

Inner-shell ionizations and satellites studied by the open-shell reference symmetry-adapted cluster/symmetry-adapted cluster configuration-interaction method

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Open-shell reference version of the symmetry-adapted cluster (SAC) and SAC-configuration-interaction (CI) methods, termed open-shell reference (OR)-SAC and OR-SAC-CI methods, are developed and applied to inner-shell ionizations of CH₄, NH₃, H₂O, and HF. The inner-shell ionization potentials and spectra calculated by the OR-SAC and OR-SAC-CI methods are in excellent agreement with the experimental data. Including both of the electron correlation and orbital relaxation is important for quantitative agreements. Timing comparisons with the SAC-CI general-*R* calculations that give similar high accuracies show an efficiency of the present OR-SAC and OR-SAC-CI methods. © 2006 American Institute of Physics.

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I. INTRODUCTION

Recently, fine spectra of inner-shell ionizations and excitations have been actively observed by the synchrotron-radiation spectroscopy.¹ Theoretically, inner-shell ionizations and excitations are characterized not only by their large electron-correlations but also by their large orbital relaxations. The delta-self-consistent-field (SCF) method that takes orbital relaxations alone effectively into account has thus given reasonable results for the study of main peaks and has been applied to many systems. However, the electron correlation effects that are neglected in the delta-SCF method should be considered for doing fine spectroscopy of inner-shell electrons including, in particular, both main and satellite peaks.

The symmetry-adapted cluster (SAC) (Ref. 2)/SAC-configuration-interaction (CI) (Ref. 3) method is, of course, a recommended choice for doing fine theoretical spectroscopy of inner-shell electrons as well as those for valence, inner-valence, and Rydberg electrons.⁴⁻⁶ This method is able to describe the electron correlation effects in many different electronic states in an accurate balanced way and therefore provides a standard methodology for studying various kinds of fine spectroscopy. Rather recently, this method has been applied to the inner-shell ionization and excitation spectra and fairly fine results have been obtained by the SAC-CI general-*R* method.⁷ The SAC-CI singles and doubles SD-*R* method was insufficient to describe the orbital reorganizations caused by the ionizations and excitations of the inner-shell electrons. This is in contrast to the ordinary valence and

Rydberg excitations and valence ionizations. For describing orbital relaxations as well as electron correlations accompanying the core-electron ionizations, we need at least two-hole, three-particle ionization operators for quantitative descriptions: this is why we use the SAC-CI general-*R* method. However, generally speaking, the orbital relaxation effects are rather easily included, if we perform SCF calculations for both initial and final states, separately. This is a starting point of the present formulation of the open-shell reference (OR)-SAC method.

The OR-SAC method, that is the SAC method with reference to an open-shell configuration, was proposed briefly in 1981 (Ref. 8) as a modification of the original SAC method² and applied only to some small number of open-shell atoms and molecules in their ground and excited states.⁹ This method has some resemblance to ionization potential (IP)-open shell (OS)-CCSD of Nooijen and Lotrich¹⁰ and spin-adapted open-shell coupled cluster by Li and Paldus,¹¹ both published later.

Recently Jana and Mukherjee developed a cluster expansion which can treat strong orbital relaxation and correlation effects, and applied it to valence and inner-shell ionized states.¹² In the OR-SAC method, the orbital relaxations are first described in the formation of the open-shell reference functions, and subsequently, the electron correlations within relaxed orbitals are expressed by the SAC method. The computational requirement is comparable with that of the SAC-SD calculations for closed-shell ground states.

Once the OR-SAC wave function is defined, the OR-SAC-CI method can be formulated naturally by analogy with the relationship between the SAC and SAC-CI methods. The OR-SAC-CI method was proposed in 1983,⁹ and a similar approach named OS-electron attachment (EA)-equation-of-

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motion coupled cluster (EOMCC) has been applied to inner-shell excited states by Nooijen and Bartlett in 1995,¹³ but no further calculations were made. For valence excitations, orbital relaxations are rather small compared to the inner-shell ionizations, and therefore ordinary SAC-CI method is sufficient for quantitative calculations. For calculating inner-shell shake-up satellite states, orbital relaxations due to the inner-shell ionizations and excitations must be considered simultaneously to the electron correlations, so that higher excitation operators than those necessary for valence shake-up states are required in the SAC-CI calculations. In the OR-SAC-CI calculations, orbital relaxations and dynamical correlations are described beforehand by the restricted open-shell Hartree-Fock (ROHF) and OR-SAC methods, respectively, and only excitations are treated in the OR-SAC-CI calculations. Consequently, computational requirements of the OR-SAC-CI calculations become comparable with those of the SAC-CI calculation for valence shake-up states.

We formulate here the OR-SAC method to apply to the inner-shell ionizations of molecules and then apply it to CH₄, NH₃, H₂O, and HF molecules to calculate the inner-core ionization energies. We further formulate the OR-SAC/SAC-CI method and apply it to the calculations of the satellite peaks accompanying the inner-shell ionization of NH₃ molecule. The accuracy and the merit of this formulation will be discussed in comparison with the SAC-CI general-R method with closed-shell reference.

II. OR-SAC METHOD

The SAC method is a single-reference coupled-cluster method that uses the symmetry-adapted excitation operators $\{S_j\}$,

$$|\Psi^{\text{SAC}}\rangle = \exp\left(\sum_I C_I S_I\right)|0\rangle, \quad (1)$$

where $|0\rangle$ is a single determinant [generally Hartree-Fock (HF) determinant].

The OR-SAC method is also a single-reference coupled-cluster method starting from the open-shell reference function and is written as

$$|\Psi^{\text{OR-SAC}}\rangle = \exp\left(\sum_I C_I S_I\right)\exp\left(\sum_J C_J S'_J\right)O_K|0'\rangle. \quad (2)$$

$|0'\rangle$ is a closed-shell determinant and O_K is the operator that makes the open-shell reference function designated by K . In this paper, $O_K|0'\rangle$ is the ROHF wave function for the inner-shell ionized state (so-called K -shell state for the first-row atoms). The operators S_I include only the excitations from occupied to virtual orbitals of $|0'\rangle$, similarly to the ordinary SAC operators for closed-shell systems. The other operators S'_J represent the deexcitations to the singly occupied inner-shell orbital. In practice, we choose single and double excitation operators from the reference function. The operators S_I consist of S_i^a and S_{ij}^{ab} , where i, j and a, b denote the occupied and unoccupied orbitals, respectively. For S'_J , we include only S_i^K and S_{ij}^{Kb} operators. Here S_i^K is a deexcitation operator from orbital i to K , and S_{ij}^{Kb} contains a deexcitation from orbital i to K and an excitation from j to b . In the present calculations, S_I and S'_J were restricted to contribute up to quadratic and linear terms, respectively. The unknown variables are determined by projecting the Schrödinger equation on the linked space composed of $\{S_I\}$ and $\{S'_J\}$, and solving the nonvariational equations as in the ordinary SAC method,

$$\langle 0'|O_K^\dagger S_I^\dagger H|\Psi^{\text{OR-SAC}}\rangle = E\langle 0'|O_K^\dagger S_I^\dagger|\Psi^{\text{OR-SAC}}\rangle, \quad (3)$$

$$\langle 0'|O_K^\dagger S'_J{}^\dagger H|\Psi^{\text{OR-SAC}}\rangle = E\langle 0'|O_K^\dagger S'_J{}^\dagger|\Psi^{\text{OR-SAC}}\rangle. \quad (4)$$

III. OR-SAC-CI METHOD

Like the relationship between the SAC and SAC-CI methods, the OR-SAC-CI wave function is defined by

$$|\Psi^{\text{OR-SAC-CI}}\rangle = Q\sum_J d_J R_J|\Psi^{\text{OR-SAC}}\rangle, \quad (5)$$

where Q is a symmetry projector and R_J is an excitation operator. If we take only the excitation operators $\{S_I\}$ in the OR-SAC method, O_K and S_I commute, and the OR-SAC-CI wave function is transformed as

TABLE I. Inner-shell IPs and CPU times of the SAC-CI and OR-SAC calculations (geometries: expt. basis sets: cc-pCVTZ for C, N, O, and F and cc-pVTZ for H).

| Molecule | SAC-CI | | OR-SAC | | Expt. |
|------------------|---------|-----------------------|---------|-----------------------|----------------------|
| | IP (eV) | CPU time ^a | IP (eV) | CPU time ^b | IP ^c (eV) |
| CH ₄ | 290.97 | 37 min 20 s | 291.04 | 8 min 50 s (24%) | 290.91 |
| NH ₃ | 405.26 | 66 min 20 s | 405.56 | 10 min 48 s (16%) | 405.56 |
| H ₂ O | 539.25 | 22 min 3 s | 539.55 | 4 min 49 s (22%) | 539.78 |
| HF | 693.44 | 7 min 24 s | 693.84 | 1 min 54 s (26%) | 694.01 |

^aOnly the SAC-CI steps (termed link923 in GAUSSIAN 03) are presented.

^bOnly the OR-SAC steps are presented. The values in parentheses are percentages relative to the SAC-CI results.

^cReference 21, average IP values are considered to be the experimental ones, if more than one value was reported in Ref. 21.

TABLE II. Total energies of the ground and inner-shell ionized states of CH₄, NH₃, H₂O, and HF by the RHF, ROHF, SAC, and OR-SAC methods (in a.u.) (geometries: expt.).

| Basis sets | Ground state | | Inner-shell ionized states | | |
|------------------|--------------|-----------|----------------------------|----------------------|-----------------------|
| | RHF | SAC | ROHF (IP) | OR-SAC (IP) | Expt. IP ^a |
| CH ₄ | | | | | |
| cc-pVTZ | -40.2134 | -40.4371 | -29.5186 (291.02 eV) | -29.7571 (290.61 eV) | 290.91 eV |
| cc-pCVTZ | -40.2136 | -40.4681 | -29.5256 (290.83 eV) | -29.7724 (291.04 eV) | |
| NH ₃ | | | | | |
| cc-pVTZ | -56.2044 | -56.4558 | -41.2966 (405.65 eV) | -41.5651 (405.19 eV) | 405.56 eV |
| cc-pCVTZ | -56.2045 | -56.4918 | -41.3079 (405.35 eV) | -41.5876 (405.56 eV) | |
| H ₂ O | | | | | |
| cc-pVTZ | -76.0572 | -76.3261 | -56.2272 (539.59 eV) | -56.5075 (539.28 eV) | 539.78 eV |
| cc-pCVTZ | -76.0574 | -76.3662 | -56.2416 (539.21 eV) | -56.5379 (539.55 eV) | |
| HF | | | | | |
| cc-pVTZ | -100.0580 | -100.3396 | -74.5674 (693.63 eV) | -74.8489 (693.63 eV) | 694.01 eV |
| cc-pCVTZ | -100.0582 | -100.3853 | -74.5845 (693.16 eV) | -74.8869 (693.84 eV) | |

^aReference 21.

$$|\Psi^{\text{OR-SAC-CI}}\rangle = Q \sum_J d_J R_J \exp\left(\sum_I C_I S_I\right) O_K |0'\rangle \quad (6)$$

$$= Q \sum_J d_J R_J O_K \exp\left(\sum_I C_I S_I\right) |0'\rangle \quad (7)$$

$$= \sum_J d_J R'_J \exp\left(\sum_I C_I S_I\right) |0'\rangle. \quad (8)$$

As a result, the OR-SAC-CI wave function has the same feature as the SAC-CI one with a closed-shell reference function, and so the coding has been done with a slight

modification of the SAC/SAC-CI code in GAUSSIAN 03.¹⁴ In this article, R_J is an identity or excitation operator and leads R'_J that is an ionization operator. By using the relaxed orbitals and the electron correlations of the hole state, the size of CI expansions is expected to be reduced for describing the shake-up states. The effects of the S'_J operators neglected in the OR-SAC method are included in R_J and R'_J like in the multi-exponentially generated (MEG)4/excited (EX)-MEG4 method.¹⁵

We can calculate the inner-shell excited states using electron attachment operators R_J . In this case, R'_J becomes an inner-shell excitation operator, and the resultant OR-SAC-CI

TABLE III. Binding energies (BE) and relative intensities of inner-shell ionized states of NH₃ calculated by OR-SAC-CI method.

| Expt. ^a | | OR-SAC-CI | | |
|--------------------|----------------------------|-----------|----------------------------|--|
| BE (peak) (eV) | Intensity ($\times 100$) | BE (eV) | Intensity ($\times 100$) | Main configuration ^b ($C > 0.3$) |
| 405.6 (0) | 100.0 | 405.45 | 100.0 | 0.96($1a_1^{-1}$) |
| 416.6 (1) | 3.0 | 416.98 | 0.31 | $-0.52(1a_1^{-1}4a_13a_1^{-1}), 0.51(3a_1^{-1}4a_11a_1^{-1})$ |
| | | 418.77 | 0.26 | $0.87(3a_1^{-1}4a_11a_1^{-1}), 0.86(1a_1^{-1}4a_13a_1^{-1})$ |
| 422.8 (2) | 2.0 | 421.50 | 0.57 | $0.50(1a_1^{-1}5a_13a_1^{-1}), -0.40(3a_1^{-1}5a_11a_1^{-1})$ |
| | | 422.48 | 0.51 | $-0.49(1a_1^{-1}2e1e^{-1})$ |
| 426.7 (3) | 13.0 | 424.98 | 0.64 | $0.35(3a_1^{-1}5a_11a_1^{-1})$ |
| | | 426.07 | 4.32 | $-0.35(1e^{-1}2e1a_1^{-1}), 0.31(3a_1^{-1}8a_11a_1^{-1})$ |
| | | 426.24 | 0.41 | $-0.31(3a_1^{-1}7a_11a_1^{-1})$ |
| | | 426.83 | 0.32 | $0.32(3a_1^{-1}9a_11a_1^{-1}), -0.30(1a_1^{-1}9a_13a_1^{-1})$ |
| | | 426.95 | 1.11 | $0.25(3a_1^{-1}8a_11a_1^{-1}), -0.23(1a_1^{-1}9a_13a_1^{-1})$ |
| | | 427.85 | 0.76 | $-0.49(3a_1^{-1}15a_11a_1^{-1}), -0.42(1a_1^{-1}12a_13a_1^{-1}),$ $-0.31(3a_1^{-1}5a_11a_1^{-1}), -0.30(1a_1^{-1}11a_13a_1^{-1})$ |
| | | 436.6 (4) | 1.0 | 436.53 |
| | | 436.61 | 0.65 | $-0.63(1e^{-1}15e1a_1^{-1}), -0.41(1a_1^{-1}15e1e^{-1}),$ $-0.32(1a_1^{-1}4a_12a_1^{-1})$ |
| | | 436.89 | 0.70 | $0.54(2a_1^{-1}4a_11a_1^{-1}), 0.49(1a_1^{-1}4a_12a_1^{-1}),$ $-0.35(1a_1^{-1}17e1e^{-1})$ |

^aReference 25.^bExcitation pairs within e symmetry orbitals are not shown.

wave function projected by Q becomes singlet or triplet. Our results for the inner-shell excitation spectra will be presented in a forthcoming paper.¹⁶

IV. APPLICATIONS

First, we demonstrate the efficiency of the OR-SAC method for the study of inner-shell ionized states. We took the experimental geometry of the ground states.¹⁷ The correlation consistent polarized core-valence triple-zeta¹⁸ (cc-pCVTZ) and cc-pVTZ (Ref. 19) basis sets were employed for heavy and hydrogen atoms, respectively, and all MOs were included in the active space. The SAC and the OR-SAC excitation operators were restricted to singles and doubles from the reference function. Perturbation selection²⁰ was done for the double excitation operators with an energy threshold of 10^{-6} a.u.. The HF and ROHF determinants were used as the reference functions for the ground and inner-shell ionized states, respectively. We adopted here core-valence separation approximation, namely, the deexcitation operators that make valence ionized configurations were not considered in the present calculations. Therefore, S_i^K was excluded here, and only spectator-type operators S_{iK}^{Kb} out of S_{ij}^{Kb} were taken into account. In the unlinked operators of the SAC and OR-SAC, we included only such operators that have the coefficients larger than 0.005 in the preliminary SDCl.

In Table I, the inner-shell IPs and CPU times of the OR-SAC calculations are compared with the results of SAC-CI general- R method. The conditions of the SAC-CI calculations are identical to those reported in Ref. 7. All calculations were performed using Compaq AlphaStation XP1000. In the CPU time, SCF and integral transformation steps were not included, and only the SAC-CI or the OR-SAC portions (termed link923 in GAUSSIAN 03) were presented. The SAC-CI results for the inner-shell IPs were somewhat lower than the experimental values, except for CH₄. On the other hand, the inner-shell IPs were well reproduced by the OR-SAC method. With respect to the CPU time, the SAC-CI calculation consists of the SAC and the SAC-CI general- R steps, and the OR-SAC calculation is comparable only with the SAC step. Consequently, the OR-SAC calculations require only 16%–26% of the SAC-CI calculations. Further acceleration is not difficult because the OR-SAC code used here was tentative.

Next, we discuss the basis-set dependence of the SAC and OR-SAC calculations. The basis-set cc-pCVTZ was chosen to represent the inner-shell electron correlations in the ground state and the polarizations in the inner-shell ionized states. The cc-pCVTZ basis sets for C, N, O, and F atoms consist of cc-pVTZ basis sets and additional $(2s2p1d)/[2s2p1d]$ functions. In Table II, the restricted Hartree-Fock (RHF) and ROHF wave functions are the reference functions of the SAC and OR-SAC methods, respectively. The values in parentheses in the ROHF and OR-SAC columns are the inner-shell IPs of the Δ SCF and OR-SAC methods, respectively.

For the ground states, the differences of the RHF total energies between cc-pCVTZ and cc-pVTZ basis sets were less than 1 mhartree, while the SAC correlation energies with

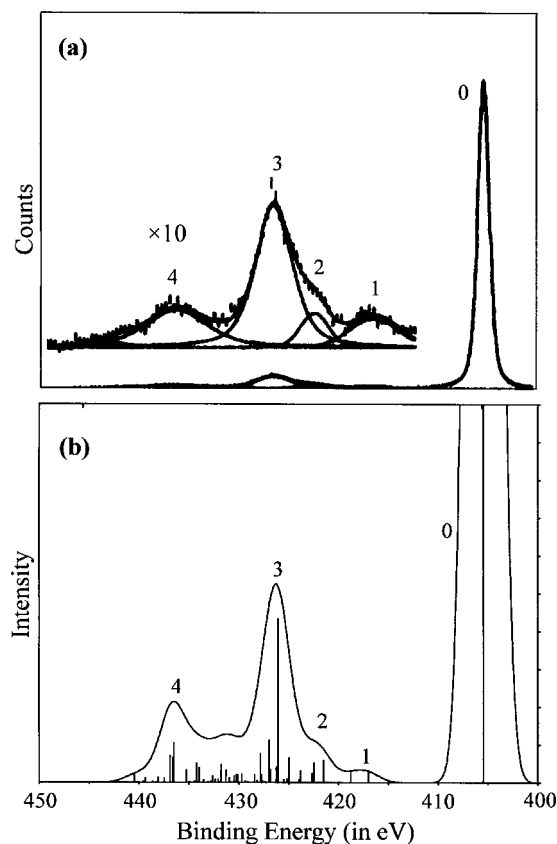


FIG. 1. (a) Core 1s level x-ray photoelectron spectrum of NH₃, (Ref. 25) and (b) theoretical inner-shell ionization spectrum by the OR-SAC-CI method. In theoretical spectrum, calculated monopole intensity is shown by the solid vertical lines at each ionization potential, and the Gaussian curves are drawn with the averaged line width [4.0 eV full width at half maximum (FWHM)].

cc-pVTZ in CH₄, NH₃, H₂O, and HF were improved by 31, 36, 40, and 46 mhartree, respectively, with the cc-pCVTZ basis set. In the inner-shell ionized states, the differences in the ROHF total energies between these basis sets were 7, 11, 14, and 17 mhartree from CH₄ to HF: they reflect the contributions of the additional functions to the orbital relaxations and polarizations. Consequently, the IPs estimated by the Δ SCF employing the cc-pCVTZ basis were 290.83, 405.35, 539.21, and 693.16 eV for CH₄, NH₃, H₂O, and HF, respectively. These are all lower as compared with the results obtained with the cc-pVTZ basis set (291.02, 405.65, 539.59, and 693.63 eV) and the experimental values (290.91, 405.56, 539.78, and 694.01 eV).²¹ The OR-SAC total energies are further improved by 15, 23, 30, and 38 mhartree, respectively, with the additional functions. However, the IPs estimated by the OR-SAC method with cc-pCVTZ, 291.04, 405.56, 539.55, and 693.84 eV, are higher and closer to the experimental values than those of cc-pVTZ, 290.61, 405.19, 539.28, and 693.63 eV, because the stabilizations of the ground states by the SAC method with cc-pCVTZ are larger than those of inner-shell ionized states by the OR-SAC method. Thus, for the quantitative calculations of the inner-shell IPs, the inner-shell electron correlations in the ground state as well as the orbital relaxations and polarizations in inner-shell ionized states should be considered in a balanced way.²²

Finally we applied the OR-SAC-CI method to the calculations of the satellite states in the inner-shell ionization spectrum of NH_3 . For the basis set of nitrogen, we used the cc-pCVTZ basis augmented with Rydberg functions $[4s4p4d]$ for the $3s3p3d4s4p4d$ orbitals²³ and with the tight s - and p -type functions $[2s2p]$. For ionization operators, R'_j were restricted to the triple excitations from $|0'\rangle$ in Eq. (8). The binding energies were calculated from the SAC ground state with the RHF reference function, and the intensities were calculated with the monopole approximation²⁴ between the RHF and OR-SAC-CI wave functions. The results were listed in Table III, and the theoretical spectrum was compared with the experimental one²⁵ in Fig. 1. The experimental spectrum was well reproduced by the OR-SAC-CI method, and the observed satellite peaks (1, 2, 3, and 4) were assigned to the excitations $(2pa_1 \rightarrow 3s)$, $(2pa_1 \rightarrow 3pa_1, 2pe \rightarrow 3pe)$, $(2pe \rightarrow 3pe, 2pa_1 \rightarrow 4pa_1)$, and $(2s \rightarrow 3s)$, respectively, that accompany the K -shell ionization. These assignments are essentially the same as those due to the experiment²⁵ and to the previous SAC-CI general- R calculations.⁷ We note that only up to triple excitations were used in the OR-SAC-CI calculations, while in the SAC-CI general- R calculations up to quadruple excitations were necessary for quantitative representations. By using the electron correlations of the OR-SAC method and the relaxed orbitals of the hole state, we could calculate with the OR-SAC-CI method the inner-shell ionization spectra at the costs that are similar for valence shake-up satellite spectra.

V. CONCLUSION

We applied the OR-SAC method to the inner-shell ionized states and the results were in agreement with the experimental values. The computational costs were those comparable to the SAC-SD calculations for the ground states. The delta-SCF results with cc-pCVTZ basis were all lower than the experimental values, and therefore the electron correlations in both the ground and inner-shell ionized states should be accurately examined for quantitative calculations.

In addition, the OR-SAC-CI method, in which the OR-SAC wave function was used as the basis of CI expansions, was applied to the inner-shell ionization spectrum of NH_3 . The results reproduced well the experimental spectrum at smaller costs compared to the SAC-CI general- R calculations based on the closed-shell ground-state orbitals and the assignments of the observed peaks were consistent with the previous results.

We have applied the OR-SAC/SAC-CI method to inner-shell ionization spectra of other molecules. We have also applied this method to the inner-shell excitation spectra. The results will be presented in forthcoming papers.

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