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## Wave-Mechanical Treatment of the LiH Molecule

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Variational treatments of the LiH molecule and  $\text{LiH}^+$  ion have been carried out in which the two electrons of the inner shell of the Li atom are represented by Slater wave functions and the orbitals of the two valence electrons are treated after the method of James and Coolidge (but without the interelectronic distance as one of the coordinates). In this treatment elliptical coordinates are used for the expression of the wave function for the outer electrons, which takes the form of an exponential times a power series. The energy matrix for the LiH molecule contain the matrix terms for the  $\text{LiH}^+$  ion, for which calculations were also made. The lowest state of the  $\text{LiH}^+$  ion is a  $^2\Sigma$  state with the dissociation products normal hydrogen and ionized lithium and is the only one-quantum state. The use of a very flexible eleven-term function gives at an internuclear distance of three Bohr radii an energy of repulsion of 0.181 ev. The slope of the potential energy curve at this point is found to be  $-0.791$  ev per Bohr radius. The lowest state of the ion is surely stable with an equilibrium

distance somewhat greater than three Bohr radii. The energies of the four two-quantum  $^2\Sigma$  states of  $\text{LiH}^+$  at the same internuclear distance are obtained from the next four roots of the eleventh-order determinantal equation used to obtain the energy of the lowest state. These states are found to be quite strongly repulsive at this distance. On applying the variational method to the ground state of the neutral LiH molecule, it is found that the best value for the calculated binding energy that can be expected is smaller than the observed value by over a half volt. The addition of two terms containing the cosine of the difference of the azimuthal angles of the two outer electrons improves the calculated energy by 0.13 ev. An eight-term wave function has been tried for the  $^3\Sigma$  state of LiH dissociating to the same products as the ground state. The energy found is a repulsion of 1.89 ev at a distance of three Bohr radii, the equilibrium distance of the ground state.

IN this paper<sup>1</sup> we wish to present variational treatments of the LiH molecule and  $\text{LiH}^+$  ion based on the method of James and Coolidge. This method, first applied<sup>2</sup> to the ground state of  $\text{H}_2$ , is the most accurate method known for the treatment of simple molecules. For the three states of the  $\text{H}_2$  molecule to which it has been applied, the binding energies obtained are in very satisfactory agreement with the experimental values. Hutchisson and Muskat<sup>3</sup> have treated the LiH molecule by wave mechanics using the Heitler-London method of atomic wave functions and a simplified Hamiltonian, obtaining results in fairly good agreement with experiment. However, James<sup>4</sup> has shown that the approximations made in such a treatment have very little justification and that the Heitler-London method, when applied in rigorous form, gives binding energies which are much too small.

The James-Coolidge method is characterized by (1) the use of an extremely flexible wave function involving a power series in all the coordinates and (2) the recognition of the importance of terms containing powers of the interelectronic distance. Elliptical coordinates are particularly suitable since in  $\text{H}_2$ , at least, the density function has approximately elliptical form. The terms containing the interelectronic distance make the function very sensitive to the relative positions of the electrons and serve to make it small in those parts of configuration space in which the two electrons are close together. Such terms were first introduced by Hylleraas<sup>5</sup> in obtaining accurate energies for the He atom. In carrying out the method a number of terms is taken and the coefficients in the series determined to make the total energy a minimum. By the variational principle, the energies obtained are upper bounds to the true energies of the system.

The LiH molecule is of particular interest because it is one of the simplest of the heteronuclear molecules. Two of its electrons are closely bound forming a closed shell about the lithium nucleus, leaving the other two as valence electrons. The

<sup>1</sup> A preliminary report on this work was presented at the Pittsburgh meeting of the Am. Phys. Society (Dec. 1934); see Phys. Rev. **47**, 339A (1935).

<sup>2</sup> James and Coolidge, Phys. Rev. **43**, 588 (1933); J. Chem. Phys. **1**, 825 (1933); J. Chem. Phys. **3**, 129 (1935). For excited states see R. Present, J. Chem. Phys. **3**, 122 (1935).

<sup>3</sup> Hutchisson and Muskat, Phys. Rev. **40**, 340 (1932).

<sup>4</sup> H. M. James, Phys. Rev. **43**, 588 (1933); J. Chem. Phys. **2**, 794 (1934). See also J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935).

<sup>5</sup> E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

unobserved molecule HeH has one less electron, but all three of its electrons play the part of valence electrons. The question of inner shells has already been investigated by James<sup>4</sup> in his treatment of Li<sub>2</sub>. He finds that they can be represented satisfactorily by Slater<sup>6</sup> one-electron functions. With such a treatment only the coordinates of the valence electrons appear in the series expression. This is a great help in simplifying the problem. However because of the mathematical complexity which still remains, it is found impracticable to include terms containing the inter-electronic distance between the valence electrons. Hence, an entirely satisfactory solution is not obtained in the cases in which inner shells are present. It has been found in the treatment of H<sub>2</sub> and Li<sub>2</sub> that the method without these terms gives binding energies which are approximately one-half volt too small. Our computations on LiH give a difference of the same sign and order of magnitude. It is presumed that the difference is due to the absence of the above-mentioned terms or their equivalent, since such is the case with H<sub>2</sub>, where no inner electrons are present.

Incidental to the solution of the problem for the neutral molecule, LiH, is the solution of the simpler problem, that of the molecular ion, LiH<sup>+</sup>. This molecule has not been observed experimentally. A detailed treatment of it is of interest because of the accuracy of the results obtainable and because these results comprise the only information we have at the present time of its properties.

#### THE LITHIUM HYDRIDE ION

Although, with the exception of H<sub>2</sub><sup>+</sup>, we have no experimental evidence of diatomic molecules having one-electron bonds,<sup>7</sup> we have reason to believe from the theory that such molecules exist having stable states. That they are not observed is due to the fact that they do not have extensive discrete band spectra. The molecule H<sub>2</sub><sup>+</sup> has been shown to have at least two stable states<sup>8</sup> and

James<sup>9</sup> has found that Li<sub>2</sub><sup>+</sup> has a stable ground state.

For purposes of comparison it is instructive to consider briefly the states of H<sub>2</sub><sup>+</sup>, the theory of which has been worked out by Morse and Stueckelberg, Teller and others. The lowest two states are <sup>2</sup>Σ states and dissociate to a normal hydrogen atom and a hydrogen ion. One is symmetrical in the nuclei and stable, having a binding energy of 2.78 ev and an equilibrium distance of 2 Bohr radii, while the other is antisymmetrical and is repulsive. There are six two-quantum states (dissociating to 2s or 2p atoms and an ion) four of which are <sup>2</sup>Σ states. One is stable, having a binding energy of 1.35 ev and an equilibrium distance of 11.5 Bohr radii. One of the two <sup>2</sup>Π states is also probably stable. The behavior of the one-quantum states can be understood qualitatively as a resonance between two unperturbed atomic states with the accompaniment of a resonance energy which is subtracted in the case of the symmetrical state and added in the case of the antisymmetrical state. A similar description of the two-quantum states can be made. Here the situation is complicated by the fact that there are four interacting states. They are successively symmetrical and antisymmetrical and it so happens that only one is stable. A more careful picture might include an examination of the effect of the three-quantum states above. It is assumed that the one- and two-quantum states, which are about ten volts apart, do not affect each other appreciably.

LiH<sup>+</sup> is a heteronuclear molecule but its energy levels approach those of H<sub>2</sub><sup>+</sup> at infinite distances for large quantum numbers. A similar behavior can be expected at ordinary distances for those high quantum number states since in such states the valence electron is so far out that the combined field of the lithium nucleus and the shell is like that of the hydrogen nucleus. There being very little overlapping of the wave functions, the effect of interchange of valence and inner electrons is small. We would thus expect every other one of the higher <sup>2</sup>Σ states to take on antisymmetrical characteristics, that is to have a node near the internuclear line. Since the lithium atom has no one-quantum state, there is

<sup>6</sup> Slater, Phys. Rev. **36**, 59 (1930).

<sup>7</sup> For a recent discussion of H<sub>2</sub> and H<sub>2</sub><sup>+</sup> comparing experimental and theoretical results, see O. W. Richardson, Proc. Roy. Soc. **A152**, 503 (1935).

<sup>8</sup> Morse and Stueckelberg, Phys. Rev. **33**, 932 (1929); Teller, Zeits. f. Physik **61**, 458 (1930); Hylleraas, Zeits. f. Physik **71**, 739 (1931). See also discussion by Bethe, *Handbuch der Physik*, Vol. 24 (1933).

<sup>9</sup> H. M. James, J. Chem. Phys. **3**, 9 (1935).

but one one-quantum state of  $\text{LiH}^+$  and it has the dissociation products, normal hydrogen and ionized lithium. The nearest  $^2\Sigma$  state is 8.17 ev higher at infinite separation and has the dissociation products, normal lithium ( $\text{Li } 2s$ ) and ionized hydrogen. Pauling<sup>10</sup> has pointed out that so great a separation implies the absence of large resonance effects, such as appear in  $\text{H}_2^+$ , and he suggests that the lower state will not be stable. The four two-quantum states of  $\text{LiH}^+$ , corresponding to a dissociation into  $\text{Li}$  or  $\text{H } 2s$  or  $2p$  and an ion, are less than 2 ev apart and hence we can expect resonance interactions and the possibility of stable states. If stable states do exist, we would expect their equilibrium distances to be large.

The lithium hydride ion is a system of three electrons and a nucleus of charge three, the lithium nucleus, separated a distance  $R$  from a nucleus of charge one, the hydrogen nucleus. Two of the electrons are closely bound forming a closed shell about the lithium nucleus. The third electron travels about one or the other or both of the nuclei as the case may be and can be thought of as a valence electron. Let distances be expressed in terms of the first Bohr radius of hydrogen and energies in a unit equal to the energy of the ground state of the hydrogen atom. The Hamiltonian of the "clamped" molecule in these atomic units is the expression

$$h = \frac{6}{R} - \sum_i^3 \left( \nabla_i^2 + \frac{6}{r_i} + \frac{2}{s_i} \right) + \sum_{i>j}^3 \frac{2}{r_{ij}}, \quad (1)$$

where  $\nabla_i^2$  is the Laplacian for electron  $i$ ,  $r_i$  is its distance from the lithium nucleus and  $s_i$  is its distance from the hydrogen nucleus. The distance from electron  $i$  to electron  $j$  is  $r_{ij}$ .

We suppose that the molecular wave function can be built up as the sum of products of one-electron functions. These functions describing the behavior of single electrons we shall call orbitals. If  $u(1, \alpha)$  is a valence electron orbital occupied by electron 1 with spin  $\alpha$ , and  $g(1, \alpha)$  and  $g(1, \beta)$  are inner electron orbitals with spin  $\alpha$  and  $\beta$ , respectively, an arbitrarily normalized wave function antisymmetrical in all the electrons is given by the determinant

$$\psi = \frac{1}{(6 \int g^2 dV)^{\frac{1}{2}}} \begin{vmatrix} u(1, \alpha) & g(1, \alpha) & g(1, \beta) \\ u(2, \alpha) & g(2, \alpha) & g(2, \beta) \\ u(3, \alpha) & g(3, \alpha) & g(3, \beta) \end{vmatrix}. \quad (2)$$

For the inner electron orbitals we shall take Slater atomic wave functions. The outer electron wave function we shall express as an exponential times a power series in elliptical coordinates. All azimuthal angles will be omitted from our function. This means that not only do we restrict ourselves to the consideration of  $\Sigma$  states, but that we also omit a detailed treatment of the effects of the interelectronic repulsions on the wave function. By proper choice of the energy values taken for the separated atoms, some of the errors introduced in the energy of the system by these approximations will cancel out in computing the difference between the molecular energy and the total atomic energy.

Our orbitals are

$$\begin{aligned} u(1, \alpha) &= \sum_f C_f f(1, \alpha), \\ f(1, \alpha) &= \lambda_1^m \mu_1^j e^{-\delta \lambda_1} \delta(\alpha, \sigma_1), \\ g(1, \alpha) &= e^{-k r_1} \delta(\alpha, \sigma_1), \quad g(1, \beta) = e^{-k r_1} \delta(\beta, \sigma_1), \end{aligned} \quad (3)$$

where  $\lambda_1 = (r_1 + s_1)/R$ ,  $\mu_1 = (r_1 - s_1)/R$  and  $\delta$  and  $k$  are parameters independent of  $m$  and  $j$ .  $\delta(\alpha, \sigma_1)$  is the spin function and takes the value 1 or 0 as the spin coordinate  $\sigma_1$  of the electron is  $\alpha$  or  $\beta$ . We can now write our wave function as a sum of determinants,

$$\psi = \sum_f C_f \psi_f, \quad \psi_f = \frac{1}{(6 \int g^2 dV)^{\frac{1}{2}}} \begin{vmatrix} f(1, \alpha) & g(1, \alpha) & g(1, \beta) \\ f(2, \alpha) & g(2, \alpha) & g(2, \beta) \\ f(3, \alpha) & g(3, \alpha) & g(3, \beta) \end{vmatrix}. \quad (4)$$

Upper bounds to the correct energies are given by minimizing the integral  $I = \int \psi^* h \psi dv$  subject to the condition for normalization  $1 = \int \psi^* \psi dv$ . The integrals are taken over all configuration space and summed over the spins. As usual in this type of problem, we obtain a secular equation for the determination of the energy values  $W$ ,

$$|(F'|h|F) - W(F'|1|F)| = 0,$$

where  $(F'|h|F)$  and  $(F'|1|F)$  are, respectively, the matrix elements of  $h$  and 1 between the functions  $\psi_f$  and  $\psi_{f'}$ . Methods for the evaluation of these quantities are discussed by James.<sup>4</sup>

<sup>10</sup> L. Pauling, J. Am. Chem. Soc. 53, 3225 (1931).

Because of the large amount of numerical computation involved in obtaining the matrix elements for any set of values of the parameters  $R$ ,  $\delta$ ,  $k$ , all work was carried out for one set only. The internuclear distance was taken as three Bohr radii, which is the experimental equilibrium distance of the ground state of the neutral molecule. The parameter  $k$  appearing in the Slater functions, if determined so as to minimize the energy of ionized lithium, must have the value 2.6875. We have used the value 2.7, which gives an energy for  $\text{Li}^+$  differing by 0.00003 atomic unit from the energy obtained by using the optimum value. This energy differs by 1.5 ev from the experimental value because of the very simple wave function used. The choice of the value of the parameter in the outer electron function is not a very critical one since the difference between an exponential having a very good value of  $\delta$  and the one used can in our case be expanded in a series and absorbed by the coefficients  $C_j$  of the general series (4).  $\delta$  is taken equal to 1.35 since that is the value used in the work on LiH.

We can safely assume, because of the diffuseness of our outer electron function, that there is no real improvement in the wave functions of the inner electrons in the molecule over those in a similar treatment of the atom or ion and therefore that the error in the energy introduced by the use of simple functions for those electrons remains essentially the same in all three cases and will cancel out. For states having normal lithium as one of the dissociation products, it is preferable to take the total energy of the atom as calculated by Wilson<sup>11</sup> ( $-14.8384\text{Rh}$ ) using a four-parameter variational method, since the simplifications made by him in the atomic problem are of the same nature as those made here. We take this value instead of the experimental one because in calculating the difference of molecular and atomic energies, to use an exact value of the atomic energy is to include the large total error of the computed molecular energy in that difference. To obtain atomic energies for the higher states, for which computations are lacking, we have added to the computed core energy the observed ionization energy for the atomic states—a step

justified by the considerable accuracy obtainable in computations of ionization energies, even when poor core functions are employed.

The matrix elements have been calculated for all functions with  $m=0, 1, 2$  and  $j=0, 1, 2, 3$  except the one having  $m=2$  and  $j=3$ . The secular equation is an eleventh order determinantal equation the roots of which are upper bounds to the lowest  $^2\Sigma$  energies of  $\text{LiH}^+$ .

Having calculated the energy at a point, we can obtain the slope of the energy curve with little extra work. Consider  $R'=Rq$  where  $q$  is nearly one, and let  $k'=k/q$  and  $\delta'=\delta$ . Since the energy of the inner shell is a minimum with respect to  $k$ , a small change in the value of  $k$  is negligible. Taking the same value of  $\delta$  at our new point is of no harm since, as we have seen, the exact value of  $\delta$  is not important.  $k$  enters in the expressions for our integrals only in the product  $kR$ , which remains unchanged. All integrals of unity contain the factor  $R^{3n}$  where  $n$  is the number of electrons. For all potential energy integrals the factor is  $R^{3n-1}$ , while for all kinetic energy integrals it is  $R^{3n-2}$ .  $R$  enters in no other way. Since the factor  $q^{3n}$  cancels out in obtaining the new energy, we retain the old matrix elements of unity and in the matrix terms for the energy multiply all potential energy integrals by  $q^{-1}$  and all kinetic energy terms by  $q^{-2}$ . From these new matrix elements the energy at a distance  $Rdq$  from the original point can be obtained and used to calculate the slope. In the computations  $q$  was taken equal to 1.01 ( $dq=0.01$ ).

From the first root of the secular determinant we find that the lowest state of  $\text{LiH}^+$  has a repulsive energy of not over 0.181 ev at a distance of three Bohr radii. The slope at this distance is  $-0.791$  ev per Bohr radius. Details are given in the two tables. Since the energy of repulsion is so small and the slope so large, we conclude, in contradiction to the prediction of Pauling, that the molecule must be stable at larger distances. This can hardly be due to inner shell effects, for James<sup>9</sup> has shown that in  $\text{Li}_2^+$ , where the behavior of these shells should be essentially the same, they give rise to a repulsion. It would therefore appear that in addition to resonance there may be polarization effects which play an important, or even predominant, part in the formation of a stable one-electron bond.

<sup>11</sup> E. B. Wilson, Jr., J. Chem. Phys. 1, 210 (1933).

An examination of the importance of the various terms is of interest. The three terms with  $mj$  equal to (20), (21), (22) together lower the energy by only 0.006 ev showing that the contributions of terms with higher powers than  $\lambda^2$  is small. The importance of terms with odd powers of  $\mu$  is great; (03,13) together lower the energy by 0.163 ev. However, this is less than one-tenth the value of terms with  $j=1$ . We can safely assume that terms with  $j=5$  would not lower the energy by more than 0.02 ev. Similar evidence for terms with  $j=4$  gives an even smaller amount for such terms. Therefore we conclude that  $0.16 \pm 0.02$  ev is a close upper bound to the lowest state of  $\text{LiH}^+$  at  $R=3$ . Wilson's calculated value for the ionization energy of Li is too small by about 0.05 ev. If we suppose this difference is due to the simplifications made in the treatment of the inner shell and make a similar correction for  $\text{LiH}^+$ , we have 0.11 ev as an estimated value of the energy of repulsion.

The next four roots give repulsive energies of 3.885, 4.292, 4.645, and 5.468 ev for the four two-quantum states dissociating into  $\text{H}^+ + \text{Li } 2s$ ,  $\text{H}^+ + \text{Li } 2p$ , and  $\text{H } 2s$  and  $2p + \text{Li}^+$ , respectively. At infinite separation the first is 1.840 ev below the second which is 0.143 ev below the other two. At  $R=3$  the separations are 2.199, 0.497, and 0.823 ev respectively, neglecting the fact that some of the computed energies may be better than others because of better wave functions. The slope for the first of these states has been computed and found to be large ( $-2.855$  ev per Bohr radius) making a stable state at considerably larger distances quite probable.

The first power terms in  $\lambda$  are the most important in these two-quantum states. The first power in  $\lambda$  corresponds to the first power of  $r$  which appears in two-quantum atomic functions. An estimate of the decrease in the energy which would be caused by more terms would require the evaluation of many numerical determinants. This has not been done, hence the energies given must be regarded as upper bounds. However, because even in the case of the fifth root there are essentially six coefficients at our disposal, we may expect the computed energies of the two-quantum states, particularly the lower ones, to be rather good.

Normalized coefficients for a simple eight-term function for the lowest state are given in Table I. The coefficients for eleven-term functions for all five states are also given. These latter coefficients have all been calculated from the same determinantal equation and therefore the corresponding wave functions are strictly orthogonal. We define the valence orbitals  $U = [1/(\int g^2 dV)^{1/2}] \{\sum C_j f + ag\}$ , the constant  $a$  being so chosen that  $U$  is orthogonal to  $g$ . If the  $C_j$  are so chosen that

TABLE I. Coefficients of normalized wave functions for  $\text{LiH}^+$ .  $C_{mj}$  for  $R=3$ ,  $\delta=1.35$ ,  $k=2.7$ . All the states are repulsive at this distance.  $W'$  is the energy referred to isolated  $\text{H}^+$  and  $\text{Li}^+$  as zero.  $W_\infty'$  is the value of  $W'$  for  $R=\infty$ .

$mj$	LOWEST STATE	LOWEST STATE	SECOND STATE
00	1.97191	2.21981	-1.78672
01	2.22048	2.29138	0.11061
02	1.17694	1.02505	0.72710
03	1.73098	1.74190	1.44001
10	-0.41862	-0.70165	1.90121
11	-0.36791	-0.45181	-0.62244
12	-0.23984	-0.05147	-2.26936
13	-0.54866	-0.55681	-1.21418
20		0.07181	-0.01359
21		0.02338	-0.21317
22		-0.05034	0.53653
$W_\infty', Rh$	-1.6667	-1.66667	-1.0597
$W', Rh$	-1.6528	-1.65329	-0.77271
$W' - W_\infty'$ ev	0.187	0.1811	3.885
$mj$	THIRD STATE	FOURTH STATE	FIFTH STATE
00	-7.91415	-9.15988	-0.21866
01	0.65278	1.17803	0.77098
02	17.16824	21.73215	-0.94663
03	-0.79811	0.62136	0.08929
10	8.14604	12.76449	0.42614
11	-2.59954	-2.21312	1.69240
12	-20.09876	-26.57546	1.14955
13	-0.05094	-0.97776	-0.03391
20	-1.94582	-3.61720	-0.63036
21	1.39377	0.66424	-1.20923
22	5.86476	6.67040	1.02214
$W_\infty', Rh$	-0.9273	-0.9167	-0.9167
$W', Rh$	-0.6102	-0.5736	-0.5127
$W' - W_\infty'$ ev	4.292	4.645	5.468

TABLE II. Energies of  $\text{LiH}^+$  for  $R=3.03$ .

	LOWEST STATE	SECOND STATE
$W_\infty'$	-1.66007	-1.0531
$W'$	-1.64844	-0.77244
$W' - W_\infty'$ ev	0.1574	3.799
$\Delta(W' - W_\infty')/\Delta R$	-0.791	-2.855

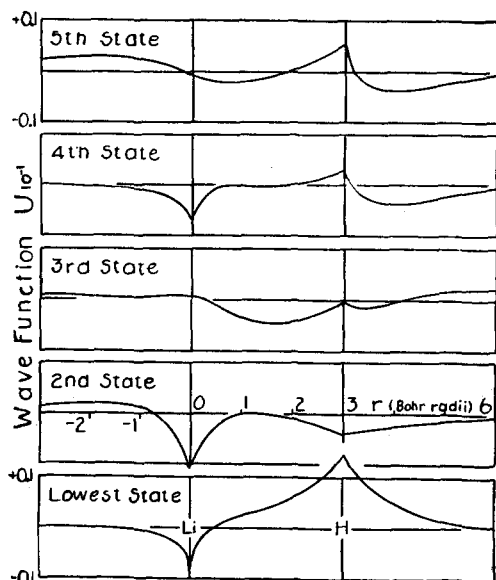


FIG. 1. Valence electron orbitals for the lowest five  $2\Sigma$  states of  $\text{LiH}^+$  plotted along the internuclear line. The functions are normalized when multiplied by a factor which is about 0.4. The lowest state dissociates into normal hydrogen and a lithium ion. The four other states are two-quantum states and dissociate into  $\text{Li } 2s + \text{H}^+$ ,  $\text{Li } 2p + \text{H}^+$ , and  $\text{Li}^+ + \text{H } 2s$  and  $\text{H } 2p$ , respectively. Atomic characteristics are noticeable in all the states. These functions are orthogonal to the inner shell functions and to each other.

$\psi$  is normalized, then  $U$  is normalized. The  $U$ 's for different states, like the corresponding  $\psi$ 's, are orthogonal. In Fig. 1 are graphs showing these functions plotted along the internuclear axis. In the fifth state an antisymmetrical tendency is in evidence.

### THE LITHIUM HYDRIDE MOLECULE

For neutral lithium hydride the Hamiltonian of the "clamped" molecule in atomic units is

$$H = \frac{6}{R} - \sum_1^4 \left( \nabla_i^2 + \frac{6}{r_i} + \frac{2}{s_i} \right) + \sum_{i>j} \frac{2}{r_{ij}}. \quad (5)$$

We are concerned in this investigation with  $\Sigma$  states only and shall suppose at first that our wave functions can be expressed as the sums of products of orbitals of the type used in the lithium hydride ion. The wave functions, being antisymmetrical in all the coordinates as required by the Pauli principle, must be symmetrical in the space coordinates of the valence electrons for singlet states and antisymmetrical in those co-

ordinates for triplet states. If  $f$  and  $h$  are two valence electron orbitals, expressions having the proper symmetry are the functions

$$\psi_{fh} = \frac{1}{(48 \int g^2 dV)^{1/2}} \sum_P (-1)^{\sigma_P} [f(1, \alpha) h(2, \beta) + h(1, \alpha) f(2, \beta)] g(3, \alpha) g(4, \beta) \quad (6)$$

for singlet states and

$$\psi_{fh} = \frac{1}{(48 \int g^2 dV)^{1/2}} \sum_P (-1)^{\sigma_P} f(1, \alpha) \times h(2, \alpha) g(3, \alpha) g(4, \beta) \quad (7)$$

for triplet states. The summations are over all the permutations of the four electrons and  $\sigma_P$  is the number of inversions of the permutations from 1234. This notation is equivalent to the use of determinants. We use it here in preference to determinants because later we shall introduce a function involving the relative coordinates of the two outer electrons and this is easily done with this system of notation.

Let us assume complete wave functions of the form

$$\psi = \sum_{f,h} C_{fh} \psi_{fh}, \quad (8)$$

in which the orbitals are the functions

$$\begin{aligned} f(1, \alpha) &= \lambda_1^m \mu_1^j e^{-\delta \lambda_1} \delta(\alpha, \sigma_1), \\ h(1, \alpha) &= \lambda_1^n \mu_1^k e^{-\delta \lambda_1} \delta(\alpha, \sigma_1), \\ g(1, \alpha) &= e^{-k r_1} \delta(\alpha, \sigma_1). \end{aligned} \quad (9)$$

$\delta$ ,  $\gamma$  and  $k$  are parameters independent of  $m, n, j, k$  and  $\delta(\alpha, \sigma_1)$  is the spin function with the spin coordinate  $\sigma_1$ . The evaluation of matrix elements and adjustment of the parameters  $C_{fh}$  is accomplished by the methods used in the treatment of  $\text{LiH}^+$ .

If we write the Slater wave functions for the H atom and for the outer electron of Li in elliptical coordinates and put  $R=3$ , we find the parameters in the exponentials to be 1.5 for H and 1.0 for Li. 1.5 and 1.0 are probably good values for our parameters  $\delta$  and  $\gamma$ . The work of Present on excited states of  $\text{H}_2$  shows that the number of terms necessary in the James-Coolidge method is much less for states with nonequivalent electrons if these parameters are taken not the

same. However, because in this case it made possible a marked decrease in the necessary numerical work,  $\delta$  and  $\gamma$  were given a common value, chosen to be 1.35. It was taken nearer the value for hydrogen since the wave function for lithium is more naturally built up out of powers of  $\lambda$  than is the hydrogen function. As in the problem of the ion, the value of  $k$  chosen was 2.70.

For the  $^1\Sigma$  ground state the eleven terms ( $m\eta jk$ : 1000, 1001, 1002, 1003, 1100, 1101, 1010, 1011, 0000, 2000, 1111) gave the energy  $W' = -2.1939$  or a binding energy of 1.82 ev ( $W_\infty' = -2.0597$ ) to be compared with the probable experimental<sup>12</sup> value 2.63 ev. The seven other terms (1102, 1103, 1020, 1030, 0001, 1012, 2001) were tried separately and each gave less than 0.03 ev to the energy. To estimate the value of further terms is hazardous. The changes in the energy caused by the terms tried seem to indicate that the energy improvement obtainable by adding seven or eight more terms to the eleven-term function would not be over 0.15 ev. It is therefore perhaps safe to say that the limiting value for the binding energy obtainable by a function with a large number of terms of the kind here considered is about 2.0 ev or six or seven-tenths of a volt from the experimental value. Coolidge and James found that their simple power series function without the interelectronic terms came within 0.46 ev of the observed value for the ground state of  $H_2$ . Present's calculation, gave a difference of about 0.37 ev for an excited two-quantum state of  $H_2$  using a thirteen-term function. James found that for the ground state of  $Li_2$  the difference of 0.5 ev remained between the experimental and computed values for the binding energy after taking eighteen terms of the series.

For the  $^3\Sigma$  state an eight-term function made up of the terms (1000, 1001, 1002, 1003, 1101, 1010, 1011, 2000) gave an energy  $W' = -1.920$  or a repulsion of 1.89 ev ( $W_\infty' = -2.0597$ ) at a distance of three Bohr radii. Other terms were not tried and the contributions of various terms were not examined. Present, working on a two-quantum  $^3\Sigma$  state of  $H_2$ , found that a six-term function of this nature but having two different exponential parameters came within 0.08 ev of the experimental value. However he also discovered that when the parameters were given the same value the convergence was very poor. The orbital antisymmetry of the triplet states, which causes the functions to vanish when the valence electrons are near each other, explains why functions not involving the interelectronic distance or the equivalent are better for triplet states than for singlet states and hence why the interelectronic terms are less important in such functions. In our case we can regard the repulsive energy 1.89 ev as an upper bound to the energy which is probably within a few tenths of a volt of the true value.

It is apparent that further improvements of any appreciable amount in the energy for the singlet state must come through the introduction of terms which account for the relative orientation of the valence electrons. We observe that the interelectronic distance is expansible in a series having in it the powers of the cosine of the difference of the azimuthal angles of the two electrons. It is proposed next to investigate the effect of adding terms containing a cosine factor.

In order that our function be single valued, we must introduce a factor which vanishes properly at the poles. Let  $P(12)$  denote the function

$$P(12) = M(12) \cos(\phi_1 - \phi_2), \quad M(12) = [(\lambda_1^2 - 1)(1 - \mu_1^2)(\lambda_2^2 - 1)(1 - \mu_2^2)]^{\frac{1}{2}}, \quad (10)$$

where  $\phi_1$  is the azimuthal angle of electron 1. We can take as additional terms functions of the form

$$\psi_{fhp} = \frac{1}{(48 \int g^2 dV)^{\frac{1}{2}} P} \sum_P (-1)^{\sigma_P} [f(1, \alpha)h(2, \beta) + h(1, \alpha)f(2, \beta)] P(12)g(3, \alpha)g(4, \beta). \quad (11)$$

<sup>12</sup> The number of observed vibrational levels for the ground state of  $LiH$  is only five. For this reason an estimate of the binding energy involves a long extrapolation. Professor Crawford has kindly informed me that the energy we require, using a Morse potential curve and recent

experimental data, is about  $2.63 \pm 0.05$  ev. This is more reliable than Nakamura's earlier value of 2.56 ev. See F. H. Crawford and T. Jorgenson, Jr., *Phys. Rev.* **47**, 932 (1935); G. Nakamura, *Zeits. f. Physik* **59**, 218 (1930).



$P(12)$  is symmetric with respect to interchange of electrons 1 and 2; hence the proper symmetry conditions are maintained. We define the quantities

$$\begin{aligned}
 M(1) &= [(\lambda_1^2 - 1)(1 - \mu_1^2)]^{\frac{1}{2}}, & H_0 &= -\left(\nabla_1^2 + \frac{6}{r_1} + \frac{2}{s_1}\right), & H_1 &= \frac{6}{R} - \sum_i \left(\nabla_i^2 + \frac{6}{r_i} + \frac{2}{s_i}\right) + \frac{2}{r_{12}}, \\
 (f'f) &= \int f'(1)f(1)dV_1, & F &= f - [(fg)/(g^2)]g, \\
 (f'M \setminus fM) &= \int f'(1)M(1)H_0f(1)M(1)dV_1 + (4/R^2)(f'f), \\
 (f'f/Ph'h) &= \int f'(1)f(1)(2/r_{12})P(12)h'(2)h(2)dV_{12}, \\
 (f'f/P^2h'h) &= \int f'(1)f(1)(2/r_{12})P^2(12)h'(2)h(2)dV_{12}, \\
 (h'hM^2) &= \int h'(1)h(1)M(1)^2dV_1.
 \end{aligned} \tag{12}$$

The matrix elements of terms involving  $P$  with terms not involving  $P$  are

$$(F'H' | H | fhP) = [(F'f/PH'h) + (F'h/PH'f)](g^2), \quad (F'H' | 1 | fhP) = 0. \tag{13}$$

We give them for the singlet state only. Matrix elements of  $P$  terms with  $P$  terms are

$$\begin{aligned}
 (f'h'P | H | fhP) &= (f'h'P | 1 | fhP)(g^2)^{-2} \int g(1)g(2)H_1g(1)g(2)dV_{12} + \frac{1}{2} \{ [(f'M \setminus fM)(g^2) \\
 &\quad + 2(f'fM^2/g^2) - (f'g/Pfg)](h'hM^2) + [(f'M \setminus hM)(g^2) + 2(f'hM^2/g^2) \\
 &\quad - (f'g/Phg)](h'fM^2) + [(h'M \setminus fM)(g^2) + 2(h'fM^2/g^2) - (h'g/Pfg)](f'hM^2) \\
 &\quad + [(h'M \setminus hM)(g^2) + 2(h'hM^2/g^2) - (h'g/Phg)](f'fM^2) \} \\
 &\quad + \{ (f'f/P^2h'h) + (f'h/P^2h'f) \}(g^2), \\
 (f'h'P | 1 | fhP) &= \frac{1}{2} \{ (f'fM^2)(h'hM^2) + (f'hM^2)(h'fM^2) \}(g^2).
 \end{aligned} \tag{14}$$

The terms (1000 $P$ , 1001 $P$ ) were added to the eleven-term wave function. The first of the two terms gave an improvement of the energy of 0.09 ev and the second an additional improvement of 0.04 ev. The thirteen-term wave function gave an energy  $W' = -2.2036$  or a binding energy of 1.95 ev. It is hardly possible that further terms of this kind would improve the energy by more than 0.1 ev. The failure of the cosine to give greater improvement probably lies in the fact that it does not vary rapidly when the electrons are close together.<sup>13</sup> An exact expansion of the inter-

electronic distance involves the use of functions with discontinuous derivatives. Higher powers of the cosine or terms having  $\cos p(\phi_1 - \phi_2)$ ,  $p$  an integer, were not used because their introduction would mean an extension of all the tables and was regarded as impracticable. Terms having  $\cos 2(\phi_1 - \phi_2)$  would probably have greater value than those used because the cosine of twice the angle varies more rapidly for small angles.

The writer wishes to express his sincere thanks to Professor E. C. Kemble for valuable criticisms on this work. He is deeply indebted and very grateful to Dr. H. M. James for the benefit of many discussions and original suggestions.

<sup>13</sup> That the wave function must depend almost linearly on the interelectronic distance is a result of the work on  $H_2$ . Consider also the wave function for  $H_2$ ,  $\psi_0(1 - be^{-\beta r_{12}}) + \dots$ , where  $\psi_0$  is the first term in the James-Coolidge function. Then if  $\beta$  and  $b$  are estimated by fitting this function to their solution, we obtain the approximate values  $\beta = 0.16$ ,  $b = 0.57$ . The value of  $\beta$  is small showing the effect to be a long range one. For the He atom a similar estimate can be made using Hylleraas' wave function. We find  $\beta = 0.18$ ,

$b = 0.67$ . This suggests that, for two electrons which can be said to be in the same state except for spin,  $\beta$  and  $b$  are roughly independent of the nuclear system in which the electrons are moving. They serve to define a sphere of influence of one equivalent electron on the other.