Theory of Optical Field Effects in Photoemission

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Our previous quantum electrodynamics (QED) Keldysh Green’s function approach provides a theoretical basis to study the radiation field screening and microscopic photon scatterings. As an application, we derive a useful formula to study low energy photoemission from extended states which incorporates the radiation field screening. This formula can describe the singular behaviors excited by photons with near plasmon energy, and is in particular suitable for the analyses of the photoemission from organic solids because it is written in terms of bond orders and effective charges on each site.

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I. INTRODUCTION

Most of the photoemission theory implicitly assumes a bare coupling to the external photon field, however, in general this external field will be influenced by the material. For example, $L_1/L_2$ transition intensity branching ratio of 3d transition metals varies considerably with atomic number $Z$, and is close to 1:1 for metals like Ti and V. This result is contrast to the result predicted by the independent electron approximation 2:1. A successful explanation is given by Ankudinov et al. taking account the radiation field screening in the time-dependent local density approximation (TDLDA) approach [1]. Another example is multilayer resonant photoemission (MARPE) spectra [2–4]. Successful theoretical explanation has been given based on the radiation field screening [5–7].

The external field is screened by the dielectric response of the material, which is much enhanced by surface plasmon generation [8]. This effect has been observed in connection with UV photoemission [9]. Though these effects are well known, the full incorporation into one-step photoemission calculation is quite difficult. Qualitative discussion based on physical insight replaces the vector potential $A$ by $e^{-1}A$. The importance of the radiation field screening is demonstrated by large change (≈ 100%) in the photoelectron current excited from the valence band of TiSe$_2$ around 20 eV [8, 10]. Barberan and Inglesfield calculated a frequency dependence of the peak intensity from the surface and Fermi level with classically screened A-field [9]. These intensities strongly vary with the photon energy, due to the screening of the electromagnetic field by the electron gas. The screening effect is calculated by use of the hydrodynamic approximation.

A new non-relativistic many-body theory to analyze XPS spectra has been developed on the basis of quantum electrodynamics (QED) Keldysh Green’s function approach [11]. We first separate longitudinal and transverse parts of these Green’s functions in the Coulomb gauge. The transverse electron selfenergy describes the electron-photon interaction, whereas the longitudinal electron selfenergy describes the electron-electron interaction. We derive the QED Hedin’s equation from which we obtain systematic skeleton expansion in the power series of the screened Coulomb interaction $W$ and the photon Green’s function $D_{kl}$. The mixed photon Green’s function $D_{0kl}$ and $D_{k0}$ which have been supposed to be unimportant for the XPS analyses, however, directly describe the radiation field screening. Beyond free photon Green’s function approximation $D_{0kl}$, photon scatterings from electron density were incorporated within the QED theory [11].

In this work the radiation field screening effects are discussed in one-step theory and applied to UPS analyses. In particular we derive a useful and practical formula to study UPS spectra from organic solids which include the radiation field screening in terms of the density matrix.

II. QED PHOTOEMISSION THEORY

A general nonrelativistic many-body theory to analyze photoemission spectroscopy spectra has been developed on the basis of QED Keldysh Green’s function approach [11]. We first separate longitudinal and transverse part of these Green’s functions in the Coulomb gauge. The transverse electron selfenergy describes the electron-photon interaction, whereas the longitudinal electron selfenergy describes the electron-electron interaction. We derive the QED Hedin’s equation from which we obtain systematic skeleton expansion in the power series of the screened Coulomb interaction $W$ and the photon Green’s function $D_{kl}$ ($k, l = x, y, z$). In this theoretical framework the photoelectron current density measuring photoelectrons with momentum $p$, kinetic energy $\varepsilon_p$ and spin $\sigma$ is given by

$$
\langle J(p, \varepsilon) \sigma \rangle = \frac{\pi}{\eta V} \delta (\varepsilon - \varepsilon_p) \left\langle J^p_{\sigma} \left| \Sigma^{T<} (\varepsilon) \right| J^p_{\sigma} \right\rangle \\
= \frac{\pi}{\eta} \delta (\varepsilon - \varepsilon_p) J^p_{\sigma} (\eta \rightarrow +0)
$$

where $V$ is the volume of the quantization box. The photoelectron Dyson orbital

$$
J^p_{\sigma} (x) = \left\langle \psi (x) \right| p \rightarrow 0, N+1 \rangle, \quad x = (r, \sigma)
$$
satisfies the outgoing boundary condition and approaches to the plane wave at detection position far from the target: \( \psi(x) \) is the annihilation field operator for electrons. In solids it propagates under the influence of the non-Hermitian nonlocal potential (advanced electron self-energy) \( \Sigma^a(\varepsilon_p) \) \([5, 6, 12]\). Our main task in the photoemission theory thus is to calculate the transverse electron self-energy function \( \Sigma^T_\perp \) and screened Coulomb interaction \( \Delta_\k \) which describes a basic photoemission process. The diagrams (b)-(d) include the radiation field screening stemming from the mixed photon Green’s function \( D_{\k \ell} \) and screened Coulomb interaction \( \Delta_\k \) in the photoemission processes. Renormalized electron Green’s function \( G \), photon Green’s function \( D_{h \ell} \) and screened Coulomb interaction \( W \) are given by fat solid line, dashed line and wavy line. Indices + and - mean the time leg on the Keldysh contour. The diagram (a) is the lowest term of the transverse electron self-energy, which describes a basic photoemission process. The diagrams (b)-(d) include the radiation field screening stemming from the mixed photon Green’s function \( D_{\k \ell} \) and \( D_{0 \ell} \).

### III. UPS THEORY

In this section we derive the photoemission amplitude from extended states excited by low energy photons, including the radiation field screening effects. In particular, the present formula is suitable to study the photoemission from organic solids. In organic systems we can use an LCAO (tight binding) approximation for the initial Dyson orbital \( g_n \) from which a photoelectron is ejected:

\[
g_n(x) = \sum_{i=0}^{C_{ni}} C_{ni}^\alpha \chi_i^\alpha(r) \quad (4)
\]

where \( \chi_i^\alpha \) is the \( \alpha \)-th atomic basis function on the site \( \alpha \), and \( C_{ni}^\alpha \) is the expansion coefficient. In usual Hartree Fock approximation, \( g_n \) is replaced by a corresponding molecular orbital; Equation (4) is simply reduced to LCAO-MO approximation.

The polarization for core electrons \( P_c \) is small in UPS region compared with the valence polarization \( P_v \) \([13]\). We thus have an expansion for the inverse dielectric function (we drop the superscript \( r \) for simplicity)

\[
\varepsilon^{-1} = \varepsilon^{-1}_v + \varepsilon^{-1}_v P_c \varepsilon^{-1}_v + \cdots ,
\]

\[
\varepsilon_v = 1 - \nu P_v . \quad (5)
\]

From Eqs. (4) and (5) we obtain an approximation for the amplitude

\[
\langle f_{p\sigma} | \Delta_\k^{eff} | g_n \rangle \sim \sum_{i=0}^{C_{ni}} C_{ni}^\lambda \langle f_{p\sigma} | \varepsilon^{-1}_v \Delta_\k | \chi_i^\lambda \rangle . \quad (6)
\]

The random phase approximation (RPA) where \( \varepsilon^{-1}_v \sim 1 + \nu P_v \) further simplifies the amplitude

\[
\langle f_{p\sigma} | \varepsilon^{-1}_v \Delta_\k | \chi_i^\lambda \rangle \sim \langle f_{p\sigma} | \Delta_\k | \chi_i^\lambda \rangle + \langle f_{p\sigma} | \nu P_v \Delta_\k | \chi_i^\lambda \rangle . \quad (7)
\]

The first term can be calculated by use of the method developed by us \([14-16]\). The second term is a new term.
associated with the radiation field screening. The valence polarization \( P_v \) is thus written
\[
P_v(x, x'; \omega) = \sum_m \{g^r_m(x, x'; \omega + \varepsilon_m)g_m^*(x') + g^a_m(x, x'; \omega + \varepsilon_m)g_m^*(x')\} ,
\]
where the sum over valence states are taken. Even in the UPS region the second term give smaller contribution than the first term because of larger energy denominator in the retarded Green’s function \( g^r \). As valence energies \( \varepsilon_m \)’s are in the small energy region, we can replace \( \varepsilon_m \approx \varepsilon_n \). In these approximations the first term of Eq. (8) is approximated in terms of the valence density matrix \( \rho^v \),
\[
g^r_m(x, x'; \varepsilon_n)g_m^*(x') = g^r_m(x, x'; \omega + \varepsilon_n)\rho^v(x', x) .
\]

We also give another local expression from Eqs. (4) and (9) for \( \rho^v \)
\[
\rho^v(x, x') = \sum_{m\alpha} \sum_{j\beta} C_{mn}^{\alpha\beta} \chi^\alpha_m(x)\chi^\beta_j(x')^* \]
\[
= \sum_{m\alpha} \sum_{j\beta} P^{\alpha\beta}_{ij} \chi^\alpha_i(x)\chi^\beta_j(x')^* ,
\]
where \( P^{\alpha\beta}_{ij} \) is defined by
\[
P^{\alpha\beta}_{ij} = \sum_{m} C_{mi}^\alpha C_{mj}^{\beta*} .
\]
When \( \alpha \neq \beta \) it is bond order between \( \chi^\alpha_i \) and \( \chi^\beta_j \), and it is valence electron charge on \( \chi^\alpha_i \) when \( \alpha = \beta \) and \( i = j \). The substitution of Eqs. (8) and (10) into the second term of Eq. (7) yields
\[
\langle f_{\rho}^{-} | \sum \rho \Delta_{kk}| \chi^\lambda \rangle \sim \int dx f_{\rho}^{-}(x)^* \left[ \sum_q \int dx' dx'' \frac{1}{|r - r'|} f_q(x')f_q^*(x'') \delta(x'' - x') - \sum_m g_m(x')g_m^*(x'') \right] \chi^\lambda(x) .
\]
where \( f_q(x) \) is the particle Dyson orbital \( f_q(x) = \langle 0, N | \psi(x) | q, N + 1 \rangle \), and we have neglected the contribution from hole term of \( g^a(\omega + \varepsilon_n) \).

To derive a useful practical formula we approximate \( \varepsilon_q - \varepsilon_n \approx \omega_p \) and take the sum over \( q \)
\[
\sum_q \omega_q \approx \frac{1}{\omega - \omega_p + i\Gamma} \left\{ \delta(x' - x'') - \sum_m g_m(x')g_m^*(x'') \right\} ,
\]
where \( \omega_p \) is the plasmon-like energy and \( \Gamma \) is its lifetime [12]. The sum over all states \( m \) yields a useful formula in terms of the density matrix \( \rho \) for all electrons and \( \rho^v \)
\[
\text{Eq. (12) } \approx \int dx f_{\rho}^{-}(x)^* \left[ \sum_q \int dx' dx'' \frac{1}{|r - r'|} \delta(x' - x'') - \rho_p(x', x'') \Delta_{kk}(x'') \right] \chi^\lambda(x) .
\]
The first energy dependent factor in Eq. (14) is responsible for the resonant feature when we tune the incident photon energy to that near \( \omega_p \). By use of the local representation (10) and use of the approximate formula for \( \chi^\alpha \)
\[
\chi^\alpha_i(r) = R_i(r_\alpha)Y_{L_i}(\hat{r}_\alpha) , \quad r_\alpha = r - R_\alpha
\]
we obtain a useful formula for the practical application
\[
\text{Eq. (14) } \approx \int dx f_{\rho}^{-}(x)^* \left[ \sum_{Ls} \sum_\lambda \left\{ f_{\rho}^{-} | a_\lambda^\alpha(r_\lambda)_{ss} Y_{L}(\hat{r}_\lambda) | \chi^\alpha \right\} A(L)_{sr} \right.
\]
\[
- \sum_{Ls} \sum_\lambda \sum_{s's'} \left\{ f_{\rho}^{-} \left[ p_{s's'}^{\lambda\alpha} + p_{ccc}^{\lambda\alpha} \delta_{\lambda\alpha} \delta_{ss'} \right] | b_\lambda^\beta(r_\lambda)_{ss'} Y_{L}(\hat{r}_\lambda) | \chi^\beta \right\} \left\{ \chi^\alpha | \Delta_{kk} | \chi^\alpha \right\} B(L)_{ss'} ,
\]
where in terms the Gaunt integral \( G(L L'| L'') = \int Y_{L}(\hat{r})Y_{L'}(\hat{r})Y_{L''}^*(\hat{r})d\hat{r} \)
\[
A(L)_{sr} = \frac{4\pi}{2l + 1} \sum L' G(L_{s} 10 | L') G(L L_s | L') ,
\]
\[
B(L)_{ss'} = \frac{4\pi}{2l + 1} G(L L_s | L'_s) ,
\]

http://www.sssj.org/ejssnt (J-Stage: http://ejssnt.jstage.jst.go.jp)
\[ a_i^s(r)_{sr} = \int \frac{r^1}{r^{1+1}} R_i^s(r') R_i^s(r') r^3 dr', \quad (19) \]

\[ b_i^s(r)_{ss'} = \int \frac{r^1}{r^{1+1}} R_i^s(r') R_i^s(r') r^2 dr'. \quad (20) \]

For the calculation of the matrix elements \( \langle f_{\sigma \lambda} \mid a_\lambda \mid Y_L \mid \chi \rangle \) and \( \langle f_{\sigma \lambda} \mid b_\lambda \mid Y_L \mid \chi \rangle \), we can apply the site-T matrix expansion and consequently multiple scattering theory [14].

So far the radiation field screening effects in the analyses of photoemission from organic solids have not been discussed, in contrast to the photoemission from some inorganic solids. They have observed prominent effects in UPS spectra [8] near \( \omega_p (\omega \approx \omega_p) \), and in photoemission from the surface states of metal [9]. In organic solids collective effects can be much smaller than those in conductive inorganic systems. This physical consideration supports rather crude approximation (16), whereas more sophisticated theoretical approach would be necessary for the UPS analyses of conductive inorganic solids.

**IV. CONCLUSION**

We derive an useful formula to study the radiation field screening in UPS spectra based on the QED theory developed by us [11]. The key formula (16) is written in terms of the density matrix, whose local representation allows us to use well-known bond-order, and net charge density on each atom. The formula includes only one parameter, "plasmon energy" \( \omega_p \) near which the radiation screening is dramatically enhanced. In near future some calculated examples will be demonstrated by use of the present approach.

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