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Simple Energy Eigenfunctions for Li_2 and LiH*

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The use of an orbital parameter which varies with internuclear distance is tested by the calculation of potential energy curves of Li_2 and LiH in a Heitler-London approximation. The best method of choosing the molecular orbital parameter is discussed. The values of the dissociation energies obtained are compared to similar calculations which determined the orbital parameter in a different manner.

L'utilisation d'un paramètre orbital qui varie avec la distance internucléaire est examinée par un calcul de courbes d'énergie pour Li_2 et LiH (dans le cadre d'une approximation Heitler-London). La meilleure méthode pour choisir le paramètre moléculaire est discutée. Les énergies de dissociation obtenues sont comparées aux résultats de calculs semblables, dans lesquels le paramètre orbital est défini d'une manière différente.

Die Verwendbarkeit eines vom Kernabstand abhängigen Bahnparameters wird durch die Berechnung von Potentialkurven für Li_2 und LiH (in einer Heitler-London-Näherung) geprüft. Die Wahl des besten Ansatzes für diesen Molekülparameter wird diskutiert. Die erhaltenen Dissoziationsenergien werden mit denen ähnlicher Rechnungen verglichen, bei denen der Bahnparameter auf andere Weise bestimmt wurde.

Introduction

One of the most commonly used types of wave functions in quantum mechanical calculations is a function containing an exponential dependence upon internuclear distance. The shape of the exponential factor depends upon an "*effective atomic number*" and the principal quantum number. For complex diatomic molecules and polyatomic molecules, the effective atomic number is computed from a screening constant selected by the use of SLATER's rules (1930). MUSULIN (1956) has suggested a semi-empirical method for determining an effective atomic number which is characteristic of the molecule under consideration.

The purpose of the present paper is to determine whether or not the molecular orbital parameter would be useful in quantum mechanical calculations. For the purpose of a test calculation which could be compared to previous calculations, the total energy and the dissociation energy of two simple diatomic molecules is computed. The molecules selected are Li_2 and LiH. These molecules represent the simplest cases involving orbitals with a principal quantum number of 2. In addition, Li_2 is a molecule which would be expected to have essentially covalent

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bonding while LiH would be expected to be primarily ionic in nature. Alternatively, another viewpoint is that the test calculation is made upon one example of a homonuclear diatom and upon one example of a heteronuclear diatom.

A second important purpose in making the calculations is to determine if the simplifications in the wave functions cause a great worsening in the energy results. Although it is possible to create highly exact wave functions which with the use of large electronic computers lead to very exact values of physical observables, there is still a great need for simple wave functions which can be used by chemists to estimate properties and which at the same time retain chemical significance [COULSON (1960)]. The simplest construction of a molecular orbital parameter involves a weighted mean value for all orbital functions. Molecules were chosen which involved electrons outside the K shell in order to test whether the use of a weighted mean molecular screening constant would provide meaningful results. Should such a technique prove useful, it would be possible to greatly simplify the computational work involved.

Different choices of wave functions and molecular orbital parameters are examined in order to determine the interrelations of these aspects in the construction of a model for quantum mechanical calculations.

Choice of Wave Function

The calculations are performed in the Heitler-London (1927) approximation considering the valence electrons only. Thus the wave function, in both cases, is of the LCAO (linear combination of atomic orbitals) type with zero spin

$$\Psi = \psi_a(1)\,\psi_b(2) + \psi_a(2)\,\psi_b(1) \tag{1}$$

where the subscripts refer to the nuclei and the numbers refer to the spatial coordinates of the valence electrons. The spin terms have been factored out in the usual manner.

It has been most common to use a nodeless function first suggested by SLATER (1930) for the atomic wave functions, ψ, in equation (1). With the use of such functions, approximately the same results are usually obtained as those found with the atomic functions derived from the exact solution of the problem of hydrogen-like ions, however, differences may be obtained when the region of interest in the calculations coincides with the location of the nodes in the true atomic functions [FISCHER (1952)]. There is no *a priori* reason to expect that nodeless wave functions and those with nodes would provide the same results when used with a molecular orbital parameter. Consequently, two parallel calculations are made; one using Slater orbitals for the atomic functions in equation (1), and one using hydrogen-like functions.

The calculations are made in the simplest possible manner, i.e., only $1s$ orbitals are used for the hydrogen electron and only $2s$ orbitals for the valence lithium electron. The normalized wave functions which were used in the calculations are

$$\begin{aligned}
\psi_{1s} &= \frac{1}{\sqrt{\pi}}\, z^{3/2}\, e^{-\varrho} \\
\psi_{2s} &= \frac{1}{4\sqrt{2\pi}}\, z^{3/2}\, (2-\varrho)\, e^{-\varrho/2} \quad \text{hydrogen-like} \\
\psi_{2s} &= \frac{1}{4\sqrt{6\pi}}\, z^{3/2}\, \varrho\, e^{-\varrho/2} \qquad \text{SLATER}
\end{aligned} \tag{2}$$

with $\varrho = zR$ where z is the molecular screening constant and R is the internuclear distance. In the case of the $1s$ orbital, the Slater and the hydrogen-like functions are identical.

Choice of Molecular Orbital Parameter

The expression for the molecular orbital parameter is

$$z = Ae^{-R} + B \tag{3}$$

where z is the constant to be used in the atomic wave functions given by equations (2), A and B are constants to be determined from the united and separated atom limits, and R is the internuclear distance in atomic units* (a.u.). Three different methods of determining A and B are used in order to find the best way of applying the use of a molecular orbital parameter. These choices are illustrated using LiH as an example.

The united atom formed by LiH is Be while the separated atoms are Li and H. (No attempt is made to consider the dissociation into ionic states in the present paper.) One method of determining A and B is to consider all four electrons. SLATER's values are used for the $1s$ and $2s$ electrons of Be and for the $1s$, $2s$ electrons of Li and the $1s$ electron of H. These values give

$$z = 0.90e^{-R} + 1.92.$$

At the known equilibrium distance [HERZBERG (1950)], a value of $z = 1.97$ is found.

Since only the valence electrons are considered in the calculation another method of choosing A and B is to use SLATER's values for the $2s$ electrons of Be and for the $2s$ electron of Li and the $1s$ electron of H. These values give

$$z = 0.80e^{-R} + 1.15.$$

In this case, $z = 1.19$ at the equilibrium distance.

Finally, if the inner shell electrons of the lithium atom are considered completely coalesced into the nucleus, then the united atom is He and the separated atoms are H and H. Applying the same procedure, the following equation for z is obtained.

$$z = 0.70e^{-R} + 1.00.$$

The equilibrium value of z is 1.03.

In the case of Li_2, the following three equations for z are obtained.

$z = 1.84e^{-R} + 2.23$	6 electron average
$z = 1.95e^{-R} + 1.30$	2 electron average
$z = 0.70e^{-R} + 1.00$	2 electron average with complete screening

Each of the different equations for z are used with Slater and hydrogen-like atomic functions. The equilibrium values of z found with these formulae are 2.24, 1.31, and 1.00, respectively.

The two electron Hamiltonian for the two-center problem is

$$\boldsymbol{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z_a}{r_{a_1}} - \frac{Z_a}{r_{a_2}} - \frac{Z_b}{r_{b_1}} - \frac{Z_b}{r_{b_2}} + \frac{1}{r_{12}} + \frac{Z_a Z_b}{R} \tag{4}$$

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* 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.

where Z_a and Z_b are the nuclear charges of centers a and b, respectively, r_{12} is the interelectronic distance, r_{ij} is the distance between center i and electron j, and R is the distance between centers a and b. The Hamiltonian is given in atomic units.

In the Heitler-London approximation, the inner shell electrons of the lithium atom are not used. These electrons are considered to be too close to the nucleus to actually take part in chemical reactions. If this view is carried to the limit, then the two inner shell electrons could be thought of as part of the nuclear core. In this case, the charge on the nuclear core for lithium is not 3 but rather 1.

Calculation Details

In the course of the calculations it is necessary to evaluate integrals of the type

$$\int \frac{\psi_a(1)\,\psi_b(2)\,\psi_a(2)\,\psi_b(1)\,d\tau}{r_{12}}\,.$$

In order to retain simplicity in the calculations, the Mulliken approximation [MULLIKEN (1949)] is used to evaluate all integrals of this type. All other integrals and expectation values are evaluated by the techniques used by MUSULIN and JAMIESON (1958).

The calculations were performed on an IBM 650 computer having no extra storage. The original programs were written in Fortran and the corrected versions were written in ILLIAD (1961). The use of an electronic computer allows the use of a great many points in the region of the equilibrium internuclear distance. However, with a single value of z, the integral evaluations are sufficiently simple that the shape of the potential curve could easily be obtained from evaluation of a limited set of points on a desk calculator. Thus, one of the objectives of the project, i.e., simplicity of use, is attained.

An independent check of the use of the Mulliken approximation was made in the case of the LiH trial function constructed from Slater atomic orbitals. The interpolation formulas given by MILLER, et al. (1959) are used to estimate at the internuclear distances the exchange integral from the values in their tables. Independent of the type of orbital parameter used, it is found that the total energy in the region of R_e and thus the dissociation energy are lowered 0.02 a.u. Although this is a small value, it is approximately of the same order of magnitude as the dissociation energy of Li_2, 0.04 a.u.

It is felt that no rationale exists for a more exact evaluation of the exchange integral within the framework of the approximations already used. Further, a great deal of the simplicity of the calculation would be lost if a more exact evaluation than the Mulliken approximation were to be used.

Results

The potential energy curves obtained for Li_2 are given in Fig. 1 and 2 and the corresponding curves for LiH are given in Fig. 3 and 4. In every case, the lowest potential curve is obtained from an LCAO valence bond function constructed from Slater atomic orbitals. The values for Li_2 and LiH of the equilibrium internuclear distance, R_e, the total energy, E, at R_e, and the dissociation energy, are presented in Tab. 1.

The total two electron energies [calculated with values from HERZBERG (1950) and MOORE (1949)] are given in Tab. 1. Either two electron orbital parameter in a hydrogen-like wave function gives a good approximation to these energies, while the average using all electrons seriously underestimates the true values. The use of Slater wave functions tends to give values of the total energy which are too low.

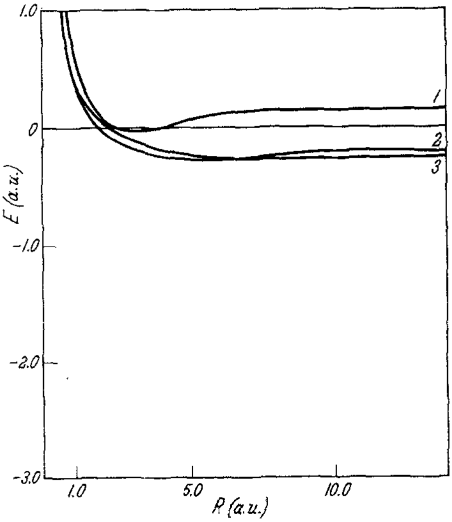

Fig. 1. Potential Energy Curves of Li_2 Obtained with Hydrogen-Like Wave Functions. *1* Six electron orbital parameter; *2* Unscreened two electron orbital parameter; *3* Screened two electron orbital parameter

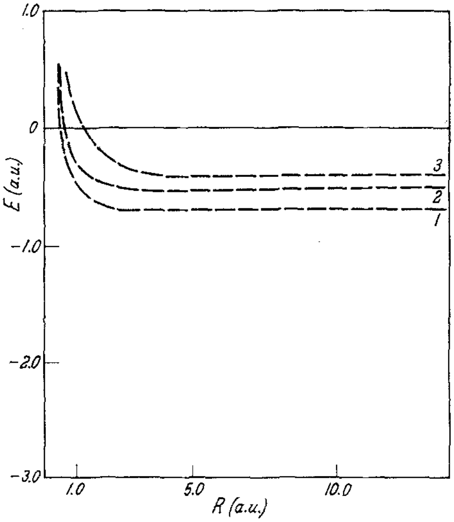

Fig. 2. Potential Energy Curves of Li_2 Obtained with Slater Wave Functions. *1* Six electron orbital parameter; *2* Unscreened two electron orbital parameter; *3* Screened two electron orbital parameter

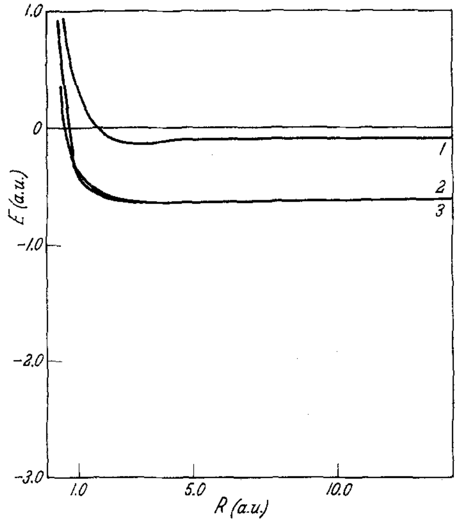

Fig. 3. Potential Energy Curves of LiH Obtained with Hydrogen-Like Wave Functions. *1* Four electron orbital parameter; *2* Unscreened two electron orbital parameter; *3* Screened two electron orbital parameter

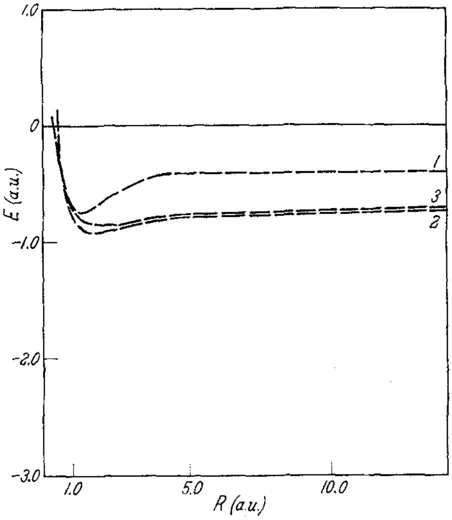

Fig. 4. Potential Energy Curves of LiH Obtained with Slater Wave Functions. *1* Four electron orbital parameter; *2* Unscreened two electron orbital parameter; *3* Screened two electron orbital parameter

The dissociation energies are calculated by taking the difference of the energy at the equilibrium distance and the asymptotic energy value. These values represent the difference of the two large energy values and, if the trial calculations are internally consistent, it may be possible to obtain excellent agreement between experiment and calculation even though the true total energy does not agree well with experiment.

The trial functions for *LiH* constructed from hydrogen-like atomic orbitals give good results when compared to the experimental value. The best of these values is obtained with a function containing a molecular orbital parameter based upon a four electron average. The value of 0.044 a.u. is approximately equal to the value obtained by Yasumori (1952) in a similar calculation using two different orbital parameters.

Table 1. *Summary of Results*

Compound	Function	Orbital Parameter	R_e (a. u.)	$-E$ (a. u.)	D_e (a. u.)	Test by Virial Theorem
Li_2	Hydrogen-like	Six electron average	3.00	0.0211	0.1493	0.84
		Two electron average	5.50	0.2756	0.0481	0.85
		Two electron average with screening	8.00	0.2733	0.0233	0.86
	Slater	Six electron average	4.00	0.7046	0.0040	0.33
		Two electron average	4.00	0.5189	0.0097	0.38
		Two electron average with screening	6.00	0.4234	0.0067	0.37
Bartlett and Furry (1931)		—	4.54	—	0.040	—
James (1934)		—	6.01	—	0.010	—
Experimental [Herzberg (1950)]		—	5.05	0.4341	0.039	1.00
LiH	Hydrogen-like	Four electron average	2.98	0.1342	0.0440	0.96
		Two electron average	4.00	0.6471	0.0362	0.95
		Two electron average with screening	4.50	0.6532	0.0280	0.95
	Slater	Four electron average	1.25	0.7461	0.3471	0.67
		Two electron average	1.75	0.9173	0.1962	0.66
		Two electron average with screening	2.00	0.8635	0.1651	0.66
	Yasumori (1952)	—	2.89	—	0.047	—
Experimental [Herzberg (1950)]		—	3.01	0.7897	0.095	1.00

In every case the Slater type functions overestimate the amount of binding in *LiH*. The difference between the results using the Slater and hydrogen-like functions is in the calculation of the kinetic energy. The values of all individual integrals and the potential energy are essentially the same for the two types of functions but the kinetic energy calculated with Slater functions is always smaller than the corresponding energy calculated with hydrogen-like functions. Apparently, the use of a single molecular orbital parameter is not an accurate enough description of the screening to allow the use of the further approximation of nodeless functions. The greater amount of binding also results in a tighter bond. Again, the equilibrium distances calculated with hydrogen-like functions agree more closely with experiment. The function using a molecular orbital parameter based upon the four electron average yields a distance within 0.1 a.u. of that found by YASUMORI and within 0.2 a.u. of the experimental distance.

Essentially the same results are found for Li_2 in that the use of Slater functions tends to give tighter bonding. On the other hand, it is the hydrogen-like functions which tend to overestimate the dissociation energy. Nevertheless, the dissociation energy calculated with hydrogen-like functions and using a two electron orbital parameter is better than that found by JAMES (1934) in a similar calculation. The equilibrium distance which is found is smaller than those found in comparable calculations.

Table 2. *Occupation Numbers of the Trial Functions at the Equilibrium Internuclear Distance*

Function	Orbital Parameter	n_1 (Li_2)	n_1 (LiH)
Hydrogen-like	Total electron average	0.9276	0.7273
	Two electron average	0.9223	0.7577
	Two electron average with screening	0.9009	0.7593
SLATER	Total electron average	0.8259	0.8656
	Two electron average	0.9693	0.8758
	Two electron average with screening	0.9009	0.8772

The final column of Tab. 1 gives the values of the ratio (—2 kinetic energy/potential energy) at the equilibrium distance. According to the Virial Theorem [SLATER (1933)] this ratio should have a value of 1.0 at the equilibrium distance. Usually if screening is introduced into the wave function, the Virial Theorem will be satisfied. However, this is not found to be true in these calculations except for the case of LiH using hydrogen-like atomic orbitals. Whether or not the Virial condition would be satisfied upon the introduction of an additional variational parameter is now being investigated. It is possible that a wave function satisfying the Virial condition cannot be constructed when a single orbital parameter is used to describe orbitals with different principal quantum numbers.

A potential maximum is found in some of the calculations with both molecules at an approximate distance of 10 a.u. These maxima are of the order of magnitude of 0.001 a.u. Since they are not known experimentally, their appearance is probably due to the approximate nature of the calculations.

SHULL (1959) has shown that a Heitler-London wave function may be transformed into a truncated two-term Natural Spin Orbital (NSO) 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. The transformation given by SHULL has been used to transform the functions of the present calculation into

NSO expansions, and the resulting occupation numbers are given in Tab. 2. The usual Heitler-London approximations which have been used have occupation numbers of the first term equal to 0.98 to 0.99. It is seen that the occupation numbers for *LiH* indicate that these wave functions are poor representations of the true natural spin orbitals. The functions for Li_2, although not as good a truncated expansion as the Heitler-London approximations for H_2, are fairly good approximations to the true NSO expansion. The "*goodness*" of the *LiH* wave function is the opposite from that found by the Virial Theorem criteria.

Conclusion

A single orbital parameter, which is a function of internuclear distance, may be used to construct a wave function, which successfully estimates dissociation energies of diatomic molecules, in the Heitler-London approximation. In the heteronuclear case the wave function should be constructed from atomic functions which are the solutions of hydrogen-like ions. The use of nodeless functions leads to excessive binding. In the homonuclear case, there is less difference between the use of the two atomic functions although in these calculations the noded function again appeared superior.

Logically, only the "unscreened" two electron average method should have been used to determine the orbital parameter in these two electron calculations. With hydrogen-like wave functions, this choice is either the best choice or differs from the best choice by an amount which is much less than the difference between the approximations and the experimental values. For Li_2, this is also true with Slater wave functions, although the results obtained with these functions are inferior to those obtained with hydrogen-like functions. In the case of *LiH*, the screened two electron orbital parameter gives better results, emphasizing the unsuitability of the use of Slater functions in these calculations.

The wave functions are not excellent wave functions either from the viewpoint of the Virial condition at the equilibrium internuclear distance or from the viewpoint of occupation numbers. The occupation number analysis indicates the method is better for the homonuclear problem than for the heteronuclear problem. However, this may result from the use of the Heitler-London approximation rather than from the use of a single orbital parameter.

Finally, the goal of simplicity has been attained. The use of a single orbital parameter which is a function of internuclear distance leads to a molecular wave function which is useful for estimation of physical quantities by quantum mechanical techniques. The resulting calculations give results comparable to those obtained with wave functions containing one or two more variables.

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