Journal of Electron Spectroscopy and Related Phenomena 207 (2016) 60–64

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Simulation of molecular Auger spectra using a two-electron Dyson propagator

Y. Hori, M. Nishida, F.H. Lim, T. Ida*, M. Mizuno

Chemistry Course, Division of Material Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

ARTICLE INFO

Article history:
Received 23 October 2015
Received in revised form 7 January 2016
Accepted 7 January 2016
Available online 26 January 2016

Keywords:
Auger electron spectroscopy
Double ionization potential
Electron propagator

ABSTRACT

In order to simulate Auger electron spectra (AES), we propose the use of the two-electron Dyson propagator with the shifted denominator approximation (SD2). The double ionization potentials (DIPs) of molecules calculated using the SD2 method have shown good agreement with experimental data. This method can be used to calculate each DIP separately, and reducing the matrix dimensionality into that of only a two-hole configurations. We carried out AES simulations of water (H_2O), ethylene (C_2H_4), and formaldehyde (H_2CO) molecules and compared with the observed spectra. Furthermore Auger line shapes of glycine and hydrated glycine molecules were simulated, it found out that the peaks of nitrogen *K-LL* Auger were broadened due to hydration. From these results, we conclude that the SD2 method is very useful for the calculation of DIPs to investigate the properties of a double ionized molecule.

1. Introduction

The double ionization potential (DIP) is defined as the energy required for the detachment of two electrons from a neutral molecule, and these have been studied extensively using a variety of both experimental and theoretical techniques [1,2]. In particular, Auger electron spectra (AES) are widely used in materials science to investigate the properties of neutral and doubly-ionized states of a molecule [3–8]. In early AES studies, the electronic energy difference method based on configuration interaction (ΔCI) [9–11] was used. More recently, coupled cluster (CC) [11] or complete active space (CAS) [12,13] methods have been used in theoretical investigations. However, using the ΔCI, CC, and CAS methods to calculate doubly-ionized states is difficult for most systems of chemical interest because a number of unnecessary excited states must be included in the calculation.

On the other hand, the particle–particle second-order algebraic diagrammatic construction (ADC(2)) [14–19] has been widely used to theoretically study the double ionization process in molecules. The ADC(2) method is based on analysis of the Feynman diagrams, which describe the second-order perturbation expansion of the electron propagator with respect to the Hartree–Fock determination reference. One advantage of the ADC(2) method is that the advanced and retarded Green's functions are treated separately. The explicit configuration space of ADC(2) comprises main space (two-hole configuration; 2*h*) and subspace (three-hole one-particle configuration; 3*hp*), and a large matrix representing the entire space must be diagonalized. For example, in the case of a formaldehyde molecule, the number of configurations of 2*h* and 3*hp* space are 36 and 10,080 dimensions, respectively, in a DIPs calculation using the Aug-cc-pVDZ basis set.

In our previous work, in contrast to ADC(2), the second-order two-electron Dyson propagator for the 2*h* configuration renormalizing the other spaces was derived from superoperator theory and applied to the shifted denominator approximation (SD2) [20]. Although the two-particle propagator can be used to simulate Auger spectra, as reported by Ortiz [21] and Liegener [22,23], our new propagator includes higher order electron correlation terms than the other propagators. The DIPs of small molecules calculated by the SD2 method have shown good agreement with experimental data [20]. However the SD2 method includes both the advanced and retarded functions, namely the causal Green's function or the Dyson propagator, each DIP is calculated separately so that the matrix dimensionality is reduced into only 2*h* configurations. Because these features are advantageous for many-core computing, it is important to investigate the accuracy of AES simulations using the SD2 methods. In this study, we focus on AES simulations of water (H_2O), ethylene (C_2H_4), and formaldehyde (H_2CO) molecules and introduce two-hole population analysis into the SD2 method to evaluate the AES peak intensity. From comparing these simulated spectra with the observed ones, we confirm the validity of our method.

---

* Corresponding author. Tel.: +81 762645688.
E-mail address: ida@se.kanazawa-u.ac.jp (T. Ida).

http://dx.doi.org/10.1016/j.elspec.2016.01.002
0368-2048/

Recently, some relaxation process from the core-hole state, such as intermolecular coulombic decay, have been reported [24,25]. Auger electron spectroscopy is also a sensitive tool for system concerned with proton-transfer [26]. Unger and co-workers revealed that the proton-transfer-mediated processes were an important role of chemical reactivity in solution by high-accuracy Auger electron spectroscopy measurement for hydrated ammonia and glycine molecules [27]. They, however, didn't directly illustrate the relationship between the measurement and the molecular structure through the AES simulation. Especially, it is a basic subject of interest how AES for the glycine molecule changes in solution. Therefore, in order to clarify that our method can be applied for systems of chemical interest, we simulate Auger spectra of the glycine and the hydrated glycine molecules.

2. Theoretical background

In order to simulate AES using the two-electron propagator, there are two steps: (1) Calculation of the vertical double ionization potentials (DIPs) and (2) peak intensity calculation. In the experimental AES, the DIPs were obtained from the following equation,

$$E_k = E_{\mathrm{CEBE}} - E_{\mathrm{DIP}} \tag{1}$$

where E_k, E_{CEBE}, and E_{DIP} are the peak position in the Auger spectrum, the core electron binding energy, and the double ionization energy, respectively. In the AES simulations, by assuming a value of the core electron binding energy, the peak position of the AES spectra can be directly compared with the calculated double ionization energy. Several DIP and peak intensity calculation methods that can be used to simulate AES are described below.

2.1. Vertical double ionization potentials (DIPs)

In this study, we used the SD2 method to calculate DIPs and simulate AES. A more detailed description of the SD2 method is given in Ref. [20], so we introduce the only critical points here.

The zeroth-order propagator restricts operator averages in the ground state to the Hartree–Fock configuration, and therefore corresponds to the double Koopmans energy. Electron correlation and relaxation effects are considered in the first- and second-order energy-independent and dependent self-energy terms. From the correlation and relaxation terms, we obtained the following explicit expression of the self-energy element of the second-order two-electron Dyson propagator (2nd):

$$\begin{aligned}
&[\Sigma(E)]_{ij,kl} = -\left\langle ij||kl\right\rangle \\
&+\frac{1}{4}\left(1-P_{ij}\right)(1-P_{kl})\sum_{m,ab}\delta_{jl}\left[\langle im\right|\left|ab\; t_{km,ab} + \langle km\right|\left|ab\; t_{im,ab}\right] \\
&+\frac{1}{2}\sum_{ab}\left[\frac{\langle ij\right|\left|ab\;\langle ab\right|\left|kl}{E-\varepsilon_a-\varepsilon_b}\right] + \left(1-P_{ij}\right)(1-P_{kl}) \\
&\times\left[\frac{1}{2}\delta_{jl}\sum_{m,n,a}\frac{\langle ia|\,|mn\rangle\langle mn|\,\left|ka\right.}{E-\left(\varepsilon_j+\varepsilon_m+\varepsilon_n-\varepsilon_a\right)} - \sum_{m,a}\frac{\langle ia|\,\left|lm\right\rangle\langle jm\right|\,\left|ka\right.}{E-\left(\varepsilon_j+\varepsilon_l+\varepsilon_m-\varepsilon_a\right)}\right]
\end{aligned} \tag{2}$$

where the indices *i*, *j* and *a*, *b* represent occupied and unoccupied spin orbitals, respectively. And P_{ij} is a permutation operator and exchanges indices *i* and *j* in the following term. $t_{im,ab}$ and $ij||kl$ correspond to the MP2 amplitude and anti-symmetrized Coulomb repulsion. A shifted denominator approximation (SD2) of the self-energy term for the 3*hp* configuration was then obtained from substitution of the following terms,

$$\begin{aligned}
&\left[E-\left(\varepsilon_i+\varepsilon_j+\varepsilon_k-\varepsilon_a\right)\right]^{-1} \\
&\quad\rightarrow\left[E-\left(\varepsilon_i+\varepsilon_j+\varepsilon_k-\varepsilon_a\right)-\left(1+P_{ij}+P_{jk}\right)\left\{\langle ja\right|\left|ja\right\rangle-\langle ik|\,\left|ik\right\rangle\right\}\right]^{-1}
\end{aligned}$$

The first order diagonal element from the 3*hp* configuration gives a particular ladder diagram up to infinite order for the second order self-energy. In a practical DIP calculation, we can construct the self-energy matrix by calculating all elements of the 2*h* space, obtaining the diagonal self-energy $\left[\sum(E)\right]_{ij}$ with respect to *E*. Using a pole search method based on the Dyson equation, a vertical DIP $\left(E_{ij}^{\mathrm{DIP}}\right)$ with two-hole orbitals *i* and *j* is obtained at the point of convergence using the following equation:

$$E_{ij}^{\mathrm{DIP}} = \varepsilon_i + \varepsilon_j + \left[\Sigma\left(E_{ij}^{\mathrm{DIP}}\right)\right]_{ij} \tag{3}$$

where $\varepsilon_i + \varepsilon_j$ is the double Koopmans energy. In the pole search, the pole strength is also obtained. The pole strength indicates the contribution of the two-hole state, which is the main configuration, to the DIP.

2.2. Peak intensity: Two-hole population analysis

For the Auger transition intensities, we employed the two-hole population analysis reported by Tarantelli, Sgamellotti, and Cederbaum [19]. This method is a simple implementation of Mulliken population analysis. We restricted the formulation to the 2*h* components of the eigenvectors in the atomic orbital (AO) basis,

$$\left|ij^{(s,t)}\right. = \sum_{p,q} U_{pq,ij}^{(s,t)}\left|pq^{(s,t)}\right. \tag{4}$$

where the superscripts *s* and *t* denote singlet and triplet spin multiplicity, respectively, and *ij* and *pq* are MO and AO hole indices, respectively. The matrix elements $U^{(s)}$ and $U^{(t)}$ can be worked out in terms of the HF eigenvector matrix of LCAO coefficients **C**,

$$U_{pq,ij}^{(s,t)} = C_{pi}C_{qj} \pm C_{qi}C_{pj}, \tag{5}$$

where plus and minus signs are corresponding to singlet and triplet states, respectively. The overlap matrices over the AO 2*h* functions are expressed as

$$O_{pq,rs}^{(s,t)} = S_{pr}S_{qs} \pm S_{ps}S_{qr} \tag{6}$$

where **S** is the basis set overlap matrix. It is straightforward to express the 2*h* part of the propagator's eigenvector $\mathbf{X}_n$ for the *n*-th two-hole state in terms of the AO 2*h* function. We obtain a new vector $\mathbf{Y}_n$ as follows,

$$\mathbf{Y}_n = \mathbf{U}\mathbf{X}_n \tag{7}$$

Therefore, the contribution of the AO 2*h* function to the total weight of the *n*-th state is

$$Q_{pq,n} = P_n Y_{pq,n}\sum_{rs} Y_{rs,n} O_{pq,rs} \tag{8}$$

where P_n is the pole strength of the *n*-th two-hole state. For intensities of the triplet final states, the values have been multiplied by factor of 1/3. The sum of terms $Q_{pq,n}$, where both *p* and *q* refer to basis functions on a given atom A, is the *one-site* localization hole on A for the *n*-th state. Similarly, we obtain the *two-site* character of a state for each pair of atoms A and B. We will discuss the validity of *one-* and *two-site* characters to the Auger transition intensities.