WaveMechanical Treatment of the Li2 Molecule

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Wave-Mechanical Treatment of the Li₂ Molecule

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A treatment of the Li₂ molecule by the Heitler-London method, with Slater wave functions for the atoms, has been carried out both with and without the customary approximations. In the absence of these approximations the binding computed is only a small fraction of that observed. It is found that the inner shells of the atoms may have an important effect on the magnitude of molecular binding, and may either increase or decrease it. Since their effect is associated with electron exchange it appears that they cannot be replaced by an equivalent potential field without serious error. Triple exchanges of electrons are found to be important, while polar binding is quite negligible in Li₂. A criterion for the applicability of the "interaction operator" is developed; the error involved in its use with Li₂ is small. A variational treatment has also been applied to this molecule. It yielded a binding energy less than that observed by about 0.5 e.v. The elimination of the residual error apparently requires the introduction of the interelectronic distances as coordinates. Convenient methods for the numerical treatment of multiple electron exchanges in complicated molecules are described.

I. INTRODUCTION

IT has not been the purpose of the present investigation to determine with great care the properties of the Li₂ molecule in its normal state, but rather to investigate the potentialities of the Heitler-London method in dealing with such problems, to evaluate in this one case the approximations commonly made in theoretical investigations of molecular binding, to gain insight into the rôle of the inner shells in chemical binding, and to illustrate the application to such problems of a variational method which has already been used in an investigation of H₂ in the normal state.[1]

Only in the treatment of two-electron molecules has it been possible to follow the Heitler-London[2] treatment of H₂ in using approximate molecular wave functions constructed as linear combinations of products of accurate atomic wave functions; in other cases accurate atomic functions are either lacking or of such character that the necessary integrations would be quite difficult. All the available information, not complicated by the introduction of other untested approximations, concerning this fundamental approximation has, therefore, been obtained from treatments of various states of the molecule H₂. The results obtained have been qualitatively correct, so far as experimental checks are available, but quantitatively unsatisfactory, particularly as concerns the normal state of the molecule. The computed binding energies have been decidedly too small, and the computed equilibrium distances too large, it being thus indicated that, as one would expect, for the internuclear distances of interest in such work the Heitler-London approximation is rather poor, and that it becomes constantly worse as the atoms approach each other.

If, instead of accurate atomic wave functions, the approximate ones of Slater[3] are employed it becomes possible to treat in a similar manner molecules which are considerably more complicated. The molecular wave functions set up by the method of Heitler and London may then be expressed as a sum of determinants of the form

$$\begin{vmatrix} f_1(1) & f_2(1) & f_3(1) & \cdots \\ f_1(2) & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ f_1(n) & \cdots\cdots\cdots & f_n(n) \end{vmatrix}$$

(notation henceforth $|f_1(1)\ f_2(2)\ \cdots\ f_n(n)|$),

if there are n electrons in the molecule, each f describing a one-electron orbit of the type used in describing the isolated atoms. The evaluation of the energy associated with such a function appears to have been carried out without approximation only by Gentile,[4] in the consideration of the interaction of an unexcited He atom with another H or He atom; no quantitative experimental checks on his results are available.

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[1] James and Coolidge, J. Chem. Phys. **1**, 825 (1933).
[2] Heitler and London, Zeits. f. Physik **44**, 455 (1927).
[3] Slater, Phys. Rev. **34**, 1293 (1929).
[4] Gentile, Zeits. f. Physik **63**, 795 (1930).

To facilitate computation two further approximations are customarily made.

First, the inner shells are omitted from consideration, a wave function being set up which involves only the outer electrons, while the effective charge of each nucleus is taken as the algebraic sum of its real charge and the charge of the inner shells. In effect the inner shells are thus treated as consolidated with the nucleus. The energy computed from such a wave function is then compared with the energy of atomic functions similarly constructed, to determine the binding energy of the molecule. Though several arguments for the validity of this process have appeared in the literature they cannot be given much weight, as they deal only with considerations of the interactions of the stripped inner shells, and neglect characteristically quantum-mechanical effects involving the outer shells along with the inner ones. Delbrück,[5] in a treatment of Li₂ in which many approximations were made, has estimated some of the terms in the energy associated with the inner shells. His conclusion that they play no essential rôle in the binding cannot be accepted, however, as he entirely neglected the most important of these terms.

It should be noted that even if it were to be granted that the inner shells are unimportant, the process used for their elimination from the problem would have to be considered to be somewhat arbitrary. For, because of the symmetry of the functions to interchanges of electrons, it is not possible to pass uniquely from a given approximate atomic function to an approximate function describing an electron in a particular state. For instance, the nodeless functions used by Rosen and Ikehara[6] to describe the outer electrons of the alkali metal atoms, could equally logically be replaced by sums of these functions with the similar functions which might be used to represent the inner shell electrons. This change would be accompanied by an arbitrary change in the computed binding energy. Only by explicit inclusion of the inner electrons in the wave function can this ambiguity be eliminated.

The second customary approximation is the use of an "interaction operator," the introduction of which is equivalent to the assumption that the wave functions are accurate solutions of the wave equation for infinite separation of the nuclei. A description of the way in which this may be set up and an analysis of the approximation involved in its use are to be found in the mathematical section of this paper.

The only results which tend to produce confidence in the quantitative value of the H.-L. method have been obtained in treating the normal states of molecules in which the binding is due to a single pair of electrons. Table I gives

TABLE I.

| | Dissociation Energy (e.v.) | | | Equilibrium Distances (A) | |
	Calc.	Obs.	Obs./Calc.	Calc.	Obs.
H₂[2]	2.87	4.44	1.55	0.87	0.74
Li₂[7]	1.09	1.14	1.05	2.28	2.67
Na₂[6]	0.81	0.76	0.94	2.83	3.08
K₂[6]	0.55	0.51	0.93	4.18	3.91
NaH[8]	2.30	2.56	1.11	1.44	1.6

the results of these computations. Except in the case of H₂ all the approximations mentioned above have been made.

One could desire in the agreement of computation with experiment little more than is obtained in the last four cases. However, the relation of the computed to the observed results for H₂ is very different from that found in those cases where inner shells were omitted from the calculation. It is clear, also, that the similarity which one would expect in this respect if the treatments were essentially similar could be obtained by the inclusion of a repulsion due to the inner shells in those cases where they were omitted. One is thus led to the idea that approximations made in these computations are responsible for their satisfactory outcome, and that they do not form a reasonable basis for the evaluation of the Heitler-London method.

As it does not seem possible to determine either sign or magnitude of the approximations from material in the literature, Li₂ has been

[5] Delbrück, Ann. d. Physik **5**, 36 (1930).
[6] Rosen and Ikehara, Phys. Rev. **43**, 5 (1933).

[7] Bartlett and Furry, Phys. Rev. **38**, 1615 (1931).
[8] Hutchisson and Muskat, Phys. Rev. **40**, 340 (1932).

chosen for such an investigation. The work carried out has been the following:

(1) H.-L. treatment of the molecule, including the inner shells, without computational approximation.

(2) H.-L. treatment of the molecule including the inner shells, using a modified Hamiltonian.

(3) H.-L. treatment without inner shells, using a modified Hamiltonian.[9]

(4) Addition of an ionic term to (1).

(5) Change of the shielding parameters in (2).

By comparison of the various results thus obtained and the experimental value for the dissociation energy, it is possible to determine the value of the H.-L. method in treating such a molecule, justify the use of the modified Hamiltonian, evaluate approximately and analyze the effect of the inner shells on the binding, and estimate the improvement in the energy to be obtained by the methods now usual when the H.-L. method proved to be inadequate. Finally,

(6) A variational treatment has been found to yield considerably more satisfactory results than could be obtained in the above work.

II. HEITLER-LONDON AND RELATED TREATMENTS

1. Method

Denoting by $s(n\alpha, i)$ the ith electron in an ns state about nucleus A, with spin α, and by $s'(n\alpha, i)$ that electron in a similar state about nucleus B, the molecular configurations of lowest energy may be designated by

$$1 \sim s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6)$$
$$2 \sim s(1\alpha, 1)s'(1\alpha, 2)s'(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s(2\beta, 6)$$
$$3 \sim s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\alpha, 6)$$
$$4 \sim s(1\alpha, 1)s'(1\alpha, 2)s(2\beta, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6).$$

To each of these there corresponds a determinant wave function such as

$$\psi_1 = (1/C_1) | s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6) |,$$

where C_1 is a normalizing factor. The H.-L. functions are constructed as sums of these which make the part of the energy matrix associated with these four functions diagonal.[10] Of these $\psi_1 + \psi_2$ describes the basic $^1\Sigma$ state, $\psi_1 - \psi_2$, ψ_3 and ψ_4 the lowest $^3\Sigma$ state.

Let

$$U_{mn} = \int \psi_m{}^* \psi_n dv; \qquad H_{mn} = \int \psi_m{}^* H \psi_n dv.$$

Here the * denotes the conjugate complex, and may be omitted, since all the wave functions are real. In terms of these quantities the energies associated with the above functions for the singlet and triplet states are $(H_{11} \pm H_{21})/(1 \pm U_{21})$, the + being associated with the singlet, the − with the triplet.

The lowest ionic configurations are similarly

$$A \sim s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s(2\beta, 6)$$
$$B \sim s(1\alpha, 1)s'(1\alpha, 2)s'(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6)$$

to which there correspond ψ_A and ψ_B, respectively. The linear combinations $\psi_A + \psi_B$ and $\psi_A - \psi_B$ are two zero order singlet ionic functions of the Heitler-London type, the first being symmetric to reflection of the function in the midplane between the nuclei, the second antisymmetric to this transformation. A simple extension of the H.-L. method can now be carried out by making diagonal the part of the energy matrix associated with the six functions $\psi_1 + \psi_2$, $\psi_1 - \psi_2$, ψ_3, ψ_4, $\psi_A + \psi_B$ and $\psi_A - \psi_B$. As the only non-zero elements off the diagonal are those between the first and fifth functions, the secular equation reduces to four linear equations giving the energies of the other functions and a quadratic equation giving the energies of the proper com-

[9] Essentially the treatment of the problem by Bartlett and Furry.

[10] For a general discussion of this method of obtaining approximate molecular wave functions see Slater, Phys. Rev. **38**, 1109 (1931).

binations of these two functions. The lower root of this equation is the interesting one, yielding for the energy of the basic state a better approximation than that given above in proportion as ionic binding is important in this molecule.

Noting equalities between the integrals H_{mn} due to the Hermitian character of the operator H, its symmetry in the electrons and nuclei, and its independence of spin, the secular equation reduces to

$$\begin{vmatrix} (H_{11}+H_{21})-E(U_{11}+U_{21}) & 2H_{1A}-E(2U_{1A}) \\ 2H_{1A}-E(2U_{1A}) & (H_{AA}+H_{BA})-E(U_{AA}+U_{BA}) \end{vmatrix}=0. \quad (1)$$

The normalized one-electron wave functions used in the construction of the molecular wave functions and evaluation of the integrals H_{mn} and U_{mn} were the following:

$$s(1\alpha, 1) = e^{-\delta_1 r_1}\delta(\alpha/\sigma_1)[(2\delta_1)^3/4\pi\cdot 2!]^{\frac{1}{2}},$$

$$s(2\alpha, 1) = r_1 e^{-\delta_2 r_1}\delta(\alpha/\sigma_1)[(2\delta_2)^5/4\pi 4!]^{\frac{1}{2}},$$

$$s'(1\alpha, 1) = e^{-\delta_1 s_1}\delta(\alpha/\sigma_1)[(2\delta_1)^3/4\pi 2!]^{\frac{1}{2}},$$

$$s'(2\alpha, 1) = s_1 e^{-\delta_2 s_1}\delta(\alpha/\sigma_1)[(2\delta_2)^5/4\pi\cdot 4!]^{\frac{1}{2}},$$

where r and s indicate distances from nuclei A and B, respectively, δ_1 and δ_2 are parameters, and σ_1 is the spin coordinate of electron 1. These functions are of the form suggested by Slater;[11] using in them the best possible values of the δ's (in the sense of the Ritz method) one finds for the Li atom an ionization energy of 5.29 e.v., as compared to the experimental 5.37 e.v. The best value for δ_1 is 2.686, and is very nearly independent of the choice of δ_2. The best value of δ_2 is 0.637; the computed energy of the atom is quite insensitive to small changes of this parameter.

Though the ionization energy of the atom computed with these functions is in error by only 0.08 e.v., the error in the total energy is 1.63 e.v. This is principally due to the error in the wave functions for the inner electrons, this error being present also in the computation of the ionic energy and cancelling out on evaluation of the ionization energy as the difference of the two quantities. Similarly it seems probable that though the computed total energy of the molecule may be in error by 3 or 4 e.v. the difference between this and the computed energy of the separated atoms should give a good representation of the binding energy, provided only

that the H.-L. method of dealing with the binding electrons is adequate.

If the procedure of Heitler and London were to be followed closely the δ's should be in the ratio $\delta_1/\delta_2=4.21$. In most of the present work, however, this ratio was taken to be 4, both to simplify the numerical work and in view of the following considerations. Wang[12] has shown that in the best wave functions for H_2 of H.-L. form the effective charge of the nuclei is different from that in the separated atoms; Rosen[13] has shown how the value of this parameter varies with the internuclear distance. To obtain the best results possible without an extensive variation of the parameters δ_1 and δ_2 (a prohibitively laborious process in the case of Li₂) it was attempted to estimate what they should be. The effective nuclear charge for the inner shells (i.e., δ_1) was taken as unchanged on formation of the molecule, just as it is essentially unchanged on formation of the atom from the ion. On the other hand, it was assumed that δ_2 would be changed in the same proportion as the δ in the H_2 function, when the internuclear distances are in the same ratio as the distances from the nuclei of the maxima of radial charge density. That is, it was assumed that the essential difference of H_2 and Li₂ in this respect is one of scale. This assumption leads, for an internuclear distance of 3A in Li₂, to $\delta_1/\delta_2=3.96 \cong 4.0$. To prove that no gross error was introduced by such a choice of δ_2 one computation was carried out with $\delta_1/\delta_2=4.25$.

The methods used in the evaluation of the integrals U_{mn} and H_{mn} with the various approximations are described in the mathematical section of this paper.

[11] Slater, Phys. Rev. **36**, 57 (1930).

[12] Wang, Phys. Rev. **31**, 579 (1928).
[13] Rosen, Phys. Rev. **38**, 2099 (1931).

2. Results

In Table II will be found the results of the computations made without further approxi-

TABLE II.

δ_1	δ_2	Inter-nuclear distance R (A)	Energy (atomic units)	$E-2E_A$ (a.u.)	(e.v.)	Δ (e.v.)
2.68	.670	2.78	−29.68815	−.0165	−.223	−.051
2.68	.670	2.98	−29.69069	−.0190	−.257	−.032
2.68	.670	3.18	−29.69130	−.0196	−.265	−.018

mations than those implied in the use of the Slater atomic functions in the H.-L. molecular functions. A Morse curve, which should have the general character of the results of such a computation, when fitted to these points has its minimum very near 3.18A, and gives a binding energy, $E-2E_A$, of −0.27 e.v. when $2E_A$, the atomic energies subtracted from the molecular energy, are the best obtainable when using Slater's form of the one-electron functions. Less conservatively one might subtract atomic energies computed with $\delta_1/\delta_2=4$, as in the molecular computation. This increases the binding energy by only 0.04 e.v.; the result is still only a small fraction of the observed binding energy, −1.14 e.v.

Introduction of the modified Hamiltonian changes the energy computed by $2E_A+\Delta$, where E_A is the atomic energy computed with the atomic wave functions appearing in the molecular function and Δ is the error involved in the assumptions leading to the use of this operator. This small quantity is given in the last column of Table II.

Table III gives the computed "interaction energy" (from the modified Hamiltonian) for the treatments of the $^1\Sigma$ state with and without

TABLE III.

State	δ_1	δ_2	R (A)	Interaction Energy (e.v.)		
				With inner shells	Without	Difference
$^1\Sigma$	2.68	.670	2.78	−.310	−.992	.682
$^1\Sigma$	2.68	.670	2.98	−.326	−.850	.524
$^1\Sigma$	2.68	.670	3.18	−.327	−.722	.395
$^1\Sigma$	2.68	.632	3.38	−.349	−.681	.332
$^3\Sigma$	2.68	.670	3.18	+.424	+.600	−.176

the inner shells included. The result of a similar computation on the repulsive $^3\Sigma$ state is also included.

The introduction of the ionic term into the function was carried out only for $R=2.98$A, the complete energy operator being used. It was found that the best result was obtained by adding three percent of the ionic function, the energy being lowered by only 0.0005 e.v.

3. Discussion

The results summarized in Table II show that a treatment of Li_2, modeled so far as possible after the H.-L. treatment (with the slight modification due to Wang), yields a computed binding energy which resembles but little that deduced from observations. The error, though smaller in magnitude than that found in the work on H_2, is much larger in proportion to the binding energy. Clearly the approximations made by Bartlett and Furry are responsible for their satisfactory results in the treatment of this problem.

The error involved in the use of the approximate Hamiltonian turns out to be small for the distances considered, and changes rapidly (apparently exponentially) with the internuclear distance. The latter of these observations was of course to be expected, as the error has its origin in the overlapping of an approximate atomic function about nucleus A, φ_A, with $(H_B-E_B)\varphi_B$, where φ_B is another atomic function which is a good approximate solution of $(H_B-E_B)\varphi_B=0$ except in the region near nucleus B. (See mathematical section.)

Since this error is small the further discussion can be carried on in terms of the interaction energies, as given in Table III. The effect of using a somewhat different value for δ_2 is indicated by the fourth entry in this table. The smaller value of δ_2 turns out to be the better, but the change to be obtained through such an adjustment is so small that the statements made above need no fundamental modification.

The effect of the inner shells on the computation, on the other hand, is very important. They seem to give rise to a repulsive potential, for the $^1\Sigma$ state, varying much more rapidly with distance than the other terms in the binding energy, and with magnitude ranging between one-half

and three-fourths of the observed binding energies for the various distances. For sufficiently large separations of the atoms this effect would presumably sink to negligibility, but for internuclear distances of the order of the equilibrium distance it is by no means unimportant. Omission of these shells tends to correct for a serious underestimate of the binding energy associated with the external electrons, such as follows from the use of the H.-L. functions, and also shifts the computed equilibrium distance strongly toward smaller values (by 0.9A, in Li₂).

Assuming that the above computations give correct values for the repulsion associated with the inner shells, then the binding energy due to the outer electrons should be about $-1.14-0.80 = -1.94$ e.v., for the equilibrium distance. Probably a better estimate would arise from assuming that the computed repulsions are 50 percent too great. (In general the H.-L. method leads to the computation of excessive repulsions as well as insufficient binding.) Then the binding energy computed for the outer electrons should be about -1.7 e.v., of which that found by Bartlett and Furry is 67 percent—a performance closely parallel to that of the same method in the treatment of H₂. The estimated value for the binding due to the 2s electrons in Li₂ is thus a little more than a third of that due to the 1s electrons in H₂, for the equilibrium distances. However, Delbrück's conclusion that the decrease of the binding in Li₂ with respect to that in H₂ is to be attributed exclusively to the fact that the binding electrons are 2s electrons cannot be accepted; the inner shells seem to be effective in this respect both through the repulsion associated with their presence and through the resulting increase in the equilibrium distance, which is apparently of considerable size.

That the inner shells in a molecule do not necessarily exert a repulsive effect is shown by the computation on the ³Σ state of Li₂, in which case they produce an attractive potential of about half the magnitude of the repulsive potential in the ¹Σ state at that distance. This surprising result is due to the fact, now to be demonstrated, that the important terms in the energy associated with the inner shells involve also the outer "binding" electrons, and will thus vary with their nature.

In order to analyze the way in which the inner shells produce their effect it will be necessary to divide the interaction energy into parts which may be thought of as associated with pairs of electrons undergoing transitions of various types in the molecule. It should be emphasized that such a division is a purely formal matter, as indeed is the whole of the discussion which follows. Such observations as can be made have the same sort of significance as the common statement that chemical binding is associated with resonant interchange of the electrons responsible for the binding, and the possibility of such an interpretation is dependent entirely on the choice of wave function for the representation of the molecule. There seems to be sufficient interest associated with the results, however, to justify their presentation.

Now, the interaction energy operator can be separated into parts, all having the same form, associated with each pair of electrons. The interaction energy is similarly divided into parts, each of which consists of an integral involving such a part of the operator, with a weighting factor arising from integrations over the coordinates of the other electrons. These weighting factors would be one or zero if the one-electron functions were all mutually orthogonal; since this is not the case they differ somewhat from these two values. The contributions to the binding energy are conveniently and reasonably grouped according to the nature of the integral which contains the energy operator. A contribution involving an integral such as $\int f_4{}^*(2)f_3{}^*(1) \times H_{12}f_2(2)f_1(1)dv_{12}$ may then be thought of as associated with a simultaneous transition of electron 1 from a state described by f_1 to one described by f_3 and of electron 2 from a state described by f_2 to one described by f_4. In Table IV are listed the contributions associated with the possible pairs of transitions, for the computation at $R=2.78A$. In this grouping the numbers and spins of the electrons and the senses of the transitions have been disregarded.

Only the first two terms here do not involve the inner shells. They do not add up to give exactly the result of a computation from which inner shells are excluded, however, the difference being due to a small difference of the normalizing factors $[2+2U_{21}]^{-\frac{1}{2}}$ in the two cases. The other

TABLE IV.

$f_4 f_3 f_2 f_1$	Contribution to the energy (e.v.)
$s(2)s'(2)s(2)s'(2)$	−0.240
$s'(2)s(2)s(2)s'(2)$	−0.828
$s'(2)s(2)s(2)s'(1)$	0.306
$s(2)s(1)s(2)s'(2)$	0.169
$s(1)s(1)s(2)s'(2)$	0.130
$s(1)s(1)s(1)s'(2)$	0.106
$s'(1)s(2)s(2)s'(1)$	0.077
$s(1)s(2)s(1)s'(2)$	−0.029
$s'(1)s(1)s(2)s'(2)$	−0.007
$s(2)s'(1)s(2)s'(2)$	0.004
$s(1)s(2)s(2)s'(2)$	0.002

terms which tend to produce binding are quite unimportant. The larger contributions producing repulsion have the common characteristic of involving at least one electron undergoing a transition between one of the $2s$ states and a $1s$ state about the other nucleus; from the usual point of view this would be taken to mean that the occurrence of electronic rearrangements involving such a transition is responsible for the repulsion. That the substitution of some kind of central field for the inner electrons in a H.-L. computation cannot be a proper simplification is clear, as the possibility of such processes is thus neglected.

One of the largest repulsive contributions of all arises from triple or higher transitions of electrons between different states. Though exceeded in magnitude by only one other contribution these were neglected by Delbrück, who assumed (as is indeed the almost universal practice) that the contributions decrease in magnitude as the number of electron transitions involved increases. Such a criterion is thus proved to be inapplicable, at least when inner shells are present. It will also be noted that three of the five important repulsive terms involve states in at least three of the four electron shells in the molecule. Thus not even by considering the atomic interaction as a sum of interactions of electron shells in pairs can one obtain a satisfactory result; indeed it seems to be exceedingly difficult to suggest any essential simplification in the treatment of such systems which does not introduce a considerable error.

The small improvement produced on introduction of the ionic term (−0.0005 e.v. for $R = 2.98A$) is not surprising in the case of the molecule Li_2. This result is, however, to be contrasted with that of Bartlett and Furry, who obtain for this distance a change of −0.05 e.v. in the energy on introduction of this term. Even more surprising is the increasing importance of ionic binding with increasing distance between the atoms which they find. These anomalous results seem to have their origin in the fact that the introduction of the ionic function is essentially a variational process, and can thus be depended upon to give proper results only when all electrons are present and the entire energy operator is used. A similar objection may be made to attempts to improve the H.-L. method by diagonalizing a larger section of the energy matrix, when inner shells are omitted or other approximations are made.[14]

III. VARIATIONAL TREATMENT

1. Method

The quantitatively unsatisfactory outcome of the work described above reveals the necessity of designing an essentially different method for dealing with such systems. The molecule H_2 was chosen as the most suitable subject for the investigation of such a method. The satisfactory outcome of the work on that problem, as described in reference 1, then led to an attempt to extend the method used there to the treatment of the present problem. The most complete generalization, which would consist in the construction of a wave function expressed in terms of the 17 coordinates of which the energy is a function, is clearly impracticable at present. Even the less ambitious project of describing the inner shells of the molecule by Slater functions and the binding electrons by functions of the sort used in treating H_2 proved to be decidedly difficult, because of the nature of the terms involving the distance between these electrons, the r_{12} terms. As a first step in the right direction the work was carried through with the omission of these terms. Then the wave function, like the H.-L. function, was expressible as a sum of products of one-electron functions.

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[14] Note, for instance, the excessively strong binding computed for a $^2\Sigma$ state of BeH by Ireland, Phys. Rev. **43**, 329 (1933).

$$\psi = \sum_{mnjk} C_{mnjk}[mnjk] = \sum_{mnjk} C_{mnjk}$$

$$\times \{\psi_{mnjk} + \psi_{nmkj})/[2(6!)]^{\frac{1}{2}}\}, \quad (2)$$

$$\psi_{mnjk} = |s(1\alpha, 1)s'(1\alpha, 2)f(mj\alpha, 3)$$

$$\times s(1\beta, 4)s'(1\beta, 5)f(nk\beta, 6)|. \quad (3)$$

Here $s(1\alpha, 1)$ and $s'(1\alpha, 1)$ are defined as before, while

$$f(mj\alpha, 1) = e^{-\gamma_2\lambda_1/2}\lambda_1{}^m\mu_1{}^j\delta(\alpha_1, \sigma_1),$$

where $\lambda_1 = (r_1 + s_1)/R$, $\mu_1 = (r_1 - s_1)/R$, and γ_2 is a parameter independent of m and j. Neither the f's nor the functions ψ_{mnjk} are normalized or orthogonal. This ψ is of the proper character for the description of a singlet state. The desired symmetry of ψ to reflection in the mid-plane is to be obtained by including only those terms $[mnjk]$ for which $j+k$ is even, each ψ_{mnjk} then being symmetric to such a transformation. The adjustment of the constants C_{mnjk} and the determination of the molecular energy were carried out by the methods described in reference 1 and the mathematical section of this paper.

2. Results and discussion

Because of the large amount of numerical work necessary a computation has been made for only one set of values for the parameters. They were chosen to be $\gamma_1 = \delta_1 R = 15$; $\gamma_2 = 4$; $R = 2.98A$, these values giving the greatest numerical convenience available in the desired range of R and γ_2.

When a wave function for the molecule was built up by adding one term at a time, the energy fell rapidly at first on the addition of each new term, but later much more slowly, until in all eighteen terms were introduced. These were all the terms of proper character that could be constructed with mj and nk equal to 00, 01, 02, 10, 11, 12 or 20. The binding energy was then -0.62 e.v., the energy taken for Li being that computed by Wilson.[15] This is to be compared with the -0.20 e.v. computed for this distance by the H.-L. method (the same energy for the separated atoms being used) and the -1.11 e.v. which is indicated by a Morse curve constructed by using experimental values for the molecular constants involved.

[15] Wilson, J. Chem. Phys. **1**, 210 (1933).

The effect of adding new terms to the wave function was somewhat different from that described in the case of H₂, the convergence toward a limit being less definite. Since the value of the secular determinant was rather far from a linear function of λ (the presence of another $^1\Sigma_g$ state in the neighborhood being thus indicated) it would have been rather troublesome to determine exactly the energy associated with each of the preliminary functions used. The average improvement found on adding the last few terms, however, was found to be between 0.02 and 0.03 e.v., as against 0.01 e.v. in the case of H₂. It was thus indicated that the result could be somewhat improved by the addition of more terms of similar character, but since the labor involved in adding each new term to such a complicated function is considerable this has not been done. It may be expected that in the presence of a few r_{12} terms the convergence would be much more satisfactory, and that an excessive number of terms would not be required in the wave function, as such behavior with respect to convergence was found with H₂.

It seems likely that the 0.5 e.v. between the computed and experimental values may be almost entirely due to the absence of the r_{12} terms. A part of this error, though hardly more than a small part, to judge from the results with H₂, might be due to a poor choice of γ_2. Another possibility is that the binding electrons have retained more of their atomic character than is the case in H₂. The binding energy in Li₂ is about 10 percent of the total energy of the outer electrons, against 20 percent in H₂. Associated with the greater ratio of intra-atomic to binding forces there should be a smaller change in the character of the functions as the atoms approach each other. The slow convergence noted might then be associated with a slowly increasing perfection in the expansion of a function of marked atomic character as a sum of an increasing number of terms of molecular character. The remedy for such a situation would be to introduce a term of atomic character—say the Wang function—as a unit in the series. One would thus attempt to expand the difference between the Wang function and the correct one, rather than the entire function, in terms of the two-center functions. Some work of Dr. A. S. Coolidge and

the writer, as yet unpublished, has shown that this scheme is quite ineffective in the treatment of either the normal or lowest $^3\Sigma_u$ state of H_2. It would then seem that no large improvement in the treatment of Li_2 could be expected from such a modification.

Introduction into the wave function of terms depending on the distance between the outer electrons, or something equivalent, would seem to be the next step in this investigation. It is hoped that a satisfactory method for doing this and simultaneously improving the treatment of the inner shells may grow out of an investigation of the Li atom now under way.

IV. MATHEMATICAL SECTION

1. The interaction operator

The use of the interaction operator involves assumptions which do not seem to have been discussed in the literature. Since consideration of these assumptions throws some little light on the range of applicability of this approximation it seems worth while to give them explicit statement. The argument below applies to a nonpolar state of a neutral diatomic molecule. The extension to polar states and polyatomic molecules is simple and obvious, and even charged systems can be treated by a proper modification of the method.

Let the molecule to be considered contain $n = Z_A + Z_B$ electrons, and nuclei with charges Z_A and Z_B, respectively. The wave equation for this molecule is then

$$\left\{\sum_i^n -\nabla_i^2 + \frac{2Z_AZ_B}{R} + \sum_{i>i}^{n,\,n-1} \frac{2}{r_{ij}} - \sum_i^n \frac{2Z_A}{r_i}\right. $$
$$\left. - \sum_i^n \frac{2Z_B}{s_i} - E\right\}\psi = 0. \quad (4)$$

Here r_i, s_i and r_{ij} are the distances of electron i from nucleus A, nucleus B and electron j, respectively, and E is the energy of the system in atomic units (13.54 e.v.). Let $\varphi(1, \cdots, n)$ be a single determinant describing a configuration of the molecule (such as $\psi_1(1, \cdots, 6)$ as defined in treating Li_2). φ can be expanded in a well-known manner as a sum of products of subdeterminants, each of which describes a configuration of one of the constituent atoms

$$|f_1(1)f_2(2)\cdots f_n(n)| = |f_1(1)\cdots f_m(m)|$$
$$\times |f_{m+1}(m+1)\cdots f_n(n)| + \text{similar terms}$$

or

$$\varphi(1, 2, \cdots, n) = \chi_A(1, \cdots m-1, m)$$
$$\times \chi_B(m+1, m+2, \cdots n)$$
$$- \chi_A(1, \cdots m-1, m+1)$$
$$\times \chi_B(m, m+2, \cdots n) + \cdots. \quad (5)$$

The functions f are to be so chosen as to make the determinants χ approximate solutions of atomic equations such as

$$\left\{-\sum_{i=1}^{m=Z_A}\left(\nabla_i^2 + \frac{2Z_A}{r_i}\right) + \sum_{i>i}^{m,\,m-1}\frac{2}{r_{ij}}\right\}\chi_A(1, \cdots m)$$
$$= E\chi_A(1\cdots m) \quad (6)$$

or $H_A\chi_A = E\chi_A$. If χ_A is an exact solution of this equation E will be the correct E for atom A. If this is not the case the root-mean-square error involved in the use of Eq. (6) can be reduced to a minimum by setting E equal, not to this true energy, but to

$$E_A = \int \chi_A^* H_A \chi_A dv \bigg/ \int \chi_A^2 dv. \quad (7)$$

For if

$$(H_A - E_A)\chi_A = \Delta_A, \quad (8)$$

then

$$(H_A - E_A')\chi_A = \Delta_A + (E_A - E_A')\chi_A, \quad (9)$$

and the root-mean-square error in putting $(H_A - E_A')\chi_A = 0$ becomes, through the use of (7) and (8),

$$\left\{\int \Delta_A^2 dv + (E_A - E_A')^2 \int \chi_A^2 dv\right\}^{\frac{1}{2}},$$

having its minimum for $E_A' = E_A$. Now

$$H = H_A(1, \cdots m) + H_B(m+1, \cdots n)$$
$$+ H_I(1, \cdots m; m+1, \cdots n), \quad (10)$$

$$H_I(1, \cdots m; m+1, \cdots n) = \sum_{i=1}^m \sum_{j=m+1}^n h_I(i, j), \quad (11)$$

$$h_I(i, j) = 2/R + 2/r_{ij} - 2/r_j - 2/s_i. \quad (12)$$

Then

$$H\chi_A(1, \cdots m)\chi_B(m+1, \cdots n)$$
$$= (E_A + E_B)\chi_A(1, \cdots m)\chi_B(m+1, \cdots n)$$
$$+ H_I(1, \cdots m; m+1, \cdots n)\chi_A(1, \cdots m)$$
$$\times \chi_B(m+1, \cdots n) + \Delta_A\chi_B + \chi_A\Delta_B. \quad (13)$$

Using this and a set of similar equations one obtains

$$H\varphi \cong (E_A + E_B)\varphi + \sum_{i \neq j} h_I'(i, j)\varphi, \qquad (14)$$

where $h_I'(i, j) = h_I(i, j)$ when multiplied into any term in φ in which electron i is assigned to a state about nucleus A and j to a state about B, and is zero otherwise. Proceeding as though the approximate equality of Eq. (14) were exact is essentially what one does in using the interaction operator, the error arising from neglect of terms similar to the last two in (13).

This error vanishes if the χ's are accurate atomic functions, as happens only in the case of one-electron atoms, or if $\Delta_A \chi_B$ and $\Delta_B \chi_A$ vanish. In general these products will not vanish unless the Δ's vanish, but it is not difficult to judge when they will be so small as to be safely neglected. When Slater functions are used the χ's will be fairly good solutions of the atomic equation except where the potential energy is very large, near the nucleus or where the electrons are close together. Thus the Δ's will be large in the neighborhood of the inner shells of alkali atoms, but relatively small outside. On the other hand, in the case of the Li⁻ ion or the atom Be, for instance, Δ will differ from zero appreciably even in the outer shell. Thus one would expect that the neglect of $\Delta_A \chi_B$ in treating a nonpolar configuration of Li₂ would not be serious for fairly large R, because Δ_A is then large only in a restricted region where χ_B is small. Similarly, in treating a polar configuration of this molecule, χ_B for the Li⁺ ion will be large in a very restricted region where Δ_A for the Li⁻, though it is fairly large in extent, will be rather small in magnitude. The error in this case would thus be expected to be of the order of that found in the nonpolar state. On the other hand, in the treatment of BeH the Δ_A for the Be atom and the χ_B for the H atom will both be extensive, and one may expect serious errors from the neglect of their product. $\Delta_B \chi_A$ in this case of course vanishes because of the vanishing of Δ_B. Since this method of estimating the errors produced in the integrals $\int \varphi_2 H \varphi_1 dv$ takes no account of the nature of the function φ_2 with which the terms $\Delta \chi$ are to be integrated, it might lead one to be unnecessarily conservative

in certain cases. One may then supplement the above argument by noticing whether or not φ_2 and $\Delta \chi$ are likely to be large in the same region in phase space.

2. Reduction of the matrix elements

The most characteristic difficulty in the computation of molecular energies is that of expressing the matrix elements, particularly those of energy, in terms of integrals over the coordinates of one or two electrons. This difficulty arises from the fact that the one-electron functions to be used are in large part not mutually orthogonal, the complexity of the expressions for the matrix elements increasing rapidly with the number of such functions involved. The use of non-orthogonal functions is a necessary outcome of the application of the H.-L. method, and is also useful in the treatment of problems of atomic interaction from other points of view. There are two ways in which one may proceed. One is to express the energy matrix element, say, in terms of integrals involving the non-orthogonal functions, so collecting terms as to obtain a sum of integrals containing parts of the Hamiltonian operator, with factors which are complicated functions of integrals over the coordinates of single electrons. The other is to obtain a simple expression for the matrix elements in terms of orthogonalized combinations of the original functions, and to construct the integrals involving the orthogonalized functions as linear combinations of the integrals involving the original functions. The first of these processes is more advantageous the more complex the system and the fewer the electronic configurations to be considered, being especially suited for work by any simple modification of the H.-L. method. After developing this process as it was applied to the treatment of Li₂ by the H.-L. method, the second process will be illustrated by explicit application to the variational treatment of this problem, for which it is preferable.

The first step in the evaluation of the integral $\int \varphi_2^* H \varphi_1 dv$, where

$$\varphi_1 = |f_1(1)f_2(2)\cdots f_n(n)|,$$
$$\varphi_2 = |f_1'(1)f_2'(2)\cdots f_n'(n)| \qquad (15)$$

and $f_1 \cdots f_n$ and $f_1' \cdots f_n'$ are sets of n linearly independent functions, is to express φ_1 and φ_2

in terms of $F_1 \cdots F_n$ and $F_1' \cdots F_n'$. Here the F's shall be normalized linear combinations of the f's and the F''s normalized linear combinations of the f''s such that F_i is orthogonal to all F''s, except, possibly, F_i'. By a familiar property of determinants

$$\varphi_1 = |g_1(1) \cdots g_n(n)|, \tag{16}$$

if

$$g_i = a_{i1}f_1 + a_{i2}f_2 + \cdots + a_{in}f_n, \quad a_{ii} = 1. \tag{17}$$

Now the constants a_{ij} may be so chosen as to produce those orthogonality relations between the g's and g''s which one wishes to hold between the F's and F''s. In the present work this could be done, for instance, by making the g's and g''s mutually orthogonal among themselves, with $g_i = g_i'$ whenever possible; it is to such a situation that the discussion which follows particularly applies. After dividing the f's into groups with respect to spin, angular momentum about the internuclear axis, etc., such that every function in a group is orthogonal to all functions not in

that group, orthogonal linear combinations of the members of each group can be made. Simple ways of doing this, depending on the symmetry properties of the system, are often available. In any case one can use the standard process, as described in Courant and Hilbert's "Methoden der Mathematischen Physik I," p. 34. From the g's one then obtains the desired F's by normalization.

$$F_i = N_i g_i, \tag{18}$$

where

$$N_i = \left\{ \sum_j \sum_k a_{ij} a_{ik} \int f_j^*(1) f_k(1) dv_1 \right\}^{-\frac{1}{2}}. \tag{19}$$

Then

$$\varphi_1 = (1/N_1 N_2 \cdots N_n) |F_1(1) \cdots F_n(n)|, \tag{20}$$

and

$$\int \varphi_1^2 dv = n! / (N_1 N_2 \cdots N_n)^2, \tag{21}$$

because of the orthogonality and normalization of the F's.

Now, because of the symmetry of H to any interchange of electrons,

$$\int |F_i'|^* H |F_i| dv = n! \int |F_i'|^* H \{ F_1(1) F_2(2) \cdots F_n(n) \} dv, \tag{22}$$

each term in the determinant $|F_i|$, when operated on by H, multiplied by $|F_i'|$ and integrated over all space giving the same result. Hence, using (21) one obtains

$$E_{12} = \int \varphi_2^* H \varphi_1 dv \Big/ \left(\int \varphi_2^* \varphi_2 dv \int \varphi_1^* \varphi_1 dv \right)^{-\frac{1}{2}} = \int |F_i'|^* H F_1(1) \cdots F_n(n) dv. \tag{23}$$

It is in the evaluation of this quantity (the integral $\int \varphi_2^* H \varphi_1 dv$ with φ_1 and φ_2 separately normalized to 1) that we shall be interested.

Because of the symmetry of H in its arguments and the fact that no part of it involves the coordinates of more than two electrons one can write

$$H = \sum_{i>j} h_{ij}. \tag{24}$$

For a neutral diatomic molecule, for instance,

$$h_{ij} = -\frac{1}{Z_A + Z_B - 1} \left(\nabla_i^2 + \nabla_j^2 + \frac{2Z_A}{r_i} + \frac{2Z_B}{s_i} + \frac{2Z_A}{r_j} + \frac{2Z_B}{s_j} \right) + \frac{2}{r_{ij}}. \tag{25}$$

Introducing this into (23), expanding the determinant and noting the orthogonality relations one finds

$$E_{12} = \sum_{i>j} S_{ij} \left(\int F_i'^*(i) F_j'^*(j) h_{ij} F_i(i) F_j(j) dv_{ij} - \int F_i'^*(j) F_j'^*(i) h_{ij} F_i(i) F_j(j) dv_{ij} \right), \tag{26}$$

where

$$S_i = \int F_i'^*(1)F_i(1)dv_1, \qquad S_{ij} = S/S_iS_j, \qquad S = \prod_i^n S_i. \tag{27}$$

Remembering that the matrix transforming the f's into the F's is

$$\|N_i a_{ij}\| = \|c_{ij}\|, \tag{28}$$

one can get out of (26) K_{pqrs}, the coefficient in E_{12} of the integral $\int\int f_r'^*(x)f_s'^*(y)h_{xy}f_p(x)f_q(y)dv_{xy}$, where the arguments no longer refer to definite electrons. This is readily seen to be

$$K_{pqrs} = \sum_{i \neq j} S_{ij}(c_{ip}c_{jq}c_{ir}'c_{js}' - c_{ip}c_{jq}c_{is}'c_{jr}') = S\sum_{i \neq j}(d_{ip}d_{jq}d_{ir}'d_{js}' - d_{ip}d_{jq}d_{is}'d_{jr}'), \tag{29}$$

if

$$d_{ip} = c_{ip}S_i^{-\frac{1}{2}}, \tag{30}$$

it being assumed that none of the S_i's vanish. (If one should vanish the energy expression is greatly simplified and the work can be started on a different basis.) Observing that (29) may be written

$$K_{pqrs} = S\{\sum_i d_{ip}d_{ir}'\sum_j d_{jq}d_{js}' - \sum_i d_{ip}d_{is}'\sum_j d_{jq}d_{jr}'\},$$

one obtains finally

$$K_{pqrs} = S\{D_{pr}D_{qs} - D_{qr}D_{ps}\}, \tag{31}$$

where

$$D_{ps} = \sum_i d_{ip}d_{is}'. \tag{32}$$

Thus $\|D_{ij}\|$ is the matrix formed by postmultiplying the conjugate of the matrix $\|d_{ij}\|$ by the matrix $\|d_{ij}'\|$. Having constructed the matrix $\|D_{ij}\|$ it is a simple matter to find the coefficient of any integral in the energy matrix element; summing over the contributions from each possible integral E_{12} is then found.

To summarize the process: Determine the matrices of real constants $\|c_{ij}\|$, $\|c_{ij}'\|$ which convert the functions f, f' into the normalized and properly orthogonalized functions F, F'. Divide the ith row of each matrix by $S_i^{\frac{1}{2}}$, and postmultiply the conjugate of the first matrix by the second. From the matrix $\|D_{ij}\|$ resulting the coefficients K_{pqrs} can then be obtained using (31).

To compute E_{12}', the interaction energy matrix element, one need only substitute the integrals $\int\int f_r^*(x)f_s^*(y)[h_1'(x, y)+h_1'(y, x)]f_p(x)$ $\times f_q(y)dv_{xy}$ for the integrals $\int\int f_r^*(x)f_s^*(y)h_{xy}f_p(x)$ $\times f_q(y)dv_{xy}$, the coefficients K_{pqrs} being computed as before.

The second method mentioned above of assembling the simple integrals into matrix elements, which will now be illustrated, is particularly useful when many electronic configurations of a system are to be considered, or a linear function of many parameters is to be used in a variational attack on the problem. One advantage lies in the fact that in the computation of extensive tables of integrals involving orthogonalized functions it is possible to construct tables of intermediate quantities which enter many of the matrix elements. A corresponding reduction in the labor of computing many sets of the coefficients K_{pqrs}, on the other hand, does not appear to be attainable. It is also possible to make immediate use of material arranged in this way for the treatment of one problem, say the normal state of Li₂, in the treatment of other problems—states of the same molecule with different symmetry characteristics, or states of related ionic molecules, as Li₂⁺.

The first problem to be considered is that of expressing $\int \psi^*_{m_2n_2j_2k_2}\psi_{m_1n_1j_1k_1}dv$ and $\int \psi^*_{m_2n_2j_2k_2}$ $\times H\psi_{m_1n_1j_1k_1}dv$ with good approximation in terms of a few integrals involving orthogonalized one-electron functions, in such a way as to make maximum use of the relations between the various matrix elements. The orthogonalized functions to be used in place of $s(1\alpha, 1)$, $f(mj\alpha, 1)$, etc., are

$$S(1\alpha, 1) = s(1\alpha, 1),$$
$$S'(1\alpha, 1) = s'(1\alpha, 1) - J_1 s(1\alpha, 1),$$
$$F(mj\alpha, 1) = f(mj\alpha, 1) + t(mj)s(1\alpha, 1) \\ + t'(mj)s'(1\alpha, 1). \tag{33}$$

It is most convenient to make $t(mj) = (-1)^j$ $\times t'(mj)$, so that $F(mj\alpha, 1)$ and $f(mj\alpha, 1)$ will have the same definite symmetry to reflection in the plane bisecting the internuclear axis.

Let $J_1 = \int s(1, 1)s'(1, 1)dv_1,$ $\qquad\qquad$ $J_{mj}' = \int f(mj, 1)s'(1, 1)dv_1 = (-1)^j J_{mj},$

$J_5 = \int S'^2(1, 1)dv_1 = 1 - J_1^2,$ $\qquad\qquad$ $J_{mj, nk} = \int f(mj, 1)f(nk, 1)dv_1,$ $\qquad$ (34)

$J_{MJ, NK} = \int F(mj, 1)F(nk, 1)dv_1.$

$J_{mj} = \int f(mj, 1)s(1, 1)dv_1,$ $\qquad\qquad$ Then $t_{mj} = (-1)^j t_{mj}' = -(J_{mj} - J_1 J_{mj}')/J_5,$ $\quad$ (35)

$$J_{MJ, NK} = \delta((-1)^{j+k}, 1)\{J_{mj, nk} - (1/J_5)(J_{mj}J_{nk} + J_{mj}'J_{nk}' - J_1[J_{mj}J_{nk}' + J_{mj}'J_{nk}])\}. \qquad (36)$$

Expressing the ψ's in terms of orthogonalized functions according to (16) and (17), and transforming the integral as in (22), one obtains immediately

$$(1/6!)\int \psi^*_{m_2 n_2 j_2 k_2}\psi_{m_1 n_1 j_1 k_1}dv = J_5^2 J_{M_1 J_1, M_2 J_2}J_{N_1 K_1, N_2 K_2}. \qquad (37)$$

Similarly

$$(1/6!)\int \psi^*_{m_2 n_2 j_2 k_2}H\psi_{m_1 n_1 j_1 k_1}dv = \int \psi^*_{m_2 n_2 j_2 k_2}HS(1\alpha, 1)S'(1\alpha, 2)F(m_1 j_1\alpha, 3)$$

$$\times S(1\beta, 4)S'(1\beta, 5)F(n_1 k_1\beta, 6)dv. \qquad (38)$$

Now, let

$$H = H_1 + H_2 + H_3 + H_4. \qquad (39)$$

H_1 shall contain those terms in H which refer only to electrons 1, 2, 4 and 5, plus the repulsion of the nuclei. H_2 shall contain those terms in the operator which involve only electrons 3 and 6, except for $2/r_{36}$, which shall be H_3. H_4 shall contain all other parts of the operator, these being electron interaction terms involving one electron in an inner and one in an outer shell. The energy integrals E_i associated with the operators H_i will be dealt with separately.

Carrying out the integrations over the coordinates of electrons 3 and 6 one obtains

$$(1/6!)\int \psi^*_{m_2 n_2 j_2 k_2}H_1\psi_{m_1 n_1 j_1 k_1}dv = J_{M_1 J_1, M_2 J_2}J_{N_1 K_1, N_2 K_2}\int |S(1\alpha, 1)S'(1\alpha, 2)S(1\beta, 4)S'(1\beta, 5)|^*$$

$$\times H_1 S(1\alpha, 1)S'(1\alpha, 2)S(1\beta, 4)S'(1\beta, 5)dv_{1245}. \qquad (40)$$

Now, the integral which appears here is just J_5^2 times the energy of Li_2^{++}, as computed by the H.-L. method. That energy differs from the energy of the separated inner shells, E_s, plus the electrostatic repulsion energy of the ions, $2/R$, by terms of the order of J_1^2, which is about 10^{-9} for the values of R which are of interest. With negligible error, then, one can write

$$E_1 = J_{M_1 J_1, M_2 J_2}J_{N_1 K_1, N_2 K_2}(2/R + E_s). \qquad (41)$$

Proceeding similarly one finds to a similar approximation

$$E_2 = J_{M_1 J_1, M_2 J_2}V_{N_1 K_1, N_2 K_2} + J_{N_1 K_1, N_2 K_2}V_{M_1 J_1, M_2 J_2}, \qquad (42)$$

where

$$V_{M_1 J_1, M_2 J_2} = \int F^*(m_2 j_2, 1)(-\nabla_1^2 - 6/r_1 - 6/s_1)F(m_1 j_1, 1)dv_1. \qquad (43)$$

$V_{M_1 J_1, M_2 J_2}$ can be considered as a matrix component of the energy of one of the outer electrons, the mutual energy with other electrons being excluded. Likewise one obtains

$$E_3 = \int F(m_2 j_2, 3)F(n_2 k_2, 6)(2/r_{36})F(m_1 j_1, 3)F(n_1 k_1, 6)dv_{12}, \qquad (44)$$

a matrix component of the mutual energy of the outer electrons. Finally, defining

$$X_{M_1J_1,\,M_2J_2} = V_{M_1J_1,\,M_2J_2} + \delta((-1)^{i_1+i_2},\,1)\Big\{8\int S^2(1,\,1)(1/r_{12})F(m_1j_1,2)F(m_2j_2,\,2)dv_{12}$$

$$-4\int S(1,\,1)F(m_1j_1,\,1)(1/r_{12})S(1,\,2)F(m_2j_2,\,2)dv_{12}\Big\},\quad (45)$$

a matrix element of the energy of an outer electron, exclusive of the interaction with the other outer electron, one obtains

$$E_4 = J_{N_1K_1,\,N_2K_2}\{X_{M_1J_1,\,M_2J_2} - V_{M_1J_1,\,M_2J_2}\} + J_{M_1J_1,\,M_2J_2}\{X_{N_1K_1,\,N_2K_2} - V_{N_1K_1,\,N_2K_2}\}.\quad (46)$$

Thus

$$(1/6!)\int \psi^*_{m_2n_2j_2k_2}H\psi_{m_1n_1j_1k_1}dv = J_{M_1J_1,\,M_2J_2}J_{N_1K_1,\,N_2K_2}(2/R+E_s) + J_{M_1J_1,\,M_2J_2}X_{N_1K_1,\,N_2K_2}$$

$$+ J_{N_1K_1,\,N_2K_2}X_{M_1J_1,\,M_2J_2} + 2\int F(m_2j_2,\,1)F(n_2k_2,\,2)(1/r_{12})F(m_1j_1,\,1)F(n_1k_1,\,2)dv_{12},\quad (47)$$

terms of the order of J_1^2 being neglected throughout.

Only the last integral in (47) is characteristic of the particular matrix element to be computed, the other quantities entering an extensive treatment of the system many times. Since $(2/R+E_s)$ enters each of the matrix elements with the corresponding element of the unity matrix as factor, the last three terms of (47) give the "matrix element of $H-2/R-E_s$." It is helpful in the computation to solve the secular equation for this more convenient quantity. This separation of the inner shell energy is essentially different from that which is usually carried out, as the exchange terms have been preserved, many of them having been lumped together into integrals in which, formally, only functions of the outer electrons appear. This again illustrates the purely formal character of the "exchange terms"; even those which appear in this work could be made to disappear by proper modification of the wave functions.

The computation of the X's is similar to, but simpler than that of the last integral in (47). That integral is a sum of 81 integrals involving the unorthogonalized functions. It is conveniently computed by the obvious 9-term formula from tables of intermediate functions, some of which appear elsewhere in the work. These are the integrals

$$\int s^2(1,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12},$$

$$\int s(1,\,1)s'(1,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12},$$

$$\int s(1,\,1)f(n_1k_1,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12}$$

and

$$\int f(n_1k_1,\,1)f(n_2k_2,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12},$$

each of which can be computed from integrals involving the original functions by a nine term formula.

3. Evaluation of integrals

The integrals encountered in this work can be evaluated as functions of the following simpler quantities.

$$A_n(\sigma,\,\gamma) = \int_\sigma^\infty \lambda^n e^{-\gamma\lambda}d\lambda, \qquad R_\tau{}^n = \int_{-1}^{+1} P_\tau(\mu)\mu^n d\mu,$$

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$$B_n(\gamma) = \int_{-1}^{+1} \mu^n e^{-\gamma\mu} d\mu, \qquad G_\tau{}^n(\gamma) = \int_{-1}^{+1} e^{-\gamma\mu} P_\tau(\mu) \mu^n d\mu,$$

$$H_\tau(m, \gamma_1, n, \gamma_2) = \int_1^\infty d\lambda_1 \int_1^\infty d\lambda_2 Q_\tau\binom{\lambda_1}{\lambda_2} P_\tau\binom{\lambda_2}{\lambda_1} \lambda_1{}^m \lambda_2{}^n e^{-(\gamma_1\lambda_1 + \gamma_2\lambda_2)} \qquad \begin{array}{l} \lambda_1 > \lambda_2 \\ \lambda_2 > \lambda_1 \end{array}.$$

Here P_τ and Q_τ are the Legendre functions of the first and second kind, respectively. Rosen[16] has discussed the integrals A, B, R and G, while Rosen[13] and James and Coolidge[1] give formulas for $H_\tau(m, \gamma_1, n, \gamma_2)$ when $\gamma_1 = \gamma_2$. The following generalizations of their formulas enable one to deal with the case of $\gamma_1 \neq \gamma_2$.

$$H_0(m, \gamma_1, n, \gamma_2) = F_m(\gamma_1) A_n(\gamma_2) + F_n(\gamma_2) A_m(\gamma_1) - T(m, \gamma_1, n, \gamma_2) - T(n, \gamma_2, m, \gamma_1), \tag{48}$$

$$\begin{aligned} H_\tau(m, \gamma_1, n, \gamma_2) = (1/\tau^2)\big[& (2\tau-1)^2 H_{\tau-1}(m+1, \gamma_1, n+1, \gamma_2) + (\tau-1)^2 H_{\tau-2}(m, \gamma_1, n, \gamma_2) \\ & - (2\tau-1)(2\tau-3)\{H_{\tau-2}(m+2, \gamma_1, n, \gamma_2) + H_{\tau-2}(m, \gamma_1, n+2, \gamma_2)\} \\ & + 2(2\tau-1)(2\tau-5) H_{\tau-3}(m+1, \gamma_1, n+1, \gamma_2) \\ & - (2\tau-1)(2\tau-7)\{H_{\tau-4}(m+2, \gamma_1, n, \gamma_2) + H_{\tau-4}(m, \gamma_1, n+2, \gamma_2)\} \\ & + 2(2\tau-1)(2\tau-9) H_{\tau-5}(m+1, \gamma_1, n+1, \gamma_2) - \cdots, \end{aligned} \tag{49}$$

until for even τ $\quad -(2\tau-1)\{H_0(m+2, \gamma_1, n, \gamma_2) + H_0(m, \gamma_1, n+2, \gamma_2) - S(m+1, \gamma_1, n, \gamma_2)$
$$-S(n+1, \gamma_2, m, \gamma_1)\}\big],$$

for odd τ $\quad +(2\tau-1)\{2H_0(m+1, \gamma_1, n+1, \gamma_2) - S(m, \gamma_1, n+1, \gamma_2) - S(n, \gamma_2, m+1, \gamma_1)\}.$

The auxiliary quantities appearing in these formulas can all be computed by means of recurrence relations.

$$T(m, \gamma_1, n, \gamma_2) = \int_1^\infty \lambda_1{}^m e^{-\gamma_1\lambda_1} Q_0(\lambda_1) d\lambda_1 \int_{\lambda_1}^\infty \lambda_2{}^n e^{-\gamma_2\lambda_2} d\lambda_2,$$

$$T(m, \gamma_1, n, \gamma_2) = (1/\gamma_2)[nT(m, \gamma_1, n-1, \gamma_2) + F_{m+n}(\gamma_1+\gamma_2)], \tag{50}$$

$$T(m, \gamma_1, 0, \gamma_2) = F_m(\gamma_1+\gamma_2)/\gamma_2, \tag{51}$$

$$F_n(\gamma) = \int_1^\infty \lambda^n e^{-\gamma\lambda} Q_0(\lambda) d\lambda,$$

$$F_n(\gamma) = F_{n-2}(\gamma) + (1/\gamma)[nF_{n-1}(\gamma) - (n-2)F_{n-3}(\gamma) - A_{n-2}(\gamma)], \tag{52}$$

$$F_0(\gamma) = \tfrac{1}{2}[(\ln 2\gamma + C)(e^{-\gamma}/\gamma) - E_i(-2\gamma)(e^\gamma/\gamma)], \tag{53}$$

$$F_1(\gamma) = \tfrac{1}{2}[(\ln 2\gamma + C)e^{-\gamma}(1/\gamma + 1/\gamma^2) - E_i(-2\gamma)e^\gamma(-1/\gamma + 1/\gamma^2)], \tag{54}$$

$$S(m, \gamma_1, n, \gamma_2) = \int_1^\infty \lambda_1{}^m e^{-\gamma_1\lambda_1} d\lambda_1 \int_1^{\lambda_1} \lambda_2{}^n e^{-\gamma_2\lambda_2} d\lambda_2,$$

$$\begin{aligned} S(m, \gamma_1, n, \gamma_2) &= (1/\gamma_1)[mS(m-1, \gamma_1, n, \gamma_2) + A_{m+n}(\gamma_1+\gamma_2)] \\ &= A_0(\gamma_2) A_m(\gamma_1) + (1/\gamma_2)[nS(m, \gamma_1, n-1, \gamma_2) - A_{m+n}(\gamma_1+\gamma_2)], \end{aligned} \tag{55}$$

$$S(0, \gamma_1, m, \gamma_2) = (1/\gamma_1) A_m(\gamma_1+\gamma_2), \tag{56}$$

$$S(m, \gamma_1, 0, \gamma_2) = A_0(\gamma_2) A_m(\gamma_1) - (1/\gamma_2) A_m(\gamma_1+\gamma_2), \tag{57}$$

$$S(m, \gamma_1, n, \gamma_2) + S(n, \gamma_2, m, \gamma_1) = A_m(\gamma_1) A_n(\gamma_2). \tag{58}$$

[16] Rosen, Phys. Rev. **38**, 255 (1931).

All the required integrals except those involving $1/r_{ij}$ are easily evaluated in terms of the functions A_n and B_n, by expressing the integrand in polar or elliptic coordinates, according to the nature of the one-electron functions involved. The more troublesome integrals $\int f_1(i)(1/r_{ij})f_2(j)dv_{ij}$ fall into two groups. If f_1, say, is simply expressible in terms of polar coordinates about one of the nuclei one may determine the potential due to this distribution.[17] Multiplying by f_2 and integrating in polar or elliptic coordinates, as may be necessary, these integrals are also found in terms of A's and B's. If neither f_1 nor f_2 has a simple potential it is usually desirable to make use of Neumann's expansion of $1/r_{12}$ in elliptic coordinates.

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\infty} D_{\tau}{}^{\nu} P_{\tau}{}^{\nu} \binom{\lambda_2}{\lambda_1} Q_{\tau}{}^{\nu} \binom{\lambda_1}{\lambda_2} P_{\tau}{}^{\nu}(\mu_1) P_{\tau}{}^{\nu}(\mu_2) \cos \nu(\varphi_1 - \varphi_2) \quad \begin{matrix} \lambda_1 > \lambda_2 \\ \lambda_2 > \lambda_1 \end{matrix},$$

$$D_{\tau}{}^0 = 2\tau+1, \qquad D_{\tau}{}^{\nu} = (-1)^{\nu} 2(2\tau+1)[(\tau-\nu)!/(\tau+\nu)!]^2, \qquad \text{for } \nu > 0.$$

Integration of f_1 and f_2 with each term of the series gives a quantity expressible in terms of functions defined above. The higher terms of the resulting series often vanish identically, but this does not happen when, for instance, exponential factors in μ appear in both f_1 and f_2. The convergence with increasing τ of the infinite series has in the cases met in this investigation been adequate, though in one case an inconvenient number of terms had to be computed.

The integrals required in the work with H.-L. type functions are not reproduced here; some of them are to be found elsewhere in the literature.[5, 7, 8] The integrals entering the variational treatment of the problem follow. Arguments are omitted where no confusion will result.

$$\gamma_1 = R\delta_1; \qquad \kappa = (\gamma_1 + \gamma_2)/2.$$

$$J_{mj} = (\pi\delta_1{}^3)^{\frac{1}{2}}(R^3/4)\{A_{m+2}(\kappa)B_j(\gamma_1/2) - A_m(\kappa)B_{j+2}(\gamma_1/2)\},$$

$$J_{mj, nk} = \delta((-1)^{j+k}, 1)\frac{\pi R^3}{2}\left\{\frac{A_{m+n+2}(\gamma_2)}{j+k+1} - \frac{A_{m+n}(\gamma_2)}{j+k+3}\right\},$$

$$\int s(1, 1)f(mj, 1)(1/r_1)dv_1 = (\pi\delta_1{}^3)^{\frac{1}{2}}(R^2/2)\{A_{m+1}(\kappa)B_j(\gamma_1/2) - A_m(\kappa)B_{j+1}(\gamma_1/2)\},$$

$$\int s'(1, 1)f(mj, 1)(1/r_1)dv_1 = (\pi\delta_1{}^3)^{\frac{1}{2}}(R^2/2)\{A_{m+1}(\kappa)B_j(-\gamma_1/2) - A_m(\kappa)B_{j+1}(-\gamma_1/2)\},$$

$$\int f(mj, 1)f(nk, 1)(1/r_1)dv_1 = \pi R^2\left\{\frac{A_{m+n+1}(\gamma_2)}{j+k+1}\delta((-1)^{j+k}, 1) - \frac{A_{m+n}(\gamma_2)}{j+k+2}\delta((-1)^{j+k}, -1)\right\},$$

$$\int f(mj, 1)\nabla_1{}^2 s(1, 1)dv_1 = \delta_1{}^2 J_{mj} - R\gamma_1(\pi\delta_1{}^3)^{\frac{1}{2}}\{A_{m+1}(\kappa)B_j(\gamma_1/2) - A_m(\kappa)B_{j+1}(\gamma_1/2)\},$$

$$\int f(mj, 1)\nabla_1{}^2 f(nk, 1)dv_1 = 2\pi R\{[k(k-1)/(j+k-1)]A_{m+n}(\gamma_2) + [1/(j+k+1)]$$
$$\times[-n(n-1)A_{m+n-2}(\gamma_2) + n\gamma_2 A_{m+n-1}(\gamma_2) + (n(n+1) - k(k+1) - (\gamma_2/2)^2)A_{m+n}(\gamma_2)$$
$$- (n+1)\gamma_2 A_{m+n+1}(\gamma_2) + (\gamma_2/2)^2 A_{m+n+2}(\gamma_2)]\}\delta((-1)^{j+k}, 1),$$

$$\int s^2(1, 1)(1/r_{12})s(1, 2)f(mj, 2)dv_{12}$$

$$= \int s(1, 1)f(mj, 1)(1/r_1)dv_1 - (\pi\delta_1{}^3)^{\frac{1}{2}}(R^2/2)\{(\gamma_1/2)(A_{m+2}(\gamma_1 + \kappa)B_j(3\gamma_1/2) - A_m B_{j+2})$$
$$+ A_{m+1}B_j - A_m B_{j+1}\},$$

[17] Jeans, *Electricity and Magnetism*, Fifth Edition, p. 224.

$$\int s^2(1, 1)(1/r_{12})s'(1, 2)f(mj, 2)dv_{12}$$

$$= \int s'(1, 1)f(mj, 1)(1/r_1)dv_1 - (\pi\delta_1{}^3)^{\frac{1}{2}}(R^2/2)\{(\gamma_1/2)(A_{m+2}(\gamma_1+\kappa)B_j(\gamma_1/2) - A_m B_{j+2})$$
$$+ A_{m+1}B_j - A_m B_{j+1}\},$$

$$\int s(1, 1)s'(1, 1)(1/r_{12})s(1, 2)f(mj, 2)dv_{12}$$

$$= (\pi\delta_1{}^3)^{\frac{1}{2}}(\gamma_1{}^3R^2/8)\{R_0{}^0G_0{}^j(\gamma_1/2)H_0(2, \gamma_1, m+2, \kappa) - R_0{}^0G_0{}^{j+2}H_0(2, m) - R_0{}^2G_0{}^jH_0(0, m+2)$$
$$+ R_0{}^2G_0{}^{j+2}H_0(0, m) - 5R_2{}^2G_2{}^jH_2(0, m+2) + 5R_2{}^2G_2{}^{j+2}H_2(0, m)\},$$

$$\int s^2(1, 1)(1/r_{12})f(mj, 2)f(nk, 2)dv_{12}$$

$$= \int f(mj, 1)f(nk, 1)(1/r_1)dv_1 - (\pi R^2/2)\{(\gamma_1/2)(A_{m+n+2}(2\kappa)B_{j+k}(\gamma_1) - A_{m+n}B_{j+k+2})$$
$$+ A_{m+n+1}B_{j+k} - A_{m+n}B_{j+k+1}\},$$

$$\int s(1, 1)s'(1, 1)(1/r_{12})f(mj, 2)f(nk, 2)dv_{12}$$

$$= (\pi R^2\gamma_1{}^3/8)\{R_0{}^0R_0{}^{j+k}H_0(2, \gamma_1, m+n+2, \gamma_2) - R_0{}^2R_0{}^{j+k}H_0(0, m+n+2)$$
$$- R_0{}^0R_0{}^{j+k+2}H_0(2, m+n) + R_0{}^2R_0{}^{j+k+2}H_0(0, m+n) - 5R_2{}^2R_2{}^{j+k}H_2(0, m+n+2)$$
$$+ 5R_2{}^2R_2{}^{j+k+2}H_2(0, m+n)\},$$

$$\int s(1, 1)f(mj, 1)(1/r_{12})\binom{s(1, 2)}{s'(1, 2)}f(nk, 2)dv_{12}$$

$$= \frac{\pi R^2\gamma_1{}^3}{8}\sum_{\tau=0}^{\infty}\binom{1}{(-1)^{k+\tau}}(2\tau+1)\{G_\tau{}^j(\gamma_1/2)G_\tau{}^k(\gamma_1/2)H_\tau(m+2, \kappa, n+2, \kappa)$$
$$- G_\tau{}^jG_\tau{}^{k+2}H_\tau(m+2, n) - G_\tau{}^{j+2}G_\tau{}^kH_\tau(m, n+2) + G_\tau{}^{j+2}G_\tau{}^{k+2}H_\tau(m, n)\},$$

$$\int s(1, 1)f(m_1j_1, 1)(1/r_{12})f(m_2j_2, 2)f(n_2k_2, 2)dv_{12}$$

$$= \frac{(\pi\delta_1)^{\frac{1}{2}}R^5}{8}\sum_{\tau=0}^{i_2+k_2+2}(2\tau+1)\{G_\tau{}^i(\gamma_1/2)R_\tau{}^{i_2+k_2}H_\tau(m_1+2, \kappa, m_2+n_2+2, \gamma_2) - G_\tau{}^{j_1}R_\tau{}^{i_2+k_2+2}$$

$$\times H_\tau(m_1+2, m_2+n_2) - G_\tau{}^{j_1+2}R_\tau{}^{i_2+k_2}H_\tau(m_1, m_2+n_2+2) + G_\tau{}^{j_1+2}R_\tau{}^{i_2+k_2+2}H_\tau(m_1, m_2+n_2)\},$$

$$\int f(m_1j_1, 1)f(n_1k_1, 1)(1/r_{12})f(m_2j_2, 2)f(n_2k_2, 2)dv_{12}$$

$$= (\pi^2R^5/8)\sum_\tau(2\tau+1)\{R_\tau{}^{j_1+k_1}R_\tau{}^{i_2+k_2}H_\tau(m_1+n_1+2, \gamma_2, m_2+n_2+2, \gamma_2) - R_\tau{}^{j_1+k_1}R_\tau{}^{i_2+k_2+2}$$
$$\times H_\tau(m_1+n_1+2, m_2+n_2) - R_\tau{}^{j_1+k_1+2}R_\tau{}^{i_2+k_2}H_\tau(m_1+n_1, m_2+n_2+2)$$
$$+ R_\tau{}^{j_1+k_1+2}R_\tau{}^{i_2+k_2+2}H_\tau(m_1+n_1, m_2+n_2)\}.$$