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# Wave Mechanical Treatment of the Molecule $\text{Li}_2^+$

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The  $\text{Li}_2^+$  molecule has been treated by methods previously applied to the study of  $\text{Li}_2$  by the writer. It appears that the dissociation energy of  $\text{Li}_2^+$  must be greater than that of  $\text{Li}_2$ , and is probably  $1.30 \pm 0.05$  e.v. The ratio of one- to two-electron bond strengths appears to be greater with  $\text{Li}_2$  than with  $\text{H}_2$  because the bonding wave functions are more diffuse. The inner shells play a deterring role in the binding in  $\text{Li}_2^+$  similar to that found in  $\text{Li}_2$ . The Heitler-

London wave function has been compared with the much more accurate series function, and the general character of the satisfactory molecular orbital is noted. The form of the variational process used here appears to be particularly suitable for the treatment of one-electron bonds, and simple functions may be used to give highly satisfactory results, as illustrated by the cases of  $\text{Li}_2^+$  and  $\text{H}_2^+$ .

## I. INTRODUCTION

IN this paper it is proposed to extend to the discussion of  $\text{Li}_2^+$ , as a typical simple molecule involving a one-electron bond, the methods previously used by the writer in the treatment of the closely related molecule  $\text{Li}_2$ .<sup>1</sup> Though there seems to be no experimental data on this molecule, the lack of it is not a serious hindrance to the discussion, which is to be concerned principally with the more general questions of the value of the available methods for treating such molecules, the nature of satisfactory but simple molecular orbital functions, and the effect of the inner shells on the properties of the system. There is also internal evidence which may lead one to have considerable confidence in the quantitative significance of the results given by one method.

## II. METHODS

For the quantitative treatment of molecules there are at present available four methods. Of these, the statistical method using the Fermi-Thomas field<sup>2</sup> is restricted in applicability to those cases in which the essential properties of the molecule are dependent on the presence of a fairly large number of electrons; it seems hardly worth while to apply it to so simple a system as  $\text{Li}_2^+$ , or indeed to any case in which there is a single bonding electron.

The Hund-Mulliken<sup>3</sup> method, that of representing the binding electrons by means of molecular orbitals constructed as linear combinations of atomic orbitals, gives in the case of  $\text{Li}_2^+$  the same molecular function as the Heitler-London<sup>4</sup> method, as applied by Slater.<sup>5</sup> Using for the atomic orbitals functions of the type suggested by Slater,<sup>6</sup> one obtains in either case the wave function

$$\psi = \frac{1}{C} \begin{vmatrix} s(1\alpha, 1) & s'(1\alpha, 1) & s(1\beta, 1) & s'(1\beta, 1) & s(2\alpha, 1) + s'(2\alpha, 1) \\ s(1\alpha, 2) & & & & \vdots \\ \vdots & & & & \vdots \\ s(1\alpha, 5) & \cdot & \cdot & \cdot & s(2\alpha, 5) + s'(2\alpha, 5) \end{vmatrix}.$$

$$\text{Here } s(1\alpha, 1) = [(2\delta_1)^3/4\pi \cdot 2!]^{1/2} e^{-\delta_1 r_1} \delta(\alpha/\sigma_1), \quad s(2\alpha, 1) = [(2\delta_2)^5/4\pi 4!]^{1/2} r_1 e^{-\delta_2 r_1} \delta(\alpha/\sigma_1),$$

$r_1$  being the distance from electron 1 to nucleus A, while  $\delta(\alpha/\sigma_1)$  is the spin function and takes

the values 1 or 0 as the spin of electron 1 is  $\alpha$  or  $\beta$ .  $s'(1\alpha, 1)$  and  $s'(2\alpha, 1)$ , respectively, have

<sup>1</sup> H. M. James, *J. Chem. Phys.* **2**, 794 (1934), hereafter referred to as I.

<sup>2</sup> F. Hund, *Zeits. f. Physik* **77**, 12 (1932).

<sup>3</sup> F. Hund, *Zeits. f. Physik* **73**, 1 (1931). R. S. Mulliken, *Phys. Rev.* **40**, 55 (1932), and subsequent papers.

<sup>4</sup> W. Heitler and F. London, *Zeits. f. Physik* **44**, 455 (1927).

<sup>5</sup> J. C. Slater, *Phys. Rev.* **38**, 1109 (1931).

<sup>6</sup> J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

similar forms in terms of  $s_1$ , the distance from electron 1 to nucleus  $B$ .

Finally, one may apply the variational method, a particularly convenient form of which has been employed in the treatment of  $H_2^+$  and  $Li_2$ . The wave function which has been used is  $\psi = \sum_m C_m \psi_m$ , where  $\psi_m$  is like the unnormalized Heitler-London function, except that  $s(2\alpha, 1) + s'(2\alpha, 1)$  is replaced by  $f(mj\alpha, 1)$ .

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

Here  $\lambda_1$  and  $\mu_1$  are the elliptic coordinates of the electron in a coordinate system with the nuclei at the foci, and  $\gamma_2$  is a parameter independent of  $m$  and  $j$ . Only terms with even  $j$  need be included in the series, since the wave function is known to be symmetric to reflection in the midplane between the nuclei. With a fixed value for  $\gamma_2$ ,  $\psi$  is made the best available approximation to the correct wave function by so choosing the parameters  $C_m$  as to make the energy associated with  $\psi$  a minimum. Thus, instead of representing the binding electron by the function  $s(2\alpha, 1) + s'(2\alpha, 1)$  (known to be a good approximation for large separations of the atoms) one uses  $\sum_m C_m f(mj\alpha, 1)$ , which in practice may be made exceedingly flexible and resembles in form the known solutions of the  $H_2^+$  problem for the internuclear distances which are of interest.

The methods used in working with these functions have been described in references 1 and 7. In fact,  $J_{M_1 J_1, M_2 J_2}$  and  $X_{M_1 J_1, M_2 J_2}$ , as defined for the treatment of  $Li_2$  in Eqs. (34) and (45) of the first of these papers, are the elements of the unity and energy matrices, respectively, needed for the variational treatment of  $Li_2^+$ . All the work necessary for the treatment of  $Li_2^+$  by this method, except for the variation of the constants  $C_m$ , was thus carried out in the normal course of the investigation of  $Li_2$ .

### III. RESULTS

The computations were all carried out for a single separation of the nuclei, chosen to be 2.98 atomic units (a.u.), principally because for this distance all the desired material was avail-

able from previous computations. This nuclear separation is 12 percent greater than that for which the minimum of the  $Li_2$  potential curve is found, and may be expected to be approximately the equilibrium distance for  $Li_2^+$ .

#### 1. Variational treatment

This computation was carried out with  $\gamma_2=4$ , a value chosen as probably suitable for  $Li_2$ . The computed values for the molecular energy were reduced to terms of binding energy by subtracting the energy of  $Li+Li^+$ , as computed by Wilson.<sup>8</sup> This energy is essentially the best which can be found for these atoms with the inner shell functions used in this work and a function for the outer electron which is independent of the position of the inner electrons; it is thus the lowest energy which could be given by a function of the character of our  $\psi$  when the nuclei are separated indefinitely.

The complete function was built up by adding one term at a time. The binding energy found after the addition of each term is given below in electron volts.

The first term was	$\psi_{00}$	giving	-0.49 e.v.
Add	$\psi_{02}$	to get	-1.116 e.v.,
then successively	$\psi_{10}$	to get	-1.143 e.v.,
	$\psi_{04}$		-1.195 e.v.,
	$\psi_{12}$		-1.221 e.v.,
	$\psi_{20}$		-1.242 e.v.,
	$\psi_{22}$		-1.242 e.v.,
and finally	$\psi_{14}$	to get	-1.243 e.v.

The improvement obtainable by adding terms involving higher powers of  $\lambda$  seems to be very small. Excluding terms with  $j=4$ , one obtains with the terms in  $\lambda^0$  a binding energy of -1.116 e.v. Adding terms in  $\lambda$  depresses this by 0.043 e.v. to -1.159 e.v. Adding terms in  $\lambda^2$  further lowers the result by 0.013 e.v. to -1.172 e.v. In view of the small importance of  $\psi_{14}$  it appears that one may expect a further improvement of only  $\sim 0.005$  e.v. from the indefinite continuation of this process. Similarly, the terms in  $\mu^0$  above gave a binding energy of -0.592 e.v. Addition of the terms in  $\mu$  depresses this to -1.172 e.v., an improvement of 0.542 e.v., while further addition of  $\mu^2$  terms yields -1.243 e.v., down 0.071 e.v. It appears, then, that 0.03 e.v. would be a sufficient allowance for

<sup>7</sup> H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933).

<sup>8</sup> E. B. Wilson, Jr., J. Chem. Phys. 1, 210 (1933).

convergence in all directions, and that we may safely take  $-1.27 \pm 0.02$  as the limiting result.

The best six-term wave function was found to be  $0.049274\psi_{00} - 0.087484\psi_{02} + 0.043777\psi_{10} + 0.051630\psi_{12} - 0.013152\psi_{20} - 0.069219\psi_{04}$ , giving a binding energy of  $-1.242$  e.v.

## 2. Heitler-London and related treatments

The Heitler-London treatment of  $\text{Li}_2^+$  was carried through without other approximations than those inherent in the derivation of the wave function given above and the choice of  $\delta_1$  and  $\delta_2$  as 2.6875 and 0.672, respectively. These values were chosen for reasons given in I, the argument for the use of the relatively higher value of  $\delta_2$  being perhaps stronger for  $\text{Li}_2^+$  than for  $\text{Li}_2$ . The binding energy found was  $-0.304$  e.v., the energy taken for the separated atoms being that computed by using the limiting form of the molecular function, lying 0.047 e.v. above that obtained by Wilson.

Replacement of the complete Hamiltonian operator by the "interaction operator," as described in I, changed the computed binding energy by  $-0.014$  e.v. With  $\text{Li}_2$  at the same nuclear separation the result was a change of  $-0.032$  e.v. in the binding energy. The approximate 1:2 ratio of these effects indicates the essential correctness of the assumption made in I, that the error associated with the use of this operator comes principally from the neglect of the overlapping of one atomic function with that part of the other where the electrons are likely to approach each other (i.e., for this case, the inner shell). Such an error would be reduced by 1/2 on removal of one of the outer electrons, while the error associated with the incorrectness of the outer electron function should almost vanish.

Omission of the inner shell functions further lowers the computed binding energy by 0.402 e.v. to  $-0.720$  e.v. With this is to be compared the 0.587 e.v. found for  $\text{Li}_2$  at this nuclear separation as the effect of the inner shells. As in that case, the important terms involving the inner shells may be associated with transitions of an electron from the outer shell of one atom to the inner shell of the other; their net effect is, however, rather larger than one would expect from a survey of the results with the neutral molecule.

## IV. DISCUSSION

The result of the variational treatment of  $\text{Li}_2^+$  definitely indicates that the dissociation energy of the molecule is at least 1.25 e.v. Further, the situation is such that even more definite significance seems to be attached to the result. The essential coordinates which had to be omitted in the treatment of the problem were all associated with the inner shell electrons. The error in the convergence limit for the computed binding energy as a measure of the actual binding energy may then all be associated with the use of approximate inner shell functions and the neglect of polarization effects between the inner and outer electrons. Since both of these errors must be expected to be small<sup>9</sup> one may safely assume for this computation a higher degree of accuracy than was obtained with  $\text{Li}_2$ , and that the dissociation energy of  $\text{Li}_2^+$  will differ essentially from 1.27 e.v. only as the equilibrium distance differs from 3A. Further, even if the computed point lies several tenths of an Angstrom unit from the minimum of the potential curve that minimum would lie only a few hundredths of an e.v. below the value found here. Thus one may confidently expect the dissociation energy of  $\text{Li}_2^+$  to be  $1.30 \pm 0.05$  e.v.

This value is somewhat greater than that for  $\text{Li}_2$  (1.12 e.v.) contrary to the prediction of Pauling,<sup>10</sup> who, in the course of a discussion of the conditions for the stability of the one-electron bond, estimated that  $\text{Li}_2^+$  would have a dissociation energy about two-thirds as great as that of  $\text{Li}_2$ . This estimate was made by reference to the situation with  $\text{H}_2^+$  and  $\text{H}_2$ , considered to be analogous systems. It is thus of interest to see

<sup>9</sup> Computations on the Li atom by Dr. A. S. Coolidge and the writer, as yet unpublished, show that essentially the same ionization energy (to 0.01 e.v.) is found whether one employs the inner shell functions used in this work, or much more accurate ones. A similar lack of influence of the form of the inner shell functions on the computed binding energy is to be anticipated. Further, with Li the modification of the wave function to take account of polarization effects will increase the computed ionization energy by about 0.05 e.v. One may expect the importance of these effects to be somewhat greater in the molecule  $\text{Li}_2^+$ , where two inner shells are involved, but hardly by a factor of 2. Introduction of this further degree of flexibility into both atomic and molecular ion functions will thus probably increase the computed dissociation energy of  $\text{Li}_2^+$ , but by less than 0.05 e.v.

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

to what degree one can associate this unexpected result with the most obvious difference between the pairs of systems, the presence of inner shells in the one pair. The inner shells are apparently involved in the production of a repulsion; the observed binding may be considered to be the resultant of the binding of the outer electrons and this repulsive effect. Since the inner shell repulsion in  $\text{Li}_2$  is greater than that in  $\text{Li}_2^+$  the outer electron bonds, which may be taken as the proper quantities for comparison, are more nearly in the ratio 3 : 2 than are the total binding energies.

Taking for the inner shell repulsions the values obtained with the Heitler-London method, one gets for the outer electron binding  $-1.95$  e.v. in the case of  $\text{Li}_2$ ,  $-1.7$  e.v. in the case of  $\text{Li}_2^+$ . Though the correction for the inner shells has thus improved the situation, it is still distinctly at variance with expectation. One can only bring the outer electron bond ratio to 3 : 2 by assuming that the Heitler-London method gives a marked underestimate of the inner shell repulsions, or that its behavior in the treatment of the two problems is very different. It seems most reasonable to assume that the Heitler-London method gives here, as elsewhere, an overestimate of repulsive effects. Taking this overestimate as one by 50 percent in the case of  $\text{Li}_2$  (an assumption which was found to bring the Heitler-London treatments of  $\text{H}_2$  and  $\text{Li}_2$  into satisfactory parallelism) and by 100 percent in the case of  $\text{Li}_2^+$  (since the method is less competent to deal with this problem), the outer electron binding is found to be  $-1.7$  e.v. for  $\text{Li}_2$ ,  $-1.5$  e.v. for  $\text{Li}_2^+$ . It thus seems clear that with Li atoms the one-electron bond must be relatively stronger than with H atoms, even when inner shell effects are excluded. This may be associated with the greater diffuseness of the bonding electron function in the atom (weaker intraatomic forces associated with the 2s character of the electron), the perturbing forces in the ionic molecule causing a greater rearrangement of the charge density toward the center of the molecule, where it is effective in producing binding.<sup>11</sup>

<sup>11</sup> With  $\text{H}_2^+$  at its equilibrium distance the Heitler-London method gives a charge density at the center of the molecule which is in error by a factor of less than 2,

In view of the relatively high ratio for the strengths of one- and two-electron bonds with Na and K atoms, and the probably smaller inner shell effect in the ionic molecules, one must expect  $\text{Na}_2^+$  and  $\text{K}_2^+$  to have higher dissociation energies than  $\text{Na}_2$  and  $\text{K}_2$ , respectively.

As in the work on  $\text{Li}_2$ , the Heitler-London and Hund-Mulliken methods do not give acceptable results, the computed binding energy being less than one-fourth of that given by the variational method. There is, of course, little reason to expect these methods to be at all satisfactory when interatomic fields of the magnitude of those in  $\text{Li}_2^+$  are present. Indeed, so poor an approximation is the Heitler-London function that each of two of the terms entering the series function is itself a distinctly better approximation to the correct function,  $\psi_{00}$  giving a binding energy of  $-0.49$  e.v.,  $\psi_{10}$  a binding energy of  $-0.57$  e.v.

A comparison of the charge distributions associated with the Heitler-London and series functions is interesting in showing the way in which the first of these is inaccurate, and in indicating the general character of a satisfactory molecular orbital. By the use of the well-known property of determinants, that to any row (or column) any multiple of another row (or column) may be added without changing the value of the determinant, each wave function may be given the form

$$\psi = \frac{1}{\sqrt{5!}} \begin{vmatrix} f_1(1) & \cdots & f_5(1) \\ \vdots & & \vdots \\ f_1(5) & \cdots & f_5(5) \end{vmatrix},$$

where  $f_n$  is normalized and orthogonal to all other  $f$ 's. Integrating  $\psi^2$  over the coordinates of electrons 2, 3, 4, 5, one obtains

$$\sum_{\text{spins}} \int \psi^2 dv_2, \dots, v_5 = \frac{1}{5} (f_1^2(1) + f_2^2(1) + f_3^2(1) + f_4^2(1) + f_5^2(1))$$

as the chance of finding electron 1 at a given point in space, taking no account of its spin or the positions of the other electrons. That is, there is one chance in 5 of finding electron 1 in

while at a corresponding distance in  $\text{Li}_2^+$  the error is one of a factor of 4.

the charge distribution associated with each of the five orbitals. Just the same result must apply for each electron, and the charge density for the entire molecule is simply a superposition of the charge densities associated with the various orbitals.  $\rho = f_1^2 + f_2^2 + f_3^2 + f_4^2 + f_5^2$ .  $\rho$  is, of course, invariant to linear transformations of the  $f$ 's which maintain their orthogonality, possessing a uniqueness of character which the  $f$ 's lack.

Now, in the case under consideration the functions  $\psi$  and  $\psi'$  which are to be compared may be expressed in terms of four common  $f$ 's, referring to the inner shells, and characteristic  $f$ 's, which we call  $f_s$  and  $f'_s$ , respectively. The difference between  $\rho$  and  $\rho'$  is then precisely the difference between  $f_s^2$  and  $f'_s{}^2$ . Further, each  $\rho$  is obtained by adding to the corresponding  $f_s^2$  the charge distribution (to terms in  $[\int s(1\alpha, 1)s'(1\alpha, 1)dv_1]^2$ ) of the two inner shells, treated separately. We are thus justified in considering the  $f_s$ 's as being significant not only for a comparison of the  $\rho$ 's, but also as indicating the nature of the molecular orbitals for the binding electron in each case.

In Table I will be found the values of the charge densities for the binding electron at various distances from the center of the molecule, measured along a line perpendicular to the internuclear axis, while in Table II are to be found similar values for points along the axis of the molecule. A nucleus is at the point 2.79 a.u. along this line. The sign (—) following a value indicates that it is the square of a negative value of  $f_s$ .

Perhaps the most striking difference in the charge distribution is to be found near the center of the molecule, where the charge density given by the Heitler-London function is only a fourth of that given by the series function. We observe with this latter function a considerably greater tendency for the charge to collect near the internuclear axis, between the nuclei. The Heitler-London function, on the other hand, places a considerable amount of charge on this axis outside of the nuclei, while the series function gives there a charge density which is exceedingly small. In the immediate neighborhood of the nuclei the Heitler-London function likewise gives much the larger density of charge, though

TABLE I.  $f_s^2$  at distance  $s$  from center of molecule along midaxial perpendicular.

$s$ (a.u.)	Series function	H.-L. function	$s$ (a.u.)	Series function	H.-L. function
0	0.01397	0.00363	3.83	0.00098	0.00077
0.89	0.01169	0.00333	4.17	.00065	.00059
1.27	.00977	.00304	4.50	.00043	.00045
1.85	.00678	.00249	4.83	.00029	.00035
2.31	.00467	.00202	5.46	.00012	.00020
2.73	.00319	.00161	6.08	.00005	.00011
3.12	.00217	.00127	6.69	.00002	.00006
3.48	.00146	.00099			

TABLE II.  $f_s^2$  at distance  $s$  from center of molecule along nuclear axis.

$s$ (a.u.)	Series function	H.-L. function	$s$ (a.u.)	Series function	H.-L. function
0	0.01397	0.00363	3.62	0.00080 (—)	0.00002
.27	.01383	.00361	3.90	.00012 (—)	.00068
.55	.01336	.00353	4.18	0	.00125
.83	.01247	.00336	4.46	.00001	.00150
1.11	.01099	.00301	4.74	.00002	.00151
1.39	.00873	.00237	5.02	.00004	.00140
1.67	.00560	.00133	5.30	.00004	.00123
1.95	.00194	.00016	5.58	.00004	.00104
2.23	.00006 (—)	.00124 (—)	6.14	.00003	.00070
2.51	.00965 (—)	.01708 (—)	6.69		.00045
2.79	.06884 (—)	.10540 (—)	7.25	.00001	.00028
3.07	.01655 (—)	.01776 (—)	7.81		.00016
3.34	.00385 (—)	.00163 (—)	8.37		.00010

the volume affected is so small that probably only a small fraction of the charge is involved in each case.

It is the particular advantage of the form of the variational treatment we have used that the most effective factor in controlling the general character of the wave function is the exponential  $e^{-\delta\lambda}$ ; it is thus especially suited for the construction of wave functions which concentrate the charge between the nuclei. It has been noted how a single term of this type which does not depend on  $\mu$ , such as  $\lambda^n e^{-\delta\lambda}$ , can give relatively satisfactory results with  $\text{Li}_2^+$ . As a further example we may mention that with the function  $\psi = ce^{-\delta\lambda}$  one obtains for  $\text{H}_2^+$  with a nuclear separation of 2 a.u. (approximately the equilibrium distance) a binding energy of  $-2.16$  e.v., in error by 0.62 e.v. This is a much more satisfactory result than that given by the Heitler-London method, and quite near the result of Finkelstein and Horowitz,<sup>12</sup> who varied the exponential parameter in a Heitler-London type function. Such a function, however, gives a charge density which is the same at all points on the axis between the nuclei, and is thus re-

<sup>12</sup> B. N. Finkelstein and G. E. Horowitz, *Zeits. f. Physik* **48**, 118 (1928).

stricted in its usefulness to relatively small internuclear distances.

The variation of the parameter  $\delta$  is a very simple matter when only one electron is present, but in the more general case where one wishes to keep fixed the part of the function referring to other electrons it may be decidedly tedious. In such cases, in the absence of empirical rules or other information concerning the proper value of  $\delta$ , it would probably be more convenient to use a series function involving several powers of  $\lambda$ , keeping  $\delta$  fixed and varying the linear parameters. If it were then desired to reduce the function to a more simple analytical form, it could be plotted and fitted approximately with a single term having an appropriate  $\delta$ .

A more satisfactory, but still very simple molecular orbital may be constructed by taking some account of the dependence of the function on  $\mu$ , as well as  $\lambda$ . As noted above, a function of the form  $e^{-\delta\lambda}(1+c\mu^2)$  has given with  $\text{Li}_2^+$  a binding energy of  $-1.116$  e.v., in satisfactory agreement with the limiting value of  $\sim -1.27$  e.v., and this without any attempt having been made to vary  $\delta$ . (It seems probable, however, that the choice of  $\delta$  was a rather fortunate one.) With  $\text{H}_2^+$  in the configuration considered above the corresponding result was a binding energy of  $-2.772$  e.v., in error by only 0.005 e.v. This highly satisfactory result was obtained with the normalized function  $e^{-1.35\lambda}(1.218+0.545\mu^2)$ . Such a function is much more easily handled than the equally accurate one of Guillemin and Zener,<sup>13</sup> since it possesses only one exponential parameter, as compared with the two used by them. It is,

of course, not so well adapted to the treatment of molecules for very large separations of the nuclei, but its range of applicability is obviously much greater than that of the function  $ce^{-\delta\lambda}$ . As in the case of that function, a variation of the parameter  $\delta$  may be avoided by the introduction of terms in several powers of  $\lambda$ , followed by the fitting to the resulting function of a simpler one with  $\delta$  properly adjusted.

This form of the variational method might be conveniently applied in conjunction with the statistical method of treating molecules,<sup>14</sup> and it possesses the advantage that one could avoid the use of an approximation to the statistical field in which an electron is to be considered as moving.

It is suggested that the function  $\lambda^n e^{-\delta\lambda}(1+c_1\mu+c_2\mu^2)$  may be of general usefulness as a simple but satisfactory form for molecular orbitals when the atoms involved are of not too different size, and that a program for the determination of rules concerning the proper magnitude for  $\delta$  would be of value. The use of orbitals of this form in molecular computations would be open to several objections which apply generally to computations with molecular orbitals—particularly that the wave functions tend to give too much importance to polar states of nonpolar molecules. This can be avoided only by the introduction and independent adjustment of terms in the function which depend on the position of two or more electrons, which will introduce an unsatisfactory but apparently unavoidable complexity into the treatment of molecules which do not have a particularly simple structure.

<sup>13</sup> V. Guillemin, Jr. and C. Zener, *Proc. Nat. Acad. Sci.* **15**, 314 (1929).

<sup>14</sup> A. Recknagel, *Zeits. f. Physik* **87**, 375 (1934).