Multiple scattering approach to photoemission from the highest occupied molecular orbital of pentacene

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ABSTRACT

Angle resolved photoemission spectroscopy (ARPES) gives detailed information about the surface electronic structures and oriented molecules. In the so-called orbital tomography method, the ARPES intensity is obtained by a simple Fourier transform of the initial state molecular orbital. While this method has given good results for a number of π-orbital systems, it is known to have strong limitations because the final state is approximated as a plane wave and thus photoelectron scattering is completely neglected. Here we propose an ARPES theory where the initial states are taken from a quantum chemistry method and the final states are calculated in multiple scattering theory. The initial molecular orbitals are reexpanded in a multi-site spherical wave basis and the multiple scattering potential is constructed from the ab initio charge density. These computations are performed algebraically using newly developed algorithms. The method is applied to pentance and the results are compared with the plane wave approximation.

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1. Introduction

In the last decades, intensive research has been done on organic semiconductors composed of π conjugated organic molecules such as pentacene [1,2]. Compared to traditional inorganic materials, organic semiconductors are flexible, lightweight and cost-effective [3,4]. As organic semiconductors absorb light in visible region and often show electronic conductivity, they have potential for the applications such as organic light emitting diodes (OLEDs), organic solar cells (OSCs), and organic field effect transistors (OFETs) [4–6].

Angle resolved photoelectron spectroscopy (ARPES) is a powerful tool to investigate the electronic structure of surfaces. For photon energies of a few tens of eV, the photoelectron has a short inelastic mean free path and so the near surface region is probed.

Recently, Puschnig et al. [7] have developed the so-called orbital tomography method, by which the real space charge density of selected molecular orbitals can be reconstructed from the ARPES

data. The orbital tomograph method relies on the plane wave (PW) approximation for the final state. Since the photoelectron energy is fairly low in ARPES, electron scattering at the molecular potential is expected to be strong and the validity of the PW approximation is questionable [8]. One of the examples where the PW approximation fails is circular dichroism in ARPES intensity [9]. Because the PW approximation gives exactly same intensity maps with a right and left handed light.

Photoelectron scattering effects can conveniently be taken account for using multiple scattering (MS) theory [10–12]. Usually single atom data is used for the construction of the scattering potentials. However, such potentials are inconsistent with the molecular orbital electronic structure. Here we overcome this shortcoming by constructing the MS potential from the electronic structure as given by a quantum chemistry method. For a Gaussian-type orbital basis (as used, e.g. in the GAUSSIAN 09 code [13]). we have developed analytical formula and algorithms for mapping the molecular orbitals onto a MS spherical harmonics basis and have constructed the corresponding MS potential.

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2. Theory

2.1. The photoemission intensity

From Fermi's golden rule, the photoemission intensity becomes

$$I(\mathbf{k}) \propto \sum_f |\langle \psi_f | \Delta | \psi_i \rangle|^2 \delta(\epsilon_f - \epsilon_i + \hbar\omega), \tag{1}$$

where, ψ_i is the initial state and ψ_f is the final state. Δ is the electron-photon interaction operator and is expressed using the polarization vector $\hat{\boldsymbol{\epsilon}}$, the momentum operator $\mathbf{p}$ and the position operator $\mathbf{r}$

$$\Delta \propto \hat{\boldsymbol{\epsilon}} \cdot \mathbf{p} \propto \hat{\boldsymbol{\epsilon}} \cdot \mathbf{r} \quad . \tag{2}$$

In the PW approximation, the final state in Eq. (1) is a plane wave. Then, $I(\mathbf{k})$ simply becomes proportional to the Fourier transform of the initial state $\tilde{\phi}_i(\mathbf{k})$

$$I(\mathbf{k}) \propto |\hat{\boldsymbol{\epsilon}} \cdot \mathbf{k} \ \tilde{\phi}_i(\mathbf{k})|^2. \tag{3}$$

If the energy of photoelectron is high enough, the scattering effects are not so strong and the PW approximation is justified to some extent. Also, scattering effects may be partly suppressed when the molecule is flat and the polarization vector is perpendicular to the molecular plane.

On the other hand, photoelectron scattering can be fully included in MS theory. Here we employ the usual muffin-tin (MT) approximation where the scattering potential is divided into spherically symmetric potential regions (MT spheres) located at atoms and the remaining "interstitial" regions where the potential is constant. The final state is a solution of the Lippmann–Schwinger equation in this potential with appropriate boundary conditions. The photoemission intensity is written as [10]

$$\begin{aligned} I(\mathbf{k}) \quad &\propto |\langle \psi_{\mathbf{k}}^- | \Delta | \phi_i \rangle|^2 \\ &\approx |\sum_\alpha e^{-i\mathbf{k} \cdot \mathbf{R}_\alpha} \sum_{AL_1L_2L_3} Y_{L_1}(\hat{\mathbf{k}}) \\ &\times [1 + X + X^2 + \cdots]_{L_1L_2}^{\alpha A} M_{L_2L_3}^A|^2. \end{aligned} \tag{4}$$

The superscript of $\psi_{\mathbf{k}}^-$ indicates the imposed boundary condition, where the wave function is formed by fully interacting incoming waves and a plane wave which describes electron into the detector. $Y_L(\hat{\mathbf{k}})$ is a spherical harmonics, and $L \equiv (l, m)$. The matrix $X_{LL'}^{\alpha\beta}$ describes the propagation of photoelectron from atom β to atom α and scattering at atom α, and $M_{LL'}^A$ are the optical transition matrix elements of atom A.

2.2. Algorithm for GAUSSIAN 09 output to MS calculations

2.2.1. Spherical averages of charge density and potential

We performed molecular orbital calculations by GAUSSIAN 09 to construct the scattering potential from the charge density and to obtain the initial state molecular orbital.

As basis sets are composed of Gaussian type orbitals (GTOs) in GAUSSIAN, the electron density can be expanded by products of GTOs. Any product of GTOs can be expanded by Hermite Gaussian functions which are defined by partial derivatives of a Gaussian function [14]

$$\Lambda_{tuv}(\mathbf{r}_p, p) = \frac{\partial^t}{\partial P_x^t} \frac{\partial^u}{\partial P_y^u} \frac{\partial^v}{\partial P_z^v} e^{-pr_p^2}, \tag{5}$$

where t, u, v are orders of partial derivatives, $\mathbf{r}_p = \mathbf{r} - \mathbf{P}$, $\mathbf{P}$ is a point between two atomic sites, and the exponent p is determined by the exponents of two GTOs. The spherical averages of Hermite Gaussian

functions in terms of a given center $\mathbf{C}$ are obtained by integrating Eq. (5)

$$\begin{aligned} \int \Lambda_{tuv} \quad &(\mathbf{r}_p, p) d\hat{\mathbf{r}}_c = \\ &\frac{2\pi}{pr_c} \sum_{t'u'v'} tC_{t'} uC_{u'} vC_{v'} F_{t-t', u-u', v-v'} S_{t'u'v'} \quad . \end{aligned} \tag{6}$$

Here, we introduced the following two terms

$$F_{tuv} = \frac{\partial^t}{\partial P_x^t} \frac{\partial^u}{\partial P_y^u} \frac{\partial^v}{\partial P_z^v} \frac{1}{R_{cp}}$$

where $\mathbf{r}_c = \mathbf{r} - \mathbf{C}$ and $\mathbf{R}_{cp} = \mathbf{C} - \mathbf{P}$. To obtain the spherically averaged density, only a finite number of F_{tuv} and S_{tuv} term are needed. They can be calculated by using recurrence equations. Once the spherically averaged density is obtained, the spherically averaged scattering potential can be constructed using the local density approximation.

2.2.2. Angular momentum expansion of an initial state

In order to use an initial state molecular orbital in MS theory, we need its angular momentum expansion on the neighboring atomic sites. Any GTO has the following form

$$\begin{aligned} \chi(\mathbf{r}) \quad &= x_g^l y_g^m z_g^n e^{-\alpha r_g^2} \\ &= e^{-\alpha(r_c^2 + R_{cg}^2)} x_g^l y_g^m z_g^n e^{-2\alpha \mathbf{r}_c \cdot \mathbf{R}_{cg}}, \end{aligned} \tag{9}$$

where l, m, n are integers which determine the angular dependence of a GTO, $\mathbf{r}_g = \mathbf{r} - \mathbf{G}$, $\mathbf{R}_{cg} = \mathbf{C} - \mathbf{G}$, $\mathbf{G}$ is the center of a GTO, and $\mathbf{C}$ is the center of the angular momentum expansion. Then, the polynomial and the later exponential in Eq. (9) depend on the direction from the center $\mathbf{C}$. The polynomial can be expanded in spherical harmonics easily, and the exponential can also be expanded by using the analytic continuation of the Rayleigh expansion [15]

$$\begin{aligned} e^{-2\alpha \mathbf{r}_c \cdot \mathbf{R}_{cg}} = \quad &4\pi \sum_L (-1)^l \\ &\times i_l(2\alpha r_c R_{cg}) Y_L(\hat{\mathbf{r}}_c) Y_L^*(\hat{\mathbf{R}}_{cg}) \quad , \end{aligned} \tag{10}$$

where i_l is a modified spherical Bessel function. So, we need to express products of spherical harmonics by a series of spherical harmonics.

3. Results and discussion

3.1. Computational details

We have applied the above theory to ARPES from the HOMO level of pentacene and compare the result with the PW approximation. A pentacene molecule consists of five linearly fused benzene rings. The calculations are performed according to the experimental conditions [7]. The photoelectron energy is 29.8 eV; the light is linearly p-polarized; the angle between the incident light $\mathbf{q}$ and the surface normal $\mathbf{n}$ is fixed to $\alpha = 40°$; $\mathbf{q}$, $\mathbf{n}$ and photoemission direction $\mathbf{k}$ lie in the same plane. The molecules lie essentially flat on the surface. The long molecular axis is in the surface plane while the short axis is tilted by $\beta = \pm 25°$ [7], see Fig. 1. We use the ground state wave function of the neutral molecule for both the PW and the MS calculations. For simplicity, scatterings off the substrate are neglected and ARPES intensity maps of a single molecule are computed.