

On the TwoQuantum Σ States of the Hydrogen Molecule

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studies⁹ of AsCl_3 lead to $101 \pm 4^\circ$ bond angles. An As—Cl separation of $2.18 \pm 0.03 \text{ \AA}$ is given by the electron diffraction study, while a value of 2.20 \AA is obtained from Pauling and Huggins' covalent radii.¹⁰ Structure II, which has $v \approx 0.805$, $x = 0.365$, $y = 0.200$, $z = 0.325$, contains AsCl_3 molecules with bond angle $95^\circ 50'$, As—Cl = 2.25 \AA , Cl—Cl = 3.34 \AA . Table IV lists all of the pertinent interatomic distances for the two structures for which we have calculated intensities. The As—Cl separation of 2.25 \AA given by structure II is nearly that expected for a covalent bond, whereas the precise significance

of the corresponding value of 2.42 \AA given by structure I would remain doubtful. Moreover the relations of caesium with chlorine are probably more satisfactory in general for structure II than for structure I.

Possible variations in the parameter values would include having z about 0.005 smaller, v from 0.005 – 0.010 smaller, and x and y a little nearer the closest-packed positions. Such changes would not materially alter our concept of covalent As—Cl bonds, but would lead to bond angles a little greater than 96° . They would result also in a somewhat smaller value than 3.71 \AA for the Cs_A —Cl_B distance, which is perhaps to be anticipated.

⁹ Brockway and Wall, *J. Am. Chem. Soc.* **56**, 2373 (1934).

¹⁰ Pauling and Huggins, *Zeits. f. Krist.* **87**, 205 (1934).

On the Two-Quantum Σ -States of the Hydrogen Molecule

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A wave function in the form of a series with coefficients to be determined by the variational method is used to calculate the dissociation energies of the hydrogen molecule in two of its excited states: $1s\sigma 2s\sigma {}^3\Sigma_u^+$ and $1s\sigma 2p\sigma {}^1\Sigma_u^+$. In the former case an 11-term wave function gives an energy less than 0.02 e.v. from the most probable experimental value and lying within the limits of experimental error. For the second state an energy less than 0.08 e.v. from

experiment is obtained by means of a function comprising 18 terms. The interelectronic distance has been introduced explicitly into the wave function and the role that it plays in reducing the energy is discussed at length. The limits of accuracy of the calculation with reference to convergence and nuclear motion are considered. Explicit wave functions are given for the two states.

INTRODUCTION

THE treatment by wave mechanics of the electronic states of a diatomic molecule has led in general to results which are unsatisfactory from a quantitative point of view. The very simplest problems, including the excited states of the hydrogen molecule, have not been carried to the point where quantitative agreement with experiment could be obtained. The successful treatment of the normal state of the hydrogen molecule by James and Coolidge¹ furnishes a method whose possibilities it seems worth while to explore more thoroughly; and with this in mind a calculation has been made on several of the two quantum states of hydrogen,² and the

results for two of these states are reported in this paper.³

Previous work on these states has been based on trial wave functions that have been constructed from hydrogen atom functions⁴ (cf. the Heitler-London method), from the wave functions for the hydrogen molecular ion,⁵ or from a combination of the two.⁶ In a molecule as closely

³ Work has also been done on the repulsive state $1s\sigma 2p\sigma {}^3\Sigma_u^+$ and will be published shortly in a joint paper by Drs. James and Coolidge with the writer.

⁴ Kemble and Zener, *Phys. Rev.* **33**, 512 (1929); Zener and Guillemin, *Phys. Rev.* **34**, 999 (1929).

⁵ E. A. Hylleraas, *Zeits. f. Physik* **71**, 739 (1931). Hylleraas fails to treat the state $1s\sigma 2s\sigma {}^3\Sigma_u^+$, but mentions results obtained by a rough extrapolation which appears to have little theoretical justification.

⁶ J. K. L. MacDonald, *Proc. Roy. Soc.* **A136**, 528 (1932). MacDonald treats all of the two-quantum states for the same internuclear distance, 2 Bohr radii. Both Hylleraas and MacDonald obtain fairly good agreement with experiment on the Π states, but their results on the Σ states are unsatisfactory.

¹ James and Coolidge, *J. Chem. Phys.* **1**, 825 (1933).

² Two-quantum molecular states dissociate upon adiabatic separation of the nuclei into one normal atom and one atom in a two-quantum state.

bound as hydrogen it is to be expected that the molecular ion function of Hylleraas and the hybrid function of MacDonald will be more effective than a Heitler-London function, as is confirmed by their results. However these wave functions, together with all others previously employed, suffer a twofold disadvantage which renders them unsatisfactory if accurate results are desired: (1) they are insufficiently flexible, if flexible at all; (2) they take no adequate account of electronic interaction; e.g., for Σ states they are functions of only four of the five essential coordinates, the interelectronic distance or its equivalent having been omitted.

The importance of taking account of electronic interaction in the wave function is to ensure that there will be a small probability for those regions of configuration space in which the electrons are close together. For example, the introduction of positive powers of the interelectronic distance (r_{12} -terms) into the wave function will serve to keep the electrons apart, and where that service is partly accounted for by other means, r_{12} -terms will be less important. Thus r_{12} -terms should be less important for triplet than for singlet states, since the wave function for a triplet state is antisymmetric in the space coordinates of the electrons and will vanish when they coincide. Also the explicit appearance of azimuthal angles in the wave function for a Π state will compensate in some measure for the absence of r_{12} -terms, if the state happens to be a triplet. In consequence we should expect that functions of the type previously used would have given somewhat better agreement for triplet than for singlet states and better for ${}^3\Pi$ than for ${}^3\Sigma$. This appears to be in agreement with the results of MacDonald, although the former effect is not so marked as one might suppose. A more detailed discussion of some of these points is reserved till later when a comparison can be made with the results of the present work.

METHOD

The observed two-quantum Σ states are $1s\sigma 2s\sigma {}^3\Sigma_g^+$ (the most probable upper state for the continuous spectrum), $1s\sigma 2p\sigma {}^1\Sigma_u^+$ (the B state) and $1s\sigma 2p\sigma {}^3\Sigma_u^+$ (the Heitler-London repulsive state). The symmetry characteristics

impose two types of conditions on the wave functions:

(1) Symmetry or antisymmetry to interchange of the space coordinates of the electrons (singlet or triplet states).

(2) Symmetry or antisymmetry to interchange of the space coordinates of the nuclei (even (g) or odd (u) positive electronic states).⁷ Furthermore the wave function of a Σ state must have rotational symmetry about the nuclear axis and can contain only the difference between the azimuthal angles of the electrons.

It is proposed to expand the wave function in terms of a power series in the five variables with an exponential factor in the elliptical coordinate λ to ensure convergence of the integrals involved. If the nuclei are designated by a and b and the electrons by 1 and 2, and the distances between the particles expressed in Bohr radii (B.R.) are denoted by the customary symbols, then the coordinates are:

$$\lambda_1 = (r_{1a} + r_{1b})/R, \quad \lambda_2 = (r_{2a} + r_{2b})/R, \\ \mu_1 = (r_{1a} - r_{1b})/R, \quad \mu_2 = (r_{2a} - r_{2b})/R, \quad \rho = 2r_{12}/R.$$

The wave function is:

$$\psi = \sum_{m n j k p} c_{m n j k p} [m \delta_1 n \delta_2 j k p],$$

where $[m \delta_1 n \delta_2 j k p]$ stands for

$$(1/2\pi) \{ e^{-\delta_1 \lambda_1 - \delta_2 \lambda_2} \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p \\ \pm e^{-\delta_2 \lambda_1 - \delta_1 \lambda_2} \lambda_1^n \lambda_2^m \mu_1^k \mu_2^j \rho^p \}.$$

No spin function is introduced, but the spin is determined implicitly by the symmetry characteristics of the wave function ψ in accordance with Pauli's principle. For singlet states the plus sign is to be used, for triplet states the minus sign. For the even (g) states $j+k$ must be even, for the odd (u) states odd. Subject to this last restriction the summation is to be extended over positive or zero values of the indices and as many terms taken as result in an effective lowering of the energy. The quantities δ_1 and δ_2 should preferably be taken as arbitrary parameters to be varied, but since there appeared to

⁷ Σ^+ terms are $\frac{\text{symmetric}}{\text{antisymmetric}}$ in the space coordinates of the nuclei if they are $\frac{\text{even}(g)}{\text{odd}(u)}$.

be no simple way of performing this variation, suitable values were selected at the outset of the calculation by a preliminary computation described below. A small error in the choice of δ_1 and δ_2 should be compensated for by a slight alteration in the coefficients of terms involving powers of λ_1 and λ_2 . The best values of these constants will depend on the internuclear distance R , and a particular choice of δ 's will give reasonably good results over a small range in R .¹ The electronic energy plotted as a function of R will be the envelope of a family of curves characterized by different pairs of values of the parameters δ_1 and δ_2 such that each pair of values will be the best for that particular R at which its curve touches the envelope.

The variational method was applied to determine a set of values for the parameters c_{mnjkp} which would give the lowest energy obtainable with the type of function used. Since only the lowest states of a particular symmetry are considered, the computed value of the energy for any trial function must always lie above the true energy. The actual computation falls naturally into three parts. In the first, extensive tables of fundamental integrals, related by convenient recursion formulas, are prepared for use in evaluating the matrix elements of the successive approximations. The principal labor occurs in the integrations over $1/r_{12}$, which is expanded by the Neumann formula, and in the evaluation of integrals between r_{12} -terms. In the second part the matrix elements corresponding to combinations of the simplest terms in the series, are evaluated and introduced into the secular equation. If the parameters δ_1 and δ_2 are approximately correct, it is found that the series converges rapidly and that only low powers (0, 1, 2 but never more than 3) are required. Since in the n th approximation there are $n(n+1)/2$ matrix elements to be computed and a secular equation of the n th degree to be solved, it is not feasible to test every term in combination with all the others nor to carry along any terms which give inappreciable contributions. As the importance of any term was generally found to decrease as the number of terms combined with it was increased, terms which yielded negligible improvement at any stage of the calculation were usually dropped. However, exceptions have

been found to this rule, notably in the case of certain pairs of functions, e.g. $[0\delta_1 0\delta_2 000]$ and $[1\delta_1 1\delta_2 000]$ in treating $^3\Sigma_g^+$ which gave in combination a better contribution to the energy than the sum of their individual contributions when inserted independently. This phenomenon, which is fortunately infrequent in occurrence, seems to indicate that the δ 's have not exactly the right values to ensure the closest convergence.

The third part of the work consists in the solution of the secular equations which arise in each approximation. The procedure is necessarily one of trial and error and involves the evaluation of large numbers of symmetric determinants.¹ Here there were no neighboring electronic states of the same symmetry, i.e., no nearby roots of the secular equation, and it was found sufficiently accurate to interpolate linearly for λ , the value of the root. The coefficients of the wave function are readily obtained from a secular determinant evaluated at the root. Before working out this determinant it is desirable to rearrange the terms by putting an important function at the end to ensure that the last factor of the determinant will reduce to a vanishingly small quantity.

THE STATE $1\sigma 2s\sigma \ ^3\Sigma_g^+$

In order to make use of tables already prepared¹ in treating the normal state of the molecule, computations were begun on the state $1\sigma 2s\sigma \ ^3\Sigma_g^+$ with a wave function for which $\delta_1 = \delta_2 = 0.75$. It was soon found that the convergence was extremely poor, and this was attributed to an unfavorable choice of shielding constants. Thereupon a preliminary investigation for determining a suitable pair of δ 's was made upon the single term $[1\delta_1 0\delta_2 000]$ which in the previous work had proved to be the most important single term of the series; this led to the selection of $\delta_1 = 0.5$ $\delta_2 = 1$ for treating this state of the molecule. The calculation was then carried out for the internuclear distance $R = 1.87$ B.R. at which occurs the minimum of the experimentally determined potential energy curve.⁸

⁸ It would have been more convincing to have established this also as the theoretical minimum. However it is well known that the experimentally determined Morse curves are quantitatively accurate in the neighborhood of the minimum.

The six terms [10020] [10200] [10000] [00000] [10110] [11000]⁹ were found to give an energy much better than any previously reported,¹⁰ less than 0.08 e.v. from experiment. Upon the insertion of r_{12} terms the energy was still further reduced and the final wave function involving [10020] [10200] [10000] [00000] [10110] [11000] [11020] [10001] [00001] [10021] [11001] gave a total energy of -0.7361 in units of twice the ionization energy of the normal hydrogen atom: $2R_{\infty}hc$ (27.074 e.v.). A number of other terms were investigated at various stages of the calculation including: [20000] [01000] [11200] [10130] [12000] [11110] [10111]; these were all found to yield 0.001 e.v. or less. The r_{12} terms contributed 0.057 e.v. in marked contrast to the improvement of 0.44 e.v. observed in the ground state (singlet) by James and Coolidge; this difference is easily understandable from the orbital antisymmetry of the triplet state. Because of the extremely rapid convergence it was possible to make an estimate of the probable contribution of remaining terms, from which the absolute minimum may be said to occur at $\lambda = -0.7367 \pm 0.0004$ (-19.945 ± 0.01 e.v.). Subtracting the zero point energy of 0.162 e.v. and the energy -16.921 e.v. of a normal and a two-quantum hydrogen atom (with fixed nuclei), we obtain 2.862 ± 0.01 e.v. for the dissociation energy of the hydrogen molecule in the state $1s\sigma 2s\sigma^3\Sigma_g^+$. The experimental value is given by Richardson as 2.867 e.v., by Mulliken as 2.86 e.v. and by Jevons as 2.85 e.v.¹¹

The unusual degree of accuracy which has been obtained for this state makes it necessary for us to consider closely the approximation which has been made in the customary assumption of "clamped nuclei." The correction to the energy for Σ states may be roughly estimated by means of the limiting case of the united atom. The electronic energy¹² is then effectively raised by an amount:^{13, 14}

⁹ $[m\delta_1 n\delta_2 jkp]$ is abbreviated to $[mnjkp]$ for $\delta_1 = 0.5$, $\delta_2 = 1$.

¹⁰ MacDonald's result is 0.40 e.v. from experiment.

¹¹ O. W. Richardson, *Molecular Hydrogen and Its Spectrum*, p. 324; R. S. Mulliken, *Rev. Mod. Phys.* **4**, 78 (1932); W. Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 268.

¹² "Electronic" energy includes energy of nuclear repulsion.

¹³ R. de L. Kronig, *Band Spectra and Molecular Structure*, pp. 14, 15.

¹⁴ R. de L. Kronig, *Physica* **1**, 7 (1934).

$$\bar{U} = \frac{\hbar^2}{8\pi^2\mu L} \left[\frac{L(L+1)}{R^2} + \sum_{\text{spin}} \int \left(\frac{\partial \Phi}{\partial R} \right)^2 d\tau_{\text{elec.}} \right],$$

where μ is the reduced mass of the molecule, L the resultant orbital angular momentum of the united atom and Φ the electronic part of the wave function. Since this expression is always positive it appears that the uncorrected electronic energy may lie below the experimental value. A consideration of the effect of nuclear motion in Hylleraas' very exact calculation on parahelium¹⁵ led to a similar result. For the state under consideration ($1s\sigma 2s\sigma^3\Sigma_g^+$) the first term in \bar{U} will vanish. It would seem to be a matter of considerable difficulty to appraise the second term; fortunately this has been done by MacDonald⁶ who finds it to be worth about 0.01 e.v. The minimum of the corrected potential energy curve will therefore occur at $\lambda = -19.935 \pm 0.01$ e.v. However, since corrections have now been made for nuclear motion, we must subtract the true value of the two-quantum asymptote (-16.912) and this leaves us with nearly the same dissociation energy as before: 2.861 ± 0.01 e.v. The approximations made in assuming the minimum of the experimentally-determined potential energy curve to be the true minimum, in estimating the convergence of the series wave function and in correcting for the effect of nuclear motion take us into a region of accuracy where spin and relativistic effects can no longer be neglected.

THE STATE $1s\sigma 2p\sigma^1\Sigma_u^+$

Next to be treated was the B state $1s\sigma 2p\sigma^1\Sigma_u^+$. In order to secure the best results, it would have been advisable to have adopted the same procedure for determining δ_1 and δ_2 as that employed in the preceding work, but this would have necessitated the entire recalculation of all the tables of fundamental integrals from the very beginning. The calculation was therefore carried out with $\delta_1 = 0.5$, $\delta_2 = 1$ at the Morse curve minimum $R = 2.42$ B.R. A great many terms were tried and it was found that few could be rejected. A wave function comprising the terms

[10010]	[10100]	[11100]	[00100]	[11010]
[10120]	[20100]	[01100]	[00300]	[02100]
[01120]	[01300]	[11120]	[00101]	[10101]

¹⁵ E. A. Hylleraas, *Zeits. f. Physik* **54**, 347 (1929).

[11101] [01101] [10121] gave the best energy of -0.7522 (-20.37 e.v.) which is approximately 0.08 e.v. from the experimental value given by Mulliken.¹⁶ The addition of r_{12} terms to the wave function lowered the energy by 0.29 e.v. The slowness of convergence is undoubtedly to be attributed primarily to the fact that δ_1 and δ_2 have not been given their best values. Since the r_{12} terms are quite important and since they were inserted last in order, it might be thought that if they had been put in somewhat earlier, several of the non- r_{12} terms would have proved to be less important and might even have been dropped altogether. The contribution of some of these terms was noticeably decreased, but it appears that none of the 18 could have been omitted without sacrificing 0.01 e.v. or more, e.g., the best 15-term wave function, whose coefficients are given in Table I, gave an energy worse by 0.06 e.v. In estimating the convergence of remaining terms, the greatest error appears to be due to the absence of those with higher powers of r_{12} . In the treatment of the normal state these terms proved to be worth about one-sixth of the energy contributed by the first power terms. Allowing from 0.04 to 0.06 e.v. for this purpose and, upon examination, from 0.01 to 0.05 e.v. for convergence of other terms, one obtains 3.44 ± 0.03 e.v. for the dissociation energy of the B state, as compared with the values 3.42, 3.44 and 3.47 e.v. given by Richardson, Mulliken and Jevons, respectively. This estimate is not quite so reliable as that made on the state $^3\Sigma_g^+$.

Relative to the total energy, the r_{12} terms in the B state are of the same order of importance as in the ground state. Thus it is clear that the greater importance of the r_{12} terms for these two states is to be attributed almost entirely to the fact that they are both singlets. One might suppose that there would be less overlapping of the electron orbits in a two-quantum state than in the normal state, and that r_{12} terms would be correspondingly less important in the former case. Thus Hylleraas and Undheim¹⁷ find that for two-quantum para-helium the r_{12} terms contribute only one-tenth as much to the

energy as in the ground state. The situation in the molecule is sufficiently different from that in the atom to make understandable the fact that the r_{12} terms do not drop off in importance in the molecule to the extent that they do in the atom as one passes from the ground state to the excited levels.¹⁸

CONCLUDING REMARKS

The best wave function for the state $^3\Sigma_g^+$ and the best 15-term wave function for the B state are given in Table I. A recalculation of the latter state with a specially selected pair of δ 's would probably reduce the number of terms considerably and provide a somewhat lower value of the energy. A preliminary examination of the term $[0\delta_1 0\delta_2 100]$ for a range of values of δ_1 and δ_2 should enable one to select a suitable pair, or else one might determine δ_1 and δ_2 by requiring a simpler function to approximate the function given in Table I or a certain number of its more important terms. Tables of matrix elements for combinations of numerous terms have been pre-

TABLE I. Coefficients of the normalized* wave functions (c_{mnpk}).

$^3\Sigma_g^+(\lambda = -0.73609, R = 1.87)$ $^1\Sigma_u^+(\lambda = -0.74986, R = 2.42)$			
[00000]	-1.161959	[00100]	1.441073
[10000]	0.499368	[10100]	-0.231754
[11000]	-0.077834	[10010]	0.002751
[10110]	-0.014422	[01100]	-0.560549
[10020]	0.071975	[11100]	0.007094
[10200]	0.034815	[11010]	-0.009393
[11020]	-0.018709	[20100]	0.019232
[00001]	0.091777	[10120]	0.207940
[10001]	-0.004742	[02100]	0.077989
[11001]	-0.000503	[01120]	-0.106513
[10021]	0.009030	[00300]	0.096702
		[00101]	0.210583
		[10101]	-0.016744
		[10101]	-0.020524
		[10121]	-0.014764

* Note the factor $1/2\pi$ in the wave function.

¹⁶ The energies calculated by Hylleraas and MacDonald are, respectively, 0.25 and 0.50 e.v. from experiment.

¹⁷ Hylleraas and Undheim, *Zeits. f. Physik* **65**, 759 (1930).

¹⁸ In the two-quantum atom the inner electron will be moving rapidly with respect to the outer electron in a smaller orbit. Classically speaking, its motion could then be represented by a spherical cloud of charge shielding the nucleus (the shielding for two-quantum para-helium is 80 percent effective). The interaction of the outer electron with this charge cloud is a function only of its distance from the center, i.e., the nucleus, so that r_{12} -terms will not be needed to describe the motion. On the other hand in the excited molecule the electrons will have lost their one- and two-quantum atomic characteristics to a large extent (all the more so for a closely bound molecule such as hydrogen), and will move with more nearly equal velocities in much the same region of space between the nuclei. Thus r_{12} -terms will be nearly as important as in the ground state.

pared for treating both even (*g*) and odd (*u*) states. These tables, although unpublished, are accessible and may be used for calculating any of the 3-quantum Σ states or the unobserved state $1s\sigma 2s\sigma^1\Sigma_g^+$. These states should appear as higher roots of the secular determinants, for to each higher root there will correspond a state of the system such that the *n*th lowest root will be an upper limit for the energy of the *n*th lowest state of the given symmetry.¹⁷

In possible extensions of the James-Coolidge method to other molecules, the present work

would indicate that where it becomes a practical impossibility to take into account r_{12} terms or their equivalent, quantitative results for Σ states can be expected only if the states are antisymmetrical in the space coordinates of all the electrons.¹⁹

In conclusion I wish to thank Dr. H. M. James and Dr. A. S. Coolidge for the use of their tables, and I am especially indebted to Dr. James for valuable advice and encouragement. I am also obliged to Professor Kemble for helpful comment on the manuscript.

APPENDIX

The procedure adopted for evaluating the matrix elements follows closely that described in the appendix of James and Coolidge, and will consequently not be reproduced in detail. Modifications of most of the formulas are needed because the previous work was restricted to the special case $\delta_1 = \delta_2$.

The required quantities can all be found in terms of the integrals:

$$X(m\alpha_1 n\alpha_2 jk p) = \frac{1}{4\pi^2} \int \int \int \int \int (\lambda_1^2 - \mu_1^2) e^{-2\delta_1\lambda_1 - 2\delta_2\lambda_2} \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

$$X(m\alpha_2 n\alpha_1 jk p) = \frac{1}{4\pi^2} \int \int \int \int \int (\lambda_1^2 - \mu_1^2) e^{-2\delta_2\lambda_1 - 2\delta_1\lambda_2} \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

$$X(m\alpha\alpha\alpha jk p) = \frac{1}{4\pi^2} \int \int \int \int \int (\lambda_1^2 - \mu_1^2) e^{-(\delta_1 + \delta_2)(\lambda_1 + \lambda_2)} \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

where $\alpha_1 = 2\delta_1$, $\alpha_2 = 2\delta_2$, $\alpha = \delta_1 + \delta_2$.

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

Consider the matrix component of unity between the two terms $[m_a \delta_1 n_a \delta_2 j_a k_a p_a]$ and $[m_b \delta_1 n_b \delta_2 j_b k_b p_b]$. Since each term is the sum or difference of two parts which we may designate ψ_a' , ψ_a'' and ψ_b' , ψ_b'' , respectively, the matrix component of unity will have four parts:

$$S_{ab} = \int \int \psi_a' \psi_b' d\tau_1 d\tau_2 + \int \int \psi_a'' \psi_b'' d\tau_1 d\tau_2 \pm \int \int \psi_a' \psi_b'' d\tau_1 d\tau_2 \pm \int \int \psi_a'' \psi_b' d\tau_1 d\tau_2,$$

where the plus sign is for singlet and the minus sign for triplet states. Remembering that

$$d\tau_1 d\tau_2 = \frac{R^6}{64} (\lambda_1^2 - \mu_1^2) (\lambda_2^2 - \mu_2^2) d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2$$

we find:

$$S_{ab} = \frac{R^6}{64} \{ 2[X(m_a + m_b, \alpha_1, n_a + n_b + 2, \alpha_2, j_a + j_b, k_a + k_b, p_a + p_b) - X(m_a + m_b, \alpha_1, n_a + n_b, \alpha_2, j_a + j_b, k_a + k_b + 2, p_a + p_b)] \\ \pm 2[X(m_a + n_b, \alpha, n_a + m_b + 2, \alpha, j_a + k_b, k_a + j_b, p_a + p_b) - X(m_a + n_b, \alpha, n_a + m_b, \alpha, j_a + k_b, k_a + j_b + 2, p_a + p_b)] \}.$$

¹⁹ Or at least in the space coordinates of the binding electrons.

The matrix component of the Hamiltonian energy will similarly consist of four parts:

$$H_{ab} = I \begin{pmatrix} m_a \delta_1 n_a \delta_2 j_a k_a p_a \\ m_b \delta_1 n_b \delta_2 j_b k_b p_b \end{pmatrix} + I \begin{pmatrix} n_a \delta_2 m_a \delta_1 k_a i_a p_a \\ n_b \delta_2 m_b \delta_1 k_b j_b p_b \end{pmatrix} \pm I \begin{pmatrix} m_a \delta_1 n_a \delta_2 j_a k_a p_a \\ n_b \delta_2 m_b \delta_1 k_b j_b p_b \end{pmatrix} \pm I \begin{pmatrix} n_a \delta_2 m_a \delta_1 k_a j_a p_a \\ -m_b \delta_1 n_b \delta_2 j_b k_b p_b \end{pmatrix}.$$

The I 's may be evaluated in terms of the X 's by means of the following general formula:

$$I \begin{pmatrix} a\gamma_1 c\gamma_3 e g p_a \\ b\gamma_2 d\gamma_4 f h p_b \end{pmatrix} = \frac{R^4}{64} \left\{ R \{ X(02000) - X(00020) - 8X(01000) + 2X(0200-1) - 2X(0002-1) \} \right. \\ - 4 \{ (d^2 + d - h^2 - h - \gamma_4^2) X(00000) - 2\gamma_4(1+d)X(01000) + \gamma_4^2 X(02000) + 2\gamma_4 d X(0-1000) \\ - d(d-1)X(0-2000) + h(h-1)X(000-20) \} - 4p_b \{ (d-h)X(00000) - \gamma_4 X(01000) \\ + (d+h+p_b+1)[X(0200-2) - X(0002-2)] + (h-d)[X(2000-2) + X(0020-2)] \\ + \gamma_4 [X(2100-2) - X(0300-2) + X(0120-2) + X(0102-2) - 2X(1011-2)] \\ \left. + 2dX(1-111-2) - 2hX(111-1-2) \right\}.$$

The abbreviation $X(rstuv)$ has here been used for the integral

$$X(a+b+r, \gamma_1+\gamma_2, c+d+s, \gamma_3+\gamma_4, e+f+i, g+h+u, p_a+p_b+v).$$

Fortunately, by virtue of the unsymmetrical nature of this formula, the bracket multiplied by p_b will drop out for all combinations of non- r_{12} terms and for all combinations of an r_{12} -term with a non- r_{12} term.

The X 's may all be evaluated in terms of generalized Z 's by the following formulae:

$$X(m\alpha_1 n\alpha_2 j k p) = Z^0(m+2, \alpha_1, n, \alpha_2, j, k, p) - Z^0(m, \alpha_1, n, \alpha_2, j+2, k, p)$$

$$Z^r(m\alpha_1 n\alpha_2 j k p) = \frac{1}{4\pi^2} \int \int \int \int \int e^{-\alpha_1 \lambda_1 - \alpha_2 \lambda_2} \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p M^r \cos^r(\varphi_1 - \varphi_2) d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

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

For the calculation of the Z 's there are needed the generalized integrals $H_r(m\alpha_1 n\alpha_2)$, and $S(m\alpha_1 n\alpha_2)$, already familiar in molecular problems for the special case $\alpha_1 = \alpha_2$. The details of these generalizations are more or less obvious and the relevant formulae²⁰ and recurrence relations may be obtained from the appendix of the James-Coolidge paper if one makes the following alteration in their formulae: replace the single α by α_1 and α_2 in such a way that m always goes with α_1 and n with α_2 . For example:

$$Z(m\alpha_1 n\alpha_2 j k 0) = 4A_m(\alpha_1)A_n(\alpha_2)/(j+1)(k+1),$$

$$Z(m\alpha_1 n\alpha_2 j k - 1) = \sum_{\tau=0}^{\infty} (2\tau+1)R_\tau(j)R_\tau(k)H_\tau(m\alpha_1 n\alpha_2),$$

$$H_1(m\alpha_1 n\alpha_2) = H_0(m+1, \alpha_1, n+1, \alpha_2) - S(m, \alpha_1, n+1, \alpha_2) - S(n, \alpha_2, m+1, \alpha_1).$$

²⁰ Some of these formulae are contained in a recent paper by H. M. James, J. Chem. Phys. 2, 794 (1934).