on a femtosecond time scale, different pump-probe photoemission experiments have been employed [2–16]. Here, we present a general theoretical framework which can be applied to simple metals where a treatment of the electron dynamics in a picture of essentially independent particles may be adequate. The formalism also accounts for relativistic effects; for example, it captures the simultaneous appearance of spin-orbit coupling and magnetic exchange splitting. In principle, it can be applied to different pump-probe photoemission setups involving valence bands as well as core levels. To keep the complexity at a reasonable level, we focus on a valence-pump–core-probe situation in the present study. We sketch the computation of the atomic contribution of the initial state to the time-dependent photocurrent and point out the necessity to implement a full time-dependent multiple-scattering technique for other contributions to the time-dependent photocurrent.

The most successful theoretical framework available to deal with photoemission from solid surfaces is the one-step model as originally implemented by Pendry and coworkers [17–19]. The main idea is to describe the excitation process, the transport of the photoelectron to the crystal surface, and the escape into the vacuum [20] as a single quantum-mechanically coherent process including all multiple-scattering events [21]. Nowadays, it allows for photocurrent calculations ranging from a few eV to more than 10 keV [22–25] at finite temperatures and from arbitrarily ordered [26] and disordered systems [27] and may also include effects of strong electron correlations [28–30]. However, a general and quantitative one-step formulation of time-resolved phenomena in angle-integrated or angle-resolved photoemission is still missing. Only a few theoretical approaches to TR-PES have been published within the last few years. Initial descriptions of TR-PES in terms of Keldysh Green's function techniques [31] were published by Freericks *et al.* [32–34] and Eckstein and M. Kollar [35], followed by work from other groups [36,37]. Moreover, the first realistic description of two-photon photoemission has been worked out [38], as well as a many-body formulation of core-level photoemission [39].

One of the major problems, as discussed in the literature, mainly in the context of strongly correlated systems, consists of the calculation of the lesser component of the Keldysh Green's function for a realistic system while avoiding an equal-time approximation or similar severe simplifications. As this function has two independent time arguments, the numerical effort can be tremendous, even for simple model systems. There is, however, another class of complications that is relevant to the theoretical description of real materials: In order to obtain the photocurrent as a function of the pump-probe delay, one has to calculate the lesser Green's function for a semi-infinite stack of atomic layers and for a realistic electronic potential, which is typically available from band-structure formalisms such as the Korringa-Kohn-Rostoker (KKR) method [40]. Furthermore, equally important, final-state multiple-scattering and matrix-element effects have to be taken into account, as well as the presence of the surface itself.

For the case of *equilibrium* photoemission, those problems have been addressed and successfully solved in the past: The first and most simple version of an independent-electron approximation for the photocurrent was given by Berglund and Spicer [20], namely, with the so-called three-step model of photoemission in which the process is divided into three independent steps (excitation, transport, and escape into the vacuum; see above). To overcome obvious deficiencies of the three-step model, a multiple-scattering or "dynamic" approach was suggested, first for the final state [41,42] and later on for both initial and final states [19] in order to treat self-energy corrections on equal footing. With Pendry's one-step approach [18] to angle-resolved photoemission a numerically tractable scheme was introduced which rests on the one-particle Green's function in the local-density approximation (LDA) of band-structure theory [43]. Photoemission is described as a single coherent quantum process. Explicit effects of strong Coulomb correlations are still disregarded. Furthermore, the use of the sudden approximation for the final state allows us to adopt an independent-particle description of the photoelectron in the framework of low-energy electron-diffraction theory [17].

Our long-term goal is to provide a numerical tool which helps to analyze time-resolved pump-probe photoemission data from real systems and which thus makes direct contact with the experiments. In the present paper, as a first step, we demonstrate that a one-step formulation is also possible in the time-dependent or nonequilibrium case. Using the Keldysh formalism [31], the lesser Green's function provides the description of the time evolution of the electronic structure on a femtosecond time scale following a strong pump pulse. In general, this requires the solution of an integral equation involving the S matrix that corresponds to multiple (all-order) scattering at the time-dependent perturbation given by the light-matter-interaction term describing the pump. The problem can be rewritten as a Dyson equation for the nonequilibrium double-time retarded Green's function starting from the equilibrium retarded (and advanced) Green's functions which are available from standard KKR theory [40] and which are homogeneous in time. However, even if one works on an LDA level and neglects explicit Coulomb correlations in the many-body system and describes the electrons as effectively independent, this is a very demanding task.

Within the sudden approximation, the descriptions of the initial state and of the final state can be separated from each other [32]. Final-state multiple-scattering effects, dipole selection rules, and, generally, all effects of the transition-matrix elements as well as multiple scattering from the surface potential are fully included by describing the final state of the photoelectron as a time-reversed low-energy electron-diffraction (LEED) state. To simplify the solution of the Dyson-type integral equation for the lesser Green's function, we adopt an "atomic approximation"; that is, we compute the atomic contribution of only the initial state. This should be reasonable for the case of a pump-probe experiment in which the time-dependent electronic structure in a valence band is probed with an x-ray pulse addressing a core state. For this valence-pump–core-probe photoemission [4,44,45] a fully relativistic four-component formalism is necessary. Our approach should thus also make contact with pump-probe photoemission from high-Z materials and allows us to study, e.g., dichroic effects in TR-PES.

This paper is organized as follows: The next section presents the general theory of time-resolved photoemission theory. The relation to the conventional (equilibrium) one-step theory and other aspects are discussed in Sec. III. Section IV is devoted to the lesser Green's function which describes the time evolution of the system's initial state after a strong pump pulse. Different types of pump-probe experiments are discussed in Sec. V, while the explicit formulation of time-resolved photoemission within the one-step approach is worked out in Sec. VI for an x-ray probe addressing a core state. Section VII provides a short summary.

II. GENERAL THEORY OF TIME-DEPENDENT PHOTOEMISSION SPECTROSCOPY

We consider the electronic properties of a system specified by a Hamiltonian $\mathcal{H}$ and assume that the system's state is a thermal state characterized by the inverse temperature β and the chemical potential μ in the distant past $t \to -\infty$. The grand-canonical density operator is given by $\rho(-\infty) = Z^{-1}\exp[-\beta(\mathcal{H} - \mu N)]$, where N is the total particle number and $Z = \operatorname{tr}\exp[-\beta(\mathcal{H} - \mu N)]$ is the partition function. Let $|\Psi_m\rangle$ be the eigenstates of $\mathcal{H}$ and E_m be the corresponding eigenenergies. We have

$$\rho(-\infty) = \sum_m p_m |\Psi_m\rangle\langle\Psi_m|, \tag{1}$$

with

$$p_m = \frac{1}{Z} e^{-\beta(E_m - \mu N_m)}, \tag{2}$$

where N_m is the total particle number in state $|\Psi_m\rangle$.

We consider a situation where the system is subjected to a strong light pulse, described by a light-matter-interaction Hamiltonian $\mathcal{V}(t)$, which drives the system state $\rho(t)$ out of equilibrium. Typically, this pump pulse has a finite duration and is followed by electronic relaxation processes on a femtosecond time scale before slower relaxation mechanisms involving lattice degrees of freedom become relevant. The time evolution of the mixed state

$$\rho(t) = \sum_m p_m |\Psi_m(t)\rangle\langle\Psi_m(t)| \tag{3}$$

must be described nonperturbatively and is formally obtained from the time propagation of each state of the grand ensemble,

$$|\Psi_m(t)\rangle = \mathcal{U}_{\text{tot}}(t, -\infty)|\Psi_m\rangle, \tag{4}$$

by means of the unitary time-evolution operator

$$\mathcal{U}_{\text{tot}}(t,t') = \mathcal{T}\exp\left(-i\int_{t'}^{t} \mathcal{H}_{\text{tot}}(\tau)d\tau\right), \tag{5}$$

where $\mathcal{T}$ denotes chronological time ordering and $\mathcal{H}_{\text{tot}}(t) = \mathcal{H} + \mathcal{V}(t)$.

After some time delay Δt following the pump, the nonequilibrium state is probed by a second pulse that is described by an interaction term $\mathcal{W}(t)$. We assume that the probe pulse is nonzero for times $t > t_0$ and $t < t_1$. As we are interested in only the electronic system properties, it is reasonable to express $\mathcal{W}(t)$ in terms of only electronic degrees of freedom. Conceptually, the electronic structure can be subdivided into the states of primary interest, namely, occupied states and states in a certain energy window around the Fermi energy (or around μ) on the one hand and high-energy scattering states on the other. To address the former, we introduce c_α, which annihilates an electron in the one-particle basis state $|\varphi_\alpha\rangle$, while the latter are addressed by an annihilator a_k with a label k for the one-particle scattering state that is occupied by the photoelectron. Therewith,

$$\mathcal{W}(t) = s_{\mathcal{W}}(t)\sum_{k,\alpha}(M_{k\alpha}a_k^\dagger c_\alpha + \text{H.c.}), \tag{6}$$

where $s_{\mathcal{W}}(t)$ describes the time profile of the probe pulse (and is nonzero only for $t_0 < t < t_1$) and $M_{k,\alpha}$ are the transition-matrix elements for processes lifting a (low-energy) electron in state $|\varphi_\alpha\rangle$ to a high-energy state $k = (\boldsymbol{k},\sigma)$ characterized by a wave vector $\boldsymbol{k}$ and a spin projection $\sigma = \uparrow,\downarrow$.

The probability $P_k(t)$ to detect a photoelectron with quantum numbers k at time t is given by the expectation value, in the system state $\rho(t)$, of the projector $\Pi(k)$ onto the subspace of all many-electron "final" states of the form

$$|f\rangle = a_k^\dagger |\Phi_n\rangle\ . \tag{7}$$

Therewith, we have adopted the sudden approximation and assumed that the Coulomb interaction of the (high-energy) photoelectron with the low-energy part of the system can be neglected. $|\Phi_n\rangle$ is an arbitrary many-electron state from an orthonormal basis set of the rest system (excluding the high-energy scattering states). We have

$$\Pi(k) = \sum |f\rangle\langle f| = \sum_n a_k^\dagger |\Phi_n\rangle\langle\Phi_n| a_k \tag{8}$$

and

$$P_k(t) = \langle \Pi(k)\rangle_{\rho(t)} = \mathrm{tr}[\rho(t)\Pi(k)]. \tag{9}$$

With Eqs. (3) and (8), the time-dependent photoemission spectrum is obtained as

$$P_k(t) = \sum_{m,n} p_m |\langle\Phi_n|a_k|\Psi_m(t)\rangle|^2\ . \tag{10}$$

The next task is to find the time dependence of states $|\Psi_m(t)\rangle$ in the presence of the additional probe pulse $\mathcal{W}(t)$, i.e., for times $t > t_0$. We have

$$|\Psi_m(t)\rangle = \mathcal{U}_1(t,-\infty)|\Psi_m\rangle, \tag{11}$$

where

$$\mathcal{U}_1(t,t') = \mathcal{T}\exp\left(-i\int_{t'}^{t}[\mathcal{H}_{\mathrm{tot}}(\tau) + \mathcal{W}(\tau)]d\tau\right). \tag{12}$$

We assume that the probe pulse is sufficiently weak and treat the time evolution perturbatively. To this end, let us introduce the corresponding S matrix:

$$\mathcal{S}_W(t,t_0) = \mathcal{U}_{\mathrm{tot}}(t_0,t)\mathcal{U}_1(t,t_0). \tag{13}$$

Taking the time derivative, we immediately get

$$i\frac{d}{dt}\mathcal{S}_W(t,t_0) = \mathcal{U}_{\mathrm{tot}}(t_0,t)\mathcal{W}(t)\mathcal{U}_1(t,t_0). \tag{14}$$

Integration then yields

$$\mathcal{S}_W(t,t_0) = 1 - i\int_{t_0}^{t} dt'\mathcal{U}_{\mathrm{tot}}(t_0,t')\mathcal{W}(t')\mathcal{U}_1(t',t_0). \tag{15}$$

Taking into account only the term first order in $\mathcal{W}(t)$, we can replace $\mathcal{U}_1(t',t_0)$ by $\mathcal{U}_{\mathrm{tot}}(t',t_0)$ on the right-hand side. Therewith, using Eqs. (11) and (13), we find

$$\begin{aligned}|\Psi_m(t)\rangle &\approx \mathcal{U}_{\mathrm{tot}}(t,-\infty)\\ &\quad\times\left(1 - i\int_{-\infty}^{t} dt'\mathcal{U}_{\mathrm{tot}}(-\infty,t')\mathcal{W}(t')\mathcal{U}_{\mathrm{tot}}(t',-\infty)\right)\\ &\quad\times|\Psi_m\rangle.\end{aligned} \tag{16}$$

Inserting this into Eq. (10) and recalling that $\mathcal{W}(t) = 0$ for $t < t_0$ yield

$$\begin{aligned}P_k(t) = \sum_{m,n} p_m \Bigg|\langle\Phi_n|a_k\int_{t_0}^{t} dt'\\ \times\,\mathcal{U}_{\mathrm{tot}}(t,t')\mathcal{W}(t')\mathcal{U}_{\mathrm{tot}}(t',-\infty)|\Psi_m\rangle\Bigg|^2.\end{aligned} \tag{17}$$

Here, we have also made use of the fact that the one-particle high-energy scattering states are, to a very good approximation, unoccupied in $|\Psi_m\rangle = |\Psi_m(-\infty)\rangle$, i.e., that $a_k|\Psi_m\rangle \approx 0$. Making, once more, use of the sudden approximation, we have

$$a_k\mathcal{U}_{\mathrm{tot}}(t,t') = \mathcal{U}_{\mathrm{tot}}(t,t')a_k e^{-i\varepsilon(k)(t-t')}, \tag{18}$$

where $\varepsilon(k)$ is the dispersion of the scattering state. Furthermore,

$$\begin{aligned}&a_k\mathcal{W}(t')\mathcal{U}_{\mathrm{tot}}(t',-\infty)|\Psi_m\rangle\\ &\quad= s_{\mathcal{W}}(t')\sum_\gamma M_{k\gamma}c_\gamma\mathcal{U}_{\mathrm{tot}}(t',-\infty)|\Psi_m\rangle.\end{aligned} \tag{19}$$

Therewith, we arrive at

$$\begin{aligned}P_k(t) = \sum_{m,n} p_m\Bigg|\langle\Phi_n|\int_{t_0}^{t} dt'\mathcal{U}_{\mathrm{tot}}(t,t')e^{i\varepsilon(k)t'}s_{\mathcal{W}}(t')\\ \times\sum_\gamma M_{k\gamma}c_\gamma\mathcal{U}_{\mathrm{tot}}(t',-\infty)|\Psi_m\rangle\Bigg|^2.\end{aligned} \tag{20}$$

Reformulating this result by expanding the modulus square and using $\sum_n |\Phi_n\rangle\langle\Phi_n| = \mathbf{1}$, we have

$$\begin{aligned}P_k(t) &= \int_{t_0}^{t}\int_{t_0}^{t} dt'dt'' s_{\mathcal{W}}(t')s_{\mathcal{W}}(t'')e^{-i\varepsilon(k)(t'-t'')}\\ &\quad\times\sum_{\alpha\beta,m} M_{k\beta}^* M_{k\alpha}p_m\langle\Psi_m|\mathcal{U}_{\mathrm{tot}}(-\infty,t')c_\beta^\dagger\mathcal{U}_{\mathrm{tot}}(t',t'')\\ &\quad\times c_\alpha\mathcal{U}_{\mathrm{tot}}(t'',-\infty)|\Psi_m\rangle.\end{aligned} \tag{21}$$

This can be written in a compact form by switching to the Heisenberg picture, i.e., $c_\alpha(t) = \mathcal{U}_{\mathrm{tot}}(-\infty,t)c_\alpha\mathcal{U}_{\mathrm{tot}}(t,-\infty)$:

$$\begin{aligned}P_k(t) &= \sum_{\alpha\beta} M_{k\beta}^* M_{k\alpha}\int_{t_0}^{t} dt' s_{\mathcal{W}}(t')\int_{t_0}^{t} dt'' s_{\mathcal{W}}(t'')e^{-i\varepsilon(k)(t'-t'')}\\ &\quad\times\langle c_\beta^\dagger(t')c_\alpha(t'')\rangle.\end{aligned} \tag{22}$$

The one-particle correlation function is the lesser component of the Keldysh Green's function. It is given by an equilibrium expectation value but is time inhomogeneous as the Heisenberg time dependence is governed by the full and explicitly time-dependent Hamiltonian $\mathcal{H}_{\mathrm{tot}}(t) = \mathcal{H} + \mathcal{V}(t)$.

III. DISCUSSION

Equation (22) was first derived by Freericks *et al.* [32] in a similar way. It nicely defines the main tasks of a theory of time-dependent pump-probe photoemission: The problem consists of computing the lesser Green's function which describes the temporal evolution of the electronic degrees of freedom after the pump pulse. As this is assumed to drive the system strongly out of equilibrium, a linear-response approach or, generally, a perturbative calculation must be disregarded, and ideally, Dyson's equation with respect to $\mathcal{V}(t)$ should be solved without approximation. Within a picture of effectively noninteracting electrons, this is equivalent to a time-dependent multiple-scattering approach where all scattering events, at all times and in the entire lattice, are summed up. This is a formidable task.

The second problem consists of the realistic computation of the transition-matrix elements in Eq. (22). For those we have to consider the light-matter-interaction term $\mathcal{W}(t)$ in Eq. (6). We apply the dipole approximation which is well justified for sufficiently large wavelengths, i.e., for photon energies below about 10 keV. In the real-space representation and using a relativistic four-component notation, which is needed for later purposes, we have

$$W(\boldsymbol{r},t) = W(t) = -s_{\mathcal{W}}(t)\boldsymbol{\alpha} \cdot \mathbf{A}_{0,\mathcal{W}}, \qquad (23)$$

where $\mathbf{A}_{0,\mathcal{W}}$ denotes the spatially constant amplitude of the electromagnetic vector potential. The three components α_k of the vector $\boldsymbol{\alpha}$ are defined as the tensor product $\alpha_k = \sigma_1 \otimes \sigma_k$ for $k = 1,2,3$, where σ_k denote the Pauli spin matrices.

While the lesser Green's function in Eq. (22) describes time-dependent multiple scattering from the pump pulse $\mathcal{V}(t)$ in the "initial" state, the matrix elements also include the "final" state of the photoemission process. This is a one-particle scattering state that is characterized by $k = (\boldsymbol{k},\sigma)$ and that has the correct asymptotic behavior, i.e., is a simple plane wave "at the detector" far away from the system. Here, we will make use of the standard layer-KKR formalism [46] to represent this state as a time-reversed LEED state [17].

The real-space representation of the pump pulse $\mathcal{V}(t)$ has the same form as the probe. In both cases the excitation is mediated by a light pulse where the corresponding electromagnetic field can essentially be described by a monochromatic plane wave. The time profile of the pump pulse $s_{\mathcal{V}}(t)$ can be different from that of the probe $s_{\mathcal{W}}(t)$. We assume that the dipole approximation is well justified for both the pump and the probe. The strength of the two pulses can be largely different. This fact is encoded in the absolute magnitude of the vector potential.

The conventional, i.e., equilibrium, expression of the photocurrent is easily rederived from Eq. (22) by assuming $\mathcal{V}(t) \equiv 0$. This immediately implies a time-homogeneous lesser Green's function. We also set $s_{\mathcal{W}}(t) \equiv 1$ and consider the limits $t_0 \to -\infty$ and $t \to \infty$. After a change of variables $dt'dt'' = dt_{\text{rel}}dt_{\text{av}}$, with $t_{\text{rel}} = t' - t''$ and $t_{\text{av}} = (t' + t'')/2$, one finds for the transition probability per unit time

$$\begin{aligned} w_k &= \frac{P_k}{t - t_0} \\ &= \sum_{\alpha\beta} M^*_{k\beta} M_{k\alpha} \int_{-\infty}^{\infty} dt_{\text{rel}}\, e^{-i\varepsilon(k)t_{\text{rel}}} \langle c^\dagger_\beta(t_{\text{rel}}) c_\alpha(0)\rangle. \end{aligned} \qquad (24)$$

Using the spectral sum rule

$$\langle c^\dagger_\beta(t) c_\alpha(0)\rangle = \int_{\infty}^{\infty} d\omega\, f(\omega) A_{\alpha\beta}(\omega) e^{i\omega t}\ , \qquad (25)$$

where $f(\omega) = 1/[\exp(\beta\omega) + 1]$ is the Fermi function, we have

$$w_k = 2\pi \sum_{\alpha\beta} M^*_{k\beta} M_{k\alpha} f(\omega) A_{\alpha\beta}(\omega), \qquad (26)$$

with $\omega = \varepsilon(k)$ and the single-electron spectral density $A_{\alpha\beta}(\omega)$. This is the well-known golden-rule formula for the equilibrium photocurrent [18].

IV. INITIAL-STATE GREEN'S FUNCTION

The time-dependent correlation function in Eq. (22) can be considered to be a component of the one-particle Keldysh Green's function $G_{\alpha\alpha'}(z,z')$. Some of its basic properties will be discussed here for the case of effectively noninteracting electrons; that is, we will not account for time-dependent correlations in the sense of many-particle interactions. Generally, the Green's function is defined for arguments z,z' on the Keldysh-Matsubara [31] contour C in the complex time plane as

$$i G_{\alpha\alpha'}(z,z') = \langle \mathcal{T} c_\alpha(z) c^\dagger_{\alpha'}(z')\rangle, \qquad (27)$$

where $\mathcal{T}$ denotes the contour ordering and the expectation value refers to the "free" system $\mathcal{H}$, while z results from time evolution with the "total" Hamiltonian $\mathcal{H}_{\text{tot}}(t) = \mathcal{H} + \mathcal{V}(t)$, with

$$\mathcal{H} = \sum_{\alpha\alpha'} T_{0;\alpha\alpha'} c^\dagger_\alpha c_{\alpha'} \qquad (28)$$

and

$$\mathcal{V}(t) = \sum_{\alpha\alpha'} V_{\alpha\alpha'}(t) c^\dagger_\alpha c_{\alpha'}. \qquad (29)$$

The Green's function can be obtained from Dyson's equation,

$$\boldsymbol{G}(z,z') = \boldsymbol{G}_0(z,z') + \int_C dz'' \boldsymbol{G}_0(z,z'')\boldsymbol{V}(z'')\boldsymbol{G}(z'',z'), \qquad (30)$$

where bold symbols refer to matrices in the orbital indices α,α'. $G_{0;\alpha\alpha'}(z,z')$ denotes the free Green's function for $\mathcal{V}(z) \equiv 0$ and is easily expressed in terms of the hopping matrix $\boldsymbol{T}_0$ as [47]

$$\begin{aligned} i\boldsymbol{G}_0(z,z') = e^{-i\boldsymbol{T}_0(z-z')} \Bigg[&\frac{\Theta_c(z,z')}{1 + \exp[-\beta(\boldsymbol{T}_0 - \mu)]} \\ &- \frac{\Theta_c(z',z)}{\exp[\beta(\boldsymbol{T}_0 - \mu)] + 1} \Bigg], \end{aligned} \qquad (31)$$

where $\Theta_c(z,z')$ is the contour step function. For our purposes it is sufficient to consider the lesser component of $\boldsymbol{G}(z,z')$ which is obtained for z on the upper branch and z' on the lower branch of the Keldysh contour; that is, z is "earlier" than z' on the contour and thus $i G^<_{\alpha\alpha'}(t,t') = -\langle c^\dagger_{\alpha'}(t') c_\alpha(t)\rangle$. This can formally be written as

$$\begin{aligned} i\boldsymbol{G}^<(t,t') = -\mathcal{T} e^{-i\int_{t_0}^{t} d\tau[\boldsymbol{T}_0 + \boldsymbol{V}(\tau)]} &\frac{1}{e^{\beta(\boldsymbol{T}_0 - \mu)} + 1} \\ &\times \tilde{\mathcal{T}} e^{i\int_{t_0}^{t'} d\tau[\boldsymbol{T}_0 + \boldsymbol{V}(\tau)]}, \end{aligned} \qquad (32)$$

where $\tilde{\mathcal{T}}$ is the antichronological time ordering.

We are seeking for a more suitable representation which also allows us to set up a time-dependent multiple-scattering approach. To this end we define the S matrix $\boldsymbol{S}_{\mathcal{V}}$ related to (all-order) perturbation theory in the pump pulse:

$$\boldsymbol{S}_{\mathcal{V}}(t,t') = \boldsymbol{U}_0(t_0,t)\boldsymbol{U}(t,t')\boldsymbol{U}_0(t',t_0). \tag{33}$$

Here, $\boldsymbol{U}_0(t,t') = \exp[-i\boldsymbol{T}_0(t-t')]$ is the matrix representation of the free time-evolution operator, and $\boldsymbol{U}(t,t') = \mathcal{T}\exp[-i\int_{t'}^{t} d\tau(\boldsymbol{T}_0 + \boldsymbol{V}(\tau))]$ is the representation of the interacting time-evolution operator. The equation of motion for $\boldsymbol{S}_{\mathcal{V}}(t,t')$ is easily derived. We have

$$i\frac{\partial}{\partial t}\boldsymbol{S}_{\mathcal{V}}(t,t') = \boldsymbol{V}_t(t)\boldsymbol{S}_{\mathcal{V}}(t,t'), \tag{34}$$

where the double time dependence appears due to the use of the interaction picture, $\boldsymbol{V}_t(t) = \boldsymbol{U}_0(t_0,t)\boldsymbol{V}(t)\boldsymbol{U}_0(t,t_0)$. The corresponding integral equation reads

$$\boldsymbol{S}_{\mathcal{V}}(t,t') = \boldsymbol{1} - i\int_{t'}^{t} dt''\,\boldsymbol{V}_{t''}(t'')\boldsymbol{S}_{\mathcal{V}}(t'',t'). \tag{35}$$

For $t > t_0$, the time-evolution matrices can also be expressed in terms of the retarded and advanced Green's functions, $i\boldsymbol{G}_0^{\mathrm{R}}(t,t') \equiv i\Theta(t-t')\boldsymbol{U}_0(t,t')$ and $i\boldsymbol{G}_0^{\mathrm{A}}(t,t') = i\Theta(t'-t)\boldsymbol{U}_0(t,t')$, i.e.,

$$\boldsymbol{V}_t(t) = \boldsymbol{G}_0^{\mathrm{A}}(t_0,t)\boldsymbol{V}(t)\boldsymbol{G}_0^{\mathrm{R}}(t,t_0). \tag{36}$$

Therewith, we have (for $t,t' > t_0$)

$$\boldsymbol{S}_{\mathcal{V}}(t,t') = \boldsymbol{1} - i\int_{t'}^{t} d\tau\,\boldsymbol{G}_0^{\mathrm{A}}(t_0,\tau)\boldsymbol{V}(\tau)\boldsymbol{G}_0^{\mathrm{R}}(\tau,t_0)\boldsymbol{S}_{\mathcal{V}}(\tau,t'), \tag{37}$$

and with Eq. (32) and the definition of the S matrix, we get

$$\begin{aligned} i\boldsymbol{G}^{<}(t,t') = {} & -\boldsymbol{G}_0^{\mathrm{R}}(t,t_0)\boldsymbol{S}_{\mathcal{V}}(t,t_0)\frac{1}{e^{\beta(\boldsymbol{T}_0-\mu)}+1} \\ & \times \boldsymbol{S}_{\mathcal{V}}(t_0,t')\boldsymbol{G}_0^{\mathrm{A}}(t_0,t'). \end{aligned} \tag{38}$$

With Eq. (32) we can write

$$i\boldsymbol{G}^{<}(t,t') = -\boldsymbol{G}^{\mathrm{R}}(t,t_0)\frac{1}{e^{\beta(\boldsymbol{T}_0-\mu)}+1}\boldsymbol{G}^{\mathrm{A}}(t_0,t'). \tag{39}$$

The retarded Green's function $\boldsymbol{G}^{\mathrm{R}}(t,t')$ can be obtained from the following integral equation:

$$\boldsymbol{G}^{\mathrm{R}}(t,t') = \boldsymbol{G}_0^{\mathrm{R}}(t,t_0) + \int_{t'}^{t} d\tau\,\boldsymbol{G}_0^{\mathrm{R}}(t,\tau)\boldsymbol{V}(\tau)\boldsymbol{G}^{\mathrm{R}}(\tau,t'), \tag{40}$$

which is derived from Eqs. (33) and (37). The advanced Green's function is given by $\boldsymbol{G}^{\mathrm{A}}(t,t') = [\boldsymbol{G}^{\mathrm{R}}(t',t)]^{\dagger}$. This completes the formal calculation of the lesser Green's function.

V. DISCUSSION OF DIFFERENT PUMP-PROBE SPECTROSCOPIES

The integral equation for $\boldsymbol{G}^{\mathrm{R}}(t,t')$ poses a time-dependent multiple-scattering problem for a three-dimensional solid or, more realistically, for a semi-infinite system bounded by a surface. In combination with Eq. (22), it provides us with a quantitative description of different pump-probe experiments. Clearly, the solution appears to be a demanding task.

Typically, the pump pulse $\mathcal{V}(t)$ excites electrons from occupied to unoccupied valence states below the vacuum level, while the probe pulse $\mathcal{W}(t)$, after some defined time delay, excites valence electrons from the explicitly time-dependent and nonequilibrium state into high-energy scattering states such that they can escape into the vacuum. For those valence-pump–valence-probe experiments, the numerical evaluation of the theory is most demanding.

A simplification of the formalism is possible, however, for the important case of two-photon photoemission experiments (2PPE) [29,48–50]. Namely, from the theoretical perspective, a 2PPE experiment actually is just a pump-probe-type experiment in which the intensity of the pump pulse is comparable to the intensity of the probe. This means that Eq. (40) can be treated perturbatively to a good approximation, and the series obtained by iteration can be cut by neglecting terms of the order $O(\boldsymbol{V}^2)$, for example. This leaves us with an expression for the Green's functions $\boldsymbol{G}^{\mathrm{R}}(t,t')$ that is amenable to a straightforward numerical calculation since it is given in terms of only $\boldsymbol{G}_0^{\mathrm{R}}(t,t') = \boldsymbol{G}_0^{\mathrm{R}}(t-t')$, i.e., in terms of the *equilibrium* retarded Green's function which is homogeneous in the time arguments. This quantity is defined as the Fourier transform of the following quantity, which is available from standard layer-dependent KKR techniques [51]:

$$\begin{aligned} G_0^R(\boldsymbol{r},\boldsymbol{r}',E) = {} & -4ik\sum_{jn\Lambda}\Psi^{+}_{jn\Lambda}(\mathbf{r}_>)\Psi^{\dagger}_{jn\Lambda}(\mathbf{r}_<) \\ & -\frac{4ik}{\Omega}\sum_{jn\Lambda\Lambda'}\Psi_{jn\Lambda}(\mathbf{r})(t_{jn\Lambda})^{-1} \\ & \times\left(\int_{\Omega} d\mathbf{k}\,\tau^{nn}_{j\Lambda\Lambda'} - \delta_{\Lambda\Lambda'}t_{jn\Lambda'}\right) \\ & \times(t_{jn\Lambda'})^{-1}\Psi^{\dagger}_{jn\Lambda'}(\mathbf{r}'). \end{aligned} \tag{41}$$

Here, we have switched to the real-space representation. Ψ^{+} and Ψ represent the single-site solutions for the nth cell in the jth layer in a semi-infinite slab geometry, and τ is the KKR scattering path operator for the jth layer. t denotes the single-scattering matrix for the nth cell in the jth layer, and Ω is the area of the layer unit cell. Besides valence-pump–valence-probe and 2PPE experiments, a valence-pump–core-probe setup is frequently used [4,44,45]. Here, the pump pulse excites valence-band electrons with a photon energy of a few eV to unoccupied valence states. After a controlled time delay, the response of a core level is probed in a second step with a corresponding x-ray probe pulse. The first part of this pump-probe experiment is described by $\boldsymbol{G}^{\mathrm{R}}(t,t')$, which must be obtained from the integral equation (40) and accounts for the time evolution of the nonequilibrium electronic structure after an intense pump pulse. In contrast to 2PPE, this time evolution usually cannot be captured in a linear-response formalism; that is, a perturbative approach expanding in $\mathcal{V}$ is not applicable here. There is, however, a simplification for the case of a probe pulse addressing *core* electrons, namely, restricting oneself to a single-scattering center in the solution of Eq. (40) for the retarded Green's functions $\boldsymbol{G}^{\mathrm{R}}(t,t_0)$. For the case of an x-ray probe addressing a core state, the propagator refers only to this core state, as is obvious from the central equation (22). Within the one-step model, this results in an "atomic contribution" of the initial state to the full time-dependent photocurrent, while a full summation over all multiple-scattering events is included in the formalism for the final state. This shall be worked out in detail in the following section. In the case of almost-dispersion-free core states, this should be an excellent starting point. Clearly, the ultimate test case for the atomic approximation will be the direct comparison with corresponding experimental data [4,44,45,52,53].

VI. ONE-STEP MODEL OF CORE-LEVEL PUMP-PROBE SPECTROSCOPY

To formulate a one-step theory of valence-pump–core-probe photoemission, a fully relativistic formalism for the final state is necessary. We therefore rewrite Eq. (22) in the real-space and a four-component spinor representation:

$$P_k(t) = \int d^3r' \int d^3r''\, f_k^\dagger(\mathbf{r}') W(t') \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' e^{-i\varepsilon(k)(t'-t'')} \times G^<(\mathbf{r}',t',\mathbf{r}'',t'') W^\dagger(t'') f_k(\mathbf{r}''). \tag{42}$$

Here, $G^<(\mathbf{r}',t',\mathbf{r}'',t'')$ is a 4×4 Green's function matrix. f_k represents a single-particle-like final state of the photoelectron in the form of a time-reversed LEED state and is a four-component spinor. The 4×4 matrix $W(t)$ is given by Eq. (23). The lesser Green's function is obtained from Eq. (39) in real-space representation,

$$G^<(\mathbf{r},t,\mathbf{r}',t') = i \int dE\, F(E) \int d^3r'' \int d^3r''' G^R(\mathbf{r},t,\mathbf{r}'',t_0) \times \Psi_E(\mathbf{r}'')\Psi_E^\dagger(\mathbf{r}''') G^A(\mathbf{r}''',t_0,\mathbf{r}',t'), \tag{43}$$

where $F(E) = 1/\{\exp[\beta(E-\mu)]+1\}$ denotes the Fermi distribution function and the spinors Ψ_E define an orthonormal basis set with $T_0\Psi_E = E\Psi_E$. The occupied energy eigenstates Ψ_E needed here can be obtained from relativistic KKR theory [46]. KKR-theory also provides us with the retarded (advanced) Green's function G_0^{R} (G_0^{A}), constructed as a tensor product of two four-spinors [54].

In the modern version of the KKR method [46], the electronic structure of a system, including valence as well as core states, is directly and efficiently represented in terms of the retarded one-electron Green's function. This appealing feature is achieved by using multiple-scattering theory. The same multiple-scattering KKR technique is used in the context of photoemission theory to construct the final state as a time-reversed LEED state. For these reasons, the KKR multiple-scattering formalism provides the initial-state Green's function and the final-state scattering state in a consistent way and on equal footing and is thus the method of choice.

As noted in the preceding section, we will focus on the "atomic" contribution of the initial state to the total time-dependent photoemission yield. For simplicity, we additionally assume spherically symmetric single-cell potentials $v(\mathbf{r}) = v(r)$. Therewith, an ansatz separating radial and angular dependencies becomes convenient. For all types of Green's functions, $G^<$, G^{R}, and G^{A}, we have

$$G^{<,\mathrm{R},\mathrm{A}}(\mathbf{r},t,\mathbf{r}',t') = \sum_{\Lambda\Lambda'} g_{\Lambda\Lambda'}^{<,\mathrm{R},\mathrm{A}}(r,t,r',t')\chi_\Lambda(\hat{\mathbf{r}})\chi_{\Lambda'}^\dagger(\hat{\mathbf{r}}'), \tag{44}$$

where $\chi_\Lambda(\hat{\mathbf{r}})$ denote the relativistic spin-angular functions [55] with the spin-orbit (κ) and the magnetic (μ) quantum numbers [55] combined as $\Lambda = (\kappa,\mu)$. Using this, the radial parts of the quantities in Eq. (43) are related by

$$g_{\Lambda\Lambda'}^<(r,t,r',t') = i \int dE\, F(E) \sum_{\Lambda'',\Lambda'''} \int dr'' r''^2 \int dr''' r'''^2 \times g_{\Lambda\Lambda''}^{\mathrm{R}}(r,t,r'',t_0)\Psi_{E,\Lambda''}(r'') \times \Psi_{E,\Lambda'''}^\dagger(r''') g_{\Lambda'''\Lambda'}^{\mathrm{A}}(r'',t_0,r',t'). \tag{45}$$

This equation is considerably simpler and very amenable to a numerical approach based on the KKR formalism.

Likewise, the central Dyson equation for the retarded Green's function, Eq. (40), can be simplified. In the real-space representation we have

$$G^{\mathrm{R}}(\mathbf{r},t,\mathbf{r}',t') = G_0^{\mathrm{R}}(\mathbf{r},t,\mathbf{r}',t') - \int_{t'}^{t} dt'' s_V(t'') \int d^3r'' \times G_0^{\mathrm{R}}(\mathbf{r},t,\mathbf{r}'',t'')\boldsymbol{\alpha}\cdot\mathbf{A}_{0,V} G^{\mathrm{R}}(\mathbf{r}'',t'',\mathbf{r}',t'). \tag{46}$$

Here, as for the probe, we assume that the dipole approximation is valid:

$$V(\mathbf{r},t) = -s_V(t)\boldsymbol{\alpha}\cdot\mathbf{A}_{0,V}. \tag{47}$$

$\boldsymbol{A}_{0,V}$ denotes the constant amplitude of the vector potential of the pump field, and $s_V(t)$ is the time profile of the pump pulse. Using the ansatz (44) to get the atomic contribution, we find a coupled system of Volterra integral equations of the second kind for the radial part of the retarded Green's function:

$$g_{\Lambda\Lambda'}^{\mathrm{R}}(r,t,r',t') = g_{0,\Lambda\Lambda'}^{\mathrm{R}}(r,t,r',t') - \sum_{\Lambda''\Lambda'''} D_{\Lambda''\Lambda'''} \int_{t'}^{t} dt'' s_V(t'') \times \int dr'' r''^2 g_{0,\Lambda\Lambda''}^{\mathrm{R}}(r,t,r'',t'') \frac{dv(r'')}{dr''} \times g_{\Lambda'''\Lambda'}^{\mathrm{R}}(r'',t'',r',t'). \tag{48}$$

We also made use of a representation of the dipole operator [see Eq. (47)] in terms of the gradient of the cell potential $v(r)$. Again, the resulting system of equations is considerably simplified and can be implemented numerically. At this point the calculation of the atomic contribution is complete.

We finally combine the results for the initial state with the layer-KKR multiple-scattering approach describing the final state. This provides us with the time-dependent photoemission yield in the following form:

$$P_k(t) = \sum_{\Lambda\Lambda'\Lambda''\Lambda'''jn} A_{jn\Lambda}^\dagger D_{\Lambda\Lambda'} M_{\Lambda\Lambda'\Lambda''\Lambda'''}(t) D_{\Lambda''\Lambda'''}^\dagger A_{jn\Lambda'''}. \tag{49}$$

Here, the radial matrix elements are defined as

$$M_{\Lambda\Lambda'\Lambda''\Lambda'''}(t) = \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' s_W(t') s_W(t'') e^{-i\varepsilon(k)(t'-t'')} \times \int dr' r'^2 \int dr'' r''^2 \phi_\Lambda^{f\dagger}(r') \frac{dv(r')}{dr'} \times g_{\Lambda'\Lambda''}^<(r',t',r'',t'') \frac{dv(r'')}{dr''} \phi_{\Lambda'''}^{f}(r''), \tag{50}$$

where v is the spherical single-cell potential. Furthermore, A denote the spherical coefficients of the high-energy wave field:

$$A_{jn\Lambda} = \sum_{\Lambda'} A_{jn\Lambda'}^{(o)} (1-X)_{\Lambda\Lambda'n}^{-1}. \tag{51}$$

The effect of multiple scattering within the jth layer can be represented by a matrix X, and the bare coefficients $A^{(o)}$ are given by

$$A^{(o)}_{jn\Lambda'} = \sum_{\mathbf{g}s} 4\pi i^{l'}(-2s)(-)^{\mu'-s} C^{\Lambda'}_{s} \big[u^{+}_{j\mathbf{g}s} Y^{s-\mu'}_{l'}(\widehat{k^{+}_{2\mathbf{g}}}) e^{i\mathbf{k}^{+}_{2\mathbf{g}}\cdot\mathbf{r}_n} + u^{-}_{j\mathbf{g}s} Y^{s-\mu'}_{l'}(\widehat{k^{-}_{2\mathbf{g}}}) e^{i\mathbf{k}^{-}_{2\mathbf{g}}\cdot\mathbf{r}_n}\big]. \tag{52}$$

$\boldsymbol{r}_n$ is the distance vector from the origin to the position of the nth atom in the layer unit cell. The plane-wave amplitudes u^{+} and u^{-} can be calculated recursively by standard (KKR) multiple-scattering techniques [21,40]. D are the relativistic angular dipole matrix elements [21]:

$$D_{\Lambda\Lambda'} = \sum_{s=\pm\frac{1}{2}} (-2s) C^{\Lambda}_{s} D^{\mathrm{NR}}_{l,\mu-s,l',\mu'+s} C^{\Lambda'}_{-s}, \tag{53}$$

where C^{Λ}_{s} denote the Clebsch-Gordan coefficients and $D^{\mathrm{NR}}_{l,\mu-s,l',\mu'+s}$ represent the nonrelativistic angular matrix elements [18], which are given by

$$D^{\mathrm{NR}}_{LL'} = \frac{4\pi}{3} A_0\, Y^{*}_{1m}(\hat{A}_0)\, C_{lml'm'1(-m-m')} \tag{54}$$

in terms of the Gaunt coefficients C.

In Eq. (49), the k dependence, i.e., the dependence on the quantum numbers of the photoelectrons, enters $P_k(t)$ through the wave field describing the final state [Eqs. (51) and (52)] and also through the time-dependent phase factor via $\varepsilon(k)$ absorbed in the radial matrix elements [Eq. (50)]. The main experimental control parameter, the time delay, enters the theory through the time distance between the two pulses with profiles $s_{\mathcal{V}}(t)$ (pump pulse) and $s_{\mathcal{W}}(t)$ (probe pulse) where the former appears in the integral equation (48) for the initial-state retarded Green's function while the latter appears more explicitly in Eq. (50).

VII. SUMMARY

We have presented a theoretical framework for time-resolved pump-probe photoemission involving only electronic degrees of freedom. The theory addresses systems in which explicit Coulomb correlations can be neglected safely and which can be treated within a picture of effectively independent electrons moving in a one-particle potential that is obtained from standard band-structure calculations. The present approach aims at an *ab initio* description of photoemission from real materials that may complement pure model studies for strongly correlated systems carried out previously.

The key quantity to describe time-revolved photoemission is the lesser Green's function. We have shown that this is theoretically and numerically accessible, even for real systems. Within the Keldysh formalism and treating the time-dependent pump pulse in all-order perturbation theory, we express the lesser Green's function in terms of the retarded and advanced Green's functions. The latter are obtained by solving a standard Dyson equation in which the perturbation is given by the pump pulse. The main point of the present paper is to show how to treat this in a real-space representation for realistic materials as opposed to model systems.

Furthermore, the description of the transition induced by the probe pulse as well as the final high-energy scattering state of the photoelectrons has been done in a fully relativistic, four-component formalism which resolves all quantum numbers of the photoelectron. Thereby, the theory covers ultraviolet as well as soft or hard x-ray photon energies and spans the same regime as the conventional equilibrium theory of angle-resolved photoemission. The central idea of our paper is to straightforwardly extend the traditional and highly successful one-step formulation. Formally, this gives access to time-resolved intensity distributions and to magnetic linear and circular dichroism, not only from real systems like simple metals but also from complex ordered compounds.

In addition, our formalism allows in a very stringent way for a quantitative description of two-photon photoemission spectroscopy. Namely, in the case of a weak pump pulse the retarded Green's function is simply given in terms of the Fourier transform of the retarded free Korringa-Kohn-Rostoker Green's function, which is available using standard KKR techniques. Last but not least, the explicit calculation of 2PPE spectra may serve as a starting point for spectroscopical investigations in the case of strong pump pulses, for which the Dyson equation for the retarded Green's function has to be solved self-consistently. This is because the lesser Keldysh Green's function, after one iteration, is available as a function of space and time coordinates, where the radial coordinates are restricted to only a single cell potential, $g^{<}(r,t,r',t')$. This provides the starting point for a self-consistent solution of the corresponding radial part of the Dyson equation, and all time-dependent multiple-scattering effects in the initial state are properly included in the calculation. Let us emphasize that treating time-dependent multiple-scattering effects for a real system, even on the level of noninteracting particles, represents a highly nontrivial problem which we believe is solvable by our approach.

In conclusion, we believe that our approach to time-resolved photoemission is emerging as an important tool for studying the electronic structures of simple metals and of complex materials in a quantitative way.

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