Multiple-Scattering Approach to Angle-Resolved Ultraviolet Photoelectron Spectroscopy of Large Molecules

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Angular dependence of ultraviolet photoelectron spectroscopy (UPS) has been discussed here by using a multiple-scattering theory and has been applied to some large organic molecules. Low kinetic energy electron (<~50eV) relatively have long mean free path. Moreover the electron-atom scattering shows isotropic scattering features. In order to analyze the local electronic and geometric structure for thin film of large organic molecules by UPS, we should consider the multiple-scattering processes of the photoelectron. In this paper, convergence features of calculated spectra have been discussed by considering scattering order analysis for the calculation of UPS for large organic molecules. Because carbon atoms in organic molecules are weak scatterers, we can neglect high order intramolecular scattering processes. However, the theoretical calculations show that we need careful consideration for near the photoemission threshold energy and for the analysis of large molecule.

Keywords: Electron-solid interactions; Green’s function methods; Photoelectron diffraction; Nano-electronics and related devices;

I. INTRODUCTION

Ultraviolet Photoelectron Spectroscopy (UPS) is useful to study valence electron state. Recently, interface region in organic material and metal substrate is important to understand super-functionality organic devices. In order to characterize the organic devices, we must know the valence state features. Therefore, the UPS analysis plays an essential role of the development for organic devices. Angle-resolved UPS (ARUPS) has been recognized as a useful tool of studying surfaces for clean and adsorbed system [1]. The ARUPS spectra have information for geometries of adsorbed molecules, valence band features, and so on. Synchrotron light source allows us to use energy-tunable highly-polarized photons and gives much information of anisotropic features.

There are three major theoretical approaches to approximate the final photoelectron state in UPS analyses. In order to analyze an isolated molecule in gas phase, molecular orbital (MO) method is widely used. For well-defined surface or periodic huge system, we can use band theory. These two methods are not suitable for studying organic devices about adsorbed molecules on surface and their interface region. MO method treats the continuum state as bound state. Band theory cannot be applied to non-periodic system (adsorbed molecules, surface, interface and so on). On the other hand, real-space multiple-scattering theory needs no long range order. If we analyze UPS of organic devices, this specific feature is useful to discuss UPS from large organic molecules adsorbed on substrate.

Because of the non-localized initial state, we should take the interference of photoelectron waves from different atomic centers. Independent atomic center (IAC) approximation was suggested by several authors [2, 3]. In this approximation, the photoelectron state is represented by sum of the amplitudes for each atomic centers. Later, scattering effects are considered in one-step theory [4]. The other one-step theories are reviewed by Braun [5]. Because of the isotropic scattering and long photoelectron mean free path, the multiple-scattering is important in the lower kinetic energy region (<~50eV). So far real-space full multiple-scattering calculations have not been applied to UPS from large organic molecules. We now apply it to some large organic molecules. We show the importance of multiple-scattering effects in UPS analyses.

In section 2, we show a derivation of the multiple-scattering formula. We apply this theory to UPS spectra of a small molecule (benzene) and a large molecule (copper phthalocyanine). The energy dependence and scattering order analyses are shown in section 3.

FIG. 1: Schematic of the energy diagram. \( E_1 \) is the final state energy from muffin-tin constant. In multiple-scattering calculation, the electron kinetic energy is defined by the \( E_1 \). \( E_2 \) is the final state energy from vacuum level and is natural definition of photoelectron kinetic energy. The length of big arrow means photon energy \( E_{ph} \). Usually, we should find the relation \( E_1 > E_2 \).
FIG. 2: Calculated UPS spectra of benzene HOMO orbital. Photoelectron kinetic energy is shown in figure. The photon energies (kinetic energies $E_1$) are (a) 26.6eV (40eV), (b) 86.6eV (100eV), and (c) 186.6eV (200eV). (d) is schematic of benzene molecule. The HOMO orbital is expressed by superposition of carbon 2p orbitals. Values on carbon atom in (d) mean coefficients of each 2p orbitals. 'direct' means the calculated result without scattering terms. 'single' and 'double' are the result of scattering order limited calculations. 'full' means the calculated result of the infinite order multiple-scattering.

II. MULTIPLE-SCATTERING FORMULA

A. Theories for photocurrent calculation

We can easily find sophisticated many-body theories of photocurrent in many literatures [6–13]. In order to use these theories for numerical calculations, we have to derive single particle formulations. The first and most simple treatment of one electron approximation for photocurrent which is so-called three-step model of photoemission has been given by Berglund and Spicer [14]. The three steps are the excitation of the photoelectron, the transportation through the crystal and the escape into the vacuum. In the framework of this model, electron self-energy corrections are not considered. In the quasi-particle spectrum, the real part and the imaginary part of the self-energy give the damping effect and the energetic shifts each other. This means that the initial and final state in the photoemission process are assume to be Bloch state with an infinite lifetime. So this theory may fail to give exact transition rates and do not suitable to apply to calculate photoemission from surface state. To solve this problem, one-step model or dynamic approach has been suggested for final state calculations by Liebsch [15] and Spanjaard et al. [16]. This theory includes multiple-scattering of the photoelectron in final state. The multiple-scattering formulation can easily include self-energy corrections. Later, multiple-scattering effects were properly included for both initial state and final state by Pendry [17, 18]. In order to apply one-step theory to the UPS of organic molecule, we need to calculate initial state wavefunction. The initial valence state are composed by molecular orbitals. Our formulation is described by the transition rate of the photoexcitation from the initial molecular-orbital state to final-state which are multiple-scattering state obtained by using scattering Green’s function.
FIG. 3: Same as Fig. 2 except for the result of copper phthalocyanine. The kinetic energies ($E_1$ in Fig. 1) are (a) 20eV, (b) 50eV, and (c) 100eV. (d) is schematic of copper phthalocyanine molecule.

B. Multiple-scattering formula for valence electron excitation

A detailed theoretical treatment within many-body theory has been discussed in ref.[19]. The photoelectron intensity $I(k,\omega)$ in atomic unit without unimportant constants is written by

$$I(k,\omega) = |\langle \Psi_k^- | \Delta | \Phi_0 \rangle |^2 \delta(E_f - E_i - \omega),$$ (1)

where $k$ is photoelectron wave vector and $\omega$ is photon frequency. $\Psi_k^-$ is photoelectron wavefunction. The $\Delta$ is electron-photon interaction operator. In dipole approximation, the explicit expression is given in a compact form neglecting unimportant constant $\Delta = rY_{1m_p}$. If we assume that the initial state can be written within the linear combination of atomic orbital (LCAO) approximation by

$$|\Phi_i\rangle = \sum_{An} c_{An} |\phi_{An}\rangle,$$ (2)

where $A$ and $n$ means a $n$th atomic orbital on a site $A$ and the orbital is written by $\phi_{A,n}$. The $c_{An}$ is the coefficients of the orbital component in the initial valence state within the LCAO approximation. By use of these, the photoelectron intensity is written by

$$I(k) = |M(k)|^2 \delta(E_f - E_i - \omega)$$ (3)

$$M(k) = \sum_{An} \sum_{\alpha} e^{-ikR_\alpha}$$

$$\times \sum_{L,L'} Y_L(k) [(1-X)^{(-1/2)}_{L,L'} m_{L',L}^{An}(k)m_{L,L'}^{An}(k)_m],$$ (4)

where $L$ means $L = (l, m)$ and $\alpha$ is atom site. The matrix element $m_{L',L}^{An}(k)_m$ is

$$m_{L',L}^{An}(k)_m = \sqrt{\frac{\pi}{2}} e^{-i\delta^{An}_L} \rho^{An}_L(k) G(L_{An}, 1m_p | L').$$ (5)

$\delta^{An}_L$ is scattering phaseshift of absorbing site, and $\rho^{An}_L(k)$ is radial dipole integral. $G(L_{An}, 1m_p | L')$ is Gaunt’s integral which gives selection rule to photoelectron excitation. The scattering phase shifts are obtained by conventional non-local Hartree-Fock calculations[20].
III. RESULTS AND DISCUSSION

First we analyze convergence features of photoelectron intensity by calculating the scattering order dependence. Electron inelastic mean free path strongly depends on the kinetic energy. The mean free path have minimum point around 50eV. In the low kinetic energy region (0 ~ 50eV), photoelectrons have long mean free path and the value rapidly decrease. In the higher kinetic energy region, the value of the mean free path grow only slowly. The convergence depends on the energy of photoelectron and scattering power of the scatterer. In the framework of the multiple-scattering theory, it is convenient to set the energy zero point to muffin-tin constant potential (See Fig. 1). If we discuss the electron inelastic mean free path in solid, the kinetic energy of the photoelectron is defined by the $E_1$ in Fig. 1. We subsequently use this definition except in special circumstances.

Figure 2 shows calculated angler distributions of UPS spectra for a benzene HOMO orbital at three photoelectron kinetic energies. All results are polar-plotted photoelectron intensities by azimuth-scan and emission angle is 45°. Molecular plane is parallel to $xy$-plane and we consider $z$-axis polarized photon in all calculations. In Fig. 2, 'direct' means the calculated result without scattering terms. 'single' and 'double' are the results of scattering-order limited calculations. 'full' means the result of infinite order multiple-scattering calculations. Grobman also have shown similar calculations within independent atomic center approximations[3]. However, their calculations do not include multiple-scattering processes and potential in interstitial region. In Fig.2, the muffin-tin constant potential is -21eV from vacuum level. The benzene molecular orbital is obtained by Gaussian 03 code[21]. The Hartree-Fock calculation is performed by STO-3G type basis functions. In this calculation, the benzene HOMO level is -7.6eV from vacuum level. Thus if we want to translate the kinetic energy $E_1$ to photon energy, $E_{ph} = E_{1} - 21 - (-7.6)$ gives the photon energy. In Fig. 2, the photon energies (the kinetic energies $E_1$) are (a) 26.6eV ($E_{1}=50$eV), (b) 86.6eV ($E_{1}=100$eV), and (c) 186.6eV ($E_{1}=200$eV). The comparison between 'direct' and 'full' in Fig. 2 shows the importance of the multiple-scattering processes in lower kinetic energy region as shown Fig. 2(a) and the higher kinetic energy region as shown Fig. 2(c). This behavior reflects energy dependence of the electron inelastic mean free path. Because of weak and small number of scatterers, the multiple-scattering contributions are not serious problems for benzene molecule.

The calculated results of UPS for copper phthalocyanine HOMO at several photoelectron kinetic energies are shown in Fig. 3. The muffin-tin constant potential is -17.8eV from vacuum level. The CuPc HOMO level is -5.4eV from vacuum level in same calculation method. In Fig. 3, the photon energies (the kinetic energies $E_1$) are (a) 7.6eV (25eV), (b) 37.6eV (50eV), and (c) 87.6eV (100eV). These result shows same convergence features as the results of benzene. The difference between 'direct' and 'full' is larger than the result of benzene. The behavior of 'direct' and 'full' depends on the molecule and the polar-angle of the detector's position. It is caused by interference of many multiple-scattering state. Therefore, theoretical analyses sometimes give wrong information if we do not consider multiple-scattering of photoelectron.

We analyzed the UPS of CuPc near the photoemission threshold energy (Fig. 4). The difference between 'full' and 'direct' is quite large in Fig. 4. In order to analyze the energy threshold region, we must consider infinite-order multiple-scattering calculation.

IV. CONCLUSION

First we have checked convergence of scattering orders. The electron mean free path play an important roles in the convergence features. For example, the energy of photon obtained by source He I is 21.2 eV. The kinetic energy of the photoelectron emitted from highest occupied molecular orbital is ~10eV. We however consider the kinetic energy defined by $E_1$ in Fig. 1 for intramolecular scattering processes. In many cases, the kinetic energy of the photoelectron for UPS is about ~30eV in the definition of $E_1$. It is in minimum region of mean free path. Moreover carbon atoms in organic molecule are weak scatterer. Multiple-scattering effects are often weak. However, we have shown importance of intramolecular multiple-scattering processes for large molecules such as copper phthalocyanine. We can also expect the importance of multiple-scatterings in UPS from multilayer system. This real-space multiple-scattering theory requires only the short range order structure and is good at calculating such kind of disordered system. Therefore, the intermolecular scattering effects should be checked in forthcoming paper. Large molecules (CuPc, polyacene, Alq$_3$ and so on) play important roles in organic devices. In order to study angle resolved UPS of these systems, we should pay attention to the multiple-scattering effects.
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