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518. *Hybridization in the Ground State of the Hydrogen Molecule-ion.*

By B. F. Gray, H. O. Pritchard, and F. H. Sumner.

Calculations have been made on an automatic machine to determine the best representation of the ground state of the hydrogen molecule-ion in terms of a linear combination of the ten hydrogen-atom wave functions 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, 4*s*, 4*p*, 4*d*, 4*f*. An error in some earlier calculations has been noted and we have found that, if the effective value of Z is maintained at unity, the best function gives only about 75% of the experimental dissociation energy. With the inclusion of a single value of Z as a variation parameter, it is possible to get a close approximation to the true dissociation energy.

A feature of the calculation is that the necessary two-centre integrals were, for the most part, evaluated in an analytical fashion by the machine.

It was stated by Pritchard and Skinner[1] that in the hydrogen molecule-ion the best 1*s*–2*p* hybrid, without variation in Z from the value unity, had a dissociation energy almost equal to that obtained by Dickinson;[2] also that the calculated bond length for this state was too small and the calculated force constant too large. It has been suggested that this surprising result was caused by a lack of orthogonality between the 1*s*–1*s* and 2*p*–2*p* molecular wave functions used,[3] but unfortunately it was due to the erroneous assumption that a particular integral in the energy expression could be equated to zero. In fact, the inclusion of higher quantum states does not lead to a very marked improvement in the calculated energy unless one allows a variation in the value of Z.

The Nature of the Calculation.—We may consider hybridization in the hydrogen molecule-ion in two different ways: as the sharing of the electron between a hybridized atomic orbital on atom A with a similar orbital on atom B, *i.e.*, we form a molecular orbital by overlapping two LCAO atomic wave functions; or as a linear combination of a number of simple LCAO molecular-orbital representations of various states of the system. In this particular case the two methods are equivalent, and we use the LCMO description as it is considerably easier to handle.

Let $\phi^a{}_0 \ldots . \phi^a{}_9$, $\phi^b{}_0 \ldots \phi^b{}_9$ be the exact 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, 4*s*, 4*p*, 4*d*, 4*f* hydrogen-atom wave functions centred respectively on atoms A and B. Confining ourselves to $\sum$ states of the system, we need only consider, where a choice exists, those wave functions having a maximum along the line of centres A—B, as wave functions of other symmetries do not contribute to the energy of these $\sum$ states. We define the ten molecular orbitals as:

$$\Phi_{ii} = (2 + 2\xi_{ii})^{-\frac{1}{2}}(\phi^a{}_i + \phi^b{}_i),\ i = 0,\ 1, \ldots .\ 9$$

and the total wave function for the system as:

$$\Psi = \sum_{i=0}^{9} c_i \Phi_{ii} = \sum_{i=0}^{9} c_i (2 + 2\xi_{ii})^{-\frac{1}{2}}(\phi^a{}_i + \phi^b{}_i)$$

Minimizing the energy with respect to the coefficients c_i leads to the tenth-order secular determinant:

$$|D_{ij}| = |H_{ij} - S_{ij}E| = 0$$

there are ten eigenvalues of this equation corresponding to the energies of ten $\sum$ states of the hydrogen molecule-ion, and ten orthogonal eigenvectors giving the values of the coefficients c_i associated with each of these levels.

The elements of $|D_{ij}|$ may readily be shown to be

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

and

$$H_{ij} = 2(2 + 2\xi_{ii})^{-\frac{1}{2}}(2 + 2\xi_{jj})^{-\frac{1}{2}}[(\xi_{ij} + \delta_{ij})(I_j + \mathbf{e}^2/R) - \mathbf{e}^2(K_{ij} + J_{ij})]$$

where the symbols have the significance: $\mathbf{e}$ = the electronic charge, R = the internuclear separation, I_j = the ionization potential of a hydrogen atom in state ϕ_j, $\xi_{ij} = \int \phi^a{}_i \phi^b{}_j \mathrm{d}\tau$ for all values of i, j, δ_{ij} = zero ($i \neq j$) or unity ($i = j$), $K_{ij} = \int \frac{\phi^a{}_i \phi^b{}_j}{r_a} \mathrm{d}\tau$ and $J_{ij} = \int \frac{\phi^a{}_i \phi^b{}_j}{r_b} \mathrm{d}\tau$, r_a and r_b being the distance of the electron from nucleus A or B. Since H is Hermitian, $H_{ji} = H_{ij}$, but the K integrals are not independent of the order of the subscripts; the compensation is achieved through the I term, I_j being taken with K_{ij} and I_i with K_{ji}.

It was in the evaluation of the H_{ij} ($i \neq j$) terms that the error arose in the previous work[1] as only the terms $\int \phi^a{}_i H \phi^b{}_j \mathrm{d}\tau$ and $\int \phi^a{}_j H \phi^b{}_i \mathrm{d}\tau$ were considered, the other two $\int \phi^a{}_i H \phi^a{}_j \mathrm{d}\tau$ and $\int \phi^b{}_i H \phi^b{}_j \mathrm{d}\tau$ being neglected. Detailed corrections have not been evaluated because we feel that the verification of Pauling's bond-strength criterion, based upon the magnitude of the angular part of the wave function, is no longer a vital issue in theoretical chemistry. However, the extent of the error in the 1*s*–2*p* case is clear from the results which are presented below.

The Method of Calculation.—The complete calculation was carried out automatically at a series of internuclear distances in the range $2a_0$—$2{\cdot}8a_0$. At each value of R, the machine evaluated the integrals ξ_{ij}, J_{ij}, and K_{ij} and manipulated them to form the required quantities S_{ij} and H_{ij} according to the formulæ given above. The 165 values of the integrals, together with the 55 resulting values each of S_{ij} and H_{ij} were printed out for checking; the machine time up to this stage was about 70 minutes. After the determinant had been set up from S_{ij} and H_{ij}, the eigenvalues and eigenvectors were determined in a relatively short time by programmes that have already been described.[4]

The mechanical calculation of the two-centre integrals ξ_{ij}, J_{ij}, and K_{ij} presents an interesting and difficult problem. Straightforward numerical integration on the scale involved in this problem is out of the question; to obtain two-dimensional integrals to the required accuracy would necessitate the evaluation of each function at several hundreds (or even thousands) of points before quadrature formulæ could be applied. This would be too time-consuming. We therefore devised a programme for the machine to perform the calculation in the same way as a human calculator would.

To facilitate transformation into elliptical co-ordinates, the wave functions were recast in terms of the variables r and $r \cos \theta$, *i.e.* :

$$\phi_i = (\text{numerical const.})(\mathrm{e}^{-r/N})(\text{polynomial in } r,\ r\cos\theta)$$

A set of storage locations was assigned to each of the ten orbitals, the most complicated one (4*s*) requiring eight 20-digit lines. The orbitals were stored in the following way : one line each for the value of the principal quantum number N and for the number of terms in the polynomial; a pair of lines for the numerical coefficient and one line each for each term in the polynomial. Terms in the polynomial were stored in the form : 5 digits for the exponent of r; 5 digits for the exponent of $r \cos \theta$; and 10 digits for the numerical coefficient and its sign. To calculate an overlap integral ξ_{ij}, the orbital ϕ_i was identified with atom A and ϕ_j with B; thus, when the transformations $u = (r_a + r_b)/R$ and $v = (r_a - r_b)/R$ were used, the exponents were regarded as operating on $\frac{1}{2}R(u + v)$ and $\frac{1}{2}R(1 + uv)$ for $\phi^a{}_i$ and on $\frac{1}{2}R(u - v)$ and $\frac{1}{2}R(1 - uv)$ for $\phi^b{}_j$. The integral ξ_{ij} was then given by :

$$2\pi \times \text{constant} \int_{-1}^{+1} \int_{1}^{\infty} (\tfrac{1}{2}R)^{w+x+y+z}(u+v)^w(1+uv)^x(u-v)^y(1-uv)^z \\ (\tfrac{1}{2}R)^3(u+v)(u-v)\mathrm{e}^{-Rut_1}\mathrm{e}^{-Rvt_2}\mathrm{d}u\,\mathrm{d}v$$

the terms $(\frac{1}{2}R)^3(u + v)(u - v)$ arising from the expression for the volume element in elliptical co-ordinates, and t_1 and t_2 depend on Z, N_i, and N_j; the factor 2π comes from the integration with respect to the angle about the line of centres.

The maximum value of w, x, y, or z occurring in the calculation was 3, and it was thus a simple matter to store in the machine, in the same way as the polynomial parts of the orbitals, two tables of u–v polynomials, one corresponding to all possible combinations of $(w + 1)$ and $(y + 1)$, and the other for all possible combinations of x and z. By use of these tables, therefore, the integral reduces to a series of terms all of the general form :

$$\text{Constant} \int_{-1}^{+1} \int_{1}^{\infty} v^m u^n \mathrm{e}^{-Rvt_2}\mathrm{e}^{-Rut_1}\mathrm{d}u\,\mathrm{d}v$$

At this stage a human calculator would collect together like terms in u and v to produce a single polynomial, but this is not a process that is worthwhile in calculation on the machine; he would then proceed to integrate the function, first with respect to v between the limits $-1 \leqslant v \leqslant 1$ and then with respect to u from $1 \leqslant u \leqslant \infty$ to obtain a power series in the argument R which he would then evaluate numerically for the various values of R. Mechanically, however, it is much faster to resort to numerical methods one stage earlier. Hence, before the calculation of the series of integrals ξ_{ij}, J_{ij}, and K_{ij} for any given R was begun, the programme constructed a master table of values of the integrals :

$$\int_{-1}^{+1} v^m \mathrm{e}^{-Rvt_2} \mathrm{d}v = \frac{m\,!}{(Rt_2)^{m+1}} \left[\mathrm{e}^{Rt_2} \sum_{k=0}^{m} \frac{(-Rt_2)^k}{k\,!} - \mathrm{e}^{-Rt_2} \sum_{k=0}^{m} \frac{(Rt_2)^k}{k\,!} \right]$$

and

$$\int_{1}^{\infty} u^n \mathrm{e}^{-Rut_1} \mathrm{d}u = \frac{n\,!\,\mathrm{e}^{-Rt_1}}{(Rt_1)^{n+1}} \sum_{k=0}^{n} \frac{(Rt_1)^k}{k\,!}$$

for that particular value of R, for each possible pair of values of t_1 and t_2, and for each possible value of m and n that would occur in the u–v polynomials; there were ten possible pairs of t_1 and t_2 which determined the number of values of m and n, the maximum values being eight in the present calculation. Returning to the calculation of a specific integral ξ_{ij}, the machine would then consider each term of the u–v polynomial in turn, multiplying together its own numerical coefficient and the two correct items from the master table of integrals, and adding the result to a running total; when every term had been added in, the result was multiplied by the correct power of $(\frac{1}{2}R)$ and the numerical constant to give the value of ξ_{ij} which was stored for future use, and also printed out for checking purposes.

The other two types of integrals were treated similarly : in the case of the K_{ij} integrals, it was only necessary to reduce w and $(w + 1)$ [the exponents of $(\frac{1}{2}R)$ and $(u + v)$] by one [*i.e.*, to divide by $r_a = \frac{1}{2}R(u + v)$] before repeating the calculation; for the J_{ij} integrals, both orbitals belong to the same atom (A) so that only terms in $(u + v)$ and $(1 + uv)$ occur, and dividing through by $r_b = \frac{1}{2}R(u - v)$ removes the $(u - v)$ term contributed by the volume element. In other words, J_{ij} and K_{ij} are treated only as special cases of the ξ_{ij} integrals.

This scheme worked very well for the simpler orbitals, but in the inter-4-quantum level ξ_{ij} integrals, values as large as 50 were printed out ! This was found to be due to a very rapid cancellation of significant digits in evaluation of the higher v integrals, so that some of the numbers used were meaningless. Without carrying double- or triple-length numbers, it is virtually impossible to overcome this difficulty, so it was decided to evaluate these particular integrals numerically. This was done using a 16-point Gaussian integration in the range $-1 \leqslant v \leqslant 1$, which gave answers of very high precision.

Even with this modification, errors occurred in the calculation of J_{3d3d}, J_{4d4d}, and probably also in J_{3d4d}. Since the same routine was used to calculate all 165 integrals, this could only be due to a chance cancellation of significant digits in the final answer; this conclusion was proved by putting all the integrals in the master table equal to unity when the correct value $(128R^{-1})$ for J_{3d3d} was obtained. The error in these J integrals ($\sim$10%) was not sufficient to affect significantly the calculated ground-state energy of the system, the only effect being to upset the hybridization coefficients. Consequently, we did not undertake the immense task of searching for the cancellation and correcting it, but instead we confine our detailed discussion to the effect of mixing *s*- and *p*-orbitals only.

RESULTS

The dissociation energies and bond lengths for a number of orbital combinations, together with the corresponding values of c_i are given in the Table. These values are for $Z = 1$ and it is obvious that the inclusion of still higher bound states* will never lead to the correct dissociation energy of 0·205 a.u. or bond length of $2{\cdot}0a_0$. The reason is that our wave function does not obey the correct boundary conditions : it should vanish at ∞ as e^{-2r} whereas the simple $Z = 1$ function vanishes roughly as e^{-r}; this causes the electron

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* The discrete hydrogen-atom wave functions do not form a complete set and the correct description will only be attained if continuum wave functions are included.[5] This is inconvenient, both practically and conceptually.

cloud to be on the average too far away from the two nuclei and the interaction energy will always, therefore, be too small.

The most interesting conclusion to be drawn from these results is that *s*-orbitals are more important than *p*-orbitals of the same quantum level. In particular this appears in the 2-quantum level where the addition of $2s$ to the $1s$ wave function leads to a significant improvement in the binding energy, but the subsequent addition of $2p$-character to the wave function has an almost insignificant effect. (The same is qualitatively true of *d*- and *f*-orbitals : the coefficients of $4d$ and $4f$ are successively less than $4p$, and their inclusion in the total wave function causes only a minute improvement in the binding energy.)

Approximation	Orbital coefficients							r_e	D_e
no.	$1s$	$2s$	$2p$	$3s$	$3p$	$4s$	$4p$	(in atomic units)	
1	1·0000	—	—	—	—	—	—	2·493	0·1297
2	1·0076	0·1014	—	—	—	—	—	2·394	0·1430
3	0·9975	0·1015	0·0157	—	—	—	—	2·406	0·1432
4	1·0096	0·1061	—	0·0447	—	—	—	2·368	0·1464
5	0·9371	0·1112	0·0398	0·0466	−0·0210	—	—	2·378	0·1471
6	1·0104	0·1078	—	0·0463	—	0·0269	—	2·357	0·1478
7	0·9926	0·1125	0·0350	0·0614	0·0121	0·0309	−0·0266	2·368	0·1487
							Actual values	2·00	0·205

The values of the coefficients all refer to a distance of $2{\cdot}4a_0$, since the character of the hybrid wave function does not vary significantly with small changes in distance. That some of the coefficients are greater than unity arises because they are associated with the series of orbitals Φ_{ii} which are not orthogonal to each other, so that the cross-products involving c_ic_j do not vanish.

In principle, the energies of nine orthogonal excited $\sum$ states can be obtained, but owing to the poorness of the above approximation they were not fully investigated. They are all highly unstable with respect to a hydrogen atom in its ground state, the first being built mainly from $2s$, the second from $2p$, and so on.

The energy of the ground state is very readily improved by allowing a variation in Z in the wave functions (but not in the actual charges of the two nuclei). A calculation similar to approximation no. 5 carried out at $R = 2{\cdot}0a_0$ and $Z = 1{\cdot}25$ gave orbital coefficients similar to those in the Table and a dissociation energy of 0·2004 a.u.; this is almost the same as the energy (0·2016 a.u.) obtained by Dickinson [2] by considering only $1s$ and $2p$, each orbital having a separate value of Z. We see that the physical interpretation of Dickinson's wave function in terms of " polarization " is not very convincing, (*a*) because the addition of $2p$ to the $1s$ wave function is no more effective than the addition of $2s$, and (*b*) because if we take enough orbitals, and vary Z from the chosen value of 1·25, we can obviously improve Dickinson's answer without inventing two values of Z. The variation of Z tends to rectify the fact that the wave function does not obey the boundary conditions at infinity by bringing the electron a little closer to the nuclei; in effect, what Dickinson has done is to choose a very effective non-linear combination of $1s$ and $2p$ orbitals which gives a good representation of the energy with a minimum of computational labour.

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THE UNIVERSITY, MANCHESTER.

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