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The Ground State of the Hydrogen Molecule¹

HUBERT M. JAMES AND ALBERT SPRAGUE COOLIDGE, *Harvard University*

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The method used by Hylleraas in treating the He atom has been extended to the H_2 molecule. The method consists of setting up a wave function as a series in the five variables required, electronic separation being introduced explicitly as one of the variables. The coefficients are then determined so as to produce the lowest energy. The energy found is within 0.03 v.e. of the most probable experimental value, while the form and location of the potential energy curve

for various internuclear distances agree with those deduced from spectra to within similar limits. The value of the function is computed for several configurations of the electrons, and compared with other approximations. Application of the method to other problems is discussed. A method is given for the numerical solution of secular equations of high degree.

INTRODUCTION

IN constructing an approximate wave function for the hydrogen molecule in its normal state (regarding the nuclei as fixed), one may follow several lines of attack. Heitler and London make use of the unchanged functions of the individual atoms, regarding the interatomic forces as small perturbations. In a molecule as close-coupled as H_2 this implied persistence of the identity of the individual atoms is quite unjustified, and the resulting wave function is a very poor approximation. In particular, it is inadequate in that it is a function of only four electronic coordinates, instead of the required five. Aside from convenience, the only advantage of the H-L scheme seems to be that it yields a result in which the energy of the molecule is represented as a sum of terms, some of which are just the energy of the separated normal atoms, so that these may be cancelled out and the remaining terms called "binding energy."

Several attempts have been made to improve the H-L method by grafting upon it the variation principle; the original atomic wave functions are modified by the introduction of one or two arbitrary parameters, which are then determined so as to give the lowest energy. Such schemes do give somewhat better results, but do not escape the essential shortcomings of the original method

—the implication of atomic individuality, and the omission of an essential coordinate. Indeed, they actually sacrifice the peculiar advantage of the pure perturbation method, since the unchanged atomic energy no longer appears in the result.

In view of the theoretical weakness and practical inadequacy of these methods, it seemed to us worth while to explore rather carefully a third possibility. Abandoning all concern with individual atoms, we have tried to build up from the ground a suitable molecular wave function, containing the full number of required coordinates. While guided by certain considerations of limiting forms of this function, we have placed our main reliance on the variation principle, introducing a large number of parameters to be determined by its use.

DISCUSSION OF METHOD

Concerning the true function, we know the following: The ground state being a Σ state, the function must have rotational symmetry about the nuclear axis; that is, it may contain only the difference between the azimuthal angles of the two electrons, and not either angle alone. It must be symmetrical in the two electrons and also in the nuclei. In those parts of phase-space corresponding to one electron at a large distance from the nuclei, the wave function should approximate the product of a H-like function for the distant electron and an H_2^+ -like function for the close electron. The last two conditions

¹ A preliminary notice appeared in *Phys. Rev.* **43**, 588 (1933). Some minor numerical inaccuracies in that notice have been corrected in the present paper.

Here λ is a Lagrangian multiplier, and the condition of compatibility is the secular equation

$$\begin{vmatrix} H_{11}-\lambda S_{11} & H_{12}-\lambda S_{12} & \cdots & H_{1s}-\lambda S_{1s} \\ H_{12}-\lambda S_{12} & H_{22}-\lambda S_{22} & \cdots & H_{2s}-\lambda S_{2s} \\ \cdot & \cdot & \cdot & \cdot \\ H_{1s}-\lambda S_{1s} & H_{2s}-\lambda S_{2s} & \cdots & H_{ss}-\lambda S_{ss} \end{vmatrix} = 0.$$

The H_{fg} and the S_{fg} are the matrix components of the Hamiltonian energy operator and of unity, respectively, between the f th and g th terms in the series, considered as numbered consecutively from 1 to s . Details of their computation, of the solution of the secular equation, and of the determination of the C 's will be reserved for the Appendix. As usual, the lowest of the s values of λ turns out to be the required minimum energy, and can be found without determining the C 's.

By way of finding out how many and which terms in the series would have to be used in order to get a good approximation for the wave function, we confined ourselves in the beginning to the equilibrium distance, $R=1.4$, and to $\delta=0.75$. It soon became apparent that the first few terms alone were capable of giving a far better energy value than any previously reported, and that incorporation of additional terms produced only rapidly diminishing improvements. In some cases, even terms involving low powers of the variables made such slight changes as to warrant leaving them out. Of course, the incorporation of each new term required the computation of its matrix elements with all the terms already in use and the solution of a new secular equation of higher degree. Strictly, a term should not be neglected until it had been tested in combination with all other terms. But it soon became clear that the improvement obtainable by any given term became progressively less important as the number of other terms present increased, so that we were justified in rejecting any term which at any stage in the building up of our function was found to produce a negligible improvement in the energy.

RESULTS

An idea of the results obtained is given in Table I, in which the energy at several stages is

TABLE I.

Function	Total energy atomic units	Binding energy electron-volts	Internuclear distance, Bohr radii
One term	-2.189	-2.56	1.40
5 terms	-2.33290	-4.507	1.40
11 terms	-2.34580	-4.682	1.40
13 terms	-2.34693	-4.697	1.40
Without r_{12}	-2.3154	-4.27	1.40
Heitler-London	-2.21	-2.9	1.40
Heitler-London	-2.24	-3.2	1.51
Wang	-2.278	-3.76	1.42
Rosen	-2.297	-4.02	1.416
Observed		-4.73 \pm 0.04	1.40

compared with that given by other methods, and with the observed value. The last is obtained by adding 0.27 v.e., the zero-point energy of the normal molecule, to the heat of dissociation, which is 4.46 ± 0.04 according to Richardson and Davidson,⁵ while Mulliken⁶ gives 4.44. Much of the table is copied from Rosen,⁷ who, however, seems to have neglected the zero-point energy in giving the observed value. The values in the last column are those for which the various functions (other than the series functions here presented) give their best results. They are sufficiently near $R=1.4$ for purposes of comparison, except the Heitler-London function, whose minimum energy lies at considerably greater R , so that it seems worth while to include also the energy given by this function at the true distance.

TABLE II.

Terms	Coefficients in normalized functions			
[00000]	1.69609	2.23779	2.29326	2.22350
[00020]		0.80483	1.19526	1.19279
[00110]		-0.27997	-0.49921	-0.45805
[10000]		-0.60985	-0.86693	-0.82767
[10200]			-0.13656	-0.17134
[10020]			-0.07214	-0.12101
[10110]			0.14330	0.12394
[20000]			0.06621	0.08323
[00001]		0.19917	0.33977	0.35076
[00021]				0.07090
[00111]			-0.03143	-0.01143
[10001]				-0.03987
[00002]			-0.02456	-0.01197

⁵ O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A123**, 466 (1929).

⁶ R. S. Mulliken, Rev. Mod. Phys. **4**, 78 (1932).

⁷ N. Rosen, Phys. Rev. **38**, 2099 (1931).

The terms used in the first four functions of Table I, together with their normalized coefficients, are given in Table II. It is interesting to note that the simple exponential wave function,

$$e^{-\delta(\lambda_1+\lambda_2)} \approx e^{-r_{1a}/2} \times e^{-r_{1b}/2} \times e^{-r_{2a}/2} \times e^{-r_{2b}/2}$$

already gives a binding energy comparable to that of the H-L function; indeed, by a suitable choice of δ the result can be made better, when for both functions $R=1.4$. In the energy thus calculated, there is nothing resembling the "exchange integrals" of the H-L treatment; this raises the question whether the importance of the "exchange terms," frequently assumed to represent the essential nature and magnitude of chemical binding, may not have been over-emphasized. The five-term function is offered as a practical compromise between simplicity and accuracy. The reason for including both 11- and 13-term functions is really accidental. Due to a mistake, we at first believed that the contributions from the terms [00021] and [10001] could be neglected, and we therefore took the 11 terms as a basis for investigating the effects of varying δ and R (discussed later). The results showed that in fact we had hit upon the best possible values of both. In going over the work, we discovered the mistake, and found that a slight improvement could be obtained by including the two given terms, and we therefore offer the 13-terms function as the best known approximation to the true wave function of H_2 . It did not seem worth while to repeat the variations of δ and R with this slightly different form of the function.

The energy given by the 13-term function is within the range fixed by experiment, but higher than the most probable value. It is beyond doubt that if still more terms were included, the result could be still further depressed. We have made a rather careful estimate of what could be gained in this way, reasoning by analogy from the contributions actually found from series of related terms; it seems safe to say that we have reached the limit of convergence within from 0.01 to 0.05 volt. The theoretical energy of the hydrogen bond is, then, 4.73 ± 0.02 volt, as compared with the experimental 4.73 ± 0.04 volt.

We found it possible to reach the value -4.27 with a combination of terms with $p=0$, and therefore not including r_{12} in the wave function.

(The coefficients were not determined in this case.) This is substantially the same as the value reported by Hylleraas⁸ as the best which he could obtain by an involved computation which he does not reproduce, and is probably close to the limit obtainable with wave functions in four coordinates.

It may be of interest to compare the magnitudes of some of the functions themselves, computed for various positions of the electrons, and to see how nearly they satisfy Schrödinger's equation. Table III shows values of ψ and of

TABLE III.

Coordinates						
r_{1a}	0.35	0.35	0.35	0.35	1.4	1.4
r_{1b}	1.4	1.4	1.4	1.4	1.4	1.4
r_{2a}	0.35	0.7	0.7	0.7	1.4	1.4
r_{2b}	1.75	0.7	1.4	1.4	1.4	1.4
r_{12}	0.525	0.7425	0.3556	1.0334	0	2.4249
$\varphi_1 - \varphi_2$	—	—	0°	180°	0°	180°
Values of ψ (normalized)						
H-L	0.0532	0.0849	0.0533	0.0533	0.0219	0.0219
Rosen	0.0702	0.1215	0.0710	0.0710	0.0249	0.0249
5-term	0.0798	0.1172	0.0698	0.0777	0.0162	0.0271
11-term	0.0783	0.1180	0.0667	0.0777	0.0130	0.0271
13-term	0.0769	0.1162	0.0656	0.0772	0.0142	0.0269
Values of $(H-E)\psi$, in 27.08 volts						
H-L	-0.0425	-0.0481	0.0460	-0.0522	0.0313/ ρ	-0.0052
Rosen	-0.0310	-0.0015	0.0879	-0.0429	0.0356/ ρ	-0.0038
5-term	0.0148	0.0093	0.0653	-0.0097	0.0102/ ρ	-0.0002
11-term	0.0117	0.0109	0.0356	-0.0060	-0.0034/ ρ	-0.0005
13-term	0.0055	0.0060	0.0269	-0.0021	0.0028/ ρ	-0.0009

$(H-E)\psi$, calculated in each case for $R=1.4$; the unit of energy is here (as in all our computations) 27.08 v.e., twice that adopted for purposes of comparison in Table I.

It is natural to regard the discrepancies between the various functions as a rough indication of their probable errors. The differences shown in Table III are representative of a large number of points which have been calculated. Evidently the H-L function is much too diffuse, giving ψ^2 only about half its proper value in the region of importance, and a corresponding excessive value in more remote regions in order to preserve normalization. Between the other functions no systematic differences are conspicuous except when we compare points in phase-space for which the elliptical coordinates of the two electrons are respectively the same, but the differences in azimuth, and hence the inter-electronic separations, are different. Columns 3

⁸ E. A. Hylleraas, *Zeits. f. Physik* **71**, 739 (1931).

and 4, 5 and 6, offer such comparisons. Here the present functions show their characteristic advantage of being able to assume smaller values for the smaller electronic separations.

The discrepancies are in general in good agreement with Eckart's⁴ criterion, which can be thus stated: the root-mean-square error in ψ is equal to $(\epsilon/\Delta E)^{1/2}$, where ϵ is the error in the calculated energy, and ΔE represents a kind of average of the separation between the lowest energy level and the other levels of the same symmetry. According to Mulliken,⁶ the second lowest $^1\Sigma_g^+$ state has an energy about 20 volts above the ground state (for $R=1.4$). The state of complete ionization of the fixed-center molecule would evidently have the positive absolute energy 19.3 volts (due to nuclear repulsion), or 51 volts above the ground state. If we take ΔE as 35 volts, ϵ as 1.8, 0.71, 0.22, 0.05, and 0.03 volts for the five functions, respectively, the mean errors should be 23 percent, 14 percent, 8 percent, 4 percent, and 3 percent. The errors in ψ^2 , and presumably in quantities calculated by its aid, will be double these figures.

Corroboratory evidence is offered by the values of $(H-E)\psi$. This quantity, which vanishes for the correct function, seems on the basis of five computed points to tend to amount to something like 80 percent, 40 percent, 12 percent, 9 percent, 6 percent, of ψ . Reasoning similar to Eckart's (see Appendix) leads to the conclusion that the root-mean-square average of these ratios should be somewhat greater than $(\epsilon \times \Delta E)^{1/2}$, or 29 percent, 19 percent, 10 percent, 5 percent, 4 percent, respectively. The magnitude of $(H-E)\psi/\psi$ varies greatly from point to point, but at each point there is a clear tendency for the values to run proportional to the square-roots of the assumed energy errors, thus indicating that those errors are indeed of the right order of magnitude, and that the correct function would give the experimental value.

It is instructive to see what happens when the electrons coincide and $r_{12}=0$. Since the term $1/r_{12}$ in the potential energy becomes infinite, Schrödinger's equation requires either that ψ vanish or that a cancelling infinite term arise from the Laplacian or kinetic energy part of the operator H . The second alternative is evidently the correct one. In the fifth column of Table III,

the entries under $(H-E)\psi$ show the coefficient of the $1/\rho$ term in $H\psi$, which outweighs all other terms as ρ becomes small. In the H-L and Rosen functions, this term comes solely from the potential energy; in the series functions, especially the 13-term function, cancellation by a term from the Laplacian is approximately complete. The function itself shows no sign of approaching zero as it is made more accurate.

In order to see whether still lower energy values could be obtained by varying δ and/or R , we computed a number of energies for different values of these quantities, using the same eleven terms in the series. As a basis of comparison, we took as "observed" values those given by a Morse curve constructed as recommended by Mulliken,

$$U(r) = D_e[1 - e^{-a(r-r_e)}]^2; \quad a = (2\pi^2\mu c\omega_e^2/hD_e)^{1/2}.$$

taking $D_e = 4.73$ e.v., $\omega_e = 4375\text{cm}^{-1}$, $r_e = 1.40 a_H$, $\mu = 0.8309 \times 10^{-24}$ g.

TABLE IV.

R	1.2	1.3	1.4	1.5	1.6	1.7
Binding energy, e.v.			-4.67	-4.63	-4.52	-4.35
electron-volts			-4.68	-4.63	-4.49	-4.40
			-4.73	-4.68	-4.57	-4.40

The results are summarized in Table IV. The significance of these results will best be seen from the graph, Fig. 1. It will be noticed, first, that the choice already discussed, $\delta=0.75$, R

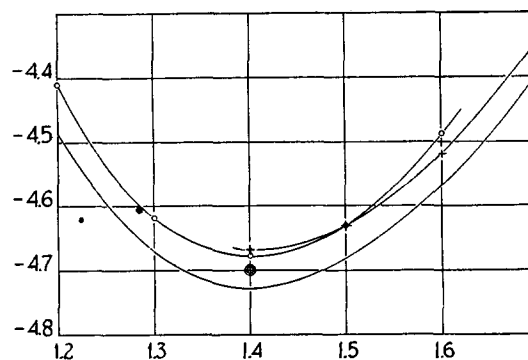


FIG. 1. Energy of H_2 in electron-volts, against separation of the nuclei, in Bohr radii. (Energy of dissociated molecule taken as zero.) Lowest curve is "experimental" Morse curve. Circle indicates point computed with $\delta=0.75$, 11-term function. Cross indicates point computed with $\delta=0.875$, 11-term function. Double circle indicates point computed with $\delta=0.75$, 13-term function.

TABLE V.

Terms	Coefficients							
	$\delta=0.75$				$\delta=0.875$			
	$R=1.2$	$R=1.3$	$R=1.4$	$R=1.5$	$R=1.4$	$R=1.5$	$R=1.6$	$R=1.7$
[00000]	2.64085	2.47282	2.29326	2.10831	2.55009	2.42055	2.28454	2.14343
[00020]	1.05889	1.14862	1.19526	1.20876	1.32769	1.46843	1.56080	1.61252
[00110]	-0.35865	-0.44227	-0.49921	-0.53385	-0.48136	-0.59679	-0.68500	-0.74964
[10000]	-0.75010	-0.82703	-0.86693	-0.87515	-0.76638	-0.84500	-0.89956	-0.92919
[10200]	-0.07001	-0.10926	-0.13656	-0.15443	-0.06026	-0.12001	-0.16569	-0.19941
[10020]	-0.00474	-0.04501	-0.07214	-0.08931	+0.03746	-0.02644	-0.07409	-0.10817
[10110]	0.05723	0.10936	0.14330	0.16388	0.03528	0.11560	0.17625	0.22060
[20000]	0.06082	0.06100	0.06621	0.07168	0.07933	0.07208	0.07421	0.07970
[00001]	0.46092	0.39769	0.33977	0.28909	0.54697	0.48577	0.42713	0.37287
[00111]	-0.01097	-0.02408	-0.03143	-0.03508	-0.00316	-0.02137	-0.03420	-0.04269
[00002]	-0.02616	-0.02596	-0.02456	-0.02264	-0.03099	-0.03198	-0.03135	-0.02974

$=1.4$, gives the lowest energy of any calculated. Second, that the curve for $\delta=0.75$ lies parallel to the Morse curve and 0.05 above it at $R=1.4$, while the same is true of the curve for $\delta=0.875$ for $R=1.6$. In view of the small effect of changes in δ , it seems safe to conclude that, within the region studied, and to an accuracy of 0.01 v.e., the envelope of a family of curves having various δ values would be given by calculating the energy for each R with $2\delta=1.08R$, and that this envelope would lie 0.05 v.e. above the observed Morse curve. It follows that the calculated equilibrium distance and fundamental vibration frequency agree sensibly with the observed. It must be admitted, however, that the cogency of this reasoning would be much re-enforced by an actual computation with $\delta=0.625$, say, in order to exclude the conceivable possibility that for some R near 1.4 a still lower result might come out.

The coefficients of each term in the series were computed for all cases. They vary in a regular manner as R and δ are changed, showing no such sharp maxima or minima as the parameters in Rosen's paper. They are shown in Table V.

OTHER POSSIBLE APPLICATIONS

The excited Σ states of H_2 which, like the normal state, are singlet, with wave functions symmetrical in the nuclei, can be attacked by the same general method. Hylleraas and Undheim⁹ have shown that the second lowest root of the secular equation is an upper limit for the

⁹ E. A. Hylleraas and B. Undheim, *Zeits. f. Physik* **65**, 759 (1930).

energy of the second lowest state of the given symmetry, and so on. Thus, by investigating the values of the higher roots for various choices of R and δ we may hope to gain approximations to the potential curves for the excited states. Of course, this may demand the use of more terms than are needed for the ground state, or even the use of the exponential $e^{-\delta_1\lambda_1-\delta_2\lambda_2}$ in place of $e^{-\delta(\lambda_1+\lambda_2)}$. The various singlet Σ states antisymmetric in the nuclei can be investigated in the same way, by using those terms in the series with $j+k$ odd, and the triplet Σ states by using the series in which differences instead of sums occur:

$$\psi = \sum_{m n j k p} C_{m n j k p} e^{-\delta(\lambda_1+\lambda_2)} (\lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p - \lambda_1^n \lambda_2^m \mu_1^k \mu_2^j \rho^p).$$

Once the computation for the singlet states has been carried out, the triplet states can be treated with very little labor. Some work on excited H_2 has been done in this laboratory, and will be communicated later. So far, the results are disappointing.

In applying a similar method to molecules with but two electrons outside closed shells, one would attempt to represent the inner shells by the usual atomic functions, the valence electrons by a series function. When only terms with $p=0$ are used, the work is straightforward and not too difficult. The introduction of the terms with r_{12} involves the evaluation of some exceedingly formidable integrals, and it seems that some modification of these terms will be needed. This is now being investigated in relation to the normal states of LiH and Li_2 .

MATHEMATICAL APPENDIX

Evaluation of matrix components

Consider the matrix components of unity and of energy arising between any two terms in the series from which the wave function is constructed, say the terms $[m_a n_a j_a k_a p_a]$ and $[m_b n_b j_b k_b p_b]$. Each term contains two sub-terms, which we may designate ψ_a, ψ_a' , and ψ_b, ψ_b' , respectively; they differ by interchange of indices between electrons. The matrix component of unity will have the form

$$S_{ab} = \int \int dV_1 dV_2 \psi_a \psi_b + \int \int dV_1 dV_2 \psi_a \psi_b' + \int \int dV_1 dV_2 \psi_a' \psi_b + \int \int dV_1 dV_2 \psi_a' \psi_b'.$$

It will be sufficient to consider the first of these integrals, which we may call s_{ab} . Four similarly related integrals will form the matrix component of the energy; the first of these will be

$$\begin{aligned} h_{ab} &= \int \int dV_1 dV_2 \psi_a H \psi_b \\ &= \int \int dV_1 dV_2 \psi_a \left[-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 + (1/R) \{ 1 + 2/\rho - 4\lambda_1/(\lambda_1^2 - \mu_1^2) - 4\lambda_2/(\lambda_2^2 - \mu_2^2) \} \right] \psi_b. \end{aligned}$$

Owing to the fact that the complete terms $\psi_a + \psi_a'$ and $\psi_b + \psi_b'$ contain the coordinates of the two electrons symmetrically, we may use instead the simpler integrals

$$h'_{ab} = \int \int dV_1 dV_2 \psi_a \left[-\nabla^2 + (1/R) \{ 1 + 2/\rho - 8\lambda_2/(\lambda_2^2 - \mu_2^2) \} \right] \psi_b.$$

Then

$$H_{ab} = h'_{ab} + h'_{a'b'} + h'_{ab'} + h'_{a'b}.$$

In performing these integrations, we were not able to utilize the device adopted by Hylleraas for He, using ρ directly as one of the variables of integration. We found it necessary to transform the powers of ρ into elliptical coordinates, by means of the equations

$$\begin{aligned} \rho^2 &= \lambda_1^2 + \lambda_2^2 + \mu_1^2 + \mu_2^2 - 2 - 2\lambda_1\lambda_2\mu_1\mu_2 - 2[(\lambda_1^2 - 1)(\lambda_2^2 - 1)(1 - \mu_1^2)(1 - \mu_2^2)]^{\frac{1}{2}} \cos(\varphi_1 - \varphi_2), \\ \rho^{-1} &= \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\infty} D_{\tau}^{\nu} P_{\tau}^{\nu} \left(\frac{\lambda_1}{\lambda_2} \right) Q_{\tau}^{\nu} \left(\frac{\lambda_2}{\lambda_1} \right) P_{\tau}^{\nu}(\mu_1) P_{\tau}^{\nu}(\mu_2) \cos \nu(\varphi_1 - \varphi_2), \quad (\text{notation of Zener and Guillemin}^{10}) \end{aligned}$$

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

Now, the required quantities may all be found in terms of integrals defined thus:

$$X(m, n, j, k, p) \equiv \frac{1}{4\pi^2} \int \int \int \int \int \int (\lambda_1^2 - \mu_1^2) e^{-2\delta(\lambda_1 + \lambda_2)} \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2.$$

The indices are all zero or positive, except that p may have the value -1 .

Remembering that $dV_1 dV_2 = (1/64) R^6 (\lambda_1^2 - \mu_1^2) (\lambda_2^2 - \mu_2^2) d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2$, we find at once

$$\begin{aligned} s_{ab} &= (1/64) R^6 [X(m_a + m_b, n_a + n_b + 2, j_a + j_b, k_a + k_b, p_a + p_b) \\ &\quad - X(m_a + m_b, n_a + n_b, j_a + j_b, k_a + k_b + 2, p_a + p_b)]. \end{aligned}$$

We shall abbreviate this to

$$s_{ab} = (1/64) R^6 [X(02000) - X(00020)].$$

¹⁰ C. Zener and V. Guillemin, Jr., Phys. Rev. **34**, 999 (1929).

In h_{ab}' , the only troublesome part is that arising from the Laplacian. Insofar as the coordinates of electron 2 are concerned, we may write ψ_b as constant $\times L_b(\lambda_2)M_b(\mu_2)P_b(\rho)$. Then

$$\nabla^2 \psi_b / \psi_b = \nabla^2 L_b / L_b + \nabla^2 M_b / M_b + \nabla^2 P_b / P_b + 2\nabla_2 L_b \cdot \nabla_2 P_b / L_b P_b + 2\nabla_2 M_b \cdot \nabla_2 P_b / M_b P_b;$$

(since the term in $\nabla_2 L_b \cdot \nabla_2 M_b$ always vanishes, the coordinates being orthogonal). Now, in general,

$$\nabla^2 f(\rho) = [4/R^2 \rho^2] \times [2\rho df/d\rho + \rho^2 d^2 f/d\rho^2];$$

$$\nabla^2 f(\lambda, \mu) = [4/R^2(\lambda^2 - \mu^2)] \times [2\lambda \partial f/\partial \lambda + (\lambda^2 - 1)\partial^2 f/\partial \lambda^2 - 2\mu \partial f/\partial \mu + (1 - \mu^2)\partial^2 f/\partial \mu^2];$$

$$\nabla f(\lambda, \mu) \cdot \nabla g(\lambda, \mu, \varphi) = [4/R^2(\lambda^2 - \mu^2)] \times [(\lambda^2 - 1)(\partial f/\partial \lambda)(\partial g/\partial \lambda) + (1 - \mu^2)(\partial f/\partial \mu)(\partial g/\partial \mu)].$$

Putting

$$L_b = e^{-\delta \lambda_2 \lambda_2^{n_b}}, \quad M_b = \mu_2^{k_b}, \quad P_b = \rho^{p_b},$$

we find

$$[(\lambda_2^2 - 1)/\lambda_2] \partial P_b / \partial \lambda_2 = \frac{1}{2} p_b P_b \rho^{-2} [\rho^2 - \lambda_1^2 + \lambda_2^2 - \mu_1^2 - \mu_2^2 + 2\lambda_1 \mu_1 \mu_2 / \lambda_2]$$

$$[(1 - \mu_2^2)/\mu_2] \partial P_b / \partial \mu_2 = -\frac{1}{2} p_b P_b \rho^{-2} [\rho^2 - \lambda_1^2 - \lambda_2^2 - \mu_1^2 + \mu_2^2 + 2\lambda_1 \lambda_2 \mu_1 / \mu_2]$$

and finally

$$\begin{aligned} \psi_a \nabla^2 \psi_b = & [4\psi_a \psi_b / R^2(\lambda_2^2 - \mu_2^2)] \times \{ 2(n_b - \delta \lambda_2) + (1 - 1/\lambda_2^2)(n_b(n_b - 1) - 2\delta n_b \lambda_2 + \delta^2 \lambda_2^2) \\ & - 2k_b + (1/\mu_2^2 - 1)(k_b(k_b - 1)) + (p_b/\rho^2)[(p_b + 1)(\lambda_2^2 - \mu_2^2) \\ & + (n_b - \delta \lambda_2)(\rho^2 - \lambda_1^2 + \lambda_2^2 - \mu_1^2 - \mu_2^2 + 2\lambda_1 \mu_1 \mu_2 / \lambda_2) - k_b(\rho^2 - \lambda_1^2 - \lambda_2^2 - \mu_1^2 + \mu_2^2 + 2\lambda_1 \lambda_2 \mu_1 / \mu_2)] \}. \end{aligned}$$

This can evidently be integrated in terms of the functions X previously defined. But a somewhat shorter expression for the integral can be found. By Greene's theorem, for properly continuous functions which vanish canonically at infinity,

$$\int dV_2 \psi_a \nabla^2 \psi_b = \frac{1}{4} \int dV_2 (\psi_a \nabla^2 \psi_b + \psi_b \nabla^2 \psi_a - 2\nabla_2 \psi_a \cdot \nabla_2 \psi_b).$$

We note

$$\begin{aligned} \nabla_2 \psi_a \cdot \nabla_2 \psi_b / \psi_a \psi_b = & \nabla_2 L_a \cdot \nabla_2 L_b / L_a L_b + \nabla_2 M_a \cdot \nabla_2 M_b / M_a M_b + \nabla_2 P_a \cdot \nabla_2 P_b / P_a P_b + \nabla_2 L_a \cdot \nabla_2 P_b / L_a P_b \\ & + \nabla_2 M_a \cdot \nabla_2 P_b / M_a P_b + \nabla_2 L_b \cdot \nabla_2 P_a / L_b P_a + \nabla_2 M_b \cdot \nabla_2 P_a / M_b P_a. \end{aligned}$$

When this is evaluated, some cancellation occurs, and the final formula is

$$\begin{aligned} h'_{ab} = & (1/64)R^5 \{ X(02000) - X(00020) + 2X(0200-1) - 2X(0002-1) - 8X(01000) \} \\ & - (1/64)R^4 \{ [(n_a - n_b)^2 - (k_a - k_b)^2 + (n_a + n_b) - (k_a + k_b) + (p_a - p_b)(n_a - n_b - k_a + k_b)] X(00000) \\ & - 4\delta X(01000) - [(n_a - n_b)^2 - (n_a + n_b)] X(0-2000) + [(k_a - k_b)^2 - (k_a + k_b)] X(000-20) \\ & + [(p_a - p_b)^2 + p_a + p_b + (p_a - p_b)(n_a - n_b + k_a - k_b)] [X(0200-2) - X(0002-2)] \\ & - (p_a - p_b)(n_a - n_b - (k_a - k_b)) [X(2000-2) + X(0020-2)] \\ & + 2(p_a - p_b)(n_a - n_b) X(1-111-2) - 2(p_a - p_b)(k_a - k_b) X(111-1-2) \}. \end{aligned}$$

(The same abbreviation as before has been made in the argument of the X 's.)

In discussing the computation of these integrals, it will be expedient to introduce the abbreviation $\alpha = 2\delta$. Let us define the more general function

$$X^\nu(m, n, j, k, p) \equiv Z^\nu(m+2, n, j, k, p) - Z^\nu(m, n, j+2, k, p);$$

$$Z^\nu(m, n, j, k, p) \equiv (1/4\pi^2) \int \int \int \int \int \int e^{-\alpha(\lambda_1 + \lambda_2)} \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p M^\nu \cos^\nu(\varphi_1 - \varphi_2) d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2;$$

$$M^2 = (\lambda_1^2 - 1)(\lambda_2^2 - 1)(1 - \mu_1^2)(1 - \mu_2^2).$$

This evidently reduces to the previously defined $X(m, n, j, k, p)$ when $\nu = 0$.

For $p = 0$, we have

$$Z(m, n, j, k, 0) = 4A_m(\alpha)A_n(\alpha)/(j+1)(k+1),$$

$$Z'(m, n, j, k, 0) = 0,$$

$$Z''(m, n, j, k, 0) = 8[A_{m+2}(\alpha) - A_m(\alpha)][A_{n+2}(\alpha) - A_n(\alpha)]/(j+1)(j+3)(k+1)(k+3),$$

when j and k are both even; otherwise the integrals vanish. (Here, as usual, $A_n(\alpha) \equiv \int_1^\infty \lambda^n e^{-\alpha\lambda} d\lambda$. For details of computation and tables, see Rosen's paper.¹¹)

For $p = -1$, the Neumann expansion of $1/\rho$ yields

$$Z(m, n, j, k, -1) = \sum_{\tau=0}^{\infty} (2\tau+1)R_\tau(j)R_\tau(k)H_\tau(m, n, \alpha),$$

$$Z'(m, n, j, k, -1) = -\sum_{\tau=1}^{\infty} [1/\tau(\tau+1)]R'_\tau(j)R'_\tau(k) \times [(2\tau+1)/\tau(\tau+1)]H'_\tau(m, n, \alpha),$$

$$\begin{aligned} Z''(m, n, j, k, -1) = & \frac{1}{2} \sum_{\tau=2}^{\infty} [1/(2\tau+3)(2\tau-1)(\tau+2)(\tau+1)\tau(\tau-1)]R''_\tau(j)R''_\tau(k) \\ & \times [(2\tau+3)(2\tau+1)(2\tau-1)/(\tau+2)(\tau+1)\tau(\tau-1)]H''_\tau(m, n, \alpha) \\ & + \frac{1}{2} \sum_{\tau=0}^{\infty} (2\tau+1)(R_\tau(j) - R_\tau(j+2))(R_\tau(k) - R_\tau(k+2)) \\ & \times [H_\tau(m+2, n+2, \alpha) - H_\tau(m+2, n, \alpha) - H_\tau(m, n+2, \alpha) + H_\tau(m, n, \alpha)]. \end{aligned}$$

Here, $R_\tau^\nu(j) \equiv \int_{-1}^{+1} d\mu (1-\mu^2)^{\nu/2} P_\tau^\nu(\mu) \mu^j$. Rosen has discussed and tabulated this integral for $\nu = 0$. The other cases are readily obtained from the elementary theory of associated harmonics. They exist only for even or for odd τ , according as $j+\nu$ is even or odd, and vanish for all values of τ greater than $j+\nu$, so that the summation over τ contains at most a few terms.

The other integral

$$H_\tau^\nu(m, n, \alpha) \equiv \int_1^\infty d\lambda_1 \int_1^\infty d\lambda_2 [(\lambda_1^2-1)(\lambda_2^2-1)]^{\nu/2} P_\tau^\nu\left(\frac{\lambda_1}{\lambda_2}\right) Q_\tau^\nu\left(\frac{\lambda_2}{\lambda_1}\right) \lambda_1^m \lambda_2^n e^{-\alpha(\lambda_1+\lambda_2)}$$

is familiar in molecular problems, at least for $\nu = 0$. Rosen gives a method for computing $H_0(m, n, \alpha)$ (his formula A19). With the aid of his function $S(m, n, \alpha)$ (formulas A13, A14), and the following recurrence relations, other values can be found readily:

$$H_1(m, n, \alpha) = H_0(m+1, n+1, \alpha) - S(m, n+1, \alpha) - S(n, m+1, \alpha).$$

$$\begin{aligned} H_\tau(m, n, \alpha) = & (1/\tau^2) [(2\tau-1)^2 H_{\tau-1}(m+1, n+1, \alpha) + (\tau-1)^2 H_{\tau-2}(m, n, \alpha) \\ & - (2\tau-1)(2\tau-3)(H_{\tau-2}(m+2, n, \alpha) + H_{\tau-2}(m, n+2, \alpha)) + 2(2\tau-1)(2\tau-5)H_{\tau-3}(m+1, n+1, \alpha) \\ & - (2\tau-1)(2\tau-7)(H_{\tau-4}(m+2, n, \alpha) + H_{\tau-4}(m, n+2, \alpha)) + 2(2\tau-1)(2\tau-9)H_{\tau-5}(m+1, n+1, \alpha) \\ & - \dots] \text{ until either} \end{aligned}$$

$$\text{(for even } \tau) \quad - (2\tau-1)[H_0(m+2, n, \alpha) + H_0(m, n+2, \alpha) - S(m+1, n, \alpha) - S(n+1, m, \alpha)] \quad \text{for } \tau > 1.$$

$$\text{(for odd } \tau) \quad + (2\tau-1)[2H_0(m+1, n+1, \alpha) - S(m, n+1, \alpha) - S(n, m+1, \alpha)].$$

$$[(2\tau+1)/\tau(\tau+1)]H'_\tau(m, n, \alpha) = (\tau+1)H_{\tau+1}(m, n, \alpha) - (2\tau+1)H_\tau(m+1, n+1, \alpha) + \tau H_{\tau-1}(m, n, \alpha).$$

¹¹ N. Rosen, Phys. Rev. **38**, 255 (1931).

$$\begin{aligned}
& [(2\tau+3)(2\tau+1)(2\tau-1)/(\tau+2)(\tau+1)\tau(\tau-1)]H''_{\tau}(m, n, \alpha) \\
& \quad = \tau(2\tau-1)[(2\tau+3)/(\tau+1)(\tau+2)]H'_{\tau+1}(m, n, \alpha) \\
& - (2\tau+3)(2\tau-1)[(2\tau+1)/\tau(\tau+1)]H'_{\tau}(m+1, n+1, \alpha) + (\tau+1)(2\tau+3)[(2\tau-1)/(\tau-1)\tau]H'_{\tau-1}(m, n, \alpha).
\end{aligned}$$

(The factors in brackets [] before H' and H'' are left in explicitly because for purposes of computation they may conveniently be considered part of the functions.)

When X^{ν} has been tabulated for $p=0$ and $p=-1$, it can easily be found for positive values of p by means of the relation (with the usual abbreviation)

$$\begin{aligned}
X^{\nu}(00002) &= X^{\nu}(20000) + X^{\nu}(02000) + X^{\nu}(00200) + X^{\nu}(00020) - 2X^{\nu}(00000) \\
&\quad - 2X^{\nu}(11110) - 2X^{\nu+1}(00000).
\end{aligned}$$

A corresponding relation holds also for Z^{ν} .

Solution of secular equation, and determination of constants

The complexity of the secular equation of course necessitates determination of the roots by trial and error. The following process seems to be the simplest available, and puts the work in a particularly satisfactory form for the determination of the constants. Choosing a trial value of λ in the proper neighborhood (known from experiment, or experience with a similar function), we may write the s equations which must be satisfied by the coefficients C in the form

$$\sum_{\tau=1}^s d_{i\tau} C_{\tau} = 0, \quad i = 1, 2, \dots, s, \quad d_{i\tau} = H_{i\tau} - \lambda S_{i\tau}.$$

This set of equations is equivalent to another set, obtained from it by progressive elimination of the variables C_{τ} , in which there is one equation involving s of the C 's, one in $(s-1)C$'s, and so on. Let these equations be

$$\sum_{\tau=1}^s D_{i\tau} C_{\tau} = 0, \quad i = 1, 2, \dots, s.$$

The D 's are conveniently found by the recurrence relation

$$D_{n\tau} = d_{n\tau} - \sum_{\nu=1}^{n-1} D_{\nu\tau} D_{\nu n} / D_{\nu\nu},$$

starting with $D_{1\tau} = d_{1\tau}$. Because the d 's form a symmetrical matrix, it will be found that $D_{n\tau}$ vanishes automatically for $\tau < n$. A convenient numerical check is provided by the fact that the quantities $\Sigma_{\tau} D_{n\tau}$ should be obtainable from the quantities $\Sigma_{\tau} d_{n\tau}$ by means of the same recurrence relation.

If λ has been properly chosen, the last factor D_{ss} will vanish, and the last equation $D_{ss}C_s = 0$ will permit C_s to be set arbitrarily equal to 1 (or any other number). Since the secular determinant is easily seen to be just the product of the diagonal factors D_{ii} , the value of λ so determined is evidently that which makes the determinant vanish. The remaining C 's may be immediately determined by successively substituting C_s in the $(s-1)$ st equation, C_s and C_{s-1} in the $(s-2)$ nd, and so on. The provisional coefficients are then used to compute $\int dV_1 dV_2 \psi^2$; upon division by the square root of this quantity, a set of normalized coefficients is obtained.

Should D_{nn} vanish for $n < s$, the meaning is that the value of λ chosen happens to be an exact solution of the secular equation containing only the first n terms. In this case (and also in practise if D_{nn} is very small), the procedure for subsequent D 's breaks down. If, nevertheless, it is desired to find the value of the whole determinant, the order of the original terms must be changed, placing at least one of the originally first n terms in a position later than the n th.

In general, of course, the chosen value of λ will prove incorrect, the last factor, and therefore the whole determinant, failing to vanish. In order to find a value of λ making D_{ss} negligibly small, the above process is carried out for two assumed values of λ lying rather near the root, and preferably enclosing it, as shown by the last factor having opposite signs in the two cases. The root can then be quite accurately determined by considering the value of the determinant (not the last factor) as linear in λ , and interpolating. If the coefficients are desired, they must be obtained by a new computation using the interpolated λ , as it is not safe to try to interpolate the individual D 's which determine the coefficients.

It may be mentioned that by this method an 11-row determinant with six significant figures can be evaluated and checked by an experienced computer in a little over two hours.

Order of magnitude of $(H-E)\psi$

Suppose our approximate wave function ψ expanded in terms of the correct wave functions ψ_n of proper symmetry, with coefficients a_n , such that a_1 is nearly unity, and $\sum_n a_n^2 = 1$. Let E be the energy calculated, and E_n the correct energy for the n th function. Then

$$\begin{aligned} E &= \int \psi H \psi dV = \int \left(\sum_{\tau} a_{\tau} \psi_{\tau} \right) \left(\sum_{\sigma} a_{\sigma} E_{\sigma} \psi_{\sigma} \right) dV = \sum_{\tau} a_{\tau}^2 E_{\tau} = a_1^2 E_1 + \sum_{\tau=2} a_{\tau}^2 E_{\tau} \\ &= a_1^2 E_1 + \bar{E} \sum_{\tau=2} a_{\tau}^2 = a_1^2 E_1 + \bar{E} (1 - a_1^2), \end{aligned}$$

where \bar{E} is some value between E_2 and E_{∞} . Similarly we can show that

$$\delta^2 = \int [(H-E)\psi]^2 dV = a_1^2 (E_1 - E)^2 + (\bar{E} - E)^2 (1 - a_1^2), \quad E_2 < \bar{E} < E_{\infty}.$$

Eliminating $1 - a_1^2$ gives $\delta^2 = (E_1 - E)[E_1 - E + \{(\bar{E} - E)^2 - (E_1 - E)^2\} / (E_1 - \bar{E})]$.

Assuming that $(\bar{E} - E) / (\bar{E} - E_1)$ is of the order of unity, and neglecting higher powers of $\epsilon = E - E_1$, we have $\delta^2 \approx (E_1 - E)(E_1 - \bar{E})$. This is a lower limit, since it can easily be shown that $\bar{E} > \bar{E}$.

Note added in proof:

A minute error has been found, affecting the energy by 0.003 e.v. Corrected coefficients will be published as soon as possible.