

A PRELIMINARY INVESTIGATION OF THE BINDING ENERGY OF LiH

BORIS MUSULIN AND DONALD R. JAMIESON
Southern Illinois University, Carbondale

In a previous paper, Musulin (1956), an empirical method for the calculation of molecular screening constants was presented. The purpose of this paper is to make an exploratory calculation of the binding energy of the LiH molecule using a wave function containing a molecular screening constant. This type of wave function, containing only one screening constant, is much simpler than conventional wave functions of heteronuclear diatomic molecules which demand the use of two parameters. The simplification is even greater for those calculations including the effect of inner shell electrons of atoms having a principal quantum number equal to or greater than two.

METHOD OF CALCULATION

The LiH molecule is the simplest diatomic molecule involving electrons of principal quantum number equal to 2. This molecule should provide an excellent test of a molecular screening constant in the place of the individual atomic screening constants suggested by Slater (1930). The molecule has a polar nature and thus provides an excellent test of the effect of ionic terms in a complete wave function.

The simplest approximation is to consider a covalent bond between the 1s electron of the hydrogen atom and the 2s electron of the lithium atom. The 1s electrons of the lithium

atom are considered to be part of the nuclear core.

The Hamiltonian operator for the system is given (in atomic units) by 1) below.

A Heitler-London (Valence Bond) approach is used. The wave function of the system being of form 2) below.

Parallel calculations were performed using hydrogenic 2s functions and Slater 2s functions for the lithium atom. They are 3) below.

The energy eigenvalue is calculated by 4) below.

The molecular screening constant is calculated by an equation of form 5) below.

The equilibrium distance is given by Herzberg (1950) as 3.01 a.u. and the calculated molecular screening constant (z) is 1.96. This value is used in both the hydrogen and lithium wave functions, replacing the atomic screening constants of 1.00 and 6.74 for hydrogen and lithium, respectively.

In practice, rather than to apply equation No. 4 directly, it is simpler to determine the expectation values of the kinetic energy (T) and the potential energy (V) and to calculate of the total energy by means of 6) below.

The expectation values are evaluated as functions of ρ in this method.

The various one-center integrals were evaluated as functions of R by direct integrations. The two-center coulomb integrals were evaluated by

$$1) \quad \underline{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{H_1}} - \frac{1}{r_{H_2}} - \frac{1}{r_{Li_1}} - \frac{1}{r_{Li_2}} + \frac{1}{r_{12}} + \frac{1}{R}$$

where $-\frac{1}{2} \nabla_1^2$ = kinetic energy of electron 1

$-1/r_{a_1}$ = potential attraction between nucleus, a, and electron, 1.

$1/r_{12}$ = potential repulsion between electrons 1 and 2

$1/R$ = potential repulsion between the nuclei.

$$2) \quad \Psi_{(1,2)} = \Psi_{Li}(1) \Psi_H(2) + \Psi_{Li}(2) \Psi_H(1).$$

$$\Psi_H = \frac{1}{\sqrt{\pi}} e^{-\rho} \quad \text{Hydrogenic and Slater}$$

$$3) \quad \Psi_{Li} = \frac{1}{4\sqrt{2\pi}} (2 - \rho) e^{-\rho/2} \quad \text{Hydrogenic}$$

$$\Psi_{Li} = \frac{1}{4\sqrt{6\pi}} \rho e^{-\rho/2} \quad \text{Slater}$$

where $\rho = zr$

z = molecular screening constant

$$4) \quad E = \frac{\int \Psi_H^* \Psi d\tau}{\int \Psi_H^* \Psi d\tau}$$

binations of two-center integrals involving Slater functions. In all cases the use of a single screening constant provided a simplification of the integral formulas.

$$5) \quad z = Ae^{-R_e} + B$$

where R_e = equilibrium distance

A, B = empirical constants

$$6) \quad E = z^2 T + zV.$$

The evaluation of the energy eigenvalue is to be done by a variational procedure involving only the parameter R . A preliminary test of this wave function was made by direct evaluation at the equilibrium distance of $\rho = 5.90$ a.u.

RESULTS

the method of Rudenberg *et al.* (1956) and the two-center exchange integrals by the method of Rudenberg (1951). The two-center integrals using hydrogenic wave functions were found to be linear com-

The values of the one-center integrals using hydrogenic wave functions agreed, to less than 10%, with those using Slater functions. The

two-center coulomb integrals differed by a factor of two. The actual numerical value of the hydrogenic coulomb integral is 0.07 and the small absolute value was responsible for the large percentage difference. The two methods of calculation failed to give agreement in the value of the exchange integral. This integral has the value of -0.03 when the Slater functions were used and -0.41 for the hydrogenic wave functions. All values of Slater function integrals were checked by interpolation or extrapolation in the tables of Kotani *et al.* (1938, 1940) and were found to agree with the present calculation.

The binding energy of LiH using Slater functions was found to be 7.99 e.v. and -3.55 e.v. with the hydrogenic function. The observed value, as given by Herzberg (1950), is -2.59 e.v. The present results should be compared to the value of -1.30 e.v. obtained by Yasumori (1952) using atomic screening constants.

A good test of a trial wave function is that the expectation values of the kinetic and potential energies satisfy the virial theorem:

$$7) \quad \frac{V}{T} = -2$$

This criterion was applied to the present wave functions. A ratio of -1.1 was obtained with Slater functions and -1.3 with hydrogenic functions.

DISCUSSION

The binding energies found in this approximation are of the correct

order of magnitude. These numbers represent the difference between two large numbers, and a slight error in the total energy of LiH causes a large error in the binding energy. The total energy, using Slater functions, is 46% of the observed total energy. This is remarkable if one considers that no account has been made of the ionic nature of LiH, of the hybridization of the 2s Li electron, and of the inner shell electrons.

There appears to be a numerical error in the exchange integral using hydrogenic functions. Not only is the value far different from that obtained with Slater functions, but the binding energy is more negative than the observed value. A theorem of the variation method states that the true energy must be approached from above.

The present calculations show that, if ionic terms, hybridization, etc. are to be included, the amount of work required can be greatly reduced by using a wave function with a single molecular screening constant. The exact degree of usefulness will depend on the rapidity of convergence to the observed value. A variational procedure, with respect to the internuclear distance, must be made to determine the usefulness of the trial function in the simplest approximation as described in this paper. Work is now in progress on these aspects of the calculation.

In order to make a complete test of the molecular screening constant, similar calculations are being performed on Li_2 . This molecule is non-polar in the ground state, and the results of the simplest approximation are expected to be closer to the observed value than in the case of LiH.

SUMMARY

A new trial wave function was used to calculate the binding energy of LiH. The binding energy of LiH, considering the valence electrons only at the observed equilibrium distance, was evaluated in the Heitler-London approximation. The new function used a single molecular screening constant and the resulting calculations were much simpler than with conventional approximate wave functions. The calculation was performed using both Slater atomic wave functions and hydrogenic atomic wave functions. The former gave a value of the binding energy of 7.99 e.v. and the latter of -3.55 e.v.

ACKNOWLEDGMENT

This work was supported in part by the Research Corporation and by the Graduate School of Southern Illinois University.

LITERATURE CITED

- HERZBERG, GERHARD. 1950. Molecular spectra and molecular structure. I. Spectra of diatomic molecules. New York, D. Van Nostrand Co., Inc., xv + 658 pp.
- KOTANI, MASAO, AYAO AMEMIYA, and TUNETO SIMOSE. 1938. Tables of integrals useful for the calculations of molecular energies. *Proc. Physico-Math. Soc. Japan*, 20 (extra no. 1): 1-70, 7 tables.
- KOTANI, MASAO, and AYAO AMEMIYA. 1940. Tables of integrals useful for the calculations of molecular energies. II. *Proc. Physico-Math. Soc. Japan*, 22 (extra no.): 1-28, 7 tables.
- MUSULIN, BORIS. 1956. Molecular screening constants. *Jour. Chem. Phys.*, 25: 801-803, 1 table, 2 figs.
- RUDENBERG, KLAUS. 1951. A study of two-center integrals useful in calculations on molecular structure. II. The two-center exchange integrals. *Jour. Chem. Phys.*, 19:1459-1477, 3 tables.
- RUDENBERG, KLAUS, C. C. J. ROTHAAAN, and W. JAUNZEMIS. 1956. A study of two-center integrals useful in calculations on molecular structure. III. A unified treatment of the hybrid, coulomb, and one-electron integrals. *Jour. Chem. Phys.*, 24:201-220, 10 tables, 4 figs.
- SLATER, J. C. 1930. Atomic shielding constants. *Phys. Rev.*, 36:57-64, 3 tables.
- YASUMORI, IWAO. 1952. On the binding energy of LiH. *Bull. Chem. Soc. Japan*, 25:358-360, 1 table.