THE VARIATION METHOD AND THE TWO-ELECTRON MODEL

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The Variation Method (Eyring, *et al.*, 1944, p. 99) has been used by chemists in energy calculations. For problems where a two-electron approximation is made and inner shells are ignored, care must be taken in the use of the Variation Method. The primary purpose of this paper is to investigate whether these two-electron calculations are a variation problem with respect to two-electron energies or a perturbation problem.

The investigation considers the usual two-electron Hamiltonian as a perturbed case of a more general two-electron Hamiltonian. The results of the present calculations with the generalized Hamiltonian should be considered as a demonstration rather than a general proof since specific wave functions are used. These results are compared to those of a usual two-electron calculation of LiH and Li_2 recently given by Harriss, Mitchell, and Musulin (1963).

James (1934) performed calculations, for Li_2 with a modified six-electron Hamiltonian, using all six electrons and using, also, a two-electron approximation. The results indicated that the serious underestimation of the binding energy with a complete calculation was corrected for by the approximation of neglect of inner shells. That is, the omission of inner shells neglects a repulsive potential due to these inner shells. This, in turn, leads to a smaller value for the equilibrium internuclear distance. In general, the Heitler-London (1927) method leads to values of the binding energy which are too low and values of inner shell repulsion which are too high.

The generalized two-electron Hamiltonian, referred to above, may be considered as one which neglects, in two-electron calculations, all screening by the inner shells. Consequently, by comparison with the results of the usual two-electron calculation, it should be possible to obtain an estimate of the inner shell repulsions. It is proposed that this method of obtaining the repulsions is an alternate method to that of James.

The Hamiltonian

The two-electron Hamiltonian for the two-center problem is

$$\mathbf{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z_a}{{}_1r_a} - \frac{Z_a}{{}_2r_a} - \frac{Z_b}{{}_1r_b} - \frac{Z_b}{{}_2r_b} + \frac{1}{r_{12}} + \frac{Z_aZ_b}{R} \qquad (1)$$

where Z_j is the nuclear charge of the i^{th} center, r_{12} is the interelectronic distance, ${}_jr_i$ is the distance between center i and electron j, and R is the distance between the centers. The Hamiltonian is given in atomic units (a.u.) (Energy: 1 a.u. = 27.210 e.v.; Charge:

1 a.u. = 4.80286×10^{-10} e.s.u.; Mass: 1 a.u. = 9.1083×10^{-28} g; Length: 1 a.u. = 0.529172×10^{-8} cm.).

In the usual Heitler-London approximation, the inner shell electrons are considered to be too close to the nucleus to actually take part in chemical reactions. This has the effect, in problems involving the lithium atom, of giving Z_i the value 1 instead of 3. In the present calculations, Z_i, where it involves a lithium atom, will be given the value 3. That is, it is assumed that the inner shells do not screen the nucleus at all.

Since

$$\frac{3}{{}_jr_i} = \frac{2}{{}_jr_j} + \frac{1}{{}_jr_i}$$

then

$$\mathbf{H} = \mathbf{H}_o + \mathbf{H}' \qquad (2)$$

where $\mathbf{H}$ is the Hamiltonian used in the present calculations, $\mathbf{H}_o$ is the usual two-electron Hamiltonian, and $\mathbf{H}'$ is the perturbing Hamiltonian, containing terms $2/{}_jr_i$.

The Wave Function

In order to thoroughly test the model, the calculations are performed with two types of atomic wave functions. The first type is the usual noded wave functions which are solutions of the hydrogen atom problem (Eyring, *et al.*, 1944, p. 89). The second set consists of the nodeless functions proposed by Slater (1930). The molecular wave function is described by the usual LCAO (linear combination of atomic orbitals) approximation in its simplest Heitler-London form. That is, only 1s orbitals are used for the hydrogen electron and only 2s orbitals for the valence lithium electron.

Eyring, *et al.* (1944, p. 216) have also shown how the exact solutions of the hydrogen atom problem may be modified and taken in linear combinations to approximate the exact solutions of molecular problems. One of the modifications which they mention is that of placing a multiplicative factor in front of the distance parameter in the exponential portion of the wave function. Through the years it has been customary to use values suggested by Slater (1930) for this multiplicative factor.

The Slater terms are obtained from values of screening in the atomic case. These, of course, are not properly valid when an atom takes part in molecular formation. However, the mathematical processes necessary to correct the situation have been so laborious that workers in the field have usually neglected the error resulting from the use of the Slater values. Since these values are based upon atoms, it appears to be suitable to describe them by the adjective atomic. Furthermore, in recent years, it has become recognizable that some of the attempts to identify these multiplicative factors with physical quantities, such as screening, are rather nebulous in the very complex wave functions being tested on today's high-speed computers. Consequently, the general categorical term, orbital parameter, has become adopted. The word, orbital, is used as part of the description insomuch as the quantum number is also part of the single, compound, multiplicative factor of the distance parameter (Eyring, *et. al.*, 1944, p. 89). Combining these terminologies, it may be said that

workers in the past have used wave functions with an atomic orbital parameter.

Musulin (1956) has shown how, for diatomic molecules, an orbital parameter, which varies with internuclear distance, may be obtained. This functional dependence is more realistic for molecules than the use of a fixed value as determined by Slater (1930). In line with the terminology of the preceding paragraph, Musulin has used the adjective, molecular, to describe his multiplicative factor. The whole term is referred to as a molecular orbital parameter. The present work uses a molecular orbital parameter in all wave functions.

The necessary constants defining the orbital parameter are computed with the following three electron groupings: (1) all electrons (4 in the case of LiH and 6 for Li_2); (2) only valence electrons in the presence of unscreened nuclei; (3) only valence electrons in the presence of completely screened nuclei. Technically, it might be better to describe the third grouping by saying "in the presence of partially screened nuclei" since Slater's (1930) rules are used to determine the orbital parameters for the united and separated atoms. However, the terminology used allows for easier tabulation.

Calculation Details

The usual techniques are used to obtain explicit expressions for all integrals except the exchange integral. Insomuch as several approximations have already been made, the Mulliken (1949) approximation is more *apropos* to the problem.

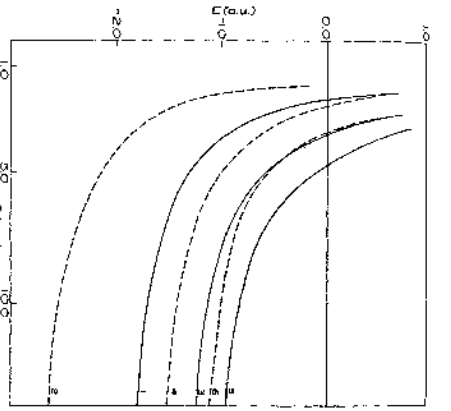

Figure 1.—Potential energy curves of Li_2. Key: 1, 2—six-electron orbital parameter; 3, 4—unscreened two-electron orbital parameter; 5, 6—screened two-electron orbital parameter; solid line—hydrogen-like wave functions; and dashed line—Slater wave functions.

The calculations were performed upon an IBM 650 computer having no extra storage. The original programs were written in Fortran and

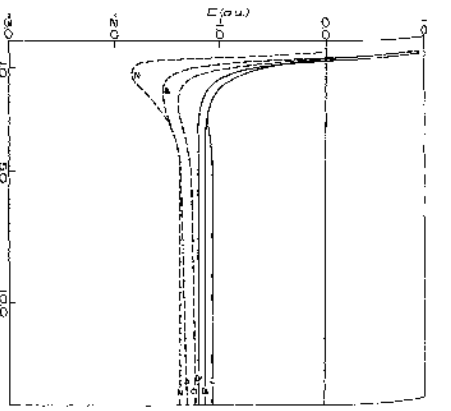

Figure 2.—Potential energy curves of LiH. Key: 1, 2—four-electron orbital parameter; 3, 4—unscreened two-electron orbital parameter; 5, 6—screened two-electron orbital parameter; solid line—hydrogen-like wave functions; and dashed line—Slater wave functions.

the corrected versions were written in Illiad (1961). The integrals were evaluated at 70 points of R between the values of 0.25 and 50.00 a.u. The greatest density of points was taken at the experimental internuclear distance (Herzberg, 1950).

The experimental values of electron energies, dissociation energies, and internuclear distances were obtained from Herzberg (1950) and Moore (1949). The calculated dissociation energies are obtained by taking the difference between the energy at the equilibrium distance and the asymptote.

Results

The potential energy curves obtained for Li_2 are given in Figure

Table 1.—Summary of Spectroscopic Results for LiH.

Function	Orbital Parameter	R_e(a.u.)	$-E_e$(a.u.)	D_e(a.u.)	$\triangle D_e$(a.u.)
Hydrogen-like	Four-electron average	2.80	1.1058	0.0531	0.0091
	Two-electron average	4.00	1.2167	0.0298	—0.0064
	Two-electron average with screening	4.75	1.1447	0.0197	—0.0083
Slater	Four-electron average	1.25	1.9653	3.5038	0.1567
	Two-electron average	1.75	1.5537	0.2570	0.0614
	Two-electron average with screening	2.20	1.4021	0.1038	0.0287
Experimental		3.01	0.793* 8.072**	0.036	

* Two-electron.
** Four-electron.

Table 2.—Summary of Test Criteria for LiH.

Function	Orbital Parameter	Virial Theorem	Occupation Numbers
Hydrogen-like	Four-electron average	0.68	0.7379
	Two electron average	0.68	0.7577
	Two-electron average with screening	0.68	0.7560
Slater	Four-electron average	0.48	0.7279
	Two-electron average	0.48	0.8758
	Two-electron average with screening	0.47	0.8733

1 and the corresponding curves for LiH are given in Figure 2. The values for LiH, of the equilibrium internuclear distance, R_e, the total energy, E, at R_e, and the dissociation energy, are summarized in Table 1. No binding was observed in L_2 for any of the six trial wave functions.

Table 2 lists the results of evaluating the present wave function for LiH by two different criteria. These results are included to insure that the wave function is of the same degree of "goodness" in calculations using both types of Hamiltonians.

The first criterion results from the use of the Virial Theorem (Slater, 1933). In Table 2, values of the ratio (-2 kinetic energy/potential energy) are presented at the equilibrium distance. According to the Virial Theorem, this ratio should have the value of 1.0 at this distance.

The second of these test criteria is the use of occupation numbers. The transformation given by Shull (1959) is used to transform the present wave function into a truncated two-term Natural Spin Orbital expansion. The square of the coefficient of the first term of the expansion is the occupation number of that term, which should be very close to unity if the truncated expansion is a good approximation to the true expansion.

Discussion

Each of the total energy values obtained in the present calculations for LiH is below the total experimental two electron energy. This is an apparent contradiction of the Variation Theorem. However, the results may be explained by a consideration of the restrictions of the Variation Theorem.

In the Variation Method, an "exact" Hamiltonian is used with approximate wave functions. On the other hand, in the Perturbation Theory, an approximate Hamiltonian is used with eigenfunctions which are exact solutions of that Hamiltonian. The Hamiltonian given by equation (1) is the "exact" Hamiltonian for a two-center, two-electron problem if the values of Z_i are correctly defined. In the present calculation, it is unrealistic to believe that the valence electrons are under the forces of unscreened nuclei. Consequently, it should not be expected that the Variation Theorem provides a lower bound for the total energy.

If this same argument is applied to the usual two-electron calculation, a similar conclusion must be reached. The assumed value of $Z_i = 1$ is also unrealistic. In fact, the valence electrons are under the influence of a partially screened nuclear field of $Z_i = 3$ (if the i^{th} center is the Li atom). Thus, one should question whether or not it is proper to state that values obtained in the usual two-electron calculations are bounded from below by the experimental two-electron energy.

If the usual two-electron calculations are considered as perturbation calculations, then the energy obtained may be either above or below the experimental energy. The usual consequence of the Variation Theorem is that a value obtained below the experimental energy is the result of a numerical error or a failure of the model selected.

It should be pointed out that the present calculation, as described in equation (2), is not a true perturbation calculation since the LCAO wave functions are not eigenfunctions of $\mathbf{H}_0$. However, one could recast the Hamiltonian so that the problem appears as a true perturbation problem. This is done by splitting $\mathbf{H}_0$ into two parts, viz.,

$$\mathbf{H}_0 = \mathbf{H}_0' + \mathbf{H}_0''$$

where $\mathbf{H}_0'$ is the Hamiltonian for a composite system of hydrogen-like atoms and $\mathbf{H}_0''$ contains the remainder of the terms of $\mathbf{H}_0$. The LCAO functions are then solutions of $\mathbf{H}_0'$, and the problem could be treated rigorously as a perturbation problem.

In the present calculations, if total energy is used as a criterion to select the best wave function, it is seen that the use of a hydrogen-like function, with a molecular parameter determined by the use of all four electrons, provides the best LCAO approximation to the wave function of LiH.

Since no binding was found for Li_2, it would not be appropriate to discuss whether or not the total energy at the stable minimum is above or below the experimental two-electron energy. On the other hand, if one examines the total energies obtained at the experimental internuclear distance, one finds that five of the six calculations yield values below the experimental energy value.

The Variation Theorem does not provide any information on bounds of dissociation energies. It might be noted that the hydrogen-like wave function, with a molecular orbital parameter using all four electrons, again provides the best value of the dissociation energy.

The essential difference between this calculation and that performed by Harriss, *et al.*, is the addition of the perturbing term, $\mathbf{H}'$, of equation (2). This term is attractive in nature and has the effect of lowering, for a given internuclear distance, the total energy. Physically, the difference corresponds to the shielding of the nuclear field by the inner shell electrons. In this framework, it might be said that the traditional two-electron calculation corresponds to the inclusion of inner shells (the assigned value of $Z_i = 1$ in the Hamiltonian corresponds to complete shielding by the inner shells) while the present calculation corresponds to the omission of inner shells. It is to be noted that this does not imply that inner shells are included in any two-electron calculation.

The results obtained, using this viewpoint, agree with those given by James. The inclusion of inner shells gives rise to a repulsive potential in the ground state of Li_2. The present calculation also indicates that this is true for LiH. However, with the present wave function, all binding is lost when the inner shells are omitted in Li_2. Thus, the binding energy is greater with the inner shells included, which is contrary to the results of James. It would appear that the use of a wave function with a molecular orbital parameter causes the repulsive potential due to inner shells to be as great or greater at large distances than at equilibrium distances; whereas, the James' wave function causes this potential to greatly diminish at large distances.

For the ionic, LiH molecule, the dissociation energy is greater with the omission of inner shells in four of the six calculations. This is indicated by the results tabulated in the final column of Table 1, which of course then are the inner shell repulsions.

Some readers may find the purely mathematical approach of the present work, and that of James (1934), too mysterious. They may be reassured that the results are similar to those obtained *in a posteriori* arguments by chemists who base their work upon experimental evidence. For example, Pitzer (1948) concludes qualitatively, based upon experimentally determined dissociation energies, that inner shells repel each other. Pitzer indicates that such repulsions are not as predominant for first row species (including Li_2) as for species of other rows in the periodic table. The present paper can make no such comparisons, but the values of Table 1 and those found by James indicate that neglect of inner shell repulsions may cause a misestimate of the binding energies of the outer electrons by as much as 40 to 60%.

The strong shifting of equilibrium distances toward smaller values found by James is not found in the present calculation. A slight indication of this effect is found, for LiH, if the orbital parameter in hydrogen-like wave functions is determined using all four electrons. It is this selection of wave function which must be considered best, if agreement with the work of James is used as a criterion.

The hydrogen-like wave functions are found to be better using the Virial Theorem criterion. However, they do not appear to be as satisfactory a function as when used with the traditional two-electron Hamiltonian.

The occupation number criterion indicates that the Slater wave functions are the better, although the difference in values is not as great as with the Virial Theorem criterion. A second point is that there is almost no change in the values of occupation numbers when the calculation is performed with the different Hamiltonians.

It would appear that there is not much difference in the "goodness" of the wave function in the calculation with the two Hamiltonians. Therefore, the conclusions concerning inner shell repulsion, based upon the use of these functions, are internally consistent.

Summary

Calculations made in the Heitler-London approximation, using a molecular orbital parameter, for Li_2 and LiH support the contention that the energy values obtained from a traditional two-electron calculation are not bounded by the experimental two-electron energy. A new method, considering the usual two-electron calculations as a perturbation problem, is introduced for interpreting the repulsion due to the inner shells. Calculations are given to estimate the amount of these repulsions.

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