

COMPLETE SET EXPANSIONS FOR MOLECULAR WAVE FUNCTIONS

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Received October 5, 1960

The wave functions for the $1s\sigma_g$, $2s\sigma_g$ and $3d\sigma_g$ states of H_2^+ have been expanded in terms of two complete sets of spherical functions, one centered on each atom. No serious difficulty was caused by overcompleteness, and excellent representations of the energies and wave functions were obtained.

Before it is possible to perform accurate calculations on small molecules, it will be necessary to find quick and efficient methods for the representation of electron-nucleus and electron-electron distribution functions. Such progress can only be expected if the basic functions used for the representation are members of a suitable complete set. Several complete sets of spherical functions are known which might be suitable for the representation of electron-nucleus distribution functions, but the simple substitution of one of these sets for, say, the hydrogen-like set in the normal l.c.a.o. treatment of H_2^+ can be expected to lead to difficulties due to overcompleteness. In principle, the wave function for H_2^+ can be expanded using only one complete set: if two complete sets are used, one of them is superfluous and the system of secular equations becomes insoluble.¹ However, the expansion of the wave function of H_2^+ in terms of only one set is very disappointing,² largely because it is difficult to reproduce the singularities at the two nuclei in terms of sums of smooth functions. On the other hand, using only the first two members of a complete set centered on each nucleus, a far better representation of H_2^+ is obtained³ than the equivalent treatment using the first ten hydrogen atom functions.⁴ It will be shown in this paper that by generalizing this treatment, an almost exact description of the H_2^+ system can be obtained before overcompleteness becomes a serious handicap.

The L.C.M.O. Method Using Epstein Functions.—The general method of calculation is essentially that used by us before⁴ in which a tenth order secular determinant was constructed by a program written for the Manchester University Mark I Computer. The substitution of the functions

$$\begin{aligned} \phi_i &= \chi_{nl}(x)Y_l(\theta) \\ &= \left[\frac{(n-l-1)!}{2n(n+l)!} \right]^{\frac{1}{2}} \cdot \left(\frac{2Z}{a_0} \right)^3 \cdot \frac{2l+1}{2} \cdot \frac{1}{2\pi} \left[\left(\frac{2Zr}{a_0} \right)^l L_{n+l}^{2l+1} \left(\frac{2Zr}{a_0} \right) P_l^0(\cos \theta) \cdot e^{-\frac{Zr}{a_0}} \right] \\ &[n = 1, 2, 3, 4; l = 0 \dots (n-1); (m = 0)] \end{aligned}$$

for the hydrogen-like set was actually a considerable simplification of the original program. There is, however, one slight complication in that, while any member of the set is orthogonal to most of the other members, it is not orthogonal to adjacent functions having the same value of l ; the relevant relations were given by Hylleraas⁵ as follows (with $x = 2Zr/a_0$)

$$\int_0^\infty \chi_{ni}^2(x) x^2 dx = 1 \quad (a)$$

$$\int_0^\infty \chi_{nl}(x) \chi_{(n \pm 1)l}(x) x^2 dx = 0 \text{ for } j = 2, 3, 4, \dots \quad (b)$$

$$\int_0^\infty \chi_{nl}(x) \chi_{(n+1)l}(x) x^2 dx = -\frac{1}{2} \left[\left(1 - \frac{l}{n} \right) \left(1 + \frac{l}{n+1} \right) \right]^{1/2} \quad (c)$$

$$\int_0^\infty \chi_{ni}^2(x) x dx = 1/2n \quad (d)$$

$$\int_0^\infty \chi_{nl}(x) \chi_{(n \pm 1)l}(x) x dx = 0 \text{ for all } j \neq 0 \quad (e)$$

As before, we define ten molecular orbitals as

$$\Phi_i = (2 + 2\xi_{ii})^{-1/2} (\phi_i^a + p_i \phi_i^b), \quad i = 0, 1 \dots 9$$

where p_i is the parity (± 1) of the wave function ϕ_i , and ξ_{ii} is the overlap integral between ϕ_i^a centered on atom A and $p_i \phi_i^b$ centered on atom B. We then write the total wave function for the system as

$$\Psi = \sum_{i=0}^9 c_i \Phi_i = \sum_{i=0}^9 c_i (2 + 2\xi_{ii})^{-1/2} (\phi_i^a + p_i \phi_i^b)$$

Minimizing the energy with respect to the coefficients c_i leads to the tenth order secular determinant $|H_{ij} - S_{ij}E| = 0$. The matrix ele-

(5) E. A. Hylleraas, *Z. Physik*, 48, 469 (1928).

(1) P.-O. Lowdin, *Advances in Phys.*, 5, 1 (1956); *Advances in Chem. Phys.*, 2, 207 (1959); *Ann. Rev. Phys. Chem.*, 11, 107 (1960).

(2) K. M. Howell and H. Shull, *J. Chem. Phys.*, 30, 627 (1959).

(3) B. F. Gray, Ph.D. Thesis, Manchester, 1957.

(4) B. F. Gray, H. O. Pritchard and F. H. Sumner, *J. Chem. Soc.*, 2631 (1956).

ments H_{ij} and S_{ij} may then be obtained, remembering that the ϕ_i are not eigenfunctions of a hydrogen-like Hamiltonian, but satisfy the equation

$$\mathcal{H}'\phi_i = \epsilon_i'\phi_i \text{ where } \mathcal{H}' = -\frac{1}{2}\nabla^2 - \frac{nZe^2}{r}$$

Thus

$$S_{ij} = 2(2 + 2\xi_{ii})^{-1/2}(2 + 2\xi_{jj})^{-1/2}(\xi_{ij} + \omega_{ij})$$

and

$$H_{ij} = 2(2 + 2\xi_{ii})^{-1/2}(2 + 2\xi_{jj})^{-1/2}[(\xi_{ij} + \omega_{ij})(\epsilon_j' + e^2/R) - e^2(J_{ij} + K_{ij}) + (Zn_j - 1)e^2(L_{ij} + K_{ji})]$$

where e is the electronic charge, R is the internuclear separation, ϵ_j' is the eigenvalue of ϕ_j for the Hamiltonian \mathcal{H}' , $\xi_{ij} = p_j \int \phi_i^a \phi_j^b d\tau$

$$\omega_{ij} = \int \phi_i^a \phi_j^a d\tau, J_{ij} = \int \phi_i^a \phi_j^a r_b^{-1} d\tau,$$

$$K_{ij} = p_j \int \phi_i^a \phi_j^b r_a^{-1} d\tau \text{ and } L_{ij} = \int \phi_i^a \phi_j^a r_a^{-1} d\tau$$

From the relations d and e given above $L_{ij} = Z/n_j$ atomic units if $i = j$ and zero otherwise; similarly, ω_{ij} may be written down from relations a , b and c . A further simplification is possible because $\epsilon_j' = Z^2 n_j^2 \epsilon_j$ where ϵ_j is the eigenvalue of ϕ_j with $Zn_j = 1$, and since ϵ_j is $(n_j)^{-2}$ times the ionization potential of hydrogen, $\epsilon_j' = -Z^2/2$ atomic units. This makes the relation between K_{ij} and K_{ji} very simple, *i.e.*

$$K_{ji} = \frac{n_i}{n_j} K_{ij}$$

Solution of the Secular Equations.—The calculations were performed initially for $Z = 1.0$ and $Z = 1.25$, at an internuclear separation of $R = 2a_0$, but because of the approach to overcompleteness, we were unable to solve either of the resulting secular determinants with the programs which then existed for dealing with this problem.⁶ Furthermore, as it was only a matter of weeks before the Mark I computer was to be dismantled, we decided to construct secular determinants for as large a range of Z as possible, and evaluate them later on the Mercury machine with which it was replaced. Unfortunately, we thought that the energy maximum of the $1s$ hydrogen-like function at $Z = 1.228$ would probably dominate throughout the calculation, with the result that we covered the range $Z = 1.0$ to $Z = 1.4$; however, although excellent representations of $1s\sigma_g$, $2s\sigma_g$ and $3d\sigma_g$ states were obtained, our chosen range of Z did not span the best value for any of these three states.

The first solutions were obtained by substituting trial values of E in the secular determinant, until a value was found for which the determinant vanished; the determinants were well-behaved functions of E and there was no difficulty. The coefficients c_i were then found by solving sets of simultaneous equations; this will be called method 1.

Subsequently, a more accurate version of our original Mark I matrix program became available. (The set of equations $|\mathcal{H} - SE| = 0$ was transformed to a new set $|\mathcal{S}^{-1}\mathcal{H} - IE| = 0$ by inverting the matrix \mathcal{S} ; $\mathcal{S}^{-1}\mathcal{H}$, being unsymmetrical, was solved by the Lanczos procedure—method 2a). The eigenvalues for the bound states obtained using

this program were identical with those from method 1, but the corresponding eigenvectors looked significantly different. Nevertheless, both sets of vectors were found to be equally acceptable solutions for the problem, and both corresponded to wave functions of equal numerical magnitude. There are two reasons why this might happen. One is that the system is so nearly overcomplete that a whole range of wave functions is more or less equally acceptable and the one found is that most favored by the particular combination of rounding errors. The other is that our original basic set of functions is not an orthogonal set, and again depending on the accumulation of rounding errors, the wave function can be equally well represented to within the accuracy of the calculation by several different combinations of these non-orthogonal functions; in a sense, this also is overcompleteness. This point will be discussed further below.

Overcompleteness causes the determinant of the overlap matrix to vanish.⁷ In the present calculations the magnitude of these determinants is about 10^{-6} ; we have therefore written a new program (method 2b) which is not only faster, but minimizes the difficulties caused by the overlap matrices being nearly singular. A real symmetric matrix \mathbf{S} can be resolved into the product of two triangular matrices,⁸ *i.e.*, $\mathbf{S} = \mathbf{L}\mathbf{U}$ where \mathbf{L} is the transpose of \mathbf{U} ; the determinants of \mathbf{L} and \mathbf{U} are now of the order 10^{-3} . Using this fact, the set of equations $(\mathcal{H} - SE)c_i = 0$ can be transformed into $(L^{-1}HU^{-1} - IE)c_i = 0$ where $\mathbf{x}_i = \mathbf{U}c_i$ (the c_i of course being normalized such that $\mathbf{c}_i\mathbf{S}\mathbf{c}_i = 1$); the new matrix is symmetric and can be solved by the very much faster Givens method. Unfortunately, in the formation of the matrix product $L^{-1}HU^{-1}$ there is severe cancellation which necessitates the use of double-length arithmetic, not only in the formation of this product, but also in the formation of \mathbf{L} and \mathbf{L}^{-1} . This limitation was unexpected, but even so method 2b is still considerably faster than method 2a, *e.g.*, for these tenth order sets, the computing times are 1.5 and 8 minutes, respectively. The new method is also more accurate, for although both methods produced identical values for the negative roots (these are accurate solutions of $|\mathcal{H} - SE| = 0$ to 8 significant figures), it gives better values for the largest positive roots.

Numerical Results

Table I compares the energies of the $1s\sigma_g$ state of H_2^+ given by various approximations (also listed are the exact solution, two sets of data for hydrogen-like functions, and results obtained using orthogonalized orbitals). It can be seen that as soon as the function $n = 2, l = 0$ is included, the energy becomes almost independent of Z , but there is a general tendency for the energy to improve as Z increases. The tenth order approximation for

(7) H. Margenau and G. M. Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand, New York, N. Y., 1943, p. 130.

(8) (a) R. A. Brooker, *Brit. J. Appl. Phys.*, **4**, 321 (1953); V. N. Faddeeva, "Computational Methods of Linear Algebra," Dover, New York, N. Y., 1959, p. 81. (b) Provided that the elements on the main diagonal are large compared to the other elements, as is always so in these calculations, the triangular matrices will always be real.

TABLE I
 (-) TOTAL ELECTRONIC ENERGY OF THE $1s\sigma_g$ STATE OF H_2^+ IN RYDBERG UNITS AT $R = 2a_0$

Z	Last function added									
	$n = 1, l = 0$	$n = 2, l = 0$	$n = 2, l = 1$	$n = 3, l = 0$	$n = 3, l = 1$	$n = 3, l = 2$	$n = 4, l = 0$	$n = 4, l = 1$	$n = 4, l = 2$	$n = 4, l = 3$
Hydrogen-like set										
1.0	2.107543	2.127838	2.127951	2.132933	2.133715	2.135466	2.136267	2.137636	2.140021	2.140098
1.25	2.172865	2.174286	2.182012	2.182826	2.183068	2.192879	2.193007	2.193952	1.197533	2.197661
Complete set										
1.0	2.107543	2.178321	2.196446	2.196875	2.202938	2.203073	2.203549	2.204534	2.204699	2.204700
1.05	2.132135	2.177150	2.197983	2.197999	2.203221	2.203397	2.204029	2.204710	2.204857	2.204857
1.10	2.150932	2.175539	2.198626	2.199177	2.203499	2.203723	2.204389	2.204819	2.204977	2.204978
1.15	2.163978	2.174109	2.198902	2.200326	2.203763	2.204042	2.204638	2.204896	2.205064	2.205065
1.20	2.171290	2.173223	2.199157	2.201376	2.203994	2.204334	2.204817	2.204951	2.205122	2.205123
1.25	2.172865	2.173029	2.199579	2.202279	2.204176	2.204582	2.204928	2.204989	2.205160	2.205162
1.30	2.168677	2.173510	2.200229	2.203009	2.204301	2.204775	2.204996	2.205018	2.205184	2.205 _g 87
1.35	2.158688	2.174540	2.201080	2.203564	2.204373	2.204913	2.205038	2.205042	2.205200	2.205203
1.40	2.142849	2.175932	2.202044	2.203955	2.204401	2.205005	2.205065	2.205065	2.205210	2.205214
Orthogonalized orbitals										
	1 term	2 terms	3 terms	4 terms	5 terms	6 terms	7 terms	8 terms	9 terms	10 terms
1.40	1.199633	1.253628	1.972751	1.984449	2.086714	2.088267	2.095059	2.181467	2.205164	2.205214
										Exact soln.
										2.20525

$Z = 1.4$ is within $0.00004I_H$ of the correct solution, and it seems likely that with a higher value of Z , this discrepancy might easily be halved. It is noted in passing that the best energy for a $1s(Z)$ function is about $2.173I_H$, not $2.166I_H$ as given by Finkelstein and Horowitz⁹; their derivation of the optimal value of Z is correct, but they did not carry sufficient terms in their energy expansion.

As soon as two or three functions (depending on the value of Z) are included, approximations to the $2s\sigma_g$ state begin to appear, and after a further two functions are added, the $3d\sigma_g$ state appears; the tenth order solutions for the energies of these two states are given in Table II. In both these sets of

TABLE II

(-) TOTAL ELECTRONIC ENERGY OF THE $2s\sigma_g$ AND $3d\sigma_g$ STATES OF H_2^+ IN RYDBERG UNITS AT $R = 2a_0$		
Z	$2s\sigma_g$	$3d\sigma_g$
Hydrogen-like set		
1.0	0.65734	0.45198
1.25	0.71034	0.45781
Complete set		
1.40	0.69935	0.40390
1.35	.70591	.41602
1.30	.71106	.42683
1.25	.71494	.43634
1.20	.71770	.44458
1.15	.71955	.45160
1.10	.72067	.45749
1.05	.72125	.46208
1.0	.72151	.46566
Exact solution		
	0.72173	0.47155

results, the trend with Z is opposite to that for the ground state; the energy of the higher of the two states is varying more rapidly and clearly the best value of Z for this state is considerably less than 1.

(9) B. N. Finkelstein and G. E. Horowitz, *Z. Physik*, **48**, 118 (1928).

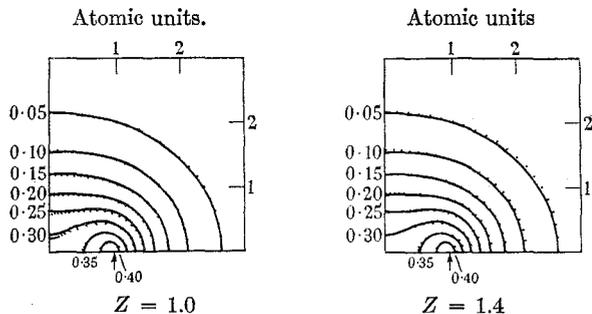


Fig. 1.—Comparison of the exact wave function for the $1s\sigma_g$ state of H_2^+ (taken from Bates, Ledsham and Stewart¹⁰) with the $Z = 1.0$ and $Z = 1.4$ complete-set approximations. (The exact wave function is reproduced by kind permission of the Royal Society.)

It would appear, therefore, that for an intermediate number of functions, the proper value of Z to use in these calculations is near η/n where η is the effective charge of the united atom and n is the quantum number of the corresponding united atom state: thus we should use $Z \approx 2$ for $1s\sigma_g$, $Z \approx 1$ for $2s\sigma_g$ and $Z \approx 2/3$ for $3d\sigma_g$.

Two alternative forms of truncation of the set were investigated to see if simpler calculations are likely to be of any value. In one case, only the $l = 0$ functions were taken: the results for $n = 1$ and $n = 1, 2$ are given in the first two columns of Table I; for $n = 1, 2, 3$ and $n = 1, 2, 3, 4$, the energy values were $2.180 \pm 0.001I_H$ and $2.1812 \pm 0.0002I_H$, respectively, virtually independent of Z . In the other case, only the functions without radial nodes were considered, i.e., $l = (n - 1)$; here, the maximum near $Z = 1.25$ was maintained, and for $n = 1, 2, 3, 4$, the energy value was $2.2040I_H$, which is about as good as the best 4-function representation in Table I. This form of truncation is equivalent to the use of Slater orbitals, but omitting the quantum number from the exponent, and as it would involve a great deal less labor, the convergence properties would merit further investigation, especially for approximate treatments.

TABLE III
COMPLETE-SET EXPANSIONS FOR H_2^+ WAVE FUNCTIONS

	$n = 1,$ $l = 0$	$n = 2,$ $l = 0$	$n = 2,$ $l = 1$	$n = 3,$ $l = 0$	$n = 3,$ $l = 1$	$n = 3,$ $l = 2$	$n = 4,$ $l = 0$	$n = 4,$ $l = 1$	$n = 4,$ $l = 2$	$n = 4,$ $l = 3$
1s σ_g state, $Z = 1.4$										
$(1 + \xi r)$	1.389995	1.639177	1.100740	1.609275	0.703473	1.063676	1.604595	0.660456	1.358266	1.016951
c_i (method 2b)	0.841401	-0.120382	0.128523	-0.014904	-0.009119	0.034439	-0.002295	-0.003538	0.005239	0.008172
2s σ_g state, $Z = 1.0$										
$(1 + \xi r)$	1.586453	1.730811	0.774441	1.737685	0.547593	1.321797	1.729284	0.474727	1.492124	0.705623
c_i (method 2b)	0.131117	0.693794	0.229268	-0.404426	0.012573	0.073721	0.066110	-0.008398	0.016481	0.011170
3d σ_g state, $Z = 1.0$										
c_i (method 2b)	0.644444	-0.167654	-1.086649	-0.179637	0.651507	0.120453	0.120182	-0.196341	-0.070844	0.005729

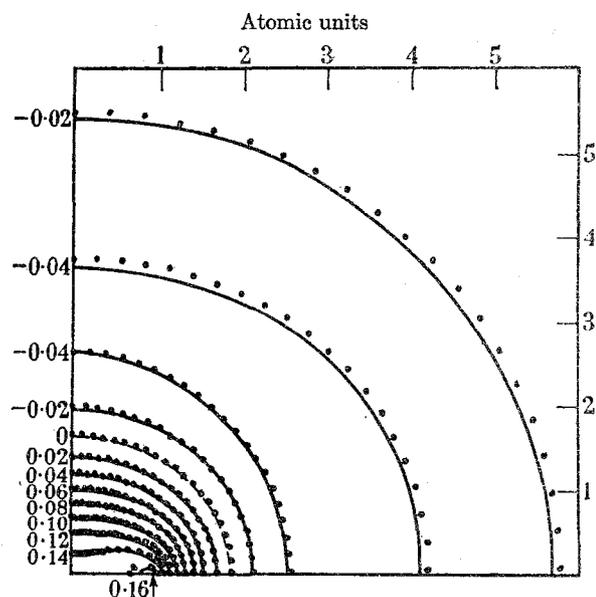


Fig. 2.—Comparison of the exact wave function for the 2s σ_g state of H_2^+ (taken from Bates, Ledsham and Stewart¹⁰) with the $Z = 1.0$ complete-set approximation. (The exact wave function is reproduced by kind permission of the Royal Society.)

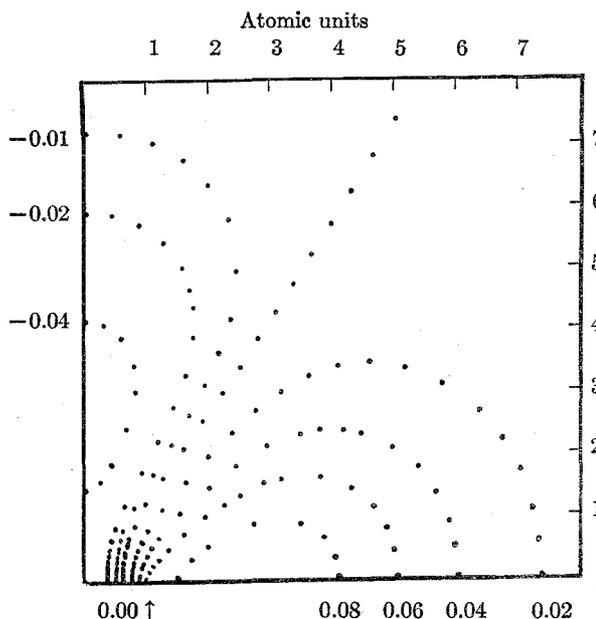


Fig. 3.— $Z = 1.0$ complete-set approximation to the wave function of the 3d σ_g state of H_2^+ .

The wave functions obtained for the 1s σ_g ($Z = 1.4$), 2s σ_g ($Z = 1$) and 3d σ_g ($Z = 1$) approximations

are given in Table III; they were also plotted out in the form of contour diagrams using the Manchester University Graphical Output, and are shown in Figs. 1, 2 and 3, respectively. Diagrams of the exact wave functions for the 1s σ_g and 2s σ_g states have been given already by Bates, Ledsham and Stewart¹⁰ and as our approximate wave functions are very similar, we have superimposed our own contour maps on photographs of their exact functions. In Fig. 1, both the approximations for $Z = 1$ and $Z = 1.4$ are compared with the exact function. It can be seen that whilst the $Z = 1.4$ function agrees reasonably with the exact function over the whole region of space, the $Z = 1$ function differs significantly near the center of the bond, despite the fact that it corresponds to an energy which is only 0.00055 I_H in error. It appears that if an unsuitable value of Z is chosen, then the truncated function cannot be made to fit satisfactorily over the whole of space, and as the more remote regions are more heavily weighted in the calculation, the function is forced to fit best at large distances. If, however, Z is chosen to be near η/n , the function automatically behaves correctly at large distances, and therefore stands a much better chance of spanning the central regions satisfactorily.

The Problem of Overcompleteness.—The question as to whether or not the ill-conditioning of our system of equations is due to overcompleteness was decided in the following way. The eigenvalues λ_k and eigenvectors x_k of the overlap matrix S were first obtained. A matrix K was then constructed such that each row consisted of an eigenvector x_k of S , the rows being written from top to bottom in descending order of the eigenvalues λ_k . The secular determinant was then transformed from $(H - SE)$ to $(KH\bar{K} - KSK\bar{E}) \equiv (KH\bar{K} - \lambda E)$ and the eigenvalues of this set of equations were determined for all orders from one to ten. The ground-state eigenvalues are listed in Table I under the heading of orthogonalized orbitals; at least five orbitals are needed before the system is bonding, and eight are required before the energy is better than a simple 1s function of the same value of Z . It is found that the difference in energy between the use of the nine functions ($x_0 \dots x_8$) and the ten functions ($x_0 \dots x_9$) is an order of magnitude greater than the difference between the original ninth and tenth order approximations: the same is true for the

(10) D. R. Bates, K. Ledsham and A. I. Stewart, *Phil. Trans. Roy. Soc. (London)*, **A146**, 215 (1953).

$2s\sigma_g$ state, and for the $3d\sigma_g$ state, the discrepancy is more than two orders of magnitude. Thus it is clear that when only the first ten members of the set are used, there is no redundancy, even though each member of the set is used twice.

We conclude that using the simple l.c.m.o. procedure, as we have done, overcompleteness is likely to become troublesome if many more than ten functions are used. However, by that time, with a suitable choice of Z for each individual state, it is possible to reproduce both the energy and the wave function to a degree of accuracy which will be sufficient for most purposes, and the wave functions obtained in this way will certainly be easier to manipulate than the exact functions. Should greater accuracy be required, we can see no obvious reason why a few more members of the set should not be included and any resulting redundancy removed by an orthogonalization procedure such as that just described; it may however be necessary to compute the basic integrals to an accuracy of better than the 1 part in 10^8 which we have used.

We wish to acknowledge our indebtedness to Dr. B. F. Gray for his collaboration in the early stages of this work and to Mr. W. B. Brown and

Mr. D. J. Evans for many discussions; also to Professor D. R. Bates, F. R. S. for permission to use his published contour maps in the construction of Fig. 1 and 2.

Appendix

The matrix elements for the hydrogen-like set, arbitrary Z , are given below. The functions are eigenfunctions of the operator

$$\mathcal{H}\epsilon'' = -\frac{1}{2}\nabla^2 - \frac{Ze^2}{r}$$

with $\epsilon_i'' = Z^2\epsilon_i$ where ϵ_i corresponds to $Z =$
Thus

$$S_{ij} = 2(2 + 2\xi_{ii})^{-1/2} (2 + 2\xi_{jj})^{-1/2} (\xi_{ij} + \delta_{ij})$$

and

$$H_{ij} = 2(2 + 2\xi_{ii})^{-1/2} (2 + 2\xi_{jj})^{-1/2} [(\xi_{ij} + \delta_{ij})(\epsilon_i'' + e^2/R) - e^2(J_{ij} + K_{ij}) + (Z - 1)e^2(L_{ij} + K_{ji})]$$

where $\delta_{ij} = 1$ if $i = j$, or $= 0$ if $i \neq j$, and the other symbols have their previous meaning; the relation between K_{ij} and K_{ji} is

$$Ze^2K_{ji} = Ze^2K_{ij} + (\xi_{ij} + \delta_{ij})(\epsilon_i'' - \epsilon_j'')$$

L_{ij} now occurs between all pairs of ϕ_i and ϕ_j having the same l -quantum number.