I. AB-INITIO EFFECTIVE POTENTIALS FOR USE IN MOLECULAR CALCULATIONS

II. THE STERNHEIMER CORRECTION, PERTURBATION THEORY, AND APPROXIMATE WAVEFUNCTIONS

III. THE THEORETICAL DETERMINATION OF THE Li_2 $B^1\Pi_u$ POTENTIAL ENERGY CURVE

Thesis by

Luis R. Kahn

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To my wife, Hazel,

and

to my Parents

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ABSTRACT

Part I

We have investigated the efficacy of ab-initio effective potentials in replacing the core electrons of atoms for use in molecular calculations. The effective potentials are obtained from ab-initio GI calculations on atoms and are unique and local. We find that the use of these effective potentials to replace the core orbitals of such molecules as LiH, Li_2, BH, or LiH_2, leads to wavefunctions in excellent agreement with all-electron ab-initio results. The use of such effective potentials should allow ab-initio quality wavefunctions to be obtained for systems too large for the ab-initio consideration of all the electrons.

Part II

We have investigated the Sternheimer correction for the calculation of the nuclear quadrupole coupling constants and its relation to the approximate nature of the zero-order wavefunction. The first-order perturbed Hartree-Fock equations, and some approximations to them, are solved for the 2 ^2P state of Li, and the resulting Sternheimer type corrections are compared with Sternheimer's approximate calculations and with results from non-perturbation theory approaches.

Part III

The Li_2 $B^1\Pi_u$ potential energy curve has been calculated with a Multi-Configuration SCF (MCSCF) wavefunction. Several different types of wavefunctions and basis sets have been examined and their accuracy determined. The most accurate wavefunction used predicts a binding energy of 0.3015 e.V. (84% of the experimental value of 0.362 e.V.), and predicts a potential hump of 0.0724 e.V. with its maximum in the vicinity of 10.6 Bohr. It is argued that the theoretical value of the hump is an upper bound to the experimental value.

TABLE OF CONTENTS

III THE THEORETICAL DETERMINATION OF THE Li_2 $B\ ^1\Pi_u$ POTENTIAL ENERGY CURVE.

I. AB-INITIO EFFECTIVE POTENTIALS FOR USE IN MOLECULAR CALCULATIONS

I. INTRODUCTION

Empirically, it seems clear that we can think of the states of a molecule or solid as if only the description of the outer or valence electrons changes significantly as the atoms are brought together to form the bound system. Thus, in considering the Na_2 molecule as a function of internuclear distance, we should be able to ignore the ten inner or core electrons on each Na and consider Na_2 as a two-electron problem. However, quantum mechanically the situation is less clear. Since the electrons are indistinguishable, there are certainly not two electrons of Na_2 that are different from the other twenty and which can be isolated out and considered as the valence electrons. Then what <u>do</u> we mean by the valence electrons of Na? In order to discuss the many-electron wavefunction in terms of one electron at a time, we must turn to one of the variational methods, such as Hartree-Fock (HF) or GI,[1] which lead to independent-particle interpretations. In these methods the many-electron wavefunction is composed of N different orbitals, each of which can be interpreted as the state of an electron moving in the field due to the other electrons. That is, each orbital is the solution of an equation

$$(h + U_i)\phi_i = \epsilon_i \phi_i \quad , \tag{1}$$

where U_i contains the interaction effects due to the other electrons. Thus, it is the orbitals we interpret, not the real electrons of the molecule. In the case of a molecule such as Na_2, twenty of the orbitals (the core orbitals) are essentially the same as for the Na atoms, and only the other two orbitals (the valence orbitals) change upon bonding. Thus, if we had some way of incorporating the effect of the core orbitals into the U_i of (1), we could then completely forget about the core orbitals and solve just the two equations (1) for the two valence orbitals of the Na_2 molecule. We could then also solve for the low-lying excited states of Na and Na_2 in the same way, and indeed we could even include correlation effects in the interactions between the valence electrons.

We will be concerned here with how to include the effects of the core orbitals into an effective potential, $\overline{U}_i$, equivalent to the U_i of (1). Progress has been made along these lines based on Hartree-Fock wavefunctions, leading to what are usually called pseudopotentials. However, certain difficulties arise involving, for example, uniqueness of the potential. We will review certain aspects of these approaches and then turn to a new method based on the GI wavefunctions.[2] Comparison between the full electron *ab-initio* calculations and the corresponding calculations using the effective potentials will be made for several systems[3] (e.g., LiH, Li_2, BH, and LiH_2). In addition some results on larger systems (e.g., Li_3, Li_2H, and BH_2) will be presented.

II. LOCAL POTENTIALS FROM HARTREE-FOCK WAVEFUNCTIONS

In this section we will review some of the previous approaches used to replace core electrons by effective potentials, with particular emphasis on the *local* representation of these effective potentials.[4]

Early work along these lines was due to Hellmann[5] and Gombás.[6] The theoretical basis was sought in a combined procedure whereby the core-electron charge distribution was described by the Thomas-Fermi theory, while the valence electrons were described by a Schrödinger equation containing a repulsive potential due to the core electrons. For practical applications, as for K_2 and KH,[5] a simple local functional form was assumed for the repulsive potential,

$$\frac{A}{r}\exp(-2Kr) \quad , \tag{1}$$

and the parameters A and K were adjusted so as to fit the appropriate atomic valence spectra. Later work using the Hellmann approach was carried out by Preuss[7] on alkali molecular ions such as Na_2^+.

An alternative theoretical basis for effective potentials can be obtained from the Hartree-Fock (HF) approximation. Consider an atom with one valence electron, say Li, Be^+, or K; the HF equation for the valence orbital is

$$\hat{H}_v^{HF}\,\phi_v = (-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \hat{V}^{HF})\,\phi_v = \epsilon_v\phi_v \quad , \tag{2}$$

where the $\hat{V}^{HF}$ is a sum of Coulomb and exchange operators constructed from the core orbitals and can be thought of as the potential due to the core electrons. [For simplicity, in Eq. (2) we have ignored the off-diagonal terms coupling the valence and core orbitals; these terms are discussed in Appendix II.] Then, assuming the core orbitals are unchanged upon going to a molecule, one can take the atomic $\hat{V}^{HF}$ to simulate the interaction of each valence electron in a molecule with the corresponding core electrons. However, note that $\hat{V}^{HF}$ is of of the form

$$\hat{V}^{HF}(1) = \sum_{c} [2\hat{J}_c(1) - \hat{K}_c(1)], \tag{3a}$$

where the sum is over all core orbitals ϕ_c and where

$$\hat{J}_c(1) = \int \phi_c(2) \ \frac{1}{r_{12}} \ \phi_c(2) \, d\tau_2 \tag{3b}$$

is the usual Coulomb potential and

$$\hat{K}_c(1) = \int \phi_c(2) \ \frac{1}{r_{12}} \ \hat{P}_{12} \, \phi_c(2) \, d\tau_2 \tag{3c}$$

is the usual exchange operator ($\hat{P}_{12}$ interchanges electrons 1 and 2). In particular, the exchange potential, $\hat{K}_c$, is a nonlocal or integral operator in the sense that it depends on the function on which it operates,

$$\hat{K}_c(1)\,\psi(1) = \phi_c(1) [\int \phi_c(2) \ \frac{1}{r_{12}} \ \psi(2) \, d\tau_2]. \tag{4}$$

Because of these nonlocal operators in $\hat{V}^{HF}$ the solution of a Hamiltonian for the valence electrons in a molecule is still of comparable difficulty to that of the original full-electron problem because all two-electron multicenter integrals between the valence and core orbitals have to be explicitly evaluated.[8] In order to avoid these difficulties, we want to replace the nonlocal potential $\hat{V}^{HF}$ by a <u>local</u> potential U^{HF}. In this way insofar as core-valence interactions are concerned only one-electron-like integrals would have to be evaluated, and the specific form of the core orbitals would not have to be explicitly included.

Toward this end we consider the local operator derived from $\hat{V}^{HF}$ by right-multiplying and dividing it by ϕ_v,

$$U^{HF}(\underset{\sim}{r}) = \frac{\hat{V}^{HF}\phi_v}{\phi_v} \tag{5}$$

With this definition of $U^{HF}(\underset{\sim}{r})$, ϕ_v is clearly a solution of

$$[-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + U^{HF}(\underset{\sim}{r})]\phi_v = \epsilon_v\phi_v \; . \tag{6}$$

However we want to use U^{HF} to solve for states in a molecule; hence in addition to satisfying (6) (this is just an identity), we want U^{HF} to be such that it has the same spectrum of states as $\hat{V}^{HF}$. If this is the case, we might hope that U^{HF} would describe the distortions and changes in the valence orbitals upon molecule formation as well as does $\hat{V}^{HF}$.

In discussing the spectrum of U^{HF},

$$[-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + U^{HF}(\underset{\sim}{r})]\phi_i = \epsilon_i\phi_i$$

we take U^{HF} to be independent of ϕ_i [being defined through ϕ_v in (5)]. From (5) we see that if the radial part of ϕ_v has a node at some $r_0 \neq 0$, then U^{HF} will be singular at r_0 unless $\hat{V}^{HF}\phi_v = 0$ at r_0. But since $\hat{V}^{HF}$ is nonlocal, $\hat{V}^{HF}\phi_v$ does not in general possess a zero at a zero of ϕ_v; hence $U^{HF}(\underset{\sim}{r})$ will in general have a $\frac{1}{(r - r_0)}$ singularity at a zero of ϕ_v. The Hartree-Fock valence orbitals are generally taken as orthogonal to the core orbitals, and hence the straightforward use of (5) would lead to singularities in the resulting local potential (5). In Fig. 1 we show a plot of such a local potential derived from the 2s HF orbital of Li.[9] Clearly the singularity at r_0 in the potential is not a physical one, but an artifact of the method. Because of this singularity in U^{HF}, all the solutions of (6) will have a node at exactly r_0.

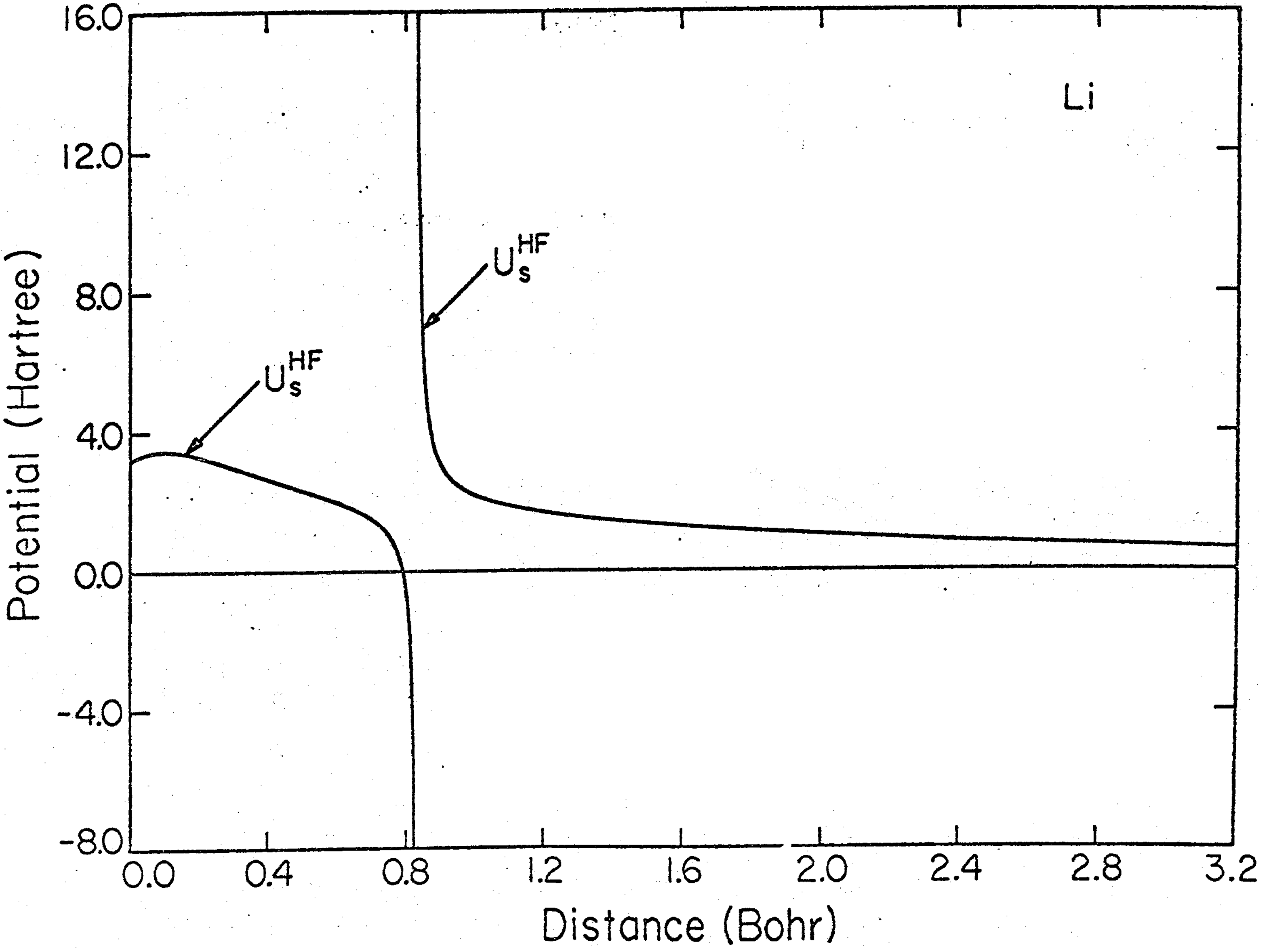

FIG. 1. The Hartree-Fock local potential for Li [From Eq. (5)]. The singularity is caused by the node in the corresponding Hartree-Fock valence orbital.

Fig. 1

An alternative to the singular HF local potential can be found in the pseudopotential formalism developed by Phillips and Kleinman.[10] Basically the idea is that the HF equation (2) can be transformed into the equivalent equation,

$$\left(-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \hat{V}^{HF} + \hat{V}^{PK}\right)\chi = \epsilon_v \chi \quad , \tag{7}$$

where

$$\hat{V}^{PK} = \sum_c (\epsilon_v - \epsilon_c) |\phi_c\rangle \langle \phi_c| \tag{8}$$

is a repulsive Hermitian nonlocal potential (called the pseudopotential) and χ is a valence-like function <u>not</u> required to be orthogonal to the core orbitals. Since both ϕ_v and ϕ_c are degenerate solutions of (7), the general form of χ must be

$$\chi = \phi_v + \sum_c a_c \phi_c, \tag{9}$$

where the coefficients a_c are <u>arbitrary</u>. In particular the a_c can generally be chosen such that χ is a <u>nodeless</u> function, and thus one can then find a corresponding nonsingular local effective potential

$$U^{HF\text{-}PK}(\underset{\frown}{r}) = \frac{\hat{V}^{HF}\chi}{\chi} + \frac{\hat{V}^{PK}\chi}{\chi} \quad . \tag{10}$$

The PK-potential (8) has been generalized by Weeks and Rice[11,12] to

$$\hat{V}^{GPK} = -\hat{H}_v^{HF}\hat{P} - \hat{P}\hat{H}_v^{HF} + \hat{P}\hat{H}_v^{HF}\hat{P} + \epsilon_v \hat{P} \quad , \tag{11a}$$

where
$$\hat{P} = \sum_c |\phi_c\rangle\langle\phi_c| \, . \tag{11b}$$

The importance of these developments is that since the transformation (9) from ϕ_v to χ leaves the total HF wavefunction and energy invariant and changes the one-particle Eq. (2) into a comparable one-particle Eq. (7), one can rigorously transfer any physical interpretation from $\hat{V}^{HF}$ and ϕ_v to $(\hat{V}^{HF} + \hat{V}^{PK})$ and χ. However, since χ is not unique, the effective <u>local</u> potential (10) is not unique.

Figure 2 shows a few of the smooth local potentials corresponding to different choices for χ. Two approaches have generally been used to choose among the infinite possibilities. One approach is to use a model potential with a physically reasonable form and to optimize parameters in this potential so as to fit experimental data [one can think of this as an attempt to approximate (10)]. Typical forms for the model potentials are the Hellmann potential (1) and generalizations of it, and Coulomb-cutoff type potentials.[11,13] A second approach would be to choose some appropriately smooth function, χ, to define a new function χ',

$$\chi' = \langle\phi_v|\chi\rangle\,\phi_v + \sum_c \langle\phi_c|\chi\rangle\,\phi_c \tag{9'}$$

so that χ' has the form of (9), and to use χ' in (10) to generate the corresponding local potential.[14]

Still, this non-uniqueness is an unsatisfactory feature. Cohen and Heine[15] suggested several criteria which might be used to obtain reasonable forms for the pseudopotential. One of their criteria which is appealing is to choose χ so as to minimize its kinetic energy. Clearly the choices are manifold, each of which might have its own characteristic set of eigenstates. Another aspect to consider is that the use of (10) for a molecular system leads to molecular orbitals which look

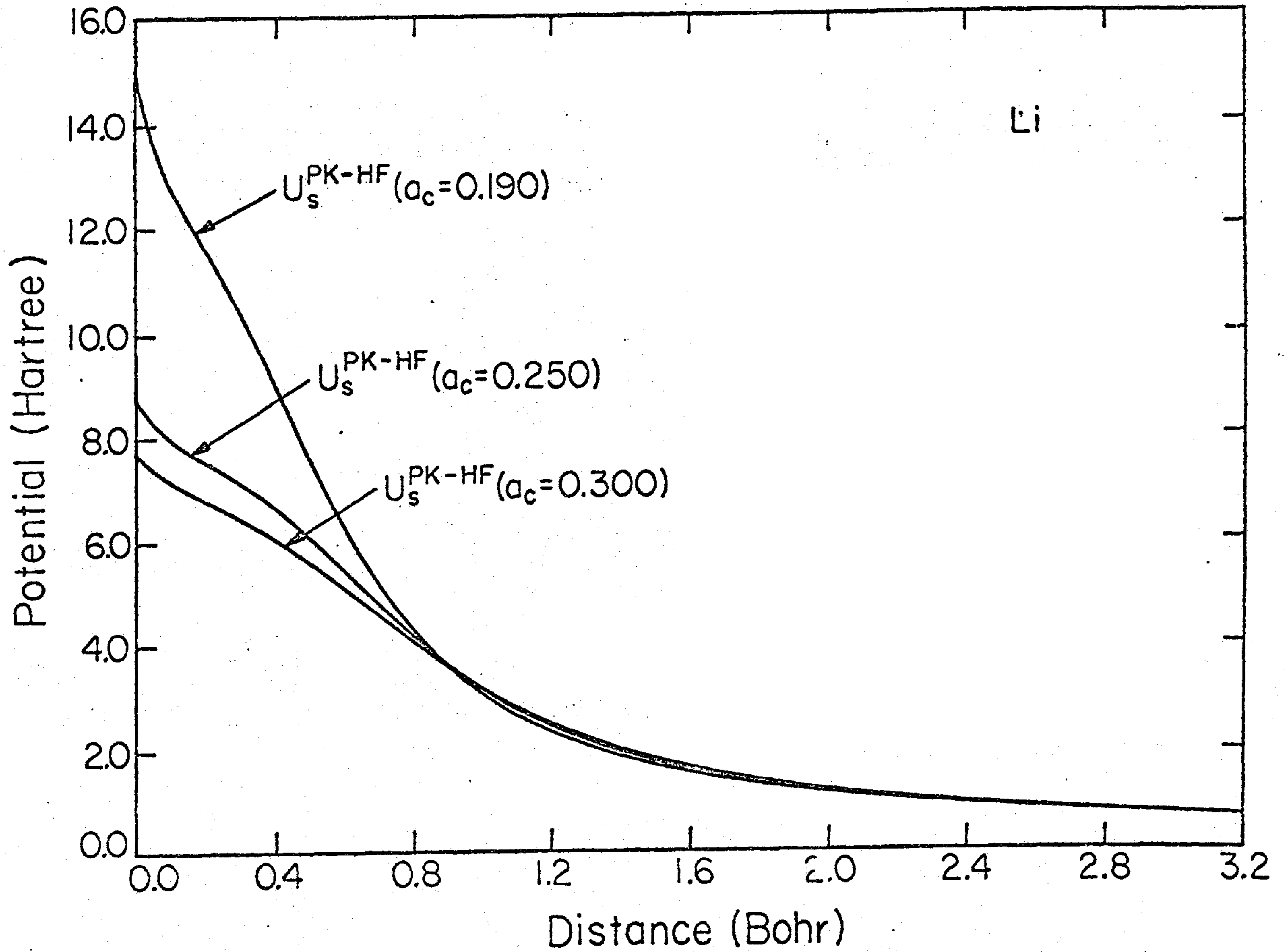

FIG. 2. Several Phillips–Kleinman Hartree–Fock local potentials. The manifold of different shapes for this local potential illustrates the nonuniqueness problem.

Fig. 2

different from those one would obtain from full-electron Hartree-Fock calculations. We will consider next an alternative approach which bypasses these ambiguities and in turn provides a basis for better understanding of (10).

III. G1 ATOMIC EFFECTIVE POTENTIALS AND THEIR USE IN MOLECULAR CALCULATIONS

In this section we will examine unique effective local potentials as derived from the G1 wavefunction and will consider their use in molecular calculations. For clarity we will consider here the Li atom, although the procedures to be outlined hold generally. The G1 wavefunction for Li can be expanded into determinants as

$$G_1(\phi_{1a}\phi_{1b}\phi_{2a}\alpha\beta\alpha) = \mathcal{A}[(\phi_{1a}\phi_{1b} + \phi_{1b}\phi_{1a})\phi_{2a}\alpha\beta\alpha] , \qquad (12)$$

where ϕ_{1a} and ϕ_{1b} are core orbitals and ϕ_{2a} is the valence orbital. We see that in contrast to the HF case, it would be a constraint to require orthogonality among any of the orbitals of (12).

The requirement that the orbitals of (12) be optimum leads to one-particle variational equations which must be solved self-consistently. The equation for the valence orbital ϕ_{2a} is

$$\hat{H}_{2a}\phi_{2a} \equiv (-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \hat{V}^{G1})\phi_{2a} = \epsilon_{2a}\phi_{2a} , \qquad (13)$$

where $\hat{V}^{G1}$ is an integral operator involving the two core orbitals. But now, in contrast to the HF case, ϕ_{2a} is the first solution of $\hat{H}_{2a}$ and is nodeless[16a] and unique.[16b] Because of this we can now proceed to find a corresponding local potential straightforwardly. First we assume (13) has been solved for ϕ_{2a} and ϵ_{2a}; then we consider the similar equation

$$[-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + U^{G1}(\underset{\sim}{r})]\phi_{2a} = \epsilon_{2a}\phi_{2a} \ , \tag{14}$$

where the nonlocal potential $\hat{V}^{G1}$ is to be replaced by a local potential $U^{G1}(\underset{\sim}{r})$. In (14) only $U^{G1}(\underset{\sim}{r})$ is unknown and we find that[2,17]

$$U^{G1}(\underset{\sim}{r}) = \epsilon_{2a} + \frac{Z}{r} + \frac{\nabla^2\phi_{2a}}{2\phi_{2a}} \ . \tag{15}$$

Note that since the valence orbital is nodeless (except at r = 0 for $\ell \neq 0$, which causes no singularity), we do not obtain a singularity in $U^{G1}(\underset{\sim}{r})$. From (13) we also obtain the alternative (but equivalent) form[18]

$$U^{G1}(\underset{\sim}{r}) = \frac{\hat{V}^{G1}\phi_{2a}}{\phi_{2a}} \ . \tag{16}$$

Factoring ϕ_{2a} into radial and angular parts

$$\phi_{2a} = \left(\frac{\theta_\ell(r)}{r}\right) Y_{\ell m}(\Omega) \ , \tag{17}$$

we obtain

$$U_\ell^{G1}(r) = \epsilon_{2a} + \frac{\ell(\ell+1)}{2r^2} + \frac{\theta''_\ell}{2\theta_\ell} \ , \tag{18}$$

where

$$\theta''_\ell(r) = \frac{d^2}{dr^2}\,\theta_\ell(r) \ .$$

The effective potential for replacing some orbitals of a system obtained as above by using the atomic GI orbitals we will refer to as the <u>G1 atomic effective potential</u> or GAEP.

In order to determine how sensitive U_ℓ^{G1} is to the angular momentum ℓ, we have used the 2s, 2p, and 3d orbitals from ab-initio calculations on the lowest ^2S, ^2P, and ^2D states of Li to derive the corresponding local potentials. (See Appendix I for details.) The resulting U_ℓ [from (18)] are shown in Fig. 3 where we see that the potentials are smooth and nonsingular and that the s potential is much more repulsive that the p and d potentials. In Fig. 4 we show $U_\ell(r)$ plus the nuclear attraction potential (for the case of U_s this is the total effective radial potential). These potentials possess the correct limiting forms of $-Z/r$ for r approaching zero and $-1/r$ for large r. Note that the total s potential is actually positive in the core region; it is this repulsion that forces the s valence orbital out of the core region. (This just reflects the radial kinetic energy of the 2s orbital; for the 2p orbital a corresponding amount of kinetic energy is separated into the angular term $\ell(\ell+1)/2r^2$.)

An important test of the validity of these local potentials is whether or not they can reproduce the excited states of (13). The results from solving (14) for the lower excited states[19] are compared in Table I with the ab-initio and experimental results. We see that the U_s, U_p, and U_d potentials reproduce quite well the respective ns, np, and nd series. From these results we conclude that the local potential derived [using (18)] from the first G1 Li valence orbital of each symmetry is a valid representation of the nonlocal potential due to the core.[20]

Since the local potential $U_\ell(\underset{\sim}{r})$ depends on the angular momentum ℓ, we need to combine these potentials into a total potential $U(\underset{\sim}{r})$ so that when $U(\underset{\sim}{r})$ operates on a general function $f(\underset{\sim}{r})$, the correct U_ℓ acts on each ℓ component of $f(\underset{\sim}{r})$; i.e.,

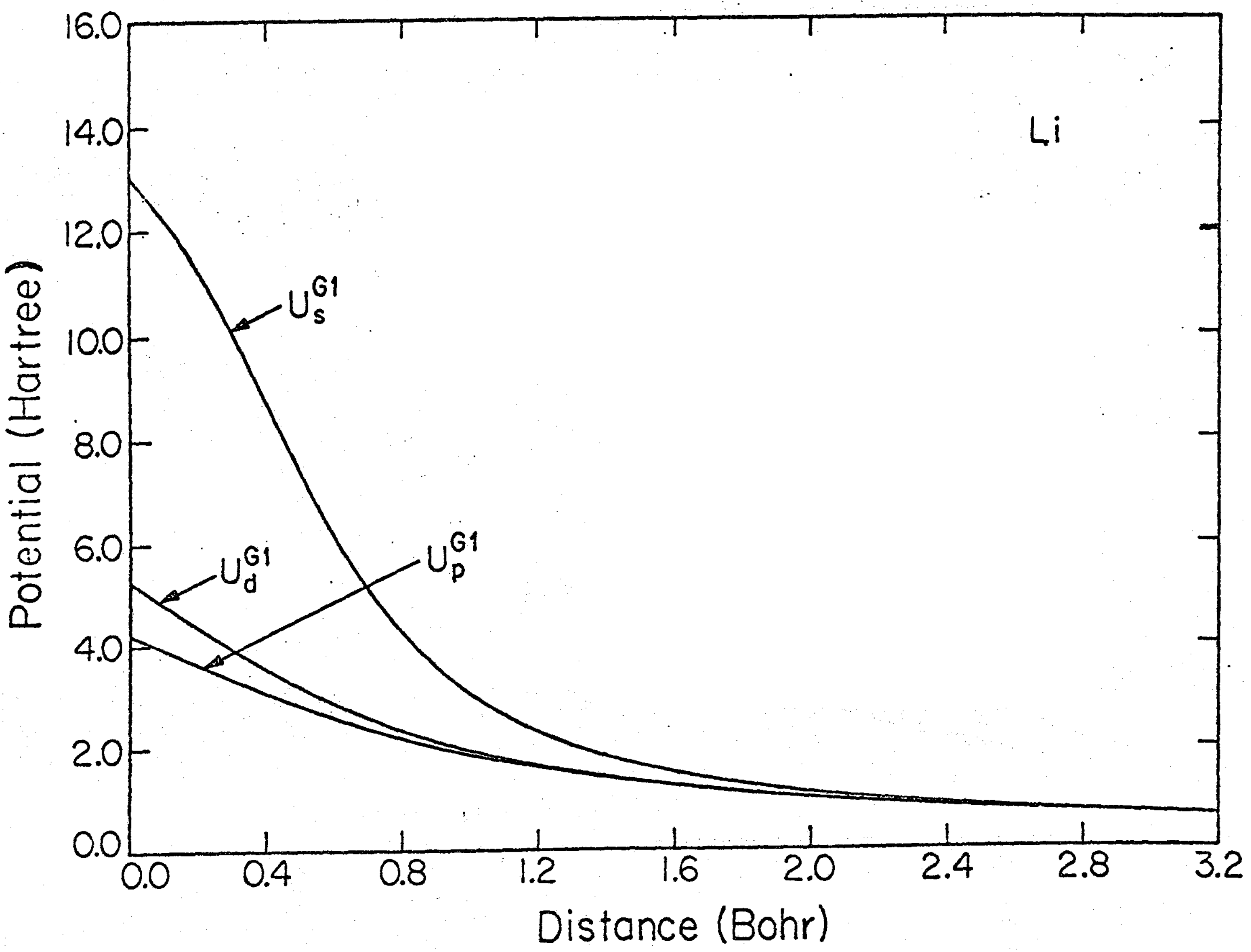

FIG. 3. The G1 *s*, *p*, and *d* local potentials for Li. These are unique *ab initio* local potentials. Note the angular momentum dependence of the potential.

Fig. 3

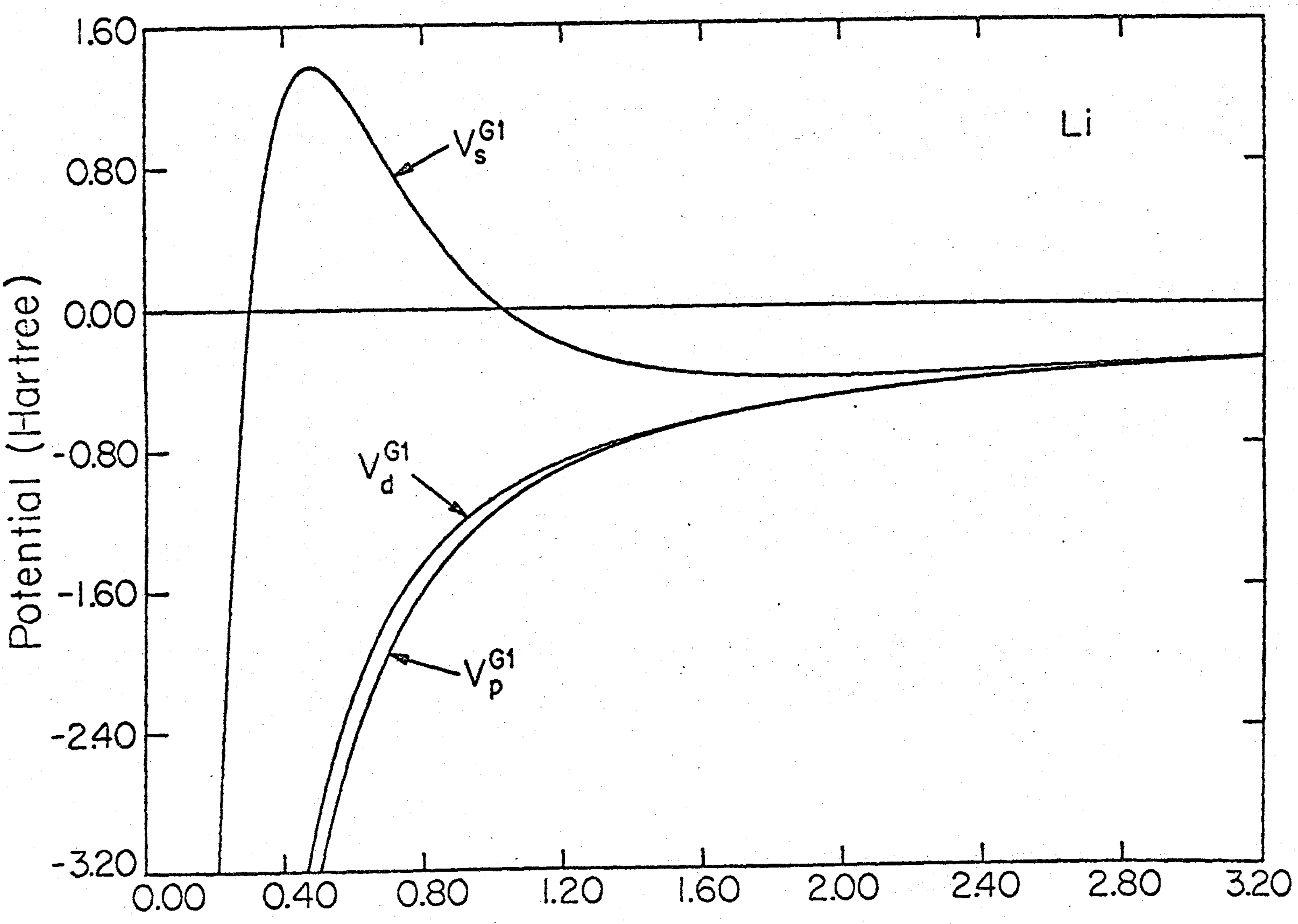

FIG. 4. The G1 *s*, *p*, and *d* local potentials of Li including the nuclear attraction potential. The *s* potential shown here is the total effective radial potential for an *s* orbital. For large *r* the potentials approach $(-1/r)$, and for small *r* they approach $(-3/r)$.

Fig. 4

TABLE I. Spectrum of Li using the G1 atomic effective potentials (GAEP) compared with the results of *ab initio* G1 calculations and experimental results. All quantities are in Hartree atomic units.[a]

ϵ_i	GAEP	G1[b]	Experiment[c]
2*s*	−0.19616	−0.19615	−0.19814
3*s*	−0.07479	−0.07376	−0.07418
4*s*	−0.03895		−0.03862
5*s*	−0.02382		−0.02364
6*s*	−0.01605		−0.01595
7*s*	−0.01136		−0.01148
2*p*	−0.12875	−0.12872	−0.13024
3*p*	−0.05685	−0.05679	−0.05724
4*p*	−0.03182		−0.03198
5*p*	−0.02030		−0.02037
6*p*	−0.01405		−0.01411
7*p*	−0.00983		−0.01034
3*d*	−0.05558	−0.05556	−0.05561
4*d*	−0.03126		−0.03127
5*d*	−0.02000		−0.02001
6*d*	−0.01388		−0.01390
7*d*	−0.00977		
8*d*	−0.00525		

[a] One atomic unit of energy ≡ 1 hartree = 27.2117 eV, and one atomic unit of length ≡ 1 bohr = 0.529177 Å; $|e| = 1$. See B. N. Taylor, W. H. Parker, and D. N. Langenberg, *The Fundamental Constants and Quantum Electrodynamics* (Academic, New York, 1969).

[b] The G1 results for the 2*s*, 2*p*, and 3*d* states are in Appendix I, and the results for the 3*s* and 3*p* states are from Ref. 37.

[c] C. Moore, *Atomic Energy Levels* (National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1949), Vol. I, p. 8.

$$U(\underset{\sim}{r})f(\underset{\sim}{r}) = \sum_{\ell,m} U_\ell(r) Y_{\ell m}(\Omega) f_{\ell m}(r) \quad , \tag{19}$$

where $f(\underset{\sim}{r})$ has been expanded as $f(\underset{\sim}{r}) = \sum_{\ell m} Y_{\ell m}(\Omega) f_{\ell m}(r)$. (The sum in (19) is from $\ell = 0$ to ∞ and from $m = -\ell$ to $+\ell$.) The general effective potential satisfying (19) is

$$U(\underset{\sim}{r}) = \sum_{\ell,m} U_\ell(r) |\ell m\rangle\langle\ell m| \quad , \tag{20}$$

where $|\ell m\rangle\langle\ell m|$ is an angular momentum projection operator (onto angular momentum ℓ) and $U_\ell(r)$ is the effective potential from (18). Although (20) involves an infinite number of U_ℓ's, in practice we find that there is an L such that

$$U_\ell(r) \cong U_L(r) \qquad \ell \geqslant L \quad , \tag{21}$$

where typically $(L - 1)$ is the largest angular momentum used by core orbitals. In particular for Li we find that $U_d \cong U_p$, and that the nd spectrum of U_d is well given by U_p. Thus for Li we will set $U_\ell = U_p$ for $\ell \geqslant 2$. In general, if we assume $U_\ell = U_L$ for $\ell \geqslant L$, we can use the closure property of the projection operators to write

$$\hat{U} \cong U_L(r) + \sum_{\ell=0}^{L-1} \sum_m (U_\ell(r) - U_L(r)) |\ell m\rangle\langle\ell m| \quad . \tag{22}$$

In Appendix I we report the data necessary to generate the s and p G1 local potentials for Li through F^{+6}.

Next, we proceed to the use of the G1 effective local potentials to replace core electrons in molecules. To illustrate the ideas we again turn to a specific case, the LiH molecule. Consider the Hamiltonian for the two valence electrons of LiH in the field of the nuclei and Li core electrons,

$$\mathcal{H}(1,2) = h_1 + h_2 + \frac{1}{r_{12}} , \qquad (23a)$$

where $h_i = -\frac{1}{2}\nabla_i^2 + \hat{U}_{Li}(\underset{\sim}{r}) - \frac{3}{r_{Li,i}} - \frac{1}{r_{H,i}}$. (23b)

In addition to the usual kinetic and potential energy terms, (23b) contains the interaction potential $\hat{U}_{Li}(\underset{\sim}{r})$ of the valence electrons with the Li core. Since the Li core orbitals are essentially unchanged upon going from the atom to the molecule, we take the interaction potential of the LiH valence electrons with the Li core to be the same as that of an Li atom valence electron with the Li core, namely, the effective potential (20).

Note that the effective valence Hamiltonian (23) is not the result of an exact reduction of the all-electron G1 description to the valence electrons, but rather is an approximate reduction motivated by physical considerations the validity of which will be investigated in the following sections. An analogous approach can also be used in the case of Hartree-Fock wavefunctions. For example, for a Hartree-Fock description of the core orbitals the two-electron Hamiltonian for the valence electrons becomes[11, 21]

$$\mathcal{H}(1,2) = \hat{P}_1\hat{P}_2[h_1 + h_2 + \frac{1}{r_{12}}]\,\hat{P}_1\hat{P}_2 , \qquad (24a)$$

where

$$h_i = -\frac{1}{2}\nabla_i^2 - \frac{3}{r} - \frac{1}{r_H} + \hat{V}_{Li}^{HF} \qquad (24b)$$

and $\hat{P}_i$ is the projection operator

$$\hat{P}_i = 1 - |\phi_c(i)\rangle\langle\phi_c(i)| , \qquad (24c)$$

which projects onto the space orthogonal to the core space of electron i. An approximation to (24a) that leads to a considerable simplification and that puts (24a) into a form comparable to (23a) is[11, 14]

$$\mathcal{H}(1,2) = h'_1 + h'_2 + \frac{1}{r_{12}} \quad , \tag{25a}$$

where

$$h'_i = -\tfrac{1}{2}\nabla_i^2 - \frac{3}{r_{Li}} - \frac{1}{r_H} + \hat{V}_{Li}^{HF} + \hat{V}_{Li}^{GPK} , \tag{25b}$$

and $\hat{V}_{Li}^{GPK}$ is the Generalized Phillips-Kleinman pseudopotential (11a). The difference between (23) and (25) is that the local representation of $(\hat{V}_{Li}^{HF} + \hat{V}_{Li}^{GPK})$ is nonunique and that, if chosen without "sufficient" repulsive character, problems can arise involving variational collapse of the valence orbitals into the core. This problem is avoided in the use of the unique G1 atomic effective potential $\hat{U}_{Li}$ since the atomic valence orbital is its lowest energy solution.

Having specified the valence electron Hamiltonian (23b) the problem remaining is to solve for the corresponding molecular valence states. To this end one could choose a Hartree-Fock or GI type of approximate wavefunction, or one could choose a configuration interaction type of wavefunction and solve the valence electron problem to a high degree of accuracy. However, in order to assess the validity of the effective valence Hamiltonian (23) we have chosen in this case to use a G1 type of wavefunction so that we might compare the resulting orbitals with those from the corresponding all-electron G1 calculation. Before giving the results, we discuss in the next section the evaluation of matrix elements of the local potential (20) necessary for the variational solution of wavefunctions for (23a).

IV. CALCULATIONAL DETAILS

In this section we will discuss the evaluation of local potential matrix elements, i.e.,

$$\langle \chi_\mu | \hat{U}(\underset{\sim}{r}) | \chi_\nu \rangle \;=\; \sum_{\ell m} \langle \chi_\mu | U_\ell(r) | \ell m \rangle \langle \ell m || \chi_\nu \rangle \quad , \tag{26}$$

where $\{\chi_u\}$ are the basis functions and the interior brackets refer to the angular spaces only. We will consider the basis functions to be either Slater-type functions or gaussian functions.[22]

In the case of Slater-type functions an integral program specific to diatomic molecules was written. We made use of the Zeta function[23,24] expansion in cases when it was necessary to expand a basis function about the center of the potential. After all angular integrations were carried out, the remaining radial integrals were evaluated by Gauss-Legendre and Gauss-Laguerre quadratures over the intervals $(0, R_{AB})$ and (R_{AB}, ∞) respectively.[24] All integrals were found to be accurate to six decimal places.

In the case of gaussian functions an integral program for polyatomic molecules was written. In contrast to the Slater-type functions, the property of gaussians[25]

$$\exp(-\alpha r_A^2)\,\exp(-\beta r_B^2) \;=\; \exp\left(-\frac{\alpha\beta}{\alpha+\beta}\,\overline{AB}^2\right)\exp(-(\alpha+\beta)r_C^2) \tag{27a}$$

allows one to avoid infinite series in the three-center integrals. Because the projection operators are fixed on the center of the potential, we use the following expansion[26] for a gaussian on center B about the center A of the potential,

$$\exp(-\zeta r_B^2) \;=\; \exp(-\zeta\overline{AB}^2)\exp(-\zeta r_A^2)\sum_{\ell=0}^{\infty}(2\ell+1)M_\ell(2\zeta\overline{AB}r_A)P_\ell(\cos\theta_A), \tag{27b}$$

where $M_\ell(\chi)$ is the Modified Spherical Bessel function of the first kind defined as[26]

$$M_\ell(\chi) \equiv \chi^\ell \left(\frac{1}{\chi} \frac{d}{d\chi} \right)^\ell \left(\frac{\sinh \chi}{\chi} \right). \tag{27c}$$

Note that since the expansion (27b) is based on the relation

$$r_B^2 = r_A^2 + \overline{AB}^2 - 2\,\overline{AB}\, r_A \cos\theta_A \,, \tag{28}$$

it is valid only if the z-axis of coordinate system A has been rotated so as to point at center B.

Using the expansion (27b), all necessary integrals are reduced to radial integrals involving the local potential $U_\ell(r)$. One approach to evaluate the integrals is direct numerical integration. First we tried Gauss-Hermite quadrature but found it not suitable for many of the integrals encountered. Then, for the calculations reported in this paper, we used a Simpson's-rule quadrature with a square-root grid distribution of points about the maximum of the integrand. However, we found that this straightforward numerical integration led to integral times of the order of ten to one hundred times longer than for the usual nuclear attraction one-electron integrals. A second approach, alternative to numerical integration, has since been developed and found to lead to integral times of the same order as those of the usual one-electron integrals. This second approach is based on least-squares fitting the local potentials with gaussian functions and then integrating analytically over the gaussian expansion functions.[27] The evaluation of some of the integrals that arise this way requires the use of the integral representation of the Modified Spherical Bessel functions $M_\ell(\chi)$.

V. RESULTS

Having established some of the properties of the G1 atomic effective potentials (20), we will now use these potentials for molecular calculations in which only the valence electrons are treated. In order to test the efficacy of these potentials we will describe the valence electrons with a G1 wavefunction and compare the resulting valence orbitals with those resulting from an all-electron G1 calculation. Thus we should have a sensitive test of the validity of the local potential approximation.

A. LiH Ground State

Consider the ground state ($X^1\Sigma$) of the LiH molecule with $R = R_e = 3.015$ Bohr. There are a total of four electrons and hence four orbitals, but we deal only with the two valence orbitals involved in bonding. One of these orbitals [Fig. 5] corresponds in the separated atoms limit to a H 1s orbital. Upon molecule formation it remains essentially a hydrogen-like orbital but with a slight increase in amplitude in the internuclear region. In contrast, the second valence orbital [Fig. 6], which in the separated-atoms limit corresponds to a Li 2s orbital, strongly sp-hybridizes towards the H atom and has a large H-like component on the H atom. The net result is a large transfer of amplitude from the Li to the internuclear region and onto the H atom, and is reflected in the large LiH dipole moment of 5.8 Debye. This latter orbital is essentially the orbital responsible for binding in LiH.[28] In Figs. 5 and 6 we show these orbitals as obtained from all-electron G1 and G1 atomic effective potential (GAEP) calculations.[29] The agreement is very good. In the same figures we also show the orbitals from a

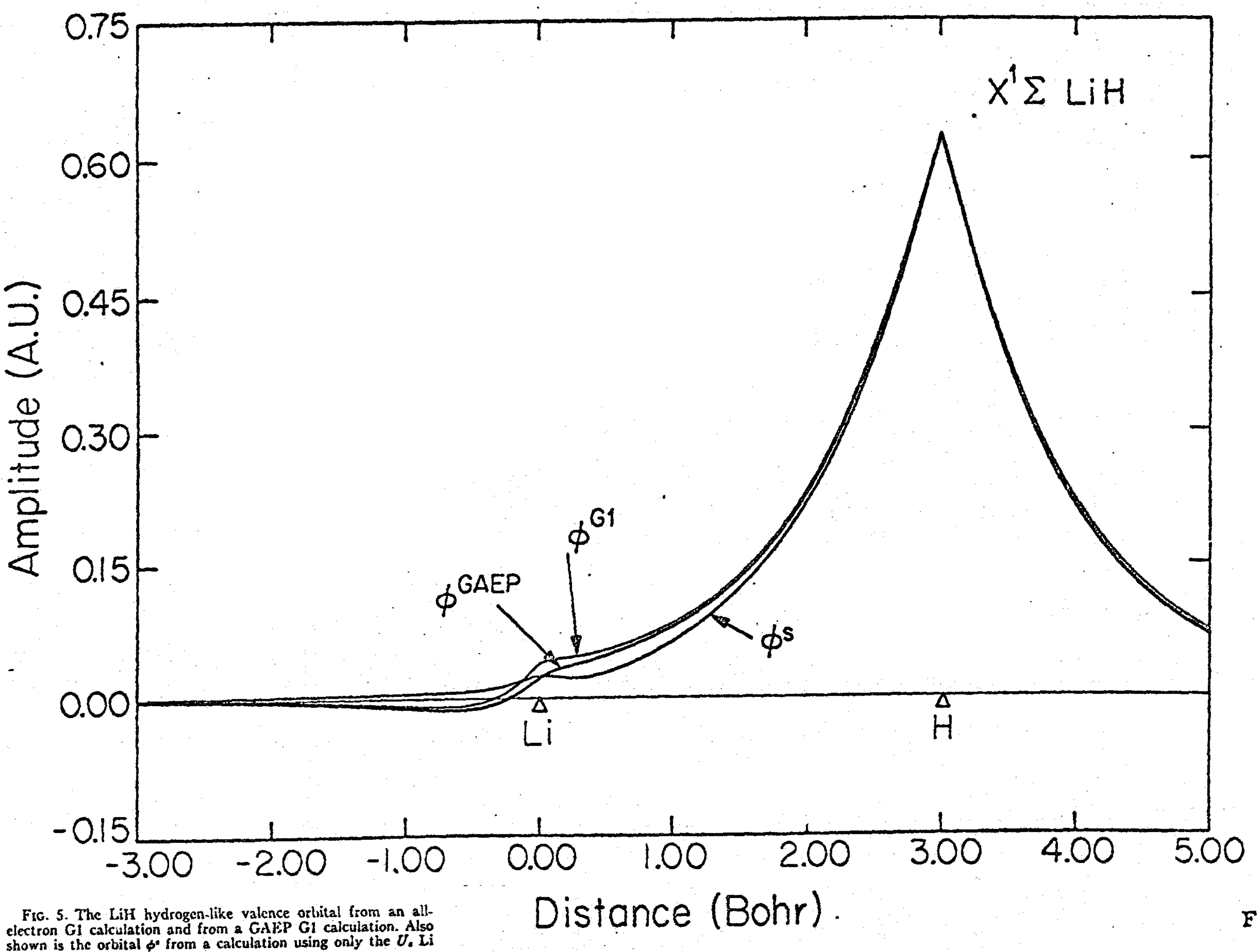

FIG. 5. The LiH hydrogen-like valence orbital from an all-electron G1 calculation and from a GAEP G1 calculation. Also shown is the orbital ϕ^s from a calculation using only the U_ℓ Li local potential.

Fig. 5

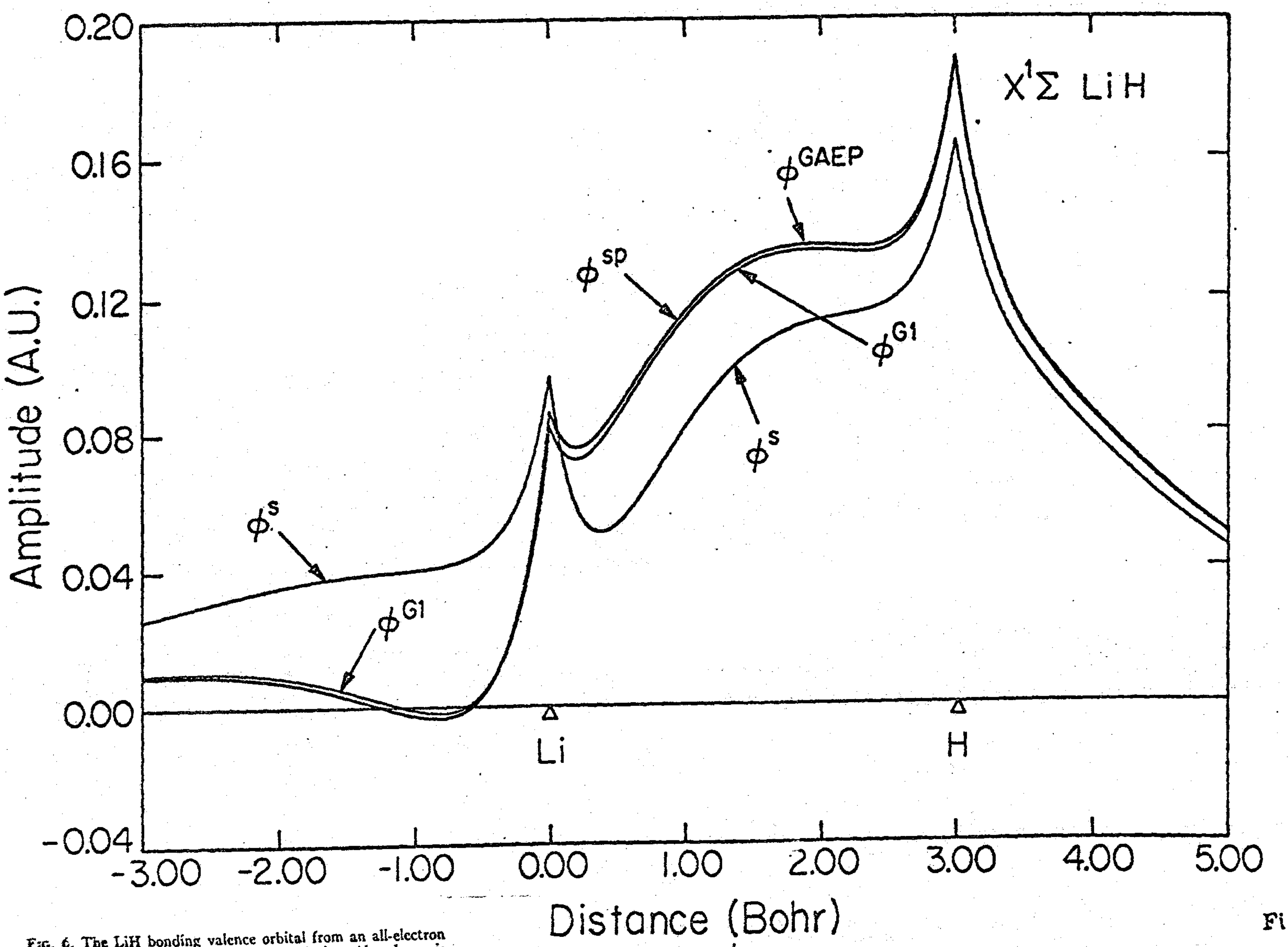

Fig. 6

FIG. 6. The LiH bonding valence orbital from an all-electron G1 calculation and from a GAEP G1 calculation. Also shown is the orbital ϕ^{sp} from a calculation using just the U_s and U_p Li potentials and the orbital ϕ^{s} from a calculation using only the U_s Li potential.

calculation using only the Li U_s potential (in this case the potential is purely local, possessing no angular momentum). The resulting orbital ϕ^s is poorly described, primarily because U_s is much more repulsive than U_p and hence leads to too little hybridization. As a result, the valence energy is higher than the GAEP energy by 0.031 Hartree. Upon using both the Li U_s and U_p potentials we obtain the orbital ϕ^{sp} which is in very good agreement with the orbital from the all-electron G1 calculation. The orbital designated ϕ^{GAEP} corresponds to using the U_s, U_p, and U_d potentials and is virtually identical to ϕ^{sp}.

In Table II we compare various electronic properties[31] for the GAEP and all-electron wavefunctions. Since the different properties sample different aspects of the electronic charge distribution, the close agreement for all these properties between the all-electron and the effective potential G1 wavefunctions indicates the usefulness of the effective potential approximation.

The total energy is calculated by adding to the valence energy the self-energy of the cores (from the atomic calculation) and coulomb interactions with other cores and nuclei (analogous to the nuclear-nuclear repulsion potential) assuming non-overlapping spherically symmetric core charge distributions. This method of estimating the total molecular energy is consistent with the philosophy behind the effective potential approximation. We have tested this approximation by calculating the four electron LiH energy as given by the corresponding four electron G1 wavefunction constructed from the two Li atom G1 core orbitals[30] and the two LiH GAEP valence orbitals, with all two-electron integrals calculated exactly. The resultant total energy of -8.01725 is in good agreement with the SCF-G1 energy, and is better than the GAEP energy estimate (see Table II).

TABLE II. Properties for $(X\,^1\Sigma)$LiH as obtained using the atomic effective potential (GAEP). Comparisons are made with *ab initio* all-electron calculations. Unless otherwise noted, all quantities are in Hartree atomic units.[a]

	GAEP[b]	G1[b]	HF[c]	CI[d]	Experiment
R	3.015	3.015	3.015	3.1047	3.015[e]
E	−8.01571	−8.01809	−7.98731	−8.06062	−8.0705[e]
D_e(eV)	1.854	1.919	1.490	2.245	2.515[e]
Dipole moment[f] (Debye)	−5.669	−5.643	−6.002	−5.965	−5.828[g]
Quadrupole moment[h] (Buckingham)	−3.545	−3.582	−4.535	−4.15[i]	
$\langle 1/r_{Li}\rangle_e$	6.0626	6.0773	6.0780	6.0748	
$\langle 1/r_H\rangle_e$	2.2226	2.2226	2.2280	2.2404	
Electric Field Gradient[j] at the Li	−0.0467	−0.0395	−0.0440	−0.0374	
at the H	0.0556	0.0610	0.0580	0.0460	
$\langle r_{Li}^2\rangle_e$	26.0023	26.1622			
Valence orbital energy, ϵ_{2a}	−0.28156	−0.28009	−0.30172		
Valence orbital energy, ϵ_{2b}	−0.47168	−0.46700	−0.30172		

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[a] One atomic unit of energy ≡ 1 hartree = 27.2117 eV, and one atomic unit of length ≡ 1 bohr = 0.529177 Å; $|e| = 1$. See B. N. Taylor, W. H. Parker, and D. N. Langenberg, *The Fundamental Constants and Quantum Electrodynamics* (Academic, New York, 1969).

[b] See Ref. 29 for the basis set.

[c] P. E. Cade and W. M. Huo, J. Chem. Phys. **47**, 614 (1967). The electronic properties were calculated with a program described in Ref. ~~31~~. 30

[d] C. F. Bender and E. R. Davidson, J. Phys. Chem. **70**, 2675 (1966).

[e] For R_e see G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950). For D_e see R. Velasco, Can. J. Phys. **35**, 1204 (1957). For atomic energies see Appendix I of footnote c.

[f] The dipole moment is defined as $\langle rP_1(\cos\theta)\rangle_{e,n}$. One atomic unit of dipole moment = 2.54177 D. 1 D = 10^{-18} *esu·cm*. The direction of the dipole is Li$^+$H$^-$.

[g] L. Wharton, L. P. Gold, and W. Klemperer, J. Chem. Phys. **37**, 2194 (1962). The value quoted is μ_e derived from μ_v data in this reference.

[h] The quadrupole moment is defined as $\langle r^2P_2(\cos\theta)\rangle_{e,n}$, with the origin at the LiH center of mass. One atomic unit of quadrupole moment = 1.34505 buckingham; 1 buckingham = 10^{-26} esu·cm^2.

[i] This value was calculated by D. P. Chong and W. B. Brown, J. Chem. Phys. **45**, 392 (1966) for a CI wavefunction by J. C. Browne and F. A. Matsen, Phys. Rev. **135A**, 1227 (1964).

[j] The electric field gradient is defined as $\langle 2P_2(\cos\theta)/r^3\rangle_{e,n}$. One atomic unit of field gradient = 3.24139 × 10^{15} esu/cm^3.

The other electronic properties,[31] such as the dipole moment, were found by calculating the valence contribution as given by the two-valence orbital wavefunction and adding to it the core contribution. This latter part, if not zero because of the spherical symmetry of the core, was calculated for the two atomic-core orbital wavefunction. However, it usually suffices (and is consistent with the effective potential assumptions) to take the core contribution to be that of a spherically symmetric charge distribution that has no amplitude outside a small region about its center. For example, we found that the explicitly calculated Li core contribution to $\langle 1/r_H \rangle$, $\langle P_1/r_H^2 \rangle$, and $\langle P_2/r_H^3 \rangle$ differed from $2/R_{LiH}$, $2/R_{LiH}^2$, and $2/R_{LiH}^3$, respectively, in the fifth to sixth decimal place.

B. Li_2 and Li_2^+

Next we consider the ground state ($X\ ^1\Sigma_g^+$) of the Li_2 molecule with $R = R_e = 5.051$ Bohr. Although there is a total of six electrons, we deal again only with the two valence orbitals involved in bonding. In the dissociated-atoms limit, each of these two valence orbitals corresponds to a Li 2s orbital. Upon molecule formation each of these orbitals sp-hybridizes towards the opposite center and thus increases the amplitude in the internuclear region. However, the orbitals remain essentially localized on their original center with little actual buildup of amplitude on the opposite Li, and a relatively weak bond is formed (experimental $D_e = 1.02$ eV). In Fig. 7 we show one of these valence orbitals (the other is symmetrically related) and we see that the agreement between the G1 atomic effective potential[32] (we used the U_s, U_p, and U_d Li potentials) and the all-electron G1[33] orbitals is very close. In Table III we present the corresponding comparison of electronic properties and again find good agreement, except for the

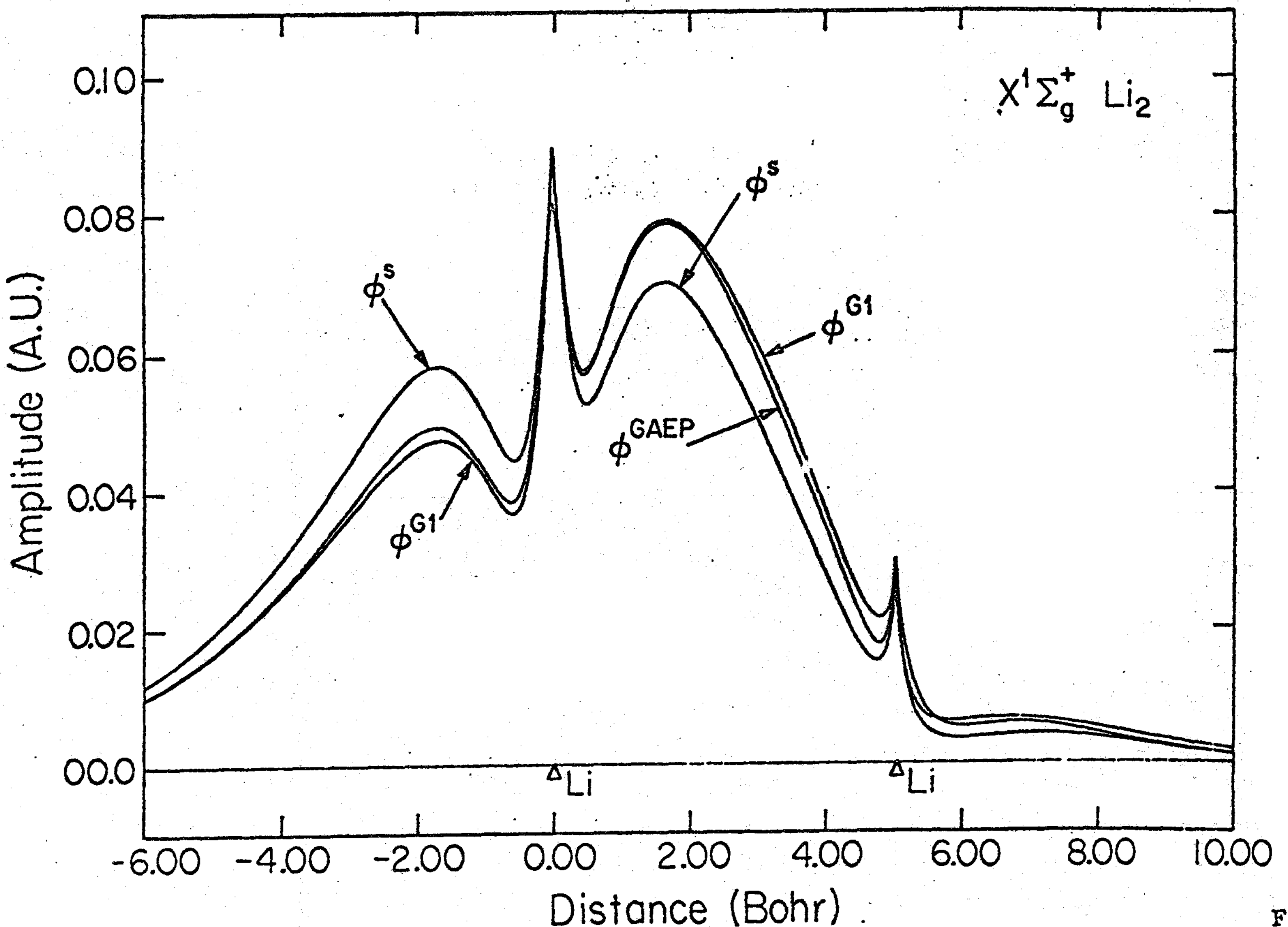


FIG. 7. One of the Li$_2$ bonding valence orbitals from an all-electron G1 calculation and from a GAEP G1 calculation. Also shown is the orbital ϕ^s from a calculation using only the U_ℓ Li local potential.

Fig. 7

TABLE III. Properties for $(X\,^1\Sigma_g^+)\,\mathrm{Li}_2$ as obtained using the atomic effective potential (GAEP). Comparisons are made with *ab initio* all electron calculations. Unless otherwise noted all quantities are in Hartree atomic units.[a]

	GAEP[b]	G1[c]	HF[d]	CI[e]	Experiment[f]
R	5.051	5.051	5.051	5.070	5.051 ~~5.049~~
E	−14.90724	−14.90998	−14.87152	−14.90260	−14.9945
D_e(eV)	0.330	0.404	0.165	1.011	1.048
Quadrupole moment (Buckingham)	10.798	11.543	13.888		
$\langle r_{\mathrm{Li}}^2\rangle_e$	104.3344		102.9948		
$\langle 1/r_{\mathrm{Li}}\rangle_e$	6.3145	6.3310	6.3372		
Electric field gradient at the Li	−0.001004	+0.001934	−0.009986		
Valence orbital energy, $\epsilon_{3\sigma}$	−0.2113	−0.2119			

[a] All units and properties are defined in footnotes to Table II.

[b] See Ref. 32. Note that the GAEP and G1 calculations were done in slightly differently contracted basis.

[c] See Ref. 33.

[d] P. E. Cade, K. D. Sales, and A. C. Wahl (unpublished).

[e] G. Das, J. Chem. Phys. 46, 1568 (1967).

[f] For R_e ~~see G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950). For~~ D_e see R. Velasco, Ch. Ottinger, and R. N. Zare J. Chem. Phys. 51, 5522 (1969). For atomic energies see Appendix I of Footnote c to Table II.

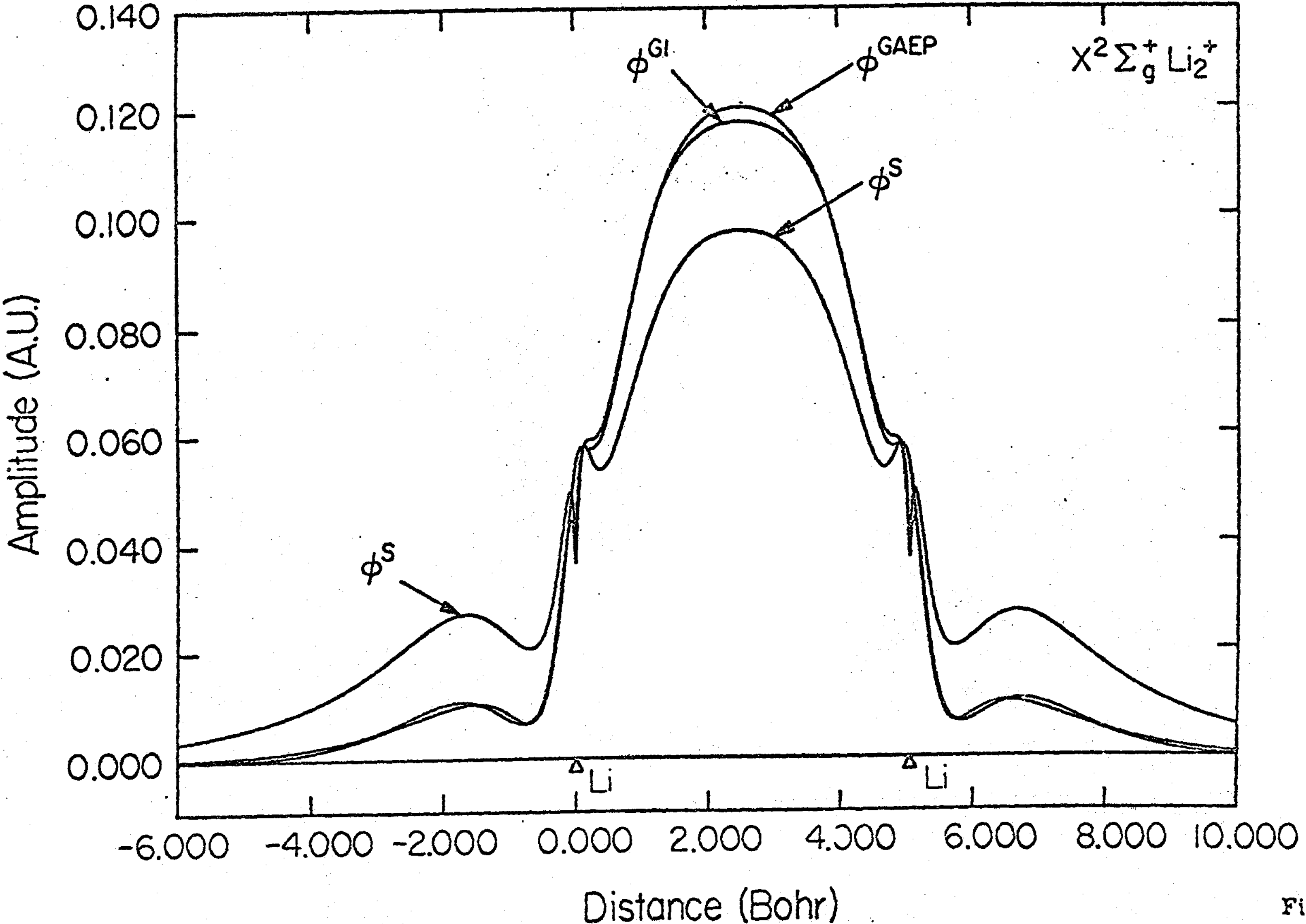


Fig. 8

FIG. 8. The Li_2^+ bonding valence orbital from an all-electron G1 calculation and from a one-electron GAEP calculation. Also shown is the orbital ϕ^s from a calculation using only the U_s Li local potential.

TABLE IV. Energy for $(X\,^2\Sigma_g^+)\mathrm{Li}_2^+$ as obtained using the atomic effective potential (GAEP). Comparisons are made with *ab initio* all-electron calculations. Unless otherwise noted all quantities are in Hartree atomic units.[a]

	GAEP[b]	GAEP[c]	G1[d]	HF[e]	Experiment
R	5.856	5.051	5.051	5.051	
E	−14.74395	−14.73625	−14.73525	−14.70971	
D_e(eV)	1.224	1.014	0.987	1.104	1.5±0.1[f]

[a] All units are defined in footnotes to Table II.

[b] This calculation corresponds to the minimum of the GAEP Li_2^+ potential curve. See Ref. 35.

[c] See Footnote b to Table III.

[d] See Ref. 33.

[e] P. E. Cade, K. D. Sales, and A. C. Wahl (to be published), quoted by M. Krauss, Nat. Bur. Std. Tech. Note 438, 18 (1967).

[f] This value was deduced using I.P. (Li) = 5.390 eV, $D_0(\mathrm{Li}_2 X\,^1\Sigma_g^+) = 1.026 \pm 0.006$ eV, and I.P. $(\mathrm{Li}_2 X\,^1\Sigma_g^+) = 4.96 \pm 0.1$ eV, resulting in $D_0(\mathrm{Li}_2 X\,^2\Sigma_g^+) = 1.46 \pm 0.1$ eV. Assuming the zero-point energy of Li_2^+ to be comparable to that of Li_2 (zero-point energy = 0.022 eV), we obtain $D_e = 1.5 \pm 0.1$. For I.P. (Li) see Footnote c to Table I. For $D_0(\mathrm{Li}_2)$ see footnote *f* to Table III. For I.P. (Li_2) see R. Velasco, Anales Real Soc. Espan. Fis. Quim. (Madrid) Ser. A **56**, 175 (1960).

total field gradient at the Li nucleus, for which the GAEP and all-electron G1 calculations yield opposite signs. However, the corresponding electronic contributions are -0.047 564 and -0.044 626 for the GAEP and all-electron G1, respectively, whereas the nuclear contribution is +0.046 561. Thus, the discrepancy is in the third decimal place of the electronic contribution[34] and the differing sign is due to the nearly canceling nuclear contribution.

In Fig. 7 we also show the orbital ϕ_s resulting from a calculation using only the U_s Li potential. Just as for LiH, this angular-momentum-independent potential leads to poor agreement with the all-electron results.

For Li_2^+ the use of the GAEP leads to a one-electron system, and assuming that the core orbitals are not involved in binding, should reproduce the experimental potential energy curve. The comparison of the results of the GAEP and all-electron G1 calculations[33] for the ground state of Li_2^+ ($X\,^2\Sigma_g^+$) are presented in Fig. 8 and Table IV. Note that in comparison to the Li_2 orbitals the Li_2^+ orbital has far more p character and has a much larger amplitude in the internuclear region, leading in turn to a stronger bond (1.5 eV as compared to 1.0 eV). Upon varying the internuclear distance[35] we found the equilibrium distance to be at 5.856 Bohr and obtained 82% of the experimental binding energy. However, our basis set contained only s and p Gaussian functions; it is well known that d functions are important in accurately describing bonding energies, and indeed are responsible for about 16% of the bonding energy in BH. Thus, it is still expected that the exact solution of the GAEP equations for Li_2^+ would account for nearly all of the bonding.

Next we consider the G1 atomic effective potential approximation in some three-center molecular systems.

C. LiH_2 ($^2\Sigma$) System.

The reaction

$$LiH + H \rightarrow Li + H_2$$

has previously been considered for linear geometries with all electron SOGI[37] calculations, leading to a saddle point near $R(Li, H_A) = 3.20$ Bohr and $R(H_A, H_B) = 3.00$ Bohr and an energy barrier of 5.14 kcal/mole.[38] Using the Li s and p G1 effective potential (GAEP) this system reduces to a three electron problem.[39] The resulting valence orbitals are compared with those from the all-electron SOGI calculations in Fig. 9, and the energies are compared in Table V. For both the orbitals and the energies the agreement is quite good. The energy barrier height obtained with the GAEP calculation is 5.43 kcal/mole, in good agreement with the ab-initio value.

D. Li_2H and Li_3 ($^2\Sigma$) Systems.

Using the Li G1 atomic effective potentials the seven and nine electron systems Li_2H and Li_3 become three electron problems leading to self-consistent calculations no more time consuming than H_3. Here we show what the GAEP SOGI valence orbitals for these systems are like.[39] There are at present no corresponding all-electron SOGI calculations with which to compare these results.

The Li_2H ($^2\Sigma$) system was considered[39] at a linear geometry with $R(Li_A, Li_B) = 5.051$ Bohr and $R(Li_B, H) = 7.0$ Bohr. The resulting SOGI orbitals are shown in Fig. 10, where we see that ϕ_2 and ϕ_3 closely resemble Li_2 bonding orbitals and ϕ_1 is essentially an H non-bonding orbital but with a node between the Li nuclei. Even for this large Li_B-H

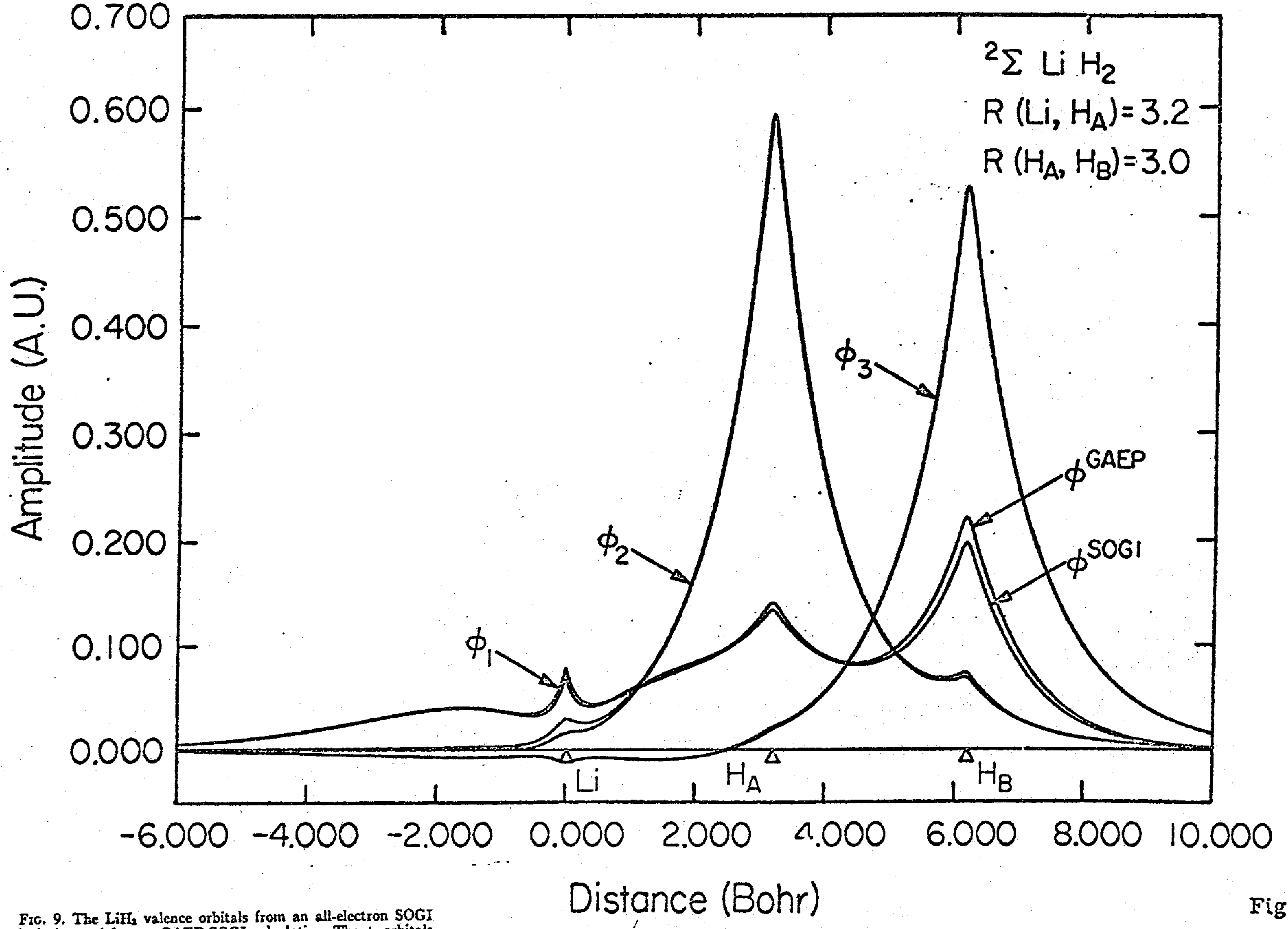


FIG. 9. The LiH_2 valence orbitals from an all-electron SOGI calculation and from a GAEP SOGI calculation. The ϕ_2 orbitals superimpose.

Fig. 9

Table V. Total energy (E) and orbital energies (ϵ_i) for LiH_2 as obtained using the G1 atomic effective potential (GAEP). Comparison is made with an *ab initio* all-electron calculation. All quantities are in atomic units.[a]

	E	ϵ_1	ϵ_2	ϵ_3
GAEP[b]	−8.509429	−0.285504	−0.478256	−0.334714
SOGI[c]	−8.509202	−0.286547	−0.481200	−0.339251

[a] All units are defined in footnotes to Table II.

[b] See Ref. 39. The LiH GAEP energy in the corresponding gaussian basis is −8.018221, and the H energy is −0.499859. This leads to an energy barrier of 0.008650 hartree = 5.43 kcal/mole.

[c] See Ref. 38. The LiH all-electron G1 energy in the corresponding gaussian basis is −8.017537 and the H energy is −0.499859. This leads to an energy barrier of 0.008193 hartree = 5.14 kcal/mole.

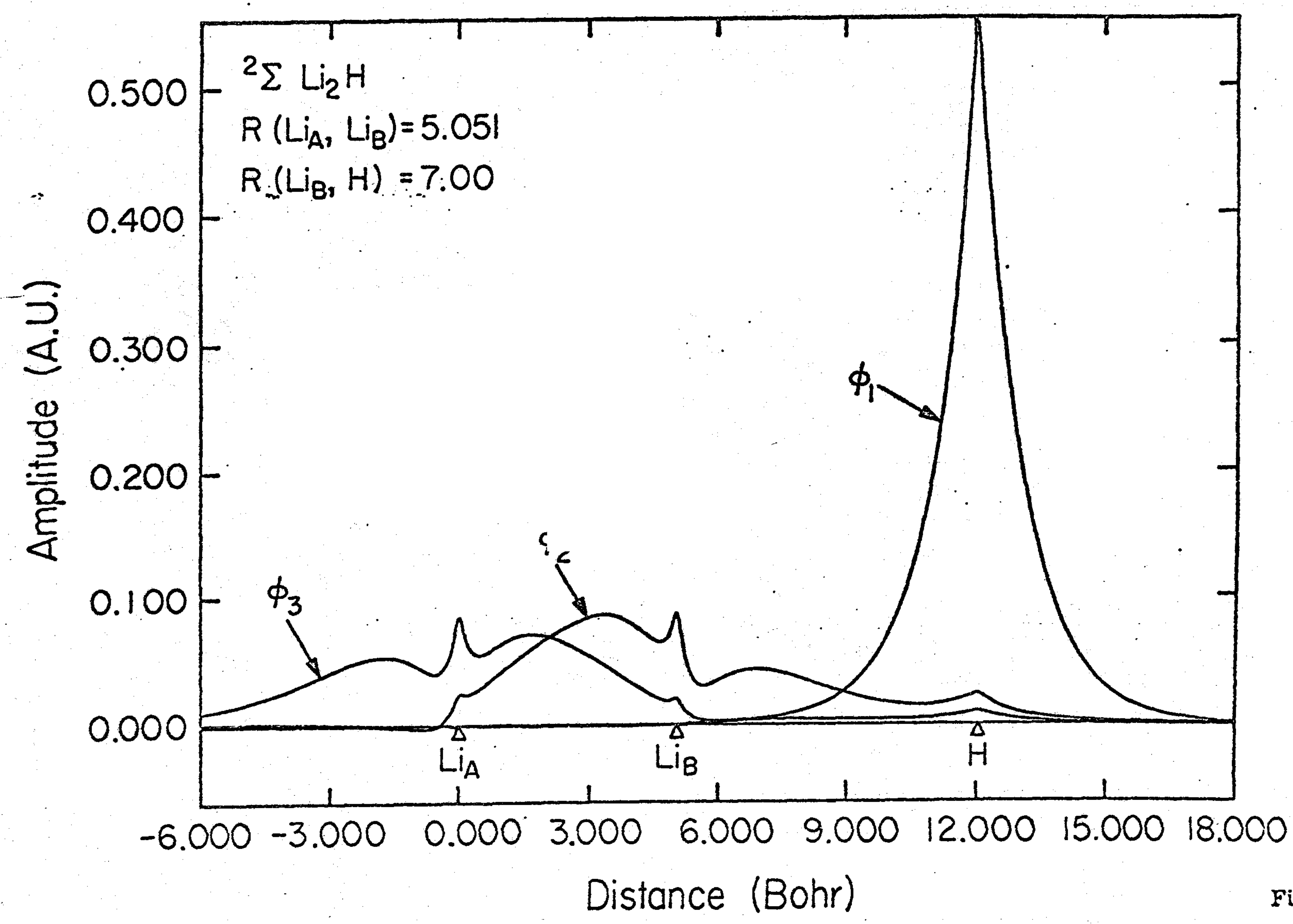


Fig. 10

FIG. 10. The Li$_2$H valence orbitals from a GAEP SOGI calculation.

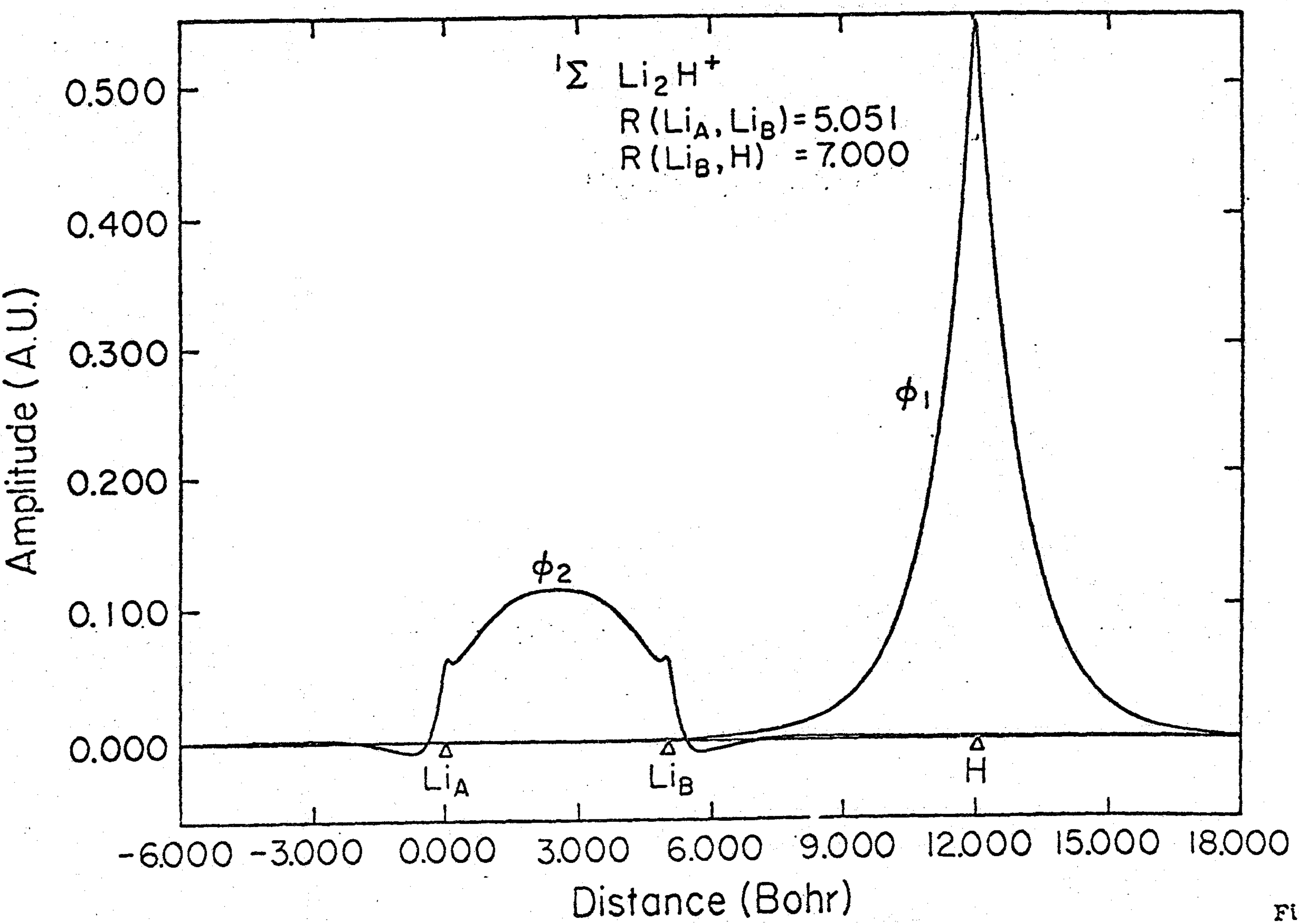


Fig. 11

FIG. 11. The Li_2H^+ valence orbitals from a GAEP G1 calculation. Note that orbital ϕ_1 is essentially unchanged from Li_2H.

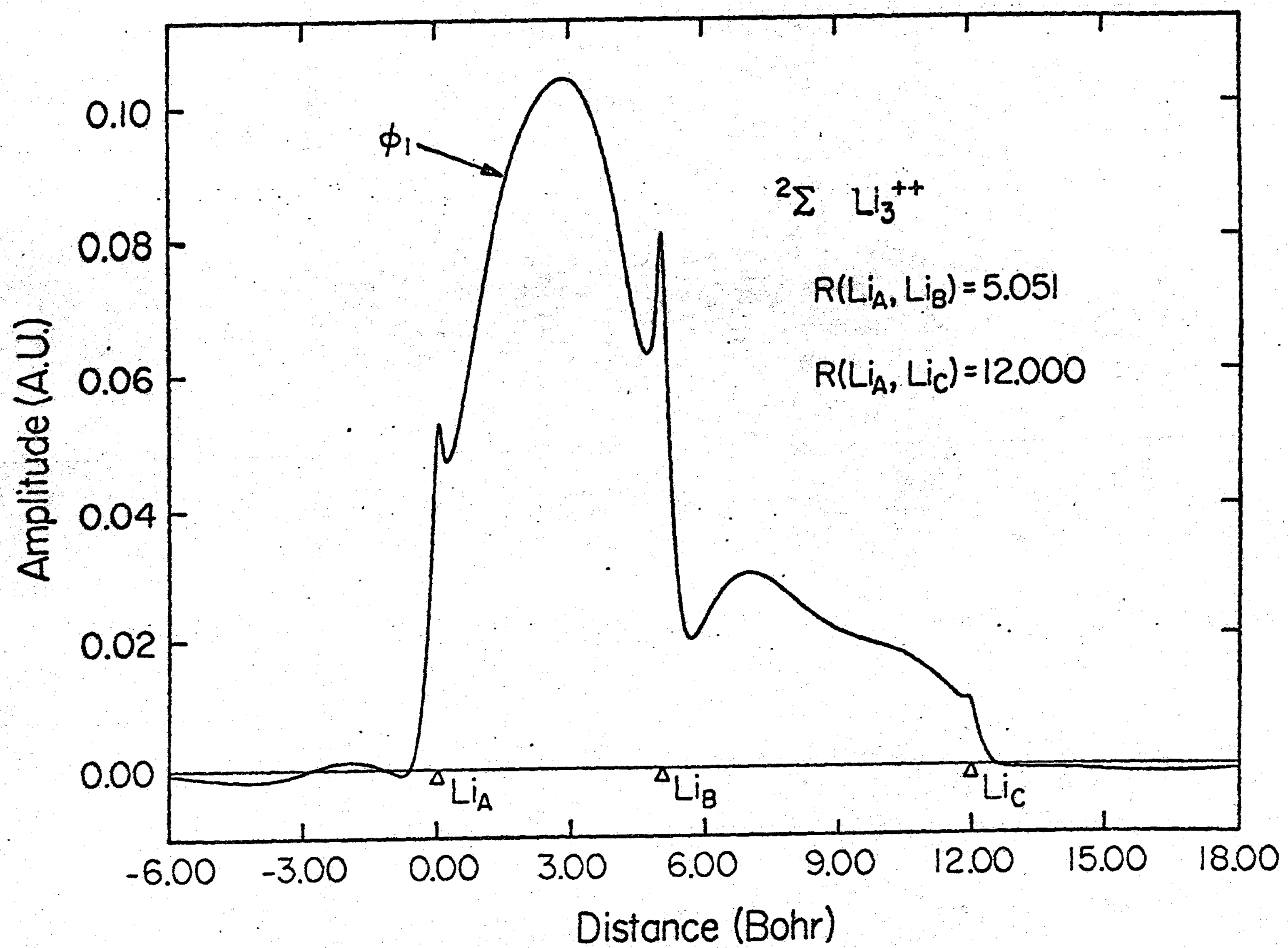


Fig. 12

FIG. 12. The Li_3^{++} valence orbital from a one-electron GAEP lculation. Note that orbital ϕ_1 is essentially unchanged from e ϕ_1 orbital in Li_3.

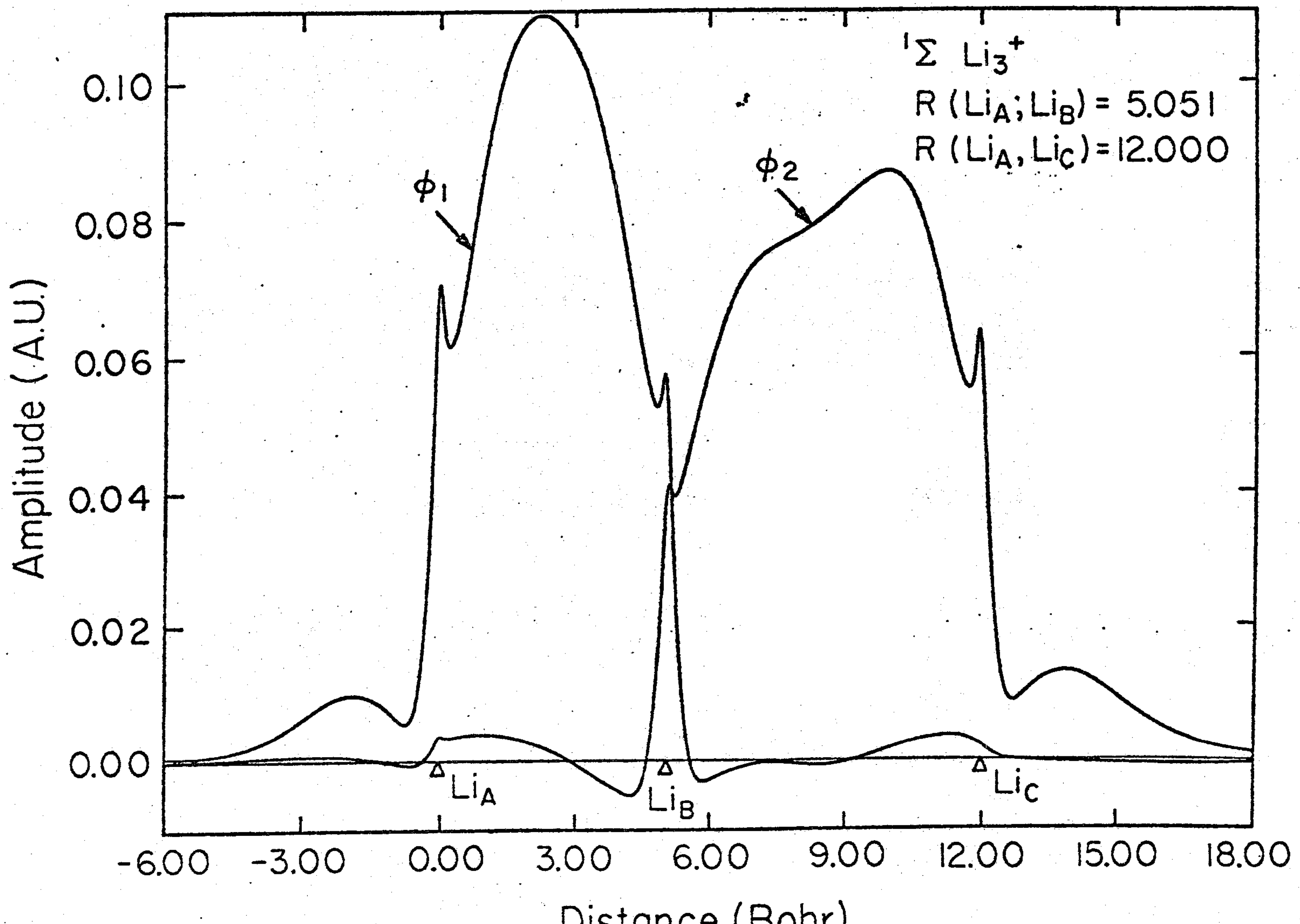


Fig. 13

FIG. 13. The Li_3^+ valence orbitals from a GAEP G1 calcuation. Note the correspondence to the ϕ_1 and ϕ_2 orbitals of Li_3.

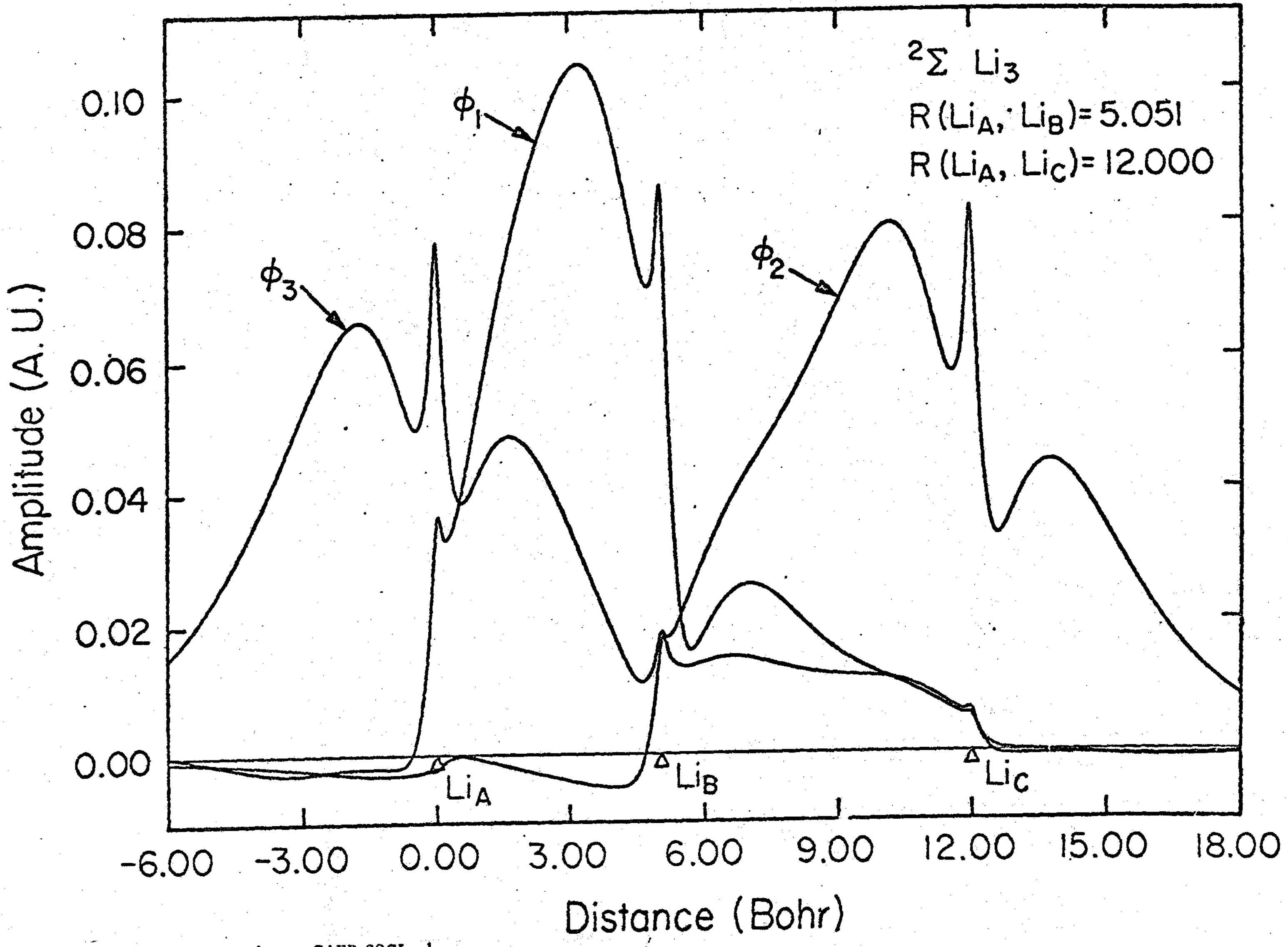


FIG. 14. The Li_3 valence orbitals from a GAEP SOGI calculation. The orbitals are labeled in order of increasing orbital energies.

Fig. 14

distance, the Li_2-like orbital ϕ_2 has delocalized a bit onto the H atom. The orbitals for the $^1\Sigma$ state of Li_2H^+ at the same geometry are shown in Fig. 11 where we see that the system is essentially an isolated Li_2^+ molecule and an isolated H atom.

The Li_3 ($^2\Sigma$) system was considered[39] for a linear geometry with $R(Li_A, Li_B) = 5.051$ Bohr and $R(Li_B, Li_C) = 6.949$ Bohr. First in Fig. 12 we consider the single valence orbital of Li_3^{++}, which is similar to a Li_2^+ orbital in the region between Li_A and Li_B with a little extra component between Li_B and Li_C. In Fig. 13 we consider next the orbitals for the $^1\Sigma$ state of Li_3^+, and we find that they are similar to Li_2^+ orbitals between Li_A and Li_B, and between Li_B and Li_C, respectively. Upon introducing the third electron to obtain the $^2\Sigma$ state of Li_3 we see from Fig. 14 that the third orbital is localized near center Li_A but hybridized away from center Li_B. At the same time, orbitals ϕ_1 and ϕ_2 are distorted toward the right, the net result being that ϕ_1 is quite similar to the orbital of Li_3^{++}.

E. Be Ground State.

In Be atom we have two core-like orbitals which are relatively unchanged upon ionization or molecule formation and two valence orbitals, responsible for the chemical properties of Be. Here we will replace the core orbitals by using the G1 effective potentials obtained for Be^+ (see Appendix I). Using this GAEP for Be leads to a two-electron system, the G1 orbitals for which are compared in Fig. 15 with the all electron G1 results.[41,42] The energies are compared in Table VI, where we see that the agreement here is not quite

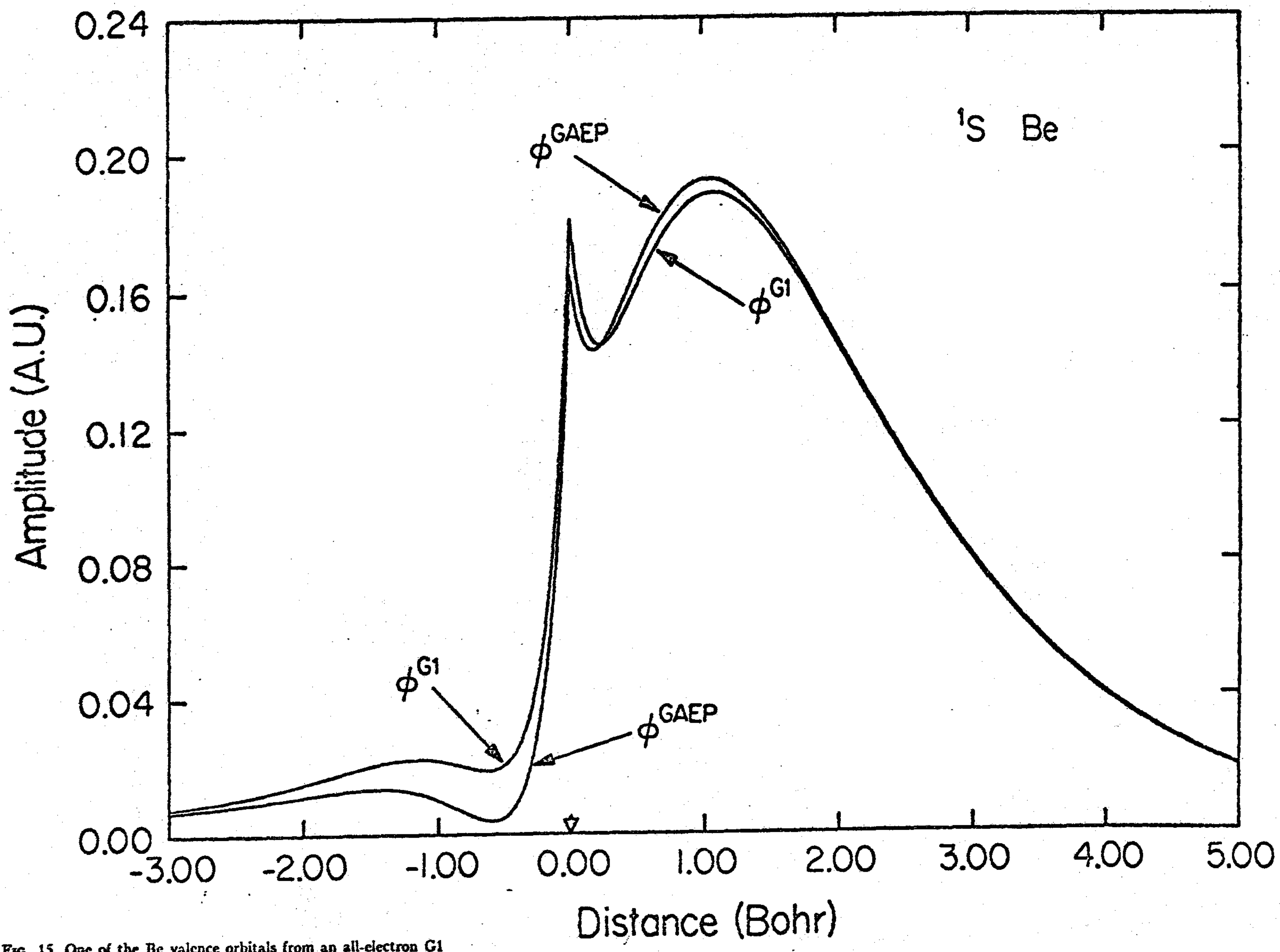


Fig. 15

FIG. 15. One of the Be valence orbitals from an all-electron G1 calculation and from a GAEP G1 calculation.

Table VI. Energies for Be, B, BH, and BH_2 as obtained using the G1 atomic effective potential (GAEP). Comparisons are made with *ab initio* all electron calculations. Unless otherwise noted all quantities are in atomic units.[a]

Be ^1S	E	ϵ_1	ϵ_2		
GAEP[b]	−14.59715	−0.34502	−0.34502		
G1[b]	−14.60432	−0.35071	−0.35071		
HF[c]	−14.57302	−0.30927	−0.30927		
Experiment[d]	−14.6685	···	···		
B ^2P	E	ϵ_1	ϵ_2	ϵ_3	
GAEP[e]	−24.54085	−0.53799	−0.53799	−0.30034	
G1[f]	−24.56077	−0.55054	−0.55054	−0.30511	
HF[e]	−24.52905	−0.49468	−0.49468	−0.30987	
Experiment[d]	−24.6581				
BH$X\,^1\Sigma$	E	ϵ_1	ϵ_2	ϵ_3	ϵ_4
GAEP[g]	−25.15105	−0.47496	−0.47496	−0.55720	−0.64773
G1[f]	−25.16336	−0.48532	−0.48532	−0.54713	−0.63515
HF[h]	−25.13137	−0.34837	−0.34837	−0.64816	−0.64816
Experiment[d]	−24.6581	···	···	···	···
$BH_2\,^2A_1$	R(BH)	θ(HBH)	E		
GAEP[i]	2.229907[j]	120°	−25.78470		
GAEP[i]	2.229907[j]	131°	−25.78554		
GAEP[i]	2.229907[j]	140°	−25.78435		
CI[k]	2.25	120°	−25.78891		
CI[k]	2.25	135°	−25.79016		
HF[k]	2.25	120°	−25.73885		
HF[k]	2.25	135°	−25.73958		

[a] All units are defined in footnotes to Table II.

[b] See Ref. 41.

[c] E. Clementi, C. C. J. Roothaan and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[d] See Appendix I of Footnote c of Table II.

[e] See Ref. 43.

[f] See Ref. 44.

[g] See Ref. 45.

[h] See Footnote c of Table II.

[i] See Ref. 46.

[j] 2.229907 bohr = 1.18 Å, which is the experimental bond length. See Ref. 47.

[k] See Ref. 48.

as good as in the previous cases. The discrepancy here is probably mainly due to the presence of a term in $\hat{V}^{G1}$ that depends upon ϕ_v in that it is proportional to ϵ_v. In cases in which ϵ_v changes significantly (as in going from Be^+ with $\epsilon_v = -0.665$ to Be with $\epsilon_v = -0.351$), U^{G1} might lead to a poorer approximation to $\hat{V}^{G1}$. Since this extra term proportional to ϵ_v is also proportional to the overlap between the core orbital and the valence orbital, it should be of much less importance for excited states.

The Be (^1S) calculations reported here are spatial-symmetry unrestricted G1 calculations in which the orbitals are allowed to mix different angular momentum components subject to minimization of the total energy. The resulting optimum orbitals have the shape of sp-like hybrids (about 19% p character).[42] One of these orbitals is shown in Fig. 15 (the other is symmetrically related).

F. BH ($X^1\Sigma$) and BH_2 (X^2A_1)

In the same manner as for Be ^1S, we considered B ^2P as a three-electron system using the G1 effective potentials obtained from B^{+2} (see Appendix I).[43] In agreement with the corresponding all-electron G1 result,[44] two of the orbitals are singlet coupled sp-like hybrids (16% p character), analogous to the Be result, and the third orbital is a p orbital orthogonal to the sp-hybrid pair. Similarly, BH becomes a four-electron problem in the field of the B and H nuclei and the B^{+2} G1 atomic effective potential.[45] The bonding orbitals for the $X\,^1\Sigma^+$ state are shown in Figs. 16 and 17, where the GAEP and all-electron G1 results[44, 45] are compared; we see that the comparison is good. These bonding orbitals can be considered as deriving from the B p

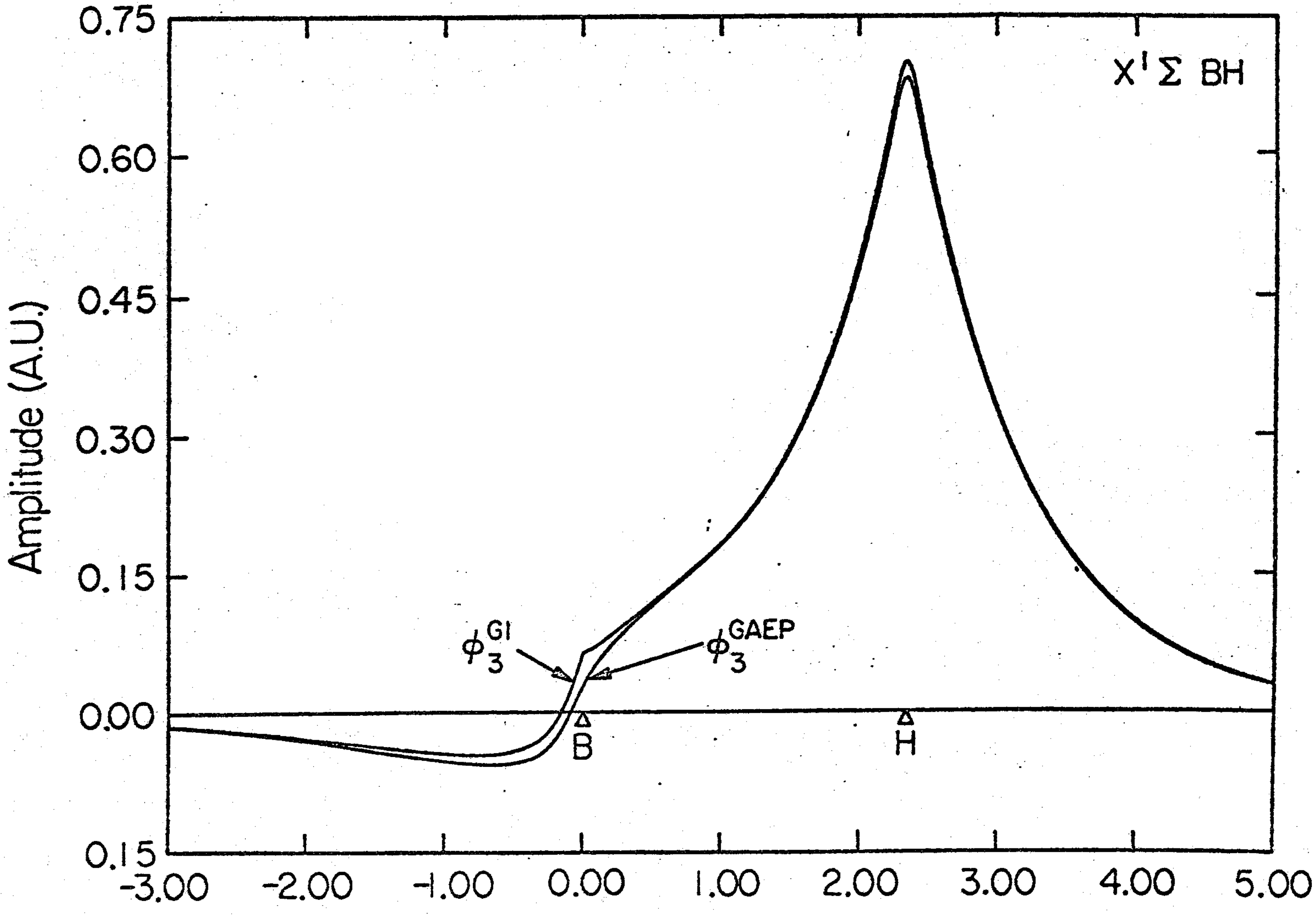


FIG. 16. The hydrogenlike bonding orbital of BH from all-electron G1 and GAEP G1 calculations.

Fig. 16

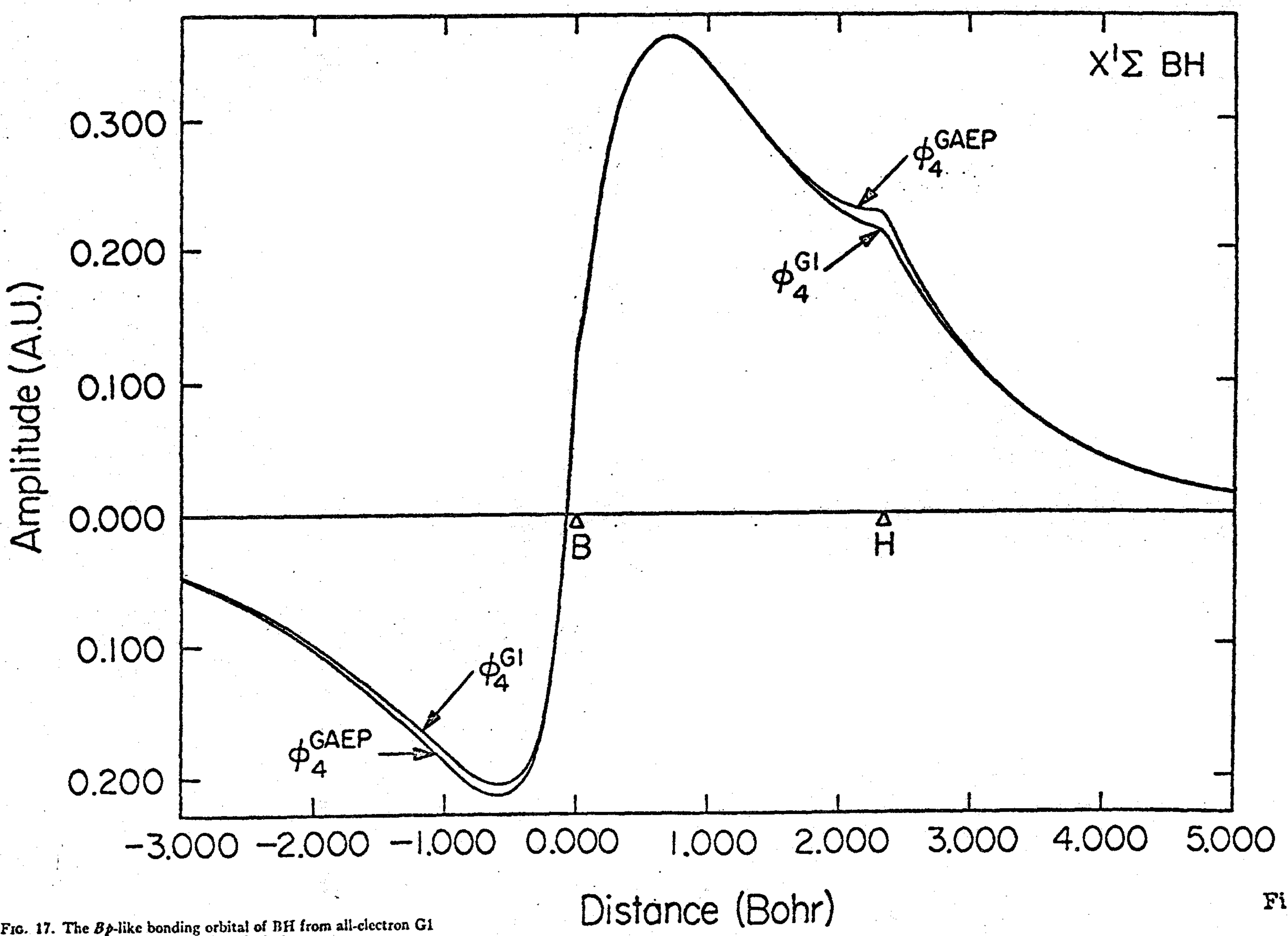


Fig. 17

FIG. 17. The Bp-like bonding orbital of BH from all-electron G1 and GAEP G1 calculations.

and the H s orbitals of the separated atoms. The other valence pair of the B bends back as shown in Fig. 18, where the GAEP and all-electron G1 results are compared (Figs. 18 and 19 each show one of the pair of orbitals, the other is symmetrically related). The spatial orientation of these latter orbitals is reminiscent of the sp^2-like hybrids (their composition is about 76% s, 17% p_x, and 6% p_z character), and they are separated by an angle of about 127°. The corresponding energies are compared in Table VI, where again the agreement is good.

Finally, using the B^{+2} GAEP we consider BH_2 as a five-electron system.[46] The experimental geometry[47] for the $^2A_1$ state of BH_2 is R(B, H) = 1.18 Å and θ(HBH) = 131°. The orbitals for this geometry are given in Fig. 20, where the orbitals of Fig. 20a and 20b correspond to one BH-like bonding pair (the other pair is symmetrically related), and Fig. 20c shows the non-bonding orbital. Upon consideration of the BH orbitals shown above one can readily rationalize the present BH_2 results by considering the coupling of a second H atom to one of the non-bonding BH orbitals. Thus, a strong second BH-like bond is formed resulting in a bent BH_2 molecule.

We varied the angle θ(HBH) keeping the bond length fixed and found the minimum angle to be at 129°, which is in good agreement with the experimental value and coincides with the result of a recent all-electron CI calculation by Bender and Schaefer.[48]

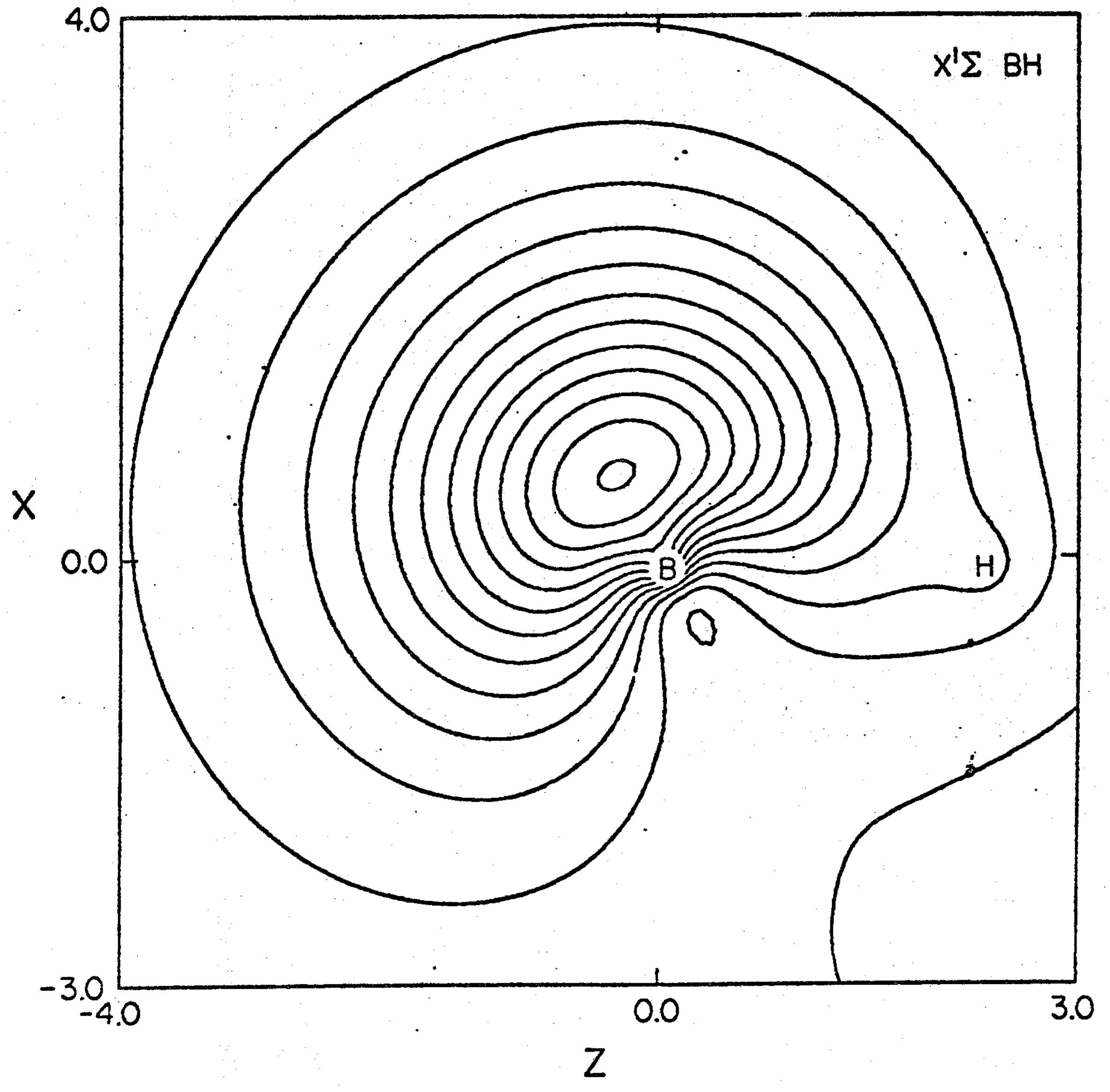


Fig.18

FIG. 18. One of the two BH nonbonding orbitals from a GAEP G1 calculation. Compare with the corresponding all-electron result in Fig. 19.

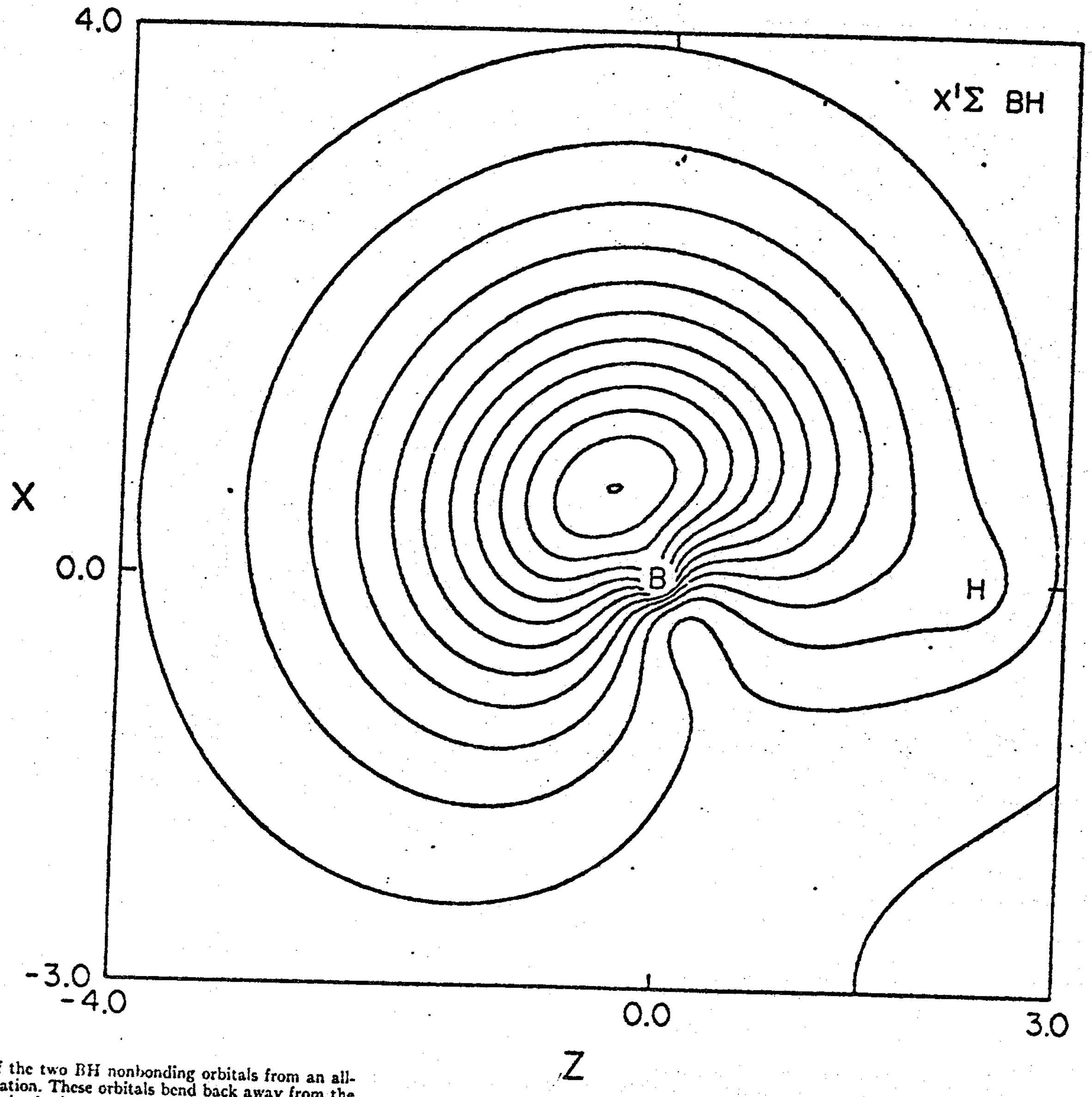


Fig. 19. One of the two BH nonbonding orbitals from an all-electron G1 calculation. These orbitals bend back away from the internuclear region in the form of sp^3-like hybrids.

Fig. 19

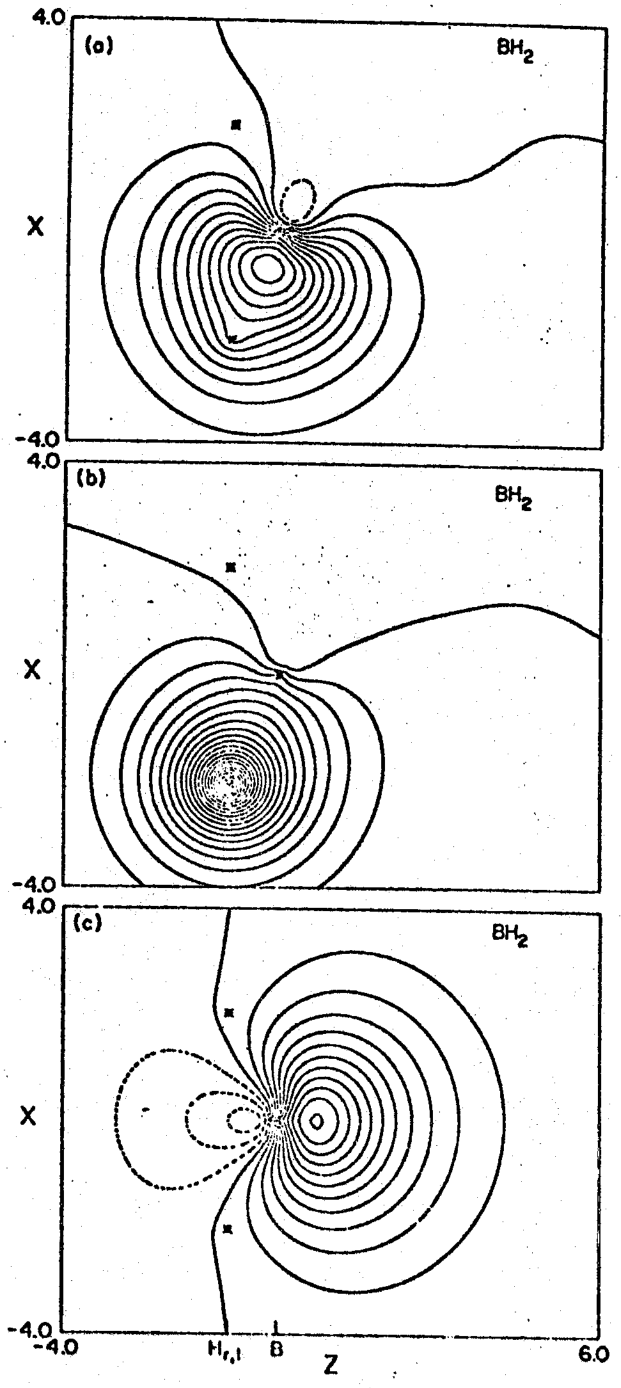


Fig. 20

Fig. 20. The BH_2($\measuredangle$HBH = 131°) valence orbitals from a GAEP GI calculation. Figures (a) and (b) show one pair of bonding orbitals; the other pair is symmetrically related and concentrated in the other bonding region. Figure (c) shows the nonbonding orbital, which points away from both bond regions.

VI. CONCLUSIONS

Unique hermitian G1 local potentials derived directly from ab initio G1 atomic calculations have been used to replace core electrons of first-row atoms in molecular systems. The molecular problem is then reduced to the description of the valence electrons in the field of the cores and nuclei. Upon solving for the GI wavefunction for the valence electrons of molecular systems such as LiH, Li_2, BH, and LiH_2 we find very good agreement with the corresponding all-electron SCF-GI results.

The approach used here differs from previous approaches in that the G1 local potential used is unique, ab initio, and that its angular momentum dependence is properly taken into account. Further, upon using it to replace core-electrons in molecules, the GI solution for the valence orbital has been directly compared to the ab initio all-electron GI solution, thus providing a direct test of the approximations involved. In addition, one-electron properties, such as the dipole moment, and geometric parameters, such as the bond angle, seem to be accurately predicted. Thus we may reasonably expect that the use of effective potentials to replace core electrons as described here may lead to ab initio quality results in larger systems, i.e., large cores and many centers, but with consideration of only the valence electrons.

In summary, the use of ab initio effective local potentials as described here yields wavefunctions which are bona fide approximations to the wavefunction of a system.

APPENDIX I. G1 Effective Potentials for Li through F Atoms

In Table A-I we present the data required to generate the U_s and U_p G1 atomic effective potentials. These potentials replace the He-like cores of the first row atoms and are taken from the ^2S and ^2P G1 wavefunctions for the ions Li, Be^+, B^{+2}, C^{+3}, N^{+4}, O^{+5} and F^{+6}. The basis set used to obtain the G1 wavefunctions for the ^2S states consists of seven optimized s-like Slater functions,[22] and for the ^2P states this s set was augmented by five optimized p-like Slater functions. These basis sets satisfy the cusp condition, and the most diffuse basis function has an exponent of $\sqrt{2|\epsilon_v|}$. The total G1 energy (E) and the virial ratio (V/2E) for each three-electron wavefunction are also included in Table A-I. In Table A-II we present the data to generate the Li U_d potential. Since we found that $U_d \approx U_p$ for Li, we have not generated the U_d for the other systems.

We find that the optimum orbital exponents of these basis functions are very nearly a linear function of the nuclear charge (Z). A few exceptions were found, and in those cases a change to an extrapolated value raised the energy very slightly (sixth decimal place). The parameters for a least-squares fit of the exponents to a linear function,

$$\zeta_i = a_i Z + b_i$$

are given in Table A-III. These adjustments in the orbital exponents would lead to a negligible change in the atomic energies.

TABLE A-I. Data for the G1 atomic effective potentials of Li through F. All quantities are in Hartree atomic units.

			Li		Be^{+}		B^{+2}		C^{+3}		N^{+4}		O^{+5}		F^{+6}
n	ℓ	ζ	ϕ_{2s}	ζ	ϕ_{2s}	ζ	ϕ_{2s}	ζ	ϕ_{2s}	ζ	ϕ_{2s}	ζ	ϕ_{2s}	ζ	ϕ_{2s}
1	0	3.0	0.031949	4.0	0.050037	5.0	0.060899	6.0	0.068092	7.0	0.073175	8.0	0.076959	9.0	0.079884
4	0	5.32615	-0.000891	7.54155	-0.000381	9.67650	-0.000219	11.85814	0.000118	14.03332	0.000135	16.2064	0.000161	18.3795	0.000171
3	0	5.3395	0.000691	6.95784	0.000835	9.22921	0.000656	11.4169	0.000575	13.66038	0.000473	15.8899	0.000407	18.11944	0.000355
3	0	2.9847	0.018339	4.16569	0.018854	5.33279	0.018149	6.49243	0.015675	7.66647	0.014604	8.8355	0.013474	10.0045	0.012519
3	0	1.37796	0.266959	2.1266	0.296325	2.87916	0.291747	3.68112	0.265630	4.43172	0.264381	5.1979	0.257940	5.96413	0.252736
3	0	0.84345	0.634049	1.41861	0.606889	2.00338	0.588908	2.61236	0.587217	3.19233	0.572564	3.7814	0.564004	4.3704	0.556696
3	0	0.62634	0.141538	1.154	0.113583	1.667	0.124501	2.175	0.146662	2.69533	0.158182	3.21123	0.170264	3.72713	0.180608
ϵ_{2s}			-0.196152		-0.665887		-1.389546		-2.364666		-3.590495		-5.066721		-6.793194
$E_{^2S}$			-7.447560		-14.291628		-23.389912		-34.739791		-48.340453		-64.191556		-82.292935
$(V/2E)_{^2S}$			1.000009		1.000003		1.000001		1.000001		1.000000		1.000000		0.999999
n	ℓ	ζ	ϕ_{2p}	ζ	ϕ_{2p}	ζ	ϕ_{2p}	ζ	ϕ_{2p}	ζ	ϕ_{2p}	ζ	ϕ_{2p}	ζ	ϕ_{2p}
2	1	1.5	0.133337	2.0	0.304385	2.5	0.427220	3.0	0.514952	3.5	0.578845	4.0	0.628426	4.5	0.667634
4	1	2.10427	0.044191	3.51069	0.017641	5.03395	0.006345	5.4610	0.008379	7.94416	0.003246	9.4090	0.002632	10.87384	0.002257
4	1	1.27373	0.331132	2.16015	0.286890	3.05208	0.205242	3.8679	0.147207	4.7571	0.112864	5.6245	0.086849	6.49196	0.069033
4	1	0.76193	0.570838	1.41949	0.477862	2.06721	0.433468	2.70588	0.383567	3.3585	0.339314	4.0065	0.302799	4.6544	0.271464
4	1	0.50736	0.090799	1.0196	0.052815	1.528	0.042886	2.0343	0.043439	2.5446	0.050484	3.0535	0.054047	3.5625	0.056452
ϵ_{2p}			-0.128716		-0.519810		-1.167931		-2.069304		-3.222362		-4.626396		-6.281043
$E_{^2P}$			-7.380113		-14.145420		-23.168001		-34.443983		-47.971747		-63.750555		-81.780021
$(V/2E)_{^2P}$			1.000007		0.999998		0.999996		0.999997		0.999997		0.999997		0.999998

TABLE A-II. Data for the G1 atomic effective potential for Li ^2D.

n	ℓ	ζ	ϕ_{3d}
1	0	3.0	0.0
4	0	5.13	0.0
3	0	5.31	0.0
3	0	2.921	0.0
3	2	1.0	0.028 299
5	2	0.98	0.129 081
5	2	0.6	0.466 498
5	2	0.404	0.490 804
5	2	1.762	0.008 777
ϵ_{3d}			-0.055 562
$E(^2D)$			-7.306 973

TABLE A-III. Analytic form for the basis function exponents. Each exponent is expressed as $\zeta_i = a_i Z + b_i$.

ζ_i	a_i	b_i
1s	1.0	0.0
4s	2.173092	-1.178329
3s	2.229530	-1.946333
3s′	1.169029	-0.516728
3s″	0.766204	-0.931708
3s‴	0.589050	-0.931025
3s″″	0.515898	-0.915956
2p	0.5	0.0
4p	1.464840	-2.309723
4p′	0.867440	-1.315033
4p″	0.647957	-1.177179
4p‴	0.508922	-1.017834

APPENDIX II. Off-Diagonal Lagrange Multipliers and the Generalized Pseudopotential

As it stands Eq. (2) and hence (7) are not quite correct since we have neglected to include the off-diagonal Lagrange multipliers.[49] Assuming a single open shell, the correct HF equation for the valence orbital is

$$\hat{H}_v^{HF}\phi_v = (-\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \hat{V}^{HF})\phi_v = \epsilon_v\phi_v + \sum_c \epsilon_{vc}\phi_c \quad , \qquad \text{(A-1)}$$

where

$$\langle\phi_v|\phi_c\rangle = 0 \qquad \text{(A-2)}$$

and

$$\epsilon_{vc} = \langle\phi_c|\hat{H}_v^{HF}|\phi_v\rangle \quad . \qquad \text{(A-3)}$$

Using (A-3) we can rewrite (A-1) as

$$\hat{H}_v^{HF}\phi_v - \sum_c \langle\phi_c|\hat{H}_v^{HF}|\phi_v\rangle\phi_c = \epsilon_v\phi_v \quad ,$$

or as

$$(1 - \hat{P})\hat{H}_v^{HF}\phi_v = \epsilon_v\phi_v \quad , \qquad \text{(A-4)}$$

where

$$\hat{P} = \sum_c |\phi_c\rangle\langle\phi_c| \quad .$$

Since

$$(1 - \hat{P})\phi_v = \phi_v$$

we can rewrite (A-4) as

$$(1 - \hat{P})\hat{H}_v^{HF}(1 - \hat{P})\phi_v = \epsilon_v(1 - \hat{P})\phi_v \qquad \text{(A-5)}$$

[where (A-2) is no longer required]. Since any function of the form

$$\chi = \phi_v + \sum_c a_c\phi_c$$

satisfies

$$(1 - \hat{P})\chi = \phi_v$$

and since $$(1-\hat{P})(1-\hat{P}) = (1-\hat{P}) \quad ,$$

we see that χ is also a solution of (A-5). Thus

$$(1-\hat{P})\hat{H}_v^{HF}(1-\hat{P})\chi = \epsilon_v(1-\hat{P})\chi \quad , \tag{A-6}$$

and expanding (A-6) we find

$$(\hat{H}_v^{HF} - \hat{P}\hat{H}_v^{HF} - \hat{H}_v^{HF}\hat{P} + \hat{P}\hat{H}_v^{HF}\hat{P} + \epsilon_v\hat{P})\chi = \epsilon_v\chi \, . \tag{A-7}$$

Upon inspection we find that the pseudopotential based on the correct HF equation, (A-1), is

$$\hat{V}^{pseudo} = -\hat{P}\hat{H}_v^{HF} - \hat{H}_v^{HF}\hat{P} + \hat{P}\hat{H}_v^{HF}\hat{P} + \epsilon_v\hat{P} \quad . \tag{A-8}$$

The pseudopotential (A-8) is just the generalized PK pseudopotential first derived by Weeks and Rice[11] by a somewhat different procedure.

Note that if the core orbitals were also solutions of $\hat{H}_v^{HF}$ (not generally true), $$\hat{H}_v^{HF}\phi_c = \epsilon_c\phi_c \quad ,$$

then (A-7) would reduce to the usual PK form (8).

APPENDIX III

Local Potential Integrals

In this Appendix we give the formulae for the integrals of the local potential necessary for variational calculations. We consider two cases depending on the type of basis function.

In the case of Slater Functions, we will restrict ourselves to two-centers since a third center would introduce integrals with infinite series. First we define and give the properties of the functions to be used. A real Slater function is defined as

$$\chi_{n,\ell,m} = N\, r^{n-1}\, e^{-\zeta r}\, P_\ell^m(\cos\theta)\, S_m^\sigma(\phi)$$

where

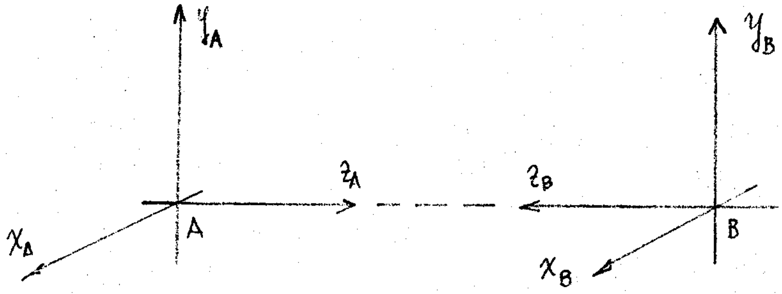
$$\text{(i)} \quad S_m^\sigma(\phi) = \begin{cases} \cos m\phi & \sigma = 0 \\ \sin m\phi & \sigma = 1 \\ 1 & m = 0 \end{cases}$$

$$\text{(ii)} \quad \int_0^{2\pi} S_{m_1}^{\sigma_1}(\phi)\, S_{m_2}^{\sigma_2}(\phi)\, d\phi = \pi\,(1+\delta_{m_1,0})\,\delta_{m_1,m_2}\,\delta_{\sigma_1,\sigma_2}$$

$$\text{(iii)} \quad \int_0^{\pi} P_{\ell_1}^{m_1}(\cos\theta)\, P_{\ell_2}^{m_2}(\cos\theta)\sin\theta\, d\theta = \frac{2}{2\ell_1+1}\,\frac{(\ell_1+m_1)!}{(\ell_1-m_1)!}\,\delta_{\ell_1\ell_2}$$

$$\text{(iv)} \quad N = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}\cdot\frac{(2\ell+1)}{2}\cdot\frac{(\ell-m)!}{(\ell+m)!}\cdot\frac{1}{\pi(1+\delta_{m,0})}}$$

If a Slater function is located on center B, its expansion in Associated Legendre Polynomials about another center A, as shown in the accompanying figure,



is given by the "zeta-function" expansion

$$r_B^{n-1}\, e^{-\zeta r_B}\, P_\ell^m(\cos\theta_B) = \sum_{\lambda=m}^{\infty} (2\lambda+1)\, \eta_{n\ell m;\lambda}(\zeta, r_A, R_{AB})\, P_\lambda^m(\cos\theta_A)$$

where

$$\eta_{n\ell m;\lambda}(\zeta, r_A, R_{AB}) = \frac{1}{\zeta^{n-1}} \cdot \frac{(\lambda-m)!}{(\lambda+m)!} \sum_i \sum_j (-1)^{i+m} \binom{\ell+m}{i+m} (\zeta r_A)^i (\zeta R_{AB})^{\ell-i} \times$$

$$\times\ \mathcal{D}_j(\lambda\, m \mid i\, m)\, e^{-\zeta|r_A - R_{AB}|}\, Z_{n-\ell, j}(\zeta r_A, \zeta R_{AB})$$

$$i = m, (1), \ell \qquad\qquad j = |\lambda - i|, (2), (\lambda + i)$$

and where

$$\mathcal{D}_\ell(\ell_1\, m_1 \mid \ell_2\, m_2) = \frac{(2\ell+1)}{2} \cdot \frac{(\ell - |m_1 - m_2|)!}{(\ell + |m_1 - m_2|)!} \left(\int_{-1}^{+1} P_{\ell_1}^{m_1}(x)\, P_{\ell_2}^{m_2}(x)\, P_\ell^{|m_1 - m_2|}(x)\, dx \right)$$

We will also need the decomposition of the product of two Associated Legendre Polynomials,

$$P_{\ell_1}^{m_1}(\cos\theta)\, P_{\ell_2}^{m_2}(\cos\theta) = \sum_{\ell} \mathcal{D}_{\ell}(\ell_1\, m_1 | \ell_2\, m_2)\, P_{\ell}^{|m_1-m_2|}(\cos\theta)$$

$$\ell = |\ell_1 - \ell_2|,\ (2),\ (\ell_1 + \ell_2)$$

Given these formulae, we can derive the needed integrals over Slater functions of the local potential

$$\hat{U} = \sum_{\ell}\sum_{m} U_{\ell}(r_A)\, |\ell m\rangle\langle \ell m|$$

There are three types of integrals depending on the centers of the basis functions and given that the potential always is on center A.

1) Type $\langle A|\hat{U}(A)|A\rangle$:

$$= \delta_{\ell_1\ell_2}\, \delta_{m_1 m_2}\, \delta_{\sigma_1\sigma_2}\, N \left(\int_0^\infty r^{n_1+n_2}\, e^{-(\zeta_1+\zeta_2)r}\, U_{\ell_1}(r)\, dr \right)$$

where

$$N = \sqrt{\frac{(2\zeta_1)^{2n_1+1}}{(2n_1)!} \cdot \frac{(2\zeta_2)^{2n_2+1}}{(2n_2)!}}$$

2) Type $\langle A|\hat{U}(A)|B\rangle$:

$$= \delta_{m_1 m_2}\, \delta_{\sigma_1\sigma_2}\, N \left[\frac{1}{(\zeta_2)^{n_2-\ell_2-1}} \sum_i \sum_j (-1)^{i+m_1} \binom{\ell_2+m_1}{i+m_1} \mathcal{D}_j(\ell_1\, m_1 | i\, m_1) \cdot R_{AB}^{\ell_2-i} \right.$$

$$\left. \cdot \left(\int_0^\infty r^{n_1+i+1}\, e^{-\zeta_1 r}\, U_{\ell_1}(r)\, e^{-\zeta_2|r-R_{AB}|}\, Z_{n_2-\ell_2,j}(\zeta_2 r, \zeta_2 R_{AB})\, dr \right) \right]$$

where $\quad i = m_1, (1), \ell_2 \qquad j = |\ell - i|, (2), (\ell + i)$

$$N = 2\sqrt{\left(\frac{(2\zeta_1)^{2n_1+1}}{(2n_1)!}\cdot\frac{(2\ell_1+1)}{2}\cdot\frac{(\ell_1-m_1)!}{(\ell_1+m_1)!}\right)\left(\frac{(2\zeta_2)^{2n_2+1}}{(2n_2)!}\cdot\frac{(2\ell_2+1)}{2}\cdot\frac{(\ell_2-m_2)!}{(\ell_2+m_2)!}\right)}$$

3) Type $\langle B|\hat{U}(A)|B\rangle$:

We take the approximation to the local potential

$$\hat{U} \simeq \underset{\text{LMAX}}{U}(r_A) + \sum_{\ell=0}^{\text{LMAX}-1}\sum_{m=\ell}^{-\ell} \Delta U_\ell(r_A)\,|\ell m\rangle\langle \ell m|$$

where

$$\Delta U_\ell(r_A) = U_\ell(r_A) - \underset{\text{LMAX}}{U}(r_A)$$

We consider the integrals of each of the two centers separately.

3-a) Type $\langle B|\underset{\text{LMAX}}{U}(r_A)|B\rangle$

$$= \delta_{m_1m_2}\,\delta_{\sigma_1\sigma_2}\,N\left[\frac{1}{(\zeta_1+\zeta_2)^{n_1+n_2-2}}\sum_\ell \vartheta_\ell(\ell_1m_1|\ell_2m_2)\,(\zeta_1+\zeta_2)^\ell\sum_{i=0}^{\ell}(-1)^i\binom{\ell}{i}R_{AB}^{\ell-i}\right.$$

$$\left.\left(\int_0^\infty r^{i+2}\,e^{-(\zeta_1+\zeta_2)|r-R_{AB}|}\,Z_{n_1+n_2-\ell-1,i}\left[(\zeta_1+\zeta_2)r,\,(\zeta_1+\zeta_2)R_{AB}\right]\underset{\text{LMAX}}{U}(r)\,dr\right)\right]$$

where $\quad \ell = |\ell_1 - \ell_2|, (2), (\ell_1 + \ell_2)$

3-b) Type $\langle B|\sum_{\ell=0}^{\text{LMAX}-1}\sum_{m=\ell}^{-\ell}\Delta U_\ell(r_A)|\ell m\rangle\langle \ell m||B\rangle$:

$$= \delta_{m_1 m_2} \delta_{\sigma_1 \sigma_2} N \left[\frac{1}{\zeta_1^{n_1-l_1-1} \zeta_2^{n_2-l_2-1}} \sum_{l=m_1}^{\mathrm{LMAX}-1} (2l+1) \frac{(l-m_1)!}{(l+m_1)!} \sum_{i_1} (-1)^{i_1} \binom{l_1+m_1}{i_1+m_1} \times \right.$$

$$R_{AB}^{l_1-i_1} \sum_{j_1} \vartheta_{j_1}(l m_1 | i_1 m_1) \sum_{i_2} (-1)^{i_2} \binom{l_2+m_1}{i_2+m_1} R_{AB}^{l_2-i_2} \sum_{j_2} \vartheta_{j_2}(l m_1 | i_2 m_1) \times$$

$$\left. \left(\int_0^\infty e^{-(\zeta_1+\zeta_2)|r-R_{AB}|} Z_{n_1-l_1, j_1}(\zeta_1 r, \zeta_1 R_{AB}) Z_{n_2-l_2, j_2}(\zeta_2 r, \zeta_2 R_{AB}) \Delta U_l(r) r^{i_1+i_2+2} dr \right) \right]$$

where

$$i_1 = m_1, (1), l_1 \qquad j_1 = |l-i_1|, (2), (l+i_1)$$

$$i_2 = m_1, (1), l_2 \qquad j_2 = |l-i_2|, (2), (l+i_2)$$

This finishes our work with Slater functions. We consider the Gaussian Function next.

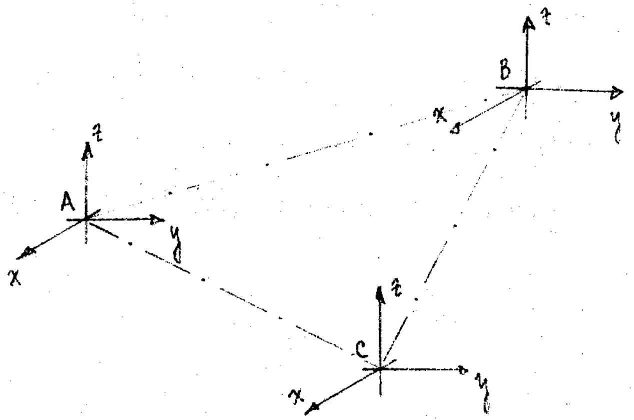
In the case of Gaussian Functions, we do not have to restrict ourselves to the case of two centers. The most difficult three-center integral still has a closed-formula expression. First, we give the properties of the functions to be used. A Gaussian basis function is defined as

$$G_{n,l,m} = N x^n y^l z^m e^{-\zeta r^2}$$

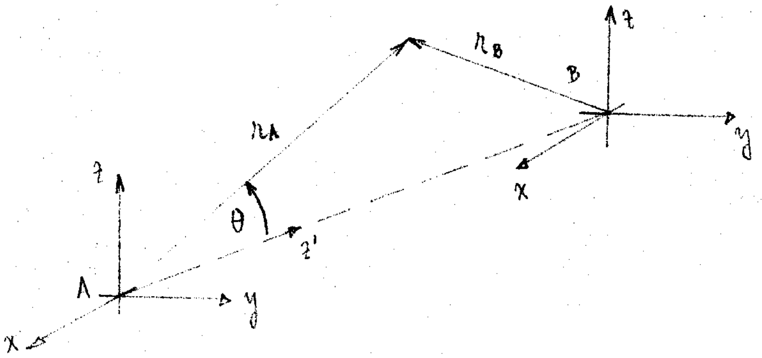
where N is an appropriate normalization factor. The general form of the integrals to be evaluated is

$$\langle G_1 | \sum_{l,m} |lm\rangle U_l(r) \langle lm| | G_2 \rangle$$

where the potential is on center A and in general the basis functions G_1 and G_2 are on centers B or C. See Fig. 1.



Since the potential, in particular the $|\ell m\rangle\langle \ell m|$ operators, are fixed on center A, it is convenient to first work out the $\langle \ell m | G \rangle$ projections of the basis functions onto center A. For this purpose it is convenient to rotate the coordinate system on A so that its new z-axis is pointing at the center of the basis function, as in Fig. 2.



In these new coordinates, one has that

$$r_B^2 = r_A^2 + \overline{BA}^2 - 2\,\overline{BA}\,r_A \cos\theta$$

and consequently the expansion of a spherical Gaussian on B onto A is

$$\begin{aligned} e^{-\zeta r_B^2} &= e^{-\zeta \overline{BA}^2}\, e^{-\zeta r_A^2}\, e^{2\zeta \overline{BA} r_A \cos\theta} \\ &= e^{-\zeta \overline{BA}^2}\, e^{-\zeta r_A^2} \sum_{l=0}^{\infty} (2l+1)\, M_l(2\zeta \overline{BA} r_A)\, P_l(\cos\theta) \end{aligned}$$

where M_l is the Modified Spherical Bessel function of the first kind defined as follows

$$M_l(x) = x^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \left(\frac{\sinh x}{x}\right)$$

or

$$= \frac{x^l}{2^{l+1}\, l!} \int_{-1}^{+1} \cosh(xt)\,(1-t^2)^l\, dt$$

The angular functions on center B are readily translated onto center A by

$$r_{B_i} = r_{A_i} - (B_i - A_i) = r_{A_i} - \overline{BA}_i \qquad i = 1,2,3 : x,y,z$$

and the appropriate rotation of coordinate system A is given by

$$r_{A_i} = \sum_{j=1}^{3} D_{ij}\, r'_{A_j} \qquad i = 1,2,3 : x,y,z$$

where the rotation matrix $\underset{\sim}{D}$ is given by

$$\mathcal{D}_{11} = \frac{\overline{BA}_x\,\overline{BA}_z}{\overline{BA}\sqrt{\overline{BA}_x^2+\overline{BA}_y^2}} \qquad \mathcal{D}_{12} = -\frac{\overline{BA}_y}{\sqrt{\overline{BA}_x^2+\overline{BA}_y^2}} \qquad \mathcal{D}_{13} = \frac{\overline{BA}_x}{\overline{BA}}$$

$$\mathcal{D}_{21} = \frac{\overline{BA}_y\,\overline{BA}_z}{\overline{BA}\sqrt{\overline{BA}_x^2+\overline{BA}_y^2}} \qquad \mathcal{D}_{22} = \frac{\overline{BA}_x}{\sqrt{\overline{BA}_x^2+\overline{BA}_y^2}} \qquad \mathcal{D}_{23} = \frac{\overline{BA}_y}{\overline{BA}}$$

$$\mathcal{D}_{31} = -\frac{\sqrt{\overline{BA}_x^2+\overline{BA}_y^2}}{\overline{BA}} \qquad \mathcal{D}_{32} = 0 \qquad \mathcal{D}_{33} = \frac{\overline{BA}_z}{\overline{BA}}$$

Using these results, one can work out the $|\ell m\rangle$ projections of a Gaussian on center B onto center A. We first define

(i) $$GM_\ell = e^{-\zeta\overline{BA}^2}\,e^{-\zeta r_A^2}\,M_\ell(2\zeta\,\overline{BA}\,r_A)$$

(ii) $Z_{\ell m}(\Omega)$ is a real Spherical Harmonic function.

In terms of these, we have:

1. $$\langle Z_{00}(\Omega_A)|\,G_B(s)\rangle = N\sqrt{4\pi}\;GM_0$$

2. $$\langle Z_{00}(\Omega_A)|\,G_B(r_i)\rangle = N\sqrt{4\pi}\;\overline{BA}_i\left[\frac{r}{\overline{BA}}\,GM_1 - GM_0\right]$$

3. $$\langle Z_{00}(\Omega_A) | G_B(r_i r_j) \rangle = N\sqrt{4\pi}\left[\left(\frac{\overline{BA}_i\,\overline{BA}_j}{\overline{BA}^2} - \frac{1}{3}\delta_{ij}\right) r^2\, GM_2 \; - \right.$$

$$\left. - \frac{2\,\overline{BA}_i\,\overline{BA}_j}{\overline{BA}}\, r\, GM_1 + \left(\overline{BA}_i\,\overline{BA}_j + \frac{r^2}{3}\delta_{ij}\right) GM_0 \right]$$

4. $$\langle Z_{1m}(\Omega_A) | G_B(r) \rangle = N\sqrt{12\pi}\;\frac{\overline{BA}_m}{\overline{BA}}\; GM_1$$

5. $$\langle Z_{1m}(\Omega_A) | G_B(r_i) \rangle = N\sqrt{12\pi}\left[\frac{\delta_{mi}}{3}\, r\, GM_0 + \left(\frac{\overline{BA}_i\,\overline{BA}_m}{\overline{BA}^2} - \frac{1}{3}\delta_{im}\right) r\, GM_2 \; - \right.$$

$$\left. - \frac{\overline{BA}_m\,\overline{BA}_i}{\overline{BA}}\; GM_1 \right]$$

6. $$\langle Z_{1m}(\Omega_A) | G_B(r_i r_j) \rangle = N\sqrt{12\pi}\left(-\frac{1}{3}\left(\overline{BA}_i\,\delta_{jm} + \overline{BA}_j\,\delta_{im}\right) r\, GM_0 \; + \right.$$

$$+ \left[\frac{1}{5}\,\frac{\left(\delta_{im}\,\overline{BA}_j + \delta_{jm}\,\overline{BA}_i + \delta_{ij}\,\overline{BA}_m\right)}{\overline{BA}}\, r^2 + \frac{\overline{BA}_i\,\overline{BA}_j\,\overline{BA}_m}{\overline{BA}}\right] GM_1 \; +$$

$$+ \left[-2\,\frac{\overline{BA}_m\,\overline{BA}_i\,\overline{BA}_j}{\overline{BA}^2} + \frac{1}{3}\left(\overline{BA}_i\,\delta_{jm} + \overline{BA}_j\,\delta_{im}\right)\right] r\, GM_2 \; +$$

$$\left. + \left[\frac{\overline{BA}_m\,\overline{BA}_i\,\overline{BA}_j}{\overline{BA}^2} - \frac{1}{5}\,\frac{\left(\delta_{im}\,\overline{BA}_j + \delta_{jm}\,\overline{BA}_i + \delta_{ij}\,\overline{BA}_m\right)}{\overline{BA}}\right] r^2\, GM_3 \right)$$

In turn one can take these projections and assemble the necessary radial integrals. These radial integrals, which contain the radial local potentials, can be directly evaluated numerically. Alternatively, the radial local potential can be expanded in Gaussians, and then each radial integral becomes a sum of radial integrals. This is the approach pursued by Mr. Carl Melius in collaboration with the author, and it has proven to be the most successful approach. We illustrate this approach for the most difficult three-center integral and postpone at this time a complete review of all the formulae. First, we define a basic radial integral

$$J_{n,\ell_C,\ell_B} = e^{-\zeta_B \overline{BA}^2} e^{-\zeta_C \overline{CA}^2} \int_0^\infty e^{-\zeta_D r^2} r^n M_{\ell_C}(2\zeta_C \overline{CA} r) M_{\ell_B}(2\zeta_B \overline{BA} r)\, dr$$

where $\zeta_D = \zeta_B + \zeta_C + \zeta_{LP}$; we will not include in our notation any powers of r, which arises from the expansion of $U(r)r^2$ in terms of spherical Gaussians, i.e., from terms in

$$U(r) r^2 = \sum_p a_p r^{n_p} e^{-\zeta_p r^2}$$

then, upon multiplying the appropriate projections and summing over all m components of ℓ we obtain the results illustrated in the next example.

1. $\langle G_C(r_k r_l) | p \rangle \langle p | G_B(r_i r_j) \rangle = 12\pi N_C N_B \sum C_{n\ell_1\ell_2} J_n(\ell_1, \ell_2)$

1. $$C_{200} = \frac{1}{9}\left[\overline{CA}_k(\delta_{\ell j}\overline{BA}_i + \delta_{\ell i}\overline{BA}_j) + \overline{CA}_\ell(\delta_{kj}\overline{BA}_i + \delta_{ki}\overline{BA}_j)\right]$$

2. $$C_{301} = -\frac{3}{5\overline{BA}}C_{200} - \frac{\delta_{ij}}{15\overline{BA}}(\overline{BA}_\ell\overline{CA}_k + \overline{BA}_k\overline{CA}_\ell)$$

3. $$C_{101} = -\frac{1}{3}\frac{\overline{\overline{BA}_i\overline{BA}_j}}{\overline{BA}}(\overline{CA}_k\overline{BA}_\ell + \overline{CA}_\ell\overline{BA}_k)$$

4. $$C_{202} = -\frac{2C_{101}}{\overline{BA}} - C_{200}$$

5. $$C_{303} = \frac{C_{101}}{\overline{BA}^2} - C_{301}$$

6. $$C_{310} = -\frac{3}{5\overline{CA}}C_{200} - \frac{\delta_{\ell k}}{15\overline{CA}}(\overline{BA}_i\overline{CA}_j + \overline{BA}_j\overline{CA}_i)$$

7. $$C_{411} = -\frac{3C_{301}}{5\overline{CA}} + \frac{\delta_{\ell k}}{25\overline{CA}\,\overline{BA}}(\overline{CA}_i\overline{BA}_j + \overline{CA}_j\overline{BA}_i + \delta_{ij}\sum_m\overline{CA}_m\overline{BA}_m)$$

8. $$C_{211} = \frac{\overline{BA}_i\overline{BA}_j}{5\overline{CA}\,\overline{BA}}(\overline{CA}_\ell\overline{BA}_k + \overline{CA}_k\overline{BA}_\ell + \delta_{\ell k}\sum_m\overline{CA}_m\overline{BA}_m)$$

9. $$C_{312} = -\frac{2C_{211}}{\overline{BA}} - C_{310}$$

10. $$C_{413} = \frac{C_{211}}{\overline{BA}^2} - C_{411}$$

11. $$C_{110} = -\frac{1}{3}\frac{\overline{\overline{CA}_k\overline{CA}_\ell}}{\overline{CA}}(\overline{CA}_j\overline{BA}_i + \overline{CA}_i\overline{BA}_j)$$

12. $$C'_{211} = \frac{\overline{CA}_k\overline{CA}_\ell}{5\,\overline{CA}\,\overline{BA}}(\overline{CA}_i\overline{BA}_j + \overline{CA}_j\overline{BA}_i + \delta_{ij}\sum_m\overline{CA}_m\overline{BA}_m)$$

13. $$C_{011} = \overline{CA}_k \overline{CA}_\ell \overline{BA}_i \overline{BA}_j \frac{(\sum_m \overline{CA}_m \overline{BA}_m)}{\overline{CA}\ \overline{BA}}$$

14. $$C_{112} = -\frac{2C_{011}}{\overline{BA}} - C_{110}$$

15. $$C_{213} = \frac{C_{011}}{\overline{BA}^2} - C'_{211}$$

16. $$C_{220} = -\frac{2C_{110}}{\overline{CA}} - C_{200}$$

17. $$C_{321} = -\frac{2C'_{211}}{\overline{CA}} - C_{301}$$

18. $$C_{121} = -\frac{2C_{011}}{\overline{CA}} - C_{101}$$

19. $$C_{222} = \frac{4C_{011}}{\overline{CA}\,\overline{BA}} + \frac{2C_{110}}{\overline{CA}} + \frac{2C_{101}}{\overline{BA}} + C_{200}$$

20. $$C_{323} = -\frac{2C_{011}}{\overline{CA}\,\overline{BA}^2} + \frac{2C'_{211}}{\overline{CA}} + \frac{C_{101}}{\overline{BA}^2} + C_{301}$$

21. $$C_{330} = \frac{C_{110}}{\overline{CA}^2} - C_{310}$$

22. $$C_{431} = \frac{C'_{211}}{\overline{CA}^2} - C_{411}$$

23. $$C_{231} = \frac{C_{011}}{\overline{CA}^2} - C_{211}$$

24. $$C_{332} = -2C_{213} - C_{303}$$

25. $$C_{433} = \frac{C_{011}}{\overline{CA}^2\,\overline{BA}^2} - \frac{C'_{211}}{\overline{CA}^2} - \frac{C_{211}}{\overline{BA}^2} + C_{411}$$

In turn, these formulae can be further simplified some by use of the recursion relation

$$M_{\ell+1}(x) = M_{\ell-1}(x) - (2\ell+1)\frac{M_\ell(x)}{x}$$

for example, we find that

$$J_1(2,1) = J_1(0,1) - \frac{3}{2\zeta_c \overline{CA}} J_0(1,1)$$

REFERENCES

[1] W.A. Goddard III, Phys. Rev. **157**, 81 (1967).

[2] W.A. Goddard III, ibid. **174**, 659 (1968).

[3] For preliminary results see L.R. Kahn and W.A. Goddard III, Chem. Phys. Letters **2**, 667 (1968). Also, for results from using G1 atomic effective potentials for molecular excited states see C. F. Melius, W. A. Goddard III, and L. R. Kahn, J. Chem. Phys. **54**, 0000 (1971).

[4] For a good review of pseudopotential theory from the Hartree-Fock point of view, see J.D. Weeks, A. Hazi, and S.A. Rice, Adv. Chem. Phys. **16**, 283 (1969).

[5] H. Hellmann, J. Chem. Phys. **3**, 61 (1935); Acta Physicochim. URSS **1**, 6 (1935); ibid. **4**, 225, 324 (1936).

[6] P. Gombás, Z. Physik **94**, 473 (1935); P. Gombás, *Pseudopotentiale* (Springer Verlag, Wien, 1967).

[7] H. Preuss, Z. Naturforsch. **10A**, 365 (1955).

[8] In addition, because $\hat{V}^{HF}$ has core-like solutions of lower energy than ϕ_v, the basis in which we expand ϕ_v has to be orthogonalized to the core-like solutions so that ϕ_v will be the lowest accessible state of $\hat{V}^{HF}$. This introduces additional multicenter two-electron integrals to be evaluated.

[9] A.W. Weiss, Astrophys. J. **138**, 1262 (1963).

[10] J.C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[11] J.D. Weeks and S.A. Rice, J. Chem. Phys. **49**, 2741 (1968).

[12] For an alternative derivation to the one in Ref. 11, see Appendix II.

[13] W. Kutzelnigg, R.J. Koch, and W.A. Bingel, Chem. Phys. Letters **2**, 197 (1968); W.A. Bingel, R.J. Koch, and W. Kutzelnigg, Acta Phys. Hung. **27**, 323 (1969); W. Kutzelnigg, Chem. Phys. Letters **4**, 435 (1969).

[14] (a) L. Szasz and G. McGinn, J. Chem. Phys. 42, 2363 (1965); *ibid.* 45, 2898 (1966); *ibid.* 47, 3495 (1967); *ibid.* 48, 2997 (1968); L. Szasz, *ibid.* 49, 679 (1968); G. McGinn, *ibid.* 50, 1404 (1969); *ibid.* 51, 1681, 3135, 5090 (1969). (b) Szasz and McGinn's procedure is to guess a smooth function χ, evaluate a localized V^{PK}, solve for the new χ' of (7) and to iterate until convergence. The result of this procedure is equivalent to starting with the usual Hartree-Fock core and valence orbitals and adjusting a_c of (9) to have maximum overlap of (9) with the originally chosen smooth function χ.

[15] M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).

[16] (a) If the potential term $\hat{V}^{G1}$ in (13) were a local potential, we could quite generally expect the lowest solution to be nodeless [see R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1961) Vol. I, p. 451]. The presence of exchange terms in $\hat{V}^{G1}$ deprives us of a rigorous proof that the G1 atomic orbitals are nodeless; however, for atomic valence orbitals we would expect the exchange terms due to the core orbitals to be dominated at all r by the local (Coulomb-like) terms, and would thus expect the GI atomic valence orbitals to be nodeless. In fact, no exceptions to this have yet been found [by nodeless we mean no nodes except those required by orbital symmetry; for example, p and d orbitals possess a node at $r = 0$ required by symmetry, but such a node presents no difficulties in obtaining effective potentials]. (b) In general there are no transformations among the orbitals of a G1 wavefunction leaving the many-electron wavefunction invariant and thus the G1 orbitals are unique. For Hartree-Fock wavefunctions one may take any non-singular transformation on the orbitals without changing the many-electron wavefunction; as a result the Hartree-Fock orbitals cannot be unique.

[17] This procedure to find the potential is also used in perturbation calculations. See, for example, R.M. Sternheimer, Phys. Rev. 105, 158 (1957).

[18] Given the exact solution to (13), both (15) and (16) lead to the same potential; however, for an approximate orbital ϕ_{2a}, they may lead to different potentials. For a complicated operator $\hat{V}^{G1}$, (15) is much simpler to evaluate and our experience is that (15) may be less sensitive to errors in the solutions of (13).

[19] Eq. (14) was solved numerically by matrix finite differences methods using a program due to N.W. Winter, F.P. Roullard, and L.R. Kahn. We used a fourth-root grid and 100 a.u. as the radial cutoff. The eigenvalues corresponding to 300, 400, and 500 points were extrapolated to zero mesh width.

[20] Since we have examined only states involving excitation of the valence orbitals, we have established the usefulness of the potential only for such states. The potential should not be useful for describing excitations of core orbitals nor need it be useful for continuum states with a significant amount of core character.

[21] V. Fock, M. Vesselov, and M. Petraschen, Zh. Eksp. Teor. Fiz. 10, 723 (1940).

[22] By a Slater basis function we mean

$$\chi = N_s r^{n-1} e^{-\zeta r} Y_{\ell m}(\theta, \phi) ,$$

and by a Gaussian basis function we mean

$$\chi = N_g x^{\ell} y^{m} z^{n} e^{-\zeta r^2} ,$$

where N_s and N_g are the appropriate normalization constants, and $Y_{\ell m}$ is the usual spherical harmonic function.

[23] M. P. Barnett and C. A. Coulson, Phil. Trans. Roy. Soc. (London) A243, 221 (1951); M. P. Barnett, Methods in Computational Physics (Academic Press, Inc., New York, 1963), Vol. II, p. 95.

[24] We thank Dr. R. M. Pitzer for the use of his zeta function and Gaussian quadrature routines.

[25] I. Shavitt, Methods in Computational Physics (Academic Press, Inc., New York, 1963), Vol. II, p. 1.

[26] M. Abramowitz and L. A. Stegun, Handbook of Mathematical Functions (National Bureau of Standards, U. S. Goverment Printing Office, Washington, D.C., 1966), p. 443.

[27] C. F. Melius, L. R. Kahn, and W. A. Goddard (unpublished results).

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

[29] The present GAEP and all electron G1 calculations on LiH were done with the following basis of Slater functions: on the Li (1s 3.0, 4s 5.33, 3s 5.4, 3s 2.999, 3s 1.347, 3s 0.841, 4s 0.732, 2p 0.690, 2p 1.77, 3d 0.78); on the H (1s 1.065, 2s 2.83, 2p 1.32). See Refs. 28 and 30 for more details on the basis used.

[30] W. A. Goddard III, Phys. Rev. 169, 120 (1968).

[31] These one-electron properties $[r^n, r^\ell P_\ell^m(\cos\theta), P_\ell^m(\cos\theta)/r^{\ell+1}]$ were evaluated with an integral program based on formulae in R. M. Pitzer, C. W. Kern, and W. N. Lipscomb, J. Chem. Phys. 37, 267 (1962), and A. C. Wahl, P. E. Cade, and C. C. J. Roothaan, ibid. 41, 2578 (1964).

[32] The GAEP calculations on Li_2 and Li_2^+ at R = 5.051 Bohr were carried out in the same basis as that of Ref. 33 but the basis was left uncontracted.

[33] R. J. Blint and W. A. Goddard III (unpublished results). The basis set on each Li consisted of the following Slater functions (1s 3.0, 4s 5.33, 3s 5.33, 3s 3.0, 2s 0.67, 2s 1.93, 2p 0.675, 3d 1.15115). For the all electron calculation this set was contracted to a [4s/1p/1d] set.

[34] Note also that the basis set used has only one p and one d basis function on each Li. More p functions (and perhaps d functions) with larger orbital exponents would be necessary to obtain a good description of the electric field gradient at the nucleus.

[35] The GAEP calculations on Li_2^+ as a function of R were done in a (10s/5p) basis. The s set was taken from Ref. 36. The p set was optimized for the Li 2^2P state [the exponents are (2.56483, 0.48593, 0.14536, 0.05292, 0.02026)--Th. Dunning, private communication.]

[36] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965); S. Huzinaga and Y. Sakai, *ibid.* **50**, 1371 (1969).

[37] R. C. Ladner and W. A. Goddard III, *ibid.* **51**, 1073 (1969).

[38] R. C. Ladner and W. A. Goddard III, to be published.

[39] The LiH_2 GAEP calculation was carried out in the same gaussian basis as the all-electron SOGI calculation described in Ref. 38.

The Li_2H and Li_3 calculations were also carried out in a gaussian basis. The basis on each Li consisted of the following primitive (7s/5p) set: s's (59.68430, 9.14413, 0.93435, 0.44102, 0.10280, 0.04928, 0.02246) and p's (2.697116, 0.535169, 0.14719, 0.052783, 0.020138), and it was obtained by energy fitting the G1 2s and 2p Li valence orbitals. The primitive gaussians on each H center consisted of a (6s/2p) set as described in Ref. 38. For the Li_2H calculation the basis was contracted down to a [5s/s/s; 3p/p/p] set on each Li, and a [4s/s/s; 2p] set on each H. For the Li_3 calculation the basis was contracted down to a [5s/s/s; 4p/p] set on each Li. See Ref. 36 for a study of gaussian basis sets, and Ref. 40 for a study of contraction schemes.

[40] Th. H. Dunning Jr., J. Chem. Phys. 53, 2823 (1970).

[41] The basis for the present GAEP and all-electron G1 calculations on Be consisted of a set of (7s/5p) Slater functions optimum for the Be^+ ^2S and ^2P states. This basis is found in Table A-I of Appendix I.

[42] The resulting wavefunction for Be is not exactly ^1S but also contains a component of ^1D (but no ^1P) character. In the analogous wavefunction[43, 44] for ^2P B a similar splitting of the 2s-pair occurs leading to a wavefunction with some ^2F (but no ^2D) character. In this case it was found[44] that spatial symmetry projection led to a decrease of only 0.008 in the energy; thus the symmetry contamination is not serious.

[43] The GAEP calculation on B was done in a (7s/5z/5x) primitive gaussian set. The p set is from Ref. 36, and the s set was modified from those in Ref. 36 by energy fitting the G1 B^{+2} orbital. This primitive set was contracted down to a [4s/s/s/s; 3z/z/z; 3x/x/x] set.

[44] R. J. Blint and W. A. Goddard III, J. Chem. Phys., to be published.

[45] The basis for the GAEP and all-electron G1 calculations on BH consisted of a [9s/9s/9s/s/s; 4z/z; 4x/x] contracted gaussians set on the B, and a [6s/6s] contracted gaussians set on the H. See Ref. 44 for details.

[46] R. J. Blint, L. R. Kahn, and W. A. Goddard III (unpublished results). The basis used is the same as in Ref. 45 except for the addition of a z and an x contracted gaussian on the B.

[47] G. Herzberg, Electronic Spectra of Polyatomic Molecules (D. Van Nostrand Co., Inc., New York, 1966), p. 583.

[48] C. F. Bender and H. F. Schaefer III, J. Chem. Phys., to be published.

[49] For further discussion of the off-diagonal Lagrange multipliers, see W. A. Goddard III, Th. H. Dunning, Jr., and W. J. Hunt, Chem. Phys. Letters **4**, 231 (1969) and W. J. Hunt, W. A. Goddard III, and Th. H. Dunning, Jr., Chem. Phys. Letters **6**, 147 (1970).

II. THE STERNHEIMER CORRECTION, PERTURBATION THEORY, AND APPROXIMATE WAVEFUNCTIONS.

I. INTRODUCTION

The electric hyperfine interaction energy is due to the interaction of the electrons of an atom or molecule with the non-spherical charge distribution of the nucleus. For a nucleus with a quadrupole moment (Q) the corresponding interaction energy is proportional to the product of Q times the electric field gradient (q) at the nucleus due to the electrons. Since only the product qQ can be measured (nuclear quadrupole coupling constant), the nuclear quadrupole moment Q can be determined from such experiments only if an accurate theoretical value of q can be calculated. A common procedure is to carry out a Hartree-Fock (HF) calculation for the wavefunction of the atom or molecule, and to use this to determine the electric field gradient, q^0. For a typical atom the HF wavefunction has a core of closed-shell doubly occupied orbitals which do not contribute to q^0 and an open shell of non-s functions which determine q^0. For example, in the 2 ^{2}P state of Li the doubly-occupied 1s orbital forms the core and the 2p orbital forms the open shell and determines q^0. Sternheimer[1, 2, 3] pointed out that the quadrupole field due to the open shell could induce quadrupole character into the closed shell which would in turn lead to an additional electric field gradient at the nucleus, q^1. In this case the total quadrupole interaction is given by

$$Q(q^0 + q^1).$$

He also pointed out that since the s-core electrons are quite close to the nucleus, q^1 might be comparable to q^0 and neglecting it might lead to erroneous values of Q. In a series of papers Sternheimer has calculated approximate values of q^1 for a number of atoms using a number of different approximations. In this paper we report an exact HF calculation of q^1 for the $2\ ^2P$ state of Li and compare the results to the values obtained using various previous approximations. In addition, we discuss the relation of the Sternheimer correction to general perturbation expansions and to spatial symmetry and orbital restrictions.

II. FIRST-ORDER PROPERTIES FOR APPROXIMATE WAVEFUNCTIONS

A. Exact Zero-Order Wavefunctions

Suppose we have the exact eigenfunction Ψ^0 for some zero-order Hamiltonian, H^0,

$$H^0\Psi^0 = E^0\Psi^0 \tag{1}$$

and that H^1 is some perturbation operator (for example due to the quadrupole moment of the nucleus) then expanding the total energy E of the system, and taking Ψ to be normalized

$$E = \langle\Psi|H^0 + H^1|\Psi\rangle,$$

we obtain the usual expression for the zero-order energy,

$$E^0 = \langle\Psi^0|H^0|\Psi^0\rangle, \tag{2}$$

but for the first-order energy we obtain

$$E^1 = \langle\Psi^0|H^1|\Psi^0\rangle + 2R_e\langle\Psi^1|H^0 - E^0|\Psi^0\rangle, \tag{3}$$

etc. However, since Ψ^0 is an exact eigenfunction of H^0,

$$\Delta E^1 \equiv 2R_e\langle\Psi^1|H^0 - E^0|\Psi^0\rangle \tag{4}$$

is zero and we obtain

$$E^1 = \langle\Psi^0|H^1|\Psi^0\rangle. \tag{5}$$

Unfortunately, we usually do not have exact eigenfunctions of H^0, and so the question arises as to whether (3) or (5) should be used in the evaluation of E^1 for an approximate Ψ^0. The use of (5) involves the contradictory assumption of that Ψ^0 is exact when it is not, but (5) is nevertheless more commonly used because, although presumably less accurate, it is simpler in that it does not require the solution of a first-order equation to obtain Ψ^1. We show below that if H^1 is the nuclear quadrupole perturbation and if Ψ^0 is the Hartree-Fock wavefunction, then ΔE^1 is just the Sternheimer correction to the quadrupole splitting. First, however, we must consider more carefully the case in which Ψ^0 is only an approximate wavefunction.

B. Approximate Zero-Order Wavefunctions

We will denote the approximate zero-order wavefunction as ψ^{00}. Although ψ^{00} is not an eigenfunction of H^0, we can define an approximate Hamiltonian, H^{00}, of which ψ^{00} is an eigenfunction. Thus, we can consider the difference between H^0 and H^{00},

$$H^{01} = H^{0} - H^{00} \tag{6}$$

as a <u>correlation</u> <u>perturbation</u> which is present along with the original perturbation H^1, which we will also denote as

$$H^{10} = H^{1}. \tag{7}$$

Thus, starting with ψ^{00} as the zero-order wavefunction and H^{00} as the zero-order Hamiltonian we must apply both perturbations H^{01} and H^{10} to obtain the exact wavefunctions and energies. This approach is known as Double Perturbation theory.[4]

In order to obtain the exact first-order energy due to H^{10}, we must include the perturbation due to correlation (H^{01}) to all orders. Hence, the E^1 of (3) is given by

$$E^{1} = E^{(1,0)} + E^{(1,1)} + E^{(1,2)} + \cdots \tag{8}$$

where $E^{(i,j)}$ is the correction energy to i¹th-order in H^{10} and j¹th-order in H^{01} (correlation); for example

$$E^{(0,0)} = \langle \psi^{00} | H^{00} | \psi^{00} \rangle = \langle \Psi^{0} | H^{0} | \Psi^{0} \rangle \tag{9}$$

$$E^{(1,0)} = \langle \psi^{00} | H^{10} | \psi^{00} \rangle = \langle \Psi^{0} | H^{1} | \Psi^{0} \rangle$$

$$E^{(1,1)} = R_e \langle \psi^{00} | H^{10} - E^{10} | \psi^{01} \rangle + R_e \langle \psi^{00} | H^{01} - E^{01} | \psi^{10} \rangle .$$

Thus, to evaluate the quadrupole coupling energy, we would have to sum (8) to all orders.

Neglecting all terms in (8) which are higher than first-order in the correlation correction, H^{01}, we obtain

$$\overline{E}^1 = \langle\psi^{00}|H^{10}|\psi^{00}\rangle + R_e\langle\psi^{00}|H^{10} - E^{10}|\psi^{01}\rangle + R_e\langle\psi^{00}|H^{01} - E^{01}|\psi^{10}\rangle. \quad (10)$$

In (10) it appears that the first-order wavefunction ψ^{10} due to the external perturbation contributes to $\overline{E}^1$. However, it is well known that the second two terms of (10) are related (Dalgarno's interchange theorem^5)

$$R_e\langle\psi^{10}|H^{01} - E^{01}|\psi^{00}\rangle = R_e\langle\psi^{01}|H^{10} - E^{10}|\psi^{00}\rangle \quad (11)$$

so that (10) can be rewritten in two equivalent forms,

$$\overline{E}^1 = \langle\psi^{00}|H^{10}|\psi^{00}\rangle + 2R_e\langle\psi^{00}|H^{10} - E^{10}|\psi^{01}\rangle \quad (12)$$

or as

$$\overline{E}^1 = \langle\psi^{00}|H^{10}|\psi^{00}\rangle + 2R_e\langle\psi^{00}|H^{01} - E^{01}|\psi^{10}\rangle. \quad (13)$$

Thus the correction term to (5) for the case of an approximate wavefunction has the two equivalent forms

$$\overline{\Delta E}^1 = 2R_e\langle\psi^{00}|H^{10} - E^{10}|\psi^{01}\rangle \quad (14)$$

$$\overline{\Delta E}^1 = 2R_e\langle\psi^{00}|H^{01} - E^{01}|\psi^{10}\rangle = 2R_e\langle\psi^{00}|H^0 - E^0|\psi^{10}\rangle, \quad (15)$$

From the appearance of H^{01}, E^{01}, and ψ^{01}, one might argue that these terms represent a correlation effect, but using the usual definition of Hartree-Fock energy,

$$E_{HF} = \langle\psi^{00} + \psi^{10} + \cdots|H^0 + H^{10}|\psi^{00} + \psi^{10} + \cdots\rangle,$$

these terms are already included so that they are not properly a correlation effect.

Next, we shall consider a specific commonly used approximate wavefunction, the Hartree-Fock wavefunction.

C. The Hartree-Fock Wavefunctions

We consider the unrestricted Hartree-Fock wavefunction

$$\psi_{UHF} = \mathcal{A}\Phi \tag{16}$$

where $\mathcal{A}$ is the antisymmetrizer,[6] and Φ is a product of spin orbitals

$$\Phi = \phi^{\alpha}_{1a}(1)\phi^{\alpha}_{2a}(2)\cdots\phi^{\alpha}_{na}(n)\phi^{\beta}_{1b}(n+1)\cdots\phi^{\beta}_{mb}(N). \tag{17}$$

Here the superscript α indicates that ϕ^{α}_{i} is a product of a spatial orbital ϕ_i and a spin function $\alpha\,(s_z = +\frac{1}{2})$, and analogously for ϕ^{β}_{i}. In the unrestricted Hartree-Fock method (UHF) we consider the total energy expression

$$E = \langle\Phi_{UHF}|H|\mathcal{A}\Phi_{UHF}\rangle \tag{18}$$

and require that the energy be stationary with respect to variations of the orbitals. The resulting variational equations are usually written as

$$H_{ka}\phi_{ka} = \epsilon_{ka}\phi_{ka} \qquad k = 1, \cdots, n \tag{19a}$$

$$H_{kb}\phi_{kb} = \epsilon_{kb}\phi_{kb} \qquad k = 1, \cdots, m \tag{19b}$$

where H_{ka} is a one-electron operator containing Coulomb and exchange operators due to the various orbitals. Alternatively, directly from (18) we see that the variational conditions equivalent to (19) are that

$$\langle \Phi^{x}_{ka} | H - E | \Phi \rangle_k = 0 \tag{20a}$$

$$\langle \Phi^{x}_{kb} | H - E | \Phi \rangle_k = 0 \tag{20b}$$

where Φ^{x}_{ka} denotes that spin orbital ϕ^{α}_{ka} has been deleted from the product Φ, and the indicated integration is then being performed over the remaining $(N - 1)$ electron coordinates.[7] These conditions are also called Brillouin's theorem.[8]

Next, consider an external perturbation H^1, and suppose that we have solved (20) using H^0 (and E^0) to obtain the optimum orbital $\{\phi^0_k\}$. We next want the new optimum orbitals $\{\phi_k\}$ obtained from (20) using $H = H^0 + H^1$ where $H^1 = \sum h^1(i)$, a one-electron perturbation. One way to solve for the new orbitals through first order is by using perturbation theory. Substituting

$$\phi_k = \phi^0_k + \phi^1_k, \tag{21}$$

$H = H^0 + H^1$, and $E = E^0 + E^1$ into (20) [or (19)], and equating terms of equal order of magnitude yields the equations defining the first-order changes ϕ'_k. In this case the first-order change in the total wavefunction is

$$\Psi^1_{UHF} = \sum_{k=1} \Phi^{k^1}_{k^0} \tag{22}$$

where $\Phi_{k^0}^{k^1}$ denotes that ϕ_k^0 is replaced by ϕ_k^1, and the sum is over all N spin-orbitals.

Now, let us consider ΔE^1 from (15) for the UHF wavefunction.

$$\overline{\Delta E}^1 = 2\mathrm{Re}\langle\Psi^1_{UHF}|H^0 - E^0|\Psi^0_{UHF}\rangle = 2\mathrm{Re}\sum_{k=1}\langle\Phi_{k^0}^{k^1}|H^0 - E^0|\mathcal{a}\Phi_{UHF}\rangle \qquad (23)$$

but from the Brillouin condition (20), each term of (23) is zero regardless of the form of ϕ_k^1, and hence for a UHF wavefunction

$$\overline{\Delta E}^1 = 0$$

for all possible one-electron perturbations.

However if the UHF method is applied to the ^2P state of Li, it is found that the up-spin orbitals are not related to the down-spin orbitals, and that the orbitals are not pure symmetry functions. Consequently the resulting many electron wavefunction (16) is neither an eigenstate of $\hat{S}^2$ nor an eigenstate of $\hat{L}^2$, i.e., it is not a pure ^2P state. If one restricts the down-spin orbitals to be equal to the up-spin orbitals [double occupation (DO) restriction],

$$\phi_{kb} = \phi_{ka} \qquad k = 1, \cdots, m \qquad (24)$$

and restricts the orbitals to be symmetry functions (e.g., pure s or p symmetry) ($\hat{L}^2$ restriction), the resulting wavefunction is denoted as restricted Hartree-Fock (RHF) or often merely as HF. Because of the double occupation restriction, new terms often appear on the right side of (20) [or (19)] involving off-diagonal Lagrange multipliers (used to force orthogonality between the orbitals; this type of new term does not appear for this state). In addition, because of the spatial symmetry restrictions, equation (21), which is valid in the unrestricted space of ϕ_k, must be replaced by the corresponding equation for the spatially restricted ϕ_k

$$\hat{P}_k \langle \Phi_k^x | H - E | \Phi \rangle_k = 0$$

where $\hat{P}_k$ projects away all undesired spatial symmetries. In summary, either because the double occupation restrictions or the spatial symmetry restrictions equation (20) is no longer satisfied, and correspondingly the terms in (23) no longer need be zero. The net result is that for a restricted HF wavefunction

$$\overline{\Delta E}^1 \neq 0$$

in general.

D. The Li ^{2}P State

The restricted Hartree-Fock wavefunction for Li ^{2}P is

$$\Psi_{\text{RHF}_m} = \mathcal{A}(\phi_{1s}\alpha\phi_{1s}\beta\phi_{2p_m}\alpha) \qquad m = 1, 0, -1 \tag{25}$$

which is an eigenfunction of $\hat{S}^2$, $\hat{S}_z$, $\hat{L}^2$, and $\hat{L}_z$ if ϕ_{1s} and ϕ_{2p_m} have the form

$$\phi_{1s} = R_{1s}Y_{0,0} \tag{26a}$$

$$\phi_{2p_m} = R_{2p}Y_{1,m} \tag{26b}$$

where $R_i(r)$ is a function of the radial coordinate and $Y_{\ell,m}$ are the usual spherical harmonics. The resulting RHF equations[9] for these orbitals are

$$H_{1s}\phi_{1s} \equiv [h + J_{1s} + \tfrac{1}{3} \sum_{m=1}^{-1} (J_{2p_m} - \tfrac{1}{2}K_{2p_m})]\phi_{1s} = \epsilon_{1s}\phi_{1s} \tag{27a}$$

$$H_{2p}\phi_{2p_m} \equiv [h + 2J_{1s} - K_{1s}]\phi_{2p_m} = \epsilon_{2p}\phi_{2p_m} \qquad m = 1, 0, -1 . \tag{27b}$$

The potential in each equation is spherically symmetric so that the solutions will be spatial-symmetry functions as assumed in (26).

If we had assumed double occupancy, i.e. (24), but had <u>not</u> restricted the orbitals to be symmetry functions, the resulting variational equations for Li ^2P would become

$$\bar{H}_{1s}\phi_{1s} \equiv [h + J_{1s} + J_{2p_m} - \tfrac{1}{2}K_{2p_m}]\phi_{1s} = \epsilon_{1s}\phi_{1s} \tag{28a}$$

$$\bar{H}_{2p}\phi_{2p_m} \equiv [h + 2J_{1s} - K_{1s}]\phi_{2p_m} = \epsilon_{2p}\phi_{2p_m} . \tag{28b}$$

Now the field terms in (28a) are not spherically symmetric, but have only $D_{\infty h}$ symmetry, and the main result is that ϕ_{1s} mixes in d character. Furthermore, since now ϕ_{1s} is no longer spherically symmetric, the field term in (28b) is also aspherical resulting in ϕ_{2p_m} mixing in f character. If equations (28) are solved for self-consistently, the resulting wavefunction will be referred to as UHF(L) to indicate that the orbital restrictions of RHF have been removed, but that the double-occupation restriction is retained. For systems such as Li these equations again lead to (20), and again we obtain

$$\overline{\Delta E}^1 = 0$$

for a UHF(L) wavefunction.

Next we will consider further the form of $\overline{\Delta E}^1$ for the case of an RHF wavefunction. Starting with (27) we make the perturbation expansions

$$\phi_k = \phi^0_k + \phi'_k$$

$$h = h^0 + h^1$$

$$\epsilon = \epsilon^0_k + \epsilon'_k$$

to obtain the zero-order and first-order RHF equations. The zero-order equations are just (27) with a superscript 0 on all terms, and the first-order equations[10] are

$$(H^0_{1s} - \epsilon^0_{1s})\phi^1_{1s} \equiv [h^0 + J^0_{1s} + \tfrac{1}{3}\sum_m (J^0_{2p_m} - \tfrac{1}{2}K^0_{2p_m}) - \epsilon^0_{1s}]\phi^1_{1s}$$

$$= [\epsilon^1_{1s} - h^1 - J^1_{1s} - \tfrac{1}{3}\sum_m (J^1_{2p_m} - \tfrac{1}{2}K^1_{2p_m})]\phi^0_{1s}$$

$$\equiv (\epsilon^1_{1s} - H^1_{1s})\phi^0_{1s} \qquad (29a)$$

$$(H^0_{2p} - \epsilon^0_{2p})\phi^1_{2p_m} \equiv [h^0 + 2J^0_{1s} - K^0_{1s} - \epsilon^0_{2p}]\phi^1_{2p_m}$$

$$= [\epsilon^1_{2p_m} - h^1 - 2J^1_{1s} + K^1_{1s}]\phi^0_{2p_m}$$

$$\equiv (\epsilon^1_{2p_m} - H^1_{2p})\phi^0_{2p_m} \qquad (29b)$$

where we have taken the many-electron perturbation to be of the form

$$H^1 = \sum_i h^1(i),$$

a sum of one-electron perturbations.

Since $J^1_{2p_m}$ and $K^1_{2p_m}$ involve $\phi^1_{2p_m}$, and since J^1_{1s} and K^1_{1s} involve ϕ^1_{1s}, we see that equations (29) are coupled. For this reason they are sometimes referred to as the coupled perturbed HF equations. We will just refer to them as the HF perturbation equations or PHF.

Note that in (29) we have taken

$$J^0_{1s}(1) \equiv \int d^3x_2 (\frac{1}{r_{12}}) \phi^{0*}_{1s}(2) \phi^0_{1s}(2) \equiv \langle \phi^0_{1s} | \frac{1}{r_{12}} | \phi^0_{1s} \rangle$$

and

$$J^1_{1s}(1) \equiv \int d^3x_2 (\frac{1}{r_{12}}) [\phi^{0*}_{1s}(2) \phi^1_{1s}(2) + \phi^{1*}_{1s}(2) \phi^0_{1s}(2)]$$

$$\equiv 2R_e \langle \phi^1_{1s} | \frac{1}{r_{12}} | \phi^0_{1s} \rangle \tag{30}$$

and similarly for the other J and K terms.

Next we consider the first-order change in the RHF wavefunction due to H^1,

$$\Psi^1_{RHF_m} = \mathcal{Q}(\phi^0_{1s}\alpha \phi^0_{1s}\beta \phi^1_{2p_m}\alpha) + \mathcal{Q}(\phi^0_{1s}\alpha \phi^1_{1s}\beta \phi^0_{2p_m}\alpha)$$

$$+ \mathcal{Q}(\phi^1_{1s}\alpha \phi^0_{1s}\beta \phi^0_{2p_m}\alpha)$$

and evaluate

$$\overline{\Delta E}^1_m = 2R_e\langle\Psi^1_{RHF_m}|H^0 - E^0|\Psi^0_{RHF_m}\rangle.$$

We have (taking $\langle\phi^1_k|\phi^0_k\rangle = 0$ for convenience)

$$R_e\langle\phi^0_{1s}\alpha\phi^0_{1s}\beta\phi^1_{2p_m}\alpha|H^0 - E^0|\mathcal{A}\Phi^0\rangle = (\epsilon^0_{2p} - E^0)R_e\langle\phi^1_{2p_m}|\phi^0_{2p_m}\rangle = 0$$

$$R_e\langle\phi^0_{1s}\alpha\phi^1_{1s}\beta\phi^0_{2p_m}\alpha|H^0 - E^0|\mathcal{A}\Phi^0\rangle = R_e\langle\phi^1_{1s}|h^0 + J^0_{1s} + J^0_{2p_m}|\phi^0_{1s}\rangle$$

$$R_e\langle\phi^1_{1s}\alpha\phi^0_{1s}\beta\phi^0_{2p_m}\alpha|H^0 - E^0|\mathcal{A}\Phi^0\rangle = R_e\langle\phi^1_{1s}|h^0 + J^0_{1s} + J^0_{2p_m} - K^0_{2p_m}|\phi^0_{1s}\rangle$$

where spin has been summed over in the one-electron expressions. Adding these terms and using the equations (29)(for the zero-order functions) we obtain that for the RHF wavefunction

$$\overline{\Delta E}^1_m = 2R_e\{\langle\phi^1_{1s}|2J^0_{2p_m} - K^0_{2p_m}|\phi^0_{1s}\rangle - \tfrac{1}{3}\langle\phi^1_{1s}|\sum_{\mu}(2J^0_{2p_\mu} - K^0_{2p_\mu})|\phi^0_{1s}\rangle\} \neq 0. \tag{31}$$

which is <u>not</u> <u>zero</u> (note however that $\sum_m \overline{\Delta E}^1_m = 0$).

Consider a perturbation H^1 to be nonspherically-symmetric so that ϕ^1_{1s} has no s component and hence the second term of (30) vanishes. The remaining term is

$$\overline{\Delta E}^1_m = 2R_e\langle\phi^1_{1s}|2J^0_{2p_m} - K^0_{2p_m}|\phi^0_{1s}\rangle. \tag{32}$$

We can also write this as

$$\overline{\Delta E}^1_m = \langle\phi^0_{2p_m}|2J^1_{1s} - K^1_{1s}|\phi^0_{2p_m}\rangle. \tag{33}$$

Comparing back to (12) and (13) we see that the expressions (31) and (32) for $\overline{\Delta E}^1_m$ are in the form of (13). However, we can use (27b) to convert (33) to resemble the form of (5). Adding (33) to

$$\langle \phi^0_{2p_m} | h^1 | \phi^0_{2p_m} \rangle,$$

we obtain

$$\overline{E}^1 = \langle \phi^0_{2p_m} | h^1 + 2J^1_{1s} - K^1_{1s} | \phi^0_{2p_m} \rangle = \langle \phi^0_{2p_m} | H^1_{2p} | \phi^0_{2p_m} \rangle . \qquad (34)$$

Thus, insofar as $\overline{E}^1$ is concerned, we can consider our system as a one-electron system ($\phi^0_{2p_m}$) and the perturbation as H^1_{2p} [i.e., $\overline{E}^1$ has the form of (5)]. The induced non-spherical field due to the core electrons is now considered part of the external perturbation.

As will be discussed in more detail in section III, the correction term (33) is referred to as the Sternheimer correction. We see below that such corrections correspond to the effect on E^1 due to relaxing the symmetry to first order.

III. NUCLEAR QUADRUPOLE COUPLING AND THE STERNHEIMER CORRECTION

The interaction between a nuclear quadrupole and the electronic charge distribution is referred to as the quadrupole coupling.[11, 12] The nuclear quadrupole moment can be described either (1) as a Cartesian tensor Q_{ij} whose components are the integrals over the nuclear charge density of $3r_ir_j - \delta_{ij}r^2$ where

$r_i = x, y, z$ depending on i, or (2) as a spherical tensor Q_m whose components are the integrals over the nuclear charge density of $2r^2C_m^{(2)}$ where the functions $C_m^{(k)}$ are defined in terms of spherical harmonics Y_{km} by $C_m^{(k)} = \sqrt{4\pi/(2k+1)}\ Y_{km}$.

The interaction operator is, for an n electron system,

$$H_Q = \sum_{\mu=1}^{n} h_Q(\mu)$$

where

$$h_Q(\mu) = \frac{1}{6}\sum_{ij} Q_{ij}q_{ij}(\mu) = \frac{1}{4}\sum_m Q_m^* q_m(\mu)$$

and the q_{ij} are the Cartesian, and q_m the spherical, electric field gradient tensor operators:

$$q_{ij}(\mu) = -e(3r_{\mu i}r_{\mu j} - \delta_{ij}r_\mu^2)/r_\mu^5$$

$$q_m(\mu) = -2eC_m^{(2)}(\theta_\mu, \varphi_\mu)/r_\mu^3.$$

Within a manifold of atomic states described by the quantum numbers I, L, S, which have their usual significance, H_Q can be reduced to an angular momentum operator equivalent form. By the Wigner-Eckart theorem the nuclear quadrupole moment tensors are proportional to the analogous angular momentum tensors:

$$Q_{ij} = Q'\left[\frac{3}{2}(I_iI_j + I_jI_i) - \delta_{ij}I^2\right]$$

where the angular momentum operators here and throughout this paper are defined without the factor of ħ.

The proportionality constant Q' is usually expressed in terms of eQ, the diagonal matrix element of Q_{zz} in the $M_I = I$ state:

$$eQ = Q' I(2I - 1).$$

For the exact non-relativistic electronic wavefunctions, the first-order energies are determined from matrix elements of H_Q so that the field gradient operator can be replaced by an orbital angular momentum operator in an analogous way using the constant q'. Then the Hamiltonian is

$$H_Q = q'Q' [(3/2)(I \cdot L)^2 + (3/4)(I \cdot L) - \tfrac{1}{2} I(I + L)L(L+1)] \tag{35a}$$

When the total electronic angular momentum quantum number J is a good quantum number, the Hamiltonian can be further reduced to

$$H_Q = q_J' Q' [(3/2)(I \cdot J)^2 + (3/4)(I \cdot J) - \tfrac{1}{2} I(I+1)J(J+1) \tag{35b}$$

where

$$q_J' = \frac{3X(X - 1) - 4L(L + 1)J(J + 1)}{2J(J + 1)(2J - 1)(2J + 3)} q'$$

and

$$X = J(J + 1) + L(L + 1) - S(S + 1).$$

The constant q_J' is related to the more usual constant q_J by

$$q_J = q_J' J(2J - 1).$$

For an approximate electronic wavefunction, the additional terms in the first-order part of the matrix elements of the total Hamiltonian are

$$\Delta E_{Qm'm} = \langle \Psi^0_{m'} | H^0 | \Psi^1_m \rangle + \langle \Psi^0_{m'} | H^0 | \Psi^1_m \rangle$$

where the subscripts refer to possibly different members of the set of functions degenerate with respect to H^0, and the wavefunctions have both nuclear spin and electronic dependence. These extra terms are usually referred to as the Sternheimer correction. When these terms are included, the quadrupole coupling Hamiltonians still have the form (35), but the constants q' and q_J will now contain additional terms dependent on the first-order wavefunctions. By analogy with (31), we see that, for the ^2P state of Li, the correction terms to the M'_L (= m′), M_L (= m) matrix element become

$$\begin{aligned}\Delta E_{Qm'm} = \; & 2\,[\varphi^1_{1s}\varphi^0_{1s} | \varphi^0_{2pm'}\varphi^0_{2pm}] + 2\,[\varphi^0_{1s}\varphi^1_{1s} | \varphi^0_{2pm'}\varphi^0_{2pm}] \\ & - [\varphi^0_{2pm'}\varphi^0_{1s} | \varphi^1_{1s}\varphi^0_{2pm}] - [\varphi^0_{2pm'}\varphi^1_{1s} | \varphi^0_{1s}\varphi^0_{2pm}] \\ & - \frac{2}{3}\,\delta_{m'm}\, R_e \,\langle \varphi^1_{1s} | \textstyle\sum_{m''} (2J^0_{2pm''} - K^0_{2pm''}) | \varphi^0_{1s} \rangle \qquad (36)\end{aligned}$$

Considering the equations for the perturbed Hartree-Fock orbitals when the perturbation is h_Q, it is clear from (29a) that φ^1_{1s} will have only d(ℓ = 2) angular dependence. Thus the last term in (36) is zero by symmetry, and the remaining terms can be rewritten as

$$\Delta E_{Qm'm} = \langle \varphi^0_{2pm'} | 2J^1_{1s} - K^1_{1s} | \varphi^0_{2pm} \rangle \tag{37}$$

where J^1_{1s} is given by (30) and K^1_{1s} is defined similarly. Thus we obtain for the total first-order matrix elements,

$$E_{Qm'm} = \langle \varphi^0_{2pm'} | h_Q + 2J^1_{1s} - K^1_{1s} | \varphi^0_{2pm} \rangle \tag{38}$$

which are the same as the matrix elements of the first-order Hartree-Fock Hamiltonian. This expression (38) is the same as if the nuclear quadrupole potential were $h_Q + 2J^1_{1s} - K^1_{1s}$ rather than h_Q. Since these additional terms are just the potential due to the quadrupole character induced in the core electrons by the nuclear quadrupole moment, the Sternheimer correction is often interpreted as the interaction between the (distributed) induced quadrupole moment of the core and the distributed electric field gradient due to the outer electrons. This interpretation seems so physical that it may not be obvious that the correction term disappears[13] as one improves the wavefunction to the exact (or even the UHF) function. Thus the Sternheimer correction is <u>not</u> a physical effect, but a correction of limited extent which is necessitated only by approximations in the zero-order wavefunction.

Next we consider the Sternheimer correction for the Li ^2P using the first-order quadrupole-perturbed Hartree-Fock wavefunction and compare the calculated "total" field gradient obtained with values obtained from CI and other calculations.

IV. STERNHEIMER CORRECTIONS FOR Li 2 ^{2}P

A. First-Order Hartree-Fock Equations

We choose our approximate unperturbed wavefunction to be the spatial-symmetry-restricted Hartree-Fock wavefunction (that is, the orbitals are restricted so that the wavefunction is an eigenfunction of L^2 and S^2). The spatial symmetry restriction for the zero-order orbitals is expressed by

$$\varphi^0_{n\ell m} = R^0_{n\ell} Y_{\ell m}. \tag{39}$$

Similarly, defining h^A_Q as the angular part of h_Q,

$$h^A_Q = r^3 h_Q,$$

the symmetry restriction for the first-order orbitals can be expressed by

$$\varphi^1_{n\ell m} = \sum_{\ell'} R^1_{n\ell\ell'} \sum_{m'} Y_{\ell' m'} \langle Y_{\ell' m'} | h^A_Q | Y_{\ell m} \rangle. \tag{40}$$

In writing the perturbed Hartree-Fock equations, we denote the zero- and first-order Hartree-Fock Hamiltonians for the $n\ell$ set of orbitals by $f^0_{n\ell}$ and $f^1_{n\ell}$. In taking account of the degeneracy of the zero-order orbitals, we need the matrix $\langle \varphi^0_{n\ell m'} | f^1_{n\ell} | \varphi^0_{n\ell m} \rangle$, which can also be written as $q^R_{n\ell} \langle Y_{\ell m'} | h^A_Q | Y_{\ell m} \rangle$ by separating the radial integrals into the quantity $q^R_{n\ell}$. The equations for the first-order orbitals are essentially (29a) and (29b), but generalized to take account of the zero-order degeneracy:

$$(f^0_{n\ell} - \epsilon^0_{n\ell})\varphi^1_{n\ell m} + f^1_{n\ell}\varphi^0_{n\ell m} - \sum_{m'} \varphi^0_{n\ell m'} \langle \varphi^0_{n\ell m'} | f^1_{n\ell} | \varphi^0_{n\ell m} \rangle = 0 \qquad (41)$$

Off-diagonal Lagrange multipliers were not included in (41) since they are not necessary for the present example.

The operators $f^0_{n\ell}$ and $f^1_{n\ell}$ contain averaged potentials defined by

$$J_{n\ell} = \frac{1}{2\ell + 1} \sum_m J_{n\ell m}$$

for Coulomb potentials, and similarly for exchange potentials. The zero- and first-order averaged Coulomb potentials are

$$J^0_{n\ell} = \langle R^0_{n\ell} | \frac{1}{r_>} | R^0_{n\ell} \rangle \qquad (42)$$

$$J^1_{n\ell} = 2h^A_Q \sum_{\ell'} \frac{2\ell' + 1}{5} \begin{pmatrix} \ell' & 2 & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \langle R^0_{n\ell} | \frac{r_<^2}{r_>^3} | R^1_{n\ell\ell'} \rangle \qquad (43)$$

where here and in the following, Wigner 3 - j and 6 - j symbols are used. Matrix elements of the zero- and first-order exchange operators are

$$\langle Y_{\ell''m''} | K^0_{n\ell} | \varphi^1_{n'\ell'm'} \rangle$$

$$= \langle Y_{\ell''m''} | h^A_Q | Y_{\ell'm'} \rangle R^0_{n\ell} \sum_k \begin{pmatrix} \ell'' & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \langle R^0_{n\ell} | \frac{r_<^k}{r_>^{k+1}} | R^1_{n'\ell'\ell''} \rangle \qquad (44)$$

$$\langle Y_{\ell''m''} | K^{1}_{n\ell} | \varphi^{0}_{n'\ell'm'} \rangle$$

$$= \langle Y_{\ell''m''} | h^{A}_{Q} | Y_{\ell'm'} \rangle (-1)^{\ell+\ell''} \sum_{\ell''',k} (2\ell''' + 1) \frac{\begin{pmatrix} \ell & 2 & \ell''' \\ 0 & 0 & 0 \end{pmatrix}}{\begin{pmatrix} \ell'' & 2 & \ell' \\ 0 & 0 & 0 \end{pmatrix}} \times$$

$$\left[\begin{Bmatrix} \ell'' & 2 & \ell' \\ \ell & k & \ell''' \end{Bmatrix} \begin{pmatrix} \ell'' & k & \ell''' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} R^{1}_{n\ell\ell'''} \langle R^{0}_{n\ell} | \frac{r_<^{\,k}}{r_>^{\,k+1}} | R^{0}_{n'\ell'} \rangle + \right.$$

$$\left. \begin{Bmatrix} \ell'' & 2 & \ell' \\ \ell''' & k & \ell \end{Bmatrix} \begin{pmatrix} \ell'' & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell''' & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} R^{0}_{n\ell} \langle R^{1}_{n\ell\ell'''} | \frac{r_<^{\,k}}{r_>^{\,k+1}} | R^{0}_{n'\ell'} \rangle \right] \qquad (45)$$

For the Li ^2P problem there are three radial functions to be found: R^1_{1sd}, R^1_{2pp}, and R^1_{2pf}. The set of three coupled equations determining them can be found from (41) by the appropriate substitution of (39), (40), and by the use of (42) through (45) as well as the properties of spherical harmonics. The resulting equations are, in atomic units,

$$\left(-\frac{1}{2}\frac{1}{r}\frac{d^2}{dr^2} r + \frac{3}{r^2} - \frac{3}{r} + \langle R^0_{1s} | \frac{1}{r_>} | R^0_{1s} \rangle + \langle R^0_{2p} | \frac{1}{r_>} | R^0_{2p} \rangle - \epsilon^0_{1s}\right) R^1_{1sd}$$

$$- \left(\frac{1}{15} \langle R^0_{2p} | \frac{r_<}{r_>^2} | R^1_{1sd} \rangle + \frac{3}{70} \langle R^0_{2p} | \frac{r_<^3}{r_>^4} | R^1_{1sd} \rangle\right) R^0_{2p}$$

$$+ \left(\frac{1}{r^3} + \frac{2}{5} \langle R^0_{1s} | \frac{r_<^2}{r_>^3} | R^1_{1sd} \rangle + \frac{4}{25} \langle R^0_{2p} | \frac{r_<^2}{r_>^3} | R^1_{2pp} \rangle + \frac{6}{25} \langle R^0_{2p} | \frac{r_<^2}{r_>^3} | R^1_{2pf} \rangle\right) R^0_{1s}$$

$$- \frac{1}{15} \langle R^0_{2p} | \frac{r_<}{r_>^2} | R^0_{1s} \rangle R^1_{2pp} - \frac{1}{10} \langle R^0_{2p} | \frac{r_<}{r_>^2} | R^0_{1s} \rangle R^1_{2pf}$$

$$- \left(\frac{1}{15} \langle R^1_{2pp} | \frac{r_<}{r_>^2} | R^0_{1s} \rangle + \frac{3}{70} \langle R^1_{2pf} | \frac{r_<^3}{r_>^4} | R^0_{1s} \rangle\right) R^0_{2p} = 0 \qquad (46)$$

$$\left(-\frac{1}{2}\frac{1}{r}\frac{d^2}{dr^2} r + \frac{1}{r^2} - \frac{3}{r} + 2\langle R^0_{1s} | \frac{1}{r_>} | R^0_{1s} \rangle - \epsilon^0_{2p}\right) R^1_{2pp} - \frac{1}{3} \langle R^0_{1s} | \frac{r_<}{r_>^2} | R^1_{2pp} \rangle R_{1s}$$

$$+ \left(\frac{1}{r^3} + \frac{4}{5} \langle R^0_{1s} | \frac{r_<^2}{r_>^3} | R^1_{1sd} \rangle - q^R_{2p}\right) R^0_{2p} - \frac{1}{3} \langle R^0_{1s} | \frac{r_<}{r_>^2} | R^0_{2p} \rangle R^1_{1sd}$$

$$- \frac{1}{3} \langle R^1_{1sd} | \frac{r_<}{r_>^2} | R^0_{2p} \rangle R^0_{1s} = 0 \qquad (47)$$

$$\left(-\frac{1}{2}\frac{1}{r}\frac{d^2}{dr^2}\, r + \frac{6}{r^2} - \frac{3}{r} + 2\langle R^0_{1s}|\frac{1}{r_>}|R^0_{1s}\rangle - \epsilon^0_{2p}\right)R^1_{2pf} - \frac{1}{7}\langle R^0_{1s}|\frac{r_<^3}{r_>^4}|R^1_{2pf}\rangle R^0_{1s}$$

$$+ \left(\frac{1}{r^3} + \frac{4}{5}\langle R^0_{1s}|\frac{r_<^2}{r_>^3}|R^1_{1sd}\rangle\right)R^0_{2p} - \frac{1}{3}\langle R^0_{1s}|\frac{r_<}{r_>^2}|R^0_{2p}\rangle R^1_{1sd} - \frac{1}{7}\langle R^1_{1sd}|\frac{r_<^3}{r_>^4}|R^0_{2p}\rangle R^0_{1s}$$

$$= 0 \qquad (48)$$

where

$$q^R_{2p} = \langle R^0_{2p}|\frac{1}{r^3}|R^0_{2p}\rangle + \frac{4}{5}\langle R^0_{2p}\langle R^0_{1s}|\frac{r_<^2}{r_>^3}|R^1_{1sd}\rangle R^0_{2p}\rangle - \frac{2}{3}\langle R^0_{2p}\langle R^0_{1s}|\frac{r_<}{r_>^2}|R^0_{2p}\rangle R^1_{1sd}\rangle \qquad (49)$$

The three equations (46) to (48) are coupled integro-differential equations, for which there are two well established solution techniques: (1) finite basis set expansion, and (2) numerical finite difference approximations. In the basis expansion approach, the expansion coefficients and orbital exponents are chosen to minimize the second-order energy. Because of the $1/r^3$ behavior of the perturbation operator, the function R^1_{1sd}, for example, behaves as $1/r$ for small r, so that the basis set must contain $1/r$ like functions if an accurate solution is to be obtained. Such functions lead to divergent terms in the second-order energy, but this difficulty can be surmounted, as has been shown in an analogous problem. Nonetheless we decided to carry out a direct numerical solution of the equations, and the procedures used will be described next.

B. Numerical Solutions of the First-Order Equations

By using central first and second differences to approximate the first and second derivatives, the integro-differential equations are reduced to three coupled sets of simultaneous linear equations. These matrix equations were solved by iteration until full selfconsistency was attained. Since the perturbation operator is very large for small r, we used a square-root grid (i.e., the coordinates were transformed from r to $X = \sqrt{r}$). The integrals of the necessary combinations of an $r_<^k/r_>^{k+1}$ function and two radial functions were evaluated by integrating successively, over the square-root grid, two first-order differential equations in a manner analogous to that described by Froese.[14] The difference equations were iterated until the results of two successive cycles differed by at most 10^{-6} at all points considered.

The behavior of the first-order radial functions for r near zero can be derived by making power series expansions just as is done in deriving cusp conditions for the zero-order radial functions. For a nuclear charge Z,

$$R^1_{1sd} = -\tfrac{1}{3}[R^0_{1s}]_{r=0}(1/r - \tfrac{2}{3}Z + 0(r) + \cdots)$$

$$R^1_{2pp} = -[R^0_{2p}/r]_{r=0}(1 - \tfrac{1}{3}Zr\ln r + 0(r) + (1/6)Z^2r^2\ln r + 0(r^2) + \cdots)$$

$$R^1_{2pf} = -(1/6)[R^0_{2p}/r]_{r=0}[1 - (2/5)Zr + 0(r^2) + \cdots].$$

In solving for R^1_{1sd} and R^1_{2pf} it was convenient to make the usual substitution $\theta^1_{n\ell\ell'} = rR^1_{n\ell\ell'}$, which, as well as removing the first derivatives in the kinetic energy, led to simple boundary conditions at r = 0:

$$\theta^1_{1sd}(0) = -\tfrac{1}{3}R^0_{1s}(0)$$

$$\theta^1_{2pf}(0) = 0.$$

The corresponding substitution for R^1_{2pp} was not used because the resulting function has a second derivative which varies as ln r for small r and hence cannot be described by a second difference approximation. The substitution $v_p = r^2 R^1_{2pp}$ was made instead; the second derivative of v_p varies as $r \ln r$ for small r, which we found to be sufficiently smoothed for the second difference approximation to be successful. The $r = 0$ boundary condition is

$$v_p(0) = 0.$$

A possible alternate substitution is

$$w_p = r(R^1_{2pp} - \tfrac{1}{3} Z\, R^0_{2p} \ln r),$$

but we did not find it necessary to investigate it.

The second boundary condition on all of the solutions is, of course, that they go to zero for large r, and the only orthogonality condition is that R^1_{2pp} be kept orthogonal to R^0_{2p}. The equations were solved for 600, 800, and 1000 points, out to 25 a.u. in each case, and the resulting Sternheimer corrections for the different mesh sizes differed only in the eighth decimal place. The program was tested by solving the corresponding hydrogenic perturbed equations,[15] and the solutions obtained agreed with the exact solutions within 10^{-6}. The calculations were carried out in double precision on an IBM 360/75 computer.

In addition to solving the coupled perturbed Hartree-Fock (PHF) equations (37) and (38), we solved the uncoupled approximation (UPHF) to PHF, obtained by removing the term

$$\tfrac{1}{3}\sum_m (J^1_{2pm} - \tfrac{1}{2}K^1_{2pm})$$

from equation (37). Doing this also makes it unnecessary to solve equation (38). The next approximation, denoted UPHF-1, was to neglect J^1_{1s} from the previous (UPHF) approximation to equation (37). The final simplification and approximation of equation (37) was to replace the average electron repulsion potential

$$J^0_{1s} + \tfrac{1}{3}\sum_m (J^0_{2pm} - \tfrac{1}{2}K^0_{2pm}),$$

which contains a nonlocal term, K^0_{2pm}, by the local potential

$$\epsilon^0_{1s} + Z/r + \tfrac{1}{2}(1/\varphi^0_{1s})\,\nabla^2\,\varphi^0_{1s}.$$

This approximation has been used by Sternheimer and we denote it by UPHF-S.

Specifically, in his latest calculation on Li 2 ^2P, Sternheimer[1] chose to approximate φ^0_{1s} by a single 1s Slater function which had an orbital exponent, ζ, of 2.69. The corresponding local potential is then just $(Z - \zeta)/r$ and φ^1_{1s} can be obtained analytically. The replacement of the nonlocal potential by a local potential in this instance seems questionable since φ^1_{1s} has d angular dependence, and thus "sees" different terms than would φ^0_{1s}, which has s angular dependence. This is merely restating the fact that local potentials are angular-momentum dependent. We found that the SCF process did not converge when we used the local potential in the UPHF approximation to equation (37).

C. Results

The contribution of a particular open shell orbital to the overall field gradient parameter q' can be expressed in terms of a $q'_{n\ell}$ parameter defined by

$$q'_{n\ell}(\varphi^{0}_{n\ell m'}|(3/2)(\ell_i\ell_j + \ell_j\ell_i) - \delta_{ij}\ell^{2}|\varphi^{0}_{n\ell m}) = q^{R}_{n\ell}(\varphi^{0}_{n\ell m'}|r^{3}q_{ij}|\varphi^{0}_{n\ell m}).$$

The ratio of $q'_{n\ell}$ to $q^{R}_{n\ell}$ can be evaluated most easily for the $m' = m = 0$, $i = j = z$ case.

$$q'_{n\ell} = q^{R}_{n\ell}[-2e(2\ell + 1)\begin{pmatrix} \ell & 2 & \ell \\ 0 & 0 & 0 \end{pmatrix}^{2}]/[-\ell(\ell+1)] = \{2/[(2\ell-1)(2\ell+3)]\}eq^{R}_{n\ell}$$

For our particular example, in atomic units,

$$\begin{aligned} q' = q'_{2p} = {} & (2/5)[\langle R^{0}_{2p}|(1/r^{3})|R^{0}_{2p}\rangle \\ & + (4/5)\langle R^{0}_{2p}|\langle R^{0}_{1s}|(r_{<}^{2}/r_{>}^{3})|R^{1}_{1sd}|R^{0}_{2p}\rangle \\ & - \tfrac{2}{3}\langle R^{0}_{2p}\langle R^{0}_{1s}|(r_{<}/r_{>}^{2})|R^{0}_{2p}\rangle R^{1}_{1sd}\rangle]. \end{aligned}$$

Sternheimer defines parameters R_D and R_E to express the ratios of the two-electron integral terms in q' to the one-electron integral term. Thus R_D is the ratio of the second (direct or coulomb) term to the first and R_E is the ratio of the third (exchange) term to the first. R is the sum of R_D and R_E.

$$q' = (2/5)(1 + R)\langle R^{0}_{2p}|(1/r^{3}|R^{0}_{2p}\rangle$$

In Table I we compare the values of these Sternheimer correction factors as calculated in the different approximations. Values of the field gradient parameter q', with and without the Sternheimer terms, are given correspondingly in Table II.

We note that the accurately solved coupled first-order PHF equations lead to a total field gradient of -0.02062 a.u., which corresponds to a change of 11.85% in the zero-order RHF field gradient of -0.02339 a.u. Moreover, we note that this value is insensitive to the coupled nature of the equations since neglect of the coupling, UPHF, leads to no change in the total field gradient. Further neglect or approximation of terms, as in UPHF-1 and UPHF-2, still leads to essentially the same change in the RHF field gradient, 12.23%, as do the PHF-corrected field gradients.

These results are unfortunately not directly comparable to the calculations by Sternheimer[1] because his zero-order field gradient, -0.02597 a.u., is derived from a 2p-orbital adjusted to empirical data rather than determined from a variationally adjusted wavefunction. Nonetheless, using a single scaled 1s-orbital for the Li core orbital, and a procedure equivalent to UPHF-2, Sternheimer finds a total field gradient of -0.02297 a.u. This value is 11.56% of his initial field gradient, and it differs from the RHF value by 0.0004 a.u. This final value is however dependent on the particular choice of the zero-order wavefunction, and the authors believe that a consistent formulation of the correction term should be based on the RHF wavefunction and not the empirical one.

TABLE I. Comparison of the Calculated Sternheimer Corrections

	R_D	R_E	R
PHF[a]	-0.18497	+0.06645	-0.11852
UPHF[a]	-0.18495	+0.06636	-0.11859
UPHF-1[a]	-0.19139	+0.06905	-0.12234
UPHF-S[a]	-0.19142	+0.06907	-0.12235
Sternheimer[b]	-0.1819	+0.0663	-0.1156
Brueckner-Goldstone[c]	-0.2630	+0.1069	-0.1561
UHF[d]			-0.11629
Brueckner-Goldstone[e]			-0.17
CI[f]			+0.0187
Bethe-Goldstone[g]			-0.0255

[a] Present work.

[b] See Ref 1.

[c] First order contribution as obtained by Brueckner-Goldstone Theory. See reference 20.

[d] Unrestricted Hartree-Fock result allowing d basis functions to mix in the $1s^2$ Li core. See Table IV.

[e] Includes higher-than-first order contributions. See reference 20.

[f] See reference 18 and 19.

[g] See reference 21.

TABLE II. Comparison of Total Field Gradients[a, b]

	Zero-Order	Total
HF	-0.02339[c]	-0.02339
PHF	-0.02339	-0.02062
UPHF	-0.02339	-0.02062
UPHF-1	-0.02339	-0.02053
UPHF-S	-0.02339	-0.02053
Sternheimer	-0.02597	-0.02297
Brueckner-Goldstone	-0.0234	-0.01974
UHF	-0.02067	-0.02067
Brueckner-Goldstone	-0.0234	-0.01941
CI	-0.02339	-0.02383
Bethe-Goldstone	-0.02342	-0.02282

[a] Atomic units are used; 1 unit of field gradient = 3.241394×10^{15} e.s.u./cm^3. See reference 22.

[b] All relevant references are the same as in Table I.

[c] Calculated using a slightly improved 9 basis function Li 2^2P wavefunction originally due to A. W. Weiss, See reference 18 and Table III.

Upon removing the spatial symmetry restrictions on the RHF wavefunction and optimizing the energy, we find that 3d-character mixed into the 1s-orbital. This is now allowed because the variational field due to the 2p-orbital is aspherical. Although the total energy change, 0.00001 a.u., was minimal, the corresponding new field gradient, -0.02067 a.u., corresponds to a change of 11.63% from the RHF value,[16] and it agrees well with the PHF-corrected field gradient of -0.02062 a.u. This close agreement is also consistent with our previous discussion of the origin of the Sternheimer correction in the spatial symmetry restrictions on approximate wavefunctions, i.e., upon removal of these restrictions, the correction is automatically included in the zero-order expectation value of the property.[17]

Although we found the UHF field gradient to be insensitive to equivalence restrictions of the core-orbitals (-0.02064 a.u.) or to spin projection of the UHF wavefunction (-0.02062 a.u.), we did find the UHF field gradient to be sensitive to the nature of the d-basis functions. For example, a preliminary calculation with three d-functions (8.7, 3.398, 2.544) resulted in a field gradient of -0.02234 a.u. which is a change of only 4.08% in the RHF value.

Using a 45 term Configuration Interaction (CI) wavefunction by Weiss,[18] Ardill and Stewart[19] found a field gradient of -0.02383 a.u., or 0.019% of the RHF value. This differs from the PHF-corrected field gradient, and the origin of the discrepancy lies in that this CI wavefunction kept the core description to a ^1S, therefore not allowing for the polarization effect needed to include the

TABLE III. The Zero-Order Wave Function Li $2^2p^{a,b}$

$n\ell$	ζ	ϕ_{1s}	ϕ_{2p}
1s	3.0	0.89125	---
3s	8.7	-0.00104	---
3s	3.398	0.10448	---
3s	2.544	0.05427	---
$2p_0$	1.5	---	0.13268
$4p_0$	2.12	---	0.04423
$4p_0$	1.275	---	0.32469
$4p_0$	0.785	---	0.50652
$4p_0$	0.566	---	0.16117
Orbital Engenvalue		-2.53073	-0.12867
Total Energy		-7.365069	

[a] Atomic units are used, i.e., one unit of energy ≡ 1 hartree = 27.211652 eV. See reference 22.

[b] This wave function is similar to that of A. W. Weiss, see reference 18, except that the s basis functions have been reoptimized for the 2^2P state.

Table IV. The UHF Wavefunction for Li 2^2P^a

$n\ell$	ζ	ϕ_{1a}	ϕ_{1b}	ϕ_{2a}
1s	3.0	0.890 678	0.891 819	0.0
3s	8.7	-0.000 967	-0.001 110	0.0
3s	3.398	0.103 267	0.105 652	0.0
3s	2.544	0.056 612	0.051 971	0.0
3d	8.7	0.000 028	-0.000 003	0.0
3d	7.0	-0.000 229	0.000 026	0.0
3d	6.3	0.000 289	-0.000 035	0.0
3d	4.6	-0.000 155	0.000 009	0.0
3d	3.398	0.000 300	0.000 361	0.0
3d	2.544	-0.000 984	-0.001 406	0.0
3d	1.5	0.001 401	-0.000 006	0.0
3d	0.8	0.000 506	0.000 001	0.0
3d	0.4	-0.000 009	-0.000 0001	0.0
2p	1.5	0.0	0.0	0.132 815
4p	2.12	0.0	0.0	0.044 292
4p	1.275	0.0	0.0	0.324 827
4p	0.785	0.0	0.0	0.506 491
4p	0.566	0.0	0.0	0.160 903
Orbital Eigenvalue		-2.531 297	-2.530 008	-0.128 703
Total Energy		-7.365 085		
V/T		-1.999 999		

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[a] Atomic units are used, i.e. one unit of energy ≡ 1 Hartree = 27.211652 eV. See reference 22.

Sternheimer correction. Alternative calculations by Lyons, Pu, and Das,[20] using Brueckner-Goldstone many-body perturbation techniques, yield a first-order correction of 15.61% in the RHF field gradient, which corresponds to a total field gradient of -0.01974 a.u. Upon extending their calculations to second-order these authors find a value of -0.0194 a.u., or 17% of the RHF value. It would thus seem that the first-order term is the dominant change above the RHF value. However, recent Bethe-Goldstone variational calculations by Nesbet[21] find that, although the first-order like terms correspond to a change of 11.88%, the second-order and higher terms lead to a final change of only 2.55% of the RHF value, or a total field gradient of -0.02282 a.u. This result would indicate that the property is not converging rapidly at all. A resolution of these questions must at this time await further calculations on more diverse systems.

V. CONCLUSIONS

We have investigated the relation of the Sternheimer correction to first-order properties to the approximate nature of the wavefunction in connection with Brillouin's theorem. In particular we have examined the case of the calculation of electronic field gradients for use in the nuclear quadrupole coupling with Hartree-Fock wavefunctions in the Li 2 ^2P state. We find that in such a case the correction is nonvanishing if there are spatial symmetry restrictions on the orbitals of the RHF wavefunction. Accurate solution of the first-order perturbed equations leads to a change in the RHF Li ^2P field gradient of 11.85% to yield a total first-order result of -0.02062 a.u. We also find that this result is insensitive to approximations in the PHF equations, and that a spatial symmetry unrestricted UHF(L) calculation yields essentially (-0.02067 a.u.) the same result, in agreement with the theoretical considerations.

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REFERENCES

1 R. M. Sternheimer, Phys. Rev. **80**, 102 102 (1950); **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957); **146**, 140 (1966); **164**, 10 (1967).

2 R. M. Sternheimer, Int. J. Quantum Chemistry **1**, 67 (1967).

3 R. M. Sternheimer, H. M. Foley, Phys. Rev. **92**, 1460 (1953).

4 J. O. Hirschfelder, W. Byers-Brown, S. T. Epstein, Advances in Quantum Chemistry **1**, 255 (1964).

5 A. Dalgarno, A. L. Stewart, Proc. Roy. Soc. (London), **A247**, 245 (1958).

6 $\mathcal{A} = \sum_{\tau}' \zeta \tau$ where the sum is over all N! permutations τ and ζ_τ is the parity of τ.

7 In $\langle\Phi_{ka}|H|\ \Phi\rangle$ of (20) the factor $\langle\Phi_{ka}|\Phi_{ka}\rangle$ is replaced by 1, and $\langle\Phi_{ka}|\Phi_{ja}\rangle$ is replaced by 0 *before* removing ϕ_{ka}.

8 L. Brillouin, Actualités Sci. Ind. **71**, **159**, **160** (1933-34).

9 C. C. J. Roothaan, Rev. Mod. Phys., **32**, 179 (1960).

10 A. Dalgarno, Proc. Roy.Soc.(London) **A251**, 282 (1959), R. M. Stevens, R. M. Pitzer, W. N. Lipscomb, J. Chem. Phys. **38**, 550 (1963).

11 N. F. Ramsey, *Molecular Beams,* Oxford University Press(1956).

12 E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants,* Academic Press, London (1969).

13 S. L. Kahalas, R. K. Nesbet, J. Chem. Phys., **39**, 529 (1963).

14 C. Froese, Can. J. Phys. **41**, 1895 (1963).

15 $R^{1}_{1sd} = -\frac{2}{3}\sqrt{Z^3}\ (1/r + \frac{1}{3}Z)e^{-Zr}$

$$R^1_{2pd} = -\sqrt{Z^5/24}\,(1 - \tfrac{1}{3}Zr\,\ln(\gamma\,Zr) + (31/36)Zr - (1/12)Z^2r^2)e^{-\frac{1}{2}Zr}$$

$$R^1_{2pf} = -(1/6)\sqrt{Z^5/24}\,(1 + (1/10)Zr)e^{-\frac{1}{2}Zr}$$

where $\ln\gamma = 0.5772157$ (Euler's Constant). See also C. Schwartz, Annals of Physics, **6**, 156 (1959).

[16] Upon completion of the work reported here, the following paper S. Larsson, Phys. Rev. **2A**, 1248 (1970), appeared reporting similar UHF field gradients.

[17] R. E. Watson, A. J. Freeman, Phys. Rev. **131**, 250 (1963); A. J. Freeman, R. E. Watson, Phys. Rev. **131**, 2566 (1963); **132**, 706 (1963).

[18] A. W. Weiss, Astrophys. J., **138**, 1262 (1963).

[19] R. W. Ardill, A. L. Stewart, J. Chem. Phys. **47**, 4853 (1967).

[20] J. D. Lyons, R. T. Pu, T. P. Das, Phys. Rev. **178**, 1 (1969).

[21] R. K. Nesbet, Phys. Rev. **A2**, 661 (1970).

[22] B. N. Taylor, W. H. Parker, D. N. Langenberg, *The Fundamental Constants and Quantum Electrodynamics,* Academic Press, New York (1969).

III. THE THEORETICAL DETERMINATION OF THE Li_2 B $^1\Pi_u$ POTENTIAL ENERGY CURVE.

1. INTRODUCTION:

In addition to any inherent features of interest, the nature of the potential curve of the $B^1\Pi_u$ electronic excited state of Li_2 has been closely connected with the spectroscopic determination of the dissociation energy of the $X^1\Sigma_g^+$ electronic ground state of Li_2. In 1931 Loomis and Nusbaum,[1] from an extrapolation of the vibrational energy spacings of the $B^1\Pi_u$ state, determined the dissociation energy of the $B^1\Pi_u$ state to be $D_0 = 3{,}738\ cm^{-1} = 0.46 \pm 0.03$ eV.[2] From this datum they then deduced the dissociation energy of the $X^1\Sigma_g^+$ ground state as follows:

$$\begin{aligned} D_0(X^1\Sigma_g^+) &= \nu_{00} + D_0(B^1\Pi_u) - \nu(Li^2S \rightarrow {}^2P) \qquad (1) \\ &= 20{,}398\ cm^{-1} + 3{,}738\ cm^{-1} - 14{,}904\ cm^{-1} \\ &= 9{,}232\ cm^{-1} = 1.14 \pm 0.03\ eV \end{aligned}$$

Here ν_{00} is the energy between the zeroth vibrational levels of the $X^1\Sigma_g^+$ and $B^1\Pi_u$ states and $\nu(Li^2S \rightarrow {}^2P)$ is the atomic excitation energy from the Li 2^2 S to the Li 2^2 P states.

Alternatively, thermochemical data by Lewis[3] indicated a dissociation energy for the $X^1\Sigma_g^+$ state of $D_0 = 1.03 \pm 0.04$ eV, and a thorough theoretical calculation by Das[4] recently placed the dissociation energy at $D_0 = 0.99$ eV (a lower limit). Thus, a need arose to reexamine the spectroscopic data.

Inherent in the analysis by Loomis and Nusbaum, as summarized by equation (1), is the assumption that the $B^1\Pi_u$ potential energy curve contains no humps at long internuclear distances. However, for molecular states which arise from a ^2S atom and a ^2P atom, such as the Li_2, $B^1\Pi_u$ state, King and Van Vleck[5, 6] have shown that the corresponding $^1\Pi_u$ potential curve is repulsive at large internuclear separations. Analogous results were also found by Mulliken[7] who reexamined the nature of these long-range interactions in great detail. Coupling this long distance behavior with the known stability of the $B^1\Pi_u$ state one can then predict that this state has a potential hump, and as a consequence the spectroscopic data by Loomis and Nusbaum is really insufficient to deduce the ground state dissociation energy of Li_2.

In 1969, Velasco, Ottinger and Zare,[8] redetermined the dissociation energy for the ground state of Li_2 by direct extrapolation of the ground state vibrational energies which they obtained from the fluorescence spectra $B^1\Pi_u \rightarrow X^1\Sigma_g^+$ of Li_2. Their value for the dissociation energy - which is independent of any assumptions about the nature of the $B^1\Pi_u$ potential curve - is $D_0 = 1.025 \pm 0.006$ eV. This value is in agreement with the previous thermochemical data by Lewis, as well as consistent with the expected accuracy of the theoretical calculations by Das. Using this new value for the ground state dissociation energy together with the previous data by Loomis and Nusbaum, Velasco et al.[8] predict that the potential energy curve for $B^1\Pi_u$ state of Li_2 has a hump of magnitude 0.115 ± 0.036 eV.

In this paper we will present the results of theoretical calculations on the Li_2 $B^1\Pi_u$ state to show the nature of the full potential energy curve and of the electronic structure which characterizes this state.

2. BASIC APPROXIMATE ELECTRONIC WAVEFUNCTION FOR THE DESCRIPTION OF THE $Li_2 B^1\Pi_u$ POTENTIAL ENERGY CURVE

The Hartree-Fock wavefunction is of the following form for the $B^1\Pi_u$ state of Li_2:

$$A[1\sigma_g^2 1\sigma_u^2 2\sigma_g 1\Pi_u \alpha\beta\alpha\beta(\alpha\beta-\beta\alpha)] \qquad (2)$$

where $1\sigma_g^2 1\sigma_u^2$ are linear combinations of the two lithium core orbitals, and $2\sigma_g 1\Pi_u$ are the valence orbitals, and A is the antisymmetrizer. Although such a wavefunction gives a reasonable description of the electronic state about the equilibrium distance, it is not adequate to describe the dissociation of the Li_2 ($B^1\Pi_u$) molecule because as $R \to \infty$ the wavefunction does not go into the correct separated-atoms limit, i.e., $Li2^2S + Li2^2P$, but into a mixture of atomic states. In order to study the potential energy curve at all R, especially about the potential hump, one needs to start with a wavefunction which allows for the correct description of the separated-atoms limit, which is

$$A[1s_L^2 1s_R^2 (2s_L 2p_R + 2s_R 2p_L)\alpha\beta\alpha\beta\alpha\beta(\alpha\beta-\beta\alpha)] \qquad (3)$$

where the orbitals are just the Li atom orbitals, and the subscripts L and R refer to the center (left or right) on which the function is localized. A wavefunction which satisfies this requirement is a slightly modified form of wavefunction (2) namely,

$$A[1\sigma_g^2 1\sigma_u^2 (2\sigma_g 1\Pi_u - \lambda^2 2\sigma_u 1\Pi_g)\alpha\beta\alpha\beta(\alpha\beta-\beta\alpha)] \qquad (4)$$

where all orbitals and the coefficient λ^2 are to be variationally optimized at all R. One can see that (3), the separated atoms wavefunction, is a special case of (4) by noting the relation

$$(2\sigma_g 1\Pi_u - \lambda^2 2\sigma_u 1\Pi_g) = \tfrac{1}{2}[(2\sigma_g + \lambda 2\sigma_u)(1\Pi_u - \lambda 1\Pi_g) + (2\sigma_g - \lambda 2\sigma_u)(1\Pi_u + \lambda 1\Pi_g)] \quad (5)$$

and that when $\lambda \rightarrow 1$ (or $R \rightarrow \infty$), then the localized molecular orbitals in the right-hand side of equation (5) become the atomic orbitals as follows

$$(2\sigma_g + \lambda 2\sigma_u) \rightarrow 2s_L \quad (6a)$$

$$(1\Pi_u - \lambda 1\Pi_g) \rightarrow 2p_R \quad (6b)$$

$$(2\sigma_g - \lambda 2\sigma_u) \rightarrow 2s_R \quad (6c)$$

$$(1\Pi_u + \lambda 1\Pi_g) \rightarrow 2p_L \quad (6d)$$

and therefore the wavefunction (3) is a special case of (4).

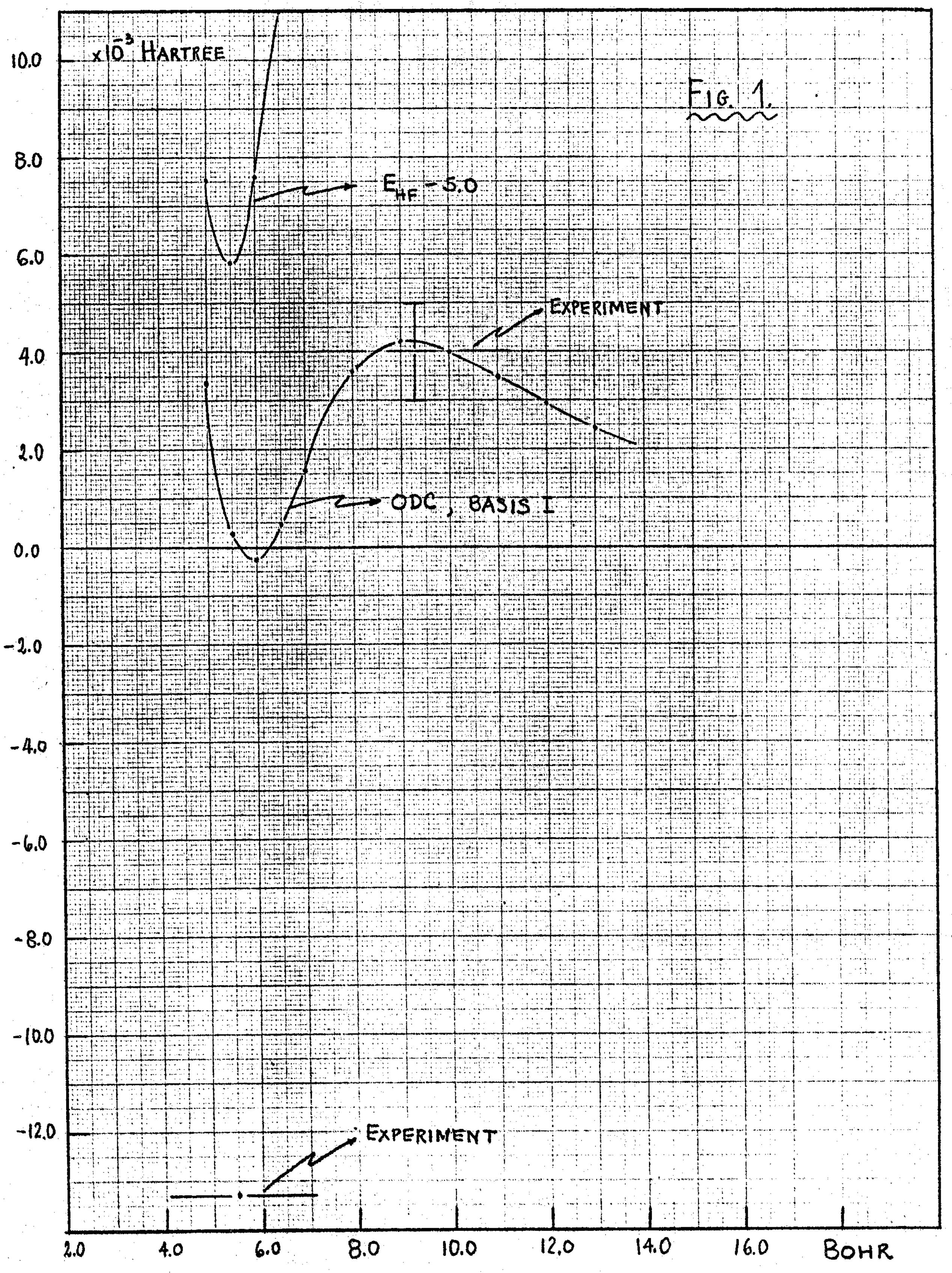
We note that with the addition of the $2\sigma_u 1\Pi_g$ configuration to the $2\sigma_g 1\Pi_u$ configuration of (2), the optimal molecular orbitals, can be put in localized form (5) instead of having to be symmetry functions as in (2). Because of this, one refers to the effect of introducing the $2\sigma_u 1\Pi_g$ configuration as "left-right" correlation.

A wavefunction of the type (4) in which all orbitals are optimized has been called the "optimized double configuration" method (ODC).[9] In general, wavefunctions consisting of a sum of Slater determinations [as in (4)] and in which all orbitals and linear coefficients are optimized are called MC-SCF wavefunctions.[10] In the next section we will describe our calculations of the $Li_2B^1\Pi_u$ potential curve first in terms of the use of an ODC wavefunction and then we will describe the changes that occur upon going to a multi-configuration wavefunction.

3. CALCULATIONS AND REFINEMENTS IN THE APPROXIMATE WAVEFUNCTION

We started our calculations with a [2(1s), 3(2s), 3(2pσ), (3dσ)/3(2pΠ), (3dΠ)] basis set of Slater functions centered on each atom with the exponents for the s and p basis functions optimized for the 2^2S and 2^2P states of the Li atom, and the d exponent chosen so as to have maximal overlap with the atomic p orbital. We call this basis set I.[11] In this basis, the 2^2S state of lithium has an energy of -7.43273 Hartree and the 2^2P state an energy of -7.36507 Hartree.

Next, we proceeded to calculate the Li_2 $B^1\Pi_u$ potential curve with the ODC wavefunction (4) and using the above basis set I to expand the orbitals. The results obtained are shown in Fig. 1 together with part of the corresponding Hartree-Fock results. The abcissa corresponds to the separated-atoms energy (-14.79780 Hartree). We note that, as expected from the discussion in the previous section, the ODC potential energy curve correctly approaches the separated atoms energy. Furthermore, we also note that the curve exhibits the potential hump predicted by King, Van Vleck, and Mulliken. In Fig. 1 we have also indicated the experimental height of the hump and its range of possible error as given by Velosco et al.[8] The ODC


x10⁻³ HARTREE
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-6.0
-8.0
-10.0
-12.0
E_HF - 5.0
EXPERIMENT
ODC, BASIS I
EXPERIMENT
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
BOHR

FIG. 1.

curve agrees closely with experiment in the region about the hump, however, it leads to a barely bound state accounting for only 0.018% of the experimental binding energy, De[12], which is 0.0133 ± 0.0002 Hartree or 0.362 ± 0.007 eV. In order to find the source of this inadequate description of the binding, which could easily have a bearing on the final calculated height and shape of the hump, we first investigated other configurations which might lead to a better description of the binding of this state.

From the wavefunction for the $X^1\Sigma_g^+$ ground state of Li_2 as calculated by Das,[4] we find that the main contributions to binding beyond the Hartree-Fock configuration $2\sigma_g^2$(~ 16% De) arise from the $2\sigma_u^2$, $3\sigma_g^2$ and $1\Pi_u^2$ configurations. The $2\sigma_u^2$ configuration corresponds to allowing the "left-right" type of correlation in the wavefunction, and it accounts for about 19% of the binding energy. The $3\sigma_g^2$ configuration corresponds to allowing the "in-out" type of correlation into the wavefunction and it accounts for about 22% of the binding energy. Finally, the $1\Pi_u^2$ configuration, which corresponds to allowing for "angular" type of correlation about the bond, has the largest contribution and accounts for about 43% of the binding energy. Thus, it is possible that inclusion of "angular" and "in-out" correlation could have a large effect upon the potential curve of the $B^1\Pi_u$ state.

"In-out" type of correlation can be introduced into the ODC wavefunction (4) by the configuration

$$3\sigma_g 2\Pi_u \qquad (7)$$

Adding this configuration to the HF configuration we obtain

$$2\sigma_g 1\Pi_u - \lambda^2 3\sigma_g 2\Pi_u = \tfrac{1}{2}\left[(2\sigma_g+\lambda 3\sigma_g)(1\Pi_u-\lambda 2\Pi_u)+(2\sigma_g-\lambda 3\sigma_g)(1\Pi_u+\lambda 2\Pi_u)\right] \quad (8)$$

In the right-hand side of relation (8) we see that in the first term the new molecular orbital $(2\sigma_g+\lambda 3\sigma_g)$ becomes more diffuse than the $2\sigma_g$ orbital, while concurrently the $(1\Pi_u-\lambda 2\Pi_u)$ molecular orbital becomes contracted in relation to the $1\Pi_u$ orbital, and vice-versa for the second term.

"Angular" type of correlation can be introduced into the ODC wavefunction (4) by adding $\delta\Pi$-like configurations, such as

$$1\delta_g 1\Pi_u \quad (9)$$

and

$$1\delta_g 2\Pi_u \quad . \quad (10)$$

Although (9) is a single excitation with respect to the Hartree-Fock wavefunction, it cannot be eliminated in this case by use of Brillouin's theorem.[13] This is because the variational condition on the $2\sigma_g$ orbital in the ODC wavefunction is not exactly the Brillouin condition

$$\langle \delta 2\sigma_g \, 1\Pi_u | \mathcal{H} | \Psi \rangle = 0 \quad (11)$$

but rather it is (11) subject to the constraint that the variations in $2\sigma_g$ be in the σ_g space; i.e., the field due to the $1\Pi_u$ orbital is cylindrically averaged in the equation (11). Thus, the $1\delta_g \, 1\Pi_u$ configuration has the dual role of allowing for the polarization of the $2\sigma_g$ orbital in the variational field of the $1\Pi_u$ orbital, and of allowing simultaneous distortion of both orbitals off the line of the nuclei, or "angular" correlation.

Having introduced the $1\delta_g 1\Pi_u$ configuration does not eliminate the need for the explicit consideration of the $1\delta_g 2\Pi_u$ configuration (10) because the variational condition on the $1\Pi_u$ orbital is not

$$\langle 1\delta_g \; \delta 1\Pi_u | H | \Psi \rangle = 0 \qquad (12)$$

thus, not necessarily leading to

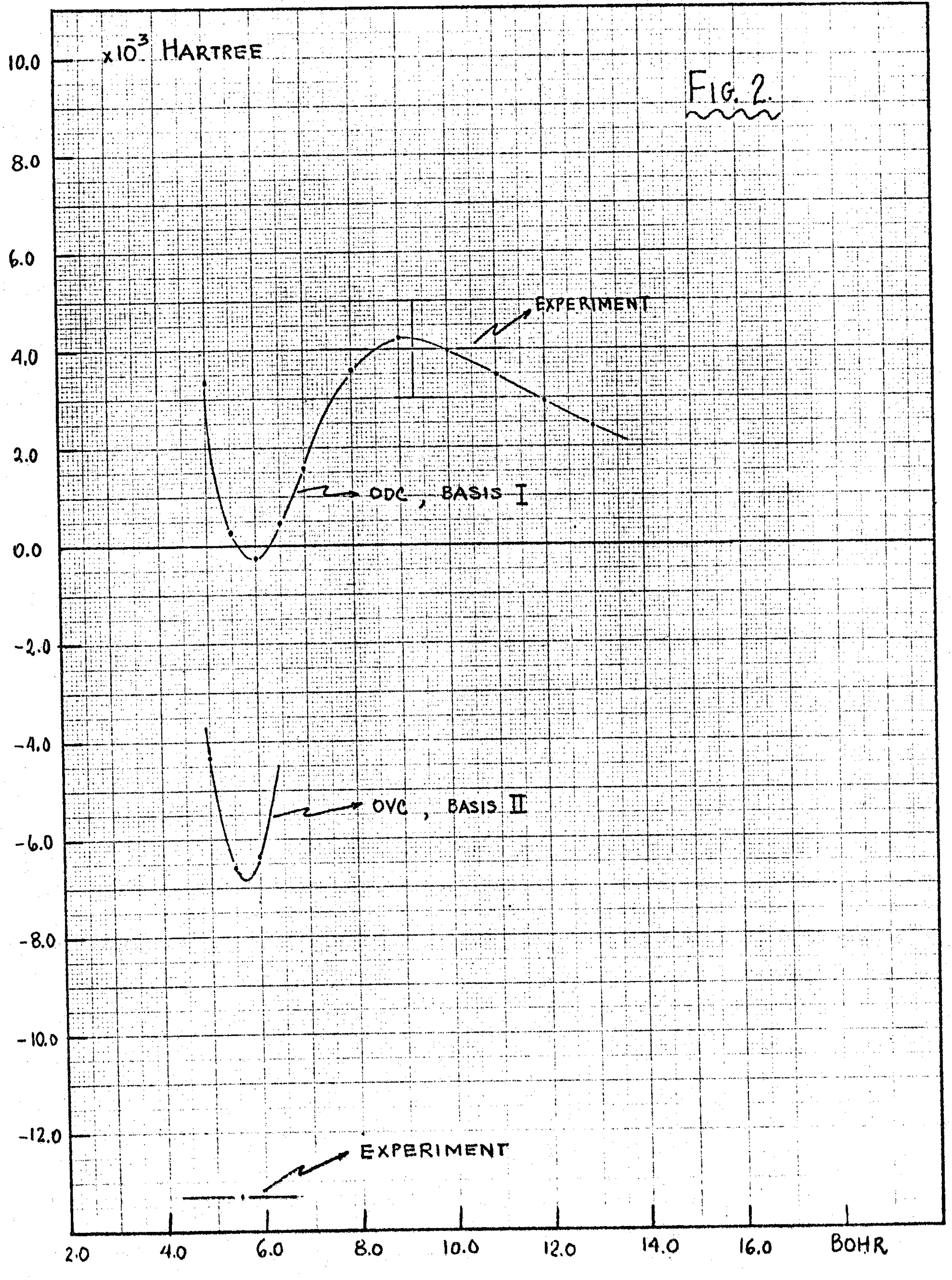
$$\langle 1\delta_g \; n\Pi_u | H | \Psi \rangle = 0$$

with n = 2 as a special case, but rather the condition is the MC-SCF equation

$$\langle 2\sigma_g \; \delta 1\Pi_u - C 1\delta_g \; \delta 1\Pi_u | H | \Psi \rangle = 0 \quad . \qquad (13)$$

The $1\delta_g 2\Pi_u$ configuration introduces solely "angular" correlation. It can in turn be analyzed in a manner analogous to (5) or (8) to show that it allows the $2\sigma_g$ orbital to mix $1\delta_g$ character and distort off of the line of the nuclei while allowing the $1\Pi_u$ orbital to mix $2\Pi_u$ character and adjust its shape in a manner corresponding to the changes in the $2\sigma_g$ orbital.

Finally, for the sake of completeness, we also included the configurations $1\delta_u 1\Pi_g$ and $1\delta_u 2\Pi_g$ which also describe angular correlation although we expected their contributions to be minor in relation to the others. The total wavefunction is now made of these seven configurations.


x10^{-3} HARTREE
10.0
8.0
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2.0
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-2.0
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-6.0
-8.0
-10.0
-12.0
EXPERIMENT
ODC, BASIS I
OVC, BASIS II
EXPERIMENT
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
BOHR

FIG. 2.

For the purpose of calculations with this seven configuration wavefunction, we added two 3dδ Slater functions on each center to the basis set I. We call this basis set II.[14] The results of the seven configuration MC-SCF calculations with basis set II on the $Li_2 B^1\Pi_u$ about the equilibrium distance $R_e = 5.51$ Bohr are shown in Fig. 2 along with the previous ODC results. We see that although there is a marked improvement in the binding energy, namely 0.00677 Hartree or 0.184 eV, we are still only accounting for 51% of the experimental binding energy. This seems anomalous when viewed against the size of the MC-SCF wavefunction employed. At this point we searched for analogous situations in other electronic systems.

The Be 2^1P atom has an electronic structure closely resembling that of the Li_2 $B^1\Pi_u$ state with the 2s2p singlet-coupled open shell of the atom analogous to the $2\sigma_g 1\Pi_u$ configuration of the molecule. A CI calculation on Be 2^1P by Dunning and Bender[15],which we have used as a guide in the choice of additional configurations, reveals an anomalous situation similar to the one we find for Li_2 $B^1\Pi_u$. These authors find that with a (4s 3p) Slater basis optimized for the Hartree-Fock configuration and augmented with 3d- and 4f- functions, a full valence electron CI accounted for only 62% of the valence correlation energy (of 0.029 Hartree). A recent CI calculation on the Be 2^1P by Tatewaki, Taketa, and Sasaki,[16] although employing fewer configurations than the previous work, yielded a much improved result, accounting for 86% of the valence correlation energy. The essential difference in the two calculations is the use of a 3p Slater function with its exponent optimized for the CI wavefunction. It would thus appear that a 3p Slater function plays an essential role in the CI wavefunction for Be, a role which may not be adequately mimicked by use of 2p-functions.

Because of this, we added a 3pΠ Slater function to basis set II, the orbital exponent being chosen on the basis of the Beryllium calculations.[17] In addition, we also modified the basis set II by deleting the tightest 2pσ function since previous calculations had shown that this function made a negligible contribution. We call this basis set III.[18] Using this basis set and the two and seven configuration wavefunction we obtained the results shown in Fig. 3 and tabulated in Tables I, II and III. We see that there is a marked improvement in the region about the equilibrium geometry. The seven configuration wavefunction now yields a binding energy of 0.26 eV, which is 71% of the experimental binding energy. Although the two configuration potential curve is also shifted down by a similar amount as the seven configuration curve, it is evidently still a rather poor representation for the Li_2 $B^1\Pi_u$ state since it only accounts for 22% of the experimental binding energy. We also note that in going from the 2 configuration result to the seven configuration result there is a marked change in the overall shape of the curve, and a significant lowering of the height of the potential hump from 0.11 eV to 0.077 eV, as well as a shift in the position of the maximum from 9.4 Bohr to 10.6 Bohr.

Finally, in order to assess the convergence of our results in terms of basis set III, we enlarged our basis set even further by:

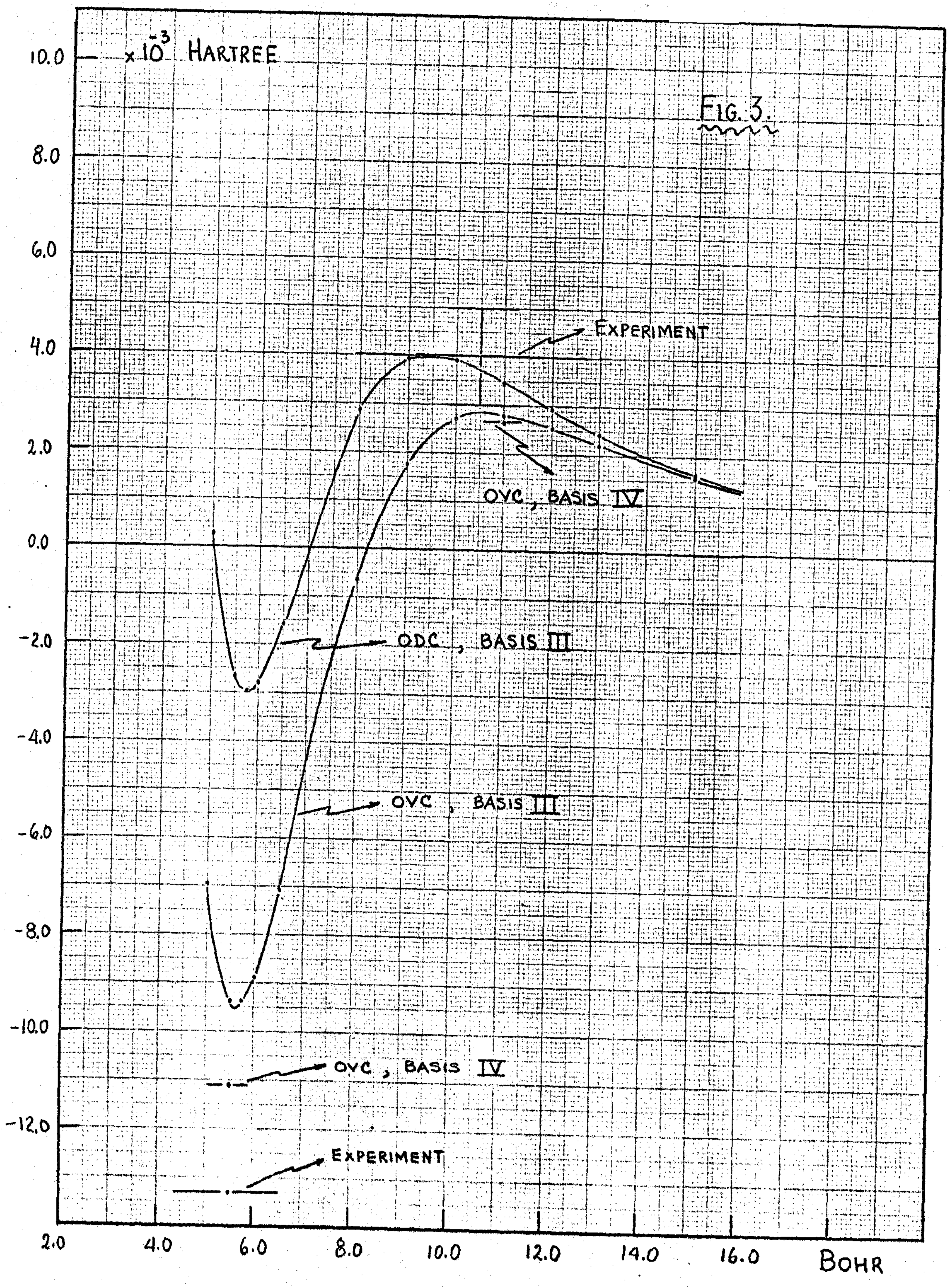

$\times 10^{-3}$ HARTREE
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
-12.0
EXPERIMENT
OVC, BASIS IV
ODC, BASIS III
OVC, BASIS III
OVC, BASIS IV
EXPERIMENT
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
BOHR

FIG. 3.

Table 1

Calculated Energies with the Two and Seven Configuration Wavefunctions in Basis Set III.[a] All Quantities are in Hartree Atomic Units.[b]

R	$E^{(2)}$	$E^{(2)}-E(\infty)$	$E^{(7)}$	$E^{(7)}-E(\infty)$
5.0	-14.797 53	0.000 27	-14.804 74	-0.006 94
5.5	-14.800 44	-0.002 64	-14.807 18	-0.009 38
5.75	-14.800 76	-0.002 96	-14.807 18	-0.009 38
6.0	-14.800 59	-0.002 79	-14.806 70	-0.008 90
6.5	-14.799 37	-0.001 57	-14.804 99	-0.007 08
8.0	-14.794 94	0.002 86	-14.798 42	-0.000 62
9.0	-14.793 86	0.003 94	-14.796 02	0.001 78
10.0	-14.793 88	0.003 92	-14.795 10	0.002 70
11.0	-14.794 34	0.003 46	-14.795 01	0.002 79
12.0	-14.794 88	0.002 92	-14.795 26	0.002 54
13.0	-14.795 38	0.002 42	-14.795 60	0.002 20
15.0	-14.796 15	0.001 65	-14.796 23	0.001 57

[a] See Reference 17.

[b] See Reference 2.

Table 2

Relative Contributions of the Terms in the Two Configuration Wavefunction in Basis Set III.[a] All Quantities are in Hartree Atomic Units.[b]

R	$2\sigma_g 1\Pi_u$	$2\sigma_u 1\Pi_g$
5.0	0.98308	-0.18317
5.5	0.97744	-0.21122
5.75	0.97381	-0.22735
6.0	0.96903	-0.24694
6.5	0.95677	-0.29086
8.0	0.89220	-0.45165
9.0	0.84743	-0.53090
10.0	0.80758	-0.58975
11.0	0.77749	-0.62890
12.0	0.75607	-0.65449
13.0	0.74110	-0.67139
15.0	0.72290	-0.69095

[a] See Reference 17.

[b] See Reference 2.

Table 3

Relative Contributions of the Terms in the Seven Configuration Wavefunction in Basis Set III.[a] All Quantities are in Hartree Atomic Units.[b]

R	$2\sigma_g 1\Pi_u$	$2\sigma_u 1\Pi_g$	$1\delta_g 1\Pi_u$	$1\delta_g 2\Pi_u$	$1\delta_g 1\Pi_g$	$1\delta_u 2\Pi_g$	$3\sigma_g 2\Pi_u$
5.0	0.96746	-0.16677	-0.14931	-0.10152	-0.01036	-0.00539	0.05896
5.5	0.96496	-0.19064	-0.14196	-0.09435	-0.00993	-0.00539	0.05764
5.75	0.96294	-0.20420	-0.13869	-0.09079	-0.00944	-0.00532	0.05873
6.0	0.95978	-0.22136	-0.13607	-0.08670	-0.00906	-0.00525	0.06062
6.5	0.95129	-0.26044	-0.13000	-0.07809	-0.00784	-0.00500	0.06428
8.0	0.90079	-0.41423	-0.10020	-0.04794	-0.00262	-0.00315	0.06807
9.0	0.86071	-0.49844	-0.07742	-0.03238	0.00292	-0.00137	0.06060
10.0	0.82048	-0.56638	-0.05624	-0.02128	0.00588	-0.00057	0.04877
11.0	0.78727	-0.61395	-0.04009	-0.01413	0.00774	-0.00074	0.03745
12.0	0.76320	-0.64477	-0.02885	-0.00965	0.00842	-0.00116	0.02841
13.0	0.74569	-0.66553	-0.02113	-0.00666	0.00841	-0.00139	0.02141
15.0	0.72545	-0.68801	-0.01212	-0.00333	0.00717	-0.00137	0.01234

[a] See Reference 17.

[b] See Reference 2.

(1) adding a 3s- and 3p- function to the σ-basis, and (2) splitting the 3p- function in the Π set into two functions. We call this basis set IV.[19] In terms of this basis and with the seven configuration wavefunction, we calculated the Li_2 $B^1\Pi_u$ energy at R = 5.5 Bohr and R = 11.0 Bohr. From these calculations we find our best binding energy to be 0.0724 eV, or 84% of experimental binding energy, which is in error by only 0.002 Hartree. In magnitude this is approximately the same error as found in the MC-SCF calculations by Das for the $X^1\Sigma_g^+$ Li_2 ground state (see Tables IV and V for the results). Furthermore, it is of interest to note that the energy lowering at R = 11.0 Bohr with respect to the results with basis set III is minimal (just .0002 Hartree). Thus we expect the shape about the hump to be insensitive to any further refinements in the wavefunction.

4. DISCUSSION

The final calculated potential energy curve for the Li_2 $B^1\Pi_u$ state is shown in Fig. 3. It shows that this state does have a hump as predicted by King, Van Vleck,[5] and Mulliken.[7]

Upon examining the corresponding wavefunction, we conclude that the qualitative nature of the electronic changes upon bringing the atoms together is as follows: the σ-orbital,[20] shown in Fig. 4, delocalizes slowly onto the opposite center until the maximum is reached; after this point the orbital hybridizes significantly toward the other center to form a stronger one-electron bond (as in Li_2^+). In turn, the Π- orbital,[20] shown in Fig. 5, is adjusting to these

Table 4

Calculated Energies with the Seven Configuration Wavefunction in Basis Set IV.[a] All Quantities are in Hartree Atomic Units.[b]

R	$E^{(7)}$	$E^{(7)}-E(\infty)$
5.5	-14.808 88	-0.01108
11.0	-14.795 14	0.00266

[a] See Reference 18.

[b] See Reference 2.

Table 5

Relative Contributions of the Terms in the Seven Configuration Wavefunction in Basis Set IV.[a] All Quantities are in Hartree Atomic Units.[b]

R	$2\sigma_g 1\Pi_u$	$2\sigma_u 1\Pi_g$	$1\delta_g 1\Pi_u$	$1\delta_g 2\Pi_u$	$1\delta_u 1\Pi_g$	$1\delta_u 2\Pi_g$	$3\sigma_g 2\Pi_u$
5.5	0.96852	-0.18139	-0.12587	-0.09596	-0.00995	0.00520	0.06240
11.0	0.78944	-0.61054	-0.04297	-0.01480	0.00810	-0.00068	0.04355

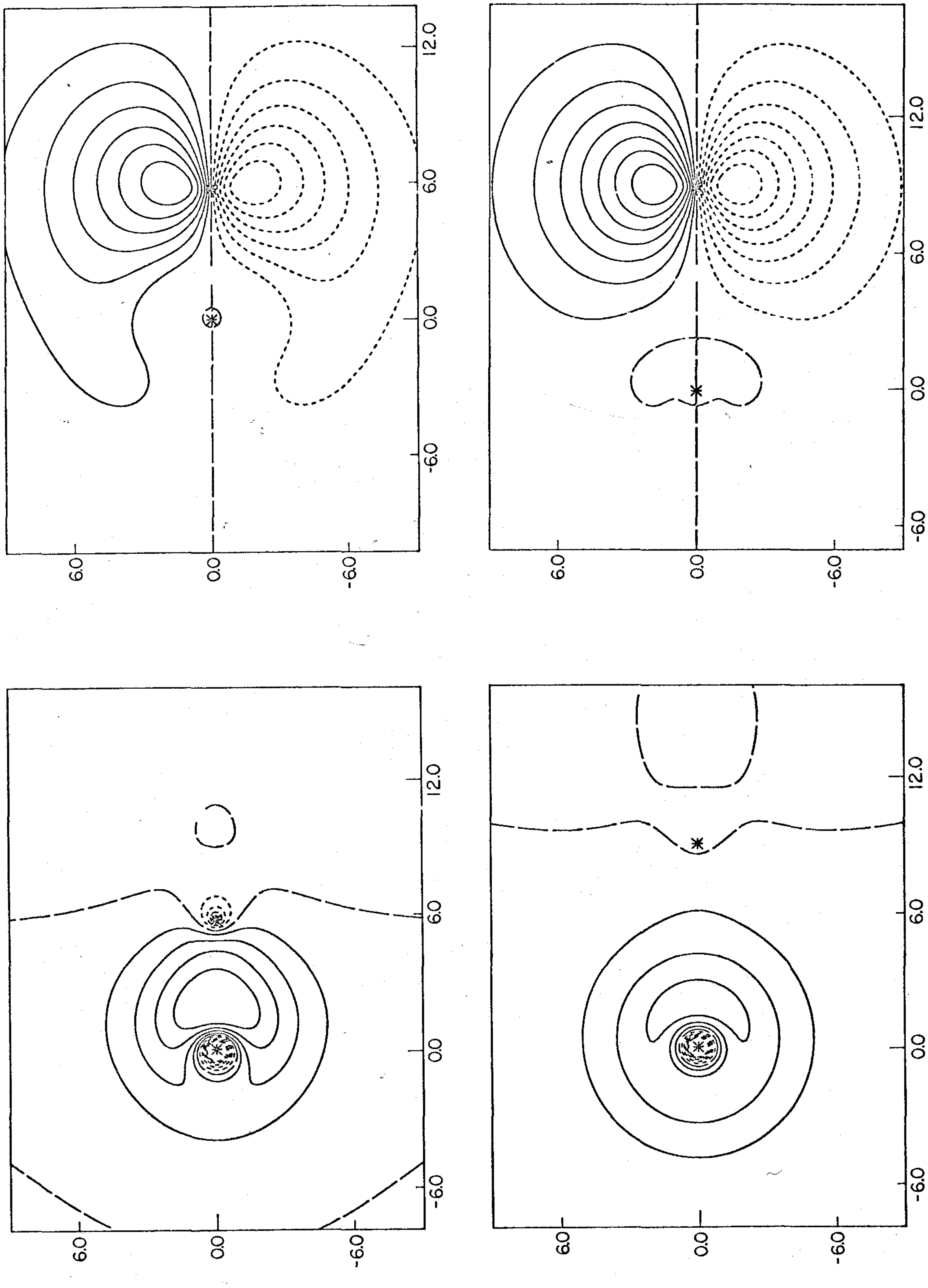
[a] See Reference 18.

[b] See Reference 2.

changes in the σ-orbital (with which is interacts via a repulsive $(\hat{J} + \hat{K})$ - potential)by becoming more diffuse. It is here that the 3pΠ function is important, as opposed to the 2pΠ's for use of it allows a localizing of the maximum farther out while diminishing the amplitude in the region near the internuclear axis.

The accuracy of the potential energy curves about the equilibrium distance is gauged best from a comparison of theoretical and experimental spectroscopic constants. These are shown in Table VI, and we note that there is good agreement.

We find that the hump in the $B^1\Pi_u$ potential curve has its maximum at R ~ 11.0 Bohr, and that the height of the hump is 0.00266 Hartree or 0.0724 eV. While this value is outside the range of error for the experimental value of 0.004 ± 0.001 Hartree, or 0.115 ± 0.036 eV, as given by Velasco et al.[8], the final experimental value depends on the accuracy of the dissociation energy for the Li_2 $B^1\Pi_u$ determined by Loomis and Nusbaum.[1] Upon reanalyzing the experimental data of Loomis and Nusbaum, Gaydon[21] suggests that perhaps larger error bounds would be safer. Alternatively, because of the use of the variational principle in our calculations, we can say that the theoretical value of the height of the hump is expected to be an upper bound on the experimental value. The only assumption involved is that the correlation energy within the Li cores and between the core and valence electrons is the same at R = 11.0 Bohr as at the separated atoms limit. Based on previous experience of the insensitivity of the cores to such relatively minor changes of environment as occur upon going from $R=\infty$ to the maximum of the hump at R = 11.0 Bohr, this is expected to be


12.0
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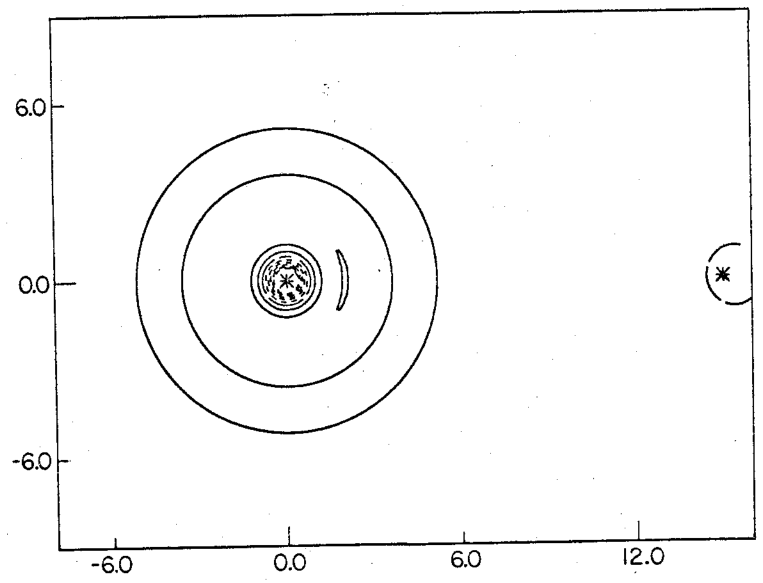
0.0
-6.0


6.0
0.0
-6.0
-6.0
0.0
6.0
12.0

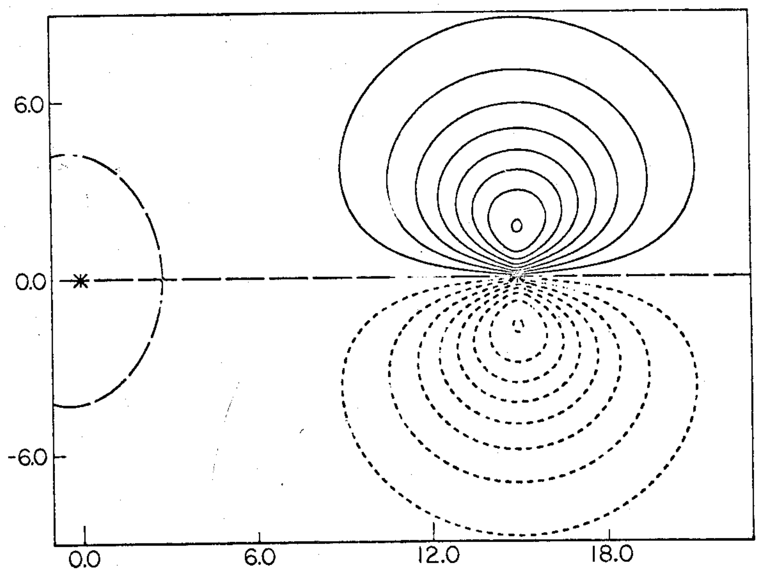

6.0
0.0
-6.0
0.0
6.0
12.0
18.0

Table 6

Calculated and Experimental Spectroscopic Constants for the $B^1\Pi_u$ State of Li_2.[a] Basis Set: $(16\sigma 10\Pi 4\delta)$

	R_e(Å)	D_e(eV)	ω_e (cm^{-1})	$x_e\omega_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	$k_e \times 10^{+6}$ (dynes/cm)
ODC[b]	3.05	0.081	240	5.7	0.52	0.01	1.19
OVC[c]	2.97	0.26	260	3.8	0.54	0.01	1.39
Exptl[d]	2.934	0.362	269.69	2.74	0.557	0.008	

[a] All units are defined in Reference 2.

[b] Optimized Double Configuration.

[c] Optimized (seven) Valence Configuration.

[d] See Reference 2.

the case.

The final test of these considerations must, however, await a more detailed experimental determination of the dissociation energy of the Li_2 $B^1\Pi_u$ state.

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REFERENCES

[1] F. W. Loomis and R. E. Nusbaum, Phys. Rev. 38 (1931) 1447.

[2] In this paper we will use atomic units, which have the following conversion factors:

$$1 \text{ Hartree} = 27.211652 \text{ eV}$$
$$1 \text{ Bohr} = 0.529177 \text{ A}$$

In addition, we also have used the conversion factor

$$1 \text{ eV} = 8.065465 \times 10^3 \text{ cm}^{-1}.$$

See B. N. Taylor, W. H. Parker, B. N. Langenberg, The Fundamental Constants and Quantum Electrodynamics, Academic Press, New York (1969).

[3] L. C. Lewis, Z. Physik 69 (1931) 786.

[4] G. Das, J. Chem. Phys. 46 (1967) 1568.

[5] G. W. King, J. H. Van Vleck, Phys. Rev. 55 (1939) 1165.

[6] The analysis used is based on the first-order dispersion force first discussed by R. E. Eisenschitz, F. London, Z. Physik. 60 (1930) 491.

[7] R. S. Mulliken, Phys. Rev. 120 (1960) 1674.

[8] R. Velasco, C. H. Ottinger, R. N. Zare, J. Chem. Phys. 51 (1969) 5522.

[9] G. Das. A. C. Wahl, J. Chem. Phys. 44 (1966) 87; W. T. Zemke, P. G, Lykos, A. C. Wahl, J. Chem. Phys. 51 (1969) 5635.

[10] J. Hinze, C. C. J. Roothaan, Prog. Theor. Phys. Suppl. No. 40 (1967) 37; A. C. Wahl, P. J. Bertoncini, G. Das, T. L.

Gilbert, Int. J. Quantum Chem. 1 (1967) 123; N. Sabelli, J. Hinze, J. Chem. Phys. 50 (1969) 684.

[11] Basis Set I: 1s(4.699, 2.478), 2s(1.770, 0.810, 0.643), $2p\sigma$ (2.869, 1.203, 0.512), $3d\sigma$(0.70), $2p\Pi$(2.869, 1.203, 0.512), $3d\Pi$(0.70).

[12] We define the binding energy, D_e, as the energy difference between the separated-atoms energy and the energy at the minimum in the potential energy curve.

[13] L. Brillouin, Act. Sci. Ind. No. 159, Hermann, Paris (1934); B. Levy, G. Berthier, Int. J. Quantum Chem. 2 (1968) 307.

[14] Basis set II, Basis set I, plus $3d\delta$(1.32, 0.60).

[15] T. H. Dunning, C. F. Bender, unpublished results.

[16] H. Tatewaki, H. Taketa, F. Sasaki, Int. J. Quantum Chem. 5 (1971) 335.

[17] The $3p\Pi$ orbital exponent was chosen to be in the same ratio to the most diffuse $2p\Pi$ exponent, as the Be 3p exponent is

[18] Basis set III; 1s(4.699, 2.478), 2s(1.770, 0.810, 0.643), $2p\sigma$(1.203, 0.512), $3d\sigma$(0.70), $2p\Pi$(2.869, 1.203, 0.512), $3p\Pi$(0.61), $3d\Pi$(0.70), $3d\delta$(1.32, 0.60).

[19] Basis set IV: 1s(4.699, 2.478), 2s(1.770, 0.810, 0.643), $2p\sigma$ (1.203, 0.512), 3s(0.56), $3p\sigma$(0.61), $3d\sigma$(0.70), $2p\Pi$(2.869, 1.203, 0.512), $3p\Pi$(1.12, 0.51), $3d\Pi$(0.70), $3d\delta$(1.10, 0.50).

[20] By σ-orbitals we mean the localized orbitals $(2\sigma_g + \lambda 2\sigma_u)$; by Π-orbital we mean the localized orbital $(1\Pi_u - \lambda 1\Pi_g)$.

[21] A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall, Ltd. London (1968) pp. 91-94.