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Kyoto University

京都大学
THEORETICAL STUDIES
ON
THE ELECTRON CORRELATION EFFECTS IN ATOMS AND MOLECULES
BY
THE MULTICONFIGURATION SELF-CONSISTENT-FIELD METHOD

KAZUHIRO ISHIDA
DEPARTMENT OF HYDROCARBON CHEMISTRY
FACULTY OF ENGINEERING
KYOTO UNIVERSITY
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Electron correlation effects in atoms and molecules have received particular attentions by theoretical chemists and physicists. Many methods for taking account of the effects have been proposed, which are described in the introduction of the present doctoral dissertation. Among them, the multiconfiguration self-consistent-field (MCSCF) method is used for the present investigations. The MCSCF method is described in Chapter II of this dissertation.

The studies presented in this dissertation are summaries of the author's works carried out from the spring of 1970 to 1975 at the Department of Hydrocarbon Chemistry of the Faculty of Engineering of Kyoto University. Chapter III had been published in Chemical Physics Letters 19, 268 (1973). Chapter IV is in press in Physical Review A. Chapters V and VI are to be submitted in the nearest future. Chapters VII and VIII had been published in Bulletin of the Chemical Society of Japan; 44, 2587 (1971) and 45, 1574 (1972), respectively.

The author would like to thank Professor Teijiro Yonezawa for continuing guidances, encouragements, and discussions. He also wishes to thank Professor Hiroshi Kato and Dr. Hiroshi Nakatsuji for helpful discussions and suggestions. The author is indebted to Professor Kenichi Fukui for academic incitements. Thanks are also due to Dr. Shingo Ishimaru and Mr. Kunihiro Kondo (B. Eng.) for active collaborations.
The author also gratefully acknowledges to Dr. Takashi Kawamura, Dr. Isao Morishima, Dr. Kimihiko Hirao, Dr. Hideyuki Konishi, Mr. Shigeki Kato (M. Eng.), and Mr. Toshikatsu Koga (M. Eng.) for kind suggestions and encouragements. He also thanks Miss Yoriko Honjo for assistances in the preparation of several manuscripts in this dissertation. Lastly, the author expresses his sincere gratitude to his parents.
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CHAPTER I
INTRODUCTION

The stationary state of atoms and molecules are described in quantum mechanics by Schrödinger equation,

$$H\psi = E\psi,$$

where \( H \) is a certain Hamiltonian of a given system and \( E \) is one of its eigenvalues corresponding to one of its eigenstates, \( \psi \). For atoms and molecules, Eq.(1) is generally a many-electron problem except for hydrogen-like atoms. It is clearly impossible to solve exactly the many-electron problem as it is so in classical mechanics.

Hartree\(^1\) proposed an "independent-particle model" which yields an approximate solution of the above problem. An \( N \)-electron problem, Eq.(1), can be reduced to \( N \)-coupled one-electron problems to be solved iteratively by his technique. After this, Fock\(^2\) improved this technique so that the above approximate solution is forced to satisfy Pauli principle completely. The improved technique is well known as Hartree-Fock method. The Hartree-Fock solution predicts over 99% of the total electronic energies of first-row atoms. However, it fails to describe many other properties of atoms and molecules; e.g., it does not predict even binding for \( F_2 \) molecule\(^3\) and the non-zero value of the experimental spin density at the nucleus of an atom among B-F,\(^4\) and so on.

Then we have to ask for a more accurate solution than the Hartree-Fock's. That is, the electron correlation effects must be taken into account.

Many techniques have been proposed for the purpose.
They may be classified into three categories; (a) perturbation method, (b) variation method, and (c) others. Works in category (a) are well reviewed up to 1963 by Hirschfelder, Byers-Brown, and Epstein. Exchange perturbation methods for describing interatomic interactions at small separations are developed and reviewed by Chipman, Bowman, and Hirschfelder. For those at large separations, Dalgarno and Davison have already given a sufficient review article. Recently, the many-body perturbation theory (MBPT) is developed by Brueckner and Goldstone. This is the second-quantized form of the ordinary Rayleigh-Schrödinger perturbation theory except for the normalization condition. Kelly first applied it to an atomic system with excellent successes. Das and his co-workers, Kelly, Hata, and others calculated atomic hyperfine structures very accurately by the MBPT. Furthermore, very accurate calculations of the MBPT have been carried out (i) for the correlation energies of atoms and molecules $H_2O$ and HF, (ii) for the hyperfine pressure shift of He atom in helium, (iii) for the van der Waals interaction between atoms, (iv) for the hyperfine structure of diatomic molecules, and so on. Thus the MBPT is very powerful for dealing with atoms and small molecules.

In category (b), two standard methods were introduced first by Hylleraas in a series of papers on helium-like systems. They are (i) the Hylleraas method, in which the interelectronic coordinates $r_{ij}$ are explicitly included in the terms of a wave function, and (ii) the configuration-interaction (CI) method, in which a wave function is
expanded by means of antisymmetrized products of spin orbitals. The both methods yield variational solutions which converge to the exact solution of a given system with any desired degree of accuracy if a sufficient number of terms are included. The Hylleraas method is applied to hydrogen molecule by James and Coolidge, to $\text{H}_4$ system by Conroy and Malli, and to the atomic systems; (i) He by Pekeris and his co-workers, and by Kinoshita, (ii) Li by Larsson and his co-workers, and by Sims and Hagstrom, (iii) Be by Sims and Hagstrom and by Perkins, and so on. There are no calculations, to the author's knowledge, for dealing with any systems which consist of more than four electrons by the use of the Hylleraas method.

The CI method are very popular so that it is applied to a great number of systems in order to describe the many properties of them. It has been reviewed by Lowdin and by Nesbet. Very accurate calculations of the method have been carried out for atoms; (i) Be, C, and Ne by Bunge and his co-workers, and (ii) B to Ne by Sasaki and Yoshimine. In the CI method, the spin orbitals mentioned above are usually not optimized, perhaps, for the sake of labor. Recently, McWeeny derived the Euler equations which determine the spin orbitals as variational parameters. The special and powerful (as is shown later in this dissertation) version of the CI method with the optimized orbitals is generally called multiconfiguration self-consistent-field (MC-SCF) method or multiconfiguration Hartree-Fock (MC-HF) method. The former name is used throughout this dissertation.
The MC-SCF method will be described in detail in the next chapter (Chapter II).

The Valence-Bond (VB) method developed by Heitler and London\textsuperscript{55} and Sugiura\textsuperscript{56} is also in the category (b). Goddard and his co-workers\textsuperscript{57} suggested that their G1 wave function is the VB type. Clearly, their G1 function is a special one of the MC-SCF wave functions with non-orthogonal orbitals. Then it seems that the VB method and the usual molecular-orbital method which has been developed by Hund\textsuperscript{58} and Mulliken\textsuperscript{59} are united into the MC-SCF method in harmony.

The spin-optimized self-consistent-field (SO-SCF) technique proposed by Kaldor and Harris,\textsuperscript{60} Lunell,\textsuperscript{61} Ladner and Goddard,\textsuperscript{62} and Hameed et al.\textsuperscript{63} is also in the framework of the MC-SCF method.

Many techniques are in the category (c). Several are mentioned here. Some methods called pair-correlation approximations have received an appreciable attention. They are (i) the "many-electron theory" (MET) by Sinanoglu,\textsuperscript{64,65} (ii) the "atomic Bethe-Goldstone" formulation by Nesbet,\textsuperscript{66} (iii) the "coupled electron pair approximation with pair natural orbitals" (CEPA-PNO) technique by Mayer\textsuperscript{67} and Ahlrichs, Kutzelnigg, and their co-workers,\textsuperscript{68} (iv) the symmetry-adapted work by Platas and Schaefer,\textsuperscript{69} in which the basic reference state is the so-called first-order wave function\textsuperscript{70} rather than the Hartree-Fock configuration, and many other works. The first idea of these techniques may be due to Rodberg,\textsuperscript{71} Nesbet,\textsuperscript{72} and Sinanoglu.\textsuperscript{73} The essential hypothesis of the pair-correlation techniques is that, for closed shell systems,
the total correlation energy $E_c$ is given as a sum of independently computed pair-correlation energies

$$E_c = \sum_{i,j} E_{e(i,j)}.$$  \hspace{1cm} (2)

Sinanoglu\textsuperscript{6} discussed why Eq.(2) should be approximately correct. Schaefer\textsuperscript{7} claimed the question of this additivity in his book, since several calculations have shown that the pair-correlation approximations usually over-estimate the correlation energy. The main reason for this is the neglect of the pair-pair interactions which can be automatically included in the CI or the MC-SCF calculations.\textsuperscript{5,1} This may cause an improved technique (which is named "pair-natural orbitals CI" (PNO-CI) method)\textsuperscript{6,7} into the framework of the CI method. For closed shell systems, this is very similar to the MC-SCF method which takes account of pair-excitations and of double-pair excitations (4 electron excitations).

Amongst the whole methods, the MC-SCF technique seems to be most powerful for many purposes. In the present dissertation, we will show, in the applications to several systems, how the MC-SCF method is powerful and how physical pictures can be extracted from MC-SCF wave functions.

The Fermi-contact hyperfine structure of the atoms Li and N is studied in Chapter III (for $^2S$ and $^2P$ states of lithium) and in Chapter IV (for $^4S$ state of nitrogen). An excellent agreement with experiment is obtained for the both atoms. A core radial-polarization mechanism which causes the spin density at the nucleus of an atom is proposed through the
studies in the both chapters. This is a new picture for core-polarization phenomena of atoms.

The dissociation energies of polyatomic molecules (CH₄, NH₃, and H₂O) are computed with sufficient accuracy in Chapter V. This study indicates that we have now a powerful tool to describe the dissociation process of polyatomic molecules with a sufficient accuracy for chemists.

In Chapter VI, floating functions⁷⁶ are used with reasonable success in the MC-SCF framework for dealing with the intra-bond pair-correlation of lone-pairs of electrons in the molecules NH₃ and H₂O.

The chemical shifts of ESCA (electron spectroscopy for chemical analysis)⁷⁷ are investigated semi-empirically in Chapters VII and VIII. A theoretical formula is given in Chapter VII for the relationship between the chemical shifts and molecular charge distributions which has been pointed out empirically. In Chapter VIII, this formula is applied to large molecules with reasonable success.

Finally, general conclusions of these studies are given at the end of this dissertation.
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4 For example, see Ref. 70.
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\textsuperscript{61} S. Lunell, Phys. Rev. 173, 85 (1968).
CHAPTER II

ON MC-SCF METHOD

In this chapter, we discuss on the MC-SCF method in detail. For a given system of atoms and molecules, the electronic Hamiltonian $H$ is usually given in atomic units by

$$H = -(1/2) \sum_i \frac{Z_i^2}{r_i} + \sum_{i<j} \frac{1}{r_{ij}},$$  \hspace{1cm} (1)

where $Z_i$ is the charge of $i$-th nucleus. Let us consider to apply the variation principle to the system described by the Hamiltonian. The trial variational function $\Psi$ can be assumed to be given by a sum of certain configurations $\{\Phi_k\}$; i.e.,

$$\Psi = \sum_k \Phi_k a_k,$$  \hspace{1cm} (2)

where $a_k$ are the configuration mixing coefficients to be determined variationally. The $\Phi_k$ are constructed by an antisymmetrized product of the component orbitals $\phi_i$ (or generally by a linear combination of the products for the symmetry considerations). A infinite sum of a complete set of $\Phi_k$ gives, of course, exactly an eigenstate of the above Hamiltonian. It is impossible, however, to take the infinite sum. Then the variation principle gives us the best $a_k$ and the best orbitals $\phi_i$ for any finite sum, via the following Euler equations:

$$\sum_k a_k [H_{KL} - \delta_{KL} E] = 0,$$  \hspace{1cm} (3)

$$\sum_j F_{ij} \phi_j = \sum_k \phi_k c_{ki} \phi_i.$$  \hspace{1cm} (4)
where $H_{KL}$ are the matrix elements of the Hamiltonian,

$$H_{KL} = \int \phi_K^* H \phi_L \, d\tau,$$

(5)

the $\delta_{KL}$ are the usual Cronecker's delta, $E$ and $\varepsilon_{ki}$ are the Lagrangean unknown multipliers, and $F_{ij}$ are the Fock-like operators derived from the variation of the matrix elements $H_{KL}$ with respect to orbitals. Equation (3) is well known as the secular equation and the unknown multiplier $E$ is clearly an upper bound of an exact energy eigenvalue of the above Hamiltonian. We may call Eq.(4) as the MC-SCF equation. Clearly, the MC-SCF equation converges to the ordinary Hartree-Fock equation at the limit of the single sum (the single configuration limit) in Eq.(2). Thus, the Fock-like operator $F_{ij}$ converges to the ordinary Fock operator in this case. It is thought in this sense that the MC-SCF method is the most natural extension of the Hartree-Fock method to that in multiconfigurations. Then the other name, multi-configuration Hartree-Fock (MC-HF) method, is also quite adequate. In the conventional SCF-CI method, the trial wave function is considered to be the same form as Eq.(2) and the Hartree-Fock equation which is the single configuration limit of the MC-SCF equation is solved. Thus the orbitals in the SCF-CI method minimize the Hartree-Fock energy rather than the upper bound $E$. (Of course, the MC-SCF orbitals minimize the upper bound.)

Next, we discuss the development and the present state of the MC-SCF method below. The first idea of the method may be due to Frenkel in second-quantized formalism.
The first calculations were carried out by Hartree, Hartree, and Swirles on O atom and its ions. The MC-SCF equation was first derived by McWeeny in his density matrix formalism. It is not so easy to ask for the density matrices. Then, several workers after McWeeny asked for the MC-SCF equation within limited choices of configurations. They are (i) the so-called "Complete multiconfiguration (CMC)-SCF" formalism by Veillard and Clementi, (ii) an atomic MC-SCF formulation by Hinze and Roothaan, (iii) the "Optimized Valence Configuration (OVC)" technique by Das and Wahl, and so on.

Of course, works without no limitation of configurations were, most recently, carried out by (i) Bagus, Bessis, and Moser for carbon atom, (ii) Sibincic for boron atom, (iii) Ishida and Nakatsuji for lithium atom, (iv) Bagus and Bauche for atoms, B, C, O, and F, (v) Wagner, Das, and Wahl for ArH system, (vi) Das for CN radical molecule, (vii) Das, Janis, and Wahl for diatomic systems CN and AlO, and (viii) Ishida for nitrogen atom. The applications of the above OVC technique have been reviewed up to 1969 in the review article by Wahl and Das.

There is a numerical difficulty in solving the MC-SCF equation, Eq.(4), by the usual SCF procedure. Then techniques for solving Eq.(4) have been studied during the last decade by (i) Hinze and Roothaan and Huzinaga (a multi-dimensional Newton-Raphson procedure), (ii) Chang and Grein, Golebiewski and Nowak-Broclawik, Mukherjee, and Hinze (a two-by-two rotation method), (iii) Das and Wahl, and Wood and Veillard (a modified single-vector diagonal-
ization technique), (iv) Hinze\textsuperscript{21} (a Gauss-Seidel procedure), and (v) Levy\textsuperscript{24} (a stepest decent method). Among them, the modified single-vector diagonalization technique by Wood and Veillard\textsuperscript{23} seems to be most promising as long as the author studied (though the Levy's stepest decent method was not tried).
References

CHAPTER III

MCSCF WAVEFUNCTIONS

FOR

THE FERMI-CONTACT HYPERFINE STRUCTURE

OF

LITHIUM ATOM
MC SCF WAVEFUNCTIONS FOR THE FERMI-CONTACT HYPERFINE STRUCTURE OF LITHIUM ATOM

MC SCF wavefunctions which describe accurately the Fermi-contact hyperfine structure of the lithium atom in lowest P and S doublet states are obtained. The physical picture of the Fermi-contact hyperfine structure of the states is discussed on the basis of the wavefunctions.

In the multi-configuration (MC) SCF method, the wavefunction of a system

$$\Psi = \sum K a_K \Phi_K$$

is optimized with respect to both the configurational coefficients $$a_K$$ and the component orbitals in the configurations $$\Phi_K$$. Consequently, this method improves the “slow convergence” of the conventional CI method so that one may achieve a good approximation for a state even with a few configurations [1]. In the present communication, we investigate the Li atom by the MC SCF method in order to search for a physical mechanism which contributes mainly to the spin density at the nucleus (hereafter referred to as $$[s\delta]$$) on the basis of the physical significance of the configurations.

In order to study the nature of the hyperfine structure of atoms, the simplest problem to treat may be the P doublet state of the Li atom. We discuss this state firstly and the S doublet state of the Li atom subsequently. The following three configurations are considered in the present calculations for the P doublet state:

$$\Phi_1 = |1s1s2p\rangle$$,

$$\Phi_2 = |2s2s2p\rangle$$,

and

$$\Phi_3 = 6^{-1/2} [2|2s1s2p\rangle - |2s1s2p\rangle - |2s1s2p\rangle]$$,

where $$\Phi_1$$ is the Hartree–Fock configuration which gives the reference state for taking into account electron correlation effects. $$\Phi_2$$ is the P doublet configuration arising from two-electron excitation from the 1s to the 2s orbital, and $$\Phi_3$$ is the singly excited configuration (this could contribute to $$[s\delta]$$ as a spin-polarization mechanism [2]).

In table 1, we summarize the results obtained from these two- and three-configuration MC SCF calculations. The nature of $$[s\delta]$$ is clarified by considering the meaning of these configurations within the MC SCF framework. Let $$u_+$$ and $$u_-$$ be the orbitals defined by the linear transformation of the MC SCF orbitals, 1s and 2s:

$$\begin{pmatrix} u_+ \\ u_- \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta \\ \cos \theta & -\sin \theta \end{pmatrix} \begin{pmatrix} 1s \\ 2s \end{pmatrix}$$

where $$0 < |\theta| < \pi/2$$. Then, an MC SCF wavefunction $$\Psi[2C]$$ consisting of the two configurations $$\Phi_1$$ and $$\Phi_2$$ is transformed to

$$\Psi[2C] = a_1 \Phi_1 + a_2 \Phi_2 = (N/2) |u_+ u_- 2p \rangle |0\rangle$$,

where $$a_1 = N \cos^2 \theta$$, $$a_2 = -N \sin^2 \theta$$ and N is the normalization constant. Eq. (3) means that configuration $$\Phi_2$$ causes the radial splitting of the 1s orbital in $$\Phi_1$$ and that the split orbitals $$u_+$$ and $$u_-$$ are occupied by an electron of $$\alpha$$ and/or $$\beta$$ spin with the same probability of 0.5. In terms of $$u_+$$ and $$u_-$$, the configuration

...
Table 1
The calculated spin density and energy of the P doublet state of the Li atom by the MC SCF method

<table>
<thead>
<tr>
<th>Configuration</th>
<th>([s, \delta]) (au)</th>
<th>Energy (au)</th>
<th>Virial theorem</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>2 conf. ([\Phi_1 \text{ and } \Phi_2])</td>
<td>0</td>
<td>-7.380082</td>
<td>2.000174</td>
<td>a)</td>
</tr>
<tr>
<td>2 conf. ([\Phi_1 \text{ and } \Phi_2])</td>
<td>-0.01402</td>
<td>-7.365088</td>
<td>2.000033</td>
<td>b)</td>
</tr>
<tr>
<td>3 conf. ([\Phi_1, \Phi_2 \text{ and } \Phi_3])</td>
<td>-0.01693</td>
<td>-7.380087</td>
<td>2.000173</td>
<td>a)</td>
</tr>
<tr>
<td>nearly full CI within (S)</td>
<td>-0.01693 ± 0.00020</td>
<td>-7.379062</td>
<td></td>
<td>[7]</td>
</tr>
<tr>
<td>experimental</td>
<td>-0.01693 ± 0.00020</td>
<td>-7.41013</td>
<td></td>
<td>[7]</td>
</tr>
</tbody>
</table>

a) This work; the basis set used in the present calculations is the same as that in ref. [6].
b) This work; the basis set is the same as in ref. [9].

Table 2
The calculated spin density and energy of the S doublet state of the Li atom by the MC SCF method

<table>
<thead>
<tr>
<th>Configuration</th>
<th>([s, \delta]) (au)</th>
<th>Energy (au)</th>
<th>Virial theorem</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 conf.</td>
<td>0.2139</td>
<td>-7.4465527</td>
<td>1.999988</td>
<td>a)</td>
</tr>
<tr>
<td>5 conf.</td>
<td>0.2265</td>
<td>-7.4475648</td>
<td>1.999990</td>
<td>a)</td>
</tr>
<tr>
<td>7 conf.</td>
<td>0.2265</td>
<td>-7.4475654</td>
<td>1.999990</td>
<td>a)</td>
</tr>
<tr>
<td>nearly full CI within (S)</td>
<td>-7.44754</td>
<td></td>
<td></td>
<td>[7]</td>
</tr>
<tr>
<td>experimental</td>
<td>0.2313</td>
<td>-7.47805</td>
<td></td>
<td>[5]</td>
</tr>
</tbody>
</table>

a) This work; the basis set used in the present calculations is the same as that in ref. [6].

\[ \Phi_3 = N' \left[ \cos^2 \theta, \sin^2 \theta, 2 \cos \theta \sin \theta \right] \]

where \(\Phi_3\) is the normalization constant. Then, the MC SCF wavefunction consisting of three configurations, \(\Phi_1, \Phi_2\) and \(\Phi_3\) can be expressed as

\[ \Psi[3C] = a_1 \Phi_1 + a_2 \Phi_2 + a_3 \Phi_3 \]

where \(a_1 = N_1 \cos^2 \theta, a_2 = N_1 \sin^2 \theta\) and \(a_3 = N_1\). As seen in the last term of eq. (5), there arises some probability that each of the split orbitals is occupied by an \(\alpha\)-spin electron. That is, the additional configuration \(\Phi_3\) causes a slight imbalance in the occupation probabilities of \(\alpha\) and \(\beta\) electrons in the split \(1s\) orbitals by the effect of the unpaired electron in the \(2p_y\) orbital. Since table 1 indicates that \(\Psi[3C]\) is superior in energy to the nearly full CI within \(S\), the S-character* of the exact wavefunction of the state may be sufficiently reproduced by \(\Psi[3C]\). As only an S-character could contribute to the \([s, \delta]\), \(\Psi[3C]\) should give a good \([s, \delta]\). Indeed, the very good value of \(-0.01693\) which just agrees with the experimental value of \(-0.01693 ± 0.00020\) can be obtained by \(\Psi[3C]\). On the other hand, as the calculated \([0, \delta]\) is \(-0.01402\) for \(a_1 \Phi_1 + a_3 \Phi_3\), the proper description of a radial correlation should be a prerequisite for a good \([s, \delta]\).

Next, we discuss the ground state of the Li atom (S doublet). The following seven configurations are considered in the present calculations for the state;

\[ \Phi_1 = |1s1s2s1\rangle, \quad \Phi_2 = |3s3s2s1\rangle, \]

\[ \Phi_3 = 6^{-1/2} [2|3s1s2s1\rangle - |3s1s2s1\rangle - |3s1s2s1\rangle, \]

\[ \Phi_4 = |1s1s3s1\rangle, \quad \Phi_5 = |1s3s3s1\rangle, \]

\[ \Phi_6 = |1s3s2s2\rangle, \quad \Phi_7 = |3s3s2s2\rangle. \]

The results are summarized in table 2. First, we take up the first three configurations on the simple analogy with the conclusion in ref. [3].

* By the "S-character", we denote a nodeless character at an origin (nucleus).
of the previous discussion of the P doublet state. However, this wavefunction gives a poor \([s_\beta]\) as table 2 shows. This is obvious since this wavefunction does not take the radial correlation sufficiently into account (compare the energies of this wavefunction and of the nearly full CI within S) and is insufficient for a 2s-orbital correction. To remedy these defects, we substitute the 2s orbital by the sum

\[
\sum_{j=1}^{3} |j s\rangle f_j,
\]

with certain coefficients \(f_j\) so that we have two configurations, \(\Phi_4\) and \(\Phi_5\), in addition to the original three ones. The configuration \(\Phi_4\) corrects the 2s orbital in \(\Phi_1\) as follows:

\[
a_1 \Phi_1 + a_4 \Phi_4 = |1s1s2s'\rangle,
\]

where the corrected orbital is

\[
|2s'\rangle = |2s\rangle a_1 + |3s\rangle a_4.
\]

The configuration \(\Phi_5\) can be interpreted as the inter- shell correlation between 1s (K shell) and 2s (L shell) electrons. Since the unpaired electron is in an s-shell, it seems that the contribution from \(\Phi_4\) and \(\Phi_5\) becomes important (spin-delocalization contribution [2]). Indeed, table 2 shows that the wavefunction of the five configurations gives the good \([s_\beta]\) value of 0.2265 (only 2% error) and that its energy may approach the S-limit. For the first-row atoms, B to F, in which unpaired electrons are all in 2p orbitals, contributions similar to those of \(\Phi_4\) and \(\Phi_5\) may be ignored just as in the case of the P doublet state of the Li atom. We further investigate two other configurations, \(\Phi_6\) and \(\Phi_7\). Table 2 indicates that these two additional configurations play no important role for the \([s_\beta]\). This suggests that one can disregard the internal correlation of \(\Phi_6\) and the semi-internal one of \(\Phi_7\) in comparison with the important semi-internal correlation included in \(\Phi_3\).

In both doublet states of P and S of the Li atom, the \([s_\beta]\) can be described excellently by the MC SCF method. Therefore, it appears that a physical mechanism for providing contributions mainly to the \([s_\beta]\) is obtained as follows:

(i) each doubly-occupied s-orbital is split radially by the pair correlation of each electron pair;

(ii) the occupational probability of an \(\alpha\) electron in each split orbital is different, to a certain extent, from that of \(\beta\) due to the unpaired electron (or generally unpaired electrons).

If the unpaired electron is in an s-shell (e.g., the ground state of alkali atoms), the orbital correction contribution, like \(\Phi_4\), and the inter-shell correlation contribution, like \(\Phi_5\), should be taken into account.

Computational details and a comparison with other work (Lunell [4], Ladner and Goddard [5], Kaldor and Harris [6], and others) will be published in the near future.

References

CHAPTER IV

CORE RADIAL-POLARIZATION AND THE CONTACT HYPERFINE STRUCTURE OF
$^4S$ STATE OF NITROGEN
Core radial-polarization and the contact hyperfine structure of \(^{1}\text{S}\) state of nitrogen

The contact hfs constant for the \(^{1}\text{S}\) state of nitrogen atom is computed variationally by a multiconfiguration self-consistent-field method. Present calculations take account of radial-correlation contributions to the spin density, but no account of any significant part of angular correlations. It is found that the calculated value of 0.0977 for the spin density is in excellent agreement with experimental value of 0.0972. A mechanism named core radial-polarization for providing contributions mainly to the spin density at the nucleus is proposed. It is noted that the mechanism provides a main contribution for the \(^{1}\text{S}\) state of nitrogen as well as for the \(^{2}\text{P}\) state of lithium. It is also claimed that the proper description of radial correlations should be a prerequisite for a good spin density.
I. Introduction

Most physical properties of atoms and molecules can be calculated by Hartree-Fock (HF) method in satisfactory agreement with experiments. Therefore, the HF theory can be considered to give a conceptual basis of the electronic structures of atoms and molecules. However, it gives only a poor description for the Fermi-contact interaction in the magnetic hyperfine structures of open-shell atoms and molecules, though it gives a sufficient description for the other magnetic hyperfine interactions. The Fermi-contact interaction is proportional to the spin density at the nucleus (hereafter written as \([s_2]\));

\[
[s_2] = \langle LSJM | \Sigma 2s_2\delta(r_i)/(4\pi r_i^2) | LSJM \rangle, \quad (J=M=L+S). \quad (1)
\]

Atomic units are used throughout this paper.

Two main approaches to improve the value of \([s_2]\) beyond the HF method have received appreciable attention. First, there are schemes based on perturbation theory. The Feynman diagrams provide conceptual pictures on the nature of electron correlation effects in these schemes. These methods have been applied to atomic systems by Kelly,\textsuperscript{1,2} Das and co-workers,\textsuperscript{3-8} Nesbet,\textsuperscript{9,10} Hata,\textsuperscript{11} and others. They obtained spin densities in very good agreement with experiments.

The second is variational approaches. Many types of trial functions have been tested.\textsuperscript{12-20} They may be well reviewed up to 1968 in the article of Schaefer, Klemm, and Harris.\textsuperscript{13} Larsson achieved very accurate calculations for lithium, using the Hylleraas-type trial functions.\textsuperscript{17}
Schaefer, Klemm, and Harris\textsuperscript{20} obtained rather good values of spin densities for the atoms B to F with their "polarization wave functions." They used a trial wave function in the form of superposition of configurations. However, the component orbitals were not optimized. Freed\textsuperscript{21} has discussed a relation of this type of wave function to that of the many-body perturbation theory.

Generally speaking, a certain physical significance can be extracted from a trial wave function chosen in the variation method. In a previous paper,\textsuperscript{22} we adopted a trial variational function in the form of the superposition of configurations and obtained a mechanism for providing contributions mainly to the spin density. We call this mechanism as core radial-polarization through the present paper. The mechanism can be briefly shown by the use of a model in the case of the P doublet state of lithium.

Figure I shows the model in which the configuration A and B are mixing with each other and the weight of A is different from that of B, leading to the spin density at the nucleus of lithium. Note that the radial-polarization of the core 1s-orbital is mainly caused by the pair-correlation of the 1s electron pair. (The exchange interaction by the odd 2p electron may merely bring about the difference of weights between A and B.) We will show that the mechanism (in the case of one core orbital) can be extended to the case of two core orbitals in the later part of the present paper.
II. Computational method

The variational method used here is well known as a multiconfiguration self-consistent-field (MCSCF) method or as a multiconfiguration Hartree-Fock (MC-HF) method.\(^{23}\) It can be briefly sketched as follows: the wave function of a Russell-Saunders term is given in the form of the superposition of configurations. The component orbitals of the configurations are optimized, making the total electronic energy of this state stationary. (Of course, the coefficients of the configurations are also optimized simultaneously.)

The orbitals can be expanded by means of a certain basis set. The s-cusp basis set of Goddard\(^{13}\) is used in the present calculations. It is expected that the basis set is sufficiently flexible for the present purpose so that the orbital exponents of the set are not reoptimized. The optimization of orbitals leads to a coupled set of equations (which may be called MCSCF equations). In order to solve it, we adopt the two-by-two rotation method by Hinze.\(^{24}\) The Hartree-Fock orbitals and its virtual orbitals are used as the initial orbitals.
III. Choice of Configurations

A guiding principle for the choice of the configurations has been obtained from our previous calculations for the $^2P$ state of lithium. That is, a core radial-polarization is well described with the configurations which arise from the single- and pair-excitation from the core s-orbital to the outer s-orbital.

For the nitrogen atom, however, there are two s-orbitals in the core. According to the above principle, we must first take into account the following four types of excitations:

(i) $1s^2 \rightarrow s_1^2$,
(ii) $1s \rightarrow s_1$,
(iii) $2s^2 \rightarrow s_II^2$,
(iv) $2s \rightarrow s_II$.

We imagine in our mind that the orbitals, $s_1$ and $s_II$, can be represented adequately by a linear combination of the MCSCF orbitals, 3s and 4s. The orbitals, $s_1$ and $s_II$, are not necessarily mutually orthogonal.

Then, we have the following ten configurations to be added to the Hartree-Fock configuration (denoted as $\Phi_0$):

$\Phi_1 : 1s^2 \rightarrow 3s^2$,
$\Phi_2 : 1s^2 \rightarrow 4s^2$,
$\Phi_3 : 1s^2 \rightarrow 3s, 4s[(3s4s)^1S]$,
$\Phi_4 : 2s^2 \rightarrow 3s^2$,
$\Phi_5 : 2s^2 \rightarrow 4s^2$,
$\Phi_6 : 2s^2 \rightarrow 3s, 4s[(3s4s)^1S]$,
$\Phi_7 : 1s \rightarrow 3s[(1s3s)^3S]$,
$\Phi_8 : 1s \rightarrow 4s[(1s4s)^3S]$. 


\[ \Phi_1 : 2s+3s[(2s3s)^3S] , \\
\Phi_{10} : 2s+4s[(2s4s)^3S], \]

where \( \Phi_1 \) to \( \Phi_6 \) take account of radial pair-correlations and no account of any coupling between core and 2p electrons; while \( \Phi_7 \) to \( \Phi_{10} \) take those couplings into account. The configurations which arise from the excitations, \( 1s+3s[(1s3s)^1S] \) etc., are further considered, but those types of single excitations have no important effects, as is shown in the succeeding section.

The whole eleven configurations lead to a picture that the radial-polarizations of \( 1s \) and \( 2s \) orbitals occur independently, because no coupling between \( 1s \) and \( 2s \) is considered explicitly.

Further, we consider the couplings by the following three types of excitations:

\[(v) \ 1s,2s+\frac{s}{s_1^2}[(1s2s)^1S] , \]
\[(vi) \ 1s,2s+\frac{s_{II}}{s_1^2}[(1s2s)^1S] , \]
\[(vii) \ 1s,2s+\frac{s}{s_1^2},s_{II}[(1s2s)^1S(s_1^2s_{II})^1S] \text{ and} \]
\[ (1s2s)^3S(s_1^2s_{II})^3S)^1S. \]

From the three excitations, we have the following four configurations to be added to the above 11 configurations:

\[ \Phi_{11} : 1s,2s+3s,4s[(1s2s)^1S(3s4s)^1S] , \]
\[ \Phi_{12} : 1s,2s+3s,4s[(1s2s)^3S(3s4s)^3S)^1S] , \]
\[ \Phi_{13} : 1s,2s+3s^2[(1s2s)^1S] , \]
\[ \Phi_{14} : 1s,2s+4s^2[(1s2s)^1S] . \]

The whole 15 configurations may take into account a significant part of radial correlations. (This is true for nitrogen, as is shown in Table I.)
The 15-term wave function has an orbital ambiguity which has been generally discussed by Gilbert.\textsuperscript{25} In order to resolve the ambiguity, we take out the two configurations of $\phi_{13}$ and $\phi_{14}$. This procedure will be discussed in the Appendix. Finally, a 13-term wave function is obtained.
IV. Results and Discussion

Table I shows the calculated results from several MCSCF wave functions for the "S state of nitrogen. In the table, the 13-term wave function is the one which is obtained in the preceding section. The 9-term function contains all of the doubly excited configurations selected in the 13-term function. This function takes account of a significant part of radial pair-correlations and no account of any coupling between core and 2p electrons. The 11-term function lacks the two configurations of \( \phi_1 \) and \( \phi_2 \) in comparison with the 13-term function. (This means the absence of any coupling between cores, 1s and 2s.) The 17-term function has, in addition, the following four configurations not included in the 13-term function:

\[
\begin{align*}
\phi_{15}: & \quad 1s+3s[(1s3s)^1S], \\
\phi_{16}: & \quad 1s+4s[(1s4s)^1S], \\
\phi_{17}: & \quad 2s+3s[(2s3s)^1S], \\
\phi_{18}: & \quad 2s+4s[(2s4s)^1S].
\end{align*}
\]

However, the four have no important contributions to the spin density and to the total electronic energy, as is shown in Table I.

The calculated value of 0.0977 for the spin density by the 13-term function is in excellent agreement with experimental value of 0.0972, as Table I shows. Since the configurations considered are chosen in the manner described in the preceding section, it seems that a physical mechanism which contributes mainly to the spin density at the nucleus is obtained as follows:
(1) Each core s-orbital is radially polarized mainly by the pair-correlation of the electron-pair which occupies this s-orbital. This electron-pair, then, occupies the two polarized orbitals in the manner as is shown schematically in Fig. I as the configurations A and B.
(2) Then, the interactions from the 2p electrons (it may be mainly the "exchange interaction." ) cause the difference of the weights between the two configurations A and B of Fig. I in each pair of the polarized orbitals individually.
(3) The polarized-orbital pairs interact finally with each other, varying themselves.

The evidence of the mechanism is discussed further below. The MCSCF orbitals of the 13-term function are very similar to those of 9-term function except for their unimportant tails, as Table II shows. This means that the MCSCF orbitals of the 13-term function are mainly determined by the effects of radial pair-correlations which have been taken into account in the 9-term function. (This is one piece of evidence for part (1) of the above mechanism.) Although the core orbitals of the 9-term function are radially polarized in the sense described in the preceding section, the 9-term function causes no spin density at the nucleus. It is found that no weight-difference occurs in the polarized orbitals, just as in $\Psi_{[2C]}$ studied in our previous paper for the $^2P$ state of lithium.\textsuperscript{22} The weight-difference is caused by the singly-excited configurations of $\Psi_7$ to $\Psi_{10}$ which take the couplings between core and 2p electrons into account in the 13-term function as well as in $\Psi_{[3C]}$ of our previous paper.\textsuperscript{22}
The interactions between the polarized pairs must be taken into account, because the 11-term function which lacks the contributions gives 0.0634 for the spin density, in poor agreement with experiment.

The 13-term wave function may reproduce the significant part of the radial-correlation contributions to either the spin density or the total electronic energy of the state, because the energy of the function reaches near the radial limit calculated by Clementi, Kraemer, and Salez and an excellent spin density is given from the wave function. It is concluded that the proper description of radial correlations should be a prerequisite for a good spin density, at least, for the $^4S$ state of nitrogen and for the $^2P$ and $^2S$ states of lithium.

Dutta, Matsubara, Pu, and Das calculated the spin density for the $^4S$ state of nitrogen by the many-body perturbation method. Their value of 0.0974±0.0014 is also in excellent agreement with experiment. Following Freed, we attempt to interpret the diagrams considered by them with the "CI language." Then, we find that the contributions from the s→d type of excitations must be very small, since the diagrams 7(h) to 7(k) of Ref. 5 include the s→d type contributions when the excited state $k$ in the diagrams is a d-wave, while the contributions from the four diagrams are individually small and totally very small. Thus, our results are consistent with those by Dutta et al., since our wave function takes no account of s→d type contributions.
Acknowledgments

I gratefully acknowledge very helpful conversations and communications with Professor T. Yonezawa, Dr. H. Nakatsuji, and Dr. J. Hata. I also wish to thank Miss Y. Honjo for typing the manuscript. All computations were carried out with a FACOM 230-75 computer at the Data Processing Center of Kyoto University.
Appendix

We will discuss in this Appendix an orbital ambiguity of the MCSCF wave functions used in the present study and show how to resolve it. First, let us define the following transformation $U$ on a set of MCSCF orbitals of $1s$ to $4s$ to the primed set of orbitals of $1s'$ to $4s'$:

\[
\begin{array}{c|c|c}
|1s'| & U & 1s \\
|2s'| & 2s \\
|3s'| & 3s \\
|4s'| & 4s \\
\end{array}
\] (A1)

where

\[
U = \begin{bmatrix}
\cos \theta & \sin \theta & 0 & 0 \\
-sin \theta & \cos \theta & 0 & 0 \\
0 & 0 & \cos \omega & \sin \omega \\
0 & 0 & -\sin \omega & \cos \omega \\
\end{bmatrix}
\] (A2)

Clearly, $U$ is an orthogonal transformation. The parameters $\theta$ and $\omega$ are entirely arbitrary. Then, we find the wave function $\psi$, which contains 19 configurations of $\phi_0$ to $\phi_{18}$, is invariant under $U$; i.e.,

\[
\psi' = \sum_{K=0}^{18} a_K' \phi_K' \psi = \sum_{K=0}^{18} a_K \phi_K, \quad (A3)
\]

where

\[
\begin{bmatrix}
\phi_0 \\
\phi_1 \\
\phi_2 \\
\vdots \\
\phi_{18}
\end{bmatrix}' = \begin{bmatrix}
T \\
\phi_0 \\
\phi_1 \\
\vdots \\
\phi_{18}
\end{bmatrix}, \quad (A4)
\]

\[
|a_0' a_1' \ldots a_{18}'| = |a_0 a_1 \ldots a_{18}|T^{-1}, \quad (A5)
\]
\[ c = \cos \theta, \quad s = \sin \theta, \quad \gamma = \cos \omega, \quad \varphi = \sin \omega, \quad t = \sqrt{2}cs, \quad \tau = \sqrt{2} \gamma \varphi, \quad a^2 = c^2 - s^2, \]
\[ \alpha^2 = \gamma^2 - \varphi^2, \quad \text{and zero-elements are not listed in Eq. (A6).} \]

The transformation \( T \) is orthogonal so that \( T^{-1} = T^t \).
Thus, the 19-term wave function \( \Psi \) has an orbital ambiguity.

Next, we will show how to resolve it. We may force the coefficients \( a_{13}' \) and \( a_{14}' \) to be zero; i.e.,
\[ 0 = a_{13}' = t[\gamma^2 (a_1 - a_4) + \varphi^2 (a_2 - a_5) + \tau (a_3 - a_6)] + a^2 [a_{11} + a_{13} \gamma^2 + a_{14} \varphi^2], \]
\[ 0 = a_{14}' = t[\gamma^2 (a_2 - a_5) + \varphi^2 (a_1 - a_4) + \tau (a_6 - a_3)] + a^2 [a_{13} \varphi^2 + a_{14} \gamma^2 - a_{11} \tau]. \]  
(A7)

This allows us to determine the arbitrary parameters \( \theta \) and \( \omega \).

After manipulating Eq. (A7), we have
\[ \tan 2\theta = \frac{-\sqrt{2} (a_{13} + a_{14})}{a_1 + a_2 - a_4 - a_5}, \quad \quad \text{(A8)} \]
\[ \tan 2\omega = \frac{\sqrt{2} [a_{14} (a_1 - a_4) - a_{13} (a_2 - a_5)]}{(a_1 + a_2 - a_4 - a_5) a_{11} - (a_{13} + a_{14}) (a_3 - a_6)} \]  
(A9)

Equations (A8) and (A9) can be always satisfied. This means that the orbital ambiguity except for orbital phases is entirely resolved, because we can always drop \( \phi_{13} \) and \( \phi_{14} \) by determining the arbitrary parameters by Eqs. (A8) and (A9).

Exactly the same discussion as this can be applied to 15-term wave function of \( \phi_0 \) to \( \phi_{14} \), leading to the 13-term function used in the present study. The 9-term function used is also given from the application of the above procedure to the 11-term function of \( \phi_0 \) to \( \phi_6 \) and \( \phi_{11} \) to \( \phi_{14} \).

Another possibility for resolving the orbital ambiguity is briefly discussed below: We can drop \( \phi_3 \) and \( \phi_6 \) instead of \( \phi_{13} \) and \( \phi_{14} \) in the 19-term function by determining the
arbitrary parameters by the following equations;

\[
\tan 2\theta = \frac{\sqrt{2} [a_3 (a_4 - a_5) - a_6 (a_1 - a_2)]}{(a_1 - a_2 + a_4 - a_5) a_1 - (a_1 - a_2 - a_4) (a_3 + a_6)} \quad (A10)
\]

\[
\tan 2\omega = \frac{\sqrt{2} (a_3 + a_6)}{a_1 - a_2 + a_4 - a_5} \quad (A11)
\]

Although we adopt Eqs. (A8) and (A9) rather than Eqs. (A10) and (A11) in the present study, there is no compelling reason for this selection. MCSCF orbitals 1s and 2s are similar to the Hartree-Fock orbitals 1s and 2s when this choice is made. (The reader may find in Table II the MCSCF orbitals chosen in this way.)
References

15. U. Kaldor and F. E. Harris, Phys. Rev. 183, 1 (1969); and succeeding papers.


23 For example, see ref. 18.


The relation between the radial- and polarized-orbitals (and/or) is completely given in Ref. 22.

The figure shows two main configurations for the $P$ state of lithium.

**Configuration A**

- Polarized LS-orbitals
  - $-d$ down
  - $+d$ up

**Configuration B**

- 2P-orbital ($m_l = 1$)
  - Down
  - Down
TABLE I. Total electronic energies and spin densities for the $^4S$ state of N atom obtained from the MCSCF wave functions in comparison with the experimental value.

<table>
<thead>
<tr>
<th>Wave function</th>
<th>Energy (a.u.)</th>
<th>Spin density (a.u.)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF 9-term</td>
<td>-54.417045</td>
<td>0.0</td>
<td>present</td>
</tr>
<tr>
<td>11-term</td>
<td>0.420557</td>
<td>0.0634</td>
<td>present</td>
</tr>
<tr>
<td>13-term</td>
<td>0.421704</td>
<td>0.0977</td>
<td>present</td>
</tr>
<tr>
<td>17-term</td>
<td>0.421704</td>
<td>0.0978</td>
<td>present</td>
</tr>
<tr>
<td>Radial limit</td>
<td>0.42225</td>
<td>0.0</td>
<td>Ref. 26</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.5892</td>
<td>0.0972</td>
<td>Ref. 5</td>
</tr>
</tbody>
</table>
TABLE II. Comparison of s-orbitals in 13-term function with those in 9-term function. The s-orbitals of 9-term function are listed under those of 13-term function.

<table>
<thead>
<tr>
<th>Basis (exponent)</th>
<th>1s-orbital</th>
<th>2s-orbital</th>
<th>3s-orbital</th>
<th>4s-orbital</th>
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</thead>
<tbody>
<tr>
<td>1s (7.02)</td>
<td>0.89945</td>
<td>-0.35515</td>
<td>0.9984</td>
<td>-0.9513</td>
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<tr>
<td></td>
<td>0.88079</td>
<td>-0.39968</td>
<td>1.0365</td>
<td>-0.9529</td>
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<tr>
<td>3s (8.20)</td>
<td>0.05525</td>
<td>-0.02159</td>
<td>-2.3714</td>
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<tr>
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<td>0.05410</td>
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<td>3s (5.49)</td>
<td>0.03768</td>
<td>0.07361</td>
<td>1.5179</td>
<td>-1.1471</td>
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<td>0.04147</td>
<td>0.07313</td>
<td>1.9621</td>
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<tr>
<td>3s (3.438)</td>
<td>0.07264</td>
<td>0.47267</td>
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<td>0.09588</td>
<td>0.46861</td>
<td>0.2342</td>
<td>1.5740</td>
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<tr>
<td>3s (2.054)</td>
<td>0.08210</td>
<td>0.48845</td>
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<td></td>
<td>0.10819</td>
<td>0.49582</td>
<td>-0.3181</td>
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<tr>
<td>3s (1.03)</td>
<td>0.02025</td>
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<td>0.01849</td>
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<td>-1.2488</td>
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<td>4s (1.13)</td>
<td>-0.01183</td>
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<td>0.8982</td>
<td>-0.7144</td>
</tr>
</tbody>
</table>
CHAPTER V

AB INITIO POTENTIAL CURVES

OF

THE BOND-DISSOCIATIONS OF XHₙ MOLECULES:

CH₄, NH₃, AND H₂O
Ab initio potential curves of the bond dissociations of \( \text{XH}_m \) molecules: \( \text{CH}_4, \text{NH}_3, \) and \( \text{H}_2\text{O} \)

The lowest potential curve of the dissociation of an \( \text{X-H} \) bond of an \( \text{XH}_m \) molecule is calculated for \( \text{CH}_4, \text{NH}_3, \) and \( \text{H}_2\text{O} \) by the use of multiconfiguration self-consistent-field (MCSCF) method. The calculated well depth of the potential curve obtained from the two configuration wave function which is constructed with MCSCF localized orbitals is 0.1707 for \( \text{CH}_4 \) (0.1656 for \( \text{NH}_3 \) and 0.1589 for \( \text{H}_2\text{O} \)), which is in good agreement with the experimental value of 0.1619 (0.1610 for \( \text{NH}_3 \) and 0.1879 for \( \text{H}_2\text{O} \)), where all quantities are in atomic units. This allows us to say that the potential curve of the dissociation process of any local bond in a polyatomic molecule can be described locally and quantitatively by the use of the two configuration wave function constructed with MCSCF localized orbitals. It is found that this wave function gives very good asymptotic behavior at a dissociation limit.
I. INTRODUCTION

Adiabatic potentials play important roles in describing the dynamics of chemical reactions or the scattering processes of atoms and molecules. Especially, for the dynamics of chemical reactions, an essential process is a dissociation and/or a formation of a certain chemical bond. Then it is in principal importance for theoretical chemists to describe properly the dissociation process of any chemical bond. The usual Hartree-Fock method is improper for the description of the dissociation process, because of the instability solution in this method.

During the last decade, Wahl and Das and co-workers\textsuperscript{1-5} calculated the potential curves of the bond-dissociation (or bond-formation) of diatomic molecules by the use of multiconfiguration self-consistent-field (MCSCF) method. They called the MCSCF method used for the special purpose as optimized valence configuration (OVC) method.\textsuperscript{1} It seems that the potential energy curves have been described properly in chemical accuracy through their pioneering works on $\text{H}_2$,\textsuperscript{2} $\text{Li}_2$,\textsuperscript{3} $\text{F}_2$,\textsuperscript{4} $\text{OH}$,\textsuperscript{5} and so on. Here organic chemists may have a question: Are the potential curves described properly in chemical accuracy even for organic molecules by the MCSCF method? This is the motive of the present study. Simple polyatomic molecules CH\textsubscript{4}, NH\textsubscript{3}, and H\textsubscript{2}O are chosen for the purpose, since these molecules have the chemical bond of C-H, N-H, and O-H which are typical for organic molecules.

On the other hand, it is well known that the localized molecular orbitals (LMO's)\textsuperscript{6} correspond closely to the chemical
concepts of inner-shell, chemical bonds, and lone-pairs of electrons. Though the LMO is in the framework of Hartree-Fock method by its definition, it is convenient to use something like the LMO in the framework of MCSCF method. This use was first suggested by Gilbert and Levy. We will call hereafter this something as "MCSCF LMO", following Levy. The MCSCF LMO's are obtained through the MCSCF procedure started from LMO's as the initial orbitals. The MCSCF LMO's are often similar to the starting LMO's especially for inner-shell and bonding orbitals. Thus the MCSCF LMO's also correspond closely to the chemical concepts mentioned above.

In the present paper, we will calculate the potential energy curves of CH₄, NH₃, and H₂O by the MCSCF method with the use of the MCSCF LMO's.
II. THEORETICAL TOOLS

In calculating potential energy curves, we will assume that the separation of electronic and nuclear motion is a good approximation (the Born-Oppenheimer approximation).

The electronic Hamiltonian is given by

$$
H = -\sum_i (\frac{Z_i}{r_i} + E \frac{1}{\alpha |r_i - R_\alpha|} + \sum_{i>j} \frac{1}{|r_i - r_j|} + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|})
$$

(1)

where $T_i$ is the kinetic energy operator of the $i$-th electron, $r_i$ is the position vector of the $i$-th electron, and $R_\alpha$ is the position vector of the $\alpha$-th nucleus (which is fixed while asking for the eigenstate of the Hamiltonian). The MCSCF method is well known in the literatures.\textsuperscript{1,10,11} Then it can be briefly sketched as follows: The wave function is expanded in terms of certain configurations,

$$
\Psi = \sum_K a_K \phi_K
$$

(2)

where $a_K$ is the mixing coefficient of a configuration $\phi_K$.

The component orbitals $\phi_i$ of the $\phi_K$ are expanded by means of basis functions $\chi_p$;

$$
\phi_i = \sum_p c_{pi} \chi_p
$$

(3)

The $\phi_i$ are mutually orthogonal. The MCSCF procedure determines the mixing coefficients and the orbital expansion coefficients $c_{pi}$ by minimizing the variational upper bound of energy eigenvalue corresponding to the wave function of Eq.(2). The variational process is based on the following iterative cycles. First initial $c_{pi}$ are supposed and the mixing coefficients
are determined from the usual secular equations with the $c_{pi}$ are fixed. Then, with the $a_k$ are fixed, a new set of $c_{pi}$ is determined (in the present study, by a two-by-two rotation technique of Hinze$^{12}$ and by a single-vector diagonalization technique of Wood and Veillard$^{13}$). With the new set of $c_{pi}$, new mixing coefficients are obtained and the entire process is repeated until convergence is achieved.
III. COMPUTATIONAL DETAILS

Basis set used here consist of contracted GTO (CGTO: recommended by Dunning\textsuperscript{14}) centered at the nucleus X and of the "STO-4G" functions\textsuperscript{15} (with the scaling factor of 1.2) centered at hydrogen nuclei.

Experimental equilibrium geometry is used in the present calculations for the ground state of an XH\textsubscript{m} molecule; for CH\textsubscript{4}, tetrahedral valence angle and C-H=1.09Å (where Å=10\textsuperscript{-10} m throughout this paper), H-N-H=106.6° and N-H=1.01Å for NH\textsubscript{3}, and H-O-H=104.45° and O-H=0.96Å for H\textsubscript{2}O. An X-H bond is lengthened in this calculations for the lowest potential curve of this local bond, leaving the other geometry is fixed except for CH\textsubscript{4}. For CH\textsubscript{4}, a planner geometry of the residual CH\textsubscript{3} is used when the length of a C-H bond is longer than 3Å. The length of a C-H bond of the CH\textsubscript{3} is fixed at 1.09Å.

The MCSCF LMO’s are obtained through the MCSCF procedure started from the Hartree-Fock LMO’s (we hereafter call the usual LMO’s like this for distinguishing them from the MCSCF LMO’s), as is mentioned in the introduction of this paper. However, at an intermediate to a large distance of an X-H bond, no Hartree-Fock LMO’s can be obtained, because of instability solution in the Hartree-Fock method. Then, the MCSCF LMO’s at these distances are obtained through the MCSCF procedure started from the MCSCF LMO’s which have been obtained at a small distance. In the MCSCF procedure, the modified single-vector diagonalization technique by Wood and Veillard\textsuperscript{13} goes to a good convergence (when λ=0.01 to 0.5) at a large distance, while the two-by-two rotation
method by Hinze\textsuperscript{12} goes into a vibrational divergence. At small distance, however, the two-by-two rotation method gives more rapid convergence than the Wood-Veillard's technique. Thus the both method are used in this study.
IV. CHOICE OF CONFIGURATIONS

In the description of the potential energy curves of a bond-dissociation process of a polyatomic molecules, it is convenient to recall the picture of localized orbitals, as is mentioned in the introduction of the present paper. Thus, for an XH$_m$ molecule (where X=C, N, or O), whole orbitals considered consist of an inner-shell orbital which is denoted as ls(X), bonding orbitals of the X-H bonds denoted as $\sigma(X-H_i)$ (i=1,2,...,m), anti-bonding orbitals of the X-H bonds denoted as $\sigma^*(X-H_i)$ (i=1,2,...,m), non-bonding orbital or orbitals denoted as $n_i(X)$ (i=1,2,...,4-m), and others denoted as $v_i(XH_m)$ (i=1,2,...). We will dissociate an X-H bond of an XH$_m$ molecule into an XH$_{m-1}$ radical molecule and an H atom. This process will be well described by a two-configuration wave function which consists of

$$\Psi[2C] = \alpha_1 \left| \text{other part} \sigma(XH_m) \bar{\sigma} (XH_m) \right| + \alpha_2 \left| \text{other part} \sigma^*(XH_m) \bar{\sigma}^*(XH_m) \right|.$$  (4)

The $\Psi[2C]$ can be analyzed below. Let us consider a Valence Bond (VB) type wave function for a local bond of an X-H in an XH$_m$ molecule. A linear combination of the atomic orbitals (LCAO) of an XH$_m$ molecule, say $\chi(X)$, and an LCAO of an H
atom, say \( \chi(H) \), construct a VB type wave function for the local bond; i.e.,

\[
\Psi[\text{VB}] = b_1 |\text{(other part)} \chi(X) \bar{\chi}(X) | + b_2 |\text{(other part)} \chi(H) \bar{\chi}(H) |
+ b_3 |\text{(other part)} [\chi(X) \bar{\chi}(H) - \chi(H) \bar{\chi}(X)] |. \tag{5}
\]

The first and second term of Eq. (5) correspond to the ionic structures of the local bond. The third term of Eq. (5) does to the covalent bond structure of the local bond. Then \( \Psi[\text{VB}] \) is equivalent to \( \Psi[2C] \), provided

\[
\sigma(X-H_m) = c_1 \chi(X) + c_2 \chi(H), \tag{6}
\]
\[
\sigma^*(X-H_m) = c_3 \chi(X) + c_4 \chi(H), \tag{7}
\]

where

\[
b_1 = a_1 c_1^2 + a_2 c_3^2, \tag{8}
\]
\[
b_2 = a_1 c_2^2 + a_2 c_4^2, \tag{9}
\]
\[
b_3 = a_1 c_1 c_2 + a_2 c_3 c_4, \tag{10}
\]
\[
S_{XH} = \int \chi(X) \chi(H) \, dt, \tag{11}
\]
\[
c_1^2 + c_2^2 + 2c_1 c_2 S_{XH} = 1, \tag{12}
\]
\[
c_3^2 + c_4^2 + 2c_3 c_4 S_{XH} = 1, \tag{13}
\]
\[
c_1 c_3 + c_2 c_4 + (c_1 c_4 + c_2 c_3) S_{XH} = 0. \tag{14}
\]

The last three relations reflect the normalization conditions of the orbitals \( \sigma(X-H_m) \) and \( \sigma^*(X-H_m) \) and the orthogonality condition between the two orbitals. Equations (6) and (7) can be almost always satisfied. Then \( \Psi[2C] \) describes well a mixing state of the ionic and the covalent bond structures of the local bond. At infinite distance of the local bond \( X-H \), the last three relations can be reduced asymptotically to the following simple relations;
\[ c_4 = -c_1, \; c_3 = c_2, \; \text{and} \; c_1^2 + c_2^2 = 1. \] \hspace{1cm} \text{(15)}

The above equality between \( \Psi[2C] \) and \( \Psi[VB] \) implies the followings: When the local bond dissociates to an \( XH_{m-1} \) radical and an \( H \) atom, at infinite distance, \( b_3 \) must be close to \( 1/\sqrt{2} \) and \( b_1 \) and \( b_2 \) must be very small so that, from Eqs. (4), (5), (6), and (7), the asymptotic relations are obtained

\[
\begin{align*}
\sigma(X-H_m) &\sim (1/\sqrt{2}) \chi(X) + (1/\sqrt{2}) \chi(H), \\
\sigma^*(X-H_m) &\sim (1/\sqrt{2}) \chi(X) - (1/\sqrt{2}) \chi(H),
\end{align*}
\]

\hspace{1cm} \text{(16)}

\[
\begin{align*}
\Psi[VB] &\sim (1/\sqrt{2}) |(\text{other part})[\chi(X)\chi(H)-\chi^2(X)\chi(H)], \\
\Psi[2C] &\sim (1/\sqrt{2}) |(\text{other part})\sigma(X-H_m)\overline{\sigma}(X-H_m)| \\
&\quad - (1/\sqrt{2}) |(\text{other part})\sigma^*(X-H_m)\overline{\sigma}^*(X-H_m)|.
\end{align*}
\]

\hspace{1cm} \text{(17)}

Thus it is considered that \( \Psi[2C] \) should be one of the simplest tools for describing properly the dissociation process. (This is true for the molecules, \( CH_4, \; NH_3, \) and \( H_2O, \) as is shown in a later part of the present paper.) The \( \Psi[2C] \) is consistent with the "base wave function" of the OVC method described in Ref. 5.

In order to investigate the contributions from the other effects to the dissociation process, we further take account of the pair-to-pair excitations from \( \sigma(X-H_i) \) \( (i=1,2, \ldots,m) \) to \( \sigma^*(X-H_i) \) \( (i=1,2, \ldots,m) \) other than from \( \sigma(X-H_m) \) to \( \sigma^*(X-H_m) \). This represents an effect from the other bond to the dissociation process. The number of configurations obtained from this choice is 17 for \( CH_4; \) 10 for \( NH_3; \) and 5 for \( H_2O. \) For discussing the effects of the lone pairs of electrons, we further take into account the pair-to-pair
excitations from $n_i(X)$ ($i=1,...,4-m$) to $\sigma^*(X-H_i)$ ($i=1,...,m$) and to $\nu_i(XH_m)$ ($i=1,...,4-m$) and from $\sigma(X-H_i)$ ($i=1,...,m$) to $\nu_i(XH_m)$ ($i=1,...,4-m$) in addition to the above. The total number of configurations from this choice is 17 for all $XH_m$ molecules. This is a wave function in the framework of so-called "Complete Multiconfiguration SCF" method of Veillard and Clementi.11
V. RESULTS AND DISCUSSION

Tables I to III show adiabatic potentials obtained from Hartree-Fock and several MCSCF wave functions for XH$_m$ molecules (where X=C, N, and O) at several distances of an X-H bond. The distance is varied up to 8Å. The usual SCF process of the Hartree-Fock method is not converged at a large distance. The preceding section describes the real forms of all multiconfiguration wave functions which appear in these tables. The well depth of the potential curve obtained from $\Psi[2C]$ can be estimated from the difference between energies obtained at experimental equilibrium geometry and at 8Å distance of an X-H bond, because the potential energies in these tables show that the distance of 8Å can be regarded as infinite. The estimated well depths are 0.1707, 0.1656, and 0.1589 (in a.u.) for CH$_4$, NH$_3$, and H$_2$O, in good agreement with the experimental values$^{16}$ of 0.1619, 0.1610, and 0.1879, respectively. Thus we now have a simple and powerful tool, $\Psi[2C]$, for describing locally and quantitatively a dissociation potential curve of a chemical bond. The advantages of $\Psi[2C]$ are as follows:

(1) The $\Psi[2C]$ is a simplest wave function which causes no instability in the process of a dissociation.

(2) By the virtue of MCSCF LMO’s, the $\Psi[2C]$ can be constructed locally for whole molecule. Then the description by $\Psi[2C]$ can be applied to any polyatomic molecules.

(3) The well depth obtained from $\Psi[2C]$ is sufficiently quantitative, at least, for CH$_4$, NH$_3$, and H$_2$O.

(4) An asymptotic behavior of $\Psi[2C]$ at infinite distance of
TABLE I. Adiabatic potentials obtained from the Hartree-Fock and from several MCSCF wave functions for CH$_4$ molecule. Energies are in atomic units.

<table>
<thead>
<tr>
<th>C-H distance (in Å)</th>
<th>Hartree-Fock</th>
<th>$\Psi(2C)^a$</th>
<th>17-configuration$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.09</td>
<td>-40.1744</td>
<td>-40.1902</td>
<td>-40.2353</td>
</tr>
<tr>
<td>1.5</td>
<td>0.1145</td>
<td>0.1445</td>
<td>0.1876</td>
</tr>
<tr>
<td>1.7</td>
<td>0.0721</td>
<td>0.1116</td>
<td>0.1536</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0105</td>
<td>...</td>
<td>0.1089</td>
</tr>
<tr>
<td>2.4</td>
<td>-39.9389</td>
<td>0.0338</td>
<td>0.0682</td>
</tr>
<tr>
<td>3.0</td>
<td>not converged</td>
<td>0.0243</td>
<td>0.0515</td>
</tr>
<tr>
<td>4.0</td>
<td>not converged</td>
<td>0.0197</td>
<td>0.0416</td>
</tr>
<tr>
<td>8.0</td>
<td>not converged</td>
<td>0.0195</td>
<td>0.0396</td>
</tr>
<tr>
<td>Energy difference$^c$</td>
<td>...</td>
<td>0.1707</td>
<td>0.1957</td>
</tr>
</tbody>
</table>

$^a$ See Eq. (4). $^b$ See section IV. $^c$ The difference between energies at 8Å and at 1.09Å.
TABLE II. Adiabatic potentials obtained from the Hartree-Fock and from several MCSCF wave functions for $\text{NH}_3$ molecule. Energies are in atomic units.

<table>
<thead>
<tr>
<th>N-H distance (in A)</th>
<th>Hartree-Fock</th>
<th>$\Psi[2C]^a$</th>
<th>10-configuration$^b$</th>
<th>17-configuration$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>-56.1574</td>
<td>-56.1758</td>
<td>-56.2111</td>
<td>-56.2132</td>
</tr>
<tr>
<td>1.2</td>
<td>...</td>
<td>.1631</td>
<td>.1977</td>
<td>...</td>
</tr>
<tr>
<td>1.5</td>
<td>.0693</td>
<td>.1107</td>
<td>.1421</td>
<td>...</td>
</tr>
<tr>
<td>1.8</td>
<td>-55.9966</td>
<td>.0623</td>
<td>.0940</td>
<td>...</td>
</tr>
<tr>
<td>2.0</td>
<td>.9530</td>
<td>.0404</td>
<td>.0700</td>
<td>.0717</td>
</tr>
<tr>
<td>4.0</td>
<td>not converged</td>
<td>.0102</td>
<td>.0267</td>
<td>.0273</td>
</tr>
<tr>
<td>8.0</td>
<td>not converged</td>
<td>.0102</td>
<td>.0266</td>
<td>.0274</td>
</tr>
<tr>
<td>Energy difference$^c$</td>
<td>...</td>
<td>.1656</td>
<td>.1845</td>
<td>.1858</td>
</tr>
</tbody>
</table>

$^a$ See Eq. (4). $^b$ See section IV. $^c$ The difference between energies at 8A and at 1.01A.
Energy difference

<table>
<thead>
<tr>
<th>Energy difference</th>
<th>1.865</th>
<th>1.706</th>
<th>1.589</th>
<th>...</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.75, 1.847</td>
<td>1.8615</td>
<td>1.8516</td>
<td>1.8516</td>
<td>...</td>
<td>4.0</td>
</tr>
<tr>
<td>...</td>
<td>1.8615</td>
<td>1.8516</td>
<td>1.8516</td>
<td>...</td>
<td>4.0</td>
</tr>
<tr>
<td>...</td>
<td>0.9235</td>
<td>0.8763</td>
<td>not converged</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>...</td>
<td>0.9234</td>
<td>0.8951</td>
<td>not converged</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>...</td>
<td>0.9274</td>
<td>0.9075</td>
<td>0.9075</td>
<td>0.9090</td>
<td>4.4</td>
</tr>
<tr>
<td>...</td>
<td>0.9274</td>
<td>0.9274</td>
<td>0.9274</td>
<td>0.9274</td>
<td>4.4</td>
</tr>
<tr>
<td>0.75, 0.9784</td>
<td>0.9589</td>
<td>0.9589</td>
<td>0.9589</td>
<td>0.9589</td>
<td>1.2</td>
</tr>
<tr>
<td>0.76, 0.8321</td>
<td>0.9698</td>
<td>0.9698</td>
<td>0.9698</td>
<td>0.9698</td>
<td>1.2</td>
</tr>
<tr>
<td>0.76, 0.5012</td>
<td>0.9796</td>
<td>0.9796</td>
<td>0.9796</td>
<td>0.9796</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Wave function

TABLE III. Adiabatic potentials obtained from the Hartree-Fock and from several MCPF wave functions for H\(_2\)O molecule. Energies are in atomic units.
an X–H bond is very good as is discussed in the preceding section. Table IV shows this asymptotic behavior. The $a_2$ defined by Eq. (4) becomes asymptotically close to $-1/\sqrt{2}$, which is consistent with Eq. (19).

Next we discuss on the contributions to the dissociation process from the other effects below. The effects from the other excitations which are described in the preceding section always deepen the potential wells for all XH$_m$ molecules, as are shown in tables I to III. However, these extra extents are not more than 20%. These are consistent with OVC calculations by Stevens et al. for OH molecule. For H$_2$O molecule, these effects improve the value of the well depth, as Table III shows. The effects of the lone pairs of electrons may be small for NH$_3$ molecule, but considerable for H$_2$O, because Table II shows that the difference between the contributions to the well depth from 17-configuration wave function and from 10-configuration one appears to be small and Table III shows that the difference between those from 17-configuration one and from 5-configuration one does to be considerable.

The geometry modifications of the residual XH$_{m-1}$ radical molecule are not considered in the present study except for CH$_4$ (see section III). However, the contributions from the modifications are in the magnitude of $10^{-2}$ (a.u.) at most, because the calculations by Stevens et al. for OH, by Bender and Schaefer for NH$_2$, and by Driessler et al. for CH$_3$ suggest. These are less than 10% of the well depth calculated. These contributions shallow the wells.
TABLE IV. Configuration mixing coefficient $a_2$ in $\Psi[2C]$ defined by Eq. (4) in the text at several distances of an X-H bond of an $XH_m$ molecule, where X=C, N, or O.

<table>
<thead>
<tr>
<th>C-H distance$^a$</th>
<th>$a_2$ for CH$_4$</th>
<th>N-H distance$^a$</th>
<th>$a_2$ for NH$_3$</th>
<th>O-H distance$^a$</th>
<th>$a_2$ for H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.09</td>
<td>-0.097</td>
<td>1.01</td>
<td>-0.102</td>
<td>0.96</td>
<td>-0.111</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.177</td>
<td>1.2</td>
<td>-0.139</td>
<td>1.2</td>
<td>-0.167</td>
</tr>
<tr>
<td>1.7</td>
<td>-0.229</td>
<td>1.5</td>
<td>-0.220</td>
<td>1.4</td>
<td>-0.227</td>
</tr>
<tr>
<td>2.4</td>
<td>-0.456</td>
<td>1.8</td>
<td>-0.328</td>
<td>1.8</td>
<td>-0.386</td>
</tr>
<tr>
<td>3.0</td>
<td>-0.602</td>
<td>2.0</td>
<td>-0.409</td>
<td>2.0</td>
<td>-0.465</td>
</tr>
<tr>
<td>4.0</td>
<td>-0.685</td>
<td>4.0</td>
<td>-0.699</td>
<td>4.0</td>
<td>-0.702</td>
</tr>
<tr>
<td>8.0</td>
<td>-0.707</td>
<td>8.0</td>
<td>-0.707</td>
<td>8.0</td>
<td>-0.707</td>
</tr>
</tbody>
</table>

$^a$ This is in Å ($Å=10^{-10}m$).
After all, in polyatomic molecules, it is concluded that a local and proper description of the dissociation process of a chemical bond is obtained by the virtue of MCSCF LMO's.

ACKNOWLEDGMENTS

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References

CHAPTER VI

A NON-BONDING EXCITED-ORBITAL
FOR DESCRIBING
THE INTRA-PAIR CORRELATION OF LONE-PAIRS OF ELECTRONS
IN
MULTICONFIGURATION SELF-CONSISTENT-FIELD METHOD
A non-bonding excited-orbital for describing the intra-pair correlation of lone-pairs of electrons in multiconfiguration self-consistent-field method

Floating functions are used in order to describe a non-bonding excited-orbital corresponding to a non-bonding (lone-pair) orbital within a multiconfiguration self-consistent-field (MC-SCF) framework with localized orbitals. Floating functions of an STO-3G type are used in the present calculations for the molecules NH$_3$ and H$_2$O as simple examples. Results indicate that a significant part of the pair-correlation of lone-pairs of electrons is taken into account by the excitation from a non-bonding (lone-pair) orbital to the corresponding non-bonding excited-orbital. It is concluded that the above non-bonding excited-orbital obtained with a floating function (or functions) is powerful in order to take account of the above correlation effects in the MC-SCF method.
I. Introduction

MC-SCF formalism has been applied to many atomic and molecular systems.\textsuperscript{1-15} It is one of the most powerful methods in order to take electron correlation into account for the systems. So-called "Complete Multiconfiguration SCF" (CMC-SCF) formalism\textsuperscript{13} seems to be most popular for dealing with the ground state of a closed-shell molecule.

Recently, Levy pointed out that the use of "MC-SCF localized molecular orbitals" (MC-SCF LMO)\textsuperscript{16} is more efficient in the CMC-SCF method than that of symmetry-adapted orbitals for Formaldehyde, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{2}H\textsubscript{4}.\textsuperscript{14,15} An intra-bond pair-correlation of a polyatomic molecule can be mainly represented by means of the excitation from the bonding to the anti-bonding orbital. For non-bonding orbitals, however, there are no such orbitals like "anti-bonding" orbitals corresponding to bonding ones. Therefore it is more advantageous to consider such orbitals for non-bonding orbitals like "anti-bonding" ones (this will be named "a non-bonding excited-orbital" (NBEO) throughout the present paper) in order to take accounts of the significant part of the intra-bond pair-correlation of lone-pairs of electrons. It seems that an NBEO is well described by means of an additional "floating function" (or functions) centered at a proper position with a proper exponent. This is the motivation of the present study.

A pioneering work of floating functions seems to be attributed to Gurnee and Magee in their Valence-Bond calculation of H\textsubscript{2} molecule. Frost pointed out that the concept of floating spherical orbitals containing pairs of electrons appears to be
due to Kimball and his students.\textsuperscript{18} He tried to represent pairs of electrons by the use of floating spherical Gaussian orbitals.\textsuperscript{18,19} The present purpose to use floating functions is different from his; they are used for describing mainly an NBEO.

In the present paper, we calculate NH\textsubscript{3} and H\textsubscript{2}O molecules as simple examples for the above purpose by the CMC-SCF method with localized orbitals.
II. Details of calculations

The CMC-SCF method is well known in the literature.\textsuperscript{13}

It is sketched as follows: The wave function of a given system can be expanded in terms of certain configurations; i.e.,

$$\psi = a_{00} \phi_{00} + \sum_{tu} a_{tu} \phi_{tu}, \quad (1)$$

where $\phi_{00}$ is a Hartree-Fock configuration, $\phi_{tu}$ is a doubly-excited configuration from the orbital $\phi_t$ (which is doubly occupied in $\phi_{00}$) to $\phi_u$ (which is unoccupied in $\phi_{00}$), and $a_{00}$ and $a_{tu}$ are certain expansion coefficients. The all component orbitals (e.g., $\phi_t$ and $\phi_u$) are optimized so that the total electronic energy of the system is stationary with respect to all orbitals. Euler equations for the variation with respect to orbitals are called "CMC-SCF equations."\textsuperscript{13} In order to solve them, we adopt here a two-by-two rotation method by Hinze.\textsuperscript{20}

Any orbital can be expanded by means of a certain basis-set. So-called "minimal STO-3G" basis-sets with Slater-rule exponents are used in the present study for convenience sake. The Gaussian expansion coefficients and "$a$" of an STO-3G function used here are given by Stewart.\textsuperscript{21} The STO-3G functions of $1s$-type are also used as floating spherical Gaussians to be added to the above basis-sets. For NH\textsubscript{3} molecule, an STO-3G $1s$-type function floated along a z-axis is used. Two of STO-3G $1s$-type functions are used for H\textsubscript{2}O molecule. Their floated centers are indicated by parameters $r$ and $\theta$ which are seen in Fig. 1. Orbital exponents and floating centers of the above $1s$-functions are roughly optimized for each molecule. The other exponents
FIG. 1. The coordinates of the centers of two floating functions in H₂O molecule. Each center is indicated by a solid circle and is on the x-z plane. The H in the figure indicates the projected position of H nucleus to the x-z plane. The r indicates a distance between O nucleus (at origin) and the center of a floating function. The θ is the angle between two centers as is shown in the figure.
of the basis-set for each molecule are not optimized, because the present purpose is to investigate the additional effects of the floating functions.

The geometry used for NH$_3$ is as follows: N-H=1.01Å, a valence angle (H-N-H)=106.60°, the three-fold axis of the molecule is taken to be a z-axis, and an x-axis is on a vertical mirror in the molecule. For H$_2$O, the followings are used: (H-O-H)=104.45°, the two-fold axis of the molecule is taken to be a z-axis, and a y-axis is on the molecular plane.
III. Results and discussion
A. For NH$_3$ molecule

Results for NH$_3$ are given in Tables I to VI. The most remarkable points are as follows:

(1) The CMC-SCF energy is varied very slowly in a range; $z=1.0$ to 1.3Å (as is seen in Table I). The minimum-energy point where the floating function is put can be roughly estimated (from a parabolic approximation) to be at the distance of about 1.15Å from N nucleus (at origin) along the z-axis. This distance is slightly longer than that of an N-H bond. The addition of the floating function lowers the CMC-SCF energy by about 0.035 hartree around the minimum point.

(2) The orbital exponent 0.6 for the floating function is most favorable in the whole basis-set of an STO-3G type (Table II). This is just the half of the Slater-rule exponent 1.2 for a hydrogen ls-basis.

(3) The most contribution to the wave function is obtained from the excitation from the orbital $\sigma$(NH) to the corresponding $\sigma^*$(NH). It is so independently whether the floating function is added or not (as is shown in Tables III and IV). The excitation from the lone-pair orbital to the NBEO (non-bonding excited orbital) contributes significantly to the wave function, though the extent of this contribution is less than that of the contribution from the above $\sigma-\sigma^*$ excitation (Table IV).

(4) The floating function contributes mainly to the NBEO as is expected (Table V). The forms of the lone-pair and the NBEO are indicated in Figs. 2 and 3, respectively.
TABLE I. Variation with respect to the center of the floating function with its exponent 0.6 for NH$_3$ molecule.$^a$

<table>
<thead>
<tr>
<th>Basis set</th>
<th>$E_{\text{HF}}$(a.u.)$^b$</th>
<th>$E_{\text{MC}}$(a.u.)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without floating function</td>
<td>-55.444588</td>
<td>-55.494363</td>
</tr>
<tr>
<td>Added floating function at origin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at $z=1.01\text{A}$</td>
<td>.461595</td>
<td>.512168</td>
</tr>
<tr>
<td>at $z=1.2625\text{A}$</td>
<td>.477320</td>
<td>.529003</td>
</tr>
<tr>
<td>at $z=1.515\text{A}$</td>
<td>.477949</td>
<td>.529230</td>
</tr>
</tbody>
</table>

$^a$ The three-fold axis of NH$_3$ is taken to be z-axis and N nucleus is put at origin.

$^b$ The Hartree-Fock energy obtained from the present basis-set.

$^c$ The CMC-SCF energy with localized orbitals; the correlation energy of inner 1s electrons is not taken into account.
<table>
<thead>
<tr>
<th>$p_{\text{MC}}(\text{a.u.})$</th>
<th>$p_{\text{HP}}(\text{a.u.})$</th>
<th>$\text{exponent (a.u.)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.517615</td>
<td>0.476137</td>
<td>0.7</td>
</tr>
<tr>
<td>0.529230</td>
<td>0.477949</td>
<td>0.6</td>
</tr>
<tr>
<td>-55.5527061</td>
<td>-55.476235</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Explaned in Table I.

Function centered at $z=1.2625$ for $\text{NH}_3$ molecule. Notations are explained in Table II. Variation with respect to the orbital exponent of the formatting.
TABLE III. Expansion coefficients $a_{00}$ and $a_{tu}$ in the CMC-SCF wave-function for NH$_3$ molecule when the floating function (centered at $z=1.2625\text{Å}$ with $\zeta=0.6$) is added to the minimal basis-set. The determinant $\phi_{tu}$ corresponding to a given $a_{tu}$ is obtained by exciting two electrons of 000 from the orbital $\phi_t$ to $\phi_u$.

<table>
<thead>
<tr>
<th>$\phi_t$</th>
<th>$\sigma^*(\text{NH}_1)$</th>
<th>$\sigma^*(\text{NH}_2)$</th>
<th>$\sigma^*(\text{NH}_3)$</th>
<th>NBOE$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma(\text{NH}_1)$</td>
<td>-.0902</td>
<td>-.0067</td>
<td>-.0067</td>
<td>-.0021</td>
</tr>
<tr>
<td>$\sigma(\text{NH}_2)$</td>
<td>-.0067</td>
<td>-.0902</td>
<td>-.0067</td>
<td>-.0021</td>
</tr>
<tr>
<td>$\sigma(\text{NH}_3)$</td>
<td>-.0067</td>
<td>-.0067</td>
<td>-.0902</td>
<td>-.0021</td>
</tr>
<tr>
<td>lone-pair</td>
<td>-.0148</td>
<td>-.0148</td>
<td>-.0148</td>
<td>-.0392</td>
</tr>
</tbody>
</table>

$a_{00} = .9865$

$^a$ The non-bonding excited-orbital, see text.
TABLE IV. Expansion coefficients $a_{00}$ and $a_{tu}$ in the CMC-SCF wave-function for NH$_3$ molecule when the minimum basis-set is used. Notations are explained in Table III.

<table>
<thead>
<tr>
<th></th>
<th>$a^*(\text{NH}_1)$</th>
<th>$a^*(\text{NH}_2)$</th>
<th>$a^*(\text{NH}_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_t$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\phi_u$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma(\text{NH}_1)$</td>
<td>-0.0927</td>
<td>-0.0067</td>
<td>-0.0067</td>
</tr>
<tr>
<td>$\sigma(\text{NH}_2)$</td>
<td>-0.0067</td>
<td>-0.0927</td>
<td>-0.0067</td>
</tr>
<tr>
<td>$\sigma(\text{NH}_3)$</td>
<td>-0.0067</td>
<td>-0.0067</td>
<td>-0.0927</td>
</tr>
<tr>
<td>lone-pair</td>
<td>-0.0170</td>
<td>-0.0170</td>
<td>-0.0170</td>
</tr>
</tbody>
</table>

$a_{00} = 0.9865$
TABLE V. MC-SCF localized orbitals of $\text{NH}_3$ when the floating function (center at $z=1.2625\text{Å}$ with $\zeta=0.6$) is added to the minimal basis-set; orbital energies and occupation numbers are listed in first two lines.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon$</th>
<th>occ. num.</th>
<th>N 1s</th>
<th>H$_1$ 1s</th>
<th>H$_2$ 1s</th>
<th>H$_3$ 1s</th>
<th>Floating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-15.392</td>
<td>2.0</td>
<td>0.99527</td>
<td>-0.00725</td>
<td>-0.00725</td>
<td>-0.00725</td>
<td>-0.00484</td>
</tr>
<tr>
<td>$\sigma$ (NH$_1$)</td>
<td>-0.72852</td>
<td>0.08019</td>
<td>0.08019</td>
<td>0.08019</td>
<td>0.08279</td>
<td>0.08279</td>
<td>0.08043</td>
</tr>
<tr>
<td>$\sigma$ (NH$_2$)</td>
<td>-0.72852</td>
<td>0.08019</td>
<td>0.08019</td>
<td>0.08019</td>
<td>0.08279</td>
<td>0.08279</td>
<td>0.08043</td>
</tr>
<tr>
<td>$\sigma$ (NH$_3$)</td>
<td>-0.72852</td>
<td>0.08019</td>
<td>0.08019</td>
<td>0.08019</td>
<td>0.08279</td>
<td>0.08279</td>
<td>0.08043</td>
</tr>
<tr>
<td>lone-pair</td>
<td>-0.60786</td>
<td>0.16640</td>
<td>0.16640</td>
<td>0.16640</td>
<td>0.16640</td>
<td>0.16640</td>
<td>0.16640</td>
</tr>
<tr>
<td>$\sigma^*$ (NH$_1$)</td>
<td>-0.01441</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
</tr>
<tr>
<td>$\sigma^*$ (NH$_2$)</td>
<td>-0.01441</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
</tr>
<tr>
<td>$\sigma^*$ (NH$_3$)</td>
<td>-0.01441</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
<td>0.09520</td>
</tr>
<tr>
<td>NBE$\sigma^a$</td>
<td>-0.00264</td>
<td>0.00310</td>
<td>0.00310</td>
<td>0.00310</td>
<td>0.00310</td>
<td>0.00310</td>
<td>0.00310</td>
</tr>
</tbody>
</table>

$^a$ The non-bonding excited-orbital, see text.
<table>
<thead>
<tr>
<th>( \langle \epsilon_{\text{HN}} \rangle )</th>
<th>( \langle \epsilon_{\text{Zn}} \rangle )</th>
<th>( \langle \epsilon_{\text{HN}} \rangle )</th>
<th>( \langle \epsilon_{\text{Zn}} \rangle )</th>
<th>( \langle \epsilon_{\text{HN}} \rangle )</th>
<th>( \langle \epsilon_{\text{Zn}} \rangle )</th>
<th>( \langle \epsilon_{\text{HN}} \rangle )</th>
<th>( \langle \epsilon_{\text{Zn}} \rangle )</th>
<th>( \langle \epsilon_{\text{HN}} \rangle )</th>
<th>( \langle \epsilon_{\text{Zn}} \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9852</td>
<td>0.9852</td>
<td>1.9852</td>
<td>0.9852</td>
<td>1.9852</td>
<td>0.9852</td>
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<td>0.9852</td>
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<tr>
<td>1.9852</td>
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<td>1.9852</td>
<td>0.9852</td>
<td>1.9852</td>
<td>0.9852</td>
<td>1.9852</td>
<td>0.9852</td>
<td>1.9852</td>
<td>0.9852</td>
</tr>
</tbody>
</table>

Eneryes and occupation numbers are also listed in first two lines.

TABLE VII. MC-SCP localized orbitals of \( \text{NH}_2 \) when the minimal basis set is used; orbital
FIG. 2. Non-bonding orbital listed in Table V for NH₃ molecule. For coordinates used, see text.
FIG. 3. Non-bonding excited orbital listed in Table V for \( \text{NH}_3 \) molecule. For coordinates used, see text.
The lone-pair orbital as an MC-SCF LMO is similar to that as an ordinary LMO (e.g., the Edmiston-Ruedenberg criteria\textsuperscript{22}). It seems that the form of the NBEO is worthy of its name (Fig. 3).

(5) The orbital energy of the lone-pair orbital is lower than that of an N-H bond before the floating function is added (Tables V and VI). It may be ascribed to the incompleteness of the present basis-set. After the addition of the floating function, the situation is improved. It seems that the floating function contributes to the dissolution of the above incompleteness to a large extent.

By the above remarks, it is concluded that the addition of a floating function to a minimal basis-set is sufficiently powerful for the description of the pair-correlation of the lone-pair of electrons in NH\textsubscript{3} molecule. The addition is straightforward to organic molecules which contain N atoms (amines, imines, amides, imides, etc.).
B. For $H_2O$ molecule

Tables VII to XIV show the results for $H_2O$. The followings are the most significant points:

(1) The CMC-SCF energy is varied very slowly around the minimum point (about $r=0.72$ Å and $\theta=205^\circ$) as is seen in Tables VII to IX. The minimum point is not the position of the "cloud" of the lone-pair orbital as the ordinary LMO (of the Edmiston-Ruedenberg criteria). The energy-lowering by the addition of the floating functions is about 0.116 hartree around the minimum point in the CMC-SCF method (Table X).

(2) The favorable value of the orbital exponent for the floating functions is near 0.6 (Table X). This is the same condition as in $NH_3$ molecule presented above.

(3) A $\sigma-\sigma^*$ excitation contributes most significantly to the wave function (Tables XI and XII). This situation is also the same as in $NH_3$. The excitation from the lone-pair orbital of a $2p\pi$-type to the corresponding NBEO (non-bonding excited orbital) has a large contribution to the wave function, while that from the lone-pair orbital of a $\sigma$-type to the corresponding one plays no important role in the description of the wave function (Table XI).

(4) The floating functions contribute mainly to both of the NBEO (as is expected) and to the lone-pair orbital of $2p\pi$-type (Table XIII). The forms of two orbitals of the lone-pair and two orbitals of NBEO are indicated in Figs. 4 to 7. It is surprising that the two orbitals of the lone-pair are very
TABLE VII. Variation with respect to the centers of floating functions 
($\zeta=0.6$ and $r=0.72\text{A}$)\(^a\) for $\text{H}_2\text{O}$ molecule.

<table>
<thead>
<tr>
<th>$\theta$ (deg.)(^a)</th>
<th>$E_{\text{HF}}$ (a.u.)(^b)</th>
<th>$E_{\text{MC}}$ (a.u.)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104.45</td>
<td>-74.955767</td>
<td>-75.083492</td>
</tr>
<tr>
<td>125</td>
<td>-75.043747</td>
<td>.090157</td>
</tr>
<tr>
<td>145</td>
<td>.049198</td>
<td>.095686</td>
</tr>
<tr>
<td>165</td>
<td>.053455</td>
<td>.101345</td>
</tr>
<tr>
<td>180</td>
<td>.055685</td>
<td>.103879</td>
</tr>
<tr>
<td>195</td>
<td>.056978</td>
<td>.105442</td>
</tr>
<tr>
<td>205</td>
<td>.057281</td>
<td>.105899</td>
</tr>
<tr>
<td>215</td>
<td>.057114</td>
<td>.105857</td>
</tr>
<tr>
<td>235</td>
<td>.055300</td>
<td>.104177</td>
</tr>
</tbody>
</table>

\(^a\) See Fig. 1 for the parameters $r$ and $\theta$. The $\zeta$ is an orbital exponent.

\(^b\) See footnote b and c in Table I.
TABLE VIII. Variation with respect to the centers of the floating functions 
($\zeta=0.6$ and $r=0.96\text{Å}$) for $\text{H}_2\text{O}$ molecule. Notations are explained in Table VII.

<table>
<thead>
<tr>
<th>$\theta$ (deg.)</th>
<th>$E_{\text{HF}}$ (a.u.)</th>
<th>$E_{\text{MC}}$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104.45</td>
<td>-75.041722</td>
<td>-75.087382</td>
</tr>
<tr>
<td>125</td>
<td>.047557</td>
<td>.093517</td>
</tr>
<tr>
<td>145</td>
<td>.051833</td>
<td>.097926</td>
</tr>
<tr>
<td>165</td>
<td>.054493</td>
<td>.102024</td>
</tr>
<tr>
<td>180</td>
<td>.055346</td>
<td>.103256</td>
</tr>
<tr>
<td>195</td>
<td>.055203</td>
<td>.103431</td>
</tr>
<tr>
<td>205</td>
<td>.054566</td>
<td>.102960</td>
</tr>
</tbody>
</table>
TABLE IX. Variation with respect to the centers of floating functions (\(\xi=0.6\) and \(\theta=205^\circ\)) for \(H_2O\) molecule. Notations are explained in Table VII.

<table>
<thead>
<tr>
<th>(r(A))</th>
<th>(E_{HF}) (a.u.)</th>
<th>(E_{MC}) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td>-75.052369</td>
<td>-75.097336</td>
</tr>
<tr>
<td>0.72</td>
<td>0.057281</td>
<td>0.105899</td>
</tr>
<tr>
<td>0.96</td>
<td>0.054566</td>
<td>0.102961</td>
</tr>
</tbody>
</table>
TABLE X. Variation with respect to the orbital exponents of the floating functions centered at \( r = 0.72 \text{Å} \) and \( \theta = 205^\circ \) for H\(_2\)O molecule. The parameters \( r \) and \( \theta \) are indicated by Fig. 3.

<table>
<thead>
<tr>
<th>Orbital exponent (a.u.)</th>
<th>( E_{\text{HF}} ) (a.u.)</th>
<th>( E_{\text{MC}} ) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0(^a)</td>
<td>-74.946706</td>
<td>-74.990058</td>
</tr>
<tr>
<td>0.4</td>
<td>-75.038980</td>
<td>-75.086442</td>
</tr>
<tr>
<td>0.5</td>
<td>0.051918</td>
<td>0.100048</td>
</tr>
<tr>
<td>0.6</td>
<td>0.057281</td>
<td>0.105899</td>
</tr>
<tr>
<td>0.7</td>
<td>0.055178</td>
<td>0.104270</td>
</tr>
<tr>
<td>0.8</td>
<td>0.047002</td>
<td>0.096559</td>
</tr>
</tbody>
</table>

\(^a\) Without floating functions.
TABLE XI. Expansion coefficients $a_{00}$ and $a_{tu}$ in the CMC-SCF wave-function for H$_2$O molecule when the floating functions (centered at $r=0.72\text{Å}$ and $\theta=205^\circ$ with $\zeta=0.6$) are added to the minimal basis-set. Notations are explained in Table III.

<table>
<thead>
<tr>
<th>$\phi_u$</th>
<th>$\phi_t$</th>
<th>$\sigma^*(\text{OH}_1)$</th>
<th>$\sigma^*(\text{OH}_2)$</th>
<th>NBOE ($\sigma$)$^a$</th>
<th>NBOE ($2p\pi$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>lone-pair($\sigma$-type)</td>
<td>$\text{(OH}_1\text{)}$</td>
<td>-.0137</td>
<td>-.0137</td>
<td>-.0076</td>
<td>-.0084</td>
</tr>
<tr>
<td></td>
<td>$\text{(OH}_2\text{)}$</td>
<td>-.1017</td>
<td>-.0057</td>
<td>-.0039</td>
<td>-.0017</td>
</tr>
<tr>
<td>lone-pair($2p\pi$-type)</td>
<td></td>
<td>-.0057</td>
<td>-.1017</td>
<td>-.0039</td>
<td>-.0017</td>
</tr>
</tbody>
</table>

$a_{00} = .9866$

$^a$ The non-bonding excited-orbital, see text.
TABLE XII. Expansion coefficients $a_{00}$ and $a_{tu}$ in the CMC-SCF wave-function for H$_2$O molecule when the minimal basis-set is used. Notations are explained in Table XI.

<table>
<thead>
<tr>
<th>$\phi_t$</th>
<th>$\phi_u$</th>
<th>$\sigma^*(\text{OH}_1)$</th>
<th>$\sigma^*(\text{OH}_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>lone-pair 1</td>
<td></td>
<td>-.0177</td>
<td>-.0177</td>
</tr>
<tr>
<td>lone-pair 2</td>
<td></td>
<td>-.0177</td>
<td>-.0177</td>
</tr>
<tr>
<td>(OH$_1$)</td>
<td></td>
<td>-.1078</td>
<td>-.0060</td>
</tr>
<tr>
<td>(OH$_2$)</td>
<td></td>
<td>-.0060</td>
<td>-.1078</td>
</tr>
</tbody>
</table>

$a_{00} = .9976$
TABLE XIII. MC-SCF localized orbitals of H$_2$O when the floating function (centered at $r=0.72\AA$ and $\theta=205^\circ$ with $\xi=0.6$) is added to the minimal basis-set; orbital energies and occupation numbers are entered in first two lines.

<table>
<thead>
<tr>
<th></th>
<th>1s(O)</th>
<th>$\sigma$(OH$_1$)</th>
<th>$\sigma$(OH$_2$)</th>
<th>lone-pair (1)</th>
<th>lone-pair (2)</th>
<th>$\sigma^*$(OH$_1$)</th>
<th>$\sigma^*$(OH$_2$)</th>
<th>NBOE(1)$^a$</th>
<th>NBOE(2)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>-20.38943</td>
<td>-0.74034</td>
<td>-0.74034</td>
<td>-1.17183</td>
<td>-0.46788</td>
<td>-0.01847</td>
<td>-0.01847</td>
<td>-0.00051</td>
<td>-0.00701</td>
</tr>
<tr>
<td>occ. num.</td>
<td>2.0</td>
<td>1.97918</td>
<td>1.97918</td>
<td>1.99899</td>
<td>1.98956</td>
<td>0.02144</td>
<td>0.02144</td>
<td>0.00052</td>
<td>0.00969</td>
</tr>
<tr>
<td>O 1s</td>
<td>1.00187</td>
<td>0.03146</td>
<td>0.03146</td>
<td>0.20855</td>
<td>-0.00009</td>
<td>0.08080</td>
<td>-0.08080</td>
<td>-0.00006</td>
<td>-0.00006</td>
</tr>
<tr>
<td>2s</td>
<td>-0.00465</td>
<td>-0.52635</td>
<td>-0.052635</td>
<td>-0.96902</td>
<td>-0.0035</td>
<td>-0.54402</td>
<td>0.54402</td>
<td>0.62616</td>
<td>0.00047</td>
</tr>
<tr>
<td>2p$_x$</td>
<td>0.00001</td>
<td>0.00009</td>
<td>0.00009</td>
<td>0.00029</td>
<td>0.79909</td>
<td>0.0014</td>
<td>-0.00014</td>
<td>-0.00039</td>
<td>0.87060</td>
</tr>
<tr>
<td>2p$_y$</td>
<td>0</td>
<td>0.45016</td>
<td>-0.45016</td>
<td>0</td>
<td>0</td>
<td>0.68047</td>
<td>0.68047</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2p$_z$</td>
<td>0.01392</td>
<td>-0.52163</td>
<td>-0.52163</td>
<td>0.29359</td>
<td>0.00002</td>
<td>-0.52261</td>
<td>0.52261</td>
<td>-0.16108</td>
<td>0.00009</td>
</tr>
<tr>
<td>H$_1$ 1s</td>
<td>-0.00412</td>
<td>-0.55159</td>
<td>0.52198</td>
<td>0.018716</td>
<td>0.00005</td>
<td>1.24512</td>
<td>-0.03866</td>
<td>0.40600</td>
<td>-0.00002</td>
</tr>
<tr>
<td>H$_2$ 1s</td>
<td>-0.00412</td>
<td>0.05220</td>
<td>-0.55159</td>
<td>0.18716</td>
<td>0.00005</td>
<td>0.03866</td>
<td>-1.24512</td>
<td>0.40600</td>
<td>-0.00002</td>
</tr>
<tr>
<td>Float. (1)</td>
<td>-0.00365</td>
<td>0.07597</td>
<td>0.07597</td>
<td>-0.02416</td>
<td>0.40078</td>
<td>-0.13155</td>
<td>0.13155</td>
<td>-0.84840</td>
<td>-1.46986</td>
</tr>
<tr>
<td>Float. (2)</td>
<td>-0.00366</td>
<td>0.75870</td>
<td>0.75870</td>
<td>-0.02442</td>
<td>-0.40076</td>
<td>-0.13108</td>
<td>0.13108</td>
<td>-0.84978</td>
<td>1.46915</td>
</tr>
</tbody>
</table>

$^a$The non-bonding excited-orbital, see text.
TABLE XIV. MC-SCF localized orbitals of $\text{H}_2\text{O}$ when the minimal basis-set is used; orbital
denergies and occupation numbers are entered in first two lines.

<table>
<thead>
<tr>
<th></th>
<th>$\epsilon$</th>
<th>$\sigma$(OH)</th>
<th>$\sigma$($\text{OH}_2$)</th>
<th>lone-pair (1)</th>
<th>lone-pair (2)</th>
<th>$\pi$(OH)</th>
<th>$\pi$($\text{OH}_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}$ 1$\text{s}$</td>
<td>1.00115</td>
<td>.01591</td>
<td>.01591</td>
<td>.15760</td>
<td>-.14992</td>
<td>-.87799</td>
<td>-.87799</td>
</tr>
<tr>
<td>2$\text{s}$</td>
<td>-.00229</td>
<td>.05527</td>
<td>.05527</td>
<td>-.72340</td>
<td>.68773</td>
<td>.61020</td>
<td>.61020</td>
</tr>
<tr>
<td>2$\text{p}_x$</td>
<td>-.00006</td>
<td>-.00001</td>
<td>-.00001</td>
<td>-.68901</td>
<td>-.72475</td>
<td>.0</td>
<td>.0</td>
</tr>
<tr>
<td>2$\text{p}_y$</td>
<td>.0</td>
<td>.41791</td>
<td>-.41791</td>
<td>.0</td>
<td>.0</td>
<td>-.70074</td>
<td>.70074</td>
</tr>
<tr>
<td>2$\text{p}_z$</td>
<td>.01299</td>
<td>-.50946</td>
<td>-.50946</td>
<td>.19197</td>
<td>-.18250</td>
<td>.53267</td>
<td>.53267</td>
</tr>
<tr>
<td>$\text{H}_1$ 1$\text{s}$</td>
<td>-.00678</td>
<td>-.57124</td>
<td>.08820</td>
<td>.00636</td>
<td>-.00604</td>
<td>-1.13651</td>
<td>.40457</td>
</tr>
<tr>
<td>$\text{H}_2$ 1$\text{s}$</td>
<td>-.00678</td>
<td>.08820</td>
<td>-.57124</td>
<td>.00636</td>
<td>-.00604</td>
<td>.04045</td>
<td>-1.13651</td>
</tr>
</tbody>
</table>
FIG. 4. The first non-bonding orbital listed in Table XIII for $\text{H}_2\text{O}$ molecule.
For coordinates and $\text{H}$ in the figure, see the caption of Fig. 1.
FIG. 5. The second non-bonding orbital listed in Table XIII for $H_2O$ molecule. For coordinates and $H$ in the figure, see the caption of Fig. 1.
FIG. 6. The first non-bonding excited orbital (NBEO) listed in Table XIII for H$_2$O molecule. For coordinates and H in the figure, see the caption of Fig. 1.
FIG. 7. The second non-bonding excited orbital (NBEO) listed in Table XIII for H₂O molecule. For coordinates and H in the figure, see the caption of Fig. 1.
similar to those symmetry-adapted. The forms of two NBEO's are thought to be worthy of their name.

(5) An equivalent-type pair of non-bonding orbitals is obtained from the minimal basis-set (Table XIV). These forms are indicated in Figs. 8 and 9. Either orbital energy of the pair is lower than that of the O-H bond. It may be due to the incompleteness of the present basis-set, since the condition is very turned out by the addition of the floating functions (Tables XIII and XIV).

The above remarks lead to the same conclusion as in NH$_3$; i.e., the addition of floating functions to a minimal basis-set is sufficiently powerful for the description of the pair correlation of the lone-pair of a 2p$_\pi$-type in H$_2$O molecule. An application to a large polyatomic-molecules containing O atom is straightforward.
FIG. 8. One of the non-bonding orbitals listed in Table XIV for H$_2$O molecule.

For coordinates and H in the figure, see the caption of Fig. 1.
FIG. 9. One of the non-bonding orbitals listed in Table XIV for H₂O molecule.

For coordinates and H in the figure, see the caption of Fig. 1.
Acknowledgments

We wish to thank Mr. S. Kato for kindly providing us his LMO program. The all computations were carried out on a FACOM 230-75 computer of the Data Processing Center of Kyoto University.
References


3 K. Ishida, to be published.


6 F. P. Billingsley II and M. Krauss, Phys. Rev. A6, 855 (1972); and succeeding papers.


8 H. Basch, J. Chem. Phys. 55, 1700 (1971); and succeeding papers.


16 This is obtained when the starting orbitals of the MC-SCF process are localized; see Ref. 5.

21 The STO-NG expansion coefficients and $\alpha$ were first given by K. O-ohata, H. Taketa, and S. Huzinaga, J. Phys. Soc. Japan, 21, 2306 (1966); more recently, the values with a more high precision than them were obtained by R. F. Stewart, J. Chem. Phys. 52, 431 (1970).
CHAPTER VII

AN MO INTERPRETATION

OF

THE CHEMICAL SHIFTS OF INNER-SHELL ELECTRONS
An MO Interpretation of the Chemical Shifts of Inner-shell Electrons

A correlation formula between the chemical shifts of inner-shell electrons and molecular-charge distributions is derived by an MO scheme with CNDO-type approximations. Errors imposed in these schemes are discussed. Reorganization energy terms are briefly discussed in the same level of approximations.

The chemical shifts of inner-shell electrons have been studied in a wide variety of organic and inorganic compounds. One interesting feature of the problem is that the chemical shifts change linearly with the charges on the atoms considered. These charges have been estimated by several methods - i.e., methods with using the oxidation number and Pauling's electronegativity differences, an iterative extended Hückel method, and several types of non-empirical calculations.

In this report, an MO interpretation of the correlation between the chemical shifts of the binding energies of inner-shell electrons in certain molecules and the atomic charges is given by introducing some approximations, and the limitations of these relations are briefly discussed.

Theoretical

By Roosnaan's SCF treatment for closed-shell systems, the orbital energy of ith MO, $e_i$, is given by:

$$e_i = F_{ii} = \sum_{r,t} C_{ri} C_{ti} F_{rt}$$

1) K. Siegbahn et al., ESCA atomic molecular and solid state structure studied by means of electron spectroscopy, Almqvist and Wiksell A.B., Stockholm (1957).
6) R. Manne, ibid., 46, 4645 (1967).
Where $C_r^t$ and $F_{rt}$ are the $r$th AO coefficient of the $t$th MO and the $F_{rt}$-element of the Fock operator, respectively.

Suppose that the $i$th MO is mainly constructed by inner-shell AO's; the following derivation can then be easily carried out with considerable accuracy, since the diagonal elements of the Fock operator for inner-shell AO's, $F_{rr}$, are very large compared with that of the off-diagonal ones $F_{rt}$:

$$
e_i = \frac{1}{2} F_{ii} C_i^t \approx 1.0, \quad (2)$$

$$F_{rt} = \left( \frac{1}{2} F_{ii} - \frac{Z_A}{r} \right) + \left( \frac{1}{2} F_{ii} - \frac{Z_B}{t} \right) + \sum_r P_{rt} \left( \frac{ss}{rt} - \frac{1}{2} \frac{ss}{st} \right). \quad (3)$$

In Eq. (3), the first term is the self-core integral, while the second is the nuclear attraction by the other nuclei and the third consists of electronic repulsions. Throughout this report, $r$, $s$, $t$, and $u$ denote atomic orbitals; especially, $s$ denotes the inner-shell MO in question belonging to the A atom. The $i$ and $j$ notations represent occupied MO's, and $k$ and $l$, vacant ones. The $P_{rt}$ notation is the bond order between $r$ and $t$ AO's.

To connect the orbital energies with the atomic charges, we use the following approximation, using the same notations as in Refs. 14 and 17:

(A) The self-core integral:

$$\left( \frac{1}{2} F_{ii} - \frac{Z_A}{r} \right) = -I_i - (N_i - 1) \left( \frac{ss}{sr} \right)$$

and the nuclear attraction:

$$\left( \frac{1}{2} F_{ii} - \frac{Z_B}{t} \right) = -Z_b \left( \frac{ss}{ns} \right) = -Z_b Y_{AB}. \quad (4)$$

The above formulae have already been given in a previous paper.\(^{14}\) (B) The electronic repulsion integrals can be estimated by a CNDO-type approximation:\(^{20}\)

Thus, Eq. (3) can be re-written as:

$$F_{rt} = -I_i + (P_{AA} - Z_A^t) Y_{AA} + \sum_{A=A} (P_{BB} - Z_B^t) Y_{AB}, \quad (6)$$

where the average Coulomb integrals are:

$$Y_{AA} = \left( \frac{ss}{ns} \right), \quad Y_{AB} = \left( \frac{ss}{ns} \right), \quad (7)$$

and where $Z_A^t$ denotes the number of valence electrons on the A atom and $n_A$ denotes valence s-type AO on the A atom.

When a Mulliken approximation with in Eq. (7) is used instead of the above CNDO-type one, and only the term of $S$(overlap) is considered, an expression similar to that in Eq. (6) is obtained, but in this case the $P_{AA}$'s in Eq. (6) become atomic populations.

From Eq. (6), the following simplified relation can be obtained by denoting $(P_{AA} - Z_A^t) = -Q_A$ ($Q_A$ is the net charge of atom A):

$$\Delta E_r = \frac{1}{2} S_{AA} - \frac{1}{2} Q_A Y_{AA} - \sum_{B=A} Q_B Y_{AB}. \quad (8)$$

That is, the shift of the inner-shell binding energy from the atomic ionization energy in certain valence state is correlated with the molecular-charge distribution. The shift of the $\Delta E_r$ for the A atom in different chemical environments, which are denoted as X and Y, is:

$$\Delta E_r(X, Y) = \{Q_A(X) - Q_A(Y)\} Y_{AA}$$

$$- \sum_{B=A} Q_B(Y) Y_{AB} + \sum_{B=A} Q_B(X) Y_{AB}(X). \quad (9)$$

Eq. (9) indicates that the chemical shifts depend not only on the atomic-charge differences of the A atom in different molecules, but also on the sum of the charges over the other parts of the molecules, since the $Y_{AB}/Y_{AA}$ ratio is not negligibly small. For diatomic molecules of the first-row elements, AB and A2, $\Delta E_r$ for AB, $Q_A(AB)=-Q_B(AB)=1.0$, $Y_{AA}(AB)=1.0$, and $Y_{AB}(AB)=0.5$ (in a.u.).\(^{20}\) The change in the inner-shell binding energy between the molecules is about 14 eV per unit charge. This is in agreement with the previous results.\(^{19}\)

Results and Discussion

Tables 1 and 2 summarize the values of some atomic integrals involving the $1s_A$ AO of formaldehyde (in a.u.). By means of these tables we can examine the approximations Eq. (5), and (B). Minimal Slater bases with Slater-rule exponents, except for that of 1.2 for hydrogen, are used throughout the calculations in the present paper. The integrals are evaluated by means of the 4-term Gaussian expansion method.\(^{20}\)

As shown in Table 1, the approximation introduced

From Eq. (6), the following simplified relation can be obtained by denoting $(P_{AA} - Z_A^t) = -Q_A$ ($Q_A$ is the net charge of atom A):

$$\Delta E_r = \frac{1}{2} S_{AA} - \frac{1}{2} Q_A Y_{AA} - \sum_{B=A} Q_B Y_{AB}. \quad (8)$$

That is, the shift of the inner-shell binding energy from the atomic ionization energy in certain valence state is correlated with the molecular-charge distribution. The shift of the $\Delta E_r$ for the A atom in different chemical environments, which are denoted as X and Y, is:

$$\Delta E_r(X, Y) = \{Q_A(X) - Q_A(Y)\} Y_{AA}$$

$$- \sum_{B=A} Q_B(Y) Y_{AB} + \sum_{B=A} Q_B(X) Y_{AB}(X). \quad (9)$$

Eq. (9) indicates that the chemical shifts depend not only on the atomic-charge differences of the A atom in different molecules, but also on the sum of the charges over the other parts of the molecules, since the $Y_{AB}/Y_{AA}$ ratio is not negligibly small. For diatomic molecules of the first-row elements, AB and A2, $\Delta E_r$ for AB, $Q_A(AB)=-Q_B(AB)=1.0$, $Y_{AA}(AB)=1.0$, and $Y_{AB}(AB)=0.5$ (in a.u.).\(^{20}\) The change in the inner-shell binding energy between the molecules is about 14 eV per unit charge. This is in agreement with the previous results.\(^{19}\)

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As shown in Table 1, the approximation introduced

\begin{table}[h]
\centering
\caption{Comparison of the nuclear attraction integrals (\(S_A (Z_B^a r_B) / S_A\) with \(Z_B Y_{AB}\) in formaldehyde (in a.u.))}
\begin{tabular}{|c|c|c|}
\hline
\(S_A\) & B & \(S_A (Z_B^a r_B) / S_A\) \(Z_B Y_{AB}\) \\
\hline
1s_0 & O & 2.6240 & 2.6160 \\
1s_0 & H & 0.4855 & 0.4727 \\
1s_0 & C & 1.7493 & 1.7089 \\
1s_0 & H & 0.2655 & 0.2654 \\
\hline
\end{tabular}
\end{table}

\(A\) A similar equation, obtained by means of an electrostatic model, is given in Ref. 19; that is, $\Delta E_r(XY) = kQ_A + \sum_{j=1} Q_j R_j$, but here $X$, which corresponds $Y_{AA}$ in Eq. (8), is taken to be an empirical parameter. The constant, $L$, is determined by means of the reference compound.


As to the integral values, refer to those in Table 2 and also those in Ref. 19.


TABLE 2. SOME ELECTRON REPULSION INTEGRALS INCLUDING CARBON 1S ORBITALS OF FORMALDEHYDE (in a.u.)

<table>
<thead>
<tr>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>((1s_1 1s_1/2s_22s_2c))</td>
<td>0.8073</td>
</tr>
<tr>
<td>((1s_1 1s_1/2p_22p_2c))</td>
<td>0.8072</td>
</tr>
<tr>
<td>((1s_1 1p_1/2s_22s_2c))</td>
<td>0.4360</td>
</tr>
<tr>
<td>((1s_1 1s_1/2p_22p_2c))</td>
<td>0.4132</td>
</tr>
<tr>
<td>((1s_1 1s_1/2s_22s_2c))</td>
<td>0.4817</td>
</tr>
</tbody>
</table>

a) The z axis is taken to be parallel with the C-O bond.

in Eq. (5) is good. Table 2 indicates that the "average Coulomb" approximation is excellent for one-center integrals and is only correct to within about a 10% error for two-center ones. The two-center Coulomb and hybrid integrals, \((1s_1 1s_1/2p_22p_2c)\) and \((1s_1 1s_1/2p_22p_2c)\), however, are not negligible; therefore, the (B) approximation, i.e., the CNDO-type integral which neglects the above type of integrals, may be bad in certain cases where the corresponding off-diagonal elements of the bond-order matrix are not negligible.

The results calculated by means of Eq. (9) are collected in Tables 3 and 4 for carbon 1s and nitrogen 1s electrons respectively; they are all shown in Figs. 1 and 2 except for anions. Figures 1 and 2 indicate a rather satisfactory correlation between the observed chemical shifts and the values of \(\delta \Delta \epsilon\). The solid lines in Figs. 1 and 2 are inclined about 45°; therefore, it seems that the chemical shifts can be evaluated semi-quantitatively in terms of the \(\delta \Delta \epsilon\), in neutral molecules, and that a relation between the molecular-charge distributions and the observed shifts may be in the form of \((Q_{A}^{2}/Q_{A}^{2} + \sum Q_{A}^{2} Q_{B}^{2})\). For the anions containing

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(E_{\text{obsd}})</th>
<th>(Q)</th>
<th>(\delta \Delta \epsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_4)</td>
<td>291.2</td>
<td>-0.064</td>
<td>-0.90</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_6)</td>
<td>290.7</td>
<td>-0.238</td>
<td>-1.73</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_6)</td>
<td>290.6</td>
<td>-0.05</td>
<td>-1.73</td>
</tr>
<tr>
<td>(\text{CH}_2\text{OH})</td>
<td>292.7</td>
<td>0.129</td>
<td>1.40</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>297.64</td>
<td>0.536</td>
<td>5.45</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{H})</td>
<td>295.79</td>
<td>0.381</td>
<td>3.40</td>
</tr>
</tbody>
</table>


b) Calculated net charges on carbon atom by CNDO/2 method.

c) Calculated by Eq. (9) with CNDO/2 net charges (in eV).

TABLE 3. CALCULATED SHIFTS FOR CARBON 1S ELECTRONS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(E_{\text{obsd}})</th>
<th>(Q)</th>
<th>(\delta \Delta \epsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2)</td>
<td>402.45</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>398.1</td>
<td>-0.234</td>
<td>-2.56 (-5.92)</td>
</tr>
<tr>
<td>(\text{CONH}_2)</td>
<td>400.4</td>
<td>-0.233</td>
<td>-1.73</td>
</tr>
<tr>
<td>(\text{CH}_2\text{N(NH)})</td>
<td>402.2</td>
<td>0.157</td>
<td>2.09</td>
</tr>
<tr>
<td>(\text{CH}_2\text{N(NH)})</td>
<td>398.0</td>
<td>-0.142</td>
<td>-2.04 (-6.27)</td>
</tr>
<tr>
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<td>-0.165</td>
<td>-2.09</td>
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<tr>
<td>(\text{NaNO}_2)</td>
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<td>0.636</td>
<td>2.59</td>
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<td>0.093</td>
<td>-10.36</td>
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<tr>
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<td>0.447</td>
<td>-6.58 (-13.0)</td>
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<tr>
<td>(\text{KCN})</td>
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<td>-0.723</td>
<td>-18.04 (-16.3)</td>
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<tr>
<td>(\text{KCN})</td>
<td>399.0</td>
<td>-0.409</td>
<td>-18.00 (-19.3)</td>
</tr>
</tbody>
</table>

a), b), c) They are the same as in Table 3.
d) Calculated as anion.
e) The values in parenthesis are evaluated by non-empirical gross atomic charges in stead of CNDO/2 net charges in Eq. (9). These gross charges have been given in references; R. Bonaccorsi, C. Peitone, O. E. Scrocco, and J. Tomasi, J. Chem. Phys., 80, 1407, 1500 (1968); E. Clementi, ibid., 46, 4731 (1977); W. E. Falke and N. N. Lipscomb, J. Amer. Chem. Soc., 88, 2384 (1966).
nitrogen atoms, the above rather good correlation is not observed; that is in these charged species, the crystal effects may be considerable. It is noticed that the values of $a$, obtained by Roothaan's closed-shell treatment are generally larger than those of the binding energy observed at about 10--20%, and open-shell SCF calculations give better results, as has been pointed out by several authors. Further it has been suggested that the main effects of these discrepancies depend on the reorganization energy. Now, let me examine the reorganization energy in the above approximation scheme. Suppose that MO's $i$ and $j$ are given by Roothaan's closed-shell treatment. Using these MO's, an open-shell wave function with an $s$ hole ($S_z = 1/2$), is obtained approximately by a CI scheme;

$$\Phi^0 = |s\bar{i}i'...j\bar{j}| + \sum_{f,a}\lambda_{ia}|s\bar{i}i'...j\bar{j}| + \sum_{a}|s\bar{i}i'...j\bar{j}|$$

$$+ \sum_{f,a}\sum_{k}\lambda_{ka}(1)|s\bar{i}i'...j\bar{j}| - |s\bar{i}i'...j\bar{j}|$$

$$+ \sum_{f,a}\sum_{k}\lambda_{ka}(2)|s\bar{i}i'...j\bar{j}| - |s\bar{i}i'...j\bar{j}| - |s\bar{i}i'...j\bar{j}|.$$  

(10)

That is, $\Phi^0$ is an approximate open SCF function and $\lambda$ is the coefficient of a related configuration, $x$. By perturbation treatment, these are;

$$\lambda_{ia} = E_{ia}/E_{ia} = 0, \quad \lambda_{ab} = (\langle ka | ks \rangle)^2/E_{ka}$$

$$\lambda_{ka}(1) = \sqrt{2} \{\langle ik | ks \rangle - \langle 1/2 | is | ks \rangle\} / E_{ka}(1)$$

$$\lambda_{ka}(2) = -\sqrt{3/2} \langle is | dk \rangle / E_{ka}(2).$$  

(11)

Where $E_{ka}$ is the energy difference between the energy of the $s\rightarrow k$ excited configuration, as shown in Eq. (10), and the ground-state configuration, and so on. Then, the energy, $E^0$, becomes;

$$E^0 = (E_0 - e_s) + \sum_k \frac{(\langle ks | ss \rangle)^2}{E_{ks}} + \sum_{i,s} \frac{\{2(\langle ik | ss \rangle - \langle 1/2 | is | ss \rangle)^2}{E_{ks}(1)}$$

$$+ \sum_{i,s} \{ -\sqrt{3/2} \langle is | ks \rangle \}^2 / E_{ks}(2) + \ldots$$  

(12)

That is, the reorganization energy is $E^0 - (E_0 - e_s)$, and the dominant contribution comes from the third term, since $E_{ka} \approx e_a - e_s$ (large), $E_{ka}(1) \approx 1E_{ka}$ (valence shell $i \rightarrow k$ singlet excitation energy for a closed-shell system, small), and $\langle ik | ss \rangle = C_iC_k^{\dagger}(r/r | ss)$ is large, and $\langle is | ks \rangle$ is small as is shown in Table 2.

The magnitude of the third term can be roughly estimated as; $E_{ka}(1) \approx 0.5$ a.u., $\langle r/r | ss \rangle \approx 1$ a.u., and $e_a \approx 10$ a.u.; hence, (the third term)$e_\sigma \approx 10^{-1}$. This order is reasonable when it is compared with the previous results, 10--20%. These results indicate that the third part is the most important in reorganization energy. Further, this third term can be approximated:

$$\sum_k \frac{2\{\sum C_iC_k^{\dagger}(r/r | ss)\}^2}{E_{ka}(1)} \approx \sum_{i,s} \sum_{r,s} \left( \frac{r\sigma}{2} - \frac{\sigma r}{2} \right) \frac{(\gamma_{ab})^3}{2E_{xy}}$$

Where $E_{xy}$ is the average excitation energy. That is, the reorganization energy is not a linear function for the atomic charges.

As to the other corrections for inner electron binding energies, that is, the correlation correction, the relativistic correction, the crystal correction, it can be pointed out that these are negligible or are proportional to the charges.

As has been shown in the above discussion, the linear relation between the charges and the inner-shell binding energy is restricted within the imposed approximations; thus, in some cases, this linearity may depend on the cancellations of various effects. We hope this point will be reexamined in the future.

The calculations have been carried out on the FACOM 230--60 Computer of Kyoto University.

26) The estimated values of the third term in the level of approximations in the present report are, e.g., 22.7 eV for the $N_1$ of pyridine.
27) For valence-electron systems, the same order values are obtained.
CHAPTER VIII

AN MO INTERPRETATION
OF
THE CHEMICAL SHIFTS OF THE BINDING ENERGIES OF INNER-SHELL ELECTRONS.
A STUDY OF INTRAMOLECULAR SHIFTS
An MO Interpretation of the Chemical Shifts of the Binding Energies of Inner-shell Electrons. II. A Study of Intramolecular Shifts

The relationship between chemical shifts in the binding energies of inner-shell electrons and molecular-charge distributions has been pointed out. For adenine and cytosine molecules, however, Barber and Clark concluded that a "simple relationship between 'shifts' in binding energies and 'charge distributions' can be misleading." In a previous paper, we have derived the following correlation formula between the chemical shifts and molecular-charge distributions within a MO framework:

\[ \Delta \sigma_s(X,Y) = \left[ \sum_{A \in X} Q_A(X) \gamma_{AA}(X) + \sum_{B \in Y} Q_B(Y) \gamma_{AB}(Y) \right] \]

where \( \Delta \sigma_s(X,Y) \) denotes the chemical shifts of an inner-shell electron, \( s \), on an atom, \( A \), in a chemical environment, \( X \), from that in another environment, \( Y \), \( Q_A(X) \), \( Q_B(Y) \), and so on denote the net charges on the \( A \), \( B \), etc. atoms in the \( X \), \( Y \), etc. environments respectively. \( \gamma_{AA}(X) \) denotes a one-center average Coulomb interaction between inner and valence electrons on an \( A \) atom. \( \gamma_{AB}(X) \) denotes a two-center average Coulomb interaction between inner electrons on an \( A \) atom and valence electrons on a \( B \) atom in an \( X \) environment.

For inter-molecular shifts of simple molecules, the results by the above formula almost entirely accorded with the experimentally obtained values. In the present note, we will report an application of the above formula to the intra-molecular shifts of adenine and cytosine molecules. The results are shown in Table 1 for carbon 1s and nitrogen 1s. Figures 1 and 2 show the plots of the observed binding energies against the calculated \( \Delta \sigma_s \) values for carbon 1s and for nitrogen 1s respectively. The figures illustrate that the correlations are fairly satisfactory. Especially, the correlation is quantitatively good for the carbon 1s of adenine in Fig. 1, in view of the fact that the solid line is drawn at 45 degree with respect to the horizontal axis. For the nitrogen 1s, the correlations are rather good, but not quantitative, as shown in Fig. 2. In view of the non-empirical calculations done on limited bases by Mely and Pullman and by Clementi, deviation of the observed binding energy from the calculated orbital energy can be not said to be constant (except for the carbon 1s of adenine). Therefore, the different slopes in Fig. 2 most probably arise from the fact that the above deviation is not constant.

4) We calculated the \( \Delta \sigma_s \) with \( \Delta \sigma_s = Q_A(X) \gamma_{AA}(X) + \sum_{B \in Y} Q_B(Y) \gamma_{AB}(X) \), using approximate net charges which has been obtained by the CNDO/2 method.

### Table 1. Calculated \( \Delta \sigma_s \) and Observed Binding Energies

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>Energy (±0.3 eV)</th>
<th>( \Delta \sigma_s ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{H\textsubscript{3}}</td>
<td>C-5</td>
<td>284.7</td>
<td>-0.44</td>
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<tr>
<td></td>
<td>C-2</td>
<td>285.7</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td>C-8</td>
<td>286.2</td>
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<tr>
<td></td>
<td>N-1</td>
<td>401.4</td>
<td>-1.33</td>
</tr>
</tbody>
</table>


The above formula means that the chemical shifts of the binding energies should be correlated with charge distributions, though not with simple local charges. Therefore, the previously-referred to suggestion by Barber and Clark is not valid in the present case.

From the above brief discussions we conclude that our formula is useful for the assignment of intra-molecular shifts so long as approximate net charges obtained by a semi-empirical method are used.
CHAPTER IX

GENERAL CONCLUSION

A reason why the electron correlation effects must be taken into account has been described in chapter I of this doctoral dissertation. Many techniques for taking account of these effects have been proposed, as described in chapter I. The MC-SCF method among them has been studied in this dissertation for showing how the method is powerful and how a new picture or model beyond the so-called independent-particle-model (of the Hartree-Fock method) can be extracted from the MC-SCF wave function.

Especially, through the studies in chapter III and IV, the calculated spin densities are in excellent agreement with experiment and a new picture for core-polarization phenomena in atoms has been obtained from an analysis of MC-SCF wave functions considered. This analysis will be a typical way for the extraction of a physical picture from MC-SCF wave functions. It is possible to apply the same method to molecules in future.

In chapter V, a proper description of the adiabatic potential of a bond-dissociation process has been obtained. The description is sufficiently quantitative in chemical accuracy and can apply to any large molecules. The model of the process obtained from a two-configuration wave function is consistent with chemical intuition.

It is shown in chapter VI that floating functions added
to basis set are efficient in (non-empirical) MC-SCF calculations of molecules containing the lone-pairs of electrons. Works in chapters VII and VIII show how the molecular charge distributions are described well within a single-configuration wave function in a moderate success.

From these studies presented in this dissertation, it is concluded that the MC-SCF method gives an excellent description in spite of few configurations and then gives a certain physical picture or model, as are expected initially.

One of the defects of the MC-SCF method is the difficulty in the solving process of the MC-SCF equation (which is described in chapter II, in detail) when the number of configurations considered increases to infinite; i.e., the process is difficult to converge and time consuming in this case. Then, in future, it is desired how to take the difficulty off.