

Use of *Ab Initio* G1 Effective Potentials for Calculations of Molecular Excited States*

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The validity of using *ab initio* G1 effective potentials for excited states of molecules is tested for a number of excited states of LiH. We find that the effective potentials lead to wavefunctions and properties which are in excellent agreement with those obtained from full-electron *ab initio* calculations.

I. INTRODUCTION

The idea of using an effective potential or pseudo-potential to replace some of the electrons of an atom or molecule has long been an attractive one.¹ It has been extensively used for solids²⁻⁶ since Phillips and Kleinman's work in 1959,² and in recent years there has been a resurgence of interest in using pseudo-potentials for molecules and even atoms.⁷ These developments have been based on finding a pseudo-potential to replace Hartree-Fock orbitals. However, the resulting pseudopotential is not unique⁸ nor necessarily even local⁴ or Hermitian.^{4,5} We have shown recently that by using the GI method^{8,9} rather than the Hartree-Fock method, we can obtain directly from *ab initio* atomic calculations *unique* effective potentials that can be used in studies of molecules and solids.¹⁰ This new type of effective potential is called the G1 atomic effective potential (GAEP). We have previously tested the validity of the GAEP to replace core electrons in the treatment of ground states of molecules¹¹ by comparison of GAEP results with those from full-electron *ab initio* calculations and found very good agreement. However, for the GAEP to be generally useful in replacing core electrons in molecules, it must be possible to use the same effective potentials to describe the excited states of molecules. In this paper we will test the validity of the GAEP for describing molecular excited states by a comparison of GAEP and *ab initio* results for the first 14 excited states of LiH. However, first we will briefly review some aspects of the G1 wavefunctions and of the corresponding effective potentials.

II. THE G1 ATOMIC EFFECTIVE POTENTIALS

In the G1 method the wavefunction for Li is

$$G_1^\mu[\phi_{1\alpha}\phi_{1\beta}\phi_{2\alpha}\alpha\beta\alpha], \quad (1)$$

where the group operator G_1^μ ensures that the total wavefunction has the proper spin symmetry and satisfies the Pauli principle. (Here α and β are the usual spin functions.) The orbitals ϕ_i are solved self-consistently as solutions of one-electron equations of the form

$$\hat{H}_i\phi_i = (h + \mathcal{U}_i^{G1}) = \epsilon_i\phi_i. \quad (2)$$

Here $h = -\frac{1}{2}\nabla^2 - (Z/r)$ (for an atom of charge Z) and \mathcal{U}_i^{G1} is an integral operator that represents essentially

the potential due to the other electrons of the system. For the valence orbital ($i=2a$) the \mathcal{U}_{2a}^{G1} in (2) represents the (nonlocal) potential due to the core electrons. We found elsewhere^{10,11} that given the G1 orbital ϕ_{2a} [by solving (2)], we can find a unique, local, Hermitian potential $U_s(r)$, which is equivalent to the nonlocal potential \mathcal{U}_{2a}^{G1} of (2). By equivalent we mean that ϕ_{2a} of (2) is also an eigenfunction of

$$[h + U_s(r)]\phi_i = \epsilon_i\phi_i \quad (3)$$

with the same energy. In addition, we found that the s -like excited states of (3) (having the same symmetry as $2a$) are close approximations to the self-consistent excited state orbitals of (2). Similarly, solving for the lowest 2P state of Li, we can find a local potential $U_p(r)$ of which the lowest 2P state is an exact solution and of which the excited p -like states are close approximations to the exact solutions. Proceeding this way for higher l , we find that the one-particle equation

$$[-\frac{1}{2}\nabla^2 - (Z/r) + U^{op}]\phi_i = \epsilon_i\phi_i \quad (4)$$

leads to a good description of all singly excited states of Li atom. The effective potential U^{op} in (4) is given by

$$U^{op} \equiv \sum_{lm} U_l(r) |lm\rangle\langle lm|, \quad (5)$$

where $|lm\rangle\langle lm|$ is a projection operator onto states of angular momentum lm , and $U_l(r)$ is a function of only the radial coordinate r (i.e., no angular variation). Thus U^{op} no longer depends on the core orbitals [as does \mathcal{U}_{2a}^{G1} in (2)] and we have effectively *replaced* the core orbitals by this unique, Hermitian potential U^{op} . Since this effective potential is based on the G1 orbitals of the atom, we refer to it as the *G1 atomic effective potential* (GAEP).

Now we will consider the valence states of LiH but with the Li core electrons replaced by the Li GAEP U^{op} . The usual four-electron LiH system is thereby reduced to a two-electron system (for the valence electrons) described by the effective Hamiltonian

$$\mathcal{H}^{eff}(1, 2) = h_1 + h_2 + r_{12}^{-1}, \quad (6a)$$

where

$$h_i = -\frac{1}{2}\nabla_i^2 + V_H(i) + V_{Li}(i) \quad (6b)$$

and

$$V_H = -1/r_H,$$

$$V_{Li} = U^{op}(r_{Li}) - (3/r_{Li}). \quad (6c)$$

FIG. 1. The LiH valence orbitals (ϕ_{2a}) for the various $^1\Sigma^+$ and $^3\Sigma^+$ states of LiH. AI and GAEP are explained in the caption to Table I.

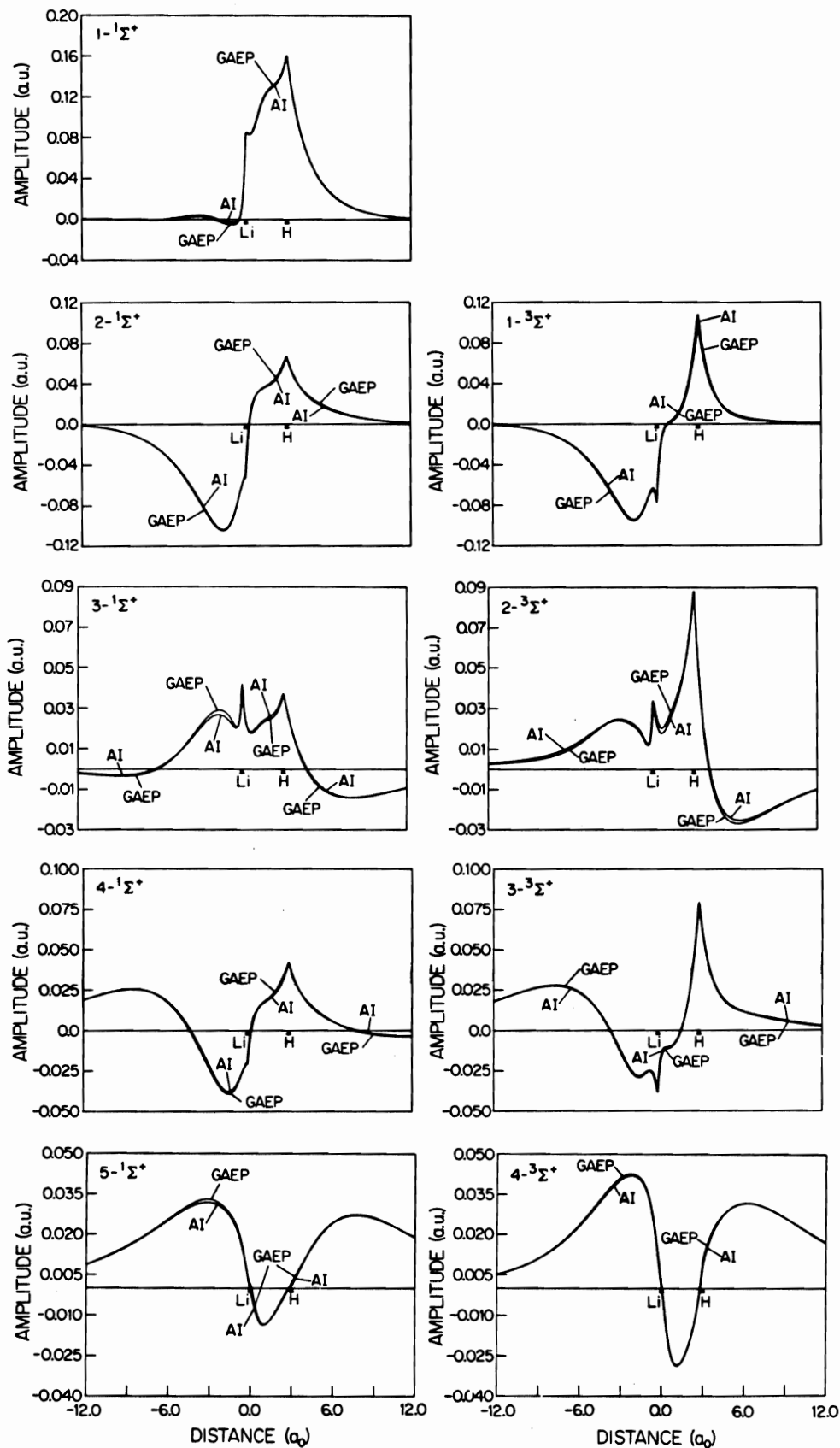


TABLE I. Overlap of molecular orbital ϕ_{2a} with atomic orbitals for the ${}^1\Sigma^+$ and ${}^2\Sigma^+$ states of LiH. AI indicates an *ab initio* G1 calculation and GAEP indicates that the G1 atomic effective potential was used.

Molecular orbitals		Atomic G1 orbital					
State	Method	Li 2s	Li 2p	Li 3s	Li 3p	Li 3d	H 1s *
$1-{}^1\Sigma^+$	AI	0.8321	0.5037	0.0957	0.1309	0.0739	0.7358
	GAEP	0.8280	0.5103	0.0935	0.1326	0.0739	0.7371
$2-{}^1\Sigma^+$	AI	0.6484	-0.7481	-0.0552	-0.0821	-0.0509	-0.1550
	GAEP	0.6444	-0.7507	-0.0581	-0.0811	-0.0523	-0.1584
$3-{}^1\Sigma^+$	AI	-0.0507	-0.1980	0.9367	0.2590	0.0976	0.0638
	GAEP	-0.0596	-0.1930	0.9415	0.2436	0.0916	0.0591
$4-{}^1\Sigma^+$	AI	-0.1038	-0.1917	-0.3248	0.8430	0.3630	0.0719
	GAEP	-0.0995	-0.1949	-0.3078	0.8515	0.3576	0.0749
$5-{}^1\Sigma^+$	AI	-0.0138	-0.0446	0.0086	-0.3990	0.9150	0.0130
	GAEP	-0.0156	-0.0470	0.0063	-0.3923	0.9180	0.0130
$1-{}^3\Sigma^+$	AI	0.8426	-0.5000	-0.0454	-0.0901	-0.0617	-0.0163
	GAEP	0.8469	-0.4960	-0.0443	-0.0859	-0.0620	-0.0037
$2-{}^3\Sigma^+$	AI	-0.1311	-0.4835	0.7041	0.4446	0.0865	-0.0130
	GAEP	-0.1377	-0.4669	0.7230	0.4295	0.0690	-0.0115
$3-{}^3\Sigma^+$	AI	0.1005	0.2578	0.6469	-0.5673	-0.4030	-0.0202
	GAEP	0.0981	0.2805	0.6207	-0.5847	-0.4048	-0.0167
$4-{}^3\Sigma^+$	AI	0.0050	-0.0439	0.1630	-0.4606	0.8645	0.0185
	GAEP	0.0051	-0.0474	0.1664	-0.4542	0.8661	0.0194

* Note that the H 1s is not orthogonal to the lithium functions.

TABLE II. Overlap of molecular orbital ϕ_{2a} with atomic orbitals for the ${}^1\Pi$ and ${}^2\Pi$ states of LiH. AI indicates an *ab initio* G1 calculation and GAEP indicates that the G1 atomic effective potential was used.

Molecular orbital		Atomic G1 orbital			
State	Method	Li 2p	Li 3p	Li 3d	H 2p *
$1-{}^1\Pi$	AI	0.9987	0.0381	-0.0182	0.7878
	GAEP	0.9985	0.0413	-0.0177	0.7887
$2-{}^1\Pi$	AI	-0.0238	0.6885	0.7248	0.3447
	GAEP	-0.0272	0.6928	0.7205	0.3412
$3-{}^1\Pi$	AI	0.0462	-0.7029	0.7093	0.2176
	GAEP	0.0482	-0.6977	0.7142	0.2218
$1-{}^2\Pi$	AI	0.9933	-0.0421	0.0575	0.8438
	GAEP	0.9933	-0.0413	0.0579	0.8441
$2-{}^2\Pi$	AI	0.0696	0.7614	-0.6386	-0.1324
	GAEP	0.0685	0.7858	-0.6085	-0.1180
$3-{}^2\Pi$	AI	-0.0215	0.6472	0.7619	0.3631
	GAEP	-0.0252	0.6170	0.7864	0.3674

* Note that the H 2p is not orthogonal to the lithium functions.

TABLE III. Energies, orbital energies, and properties for the $1\Sigma^+$ and $2\Sigma^+$ states of LiH^+ . AI and GAEP are explained in the caption of Table I.

Property ^b	Method	State								
		$1^{-1}\Sigma^+$	$2^{-1}\Sigma^+$	$3^{-1}\Sigma^+$	$4^{-1}\Sigma^+$	$5^{-1}\Sigma^+$	$1^{-3}\Sigma^+$	$2^{-3}\Sigma^+$	$3^{-3}\Sigma^+$	$4^{-3}\Sigma^+$
Energy	AI	-8.01605 ^c	-7.89982	-7.81839	-7.80486	-7.79907	-7.91520	-7.82737	-7.81041	-7.80163
	GAEP	-8.01377	-7.89922	-7.81868	-7.80466	-7.79875	-7.91454	-7.82777	-7.81057	-7.80129
Orbital Energies Valence Orbital d	AI	-0.2793	-0.1579	-0.0753	-0.0618	-0.0560	-0.1735	-0.0844	-0.0674	-0.0586
	GAEP	-0.2780	-0.1575	-0.0760	-0.0620	-0.0561	-0.1732	-0.0852	-0.0680	-0.0587
H 1s-like Orbital	AI	-0.4800	-0.6354	-0.7016	-0.7317	-0.7068	-0.6364	-0.6774	-0.7251	-0.6989
	GAEP	-0.4758	-0.6358	-0.6999	-0.7308	-0.7051	-0.6352	-0.6748	-0.7238	-0.6979
Dipole Moment, μ^e	AI	2.166 ^f	-2.133	3.081	-6.933	3.513	-1.880	4.296	-7.613	2.701
	GAEP	2.170	-2.175	2.952	-6.972	3.377	-1.885	4.369	-7.697	2.586
Quadrupole Moment, Q^g	AI	-2.70	-5.95	6.23	-69.45	-38.32	-1.74	-7.34	-57.78	-17.85
	GAEP	-2.67	-6.12	5.33	-69.48	-37.01	-1.92	-7.41	-58.81	-16.53
Electric Field Gradient, q^h	AI	-0.0187	-0.0193	-0.0026	-0.0049	-0.0040	-0.0065	-0.0040	-0.0015	-0.0062
	GAEP	-0.0208	-0.0205	-0.0050	-0.0070	-0.0064	-0.0077	-0.0067	-0.0034	-0.0085
3L_1	AI	0.0287 ⁱ	0.0285	0.0302	0.0302	0.0295	0.0289	0.0289	0.0302	0.0287
	GAEP	0.0257	0.0285	0.0296	0.0297	0.0292	0.0285	0.0291	0.0297	0.0282
$\langle \sum_e r_{Li}^2 \rangle$	AI	7.89	8.65	14.57	15.85	15.06	8.47	13.43	14.86	14.49
	GAEP	7.87	8.61	14.48	15.81	14.92	8.40	13.36	14.80	14.41
$\langle \sum_e r_{Li}^2 \rangle$	AI	26.8	34.3	131.5	164.6	145.8	32.3	108.1	141.2	134.4
	GAEP	26.6	34.0	130.6	163.9	142.7	31.8	107.0	140.4	132.8

^a All properties are listed in atomic units, $\hbar = 1$, $|e| = 1$, $m_e = 1$. One unit of energy = 1 hartree = 27.2117 eV. See B. N. Taylor, W. H. Parker, and D. N. Langenberg, *The Fundamental Constants and Quantum Electrodynamics* (Academic Press, New York, 1969).

^b For GAEP, the total property is the sum of the properties for the Li^+ core orbital wavefunction and for the two-electron valence orbital wavefunction.

^c Experimental energy is -8.0705. See P. E. Cade and W. M. Huo, *J. Chem. Phys.* **47**, 614 (1967).

^d The valence orbital is the orbital which is least bound (taken as ϕ_{1a} in Ref. 13).

^e $\mu = (-\sum_{e,n} q_n r_n)$. The direction of a positive dipole is Li^+H^- . One atomic unit = 2.54177 D.

^f Experimental value is 2.293. See L. Wharton, L. P. Gold, and W. Klemperer, *J. Chem. Phys.* **37**, 2149 (1962).

^g $Q = \langle \sum_{e,n} q_n [(3z_{en}^2 - r_{en}^2)/2r_{en}^3] \rangle$. One atomic unit = 1.34505 Buckingham = 1.34505 $\times 10^{-18}$ esu cm^2 .

^h $q_{Li} = \langle \sum_{e,n} q_n [(3z_{en}^2 - r_{en}^2)/2r_{en}^3] \rangle$. One atomic unit = 3.24140 $\times 10^{16}$ esu/ cm^3 .

ⁱ Experimental value is 0.0249. See footnote f.

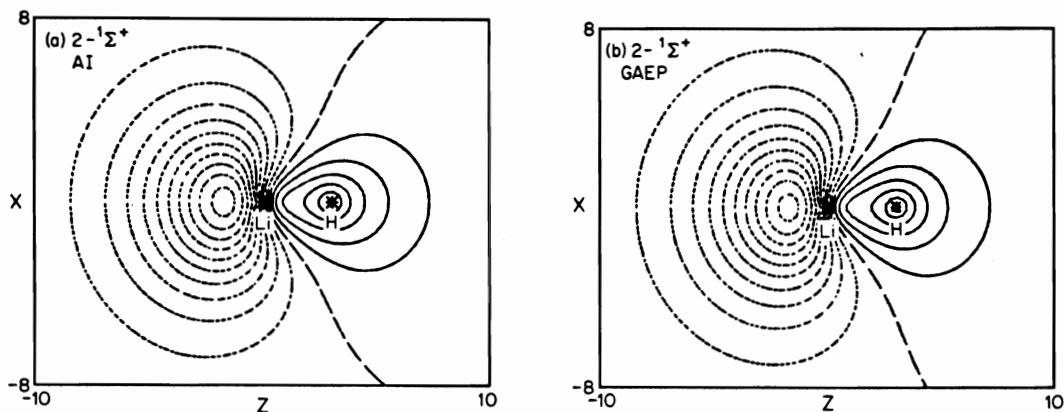


FIG. 2. The G1 $\phi_{2\sigma}$ orbital for the $2-1\Sigma^+$ state of LiH. Dashed lines (---) represent nodal lines, solid lines are positive contours, and dotted lines are negative contours (the intervals are 0.01 a.u.).

TABLE IV. Energies and orbital energies of the 1Π and 2Π states of LiH and the $2\Sigma^+$ state of LiH^+ for *ab initio* (AI) and G1 atomic effective potential (GAEP) G1 wavefunctions.^a

		State						
		$1-1\Pi$	$2-1\Pi$	$3-1\Pi$	$1-2\Pi$	$2-2\Pi$	$3-2\Pi$	LiH^+
Energy	AI	-7.86165	-7.79605	-7.79374	-7.87555	-7.79866	-7.79647	-7.74309
	GAEP	-7.86076	-7.79549	-7.79314	-7.87483	-7.79814	-7.79594	-7.74267
Orbital energy ^b								
	Valence orbital	AI	-0.1225	-0.0559	-0.0537	-0.1364	-0.0586	-0.0563
	GAEP	-0.1223	-0.0560	-0.0537	-0.1363	-0.0587	-0.0564	-0.0
H 1s-like orbital	AI	-0.6153	-0.7080	-0.7141	-0.6051	-0.7165	-0.7066	-0.8234
	GAEP	-0.6149	-0.7073	-0.7134	-0.6044	-0.7165	-0.7054	-0.8229

^a Energies are given in atomic units (1 hartree = 27.2117 eV).

^b The valence orbital is taken as the least bound orbital of LiH.

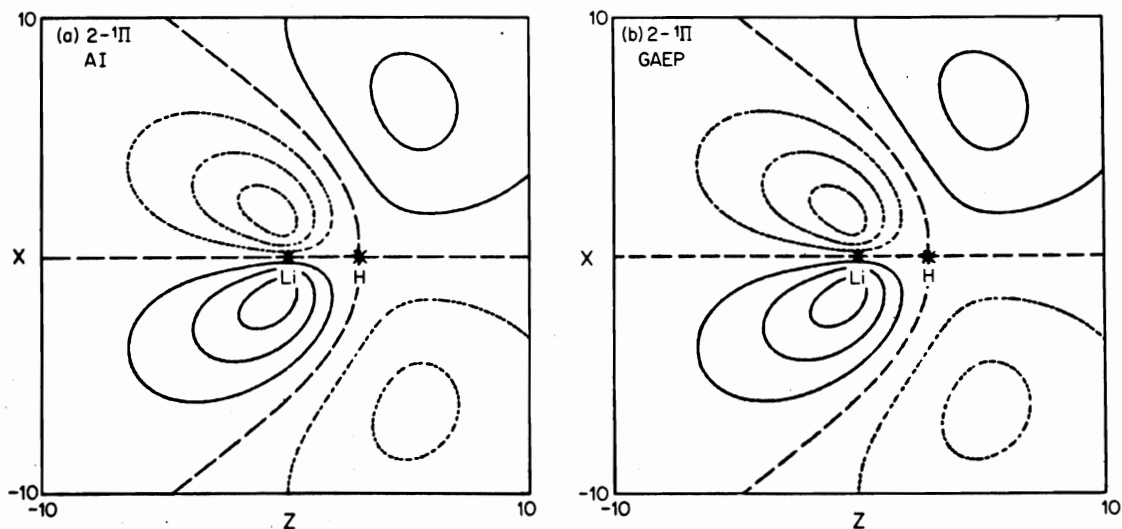


FIG. 3. The G1 $\phi_{2\pi}$ orbital for the $2-1\Pi$ state of LiH. See caption on Fig. 2 for plot conventions.

That is, the usual Li nuclear attraction term $-3/r_{Li}$ is replaced by the total effective potential due to the Li core, V_{Li} . For large r_{Li} , $U^{sp}(r_{Li}) \sim 2/r_{Li}$ so that $V_{Li} \sim -1/z_{Li}$ as expected.

Given the two-electron valence Hamiltonian (6a) we can solve for the corresponding wavefunction in many ways. For example, we could use the G1 or Hartree-Fock approaches or we could carry out an extensive (two-electron) configuration interaction (CI) calculation (with or without r_{12}) to get essentially the exact eigenfunctions of (6a).

For a system such as LiH, the energy curve and properties from the CI solutions of (6) should be very close to the exact four-electron *ab initio* values since the core states do not change significantly. However the use of the effective Hamiltonian (6a) in place of the many-electron Hamiltonian involves some approximations and hence even an exact solution for the eigenstates of (6) would not yield the exact energy and properties of LiH.

In order to assess the error in the use of the GAEP, we will solve for the various G1 solutions of (6a) and compare the orbitals and properties with the corresponding all-electron G1 solutions. Thus, we take our valence wavefunction as

$$G_1 \phi_{av} \phi_{bv} \alpha \beta = \frac{1}{2} (\phi_{av} \phi_{bv} \pm \phi_{bv} \phi_{av}) (\alpha \beta \mp \beta \alpha) \quad (7)$$

depending on whether the singlet or triplet state is wanted. The total wavefunction is then visualized as

$$G_1 [\phi_{1a}(1) \phi_{1b}(2) \Theta(3, 4) \alpha \beta \alpha \beta] \quad (8)$$

for a general two-electron valence function Θ . For the G1 approximation (7) we have

$$\Theta = (\phi_{av} \phi_{bv} \pm \phi_{bv} \phi_{av}) \quad (7')$$

and (8) becomes

$$G_1 [\phi_{1a} \phi_{1b} \phi_{av} \phi_{bv} \alpha \beta \alpha \beta], \quad (9)$$

the four-electron G1 wavefunction.

For wavefunctions of the form (1) or (9) we can optimize the spin coupling to obtain the spin-coupling optimized G1 (SOGI)¹² solution, but the energy drops by less than one part in 10^6 for the states of Li and LiH^{12,13} we are considering. Since (i) the change in spin coupling involves changing the core orbitals (which we take to be frozen or invariant in the effective potential approximation), since (ii) the two Li core orbitals by themselves (Li⁺) are singlet coupled [which corresponds to the G1 coupling of (1) or (9)], and since (iii) the optimum spin-coupling for each state of Li^{12,13} remained nearly G1, we use effective potentials derived from G1 (rather than SOGI) wavefunctions.

We have found¹¹ that $U_d \approx U_p$ in (5) and expect that $U_l = U_d$ should be a good approximation for $l > 2$. We have used this relation in the calculations reported here.

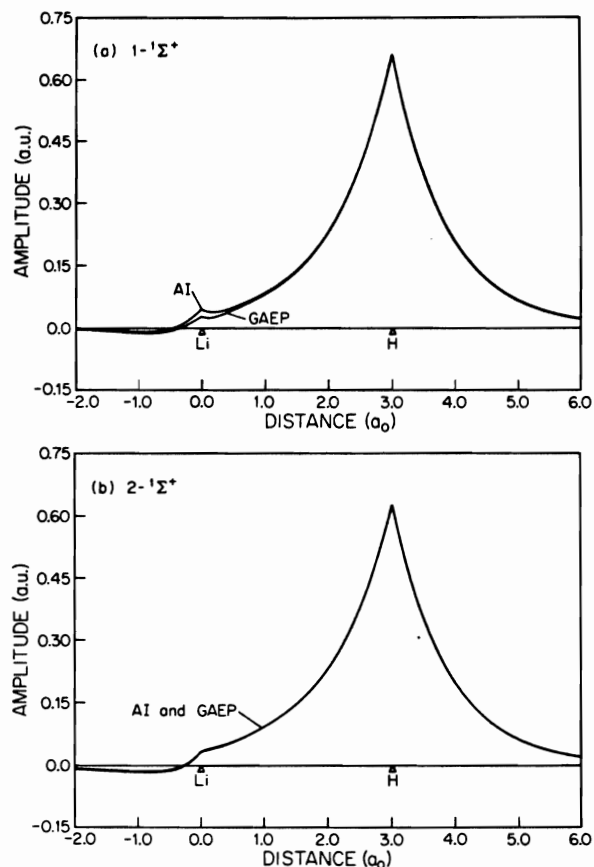


FIG. 4. The H 1s-like orbitals (ϕ_{2s}) from AI and GAEP calculations on (a) the $1-^1\Sigma^+$ state of LiH and (b) the $2-^1\Sigma^+$ state of LiH [for (b), the plots almost coincide].

III. RESULTS

Comparisons of the pseudopotential and *ab initio*¹³ calculations are made for the first four $^1\Sigma^+$ and $^3\Sigma^+$ excited states and first three $^1\Pi$ and $^3\Pi$ states of LiH. In Fig. 1 we show comparisons of the excited valence orbitals for the Σ states, and in Figs. 2 and 3 we show comparisons of the contour plots for the $2^1\Sigma^+$ and the $2^1\Pi$ excited state orbitals. Comparisons of the contour plots for the other Π state orbitals are not given since the pseudopotential and *ab initio* orbitals are essentially superimposable, just as for the $2^1\Pi$ orbitals. In Fig. 4, we show a comparison of the H 1s-like orbital for the $1-^1\Sigma^+$ and $2-^1\Sigma^+$ states. Comparisons of the H 1s-like orbital for the other excited states yield agreement similar to the $2-^1\Sigma^+$ state and therefore are not shown here. Note that although these orbitals are extremely similar as indicated by the plots, the expansion coefficients differ markedly due to the near-linear dependence of the basis set.¹⁴ Therefore, we list in Tables I and II a comparison of the overlaps of the orbitals with the excited state atomic orbitals for clearer interpretation of the differences. In Tables III and IV we list comparisons of the energies, orbital energies, and selected properties for each of the excited states. For

each excited state we find excellent agreement between the pseudopotential and *ab initio* calculations.

This excellent agreement should be expected, since the *ab initio* calculations showed that the Li core remains essentially the same for various excitations of the molecule. Therefore replacement of this core by an appropriate effective potential should, and in fact does, yield reasonably similar results, not only for calculated properties of the total wavefunction, in which errors could be canceled, but also for the individual orbital wavefunctions, thereby preserving the "independent particle interpretation."

This close agreement between the GAEP and *ab initio* wavefunctions for the molecular excited states of LiH indicates that the GAEP approach may allow the study of the wavefunction of systems too large for complete *ab initio* calculations, while retaining *ab initio* quality results.

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¹⁴ For the comparison, we used the same basis set for both approaches.¹³ For actual pseudopotential calculations, one no longer needs the large number of core basis functions.