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METHODOLOGICAL STUDIES ON THE THEORIES OF ELECTRONIC STRUCTURE AND ELECTRON SCATTERING OF ATOMS AND MOLECULES

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PREFACE

It is a widely spread belief that the electronic structures of atoms and molecules can, at least in principle, be described completely by quantum mechanics. The view is gaining increasing support from the current uplift of the computational accuracy which has been brought about by both the advances in the methodology of quantum theories and the improvement of high-speed digital computers. Conversely, theoretically essential understanding of the atomic and molecular phenomena cannot be obtained without solving, even approximately, the Schrödinger equations. Thus, the methodology of solving the equations has in itself been a traditional problem of quantum chemistry.

This thesis is concerned mainly with the methodological approaches to the electronic structures and scattering-processes of atoms and molecules. For the bound states a spin orbital theory will be presented, and a variational theory will be developed for the scattering problem. In each branch, a new theoretical scheme will be proposed, which can supply an evidently more accurate wavefunction than does any other existing theory.

Part I proposed a new orbital theory, named the theory of spin-optimized SCF general spin orbitals. It provides the most general and flexible wavefunction in the realm of orbital scheme. The wavefunction is expected to yield a highly accurate energy as well as models of the electronic structures of atoms and molecules.

In Part II, a new guiding variational principle to construct wavefunctions in the scattering theory is proposed. This is aimed at analyzing and avoiding the spurious resonances inherent in some traditional approaches. The interrelationship between the algebraic theories (or the expansion ones) and the variational approaches is also elucidated.

The present thesis is a collection of the author's studies which have been carried out at the Department of Chemistry, Faculty of engineering Science, Osaka University from 1973 to 1978. It is a great pleasure of the author to acknowlege Professor Takayuki Fueno for both his introducing the author into the field of quantum chemistry and his guidance through profound discussions. Without these, it would have been an extreme hazzard for the author to accomplish the study.

The author are indebted to Dr. Kizashi Yamaguchi and Dr. Shigeru Nagase for their constant encouragement and exciting discussions. He also thanks to Dr. Tadashi Okuyama, Dr. Kunihisa Yoshida, and Dr. Okitsugu Kajimoto for their stimulating him through their active studies, and to Dr. Takashi Okada, Dr. Kazuyuki Tatsumi, Mr. Yasunori Yoshioka, Mr. Akinobu Nishio, Mr. Satoshi Yabushita, and many other members of the Fueno Laboratory for their helpful discussions. Miss Emiko Inoue is also indebted to for laborious typing of the manuscript. Finally, the author thanks to his wife Kazuko Takatsuka and their parents.

Kazuo Takatsuka

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PART I

GENERAL SPIN ORBITALS IN ATOMS AND MOLECULES

CHAPTER 1

Introduction

The orbital theories have doubtlessly played a great role in the field of quantum chemistry. For example, the Hückel method[1] and the semi-emprical[2] (or ab initio[3]) SCF-molecular orbital theory lie in the fundamental part of almost all theories in this field.

The orbital theories may be classified into three categorie if they are looked at from the viewpoint of the canonical Hartree-Fock orbitals.[4]

(1) Hartree-Fock orbitals which are unitarily transformed into convinient forms for physical purposes. The localized molecular orbital[5] is a typical example. Although these orbitals appear to differ greatly from the original Hartree-Fock orbitals, the wavefunctions themselves are invariant except for the phase factor.

(2) Correlated orbitals. They are designed so as to incorporate the correlation effects into the orbital form. This kind of theory was developed mainly by Löwdin,[6] Goddard,[7] and their co-workers.

(3) Purely mathematical orbitals. The orbitals of this type, such as the natural orbital[8] and the MC-SCF orbitals,[9] are made use of mostly in order to simulate the configurations involved in the configuration-interaction wavefunction.[8]

The purpose of this Part is to explore the orbitals of the second kind. A new method is proposed, in which the general spin orbitals (two-component spinors) are introduced into the so-called spin-optimized SCF (SO-SCF) scheme.[6] The new wavefunction (SO-SCF-GSO function) is more extended or general in form than any other single-configuration function hitherto available. Naturally, it takes account of the electron correlation to a maximal extent that orbital theories can incorporate. In Chapter 1, theoretical formulation and general properties of the SO-SCF-GSO wavefunctions are presented in a general manner. In Chapter 2, the theory is applied to the 2^2S and 2^2P states of the lithium atom. Through the comparison with other methods, the SO-SCF-GSO wavefunction is analyzed especially in connection with the relation between the energy and the spin density at nucleus. The results have had enough as a motivation of Chapter 3, in which the distribution function for odd electrons which are generated in ground-state molecules having even electrons is described. These odd electrons are regarded to show up in strong correlation systems such as the biradical species and the intermediate states of concerted reaction.

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CHAPTER 2

Formulation of the Spin-Optimized SCF General Spin Orbitals

A new orbital theory is proposed, in which general spin orbitals (GSO) are introduced in the spin-optimized (SO) SCF scheme. In this SO-SCF-GSO theory, the effective Hamiltonian for each orbital takes the form of a 2×2 matrix composed of the eigenfunctions for two-component spinors. It is found that the GSO's thus defined should still satisfy a general form of Koopmans' theorem. The SO-SCF GSO's are to be obtained by solving two sets of coupled SCF equations for the spin coupling coefficients and the linear combination coefficients for basis functions. Using an STO-6G basis set of the double ζ quality, sample calculations have been carried out for the doublet state of the linear H_3 system for which the bond lengths are fixed at 1.470 and 2.984 bohrs. The total energy obtained is ca. 3 kcal/mol lower than the values which have resulted from the SO-SCF-DODS and the spin-extended Hartree-Fock(SEHF) GSO calculations with the same basis set. The resulting orbitals are found to be more delocalized over the entire system than those obtained by the SO-SCF-DODS theory.

I. INTRODUCTION

The Hamiltonian operator H for any electronic state of spin-independent quantum systems in the Born-Oppenheimer approximation satisfies the symmetry relations:

$$[\,H,\, S^2\,] \;=\; 0 \tag{1}$$

and

$$[\,H,\, \hat{S}_z\,] \;=\; 0 \tag{2}$$

where S is the total spin operator and $\hat{S}_z$ is its z-component. The spin symmetry condition (1) is equivalent to[1]

$$[\,H,\, P\,] \;=\; 0\;, \tag{3}$$

where P is an arbitrary permutation operator for the spatial variables. Because of these conditions together with Pauli's exclusion principle, any trial wave function should necessarily be spin-symmetry adapted and antisymmetrized.

The simplest spin-symmetry adapted wave function is the restricted Hartree-Fock (RHF) wave function,[2] which is composed of doubly occupied spatial orbitals. As is well known, however, the RHF wave functions provide results which are seriously in error for molecular systems whose geometry is far apart from that in equilibrium.[3] The difficulty can be overcome by removing the strong constraint of orbital double occupancy and instead by assuming different orbitals for different spins (DODS). The spin polarized Hartree-Fock (SPHF) or unrestricted Hartree-Fock (UHF) orbitals[4] thus derived are still defective in that the wave functions built up thereof are contaminated by those for some irrelevant spin states.[5] To cope with the situation, Löwdin proposed, some twenty years ago, the projected Hartree-Fock or spin-extended Hartree-Fock (SEHF) method,[6] in which a spin-projected Slater determinant is optimized for the total electronic energy.

In 1967, Goddard[7] proposed an SCF procedure (GI-method) for the following type of wave functions:

$$\psi_{GI} = \mathcal{A}\Phi\theta_i^\lambda \tag{4}$$

where θ_i^λ is the ith spin eigenfunction of S^2 with the permutation symmetry λ, Φ is the product of nonorthogonal orbitals, and $\mathcal{A}$ is an antisymmetrizer. Equation (4) is a special case of the generel wave functions set forth earlier by Kotani et al.[8]

$$\Psi = \sum_i \mathcal{A}\Phi_i\theta_i^\lambda . \tag{5}$$

Recently, Ladner and Goddard [9a] and Kaldor and Harris[9b] performed the optimization of the wave function which is a linear combination of Eq. (4), namely,

$$\Psi^\lambda = \mathcal{A}\Phi(\sum_i C_i\theta_i^\lambda) \ . \tag{6}$$

Equation (6) is called the spin-optimized self-consistent-field (SO-SCF) wave function. According to Goddard,[10] the SEHF-DODS theory is merely a special case of the SO-SCF theory applied to the DODS nonorthogonal orbitals (SO-SCF-DODS).

Alternatively, a number of workers[11] have explored the utility of the general spin orbitals (GSO) defined as the two-component spinors

$$\phi_k = \begin{pmatrix} a_k \\ b_k \end{pmatrix} = a_k\alpha + b_k\beta \tag{7}$$

where a_k and b_k are the apatial functions for the α- and β-spin components, respectively. So far, the best wave function for many-electron systems that explicitly retains the concept of the orbitals for electrons without recourse to configuration interaction treatments,[12] appears to be the one based on the SEHF procedure for GSO's (SEHF-GSO).[11] In fact, Lunell[11d] has pointed out that for systems of a limited number of electrons the SEHF-GSO theory is seemingly more accurate than the SO-SCF-DODS theory. It now appears very likely that, when GSO's are introduced into the SO-SCF scheme (SO-SCF-GSO), then both the SEHF-GSO and the SO-SCF-DODS theories would be embraced as special cases of the SO-SCF-GSO formalism. Scrutiny of this last point is the purpose of the present paper. In Table I, several existing orbital theories are classified in order to clarify the position of the SO-SCF-GSO method to be developed herewith.

The scope of this work is briefly outlined as follows. First, the spin-optimized general-spin-orbital (SO-GSO) wave function is defined in Section II. Next, in Section III, a set of SCF equations to be used for the determinations of the orbitals and spin coupling coefficients are presented in a general manner. In Section IV, we will deal with some properties of our SO-SCF-GSO wave functions and energies. Section V will be devoted to sample calculations of a linear H_3 molecule in order to demonstrate how the SO-SCF-GSO method improves the results obtained by the already familiar SO-SCF-DODS and SEHF-GSO theories.

II. WAVE FUNCTION AND THE ENERGY EXPRESSION

A. The SO-GSO wave function

We will be concerned primarily with a spin state of the least nonnegative $\hat{S}_z$-eigenvalue, q. By use of the S_z-projection operator

$$P_z^q = \prod_{\ell \neq q} \frac{\hat{S}_z - \ell}{q - \ell} \qquad (8)$$

and the fundamental units e_{ij}^{λ} of the algebra for a symmetric group S_N (Appendix A), we express the SO-GSO wave function as

$$\Psi_q^{\lambda} = P_z^q \sum_{ij} e_{ij}^{\tilde{\lambda}} e_{ij}^{\lambda} C_j \phi_1 \phi_2 \cdots \phi_N \qquad (9)$$

where the orbitals $\phi_1, \phi_2, \ldots, \phi_N$ are the two-component spinors, Eq. (7). In Eq. (9), the spin symmetry of the system is characterized by the irreducible representation λ. The symbol $\tilde{\lambda}$ denotes the conjugate representation associated with λ. The suffixes i and j refer to the relevant spin eigenstates. A convention that e_{ij}^{λ} and $e_{ij}^{\tilde{\lambda}}$ operate respectively on the spin and spatial coordinates, is employed throughout this paper. The coefficients C_j's are called the spin coupling coefficients and to be determined by variation.

The wave function defined as Eq. (9) satisfies the following eigenvalue equations:

$$S^2 \Psi_q^{\lambda} = S_{\lambda}(S_{\lambda} + 1)\Psi_q^{\lambda} \qquad (10)$$

$$\hat{S}_z \Psi_q^{\lambda} = q \Psi_q^{\lambda} \qquad (11)$$

$$P\Psi^{\lambda}_{q} = \varepsilon_{P}\Psi^{\lambda}_{q} , \tag{12}$$

where P is an arbitrary element of the symmetric group S_N, the quantity ε_P being its parity.

The $\hat{S}_z$- projected function of the simple product of GSO's can be expanded as follows:

$$P^{q}_{z}\phi_1\phi_2\ldots\phi_N = \sum_{u}\psi_u\eta_u \tag{13}$$

where η_u is the uth spin function of simple product of the α and β functions with the net eigenvalue q, ψ_u being the spatial function associated with η_u. We then make use of the irreducible representation matrix Γ^{λ} and the linear combination coefficients k's for the spin products (Appendix A) to obtain the normalized wave function:

$$\Psi^{\lambda}_{q} = \frac{f^{\lambda}}{N!}\sum_{ij}^{f^{\lambda}}\sum_{u}\sum_{t} C_j\tilde{\Gamma}^{\lambda}_{ji}(t^{-1})k^{u}_{j}(t\psi_u)\theta^{\lambda}_{i} , \tag{14}$$

where f^{λ} is the dimension of the irreducible representation λ, t is an element of S_N, and θ^{λ}_{i} is the ith spin eigenfunction of S^2 and $\hat{S}_z$ with the eigenvalues $S_{\lambda}(S_{\lambda} + 1)$ and q, respectively.

Clearly, the SEHF wave functions are obtained by taking all the spin coupling coefficients identical, i.e., $C_1 = C_2 = \ldots = C_{f^{\lambda}}$. If one forces either a_k or b_k (k=1,2,...,N) to be 0, then the DODS wave functions are attained. Further, the RHF wave function, for which each orbital is doubly occupied, results from the constraints that $a_1=b_2$, $a_3=b_4$ and so forth.

The SO-GSO wave function can also be written as the linear combination of the DODS wave functions, viz.,

$$\Psi_q^\lambda = \sum_i C_i \mathcal{A}\Phi_i(r_1,\ldots,r_N)\theta_i^\lambda \tag{15}$$

The spatial functions Φ_i are obtained by operating

$$P_i = \frac{f^\lambda}{N!}\sum_t \Gamma_{ii}^\lambda(t^{-1})t^n \cdot t^c \tag{16}$$

on a primitive spatial function

$$\psi = a_1(r_1)b_2(r_2)a_3(r_3)\ldots \quad . \tag{17}$$

In Eq. (16), Γ_{ii}^λ denotes the (i,i) element of Γ^λ, and t^n and t^c the permutation operators which operate respectively on the numberings of the a- or b-functions and on the spatial coordinates. The number of the a-functions present in Eq. (17) should exceed that of the b-functions by 2q.

B. Spinless density matrix and the energy expectation value

We will formulate explicitly the second-order spinless density matrix for our SO-GSO wave function. The expression for the energy expectation value can readily be derived from it.

By use of the wave function (14), the Nth-order spinless density matrix defined as[13]

$$\rho^{(N)}(r',r) = \int\Psi^*(r_1's_1,\ldots,r_N's_N)\Psi(r_1s_1,\ldots,r_Ns_N)ds_1\ldots ds_N \tag{18}$$

is transformed into

$$\rho^{(N)}(r',r) = \sum_{uv}\sum_{ts}\mathcal{B}^{uv}_{ts}(t\psi_u(r'))^*(s\psi_v(r)) \ , \tag{19}$$

where

$$\mathcal{B}^{uv}_{ts} = C^+K^{uv}_{ts}C \tag{20}$$

with

$$C = \mathrm{Col}(C_1,C_2,\ldots,C_{f^\lambda}) \tag{21}$$

and

$$(K^{uv}_{ts})_{ij} = \left(\frac{f^\lambda}{N!}\right)^2 k^u_i k^v_j \Gamma^{\tilde{\lambda}}_{ji}(s^{-1}t) \ . \tag{22}$$

The second-order spinless density matrix for our use can be expressed as

$$\rho^{(2)}(y_1',y_2';y_1,y_2) = \int\rho^{(N)}(r',r)D_2(y_1',y_2';y_1,y_2|r',r)dr'dr. \tag{23}$$

Here, y_1 etc. are the spatial coordinates and D_2 is a density matrix generating function defined as

$$D_2(y_1',y_2';y_1,y_2|r',r) = \frac{1}{N(N-1)}\sum_{m\neq n}\delta(r_m' - y_1')\delta(r_m - y_1) \times \delta(r_n' - y_2')\delta(r_n - y_2)\prod_{h\neq m,n}\delta(r_h' - r_h) \ , \tag{24}$$

where $\delta(r_m' - y_1')$ etc. are Dirac's δ-functions.

Let $H_R(y_1,y_2)$ be a reduced Hamiltonian given by

$$H_R(y_1,y_2) = \frac{N}{2}(h_1 + h_2) + \binom{N}{2}g_{12} \ , \tag{25}$$

where h_1 and h_2 are the one-electron Hamiltonians operating on y_1 and y_2, respectively, and g_{12} is the electron-repulsion operator. The energy expectation value E is then simply given by

$$E = \mathrm{Tr}\{H_R(y_1,y_2)\rho^{(2)}(y_1',y_2';y_1,y_2)\} \; . \tag{26}$$

By virtue of the symmetric property of D_2 with respect to r' and r, E can be expressed as

$$E = \sum_{uv}\sum_{ts}\mathcal{D}_{ts}^{uv}\int dr'\,dr\,dy_1dy_2\psi_u^*(r')\psi_v(r)$$
$$\times\ [H_R(y_1,y_2)D_2(y_1',y_2';y_1,y_2|r',t^{-1}sr)] \; . \tag{27}$$

In Eq. (27), use should be made of the usual convention[13] that y_1' and y_2' are set equal to y_1 and y_2, respectively, immediately before performing the integration for y_1 and y_2.

Our attention is now focused on the <u>k</u>th orbital ϕ_k in particular. Clearly, any ψ_u is the product of a's and b's involving either a_k or b_k. In case where a_k is involved in ψ_u, we may write

$$\psi_u(r) = a_k(r_k)A_k^u(\tau_k) \; , \tag{28a}$$

where τ_k denotes all the spatial coordinates except for r_k. Conversely, if b_k happens to show up in ψ_u, then $\psi_u(r)$ should be written as

$$\psi_u(r) = b_k(r_k)B_k^u(\tau_k) \; . \tag{28b}$$

Because of this dual character of $\psi_u(r)$, E should take the form

$$E = \int(a_k^*(r_k')b_k^*(r_k'))G^k(r_k',r_k)\begin{pmatrix} a_k(r_k) \\ b_k(r_k) \end{pmatrix} dr_k'dr_k \; , \tag{29}$$

where $G^k(r_k',r_k)$ is an effective reduced Hamiltonian operator which is defined as follows:

$$G^k(r_k',r_k) = \sum_{uv}\sum_{ts}\int_{y_1'=y_1,y_2'=y_2} d\tau_k' d\tau_k dy_1 dy_2$$
$$\times \mathcal{O}_{ts}^{uv}[H_R(y_1,y_2)D_2(y_1',y_2';y_1,y_2|r',t^{-1}sr)]$$
$$\times \begin{pmatrix} A_k^{u*}(\tau_k')A_k^v(\tau_k) & A_k^{u*}(\tau_k)B_k^v(\tau_k) \\ B_k^{u*}(\tau_k')A_k^v(\tau_k) & B_k^{u*}(\tau_k)B_k^v(\tau_k) \end{pmatrix} . \qquad (30)$$

III. THE SCF PROCEDURE

In the light of the variational principle, we now search for the optimum form of the wave function. In doing this, two conditions are imposed: (1) The norm of the total wave function should be finite and (2) the norm of each orbital should be finite. Condition (1) permits unique determination of the spin coupling coefficients. The pseudo-eigenvalue equations to obtain the SCF orbitals are derived by use of both conditions (1) and (2). The wave function in question should satisfy the generalized Brillouin theorem[9b,11b,14]:

$$\langle\delta\Psi|H-E|\Psi\rangle = \langle\Psi_{k\to k'}|H-E|\Psi\rangle$$
$$= 0 , \qquad (31)$$

where $\Psi_{k\to k'}$ is the wave function with a virtual orbital k' in place of the ground-state orbital k.

A. Determination of the orbitals

In this subsection, we formulate two types of one-body Schrödinger equations to determine the orbitals; one is the direct consequence of

Eqs. (29) and (31) while the other is a modification of the former such that the orbital energies are given as the solutions of an eigenvalue problem.

Let us now define an operator $S^k(r_k', r_k)$ by replacing $H_R(y_1, y_2)$ by 1 in Eq. (30). It is then obvious that

$$<\Psi|H|\Psi> = <\phi_k|G^k|\phi_k> \tag{32a}$$

and

$$<\Psi|\Psi> = <\phi_k|S^k|\phi_k>. \tag{32b}$$

Noting that neither G^k nor S^k depends on ϕ_k itself, we can take the variational form of Eq. (31)

$$<\delta\phi_k|G^k|\phi_k> = E <\delta\phi_k|S^k|\phi_k> , \tag{33}$$

which directly leads to

$$G^k|\phi_k> = ES^k|\phi_k> . \tag{34}$$

It should be noted that in Eq. (34) both G^k and S^k are the function of all the orbitals other than ϕ_k but that the spin coupling coefficients involved in both of them still remain to be determined.

We are now in a position to formulate an eigenvalue problem which gives the orbital energies. In the integral $<\Psi|(H-E)|\Psi>$ one finds two types of elements; one is proportional to $<\phi_k|\phi_k>$ while the other is not. The situation permits the formal expression:

$$<\Psi|(H-E)|\Psi> = <\phi_k|F^k|\phi_k> - \varepsilon_k<\phi_k|\phi_k> , \tag{35}$$

where ε_k is a constant and $<\phi_k|F^k|\phi_k>$ is the matrix element not proportional to $<\phi_k|\phi_k>$. It follows that

$$<\delta\phi_k|F^k|\phi_k> - \varepsilon_k<\delta\phi_k|\phi_k> = 0 \tag{36}$$

provided F_k is not a function of ϕ_k. As a consequence, one may write

$$F^k|\phi_k> = \varepsilon_k|\phi_k> . \tag{37}$$

Since $\delta<\phi_k|\phi_k> = 0$, ε_k has been treated as a Lagrangian multiplier as usual and may be regarded as the orbital energy of ϕ_k. It is given as an eigenvalue of the operator F^k whose explicit form has not yet been given.

The explicit expression of ε_k can be obtained in the following manner. In the expression $<\Psi|(H-E)|\Psi>$, one finds the elements

$$A_k<a_k|a_k> + B_k<b_k|b_k> , \tag{38}$$

where A_k and B_k are some constants which may be dependent on orbital ϕ_k. Eq. (38) can be rewritten as

$$\begin{aligned} A_k<a_k|a_k> + B_k<b_k|b_k> &= \frac{1}{2}(A_k + B_k)(<a_k| \;\; <b_k|)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}|a_k>\\ |b_k>\end{pmatrix} \\ &+ \frac{1}{2}(A_k - B_k)(<a_k| \;\; <b_k|)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}|a_k>\\ |b_k>\end{pmatrix} . \end{aligned} \tag{39}$$

The first term of the right-hand side of Eq. (39) is all that is proportional to $<\phi_k|\phi_k> = <a_k|a_k> + <b_k|b_k>$, whereas the 2×2 matrix in the second term is traceless. If follows that

$$\varepsilon_k = -\frac{1}{2}(A_k + B_k). \tag{40}$$

Explicit formalation of A_k and B_k is straightforward. Thus, A_k is given as

$$\begin{aligned} A_k\delta(r_k' - r_k) = {} & \sum_{uv} \sum_{ts}^{(k)} \mathcal{A}_{ts}^{uv} \int d\tau_k' d\tau_k dy_1 dy_2 \\ & \times A_k^{u*}(\tau_k')A_k^{v}(\tau_k) \times (s^{-1}t)_r \\ & \times [\, N \sum_{m(\neq k)} \delta(r_m' - y_1)\delta(r_m - y_1) \prod_{h(\neq m)} \delta(r_h' - r_h)h(y_1) \\ & + \frac{N(N-1)}{2} \sum_{m\neq n(\neq k)} \delta(r_m' - y_1)\delta(r_m - y_1)\delta(r_n' - y_2)\delta(r_n - y_2) \\ & \times \sum_{h(\neq m,n)} \delta(r_h' - r_h)g(y_1,y_2) - E \,] \quad , \end{aligned} \tag{41}$$

where $\sum_{ts}^{(k)}$ means the summation over all pairs of elements (t, s) of S_N, which do not involve the letter k in the product $s^{-1}t$, and $(s^{-1}t)_r$ denotes the permutation operator operating on coordinate r. $B_k\delta(r_k' - r_k)$ can be obtained by introducing $B_k^u(\tau_k')B_k^v(\tau_k)$ in place of $A_k^u(\tau_k')A_k^v(\tau_k)$ in Eq. (41).

It is interesting to relate $G^k(r_k',r_k)$ and $S^k(r_k',r_k)$ with $F^k(r_k',r_k)$. From Eqs. (32) and (35), we have

$$F^k(r_k',r_k) = G^k(r_k',r_k) - ES^k(r_k',r_k) + \varepsilon_k I_2 \ , \tag{42}$$

where

$$I_2 = \delta(r_k' - r_k)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \ . \tag{43}$$

It is evident from Eq. (42) that, when Eq. (34) holds, so does Eq. (37) automatically, and vice versa. In this connection, it must be cautioned that Eq. (37) may hold occasionally even when

$$G^k|\phi_k> = 0 , \qquad S^k|\phi_k> = 0 . \tag{44}$$

Obviously, this is an artefact arising as a consequence of the violation of Pauli's exclusion principle. Such false solutions are liable to diverge as has often been encountered in actual SCF computations.

Both equations (34) and (37) are coupled integro-differential equations, but the expansion technique may be applied as usual. Thus, the GSO ϕ_k is expanded in terms of basis functions $\{\chi_1,\chi_2,\ldots,\chi_M\}$ as

$$\phi_k = \sum_r A_{rk}\chi_r\alpha + \sum_r B_{rk}\chi_r\beta . \tag{45}$$

Both Eqs. (34) and (37) are reduced to a set of simultaneous pseudo-eigenvalue equations in the matrix forms:

$$\begin{pmatrix} G_{11}^k & G_{12}^k \\ G_{21}^k & G_{22} \end{pmatrix}\begin{pmatrix} A_k \\ B_k \end{pmatrix} = E\begin{pmatrix} S_{11}^k & S_{12}^k \\ S_{21}^k & S_{22}^k \end{pmatrix}\begin{pmatrix} A_k \\ B_k \end{pmatrix} \tag{46}$$

and

$$\begin{pmatrix} F_{11}^k & F_{12}^k \\ F_{21}^k & F_{22}^k \end{pmatrix}\begin{pmatrix} A_k \\ B_k \end{pmatrix} = \varepsilon_k\begin{pmatrix} X & 0 \\ 0 & X \end{pmatrix}\begin{pmatrix} A_k \\ B_k \end{pmatrix} , \tag{47}$$

where

$$(G_{mn}^k)_{rs} = <\chi_r|G_{mn}^k|\chi_s> \tag{48}$$

$$(S_{mn}^k)_{rs} = <\chi_r|S_{mn}^k|\chi_s> \tag{49}$$

$$(F_{mn}^k)_{rs} = <\chi_r|F_{mn}^k|\chi_s> \qquad (m,n = 1,2) \tag{50}$$

$$X_{rs} = <\chi_r|\chi_s> \tag{51}$$

and

$$A_k = \begin{pmatrix} A_{1k} \\ \vdots \\ A_{Mk} \end{pmatrix}, \qquad B_k = \begin{pmatrix} B_{1k} \\ \vdots \\ B_{Mk} \end{pmatrix}, \tag{52}$$

the operators G^k_{mn}, S^k_{mn} and F^k_{mn} being the (m,n) elements of G^k, S^k and F^k, respectively.

B. Spin coupling coefficients

The energy expression, Eq. (29), is quadratic in form in regard to the spin coupling coefficients, Eq. (21). That is,

$$C^+QC = EC^+OC \tag{53}$$

where the matrices Q and O are defined using the matrix K, Eq. (22), as follows:

$$Q_{ij} = \sum_{uv} \sum_{ts} \langle\psi_u|Ht^{-1}s|\psi_v\rangle(K^{uv}_{ts})_{ij} \tag{54a}$$

$$O_{ij} = \sum_{uv} \sum_{ts} \langle\psi_u|t^{-1}s|\psi_v\rangle(K^{uv}_{ts})_{ij} \quad . \tag{54b}$$

Direct application of the variation principle to Eq. (53) with regard to C leads to a secular equation

$$(Q - EO)C = 0. \tag{55}$$

The total energy and the spin coupling coefficients are obtained by solving Eq. (55). Equation (34) or (37), or more practically Eq. (46) or (47), is coupled with Eq. (55), so that they may be solved for the SO-SCF-GSO's in an iterative manner.

IV. SOME CHARACTERISTICS OF THE WAVE FUNCTION AND ORBITALS

A. Orthogonality and the unitary transformation property of orbitals

In both the SEHF and RHF formalisms, all the spin-orbitals are automatically chosen to be orthogonal to one another. This is not generally the case with the SO-SCF-GSO wave function. The N-body SO-SCF-GSO wave function has at best [N/2] orbital groups, each containing two GSO's which can be chosen to be mutually orthogonal and are allowed to transform to new GSO's by unitary transformation. Here, [N/2] denotes the largest possible integer not exceeding N/2.

The above statement can be proven as follows. By the aid of Serber's spin functions,[15] which diagonalize the representations of the permutations $P_k = (2k - 1, 2k)$ for $k = 1,2,\cdots,[N/2]$, we express the fundamental unit e^{λ}_{ii} in a ket-bra form (Appendix A):

$$e_{ii} = |\theta^{\lambda}_{i}\rangle\langle\theta^{\lambda}_{i}| \ . \tag{56}$$

It can then be readily seen that e^{λ}_{ii} commutes with such P_k's. Hence,

$$\begin{aligned}\Psi_{\lambda} &= \mathcal{A}(\sum_{i} C_i e^{\lambda}_{ii})(\phi_1 \cdots \phi_{2k-1}\phi_{2k} \cdots \phi_N) \\ &= \mathcal{A}(\sum_{i} C_i e^{\lambda}_{ii})P^{o}_{k}P^{s}_{k}(\phi_1 \cdots \phi_{2k}\phi_{2k-1} \cdots \phi_N) \\ &= -\mathcal{A}(\sum_{i} C_i e_{ii})(\phi_1 \cdots \phi_{2k}\phi_{2k-1} \cdots \phi_N) \ ,\end{aligned} \tag{57}$$

where P^{o}_{k} and P^{s}_{k} are the permutation operating on the space and spin coordinates, respectively. Equation (57) states that the functional component ϕ_{2k-1} involved in ϕ_{2k}, which has been the origin of their nonorthogonality, should disappear automatically. The unitary transformation between ϕ_{2k-1} and ϕ_{2k} ($k = 1,2,\cdots,[N/2]$) are thus assured.

B. Hellman-Feynman theorem

The SO-SCF-GSO wave function satisfies the Hellman-Feynman theorem[16] just as Hartree-Fock,[17] SEHF,[18] GI[18] and SO-SCF-DODS[9a] wave functions do. The proof of this theorem for the SO-SCF-GSO wave function is exactly identical with that for other wave functions.

$$\frac{\partial}{\partial\lambda}\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{1}{\langle\Psi|\Psi\rangle}\langle\Psi|\frac{\partial H}{\partial\lambda}|\Psi\rangle . \qquad (58)$$

C. Ionization and "Koopmans' theorem"

In the SO-SCF scheme, a state of pure spin symmetry turns upon ionization to a mixed spin symmetry state. This may have a bearing with the observation[19] that both singlet and triplet states are generated from a doublet state by ionization. The (N - 1)-body wave function given by deleting any one orbital, say the Mth orbital, from the parent wave function should be a mixture of the singlet and triplet states with certain weighting factors. Figure 1 illustrates an ionization process by use of Young's diagram,[20] the ground state $\lambda = [N - p, p]$ ionizing into two different states denoted by $\lambda_1 = [N - p, p - 1]$ and $\lambda_2 = [N - p - 1, p]$. In addition, in the GSO scheme, the wave function of the ionized state is not an eigenfunction of $\hat{S}_z$.

According to the present SO-SCF-GSO theory, the energy of the Mth orbital in the parent N-electron system is given by

$$\varepsilon_M = \frac{1}{2N} \sum_{p=1,2} \{ <\Psi^{\lambda_p}_{q+1/2}|\Psi^{\lambda_p}_{q+1/2}>(E_0 - E^{\lambda_p}_{q+1/2})$$

$$+ <\Psi^{\lambda_p}_{q-1/2}|\Psi^{\lambda_p}_{q-1/2}>(E_0 - E^{\lambda_p}_{q-1/2})\} \times <\Psi^{\lambda}_{q}|\Psi^{\lambda}_{q}>^{-1} , \qquad (59)$$

where Ψ^{λ}_{q} is an N-body wave function with the spin symmetry λ, the $\hat{S}_z$ eigenvalue q and energy E_0, while $\Psi^{\lambda_p}_{q\pm 1/2}$ are the ionized-state (N - 1)-body wave functions with the spin symmetry λ_p (p = 1,2), the $\hat{S}_z$-eigenvalues q±1/2 and energy $E^{\lambda_p}_{q\pm 1/2}$.

Equation (59) expresses that the orbital energy ε_M is just the difference in energy between the ground and ionized states with proper weighting factors associated with the extent to which the two ionized-state wave functions contribute to the ions. Therefore, Eq. (59) may be regarded as an extention of the familiar Koopmans theorem.[21] For a special case where N = 2, Eq. (59) reduces to

$$\varepsilon_2 = \frac{1}{2}(E_0 - <\phi_1|H_1|\phi_1>) , \qquad (60)$$

where ϕ_1 stands for the first orbital and H_1 is the one-body Hamiltonian for the ionized state. This last equation is exactly what was derived by Lunell[11c] for a two-electron system in the SEHF-GSO formalism.

D. Excitation and virtual orbitals

The eigenvalue equation (34) provides solutions other than the ground-state filled orbitals. They are called virtual orbitals. To distinguish between these two classes of orbitals, we will denote the former orbitals by $\phi_k^{(0)}$ and the latter by $\phi_k^{(n)}$, n>0.

Lunell[22] and Goddard[23] showed for the cases of the Hartree-Fock and the GF methods, respectively, that the resulting virtual orbitals are sufficiently accurate to describe the excited electronic states to a zeroth-order approximation. More specifically, the energy gaps between the virtual and ground-state orbitals are good approximations to one-electron excitation energies.

Similar trends can well be expected of our $\phi_k^{(n)}$. Let us denote by $\Psi_k^{(n)}$ the wave function for the excited state arising from the one-electron transition $\phi_k^{(0)} \rightarrow \phi_k^{(n)}$. Then, it can readily been shown that the $\Psi_k^{(n)}$ functions have the following properties:

$$<\Psi_k^{(n)}|H|\Psi> = 0 \tag{61}$$

$$<\Psi_k^{(n)}|H|\Psi_k^{(m)}> = 0 \qquad (m \neq n) \tag{62}$$

As a result, $\Psi_k^{(n)}$ $(n = 1,2,\cdots)$ together with $\Psi_k^{(0)}$ completely diagonalize the Hamiltonian matrix in each k-space, so that $E_k^{(n)}$ $(n = 1,2,\cdots)$ could in principle be good approximations to one-electron excitation energies.

V. SAMPLE CALCULATIONS

For the purpose of illustration, we here apply the present theory to the doublet state of a linear H_3 system with two bond lengths fixed at 1.470 and 2.984 bohrs. Comparisons of the results attained by the various theories, RHF, SEHF-DODS, SO-SCF-DODS, SEHF-GSO and SO-SCF-GSO, are another purpose.

The three-electron doublet system is the simplest possible system in which the spin degeneracy problem[20b] arises. According to Eqs. (9) and (13), the SO-SCF-GSO wave function pertinent to the system in question is

$$\Psi_{\text{SO-SCF-GSO}} = \mathcal{A}[C_1 2^{-1/2}(a_1 b_2 a_3 - b_1 a_2 a_3)\theta_1 + C_2 6^{-1/2}(a_1 b_2 a_3 + b_1 a_2 a_3 - 2a_1 a_2 b_3)\theta_2] \ , \tag{63}$$

where

$$\theta_1 = 2^{-1/2}(\alpha\beta\alpha - \beta\alpha\alpha) \tag{64a}$$

$$\theta_2 = 6^{-1/2}(\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta) \ . \tag{64b}$$

As stated in section IVA, two GSO's can be chosen to be orthogonal to each other. Since we have adopted the genealogical spin functions,[8] the GSO's, ϕ_1 and ϕ_2, are mutually orthogonal, and the wave function is invariant to any unitary transformation of ϕ_1 and ϕ_2. Also, we have chosen the unitary transformation so as to maximize the norms of a_1 and b_2 (or to minimize the norms of b_1 and a_2), $\langle a_1|a_1\rangle^2 + \langle a_2|a_2\rangle^2$ and $\langle b_1|b_1\rangle^2 + \langle b_2|b_2\rangle^2$ being invariant to any unitary transformation.

For the DODS cases, we simply set $b_1 = a_2 = b_3 = 0$. Thus, the SO-SCF-DODS wave function takes the form

$$\Psi_{\text{SO-SCF-DODS}} = \mathcal{A}[a_1 b_2 a_3 (C_1\theta_1 + 3^{-1/2}C_2\theta_2)] \ . \tag{65}$$

The SEHF functions corresponding to Eqs. (63) and (65) arise from the constraint $C_1 = C_2$:

$$\Psi_{\text{SEHF-GSO}} = (\Psi_{\text{SO-SCF-GSO}})_{C_1=C_2} \tag{66}$$

$$\Psi_{\text{SEHF-DODS}} = (\Psi_{\text{SO-SCF-DODS}})_{C_1=C_2} \tag{67}$$

Needless to say, the DODS theories lack the elements which allow the two spin components, α and β, to mix with each other. As a result, GSO solutions generally cannot be attained when DODS solutions are used as initial guesses. It is worth noting that, none the less, the SO-SCF-DODS wave function occasionally gives a local minimum in the GSO space. Conversely, when calculations are started from certain GSO's the solutions may in cases converge to the SO-SCF-DODS results. In actual computations, therefore, several trial GSO's as initial guesses were tested in order to confirm the convergence of the iterations to the SO-SCF-GSO results.

The SO-SCF-GSO calculations were carried out by use of the double ζ basis functions (1s and 1s$'$ Slater-type orbitals) for each hydrogen atom. For the sake of simplicity, p orbitals were set aside. The STO's were assigned the exponents given by Shavitt et al.[24] They were expanded in terms of six Gaussian type orbitals. In order to compare the results on a common base, the same basis functions were used for the other orbital theories. The SCF procedure was iterated until the energy difference between successive two steps did not exceed 10^{-6} hartree.

Table II shows the LCAO coefficients for the SO-SCF-GSO's obtained. Functional profiles of these GSO's are presented in Fig. 2. The first and the second orbitals, ϕ_1 and ϕ_2, are mutually orthogonal and delocalized over the whole molecule. The third orbital ϕ_3 is somewhat localized on the H3 atom, which will become an isolated atom in the dissociation limit. In all these orbitals the α- and β-components have different nodal structures, thus making different contributions to the chemical bonds.

In Table III, the total (E), electronic (E_e), kinetic (T), nuclear-attraction (V_{en}) and electron-repulsion (V_{ee}) energies calculated by means of the various orbital theories are compared. It can be seen that the SO-SCF-GSO method gives the lowest total energy. The difference in E(0.00474 hartree) between the SO-SCF-DODS and the SO-SCF-GSO theories is much greater than that (0.00098 hartree) between the SO-SCF-DODS and the SEHF-GSO methods. The SEHF-GSO total energy was improved significantly by the SO-SCF-GSO method as a result of the orbital nonorthogonality and the spin-optimization; $C_1 \neq C_2$. The energy improvement (0.00376 hartree) is comparable in magnitude to the difference (0.00526 hartree) between the RHF and the SEHF-DODS total energies.

Although the SO-SCF-GSO wave function provides apparently better results than does any other existing orbital theory, the total energy obtained is still too high by ca. 12 kcal/mol as compared with that resulting from the CI treatment.[24] A great part of this energy difference is no doubt due to the dynamical correlation; orbital approximations are incapable of taking due account of the dynamical motion of electrons.

VI. CONCLUDING REMARKS

The SO-SCF-GSO theory as an extention of the SO-SCF-DODS and SEHF-GSO methods takes maximal account of the degrees of freedom for variation. As a consequence, the theory is in principle by far more flexible than any other orbital theory so far presented, thus providing the most accurate results for atomic and molecular systems which are represented by given basis set functions.

Generally, GSO's are expected to gain further flexibility by the introduction of complex variable; while real GSO's have only two-dimensional spin structure, the complex component of GSO's should give an additional dimension, i.e. the component in the y direction. The treatment of Eq. (34) involving complex variables is straightforward. We believe that such a treatment will be important not only for the consideration of the electron correlation effect, but also for the argument of the continuity of the orbital phase when the electronic states of highly symmetric molecules or degenerate states are investigated. It would hardly be possible to deal with this latter problem properly by means of any other orbital theory.

In this paper we have examined only the energy to compare the SO-SCF-GSO method with other methods. However, it is expected that the theory will be capable of providing improved expectation values for other quantities, such as the Fermi contact shift of atoms, as well. This phase of the problem will be discussed elsewhere.

APPENDIX A: GROUP ALGEBRA AND k-COEFFICIENT

Group algebra[20] may be considered as a set of all linear combinations of the elements of a group. The structure of a group algebra is characterized by means of the fundamental units e^{λ}_{ij}'s for an irreducible representation Γ^{λ}, which satisfy the following fundamental relation:

$$e^{\lambda}_{ij} e^{\mu}_{k\ell} = \delta_{\lambda\mu} \delta_{jk} e^{\lambda}_{i\ell} \quad . \tag{A1}$$

e^{λ}_{ij}'s are constructed in various ways. It was shown by Wigner[25] that, for a given group G,

$$e^{\lambda}_{ij} = \frac{f^{\lambda}}{|G|} \sum_{t \in G} \Gamma^{\lambda}_{ji}(t^{-1}) t \tag{A2}$$

where f^{λ} is the dimension of Γ^{λ}. The essential properties of the algebra for a symmetric group S_N are

$$S^2 e^{\lambda}_{ii} = S_{\lambda}(S_{\lambda} + 1) e^{\lambda}_{ii} \tag{A3}$$

and

$$\begin{aligned} \frac{1}{f^{\lambda}} P^o P^s \sum_{ij} \tilde{e}^{\lambda}_{ij} e^{\lambda}_{ij} C_j &= P^o P^s \mathcal{A} \sum_{i} C_i e^{\lambda}_{ii} \\ &= - \mathcal{A} \sum_{i} C_i e^{\lambda}_{ii} \end{aligned} \tag{A4}$$

where P^o and P^s are the permutations operating concurrently on the spatial and spin coordinate, respectively. A very wide and profound review was given by Löwdin and Goscinski.[20b]

In treating a spin symmetry λ, the ith spin function θ^{λ}_{i} is written in terms of the linear combination of the products of one-electron spin functions (α or β) such that

$$\theta_i^\lambda = \sum_u k_i^u \eta_u \tag{A5}$$

where $\eta_u = \alpha(1)\beta(2)\cdots$ (with a given S_z value). With the aid of the orthogonality $\langle\eta_u|\eta_v\rangle = \delta_{uv}$ and the ket-bra expression $e_{ij}^\lambda = |\theta_i^\lambda\rangle\langle\theta_j^\lambda|$, which evidently satisfies the fundamental multiplication relation (A1), one can easily derive the relationship:

$$e_{ij}^\lambda \eta_u = k_j^u \theta_i^\lambda \tag{A6}$$

The relation (A6) has been used to derive Eq. (14). In particular, since

$$e_{ii}^\lambda \eta_u = k_i^u \theta_i^\lambda \, , \tag{A7}$$

the diagonal element e_{ii}^λ is regarded as an operator which projects an arbitrary spin product η_u on the space of a given spin function θ_i^λ.

APPENDIX B: PROOF OF "KOOPMANS' THEOREM"

The theorem is proven for Mth orbital here. The N-particle SO-GSO wave function, Eq. (9), can be written as

$$\Psi = P_z^q \, \mathcal{A}\Big(\sum_{ij} R_{ij} e_{ij}^\lambda\Big)(\phi_1 \cdots \phi_N \cdots \phi_{N-1}\phi_M) \tag{B1}$$

where

$$R_{ij} = -\sum_m \Gamma_{im}^\lambda(p)\Gamma_{jm}^{\lambda *}(p) C_m \tag{B2}$$

and $(\phi_1 \cdots \phi_N \cdots \phi_M) = P(\phi_1 \cdots \phi_M \cdots \phi_N)$, i.e., $p = (M,N)$.

An $\hat{S}_z$-projection of the product of GSO's can be split into

$$
\begin{aligned}
&P_z^q(\phi_1 \cdots \phi_N \cdots \phi_{N-1}\phi_M) \\
&= \{P_z^{q-1/2}\phi_1 \cdots \phi_N \cdots \phi_{N-1}\}\begin{pmatrix} a_M \\ 0 \end{pmatrix} + \{P_z^{q+1/2}\phi_1 \cdots \phi_N \cdots \phi_{N-1}\}\begin{pmatrix} 0 \\ b_M \end{pmatrix} \\
&= f_M^- \, a_M \, \alpha \; + \; f_M^+ \, b_M \, \beta
\end{aligned}
\tag{B3}
$$

It follows that

$$
\begin{aligned}
&\langle\Psi|(H - E)|\Psi\rangle \\
&= \sum_{ij}\sum_{mn} R_{ij}^{*} R_{mn} \langle e_{ij}^{\lambda}(f_M^- a_M \alpha + f_M^+ b_M \beta)|(H - E)\,\mathcal{A}_N| \\
&\qquad\qquad \times e_{mn}^{\lambda}(f_M^- a_M \alpha + f_M^+ b_M \beta)\rangle \; .
\end{aligned}
\tag{B4}
$$

The term proportional to $\langle\phi_M|\phi_M\rangle = \langle a_M|a_M\rangle + \langle b_M|b_M\rangle$ should be the object of our search.

First, let us derive the term proportional to $\langle a_M|a_M\rangle$. It now suffices to consider

$$
\sum_{ij}\sum_{mn} R_{ij}^{*} R_{mn} \langle e_{ij}^{\lambda} f_M^- a_M \alpha|(H - E)\,\mathcal{A}_N|e_{mn}^{\lambda} f_M^- a_M \alpha\rangle \; .
\tag{B5}
$$

The GSO product f_M^- is expanded as

$$
f_M^- = \sum_u \psi_u^- \, \eta_u^- \; ,
\tag{B6}
$$

where η_u^- is the simple product of one-particle spin functions with the net eigenvalue q-1/2 of $\hat{S}_z$, while ψ_u^- is its associated spatial function. We can write

$$
\sum_j R_{ij} e_{ij}^{\lambda} f_M^- \, a_M \, \alpha = \chi_i^- \, a_M \, \theta_i^{\lambda}
\tag{B7}
$$

with

$$\chi_i^- = \sum_{ju}\sum R_{ij} \langle\theta_j^\lambda|\eta_u^-\alpha\rangle\, \psi_u^- \tag{B8}$$

Hence, Eq. (B5) becomes

$$\sum_{ij} \langle\chi_i^-\, a_M\, \theta_i^\lambda|(H - E)\,\mathcal{A}_N|\chi_j^-\, a_M\, \theta_j^\lambda\rangle\ . \tag{B9}$$

On the other hand, θ_i^λ is known to be decomposed into two parts:[8]

$$\theta_i^\lambda = d_-^{\lambda_1}\, \theta_{i,q-1/2}^{\lambda_1}\, \alpha \;+\; d_+^{\lambda_1}\, \theta_{1,q+1/2}^{\lambda_1}\, \beta \qquad \text{for}\quad i = 1,2,\ldots,f^{\lambda_1} \tag{B10a}$$

$$\theta_i^\lambda = d_-^{\lambda_2}\, \theta_{i,q-1/2}^{\lambda_2}\, \alpha \;+\; d_+^{\lambda_2}\, \theta_{i,q+1/2}^{\lambda_2}\, \beta \qquad \text{for}\quad i = f^{\lambda_1} + 1,\ldots,f^\lambda \tag{B10b}$$

where

$$\begin{aligned} d_-^{\lambda_1} &= -[(S_\lambda - q + 1)/(2S_\lambda + 2)]^{1/2} \\ d_+^{\lambda_1} &= [(S_\lambda + q + 1)/(2S_\lambda + 2)]^{1/2} \\ d_-^{\lambda_2} &= [(S_\lambda + q)/2S_\lambda]^{1/2} \\ d_+^{\lambda_2} &= [(S_\lambda - q)/2S_\lambda]^{1/2}\quad . \end{aligned} \tag{B11}$$

The decomposition stated above is as illustrated in Fig. 1. The term proportional to $\langle a_M|a_M\rangle$ is extracted from Eq. (B9) with the help of Eq. (B10) and $(d_+^{\lambda_p})^2 + (d_-^{\lambda_p})^2 = 1$. The proportionality factor is

$$A_M = \frac{1}{N}\sum_{\lambda_p}\sum_{ij}^{(\lambda_p)} \langle\chi_i^-\, \theta_{i,q-1/2}^{\lambda_p}|(H_{N-1} - E)\,\mathcal{A}_{N-1}|\chi_j^-\, \theta_{j,q-1/2}^{\lambda_p}\rangle\ , \tag{B12}$$

where H_{N-1} and $\mathcal{A}_{N-1}$ are the (N - 1)-body Hamiltonian and antisymmetrizer, respectively.

In exactly the same manner, the term proportional to $\langle b_M|b_M\rangle$ can be obtained. The resulting factor B_M is simply what is obtained from Eq. (B12) by replacing χ_i^- and q-1/2 by χ_i^+ and q+1/2, respectively.

Because

$$A_M\langle a_M|a_M\rangle + B_M\langle b_M|b_M\rangle = \frac{1}{2}(A_M + B_M)\langle\phi_M|\phi_M\rangle + \frac{1}{2}(A_M - B_M)(\langle a_M|a_M\rangle - \langle b_M|b_M\rangle) , \tag{B13}$$

the orbital energy ε_M, according to Eq. (40), is

$$\begin{aligned}\varepsilon_M &= -\frac{1}{2}(A_M + B_M)\\ &= -\frac{1}{2N}\sum_{\lambda_p}\sum_{ij}^{(\lambda_p)}(\langle\chi_i^- \theta_{i,q-1/2}^{\lambda_p}|(H_{N-1} - E)\mathcal{A}_{N-1}|\chi_j^- \theta_{j,q-1/2}^{\lambda_p}\rangle\\ &\quad + \langle\chi_i^+ \theta_{i,q-1/2}^{\lambda_p}|(H_{N-1} - E)\mathcal{A}_{N-1}|\chi_j^- \theta_{j,q-1/2}^{\lambda_p}\rangle) .\end{aligned} \tag{B14}$$

If the (N - 1)-body wave functions is denoted as

$$\Psi_{q\pm1/2}^{\lambda_p} = \mathcal{A}_{N-1}\sum_i^{(\lambda_p)} \chi_i^\pm \theta_{i,q\pm1/2}^{\lambda_p} \qquad (p = 1,2) , \tag{B15}$$

Eq. (B14) reduces to

$$\varepsilon_M = \frac{1}{2N}\sum_{\lambda_p}\{\langle\Psi_{q+1/2}^{\lambda_p}|\Psi_{q+1/2}^{\lambda_p}\rangle(E - E_{q+1/2}^{\lambda_p}) + \langle\Psi_{q-1/2}^{\lambda_p}|\Psi_{q-1/2}^{\lambda_p}\rangle(E - E_{q-1/2}^{\lambda_p})\}, \tag{B16}$$

with the energies of the ionized state expressed as

$$E^{\lambda_p}_{q\pm 1/2} = \frac{\langle \Psi^{\lambda_p}_{q\pm 1/2} | H_{N-1} | \Psi^{\lambda_p}_{q\pm 1/2} \rangle}{\langle \Psi^{\lambda_p}_{q\pm 1/2} | \Psi^{\lambda_p}_{q\pm 1/2} \rangle} \quad . \tag{B17}$$

This completes the proof of "the Koopmans theorem" for the Mth SO-SCF-GSO.

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TABLE I. Typical SCF orbital theories

Orbital	HF	SEHF	SO-SCF
DOUBLY OCCUPIED	RHF[a]	——	——
DODS	SPHF[b]	SEHF-DODS[d]	SO-SCF-DODS[f]
GSO	SDW[c]	SEHF-GSO[e]	SO-SCF-GSO[g]

a Roothaan (Ref. 2). b Pople et al. (Ref. 4)

c Spin Density Wave, A. W. Overhauser, Phys. Rev. Lett. **4**, 462 (1960). d Löwdin (Ref. 6).

e Löwdin et al. (Ref. 6,11). f Kaldor et al. and Goddard (Ref. 9). g This study

TABLE II. LCAO coefficients for the SO-SCF-GSO's of a linear H_3 system[a]

Basis function[b]			ϕ_1		ϕ_2		ϕ_3	
			a_1	b_1	a_2	b_2	a_3	b_3
H1	1S	(0.986)	0.45745	0.35669	-0.22212	-0.04429	-0.21085	-0.27085
	1S'	(1.371)	0.24500	-0.04475	0.64441	0.14466	0.11832	0.10204
H2	1S	(1.054)	-0.01121	0.39468	-0.50520	-0.28896	-0.09574	-0.17880
	1S'	(1.297)	-0.15022	-0.15237	0.91679	0.06588	0.26743	-0.16162
H3	1S	(0.943)	-0.30363	-0.31282	0.27430	0.37513	0.40388	0.91787
	1S'	(1.066)	-0.33610	0.33864	0.20588	-0.00533	0.44645	-0.60572

[a] The coordinates (x, y, z) in bohr of each H-atom are H1 = (-1.47, 0, 0), H2 = (0, 0, 0), H3 = (2.984, 0, 0). [b] The values in parentheses are the orbital exponents for STO's, taken from Ref. 24.

TABLE III. Comparisons of the energies (hartree) for linear H_3[a] obtained by typical orbital theories[b].

Energy	RHF	DODS		GSO	
		SEHF	SO-SCF	SEHF	SO-SCF
E[c]	-1.61796	-1.62322	-1.63847	-1.63945	-1.64321
E_e[d]	-2.85787	-2.86313	-2.87838	-2.87936	-2.88312
T[e]	1.61725	1.62189	1.66168	1.65911	1.65607
V_{en}[f]	-5.64887	-5.64283	-5.67909	-5.67618	-5.66824
V_{ee}[g]	1.17375	1.15781	1.13902	1.13771	1.12905
C_2/C_1	——	——	0.105959	——	0.277304

[a] Geometry is the same as given in Table II.

[b] The same orbital exponents as listed in Table II were used.

[c] Total energy; the CI treatment in which a 2p orbital is also incorporated gives E = -1.66304 hartrees (Ref. 24).

[d] Electronic energy.

[e] Kinetic energy.

[f] Nuclear-attraction energy.

[g] Electron-repulsion energy.

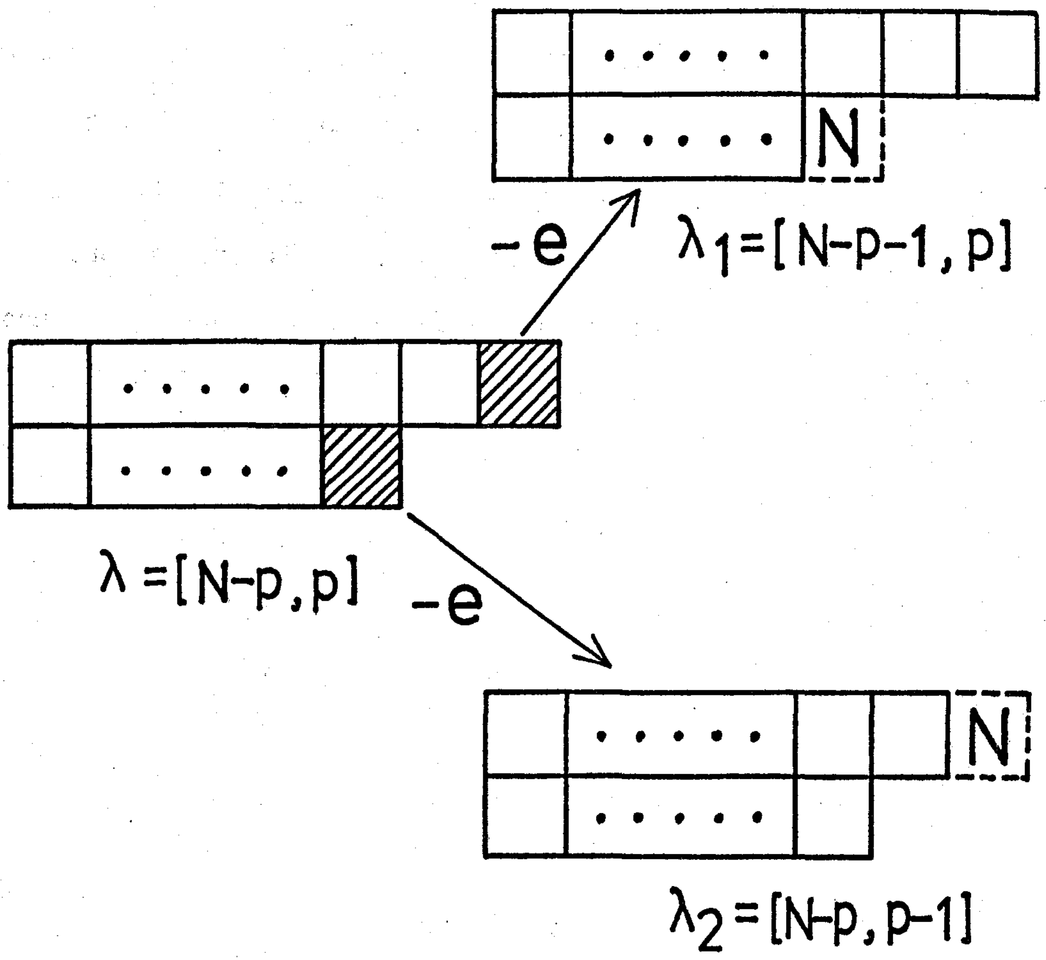

Figure 1. Ionization to two species with different spin symmetries.

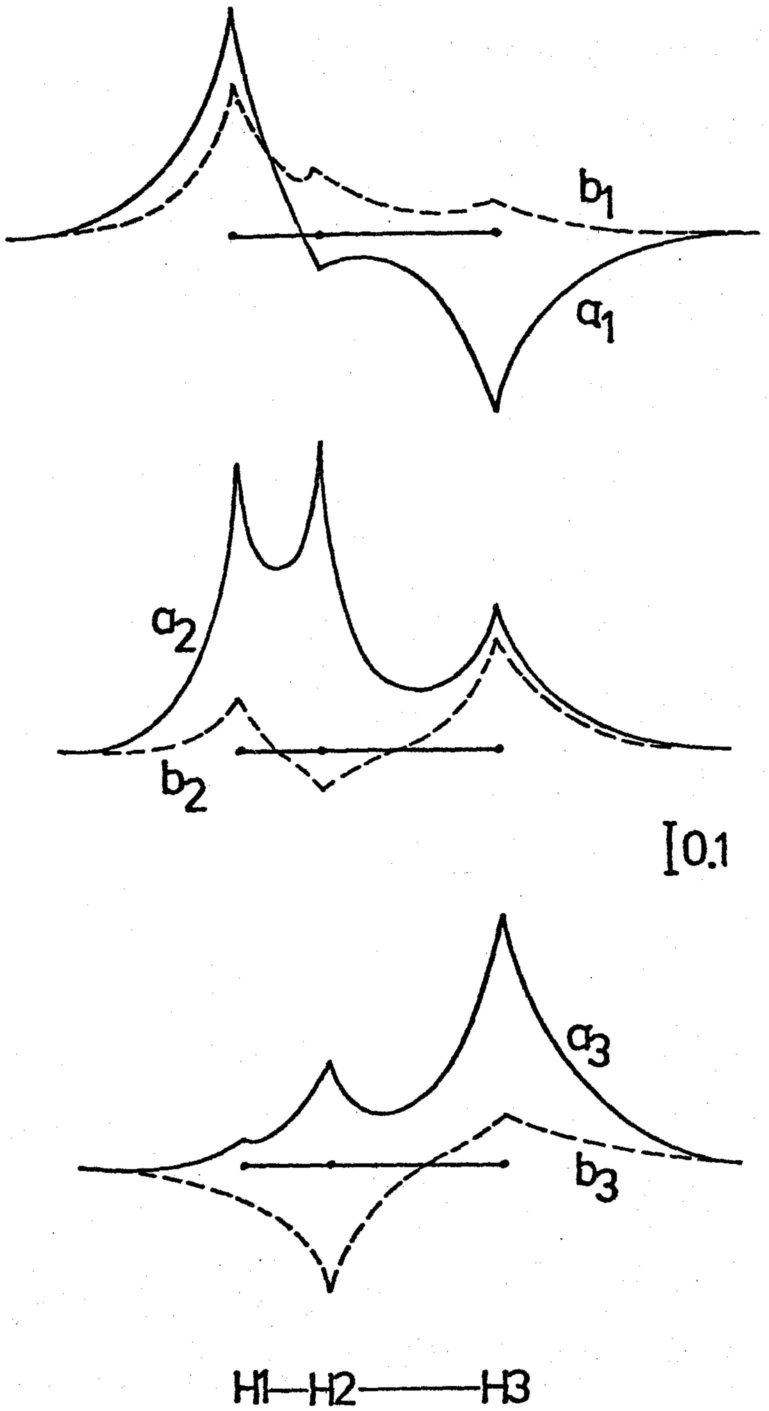

Figure 2. Profiles of the GSO's for the linear H_3 system with bond lengths 1.470 and 2.984 bohrs. The ith orbital ϕ_i is denoted as $\phi_i = a_i\alpha + b_i\beta$.

CHAPTER 3

Spin-Optimized SCF General Spin Orbitals in the 2^2S and 2^2P States of the Lithium Atom

The spin-optimized SCF general-spin-orbital (SQ—SCF—GSO) method, which has previously been proposed by us, is applied to the 2^2S and 2^2P states of a lithium atom. The energies obtained are -7.448522 and -7.381053 hartrees, respectively, which account for as much as 99.7% (2^2S) and 97.7% (2^2P) of the radical limits of electron correlation. However, the Fermi contact terms calculated, 2.750 (2^2S) and -0.1953 (2^2P), are not necessarily improvements over the values obtained by hitherto-known orbital theories. This latter result is ascribable to the functional forms of the orbitals, which cannot fully account for the electron correlation without unduly reducing the weight for the configurations of spin polarization. The situation has been clarified for the case of the 2^2P state through comparative analyses of various existing orbital theories.

I. INTRODUCTION

The spin-optimized SCF general-spin-orbital (SO—SCF—GSO) wavefunction is defined[1] as

$$\Psi = P_z^q \mathcal{A} \sum_i^{f^\lambda} C_i e_{ii}^\lambda \phi_1 \phi_2 \cdots \phi_N, \tag{1}$$

where ϕ_k is a two-component spinor

$$\phi_k = \begin{pmatrix} a_k(r) \\ b_k(r) \end{pmatrix} = a_k(r)\alpha + b_k(r)\beta, \tag{2}$$

which is termed a general spin orbital (GSO).[2] $\mathcal{A}$ and P_z^q are the antisymmetrizer and the $\hat{S}_z$-projection operator for the least nonnegative $\hat{S}_z$ eigenvalue q, respectively; e_{ii}^λ is the ith generating operator for the spin function of the symmetry λ; and C_i is a variation parameter called the spin-coupling coefficient associated with e_{ii}^λ. General properties of the SO—SCF—GSO wavefunction have been discussed in detail previously (Part I[1] of this series). Suffice it to mention here that our GSO theory can be reduced to a one-body quasieigenvalue problem expressed as

$$\begin{pmatrix} G_{11}^k & G_{12}^k \\ G_{21}^k & G_{22}^k \end{pmatrix} \begin{pmatrix} a_k(r) \\ b_k(r) \end{pmatrix} = E \begin{pmatrix} S_{11}^k & S_{12}^k \\ S_{21}^k & S_{22}^k \end{pmatrix} \begin{pmatrix} a_k(r) \\ b_k(r) \end{pmatrix} \tag{3}$$

For explicit functional forms of the operators G_{ij}^k and S_{ij}^k, Paper I[1] should be referred.

The GSO wavefunction thus defined should in principle embrace all the known orbital functions of correct spin symmetry. Thus, the restricted Hartree-Fock (RHF) function,[3] the SO−SCF function in the different-orbitals-for-different-spins scheme (SO−SCF−DODS),[4] and the spin-extended Hartree-Fock functions[2,5a] in both the DODS (SEHF−DODS)[5a] and GSO (SEHF−GSO)[2,5] schemes could all be regarded as its special cases.

The purpose of this paper is to apply the SO−SCF−GSO theory to the 2^2S and 2^2P states of a lithium atom and to compare the results with those[6] that have been obtained by the various other theories. It has been found that the present GSO theory can indeed give the lowest energy as expected but is not necessarily best suited to the prediction of hyperfine structural parameters. The problem of the coupling between energy and spin polarization inherent in each orbital theory will be discussed in a comparative manner, taking the 2^2P state as an example.

II. BASIS FUNCTION

For a three-electron doublet system, f^λ is 2 and the spin functions generated by e^λ_{ii} are

$$\theta_1 = 2^{-1/2}(\alpha\beta\alpha - \beta\alpha\alpha), \tag{4a}$$

$$\theta_2 = 6^{-1/2}(\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta). \tag{4b}$$

Using these spin functions together with the spatial functions

$$\Phi_1(r_1, r_2, r_3) = 2^{-1/2}[a_1(r_1)b_2(r_2)a_3(r_3) - b_1(r_1)a_2(r_2)a_3(r_3)] \tag{5a}$$

$$\Phi_2(r_1, r_2, r_3) = 6^{-1/2}[a_1(r_1)b_2(r_2)a_3(r_3) + b_1(r_1)a_2(r_2)a_3(r_3) - 2a_1(r_1)a_2(r_2)b_3(r_3)], \quad (5b)$$

one can rewrite the SO—SCF—GSO wavefunction, Eq. (1), into

$$\Psi = \mathcal{A}[C_1\Phi_1\theta_1 + C_2\Phi_2\theta_2]. \quad (6)$$

For the sake of brevity, the SO—SCF—GSO method will hereafter be referred to as the "OG" theory.

The SEHF—GSO, SO—SCF—DODS, and SEHF—DODS wavefunctions, which will be abbreviated as the "EG," "OD," and "ED" functions, are obtained by imposing the following conditions on Eqs. (5) and (6):

(i) SEHF—GSO (EG), by letting $C_1 = C_2$;

(ii) SO—SCF—DODS (OD), by setting $b_1 = a_2 = b_3 = 0$;

(iii) SEHF—DODS (ED), by adopting the two constraints $C_1 = C_2$ and $b_1 = a_2 = b_3 = 0$, simultaneously.

Calculation of the GSO's, Eq. (3), were performed on the basis of the expansion technique of Roothaan.[3] One crucial problem in this connection is how to select a basis set such that the cusp condition is fulfilled. However, we will not be strict to those extremely complicated cusp conditions to be imposed on the orbitals.[7] Instead, we will be cautious about the cusp conditions for both the charge and spin densities denoted by γ_c and γ_s, respectively. Steiner showed,[8] on the basis of Kato's theory,[9] the following identity for the exact charge density:

$$\frac{d}{dr}\gamma_c(r)\Big|_{r=0} = -2Z\gamma_c(0) \quad (7a)$$

where Z is the nuclear charge. The basis-set dependence of $\gamma_s(0)$ should also be considered. As will be shown in Appendix A, the cusp condition pertaining to the spin density is

$$\frac{d}{dr}\gamma_s(r)|_{r=0} = -2Z\gamma_s(0). \qquad (7b)$$

The cusp values of $Z_c = -\gamma_c'(0)/2\gamma_c(0)$ and $Z_s = -\gamma_s'(0)/2\gamma_s(0)$ resulting from the use of a trial wavefunction must not deviate greatly from Z in order for the function to be acceptable as a sufficiently good approximation.

The basis set actually selected for use for the 2^2S state was the same as that used by Kaldor and Harris.[4b] The various orbital wavefunctions of the 2^2P state were calculated on the basis of the basis set given by Lunell,[10] although we neglected two Slater-type orbitals having very small coefficients in his OD calculation,[10] namely, the 3s and $2p_+$ orbitals with the exponents 0.8451 and 4.5, respectively. The wavefunctions of 2^2S fulfilled the cusp condition for the spin density, Eq. (7b), but those of 2^2P generally did not. Incidentally, all the wavefunctions under study can only account for the radical electron correlation, because the basis sets contain s-type functions alone for the core.

III. RESULTS OF THE SO—SCF—GSO COMPUTATION

A. Orbitals

The amplitudes of the spatial orbitals obtained for the 2^2S and

2^2P states are shown in Figs. 1 and 2, respectively. As has been mentioned previously,[1] orbitals $1(\phi_1)$ and $2(\phi_2)$ (both being the core orbitals) have been transformed so as to maximize the norm of the $\alpha(\beta)$-spin part of $\phi_1(\phi_2)$. They are orthogonal to each other in the sense of spin-orbital orthogonality; $<\phi_1|\phi_2> = <a_1|a_2> + <b_1|b_2> = 0$.

The most striking feature of Figs. 1 and 2 is the presence of a node[4,11,13a] in one component of each spinor. The components a_1, b_2, a_3 are nodeless just as those of the OD orbitals. On the other hand, the components b_1 and a_2 for either of the 2^2S and 2^2P states exhibit a functional form analogous to that of the 2s Hartree-Fock orbital, which does possess a node. b_3 for the 2^2S state also has a node and is more attracted toward the nucleus than is a_3. In the 2^2P state, neither a_3 nor b_3 has a node. As in the case of 2^2S, a_3 is diffused but b_3 has a large maximum in the vicinity of the nucleus. Such nodal properties of the GSO's will eventually allow the wavefunction to take more electron correlation into account as compared with other types of wavefunctions.

B. Expectation values

The total energy E, the radical electron correlation ΔE, the hyperfine structure parameters f and ℓ, and the electron density at nucleus $\gamma_c(0)$ calculated by the OG method are listed in Table I, together with those obtained by other orbital theories (including the RHF theory[12]) as well as the radical CI treatment.[5g] For the sake of reference, the experimental data[14-16] are also given. For the 2^2P state, the ED, OD and EG calculations were repeated by use of the same basis set as used for the present OG calculation.

Inspection of the total energies given in Table I shows that the OG theory has improved both the EG and OD results by ca. 6% in electron correlation. Obviously, the improvement is a consequence of the reality that the OG method is variationally more general than the other two theories. Notice that the OG method is able to account for as much as 99.7% (2^2S) and 97.7% (2^2P) of the radical electron correlation.

Considered next are three hyperfine parameters, i.e., the Fermi contact term f, the orbital azimuthal index ℓ and the spin dipole d which are defined respectively by

$$f = 8\pi \left\langle \sum_i \delta(r_i) \hat{S}_{Z_i} \right\rangle , \tag{8a}$$

$$\ell = \left\langle \sum_i \frac{\ell_{Z_i}}{r_i^3} \right\rangle , \tag{8b}$$

and

$$d = \left\langle \sum_i \frac{3Z_i^2 - r_i^2}{r_i^5} \hat{S}_{Z_i} \right\rangle . \tag{8c}$$

The relationship $d = -\ell/5$ holds exactly for the basis set chosen in this work. The absolute values of f obtained by the OG theory are smaller than those calculated by other theories. The agreements of the OG f values with the experimental data are apparently worse than those of the OD, EG, and CI f values. As for the ℓ and $\gamma_c(0)$ values, the calculated results are not much different from one another, even though the ED theory tends to give somewhat smaller values of $\gamma_c(0)$.

Table I also lists the cusp values Z_c and Z_s. Seemingly, all the wavefunctions satisfy the cusp condition for the charge density. The spin cusp condition, however, seems to be more difficult to be satisfied. These results together strongly suggest that Z_s is generally more sensitive to the choice of basis sets than is Z_c.

IV. COMPARATIVE ANALYSES OF VARIOUS ORBITAL THEORIES

Although our OG (i.e., SO–SCF–GSO) theory provides the state energies of a lithium atom more accurately than does any other orbital theory hitherto proposed, it is apparently less reliable for the prediction of the Fermi contact term f. For Li(2^2P), the state energy decreases in the order

$$\mathrm{ED} > \mathrm{OD} \gtrsim \mathrm{EG} > \underline{\mathrm{OG}} \gtrsim \mathrm{CI} \tag{9a}$$

while $|f|$ diminishes in the order as follows:

$$\mathrm{ED} > \mathrm{CI} \gtrsim \mathrm{EG} \gtrsim \mathrm{OD} > \underline{\mathrm{OG}}\,. \tag{9b}$$

It is generally accepted that the spin polarization configurations, which dominantly govern the spin density distribution, do not strongly contribute to the correlation energy. It is mainly the doubly-excited configurations[17] that can account for the correlation energy. These two types of configurations should be varied independently if <u>both</u> the spin density and energy are to be calculated with fair accuracy. In orbital theories, however, these configurations are coupled with each other through some parameters involved in the mathematical formalisms for the determination of orbitals.[18,19] Thus, the orbital form fixed most favorably for the energy tends to place a stumbling block against reliable evaluations of the f values. In what follows, we will consider in some detail how the energy and the spin polarization are to be coupled with each other in the various orbital theories applied to Li(2^2P).

A. Spin-optimization of the DODS wavefunctions (ED vs. OD)

The OD theory is apparently superior to the ED in both E and f, a trend which suggests a basic significance of the spin optimization effect. We will take a closer look at this effect from the viewpoint of the core orbital splitting.

Denoting the two core orbitals by a and b and the valence p orbital by v, one can write the (unnormalized) DODS wavefunction as

$$\Psi_{DODS} = \mathcal{A} abv(\theta_1 + 3^{-1/2}\sigma\theta_2), \tag{10}$$

where $\sigma(= C_2/C_1)$ is fixed at unity in the ED theory whereas it is optimized by variation in the OD method. Since v's of ED and OD coincide with each other to within 10^{-3} in the coefficients for atomic orbitals, we will leave v out of discussion.

The DODS core orbitals a and b can be expanded over a natural orbital set $\{\phi_k\}$. Suppose that the expanded orbitals are expressible with deviation parameters τ_k's as[19]

$$a = \phi_1 + \sum_{k=1} (A_k + \tau_k)\phi_k, \tag{11a}$$

$$b = \phi_1 - \sum_{k=1} (A_k - \tau_k)\phi_k. \tag{11b}$$

The DODS wavefunction would then take the form:

$$\Psi_{\mathrm{DODS}} = \mathcal{A}\Phi^{\circ}_1\theta_1 + \sigma\mathcal{A}\Phi^{\circ}_2\theta_2, \tag{12}$$

where the first term represents the singlet-type core structure

$$\begin{aligned} \mathcal{A}\Phi^{\circ}_1\theta_1 &= \mathcal{A}(\phi_1\phi_1 v\theta_1) + 2\sum_k \tau_k \mathcal{A}(\phi_k\phi_1 v\theta_1) \\ &\quad - \sum_{k\neq 1}\sum_{\ell\neq 1} (A_k + \tau_k)(A_\ell - \tau_\ell)\mathcal{A}(\phi_k\phi_\ell v\theta_1), \end{aligned} \tag{13a}$$

while the second, the core structure of the triplet type

$$\begin{aligned} \Phi^{\circ}_2\theta_2 &= 2\cdot 3^{-1/2} \sum_{k\neq 1} A_k \mathcal{A}(\phi_k\phi_1 v\theta_2) \\ &\quad - 3^{-1/2} \sum_{k\neq 1}\sum_{\ell\neq 1} (A_k + \tau_k)(A_\ell - \tau_\ell)\mathcal{A}(\phi_k\phi_\ell v\theta_2). \end{aligned} \tag{13b}$$

Both the ED and OD core-orbitals for Li(2^2P) were expanded over the natural orbitals derived from the ED orbitals. The results are given in Table II. The most salient points of Table II are the following:

(i) In the ED case, the core orbitals a and b are only slightly polarized ($|A_k| << 1$) in a symmetric manner ($\tau_k \simeq 0$);

(ii) In the OD case, the spin polarization is not only relatively large but less symmetrical ($0 \neq |\tau_k| << |A_k| < 1$).

As is apparent from Eq. (13), an increasing spin polarization, $|A_k|$, tends to lower the energy of the singlet-type part E_{11} =

$\langle \mathcal{A}\Phi^{\circ}\theta_1|H|\mathcal{A}\Phi^{\circ}\theta_1\rangle$ but elevate that of the triplet-type counterpart $E_{22} = \langle \mathcal{A}\Phi_2^{\circ}\theta_2|H|\mathcal{A}\Phi_2^{\circ}\theta_2\rangle$. The total DODS energy is determined by a compromise between these two opposing contributions. In the ED formalism, in which σ is fixed at unity, it is a necessity to keep the core spin polarization relatively small[20] in order to avert from a rapid rise of E_{22} as the function of $\sum_k |A_k|^2$ (Fig. 3). By contrast, the OD wavefunction, for which σ is optimized to be 0.0060, requires no such suppression of the core-orbital splitting. It gives a far lower energy determined principally by $\mathcal{A}\Phi_1^{\circ}\theta_1$ to which the doubly-excited configurations $\mathcal{A}(\phi_k\phi_\ell v\theta_1)$ are allowed to contribute appreciably. Clearly, the SEHF condition $\sigma = 1$ lays a strong restraint on the DODS scheme.

As for the Fermi contact values, it is most illuminating to compare the two theories in an iterative manner as follows. By use of the ED orbitals, we obtain a first-order OD approximation to σ:

$$\sigma^{(0)} = -\frac{H_{12}}{H_{22} - E_{ED}S_{22}} \tag{14}$$

where S_{ij} and H_{ij} respectively stand for the overlap integral $\langle \mathcal{A}\Phi_i\theta_i|\mathcal{A}\Phi_j\theta_j\rangle$ and the corresponding Hamiltonian matrix element. Evaluation of Eq. (14) results in $\sigma^{(0)} = 0.8460$, which in turn gives the first-order approximation to f_{OD}:

$$f^{\circ}_{OD} = 2\langle \mathcal{A}\Phi_1^{\circ}\theta_1|\hat{f}|\sigma\mathcal{A}\Phi_2^{\circ}\theta_2\rangle = 0.8460\ f_{ED} \tag{15}$$

Thus, $f^{\circ}_{OD} = -0.2514$ while $f_{ED} = -0.2972$. It is quite natural that the OD orbitals adjusted by use of $\sigma^{(0)}$ will further lower σ at the expense of core spin polarization. The net effect is to diminish the $|f|$ value further. It is expected, therefore, that in the limit of spin optimization we have

$$|f_{ED}| > |f_{OD}|. \tag{16}$$

The OD energy (-7.380119 hartree) agrees nearly perfectly with the energy (-7.380115 hartree) obtained by the G1 — SCF ($\sigma = 0$) theory.[13a] Thus, it seems reasonable to consider[5a,21] that the OD orbitals are variationally fixed by the electron correlation effect due to $\mathcal{A}(\phi_k \phi_\ell v \theta_1)$ rather than by the spin polarization arising from $\mathcal{A}(\phi_k \phi_1 v \theta_2)$. Ladner and Goddard[4a] confirmed this point by direct calculations of G1 and OD orbitals for Li(2^2S).

The above view can be rationalized from a similarity between the OD and G1 orbitals (Appendix B). It is thus definite that, like the G1 orbitals, the OD orbitals are split almost exclusively by electron correlation. This supports the conclusion reached by Ishida and Nakatsuji[21] from the results of MC — SCF calculation. In fact, we can reproduce the OD f-value by use of the G1 orbitals through the approximate expression

$$f^{\circ}_{OD} = - \frac{2H_{12}}{9S_{11}(H_{22} - E_{G1}S_{22})} [a^{\circ}(0)^2 - b^{\circ}(0)^2]$$

$$= -0.213 \tag{17}$$

in good agreement with $f_{OD} = -0.2142$.

B. Spin rotation in the SEHF theory (OD vs. EG)

The SEHF condition $C_1 = C_2$ places a serious restriction on the DODS scheme, as was argued in the preceding subsection. However, the defect can well be remedied within the framework of the SEHF scheme by the introduction of GSO[22] in place of DODS.

If the spin functions quantized in the x axis

$$\alpha_x = 2^{-1/2}(\alpha + \beta) \tag{18a}$$

$$\beta_x = 2^{-1/2}(\alpha - \beta) \tag{18b}$$

are used in the SEHF scheme, a simple EG function results:

$$\Psi^{\circ}_{EG} = \frac{1}{2} P^q_z \mathcal{A}(e_{11} + e_{22}) \begin{pmatrix} a \\ a \end{pmatrix} \begin{pmatrix} -b \\ b \end{pmatrix} \begin{pmatrix} v \\ 0 \end{pmatrix} \tag{19}$$

Since P^q_z and $\mathcal{A}(e_{11} + e_{22})$ commute with each other and since

$$\begin{aligned} P^q_z\, \alpha_x \beta_x \alpha &= -(\alpha\beta - \beta\alpha)\alpha/2 \\ &= -2^{-1/2}\theta_1 , \end{aligned} \tag{20}$$

Eq. (19) reduces to

$$\Psi^{\circ}_{EG} = 2^{-1/2} \mathcal{A}\, abv\theta_1 \tag{21}$$

Equation (21) is essentially equivalent to the G1 function, so that the adverse effect of the triplet-type core structure on E has been removed.

Let us now examine the relationship between the OD and EG theory. An OD wavefunction can readily be obtained by introducing the spin-optimization parameter σ into Eq. (19):

$$\Psi_{OD} = \frac{1}{2} P^q_z \mathcal{A}(e_{11} + e_{22}) \begin{pmatrix} a \\ a \end{pmatrix} \begin{pmatrix} -b \\ b \end{pmatrix} \begin{pmatrix} v \\ \sigma v \end{pmatrix} . \tag{22}$$

Correspondingly, the exact EG function is obtained by the optimization through further distortion of each spatial component:

$$\Psi_{EG} = \frac{1}{2} P_z^q \mathcal{A}(e_{11} + e_{22}) \begin{pmatrix} a + \delta a \\ a - \delta a \end{pmatrix} \begin{pmatrix} -b - \delta b \\ b - \delta b \end{pmatrix} \begin{pmatrix} v \\ \sigma v + \delta v \end{pmatrix}, \tag{23}$$

where δa, δb and δv are the first-order variations in orbital. It follows that

$$\Psi_{EG} = \Psi_{OD} + \delta\Psi_{EG}^{opt} \tag{24}$$

with

$$\delta\Psi_{EG}^{opt} = 3^{-1/2}\mathcal{A}[(\delta ab - a\delta b)v + ab\delta v]\theta_2, \tag{25}$$

as a first-order correction of spin polarization.[23]

Equation (24) together with Eq. (25) suggests the following:

(i) $\delta\Psi_{EG}^{opt}$ is not expected to greatly improve E_{OD}. In fact, $E_{EG} - E_{OD}$ is only -0.000105 hartree, namely, 0.6% of the radical electron correlation.

(ii) $\delta\Psi_{EG}^{opt}$ must correct the somewhat rigid property of $\mathcal{A}\Phi_2\theta_2$ of the OD formalism, to assure

$$|f_{CI} - f_{EG}| < |f_{CI} - f_{OD}|. \tag{26}$$

According to numerical calculations, $|f_{CI}| = 0.2306$ is greater than $|f_{OD}| = 0.2141$. The relationship (26) is, therefore, tantamount to the inequality

$$|f_{EG}| > |f_{OD}|, \tag{27}$$

insofar as $|f_{ED}|$ can never exceed $|f_{CI}|$.

C. Spin-optimization of the GSO wavefunctions (EG vs. OG)

The OG wavefunction can formally be derived from Ψ_{EG} [Eq. (23)] by introducing a spin optimization parameter $T(= C_2/C_1)$:

$$\Psi_{OG} = \frac{1}{2} P_z^q \mathcal{A}(e_{11} + Te_{22}) \begin{pmatrix} a + \delta a \\ a - \delta a \end{pmatrix} \begin{pmatrix} -b - \delta b \\ b - \delta b \end{pmatrix} \begin{pmatrix} v \\ \sigma v + \delta v \end{pmatrix}$$

$$= \Psi_{OD} + (T - 1)\sigma \mathcal{A} \overset{\circ}{\Phi}_2 \theta_2 + T\delta\Psi_{EG}^{opt} \tag{28}$$

where $\overset{\circ}{\Phi}_2$ is the OD spatial function. In the special case where $T = 1$, Eq. (28) reduces to Eq. (24). Note that, when Ψ_{OD} is expressed in the form of Eq. (12), Eq. (28) takes the form

$$\Psi_{OG} = \mathcal{A} \overset{\circ}{\Phi}_1 \theta_1 + T(\sigma \mathcal{A} \overset{\circ}{\Phi}_2 \theta_2 + \delta\Psi_{EG}^{opt}). \tag{29}$$

Starting from the EG function ($T = 1$, $\delta\Psi_{EG}^{opt} = 0$), we may now examine the effect of spin-polarization in the OG function. Just as in the case of DODS functions [Eq. (14)], one obtains upon spin optimization an approximate T value:

$$T^{(0)} \simeq - \frac{H_{12}}{H_{22} - E_{EG}S_{22}} \tag{30}$$

Because of the inequality $S_{11} >> S_{22}$ ($S_{22}/S_{11} \simeq 10^{-5}$), we can neglect the effect of renormalization. By reoptimizing the orbitals with this $T^{(0)}$ and recycling the process, one could reach a fully optimized OG wavefunction. However, preliminary calculations showed that the convergence of this SCF process is very slow, which suggests that the EG solution is considerably stable in the variational space of the OG solution. At this conjuncture, we have decided to look into the relationship between the EG and OG theories indirectly, adopting the OD wavefunction as a common basis.

In conformity to Eq. (24), the Fermi f value in the EG theory is expressed as

$$f_{EG} \simeq f_{OD} + 2\langle \mathcal{A}\Phi_1^{\circ}\theta_1 | \hat{f} | \delta\Psi_{EG}^{opt} \rangle . \tag{31}$$

Likewise, Eq. (28), when combined with Eq. (30), leads to a first-order approximation of f_{OG}:

$$\begin{aligned} f_{OG}^{\circ} \simeq f_{OD} &+ 2(T^{(0)} - 1)\langle \mathcal{A}\Phi_1^{\circ}\theta_1 | \hat{f} | \sigma\mathcal{A}\Phi_2\theta_2 \rangle \\ &+ 2T^{(0)}\langle \mathcal{A}\Phi_1^{\circ}\theta_1 | \hat{f} | \delta\Psi_{EG}^{opt} \rangle . \end{aligned} \tag{32}$$

Noting that

$$f_{OD} = 2\langle \mathcal{A}\Phi_1^{\circ}\theta_1 | \hat{f} | \sigma\mathcal{A}\Phi_2\theta_2 \rangle \tag{33}$$

one can readily show from Eqs. (31) and (32) that f_{OG}° can never be more negative than f_{OD} unless

$$T^{(0)} > \frac{f_{OD}}{f_{EG}} = \frac{-0.2141}{-0.2152} = 0.995 \tag{34}$$

In reality, the $T^{(0)}$ value (0.953) calculated from Eq. (30) does not satisfy the condition (34). This is due mainly to the third term of Eq. (25), $3^{-1/3}\mathcal{A}ab\delta v\theta_2$, which takes account of the core-valence correlation effect. Because this additional configuration is of high energy, the OG function involving it should naturally have $T^{(0)}$ which is at least discernibly smaller than unity. The nature of the configuration in question will be discussed in greater detail in the next subsection.

Using $f_{OD} = -0.2141$ [Eq. (33)] and $f_{EG} - f_{OD} = -0.0011$ [Eq. (31)] in place of the integrals and adopting $T^{(0)} = 0.953$, we can evaluate the first-order approximation f°_{OG} [Eq. (32)]. The result is $f^{\circ}_{OG} = f_{OD} + 0.0090 = -0.2051$, in reasonable agreement with $f_{OG} = -0.1953$. The ordering

$$|f_{EG}| \gtrsim |f_{OD}| > |f_{OG}| \tag{35}$$

has thus been rationalized.

D. Structure of $\mathcal{A}\Phi_2\theta_2$ (ED, OD, and EG vs. OG)

As has been stressed above, $\mathcal{A}\Phi_1\theta_1$ and $\mathcal{A}\Phi_2\theta_2$ couple with each other through common parameters involved in both of them. Hence, it strongly depends on the functional structure of $\mathcal{A}\Phi_2\theta_2$ whether or not the wavefunctions could yield good f values. Here we expand $\mathcal{A}\Phi_2\theta_2$ of the four functions over the common natural orbitals which have been derived from the ED solutions. Denote the s- and p-type natural orbitals by $\{\phi_i\}$ and $\{\psi_i\}$ (i = 1, 2,...), respectively. Then the f value is given principally by the matrix elements between the ground configuration $F_{11} = |\phi_1\bar{\phi}_1\psi_1|$ and the singly-excited configurations

$$F_{k1} = 6^{-1/2}\{|\phi_k\bar{\phi}_1\psi_1| + |\bar{\phi}_k\phi_1\psi_1| - 2|\phi_k\phi_1\bar{\psi}_1|\} \quad (k \neq 1) \tag{36}$$

which are contained in $\mathcal{A}\Phi_2\theta_2$.

Table III summarizes the expansion coefficients d_{k1}'s ($k = 1$) in the normalized $\Phi_2\theta_2$. In the GSO theories (i.e., EG and OG), the total weights of F_{k1}'s are relatively small; 0.4523 for EG and 0.3939 for OG. Other configurations which should contribute appreciably to the GSO functions are the doubly-excited configurations

$$F_{km} = 6^{-1/2}\{|\phi_k\bar{\phi}_1\psi_m| + |\bar{\phi}_k\phi_1\psi_m| - 2|\phi_k\phi_1\psi_m|\} \quad (k,m \neq 1) \qquad (37)$$

This is due to the orbital b_3 in Eq. (5b); it has large expansion coefficients over ψ_m ($m \neq 1$), in contrast to a_2, which is almost identical with ψ_1 itself. Because the configurations F_{km} hardly contribute to f, the increase in the weights of these configurations should in effect diminish $|f|$. Obviously, this diminution depends on the spin-coupling parameter σ also.

On the basis of the expansion coefficients for F_{k1} (Table III) together with the relevant σ values, each contribution f_k from F_{k1} to the total f

$$f_k = 2(S_{22}/S_{11})^{1/2} d_{k1}\sigma \langle F_{11}|\hat{f}|F_{k1}\rangle \qquad (38)$$

has been evaluated. The results are summarized in Table IV.

Table IV indicates, first, that

$$f \simeq \sum_{k\neq 1}^{7} f_k \qquad (39)$$

Second, the distribution patterns of f_k's in the OD and OG descriptions are similar to each other, and so are those of the ED and EG formalisms. In these latter cases, the contribution of f_2 is dominant over the rest.

It is interesting to note that the OD and EG have different structures of f while the net f values agree closely with each other.

In conclusion, we emphasize two important types of electron correlation effects on f, which are characteristic of the OG scheme. One is the effect based on the interaction between core and valence-shell electrons, as is endorsed by the significantly large contributions of F_{km}'s to the GSO functions. The other is based on the interaction between core electrons themselves, which brings forth the relatively large expansion coefficients to F_{kl}'s in the SO—SCF functions. Both these effects, which can be interpreted in terms of the functional structure of $\mathcal{A}\Phi_2\theta_2$, are implicitly reflected in E_{22} (Table III); the greater the weights of the excited configuration, the less stable is the triplet-type state $\mathcal{A}\Phi_2\theta_2$. It is noteworthy that the f values calculated by the four orbital theories increase in the same order as the E_{22} values.

V. DISCUSSION

In connection with the spin density in Li(2^2P), we will briefly discuss a special significance of the functional form of natural spin orbitals[5a] (NSO) as well as the occupation numbers of natural orbitals[5a] (NO). The charge and spin density functions, denoted by γ_c and γ_s, respectively, are split into the s and p components:

$$\gamma_c = \gamma_c^s + \gamma_c^p \tag{40}$$

$$\gamma_s = \gamma_s^s + \gamma_s^p \tag{41}$$

Here, we will focus our attention on the s-component because what we are considering about is specifically the splitting of the core due to the spin and electron correlations.

A. NSO and spin density

The NSO's with the s-symmetry are slightly split symmetrically from the corresponding NO in such a manner that

$$\phi_i^\alpha = \phi_i + \delta_i \tag{42a}$$

$$\phi_i^\beta = \phi_i - \delta_i \tag{42b}$$

This is simply because, in the expressions

$$\gamma_\alpha^s = \frac{1}{2}\gamma_c^s + \frac{1}{2}\gamma_s^s \tag{43a}$$

and

$$\gamma_\beta^s = \frac{1}{2}\gamma_c^s - \frac{1}{2}\gamma_s^s \tag{43b}$$

γ_s^s is sufficiently smaller than γ_c to be treated as a small perturbation.

Using an approximate OD wavefunction, Lunell[5d] demonstrated that the f value for Li(2^2P) can be calculated almost exclusively from the first natural determinant which involves the first three NSO's of large occupation numbers. Larsson and Smith[24] confirmed this for Li(2^2S) on the basis of a highly accurate wavefunction. We have checked this problem for the various wavefunctions of our concern. The results are shown in Table V. In every case studied, the f_0 value arising from the first natural determinant has proved to be a sufficiently good approximation to f. Thus, it seems generally valid that the spin density

$\gamma_s^s(0)$ is determined primarily by the functional form of the first NSO ϕ_1:

$$\gamma_s(0) = 4\phi_1(0)\delta_1(0) \tag{44}$$

B. NO and electron correlation

The oozing of the two core electrons out of a doubly occupied orbital by their dynamical correlation must be represented in terms of the first-order density matrix, just as the spin polarization can be expressed by a first-order spin density matrix. We have previously defined a density function[25]

$$D(r) = 2\gamma_c(r, r) - \int \gamma_c(r, r')\gamma_c(r', r)dr' \tag{45}$$

which represents the spatial distribution of split-pair electrons and unpaired spins, both being regarded as sort of odd electrons in the lump. The trace of D(r), which is expressible in terms of the occupation numbers n_i of the NO's in the form

$$\mathrm{Tr}D(r) = \sum_i n_i(2 - n_i) \tag{46}$$

is essentially the total number of such odd electrons.

D(r) could also be divided into s and p components, namely,

$$D(r) = D^s(r) + D^p(r). \tag{47}$$

$\mathrm{Tr}D^s(r)$ could then be considered to represent the number of core odd electrons arising as a result of both spin and dynamical polarizations.

Table VI shows the values of $\mathrm{Tr}D^s(r)$ for $\mathrm{Li}(2^2P)$ in various orbital treatments. Because the generation of odd electrons in the ED scheme is due exclusively to the spin polarization, and because the spin polarization is allowed to an utmost extent in ED, the contribution from the spin polarization to $\mathrm{Tr}D^{s}(r)$ will in no case exceed 0.000060 ($\mathrm{Tr}D^{s}(r)$ of ED). The values of $\mathrm{Tr}D^{s}(r)$ calculated decrease in the order

$$\mathrm{OG} > \mathrm{EG} \gtrsim \mathrm{OD} \gg \mathrm{ED} \tag{48}$$

which is in agreement with the decreasing order of the correlation energies involved in the calculated total energies. The extent of the electron correlation is considered to be reflected most vividly in the distribution of the occupation numbers of NO's.

VI. CONCLUSIONS

Of the orbital theories hitherto proposed, the SO—SCF—GSO wavefunction is the most extended one. Application of the theory to a lithium atom has improved the OD and EG results by $5\sim6$ % in electron correlation, to approach the radical limit most closely. This can also be confirmed by the trace of $D^{s}(r)$. However, it is also true that the electron correlation can only be taken into account to a maximal extent at sacrifice of the functional structure of $\mathcal{A}\Phi_2\theta_2$. The effects of this distortion in $\mathcal{A}\Phi_2\theta_2$ have been examined in a comparative manner for various orbital theories. The results shed light on the roles of spin-optimization in the orbital theories, especially in the GSO treatment.

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We are indebted to Dr. H. Nakatsuji of Kyoto University and Dr. K. Yamaguchi of this Laboratory for helpful discussions.

APPENDIX A: CUSP CONDISION FOR SPIN DENSITY

According to Cohen and Frishberg[27] and Nakatsuji,[28] the exact first-order density matrix[5a,29]

$$\rho_1(x_1', x_1) = \gamma_\alpha(r_1', r_1)\alpha(\sigma_1')\alpha(\sigma_1) + \gamma_\beta(r_1', r_1)\beta(\sigma_1')\beta(\sigma_1) \tag{A1}$$

should satisfy the reduced Sohrödinger equation

$$h_1\rho_1 = E\rho_1 - 2\int(h_2 + V_{12})\rho_2 dx_2 - 3\int V_{23}\rho_3 dx_2 dx_3, \tag{A2}$$

where ρ_2 and ρ_3 are the second- and third-order density matrices, respectively, V_{ij} is the electron repulsion between electrons i and j, and h_i is a one-body Hamiltonian

$$h_1 = \left(-\frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{\vec{\ell}^2}{2r^2} \right) - \frac{1}{r}\left(\frac{\partial}{\partial r} + Z \right) \tag{A3}$$

with Z as the nuclear charge. The right-hand side of Eq. (A2) is finite everywhere. Therefore, removal of the singularity for s functions in $h_1\rho_1$ necessitates the following relationship:

$$\frac{\partial}{\partial r_1} \rho(x_1', x_1)\big|_{r_1=0} = -Z\rho(x_1', x_1)\big|_{r_1=0} \tag{A4}$$

Multiplying both sides of Eq. (A4) by $\alpha(\sigma)\alpha(\sigma')$ or $\beta(\sigma)\beta(\sigma')$ and integrating the products over σ' and σ, one obtains

$$\frac{\partial}{\partial r_1} \gamma_\alpha(r_1', r_1)\big|_{r_1=0} = -Z\gamma_\alpha(r_1', r_1)\big|_{r_1=0} \tag{A5}$$

$$\frac{\partial}{\partial r_1} \gamma_\beta(r_1', r_1)\big|_{r_1=0} = -Z\gamma_\beta(r_1', r_1)\big|_{r_1=0} . \tag{A6}$$

The cusp conditions, Eqs. (7a) and (7b), for the charge and spin densities, respectively, can be obtained simply by adding Eq. (A5) to (A6) or by subtracting Eq. (A6) from (A5) after r_1' has been set equal to r_1.

APPENDIX B: THE OD AND G1 EQUATIONS

For the 2^2P state, the OD equations relates to the corresponding G1 equations in a simple manner. When the G1 equation for the core orbital a° and b° are given as[13a]

$$H_a^{G1} a^\circ = \varepsilon_a^\circ a^\circ \tag{B1a}$$

$$H_b^{G1} b^\circ = \varepsilon_b^\circ b^\circ , \tag{B1b}$$

the OD equations become[30]

$$(H_a^{G1} + \frac{1}{36} \sigma K_V) a \simeq \varepsilon_a a \tag{B2a}$$

$$(H_b^{G1} - \frac{1}{36} \sigma K_V) b \simeq \varepsilon_b b , \tag{B2b}$$

where

$$K_v \psi(1) = \int v(1) \frac{1}{r_{12}} v(2) \psi(2) dr_2 . \tag{B3}$$

According to the results of OD calculations, $|\sigma| \simeq 0.012$ and both $< a|K_v|a >$ and $< b|K_v|b >$ are of the order of 10^{-3} hartree. Hence, the exchange terms in Eqs. (B2)'s can be neglected relative to both H_a^{G1} and H_b^{G1}, so that

$$|| a - a^\circ || \simeq 0, \quad || b - b^\circ || \simeq 0. \tag{B4}$$

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[23] In Eq. (25), we have omitted the term $2\sigma\mathcal{A}(a\delta a + \delta ab)v\theta_2$, because σ itself is also a small quantity.

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TABLE I. Expectation values obtained by various orbital theories.

Method		-E(hartree)	ΔE(%)	f	ℓ	$\gamma_c(0)$	Z_c	Z_s	Ref.
					Li(2^2S)				
RHF		7.432727	0	2.094	0	13.8160			12
DODS	ED	7.432813	0.5	3.020	0	13.8159			13b
	OD	7.447565	93.6	2.849	0	13.8646	3.0	3.0	4a, 4b
GSO	EG	7.447596	93.8	2.802	0		3.0	3.0	5g
	OG	7.448522	99.7	2.750	0	13.8672	3.0	3.0	This work
CI		7.448571	100	2.801	0	13.8669	3.0	3.0	5g
Expt.		7.47807	——	2.906	0	——	——	——	14[c], 15[d]
					Li(2^2P)				
RHF		7.365069	0	0.0	0.05848				4a
DODS	ED	7.365091	0.1	-0.2895	0.05861				4a
		7.365097	0.2	-0.2972	0.05878	13.6505	2.999	2.770	This work
	OD	7.380119	92.0	-0.2132	0.05876				10
		7.380119[a]	92.0	-0.2141	0.05881	13.6942	2.997	2.916	This work
GSO	EG	7.380191	92.4	-0.2243	0.05926				5g
		7.380224	92.6	-0.2152	0.05928	13.6952	2.996	2.745	This work
	OG	7.381053[b]	97.7	-0.1953	0.05895	13.6989	2.996	3.170	This work
CI		7.381428	100	-0.2306	0.06070	13.6576			5g
Expt.		7.41016	——	-0.2128	0.06258	——	——	——	14[c], 16[d]

[a] $C_2/C_1 = 0.0060$. [b] $C_2/C_1 = 0.0117$. [c] For E. [d] For f and ℓ.

TABLE II. Expansions of the DODS core orbitals over the ED natural orbitals.

Natural orbital[a]	ED		OD	
	a(r)	b(r)	a(r)	b(r)
ϕ_1	0.99999	0.99999	0.98199	0.98157
ϕ_2	-0.00473	0.00473	0.12175	-0.12540
ϕ_3	0.00001	0.00000	0.13228	-0.13293
ϕ_4	0.00000	0.00000	0.05371	-0.05167
ϕ_5	-0.00001	-0.00000	0.01794	-0.01733
ϕ_6	0.00031	-0.00031	-0.01283	0.01264
ϕ_7	-0.00003	0.00007	0.00213	-0.00209

[a] ϕ_k denotes the kth ED natural orbital having k - 1 nodes.

TABLE III. Coefficients d_{k1} of the configurations F_{k1} in the normalized $\mathcal{A}\Phi_2\theta_2$ of Li(2^2P).

	DODS		GSO	
k	ED	OD	EG	OG
2	0.9978	0.6501	0.6674	0.4785
3	0.0006	0.6979	-0.0571	0.3931
4	0.0005	0.2772	-0.0313	0.0011
5	-0.0006	0.0929	-0.0066	0.0737
6	-0.0652	-0.0671	-0.0507	-0.0705
7	0.0100	0.0112	0.0063	-0.0003
Total weight	0.9999_9	0.9998	0.4523	0.3939
E_{22}(a.u.)	-5.136218	-2.443656	-2.924433	-1.315152

TABLE IV. Contributions of the excited configurations F_{k1} to f.

f_k	DODS		GSO	
	ED	OD	EG	OG
f_2	-0.3324	-0.0531	-0.3180	-0.1091
f_3	-0.0005	-0.1000	0.0477	-0.1573
f_4	-0.0013	-0.1224	0.0808	-0.0013
f_5	-0.0019	0.0524	-0.0218	0.1159
f_6	-0.0487	-0.0123	-0.0540	-0.0359
f_7	0.0726	0.0195	0.0636	-0.0015
$\sum_k f_k$	-0.3122	-0.2159	-0.2017	-0.1892
f^a	-0.2972	-0.2141	-0.2152	-0.1953

[a] Table I.

TABLE V. The Fermi contact term f_0 obtained from the first natural determinant

State	Method	f_0
2^2S	OG	2.747
2^2S	ED	-0.2972
	OD	-0.2139
	EG	-0.2103
	OG	-0.1921

TABLE VI. Trace of $D^s(r)$ for Li(2^2P).

Method	$TrD^s(r)$
RHF	0.0
ED	0.000060
OD	0.011198
EG	0.011590
OG	0.012017

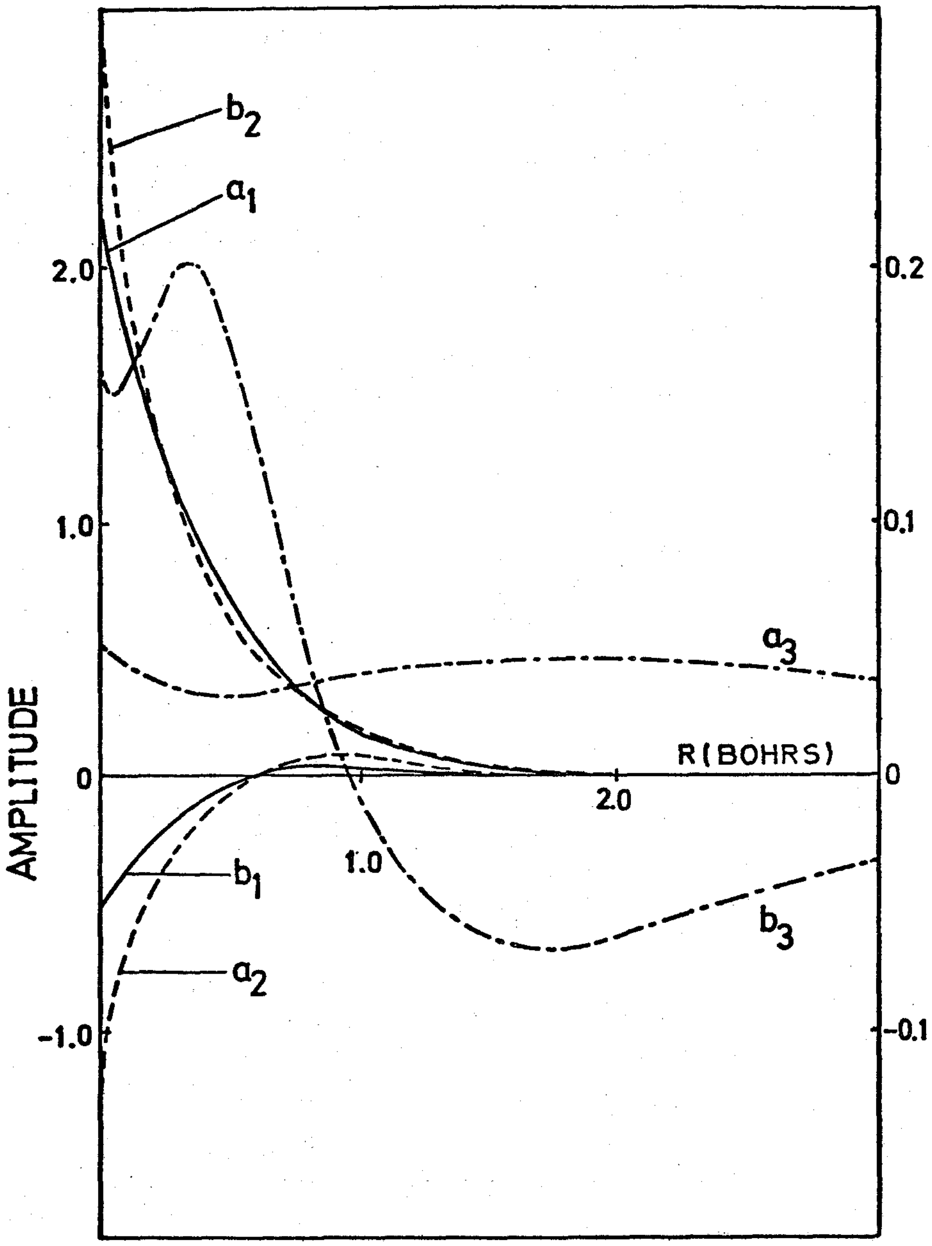

FIG. 1. Amplitudes of the SO–SCF–GSO's for the 2^2S state of Li. The core orbitals, $\phi_1 = a_1\alpha + b_1\beta$ and $\phi_2 = a_2\alpha + b_2\beta_1$, should be scaled by the left vertical axis, whereas the valence orbital, $\phi_3 = a_3\alpha + b_3\beta$, should be scaled by the right one.

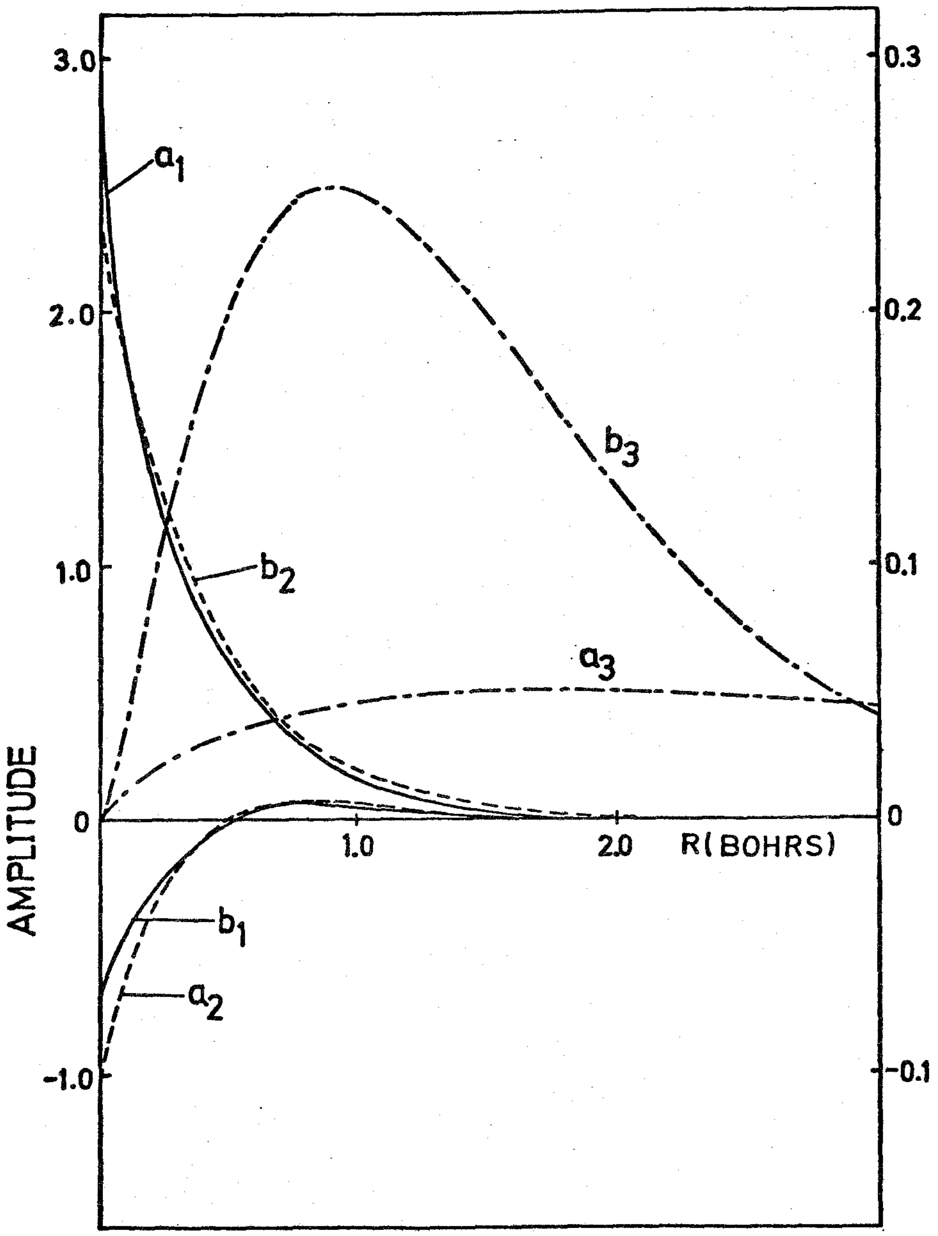

FIG. 2. Amplitudes of the SO–SCF–GSO's for the 2^2P state of Li. The scales of the orbitals are the same as in Fig. 1.

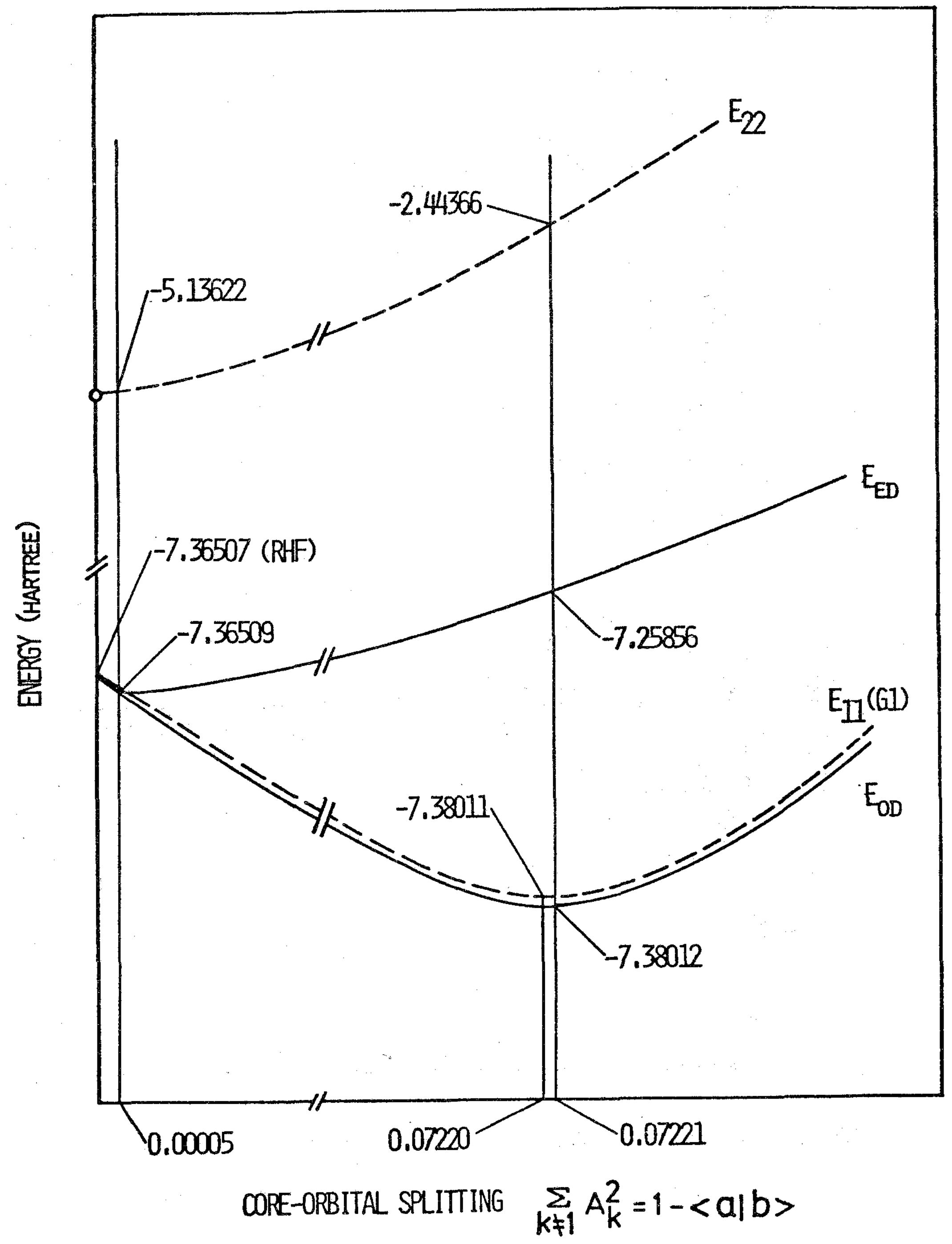

FIG. 3. Expectation values of the DODS total energy for Li(2^2P) as the functions of the core orbital splitting.

CHAPTER 4

Distribution of Odd Electrons in Ground-State Molecules

A density function $D(r) = 2\gamma(r,r) - \int \gamma(r,r')\gamma(r',r)dr'$, where $\gamma(r,r')$ is a spinless first-order density matrix, has been proposed as fundamental formula representing the spatial distribution of odd electrons in molecules. The bonding properties of π electrons in some representative triatomic species have been examined in the light of $D(r)$. The density function can also be used successfully to assess the diradical character of unstable singlet ground-state molecules.

I. INTRODUCTION

When electron correlation is utterly ignored, each orbital in the singlet ground state of atoms and molecules can be considered to be doubly occupied by a pair of electrons having α and β spins. The concept of such a double occupancy of spatial orbitals has provided a useful guiding principle to the understanding of electronic structures of stable molecules, as is endorsed by the success of the restricted Hartree-Fock (RHF) theory.[1] However, the concept apparently breaks down, when the electron correlation is duly taken into account.[2] An RHF orbital is then more or less split into two spatial orbitals, each of which now accomodates either one of the paired electrons separately. An electron pair will thus be split spatially to assume a partial odd-electron character even in a singlet ground-state molecule. The nature of such split electron pairs should have a particularly significant bearing on the properties of the so-called singlet diradical species[3] as well as the transition state of certain concerted reactions.[4]

The electronic structure of molecular systems involving the electron pair splitting can be represented satisfactorily well by some specific wavefunctions such as the generalized valence bond (GVB) wavefunction.[5] Yet, it seems desirable to invent a general method of drawing informations about the splitting of electron pairs from exact or any trial wavefunctions. Particular efforts along this line are the main purpose of the present work. It is also a formal complement to our general considerations[6] of Lewis' electron pair concept.

II. DEFINITION OF THE ODD ELECTRON DENSITY

Consider a singlet ground state. The first-order reduced density matrix[7] is written as

$$\rho^{(1)}(x,x') = \frac{1}{2}\gamma(r,r')[\alpha(s)\alpha(s') + \beta(s)\beta(s')], \tag{1}$$

where r and s respectively denote the space and spin coordinates and where $\gamma(r,r')$ is the spinless first-order density matrix. The necessary and sufficient condition[7] for a wavefunction to be reduced to a single Slater determinant is

$$\begin{aligned} &\rho^{(1)}(x,x') - \int\rho^{(1)}(x,x'')\rho^{(1)}(x'',x)dx'' \\ &= \frac{1}{4}[2\gamma(r,r') - \int\gamma(r,r'')\gamma(r'',r')dr''][\alpha(s)\alpha(s') + \beta(s)\beta(s')] \\ &= 0 . \end{aligned} \tag{2}$$

It follows that

$$2\gamma(r,r') - \gamma^2(r,r') = 0 \tag{3}$$

where $\gamma^2(r,r')$ has been defined as

$$\gamma^2(r,r') = \int\gamma(r,r'')\gamma(r'',r')dr'' . \tag{4}$$

Equation (3) means that the natural orbitals[7] should be doubly occupied, as long as the wavefunction for which $\langle S^2\rangle = 0$ can be represented by a single Slater determinant. On the contrary, when the exact wavefunction cannot be expressed by one determinant alone, $2\gamma(r,r') - \gamma^2(r,r')$ should be nonzero. In such latter cases, at least one of the natural orbital pairs must be split to a certain extent. Thus, a spinless density function defined as

$$D(r,r') = 2\gamma(r,r') - \gamma^2(r,r') \tag{5}$$

is expected to provide a theoretical clue to the spatial splitting of electron pairs in a given molecular system. Each counterpart electron of an electron pair which is thus split to occupy different portions of space orthogonally will hereafter be referred to as an "odd electron." The extent of generation of such odd electrons and their distribution in molecules are the central problem of our present concern.

Let us concern ourselves here primarily with the diagonal element of Eq. (5). We will express the diagonal element as

$$D(r) = 2\gamma(r) - \gamma^2(r) \ . \tag{6}$$

The density function D(r) can be expanded diagonaly in terms of the natural orbitals ϕ_k's and their occupation numbers n_k's $(0 \leqq n_k \leqq 2)$. The result is written as

$$D(r) = \sum_k n_k(2 - n_k)\phi_k^*(r)\phi_k(r) . \tag{7}$$

Equation (7) indicates that the intensity factor of a natural orbital ϕ_k contributing to the density function D(r) is $n_k(2 - n_k)$. Obviously, the factor $n_k(2 - n_k)$ takes a maximal value of 1 when $n_k = 1$, and diminishes monotonously down to 0 as n_k approaches 0 or 2. This could be taken as an implication that $n_k(2 - n_k)$ is the probability that the electron(s) in ϕ_k is left unpaired as if it were an odd electron in the singly occupied molecular orbital of a doublet radical. Our density function D(r) could then be regarded as a formal expression giving the spatial distribution of the total odd electrons in a given molecule.

In open-shell ground states, unpaired spin densities do exist at the outset. The first-order density matrix is

$$\rho^{(1)}(x,x') = \gamma_\alpha(r,r')\alpha(s)\alpha(s') + \gamma_\beta(r,r')\beta(s)\beta(s') \ , \tag{8}$$

the spinless first-order density matrix being written as

$$\gamma(r,r') = \gamma_\alpha(r,r') + \gamma_\beta(r,r') \ . \tag{9}$$

In this case, the density function for odd electrons D(r) is formally expressed as

$$\begin{aligned} D(r) &= 2\gamma(r) - \gamma^2(r) \\ &= 2[\{\gamma_\alpha(r) - \gamma_\alpha{}^2(r)\} + \{\gamma_\beta(r) - \gamma_\beta{}^2(r)\}] + (\gamma_\alpha - \gamma_\beta)^2(r) \end{aligned} \tag{10}$$

where the term $(\gamma_\alpha - \gamma_\beta)^2(r)$ is the diagonal element of the integrated square [Eq. (4)] of the customary spin density function $\gamma_\alpha(r) - \gamma_\beta(r)$. Clearly, $\gamma_\alpha(r) - \gamma_\beta(r)$ is due to the presence of unpaired spin(s) in the ground configuration. In case where the wavefunction happens to be given by a single determinant, we have

$$\gamma_\alpha(r) - \gamma_\alpha{}^2(r) = 0 \ , \quad \gamma_\beta(r) - \gamma_\beta{}^2(r) = 0 \ , \tag{11}$$

which give an obvious result for the unpaired spin(s):

$$D(r) = (\gamma_\alpha - \gamma_\beta)^2(r) \ . \tag{12}$$

Thus, the unpaired spin(s) has already been incorporated in our D(r) as a part of the odd electron density. It is the first term of the right-hand side of Eq. (10) that represents the splitting of paired electrons themselves.

With the distribution function D(r) at hand, we can readily calculate the populations of the odd electrons on given atomic sites in a given molecule. Thus, D(r) is expanded over the atomic orbitals $\{\chi_t(r)\}$:

$$D(r) = \sum_t \sum_u d_{tu} \chi_t^*(r) \chi_u(r) \ . \tag{13}$$

After the manner of Mulliken [8], the atomic-orbital population of odd electrons can be defined by

$$D_t = \sum_u d_{tu} \langle \chi_t | \chi_u \rangle \ . \tag{14}$$

The gross population on atom A is simply a sum

$$D_A = \sum_t^A D_t \ . \tag{15}$$

Needless to say, the total sum of D_A's over the atoms involved should be finite:

$$\sum_A D_A = \mathrm{Tr} D(r) \leq N \ , \tag{16}$$

where N is the total number of electrons.

III. APPLICATIONS TO SOME SPECIFIC ORBITAL THEORIES

Prior to the application of the theory to existing molecules, we will here derive the expressions of D(r) pertinent to a few typical orbital theories. It is hoped that such expressions will assist a proper understanding of the features of numerical results for molecules which will be presented in Section 4.

A. Doubly occupied orbital CI wavefunction

For the sake of simplicity, we choose the configuration-interaction (CI) wavefunction composed of doubly occupied (DO) spatial orbitals[9]

$$\Psi = C_0\Phi_0 + \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{unocc}} C_i^a \Phi_{ii}^{aa} , \tag{16}$$

where Φ_0 stands for the ground configuration and Φ_{ii}^{aa} is a Slater determinant having two (α- and β-spin) virtual orbitals ϕ_a in place of two occupied ones ϕ_i. Form Eq. (7), D(r) becomes

$$\begin{aligned} D(r) = {} & 4 \sum_{i}^{\mathrm{occ}} [\sum_{a}^{\mathrm{unocc}} (C_i^a)^2 - \{ \sum_{a}^{\mathrm{unocc}} (C_i^a)^2 \}^2] \phi_i^*(r)\phi_i(r) \\ & + 4 \sum_{a}^{\mathrm{unocc}} [\sum_{i}^{\mathrm{occ}} (C_i^a)^2 - \{ \sum_{i}^{\mathrm{occ}} (C_i^a)^2 \}^2] \phi_a^*(r)\phi_a(r) . \end{aligned} \tag{17}$$

In the simplest DOCI theory, we only consider the highest occupied (HO) and the lowest vacant (LV) MO's as the ϕ_i and ϕ_a, respectively. Further, if we reoptimize ϕ_{HO} and ϕ_{LV} simultaneously with C_{HO}^{LV}, the optimized double-configuration (ODC) version[10] will be obtained. In either case, Eq. (17) is simplified into

$$D(r) = 4(C_{HO}^{LV})^2 [1 - (C_{HO}^{LV})^2] [\phi_{HO}^*(r)\phi_{HO}(r) + \phi_{LV}^*(r)\phi_{LV}(r)] . \tag{18}$$

The expression is useful for the consideration of the diradical character of singlet molecules, as will be discussed later.

B. Singlet UHF wavefunction

By use of the corresponding orbitals,[11] the unrestricted Hartree-Fock (UHF) wavefunction for a singlet state can be written as[12]

$$\Psi = |a_1\bar{b}_1a_2\bar{b}_2\ldots\ldots| \, , \tag{19}$$

where the bar denotes β-spin orbitals. The corresponding orbitals satisfy the following relation:

$$\langle a_k|b_l\rangle = S_k\delta_{kl} \, . \tag{20}$$

Since the UHF wavefunction is a single Slater determinant, D(r) should consist only of the spin density term. Thus,

$$\begin{aligned} D(r) &= (\gamma_\alpha - \gamma_\beta)^2(r) \\ &= \sum_k\{a_k^*(r)a_k(r) + b_k^*(r)b_k(r) \\ &\qquad - S_k[a_k^*(r)b_k(r) + b_k^*(r)a_k(r)]\} \, . \end{aligned} \tag{21}$$

Equation (21) suggests separate contributions of $a_k(r)$ and $b_k(r)$ to the D(r) function. The spatial splitting of the α- and β-spin electrons is thus apparent in this case.

C. Generalized valence bond (GVB) wavefunction

The GVB wavefunction[5] has also been applied to the studies of diradical species.[13] It is generally written as

$$\Psi = \mathcal{A}\, a_1(1)b_1(2)(\alpha\beta - \beta\alpha)a_2(3)b_2(4)(\alpha\beta - \beta\alpha)\cdots \tag{22}$$

where $\mathcal{A}$ is an antisymmetrizing operator. The orbitals a_k and b_k constitute a pair, and every pair is orthogonal to others, i.e., $\langle a_k|a_1\rangle = \langle b_k|b_1\rangle = \langle a_k|b_1\rangle = 0 \ (k \neq 1)$.

Use of Eq. (22) leads to

$$D(r) = \sum_k \frac{1 - S_k^2}{(1 + S_k^2)^2} \{a_k^*(r)a_k(r) + b_k^*(r)b_k(r) - S_k[a_k^*(r)b_k(r) + b_k^*(r)a_k(r)]\} \ . \tag{23}$$

Aside from the factor $(1 - S_k^2)/(1 + S_k^2)^2$, Eq. (23) is identical in form with Eq. (21). It is likely that the UHF and GVB theories provide similar distribution patterns of split spins, insofor as the spatial orbitals used in these theories do not differ appreciably.

IV. NUMERICAL EXAMPLES

In this section, we will apply the present theory to some existing three-atom species and to the transition state of concerted reactions.

A. Triatomic species

A few triatomic three-electron π systems (together with their two- and four-electron family systems) were chosen as examples. They include allyl raidcal $C_3H_5(C_3H_5^+, C_3H_5^-)$, formyl radical $HCO_2(HCO_2^+, HCO_2^-)$, nitric oxide $NO_2(NO_2^+, NO_2^-)$ and ozone cation $O_3^+(O_3^{2+}, O_3)$. For all of these species, various types of wavefunctions were calculated by Linnett et al.[14] Among others, their RHF, full-CI and Heitler-London (HL) wavefunctions will be adopted for our present purpose. The populations of odd π electrons calculated therefrom are summarized in Table 1.

The salient points noticed in Table 1 are the following:

1) The odd electron populations given by the HL method is always larger than those given by the CI treatment, as is expected. The populations obtained from the RHF wavefunction reflect the unpaired spin term, Eq. (12), only.
2) In the CI case, the results for the two- and four-electron systems nearly coincide with each other. In either system, the splitting of pairs is due almost exclusively to that of the highest occupied MO.
3) In both the CI and HL treatments, all the triatomic species examined have a fairly large odd electron density on thier central atoms.
4) Roughly speaking, the population of odd electrons increases with the decreasing overlap $<\chi_a|\chi_b>$ between the neighboring atomic orbitals (Table 2).
5) For O_3^+ the total population (2.437) calculated by the CI method exceeds 2, indicative of a partial triradical character.

As has been shown in the above examples, D(r) could be used for the comparisons of the features of various model wavefunctions. For preciser displays of these features, it will be more advantageous to use contour density maps of D(r).

B. Concerted reactions

We here treat two types of cycloaddition reactions. One is a $(2_s + 2_s)$ cyclodimerization of ethylene, which is a typical orbital-symmetry forbidden reaction. The other is a $(2_s + 2_s + 2_s)$ allowed reaction of three ethylenes to give cyclohexane. The wavefunctions of these two concerted reactions were traced by Porter and Raff[15] and by Wilson and Wang,[16] respectively. The latter workers noted that in forbidden reactions the occupation numbers of the natural orbitals normally show a crossing between the orbitals of high and low occupation numbers but that no such crossing takes place in allowed reactions. The crossing should naturally be accompanied by the generation of odd electrons.

The populations of odd electrons on a carbon atom at the transition states were calculated by use of the occupation numbers given by Wilson and Wang.[16] The results were 0.55 and 0.2 for the $(2_s + 2_s)$ and $(2_s + 2_s + 2_s)$ reactions, respectively. In the allowed reaction, apparently more electrons are kept paired during the course of bond interchange.

C. Diradical character

In connection with the foregoing argument, it seems particularly interesting to consider the diradical character of singlet species. The diradical character is believed to show up also in the intermediary state of the Woodward-Hoffmann forbidden reactions.[4]

Hayes and Siu[17] defined the diradical character by

$$y = 2(C^{d}_{H-L})^{2}, \tag{24}$$

where $(C^{d}_{H-L})^{2}$ is the weight of the doubly excited configuration due to the electron transition from the highest occupied to the lowest unoccupied molecular orbital. Although Eq. (24) can well be understood intuitively, it is yet unsatisfactory on the following three grounds:

1) Virtual molecular orbitals to be made use of in the CI calculation can always be transformed unitarily among them,[18] so that no uniqueness can be attached to the values of $(C^{d}_{H-L})^2$.
2) The existence of more than two odd electrons as in a triradical should not be precluded in general cases.
3) It provides no information at all about the distribution of odd electrons.

All these ambiguities can be removed by use of our D(r). To clarify the situation, let us consider the D(r) function in the DOCI approximation, Eq. (18). Obviously, the trace of D(r)

$$\mathrm{TrD(r)} = 8(C^{LV}_{HO})^2[1 - (C^{LV}_{HO})^2] \tag{25}$$

satisfies

$$0 \leqq \mathrm{TrD(r)} \leqq 2 \ , \tag{26}$$

as long as

$$0 \leqq (C^{LV}_{HO})^2 \leqq 1/2 \ . \tag{27}$$

Hence, one half of TrD(r) must correspond to the diradical character

$$y_D = (1/2)\mathrm{TrD(r)} . \tag{28}$$

The y_D here defined is always larger than or equal to the Hayes—Siu quantity, Eq. (24), so far as the condition (27) is satisfied. The diradical characters of the various two-electron systems obtained by the full CI treatment were 0.546, 0.295, 0.318 and 0.235 for O_3^{2+}, NO_2^{+}, HCO_2^{+} and $C_3H_5^{+}$, respectively.

The diradical character which can be defined likewise form Eq. (17) should be more general than that based on Eq. (18). The UHF and GVB expressions, Eqs. (21) and (23), may also be used. In either of these latter formalisms, it is apparent that the diradical character of a singlet state stems from the splittings of the corresponding orbital pairs. Clearly, the diradical character should be the greater, the smaller the orbital overlap S_k.

V. CONCLUDING REMARKS

We have defined a density function D(r) which describes the distribution of odd electrons in molecules. The definition is based on the spinless first-order density matrix, so that it precludes all the uncertainties originating from the arbitrariness in selecting the basis sets, virtual orbitals and configurations. Use of the density function sheds light on the nature of thermal reactions as well as isolated molecules. It is emphasized that the traditional term "diradical" is a physically acceptable one. Further, in the sense that D(r) expresses the distribution of electrons still capable of forming a new pairing, it could also been taken as a conceptual generalization of Coulson's free valence.[19]

Although we have defined D(r) for the ground state only, it may also be applicable to excited states. However, in the virtual orbital approximation, excited singlet and triplet states of homopolar molecules cannot be distinguished; the former state should be zwitterionic[3] (not necessarily identical with zwitterion itself) while the latter, diradical. In such a case, recourse to the second-order density matrix would be unavoidable.

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Table 1. Odd π electron populations in some ground-state triatomic species

Wave-function	C_3H_5		HCO_2		NO_2		O_3^+	
	C_t^a	C_c^b	O	C	O	N	O_t^a	O_c^b
Two-electron systems								
RHF	0	0	0	0	0	0	0	0
CI	0.164	0.141	0.239	0.158	0.214	0.162	0.393	0.306
HL	0.296	0.593	0.351	0.701	0.398	0.795	0.444	0.889
Three-electron systems								
RHF	0.500	0	0.500	0	0.500	0	0.500	0
CI	0.663	0.326	0.632	0.265	0.675	0.350	0.859	0.719
HL	0.871	0.742	0.909	0.817	0.939	0.878	0.968	0.936
Four-electron systems								
RHF	0	0	0	0	0	0	0	0
CI	0.188	0.141	0.295	0.133	0.295	0.163	0.411	0.297
HL	0.296	0.593	0.351	0.701	0.398	0.795	0.444	0.889

a. Terminal atoms. b. Cetral atom.

Table 2. Overlap integrals between the atomic orbitals.[a]

	O_3	NO_2	HCO_2	C_3H_5
	O_1-O_2-O_3	O_1-N_2-O_3	O_1-C_2-O_3	C_1-C_2-C_3
$<\chi_1\|\chi_2>$	0.12179	0.17005	0.21130	0.25995
$<\chi_1\|\chi_3>$	0.00862	0.01137	0.00865	0.03887

a. These overlap integrals are common to the ionized states of given systems.

PART II

VARIATIONAL THEORETICAL APPROACHES TO THE ELECTRON SCATTERING PROBLEMS

CHAPTER 1

Introduction

It is well known that useful informations about the electronic structures of atoms as well as molecules and about the vibrational structures of molecules can be obtained by the experiments of electron impact on atoms and molecules.[1] In order to interpret and moreover to predict the results, help of the quantum scattering theory[2] is indispensable. Although the history of quantum scattering theory is almost as old as that of quantum mechanics itself, the theories which are really applicable to the electron impact on electron systems have not been developed until recent years.[3] This is because accurate calculations of the electronic structure of bound states have become possible only quite recently by means of recent high-speed digital computers. The variational theory[2-4] seems to be a promising tool with which to deal with the scattering processes.

The variational theory was initiated by Hulthén and developed by Kohn, Rubinow, Schwinger, Kato, and others.[2,3] Although the theory has many advantages over the other methods as an alternative theory, it is inherently faced with some difficulties. In the Kohn method,[5] divergent solutions which have nothing to do with true resonances appear inevitably, as was pointed out by Schwartz.[6] In Chapter 2, two kinds of divergence are mathematically distinguished. One of them shows up in the Kohn method as stated above and can be always avoided. The other is unavoidable by any means and occurs in some algebraic approaches at common momentum, as long as they use a common basis set. This distinction is accomplished by the basis transformation. In this connection, the methods for single-channel scattering proposed so far are treated in a unified manner. Further, a new method, which is to be termed the minimum basis-dependence method, is proposed.

In multi-channel scattering theory, some algebraic (or expansion) approaches,[7] such as the minimum-norm method,[7] were seriously disadvantageous in that they are not necessarily accompanied by a corresponding variational functional. This means that the reactance matrix which is yielded by the algebraic method has no unique first-order correction. In Chapter 3, the existence of a general functional for the algebraic method is proved explicitly. Use of the functional proposed makes the reactance matrix accurate to first order. Moreover, the correspondence of the algebraic method to the variational theory is clarified. The minimum basis-dependence method is extended to multi-channel scattering.

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CHAPTER 2

Optimized Kohn Method for the Single-Channel Scattering

A new algebraic variational procedure has been proposed for the calculation of the phase shift ρ of the radial wavefunction for a particle undergoing single-channel scattering. The method is essentially an optimization of Kohn's theory with respect to the phase parameter θ as involved in Kato's wavefunction. Specifically, the basis set has been transformed linearly so as to permit distinction between avoidable (spurious) and unavoidable (innate) singularities. On this basis, various standard variational theories have been reformulated in a unified manner, and their mutual relationships have been clarified. A criterion of the minimum basis dependence (MBD) is proposed in this connection. Sample basis-set calculations of ρ have been carried out for the Hazi-Taylor model potentials in order to demonstrate the relative merits of the MBD method.

I. INTRODUCTION

The wavefunction $\psi(\mathbf{r})$ of a spin-less particle scattering off a spherically symmetric potential $V(r)$ can generally be expressed as

$$\psi(\mathbf{r}) = \sum_{\ell} A_\ell r^{-1}\Psi_\ell(r)P_\ell(\cos\theta) \ , \tag{1}$$

where A_ℓ is a constant and $P_\ell(\cos\theta)$ is the Legendre polynomial of order ℓ. The radial function $\Psi_\ell(r)$ in its exact form satisfies

$$\hat{H}\Psi_\ell(r) = 0 \ , \tag{2}$$

where $\hat{H}$ is an operator defined in atomic units as

$$\hat{H} = E - \left\{-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + V(r)\right\} \tag{3}$$

$E = k^2/2$ being the total energy of the system.

In the algebraic variational theories,[1] the trial radial wavefunction $\Psi_\ell(r)$ is expanded in basis functions. After Hulthén,[2,3] Kohn,[4] and Lippmann and Schwinger[5] had developed such variational methods, Kato[6] extended them into a slightly more general form involving a phase parameter θ. His trial wavefunction is written as

$$\Psi_{\ell\theta}(r) = S_{\ell\theta}(r) + \lambda_\theta C_{\ell\theta}(r) + \sum_{i=1}^{N} D_{\theta i}\chi_i(r) \ , \tag{4}$$

where $S_{\ell\theta}(r)$ and $C_{\ell\theta}(r)$ are asymptotically

$$S_{\ell\theta}(r)_{r\to\infty} \sim k^{-1/2}\sin(kr - \ell\pi/2 + \theta) \tag{5a}$$

$$C_{\ell\theta}(r)_{r\to\infty} \sim k^{-1/2}\cos(kr - \ell\pi/2 + \theta) \ , \tag{5b}$$

and where $\chi_i(r)$'s are square-integrable basis functions. The coefficients λ_θ and $D_{\theta i}$'s are to be determined by variation of the functional

$$[\lambda_\theta] = \lambda_\theta + 2\left\langle \Psi_{\ell\theta}|\hat{H}|\Psi_{\ell\theta}\right\rangle , \tag{6}$$

namely, by imposing the conditions

$$\left\langle \chi_i|\hat{H}|\Psi_{\ell\theta}\right\rangle = 0 \qquad i = 1,2,\ldots,N \tag{7}$$

and

$$\left\langle C_{\ell\theta}|\hat{H}|\Psi_{\ell\theta}\right\rangle = 0 \ . \tag{8}$$

The λ_θ value thus obtained is a trial (zeroth-order) λ_θ. The value $[\lambda_\theta]$ correct to the first order is calculated by Eq. (6). The procedures for obtaining such $[\lambda_\theta]$ values have been a problem of central importance since it is related directly to the phase shift ρ and eventually to the cross sections for scattering.

Schwartz[7] pointed out through his accurate and extensive calculations that Kohn's method ($\theta = 0$) gives rise to anomalous singular solutions at certain k's, none of which has anything to do with a resonance phenomenon. Nesbest[8] showed that Rubinow's method[9] ($\theta = \pi/2$), which is also called the second Hulthén or inverse Kohn method,[1] never gives this type of singularity at the k's of the Kohn singularity, and thus proposed alternate use of the two theories. The procedure was named the anomaly-free (AF) method. The optimized anomaly-free (OAF) method proposed recently by Nesbet and Oberoi[10] has been aimed at a removal of the discontinuity of λ against k. The minimum-norm (MN) method of Harris and Michels[11] can be regared, like the OAF theory, as one of the methods which search an optimum θ automatically.

In this paper, we will investigate the dependence of λ upon θ in single-channel scattering. It seems natural to consider that the anomaly arises from the choice of θ rather than from k; the singularity is in cases avoidable depending on the θ value chosen. In order to demonstrate the situation, we will perform a specific transformation among the basis functions {S, C, and χ_i's} and propose two promising methods to evaluate an optimum [λ]. In this light, we will reformulate the various other theories in a unified manner, clarifying the essential properties of the singularities inherent in these theories.

II. THEORETICAL FORMULATIONS

A. Basis transformation

For our purpose, it is more advantageous to base the theory on Kohn's original trial function ($\theta = 0$) of the form:

$$\Psi = S + \lambda C + \sum_{i=1}^{N} D_i \chi_i \tag{9}$$

where S and C are

$$S \underset{r\to\infty}{\sim} k^{-1/2}\sin(kr - \ell\pi/2) \tag{10a}$$

$$C \underset{r\to\infty}{\sim} k^{-1/2}\cos(kr - \ell\pi/2) \tag{10b}$$

and where λ is the tangent of the phase shift ρ. For the sake of simplicity, both the specifications of the subscript ℓ and the radial coordinate r will be dropped off throughout.

Using the relation

$$\begin{pmatrix} S_\theta \\ C_\theta \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \mathrm{con}\,\theta \end{pmatrix} \begin{pmatrix} S \\ C \end{pmatrix}, \tag{11}$$

one can rewrite Eqs. (7) and (8) into

$$\langle \chi_i | \hat{H} | \Psi \rangle = 0 \qquad i = 1,2,\ldots,N \tag{12}$$

and

$$\langle C - \omega S | \hat{H} | \Psi \rangle = 0 \ , \tag{13}$$

where $\omega = \tan\theta$. λ is related to λ_θ accordingly:

$$\lambda = (\omega + \lambda_\theta)/(1 - \omega\lambda_\theta). \tag{14}$$

Equations (12) and (13) are simple simultaneous equations in the unknown variables λ and D_i's such that

$$K \begin{pmatrix} \lambda \\ D_1 \\ \cdot \\ \cdot \\ \cdot \\ D_N \end{pmatrix} = - \begin{pmatrix} \langle C - \omega S | \hat{H} | S \rangle \\ \langle \chi_1 | \hat{H} | S \rangle \\ \cdot \\ \cdot \\ \cdot \\ \langle \chi_N | \hat{H} | S \rangle \end{pmatrix} \tag{15}$$

where

$$K = \begin{pmatrix} \langle C - \omega S|\hat{H}|C\rangle & \langle C - \omega S|\hat{H}|\chi_1\rangle & \cdots & \langle C - \omega S|\hat{H}|\chi_N\rangle \\ \langle \chi_1|\hat{H}|C\rangle & \langle \chi_1|\hat{H}|\chi_1\rangle & \cdots & \langle \chi_1|\hat{H}|\chi_N\rangle \\ \vdots & \vdots & & \vdots \\ \langle \chi_N|\hat{H}|C\rangle & \langle \chi_N|\hat{H}|\chi_1\rangle & & \langle \chi_N|\hat{H}|\chi_N\rangle \end{pmatrix} \quad (16)$$

The solutions of Eqs. (12) and (13) should depend on θ if the basis set $\{\chi_i\}$ is not complete. Hereafter, we will refer to Eqs. (12) and (13) as the first and second Kohn conditions, respectively.

It may be extremely difficult to find an explicit dependence of λ on ω (and, hence, on θ) through the direct solutions of Eq. (15). Since we are now discussing on the singularity of the inverse of K [Eq. (16)], it may be more beneficial to investigate the property of det K. To accomplish this, we introduce a new basis set $\{\zeta_i\}$ by transforming {S, C, χ_i's} in such a manner that

$$\zeta_i = \chi_i + P_i^s S + P_i^c C \qquad (i = 1,2,\ldots N) \quad (17)$$

on the conditions

$$\langle S|\hat{H}|\zeta_i\rangle = 0 \quad (18a)$$

and

$$\langle C|\hat{H}|\zeta_i\rangle = 0 \ . \quad (18b)$$

The coefficients P_i^s and P_i^c may be given by

$$\begin{pmatrix} P_i^s \\ P_i^c \end{pmatrix} = M_0^{-1} \begin{pmatrix} M_i^s \\ M_i^c \end{pmatrix} \quad (19)$$

with

$$M_0 = \begin{pmatrix} M^{ss} & M^{sc} \\ M^{cs} & M^{cc} \end{pmatrix} \tag{20}$$

where

$$\begin{aligned} M_i^s &= \langle S|\hat{H}|\chi_i\rangle = \langle\chi_i|\hat{H}|S\rangle \\ M_i^c &= \langle C|\hat{H}|\chi_i\rangle = \langle\chi_i|\hat{H}|C\rangle \end{aligned} \tag{21}$$

and

$$\begin{aligned} M^{ss} &= \langle S|\hat{H}|S\rangle, \quad M^{sc} = \langle S|\hat{H}|C\rangle \\ M^{cs} &= \langle C|\hat{H}|S\rangle, \quad M^{cc} = \langle C|\hat{H}|C\rangle. \end{aligned} \tag{22}$$

We can always make det M_0 be nonzoro by adding some square-integrable functions to S and/or C. Furthermore if M_0 = det M_0 happens to be zero, all the λ's given by the methods of Kohn, Rubinow, and Hulthén are proved[1d,8,11b] to coincide with one another.

By use of $\{\zeta_i\}$, the wavefunction is now rewritten as

$$\Psi = T^s S + T^c C + \sum_{i=1}^{N} D_i\zeta_i \tag{23}$$

Comparison of Eq. (23) with Eq. (9) brings about the equalities:

$$T^s + \sum_i D_i P_i^s = 1 \tag{24a}$$

$$T^c + \sum_i D_i P_i^c = \lambda\ . \tag{24b}$$

The algebraic equation [Eq. (15)] is reduced to

$$K_0 \begin{pmatrix} T^c \\ D_1 \\ \vdots \\ D_N \end{pmatrix} = - T^s \begin{pmatrix} \langle C - \omega S|\hat{H}|S\rangle \\ \langle \chi_1|\hat{H}|S\rangle \\ \vdots \\ \langle \chi_N|\hat{H}|S\rangle \end{pmatrix}, \tag{25}$$

where

$$K_0 = \left(\begin{array}{c|c} \langle C - \omega S|\hat{H}|C\rangle & 0 \\ \hline \langle \chi_1|\hat{H}|C\rangle & \\ \vdots & X \\ \langle \chi_N|\hat{H}|C\rangle & \end{array}\right) \tag{26}$$

with

$$X = \begin{pmatrix} \langle \chi_1|\hat{H}|\zeta_1\rangle & \cdots & \langle \chi_1|\hat{H}|\zeta_N\rangle \\ \vdots & & \vdots \\ \langle \chi_N|\hat{H}|\zeta_1\rangle & \cdots & \langle \chi_N|\hat{H}|\zeta_N\rangle \end{pmatrix} \tag{27}$$

From Eq. (26) we have

$$\det K_0 = \langle C - \omega S|\hat{H}|C\rangle \det X. \tag{28}$$

Note that X is independent of ω. The determinant of X might vanish at certain energies and the singularities thus arising are unavoidable. On the other hand, the singularity which originates from a specified ω should be perfectly avoidable. We will consider these two types of singularities separately below.

B. Avoidable singularity

In order to eliminate D_i from Eqs. (24), we will introduce the first Kohn condition. Thus,

$$\sum_j \langle \chi_i|\hat{H}|\zeta_j\rangle D_j = - T^s \langle \chi_i|\hat{H}|S\rangle - T^c \langle \chi_i|\hat{H}|C\rangle \ . \tag{29}$$

Therefore, when detX is not zero,

$$D = - X^{-1}M^sT^s - X^{-1}M^cT^c \tag{30}$$

where D, M^s, and M^c are the column vectors constructed of $\{D_i\}$, $\{M_i^s\}$, and $\{M_i^c\}$, respectively. Insertion of Eq. (30) into Eq. (24) leads to

$$A^{ss}T^s + A^{sc}T^c = 1 \tag{31a}$$

$$A^{cs}T^s + A^{cc}T^c = \lambda , \tag{31b}$$

where

$$\begin{aligned} A^{ss} &= 1 - P^sX^{-1}M^s \\ A^{sc} &= - P^sX^{-1}M^c \\ A^{cs} &= - P^cX^{-1}M^s \\ A^{cc} &= 1 - P^cX^{-1}M^c \ , \end{aligned} \tag{32}$$

and where P^s and P^c are the row vectors of $\{P_i^s\}$ and $\{P_i^c\}$, respectively. Notice that none of A^{ss} to A^{cc} depends on ω.

On the other hand, from the second Kohn condition [Eq. (13)] and the property of ζ_i [Eqs. (18)], one obtains

$$\langle C - \omega S|\hat{H}|T^sS + T^cC\rangle = 0 \ . \tag{33}$$

Use of Eqs. (31) and (33) gives

$$\lambda = \frac{\beta - \alpha\omega}{\gamma\omega - \delta} \tag{34}$$

$$T^s = \frac{M^{sc}\omega - M^{cc}}{\gamma\omega - \delta} \qquad (35)$$

$$T^c = \frac{M^{cs} - M^{ss}\omega}{\gamma\omega - \delta} \qquad (36)$$

where

$$\begin{aligned} \alpha &= A^{cc}M^{ss} - A^{cs}M^{sc} \\ \beta &= A^{cc}M^{cs} - A^{cs}M^{cc} \\ \gamma &= A^{ss}M^{sc} - A^{sc}M^{ss} \\ \delta &= A^{ss}M^{cc} - A^{sc}M^{cs} \end{aligned} \qquad (37)$$

Clearly, λ depends on ω in a hyperbolic manner. That is, for any given k, there exists one, and only one, spurious singularity on the ω axis at

$$\omega_d = \delta/\gamma \qquad (38)$$

Conversely, if one chooses ω different from ω_d, such a kind of singularity can be avoided. Therefore, it never concerns a true resonance but is merely a spurious resonance. The singularity pointed out by Schwartz[7] is to take place when k passes through the point at which $\delta = 0$.

C. Variational first-order correction

In general, the λ obtained by Eq. (34) is not sufficiently accurate; it contains the first-order error. According to Kato,[6] λ_θ involved in $\Psi_{\ell\theta}$ should be corrected by Eq. (6) to give $[\lambda_\theta]$. The $[\lambda_\theta]$ may be converted to the corresponding first-order correction of λ by the relationship analogous to Eq. (14). If we denote this correction of λ as $[\lambda]_k$, it becomes

$$[\lambda]_k = \frac{\omega - [\lambda_\theta]}{1 - [\lambda_\theta]\omega} = \frac{\lambda + \lambda^2\omega + 2\langle\Psi|\hat{H}|\Psi\rangle}{1 + \lambda\omega - 2\langle\Psi|\hat{H}|\Psi\rangle} \,. \tag{39}$$

Before we express $[\lambda]_k$ in terms of ω, we discuss the mathematical meaning of Eq. (39) from another viewpoint. Kato's identity,[6] Eq. (6), is essentially

$$\bar{\lambda} = \lambda + 2\langle\bar{\Psi}|\hat{H}|\Psi\rangle \,, \tag{40}$$

where $\bar{\Psi}$ is the exact wavefunction

$$\bar{\Psi} = S + \bar{\lambda}C + \sum_{i=1}^{N} \bar{d}_i\chi_i + \sum_{m=N+1}^{\infty} \bar{d}_m\chi_m \,. \tag{41}$$

The square-integrable functions χ_m are those not to be used in the approximate wavefunction Ψ. Inserting Eq. (41) into Eq. (40) and using the first Kohn condition, Eq. (12), one gets easily

$$(1 - 2\langle C|\hat{H}|\Psi\rangle)\bar{\lambda} = \lambda + 2\langle S|\hat{H}|\Psi\rangle + 2\sum_{m=N+1}^{\infty} \bar{d}_m\langle\chi_m|\hat{H}|\Psi\rangle \tag{42}$$

If the basis set $\{\chi_i\}$ used for Ψ is sufficient, we may neglect the last sum in the right-hand side of Eq. (36). Apparently, this last term is second order as to $\delta\Psi = \bar{\Psi} - \Psi$. Thus we have obtained a first-order correction formula

$$[\lambda]_0 = \frac{\lambda + 2\langle S|\hat{H}|\Psi\rangle}{1 - 2\langle C|\hat{H}|\Psi\rangle} . \tag{43}$$

Now, it is easy to show that $[\lambda]_k$ is identical with $[\lambda]_0$. Owing to the second Kohn condition, Eq. (13), $[\lambda]_k$ becomes

$$\begin{aligned} [\lambda]_k &= \frac{(1 + \lambda\omega)(\lambda + 2\langle S|\hat{H}|\Psi\rangle)}{(1 + \lambda\omega)(1 - 2\langle C|\hat{H}|\Psi\rangle)} \\ &= [\lambda]_0. \end{aligned} \tag{44}$$

In such cases as the minimum-norm method where we need not calculate ω directly, calculations of $[\lambda]_0$ just suffice.

Finally, we will express $[\lambda]$ in terms of ω as

$$[\lambda] = \frac{(\beta - 2M_0) - \alpha\omega}{(\gamma + 2M_0)\omega - \delta} . \tag{45}$$

It should be noted that $[\lambda]$ itself also has a singularity at $\omega = \delta/(\gamma + 2M_0)$. However, we can expect this divergence to be seldom met with because this divergence condition, $\langle C|\hat{H}|\Psi\rangle = 1/2$, is hard to be fulfilled if the basis is sufficient. In order words, a basis set ought to be altered if the resultant $[\lambda]$ diverges.

D. Unavoidable singularity

For any choice of ω, all of the λ and D_i's may undergo a divergence as E passes through certain energies. True resonances must have bearing with such singularities. As was stated previously, this is ascribed to det $X = 0$ and is unavoidable. Although Eq. (15) has no solution in this case, we can instead extract a correct Kohn solution from the equality det X = 0 itself.

If det X = 0, then X should posses an eigenvalue of zero and the corresponding eigenvector ζ_0^{tr} which is expressed by a linear combination of $\{\zeta_i\}$. According to a theorem of linear algebra one can always have ζ_0^{tr} satisfy

$$\langle \chi_0^{tr} | \hat{H} | \zeta_0^{tr} \rangle = 0 \tag{46}$$

$$\langle \chi_k^{tr} | \hat{H} | \zeta_0^{tr} \rangle = 0 \, , \qquad k = 1,2,\ldots N-1 \tag{47}$$

where χ_0^{tr} and χ_k^{tr} are given by a unitary transformation of $\{\chi_i\}$. Equations (46) and (47) together with Eqs. (18) give

$$\langle S | \hat{H} | \zeta_0^{tr} \rangle = 0 \tag{48a}$$

$$\langle C | \hat{H} | \zeta_0^{tr} \rangle = 0 \tag{48b}$$

$$\langle \chi_i | \hat{H} | \zeta_0^{tr} \rangle = 0 \, . \qquad (i = 1,2,\ldots N) \tag{48c}$$

It follows that ζ_0^{tr} is nothing but the solution of the Kohn method. Further, it fulfills Hulthén's condition

$$\langle \zeta_0^{tr} | \hat{H} | \zeta_0^{tr} \rangle = 0 \, . \tag{49}$$

That is, at an unavoidably singular point, the solutions of Kohn's and Hulthén's methods coincide with each other. In addition, the energy where this singularity occurs does not depend on the methods adopted but on the basis set chosen as long as the first Kohn condition is used.

III. PROPOSAL OF METHODS

A. Minimum basis-dependence (MBD) condition

If the basis set $\{\chi_i\}$ by itself approaches a complete one, both the coefficients T^s and T^c should come to zero. This is evident from the the following two points. First, if the wavefunction is exact, neither λ nor D_i's involved in it depends on ω, so that both T^s and T^c should be constants, regardless of ω. Second, T^s and T^c should identically fulfill Eq. (33), which forces them to depend on ω unless $T^s = T^c = 0$. On the contrary, we may expect either T^s or T^c, or occasionally both of them, to depend strongly on ω and moreover to have large magnitudes, if the basis set chosen is insufficient or if the ω in Eq. (13) is fixed at a wrong point, such as $\omega = \delta/\gamma$.

The situations delineated above provide a good reason for demanding the norm

$$I_{MBD} = (T^s)^2 + (T^c)^2 \tag{50}$$

to take on a minimal value possible. There exists a single point which minimizes I_{MBD} on the ω-axis. It is

$$\omega_{MBD} = -\frac{\delta Y + 2\gamma Z}{\gamma Y} \tag{51}$$

where

$$Y = 2\frac{\delta}{\gamma}\{(M^{sc})^2 + (M^{ss})^2\} - 2(M^{sc}M^{cc} + M^{ss}M^{cs}) \tag{52a}$$

and

$$Z = (M^{cc})^2 + (M^{cs})^2 - \frac{Z^2}{\gamma^2}\{(M^{sc})^2 + (M^{ss})^2\} . \tag{52b}$$

Once we obtain ω_{MBD}, the calculations of Ψ and $[\lambda]$ are made in a straightforward way. It is clear that λ obtained by this method does not experience the avoidable singularity; if T^s and T^c are bounded, so will λ be [Eqs. (34) — (36)]. The present minimum basis-dependence (MBD) method can readily be extended to multi-channel scatterings.

B. Minimum error (ME) condition

From Eq. (42), the origin of the error of $[\lambda]$ is seen to be

$$2\sum_m \bar{d}_m \langle \chi_m | \hat{H} | \Psi \rangle = (\bar{\lambda} - \lambda) - 2\langle S | \hat{H} | \Psi \rangle - 2\bar{\lambda}\langle C | \hat{H} | \Psi \rangle. \tag{53}$$

We will seek for the ω which minimizes

$$I_{ME} = (\bar{\lambda} - \lambda)^2 + 4\langle S | \hat{H} | \Psi \rangle^2 + 4\bar{\lambda}^2 \langle C | \hat{H} | \Psi \rangle^2 . \tag{54}$$

Imposing the condition $dI_e/d\omega = 0$, we have

$$\begin{aligned} &[(\alpha\delta - \gamma\beta)(\alpha + \bar{\lambda}\gamma) + 4\bar{\lambda}^2 M_0^2 \delta]\omega_{ME} \\ &\qquad = (\alpha\delta - \gamma\beta)(\bar{\lambda}\delta + \beta) - 4M_0^2\gamma . \end{aligned} \tag{55}$$

Equation (55) as it stands is useless because $\bar{\lambda}$ is unknown. We are thus obliged to place $\bar{\lambda}$ by Eq. (45). The resulting equation is cubic in ω. Of the three ω values obtained by solving it, the ω which actually gives the smallest I_{ME} is physically acceptable.

IV. COMMENTS ON OTHER THEORIES

In this section, we will comment on some typical variational methods to calculate λ, from the viewpoint of our own. All the methods treated here are reduced to the problem to search the respective ω.

A. The Kohn and Rubinow methods

Neither the Kohn[4] ($\omega = 0$) nor Rubinow[9] ($\omega = \infty$) method can escape from a spurious singularity. Equations (34) and (45) shows that the Kohn method gives

$$\lambda = -\frac{\beta}{\delta} \tag{56}$$

$$[\lambda] = \frac{2M_0 - \beta}{\delta}, \tag{57}$$

while the Rubinow method results in

$$\lambda = -\frac{\alpha}{\gamma} \tag{58}$$

and

$$[\lambda] = -\frac{\alpha}{\gamma + 2M_0} \tag{59}$$

B. Hulthen's method and its extension

Hulthén[2,3] used the condition

$$\langle \Psi | \hat{H} | \Psi \rangle = 0 \tag{60}$$

in place of the second Kohn condition. By use of Eqs. (34) — (36) we have

$$\langle\Psi|\hat{H}|\Psi\rangle = M_0 \frac{\alpha\omega^2 - (\beta + \gamma)\omega + \delta}{(\gamma\omega - \delta)^2} . \tag{61}$$

We consider two cases below.

(i) The case where $(\beta + \gamma)^2 - 4\alpha\delta \geq 0$.

Equation (60) is equivalent to $\langle S - C/\omega|\hat{H}|\Psi\rangle = 0$, so that

$$\lambda = -\frac{1}{\omega} \tag{62}$$

and

$$\omega = \frac{\beta + \gamma \pm \{(\beta + \gamma)^2 - 4\alpha\delta\}^{1/2}}{2\alpha} . \tag{63}$$

The choice of the sign in Eq. (63) is also determined by the function I_{MBD}, Eq. (50). Here, the Demkov[5c] condition cannot be applicable.

(ii) The case where $(\beta + \gamma)^2 - 4\alpha\delta < 0$

Nesbet[8] and Shimamura[12] have already shown that Eq. (60) cannot necessarily hold in the vicinity of the eigenvalues of the matrix $\langle\chi_i|H|\chi_i\rangle$ as long as the first Kohn condition is imposed on Ψ. For such cases, Hulthén's method had better be extended to a form such that ω minimizes $|\langle\Psi|\hat{H}|\Psi\rangle|$. The ω value is then

$$\omega = \frac{\delta(\gamma - \beta)}{\gamma(\gamma + \beta) - 2\alpha\delta} . \tag{64}$$

It is easy to prove that the two ω's of Eqs. (63) and (64) are connected continuously when k is varied. The extension enables to define Hulthén's ω everywhere. Calculations of $[\lambda]$ are required only in Case (ii);

in Case (i), $[\lambda] = \lambda$.

C. The minimum-norm method

Harris and Michels[11] proposed the minimum-norm (MN) method originally for multi-channel scatterings. The wavefunction is determined so as to minimize

$$I_M = \left(\langle S|\hat{H}|\Psi\rangle \quad \langle C|\hat{H}|\Psi\rangle \right) \begin{pmatrix} \langle S|\hat{H}|\Psi\rangle \\ \langle C|\hat{H}|\Psi\rangle \end{pmatrix} \tag{65}$$

and to satisfy the first Kohn condition.

For single-channel cases, it is convinient to write T^s and T^c as

$$T^s = -\langle C_\theta|\hat{H}|C\rangle f \tag{66a}$$

and

$$T^c = \langle C_\theta|\hat{H}|S\rangle f \ . \tag{66b}$$

By use of these expressions, one obtains

$$I_M = M_0^2 f^2 \ , \tag{67}$$

and

$$f = (\gamma \sin\theta - \delta\cos\theta)^{-1} \ . \tag{68}$$

I_M may attain its minimum when

$$\omega = -\frac{A^{ss}M^{sc} - A^{sc}M^{ss}}{A^{ss}M^{cc} - A^{sc}M^{cs}} \ . \tag{69}$$

Because both $\langle S|\hat{H}|\Psi\rangle$ and $\langle C|\hat{H}|\Psi\rangle$ have a singular point at $\omega = \delta/\gamma$ as well as T^s and T^c, the above condition will avoid the spurious singularity. The first-order variational correction of λ ought to be calculated by Eq. (39), as was argued by Nesbet.[10]

D. The optimized anomaly-free method

Nesbet and Oberoi[10] imposed the condition $\lambda_\theta = 0$ as well as the first Kohn condition on the wavefunction

$$\Psi_\theta = S(\cos\theta - \lambda_\theta \sin\theta) + C(\sin\theta + \lambda_\theta \cos\theta) + \sum_i D_{\theta i}\chi_i. \tag{70}$$

The second Kohn condition, Eq. (13), is equivalent to their $m'_{10} = 0$[10] for the single-channel case. The wavefunction Eq. (70) reduces to

$$\Psi_\theta = S\cos\theta + C\sin\theta + \sum D_{\theta i}\chi_i \tag{71}$$

when $\lambda_\theta = 0$. Hence,

$$\lambda \equiv \tan\theta = \omega \tag{72}$$

or using Eq. (34)

$$\frac{\beta - \alpha\omega}{\gamma\omega - \delta} = \omega. \tag{73}$$

Equation (73) does not necessarily have real solutions. In this case, the procedure would have to return Eq. (11). There, the orthogonal matrix has to be replaced by a unitary one. Further, even if real solutions are obtained, a criterion with which to select the correct solution, such as I_{MBD}, will be needed.

V. NUMERICAL EXAMPLES

We have performed sample calculations of the phase shift $\rho = \tan^{-1}\lambda$ by the various methods mentioned in the foregoing sections: the Kohn (Eq. (56)), Rubinow (Eq. (58)), Hulthén (Eqs. (63) or (64)), the minimum-norm (MN, Eq. (69)) and optimized anomaly-free (OAF, Eq. (73)) methods in addition to our minimum-error (ME, Eq. (55)) and minimum basis-dependence (MBD, Eq. (51)) methods. Their variational corrections $[\rho] = \tan^{-1}[\lambda]$ are all given through Eq. (43). In place of the effective potential $V_{eff}(r) = V(r) + \ell(\ell + 1)/2r^2$, the model potential function of Hazi and Taylor[13] was used:

$$V(x) = \begin{cases} \frac{1}{2} x^2 & (x < 0) \\ \frac{1}{2} x^2 e^{-ax^2} & (x > 0) \end{cases} \tag{74}$$

The square-integrable basis functions χ_i's used were the Hermite functions. The size N of the basis was varied between 5 and 40. As the asymptotic functions S and C, the following functions were adopted:

$$S = \begin{cases} k^{-1/2}\sin kx & (x > 0) \\ k^{-1/2}e^{-bx^2}\sin kx & (x < 0) \end{cases} \tag{75a}$$

and

$$C = \begin{cases} k^{-1/2}\cos kx & (x > 0) \\ k^{-1/2}e^{-bx^2}\cos kx & (x < 0) \end{cases} \tag{75b}$$

with the damping factor b being fixed at 0.15.

First, we have examined the energy dependences of the various phase shifts for two different potentials for which a = 0.15 and 0.225. The results are summarized in Table I and II, respectively. The size N = 20 of $\{\chi_i\}$ yielded fairly good [ρ] values in all methods. Especially, all the results for a = 0.225 (Table II) for which the potential barrier is lower than for the case of a = 0.15 (Table I), are nearly in the exact limit. The very small deviations from the exact values may be due to the choice of a fixed damping factor b. The results are satisfactory for the relatively small size of $\{\chi_i\}$ used; the stabilization method would need more χ functions in order to obtain the comparable accuracy.[13]

In Table III, the basis size dependences of both ρ and [ρ] are shown for a case of E = 0.1986012 and a = 0.15. The [ρ] values are sufficiently close to the exact phase shift (0.25441) when N is larger than 15. With N greater than 30, exact ρ values are obtainable by any of the methods here examined. For the sake of comparison, the values of I_{MBD} and I_{ME} calculated at varying N are also listed. Both these I's converges to zero in a monotonous manner. However, in case where E is in the vicinity of the critical E at which det $X = 0$, these monotonous behaviors break down. Nonetheless, we may regard these I's as useful measures of the accuracy of the basis-set calculations.

Generally, the OAF method seems to give slightly more accurate results than do the MN and MBD. The latter two methods yield nearly the same [ρ] values. The agreement seems to be essential, as will be discussed in a forthcoming paper. Both of them are also reliable enough. Furthermore, they can be treated within a framework of real number, in contrast to the OAF method.

Finally, the way how λ is corrected to $[\lambda]$ is illustrated in Fig. 1 for the case of a = 0.15, N = 15, and E = 0.3067471 (a.u.). Both λ and $[\lambda]$ vary hyperbolically with :

$$\lambda = -0.33122 - \frac{0.07503}{\omega - 0.37129} \tag{76}$$

$$[\lambda] = -0.35956 - \frac{0.00732}{\omega - 0.40305} \tag{77}$$

The constant term for $[\lambda]$ (-0.35956) is much nearer to the exact value (-0.35015) than is that for λ (-0.33122). The numerator for $[\lambda]$ (0.00732) is about one-tenth that for λ (0.07503). The latter result indicates that the dependence of $[\lambda]$ on ω is relatively small and hence on the methods. Further, the range of ω for divergence is narrower.

VI. CONCLUDING REMARKS

We have examined the dependences both λ and $[\lambda]$ upon $\omega = \tan\theta$ in a systematic manner, to clarify mutual relationships among various variational methods. This was accomplished by the help of the basis transformation. In this connection we have proposed two new methods. Another merit of the transformation lies in its character that enable to avoid the trouble originated from the singularity of the matrix $\langle \chi_i | H | \chi_j \rangle$, which Schwartz[7] took for the origin of the singularity of Eq. (15) itself. Incidentally, the procedure of constructing $\{\zeta_i\}$ and X^{-1} does not require much of calculation time as compared to other methods such as Nesbet's[8] procedure.

Among the methods examined here, the MBD, MN (OMN) and OAF methods appear to be equally promising. However, one major drawback of the OAF method is that it involves a procedure of solving non-linear equations. The MBD as well as MN method can readily be extended to cover multichannel scatterings, as will be dealt with in the succeeding paper.

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TABLE I. Phase shifts calculated by various methods for the case of N = 20 and a = 0.15. The entries are 10^5 times the deviations from the exact ρ value[a]

Method	E =	0.1986012	0.3067471	0.4660346	0.4661227	0.4662291	0.4663029
	ρ_{exact} =	0.25441	-0.33681	0.19811	0.71752	1.26965	1.50066
Kohn	ρ	2804	-3812	1455	1176	306	49
	[ρ]	-25	-82	-9	-18	-61	-19
Rubinow	ρ	-663	398	4081	13437	13672	-303252
	[ρ]	-93	-30	234	262	110	87
Hulthén	[ρ]	-81	-35	-220	-50	-66	-20
MN	ρ	636	-3	1470	1244	362	0
	[ρ]	-67	-35	-7	-16	-60	-19
OAF	ρ	5178	—[b]	1498	2000	3544	—[b]
	[ρ]	21	—[b]	-4	4	-18	—[b]
ME	ρ	-267	134	1255	660	126	15
	[ρ]	-85	-33	-31	-31	-63	-19
MBD	ρ	1585	-68	1455	1173	284	-39
	[ρ]	-48	-35	-9	-18	-61	-20

[a] Hazi and Taylor ref. 13.

[b] Real solution was not found.

TABLE II. Phase shifts calculated by various methods for the case of $N = 20$ and $a = 0.225$. The entries are 10^5 times the deviations from the exact ρ value[a]

Method	E =	0.1829543	0.4356381	0.4400106	0.4426438	0.5338320	0.7886753
	ρ_{exact} =	1.16758	1.00578	1.61273	2.17635	3.25045	3.07880
Kohn	ρ	-25	-45	-8	24	54	-313
	$[\rho]$	-4	-7	-11	-8	-2	-2
Rubinow	ρ	47	-212	-295	-199	-18	2
	$[\rho]$	-4	-7	-11	-7	-2	-2
Hulthén	$[\rho]$	-4	-7	-11	-8	-2	-2
MN	ρ	9	-57	-24	12	45	-11
	$[\rho]$	-4	-7	-11	-8	-2	-2
OAF	ρ	107	-97	-346	139	57	-469
	$[\rho]$	-5	-7	-11	-8	-2	-2
ME	ρ	-13	-33	-9	3	-6	0
	$[\rho]$	-4	-7	-11	-8	-2	-2
MBD	ρ	-13	-47	-11	22	47	-12
	$[\rho]$	-4	-7	-11	-8	-2	-2

[a] Hazi and Taylor ref. 13.

TABLE III. The basis size dependences of the phase shifts at E = 0.1986012 a.u. and a = 0.15. The entries for ρ and [ρ] are 10^5 times the deviations from the exact ρ value (0.25441)

Methods	N =	5	10	15	20	30	40
Kohn	ρ	34650	22161	8021	2804	-134	-1
	[ρ]	-146240	-9982	-617	-25	0	0
Rubinow	ρ	8835	91492	-7465	-663	-8	-1
	[ρ]	8330	16617	-2917	-93	0	0
Hulthén	[ρ]	-165881[a]	-45555[a]	-1990	-81	0	0
MN	ρ	54455	23182	5464	636	-15	-1
	[ρ]	-99578	-8957	-923	-67	0	0
	I_M[b,c]	0.9646(0)	0.1276(-1)	0.7277(-3)	0.3422(-4)	0.1041(-7)	0.6015(-11)
OAF	ρ	82123	28957	11103	5178	-68	-1
	[ρ]	-28123	-4021	-230	21	0	0
ME	ρ	86077	-4731	-2656	279	-5	0
	[ρ]	-20084	-87684	-2095	473	0	0
MBD	ρ	27793	20167	6364	1585	-15	-1
	[ρ]	-158456	-12150	-807	-48	0	0
	I_{MBD}[d,c]	0.9607(-1)	0.1049(-2)	0.5725(-4)	0.3826(-6)	0.3729(-8)	0.7905(-12)

[a] The extended Hulthen method, Eq. (64). [b] Eq. (67).

[c] The figures given in parentheses indicate the multiplicative power of 10. [d] Eq. (50).

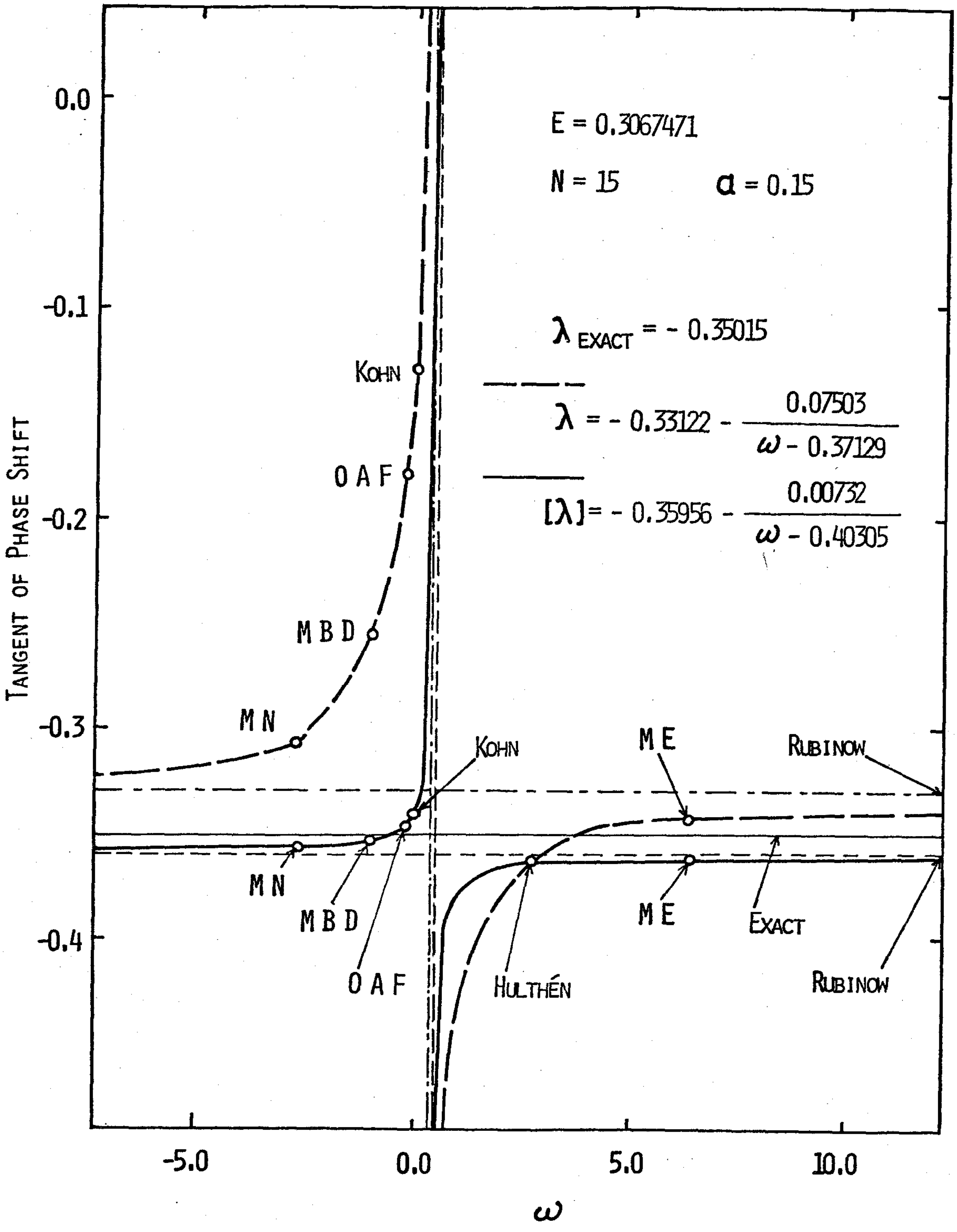

Fig. 1. Schematic representation of the hyperbolic curves of λ and [λ] vs ω.

CHAPTER 3

Optimized Kohn Method for the Multi-Channel Scattering

The minimum basis-dependence (MBD) method previously proposed for the single-channel scattering is extended to the multi-channel case. This is accomplished by the basis transformation just as was done in the single-channel scattering. The minimum-norm (MN) method, reformulated within our scheme, is also discussed in connection with the MBD method. Both of them are accompanied by a set of simultaneous equation which is more general than that of the Kohn method. A general variational functional is proposed explicitly for a wavefunction which is determined by any algebraic equation. This functional can be made use of as a correction formula for a reactance matrix which is obtained as the solution of the algebraic equation.

I. INTRODUCTION

In our previous paper[1] (referred to as Paper I hereafter), we proposed two methods to calculate the wavefunction for single-channel scattering, and discussed other theoretical methods, such as the optimized-anomaly free method[2], on the basis of our own viewpoint. In this paper, we will treat multi-channel scattering.

To begin with, we will transform a basis set, and then extend the minimum basis-dependence (MBD) method[1] by matrix calculus. The minimum-norm (MN) method[3] is also reformulated along our own way. The mathematical similarity between the two will be clarified. The resultant equation are, in both methods, a simple linear-algebraic one. In a later section of this paper, we will concentrate, in a general manner, on a variational functional, from which the linear-algebraic equation can be derived by variation.

In the single-channel scattering the relationship between a given linear-algebraic equation and the corresponding variational method was very simple. By use of the wavefunction of θ-normalization, namely Ψ_θ, defined by Kato[4]

$$\Psi_\theta = S(\theta) + \lambda_\theta C(\theta) + \sum_i D_{\theta i}\chi_i \tag{1}$$

one can construct a variational functional, $[\lambda_\theta]$,

$$[\lambda_\theta] = \lambda_\theta + 2\langle\Psi_\theta|\hat{H}|\Psi_\theta\rangle \tag{2}$$

which gives the simple algebraic equations when it is varied by λ_θ and

$D_{\theta i}$'s:

$$\langle \chi_i | \hat{H} | \Psi \rangle = 0, \tag{3a}$$

$$\langle C - \omega S | \hat{H} | \Psi \rangle = 0. \tag{3b}$$

The various symbols appearing in Eqs.(1)—(3) have the same meanings as in Paper I. Furthermore, the λ, the tangent of the phase shift, and its variational correction $[\lambda]$ were shown to depend on ω in a hyperbolic manner. Conversely, it can be said that the algebraic equations, Eq.(3), are always accompanied by the variational functional, Eq.(2), which can be made use of as a first-order correction.

On the other hand, in multi-channel scattering theory, the situation is neither so simple nor analogous. Let us assume that the following algebraic equations similar to Eqs.(3) are valid:

$$\langle \chi_i | \hat{H} | \Psi_\alpha \rangle = 0 \qquad \text{(first Kohn condition)}, \tag{4a}$$

$$\langle S_\mu + \sum_\nu^L C_\nu w_{\nu\mu} | \hat{H} | \Psi_\alpha \rangle = 0 \qquad \text{(second Kohn condition)}, \tag{4b}$$

where C_μ and S_μ are the asymptotic functions of the channel μ with cosine- and sine-like behavior, respectively, and $w_{\nu\mu}$ is a given numerical value. The wavefunction of the channel α, Ψ_α, is defined by the reactance matrix R

$$\Psi_\alpha = S_\alpha + \sum_\nu C_\nu R_{\nu\alpha} + \sum_i \chi_i D_{i\alpha}. \tag{5}$$

The wavefunctions of both the MBD and MN must fulfill Eqs.(4). Our problem now is to consider whether or not there exists a variational functional from which the general algebraic equations, Eqs.(4), can be yielded by variation. If it exists, what will its explicit form look like?

In Section II, we will extend the basis transformation of Paper I to the multi-channel case. The minimum basis-dependence method will then be proposed for the multi-channel scattering in a slightly different manner. Section III will provide a general variational functional as stated above. Further, we will discuss the conditions upon which the variational functional exists.

II. PRELIMINARY

A. Basis transformation

Define a new basis function $\{\eta_i\}$ by

$$\langle S_\nu|\hat{H}|\eta_i\rangle = 0 \tag{6a}$$

$$\langle C_\nu|\hat{H}|\eta_i\rangle = 0 \tag{6b}$$

$$\text{for}\quad i = 1,2,\ldots,N \qquad \nu = 1.2,\ldots,L$$

and

$$\eta_i = \chi_i + \sum_\mu S_\mu P^s_{\mu i} + \sum_\mu C_\mu P^c_{\mu i}. \tag{7}$$

The matrices P^s and P^c whose (μ,i) elements, denoted as $P^s_{\mu i}$ and $P^c_{\mu i}$, respectively, are determined by

$$\begin{pmatrix} P^s \\ P^c \end{pmatrix} = -\begin{pmatrix} M^{ss} & M^{sc} \\ M^{cs} & M^{cc} \end{pmatrix}^{-1} \begin{pmatrix} M^{s\chi} \\ M^{c\chi} \end{pmatrix}, \tag{8}$$

where the (ν,μ) element of M^{sc}, for instance is

$$M^{sc}_{\nu\mu} = \langle S_\nu|\hat{H}|C_\mu\rangle \tag{9}$$

and the (ν,i) element of $M^{s\chi}$ is

$$M^{s\chi}_{\nu i} = \langle s_\nu | \hat{H} | \chi_i \rangle = \langle \chi_i | \hat{H} | s_\nu \rangle . \tag{10}$$

The certainty for the existence of the inverse matrix involved in Eq.(8) is similar to that for the single-channel case.

The wavefunction of channel α, Eq.(5), is written in terms of the $\{\eta_i\}$ as

$$\Psi_\alpha = \sum_\mu^L (S_\mu T^s_{\mu\alpha} + C_\mu T^c_{\mu\alpha}) + \sum_i^N \eta_i D_{i\alpha}, \tag{11}$$

or in a matrix notation

$$\Psi = ST^s + CT^c + \eta D, \tag{12}$$

where

$$\Psi = (\Psi_1\ \Psi_2\ \ldots\ \Psi_L), \tag{13a}$$

$$S = (S_1\ S_2\ \ldots\ S_L), \tag{13b}$$

$$C = (C_1\ C_2\ \ldots\ C_L), \tag{13c}$$

$$\eta = (\eta_1\ \eta_2\ \ldots\ \eta_L). \tag{13d}$$

Comparing Eq.(11) with Eq.(5). one obtains

$$T^s + P^s D = I, \tag{14a}$$

$$T^c + P^c D = R. \tag{14b}$$

When we introduce the first Kohn condition, we have

$$XD = - M^{\chi s} T^s - M^{\chi c} T^c, \tag{15}$$

where

$$X_{ij} = \langle \chi_i | \hat{H} | \eta_j \rangle , \tag{16}$$

and $M^{\chi s}$ and $M^{\chi c}$ are the transposed matrices of $M^{s\chi}$ and $M^{c\chi}$, respectivrly.

When the determinant of X happens to be zero, unavoidable singularity will occur[1]. In this case, the eigenvector which belongs to the eigenvalue zero of X is the solution of the Kohn[5] method. The other wavefunctions should be expanded by the new basis set in which the above eigenvector is projected out of $\{\eta_i\}$. A new X constructed of this new basis set should have its own inverse. In what follows, we presume the existence of X^{-1}. Therefore, Eq.(15) will bring out D. Introducing the D thus obtained into Eqs.(14), we get

$$(I - P^s X^{-1} M X^s) T^s + (- P^s X^{-1} M X^c) T^c = I, \tag{17a}$$

$$(- P^c X^{-1} M X^s) T^s + (I - P^c X^{-1} M X^c) T^c = R, \tag{17b}$$

or

$$A^{ss} T^s + A^{sc} T^c = I, \tag{18a}$$

$$A^{cs} T^s + A^{cc} T^c = R, \tag{18b}$$

where the matrices A^{sc} etc. are defined in correspondence to Eqs.(17), and are independent of W. Here, we set the assumption: Both of the matrices $\begin{pmatrix} A^{ss} & A^{sc} \\ A^{cs} & A^{cc} \end{pmatrix}$ and A^{sc} have their inverse matrices. The assumption seems to be acceptable because both T^s and T^c must be definitely obtained when R is given by Eqs.(18a) and (18b) and because T^c should be yielded by Eq.(17a) if T^s is arbitrarily assumed. Judging from Eq.(18), one needs to introduce another condition in order for all the T^s, T^c, and R to be determined.

B. Matrix calculus

Lest any confusion should arise in later sections, we here lay down a few rules of matrix notation and its calculus. The matrix of $\hat{H} = E - H$ composed of S_μ and C_ν is defined by

$$\langle {}^{t}S|\hat{H}|C\rangle = \begin{pmatrix} \langle S_1|\hat{H}|C_1\rangle & \cdots\cdots & \langle S_1|\hat{H}|C_L\rangle \\ \vdots & & \vdots \\ \langle S_L|\hat{H}|C_1\rangle & \cdots\cdots & \langle S_L|\hat{H}|C_L\rangle \end{pmatrix}, \tag{19}$$

where t on the left shoulder of S denotes the transposition. The transposition of $\langle {}^{t}S|\hat{H}|C\rangle$ is

$${}^{t}\langle {}^{t}S|\hat{H}|C\rangle = \begin{pmatrix} \langle S_1|\hat{H}|C_1\rangle & \cdots\cdots & \langle S_L|\hat{H}|C_1\rangle \\ \vdots & & \vdots \\ \langle S_1|\hat{H}|C_L\rangle & \cdots\cdots & \langle S_L|\hat{H}|C_L\rangle \end{pmatrix}. \tag{20}$$

By use of a fundamental identity

$$\langle S_\mu|\hat{H}|C_\nu\rangle = {}^{*}\langle C_\nu|\hat{H}|S_\mu\rangle - \frac{1}{2}\,\delta_{\mu\nu}, \tag{21}$$

one gets

$$\langle {}^{t}S|\hat{H}|C\rangle = {}^{\dagger}\langle {}^{t}C|\hat{H}|S\rangle - \frac{1}{2}\,I,$$

where the symbols * and † denote the complex and hermitian conjugate, respectively. For two given (L,L)-dimensional matrices U and W, the following equality holds:

$$\langle {}^{t}U{}^{t}S|\hat{H}|CW\rangle = {}^{\dagger}\langle {}^{t}W{}^{t}C|\hat{H}|SU\rangle - \frac{1}{2}{}^{\dagger}UW. \tag{23}$$

III. MINIMUM BASIS-DEPENDENCE METHOD

A. Minimum basis-dependence (MBD) procedure

The minimum basis-dependence (MBD) procedure in a single-channel scattering is also applicable to multi-channel scattering with a slight modification. In an exact wavefunction, it is true that

$$T^s = T^c = 0, \tag{24}$$

where 0 is zero-matrix. For an approximate wavefunction, therefore, we may demmand the following functional I_{MBD} to be minimum

$$I_{MBD} = \mathrm{Tr}({}^{\dagger}T^sT^s + {}^{\dagger}T^cT^c), \tag{25}$$

where Tr denotes the trace of the matrix. The first-order variation of I_{MBD} with respect to T^s and T^c becomes

$$\delta I_{MBD} = \mathrm{Tr}(\delta^{\dagger}T^sT^s + \delta^{\dagger}T^cT^c + {}^{\dagger}T^s\delta T^s + {}^{\dagger}T^c\delta T^c). \tag{26}$$

In Eq.(26) both T^s and T^c should be varied subject to the condition Eq.(18a), namely,

$$A^{ss}\delta T^s = - A^{sc}\delta T^c. \tag{27}$$

Defining ${}^{\dagger}\Lambda = - (A^{sc})^{-1}A^{ss}$ and also introducing it into Eq.(25), we have

$$\delta I_{MBD} = \mathrm{Tr}[({}^{\dagger}T^s + {}^{\dagger}T^c\,{}^{\dagger}\Lambda)\delta T^s + \delta^{\dagger}T^s(T^s + \Lambda T^c)]. \tag{28}$$

The minimum condition $\delta I_{MBD} = 0$ necessitates

$$T^s + \Lambda T^c = 0, \tag{29}$$

because δT^s is here completely arbitrary. Combining Eqs.(29) with (18a), we finally reach the objective equation,

$$\begin{pmatrix} A^{ss} & A^{sc} \\ I & \mathcal{A} \end{pmatrix} \begin{pmatrix} T^{s} \\ T^{c} \end{pmatrix} = \begin{pmatrix} I \\ 0 \end{pmatrix} \tag{30a}$$

or

$$T^{c} = {}^{\dagger}A^{sc}(A^{ss\dagger}A^{ss} + A^{sc\dagger}A^{sc})^{-1}. \tag{30b}$$

T^{s} is given by Eq.(29). The matrix $(A^{ss\dagger}A^{ss} + A^{sc\dagger}A^{sc})$ is positive definite as long as the determinant of A^{sc} is not zero.

B. Minimum-norm method (MN)

We would like to formulate the MN in order to clarify the relationship between the MBD and MN. In the MN, Harris and Michels[3] had the following functional minimized.

$$\begin{aligned} J &= \mathrm{Tr}({}^{\dagger}\langle{}^{t}C|\hat{H}|\Psi\rangle\langle{}^{t}C|\hat{H}|\Psi\rangle + {}^{\dagger}\langle{}^{t}S|\hat{H}|\Psi\rangle\langle{}^{t}S|\hat{H}|\Psi\rangle) \\ &= \mathrm{Tr}[{}^{\dagger}(T^{s}\ \ T^{c})\,{}^{\dagger}\begin{pmatrix} M^{ss} & M^{sc} \\ M^{cs} & M^{cc} \end{pmatrix} \begin{pmatrix} M^{ss} & M^{sc} \\ M^{cs} & M^{cc} \end{pmatrix} \begin{pmatrix} T^{s} \\ T^{c} \end{pmatrix}] \\ &= \mathrm{Tr}\ Q. \end{aligned} \tag{31}$$

If we denote

$${}^{\dagger}\begin{pmatrix} M^{ss} & M^{sc} \\ M^{cs} & M^{cc} \end{pmatrix} \begin{pmatrix} M^{ss} & M^{sc} \\ M^{cs} & M^{cc} \end{pmatrix} = \begin{pmatrix} F^{ss} & F^{sc} \\ F^{cs} & F^{cc} \end{pmatrix}, \tag{32}$$

the variation of Q becomes

$$\begin{aligned} \delta Q = {} & \delta^{\dagger}T^{s}(F^{ss}T^{s} + F^{sc}T^{c}) + \delta^{\dagger}T^{c}(F^{cs}T^{s} + F^{cc}T^{c}) \\ & + ({}^{\dagger}T^{s}F^{ss} + {}^{\dagger}T^{c}F^{cs})\delta T^{s} + ({}^{\dagger}T^{s}F^{sc} + {}^{\dagger}T^{c}F^{cc})\delta T^{c}. \end{aligned} \tag{33}$$

As has been done in the MBD, Eq.(27) is introduced here:

$$\begin{aligned} \delta Q = {} & \delta^{\dagger}T^{s}[(F^{ss} + \mathcal{A}F^{cs})T^{s} + (F^{sc} + \mathcal{A}F^{cc})T^{c}] \\ & + [{}^{\dagger}T^{s\dagger}(F^{ss} + \mathcal{A}F^{cs}) + {}^{\dagger}T^{c\dagger}(F^{sc} + \mathcal{A}F^{cc})]\delta^{\dagger}T^{c}, \end{aligned} \tag{34}$$

so that

$$(F^{ss} + \lambda F^{cs})T^{s} + (F^{sc} + \lambda F^{cc})T^{c} = 0. \tag{35}$$

The final equation to be solved is

$$\begin{pmatrix} A^{ss} & A^{sc} \\ F^{ss} + \lambda F^{cs} & F^{sc} + \lambda F^{cc} \end{pmatrix} \begin{pmatrix} T^{s} \\ T^{c} \end{pmatrix} = \begin{pmatrix} I \\ 0 \end{pmatrix}. \tag{36}$$

Although the original formula of the MN derived by Harris and Michels looks quite different from our MBD expression, a kind of similarity is found through our formalisms. The MN formula, Eq.(36), is somewhat more combersome to handle than is the MBD expression, Eq.(36). Yet, Eq.(36) has an advantage over the original MN: No other formulation is needed, even when the energy comes close to the vicinity of the eigenvalues of the matrix $\langle \chi_i | H | \chi_j \rangle$.

C. The second Kohn condition

We have not used the second Kohn condition so far. However, both the MBD and MN wavefunctions do have to satisfy Eq.(4b). If the wave function Eq.(12) is inserted into Eq.(4b),

$$(M^{ss} + {}^{\dagger}wM^{cs})T^{s} + (M^{sc} + {}^{\dagger}wM^{cc})T^{c} = 0. \tag{37}$$

Both T^{s} and T^{c} have already been obtained, so that w can be directly obtained from Eq.(37).

If the w given above were accidentally a diagonal matrix, the variational functional might be simply reduced to

$$[R_\theta] = R_\theta + 2\langle {}^{t}\Psi_\theta | \hat{H} | \Psi_\theta \rangle, \tag{38}$$

where

$$\Psi_\alpha = S_\alpha(\theta_\alpha) + \sum_\nu C_\nu(\theta_\nu)(R_\theta)_{\nu\alpha} + \sum_i \chi_i D^\theta_{i\alpha}, \tag{39}$$

and

$$W = \begin{pmatrix} -\cot\theta_1 & & & 0 \\ & -\cot\theta_2 & & \\ & & \ddots & \\ 0 & & & -\cot\theta_L \end{pmatrix}. \tag{40}$$

This is a simple analog[6] of Kato's expression[4] for the single-channel scattering. However, the W to be obtained from Eq.(37) is not necessarily diagonal. Therefore, a variational functional cannot easily be found. In the next section, we will show an explicit variational functional for a wavefunction satisfying both Eqs.(4a) and (4b).

IV. VARIATIONAL FUNCTIONAL

A. General wavefunction

The wavefunction of our research is redefined as

$$\Psi = S(a_s + b_sG) + C(a_c + b_cG) + \chi D, \tag{41}$$

where a_s, b_s, a_c, and b_c are certain given and fixed matrices, named parameter matrices while both G and D are determined variationally. χ is a row vector composed of $\{\chi_i\}$. Then, the R matrix becomes

$$R = (a_c + b_cG)(a_s + b_sG)^{-1}, \tag{42}$$

and the variationally corrected reactance matrix [R] is

$$[R] = (a_c + b_c[G])(a_s + b_s[G])^{-1}, \tag{43}$$

where [G] is a corrected G. Our aim in what follows is to search a variational functional giving [G]. In addition, we will find the parameter matrices which would facilitate the calculation of [G]. Incidentally, the wavefunction of Eq.(41) coincides with Nesbet's one[2] if

$$B = \begin{pmatrix} a_s & b_s \\ a_c & b_c \end{pmatrix} \tag{44}$$

is chosen as a unitary matrix.

B. Kato's type functional

The most familiar type of variational functional is the one of Kato's type[4]:

$$[G] = G + 2\langle \Psi | \hat{H} | \Psi \rangle. \tag{45}$$

In this case, the variation of [G] becomes

$$\begin{aligned} \delta[G] = {} & 2\langle \delta {}^tD {}^t\chi | \hat{H} | \Psi \rangle + 2\langle {}^t\Psi | \hat{H} | \chi \delta D \rangle \\ & + 2\langle \delta {}^tG ({}^tb_s {}^tS + {}^tb_c {}^tC) | \hat{H} | \Psi \rangle \\ & + 2^{\dagger}\langle \delta {}^tG ({}^tb_s {}^tS + {}^tb_c {}^tC) | \hat{H} | \Psi \rangle = 0, \end{aligned} \tag{46}$$

and hence

$$\langle {}^t\chi | \hat{H} | \Psi \rangle = 0 \tag{47a}$$

and

$$\langle {}^tb_s {}^tS + {}^tb_c {}^tC | \hat{H} | \Psi \rangle = 0. \tag{47b}$$

The last two equations are nothing but Kohn's conditions.

We are now going to research the conditions imposed on the parameter matrices from which Eq.(45) can be resulted. With the help of the equality, Eq.(23), one has

$$2\langle {}^t\overline{\Psi}|\hat{H}|\Psi\rangle = ({}^\dagger a_c a_s - {}^\dagger a_s a_c)$$
$$+ {}^\dagger\overline{G}({}^\dagger b_c a_s - {}^\dagger b_s a_c) - {}^\dagger({}^\dagger b_c a_s - {}^\dagger b_s a_c)G$$
$$+ {}^\dagger\overline{G}({}^\dagger b_c b_s - {}^\dagger b_s b_c)G, \tag{48}$$

where $\overline{\Psi}$ is the vector composed of the exact wavefunctions

$$\overline{\Psi} = S(a_s + b_s\overline{G}) + C(a_c + b_c\overline{G}) + \chi\overline{D}. \tag{49}$$

In order that we could obtain Eq.(45) from Eq.(48), the following three conditions are necessary:

$$\text{(i)} \quad {}^\dagger a_c a_s = {}^\dagger a_s a_c, \tag{50a}$$

$$\text{(ii)} \quad {}^\dagger b_c a_s - {}^\dagger b_s a_c = I, \tag{50b}$$

$$\text{(iii)} \quad {}^\dagger\overline{G}({}^\dagger b_c b_s - {}^\dagger b_s b_c)G = 0. \tag{50c}$$

Then, we have

$$\begin{aligned} {}^t\overline{G} &= G + 2\langle {}^t\overline{\Psi}|\hat{H}|\Psi\rangle \\ &= G + 2\langle {}^t\Psi|\hat{H}|\Psi\rangle - 2\langle \delta^t\Psi|\hat{H}|\delta\Psi\rangle, \end{aligned} \tag{51}$$

where $\delta\Psi = \overline{\Psi} - \Psi$. The first-order error term as to $\delta\Psi$ involved in Eq.(51) has been replaced by $[G]$ to give Eq.(45).

The first two conditions, Eqs.(50a) and (50b), are never essential to define a variational functional; in comparison with Eq. (45), only constant factors are mixed in Eq.(48). By contrast, the third condition is of crucial importance. There are two possibilities to fulfill (iii), i.e., (1) $G = 0$ and (2) ${}^\dagger b_c b_s = {}^\dagger b_s b_c$. The former identity was adopted by Nesbet and Oberoi[2] in their optimized anomaly-free (OAF) method. However, in compensation for fixing $G = 0$, another nonlinear search procedure for the unitary matrix, Eq.(44), which should satisfy

$$\langle {}^t b_s {}^t S + {}^t b_c {}^t C | \hat{H} | S a_s + C a_c + \chi D \rangle = 0 \tag{47c}$$

becomes necessary. Further, the second condition (ii), Eq.(50b), does not necessarily hold.

In the latter case (2), G can be varied freely, but a severe restraint is imposed on the matrix w of the second Kohn condition. w can be expressed in terms of both b_s and b_c as

$$w = b_c b_s^{-1}. \tag{52}$$

As a direct consequence of ${}^\dagger b_c b_s = {}^\dagger b_s b_c$, we have ${}^\dagger w = w$, that is, w must be a hermitian matrix. In usual case, it is sufficient for us to choose the parameter matrices to be real, so that w should be a real symmetric matrix. This case corresponds to the optimized minimum-norm (OMN) method proposed by Nesbet and Oberoi[2]. Strictly speaking, however, their procedure is theoretically unsatisfactory, because the w of MN which is defined by Eq.(37) cannot be symmetric in general. As a result, Eq.(45) should be applied to neither the MBD nor the MN.

C. General variational functional

When the general wavefunction, Eq.(41), is expanded over the basis set $\{\eta_i\}$, Eq.(18) should be modified into a form

$$\begin{pmatrix} A^{ss} & A^{sc} \\ A^{cs} & A^{cc} \end{pmatrix} \begin{pmatrix} T^s \\ T^c \end{pmatrix} = \begin{pmatrix} a_s + b_s G \\ a_c + b_c G \end{pmatrix} \tag{53}$$

or

$$\begin{pmatrix} T^s \\ T^c \end{pmatrix} = \begin{pmatrix} A^{ss} & A^{sc} \\ A^{cs} & A^{cc} \end{pmatrix}^{-1} \begin{pmatrix} a_s + b_s G \\ a_c + b_c G \end{pmatrix}$$

$$= \begin{pmatrix} K_s^0 + K_s G \\ K_c^0 + K_c G \end{pmatrix}. \tag{54}$$

Because none of A^{mn} $(m,n = s,c)$ and the parameter matrices depend on D, both T^s and T^c can be taken as the functions of G alone. Therefore,

$$\begin{pmatrix} \delta T^s \\ \delta T^c \end{pmatrix} = \begin{pmatrix} K_s \delta G \\ K_c \delta G \end{pmatrix}. \tag{55}$$

Now let us define a variational functional V,

$$\begin{aligned} V = {} & \langle {}^t\Psi|\hat{H}|\Psi\rangle \\ & + \langle {}^tG({}^te\,{}^tS + {}^tf\,{}^tC)|\hat{H}|ST^s + CT^c\rangle \\ & + {}^\dagger\langle {}^tG({}^te\,{}^tS + {}^tf\,{}^tC)|\hat{H}|ST^s + CT^c\rangle \\ & + G/2. \end{aligned} \tag{56}$$

The variation of V is

$$\begin{aligned} \delta V = {} & \langle \delta {}^tD\,{}^t\chi|\hat{H}|\Psi\rangle + {}^\dagger\langle \delta {}^tD\,{}^t\chi|\hat{H}|\Psi\rangle \\ & + \langle \delta {}^tG\{({}^tb_s + {}^te)\,{}^tS + ({}^tb_c + {}^tf)\,{}^tC\}|\hat{H}|\Psi\rangle \\ & + {}^\dagger\langle \delta {}^tG\{({}^tb_s + {}^te)\,{}^tS + ({}^tb_c + {}^tf)\,{}^tC\}|\hat{H}|\Psi\rangle \\ & + \langle {}^tG({}^te\,{}^tS + {}^tf\,{}^tC)|\hat{H}|(SK_s + CK_c)\delta G\rangle \\ & + {}^\dagger\langle {}^tG({}^te\,{}^tS + {}^tf\,{}^tC)|\hat{H}|(SK_s + CK_c)\delta G\rangle \\ = {} & 0 \end{aligned} \tag{57}$$

In Eq.(57), the relations

$$\text{(iii')} \quad {}^\dagger b_c b_s = {}^\dagger b_s b_c \tag{50d}$$

have been used in addition to Eqs.(50a) and (50b). Further, the following conditions

$$\text{(iv)} \quad b_s + e = I \tag{58a}$$

$$\text{(v)}\quad b_c + f = w \tag{58b}$$

$$\text{(vi)}\quad \left\langle {}^t e\,{}^t S + {}^t f\,{}^t C \middle| \hat{H} \middle| S K_s + C K_c \right\rangle = 0 \tag{58c}$$

may bring about

$$\delta V = \left\langle \delta\,{}^t D\,{}^t \chi \middle| \hat{H} \middle| \Psi \right\rangle + \left\langle \delta\,{}^t G({}^t S + {}^t w\,{}^t C) \middle| \hat{H} \middle| \Psi \right\rangle$$

$$+ \text{ (hermitian conjugate).} \tag{59}$$

It is easy to show that Eq.(59) leads to the Kohn conditions. We would like to stress that w in Eq.(59) is not required to be a symmetric matrix.

If an approximate wavefunction is such that the δV calculated therefrom is zero, then the V may yield $[G]/2$ which is correct to first order. Note that the exact V, namely $\overline{V}$, for which the exact wavefunction is used, is

$$\begin{aligned} \overline{V} &= \overline{G}/2 + \left\langle {}^t\overline{\Psi} \middle| \hat{H} \middle| \overline{\Psi} \right\rangle \\ &\quad + \left\langle {}^t G({}^t e\,{}^t S + {}^t f\,{}^t C) \middle| \hat{H} \middle| S\overline{T}^s_s + C\overline{T}^c \right\rangle \\ &\quad +^{\dagger}\left\langle {}^t G({}^t e\,{}^t S + {}^t f\,{}^t C) \middle| \hat{H} \middle| S\overline{T}^s + C\overline{T}^c \right\rangle \\ &= \overline{G}/2. \end{aligned} \tag{60}$$

In Eq.(60) $\overline{T}^s = \overline{T}^c = 0$ has been used. In case like this, V is the first-order crrection of $G/2$, i.e., $[G]/2$.

D. Determination of the parameter matrices

In the preceding subsection, we have shown the conditions to be imposed on the parameter matrices as well as e and f, from which V can be obtained. These six conditions, Eqs.(50) and (58), are not sufficient to define the matrices uniquely. In other words, there remains some arbitrariness that we can make use of to simplify the calculation.

One of the general approaches to this problem may be as follows: Given two hermitian matrices Y and Z which satisfy

$$a_c = Ya_s \qquad \text{(from condition (i))} \tag{61}$$

and

$$b_s = Zb_c, \qquad \text{(from condition (iii'))} \tag{62}$$

the a_c and b_s can rewrite condition (ii) as

$$^{\dagger}b_c(I - ZY)a_s = I. \tag{63}$$

On the other hand, using $e = I - Zb_c$ and $f = w - b_c$, one can easily show condition (vi) to be converted to

$$^{\dagger}b_c\langle {}^{*}Z\,{}^{t}S + {}^{t}C|\hat{H}|SK_s + CK_c\rangle = \langle {}^{t}S + {}^{t}w\,{}^{t}C|\hat{H}|SK_s + CK_c\rangle. \tag{64}$$

A good choice of Z will give

$$^{\dagger}b_c = \langle {}^{t}S + {}^{t}w\,{}^{t}C|\hat{H}|SK_s + CK_c\rangle\langle {}^{*}Z\,{}^{t}S + {}^{t}C|\hat{H}|SK_s + CK_c\rangle^{-1}. \tag{65}$$

Although both K_s and K_c depend on b_s and b_c, we can eliminate b_s and b_c from the right-hand side of Eq.(65) in the following manner. From the definitions of K_s and K_c, Eq.(54), and of Z,Eq.(62), we have

$$SK_s + CK_c = (S\quad C)\bar{A}\begin{pmatrix} Z \\ I \end{pmatrix} b_c, \tag{66}$$

where

$$\bar{A} = \begin{pmatrix} A^{ss} & A^{sc} \\ A^{cs} & A^{cc} \end{pmatrix}^{-1}. \tag{67}$$

Using Eq.(66), we finally obtain

$$^{\dagger}b_c = \langle {}^{t}S + {}^{t}w\,{}^{t}C|\hat{H}|(S\quad C)\bar{A}\begin{pmatrix} Z \\ I \end{pmatrix}\rangle$$

$$\times\langle {}^{*}Z\,{}^{t}S + {}^{t}C|\hat{H}|(S\quad C)\bar{A}\begin{pmatrix} Z \\ I \end{pmatrix}\rangle^{-1}. \tag{68}$$

Here, Z must be chosen so as not to make the determinant of $\left\langle {}^tS + {}^tw\,{}^tC|\hat{H}|(S\quad C)\bar{A}\begin{pmatrix} Z \\ I \end{pmatrix}\right\rangle$ vanish. If this is not fulfilled, the procedure from Eq.(66) to (68) is inconsistent with the assumption that b_c^{-1} exists. We have thus obtained both the parameter matrices, e and f.

The simplest choice of Y and Z is to set Y = YI and Z = ZI, where both Y and Z are constant. Further, if we set Y = Z = 0 the time required for computation will be reduced appreciably. However, it should be noted that $\det\left\langle {}^tS + {}^tw\,{}^tC|\hat{H}|(S\quad C)\bar{A}\begin{pmatrix} 0 \\ I \end{pmatrix}\right\rangle$ or $\det\left\langle {}^tC|\hat{H}|(S\quad C)\bar{A}\begin{pmatrix} 0 \\ I \end{pmatrix}\right\rangle$, both included in Eq.(68)will vanish at certain energies. Therefore, it is desirous to let Z vary continuously with E.

V. CONCLUDING REMARKS

We have shown that the MBD method is also applicable to multi-channel scattering. The MN method was reformulated by our basis-transformation scheme. In both cases, the second Kohn condition need not be used when R is calculable, a result which is in clear contrast to the single-channel case.

A general theory of variational functional has also been presented. Any wavefunction which is defined to satisfy Kohn's conditions has been shown explicitly to connect with the variational theory. These wavefunctions including the MBD and MN functions should be corrected by the variational functional V when w is not symmetric. This explicit formulation of V is theoretically important, even though calculation of it may be a somewhat cumbersome procedure. In actual calculations, a correction formula[1] for the reactance matrix

$$[{}^{t}R] = (R + 2\langle {}^{t}S|\hat{H}|\Psi\rangle)(I - 2\langle {}^{t}C|\hat{H}|\Psi\rangle)^{-1} \tag{69}$$

will also be useful. Derivation of Eq.(69) is almost entirely analogous to that for single-channel case. The error estimeted from Eq.(69) is second order.

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