

## Electronic Structure of LiH According to a Generalization of the Valence-Bond Method\*

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The wavefunction of LiH has been calculated according to a generalization of the valence-bond method, called the *G1* method, which leads to significantly better energies than the Hartree-Fock method, yet retains an independent-particle interpretation. The total energy of the LiH *G1* wavefunction is  $-8.017$  a.u., which accounts for 36% of the difference between the Hartree-Fock and experimental energies. The *G1* molecular orbitals, which are discussed in detail, correspond closely to chemists' intuitive concepts of electron orbitals and display bonding properties more clearly than do the Hartree-Fock orbitals. In particular, the bonding orbitals are nodeless between the nuclei and, when compared to the corresponding atomic orbitals, show increased amplitude over essentially the entire internuclear region. Finally, several one-electron properties calculated from the *G1* wavefunction are presented.

## I. INTRODUCTION

The theory of atomic and molecular structure has made extensive use of the concept of electronic orbitals. Indeed, most of our intuitive ideas about atoms and molecules are based on the approximation that each electron moves in an orbital in the field of the nuclei plus the *average* field of the other electrons of the system. This concept of electronic motion determined not by the instantaneous position of every other electron in the molecule but only by the field of the average distribution of the other electrons is called an independent particle interpretation.

The most commonly used method for computing electronic wavefunctions which can be given an independent particle interpretation is the Hartree-Fock method.<sup>1</sup> However, there are conceptual drawbacks to the Hartree-Fock method, perhaps the most serious of which is that it usually predicts molecular dissociation incorrectly. For example, the Hartree-Fock wavefunction for LiH dissociates into  $\text{Li}^+$  and  $\text{H}^-$  rather than Li and H as the two nuclei are moved to infinite separation.<sup>2</sup>

We consider here a generalization of the valence-bond method, called the *G1* method,<sup>3</sup> which retains the independent particle interpretation but removes some of the deficiencies present in the Hartree-Fock method.

This method can be considered as a generalization of the valence-bond method in which no restrictions are made on the forms of the orbitals and the core

orbitals are not required to be doubly occupied.<sup>4</sup> Wavefunctions computed according to the *G1* method do behave correctly as the molecule dissociates, and furthermore, these wavefunctions necessarily have better energies than Hartree-Fock wavefunctions. In the present work we examine *G1* wavefunctions for the LiH molecule. The computed energy is significantly lower than the Hartree-Fock energy, and several one-electron properties are fairly accurately predicted. The major interest, however, is in the independent particle orbitals. These *G1* orbitals differ considerably from the Hartree-Fock orbitals and lead to a more physically reasonable picture of the bonding in LiH.

## II. THE WAVEFUNCTION

The general form for a VB wavefunction for a four-electron system can be written as<sup>5</sup>

$$\mathcal{A}\{[\phi_{1a}(1)\phi_{1b}(2)+\phi_{1b}(1)\phi_{1a}(2)] \times [\phi_{2a}(3)\phi_{2b}(4)+\phi_{2b}(3)\phi_{2a}(4)]\alpha(1)\beta(2)\alpha(3)\beta(4)\}, \quad (1)$$

where  $\mathcal{A}$  is the antisymmetrizer and  $\alpha$  and  $\beta$  are the spin-up and spin-down eigenfunctions of  $\hat{s}_z$ . In a valence-bond wavefunction the orbitals  $\phi_i$  are usually taken as atomic orbitals, and the core orbitals for an atom ( $\phi_c$ ) are usually taken as doubly occupied. Thus for LiH we would obtain

$$\psi^{\text{VB}} = \mathcal{A}\{\phi_c(1)\phi_c(2) \times [\phi_{2a}^{\text{Li}}(3)\phi_{2b}^{\text{H}}(4)+\phi_{2b}^{\text{H}}(3)\phi_{2a}^{\text{Li}}(4)]\alpha\beta\alpha\beta\}. \quad (2)$$

In addition other terms in which, for instance,  $\phi_{2a}^{\text{Li}}$  is replaced by an orbital centered on the H, may be added. An extension of the valence-bond method due to Hurley *et al.*<sup>6</sup> and Slater<sup>5</sup> allows the  $\phi_{2a}$  and  $\phi_{2b}$  to be of more general form but restricts the orbitals in

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<sup>1</sup> C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

<sup>2</sup> There are, of course, other methods of correcting for the improper dissociation of HF wavefunctions. The simplest is to obtain the optimum linear combination of several appropriate determinants (configuration interaction). However, this approach does not retain the independent-particle interpretation.

<sup>3</sup> W. A. Goddard, III, *Phys. Rev.* **157**, 81 (1967).

<sup>4</sup> W. A. Goddard, III, *Phys. Rev.* **169**, 120 (1968).

<sup>5</sup> J. C. Slater, *Quantum Theory of Molecules and Solids*, (McGraw-Hill Book Co., New York, 1963), Vol. 1.

<sup>6</sup> A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc. (London)* **A220**, 446 (1953).

different pairs to be orthogonal; this method is called the extended valence-bond method.<sup>5</sup>

The wavefunction in (1) can be expressed as<sup>7,8</sup>

$$G_1\Phi\chi = \sum_r \zeta_{or1}(O_{r1}\Phi)(\omega_{r1}\chi), \quad (3)$$

where

$$\begin{aligned} \Phi &= \phi_{1a}(1)\phi_{1b}(2)\phi_{2a}(3)\phi_{2b}(4), \\ \chi &= \alpha(1)\beta(2)\alpha(3)\beta(4), \end{aligned} \quad (4)$$

and  $O$  and  $\omega$  are Wigner projection operators<sup>9</sup> for the symmetric group. In this case the Wigner projection operators are based on the orthogonal representations of Young<sup>10</sup> and Yamanouchi,<sup>11</sup> and the choice in (2) corresponds to the first Young's tableau<sup>10</sup> or first branching diagram.

It was shown previously that the exact wavefunction can be written as

$$\Psi^{\text{exact}} = G_1\Phi^{\text{ex}}\chi, \quad (5)$$

where  $\Phi^{\text{ex}}$  is a complicated function of the spatial coordinates of the  $N$  electrons. Thus we can consider approximate wavefunctions by considering approximate forms for  $\Phi$  and proceed arbitrarily close to  $\Psi^{\text{exact}}$  by using sufficiently accurate  $\Phi^{\text{approx}}$ . In particular we may consider the best approximation to  $\Psi^{\text{exact}}$  for which  $\Phi$  is restricted to be a product of orbitals as in (4).<sup>3</sup> If we make no restrictions on these orbitals except that they be normalized, we obtain a set of equations<sup>3</sup>

$$H_i\phi_i = \epsilon_i\phi_i, \quad i = 1a, 1b, 2a, 2b, \quad (6)$$

for the optimum orbitals, where the operator  $H_i$  contains integrations over the other three orbitals.<sup>3</sup> We call the wavefunction of type (3) with these optimum orbitals the  $G_1$  wavefunction. Thus if the orbitals from (6) are placed into the wavefunction (1) or (3), we obtain a generalized valence-bond wavefunction in which no restrictions are made on the form of the orbitals. That is, the core orbitals are not restricted to be doubly occupied and the orbitals of different pairs are not restricted to be orthogonal. In addition all orbitals, including the core orbitals, are allowed to be distributed over the whole molecule. Since we do not force our wavefunction to exhibit such characteristics as hybridization, covalency, or localization, we would hope to be able to extract from our wavefunction

such concepts as are valid and gain a more fundamental understanding of the origin of such effects.

Since the optimum orbitals from (6) are not at all similar to what are usually called valence-bond orbitals and since the wavefunction of (1) can be written in terms of the  $G_1$  operator as in (3), we refer to these optimum orbitals as the  $G_1$  orbitals.<sup>3</sup> The details of constructing and solving (6) have been discussed elsewhere.<sup>3</sup> The functional optimization of the orbitals in (1) or (3) is analogous to the similar procedure used in the Hartree-Fock and projected Hartree-Fock methods by Fock<sup>12</sup> and Löwdin,<sup>13</sup> respectively. It should be noted that the wavefunction in (1) and (3) does not in general correspond to a spin projected Slater determinant.

The  $H_i$  of (6) can be written  $H_i = h_i + U_i$ , where  $h_i = -\frac{1}{2}\nabla_i^2 + V(r)$ ,  $V(r)$  is the potential due to the nuclei, and  $U_i$  is an average potential due to the other electrons. Thus, each  $G_1$  orbital  $\phi_i$  is the orbital of an electron moving in the field of the nuclei plus the average field of the other electrons and is not a function of the instantaneous position of the other electrons. Therefore, these one-electron orbitals can be given an independent particle interpretation. Furthermore, these orbitals are not bound by any orthogonality constraints such as occur in the Hartree-Fock and valence bond methods.

Since each orbital is the optimum for an electron moving in the average field of the other electrons, we interpret the correlation energy accounted for by the  $G_1$  wavefunction as due to static correlation of the electrons and refer to the remaining error in the wavefunction as due to instantaneous or dynamic correlation among the electrons. In addition to being an eigenfunction of total spin and satisfying Pauli's principle, the  $G_1$  wavefunction satisfies the Koopmans, Brillouin, Hellmann-Feynman, and virial theorems.<sup>14</sup>

If we would place the restriction on the  $G_1$  orbitals that  $\phi_{1a} = \phi_{1b}$ ,  $\phi_{2a} = \phi_{2b}$ , etc., the  $G_1$  wavefunction would reduce to the Hartree-Fock wavefunctions.<sup>15</sup> Thus we see that the Hartree-Fock method is a special case of the  $G_1$  method in which the orbitals are forced to be equal in pairs.

### III. CALCULATIONS

The  $G_1$  equations are solved by the standard method of expanding each orbital  $\phi_i$  in terms of basis functions<sup>1</sup>  $\chi_{\mu}$ :  $\phi_i = \sum_{\mu} \chi_{\mu} C_{\mu i}$ . The  $C_{\mu i}$  are coefficients which must be varied to determine those  $\phi_i$  which give the lowest value of the total electronic energy. An iterative procedure similar to that commonly used in Hartree-Fock calculations is used to determine the best  $\phi_i$ 's. Since each one-electron  $G_1$  orbital is an eigenfunction of a

<sup>7</sup> M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen Co., Ltd., Tokyo, 1963).

<sup>8</sup> W. A. Goddard, III, *Phys. Rev.* **157**, 73 (1967).

<sup>9</sup> E. P. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), p. 118.

<sup>10</sup> A. Young, *Proc. London Math. Soc.* **34**, 196 (1931); R. M. Thrall, *Duke Math. J.* **8**, 611 (1941); D. E. Rutherford, *Substitutional Analysis* (Edinburgh University Press, Edinburgh, England, 1948), now in a photocopy edition from Hafner Publ. Co., New York, 1968.

<sup>11</sup> T. Yamanouchi, *Proc. Phys. Math. Soc. Japan* **19**, 436 (1937); **18**, 623 (1936); **20**, 560 (1938); see also M. Kotani and M. Siga *ibid.* **19**, 471 (1937).

<sup>12</sup> V. Fock, *Z. Physik* **61**, 126 (1930).

<sup>13</sup> P.-O. Löwdin, *Phys. Rev.* **97**, 1509 (1955).

<sup>14</sup> W. A. Goddard, III, *J. Chem. Phys.* **48**, 5337 (1968).

<sup>15</sup> See Appendix A of Ref. 3.

TABLE I. The basis sets and energies for the LiH calculations. The orbital exponents for the sets with six and seven basis functions, 6BF and 7BF, are optimized.  $V/2E$  is the ratio of the potential energy to twice the total energy. Energies are in hartrees.

	6BF	7BF	10BF
Li	Li	Li	Li
1s	3.773	3.773	3.786
1s'	2.266	2.266	2.317
2s	0.718	0.724	0.751
2p	0.743	0.743	3s 3.751
		3d 0.80	2p 0.690
H			2p' 1.77
1s	1.052	H	3d 0.78
2p	1.34	1s 1.111	
		2p 1.23	H
			1s 1.035
			2s 2.83
			2p 1.32
Energy	-8.013 816	-8.015 420	-8.017 327
$V/2E$	1.001 097	1.001 299	1.001 332

different Hamiltonian, the iterative procedure of solving for the self-consistent  $G1$  orbitals is somewhat more complicated and time consuming than that for the Hartree-Fock method.

Calculations were made on LiH with an internuclear

TABLE II. The wavefunction and energies for the optimized basis set 7BF.

Basis orbital	Molecular orbital coefficients			
	$\phi_{1a}$	$\phi_{1b}$	$\phi_{2b}$	$\phi_{2a}$
H1s	0.00406	0.00465	0.99946	0.08704
H2p $\sigma^a$	0.00083	-0.00547	0.03553	-0.02443
Li1s	0.72598	-0.15782	0.02203	0.04357
Li1s'	0.29274	1.14544	-0.03197	-0.04667
Li2s	0.00141	-0.01224	-0.00292	0.80623
Li2p $\sigma^a$	-0.00276	-0.00889	0.00882	0.48793
Li3d $\sigma$	-0.00051	-0.00254	-0.00279	0.11049
Orbital eigenvalue	-2.80448	-2.43032	-0.46955	-0.28142
Electronic energy	= -9.010 445			
Total energy	= -8.015 420			
Kinetic energy	= 8.036 245			

<sup>a</sup> The  $z$  axis on each nucleus points toward the other nucleus.

separation of 3.015 a.u. using the three Slater-orbital<sup>16</sup> basis sets listed in Table I. The first calculations used a set of six basis orbitals consisting of two 1s's, one 2s, and one 2p $\sigma$  on Li and a 1s and a 2p $\sigma$  on H. All orbital exponents were chain optimized until the energy decrease of an entire cycle was less than  $10^{-5}$  a.u. The orbital exponents are optimized to about  $\pm 5$  in the least significant figure quoted in Table I.

An Li 3d $\sigma$  orbital was added to this set, and all orbital exponents except the two Li 1s exponents were reoptimized by the same procedure as above, resulting in an energy decrease of 0.0016 a.u. The addition of the 3d $\sigma$  orbital produced significant changes in some

TABLE III. The wavefunction and energies for the basis set 10BF.

Basis orbital	Molecular orbital coefficients			
	$\phi_{1a}$	$\phi_{1b}$	$\phi_{2b}$	$\phi_{2a}$
H1s	-0.00312	0.01026	1.04121	0.18378
H2s	0.00208	-0.00226	0.03812	-0.04942
H2p $\sigma^a$	-0.00271	0.00687	0.04267	-0.00976
Li1s	0.45861	0.13574	0.01252	0.01513
Li1s'	0.74154	0.60073	-0.01775	0.00876
Li2s	-0.00415	0.00009	-0.06787	0.76065
Li3s	-0.22836	0.30261	-0.00751	-0.03850
Li2p $\sigma^a$	0.00066	0.00057	-0.07287	0.45340
Li2p $\sigma'^a$	-0.00028	-0.02211	0.03916	0.00776
Li3d $\sigma$	0.00043	-0.00133	-0.03478	0.08969
Orbital eigenvalue	-2.79984	-2.41445	-0.46735	-0.28100
Electronic energy	= -9.012 352			
Total energy	= -8.017 327			
Kinetic energy	= 8.038 692			

<sup>a</sup> The  $z$  axis on each nucleus points toward the other nucleus.

of the orbital exponents, as can be seen in Table I. The wavefunction and energies for this optimized basis set are listed in Table II. The final calculation used a basis set of 10 functions, the Li core basis orbitals (1s, 1s', 3s) of which were taken from an optimized four-basis-function  $G1$  calculation on the Li atom.<sup>4</sup> The outer orbital exponents of this set are those of a 10-basis-function LiH set optimized in the Hartree-Fock approximation.<sup>17</sup> The energy obtained using this basis set is significantly below those of the smaller sets, and the virial ratio is only slightly changed, so it appears that the lack of optimization of this basis

<sup>16</sup> Slater orbitals have the form  $\chi_{nlm} = A r^{n-1} e^{-\zeta r} Y_{lm}$ , where  $A$  is a normalization constant and  $\zeta$  is an adjustable parameter called the orbital exponent.

<sup>17</sup> W. A. Goddard, III (unpublished results), total energy = -7.98701.

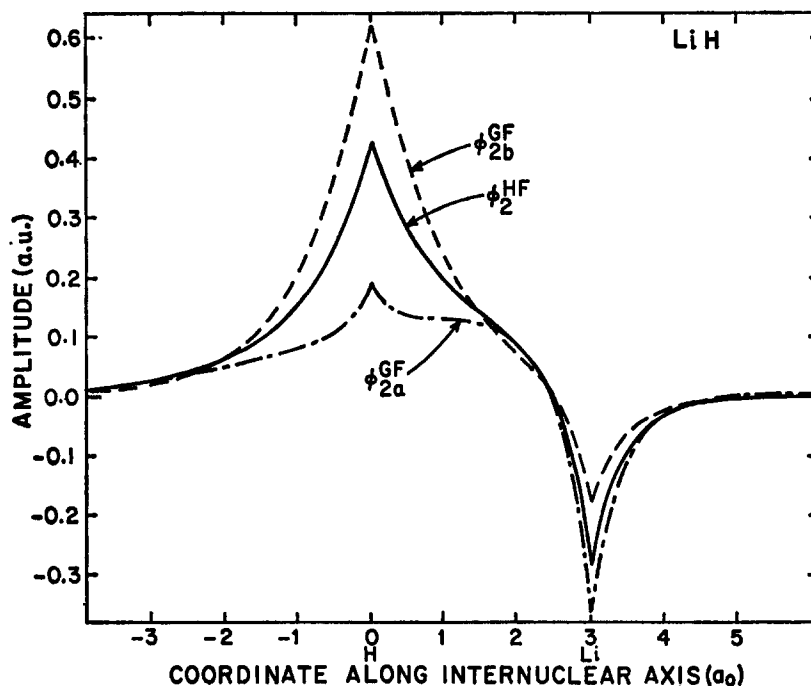


FIG. 1. Plots of the Hartree-Fock and GF LiH bonding orbitals.

set is not a serious restraint on the wavefunction. The energy for this wavefunction is probably within 0.0015 a.u. of the  $G1$  limit (the lowest energy obtainable in the  $G1$  method). The changes in the molecular orbitals and calculated properties brought about by further enlargement and optimization of the basis set are expected to be small. The coefficients and energies for this wavefunction are given in Table III, and the properties calculated from it are presented in Sec. V. We now proceed to discuss the nature of the  $G1$  orbitals of this wavefunction.

#### IV. THE $G1$ ORBITALS

Perhaps the most important information one might hope to glean from a theoretical calculation of the wavefunction of a molecule is a clear description of the bonding phenomenon. Indeed, the primary reason for considering independent particle type wavefunctions is to facilitate extraction of such information. As Slater has pointed out, a necessary requirement for bonding in a molecule seems to be a concentration of charge between the nuclei.<sup>5</sup> Thus a "bonding" molecular orbital should be one which shows a buildup of charge in the internuclear region. That is, a bonding molecular orbital should have larger amplitude in the internuclear region than the atomic orbital into which it transforms on dissociation. Correspondingly, this orbital would have smaller amplitudes outside the bonding region.

In view of these expectations, it is surprising that the Hartree-Fock and GF methods lead to bonding orbitals (depicted in Fig. 1) with nodes between the

bonded nuclei. Such an orbital contributes very little electron density in the region near the node; this behavior does not aid in concentrating charge between the nuclei.

These nodes appear physically unreasonable from another point of view also. Each orbital is the optimum one for an electron moving in the potential due to the other electrons, but if this average potential were local, then the ground state would be nodeless.<sup>18</sup> Thus in the event that exchange terms, which make the actual potential nonlocal, are small in comparison to Coulomb terms, we would expect the bonding orbitals to be nodeless. Upon examining the form of the Hartree-Fock and GF many-electron wavefunctions, we find an explanation of the above problem. These many-electron wavefunctions are forced to be antisymmetric with respect to interchanges of orbitals, resulting in orthogonality conditions on the orbitals.<sup>19</sup> That is, the nodes<sup>20</sup> in valence and bonding orbitals in Hartree-Fock and GF wavefunctions occur only because of constraints in the form of the many-electron wavefunctions.

Now consider the  $G1$  bonding orbitals for LiH shown in Figs. 2 and 3. We see that these do *not* have nodes in the internuclear region, that the amplitudes of the bonding orbitals are larger than those of the corresponding atomic orbitals in nearly the entire internuclear region, and that at most only very slightly

<sup>18</sup> L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), p. 56.

<sup>19</sup> W. A. Goddard, III, *J. Chem. Phys.* **48**, 450 (1967).

<sup>20</sup> We mean here nodes which are not required by symmetry. In the case of a  $p$  or  $\pi$  orbital, a nodal plane would appear.

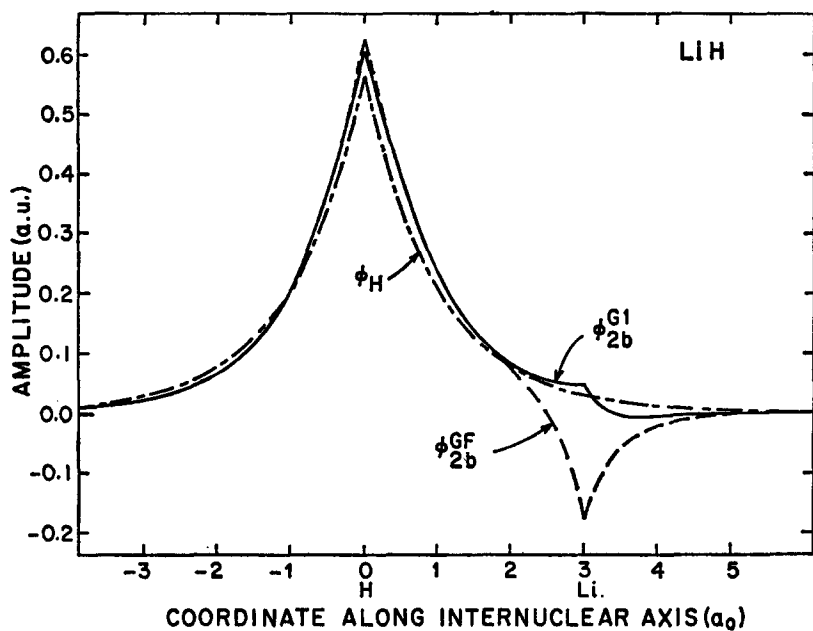


FIG. 2. Plots of the LiH  $\phi_{2b}$  orbitals of the G1 and GF methods compared to the atomic orbital for a free hydrogen atom,  $\phi_H$ .

FIG. 3. Plots of the G1 LiH orbital  $\phi_{2a}$ , the lithium hybrid portion of this orbital, and the Li-atom G1 valence orbital  $\phi_{2a(Li)}^{G1}$ .

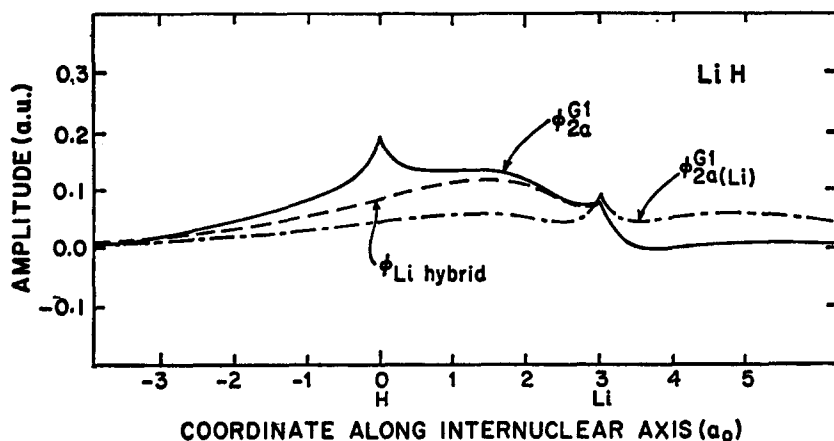
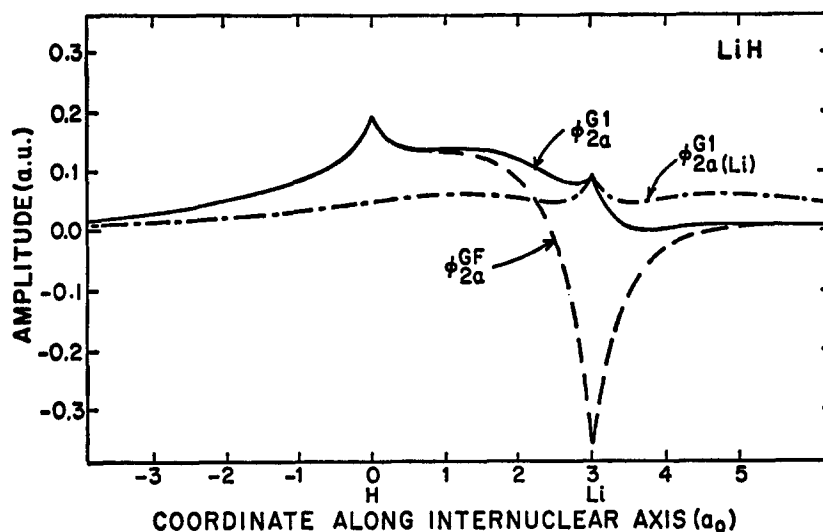


FIG. 4. Plots of the LiH  $\phi_{2a}$  orbitals of the G1 and GF methods compared to the Li-atom G1 valence orbital  $\phi_{2a(Li)}^{G1}$ .

negative amplitudes occur in the nonbonding regions. Since of the three methods leading to independent particle interpretations only the  $G1$  does not require orthogonality of the orbitals, since the variationally determined orbitals obtained from this method are essentially nodeless, and since nodes in the internuclear region are physically unreasonable, we conclude that the nodes<sup>20</sup> occurring in the valence and bonding orbitals of the Hartree-Fock and GF methods are just peculiarities of these methods with no physical or chemical significance.

Proceeding from another point of view, since the  $G1$  orbitals yield a far better energy for LiH than does any other known set of orbitals, we may consider this method to be the theoretical foundation for the following rules for bonding in LiH. (The rules are general if calculations on other molecules show that the same rules apply; this seems likely, but the calculations have not been carried out yet.)

1. Compared to the corresponding atomic orbital, a bonding orbital has a larger amplitude throughout the internuclear region (of the two nuclei being bound, note that a three-center bond has not yet been examined by this method).
2. The inner-shell orbitals (the  $1s$  orbitals for the first row of the periodic table) change only very slightly on formation of the molecular bond.

Corollaries of these rules are that the amplitude of a bonding orbital does not have deeply negative regions and drops rapidly to zero outside the bonding region. Also in the event that low-lying states of appropriate symmetry are present, an effective way to build up amplitude in the bonding region and remove it from the nonbonding region is to hybridize (e.g., mix  $p\sigma$  character into the Li  $2s$  orbital in the case of LiH).

Thus we seem to have a start toward deducing concepts concerning molecular bonding based entirely on *ab initio* calculations starting with the Schrödinger equation and independent of chemical prejudices. (Of course, the resulting concepts may on the whole correspond closely with ideas obtained by other means; in this case we would have an independent theoretical foundation for these principles.) Now we will discuss the  $G1$  orbitals of LiH in somewhat more detail.

### The $G1$ Orbitals of LiH

Orbital  $\phi_{2b}$  is primarily a hydrogen  $1s$  orbital with very small contributions from the other basis functions; its strong similarity to the hydrogen atomic orbital is apparent in Fig. 2. It is somewhat more concentrated in the internuclear region and in the region near the proton than is the free-hydrogen orbital; thus it appears to be weakly bonding. Note, however, that its eigenvalue ( $-0.467$  a.u.) is slightly less negative than the free-hydrogen eigenvalue of  $-0.5$  a.u.

The  $\phi_{2a}$  bonding orbital gradually changes into a Li  $2s$  orbital<sup>21</sup> as the internuclear distance is increased to infinity; indeed only this orbital is greatly modified in the molecule formation. Compared to the atomic Li  $2s$  orbital in Fig. 3,  $\phi_{2a}$  is changed in two major respects.  $\phi_{2a}$  displays a significant H  $1s$ -like component near the proton, and the lithium portion of the orbital has become hybridized with 72%  $s$ , 27%  $p$ , and 1%  $d$  character.<sup>22</sup> This lithium hybrid portion of  $\phi_{2a}$  ( $\phi_{2a}$  with the coefficients of the hydrogen basis functions set to zero) is also plotted in Fig. 4. It is clear that hybridization has very effectively transferred charge into the internuclear region from the region behind the Li nucleus. The net result of these changes is to more than double the amplitude of the  $\phi_{2a}$  in most of the region between the H and Li nuclei and to decrease the orbital eigenvalue from  $-0.196$  to  $-0.281$  a.u.

The remarkable similarity of the GF bonding orbitals to these  $G1$  bonding orbitals in the vicinity of the hydrogen is apparent in Figs. 2 and 3, but the orthogonality requirements on the GF orbitals force them to have nodes near the lithium. The inner shell  $G1$  orbitals  $\phi_{1a}$  and  $\phi_{1b}$  for LiH are essentially the same as the  $1s$   $G1$  orbitals of Li. We note from Fig. 5 and from the differences in the orbital eigenvalues that these inner-shell LiH  $G1$  orbitals are significantly different. The overlap of orbitals  $\phi_{1a}$  and  $\phi_{1b}$  is 0.92714 for LiH and 0.92812 for Li compared to 0.99989 for the GF<sup>2b</sup> and 1.0 for the Hartree-Fock orbitals. This large  $1s$  orbital splitting in the  $G1$  case allows a static in-out electron avoidance which significantly reduces the electron-repulsion energy. (This accounts for most of the radial correlation energy for Li.<sup>4</sup>) For LiH the two inner GF orbitals and the inner Hartree-Fock orbital differ so little that plots of all three functions are essentially indistinguishable, hence only one plot is given in Fig. 5. Likewise, plots of the atomic lithium  $1s$  orbitals are superimposable on the LiH inner  $G1$  orbitals and are not included.

Each of the  $G1$  orbitals  $\phi_{1a}$ ,  $\phi_{1b}$ , and  $\phi_{2b}$  plotted in Figs. 2 and 5 has a region of very shallow negative amplitude (never less than  $-0.01$  a.u.) in the nonbonding area of the orbital. This could be due to the unoptimized basis set because the corresponding plots for the completely optimized six and seven basis orbital wavefunctions did not have these negative regions. Orbital  $\phi_{2a}$  has a very small region of negative amplitude ( $-0.001$  a.u. deep) behind the Li nucleus which

<sup>21</sup> For convenience we will refer to the Li valence orbital as the  $2s$  orbital, as is usual. A more consistent notation would be the Li  $2as$  orbital.

<sup>22</sup> The  $s$  ( $p$  or  $d$ ) character of orbital  $\phi_i$  has been defined as  $\sum_{\mu\nu} C_{\mu i} C_{\nu i} S_{\mu\nu}$ , where the  $\mu$  and  $\nu$  sums are over all  $s$ - ( $p$ - or  $d$ -) type basis functions on Li, and  $C$  and  $S$  are the coefficient and overlap matrices. The percentage is normalized with respect to contributions from the Li basis functions.

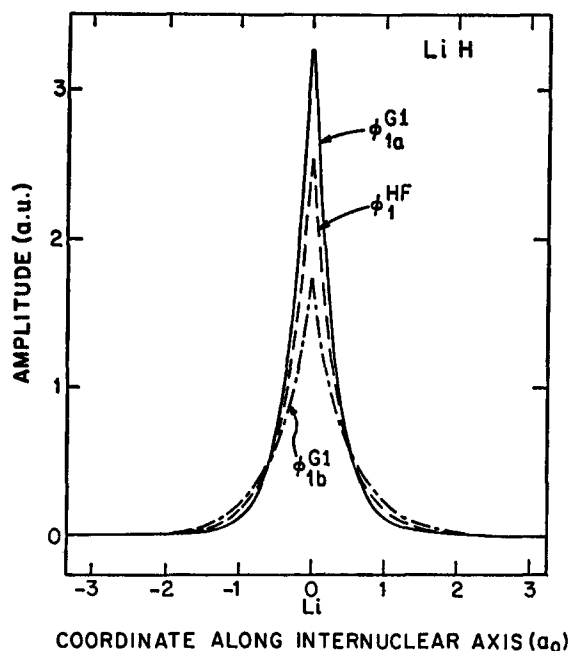


FIG. 5. Plots of the two LiH inner-shell orbitals according to the G1 method (the G1 inner-shell orbitals for a free Li atom are essentially identical to these and are not plotted here) and the inner-shell Hartree-Fock LiH orbital. (Both GF inner-shell LiH orbitals are essentially superimposable on the Hartree-Fock orbital and are not given here.)

was present and larger in the seven-basis-function calculation and larger still for the calculation with six basis functions.

The G1 molecular orbitals are very much like valence-bond orbitals with two quite localized inner-shell orbitals on Li and a rather localized orbital on hydrogen. The fourth orbital is less localized, being mostly a lithium hybrid orbital with a significant contribution from hydrogen basis functions. Indeed, if strong orthogonality were assumed for the G1 molecular orbitals, the method would reduce to the extended valence-bond method.<sup>4</sup> Strong orthogonality definitely does not hold here, as can be seen from the table of molecular orbital overlaps (Table IV), and it is clear that its imposition as a constraint in the calculation would raise the energy and would cause nodes in the bonding orbitals.

In summary, we have seen that the G1 method predicts molecular orbitals which are quite different from those of the Hartree-Fock or GF methods. The fact that the inner-shell orbitals are significantly different permits a static in-out electron avoidance. The bonding molecular orbitals, since they are nodeless in the internuclear region, show in a clear way the concentration of charge in that area. And finally, this method predicts the correct molecular dissociation products.

## V. CALCULATED PROPERTIES

The expectation values of several one-electron operators are given in Table V; experimental values as well

as values calculated with other approximations are included for comparison. Cade and Huo's calculation<sup>23</sup> is essentially the Hartree-Fock limit for LiH and Browne and Matsen's<sup>24</sup> and Bender and Davidson's<sup>25</sup> are configuration-interaction calculations.

The virial ratio  $V/2E$  is about 1.0013 for all three bases, which indicates that the calculated equilibrium separation would be larger than the experimental value. This has been observed in most calculations on LiH.<sup>23,24</sup> The energy of LiH in the G1 approximation accounts for 36% of the difference between the Hartree-Fock and experimental energies, yet as discussed above, the G1 wavefunction does not include dynamic correlation among the electrons. For LiH the GF method yields an energy<sup>3</sup> about midway between the Hartree-Fock and G1 energies. The dissociation energy of LiH was obtained by subtracting the G1 limit energies of Li and H atoms from the calculated LiH energy. The resulting 1.898 eV is 75% of the experimental result. It should be noted that the GF method predicts an equally good dissociation energy of 1.928 eV. These values are larger than the Hartree-Fock prediction, but are still smaller than both the experimental value and the values from the most accurate correlated wavefunctions.<sup>24,25</sup> The dipole moment is calculated to be 5.645 D in the direction  $\text{Li}^+\text{H}^-$ .

## The Sigma Limit

The sigma limit is defined as the best possible energy for a configuration interaction wavefunction which uses only  $\sigma$ -type orbitals. The best value for this limit for LiH is apparently  $-8.01872$  a.u. for a seven-basis-function calculation by Ebbing.<sup>26</sup> We see from Table II that the seven-basis-function G1 calculation leads to  $-8.01542$  a.u. and the 10-basis-function G1 calculation leads to  $-8.01733$  a.u. Since the Hartree-Fock energy for seven basis functions is  $-7.98315$ ,<sup>26</sup> we see that the G1 method accounts for about 90% of the non-angular Hartree-Fock correlation energy accounted for by Ebbing's calculation. Ebbing estimates the Hartree-Fock correlation error to be 0.084 a.u. of which 0.054 a.u. is sigma and 0.030 a.u. is angular

TABLE IV. G1 orbital overlaps for the 10-basis function wavefunction of LiH.

	$\phi_{1a}$	$\phi_{1b}$	$\phi_{2a}$	$\phi_{2b}$
$\phi_{1a}$	1.0	0.92714	0.13457	0.06295
$\phi_{1b}$		1.0	0.22219	0.10419
$\phi_{2a}$			1.0	0.75454
$\phi_{2b}$				1.0

<sup>23</sup> P. E. Cade and W. M. Huo, *J. Chem. Phys.* **47**, 614 (1967).

<sup>24</sup> J. C. Browne and F. A. Matsen, *Phys. Rev.* **135A**, 1227 (1964).

<sup>25</sup> C. F. Bender and E. R. Davidson, *J. Phys. Chem.* **70**, 2675 (1966).

<sup>26</sup> D. D. Ebbing, *J. Chem. Phys.* **36**, 1361 (1962).

TABLE V. Calculated properties in atomic units unless designated otherwise.

	G1	GF	HF	CI	CI	
	Experiment <sup>a</sup>	Present work	Goddard <sup>b</sup> GF	Cade <sup>c</sup> Huo	Bender <sup>e</sup> Davidson	Browne <sup>f</sup> Matsen
$R_e$	3.015	3.015	3.015	3.015	3.0147	3.046 <sup>g</sup>
$E$	-8.0705	-8.0173	-8.0037	-7.9873	-8.0606	-8.046
$D_e$ (eV)	2.515	1.898	1.928	1.49	2.25	>2.12
$\mu$ (D)	5.828	5.645		6.002	5.965	5.93
$\langle r_{\text{H}}^2 \rangle_{e1}$		30.615				
$\langle r_{\text{Li}}^2 \rangle_{e1}$		25.827				
Quadrupole moment (Buckingham) <sup>d</sup>		-3.686		-4.58 <sup>d</sup>		-4.15 <sup>h</sup>
$\langle 1/r_{\text{H}} \rangle_{e1}$		2.2239			2.2404	
$\langle 1/r_{\text{Li}} \rangle_{e1}$		6.0848			6.0748	
$\langle q/2e \rangle_{\text{H}}$	0.0249	0.0292			0.0230	0.0256
$\langle q/2e \rangle_{\text{Li}}$		-0.0202			-0.0187	-0.0173

<sup>a</sup> See G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Princeton, N. J., 1950); R. Velasco, *Can. J. Phys.* **35**, 1204 (1957); F. H. Crawford and T. Jorgensen, Jr., *Phys. Rev.* **49**, 745 (1936) and Appendix I of Ref. 11 for experimental energies and  $R_e$ . See L. Wharton, L. P. Gold and W. Klemperer, *J. Chem. Phys.* **37**, 2149 (1962) for  $\mu$  and  $q/2e$ . Wharton gives  $\mu_0 = 5.882$  D,  $\mu_1 = 5.990$  D, and  $\mu_2 = 6.098$  D. To estimate  $\mu_e$ , which should be compared to the calculated value, we assumed  $\mu(R)$  to be linear and  $\mu_e = \mu_{-1/2}$ .

<sup>b</sup> See Ref. 3.

<sup>c</sup> See Ref. 23.

<sup>d</sup> Quoted by D. E. Stogryn and A. P. Stogryn, *Mol. Phys.* **11**, 371 (1966).

<sup>e</sup> See Ref. 25.

<sup>f</sup> See Ref. 24. Due to a typographical error in Browne and Matsen's paper, their value of  $\langle q/2e \rangle_{\text{H}}$  is incorrect. The corrected value is given here. [J. C. Browne (private communication).]

<sup>g</sup> This is the value of  $R_e$  computed by Browne and Matsen.

<sup>h</sup> This was calculated by D. P. Chong and W. B. Brown, *J. Chem. Phys.* **45**, 392 (1966), from Browne and Matsen's wavefunction.

correlation. As compared to the Hartree-Fock method the G1 method allows a static left-right (along the internuclear axis) and in-out correlation of electrons. Since the wavefunction for LiH,  $G_1\Phi_X$ , must describe a  $^1\Sigma_g^+$  state and since the  $\Phi$  is a single product of orbitals, each orbital must be a  $\sigma$  orbital. In order to mix in  $\pi$  orbitals we would have to let  $\Phi$  be a sum of orbital products and hence would lose the interpretation of the wavefunction in terms of four simple orbitals. Thus by our previous definition, all angular correlation is dynamic correlation and is missed by the G1 wavefunction. Since the G1 energy for LiH is about 0.030 a.u. better than the Hartree-Fock value, the total dynamic sigma correlation energy is 0.024 a.u., and the total dynamic angular correlation is 0.030 a.u. Thus, for LiH, angular correlation is about 56% of the total dynamic correlation, which is about the same percentage as for  $\text{H}_2$  (60%).<sup>3</sup>

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#### APPENDIX A

The  $G_i^\mu$  operators and  $G_i^\mu\Phi$  wavefunctions have been discussed elsewhere; however, for the convenience of

the reader we give sufficient information here for the evaluation of expectation values of spatial operators. The total energy is given by<sup>3</sup>

$$E = \langle G_1^\mu\Phi_X | H | G_1^\mu\Phi_X \rangle / \langle G_1^\mu\Phi_X | G_1^\mu\Phi_X \rangle \\ = \langle \Phi | H | O_{11}^\mu\Phi \rangle / \langle \Phi | O_{11}^\mu\Phi \rangle, \quad (\text{A1})$$

where for a four-electron singlet ( $\mu = [2^2]$ )  $O_{11}^\mu$  is given by

$$O_{11}^\mu = \frac{1}{12} [e - \frac{1}{2}(13) - \frac{1}{2}(14)] [e + (13)(24)] \\ \times [e + (12)] [e + (34)], \quad (\text{A2})$$

and  $e$  is the identity operator.

#### APPENDIX B

Here we prove that the GF and G1 methods yield identical wavefunctions for a  $2m$ -electron singlet state if all except one pair of orbitals are taken to be equal in pairs. That is, we show that

$$G_f^{[2^m]}(\Phi_f\chi_f) = cG_1^{[2^m]}(\Phi_1\chi_1), \quad (\text{B1})$$

$$S_f^{[2^m]} = \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & 4 \\ \hline 5 & 6 \\ \hline \vdots & \vdots \\ \hline 2m-1 & 2m \\ \hline \end{array} \quad S_f^{[2^m]} = \begin{array}{|c|c|} \hline 1 & m+1 \\ \hline 2 & m+2 \\ \hline 3 & m+3 \\ \hline \vdots & \vdots \\ \hline m & 2m \\ \hline \end{array}$$

FIG. 6. The  $S_f^{[2^m]}$  and  $S_f^{[2^m]}$  tableaux.



where

$$G_f(\Phi_f \chi_f) = \sum_{r=1}^f \zeta \sigma_{rf} (O_{rf} \Phi_f) (\omega_{\bar{r}f} \chi_f),$$

$$G_1 \Phi_1 \chi_1 = \sum_{r=1}^f \zeta \sigma_{r1} (O_{r1} \Phi_1) (\omega_{\bar{r}f} \chi_1),$$

$$\Phi_j = \phi_{1a} \phi_{2a} \cdots \phi_{ma} \phi_{1b} \phi_{2b} \cdots \phi_{mb},$$

$$\Phi_1 = \phi_{1a} \phi_{1b} \phi_{2a} \phi_{2b} \cdots \phi_{ma} \phi_{mb},$$

$$\chi_f = \alpha \alpha \cdots \alpha \beta \beta \cdots \beta,$$

$$\chi_1 = \alpha \beta \alpha \beta \cdots \alpha \beta,$$

and where

$$\phi_{ia} = \phi_{ib} \quad \text{for } i \leq m-1. \quad (\text{B2})$$

Let  $\tau$  be a permutation such that  $\Phi_f = \tau \Phi_1$ ; then expanding  $\tau$  in terms of the  $O_{ij}^\alpha$  and using the orthogonality relations, we find

$$O_{rf} \Phi_f = \sum_{j=1}^f U_{fjr} O_{rj} \Phi_1.$$

But because of (B2), each array  $S_j^{[2^m]}(\Phi_1)$ , except for  $j=1$ , will have the same orbital repeated in the same column (see Fig. 6 for the  $S_1^{[2^m]}$  and  $S_f^{[2^m]}$  tableaux). Thus by the theorem of Appendix D of Ref. 8 we have  $O_{rj} \Phi_1 = 0$ , unless  $j=1$ . Hence

$$O_{rf} \Phi_f = c O_{r1} \Phi_1,$$

where  $c = U_{f1r}$  is nonzero and independent of  $r$ . Similarly  $\omega_{\bar{r}1} \chi_1 = c' \omega_{\bar{r}f} \chi_f$ . Consequently we obtain (B1).

## Ligand ENDOR of Cu-8-Hydroxyquinolate Substituted into Organic Single Crystals

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The technique of electron-nuclear double resonance (ENDOR) has been applied to copper-8-hydroxyquinolate substituted into single crystals of phthalimide and of 8-hydroxyquinoline. This method has permitted determination of the nitrogen hyperfine tensor, with sufficient accuracy to detect small orthorhombic deviations from axial symmetry, and the nitrogen quadrupole tensor. These tensors have the same principal axes and the coupling constants of the two interactions have opposite sign. The axis corresponding to the largest quadrupole splitting is oriented along the nitrogen lone pair in the plane of the metal complex. One  $g$  axis of the slightly monoclinic copper-8-hydroxyquinolate complex is oriented approximately along the oxygen-copper axis, and the other in-plane  $g$  axis is at a small angle with respect to the nitrogen-copper direction. The delocalization of the unpaired electron density to the ligand protons depends on the host lattice. The quadrupole tensor and its dependence on the host lattice are discussed. It is shown that the unpaired electron in the aromatic rings of 8-hydroxyquinoline resides mainly in the  $\sigma$  system, in accordance with the symmetry of the ground state. The isotropic and anisotropic coupling constants of the proton adjacent to the nitrogen and some coupling components of other protons in the aromatic ligands and in the neighbouring molecules of the host lattice have been determined. The spin densities in the aromatic rings are positive.

### INTRODUCTION

Hyperfine coupling constants of protons in the aromatic ligands of paramagnetic metal complexes give information about the delocalization of the unpaired electron, the orbitals in which the unpaired electron resides, and about the metal-ligand interaction. However, these coupling constants are usually below the resolving power of electron paramagnetic resonance (EPR). For certain classes of paramagnetic metal compounds<sup>1a,1b</sup> with short correlation times for the hyperfine interactions, mainly nickel and cobalt complexes, the isotropic part of the electron-proton interaction can be measured by nuclear magnetic resonance (NMR) in solution. The technique of NMR is not applicable, however, to the determination of

the anisotropic part of the electron-proton interaction or to the study of planar  $d^9$  systems. The technique of electron-nuclear double resonance (ENDOR)<sup>2</sup> is appropriate for these measurements.

The parameters which describe the covalency of a metal-ligand bond usually are deduced from the Fermi contact between the unpaired electron and the ligand nuclei. In the last few years, it has been shown<sup>3</sup> that information about the metal-ligand bond can be obtained from the quadrupole resonance (NQR) of ligand nuclei. In metal complexes, nitrogen is a frequently encountered ligand. A disadvantage of quadrupole resonance is that the nitrogen signals are weak and a large amount of sample is necessary to detect a signal. Usually the available single crystals are not

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