Theory of pump–probe ultrafast photoemission and X-ray absorption spectra

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ABSTRACT

Keldysh Green's function approach is extensively used in order to derive practical formulas to analyze pump–probe ultrafast photoemission and X-ray absorption spectra. Here the pump pulse is strong enough whereas the probe X-ray pulse can be treated by use of a perturbation theory. We expand full Green's function in terms of renormalized Green's function without the interaction between electrons and probe pulse. The present theoretical formulas allow us to handle the intrinsic and extrinsic losses, and furthermore resonant effects in X-ray Absorption Fine Structures (XAFS). To understand the radiation field screening in XPS spectra, we have to use more sophisticated theoretical approach. In the ultrafast XPS and XAFS analyses the intrinsic and extrinsic loss effects can interfere as well. In the XAFS studies careful analyses are necessary to handle extrinsic losses in terms of damped photoelectron propagation. The nonequilibrium dynamics after the pump pulse irradiation is well described by use of the time-dependent Dyson orbitals. Well above the edge threshold, ultrafast photoelectron diffraction and extended X-ray absorption fine structure (EXAFS) provide us with transient structural change after the laser pump excitations. In addition to these slow processes, the rapid oscillation in time plays an important role related to pump electronic excitations. Near threshold detailed information could be obtained for the combined electronic and structural dynamics. In particular high-energy photoemission and EXAFS are not so influenced by the details of excited states by pump pulse. Random-Phase Approximation (RPA)-boson approach is introduced to derive some practical formulas for time-dependent intrinsic amplitudes.

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1. Introduction

A pump–probe photoemission technique is now a useful tool to investigate nonequilibrium dynamics of excited molecules and solids on a femto-second time scale. So far some interesting theoretical methods have been proposed to study the nonequilibrium dynamics observed in ultrafast photoemission spectra excited by pump laser pulse [1,2]. They have provided us with quite interesting information on electron dynamics in strongly correlated systems. These approaches are based on the intrinsic approximation, so that extrinsic losses and resonant processes cannot be discussed. Braun et al. [3] have proposed an interesting one-step theory of pump–probe photoemission based on Keldysh Green's function theory in a fully relativistic four-component formalism. The extrinsic and further complicated many-body effects are not considered there. A much simpler approach based on a model Hamiltonian is

developed by Lee, and applied to attosecond resonant photoemission of copper dichloride [4].

Rolle et al. [5] have presented time-resolved femtosecond X-ray photoelectron diffraction (XPD) measurements on laser-aligned 1,4-dibromobenzene molecules which were compared with density functional theory calculations. They try to extract useful information about time-dependent structural changes after the pump pulse irradiation. They, however, observe no clear time dependence: They use rather low kinetic energy (ε_p = 20 and 35 eV). It is, however, not exactly "XPD" from molecules fixed in space. First successful photoelectron diffraction measurement is reported by Nakajima et al. [6] from laser aligned I_2 molecule using X-ray free-electron laser (XFEL) pulses. The XPD patterns of the I_2 molecules aligned to the polarization vector of the XFEL are well explained by multiple scattering calculations. Kazama et al. [7,8] have studied the sensitivity of the XPD angular patterns to the structural changes at rather high energy region (ε_p > 100 eV). They show that the XPD patterns are sensitive to the structural changes, and the time-dependent XPD can be a promising tool to study nuclear dynamics after the laser pump excitation. We still have a question whether we can directly observe the time-dependent XPD spectra from the

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pump–probe XPS. Kuleff and Cederbaum [9] have reviewed their recent theoretical results and some important applications after molecules are exposed to ultrashort laser pulses. They focus on electron and nuclear dynamics after the excitation, in particular on charge migration. Detailed discussion on pump–probe XPS spectra has not been given there.

Ultrafast X-ray absorption fine structures (XAFS) measurements have been applied to study transient structures after laser pump excitation [10]. Their analyses are based on the assumption where ultrafast XAFS provides us with snapshot spectra. We have again a similar question whether these analyses can be built on a sound theoretical basis or not. Ultrafast XAFS based on XFEL measurements are very promising, however so far only preliminary results have been reported [11,12]. Mukamel and his coworkers have greatly contributed to the development of the pump–probe XAFS theory based on nonlinear response theory by use of Liouville space pathways [13,14]. They have applied their formulas to X-ray absorption near edge structure (XANES) analyses [15]. Their interests are mainly focused on near edge structures.

Here we propose a new theory to study these pump–probe ultrafast XPS spectra and X-ray absorption spectra, based on Keldysh Green's function approach which can incorporate both intrinsic and extrinsic losses and also resonant effects within nonrelativistic theoretical framework. The pump pulse is strong enough, so that we should go beyond weak perturbation theory. For this purpose time-dependent Dyson orbital theory is quite useful and is physically transparent, which is direct extension of ordinary time-independent Dyson orbital. For practical purposes, quasi-boson approximation is introduced which allows us to calculate these time-dependent Dyson orbitals and intrinsic amplitudes.

2. Ultrafast XPS theory

2.1. Basic formulas of photoemission intensity

In the pump–probe photoemission experiments, we use two photon pulses; pump and probe pulses. The photoemission current $\mathbf{j}$ at the detection site $\mathbf{r}$ ($r \rightarrow \infty$) and time t is given within the nonrelativistic framework neglecting diamagnetic current [16]

$$\mathbf{j}(\mathbf{r}, t) \propto \sum_\sigma \left(\frac{\partial}{\partial \mathbf{r}'} - \frac{\partial}{\partial \mathbf{r}} \right) g^<(xt, x't)|_{x=x'}, \tag{1}$$

where we use $x = (\mathbf{r}, \sigma)$ ($\sigma = \pm 1$) and take $\mathbf{r}' = \mathbf{r}$ after the differential operation. Our task is thus to calculate the Green's function $g^<$ including all interaction. For that purpose we notice that the full Keldysh Green's function $G(1, 2)$ ($1 = (x_1, t_1)$) satisfies the Dyson equation

$$\left[i\frac{\partial}{\partial t_1} - h(1) - A(1) - B(1) - V_H(1) \right] G(1, 2)$$

$$- \int_c d3 \Sigma(1, 3) G(3, 2) = \delta_c(1, 2) \tag{2}$$

In the above equation $\int_c$ means the time integration on the Keldysh contour from $-\infty$ to ∞ ($-$ leg) and back to $-\infty$ ($+$ leg), and δ_c is the delta function on the closed path. We use one-electron operators $h(1)$, $A(1)$ defined as

$$h(1) = T_e(1) - \sum_\alpha \frac{Z_\alpha}{|\mathbf{r}_1 - \mathbf{R}_\alpha|}, \tag{3}$$

$$A(1) = a(t_1)\Delta(\mathbf{r}_1) + c.c., \tag{4}$$

where h is one-electron operator composed of the kinetic energy T_e and the electron–nuclei Coulomb interaction, and A shows the

interaction between the probe X-ray pulse and the system after the pump pulse irradiation, c.c. means the complex conjugation of the first term. In addition to the probe photon field the pump photon–electron interaction B is to be taken into account defined by

$$B(1) = b(t_1)\Delta(\mathbf{r}_1) + b_2(t_1)\Delta_2(\mathbf{r}_1) + c.c. \tag{5}$$

where B show the interaction between the strong laser pulse and the system in the ground state or in thermal equilibrium. For simplicity we focus on the former cases. The factors a and b describe the time dependence of probe X-rays and laser pulse: $a(t)$ is non-zero only for the interval $t_1 < t < t_2$, and $b(t)$ and $b_2(t)$ are only non-zero for $0 < t < t_0$, ($t_0 < t_1$). Typically the strong laser field is used for the pumping processes, so that 2-photon term Δ_2 is also used for B, but only 1-photon electron–photon interaction Δ is used for the probe X-rays. In eq.(2) V_H is the Hartree potential. The electron selfenergy $\Sigma(1, 2)$ is given in the formally same as the usual electron selfenergy

$$\Sigma(1, 2) = i \int_c d3d4 G(1, 3)\Gamma(32; 4)W(4, 1^+), \tag{6}$$

where Γ and W are the vertex and screened Coulomb interaction [17], 1^+ means that t_1^+ is infinitesimally later than t_1 on the closed time path c. As demonstrated by Eq. (2), the total Green's function G includes the influence from A. Let G_B be the Green's function with no influence from the X-ray probe pulse, which satisfies the Dyson equation without A

$$\left[i\frac{\partial}{\partial t_1} - h(1) - B(1) - V_H(1) \right] G_B(1, 2)$$

$$- \int_c d3 \Sigma_B(1, 3) G_B(3, 2) = \delta_c(1, 2) \tag{7}$$

where Σ_B is the electron selfenergy with no influence from the probe X-rays. Within the GW approximation, the selfenergy is written [17]

$$\Sigma(1, 2) \approx iG(1, 2)W(2, 1^+). \tag{8}$$

The screened Coulomb interaction W includes electron screening caused by Coulomb interaction between composite electrons and nuclei, so that W is not so affected by A in the low orders. The total Green's function G on the other hand can be influenced by A as shown by Eq. (2). We thus have Σ_B in the GW approximation

$$\Sigma_B(1, 2) \approx iG_B(1, 2)W(2, 1^+) \tag{9}$$

Now we define the correction $\delta\Sigma$ due to the X-ray probe pulse A: $\delta\Sigma = \Sigma - \Sigma_B$. We thus can expand G in terms of G_B, $\delta\Sigma$ and A from Eqs. (2) and (7),

$$G = G_B + G_B(\delta\Sigma + A)G_B + G_B(\delta\Sigma + A)G_B(\delta\Sigma + A)G_B + \ldots \tag{10}$$

The first and the second order corrections to Σ_B due to the pulse A are then given from Eq. (8)

$$\delta\Sigma^{(1)}(1, 2) = i(G_B A G_B)(1, 2)W(2, 1^+), \tag{11}$$

$$\delta\Sigma^{(2)}(1, 2) = i(G_B A G_B A G_B)(1, 2)W(2, 1^+). \tag{12}$$

We measure stationary photoelectron current which should be caused by 2nd order processes in regard to A. We pick up all possible terms in the order of A^2 from the full Green's function G:

$$G_B A G_B A G_B + G_B A G_B \delta\Sigma^{(1)} G_B + G_B \delta\Sigma^{(1)} G_B A G_B + G_B \delta\Sigma^{(2)} G_B \tag{13}$$

Next we project out the lesser components of the terms in the above formula (13) because only $g^<$ contributes to the photoelectron current as shown by Eq. (1). Langreth theorem coverts the time