THEORETICAL STUDIES

ON

THE ELECTRON CORRELATION EFFECTS IN ATOMS AND MOLECULES

BY

THE MULTICONFIGURATION SELF-CONSISTENT-FIELD METHOD

KAZUHIRO ISHIDA

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PREFACE

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 doctral 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.

CONTENTS

CHAPTER I

INTRODUCTION

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

$$H\Psi = E\Psi , \qquad\qquad (1)$$

where H is a certain Hamiltonian of a given system and E is one of its eigenvalues corresponding to one of its eigenstates, Ψ. 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.[5] Exchange perturbation methods for describing interatomic interactions at small separations are developed and reviewed by Chipman, Bowman, and Hirschfelder.[6] For those at large separations, Dalgarno and Davison[7] have already given a sufficient review article. Recently, the many-body perturbation theory (MBPT) is developed by Brueckner[8,9] and Goldstone.[10] This is the second-quantized form of the ordinary Rayleigh-Schrodinger perturbation theory except for the normalization condition. Kelly first applied it to an atomic system with excellent successes.[11] Das and his co-workers,[12-16] Kelly,[17] Hata,[18] 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[11,19-22] and molecules H_2O[23] and HF,[24] (ii) for the hyperfine pressure shift of He atom in helium,[25] (iii) for the van der Waals interaction between atoms,[26] (iv) for the hyperfine structure of diatomic molecules,[27,28] 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.[29-32] They are (i) the Hylleraas method,[30-33] in which the interelectronic coordinates r_{ij} are explicitly included in the terms of a wave function, and (ii) the cofiguration-interaction (CI) method,[29,33] in which a wave function is

expanded by means of antisymmetrized products of spin orb-
itals.[34,35] 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.[35] The Hylleraas method is applied to
hydrogen molecule by James and Coolidge,[36] to H_4 system by
Conroy and Malli,[37] and to the atomic systems; (i) He by
Pekeris and his co-workers,[38,39] and by Kinoshita,[40] (ii) Li
by Larsson and his co-workers,[41,42] and by Sims and Hagstrom,[43]
(iii) Be by Sims and Hagstrom[44] and by Perkins,[45] 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 prop-
erties of them. It has been reviewed by Lowdin[46] and by
Nesbet.[47] Very accurate calculations of the method have
been carried out for atoms; (i) Be,[48] C,[49] and Ne[50] by Bunge
and his co-workers, and (ii) B to Ne by Sasaki and Yoshimine.[51]
In the CI method, the spin orbitals mentioned above are usually
not optimized, perhaps, for the sake of labor. Recently,
McWeeny[52] 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[53] or multiconfiguration Hartree-Fock (MC-HF) method.[54]
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[55] and Sugiura[56] is also in the category (b). Goddard and his co-workers[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[58] and Mulliken[59] are united into the MC-SCF method in harmony. The spin-optimized self-consistent-field (SO-SCF) technique proposed by Kaldor and Harris,[60] Lunell,[61] Ladner and Goddard,[62] and Hameed et al.[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,[64,65] (ii) the "atomic Bethe-Goldstone" formulation by Nesbet,[66] (iii) the "coupled electron pair approximation with pair natural orbitals" (CEPA-PNO) technique by Mayer[67] and Ahlrichs, Kutzelnigg, and their co-workers,[68] (iv) the symmetry-adapted work by Platas and Schaefer,[69] in which the basic reference state is the so-called first-order wave function[70] rather than the Hartree-Fock configuration, and many other works. The first idea of these techniques may be due to Rodberg,[71] Nesbet,[72] and Sinanoglu.[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

$$E_c = \sum_{i,j} e(i,j). \tag{2}$$

Sinanoglu[64] discussed why Eq.(2) should be approximately correct. Schaefer[74] 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.[51] This may cause an improved technique (which is named "pair-natural orbitals CI" (PNO-CI) method)[68,75] 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 ^{2}S and ^{2}P states of lithium) and in Chapter IV (for ^{4}S 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 (CH_4, NH_3, and H_2O) 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 functions[76] 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 NH_3 and H_2O.

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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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

$$H= -(1/2)\sum_i \nabla_i^2 - \sum_{iN} \frac{Z_N}{r_{iN}} + \sum_{i>j}\sum \frac{1}{r_{ij}} \quad , \qquad (1)$$

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

$$\Psi= \sum_K \Phi_K a_K \quad , \qquad (2)$$

where a_K are the configuration mixing coefficients to be determined variationally. The Φ_K are constructed by an antisymmetrized product of the component orbitals ϕ_i (or generally by a linear combination of the products for the symmetry considerations). A infinite sum of a complete set of Φ_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 ϕ_i for any finite sum, via the following Euler equations:

$$\sum_K a_K[H_{KL}-\delta_{KL}E]=0 \quad , \qquad (3)$$

$$\sum_j F_{ij}\phi_j= \sum_k \phi_k \varepsilon_{ki} \quad , \qquad (4)$$

where H_{KL} are the matrix ele ents of the Hamiltonian,

$$H_{KL} = \int \Phi_K{}^* H \Phi_L \, d\tau , \qquad\qquad (5)$$

the δ_{KL} are the usual Cronecker's delta, E and ε_{ki} are the
Lagrangean unkown 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 sence 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,[1] is also quitely
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.[2]

The first calculations were carried out by Hartree, Hartree, and Swirles on O atom and its ions.[3] The MC-SCF equation was first derived by McWeeny in his density matrix formalism.[4] 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,[5] (ii) an atomic MC-SCF formulation by Hinze and Roothaan,[6] (iii) the "Optimized Valence Configuration (OVC)" technique by Das and Wahl,[7] and so on. Of course, works without no limitation of configurations were, most recently, carried out by (i) Bagus, Bessis, and Moser[8] for carbon atom, (ii) Sibincic[9] for boron atom, (iii) Ishida and Nakatsuji[10] for lithium atom, (iv) Bagus and Bauche[11] for atoms, B, C, O, and F, (v) Wagner, Das, and Wahl[12] for ArH system, (vi) Das[13] for CN radical molecule, (vii) Das, Janis, and Wahl[14] for diatomic systems CN and AlO, and (viii) Ishida[15] for nitrogen atom. The applications of the above OVC technique have been reviewed up to 1969 in the review article by Wahl and Das.[16]

There is a numerical dificulty 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[6] and Huzinaga[17] (a multi-dimensional Newton-Raphson procedure), (ii) Chang and Grein,[18] Golebiewski and Nowak-Broclawik,[19] Mukherjee,[20] and Hinze[21] (a two-by-two rotation method), (iii) Das and Wahl,[7,22] and Wood and Veillard[23] (a modified single-vector diagonal-

ization technique), (iv) Hinze[21] (a Gauss-Seidel procedure), and (v) Levy[24] (a stepest decent method). Among them, the modified single-vector diagonalization technique by Wood and Veillard[23] seems to be most promising as long as the author studied (though the Levy's stepest decent method was not tried).

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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

$$\Psi = \sum_K a_K \Phi_K \qquad (1)$$

is optimized with respect to both the configurational coefficients a_K and the component orbitals in the configurations Φ_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 $[s_z \delta]$) 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:

$$\Phi_1 = |1s\bar{1}s2p_+| , \qquad \Phi_2 = |2s\bar{2}s2p_+| ,$$

and

$$\Phi_3 = 6^{-1/2} [2|2s1s\bar{2p_+}| - |2s\bar{1}s2p_+| - |\bar{2}s1s2p_+|] ,$$

where Φ_1 is the Hartree–Fock configuration which gives the reference state for taking into account electron correlation effects. Φ_2 is the P doublet configuration arising from two-electron excitation from the 1s to the 2s orbital, and Φ_3 is the singly excited configuration (this could contribute to $[s_z \delta]$ 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 $[s_z \delta]$ 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;

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

where $0 < |\theta| \ll \pi/2$. Then, an MC SCF wavefunction $\Psi[2C]$ consisting of the two configurations Φ_1 and Φ_2 is transformed to

$$\Psi[2C] = a_1 \Phi_1 + a_2 \Phi_2 = (N/2)|u_+ u_- 2p_+ (\alpha\beta - \beta\alpha)\alpha| , \qquad (3)$$

where $a_1 = N \cos^2\theta$, $a_2 = -N \sin^2\theta$ and N is the normalization constant. Eq. (3) means that configuration Φ_2 causes the radial splitting of the 1s orbital in Φ_1 and that the split orbitals u_+ and u_- are occupied by an electron of α and/or β 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

Configuration	$[s_z \delta]$ (au)	Energy (au)	Virial theorem	Ref.
2 conf. (Φ_1 and Φ_2)	0	−7.380082	2.000174	a)
2 conf. (Φ_1 and Φ_3)	−0.01402	−7.365088	2.000033	b)
3 conf. (Φ_1, Φ_2 and Φ_3)	−0.01693	−7.380087	2.000173	a)
nearly full CI within S		−7.379062		[7]
experimental	−0.01693 ± 0.00020	−7.41013		[8]

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

Configuration	$[s_z \delta]$ (au)	Energy (au)	Virial theorem	Ref.
3 conf.	0.2139	−7.4465527	1.999988	a)
5 conf.	0.2265	−7.4475648	1.999990	a)
7 conf.	0.2265	−7.4475654	1.999990	a)
nearly full CI within S		−7.44754		[7]
experimental	0.2313	−7.47805		[5]

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

Φ_3 can be rewritten as

$$\Phi_3 = N' |u_+ u_- 2p_+ (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)| , \qquad (4)$$

where N' is the normalization constant. Then, the MC SCF wavefunction consisting of three configurations, Φ_1, Φ_2 and Φ_3 can be expressed as

$$\Psi[3C] = a_1 \Phi_1 + a_2 \Phi_2 + a_3 \Phi_3$$
$$= |u_+ u_- 2p_+ [(Nc_1/2)(\alpha\beta - \beta\alpha)\alpha \qquad (5)$$
$$+ N'c_2(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)]| ,$$

where $a_1 = Nc_1 \cos^2\theta$, $a_2 = -Nc_1 \sin^2\theta$ and $a_3 = c_2$. As seen in the last term of eq. (5), there arises some probability that each of the split orbitals is occupied by an α-spin electron. That is, the additional configuration Φ_3 causes a slight imbalance in the occupational probabilities of α and β electrons in the split 1s orbitals by the effect of the unpaired electron in the 2p$_+$ 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

* By the "S-character", we denote a nodeless character at an origin (nucleus).

may be sufficiently reproduced by $\Psi[3C]$. As only an S-character could contribute to the $[s_z \delta]$, $\Psi[3C]$ should give a good $[s_z \delta]$. 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 $[s_z \delta]$ 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 $[s_z \delta]$†.

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;

$$\Phi_1 = |1s\overline{1s}2s| , \quad \Phi_2 = |3s\overline{3s}2s| ,$$

$$\Phi_3 = 6^{-1/2} [2|3s1s\overline{2s}| - |3s\overline{1s}2s| - |\overline{3s}1s2s|] ,$$

$$\Phi_4 = |1s\overline{1s}3s| , \quad \Phi_5 = |1s\overline{3s}3s| ,$$

$$\Phi_6 = |1s\overline{2s}2s| , \quad \Phi_7 = |3s\overline{2s}2s| .$$

The results are summarized in table 2. First, we take up the first three configurations on the simple analogy

† This agrees with the conclusion in ref. [3].

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of the previous discussion of the P doublet state. However, this wavefunction gives a poor $[s_z \delta]$ 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

$$\sum_{j=1}^{3} |js\rangle f_j , \qquad (6)$$

with certain coefficients f_j so that we have two configurations, Φ_4 and Φ_5, in addition to the original three ones. The configuration Φ_4 corrects the 2s orbital in Φ_1 as follows:

$$a_1 \Phi_1 + a_4 \Phi_4 = |1s1s2s'| , \qquad (7)$$

where the corrected orbital is

$$|2s'\rangle = |2s\rangle a_1 + |3s\rangle a_4 . \qquad (8)$$

The configuration Φ_5 can be interpreted as the intershell 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 Φ_4 and Φ_5 becomes important (spin-delocalization contribution [2]). Indeed, table 2 shows that the wavefunction of the five configurations gives the good $[s_z \delta]$ 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 Φ_4 and Φ_5 may be ignored just as in the case of the P doublet state of the Li atom. We further investigate two other configurations, Φ_6 and Φ_7. Table 2 indicates that these two additional configurations play no important role for the $[s_z \delta]$. This suggests that one can disregard the internal correlation of Φ_6 and the semi-internal

one of Φ_7 in comparison with the important semi-internal correlation included in Φ_3.

In both doublet states of P and S of the Li atom, the $[s_z \delta]$ can be described excellently by the MC SCF method. Therefore, it appears that a physical mechanism for providing contributions mainly to the $[s_z \delta]$ 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 α electron in each split orbital is different, to a certain extent, from that of β 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 Φ_4, and the intershell correlation contribution, like Φ_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.

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CHAPTER IV

CORE RADIAL-POLARIZATION AND THE CONTACT HYPERFINE STRUCTURE

OF

^{4}S STATE OF NITROGEN

Core radial-polarization and the contact hyperfine

structure of ^{4}S state of nitrogen

The contact hfs constant for the ^{4}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 ^{4}S
state of nitrogen as well as for the ^{2}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 $[s_z\delta]$);

$$[s_z\delta] = <LSJM|\Sigma 2s_z\delta(r_i)/(4\pi r_i^2)|LSJM>, \quad (J=M=L+S). \quad (1)$$

Atomic units are used throughout this paper.

Two main approaches to improve the value of $[s_z\delta]$ 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,[1,2] Das and co-workers,[3-8] Nesbet,[9,10] Hata,[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.[12-20] They may be well reviewed up to 1968 in the article of Schaefer, Klemm, and Harris.[19] Larsson achieved very acculate calculations for lithium, using the Hylleraas-type trial functions.[17]

Schaefer, Klemm, and Harris[20] obtained rather good values

of spin densities for the atoms B to F with their "polar-

ization wave functions." They used a trial wave function

in the form of superposition of configurations. However,

the component orbitals were not optimized. Freed[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,[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 canbe 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 ls-orbital is mainly caused by the pair-correlation

of the ls 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 skeched 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.[22] 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) $1s^2 \rightarrow s_I^2$,

(ii) $1s \rightarrow s_I$,

(iii) $2s^2 \rightarrow s_{II}^2$,

(iv) $2s \rightarrow s_{II}$.

We imagine in our mind that the orbitals, s_I and s_{II}, can be represented adequately by a linear combination of the MCSCF orbitals, 3s and 4s. The orbitals, s_I 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 Φ_0);

Φ_1 : $1s^2 \rightarrow 3s^2$,

Φ_2 : $1s^2 \rightarrow 4s^2$,

Φ_3 : $1s^2 \rightarrow 3s,4s[(3s4s)^1S]$,

Φ_4 : $2s^2 \rightarrow 3s^2$,

Φ_5 : $2s^2 \rightarrow 4s^2$,

Φ_6 : $2s^2 \rightarrow 3s,4s[(3s4s)^1S]$,

Φ_7 : $1s \rightarrow 3s[(1s3s)^3S]$,

Φ_8 : $1s \rightarrow 4s[(1s4s)^3S]$,

Φ_9 : $2s \to 3s[(2s3s)^3S]$,

Φ_{10}: $2s \to 4s[(2s4s)^3S]$,

where Φ_1 to Φ_6 take account of radial pair-correlations and no account of any coupling between core and 2p electrons: While Φ_7 to Φ_{10} take those couplings into account. The configurations which arise from the excitations, $1s \to 3s[(1s3s)^1S]$ 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 occurr independently, because no coupling between 1s and 2s is considered explicitly.

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

(v) $\quad 1s,2s \to s_I^2[(1s2s)^1S]$,

(vi) $\quad 1s,2s \to s_{II}^2[(1s2s)^1S]$,

(vii) $1s,2s \to s_I,s_{II}[(1s2s)^1S(s_Is_{II})^1S]$ and
$$[(1s2s)^3S(s_Is_{II})^3S]^1S.$$

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

Φ_{11} : $1s,2s \to 3s,4s[(1s2s)^1S(3s4s)^1S]$,

Φ_{12} : $1s,2s \to 3s,4s[(1s2s)^3S(3s4s)^3S]^1S$,

Φ_{13} : $1s,2s \to 3s^2[(1s2s)^1S]$,

Φ_{14} : $1s,2s \to 4s^2[(1s2s)^1S]$.

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.[25] In order to resolve the ambiguity, we take out the two configurations of Φ_{13} and Φ_{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 ^4S state of nitrogen. In the table, the 13-term wave function is the one which is obtained in the preceeding section. The 9-term function contains the 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 Φ_{11} and Φ_{12} 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;

$$\Phi_{15}: \quad 1s \to 3s\,[(1s3s)^1S] \ ,$$
$$\Phi_{16}: \quad 1s \to 4s\,[(1s4s)^1S] \ ,$$
$$\Phi_{17}: \quad 2s \to 3s\,[(2s3s)^1S] \ ,$$
$$\Phi_{18}: \quad 2s \to 4s\,[(2s4s)^1S] \ .$$

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 preceeding 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, varing 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 preceeding 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.[22] The weight-difference is caused by the singly-excited configurations of Φ_7 to Φ_{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.[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[26] 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[5] 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,[21] we attempt to interprete 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.[5], since our wave function takes no account of s→d type contributions.

Acknowledgments

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';

$$
\begin{vmatrix} 1s' \\ 2s' \\ 3s' \\ 4s' \end{vmatrix} = U \begin{vmatrix} 1s \\ 2s \\ 3s \\ 4s \end{vmatrix} , \tag{A1}
$$

where

$$
U = \begin{vmatrix} \cos\theta & \sin\theta & 0 & 0 \\ -\sin\theta & \cos\theta & 0 & 0 \\ 0 & 0 & \cos\omega & \sin\omega \\ 0 & 0 & -\sin\omega & \cos\omega \end{vmatrix} . \tag{A2}
$$

Clearly, U is an orthogonal transformation. The parameters θ and ω are entirely arbitrary. Then, we find the wave function Ψ, which contains 19 configurations of Φ_0 to Φ_{18}, is invariant under U; i.e.,

$$
\Psi' = \sum_{K=0}^{18} a_K' \Phi_K' = \Psi = \sum_{K=0}^{18} a_K \Phi_K , \tag{A3}
$$

where

$$
\begin{vmatrix} \Phi_0' \\ \Phi_1' \\ \Phi_2' \\ \vdots \\ \Phi_{18}' \end{vmatrix} = T \begin{vmatrix} \Phi_0 \\ \Phi_1 \\ \Phi_2 \\ \vdots \\ \Phi_{18} \end{vmatrix} , \tag{A4}
$$

$$
\begin{vmatrix} a_0' & a_1' & \dots & a_{18}' \end{vmatrix} = \begin{vmatrix} a_0 & a_1 & \dots & a_{18} \end{vmatrix} T^{-1} , \tag{A5}
$$

$$
T = \left|
\begin{array}{*{13}{c}}
1 \\[2pt]
& c^2\gamma^2 & c^2\sigma^2 & c^2\tau & s^2\gamma^2 & s^2\sigma^2 & s^2\tau & & & & t\tau & -t\gamma^2 & -t\sigma^2 \\
& c^2\sigma^2 & c^2\gamma^2 & -c^2\tau & s^2\sigma^2 & s^2\gamma^2 & -s^2\tau & & & & -t\tau & -t\sigma^2 & -t\gamma^2 \\
& -c^2\tau & c^2\tau & c^2\alpha^2 & s^2\tau & -s^2\tau & s^2\alpha^2 & & & & -t\alpha^2 & -t\tau & t\tau \\
& s^2\gamma^2 & s^2\sigma^2 & -s^2\tau & c^2\gamma^2 & c^2\sigma^2 & c^2\tau & & & & -t\tau & t\gamma^2 & t\sigma^2 \\
& s^2\sigma^2 & s^2\gamma^2 & s^2\tau & c^2\sigma^2 & c^2\gamma^2 & -c^2\tau & & & & t\tau & t\sigma^2 & t\gamma^2 \\
& -s^2\tau & s^2\tau & s^2\alpha^2 & -c^2\tau & c^2\tau & c^2\alpha^2 & & & & t\alpha^2 & t\tau & -t\tau \\
& & & & & & & c\gamma & c\sigma & s\gamma & s\sigma \\
& & & & & & & -c\sigma & c\gamma & -s\sigma & s\gamma \\
& & & & & & & -s\gamma & -s\sigma & c\gamma & c\sigma \\
& & & & & & & s\sigma & -s\gamma & -c\sigma & c\gamma \\
-t\tau & t\tau & t\alpha^2 & t\tau & -t\tau & -t\alpha^2 & & & & a^2\alpha^2 & -a^2\tau & a^2\tau \\
& & & & & & & & 1 \\
t\gamma^2 & t\sigma^2 & t\tau & -t\gamma^2 & -t\sigma^2 & -t\tau & & & & a^2\tau & a^2\gamma^2 & a^2\sigma^2 \\
t\sigma^2 & t\gamma^2 & -t\tau & -t\sigma^2 & -t\gamma^2 & t\tau & & & & -a^2\tau & a^2\sigma^2 & a^2\gamma^2 \\
& & & & & & & & & c\gamma & c\sigma & s\gamma & s\sigma \\
& & & & & & & & & -c\sigma & c\gamma & -s\sigma & s\gamma \\
& & & & & & & & & -s\gamma & -s\sigma & c\gamma & c\sigma \\
& & & & & & & & & s\sigma & -s\gamma & -c\sigma & c\gamma
\end{array}
\right| , \quad (A6)
$$

$c=\cos\theta$, $s=\sin\theta$, $\gamma=\cos\omega$, $\sigma=\sin\omega$, $t=\sqrt{2}cs$, $\tau=\sqrt{2}\gamma\sigma$, $a^2=c^2-s^2$, $\alpha^2=\gamma^2-\sigma^2$, 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 Ψ 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.,

$$0=a_{13}'=t[\gamma^2(a_1-a_4)+\sigma^2(a_2-a_5)+\tau(a_3-a_6)]+a^2[a_{11}\tau+a_{13}\gamma^2+a_{14}\sigma^2],$$

$$0=a_{14}'=t[\gamma^2(a_2-a_5)+\sigma^2(a_1-a_4)+\tau(a_6-a_3)]+a^2[a_{13}\sigma^2+a_{14}\gamma^2-a_{11}\tau].$$

$$(A7)$$

This allows us to determine the arbitrary parameters θ and ω. After manipulating Eq. (A7), we have

$$\tan2\theta=\frac{-\sqrt{2}(a_{13}+a_{14})}{a_1+a_2-a_4-a_5}, \qquad (A8)$$

$$\tan2\omega=\frac{\sqrt{2}[a_{14}(a_1-a_4)-a_{13}(a_2-a_5)]}{(a_1+a_2-a_4-a_5)a_{11}-(a_{13}+a_{14})(a_3-a_6)}. \qquad (A9)$$

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 Φ_{13} and Φ_{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 Φ_0 to Φ_{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 Φ_0 to Φ_6 and Φ_{11} to Φ_{14}.

Another possibility for resolving the orbital ambiguity is briefly discussed below: We can drop Φ_3 and Φ_6 instead of Φ_{13} and Φ_{14} in the 19-term function by determining the

arbitrary parameters by the following equations;

$$\tan 2\theta = \frac{\sqrt{2}\,[a_3\,(a_4-a_5)-a_6\,(a_1-a_2)]}{(a_1-a_2+a_4-a_5)a_{11}-(a_{13}-a_{14})(a_3+a_6)} \quad , \quad (A10)$$

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

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.)

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2p-orbital($m = +1$)

Polarized 1s-orbitals
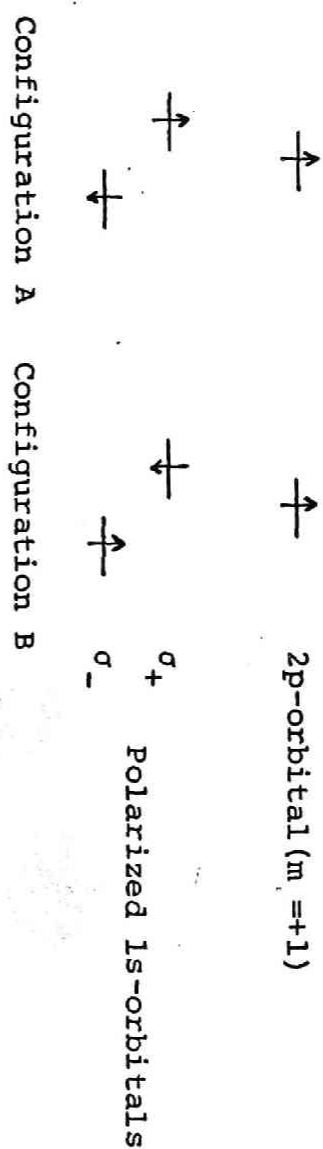
σ_+

σ_-

Configuration A   Configuration B

FIG. I. Two main configurations for the ^{2}P state of lithium. The relation between the radially-polarized orbitals(σ_+ and σ_-) and the MCSCF orbitals(1s and 2s) is completely given in Ref. 22.

TABLE I.   Total electronic energies and spin densities for the ^{4}S state of N atom obtained from the MCSCF wave functions in comparison with the experimental value.

Wave function	Energy(a.u.)	Spin density(a.u.)	Reference
MCSCF 9-term	-54.417045	0.0	present
11-term	.420557	.0634	present
13-term	.421704	.0977	present
17-term	.421704	.0978	present
Radial limit	.42225	——	Ref. 26
Experimental	.5892	.0972	Ref. 5

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.

Basis(exponent)	1s-orbital	2s-orbital	3s-orbital	4s-orbital
1s(7.02)	.89945	-.35515	.9984	-.9513
	.88079	-.39968	1.0365	-.9529
3s(8.20)	.05525	-.02159	-2.3714	1.6612
	.05410	-.02457	-2.7120	1.5570
3s(5.49)	.03768	.07361	1.5179	-1.1471
	.04147	.07313	1.9621	-.9875
3s(3.438)	.07264	.47267	.0453	1.4397
	.09588	.46861	.2342	1.5740
3s(2.054)	.08210	.48845	.5614	-1.0224
	.10819	.49582	-.3181	-1.6066
3s(1.03)	.02025	.14415	-2.9787	-.3715
	.01849	.10315	-1.2488	.9120
4s(1.13)	-.01183	-.08735	2.0947	.1737
	-.01065	-.06210	.8982	-.7144

CHAPTER V

AB INITIO POTENTIAL CURVES

OF

THE BOND-DISSOCIATIONS OF XH_n MOLECULES:

CH_4, NH_3, AND H_2O

Ab initio potential curves of the bond dissociations of XH_m

molecules: CH_4, NH_3, and H_2O

The lowest potential curve of the dissociation of an

X-H bond of an XH_m molecule is calculated for CH_4, NH_3, and

H_2O 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 CH_4 (0.1656 for NH_3 and 0.1589 for H_2O), which is in

good agreement with the experimental value of 0.1619 (0.1610

for NH_3 and 0.1879 for H_2O), 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 asymtotic 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[1-5] calculated the potential curves of the bond-dissociation (or the 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.[1] It seems that the potential energy curves have been described properly in chemical accuracy through their pioneering works on H_2,[2] Li_2,[3] F_2,[4] OH,[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_4, NH_3, and H_2O 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)[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 framwork of MCSCF method. This use was first suggested by Gilbert[7,8] and Levy.[9] We will call hereafter this something as "MCSCF LMO", following Levy.[9] 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 CH_4, NH_3, and H_2O 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

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

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_α is the position vector of the α-th nucleus (which is fixed while asking for the eigenstate of the Hamiltonian). The MCSCF method is well known in the literatures.[1,10,11] Then it can be briefly sketched as follows: The wave function is expanded in terms of certain configurations,

$$\Psi= \sum_K \Phi_K a_K , \qquad (2)$$

where a_K is the mixing coefficient of a configuration Φ_K. The component orbitals ϕ_i of the Φ_K are expanded by means of basis functions χ_p;

$$\phi_i = \sum_p \chi_p c_{pi} , \qquad (3)$$

The ϕ_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 tecnique 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[14]) centered at the nucleus X and of the "STO-4G" functions[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_m molecule; for CH_4, tetrahedral valence angle and C-H=1.09A (where A=10^{-10} m throughout this paper), H-N-H=106.6° and N-H=1.01A for NH_3, and H-O-H=104.45° and O-H=0.96A for H_2O. 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_4. For CH_4, a planner geometry of the residual CH_3 is used when the length of a C-H bond is longer than 3A. The length of a C-H bond of the CH_3 is fixed at 1.09A.

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[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[12] goes into a vibrational divergence.
At small distace, 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 convinient 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 $1s(X)$, 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

$$1s(X)^2\sigma(X-H_1)^2...\sigma(X-H_m)^2n_1(X)^2...n_{4-m}(X)^2$$

(which is the usual Hartree-Fock configuration) and

$$1s(X)^2\sigma(X-H_1)^2...\sigma^*(X-H_m)^2n_1(X)^2...n_{4-m}(X)^2$$

(which is a doubly-excited configuration arising from the pair excitation from $\sigma(X-H_m)$ to $\sigma^*(X-H_m)$; from a bonding to its anti-bonding orbital excitation). Thus the two-config-uration wave function (denoted as $\Psi[2C]$) can be expressed by

$$\Psi[2C]= a_1|(\text{other part})\sigma(X-H_m)\bar{\sigma}(X-H_m)|$$
$$+a_2|(\text{other part})\sigma^*(X-H_m)\bar{\sigma}^*(X-H_m)|. \qquad (4)$$

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-1} 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.,

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

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 $\Psi[VB]$ is equivalent to $\Psi[2C]$, provided

$$\sigma(X-H_m) = c_1 \chi(X) + c_2 \chi(H) , \quad (6)$$
$$\sigma^*(X-H_m) = c_3 \chi(X) + c_4 \chi(H) , \quad (7)$$

where

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

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 asymtotically to the following simple relations;

$$c_4 = -c_1, \quad c_3 = c_2, \quad \text{and} \quad c_1{}^2 + c_2{}^2 = 1 . \qquad (15)$$

The above equlity 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 asymtotic relations are obtained

$$\sigma(X-H_m) \sim (1/\sqrt{2})\chi(X) + (1/\sqrt{2})\chi(H) , \qquad (16)$$

$$\sigma^*(X-H_m) \sim (1/\sqrt{2})\chi(X) - (1/\sqrt{2})\chi(H) , \qquad (17)$$

$$\Psi[VB] \sim (1/\sqrt{2}) | (\text{other part}) [\chi(X)\overline{\chi}(H) - \overline{\chi}(X)\chi(H)| , \qquad (18)$$

$$\Psi[2C] \sim (1/\sqrt{2}) | (\text{other part}) \sigma(X-H_m)\overline{\sigma}(X-H_m) |$$
$$- (1/\sqrt{2}) | (\text{other part}) \sigma^*(X-H_m)\overline{\sigma}^*(X-H_m) | . \qquad (19)$$

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, ...,m) to $\sigma^*(X-H_i)$ (i=1,2,...,m) other than from $\sigma(X-H_m)$ to $\sigma^*(X-H_m)$. This represents a 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 $n_i(X)$ $(i=1,\ldots,4-m)$ to $\sigma^*(X-H_i)$ $(i=1,\ldots,m)$ and to $v_i(XH_m)$ $(i=1,\ldots,4-m)$ and from $\sigma(X-H_i)$ $(i=1,\ldots,m)$ to $v_i(XH_m)$ $(i=1,\ldots,4-m)$ 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 8A. The usual SCF process of the Hartree-Fock method is not converged at a large distance. The preceeding 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 8A distance of an X-H bond, because the potential energies in these tables show that the distance of 8A can be regarded as infinite. The estimated well depths are 0.1707, 0.1656, and o.1589 (in a.u.) for CH_4, NH_3, and H_2O, 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_2O.

(4) An asymtotic 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.

C-H distance(in A)	Wave function		
	Hartree-Fock	$\Psi[2C]$[a]	17-configuration[b]
1.09	−40.1744	−40.1902	−40.2353
1.5	.1145	.1443	.1876
1.7	.0721	.1116	.1536
2.0	.0105	...	.1089
2.4	−39.9389	.0338	.0682
3.0	not converged	.0243	.0515
4.0	not converged	.0197	.0416
8.0	not converged	.0195	.0396
Energy difference[c]	...	.1707	.1957

[a] See Eq.(4). [b] See section IV. [c] The difference between energies at 8A and at 1.09A.

TABLE II. Adiabatic potentials obtained from the Hartree-Fock and from several MCSCF wave

functions for NH_3 molecule. Energies are in atomic units.

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

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

TABLE III. Adiabatic potentials obtained from the Hartree-Fock and from several MCSCF wave functions for H_2O molecule. Energies are in atomic units.

O-H distance (in A)	Wave function			
	Hartree-Fock	$\psi[2C]$[a]	5-configuration[b]	17-configuration[b]
0.96	-75.9883	-76.0105	-76.0321	-76.0512
1.2	.9589	-75.9919	...	...
1.4	.9090	.9535	-75.9784	...
1.8	not converged	.8951	.9134	...
2.0	not converged	.8763	.8935	...
4.0	...	.8516	.8615	...
8.0	...	.8516	.8615	-75.8647
Energy difference[c]	...	.1589	.1706	.1865

a See Eq.(4).   b See section IV.   c The difference between energies at 8A and at 0.96A.

an X-H bond is very good as is discussed in the preceeding section. Table IV shows this asymtotic behavior. The a_2 defined by Eq.(4) becomes asymtotically 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 preceeding 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.[5] for OH molecule. For H_2O 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_2O, 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.[5] for OH, by Bender and Schaefer[17] for NH_2, and by Driessler et al.[18] 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.

C-H distance[a]	a_2 for CH_4	N-H distance[a]	a_2 for NH_3	O-H distance[a]	a_2 for H_2O
1.09	-.097	1.01	-.102	0.96	-.111
1.5	-.177	1.2	-.139	1.2	-.167
1.7	-.229	1.5	-.220	1.4	-.227
2.4	-.456	1.8	-.328	1.8	-.386
3.0	-.602	2.0	-.409	2.0	-.465
4.0	-.685	4.0	-.699	4.0	-.702
8.0	-.707	8.0	-.707	8.0	-.707

[a] This is in A ($A=10^{-10}$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.
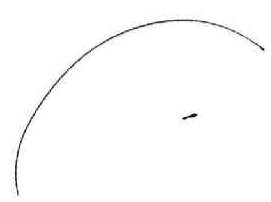
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CHAPTER VI

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 multiconfigration
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_2O 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.[1-15] It is one of the most powerful method in order to take electron correlation into account for the systems. So-called "Complete Multiconfiguration SCF" (CMC-SCF) formalism[13] seems to be most popular for dealing with the ground state of a closed-sell molecule.

Recently, Levy pointed out that the use of "MC-SCF localized molecular orbitals" (MC-SCF LMO)[16] is more efficient in the CMC-SCF method than that of symmetry-adapted orbitals for Formaldehyde, CH_4, C_2H_6, and C_2H_4.[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_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.[18] He tried to represent pairs
of electrons by the use of floating spherical Gaussian orbit-
als.[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_3 and H_2O 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.[13]
It is sketched as follows: The wave function of a given system
can be expanded in terms of certain configurations; i.e.,

$$\Psi = a_{00}\Phi_{00} + \sum_{tu} a_{tu}\Phi_{tu} , \tag{1}$$

where Φ_{00} is a Hartree-Fock configuration, Φ_{tu} is a doubly-excited
configuration from the orbital ϕ_t (which is doubly occupied in
Φ_{00}) to ϕ_u (which is unoccupied in Φ_{00}), and a_{00} and a_{tu} are
certain expansion coefficients. The all component orbitals
(e.g., ϕ_t and ϕ_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."[13] In order to solve them, we adopt
here a two-by-two rotation method by Hinze.[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 "α" of an STO-3G func-
tion used here are given by Stewart.[21] The STO-3G functions of
1s-type are also used as floatig spherical Gaussians to be added
to the above basis-sets. For NH_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_2O molecule. Their floated centers are
indicated by parameters r and θ which are seen in Fig. 1.
Orbital exponents and floating centers of the above 1s-functions
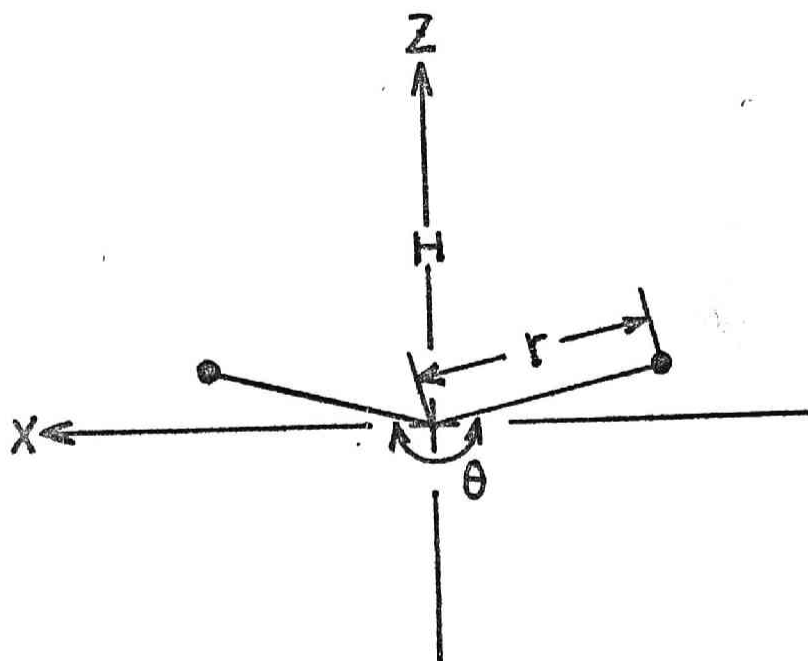are roughly optimized for each molecule. The other exponents

FIG. 1. The coordinates of the centers of two floating functions in H_2O molecule. Each center is indicated by a solid circle and is on the x-z plane. The H in the figure indicates the projected posion 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=1.01A, 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_2O, 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 1.3A (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 1.15A 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 1s-basis.

(3) The most contribution to the wave function is obtained from the excitation from the orbital σ(NH) to the corresponding σ*(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 σ-σ* 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]

Basis set	E_{HF} (a.u.)[b]	E_{MC} (a.u.)[c]
Without floating function	−55.444588	−55.494363
Added floating function at origin	.461595	.512168
at z=1.01A	.477320	.529003
at z=1.2625A	.477949	.529230
at z=1.515A	.474841	.525516

[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 II. Variation with respect to the orbital exponent of the floating function centered at z=1.2625A for NH_3 molecule. Notations are explained in Table I.

Orbital exponent(a.u.)	E_{HF}(a.u.)	E_{MC}(a.u.)
0.5	-55.476235	-55.527061
0.6	.477949	.529230
0.7	.476137	.527615

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=1.2625A with $\zeta=0.6$) is added to the minimal basis-set. The determinant Φ_{tu} corresponding to a given a_{tu} is obtained by exciting two electrons of Φ_{00} from the orbital ϕ_t to ϕ_u.

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ϕ_t \ ϕ_u	$\sigma^*(NH_1)$	$\sigma^*(NH_2)$	$\sigma^*(NH_3)$	NBEO[a]
$\sigma(NH_1)$	-.0902	-.0067	-.0067	-.0021
$\sigma(NH_2)$	-.0067	-.0902	-.0067	-.0021
$\sigma(NH_3)$	-.0067	-.0067	-.0902	-.0021
lone-pair	-.0148	-.0148	-.0148	-.0392

$$a_{00} = .9865$$

[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.

ϕ_t \ ϕ_u	$\sigma^*(NH_1)$	$\sigma^*(NH_2)$	$\sigma^*(NH_3)$
$\sigma(NH_1)$	-.0927	-.0067	-.0067
$\sigma(NH_2)$	-.0067	-.0927	-.0067
$\sigma(NH_3)$	-.0067	-.0067	-.0927
lone-pair	-.0170	-.0170	-.0170
a_{00}= .9865			

TABLE V. MC-SCF localized orbitals of NH_3 when the floating function (center at z=1.2625A with ζ=0.6) is added to the minimal basis-set; orbital energies and occupation numbers are listed in first two lines.

	1s(N)	$\sigma(NH_1)$	$\sigma(NH_2)$	$\sigma(NH_3)$	lone-pair	$\sigma^*(NH_1)$	$\sigma^*(NH_2)$	$\sigma^*(NH_3)$	NBEO[a]
ε	-15.392	-.72852	-.72852	-.72852	-.60786	-.01441	-.01441	-.01441	-.00264
occ. num.	2.0	1.98356	1.98356	1.98356	1.99560	.01688	.01688	.01688	.00310
N 1s	.99527	.08019	.08019	-.08019	.16640	.09520	.09520	.09520	.07205
2s	.02716	-.25099	-.25099	.25099	-.70929	-.70838	-.70838	-.70838	-.49957
$2p_x$	.0	-.49052	.24526	-.24526	.0	-.86012	.43006	.43006	.0
$2p_y$	.0	.0	-.42480	-.42480	.0	.0	-.74488	.74488	.0
$2p_z$	-.00924	.32225	.32225	-.32225	-.61814	.35059	.35059	.35059	-.46853
H_1 1s	-.00725	-.52049	.08279	-.08279	.03231	1.25513	.01017	.01017	-.07241
H_2 1s	-.00725	.08279	-.52049	-.08279	.03231	.01017	1.25513	.01017	-.07241
H_3 1s	-.00725	.08279	.08279	.52049	.03231	.01017	.01017	1.25513	-.07241
Floating	-.00484	.08043	.08043	.08043	-.17513	-.10072	-.10072	-.10072	1.18211

[a] The non-bonding excited-orbital, see text.

TABLE VI. MC-SCF localized orbitals of NH₃ when the minimal basis-set is used; orbital energies and occupation numbers are also listed in first two lines.

|	1s(N)	lone-pair	σ(NH₁)	σ(NH₂)	σ(NH₃)	σ*(NH₁)	σ*(NH₂)	σ*(NH₃)
ε	-15.295	-.67993	-.66340	-.66340	-.66340	-.01445	-.01445	-.01445
occ. num.	2.0	1.99826	1.98265	1.98265	1.98265	.01793	.01793	.01793
N 1s	-.99889	-.17268	-.06152	-.06152	-.06152	.09964	.09964	.09964
2s	-.01043	.82572	.15400	.15400	.15400	-.73676	-.73676	-.73676
2pₓ	.0	.0	.47780	.23890	-.23890	-.86725	.43362	.43362
2p_y	.0	.0	.0	-.41379	-.41379	.0	-.75106	.75106
2p_z	.02216	.59402	-.38841	.38841	.38841	.32873	.32873	.32873
H₁ 1s	.00811	-.00027	.53286	.08868	-.08868	1.23494	-.00100	-.00100
H₂ 1s	.00811	-.00027	.08868	-.53286	-.08868	-.00100	1.23494	-.00100
H₃ 1s	.00811	-.00027	-.08868	-.08868	.63286	-.00100	-.00100	1.23494
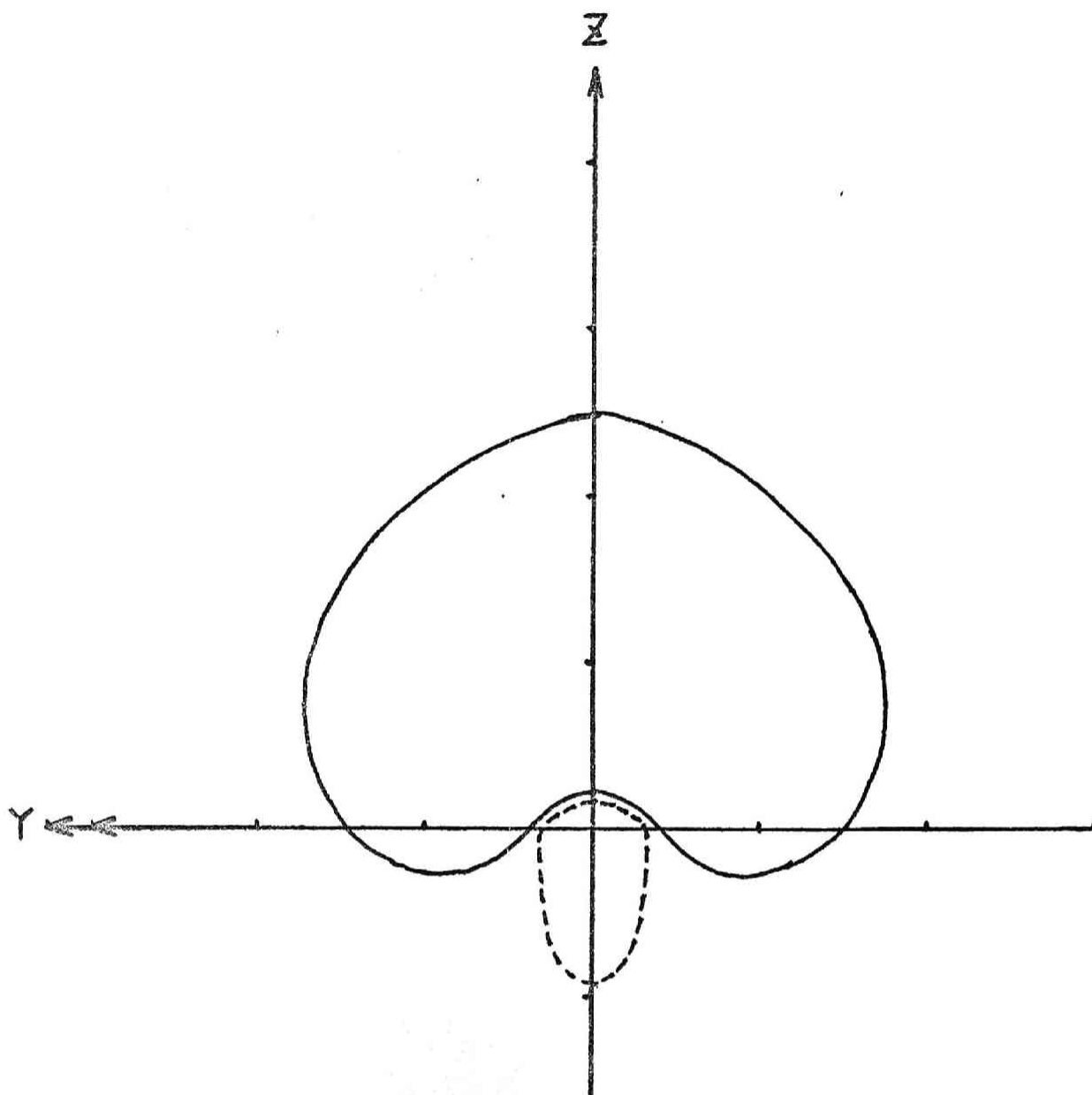
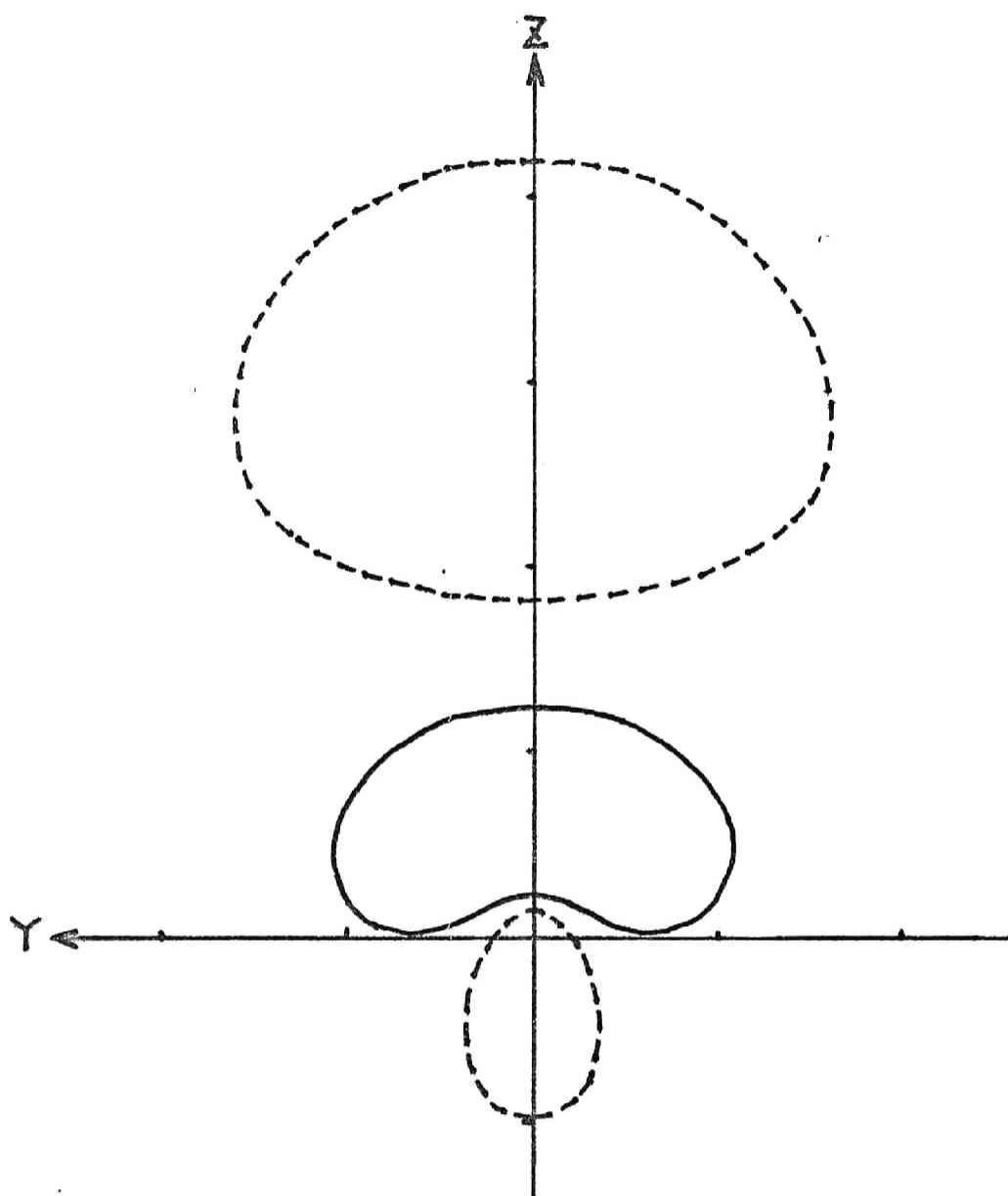FIG. 2. Non-bonding orbital listed in Table V for NH_3 molecule. For coordinates used, see text.

FIG. 3. Non-bonding excited orbital listed in Table V for 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[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_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 follow-
ings are the most significant points:

(1) The CMC-SCF energy is varied very slowly around the minimum
point (about r=0.72A and θ=205°) 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[22]).   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 σ-σ* excitation contributes most sognificantly 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 2pπ-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 σ-type to the correspond-
ing one plays no impotant 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 2pπ-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=0.72A)[a] for H_2O molecule.

θ (deg.)[a]	E_{HF} (a.u.)[b]	E_{MC} (a.u.)[b]
104.45	-74.955767	-75.083492
125	-75.043747	.090157
145	.049198	.095686
165	.053455	.101345
180	.055685	.103879
195	.056978	.105442
205	.057281	.105899
215	.057114	.105857
235	.055300	.104177

[a] See Fig. 1 for the parameters r and θ. The ζ 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
(ζ=0.6 and r=0.96A) for H_2O molecule.   Notations are explained
in Table VII.

θ (deg.)	E_{HF} (a.u.)	E_{MC} (a.u.)
104.45	-75.041722	-75.087382
125	.047557	.093517
145	.051833	.097926
165	.054493	.102024
180	.055346	.103256
195	.055203	.103431
205	.054566	.102960

TABLE IX. Variation with respect to the centers of floating functions ($\zeta = 0.6$ and $\theta = 205^{\circ}$) for H_2O molecule. Notations are explained in Table VII.

r (A)	E_{HF} (a.u.)	E_{MC} (a.u.)
0.48	−75.052369	−75.097336
0.72	.057281	.105899
0.96	.054566	.102961

TABLE X. Variation with respect to the orbital exponents of the floating

functions centered at r=0.72A and $\theta=205^{\circ}$ for H_2O molecule.

The parameters r and θ are indicated by Fig. 3.

Orbital exponent(a.u.)	E_{HF} (a.u.)	E_{MC} (a.u.)
0.0[a]	-74.946706	-74.990058
0.4	-75.038980	-75.086442
0.5	.051918	.100048
0.6	.057281	.105899
0.7	.055178	.104270
0.8	.047002	.096559

[a] Without floating functions.

TABLE XI. Expansion coefficients a_{00} and a_{tu} in the CMC-SCF wave-function

for H_2O molecule when the floating functions (centered at r=0.72A

and $\theta=205^{\circ}$ with $\zeta=0.6$) are added to the minimal basis-set.

Notations are explained in Table III.

ϕ_t \ ϕ_u	$\sigma^*(OH_1)$	$\sigma^*(OH_2)$	NBEO(σ) [a]	NBEO$(2p\pi)$ [a]
lone-pair(σ-type)	-.0137	-.0137	-.0076	-.0084
(OH_1)	-.1017	-.0057	-.0039	-.0017
(OH_2)	-.0057	-.1017	-.0039	-.0017
lone-pair($2p\pi$-type)	-.0118	-.0118	-.0132	-.0690

$a_{00} = .9866$

[a] The non-bonding excited-orbital, see text.

TABLE XII. Expansion coeffients a_{00} and a_{tu} in the CMC-SCF wave-function for H_2O molecule when the minimal basis-set is used. Notations are explained in Table XI.

ϕ_t ϕ_u	$\sigma*(OH_1)$	$\sigma*(OH_2)$
lone-pair 1	-.0177	-.0177
lone-pair 2	-.0177	-.0177
(OH_1)	-.1078	-.0060
(OH_2)	-.0060	-.1078
$a_{00}=$ .9976		

TABLE XIII. MC-SCF localized orbitals of H_2O when the floating function (centered at r=0.72A and θ=205 with ζ=0.6) is added to the minimal basis-set; orbital energies and oc-upation numbers are entered in first two lines.

	1s(O)	σ(OH₁)	σ(OH₂)	lone-pair (1)	lone-pair (2)	σ*(OH₁)	σ*(OH₂)	NBEO(1)[a]	NBEO(2)[a]
ε	-20.38943	-.74034	-.74034	-1.17183	-.46788	-.01847	-.01847	-.00051	-.00701
occ. num.	2.0	1.97918	1.97918	1.99899	1.98956	.02144	.02144	.00052	.00969
O 1s	1.00187	.03146	.03146	.20855	-.00009	.08080	-.08080	-.06840	-.00006
2s	-.00465	-.52635	-.052635	-.96902	.00035	-.54402	.54402	.62616	.00047
2p$_x$	.00001	.00009	.00009	.00029	.79909	.00014	-.00014	-.00039	.87060
2p$_y$	.0	.45016	-.45016	.0	.0	.68047	.68047	.0	.0
2p$_z$	.01392	-.52163	-.52163	.29359	.00002	-.52261	.52261	-.16108	.00009
H₁ 1s	-.00412	-.55159	.52198	.018716	.00005	1.24512	-.03866	.40600	-.00002
H₂ 1s	-.00412	.05220	-.55159	.18716	.00005	.03866	-1.24512	.40600	-.00002
Float.(1)	-.00365	.07597	.07597	-.02416	.40078	-.13155	.13155	-.84840	-1.46986
Float.(2)	-.00366	.75870	.75870	-.02442	-.40076	-.13108	.13108	-.84978	1.46915

[a] The non-bonding excited-orbital, see text.

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TABLE XIV.   MC-SCF localized orbitals of H_2O when the minimal basis-set is used; orbital energies and occupation numbers are entered in first two lines.

	1s(O)	$\sigma(OH_1)$	$\sigma(OH_2)$	lone-pair (1)	lone-pair (2)	$\sigma^*(OH_1)$	$\sigma^*(OH_2)$
ε	-20.17550	-.64280	-.64280	-.76069	-.72514	-.01926	-.01926
occ. num.	2.0	1.97670	1.97670	1.99875	1.99874	.02456	.02456
O 1s	1.00115	.01591	.01591	.15760	-.14992	-.87799	-.87799
2s	-.00229	.05527	.05527	-.72340	.68773	.61020	.61020
$2p_x$	-.00006	-.00001	-.00001	-.68901	-.72475	.0	.0
$2p_y$	.0	.41791	-.41791	.0	.0	-.70074	.70074
$2p_z$	.01299	-.50946	-.50946	.19197	-.18250	.53267	.53267
H_1 1s	-.00678	-.57124	.08820	.00636	-.00604	-1.13651	.40457
H_2 1s	-.00678	.08820	-.57124	.00636	-.00604	.04045	-1.13651
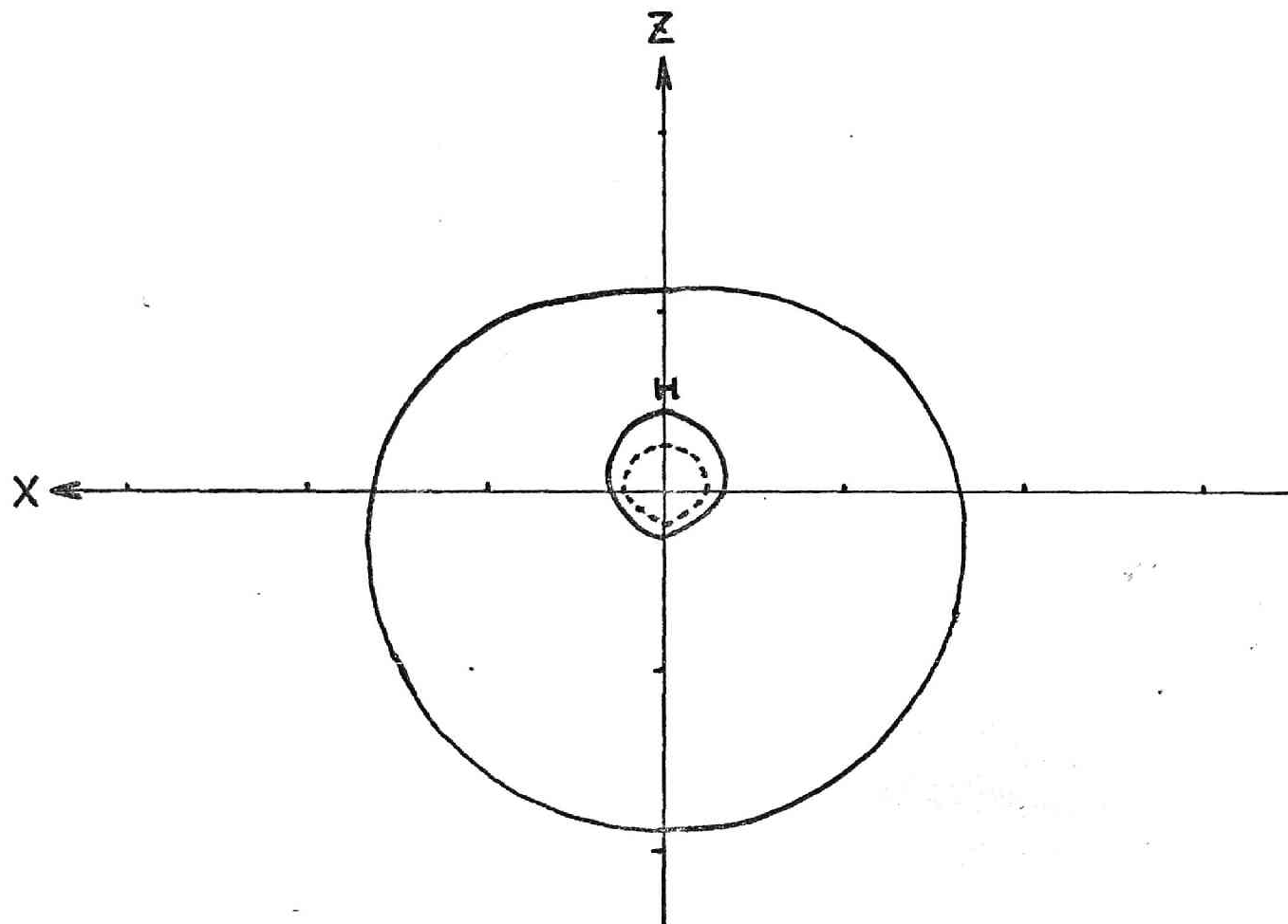
FIG. 4. The first non-bonding orbital listed in Table XIII for H_2O molecule. For coordinates and H in the figure, see the caption of Fig. 1.
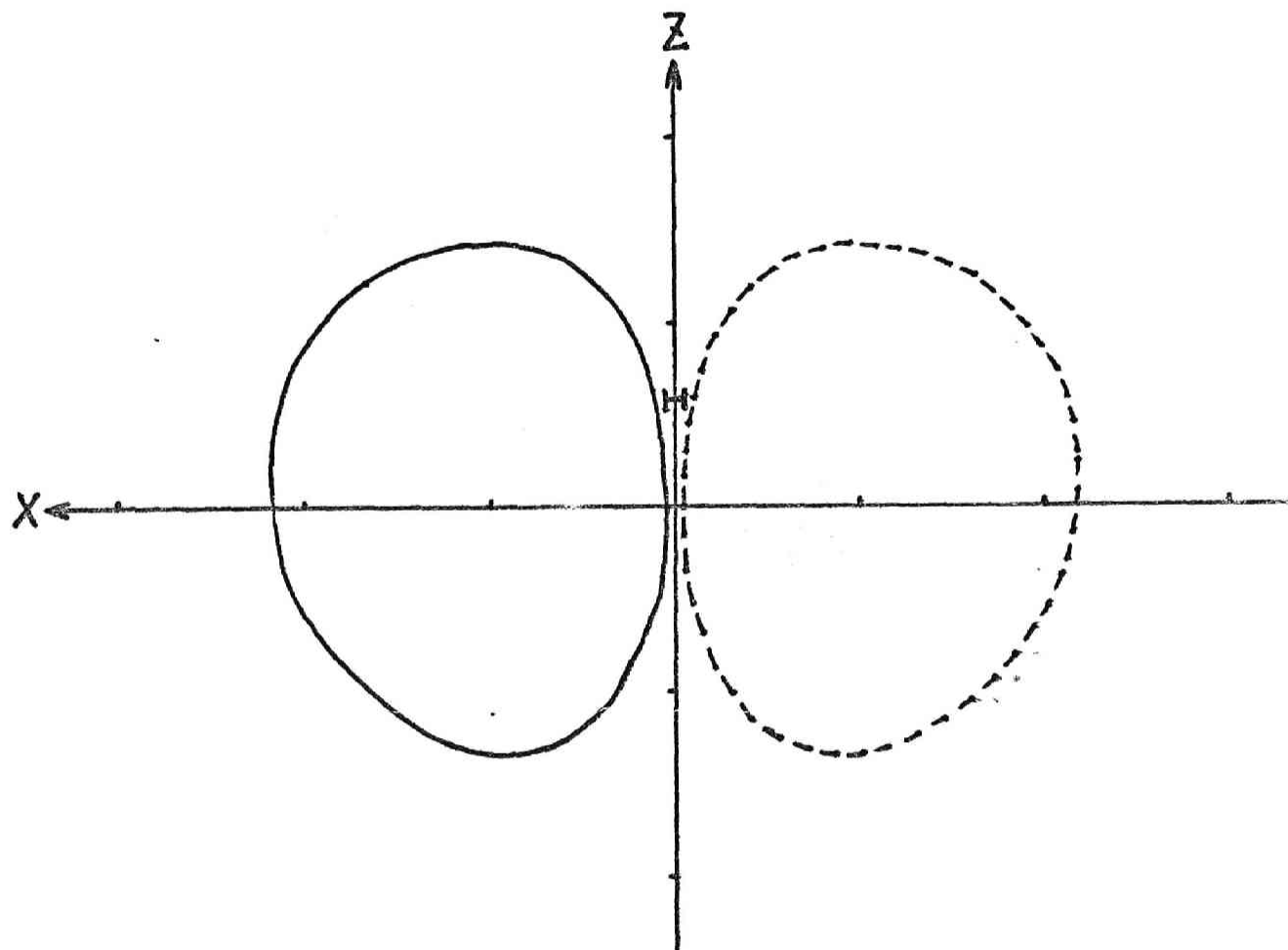
FIG. 5. The second non-bonding orbital listed in Table XIII for H_2O molecule.
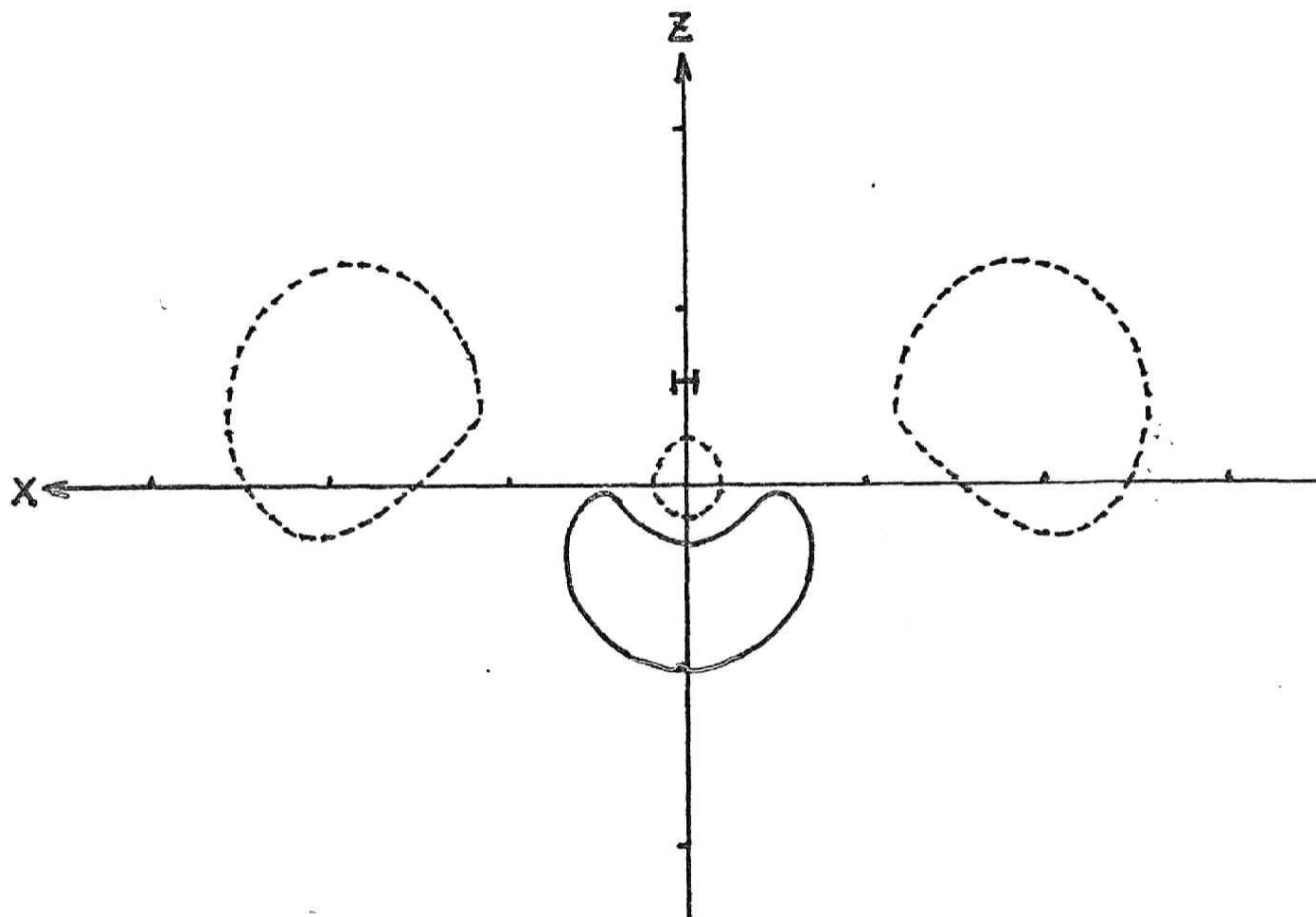For coordinates and H in the figure, see the caption of Fig. 1.

FIG. 6. The first non-bonding excited orbital (NBEO) listed in Table XIII for H_2O molecule. For coordinates and H in the figure, see the caption of Fig. 1.
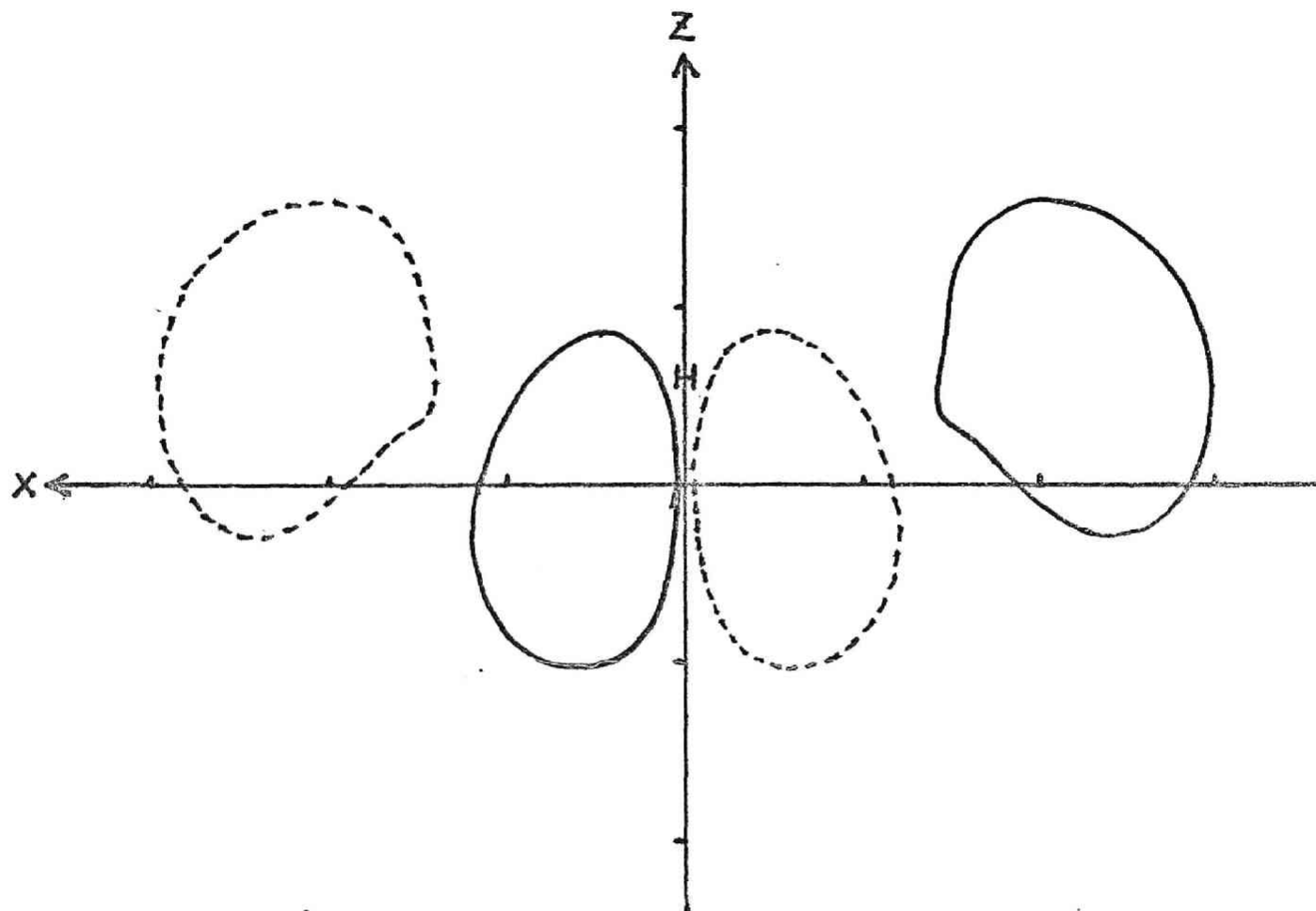
FIG. 7. The second non-bonding excited orbital (NBEO) listed in Table XIII for H_2O molecule. For coordinates and H in the figure, see the caption of Fig. 1.

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_2O molecule. An apprication to a large polyatomic-molecules containing O atom is straightforward.

FIG. 8. One of the non-bonding orbitals listed in Table XIV for H_2O molecule. For coordinates and H in the figure, see the caption of Fig. 1.
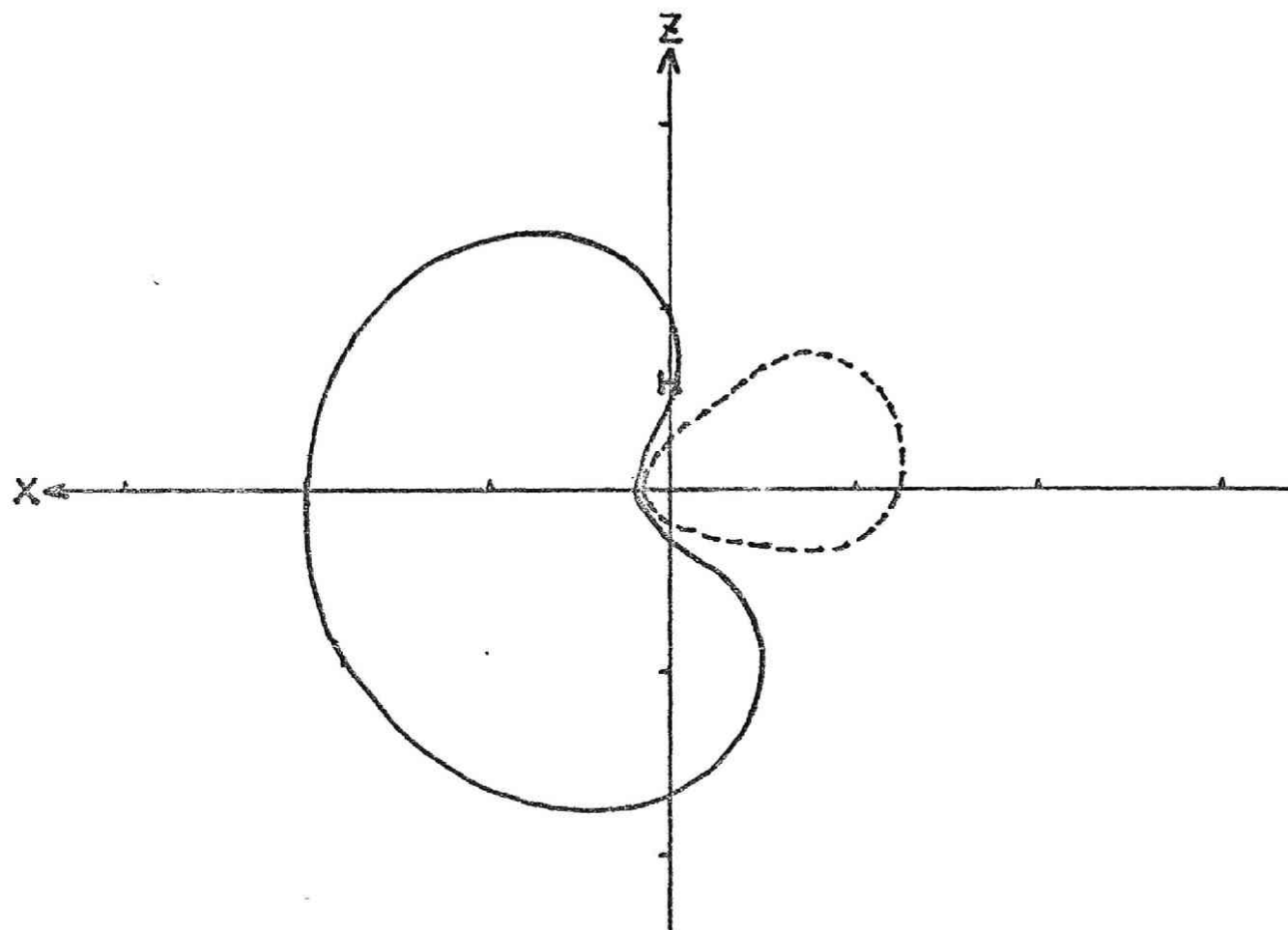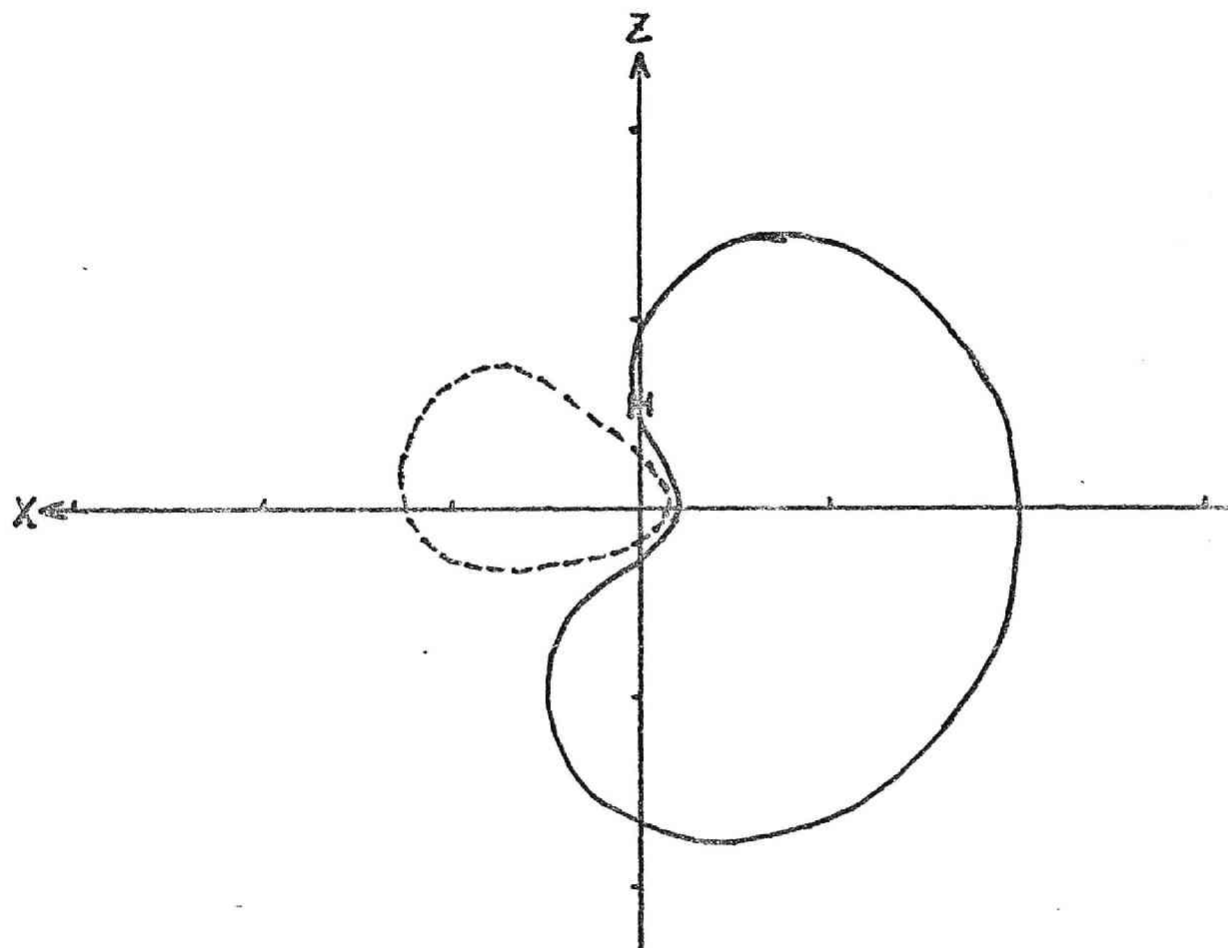
FIG. 9. One of the non-bonding orbitals listed in Table XIV for H_2O molecule.
For coordinates and H in the figure, see the caption of Fig. 1.

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

[22] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. $\underline{35}$, 457 (1963).

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.[1,2] 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,[1,3] an iterative extended Hückel method,[4] CNDO method,[5] and several types of non-empirical calculations.[6-11]

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 Roothaan's SCF treatment for closed-shell systems, the orbital energy of ith MO, ε_i, is given by:

$$\varepsilon_i = F_{ii} = \sum_{r,t} C_r{}^i C_t{}^i F_{rt} \qquad (1)$$

1) K. Siegbahn *et al.*, ESCA atomic molecular and solid state structure studied by means of electron spectroscopy, Almqvist and Wiksills A. B., Stockholm (1967).

2) D. M. Hercules, *Anal. Chem.*, **42**, 20A (1970).

3) R. G. Albridge, U. Erickson, J. Hedman, C. Nardling, and K. Siebahn, *Ark. Kemi*, **28**, 257 (1968).

4) M. Pelavin, D. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

5) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968).

6) R. Manne, *ibid.*, **46**, 4645 (1967).

7) F. A. Gianturco, and C. A. Coulson, *Mol. Phys.*, **14**, 223 (1968).

8) H. Basch, and L. C. Snyder, *Chem. Phys. Lett.*, **3**, 333 (1969).

9) M. E. Schwartz, C. A. Coulson, and S. D. Allen, *J. Amer. Chem. Soc.*, **92**, 447 (1970).

10) M. E. Schwartz, *Chem. Phys. Lett.*, **5**, 50 (1970).

11) C. A. Coulson, and F. A. Gianturco, *Mol. Phys.*, **18**, 607 (1970).

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Where $C_r{}^i$ and F_{rs} are the rth AO coefficient of the ith MO and the F_{rs}-element of the Fock operator respectively.

Suppose that the ith 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_{ss}, is very large compared with that of the off-diagonal ones F_{rs}:[12,13]

$$\varepsilon_i \simeq \varepsilon_s = F_{ss}, \qquad C_s{}^i \simeq 1.0, \qquad (2)$$

$$F_{ss} = \left(s \left| -\frac{1}{2}\Delta - \frac{Z_A}{r_A} \right| s \right) + \left(s \left| -\sum_{B \neq A} \frac{Z_B}{r_B} \right| s \right)$$

$$+ \sum_{r,t} P_{rt} \left\{ (ss/rt) - \frac{1}{2}(sr/st) \right\}. \qquad (3)$$

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 AO 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:

$$\left(s \left| -\frac{1}{2}\Delta - \frac{Z_A}{r_A} \right| s \right) = -I_s - (N_s - 1)(ss/ss)$$

$$- \sum_r^{\text{on } A} N_r \left\{ (ss/rr) - \frac{1}{2}(rs/rs) \right\} \qquad (4)$$

and the nuclear attraction:

$$\left(s \left| -\frac{Z_B}{r_B} \right| s \right) = -Z_B(ss/ns_B ns_B) = -Z_B \gamma_{AB}. \qquad (5)[15]$$

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[17]:
Thus, Eq. (3) can be re-written as:

$$F_{ss} = -I_s + (P_{AA} - Z_A{}^v)\gamma_{AA} + \sum_{A \neq B}(P_{BB} - Z_B{}^v)\gamma_{AB}, \qquad (6)$$

where the average Coulomb integrals are:

$$\gamma_{AA} = (ss/ns_A ns_A), \qquad \gamma_{AB} = (ss/ns_B ns_B), \qquad (7)$$

and where $Z_A{}^v$ denotes the number of valence electrons on the A atom and ns_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 $(P_{AA} - Z_A{}^v) = -Q_A$ (Q_A is the net charge of atom A):

$$\Delta \varepsilon_s = \varepsilon_s + I_s = -Q_A \gamma_{AA} - \sum_{B \neq A} Q_B \gamma_{AB}. \qquad (8)[18]$$

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 $\Delta \varepsilon_s$ for the A atom in different chemical environments, which are denoted as X and Y, is:

$$\delta \Delta \varepsilon_s(X, Y) = \{Q_A(X) - Q_A(Y)\}\gamma_{AA}$$

$$- \sum_{B \neq A}^{\text{in } Y} Q_B(Y)\gamma_{AB}(Y) + \sum_{B \neq A}^{\text{in } X} Q_B(X)\gamma_{AB}(X). \qquad (9)$$

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 γ_{AB}/γ_{AA} ratio is not negligibly small. For diatomic molecules of the first-row elements, AB and A_2, $\delta \Delta \varepsilon_s$(AB, A_2)=0.5, if Q_A(AB)=$-Q_B$(AB)=1.0, γ_{AA}(AB)=1.0, and γ_{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 $1S_O$ 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

TABLE 1. COMPARISON OF THE NUCLEAR ATTRACTION INTEGRALS $(S_A | (Z_B/r_B) | S_A)$ WITH $Z_B \gamma_{AB}$ IN FORMALDEHYDE (in a.u.)

S_A	B	$(S_A \| (Z_B/r_B) \| S_A)$	$Z_B \gamma_{AB}$
$1S_O$	O	2.6240	2.6160
$1S_C$	H	0.4855	0.4727
$1S_O$	C	1.7493	1.7089
$1S_O$	H	0.2655	0.2654

12) e.g., W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966).
13) E. Clementi, *Chem. Rev.*, **68**, 341 (1968).
14) T. Yonezawa, H. Kato, and K. Yamaguchi, This Bulletin, **40**, 536 (1967).
15) While this work, was in progress, the same relation was pointed out in Ref. 16.
16) See Ref. 22.
17) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).
18) A similar equation, obtained by means of an electrostatic model, is given in Ref. 19; that is, $\delta \Delta \varepsilon_s(XY) = kQ_s + \sum_{j \neq i} \frac{Q_j}{R_{ij}} + l_y$ but here K, which corresponds γ_{AA} in Eq. (8), is taken to be an empirical parameter. The constant, l_y, is determined by means of the reference compound.
19) U. Gelius, B. Roos, and K. Siegbahn, *Chem. Phys. Lett.*, **4**, 471 (1970).
20) As to the integral values, refer to those in Table 2 and also those in Ref. 12.
20) H. Taketa, S. Huzinaga, and K. O-ohata, *J. Phys. Soc. Japan*, **21**, 2323 (1966); S. Huzinaga, *Suppl. Progr. Theor. Phys.*, No. **40**, 52 (1967). R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

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

Type		Type	
$(1S_C1S_C/2S_C2S_C)$	0.8073	$(1S_C1S_C/1S_O1S_O)$	0.4373
$(1S_C1S_C/2P_{xC}2P_{xC})$	0.8072	$(1S_C1S_C/2P_{zO}2P_{zO})$	−0.2452
$(1S_C1S_C/2S_O2So)$	0.4360	$(1S_C1S_C/2S_O2P_{zO})$	−0.1190
$(1S_C1S_C/2P_{xO}2P_{xO})$	0.4132	$(1S_C1S_C/2S_O2P_{zO})$	−0.2582
$(1S_C1S_C/2P_{zO}2P_{zO})$	0.4817	$(1S_C2S_C/2S_C2S_C)$	0.0812

a) The z axis is taken to be paralled 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 integrels, $(1s_A1s_A/2s_B2p_B)$ and $(1s_A1s_A/2s_A2p_B)$ types, however, are not negligible; therefore, the (B) approximation, i.e., the CNDO-type integal which neglects the above type of integrals, may be

TABLE 3. CALCULATED SHIFTS FOR CARBON $1S$ ELECTRONS

Compounds	E_{obsd} [a]	Q_A [b]	$\delta\Delta\varepsilon$ [c]
C_2H_2	291.2	−0.064	−0.90
C_2H_4	290.7	−0.33	−0.41
C_2H_6	290.6	−0.006	−0.07
CH_3OH	292.7	+0.129	1.40
CO_2	297.64	+0.536	5.45
HCO_2H	295.79	+0.381	3.40

a) Observed binding energies (in eV), T. D. Yhomas, *J. Chem. Phys.*, **52**, 1373 (1970); D. W. Davis, J. M. Hollander, and D. A. Shirley, and T. D. Thosmas, *ibid.*, **52**, 3295 (1970).

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

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

TABLE 4. CALCULATED SHIFTS FOR NITROGEN $1S$ ELECTRONS

Compounds	E_{obsd} [a]	Q_A [b]	$\delta\Delta\varepsilon$ [c,e]	
N_2	402.45	0.0	0.0	
NH_3	398.1	−0.234	−2.96	(−5.92)
$(CONH_2)_2$	400.0	−0.238	−1.73	
$(CH_3)_3NO$	402.2	+0.157	2.09	
C_5H_5N(pyridine)	398.0	−0.142	−2.04	(−6.27)
C_6H_5CN	398.4	−0.165	−2.99	
$NaNO_3$ [d]	407.4	+0.636	−2.59	
$NaNO_2$ [d]	404.1	+0.083	−10.36	
NaN_3 [d] (middle N)	403.7	+0.447	−6.58	(−13.0)
(terminal N)	399.3	−0.723	−18.04	(−16.3)
KCN [d]	399.0	−0.409	−18.00	(−19.3)

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. Petorngolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **48**, 1497, 1500 (1968); E. Clementi, *ibid.*, **46**, 4731 (1967); W. E. Palke and N. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966).

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 $\delta\Delta\varepsilon_s$. 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 $\delta\Delta\varepsilon_s$ in neutral molecules, and that a relation between the molecular-charge distributions and the observed shifts may be in the form of $(Q_A\gamma_{AA}+\sum_{B\neq A}Q_B\gamma_{AB})$. For the anious containing
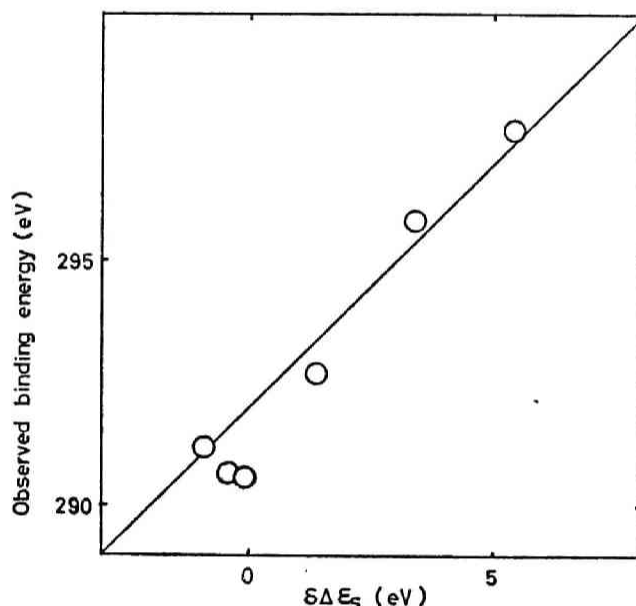

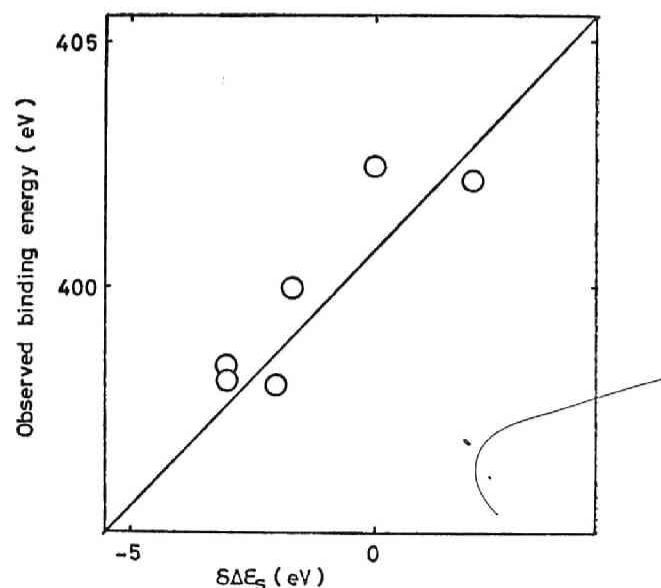Fig. 1. The observed binding energies of carbon $1s$ electron plotted against the $\delta\Delta\delta_s$'s.

Fig. 2. The observed binding energies of nitrogen $1s$ electrons plotted against the $\delta\Delta\varepsilon_s$'s.

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nitrogen atoms, the above rather good correlation is not observed; that is in these charged species, the crystal effects may be considerable.[5]

It is noticed that the values of ε_s 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[7-11,13,21,22]. Further it has been suggested that the main effects of these discrepancies depend on the reorganization energy.[19]

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;

$$\Phi_s^0 = |s i \bar{i} \cdots j \bar{j}| + \sum_{j(\neq s)}^{occ.} \lambda_{is}|s s \bar{i} \bar{i} \cdots j| + \sum_k^{vac} \lambda_{sk}|k i \bar{i} \cdots j \bar{j}|$$

$$+ \sum_{j(\neq s)}^{occ} \sum_k^{vac} \lambda_{jk}(1)\{|s i \bar{i} \cdots j \bar{k}| - |s i \bar{i} \cdots \bar{j} k|\}$$

$$+ \sum_{j(\neq s)}^{occ} \sum_k^{vac} \lambda_{jk}(2)\{2|\bar{s} i \bar{i} \cdots j k| - |s i \bar{i} \cdots j \bar{k}| - |s i \bar{i} \cdots \bar{j} k|\}.$$

$$(10)^{23)}$$

That is, Φ_s^0 is an approximate open SCF function[24] and λ_x is the coefficient of a related configuration, x. By perturbation treatment, these are[25];

$$\lambda_{js} = F_{js}/E_{js} = 0, \qquad \lambda_{sk} = \frac{(ks/ss)}{E_{sk}},$$

$$\lambda_{ik}(1) = \frac{\sqrt{2}\{(ik/ss)-(1/2)(is/ks)\}}{E_{ik}(1)},$$

$$\lambda_{ik}(2) = \frac{-\sqrt{3/2}(is/sk)}{E_{ik}(2)}. \qquad (11)$$

Where E_{sk} 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_s^0 becomes;

$$E_s^0 = (E_0-\varepsilon_s) + \sum_k \frac{(ks/ss)^2}{E_{sk}} + \sum_{k,i\neq s} \frac{2\{(ik/ss)-(1/2)(is/ks)\}^2}{E_{ik}(1)}$$

$$+ \sum_{k,i\neq s} \frac{\{-\sqrt{3/2}(is/ks)\}^2}{E_{ik}(2)} + \cdots \qquad (12)$$

That is, the reorganization energy is $E_s^0-(E_0-\varepsilon_s)$, and the dominant contribution comes from the third term, since $E_{sk}\sim\varepsilon_k-\varepsilon_s$(large), $E_{ik}(1)\sim{}^1E_{ik}$ (valence shell $i\rightarrow k$ singlet excitation energy for a closed-shell system, small), and $(ik/ss)\simeq C_r^iC_r^k(rr/ss)$ is large, and (is/ks) is small as is shown in Table 2.

The magnitude of the third term can be roughly estimated as; $E_{ik}(1) \sim0.5$ a.u., $(rr/ss) \sim1$ a.u., and $\varepsilon_s\sim10$ a.u.; hence, (the third term)$/\varepsilon_s \sim10^{-1}$ [26]. This order is reasonable when it is compared with the previous results, $10\sim20\%$.[10,13,19,27]

These results indicate that the third part is the most important in reorganization energy. Further, this third term can be approximated:

$$\sum_i \sum_k \frac{2\{\sum_r C_r^i C_r^k(rr/ss)\}^2}{E_{ik}(1)} \sim \sum_B^{all\ on\ B} \sum_r p_{rr}(2-p_{rr})\frac{(\gamma_{AB})^2}{2E_{av}}$$

Where E_{av} 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,[13,28] the relativistic correction[29] and the crystal correction,[3,30] 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 linearities 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.

21) P. S. Bagus, *Phys. Revs.*, **A619**, 139 (1965).
22) M. E. Schwartz, *Chem. Phys. Lett.*, 5, 50; 6, 631; 7, 78 (1970).
23) The last configuration does not appear in the difference between the zero-th order configuration (the first term) and Roothaan's open SCF configuration. The contribution from this configuration is certainly very small as will be shown later in this report.
24) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
25) For example, R. Zahradnik, and P. Carsky, *J. Phy. Chem.*, **74**, 1235 (1970).

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_{1s} of pyridine.
27) For valence-electron systems, the same order values are obtained.
28) E. Clementi, *J. Chem. Phys.*, **47**, 4485 (1967).
29) P. Palmiele, and C. Zauli, *Theor. Chim. Acta*, **7**, 89 (1967).
30) C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968).

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
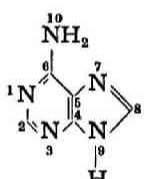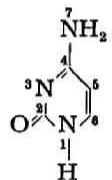
The relationship between chemical shifts in the binding energies of inner-shell electrons and molecular-charge distributions has been pointed out.[1] For adenine and cytosine molecules, however, Barber and Clark[2] concluded that a "simple relationship between 'shifts' in binding energies and 'charge distributions' can be misleading." In a previous paper,[3] we have derived the following correlation formula between the chemical shifts and molecular-charge distributions within a MO framework:

$$\delta\Delta\varepsilon_s(X, Y) = [Q_A(X) - Q_A(Y)]\gamma_{AA} + \sum_{B(\neq A)}^{in\ X} Q_B(X)\gamma_{AB}(X)$$
$$- \sum_{B(\neq A)}^{in\ Y} Q_B(Y)\gamma_{AB}(Y)$$

where $\delta\Delta\varepsilon_s(X,Y)$ 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. γ_{AA} 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 $\Delta\varepsilon_s$[4] 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[5] and by Clementi,[6] 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.

TABLE 1. CALCULATED $\Delta\varepsilon_s$ AND OBSERVED BINDING ENERGIES

Molecule	Atom	$1s$ Binding Energy[a] (±0.3 eV)	$\Delta\varepsilon_s$ (eV)
	C-5	284.7	−0.44
	C-2	285.7	1.63
	C-8	286.2	1.88
	C-4	286.6	2.40
	C-6	287.8	3.04
	N-1	398.6	−5.98
	N-3	399.1	−4.68
	N-7	399.5	−2.67
	N-10	399.6	−4.73
	N-9	400.9	1.24
	C-5	285.4	−0.28
	C-6	286.5	3.29
	C-4	287.9	4.75
	C-2	289.4	4.22
	N-3	399.6	−5.87
	N-7	400.5	−1.90
	N-1	401.4	−1.33

a) M. Barber and D. T. Clark, *Chem. Commun.*, 1970, 22, 24.

1) *E.g.* K. Siegbahn *et al.*, ESCA "Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, (1967); D. M. Hercules, *Anal. Chem.*, **42**, 20A (1970).

2) M. Barber and D. T. Clark, *Chem. Commun.*, 1970, 22.

3) H. Kato, K. A. Ishida, H. Nakatsuji, and T. Yonezawa, This Bulletin, **44**, 2587 (1971).

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

5) B. Mely and A. Pullman, *Theor. Chim. Acta*, **13**, 278 (1969).

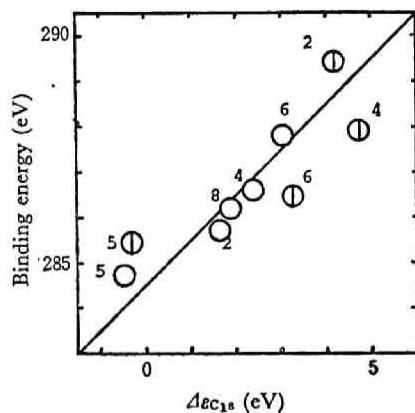6) E. Clementi, *Int. J. Quant. Chem.*, **IIIs**, 179 (1969).

Fig. 1. Observed binding energy *vs.* calculated $\Delta\varepsilon_s$ plots for carbon 1*s* in adenine and cytosine.

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-refered to suggestion by Barber and Clark is not valid in the present case.
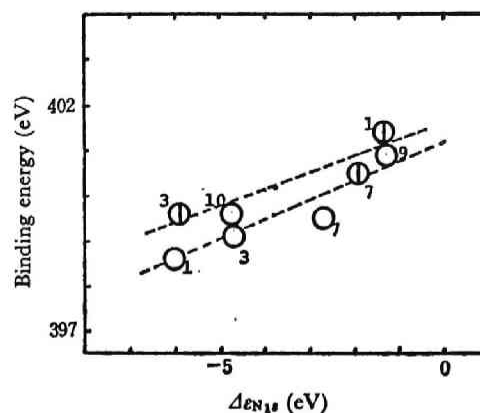

Fig. 2. Observed binding energy *vs.* calculated $\Delta\varepsilon_s$ plots for nitrogen 1*s* in adenine and cytosine.

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 doctral 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 calcu-
lations 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-configu-
ration 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 ini-
tially.

One of the defects of the MC-SCF method is the diffi-
culty 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 diffi-
culty off.