

A DIRECT TEST OF THE VALIDITY OF THE USE  
OF PSEUDOPOTENTIALS IN MOLECULES \*

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Unique and Hermitean pseudopotentials taken directly from *ab initio* calculations on Li atom have been applied to calculations on LiH and Li<sub>2</sub>. These results have been compared with the full electron *ab initio* solutions on LiH and Li<sub>2</sub> in the first such direct test of the validity of the use of pseudopotentials in molecules and solids.

In recent years there has been a great deal of interest in replacing some of the electrons, say the core electrons, of a molecule, atom, or solid by an effective potential, called a pseudopotential [1-4]†. In order to avoid orthogonalizing the valence orbitals to the core orbitals it is necessary to incorporate a term in the pseudopotential which leads to nodeless valence orbitals with the same energy as the usual Hartree-Fock orbital [2]. That is, we essentially unorthogonalize the valence orbital to the core orbitals. As might be expected and as shown by Cohen and Heine [5], the resulting pseudo-orbitals are not unique and thus the pseudopotential is not unique [6]. In addition, the Hartree-Fock generalized pseudopotential is nonlocal and non-Hermitean [4].

We have found that another approach to electronic wave functions, the G1 method [7]††, automatically leads to atomic valence orbitals which are smooth in the core region and are *not* orthogonal to the core orbitals. Thus, the direct self-consistent potential from these atomic G1 calcu-

lations can be used as the pseudopotential in molecular calculations. Such a G1 pseudopotential (call it  $V_{G1PP}$  or just  $V_{PP}$ ) is obtained uniquely and directly from *ab initio* calculations, and it is Hermitean and local. In addition a G1PP calculation is directly related to a full-electron, *ab initio* G1 calculation on the same molecule. Thus for small molecules we can carry out the calculations both ways and determine just how valid the use of the pseudopotential is. We will now present such comparisons for the LiH and Li<sub>2</sub> molecules.

The G1 wave function for the 2<sup>2</sup>S state of Li has been reported earlier [8]. Since the valence orbital is nodeless, there is no problem in solving for the local potential,  $V_s$ , of which it is an eigenstate. Similarly, from the valence orbitals of the 2<sup>2</sup>P and 3<sup>2</sup>D states, we can obtain the pseudopotentials,  $V_p$  and  $V_d$ , for the p and d states, respectively. We find that  $V_p$  and  $V_d$  are similar but differ greatly from  $V_s$ . In addition, the energies of the excited states in the potentials,  $V_s$  [9],  $V_p$  and  $V_d$ , correspond quite accurately to the experimental energies in the ns, np, and nd series of Li, respectively. On the other hand,  $V_s$  leads to poor values for the np and nd series†††, but  $V_p$  leads to good values for the np and nd series. Thus, since in a molecule each valence orbital in general has s, p, and higher  $l$  components, we would expect that the use of  $V_s$

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† The idea is originally due to Hellmann [1] but more recent work was stimulated by Phillips and Kleinman and summarized by Harrison [3].

†† The G1 wave function is based on the Wigner projection operators for the symmetric group [7]. It can be considered [8] as a generalization of the valence bond-type wave function in which each orbital is functionally optimized (no restrictions are made on the form of any of the orbitals). For a two-electron singlet the spatial part of the wave function has just the form  $\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)$ , where  $\phi_a$  and  $\phi_b$  are *not* restricted to be atomic orbitals.

††† The Phillips-Kleinman pseudopotential is Hermitean and, of course, any such nonlocal operator can be localized by multiplying and dividing by the eigenfunction [6c], although singularities would result when the orbital has nodes.

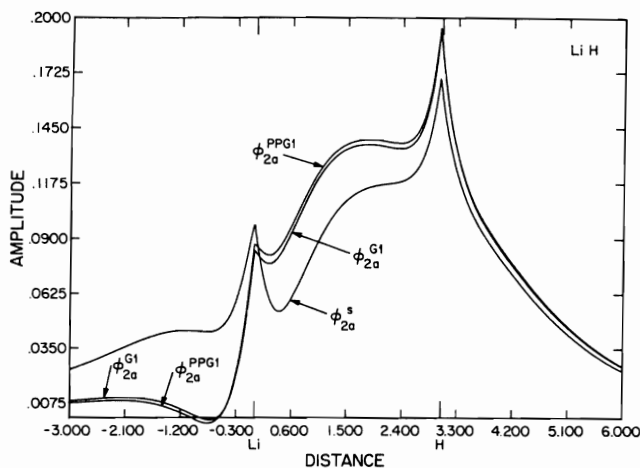


Fig. 1. The LiH valence orbital,  $\phi_{2a}$ , as obtained from *ab initio* ( $\phi_{2a}^{G1}$ ) and from pseudopotential ( $\phi_{2a}^{PPG1}$ ) G1 calculations.  $\phi_{2a}^s$  is the orbital calculated using the approximation that  $V^{PPG1} = V_s$ .

alone would lead to poor results (it does, *vide infra*).

In considering LiH and Li<sub>2</sub> we replace the Li core electrons by a pseudopotential,  $V^{PP}$  centered at each Li nucleus, thus reducing the system to a two-electron molecule. Because the pseudopotential is angular-momentum dependent, we take it to be

$$V^{PP} = \sum_l V_l^{PP} |l\rangle\langle l|,$$

where  $|l\rangle$  and  $\langle l|$  are angular-momentum projection operators. We found that for  $l > 2$ , we could take  $V_l^{PP} = V_d^{PP}$ .

In fig. 1 we show one of the valence orbitals of LiH as obtained from four-electron *ab initio* G1 calculations and from the pseudopotential calculations using  $V^{PP}$ . We see that the orbitals agree quite closely. For comparison we show the valence orbital calculated using just the s pseudopotential,  $V^{PP} = V_s$ . This latter approximation is of the type which is usually made in Hartree-Fock pseudopotential calculations since there are no p or d electrons in the Li core. We see that this approximation leads to a very poor result for this valence orbital. In fig. 2 we show the comparisons for the other valence orbital of LiH, and in fig. 3 we show the comparisons for one of the valence orbitals of Li<sub>2</sub> (the other orbital is symmetrically related but peaked on the other Li). In both cases we again find good agreement between the pseudopotential and *ab initio* calculations.

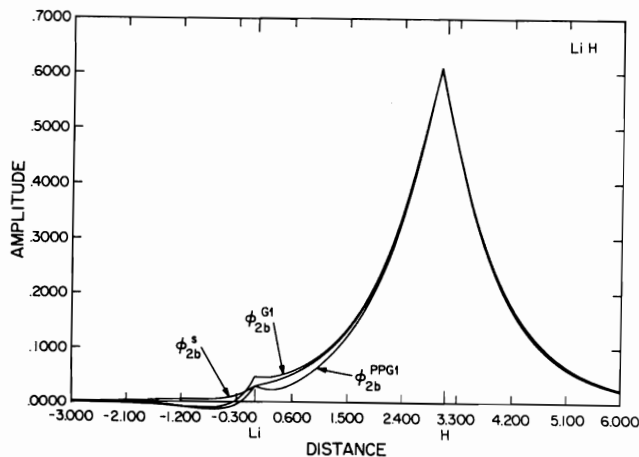


Fig. 2. The LiH valence orbital,  $\phi_{2b}$ , as obtained from *ab initio* ( $\phi_{2b}^{G1}$ ) and from pseudopotential ( $\phi_{2b}^{PPG1}$ ) G1 calculations.  $\phi_{2b}^s$  is the orbital calculated using the approximation that  $V^{PPG1} = V_s$ .

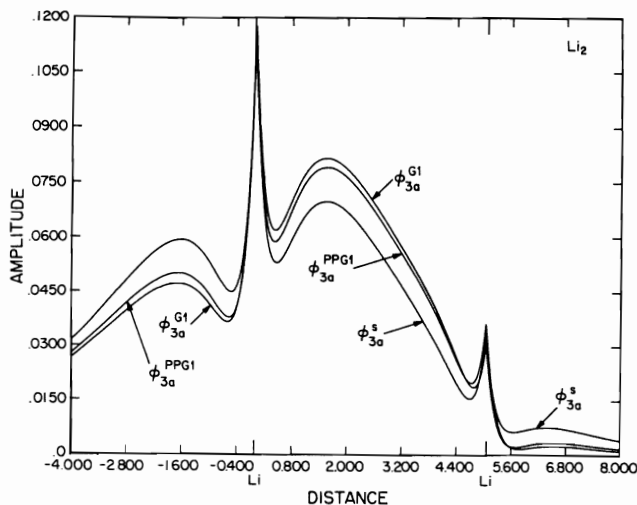


Fig. 3. The Li<sub>2</sub> valence orbital,  $\phi_{3a}$ , as obtained from *ab initio* ( $\phi_{3a}^{G1}$ ) and from pseudopotential ( $\phi_{3a}^{PPG1}$ ) G1 calculations.  $\phi_{3a}^s$  is the orbital calculated using the approximation that  $V^{PPG1} = V_s$ .

Comparison of the orbitals as in figs. 1, 2 and 3 is a quite sensitive test of the accuracy of the calculated wave functions, even more so than a comparison of calculated properties, since in the latter case many of the errors may be averaged out. Table 1 compares the total energy, dipole moment, and electric field gradients\* as obtained

\* See footnote on next page.

Table 1  
Comparison of properties for LiH as obtained from *ab initio* (G1) and pseudopotential (PPG1) calculations<sup>a)</sup>

	PP-G1	G1 b)	HF c)	CI d)	Experiment g)
$R_e$	3.015	3.015	3.015	3.0147	3.015
$E$	-8.0144	-8.0173	-7.9873	-8.0606	-8.0705
$\langle -\sum_{e,n} qz \rangle^e$	5.665	5.645	6.002	5.965	5.828
$\langle \sum_{e,n} q \left( \frac{3z_{Li}^2 - r_{Li}^2}{2r_{Li}^5} \right) \rangle$	-0.0239	-0.0202	-0.0220	-0.0187	
$\langle \sum_{e,n} q \left( \frac{3z_H^2 - r_H^2}{2r_H^5} \right) \rangle$	0.0259	0.0292	0.0290	0.0230	0.0249
$\langle \sum_e \frac{1}{r_{Li}} \rangle$	6.0706	6.0848	6.0780	6.0748	
$\langle \sum_e \frac{1}{r_H} \rangle$	2.2251	2.2239	2.2280	2.2404	
$\langle \sum_{e,n} q \left( \frac{3Z_{CM}^2 - r_{CM}^2}{2} \right) \rangle^f$	-3.681	-3.686	-4.535		

a) Atomic units are used unless designated otherwise, i.e., one unit of energy  $\equiv$  1 hartree = 27.211 eV and one unit of length  $\equiv$  1 bohr = 0.52917 Å;  $|e| = 1$ .

b) See ref. [10].

c) P. E. Cade and W. M. Huo, J. Chem. Phys. 45 (1966) 1063; 47 (1966) 614.

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

e) The dipole moment is quoted in Debye's, i.e., one atomic unit of dipole moment = 2.54158 Debye. The direction of the dipole is  $Li^+H^-$ .

f) The quadrupole moment is quoted in Buckingham, i.e., one atomic unit of quadrupole moment = 1.34492 Buckingham =  $1.34492 \times 10^{-26}$  esu cm<sup>2</sup>; the quadrupole moment is calculated at the center of mass.

g) See G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Co., Princeton, New Jersey, 1950); R. Velasco, Can. J. Phys. 35 (1957) 1204; F. H. Crawford and T. Jorgensen Jr., Phys. Rev. 49 (1936) 745; and Appendix I of footnote C, for experimental energies and  $R_e$ . See L. Wharton, L. P. Gold and W. Klemperer, J. Chem. Phys. 37 (1962) 2149, for dipole moment and field gradients.

from the G1PP and G1 calculations. We see that the agreement is quite good.

Detailed comparisons have been made between the G1 pseudopotential wave functions and the *ab initio* G1 wave functions [10] for LiH and Li<sub>2</sub> in the first such test of the fundamental validity of pseudopotential theory. The excellent agreement here gives us confidence of the potential accuracy of band structure calculations using these pseudopotentials now being carried out on Li metal. In addition we have shown that the dependence of the pseudopotential on angular momentum must be included for reliable results. These results should apply to other studies using pseudopotentials (e.g., Rydberg states in molecules, correlation effects in the bonding pairs, and band

structure calculations in metals) for which complete *ab initio* calculations cannot now be carried out. Thus the use of *ab initio* pseudopotentials as described here yields wave functions which provide a bona fide approximation (comparable to *ab initio* wave functions, such as Hartree-Fock or G1) to the wave function of a system.

#### REFERENCES

- [1] H. Hellmann, J. Chem. Phys. 3 (1935) 61; Acta Physicochimica 1 (1935) 913; 4 (1936) 225.
- [2] J. C. Phillips and L. Kleinman, Phys. Rev. 116 (1959) 287.
- [3] W. A. Harrison, Pseudopotentials in the Theory of Metals (Benjamin, Inc., New York, 1966).
- [4] B. J. Austin, V. Heine and L. J. Sham, Phys. Rev. 127 (1962) 276.
- [5] M. H. Cohen and V. Heine, Phys. Rev. 122 (1961) 1821.

\* Except for the energy, all properties in table 1 for the PPG1 and G1 wave functions were calculated from a program due to S. Aung and R. M. Pitzer, and the properties for the HF wave function were calculated using formulae based upon [11].

- [6] Recent work using pseudopotentials for small molecules include:
- a) W. Kutzelnigg, R. J. Koch and W. A. Bingel, Chem. Phys. Letters 2 (1968) 197;
  - b) P. W. Anderson, Phys. Rev. Letters 20 (1968) 413;
  - c) L. Szasz and G. McGinn, J. Chem. Phys. 48 (1968) 2997.
- [7] W. A. Goddard III, Phys. Rev. 157 (1967) 73, 81.
- [8] W. A. Goddard III, Phys. Rev. 169 (1968) 120.
- [9] W. A. Goddard III, Phys. Rev. 174 (1958) 659.
- [10] W. E. Palke and W. A. Goddard III, to be published.
- [11] R. M. Pitzer, C. W. Kern and W. N. Lipscomb, J. Chem. Phys. 37 (1962) 267.