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Application of Koopmans' theorem for density functional theory to full valence-band photoemission spectroscopy modeling

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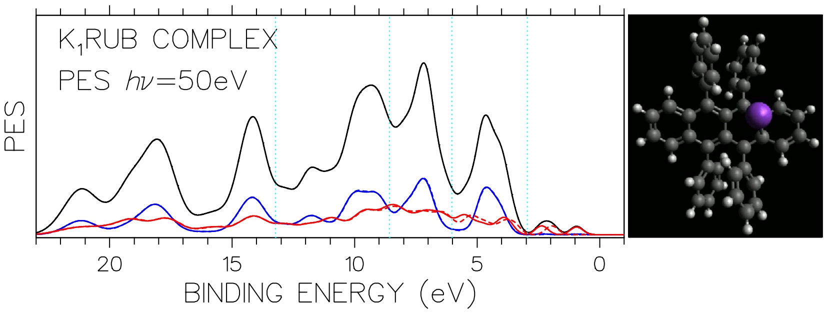
HIGHLIGHTS

- A photoemission (PES) modeling scheme is developed.
- The PES spectra of rubrene and potassium–rubrene complex are computed.
- Koopmans' theorem for KS-DFT is verified over the full valence-band.
- The anionic approximation to potassium–rubrene complex is justified.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, Koopmans' theorem for Kohn-Sham density functional theory (KS-DFT) is applied to the photoemission spectra (PES) modeling over the entire valence-band. To examine the validity of this application, a PES modeling scheme is developed to facilitate a full valence-band comparison of theoretical PES spectra with experiments. The PES model incorporates the variations of electron ionization cross-sections over atomic orbitals and a linear dispersion of spectral broadening widths. KS-DFT simulations of pristine rubrene (5,6,11,12-tetraphenyltetracene) and potassium–rubrene complex are performed, and the simulation results are used as the input to the PES models. Two conclusions are reached. First, decompositions of the theoretical total spectra show that the dissociated electron of the potassium mainly remains on the backbone and has little effect on the electronic structures of phenyl side groups. This and other electronic-structure results deduced from the spectral decompositions have been qualitatively obtained with the anionic approximation to potassium–rubrene complexes. The qualitative validity of the anionic approximation is thus verified. Second, comparison of the theoretical PES with the experiments shows that the full-scale simulations combined with the PES modeling methods greatly enhance the agreement on spectral shapes over the anionic approximation. This agreement of the theoretical PES spectra with the experiments over the full valence-band can be regarded, to some extent, as a collective validation of the application of Koopmans' theorem for KS-DFT to valence-band PES, at least, for this hydrocarbon and its alkali-adsorbed complex.

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Introduction

Koopmans' theorem states that the unrelaxed vertical ionization potential for removing an electron in a spin-orbital of the

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Hartree-Fock (HF) single-determinant wavefunction is just the negative of the spin-orbital energy [1,2]. Since its first publication in 1934, the theorem has played an important role in quantum chemistry and has been frequently used for the interpretation of photoemission spectra [3]. Since the first inception of Kohn-Sham density functional theory (KS-DFT) in the 1960s [4,5], the subsequent developments in simulation algorithms and computation technologies have expedited the advances of KS-DFT and demonstrated its advantage on computational efficiency [6]. At the beginning of the 21st century, D. P. Chong and coworkers showed that the negative of the KS-DFT eigenenergy is an approximation to the relaxed vertical ionization potential and the accuracy of this approximation appears to be good for outer valence orbitals [7]. In short, they called this application of "Koopmans' theorem for KS-DFT" the "$-\epsilon$ method." Recently the application of Koopmans' theorem to KS-DFT binding energies has been validated for core-level electrons [8].

The relaxed vertical ionization potentials are associated with the binding energies obtained by the photoemission spectroscopy (PES). The PES is an important technology for the exploration of electronic structures of materials. In the literature, the experimental PES spectra are frequently compared with the density of states (DOS) spectra or the stick spectra of the orbital energies obtained by the KS-DFT. Satisfactory results of these comparisons have been reported [9–14]. However, aspects of spectral comparison include peak energies and spectral shapes, and the shapes of spectra are, at least, characterized by the relative peak intensities and widths. Hence, using the DOS or stick spectra for spectral comparison has deficiencies in addressing two issues on the application of Koopmans' theorem to KS-DFT valence-band PES spectra. First, the DOS-based spectral comparison often focuses on peak energy comparison, and pays less attention to the spectral shape comparison. Second, the examination of the validity of Koopmans' theorem for KS-DFT in the entire valence-band is less achievable with an indirect comparison of PES with DOS spectral shapes.

To alleviate the above two deficiencies, a PES modeling method has to be developed for a more direct comparison of the theoretical and experimental spectra. In this article, a PES modeling method is presented with two important aspects taken into account. First, the effects of variations of electron ionization cross-sections with atomic orbitals are introduced to the modeling. Second, the dependencies of ionization cross-sections on binding energies are empirically incorporated into the models. With these effects taken into account, the shapes of theoretical PES spectra can be directly compared with the experiments, which enables a new way to examine the validity of the KS-DFT version of Koopmans' theorem over full valence-bands.

In the literature, Koopmans' theorem is often verified by comparing individual KS-DFT orbital energies with the PES experiments of small molecules [7]. Since there are numerous KS-DFT orbitals in the full valence-bands of moderate-sized molecules, the one-by-one comparison of KS-DFT orbital energies becomes impractical. The direct comparison of the theoretical PES spectra with the experiments is more achievable, and can be considered as a collective means to examine the validity of the KS-DFT version of Koopmans' theorem applied to full valence-bands.

To realize and verify the above ideas, the PES modeling methods are applied to pristine and potassium-adsorbed rubrenes. Rubrene (5,6,11,12-tetraphenyltetracene, $C_{42}H_{28}$) has a tetracene-like backbone and four phenyl side groups [15–17]. There are two stable rubrene isomers. The D_2 isomer has a twisted backbone, whereas the C_{2h} isomer planar [18]. Rubrene is an organic semiconductive material with many applications in flexible electronics [19–22]. This material is frequently electrically doped in applications to enhance the electron mobility [23,24]. The experimental PES spectra of pristine and potassium-doped rubrene thin films are available for the full valence-band in the literature. The anionic approximation is utilized to analyze the electronic structures of potassium–rubrene complex and qualitative agreement with the experiments has been reached [25]. In this approximation, the potassium–rubrene complex is modeled as a rubrene anion with -1 charge. The validity of this anionic approximation is also to be verified by the full-scale simulations of this work.

Photoemission spectroscopy modeling

At the incidence of synchrotron radiations of energy $\hbar\omega$ larger than the electron binding energies, some of the electrons in the materials are stricken loose and escape from the material surface. The experimental PES spectra attained by collecting these photoelectrons are modeled by taking the orbital- and energy-dependencies of the ionization cross-sections of photoelectrons into account.

Effects of ionization cross-sections

The effects of ionization cross-sections on PES spectra are modeled in this subsection. The number of photoelectrons p_i contributed by the ith molecular orbital is modeled by

$$p_i = n_i \sum_{\mu=1}^{K} \sigma_\mu M_{\mu i} = \sum_{g=1}^{n_G} p_g^i \quad \text{for} \quad i = 1, 2, \ldots, L, \tag{1}$$

where the number of photoelectrons is in an arbitrary unit, and $\sigma_\mu = \sigma_\mu(\hbar\omega)$ is the photoionization cross-section of the electron in the μth atomic orbital at the radiation energy of $\hbar\omega$. The atomic subshell photoionization cross-sections are available in the literature [26]. $M_{\mu i}$ is the population contribution of the μth atomic orbital to the ith molecular orbital. The population contribution must satisfy the conservation relation $\sum_{\mu=1}^{K} M_{\mu i} = 1$ for all i because a molecular orbital always represents one and only one quantum level of the molecular system for each spin component. The occupation number n_i of the ith molecular orbital is 1 if the orbital is occupied, and 0 otherwise. K and L are the numbers of atomic and molecular orbitals, respectively. In the second half of the equation, the atomic orbitals are divided into n_G groups of different characteristics, the number of photoelectrons contributed by the gth group G of atomic orbitals to the ith molecular orbital is thus given by $p_g^i = n_i \sum_{\mu \in G} \sigma_\mu M_{\mu i}$.

With the above photoelectron contribution factor, the total spectra $\mathrm{PES}(E)$ can be written as the sum of partial spectra $\mathrm{PES}_g(E)$ and can be computed by

$$\mathrm{PES}(E) = \sum_{g=1}^{n_G} \mathrm{PES}_g(E) \quad \text{with}$$

$$\mathrm{PES}_g(E) = \sum_{i=1}^{L} \frac{p_g^i}{\sigma_i \sqrt{2\pi}} \exp\left[-\frac{(E - E_i)^2}{2\sigma_i^2}\right], \tag{2}$$

where E is the spectral energy. Each energy level of a molecular orbital is broadened by a Gaussian function of unit area to take the intrinsic and extrinsic broadening effects [3] into account. E_i and σ_i are the scaled-and-shifted level energy and the standard deviation of the ith molecular orbital, respectively. Notationally, the standard deviation σ_i is not to be confused with the photoionization cross-section σ_μ in Eq. (1). $\mathrm{PES}_g(E)$ is the partial PES spectra associated with the gth group of atomic orbitals. The total PES spectrum is decomposed into these partial spectra associated with different groups of atomic orbitals.

It has been reported that, for a given molecule, the KS-DFT orbital energies differ from the experimental binding energies with an amount roughly same for all valence orbitals [27]. This difference may be attributed to the fact that the reference levels for

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