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Interpretation of Shake-up Satellites in the X-Ray Photoelectron Spectra of Small Hydride Molecules by One-Center-Expansion *ab initio* Calculation with Equivalent-Core Approximation

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One-center-expansion *ab initio* calculations with STO basis set were carried out on H_2O, NH_3, CH_4 and BH_3, to estimate the energies and probabilities of shake-up processes accompanying the photoionization of a core level. A method based on equivalent-core approximation and that based on configuration interaction procedure were applied to obtain wave functions of core-hole ions. It is shown that the calculations by the former method yield very satisfactory results, not only for the core ionization potential, but also for the energies and intensities of shake-up satellites.

Recent development of X-ray photoelectron spectroscopy of gaseous molecules has revealed that core-electron peaks of X-ray photoelectron spectra are often accompanied by satellite bands arising from the two-electron process where a secondary excitation (shake-up) or ejection (shake-off) of an outer shell electron takes place simultaneously with the ionization of a core level.[1–5] These phenomena are of great theoretical interest since they are closely related to the relaxation accompanied with the ejection of a core electron.

Several authors[4–9] have attempted to calculate the energies and intensities of shake-up satellites on the basis of sudden approximation[10,11] where the secondary excitation (or ejection) of an outer-shell electron is treated as arising from the sudden perturbation of potential due to the removal of a core electron. On the core-hole states of small first-row molecules, Aarons *et al.*[4] carried out an *ab initio* unrestricted Hartree-Fock (UHF) calculation with Gaussian basis set, and calculated shake-up satellites of these molecules, with reasonable success. Another type of approach was done by Guest *et al.*[7] and, more recently, by Wood.[8] These authors treated the relaxed core-hole state with a configuration interaction (CI) procedure using molecular orbitals obtained by *ab initio* SCF-MO calculations on the neutral molecules. For relatively complex molecules, semi-empirical molecular orbital methods incorporated with equivalent-core approximation have been applied to calculate the energies and intensities of shake-up satellites, and found to give reasonable results.[5,6] Equivalent-core approximation[12] has been known to be a useful tool for calculating core ionization potentials. In effect, Adams and Clark[13,14] have shown that an *ab initio* calculation combined with this approximation can provide satisfactory predictions of core ionization potential. Hitherto, however, no attempt has been done to use this approximation in calculating shake-up transitions by *ab initio* molecular orbital methods.

In the present study, we carried out *ab initio* calculations by one-center-expansion method on the neutral molecules and core-hole ions of small hydrides of first-row atoms, using equivalent-core approximation, and calculated the energies and intensities of the shake-up satellites accompanying the core-electron peaks in their X-ray photoelectron spectra. The results obtained by core-hole CI method will be also given for the sake of comparison.

Methods of Calculation

According to the sudden approximation, the probability of the transition which yields the final core-hole state $\Psi_f(2n-1)$ is given by,[10,11]

$$P_f = |\langle\Psi_f(2n-1)|\Phi_0(2n-1)\rangle|^2 \tag{1}$$

where $\Phi_0(2n-1)$ is the core-hole wave function in which all molecular orbitals have been frozen as they are in the neutral molecule.[15] We may construct the ground-state wave function $\Phi_G(2n)$ of a neutral molecule from the one-electron molecular orbitals $\{\phi_i\}$.[16]

$$\Phi_G(2n) = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_n\bar{\phi}_n| \tag{2}$$

Then, $\Phi_0(2n-1)$ can be written as follows by taking ϕ_1 as the ionizing core orbital;

$$\Phi_0(2n-1) = |\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_n\bar{\phi}_n| \tag{3}$$

In the present study, we obtained the one-electron molecular orbitals through one-center-expansion (OCE) *ab initio* calculation with Slater-type-orbital (STO) basis set. This method has been successfully applied by Hartmann *et al.*[17] to calculate the ground-state properties of various hydride molecules. We used 25 STO basis functions except in the case of H_2O where 19 basis functions were used; the zeta values of the used STO bases are given in Table 1.

In order to obtain the final-state wave function, we used two different methods; the equivalent-core approximation method and the core-hole CI method.

(a) Equivalent-Core Approximation (ECA) Method. In the equivalent-core approximation, it is assumed that, when a core electron is removed from an atom, the outer-shell electrons adjust themselves as if the nuclear charge of the ionized atom has increased by one unit.[13] This means that, in the case of CH_4, one can get the valence-electron orbitals of the core-hole ion by performing a calculation on the N^+H_4 system, in which the molecular geometry has been taken the same as that of CH_4 molecule, instead of directly calculating on the core-hole ion, $C^{*+}H_4$.[18] Thus, we carried out calculations on the equivalent-core models, C^+H_3, N^+H_4, O^+H_3 and F^+H_2, to obtain the relaxed valence-electron orbitals of the core-hole ions, $B^{*+}H_3$, $C^{*+}H_4$, $N^{*+}H_3$ and $O^{*+}H_2$, respectively.

In each case, the zeta values of the first five STO basis functions only were replaced with those corresponding to the change of the nuclear charge as shown in Table 1.

By using the relaxed one-electron orbitals $\{\psi_i\}$, the wave functions of the ground and excited configurations of a core-hole ion can be expressed as follows;

$$\Psi_0(2n-1) = |\bar{\psi}_1\psi_2\bar{\psi}_2\cdots\psi_n\bar{\psi}_n| \tag{4}$$

$$\Psi_{i\to j}(2n-1) = |\bar{\psi}_1\psi_2\bar{\psi}_2\cdots\bar{\psi}_{i-1}\psi_j\bar{\psi}_i\psi_{i+1}\cdots\psi_n\bar{\psi}_n| \tag{5}$$

where the core orbital ψ_1 is assumed to be the same as ϕ_1 by adopting the frozen-core approximation. Then, the probabilities of the transition to Ψ_0 and that to $\Psi_{i\to j}$ are given as follows according to Eq. (1);[19)]

$$P_0 = |\mathbf{S}_0|^4, \qquad P_{i\to j} = |\mathbf{S}_0|^2|\mathbf{S}_{i\to j}|^2 \tag{6}$$

where

$$\mathbf{S}_0 = \left|\begin{array}{ccccc} \langle\psi_2 & | & \phi_2\rangle\cdots\cdots\cdots\langle\psi_2 & | & \phi_n\rangle \\ & \vdots & \ddots & \vdots & \\ \langle\psi_n & | & \phi_2\rangle\cdots\cdots\cdots\langle\psi_n & | & \phi_n\rangle \end{array}\right|$$

and

$$\mathbf{S}_{i\to j} = \begin{array}{|ccccc|c} \langle\psi_2 & | & \phi_2\rangle\cdots\cdots\cdots\langle\psi_2 & | & \phi_n\rangle & \\ & \vdots & \ddots & \vdots & & \\ \langle\psi_{i-1} & | & \phi_2\rangle\cdots\cdots\cdots\langle\psi_{i-1} & | & \phi_n\rangle & \\ \langle\psi_j & | & \phi_2\rangle\cdots\cdots\cdots\langle\psi_j & | & \phi_n\rangle & <i \\ \langle\psi_{i+1} & | & \phi_2\rangle\cdots\cdots\cdots\langle\psi_{i+1} & | & \phi_n\rangle & \\ & \vdots & \ddots & \vdots & & \\ \langle\psi_n & | & \phi_2\rangle\cdots\cdots\cdots\langle\psi_n & | & \phi_n\rangle & \end{array}$$

The relative probability of shake-up, $\bar{P}_{i\to j}=P_{i\to j}/P_0$, is given as,

$$\bar{P}_{i\to j} = |\mathbf{S}_{i\to j}|^2/|\mathbf{S}_0|^2 \tag{7}$$

For the excited states of each core-hole ion, we carried out a configuration interaction calculation, extensively taking into account singly-excited configurations. Then, the relative probability of the shake-up process which yields the k-th excited state of the core-hole ion, was obtained by the following relation by using the weight ($w^k_{i\to j}$) of each configuration;[20)]

$$\bar{P}_k = \sum_{i\to j} w^k_{i\to j}\bar{P}_{i\to j} \tag{8}$$

The total probability of shake-up (P_{up}) and that of shake-off (P_{off}) are given as follows;

$$P_{\text{up}} = \sum_k \bar{P}_k\cdot P_0 \tag{9}$$

$$P_{\text{off}} = 1 - (P_0+P_{\text{up}}) \tag{10}$$

The procedure proposed by Adams and Clark[13)] was used to estimate the core ionization potentials from the calculations by ECA method.[21)]

(b) Core-hole CI (CH-CI) Method. In the core-hole CI procedure, a wave function of a relaxed core-hole ion is described as follows; for the ground state,

$$\Psi_0(2n-1) = a^0_0\Phi_0(2n-1) + \sum_{(i\to j)} a^0_{i\to j}\Phi_{i\to j}(2n-1) \tag{11}$$

and, for the k-th excited state,

$$\Psi_{\text{k}}(2n-1) = a^k_0\Phi_0(2n-1) + \sum a^k_{i\to j}\Phi_{i\to j}(2n-1) \tag{12}$$

where Φ_0 and $\Phi_{i\to j}$ are the frozen-orbital wave functions of core-hole configurations and a^k_0 and $a^k_{i\to j}$ are the coefficients. Then, the probabilities of the transitions to Ψ_0 $(2n-1)$ and to Ψ_k $(2n-1)$, can be given as,

$$P_0 = |a^0_0|^2 \tag{13}$$

$$P_k = |a^k_0|^2 \qquad \text{thus} \quad \bar{P}_k = |a^k_0|^2/|a^0_0|^2 \tag{14}$$

Therefore, the energies and probabilities of shake-up transitions are obtainable through the diagonalization of CI matrix. The core ionization potential can be calculated by the following formula,

$$\begin{aligned} I_{\text{p}}(\text{core}) &= \langle\Psi_0(2n-1)|H(2n-1)|\Psi_0(2n-1)\rangle \\ &\quad -\langle\Phi_{\text{G}}(2n)|H(2n)|\Phi_{\text{G}}(2n)\rangle \end{aligned} \tag{15}$$

We carried out the calculations described above, using the frozen-orbital wave functions constructed from the one-electron molecular orbitals which have been obtained by the one-center-expansion *ab initio* calculations on the neutral molecules with the STO basis sets given in Table 1.

All computations were performed with HITAC 8700/8800 at the computer center of the University of Tokyo, by using the programs written by ourselves. In the present calculations, we used the observed molecular geometries of free hydrides molecules, except in the case of BH_3.

Results and Discussion

In Tables 2(a)—(d), we show the orbital energies obtained by the present calculations of the neutral molecules of H_2O, NH_3, CH_4 and BH_3. As for the virtual orbitals, we have given there only three or four lower-energy ones, omitting all others of higher energies. On these molecules, *ab initio* LCAO calculations with Gaussian basis set have been carried out by other authors,[22–24)] the results of which are shown in the same table for the sake of comparison.

The ionization potentials of the molecular orbitals of H_2O, NH_3 and CH_4 have been experimentally determined by use of photoelectron spectroscopy.[25–27)] These experimental values are also given in Tables 2(a)—(c). We can see that the experimental ionization potentials are smaller than the values expected from the calculated orbital energies according to Koopmans' theorem. The discrepancy is especially significant in the case of the ionization potentials of core levels. As it is known, this discrepancy is mainly associated with the electronic relaxation of core-hole state.

The values of the core ionization potential which we have calculated by CH-CI method and by ECA method

TABLE 1. ZETA VALUES OF STO BASES

(a) H_2O

Neutral molecule (19 basis)			Equivalent-core model (19 basis)		
n	*l*	zeta	*n*	*l*	zeta
1	0	7.6579	1	0	8.6501
2	0	2.2458	2	0	2.5638
2	1	2.2266	2	1	2.5500
3	0	2.2000	3	0	2.3500
3	1	2.1000	3	1	2.2500
3	2	1.9000	3	2	1.9000
4	0	2.2000	4	0	2.2000
4	1	1.7000	4	1	1.7000
5	0	2.2000	5	0	2.2000

(b) NH_3

Neutral molecule (25 basis)			Equivalent-core model (25 basis)		
n	*l*	zeta	*n*	*l*	zeta
1	0	6.6651	1	0	7.6579
2	0	1.9237	2	0	2.2458
2	1	1.9170	2	1	2.2266
3	0	1.9000	3	0	2.0500
3	1	1.8500	3	1	2.0000
3	2	1.8000	3	2	1.8000
4	0	1.9000	4	0	1.9000
4	1	1.8000	4	1	1.8000
4	3	2.0000	4	3	2.0000

(c) CH_4

Neutral molecule (25 basis)			Equivalent-core model (25 basis)		
n	*l*	zeta	*n*	*l*	zeta
1	0	5.6727	1	0	6.6651
2	0	1.6083	2	0	1.9237
2	1	1.5679	2	1	1.9170
3	0	1.6000	3	0	1.6000
3	1	1.5600	3	1	1.5600
3	2	1.4500	3	2	1.4500
4	0	1.5400	4	0	1.5400
4	1	1.5000	4	1	1.5000
4	3	1.6000	4	3	1.6000

(d) BH_3

Neutral molecule (25 basis)			Equivalent-core model (25 basis)		
n	*l*	zeta	*n*	*l*	zeta
1	0	4.6795	1	0	5.6727
2	0	1.2881	2	0	1.6083
2	1	1.2107	2	1	1.5679
3	0	1.2680	3	0	1.2680
3	1	1.1800	3	1	1.1900
3	2	1.2600	3	2	1.2600
4	0	1.2400	4	0	1.2400
4	1	1.1700	4	1	1.1700
4	3	1.4900	4	3	1.4900

TABLE 2. CALCULATED ORBITAL ENERGIES OF NEUTRAL MOLECULES OF H_2O, NH_3, CH_4 AND BH_3

(a) H_2O

Orbital	Orbital energy (eV) (calcd)		I_p (eV)[25] (obsd)
	Present study	Neumann and Moskowitz[22]	
$4a_1$	15.08		
$2b_2$	13.40		
$3a_1$	7.72		
$1b_1$	−13.34	−13.80	12.6
$2a_1$	−15.15	−15.84	14.7
$1b_2$	−18.59	−19.56	18.4
$1a_1$	−36.76	−36.79	32.2
core	−561.50	−559.40	539.7

(b) NH_3

Orbital	Orbital energy (eV)		I_p (eV) (obsd)
	Present study	Palke and Lipscomb[23]	
3e	23.37		
$4a_1$	18.10		
2e	16.32		
$3a_1$	10.19	15.90	
$2a_1$	−11.13	−9.96	10.16[26]
1e	−15.92	−15.85	14.8[26]
$1a_1$	−30.59	−29.97	
core	−422.34	−422.38	405.6[2]

(c) CH_4

Orbital	Orbital energy (eV)		I_p (eV) (obsd)
	Present study	Clementi and Routh[24]	
$2t_2$	12.57		
$3a_1$	7.57		
$1t_2$	−13.53	−14.81	13[25]
$1a_1$	−25.18	−25.71	23[25]
core	−304.14	−305.17	290.8[27]

(d) BH_3

Orbital	Orbital energy (eV)	
	Present study	Clementi and Routh
$2e'$	6.476	
$1a_1'$	4.753	
$1a_2''$	1.436	
$1e'$	−12.41	−13.888
$1a_1'$	−18.76	−19.398
core	−206.71	−208.96

according to the procedures given in the preceding section, are given in Table 3, together with the results obtained of the probability of one-electron process (P_0), and the total probabilities of shake-up (P_{up}) and shake-off (P_{off}) processes. We see that, while both CH-CI and ECA methods yield reasonable values of core ionization potential, the agreement with observa-

TABLE 3. CALCULATED VALUES OF I_p(core), P_0, P_up AND P_off

	OCE		CNDO/2 (ECA)	Aarons *et al.*[4]	Obsd
	CH-CI	ECA		UHF	
H_2O					
I_p[eV]	542.0	540.1		539.7	539.7[28]
P_0[%]	80.8	74.7	87.6	79.2	
P_up[%]	19.2	10.9	5.9	18.8	
P_off[%]	—	14.4	6.5	2.0	
NH_3					
I_p[eV]	409.1	407.7		405.6	405.6[25]
P_0[%]	79.6	74.4	87.6	77.8	
P_up[%]	20.4	10.5	5.9	19.7	
P_off[%]	—	15.1	6.5	2.5	
CH_4					
I_p[eV]	294.1	288.0		291.1	290.8[25]
P_0[%]	81.2	74.1	87.0	77.1	
P_up[%]	18.8	11.1	6.1	20.4	
P_off[%]	—	14.8	6.9	2.5	
BH_3					
I_p[eV]	200.3	192.4			
P_0[%]	80.8	72.1	89.3		
P_up[%]	19.2	13.3	5.1		
P_off[%]	—	14.6	5.6		

tion is much better in the cases when ECA method has been used.

The P_0 values by CH-CI method are generally larger as compared with those by ECA method. Probably, this is due to the neglect of shake-off configurations in the present CH-CI calculation. Incidentally, the P_0 values obtained by Aarons *et al.*[4] through their UHF calculations on the same molecules fall in between our values by CH-CI method and those by ECA method. It may be worthwhile to compare the above P_0 values with those by the CNDO/2 calculation with equivalent-core approximation, since the last method has been conveniently used for more complex molecules. The values which we have obtained by this method are given in Table 3. We note that the CNDO/2 calculations yielded P_0 values considerably larger than those by *ab initio* calculations. Seemingly, this is reflecting the situation that the virtual orbitals which appear in CNDO/2 calculations, are quite limited as compared with those in *ab initio* calculations.

The energies and relative intensities of shake-up satellites obtained from the present calculations are summarized in Table 4. First of all, we note that CH-CI method has given unreasonably large values for the energies of shake-up transitions. The same conclusion has been reported by Guest *et al.*,[7] who have carried out an *ab initio* calculation by core-hole CI method on similar molecules. Recently it was pointed out by Wood[8] that a good result is obtainable if the effect of valence-orbital relaxation is taken into account in a core-hole CI method.

On the other hand, our results by ECA method seem to be quite reasonable when they are compared with the reported experimental data. Recently, Siegbahn[28] observed the satellite bands accompanying the O1s peak of the X-ray photoelectron spectrum of H_2O, with a high resolution technique employing monochromatized X-ray as the stimulating radiation. The satellite spectrum reported by Siegbahn is reproduced in Fig. 1, where the shake-up transitions predicted from our calculations by ECA method are indicated as vertical lines. The calculated results are

TABLE 4. ENERGIES OF SHAKE-UP SATELLITES OF THE CORE-ELECTRON PEAKS FOR H_2O, NH_3, CH_4 AND BH_3[a]

Transition	Calculation			Observation[4,28]
	Present study CH-CI	ECA	UHF[4]	
H_2O(O1s)				
$2a_1 \rightarrow 3a_1$	40.59(0.54)	17.92(0.44)	17.8(3.1)	~15(shoulder)
$1b_1 \rightarrow 2b_1$	43.92(4.82)	23.98(3.11)	23.8(8.1)	~24(17)
$2a_1 \rightarrow 4a_1$	47.43(4.41)	24.93(2.77)		
$1b_2 \rightarrow 2b_2$	59.74(4.73)	33.22(2.76)		
NH_3(N1s)				
$2a_1 \rightarrow 3a_1$	29.81(0.47)	14.18(0.74)		(~13)
$2a_1 \rightarrow 4a_1$	36.16(8.53)	22.38(3.11)	21.1(14.1)	~22(8)
$1e \rightarrow 2e$	37.74(10.04)	23.02(5.15)		
$1e \rightarrow 3e$		30.20(0.03)		~30(weak)
$1a_1 \rightarrow 3a_1$	50.03(2.46)	39.22(2.64)		
CH_4(C1s)				
$1t_2 \rightarrow 2t_2$	29.02(13.03)	17.49(8.06)	18.8(18.4)	~18(18)
$1a_1 \rightarrow 2a_1$	37.61(3.64)	31.17(3.34)		~30(3)
$1t_2 \rightarrow 3t_2$	50.55(4.09)	20.51(0.26)		
BH_3(B1s)				
$1e' \rightarrow 2e'$	20.9(8.22)	15.49(5.82)		
$1a_1' \rightarrow 2a_1'$	33.1(2.33)	23.55(4.38)		
$1e' \rightarrow 3e'$	24.6(4.26)	17.16(1.16)		

a) Relative intensities are listed in the parentheses.

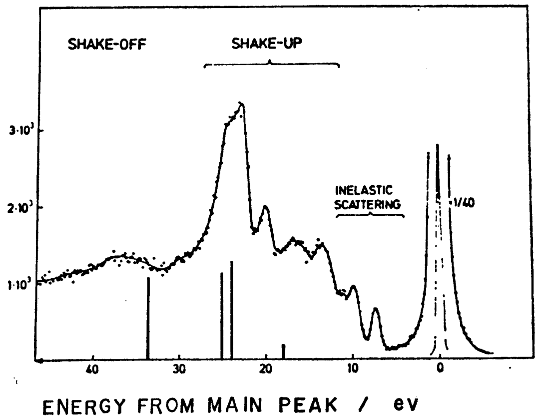

Fig. 1. Satellite bands of the Ols peak of H_2O (Siegbahn, Ref. 28). The shake-up bands predicted by the present study are shown by vertical lines.

quite satisfactory as regards the prediction of main shake-up band. In the observed spectrum, the main shake-up band is at about 24 eV from the Ols peak with an indication that it is composed of more than one components. This is in good agreement with our calculation which predicts two strong shake-up bands, at 23.98 eV ($1b_1 \rightarrow 2b_1$) and at 24.93 eV ($2a_1 \rightarrow 4a_1$). However, there is a problem concerning the interpretation of the weak satellite bands observed at lower energies. In the observed spectrum, there are three weak bands in the 11—22 eV region, their maxima being at about 13, 17 and 20 eV, respectively. All of them have been attributed by Siegbahn[28] to shake-up processes. On the other hand, our calculation predicts only one shake-up band at 17.92 eV ($2a_1 \rightarrow 3a_1$). A similar conclusion has been given by Aarons *et al.*,[4] who obtained also only one shake-up transition at 17.8 eV by UHF calculation. Seemingly, it is rather hard to explain why there are three shake-up bands in the 11—22 eV region. Siegbahn[28] attributed a broad maximum observed at about 33 eV to shake-off process. In effect, this is the energy region where we can expect a shake-off satellite. However, it should be noted also that our calculation predicts a relatively strong shake-up band at 33.22 eV ($1b_2 \rightarrow 2b_2$). Thus, there is a possibility that the 33 eV band in the observed spectrum is, at least partly, associated with a shake-up process.

For NH_3, our calculation predicts two relatively strong shake-up bands at 22.38 and 23.02 eV, which are associated with $2a_1 \rightarrow 4a_1$ and $1e \rightarrow 2e$ transitions, respectively. This is in agreement with the observation reported by Aarons *et al.*,[4] who found that the main satellite band accompanying the N1s peak of NH_3 is in the 18—25 eV region with a maximum at about 22 eV. According to our calculation, we should expect a weak shake-up band at about 14 eV. Unfortunately, however, it is difficult to judge from the reported data if there is any band corresponding to the predicted one or not.

In the case of CH_4, a relatively strong shake-up transition ($1t_2 \rightarrow 2t_2$) is predicted at 17.49 eV and a weak one ($1a_1 \rightarrow 2a_1$) at 31.17 eV. According to Aarons *et al.*,[4] the C1s spectrum of CH_4 exhibits a strong shake-up satellite at 18.1 eV, and a weak one at about 30 eV. Although they observed a weak band at about 26 eV, they attributed it to shake-off process. Seemingly, the observed spectrum is consistent with the results of our calculation.

As described above, our calculation by equivalent-core approximation (ECA) method yielded quite satisfactory results not only for the core ionization potentials, but also for the energies and intensities of shake-up satellites. On the other hand, calculations by core-hole CI(CH-CI) method failed to predict the energies of shake-up transitions correctly, while it gave reasonably good results as regards the core ionization potentials. Although we could improve the core-hole CI method by taking into account the relaxation of valence-electron orbitals as it has been proposed by Wood,[8] the equivalent core approximation method seems to have much advantage because good results are obtainable through a relatively simple computation, and, seemingly, this method can be a convenient tool for the interpretation of X-ray photoelectron spectra of molecules.

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15) The probabilities that the system will make the corresponding transition after the removal of a core electron.

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18) $C^{*+}H_4$ represents the state that an electron has been removed from the core orbital (Cls) of the carbon atom of CH_4.

19) The effect of this approximation on the estimation of probability is almost negligible since $\langle \phi_1 / \phi_l \rangle \fallingdotseq 0 (l=2, 3, \cdots\cdots)$ and $\langle \phi_1 | \phi_1 \rangle$ is nearly equal to 1 from the calculation by use of Slater's rule.

20) Strictly speaking, $P_k = |\langle \sum_{i \to j} C^k_{i \to j} \phi_{i \to j} | \Phi_0 \rangle|^2$

$$= \sum_{(i\to j)} |C^k_{i\to j}|^2 |\langle \psi_{i\to j} | \Phi_0 \rangle|^2 + 2 \sum_{(i\to j)} \sum_{(l\to m)} C^k_{i\to j} C^k_{l\to m} \langle \psi_{i\to j} | \Phi_0 \rangle$$

$$\times \langle \psi^k_{l\to m} | \Phi_0 \rangle$$

where $C^k_{i\to j}$ is the coefficient of the $(i\to j)$ excitation configuration of the k-th excited state.

However, since the second sum of the above equation was negligibly small in most cases, P_k can be expressed as follows,

$$P_k = \sum_{(i\to j)} |C^k_{i\to j}|^2 |\langle \psi_{i\to j} | \Phi_0 \rangle|^2$$

On the other hand, P_0 is reasonably assumed to be $|\langle \psi_0 | \Phi_0 \rangle|^2$.

Thus, we obtain Eq. (8).

21) For example, the ionization potential of the Ols level of H_2O is estimated as follows;

$I_p(\text{Ols}; H_2O) = E(H_2F^+) - E(H_2O) + E(O^{*\,7+}) - E(F^{7+}) - \delta_0$

where $E(H_2O)$ and $E(H_2F^+)$ are the total energies calculated of H_2O and the equivalent-core model (H_2F^+) of the core-hole ion, respectively. $E(O^{*7+})$ and $E(F^{7+})$ were also obtained by calculation. For the correction term δ_0, we assumed the values proposed by Adams and Clark.[12]

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