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First principles *T*-matrix calculations for Auger spectra of hydrocarbon systems

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Auger spectra of hydrocarbon systems (CH_4, C_2H_2, C_2H_4, and C_6H_6 molecules) are calculated from the first principles using Green's function method based on the many-body perturbation theory beyond the framework of the density functional theory. The ladder approximation to the two-particle Green's function (T matrix), which describes the short-range electron correlations between two holes or electrons, can accurately determine in a single calculation the whole spectrum of doubly ionized final states of the Auger process. The two-particle eigenvalues and eigenfunctions are determined from the Bethe-Salpeter equation for the T matrix. The obtained results are in good agreement with the experimental data.

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I. INTRODUCTION

Because of their sensitivity to the chemical environment in various substances, the Auger spectra have been extensively used for composition analysis or surface structure analysis. For isolated systems such as atoms or molecules, the Auger electron spectroscopy (AES) is used as a complementary tool to a new coincidence spectroscopy or a doubly charge transfer (DCT) experiment. On the other hand, theoretical studies, especially from the first principles, have been very limited in spite of significant interest. The first theoretical work on Auger spectra was performed by Ortenburger and Bagus in 1975.[1] They calculated the Auger spectra of CH_4 molecule by taking differences of the self-consistent-field total energies between neutral and dicationic states (this method is sometimes called the delta self-consistent field: ΔSCF) and succeeded in explaining the multiplet splittings of the experimentally observed spectra. More recently, the algebraic diagrammatic construction method based on the perturbation theory was applied to small molecules.[2–5] The calculated individual double ionization energies are in *relatively* good agreement with the experimental data. Note, however, that the remaining error is of the order of a few electron volts because the terms treated in this method are very limited, up to the second or third order.

There are mainly two reasons which hamper the theoretical study of the Auger spectra. One is the difficulty in evaluating the short-range electron correlations between two holes created in the valence levels. For example, from the analysis of the Coulomb hole in an electron gas, it is known that neither the bare Coulomb interaction itself nor its screening within random phase approximation (RPA) adequately describes the behavior of two particles at short distances.[6–8] Therefore, in order to treat the short-range Coulomb interaction accurately, it is essential to go beyond RPA and to sum up electron-electron or hole-hole ladder diagrams up to infinite order, which constitutes the basis of the T-matrix approach.[7–9] Another reason is the existence of a large number of possible doubly ionized states, being equal to the square of the number of the valence levels. Therefore, it is difficult to obtain the whole spectra using the conventional methods in which the doubly ionized states are estimated one by one in separate calculations.

In this study, we propose a different computational method, the first principles T-matrix method for the Auger spectra, and directly compare the present results with the available experimental data. The method allows us to treat the short-range electron correlations, which play an important role in the description of the dicationic final states created in the Auger processes.[10–12] In addition, since our method is based on the direct solution of the Bethe-Salpeter equations for the two-particle eigenvalues and eigenfunctions, it can treat simultaneously the double ionization energies (or double electron affinities) and the probabilities of transitions from the neutral N-electron state to the doubly excited ($N\pm2$)-electron states. Therefore, the whole Auger spectra, involving the peak positions and their heights, can be obtained in a single calculation. Finally, we apply this method to small hydrocarbon systems (CH_4, C_2H_2, C_2H_4, and C_6H_6 molecules) and obtain good agreement with the experimental C(KVV) Auger spectra.

II. METHODOLOGY

We calculate the doubly ionized final states of the Auger process from the first principles T-matrix theory, which treats the short-range electron correlations between holes created in the valence band. Our method consists of two steps. The first step is the GW approximation (GWA),[13,14] where the one-particle Green's function G_1^0 and the dynamically screened Coulomb interaction W^0, within RPA, are used to construct the self-energy Σ, which is then used to derive the quasiparticle energies. Here, the eigenvalues and wave functions ob-

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tained in the local density approximation (LDA) are used as the input data to construct G_1^0 and W^0, and the latter is evaluated within RPA. The second step is based on the T-matrix theory.[15] Here, we expand the two-particle Green's function G_2^T into the hole-hole (or electron-electron) ladder diagrams up to infinite order and find its eigenvalues and eigenfunctions. The T matrix satisfies the following integral equation:

$$\int d3'd4'T(1,2|3',4')G_1^{GW}(3,3')G_1^{GW}(4,4') = U^b(1,2)G_2^T(1,2|3,4), \tag{1}$$

$$T(1,2|3,4) = U^b(1,2)\delta(1-3)\delta(2-4) + U^b(1,2)\int d1'd2'G_2^0(1,2|1',2')T(1',2'|3,4), \tag{2}$$

where U^b is the bare Coulomb interaction and G_2^0 is the zeroth two-particle Green's function constructed as the product of two one-particle Green's functions ($=iG_1^{GW}G_1^{GW}$). Here, we introduce the short-hand notation $1\equiv(\boldsymbol{r}_1,t_1)$. The integral equation (2) is easily rewritten as a matrix equation and is reduced to the eigenvalue problem

$$\sum_{\nu\mu} H_{\alpha\beta\nu\mu}A_{\nu\mu}(\Omega) = \Omega A_{\alpha\beta}(\Omega), \tag{3}$$

where

$$H_{\alpha\beta\nu\mu} \equiv \left(\frac{f_{\nu\mu}}{G_{2\nu\mu}^0(\omega)} - \omega\right)\delta_{\alpha\nu}\delta_{\beta\mu} - U_{\alpha\beta\nu\mu}^b f_{\nu\mu} \tag{4}$$

is defined as the two-particle Hamiltonian and $f_{\nu\mu}=-\delta_\nu^{occ}\delta_\mu^{occ}+\delta_\nu^{emp}\delta_\mu^{emp}$. The detailed procedure is given in Refs. 10–12. Then, the eigenvalues Ω, which are the poles of the two-particle Green function, G_2^T, should be able to reproduce the double ionization energy spectra,[10] and the squares of the eigenfunctions $A_{\nu\mu}(\Omega)=\langle \mathrm{N}-2|\psi_\nu\psi_\mu|\mathrm{N}\rangle$ are proportional to the transition probability amplitudes, from the N-electron ground state to the doubly excited $(N-2)$-electron states.[16] Note that, in this study, we employed in the determination of the peak heights only the absolute square of the transition amplitude, composed of the main two-hole configuration $|A_{\nu\mu}(\Omega)|_{\max}^2$ at each dicationic state Ω, because of the orthogonality of the eigenfunctions $\Sigma_{\nu\mu}|A_{\nu\mu}(\Omega)|^2=1$. Therefore, the peak positions and heights in the Auger spectra are accurately determined from the eigenvalues and the eigenfunctions, respectively. The maximal error bar of our calculations of Ω is about 1 eV, or even less, depending on the size of the molecule.[10,11]

In this study, the one-particle wave functions are expanded in a linear combination of atomic orbitals and plane waves (PWs) using the all-electron mixed basis approach.[17,18] This approach can describe all the states from core to free-electron states efficiently. We employ a fcc supercell with cubic edges of 25.9, 36.2, 31.2, and 34.5 bohr and corresponding PW cutoff energies of 30.2, 17.4, 15.9, and 17.0 Ry. The cutoff energies of the **G** vectors in the calculation of Σ_x and U^b are 38.2, 34.4, 39.2, and 21.5 Ry for CH_4, C_2H_4, C_2H_2, and C_6H_6, respectively. In addition, in the calculation of Σ_c, the cutoff energies of **G** (**G′**) required to achieve good convergence up to 0.1 eV are 11.8, 13.6, 11.7, and 6.6 Ry for 7200 (288 eV), 8000 (215 eV), 4800 (151 eV), and 4800 levels (123 eV), respectively.

TABLE I. The first ionization energies evaluated in LDA and GWA for the CH_4, C_2H_4, C_2H_2, and C_6H_6 molecules (in eV). The experimental values are also shown in the column "EXPT."

	LDA	GWA	EXPT.
CH_4	9.50	14.20	14.25[a]
C_2H_4	6.73	10.24	10.51[b]
C_2H_2	7.32	11.18	11.40[b]
C_6H_6	6.63	9.30	9.24[b]

[a] Reference 19.

[b] Reference 20.

III. FIRST IONIZATION ENERGIES

Before going to discussions of the double ionization energies, we briefly compare the results of the first ionization energies obtained in LDA and GWA with the experimental data available for the CH_4, C_2H_4, C_2H_2, and C_6H_6 molecules (Table I).[19,20] As is well known, the LDA underestimates the first ionization energy, for which the LDA values are found to be about 2.6–4.1 eV smaller in comparison with the experimental data. On the other hand, GWA significantly improves the agreement and the typical error varies from 0.4% in the case of CH_4 to about 2.6% in the case of C_2H_2. Thus, GWA reproduces the experimental situation very well.

IV. AUGER SPECTRA

As already known, the final doubly ionized states in the Auger process are generated via the multistep process as schematically shown in Figs. 1(a)–1(d). In the first step of AES experiment [Fig. 1(b)], one core electron is ionized by one photon and the system changes from the neutral N-electron state to a cationic $(N-1)$-electron state. However, the cationic state with one core hole is very unstable and the system tends to relax by electron transition from the valence band to the core level [second step, Fig. 1(c)]. Finally, the energy gain $E_c-E_v^{1st}$ acquired in the previous step (where E_c is a core electron binding energy and E_v^{1st} is the first ionization energy) is released by emitting the second electron (also known as the Auger electron), with the kinetic energy K_f:

$$E_c - E_v^{1st} = E_v^{2nd} + K_f + E_r, \tag{5}$$

where E_v^{2nd} is the second ionization energy and E_r is the atomic relaxation energy. Equation (5) can be rewritten in terms of the double ionization energy Ω_f, defined as the sum of the first and second ionization energies, $\Omega_f=E_v^{1st}+E_v^{2nd}$, as follows:

$$\Omega_f = E_c - K_f - E_r. \tag{6}$$

The above expression relates the experimentally measured kinetic energies of the Auger electrons with the double ion-

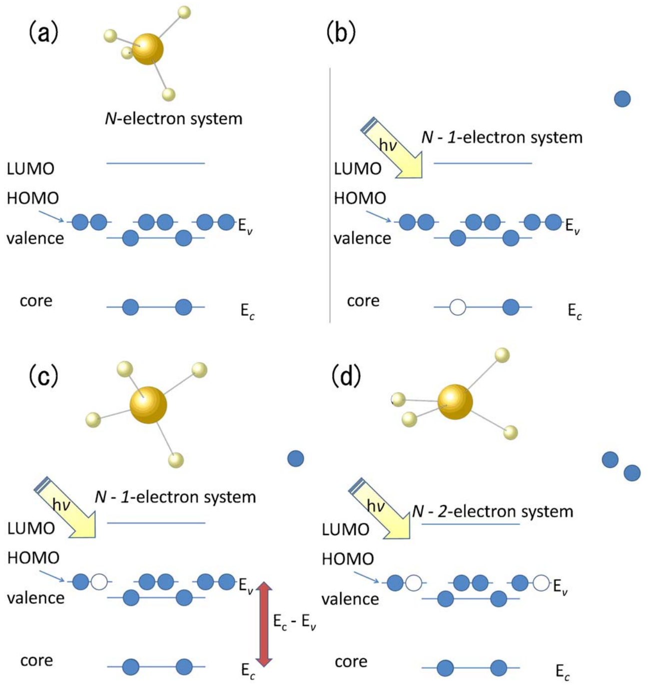

FIG. 1. (Color online) Schematic representation of Auger process. (a) The ground state of CH_4 molecules. (b) The cationic state with one core hole. (c) The cationic state with one valence hole. (d) The dicationic final state.

ization energies, which can be derived from our calculations. The atomic relaxation energy E_r will be evaluated in the next section. The C(1*s*) binding energies E_c are typically well known and are tabulated in Table II. We chose the simplest broadening method, the Gaussian broadening, for comparison with the experimental spectra [also, the values of the full width at half maximum (FWHM) are listed in Table II]. Therefore, we do not discuss here the detail of the spectra such as the vibrational structure. In order to reproduce the vibrational structure, more efficient broadening method is required (see, for example, Refs. 22 and 23). Finally, the intensities of the Auger processes corresponding to the formation of the spin-singlet and spin-triplet states are weighted 3:1 as suggested by theoretical works.[24,25]

TABLE II. The parameters used in this study (in eV). The carbon 1*s* binding energies given in the column of "C(1*s*)" are the experimental data (Ref. 21).

	C(1*s*)	FWHM
CH_4	290.8	3.7
C_2H_4	290.9	3.0
C_2H_2	291.1	3.2
C_6H_6	290.3	0.7

TABLE III. The first, second, and double ionization energies (IEs) of the CH_4 molecule (in eV). These values are calculated from the total energy difference between the neutral and cation, cation and the dication, and the neutral and dication, respectively. The values in the column of the "Double IE" are the minimal double ionization energy characterized as $^3T_1$. The adiabatic calculations take into account the structural relaxation for each configuration. The vertical calculations have been performed for the most stable geometry, corresponding to the ground state.

	First IE	Sedond IE	Double IE
Adiabatic	13.09	22.97	36.05
Vertical	14.81	24.08 (25.03[a])	38.88

[a]The value obtained for the equilibrium structural configuration of the cation.

A. CH_4 molecule

First, let us estimate the atomic relaxation energy, $E_r = E_r^{1\mathrm{st}} + E_r^{2\mathrm{nd}}$. For these purposes, we have performed the ΔSCF calculations by using the GAUSSIAN 03 package, and determined the adiabatic and vertical excitation energies for the processes corresponding to the transitions (a) → (c), (c) → (d), and (a) → (d) in Fig. 1. The experimental Auger spectra may include the effect of the atomic or electronic structure relaxation, where two holes in the valence band are created one by one in each step of the Auger process shown in Figs. 1(c) and 1(d). The most stable structures of CH_4 molecule in different steps are clearly different from each other as shown in Figs. 1(a), 1(c), and 1(d), i.e., we clearly observe a regular tetrahedral structure for neutral (a), a little flattened tetrahedral structure for cation (c), and a tetrahedral structure with slightly longer C–H bond for dication (d). In Table III, we list the adiabatic first, second, and double ionization energies of CH_4 molecule together with corresponding vertical values. From the difference between the adiabatic and vertical first ionization energies, the atomic structure relaxation energy in the process (a) → (c), E_r^{1st}, can be estimated to be 1.8 eV. This result is in agreement with the experimental photoelectron spectroscopy data and can explain the difference between the experimental adiabatic first ionization energy [about 12.5–13.0 eV (Ref. 20)] and the "vertical" ionization energy [about 14.3 eV (Ref. 19)]. The atomic structure relaxation energy in the process (c) → (d), E_r^{2nd}, calculated in a similar way, is about 1.1 (2.1) eV, where the value in parentheses is calculated using the geometry optimized for a cation. In comparison with E_r^{1st} (=1.8 eV), the atomic relaxation energy E_r^{2nd} is clearly smaller. Therefore, the total atomic relaxation energy in the double ionization process, E_r, is of the order of 3 eV. This value may be somewhat overestimated, because ΔSCF somewhat overestimates the vertical first ionization energy in comparison with the experimental data (shown in Table I). Moreover, it is known that the Auger process occurs in quite a smaller time scale ($\sim 10^{-9}$ s) than the change of the nuclear positions. In these above viewpoints, one can easily imagine that the expected discrepancies with experimental data due to the lack of the effect of atomic relation in our method are quite small and that the experimental values can be "roughly" regarded as the vertical ones.

Figure 2 shows the calculated and the experimental Auger spectra of the CH_4 molecule. The ground state configuration

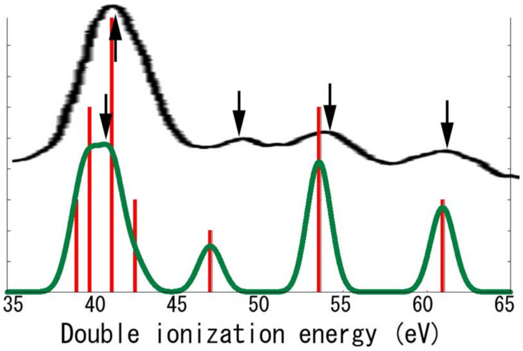

FIG. 2. (Color online) The Auger spectra calculated for the CH_4 molecule. The vertical bars show individual states while the curves correspond to their Gaussian broadening, with FWHM=3.7 eV. The upper curve denotes the corresponding experimental spectra (Ref. 26). The abscissa is in units of eV, while the ordinate is in arbitrary unit.

of valence levels of the CH_4 molecule is constructed from one inner valence level (a_1) and threefold degenerate outer valence levels (t_2). Therefore, four peaks, which are observed in the present calculations (lower curve) and in the experimental spectra (upper curve),[26] can be separated into three parts according to the combinations of outer-outer, inner-outer, and inner-inner valence levels. Four dicationic states (at 39.1, 39.9, 41.2, and 42.6 eV) in the first peak, denoted as four vertical bars in Fig. 2, is the multiplet structure obtained from the outer-outer valence levels. Two middle states (at 47.1 and 53.6 eV) and the single state (at 61.0 eV) are attributed to the inner-outer and inner-inner configurations, respectively. These four peak positions, namely, the double ionization energies, agree with the experimental spectra very well. Moreover, our method also reproduces the peak heights of the experimental spectra at each dicationic state. For example, the first peak is the highest one, and the second peak is the lowest one. As a whole, the calculated spectra agree with the experiment very well.

Next, in order to discuss the dicationic states of the CH_4 molecule in more detail, we compare the double ionization energy spectra with the available experimental data obtained by the AES[26] and DCT.[27] The double ionization energies, which are directly obtained from the eigenvalues Ω in our formulation, are important physical quantities to determine the dicationic final states, and, in turn, the peak positions in the Auger spectra.

As we have already reported in Refs. 10 and 11 the treatment of the huge repulsive Coulomb interactions between two holes is an essential part in the calculations of the double ionization energy spectra. Moreover, for small-size systems, such as atoms or molecules, it is also essential to go beyond the second- (or third-) order perturbation theory and accurately evaluate the effect of multiple scattering by two holes confined in the small space. Table IV shows the calculated and experimental double ionization energies of the CH_4 molecule. The present results are listed in the column "G_2^T" and are based on the accurate treatment of the short-range Coulomb interactions between two holes in the valence band. They agree reasonably well with the AES data ("EXPT."). The remaining errors can be estimated as 2.8, 2.7, 1.0, and 0.9 eV for the configurations $^3T_1$, $^3T_2$, $^1T_2$, and $^1A_1$, respectively. We also note that for the $^3T_1$ state, which has worse agreement with the AES data, a much better agreement is obtained with the DCT experiment (38.9 ± 0.7 eV).[27] In the AES experiment, the highest positions of each peak marked by the arrows in Fig. 2 are regarded as the double ionization energies and, therefore, at only broad first peak, do not correspond to the minimal double ionization energy in our calculation because the first peak is composed of four dicationic states as discussed above. If we determine the double ionization energy in the same way as in the AES experiment, the minimal double ionization energy (given in parentheses in column "G_2^T") is about 40.8 eV, which agrees with the AES data.

Since zeroth-order approximation to the two-particle Green's function does not include any Coulomb interactions between one-particle Green's functions, the poles of G_2^0 are

TABLE IV. The double ionization energies of the CH_4 molecule calculated in the zeroth-order approximation "G_2^0" and the T-matrix "G_2^T" (in eV). The values in parentheses in the column "G_2^T" is a double ionization energy at the highest peak position (see the text). The corresponding experimental values by the AES (Ref. 26) and DCT (Ref. 27) are also listed for comparison. The column of "2h configuration," "U^b," and "U^T" denote the two-hole configuration, the matrix element of bare Coulomb interaction carrying the largest contributions to each double ionization energy, and the short-range Coulomb interaction estimated in the T-matrix approach, respectively.

	2h configuration	U^b	U^T	G_2^0	G_2^T	EXPT.
$^3T_1$	$(1t_2)^2$	14.03	10.70	28.42	39.12 (40.83)	41.9,[a] 38.9 ± 0.7[b]
^1E	$(1t_2)^2$	13.29	11.48	28.42	39.90	
$^1T_2$	$(1t_2)^2$	14.16	12.80	28.42	41.22	
$^1A_1$	$(1t_2)^2$	14.16	14.20	28.42	42.62	
$^3T_2$	$(2a_1)(1t_2)$	13.21	10.29	36.81	47.10	49.8[a]
$^1T_2$	$(2a_1)(1t_2)$	13.21	16.77	36.81	53.58	54.6[a]
$^1A_1$	$(2a_1)^2$	14.19	15.74	45.21	60.95	61.8[a]

[a] Reference 26.

[b] Reference 27.

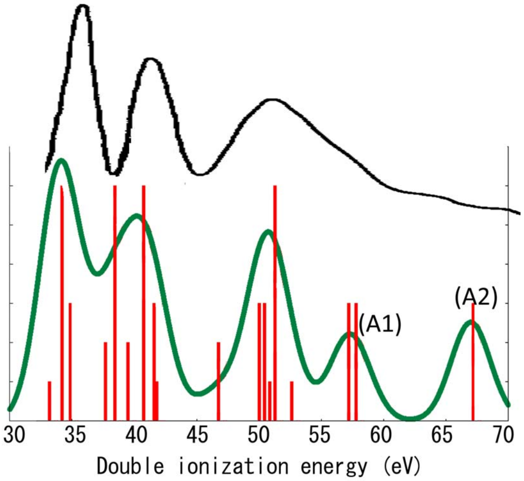

FIG. 3. (Color online) The Auger spectra calculated for the C_2H_2 molecule. The vertical bars show individual states while the curves correspond to their Gaussian broadening, with FWHM =3.0 eV. The upper curve denotes the corresponding experimental spectra (Ref. 26). The abscissa is in units of eV, while the ordinate is in arbitrary unit.

nothing but the sum of two quasiparticle energies in the valence band.

Therefore, it is instructive to compare the poles of the true two-particle Green's function, G_2^T, and G_2^0 in order to estimate the magnitude of short-range repulsive Coulomb interaction between the holes, and its dependence on the size of the molecule.

Let us start with the bare Coulomb interaction between the holes, U^b, which denotes the largest matrix element of the bare Coulomb interaction. For the small-size molecule, this interaction is of the order of 13 eV (Table IV), which is huge. If we neglect for a while the renormalization in the *T*-matrix theory and drop off off-diagonal elements in Eq. (4), the double ionization energies can be estimated by summing up the values in the columns "U^b" and "G_2^0." The obtained results would be almost in agreement with the experimental data. However, it is not enough and it is important to consider the contribution of the short-range Coulomb interactions, which appears in the *T*-matrix theory. The *corrected* value is denoted as "U^T," which is nothing but the difference of the columns "G_2^T" and "G_2^0." It differs rather substantially from U^b. This difference can easily reach several electron volts and the singlet-triplet splitting of the T_2 state. These comparisons show that the short-range Coulomb interactions in CH_4 are quite important and cannot be neglected.

B. Larger hydrocarbon molecules

Figures 3–5 show the experimental (upper curves) and theoretical (lower curves) Auger spectra for C_2H_2, C_2H_4, and C_6H_6 molecules.[26,28] We note a good overall agreement with the experimental Auger spectra regarding both the positions of the main peaks and their magnitude. For the minimal double ionization energy, the discrepancies with experimental DCT and AES data are less than 1 eV, about 0.5 eV for C_2H_4 and 0.9 eV for C_6H_6 (the case of C_2H_2 has been discussed in detail in Ref. 10).

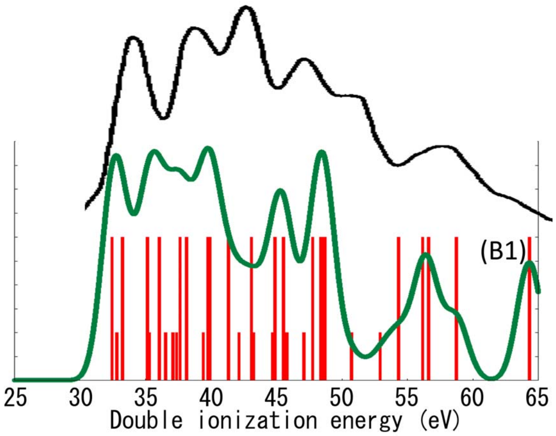

FIG. 4. (Color online) The Auger spectra calculated for the C_2H_4 molecule. The vertical bars show individual states while the curves correspond to their Gaussian broadening with FWHM =3.2 eV. The upper curve denotes the corresponding experimental spectra (Ref. 26). The abscissa is in units of eV, while the ordinate is in arbitrary unit.

Due to the large number of possible dicationic states for the large molecules (for example, 225 dicationic states can be found for C_6H_6 molecule in the range of 20–50 eV), it is impossible to compare each individual state in the theoretical and experimental spectra. Although, in general, there is good correspondence between theoretical and experimental Auger spectra, there is also a number of discrepancies for these molecules, which, in the case of the C_2H_2 and C_2H_4 molecule, we would like to discuss in more detail.

The ground state configuration of the C_2H_2 molecule consists of four core and ten valence electrons,

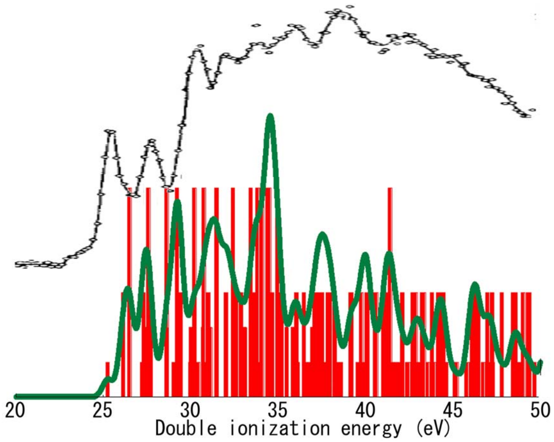

FIG. 5. (Color online) The Auger spectra calculated for the C_6H_6 (benzene) molecule. The vertical bars show individual states while the curves correspond to their Gaussian broadening, with FWHM=0.7 eV. The upper curve denotes the corresponding experimental spectra (Ref. 26). The abscissa is in units of eV, while the ordinate is in arbitrary unit.

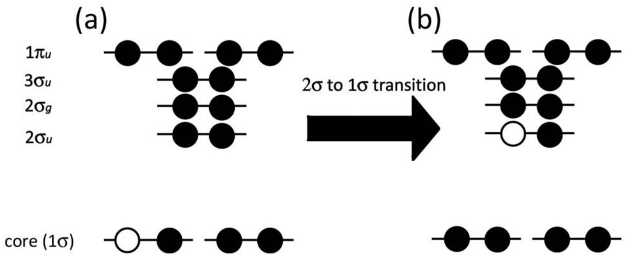

FIG. 6. One example of the forbidden transition of $2\sigma_u$ to 1σ in the C_2H_2 molecule, $(N-1)$-electron excited state with (a) one core hole (1σ) and (b) one valence hole $(2\sigma_u)$.

$(\text{core})^4(2\sigma_u)^2(2\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4$. The agreement between three peaks up to 54 eV of the present result and the experimental result[26] is very good in both the peak positions and their heights (see Fig. 3). In the present result, however, two extra peaks appear at 58 and 67.7 eV, which are marked as (A1) and (A2), respectively. From the eigenfunctions $A_{\nu\mu}(\Omega)$, we can find that both peaks correspond to the configuration $(2\sigma)^{-2}$. In actual Auger process, these two-hole configurations $(2\sigma)^{-2}$ are mainly generated via the electron transition from 2σ to core hole (1σ) [Fig. 6(a) and 6(b)]. According to the selection rule, however, the transition from σ to σ is forbidden. Therefore, experimentally, the corresponding Auger amplitude is very weak and not clearly observed due to the low resolution. On the other hand, our method based on the two-particle Green's function simulates the direct transition from N-electron ground state to $(N$-2)-electron final state, i.e., two electrons are ejected at the same time from the ground state, and this situation does not take into account the existence of the intermediate state shown in Fig. 6. The heights of two extra peaks found in the present results should be lower in actual Auger spectra [similar situation occur in the C_2H_4 molecule, where an the extra peak (B1) at 64.3 eV also results from the forbidden transition].[29] There is also a number of final doubly ionized states generated via the forbidden transitions in the middle-to-high energy region. Therefore, some peak heights in the higher energy region may not exactly agree with the experimental ones. However, at the lower energy side, the agreement with the experiments is very good.

V. SUMMARY

In summary, using first principles T-matrix method, we have evaluated the doubly ionized final states of the hydrocarbon molecules (CH_4, C_2H_2, C_2H_4, and C_6H_6) and compared them with available experimental C(KVV) Auger spectra. In these calculations, the eigenvalues Ω and eigenfunctions $A_{\nu\mu}(\Omega)$ derived from the Bethe-Salpeter equations were compared, correspondingly, with the energies and probabilities of the Auger process. The theoretical Auger spectra take into account the effects of short-range electron correlations between two holes created in the valence band.

For the CH_4 molecule, we also discussed here the double ionization energies and compared them with the DCT and AES experimental data. The case of the C_2H_2 molecule has been considered in our previous work.[10,11] Our calculation method can treat the two-electron excited energies including the short-range electron correlations and, consequently, evaluate the Auger spectra quite well. Generally, we have found good agreement between theoretical and experimental data, including the two-electron excitation energies and the Auger spectra.

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