Improved Quantum Theory of Many-Electron Systems. V. The Spin-Coupling Optimized GI Method*

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The previously developed GI methods have an arbitrary aspect since they are based on a particular representation of the symmetric group. Here we remove this arbitrariness by optimizing the representation, that is, optimizing the spin-coupling scheme simultaneously with the optimization of the orbitals. The resulting wavefunctions, called the spin-coupling optimized GI or SOGI wavefunctions, have all of the general properties of GI wavefunctions including the independent particle interpretation and are found as the solutions to a set of coupled differential equations which differ from the GI equations only in that the equations are constructed from a different representation of the symmetric group. We have applied this method to the ground state and some excited states of Li, to the ground states of Be$^+$ and B^{++} and to the ground state of LiH. In each of these cases, we found that the SOGI wavefunction was only slightly different from the G1 wavefunction and led to very similar energies and other spatial properties. For the spin density at the nucleus, however, SOGI led to much better results. In order to illustrate the effects of spatial symmetry on the SOGI orbitals, we examined the lowest $^1B_{1g}$, $^3A_{2g}$, and ^3E_u states of square H$_4$ and the $^2\Sigma_u{}^+$ state of linear symmetrical H$_3$. We find that in three of these cases optimization of the spin representation is crucial to providing an adequate description of the state. To investigate how the SOGI method would describe chemical reactions, the SOGI wavefunctions were computed for several other nuclear configurations of the H$_3$ system along the reaction path. These calculations showed that the spin coupling changed significantly during the reaction H$_2$+H$\rightleftharpoons$H+H$_2$ and that the variation of the SOGI orbitals provides a clear description of the changes in bonding which occur during this reaction.

I. INTRODUCTION

In Paper I[1] of this series, we considered a set of operators $G_i{}^\mu$ having the property that $G_i{}^\mu\Phi\chi$ is an eigenfunction of $\hat{S}^2$ and satisfies Pauli's principle for arbitrary functions Φ of the spatial coordinates of the N electrons and χ of the spin coordinates. For a given value of S and M_s, we can generally find several, say f^μ, linearly independent spin functions or ways of coupling the individual electron spins. The superscript μ of $G_i{}^\mu$ is determined by the total spin S and the subscript i indicates which of the f^μ coupling schemes is used. The spin functions used in Papers I[1] and II[2] are constructed with Wigner projection operators[3] based on Young's orthogonal irreducible representation[4] of S_N; the construction of this representation is considerably facilitated through the use of Young tableaux.[1,4] The quantity μ corresponds to a Young shape of one or two columns and i corresponds to a particular standard tableau. We will call the spin functions based on Young's orthogonal representation standard spin functions.

We showed in Paper I that, although the f^μ different operators $G_i{}^\mu$ are linearly independent, the *exact* wavefunction can be written in the form $G_i{}^\mu\Phi\chi$ using *any*

one $G_i{}^\mu$ operator and a suitable *product* of spin functions in χ if the spatial function Φ is sufficiently general,

$$\Psi^{\text{exact}}=G_i{}^\mu\Phi^{i,\text{exact}}\chi. \qquad (1)$$

(The $\Phi^{i,\text{exact}}$ will be different for different values of i.)

In Paper II,[2] we considered a function of the form

$$\Psi_{\text{GI}}=G_i{}^\mu\Phi^{i,\text{product}}\chi, \qquad (2)$$

where $\Phi^{i,\text{product}}$ is restricted to be a product of one-electron spatial orbitals and required that these spatial orbitals be the *best possible* ones. The result was a coupled set of integro-differential equations,

$$\hat{H}_k{}^{\mu i}\phi_k=\epsilon_k\phi_k \qquad k=1, 2, \cdots, N \qquad (3)$$

for the best orbitals. (The integro-differential–permutational operator $\hat{H}_k{}^{\mu i}$ depends on μ, i, and all the orbitals ϕ_j, except ϕ_k.) Since the orbitals $\{\phi_k\}$ optimize the energy for the wavefunction Ψ_{GI}, they are referred to as the GI orbitals, and the equations (3) for these orbitals are called the GI equations.

Even though the exact wavefunctions can be written in the form of (1) for *any* i, the constraint implied by a product Φ may be more restrictive for some i's than for others; that is, our approximate wavefunction Ψ_{GI} depends on which of the spin-coupling schemes (denoted by i) we have selected. The standard spin functions are used in the GI method because Young's orthogonal representation of S_N is easier to construct than other equivalent representations. This imposes an arbitrary restriction on the wavefunction because there is nothing physically special about the standard spin functions and because we can construct a new $G_i{}^\mu$-like operator, $G_i{}^{\mu L}$, which yields a wavefunction in which the spin part is a general linear combination of

[1] W. A. Goddard III, Phys. Rev. **157**, 73 (1967), hereafter referred to as Paper I.
[2] W. A. Goddard III, Phys. Rev. **157**, 81 (1967), hereafter referred to as Paper II.
[3] E. P. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), p. 118.
[4] D. E. Rutherford, *Substitutional Analysis* (Edinburgh University Press, Edinburgh, Scotland, 1948).
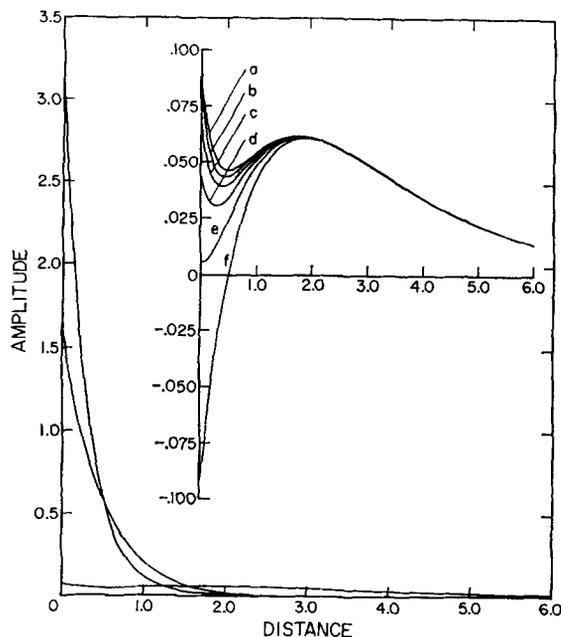
FIG. 1. Orbitals for the 2^2S state of Li. The large drawing is of the SOGI orbitals ($\Xi = 0.434°$); the core orbitals remain essentially unchanged when Ξ is within 10° of 0. The insert shows the valence orbital for various values of Ξ; a: $\Xi = 0$, b: $\Xi = 0.434°$, c: $\Xi = 1.0°$, d: $\Xi = 2.0°$, e: $\Xi = 4.0°$, f: $\Xi = 10°$. Distance is in atomic units.

the standard spin functions. The exact wavefunctions can again be written as

$$\Psi^{\text{exact}} = G_i{}^{\mu L} \Phi^{i,L,\text{exact}} \chi. \tag{4}$$

We now consider approximate wavefunctions of the form

$$\Psi_{\text{GIL}} = G_i{}^{\mu L} \Phi^{i,L,\text{product}} \chi \tag{5}$$

and select i, $\mathbf{L}$, and $\Phi^{i,L,\text{product}}$ such that the energy is the lowest possible, which leads to a new set of coupled integro-differential equations analogous to (3),

$$\hat{H}_k{}^{\mu i L} \phi_k = \epsilon_k \phi_k \qquad k = 1, \cdots N \tag{6}$$

for the best orbitals. Since this approach is a generalization of the GI method, which eliminates the arbitrariness in choice of spin function and yet retains the independent particle interpretation, we will refer to it as the spin-coupling optimized GI or SOGI method. We will show that the SOGI wavefunction, referred to in (5) as Ψ_{GIL}, is the best possible wavefunction which can be interpreted in terms of N spatial orbitals as if an electron were moving in each orbital in the self-consistent field due to the electrons in the $N-1$ other orbitals. In addition, we will show that the SOGI wavefunction has all the general properties of GI wavefunctions; e.g., the virial, Hellmann–Feynman, Brillouin, and Koopmans theorems still apply[5] (for a fixed spin function). We also show that the SOGI method can be considered as the synthesis of the valence bond and Hartree–Fock methods.

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[5] W. A. Goddard III, J. Chem. Phys. **48**, 5337 (1968).

In Sec. II we derive the general equations for determining the SOGI orbitals and consider some aspects of spatial symmetry restrictions. In order to demonstrate various aspects of the SOGI method we report in Sec. III the results of SOGI calculations on some three- and four-electron atoms and molecules.

II. THE SPIN-COUPLING OPTIMIZED GI METHOD

A. The SOGI Equations

The $G_i{}^\mu$ operators were defined in Paper I by the equation

$$G_i{}^\mu = \sum_r \zeta_{\lambda_{ri}} O_{ri}{}^\mu \omega_{\bar{r}\bar{i}}{}^{\bar{\mu}}, \tag{7}$$

where $O_{ri}{}^\mu$ and $\omega_{\bar{r}\bar{i}}{}^{\bar{\mu}}$ are orthogonal Wigner projection operators[3] based on Young's orthogonal representation of S_N, and $\zeta_{\lambda_{ri}}$ is the parity of the permutation λ_{ri} which changes the ith standard Young tableau $S_i{}^\mu$ into the rth standard Young tableau $S_r{}^\mu$. For a spin-independent Hamiltonian H the energy is given by Eq. (15) of Paper I

$$E = \langle G_i{}^\mu \Phi \chi \mid H \mid G_i{}^\mu \Phi \chi \rangle / \langle G_i{}^\mu \Phi \chi \mid G_i{}^\mu \Phi \chi \rangle$$
$$= \langle \Phi \mid H \mid O_{ii}{}^\mu \Phi \rangle / \langle \Phi \mid O_{ii}{}^\mu \Phi \rangle \tag{8}$$

which results from the fact that the orthogonal units obey the following equations[1,3,4]:

$$O_{ij}{}^\alpha O_{kl}{}^\beta = \delta_{\alpha\beta} \delta_{jk} O_{il}{}^\alpha, \tag{9a}$$

$$\omega_{\bar{i}\bar{j}}{}^{\bar{\alpha}} \omega_{\bar{m}\bar{n}}{}^{\bar{\mu}} = \delta_{\alpha\mu} \delta_{jm} \omega_{\bar{i}\bar{n}}{}^{\bar{\mu}} \tag{9b}$$

and

$$\langle O_{ij}{}^\mu \Phi_1 \mid \Phi_2 \rangle = \langle \Phi_1 \mid O_{ji}{}^\mu \Phi_2 \rangle, \tag{10a}$$

$$\langle \omega_{\bar{m}\bar{n}}{}^{\bar{\alpha}} \chi_1 \mid \chi_2 \rangle = \langle \chi_1 \mid \omega_{\bar{n}\bar{m}}{}^{\bar{\alpha}} \chi_2 \rangle. \tag{10b}$$

The orthogonal units are defined by[1,3,4]

$$O_{ri}{}^\mu = (f^\mu/N!) \sum_{\tau \in S_N} U_{ri(\tau)}{}^\mu \hat{\tau}, \tag{11a}$$

$$\omega_{\bar{r}\bar{i}}{}^{\bar{\mu}} = \zeta_{\lambda_{ri}} (f^\mu/N!) \sum_{\sigma \in S_N} \zeta_\sigma U_{ri(\sigma)}{}^\mu \hat{\sigma}, \tag{11b}$$

where the $\mathbf{U}^\mu(\tau)$ are orthogonal matrices which yield the μth irreducible representation of S_N. Picking a set of representative matrices is equivalent to picking a set of orthogonal (not necessarily normalized) basis vectors in the f^μ-dimensional space of spin functions. A convenient way of constructing the $\mathbf{U}^\mu$'s is described in Paper I and involves the use of Young tableaux. The arbitrariness in the GI method results from choosing our one spin function to be one of the arbitrarily chosen basis vectors in the f^μ-dimensional space of spin functions. This arbitrariness can be removed by allowing for a general rotation of the coordinate axes in our space of spin functions. We will require that this rotation give the best single spin function possible. We now derive the necessary equations for finding this optimum spin function.

The rotation is most easily obtained by applying an

orthogonal transformation to the representative matrices, $\mathbf{U}^\mu(\tau)$, to obtain

$$\mathbf{U}^{\mu L}(\tau) = \mathbf{L}\mathbf{U}^\mu(\tau)\mathbf{L}^{-1}, \qquad (12)$$

where $\mathbf{L}$ is a general orthogonal matrix. We can define new orthogonal units with these transformed matrices

$$O_{ri}{}^{\mu L} = (f^\mu/N!)\sum_{\tau\epsilon S_N} U_{ri(\tau)}{}^{\mu L}\hat\tau$$

$$= \sum_{kl} L_{rk}L_{il}O_{kl}{}^\mu, \qquad (13a)$$

$$\omega_{\bar\tau i}{}^{\bar\mu L} = \zeta_{\lambda ri}(f^\mu/N!)\sum_{\sigma\epsilon S_N}\zeta_\sigma U_{ri(\sigma)}{}^{\mu L}\hat\sigma$$

$$= \zeta_{\lambda ri}\sum_{kl}\zeta_{\lambda kl}L_{rk}L_{il}\omega_{\bar k \bar l}{}^{\bar\mu}. \qquad (13b)$$

Now we define a new $G_i{}^\mu$-like operator $G_i{}^{\mu L}$ as

$$G_i{}^{\mu L} \equiv \sum_r \zeta_{\lambda ri}O_{ri}{}^{\mu L}\omega_{\bar\tau i}{}^{\bar\mu L}. \qquad (14)$$

Since $\mathbf{L}$ is a completely general rotation, the initial orientation of our spin function (specified by i) is of no consequence, but for the sake of definiteness we will fix i to be 1. Since i is always 1, we will normally omit it and write $G_1{}^{\mu L}$ as $G^{\mu L}$. In discussing a particular system, we will fix μ and omit it thereafter writing G^L for $G^{\mu L}$.

Since the transformed orthogonal units satisfy Eqs. (9) and (10), the arguments of Sec. I of Paper I apply directly to show that $G^{\mu L}\Phi\chi$ is an eigenfunction of $\hat S^2$ and satisfies Pauli's principle. Similarly from the arguments of Sec. II of Paper I we have that

$$E = \langle G^{\mu L}\Phi\chi \mid H \mid G^{\mu L}\Phi\chi\rangle/\langle G^{\mu L}\Phi\chi \mid G^{\mu L}\Phi\chi\rangle$$

$$= \langle \Phi \mid H \mid O_{11}{}^{\mu L}\Phi\rangle\langle\chi\mid\omega_{ff}{}^{\bar\mu L}\chi\rangle/(\langle\Phi\mid O_{11}{}^{\mu L}\Phi\rangle\langle\chi\mid\omega_{ff}{}^{\bar\mu L}\chi\rangle)$$

$$= \langle\Phi\mid H\mid O_{11}{}^{\mu L}\Phi\rangle/\langle\Phi\mid O_{11}{}^{\mu L}\Phi\rangle. \qquad (15)$$

At this point we will restrict Φ to be a product of one-electron spatial orbitals and require that the energy be stationary not only against first-order variations in each orbital but also against first-order variations in $\mathbf{L}$. That is, we require that the spatial orbitals and the spin coupling scheme be optimal simultaneously.

The energy expression can be rewritten as

$$E = \sum_{ij} L_{1i}L_{1j}\langle\Phi\mid H\mid O_{ij}{}^\mu\Phi\rangle/\sum_{kl}L_{1k}L_{1l}\langle\Phi\mid O_{kl}{}^\mu\Phi\rangle. \qquad (16)$$

We must minimize the energy subject to the constraints that $\sum_k L_{1k}{}^2 = 1$ and that $\langle\phi_m\mid\phi_m\rangle = 1$ for all m. Therefore we introduce Lagrange multipliers and minimize the expression

$$I = (\sum_{ij} L_{1i}L_{1j}\langle\Phi\mid H\mid O_{ij}{}^\mu\Phi\rangle/\sum_{mn}L_{1m}L_{1n}\langle\Phi\mid O_{mn}{}^\mu\Phi\rangle) - \sum_k \epsilon_k\langle\phi_k\mid\phi_k\rangle - \lambda\sum_n L_{1n}{}^2. \qquad (17a)$$

This leads to a set of $N + f^\mu$ coupled equations for the best Φ and L. The N equations for the best Φ are integro-differential equations and we will call them the spatial SOGI equations. They can be written so that the only permutational operator which appears is the transformed orthogonal unit $O_{11}{}^{\mu L}$. The f^μ equations for the best $\mathbf{L}$ are nonlinear algebraic equations which involve Φ only in the integrals $\langle\Phi\mid H\mid O_{ij}{}^\mu\Phi\rangle$ and $\langle\Phi\mid O_{ij}{}^\mu\Phi\rangle$ and these occur as coefficients; we will refer to these equations as the spin SOGI equations, since $\mathbf{L}$ determines the spin coupling scheme.

When making variations in Φ, we can take the sums over i and j of Eq. (17a) back into the integral to give

$$I = (\langle\Phi\mid H\mid O_{11}{}^{\mu L}\Phi\rangle/\langle\Phi\mid O_{11}{}^{\mu L}\Phi\rangle) + \sum_k \epsilon_k\langle\phi_k\mid\phi_k\rangle + \lambda\sum_n L_{1n}{}^2. \qquad (17b)$$

From this expression we obtain the following set of equations, using exactly the arguments of Sec. I of Paper II:

$$H^L(k)\phi_k = \epsilon_{kk}\phi_k \qquad k = 1, 2, \cdots, N, \qquad (18)$$

where

$$H^L(k)\phi_k = \Bigg\{ D_k{}^k\hat h\phi_k + \sum_{j,v\neq k}\langle v\mid k\rangle D_{jk}{}^{kv}\hat h\phi_j + \sum_{s,u\neq k}\langle s\mid\hat h\mid k\rangle D_{uk}{}^{ks}\phi_u + \sum_{uvst\neq k}\langle s\mid\hat h\mid t\rangle\langle v\mid k\rangle D_{tku}{}^{svk}\phi_u$$

$$+ \sum_{j,t\neq k}\Bigg[\Big(\int\phi_j\hat g\phi_t\Big)D_{kt}{}^{kj}\phi_k + \Big(\int\phi_j\hat g\phi_k\Big)D_{tk}{}^{kj}\phi_t\Bigg] + \sum_{jst v\neq k}\Big(\int\phi_j\hat g\phi_t\Big)\langle v\mid k\rangle D_{tsk}{}^{jkv}\phi_s$$

$$+ \sum_{jst u\neq k}\langle st\mid\hat g\mid kj\rangle D_{kju}{}^{stk}\phi_u + \frac12\sum_{ijst uv\neq k}{}'\langle st\mid\hat g\mid ij\rangle\langle v\mid k\rangle D_{ijku}{}^{stvk}\phi_u - E\sum_{u,v\neq k}\langle v\mid k\rangle D_{ku}{}^{vk}\phi_u\Bigg\}. \qquad (19)$$

Here we have redefined $D_j{}^i$ to be the coefficient of $\phi_i^*(i)\phi_j(i)$ in $\int\Phi^*O_{11}{}^{\mu L}\Phi(dx_i{}')$, $D_{ji}{}^{ik}$ to be the coefficient of $\phi_i^*(i)\phi_k^*(k)\phi_j(i)\phi_l(k)$ in $\int\Phi^*O_{11}{}^{\mu L}\Phi(dx_{ik}{}'')$, etc. This redefinition of the D matrices is the only difference between the spatial SOGI equations and the GI equations.

If we define $\mathfrak{K}_{ij}\equiv\langle\Phi\mid H\mid O_{ij}{}^\mu\Phi\rangle$ and $\mathfrak{N}_{ij}\equiv\langle\Phi\mid O_{ij}{}^\mu\Phi\rangle$, the spin SOGI equations are

$$\Big[\sum_i L_{1i}(\mathfrak{K}_{ip}+\mathfrak{K}_{pi})\Big]\Big(\sum_{kl}L_{1k}L_{1l}\mathfrak{N}_{kl}\Big) - \Big(\sum_{ij}L_{1i}L_{1j}\mathfrak{K}_{ij}\Big)\Big[\sum_k L_{1k}(\mathfrak{N}_{pk}+\mathfrak{N}_{kp})\Big] - 2\lambda L_p\Big(\sum_{ij}L_{1i}L_{1j}\mathfrak{N}_{ij}\Big)^2 = 0 \qquad p = 1, \cdots f^\mu.$$
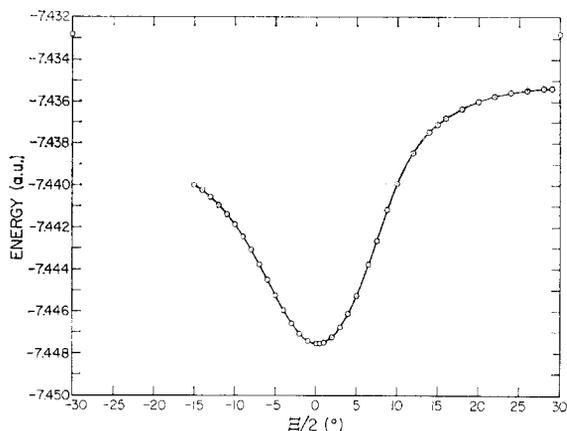
$$(20)$$

FIG. 2. Energy as a function on representation parameter, Ξ, for the 2^2S state of Li.

These equations are simple nonlinear algebraic equations. Since they involve $\mathcal{H}_{ij}$ and $\mathcal{R}_{ij}$ for all i and j, and since the evaluation of all of these quantities frequently requires a great deal of effort, it will often be expedient to find the optimum **L** by actually calculating the energy for various values of the parameters of **L** until a minimum is found.

B. The Independent Particle Interpretation and Other Properties of SOGI Wavefunctions

Each $H^L(k)$ operator in (18) is equivalent to the Hamiltonian of an electron moving in the (nonlocal) field due to electrons in the $N-1$ other orbitals. Since ϕ_k is an eigenfunction of this operator, we can interpret each ϕ_k as the eigenstate of an electron moving in the field due to $N-1$ other electrons. That is, the SOGI orbitals can be given an independent particle interpretation (IPI) just as the GI orbitals were.[2]

In the independent particle interpretation we interpret each spatial orbital of the N-electron wavefunction as the eigenstate of an electron moving in the average (self-consistent) potential due to electrons in the other $N-1$ orbitals. The criteria we use for such an independent particle interpretation are the following: (i) There must be no more than N different spatial orbitals since there are only N electrons. (ii) Each spatial orbital must be an eigenfunction of an operator equivalent to the Hamiltonian for an electron moving in the field due to the nuclei and in some average field due to electrons in the other $N-1$ orbitals. (iii) This average field in (ii) can be nonlocal but it must be obtained directly from applying the variational principle to the energy. As discussed elsewhere[2] the Hartree–Fock, UHF, and GI wavefunctions satisfy these criteria and can be given an independent particle interpretation (IPI). However configuration-interaction (CI) and

multiconfiguration SCF[6] (MC–SCF) wavefunctions do not satisfy (ii) and usually not (i) and cannot be given the IPI. In addition extended Hartree–Fock methods which use spatial projection operators[7] do not necessarily satisfy (i) [e.g., for H_2 such a wavefunction[7] might involve two σ orbitals, four π orbitals (two π_x and two π_y), four δ orbitals, etc.] and thus cannot be given the above IPI. In the valence bond (VB) wavefunction,[8] (i) is satisfied but the orbitals are not functionally optimized so that (ii) and (iii) are not satisfied and the VB wavefunction cannot be given the IPI. However we have shown[9] that the G1 wavefunction corresponds to a generalization of the VB wavefunction in which all orthogonality and double occupation constraints are removed and the orbitals are functionally optimized, and thus the G1 method is the direct generalization of the VB method which does lead to the IPI.

The criteria in (i)–(iii) are sufficient to require that the many-electron wavefunction be expressible as a product of N spatial orbitals and a suitable spin function with this perhaps operated on with an operator which does not change the form of the orbitals (if they were changed the space spanned by the orbitals would in general enlarge to dimensions larger than N). Thus the operator may involve permutations but not spatial projection operators. If all the orbitals in Φ are allowed to be different the operator must take care of both the spin symmetry and Pauli principle. The most general operator which does this and nothing more is
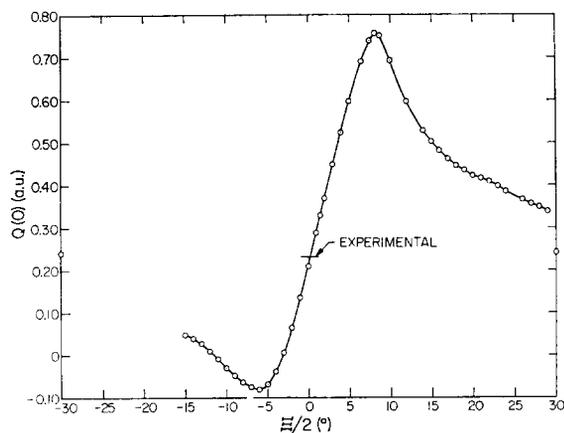
$$\sum_i c_i G_i^\mu,$$

FIG. 3. Spin density at the nucleus, $Q(0)$, as a function of representation parameter Ξ for the 2^2S state of Li.

[6] G. Das and A. C. Wahl, J. Chem. Phys. **44**, 87 (1966); A. C. Wahl, P. J. Bertoncini, G. Das, and T. L. Gilbert, Intern. J. Quant. Chem. IS, 123 (1967).
[7] E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962); C. F. Bunge, Phys. Rev. **154**, 70 (1967).
[8] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 218.
[9] W. A. Goddard III, Phys. Rev. **169**, 120 (1968).

where the c_i are arbitrary. But from Appendix C of Paper I we have[10]

$$G_i{}^\mu \Phi \chi = f^\mu \mathcal{Q} [\Phi (\omega_{\bar{i}\bar{i}}{}^{\bar{\mu}} \chi)], \tag{21a}$$

and thus we have

$$\sum_i G_i{}^\mu \Phi \chi = f^\mu \mathcal{Q} [\Phi (\sum_i c_i \omega_{\bar{i}\bar{i}}{}^{\bar{\mu}} \chi)]. \tag{21b}$$

But $\sum_i c_i \omega_{\bar{i}\bar{i}}{}^{\bar{\mu}} \chi$ is just some arbitrary vector in the f^μ-dimensional spin space and hence can be written as

$$\sum_i c_i \omega_{\bar{i}\bar{i}}{}^{\bar{\mu}} \chi = \omega_{11}{}^{L\bar{\mu}} \chi$$

in terms of the L-transformed representation. Thus

$$\sum_i c_i G_i{}^\mu \Phi \chi = f^\mu \mathcal{Q} [\Phi (\sum_i c_i \omega_{\bar{i}\bar{i}}{}^{\bar{\mu}} \chi)]$$

$$= G^{\mu L} \Phi \chi, \tag{21c}$$

and the SOGI wavefunction is the optimum wavefunction yielding the above described independent particle interpretation.

In the early years of the application of quantum mechanics, two popular types of wavefunctions were the MO and valence-bond (VB) or Heitler–London wavefunctions where the MO wavefunction was just a special case of HF using a minimum set of basis functions. Since these methods led to somewhat different wavefunctions, questions concerning which was best arose. This was partly settled by Van Vleck and Sherman[11] who showed that starting with either function inclusion of sufficient other configurations would eventually lead to the same final wavefunction. For example, for H_2 with a minimum basis set, the VB and HF wavefunctions are both special cases of the Weinbaum[12]
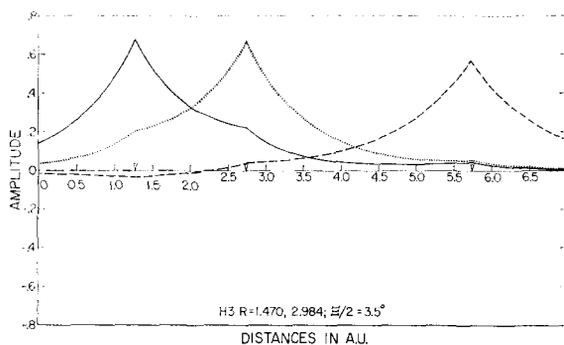

Fig. 4. SOGI orbitals for H_3: $R_{AB} = 1.470$, $R_{BC} = 2.984$; $\Xi/2 = 3.5°$. —— orbital 1, $\cdots$ orbital 2, $---$ orbital 3.

[10] $\mathcal{Q}$ is the antisymmetrizer,

$$\mathcal{Q} = (1/N!) \sum_\tau \zeta_\tau \tau,$$

where τ operates on both spatial and spin coordinates and ζ_τ is the parity of τ.
[11] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935).
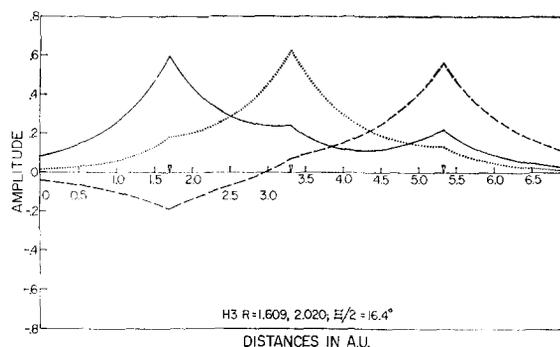[12] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933); C. A. Coulson and I. Fischer, Phil. Mag. **40**, 386 (1949).

Fig. 5. SOGI orbitals for H_3: $R_{AB} = 1.609$, $R_{BC} = 2.020$; $\Xi/2 = 16.4°$. —— orbital 1, $\cdots$ orbital 2, $---$ orbital 3.

wavefunction. However the Weinbaum wavefunction for H_2 is equivalent to the SOGI wavefunction for a minimum basis set (also equivalent to G1 and GF).[2] In fact for any number of electrons the VB (or Heitler–London) and HF methods and their natural generalizations the G1 and GF methods are special cases of the SOGI method. Hence we can consider the SOGI wavefunction as the generalization and synthesis of the HF and VB or Heitler–London methods which in addition still yields an interpretation in terms of independent particle states.

In addition to the IPI all other general properties of GI wavefunctions (e.g., the Hellmann–Feynman, Brillouin, virial, and Koopmans theorems[5]) hold also for the SOGI wavefunction (for fixed **L**) as can be seen in Ref. 5.

Wavefunctions of the form

$$\mathcal{Q} [\Phi (\sum_i c_i \Theta_i)], \tag{21d}$$

where Θ_i are the orthogonal spin coupling functions and Φ is a product of orbitals that have been dealt with by several other workers. Lunell[13] has solved for the wavefunction of the ground state Li using a form like (21d) where he optimized both the C_i and one of the orbitals of Φ and Kaldor[14] has solved for both the $2\,^2S$ and $2\,^2P$ states of Li using a wavefunction of the form (21d) with optimized orbitals. By (21b) and (21c) Kaldor's wavefunction can be considered as a SOGI wavefunction and Lunell's is a special case in which the orbitals were not all solved for self-consistency. In addition Musher[15a] has taken published G1 and GF calculations for Li and calculated the coefficients C_i in (21d) without reoptimizing the orbitals, and Taylor and Harris[15b] have optimized the coefficients C_i in (21d) for several systems without functionally optimizing the orbitals.

[13] S. Lunell, Phys. Rev. **173**, 85 (1968).
[14] U. Kaldor (private communication).
[15] (a) J. Musher (to be published); (b) H. S. Taylor, J. Chem. Phys. **39**, 3382 (1963); H. S. Taylor and F. Harris, *ibid*. 1012 (1963).
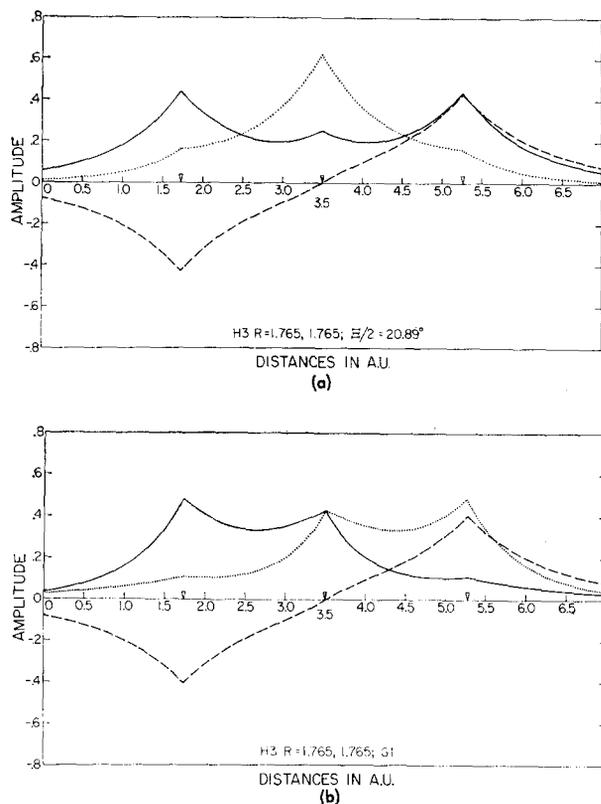
FIG. 6. (a) SOGI orbitals for the saddle point of H_3: $R_{AB} = R_{BC} = 1.765$, $\Xi/2 = 20.89°$. —— orbital 1, $\cdots$ orbital 2, --- orbital 3. (b) Optimum left–right correlated (G1) orbitals for the saddle point of H_3: $R_{AB} = R_{BC} = 1.765$, —— orbital 1, $\cdots$ orbital 2, --- orbital 3.

C. Spatial Symmetry

Although the SOGI wavefunction has the correct spin and permutational symmetry, we must also ensure that our SOGI many-electron wavefunction transforms as a basis function for some irreducible representation of the group $\mathcal{G}$ of spatial transformations which leave the nuclei unchanged. Just as for GI,[2,5] in some cases the SOGI orbitals are symmetry functions[16] for $\mathcal{G}$ and in some cases they have lower symmetry. In addition, if the SOGI orbitals are *not* symmetry functions for $\mathcal{G}$, there may be some constraints on $\mathbf{L}$ in order that the many-electron wavefunctions have the correct symmetry.

We will consider only spatially nondegenerate states for which $\hat{R}\Psi_{SOGI} = \pm\Psi_{SOGI}$ where $\hat{R}$ is some symmetry operation. Since $\hat{R}$ is symmetric in the electron coordinates, it commutes with α and $O_{11}{}^{\mu L}$ and we have that

$$\hat{R}\Psi_{SOGI} = \alpha[(O_{11}{}^{\mu L}(\hat{R}\Phi))\chi]. \qquad (22)$$

Let $\hat{R}$ be a generator of $\mathcal{G}$ for which $\hat{R}\Psi_{SOGI} = +\Psi_{SOGI}$, then

$$\alpha[(O_{11}{}^{\mu L}(\hat{R}\Phi))\chi] = \alpha[(O_{11}{}^{\mu L}\Phi)\chi]. \qquad (23)$$

[16] By a symmetry function for $\mathcal{G}$ we mean a basis function for an irreducible representation of $\mathcal{G}$.

This equation can usually be satisfied if Φ is composed of symmetry functions, but this is not a necessary condition. Suppose that Φ is constructed from orbitals which are symmetry functions of the subgroup $\mathcal{G}'$ which is obtained by deleting the generator $\hat{R}$ from $\mathcal{G}$. Further suppose that Φ is such that the effect of $\hat{R}$ is merely to interchange the orbitals among themselves; that is, $\hat{R}\Phi = \pm\hat{\tau}_R\Phi$ where τ_R is some permutation. Now if $O_{11}{}^{\mu L}\tau_R = \pm O_{11}{}^{\mu L}$, Eq. (23) is satisfied despite the fact that the orbitals of Φ are symmetry functions only of the subgroup $\mathcal{G}'$. If $\hat{R}$ is such that $\hat{R}\Psi = -\Psi$, we have the same results if $\hat{R}\Phi = \pm\tau_R\Phi$ and $O_{11}{}^{\mu L}\tau_R = \mp O_{11}{}^{\mu L}$.

To see what condition this imposes on $\mathbf{L}$, we expand τ_R in terms of the transformed orthogonal units (letting $\mathbf{L}^\alpha$ be the f^α-dimensional unit matrix if $\alpha \neq \gamma$, and $\mathbf{L}^\mu = \mathbf{L}$)

$$\tau_R = \sum_{ij\alpha} O_{ij}{}^{\alpha L^\alpha} U_{ij}{}^{\alpha L^\alpha}(\tau_R), \qquad (24)$$

then

$$O_{11}{}^{\mu L}\tau_R = O_{11}{}^{\mu L} \sum_{ij\alpha} U_{ij}{}^{\alpha L^\alpha}(\tau_R) O_{ij}{}^{\alpha L^\alpha}$$

$$= \sum_j O_{1j}{}^{\mu L} U_{1j}{}^{\mu L}(\tau_R). \qquad (25)$$

Since the $O_{ij}{}^{\mu L}$ are linearly independent, we have that $O_{ii}{}^{\mu L}\hat{\tau}_R = \pm O_{11}{}^{\mu L}$ only if $U_{1j}{}^{\mu L}(\tau_R) = \delta_{ij}$, which imposes one constraint on $\mathbf{L}$. Under some circumstances this condition cannot be satisfied, in which case the SOGI orbitals must be symmetry functions. In many cases, however, the condition on $\mathbf{L}$ can be satisfied and the use of nonsymmetry orbitals is possible. Some examples will be considered in the discussion of the H_3 and H_4 calculations below.

Consider a molecular system such as linear, equidistant H_3 which is stretched or compressed symmetrically. For large spacing, it is energetically favorable for orbitals to localize about the various nuclei, and we expect the SOGI wavefunction to have a spin part ($\mathbf{L}$) which allows this localization and a spatial part composed of permutationally related nonsymmetry functions (an orbital on each H). For small internuclear distances, delocalization of the orbitals is energetically favorable, and we expect the SOGI wavefunction to have a spatial part composed of symmetry functions and a completely general spin part. This means that, for systems which are pulled apart symmetrically, there will be a discontinuity in the slope of the energy vs distances curve where we switch from localized to delocalized bonding. Although this discontinuity of slope is not a real effect, it is interesting to see how the ideas of localized and delocalized independent particle states arise naturally and how a choice can be made for each system on purely energetic grounds. In polyatomic systems, the physically interesting processes usually do not involve symmetrical dissociations so that the discontinuity of slope is of little physical or chemical consequence. However, such
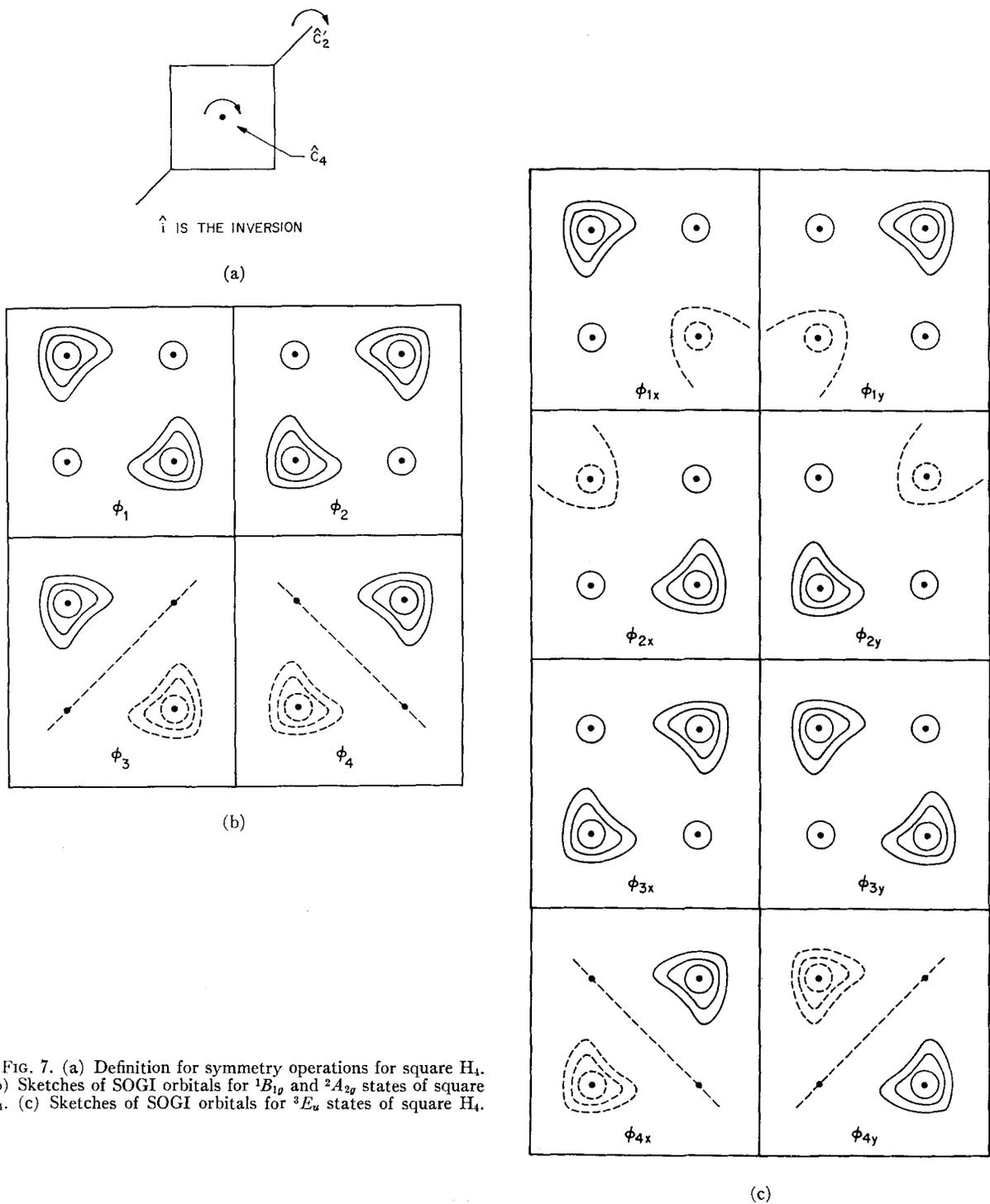
FIG. 7. (a) Definition for symmetry operations for square H_4. (b) Sketches of SOGI orbitals for $^1B_{1g}$ and $^2A_{2g}$ states of square H_4. (c) Sketches of SOGI orbitals for ^3E_u states of square H_4.

TABLE I. SOGI and G1 wavefunctions for the ground state of Li ($\Xi/2 = 0.217° \pm 0.001°$).

Function	ζ	ϕ_1SOGI	ϕ_1G1	ϕ_2SOGI	ϕ_2G1	ϕ_3SOGI	ϕ_3G1
1s	3.0	1.14368	1.14370	0.60987	0.60984	0.02804	0.03189
4s	5.33	−0.10348	−0.10348	0.12715	0.12709	−0.00228	−0.00208
3s	5.40	−0.07808	−0.07810	0.07854	0.07853	0.00060	0.00069
3s	3.00	0.00542	0.00550	0.27260	0.27246	0.02045	0.02124
3s	1.347	0.01569	0.01549	−0.00398	−0.00362	0.28602	0.28571
3s	0.841	−0.00255	−0.00292	−0.00004	0.00063	0.63560	0.63501
4s	0.732	0.03458	0.03446	−0.01551	−0.01531	0.06863	0.06854
3s	0.62	−0.03799	−0.03793	0.01738	0.01731	0.05573	0.05576
ϵ (orbital energy)		−2.84409	−2.8427	−2.46128	−2.4588	−0.19616	−0.19615

transitions are of theoretical interest and have been suggested by Mott[17] to be relevant in the discussion of conduction and other properties of such solids as NiO. Since the SOGI wavefunctions dissociate correctly and can naturally lead directly to either localized or delocalized orbitals without requiring additional Wannier-like localizations as in the HF method, it would seem that the SOGI wavefunctions would form a suitable foundation on which to discuss ideas such as the Mott transition.

III. RESULTS AND DISCUSSIONS

Since the spatial SOGI equations are of exactly the same form as the G1 equations, we solve them in the same way. We expand the unknown orbitals in terms of a finite basis set

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i} \tag{26}$$

and solve for the coefficients iteratively. (The equations could also be solved numerically.) Existing three- and four-electron G1 programs were adapted to do SOGI calculations by changing only the sections which calculate the D matrices.

A. Three-Electron Doublet States

First we will consider some three-electron doublet states. In this case there are two linearly independent spin states, $f^\mu = 2$. The standard representation is given in Paper I (Appendix A) and the general transformations $\mathbf{L}$ to new spin functions is given by

$$\mathbf{L}(\Xi) = \begin{pmatrix} \cos(\Xi/2) & \sin(\Xi/2) \\ -\sin(\Xi/2) & \cos(\Xi/2) \end{pmatrix}. \tag{27}$$

Thus in addition to optimizing the three orbitals ϕ_a, ϕ_b, and ϕ_c, we must optimize the single parameter Ξ, which

just corresponds to a rotation angle in the two-dimensional space of spin functions. From (21) we have that

$$G^{\mu L}\Phi\chi = f^\mu \mathcal{Q}(\Phi\omega_{ff}{}^{\mu L}\chi) \tag{28}$$

or expanding ω

$$G^{\mu L}\phi_a\phi_b\phi_c\alpha\beta\alpha = \tfrac{2}{3}\mathcal{Q}\{\phi_a\phi_b\phi_c[\alpha\beta\alpha(1+\tfrac{1}{2}\cos\Xi+\tfrac{1}{2}\sqrt{3}\sin\Xi)$$

$$+\alpha\alpha\beta(-\tfrac{1}{2}+\tfrac{1}{2}\cos\Xi-\tfrac{1}{2}\sqrt{3}\sin\Xi)+\beta\alpha\alpha(-\tfrac{1}{2}-\cos\Xi)]\}. \tag{29}$$

In (27) we have that $\mathbf{L}(\Xi+360°) = -\mathbf{L}(\Xi)$; however in (29) we see that Ξ, $\Xi+120°$, and $\Xi+240°$ lead to equivalent wavefunctions if we interchange the orbitals appropriately. Thus we need consider only a 120° range of Ξ, which we will usually take as −60° to +60°. If $\Xi=0$ we have

$$G^{\mu L}\phi_a\phi_b\phi_c\alpha\beta\alpha = G_1{}^\mu\phi_a\phi_b\phi_c\alpha\beta\alpha \tag{30a}$$

and by optimizing the orbitals we get the G1 wavefunction. If $\Xi=60°$,

$$G^{\mu L}\phi_a\phi_b\phi_c\alpha\beta\alpha = -G_f{}^\mu\phi_a\phi_c\phi_b\alpha\alpha\beta, \tag{30b}$$

and by optimizing the orbitals we get the GF wavefunction [note that in (30b) the roles of the second and third orbitals are interchanged]. If $\Xi = -60°$ we obtain

$$G^{\mu L}\phi_a\phi_b\phi_c\alpha\beta\alpha = \tfrac{1}{2}G_f{}^\mu\phi_c\phi_b\phi_a\alpha\alpha\beta \tag{30c}$$

and by optimizing the orbitals we again get the GF wavefunction (here the roles of the first and third orbitals have been interchanged). Thus by varying Ξ we can go continuously from G1 to GF. We will find below that in most cases the optimum angle Ξ is near zero and the G1 wavefunction is nearly as good as the SOGI wavefunction. However, for H_3 near the transition states the optimum angle Ξ is significantly different from zero.

[17] N. F. Mott, Proc. Phys. Soc. (London) A62, 416 (1949).

TABLE II. Properties for three-electron atoms (entries for GF, HF, UHF, CI, and experimental are taken directly from Ref. 19).

	G1	SOGI	GF	HF	CI	Exptl
			A. Energies			
2^2S Li	−7.44756038	−7.44756516	−7.432813	−7.432725	−7.4779	−7.47807
3^2S Li	−7.32517867	−7.32517894	−7.310216	−7.310210	⋯	−7.35410
2^2P Li	−7.38011191	−7.38011631	−7.365091	−7.365069	−7.40838	−7.41016
3^2P Li	−7.30819798	−7.30819844	−7.293189	−7.293186	⋯	−7.33715
2^2S Be$^+$	−14.29162398	−14.29163664	−14.27762	⋯	⋯	⋯
2^2S B^{++}	−23.38990151	−23.38991969	−23.37632	⋯	⋯	⋯

	G1	SOGI	GF	HF	UHF	
			B. Density at the nucleus, $\langle \sum_i \delta(r_i) \rangle$			
2^2S Li	13.8646	13.8646	13.8159	13.8160	13.8159	
3^2S Li	13.7594	13.7594	13.7067	13.7080	13.7067	
2^2P Li	13.7052	13.7052	13.6534	13.6534	13.6535	
3^2P Li	13.7179	13.7180	13.6661	13.6660	13.6661	
2^2S Be$^+$	35.1392	35.1392	35.111	⋯	⋯	
2^2S B^{++}	71.4976	71.4975	71.493	⋯	⋯	

	G1	SOGI	GF	HF	UHF	CI	Exptl
			C. Spin density at the nucleus, $Q(0) = 2\langle \sum_i \delta(r_i)\hat{s}_z(\sigma_i) \rangle$				
2^2S Li	0.20957	0.22654±0.0001	0.2406	0.1667	0.2248	0.2249	0.2313
3^2S Li	0.04873	0.0529	0.05622	0.03864	0.05253	⋯	⋯
2^2P Li	0.0	−0.0172	−0.02304	0.0	−0.01747	−0.02222	
3^2P Li	0.0	−0.00547±0.0001	−0.007318	0.0	−0.005531	⋯	⋯
2^2S Be$^+$	0.94671	0.9938±0.0015	1.008	⋯	⋯	⋯	⋯
2^2S B^{++}	2.4303	2.516±0.001	2.521	⋯	⋯	⋯	⋯

	G1	SOGI	GF	HF	UHF	CI
			D. Orbital dipole constant, $\langle \sum_i [l_z(r_i)/r_i^3] \rangle$			
2^2P Li	0.058693	0.058725	0.05861	0.05848	0.05852	a
3^2P Li	0.0176467	0.017649	0.01760	0.01759	0.01760	⋯

	G1	SOGI	GF	HF	
			E. Second moment of r, $\langle \sum_i r_i^2 \rangle$		
2^2S Li	18.6642	18.6626	18.6090	18.6376	
3^2S Li	119.571	119.569	119.447	119.480	
2^2P Li	28.690	28.685	28.692	28.716	
3^2P Li	172.203	172.198	172.511	172.536	
2^2S Be$^+$	6.559	6.559	6.545	⋯	
2^2S B^{++}	3.4136	3.4135	3.4094	⋯	

a $\langle 1/r^3 \rangle_{orb} = 0.05974$, $\langle 1/r^3 \rangle_{dip} = 0.05923$.

TABLE III. Optimum values of Ξ for three-electron atoms.

		Optimum Ξ (deg)
Li	2^2S	0.434 ± 0.002
Li	3^2S	0.098 ± 0.001
Li	2^2P	-0.396 ± 0.001
Li	3^2P	-0.118 ± 0.002
Be$^+$	2^2S	0.626 ± 0.004
B^{++}	2^2S	0.680 ± 0.008

1. Three-Electron Atoms and Ions

Calculations were carried out on the ground states (2^2S) of Li, Be$^+$, and B^{++} and on the 3^2S, 2^2P, and 3^2P excited states of Li.

Both G1[9] and GF[18] calculations for the ground states (2^2S) of Li, Be$^+$, and B^{++} have been reported elsewhere. GF calculations for the excited states of Li[19] have also been reported. Here we use similar but slightly larger basis sets of 7 to 9 Slater orbitals, chosen so that the cusp condition is satisfied exactly.[20] For a given nuclear charge, the core orbitals of all states can be described well by four or five functions. Once the orbital exponents of these functions have been optimized for one state, they can be transferred to other states and only the exponents of functions used in describing the valence orbital need to be reoptimized. The orbital exponents of the s functions were optimized for G1, and, since the G1 and SOGI orbitals were very similar, the exponents were not reoptimized for the optimum value of L. We found that the p functions used in GF calculations were also appropriate for SOGI calculations.

Calculations and Discussion: The most prominent result of these calculations is that the spatial properties of these systems are described in essentially the same way by both the G1 and SOGI wavefunctions. In Table I and Fig. 1[21] we compare the G1 and SOGI orbitals for the 2^2S state of Li. For all states considered the optimum Ξ was within 1° of zero (which corresponds to G1) as shown in Table II. As shown in Table III this led to similar values of energy, density at the nucleus, and other measures of the spatial charge distribution, but for the spin density at the nucleus, $Q(0)$, this small difference in spin coupling led to significant changes. The G1 wavefunction led to good values for all these properties except $Q(0)$,[5] and we

see in Table III that the SOGI value of $Q(0)$ is much improved over the G1 value. For the Li 2^2S state we obtain 0.2265 for SOGI which is 2.1% smaller than the experimental value of 0.2313; for this state the G1 value is 0.2096, the GF value is 0.2406, and the HF value is 0.1667. For the Li 2^2P state we obtain a $Q(0)$ of -0.0172 as compared to a G1 and HF value of zero, a GF value of -0.0230, and a CI value of -0.0222. In this case the experimental value of -0.0182 is obtained indirectly and may not be reliable.[19,22] Lunell[13] has carried out a calculation on the 2^2S state Li which is nearly equivalent[23] to SOGI and which yields $Q(0) = 0.2264$ and $E = -7.447536$ as compared to the SOGI results of $Q(0) = 0.2265$ and $E = -7.447565$.

We see from Table II that the optimum angles Ξ in the 2^2S and 2^2P states have nearly the same magnitude but opposite sign and similarly for the 3^2S and 3^2P states. In the case of positive Ξ the spin polarization (or core polarization) induced in the core is positive (2^2S and 3^2S) and for negative Ξ it is negative (2^2P and 3^2P). As we go from the $n=2$ to the $n=3$ states the magnitude of Ξ gets smaller which means that core is more nearly correctly described as a singlet pair. This is reasonable since in the limit of $n=\infty$ we have Li$^+$ and the core is exactly singlet coupled as in G1.

Although only the case of the optimum Ξ is of physical importance, it is of some interest to compare the properties and optimum orbitals for various Ξ and examine how the wavefunctions change as we go from G1 through SOGI to GF. In Fig. 2 we show $Q(0)$ as a function of Ξ. We see that near $\Xi = 0$ (i.e., G1), $Q(0)$ varies linearly but rapidly with Ξ. From Fig. 2 we see that except near G1 and GF most wavefunctions lead to quite poor values of $Q(0)$ [e.g., $Q(0) = 0.76$ at $\Xi = 16°$] even though they have the correct spin and interchange symmetry and satisfy a variational principle on the orbitals. In Fig. 3 we show the variation of energy with Ξ. The minimum is at $\Xi = 0.434 \pm 0.004°$ and was unchanged by an increase in the size of the basis set. The difference in $Q(0)$ for $\Xi = 0$ and the optimum Ξ is due primarily to differences in the spin part of the wavefunction. In fact, if we calculate $Q(0)$ with $\Xi = 0.434$ but use the G1 orbitals, we obtain $Q(0) = 0.2296$ as compared to 0.2265 for the SOGI orbitals. For Ξ in the region 50° to 60° we experienced some difficulty in convergence because of near linear

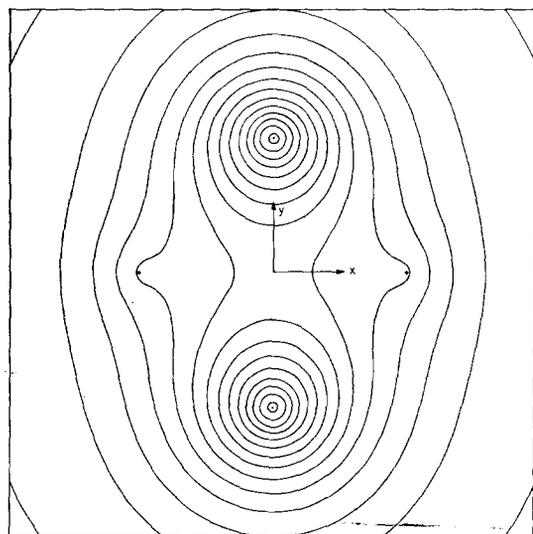[18] W. A. Goddard III, J. Chem. Phys. **48**, 1008 (1968).
[19] W. A. Goddard III, Phys. Rev. **176**, 106 (1968).
[20] That is we use one 1s Slater orbital with $\zeta = Z$ and all other s orbitals with $n \geq 3$, one 2p Slater orbital with $\zeta = Z/2$ and all other p orbitals with $n \geq 4$. See C. C. J. Roothaan and P. S. Kelly, Phys. Rev. **131**, 1177 (1963).
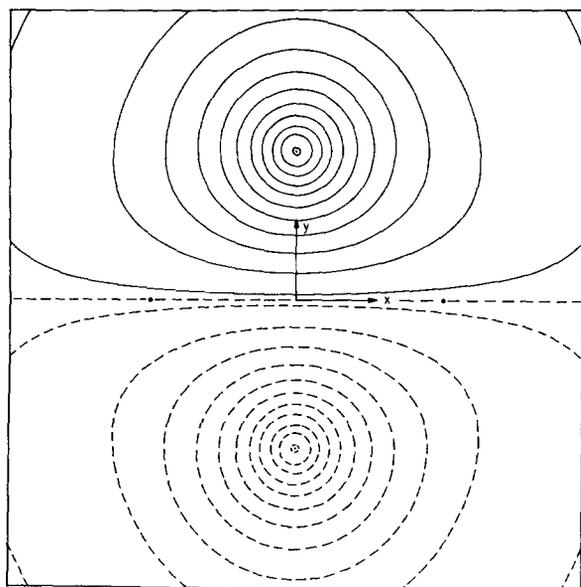[21] The expansion coefficients for the orbitals of this and all other systems discussed in the paper are available upon request.

[22] K. C. Brog, T. G. Eck, and H. Wieder, Phys. Rev. **153**, 91 (1967); see also Ref. 19.
[23] Lunell[13] states that he has used a general form of spin orbital. His use of only one spatial function for each spin orbital, however, allows his wavefunction to be reduced to the form

$$\mathcal{C}[\phi_a(1)\phi_b(2)\phi_c(3)\omega_{1f}{}^{\mu L}\alpha\beta\alpha], \qquad (31)$$

which is equivalent to the SOGI wavefunction (see Sec. II). Furthermore, Lunell has chosen his core orbitals to be those appropriate for Li$^+$ rather than solving for them self-consistently for Li.

dependence of the orbitals. The point at 60° agrees with independent GF calculations. However, the wavefunctions near $\Xi = 60°$ do not connect smoothly with the GF function indicating an instability in the GF function. It is interesting to note that for all four states of Li the UHF value of $Q(0)$ is quite close to the SOGI value (see Table IIc).

In summary, these calculations indicate that the G1 description of the spatial properties of three-electron atoms is quite good. That is, to a very good approxi-
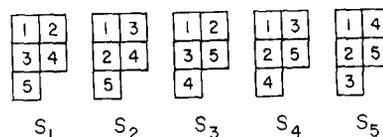

FIG. 9. The standard Young tableaux for the shape [3, 2].

mation, the two core electrons are singlet paired (as in G1); only for spin-dependent properties is it important to allow for a more general coupling of the electron spins. When this more general coupling is introduced, we obtain a very good value for $Q(0)$ for the $2\,^2S$ state and perhaps the $2\,^2P$ state of Li.

2. The H_3 System

Physically it is clear that, for three-electron atoms, Ξ should be near zero since Ξ should be determined primarily by the core electrons (for a two-electron ion the ground state is a singlet which corresponds to $\Xi = 0$, the addition of valence electrons should not change this appreciably since they are much further from the nucleus). In addition, for a system such as HeH at typical molecular distances, we expect Ξ to be primarily determined by the pair of orbitals on the He and hence to be near zero. However, for a system of three hydrogen atoms the optimum pairing should be a function of nuclear configuration and should be significantly different from zero for some configurations. We have carried out SOGI calculations for several points on the reaction path of $H_2 + D \rightarrow H + HD$ with the primary objectives being to determine (1) how well the SOGI method will predict potential energy surfaces for chemical reactions, (2) how the SOGI orbitals change as the system moves along the minimum energy reaction path, and (3) how spatial symmetry restrictions enter into our descriptions of a chemical reaction.

Basis Sets and Configurations: We used the following linear nuclear configurations which were on the minimum-energy path reported by Shavitt et al.[24]: point 1, $R_{AB} = 1.40$, $R_{BC} = \infty$; point 2, $R_{AB} = 1.470$, $R_{BC} = 2.984$; point 3, $R_{AB} = 1.609$, $R_{BC} = 2.020$; point 4, $R_{AB} = R_{BC} = 1.765$. For points 2–4 we used a basis set of nine Slater orbitals composed of two $1s$ functions and a $2p\sigma$ on each center. The orbital exponents for points 2[25] and 3[25] were estimated from data given in the paper by Shavitt et al.[24] The orbital exponents for point 4[26] are the same as those used by Shavitt et al.[24] For point 1, we used seven Slater orbitals, three on each of the protons in H_2 $(1s, 2s, 2p\sigma)^2$ and a $1s$ on the lone proton.

FIG. 8. (a) Orbital 1 of the $^3A_{2g}$ state of square H_4. The edge of the figure is 7.0 a.u. long; shortest distance between protons is 2.54 a.u. The lowest contour is 0.01 and the interval between contours is 0.024; the highest contour is 0.322. Based on the Gaussian basis set (see text). (b) Orbital 3 of the $^3A_{2g}$ state of square H_4. Scale as in (a). Lowest contour 0.01, highest contour 0.41, interval 0.04.

[24] I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, J. Chem. Phys. **48**, 2700 (1968).

[25] The integrals for this calculation were carried out with the Palke–Pitzer version of the Cambridge Slater integral program.

[26] The integrals for this calculation were carried out with the McLYOSH polyatomic Slater integral program (QCPE #104).

TABLE IV. G1, SOGI, and CI energies for various linear configurations of H_3.

R_{AB}	R_{BC}	E_{G1}	E_{SOGI}	Ξ	E_{CI}[a]
1.4	∞	-1.651526	-1.651526	$0°$	-1.66959
1.470	2.984	-1.641824	-1.642236	$3.5°$	-1.663036
1.609	2.020	-1.620887	-1.626282	$16.4°$	-1.653359
1.765	1.765	-1.599776[b]	-1.623820	$20.9°$	-1.652073

[a] The CI energy is from Ref. 24 and was calculated with a 15 basis function set.

[b] This calculation was restricted so that orbitals 1 and 2 were symmetry related (see Sec. III.A.2); this is not necessarily the best G1 wavefunction.

Results and Discussion for H_3: Let us first consider the symmetry properties of the orbitals for the saddle point, linear equidistant H_3. The symmetry group is $D_{\infty h}$ and the lowest electronic state has $^2\Sigma_u^+$ symmetry. One way for the many-electron wavefunction Ψ to have the proper symmetry is to construct Φ from two σ_g orbitals and one σ_u orbital. In this case, there are no restrictions on L. Another way for Ψ to have the proper symmetry is to have Φ such that the effect of $\hat{m}$ (the mirror plane perpendicular to the molecular axis) interchange orbitals 1 and 2 while orbital 3 is a σ_u function. From Sec. II.A, we see that the many-electron wavefunction will have $^2\Sigma_u^+$ symmetry if

$$U_{11}^{[2,1]L}((12)) = 1. \qquad (31)$$

Since, for a general Ξ, $U_{11}^{[2,1]L}((12)) = \cos\Xi$, the constraint (31) is satisfied only if $\Xi = 0$. Therefore there are two possible (spatial symmetry allowed) descriptions of saddle point. We can use symmetry orbitals (σ_g and σ_u) and couple the spins in a general way or we can have orbitals 1 and 2 be symmetrically related nonsymmetry functions coupled by the G1 spin function. For the saddle point found by Shavitt et al.[24] ($R_{AB} = R_{BC} = 1.765$ a.u.), we have carried out the calculation both ways and find that the optimum wavefunction using nonsymmetry functions leads to an energy of -1.59978 a.u., whereas the optimum SOGI wavefunction using symmetry functions yields an energy of -1.62382 a.u. Thus at the saddle point the optimum orbitals are symmetry functions.

Figures 4–6 are plots of the SOGI orbitals for nuclear configurations 2–4. The G1, SOGI, and CI energies, the optimum values of Ξ, and the SOGI orbital energies are given in Table IV. The barrier height from the SOGI calculations is ~17 kcal as compared to an experimental value[27] of 9.8 kcal and a value from the CI calculations[24] of 11 kcal. The predicted barrier height might be slightly lower if basis functions and saddle-point configurations appropriate for the SOGI wavefunction were used rather than those from the CI calculations. However, the decrease would probably not be large.

From Figs. 4, 5, and 6 we see that the best independent-particle description of the reaction is as follows: For large separations between H_2 and H, the orbitals 1 and 2 which are localized on H_A (the H farther from the lone H) and H_B (the H nearer the lone H) form a bond between H_A and H_B and are also weakly bonding to H_C (the lone H). Orbital 3 which is localized on H_C has a node midway between H_A and H_B and is weakly bonding to H_B and antibonding to H_A, with these two effects roughly cancelling. As we move along the minimum-energy path, orbitals 1 and 2 remain approximately equally bonding by strengthening the H_B–H_C bond and weakening the H_A–H_B bond. At the saddle point, these two orbitals are σ_g functions and the H_A–H_B and H_B–H_C bonds are equivalent. In response to these changes in orbitals 1 and 2, the negative lobe of orbital 3 gets larger and larger until at the saddle point it becomes the σ_u orbital. Thus, even at the saddle point, this orbital is roughly nonbonding. As we pass over the saddle point in the exchange reaction the σ_u orbital begins to localize on H_A and the σ_g orbitals begin to localize on H_B and H_C and eventually form $H + H_2$. We see that throughout the reaction there are two strongly bonding orbitals and one nonbonding orbital and that it is not necessary to break a bond during the chemical reaction. Thus the SOGI orbitals yield a clear and reasonable description of the $H + H_2$ reaction.

An alternate independent-particle description of the saddle point is for orbitals 1 and 2 to localize the right and left, but we have shown above that this is possible only if the G1 spin coupling is used. The best (G1) localized orbitals are shown in Fig. 6, but, since the energy of this (G1) wavefunction is so much worse than that of the optimum wavefunction using symmetry orbitals, we see that this is not a very good description of the system for this spacing.

B. Four-Electron Systems

1. The LiH Molecule

The ground state of LiH is a singlet and the spin representation is two dimensional. In this case the representation matrices are just the same as for a three-electron doublet (four elements of S_4 map onto each matrix). Thus $\Xi = 0$ corresponds to G1 and $\Xi = 60°$

[27] I. Shavitt, J. Chem. Phys. 49, 4048 (1968).

TABLE V. G1, SOGI, and CI energies for square H_4 (length of side = 2.54 a.u.). See Sec. II.A.2 for basis set information.

	G1	SOGI	Ξ	Υ	CI
			A. Minimum basis set		
$^1B_{1g}$	−1.96926	−2.057685	62.4°±0.2°	···	−2.057685
$^3A_{2g}$	−1.983395	−2.036985	70.50°	70.52878°	−2.036985
^3E_u	−1.865595	−1.865595	0.	···	−1.865595
		SOGI	Ξ	Υ	
			B. Ten basis functions		
$^1B_{1g}$		−2.06235	62.5	···	
$^3A_{2g}$		−2.048271	69.2	70.52878°	
^3E_u		−1.87863	0.0	···	

is GF. Here we would expect for the coupling in the core orbitals on the Li atom to be dominant and hence the optimum angle should be close to zero. In fact this is the case, $\Xi = -0.105 \pm 0.002°$ and the energy decreases by about 3×10^{-7} in going from G1[28] to SOGI.[29] Thus the G1 wavefunction for LiH has nearly the optimum spin coupling.

2. The H_4 System

We expect the greatest departures from G1 to occur in a system such as H_4 for which the spin coupling is determined by the nuclear configuration. In order to illustrate various aspects for the SOGI wavefunctions for such systems we will consider some low-lying singlet and triplet states of square H_4.

Basis sets and configurations: All calculations were for the nuclear configuration with the H's at the corners of a square with a side of length $2.54a_0$.[30] We considered the lowest two states for this configuration, $^1B_{1g}$ and $^3A_{2g}$, and also a higher-lying ^3E_u state. Two different basis sets were used. The smaller[25] was a minimum basis set of four Slater orbitals, one centered at each proton and with an orbital exponent of $\zeta = 1.05$ (this is approximately optimum for the $^1B_{1g}$ state[31]). A larger basis set based upon four $1s$ Gaussians and one $2p$ Gaussian on each center and contracted to one s-like and one p-like orbital on each center was also used.[32] For this basis set the contraction was carried out[33] so that the four Gaussians approximated a Slater $1s$ orbital with $\zeta = 1.05$.

[28] W. E. Palke and W. A. Goddard III, J. Chem. Phys. **50**, 4524 (1969).

[29] The integrals for this calculation were carried out with the Nesbet–Stevens diatomic Slater integral program.

[30] This distance was found to be near the optimum R for the $^1B_{1g}$ state of $D_{4h}H_4$ by minimum basis set CI calculations.[31]

[31] C. W. Wilson, Jr., and W. A. Goddard III, J. Chem. Phys. **51**, 716 (1969).

[32] The integrals for this calculation were carried out with the Dunning version of the Murray Geller Gaussian integrals program.

[33] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

Four-Electron Triplet States: The SOGI spin variation for the four-electron singlet state was considered above; here we will discuss the spin variation for triplet states. In this case $f^{\mu} = 3$ and the general transformation **L** is a function of two parameters Ξ and Υ and is given by

$$\mathbf{L}(\Xi, \Upsilon)$$

$$= \begin{pmatrix} \cos\Xi/2 & \sin\Xi/2 \sin\Upsilon/2 & \sin\Xi/2 \cos\Upsilon/2 \\ -\sin\Xi/2 & \cos\Xi/2 \sin\Upsilon/2 & \cos\Xi/2 \cos\Upsilon/2 \\ 0 & -\cos\Upsilon/2 & \sin\Upsilon/2 \end{pmatrix}.$$

$$(32)$$

In this case $\Xi = 0$ corresponds to G1; $\Xi = 180°$ and $\Upsilon = 0$ corresponds to GF; and $\Xi = 180°$ and $\Upsilon = 180°$ corresponds to G2.

Spatial Symmetry Restrictions: We will discuss the symmetry properties of the orbitals for all three states first, beginning with the $^3A_{2g}$ and $^1B_{1g}$ states, since they are closely related. It is only necessary to consider the generators of D_{4h} (the symmetry of the nuclear configuration) and, in each case, we will examine the effect of the C_4 element of D_{4h} and determine if the orbitals can be related in such a way that they are symmetry functions only for the subgroup D_{2h}. The orbitals used to construct the $^3A_{2g}$ and $^1B_{1g}$ states have the same symmetry; the different spatial symmetry of the many-electron wavefunctions arises through the difference in the spin coupling. These orbitals are sketched in Fig. 7(b). The product function $\Phi = \phi_1\phi_2\phi_3\phi_4$ has the following properties:

$$\hat{C}_4\Phi = -(12)(34)\Phi, \qquad (33a)$$

$$C_2\Phi = (12)(34)\Phi, \qquad (33b)$$

$$\hat{i}\Phi = \Phi. \qquad (33c)$$

From (32c) we see that the state must be "g." From Sec. II.A, we know that the state will be A_{2g} if

$$U_{11}{}^{\mu L}[(12)(34)] = -1$$

and B_{1g} if

$$U_{11}{}^{\mu L}[(12)(34)] = +1.$$

For a $^3A_{2g}$ state, this gives the condition that

$$U_{11}{}^{[2,1^2]L}((12 \ (34)) = -\cos^2\tfrac{1}{2}\Xi$$
$$+ \tfrac{1}{3}\sin^2\tfrac{1}{2}\Xi \sin^2\tfrac{1}{2}\Upsilon - (4\sqrt{2}/3)\sin^2\tfrac{1}{2}\Xi \cos\tfrac{1}{2}\Upsilon \sin\tfrac{1}{2}\Upsilon$$
$$- \tfrac{1}{3}\sin^2\tfrac{1}{2}\Xi \cos^2\tfrac{1}{2}\Upsilon = -1. \quad (34)$$

This condition is satisfied if

$$-\tfrac{1}{3}\sin^2\tfrac{1}{2}\Upsilon + (4\sqrt{2}/3)\cos\tfrac{1}{2}\Upsilon \sin\tfrac{1}{2}\Upsilon + \tfrac{1}{3}\cos^2\tfrac{1}{2}\Upsilon = 1, \quad (35a)$$

or

$$(2\sqrt{2}/3)\sin\Upsilon + \tfrac{1}{3}\cos\Upsilon = 1, \quad (35b)$$

or

$$\sin\Upsilon = 2\sqrt{2}/3 \quad \text{and} \quad \cos\Upsilon = \tfrac{1}{3} \quad (35c)$$

or finally

$$\Upsilon = 70.52878\cdots° \quad (35d)$$

(there is no condition on Ξ).

For the $^1B_{1g}$ state, we have the condition that $U_{11}{}^{[2,2]L}((12)(34)) = +1$, but this condition is always satisfied since (12)(34) is an element of the invariant subgroup and is represented by the unit matrix in this representation.

We have not discussed the case of a spatially degenerate state, but an example should make the procedure clear. Consider the orbitals sketched in Fig. 7(c). The following relations are easily seen:

$$\hat{C}_4\Phi_x = \Phi_y, \qquad \hat{C}_4\Phi_y = -(12)\Phi_x,$$
$$\hat{\imath}\Phi_x = -(12)\Phi_x, \qquad \hat{\imath}\Phi_y = -(12)\Phi_y,$$
$$\hat{C}_2'\Phi_x = (12)\Phi_x, \qquad \hat{C}_2'\Phi_y = -\Phi_y, \quad (36)$$

where $\Phi_x = \phi_{1x}\phi_{2x}\phi_{3x}\phi_{4x}$ and $\Phi_y = \phi_{1y}\phi_{2y}\phi_{3y}\phi_{4y}$. For the many-electron functions $\Psi_x = G^{\mu L}\Phi_x\chi$ and $\Psi_y = G^{\mu L}\Phi_y\chi$ to form an E_u state, it is necessary that

$$\hat{C}_4\Psi_x = \Psi_y, \qquad \hat{C}_4\Psi_y = -\Psi_x,$$
$$\hat{\imath}\Psi_x = -\Psi_x, \qquad \hat{\imath}\Psi_y = -\Psi_y,$$
$$\hat{C}_2'\Psi_x = \Psi_x, \qquad \hat{C}_2'\Psi_y = -\Psi_y. \quad (37)$$

The relations in (37) are satisfied if $O_{11}{}^{\mu L}(12) = O_{11}{}^{\mu L}$, which implies that $U_{11}{}^{\mu L}((12)) = +1$. For a general Ξ, $U_{11}{}^{[2,1^2]}((12)) = \cos\Xi$, so that only G1 allows the use of symmetrically related nonsymmetry functions.

In summary we find that: (1) For the $^1B_{1g}$ state the SOGI orbitals need only have D_{2h} symmetry rather than D_{4h}. (2) For the $^3A_{2g}$ state the SOGI orbitals must have D_{4h} symmetry unless the angle Υ is $70.52878\cdots°$. In this case the orbitals need only have D_{2h} symmetry and the restriction on Υ implies a constant relative proportion of G2 and GF coupling with an arbitrary

amount of G1 coupling. (3) For the ^3E_u state the orbitals must have D_{4h} symmetry unless $\Xi = 0$ (i.e., G1). In this latter case the orbitals may have D_{2h} symmetry. In none of these cases are the SOGI orbitals *forced* to have lower than D_{4h} symmetry. Rather we have just catalogued the possible regions where lower symmetry orbitals are *allowed*.

Results and Discussion for H_4: We find from the calculations with both basis sets that the SOGI orbitals for the $^1B_{1g}$ and $^3A_{2g}$ states do *not* have D_{4h} symmetry and have symmetries just as outlined above. In fact we find that the SOGI orbitals for these two states are nearly indistinguishable; the many-electron wavefunctions differ mainly in the spin coupling used. We see from the sketches in Fig. 7, and plots in Fig. 8, that in both $^1B_{1g}$ and $^3A_{2g}$ states there is essentially a bond and antibond along each diagonal. The presence of these antibonding orbitals explains why the energy of H_4 is so very much higher than that of $H_2 + H_2$. It is interesting to note here that the SOGI energy for the minimum basis set is identical with the complete CI energy[31] for the same basis set. Thus while these wavefunctions are equivalent, the SOGI wavefunction through the independent particle interpretation allows a visualization of the wavefunction which might be completely lost in the CI form.

From Table V we see that the addition of p basis functions lowered the energies slightly but did not change the spin representations significantly. The optimum angle for the $^1B_{1g}$ state is $\Xi = 62.5°$ which is very close to the GF value of $60°$.

We see that in the lowest singlet state, $^1B_{1g}$, for square H_4 with $R = 2.54a_0$ the orbitals are delocalized over pairs of atoms (along the diagonal). However, for squares of very large R the lowest state must be $^1A_{2g}$ for which each orbital is localized on one atom. In addition for very small R it would seem that the optimum orbitals would have D_{4h} symmetry and be delocalized over all four atoms. Thus if we start at $R = \infty$ and retain square symmetry for all R we pass through regions in which the orbitals are successively delocalized in what approximates a series of Mott transitions.[17] This point will be further developed elsewhere.

C. Considerations for Larger Numbers of Electrons

At this point we will discuss briefly a set of calculations which we have not yet carried out in order to illustrate simplifications in applying SOGI which are expected to be appropriate for larger numbers of electrons.

Consider the reaction

$$\text{LiH} + \text{H} \rightleftharpoons \text{Li} + \text{H}_2. \quad (38)$$
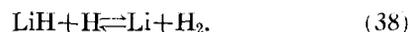
The system is a five-electron doublet and the appropriate representation of S_5 is five dimensional. If we were to allow a completely general coupling of the electron

spins, we would have to simultaneously optimize four parameters controlling the spin coupling as well as the five spatial orbitals; all of this for each nuclear configuration. However, on physical grounds, and on the basis of the calculations on Li and LiH, we expect the core electrons to be very nearly singlet paired for all nuclear geometries. From this we can see that only the mixing of the first and third standard spin basis functions (Fig. 9) is important since all others correspond to breaking the pairing of the Li core. Thus by introducing only one spin-coupling parameter, we can expect to obtain an accurate description of this reaction. This approach becomes increasingly more important as the system becomes larger. For the reaction $CH_4+H \rightleftharpoons CH_3+H_2$ or $CH_4+H^- \rightleftharpoons CH_3^-+H_2$, there are 132 different spin-coupling states. Hence to allow for a general spin-coupling scheme, we would have to introduce 131 new nonlinear parameters. If we assume, however, that the electrons in the unbroken bonds and in the core of the carbon atom remained paired, we need introduce only one new parameter to allow a general coupling among the electrons in the bonds being broken and formed.

IV. CONCLUSIONS

We have developed a way of eliminating the arbitrariness in the choice of spin function in the GI method. This method has been applied to three-electron atoms and three- and four-electron molecules. For three-electron atoms it was found that the G1 wavefunction is very nearly optimum and that only the spin-depend-

ent properties changed significantly when the spin coupling was optimized. A very good value for the spin density at the nucleus was obtained for the ground state of Li, and for the $2\,^2P$ state the results were much improved over the G1 values. Similarly for LiH the G1 wavefunction had nearly the optimum spin coupling and only a minor improvement occurred in the energy in going to SOGI. For the unstable molecular systems H_3 and H_4, however, we found that optimization of the spin-coupling was necessary in order to properly and consistently describe the system.

Thus these calculations indicate that the SOGI method may allow a proper description of the Fermi contact portion of the hyperfine interaction of atoms and molecules. More importantly however is that the SOGI method may allow a good description of the changes which occur as bonds are formed, broken, and distorted during chemical reactions.