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# Nonrelativistic quantum electrodynamic approach to photoemission theory I. Basic theoretical framework

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**Abstract**

A new nonrelativistic many-body theory to analyze X-ray photoelectron spectroscopy (XPS) spectra has been developed on the basis of quantum electrodynamic (QED) Keldysh Green's function approach. To obtain XPS current density we calculate electron Green's function $g^<$ which partly includes electron–photon interactions. 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 $D_{kl}$. We show the present theory provides a sound theoretical tool to study complicated many-body processes such as the electron propagation damping, intrinsic, extrinsic losses and their interference, and furthermore, resonant photoemission processes. We have also found the importance of the mixed photon Green's functions $D_{0k}$ and $D_{k0}$ which have been supposed to be unimportant for the XPS analyses. They, however, directly describe the radiation field screening. In this work, photon field screening effects are discussed in one-step theory, where the electron–photon interaction operator $\Delta$ is proved to be replaced by $\varepsilon^{-1}\Delta$ beyond linear approximation. Beyond free photon Green's function approximation, photon scatterings from the electron density are incorporated within the present QED theory. These photon field effects can directly describe the microscopic photon field spatial variation specific to near the surface region and nanoparticle systems.


*Keywords:* XPS theory; QED; Resonant photoemission; Intrinsic and extrinsic losses; Radiation field screening; Nanoparticle

## 1. Introduction

A useful and practical many-body approach to the analyses of X-ray photoelectron spectroscopy (XPS) spectra has been developed by Bardyszewski and Hedin by use of the projection operator techniques [1]. Further refinement is found in [2]. The above theoretical approach is practically useful to describe the photoemission processes in terms of the damping photoelectron wave functions under the influence of the optical potentials [3–5], for which they can easily handle the hole effects. Natoli et al. have developed a multichannel multiple-scattering theory, which in principle is able to incorporate the local atomic multiplet feature [6].

For the discussion of X-ray photoelectron diffraction (XPD) spectra [7,8], both of the Debye–Waller factor and the Franck–Condon factor play an important role [9–11]. To calculate these factors within the projection operator technique, we first obtain the XPD intensity at some fixed nuclear configuration and take average over all phonon states; this direct

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approach has been applied to the X-ray absorption fine structure (XAFS) analyses [10,11]. It is, however, difficult to go beyond the harmonic approximation for nuclear vibration or the single-scattering approximation for the photoelectron propagation.

First principle formal XPS theories have been developed based on Keldysh Green's functions [12–15]. These theories gave formally exact perturbation expansion of the photoemission intensity. However, these theories have proposed no convenient and applicable formulas to analyze XPD spectra. In a Keldysh Green's function method each renormalized one-electron Green's function already includes phonon effects, whereas it is difficult to include core-hole effects for the optical potentials. So far the nonequilibrium Green's function approach has successfully been developed in order to discuss the finite temperature XPS spectra and in particular refs. [16,17] provide convenient and applicable formulas to analyze multiatom resonant photoemission (MARPE) spectra [18–21] and loss spectra. These papers demonstrate the importance of symmetry lowering around the photoemission atom to give rise to prominent MARPE spectra [16,17].

Most of the XPS theories implicitly assume a bare coupling to the external photon field, however, in general this external field will be influenced by the material. Chasse and Niebergall approximated the radiation field outside and inside the solid by the classical electrodynamical local field [22,23]. They derived analytical expressions within a real-angle representation of Fresnel equations to reveal the influence of reflection, refraction and absorption of radiation at the vacuum–solid boundary. This affects photoelectron diffraction excited with polarized light of energy $\hbar\omega$ =30–100 eV [23]. This result is quite interesting, however it also raises a question about the applicability of the classical macrospically local field approximation used there. The external field is screened by the dielectric response of the material, which is much enhanced by surface plasmon generation [14]. This effect has been observed in connection with UV photoemission [24]. Though these effects are well known, the full incorporation into one-step photoemission calculations is still lacking. Qualitative discussion based on physical insight [25] or the time-dependent local density approximation (TDLDA) introduced by Zangwill and Soven [26] replaces the vector potential $\mathbf{A}$ by $\varepsilon^{-1}\mathbf{A}$. The importance of the radiation field screening is demonstrated by large changes ($\approx$100%) in the photoelectron current excited from the valence band of $TiSe_2$ around 20 eV [27,28]. Another interesting example is the $L_{2,3}$ edge intensity ratio of 3d transition metals. For these metals, the independent electron approximation predicts an $L_3/L_2$ transition intensity branching ratio near 2:1, while the observed ratio varies considerably with atomic number $Z$, and is closer to 1:1 for metals like Ti and V. A successful explanation is given by Ankudinov et al. taking account the radiation field screening in the TDLDA approach [29]. To discuss the resonant photoemission processes, the radiation field screening plays an important role, however no first principle derivation of the radiation field screening term has been found yet [17].

To discuss the many-body effects related to the optical field, we should apply the most reliable theoretical framework, quantum electrodynamic (QED) theory where electron and photon fields are simultaneously quantized. So far relativistic QED theory has been applied to XPS and XAFS analyses, which provides us with relativistic many-body theory to analyze those spectra [30]. Only short discussion is given there for the optical field effects.

In this work a new nonrelativistic QED theory is developed to discuss the complicated many-body effects such as resonant photoemission and the optical field effects by use of Keldysh Green's functions. In this theoretical framework we have to solve coupled equations for the electron and photon Green's functions. The electron selfenergy $\Sigma$ includes the photon Green's functions and the photon selfenergies $P_{lm}$ include the electron Green's functions. We derive QED Hedin's equations to construct systematic approximations. The present theory gives clear physical meanings to each term in comparison with the relativistic QED theory. So far first principle theoretical derivation of the radiation field screening has not been given. We find mixed photon Green's functions – transverse and longitudinal mixed functions – implicitly include the radiation field screening. When the free photon Green's functions are used, we again obtain the previous one-step XPS formulas to discuss the loss and resonance effects [16,17]. Beyond the free photon Green's function approximation, we can discuss the microscopic photon propagation effects on the photoemission excitation processes, which is difficult to be described without use of the QED theory. These optical field effects should be important to study the photoemission from near surface region and from nano-particles, where the photon fields rapidly change in microscopic spatial order.

## 2. Quantum electrodynamic Green's functions

In this section, we discuss nonrelativistic QED Keldysh Green's function theory on the basis of DuBois theory [31], which will extensively be applied to XPS and UPS analyses.

### *2.1. Photon Green's functions*

The nonrelativistic Hamiltonian is written for a system of interacting electrons and nuclei, coupled with the radiation field in atomic unit [31]