

Self-consistent-field calculation on lithium hydride for undergraduates

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Students generally acquire an understanding of theoretical concepts only after they have attempted actual calculations based on those concepts. Consequently there is a need for realistic calculations in quantum theory which can be used with undergraduates to illustrate its important concepts. In this paper we describe a self-consistent-field-linear combination of atomic orbitals-molecular orbital calculation on the valence electrons of LiH using the method of Roothaan. The calculation is modest in scope, mathematically simple, and easy to program. These factors enhance its usefulness with undergraduates.

The recent literature in physics and chemistry contains several interesting examples of quantum-mechanical calculations for undergraduates.¹⁻⁵ These calculations are extremely useful in augmenting classroom work on quantum theory with "laboratory-like" experiences. They provide students with an opportunity to "do quantum mechanics," which increases the likelihood that they will master the associated formalism and conceptual framework. In addition, the exercises bring the students to the computer confronting them with many important numerical methods.

The student exercise presented here is a self-consistent-field-linear combination of atomic orbitals-molecular orbital (SCF-LCAO-MO) calculation on the valence electrons of LiH using the method of Roothaan,^{6,7} an iterative procedure which yields a self-consistent set of wave functions and energies. The calculation is based on the work of Karo and Olsen^{8,9} and was used by Murrell, Kettle, and Tedder¹⁰ to illustrate SCF calculations. Given the importance of Roothaan's method in contemporary theoretical work, we thought that a more detailed discussion of the LiH calculation was justified.

SELF-CONSISTENT-FIELD THEORY

Using the fixed nuclei approximation and assuming that the 1s electrons of Li are not involved in bonding, reduces the LiH calculation to a two-electron (the classical valence electrons) problem. In the SCF treatment of the valence electrons, the two-electron Schrödinger equation is approximated by two one-electron equations of the form

$$(H_i^{\text{eff}} - \epsilon_i)\psi_i = 0, \quad i = 1, 2, \quad (1)$$

where H_i^{eff} , the one-electron effective Hamiltonian is, in atomic units,

$$H_i^{\text{eff}} = -\frac{1}{2}\nabla_i^2 - \frac{1}{r_{\text{H}}} - \frac{3}{r_{\text{Li}}} + 2 \int \frac{1}{r_{i,1s}} \phi_s^2 d\tau_{s'} + \int \frac{1}{r_{ij}} \psi_j^2 d\tau_j. \quad (2)$$

The first term on the right-hand side is the kinetic energy operator for the i th electron, the second term represents its interaction with the hydrogen nucleus, and the third term is its interaction with the lithium nucleus. The fourth term is the average interaction of the i th valence electron with the two 1s electrons of lithium and the last term represents its average interaction with the other (j th) valence electron.

LINEAR COMBINATION OF ATOMIC ORBITALS-MOLECULAR ORBITAL

In an SCF calculation, the effective Hamiltonian cannot be determined until a trial wave function is chosen. In the most commonly used version of molecular orbital theory, the wave function is formed as a linear combination of atomic orbitals. In this case the atomic orbitals chosen are the valence orbitals, namely, the 1s of hydrogen (ϕ_h) and the 2s (ϕ_s) and 2p (ϕ_p) of lithium:

$$\psi = c_h \phi_h + c_s \phi_s + c_p \phi_p. \quad (3)$$

The effective Hamiltonian can now be written as

$$H_i^{\text{eff}} = -\frac{1}{2}\nabla_i^2 - \frac{1}{r_{\text{H}}} - \frac{3}{r_{\text{Li}}} + 2(s'|s') + c_h^2(h|h) + c_s^2(s|s) + c_p^2(p|p) + 2c_h c_s (h|s) + 2c_h c_p (h|p) + 2c_s c_p (s|p), \quad (4)$$

where

$$(s'|s') = (\phi_{s'} | (1/r_{i,1s}) | \phi_{s'})$$

and, for instance,

$$(h|p) = (\phi_h | (1/r_{ij}) | \phi_p)$$

Note that s' represents the lithium 1s orbital, while s represents the lithium 2s orbital.

Equations (3) and (4) are substituted into (1). Multiplication on the left by each member of the basis set (3) in turn and integration over all space yields three simultaneous, linear, and homogeneous equations in the coefficients c_h , c_s , and c_p :

$$\begin{aligned}
c_h(H_{hh} - \epsilon S_{hh}) + c_s(H_{hs} - \epsilon S_{hs}) + c_p(H_{hp} - \epsilon S_{hp}) &= 0 \\
c_h(H_{hs} - \epsilon S_{hs}) + c_s(H_{ss} - \epsilon S_{ss}) + c_p(H_{sp} - \epsilon S_{sp}) &= 0 \\
c_h(H_{hp} - \epsilon S_{hp}) + c_s(H_{sp} - \epsilon S_{sp}) + c_p(H_{pp} - \epsilon S_{pp}) &= 0.
\end{aligned} \quad (5)$$

The notation used in Eqs. (5) is,

$$H_{hh} = (\phi_h | H_i^{\text{eff}} | \phi_h), \quad (6)$$

$$S_{hs} = (\phi_h | \phi_s). \quad (7)$$

Substitution of H_i^{eff} into Eq. (6) and using $r' = r_H$ and $r = r_{Li}$ yields,

$$\begin{aligned}
H_{hh} = & (h | -\frac{1}{2}\nabla_i^2 | h) - (h | (1/r') | h) - 3(h | (1/r) | h) \\
& + 2(hh | s's') + c_h^2(hh | hh) + c_s^2(hh | ss) \\
& + c_p^2(hh | pp) + 2c_h c_s (hh | hs) \\
& + 2c_h c_p (hh | hp) + 2c_s c_p (hh | sp). \quad (8)
\end{aligned}$$

For the two electron integrals we have, for example,

$$\begin{aligned}
(hh | hp) = & \int \int \phi_h(1)\phi_h(2) | (1/r_{12}) | \\
& \times \phi_p(2)\phi_h(1) d\tau_1 d\tau_2. \quad (9)
\end{aligned}$$

The orbitals of electron 1 are written to the left of the vertical bar and the orbitals of electron 2 to the right. The remaining elements of the determinant are given in the Appendix.

SELF-CONSISTENT-FIELD METHOD

Before the SCF calculation can begin, the integrals in Eq. (8) and those in the Appendix must be known. This is the most difficult and time consuming aspect of a molecular SCF calculation. Fortunately, the paper by Karo and Olsen⁸ contains values for these integrals for LiH at nine internuclear distances. The calculation described in this paper is for the equilibrium internuclear distance of 3.0 bohr.

With the preliminary discussion of SCF theory completed, the students are given the following outline of the SCF method;

- (i) Obtain the values of the necessary integrals from Ref. 8.
- (ii) Choose initial values for the coefficients c_h , c_s , and c_p .
- (iii) Calculate H_{ij} and S_{ij} . (Actually the overlap integrals do not vary from one iteration to the next.)
- (iv) Expand the determinant of Eqs. (5) and solve the resulting polynomial for the lowest energy root.
- (v) Use this value of ϵ in Eqs. (5) to obtain new and improved values for the coefficients.
- (vi) Normalize the coefficients and return to step iii. The coefficients are normalized by multiplication by the normalization constant which is

$$\begin{aligned}
N = & 1/(c_h^2 + c_s^2 + c_p^2 + 2c_h c_s S_{hs} \\
& + 2c_h c_p S_{hp} + 2c_s c_p S_{sp})^{1/2}.
\end{aligned}$$

This iterative technique is continued until the calculation is self-consistent. That is, until the energy and the coefficients remain invariant from one iteration to the next. The calculation described above takes approximately two four-hour lab periods. One period to write the program and a second period to proofread the program, debug it, and run it.

RESULTS AND DISCUSSION

Table I contains the results of the calculation at 3.0 bohr as described above. Eighteen iterations were required for the calculation to achieve self-consistency to three significant figures. The last line of the table contains the results of Karo's calculation.⁹ It can be seen that this calculation is in good agreement with the more accurate work of Karo.

According to Koopmans' theorem¹¹ the negatives of the one-electron energies approximate the ionization energies of the molecule. This calculation yields a first ionization energy of 8.3 eV for LiH, which compares favorably with the experimental value of 8.0 eV.¹²

Including the core electrons in the 1s orbital on Li, the electron density in the LiH molecule is given by

$$\begin{aligned}
\rho = & 2(1s_{Li})^2 + 2(c_h^2\phi_h^2 + c_s^2\phi_s^2 + c_p^2\phi_p^2 + 2c_h c_s \phi_h \phi_s \\
& + 2c_h c_p \phi_h \phi_p + 2c_s c_p \phi_s \phi_p). \quad (10)
\end{aligned}$$

An estimate of the relative distribution of charge between Li and H can be obtained by dividing the overlap density ($\phi_h\phi_s$, $\phi_h\phi_p$, and $\phi_s\phi_p$) equally between the two orbitals.¹³ For instance,

$$\phi_h\phi_s = \frac{1}{2}S_{hs}(\phi_h^2 + \phi_s^2). \quad (11)$$

This approximation yields the following ionic character for the LiH molecule $-\text{Li}^{+0.44}\text{H}^{-0.44}$. This result is consistent with the fact that hydrogen is more electronegative than lithium.

CONCLUSION

Theoretical concepts generally acquire meaning for students only after they have attempted actual calculations. The calculation outlined above is a suitable exercise for undergraduates and, therefore, should aid the student in gaining insight into Roothaan's SCF method. In addition it should serve as a useful introduction to the literature in this area.

Table I. Summary of SCF orbital energy calculation for valence electrons of LiH.

Iteration	c_h	c_s	c_p	$-\epsilon$ (Hartrees)
1	0.707	0.500	0.500	0.410
2	0.867	-0.144	0.112	0.275
3	0.662	-0.390	0.193	0.330
4	0.799	-0.232	0.141	0.292
5	0.711	-0.333	0.179	0.315
6	0.769	-0.266	0.155	0.299
7	0.731	-0.310	0.171	0.310
8	0.756	-0.281	0.161	0.303
9	0.740	-0.300	0.168	0.307
10	0.751	-0.288	0.164	0.304
11	0.744	-0.296	0.166	0.306
12	0.748	-0.291	0.164	0.305
13	0.745	-0.294	0.166	0.306
14	0.747	-0.292	0.165	0.305
15	0.746	-0.293	0.166	0.306
16	0.747	-0.292	0.165	0.305
17	0.746	-0.293	0.165	0.305
18	0.746	-0.293	0.165	0.305
⋮	⋮	⋮	⋮	⋮
30	0.746	-0.293	0.165	0.305342
Ref. 9	(0.702)	(-0.329)	(0.205)	(0.305452)

APPENDIX

The remaining elements, H_{ij} , of Eqs. (5) are:

$$H_{ss} = (s | -\frac{1}{2}\nabla^2 | s) - (s | (1/r') | s) - 3(s | (1/r) | s) + 2(ss | s's') \\ + c_h^2(ss | hh) + c_s^2(ss | ss) + c_p^2(ss | pp) + 2c_h c_s(ss | hs) \\ + 2c_h c_p(ss | hp) + 2c_s c_p(ss | sp);$$

$$H_{pp} = (p | -\frac{1}{2}\nabla^2 | p) - (p | (1/r') | p) - 3(p | (1/r) | p) + 2(pp | s's') \\ + c_h^2(pp | hh) + c_s^2(pp | ss) + c_p^2(pp | pp) + 2c_h c_s(pp | hs) \\ + 2c_h c_p(pp | hp) + 2c_s c_p(pp | sp);$$

$$H_{hs} = (h | -\frac{1}{2}\nabla^2 | s) - (h | (1/r') | s) - 3(h | (1/r) | s) + 2(hs | s's') \\ + c_h^2(hs | hh) + c_s^2(hs | ss) + c_p^2(hs | pp) + 2c_h c_s(hs | hs) \\ + 2c_h c_p(hs | hp) + 2c_s c_p(hs | sp);$$

$$H_{hp} = (h | -\frac{1}{2}\nabla^2 | p) - (h | (1/r') | p) - 3(h | (1/r) | p) + 2(hp | s's') \\ + c_h^2(hp | hh) + c_s^2(hp | ss) + c_p^2(hp | pp) + 2c_h c_s(hp | hs) \\ + 2c_h c_p(hp | hp) + 2c_s c_p(hp | sp);$$

$$H_{sp} = (s | -\frac{1}{2}\nabla^2 | p) - (s | (1/r') | p) - 3(s | (1/r) | p) + 2(sp | s's') \\ + c_h^2(sp | hh) + c_s^2(sp | ss) + c_p^2(sp | pp) + 2c_h c_s(sp | hs) \\ + 2c_h c_p(sp | hp) + 2c_s c_p(sp | sp).$$

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