

The HeitlerLondon Repulsive State of Hydrogen

Hubert M. James, Albert Sprague Coolidge, and Richard D. Present

Citation: *J. Chem. Phys.* **4**, 187 (1936); doi: 10.1063/1.1749817

View online: <http://dx.doi.org/10.1063/1.1749817>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v4/i3>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



Explore the **Most Cited**
Collection in Applied Physics

AIP
Publishing

TABLE VI.

<i>T</i>	499°K		574.5°K		612°K	
	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.
$k(\text{H}_2 + \text{Br})$	1.16×10^6	1.01×10^6	1.25×10^7	1.25×10^7	3.01×10^7	3.46×10^7
$k(\text{H}_2 + \text{Br})$	7.15	4.19	5.4	2.91	4.8	2.5
$k(\text{D}_2 + \text{Br})$						

ing Table VI the frequencies and moments of inertia for the two reactions were taken from Table V and E_0' was taken as 20.45 in order to obtain agreement for the middle temperature. This value is directly comparable with the calculated value of 25.1 above. Rates for (7) and (8) at other temperatures as well as for (9) and (10) are readily obtained from Eq. (28) and Table V.

The foregoing considerations show clearly that the new theory of absolute reaction rates with reasonable potential energy surfaces will agree perfectly with the experimental findings. Conversely with sufficiently good experimental rates we can get an accurate picture of the potential surface in the neighborhood of the activated state using the general theory. Morris and Pease¹⁸ have recently reviewed the experimental

¹⁸ Morris and Pease, *J. Chem. Phys.* **3**, 796 (1935).

data for the reactions of hydrogen with the halogens and proposed tentative activation energies. Our potential surfaces for $\text{H}_2 + \text{I}_2$ give the rather surprising result that the total zero-point energy in the activated state exceeds that for the initial states. The available experimental results suggest that these calculated zero-point energies of the activated states are probably a little too large. It is noteworthy, however, in spite of this apparent shortcoming that these surfaces still indicate that hydrogen is considerably more reactive than deuterium in agreement with experiment. New accurate experiments should point the way to improvements in the general methods of calculating potential energy surfaces.

We wish to thank Dr. William Altar for helpful discussion.

MARCH, 1936

JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

The Heitler-London Repulsive State of Hydrogen

HUBERT M. JAMES, ALBERT SPRAGUE COOLIDGE AND RICHARD D. PRESENT, *Harvard University and Purdue University*

(Received November 25, 1935)

A variational method has been used in the study of the $1s\sigma 2p\sigma {}^3\Sigma_u$ state of H_2 . Two independent computations with formally different functions gave, for a nuclear separation of $1.5 a_{\text{H}}$, energies which agreed to within 0.03 ev and functions with a root-mean-square fractional difference of about 2 percent. A study of the way in which the computed energies converged to a limit, as the complexity of the varied functions was increased, indicates that the interaction energy of the atoms at this distance is $+5.145 \pm 0.02$ ev. Computations were also made for nuclear separations of $1.6 a_{\text{H}}$ and $1.87 a_{\text{H}}$. A potential curve passed through

points thus determined and approaching the Heitler-London curve asymptotically for large nuclear separations is believed to be accurate to 0.2 ev for nuclear separations greater than $1.35 a_{\text{H}}$. This curve is compared with the results of previous computations and the curve constructed by Finkelburg and Weizel to account for the variation with wave-length of the excitation potential of the continuous spectrum. Discussion of the disagreement with the results of Finkelburg and Weizel is deferred to a later paper.

IN two previous papers,^{1, 2} the authors have described a method for constructing wave functions for the lower states of the H_2 molecule,

¹ H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).

² R. D. Present, *J. Chem. Phys.* **3**, 122 (1935).

based upon the variation principle, and adapted from the work of Hylleraas upon the He atom. The states heretofore discussed have been the attractive states ${}^1\Sigma_g$ (the ground state), ${}^1\Sigma_u$ (the *B* state), and ${}^3\Sigma_g$ (the upper state for the continuous spectrum, according to Winans and

Stueckelberg³). In all these cases, the results could be checked by comparing the energy as calculated from the wave function with that yielded by a study of the vibration terms in the spectrum. It is of interest to apply the method to a repulsive state, the most easily treated one being the $^3\Sigma_u$ state predicted by Heitler and London (the lower state for the continuous spectrum). Here, however, we have no adequate experimental check; our only empirical information about this state is due to Finkelburg and Weizel,⁴ who have roughly located a portion of its potential energy curve by studying the excitation potential of various wave-lengths in the continuous spectrum, with the aid of the Franck-Condon principle. The success of our method must therefore be judged by internal evidence, such as the rapidity of convergence to a limit of energies computed using functions of increasing complexity, and the degree to which the limit approached is independent of the arbitrary parameters introduced. In the present paper we communicate the results of our computations and compare them with those of previous, more approximate methods of attack, reserving for the following paper a discussion of the numerous problems that arise when we attempt to make a careful comparison between these results and those obtained by Finkelburg and Weizel. Since we have already fully described our method, it is unnecessary to give the details here; we have, however, thought it worth while to discuss and illustrate the estimation of the limits of convergence somewhat more fully than in the previous papers, as certain new aspects of this question appeared during the present work.

The calculations were made by using the same basic material as in the other papers. If the nuclei are designated by a and b , the electrons by 1 and 2, and the distances between them in Bohr radii a_H are denoted by the customary symbols, then the coordinates are

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

³J. G. Winans and E. C. G. Stueckelberg, Proc. Nat. Acad. Sci. **14**, 867 (1928).

⁴W. Finkelburg and W. Weizel, Zeits. f. Physik **68**, 577 (1931).

The wave function is then

$$\psi = \sum_{mnjkp} C_{mnjkp} [m\delta_1 n\delta_2 jkp], \quad j+k \text{ odd},$$

where $[m\delta_1 n\delta_2 jkp]$ stands for

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

The material at hand permitted us to compute with $\delta_1 = \delta_2 = 0.75$ and with $\delta_1 = 0.5$, $\delta_2 = 1$. Table I gives the results obtained for the internuclear distance $R = 1.5a_H$ with several selections of terms in the series. Each function, designated by a capital letter at the top of the table, contains those terms which are marked by stars under the designating letter and opposite the abbreviations at the left. (These abbreviations have the form $[mnjkp]$, the values of δ_1 and δ_2 being understood.) At the bottom of the table are given the corresponding calculated energies, in units of 27.08 ev. In the case of the best functions obtained with each choice of δ 's there is also given the limit of convergence, estimated as discussed later.

The agreement of the two parallel calculations is remarkably satisfactory. Functions E and G give energies differing by 0.01 ev, and may be accepted as good approximations to the best function which can be constructed without explicitly introducing r_{12} . (The addition to G of eight more terms with $p=0$ improved the energy by less than 0.02 ev.) This best function is evidently the one which would be obtained as an exact solution of a wave equation in which the term $1/r_{12}$, a function of the elliptical coordinates λ_1 , μ_1 , λ_2 , μ_2 , and $(\varphi_2 - \varphi_1)$, is replaced by its average value over $(\varphi_2 - \varphi_1)$ for every λ_1 , μ_1 , λ_2 , μ_2 . When E and G , respectively, are converted into F and H by applying a correction for dependence upon r_{12} , a somewhat greater discrepancy makes its appearance; but this is removed entirely, within the probable error, when the appropriate allowances are made for convergence of the series. The calculation with different δ 's is undoubtedly to be preferred, as it allows explicitly for the promotion of one electron which must take place as the nuclei are brought near each other and the molecular wave function approaches the $1s2p$ function of the helium atom. The superiority of the function with two δ 's is

TABLE I.

TERMS	A	B	$\delta_1 = \delta_2 = 0.75$			$\delta_1 = 0.5\delta_2 = 1$		
			C	D	E	F	G	H
[00100]		*		*	*	*	*	*
[01100]	*	*	*	*	*	*	*	*
[02100]					*	*		
[10100]	*	*	*	*	*	*	*	*
[11100]	*	*	*	*	*	*	*	*
[12100]					*	*		
[20100]			*	*	*	*		
[21100]			*	*	*	*		
[00120]	*	*	*	*	*	*	*	*
[01120]							*	*
[10120]	*	*	*	*	*	*		
[00300]					*	*	*	*
[01300]					*	*		
[00101]								*
[10101]						*		*
[11101]						*		
energy	-0.7967	-0.7972	-0.7983	-0.8012	-0.8064	-0.8080	-0.8067	-0.80906
limit						-0.812		-0.8100
uncertainty						± 0.003		± 0.0007

In addition to the terms shown, a number of other terms were tried out and discarded; these were [00211] in the case $\delta_1 = \delta_2 = 0.75$, and [02100], [20100], [00010], [10010], [11010], [10120], [11120], [01300], [01101], [11101], and [10121] for $\delta_1 = 0.5$, $\delta_2 = 1$.

manifested by the more regular convergence and the smaller number of terms required to get a satisfactory approximation.

The importance of the r_{12} terms is small, as is to be expected from the triplet character of the state. Because of the antisymmetry to exchange of the space coordinates of the electrons the terms in the wave function which do not explicitly involve r_{12} vanish to the first order with r_{12} . The terms with $p=1$ vanish to the second order, and may thus be expected to produce a lowering of the computed energy of the order of that given by the $p=2$ terms in singlet functions, which also vanish with r_{12} to the second order. In fact, in our treatments of a $^3\Sigma_g$ and a $^3\Sigma_u$ state of this molecule the $p=1$ terms gave improvements of 0.06 ev in each case, as against improvements of 0.07 ev and 0.05 ev, respectively, given by terms with $p=2$ in treatments of $^1\Sigma_g$ and $^1\Sigma_u$ states.

In the case of attractive states, it has heretofore always been found that when a series converges regularly and rapidly upon a limit, this limit is in excellent agreement with experiment; we are hence in all probability justified in concluding that the results obtained by correcting function H for convergence are very nearly

right. Strong internal corroboratory evidence is furnished by the agreement with function F . However, it must be admitted as possible that the functions used cannot approximate indefinitely closely to the true functions or that the analysis of convergence has not been exhaustive, so that the true value of the energy lies appreciably lower than estimated, and only by chance do the two functions give energies which are in error by the same amount. Were this true, it would still be exceedingly unlikely that the errors in the functions themselves would be everywhere the same, since they differ from each other not only in the parameters δ but also in the coefficients. A detailed agreement between them must be taken to indicate their individual agreement with a third limiting function, the one which we desire. We have accordingly determined the coefficients in F and H (given in Table II) and have computed the values of the two functions for forty different configurations of the electrons, well distributed through the region within which $\lambda_1, \lambda_2 \leq 2$. With the exception of two points near nodal surfaces, where small absolute differences become relatively large, the maximum relative difference $(F-H)/H$ was 5 percent, and its root-mean-square average was

TABLE II.

R in aH δ_1, δ_2	1.5 0.75, 0.75	1.5 0.5, 1	1.6 0.5, 1	1.87 0.5, 1
TOTAL ENERGY, (atomic units)	-0.8080	-0.80906	-0.83097	-0.87472
REPULSION ENERGY (ev)	5.20	5.17	4.58	3.39
COEFFICIENTS OF TERMS BELOW				
[00100]	1.21236	1.548772	1.897818	2.416480
[01100]	.01928	-0.027247	-0.159414	-0.373883
[02100]	-.02644			
[10100]	.86174	0.204526	0.017095	-0.342534
[11100]	-.45434	-0.048833	-0.034078	0.014003
[12100]	.06103			
[20100]	.12237			
[21100]	-.01610			
[00120]	.36873	0.683718	0.728560	0.801804
[01120]		0.039157	-0.020635	-0.135245
[10120]	.28495			
[00300]	.27807	0.205257	0.208275	0.205674
[01300]	-.03385			
[00101]		0.248869	0.237395	0.134036
[10101]	.12211	-0.017416	-0.017510	0.001903
[11101]	-.02542			

2 percent. This figure was obtained by evaluating $\Sigma(F-H)^2/\Sigma H^2$ over the forty points, in order to avoid the integrations required in computing $\int(F-H)^2dV/\int H^2dV$, the root-mean-square relative difference of the functions. It is possible that the integral would come out somewhat greater, because of the contributions from remote regions (larger values of λ_1 , or λ_2). As the energy does not depend much upon the function in these regions, it is to be expected that approximate functions obtained by minimizing the energy will be subject to larger errors there.

By reasoning similar to Eckart's,⁵ if we assume that there is no coherence between the errors in the two functions, and take the apparent convergence limit as the true energy, we can estimate the mean discrepancy from the errors in the computed energies. It comes out somewhat greater than 2 percent, in agreement with the above. We have thus an additional check on the correctness of our results.

To extend our information about the repulsive state, we have made computations for other values of R . To judge by analogy with the ground state, the values $\delta_1=0.5$, $\delta_2=1$ should be good for a considerable variation in R . Table II shows the energy computed for three separations, using these values of δ and the same nine terms

of the series as are contained in function H ; the coefficients are also given. No special estimate of convergence has been made for the other separations; doubtless the allowance for it when $R=1.87$ should be increased somewhat over that for $R=1.5$, or additional terms in the series included, if the greatest possible accuracy is required, because the values of δ become less appropriate as R increases. For $R>2$, we shall have to use different δ 's. This work is now in progress.

Fig. 1 will make possible a comparison of our work with that in the literature. We have drawn a curve passing through the points representing our corrected value at $R=1.5$, the same distance below the uncorrected point at $R=1.6$, somewhat more below that at $R=1.87$, and approaching asymptotically from below the Heitler-London curve as calculated by Sugiura's⁶ method. Pending the investigation of the region $2<R<4$, we believe this may be accepted as lying within 0.2 ev of the correct potential curve over the whole range, and much nearer for the smaller values of R . We have also included the results of Hylleraas⁷ and MacDonald.⁸ Those of Hylleraas (with which MacDonald's closely

⁶ Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

⁷ E. A. Hylleraas, Zeits. f. Physik **71**, 739 (1931).

⁸ J. K. L. MacDonald, Proc. Roy. Soc. **A136**, 528 (1932).

⁵ C. Eckart, Phys. Rev. **36**, 878 (1930).

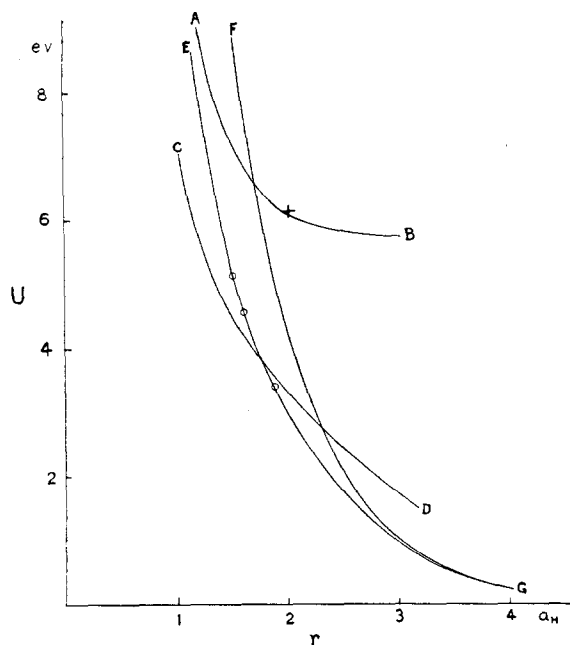


FIG. 1. Energy of the $1\sigma 2p\sigma^3\Sigma_u$ state of H_2 . *AB*, computation of Hylleraas; *CD*, estimate of Finkelburg and Weizel; *FG*, Heitler-London method; *EG*, estimate of the present authors; +, computation of MacDonald; 0, computation of the authors.

agree) lie above the H-L curve at $R=2$, but below it at $R=1.5$. Evidently both methods are subject to large errors in this region, the H-L method being much better for larger R , as is well understood, while those of Hylleraas and MacDonald, involving the use of H_2^+ functions as a basis of approximation, work best at smaller separations and for more highly excited molecular states.

The "experimental" curve of Finkelburg and Weizel is also shown. It is very far indeed from confirming our computations. We do not believe, however, that this proves our results to be in error. We shall show in the following paper that it is possible to make very plausible assumptions by which our theoretical curve may be brought into harmony with what Finkelburg and Weizel actually observed.

ON THE CHOICE OF PARAMETERS δ

The choice of values for the exponents δ_1 , δ_2 is in principle arbitrary; in practice it is a matter of convenience. There is, to be sure, one choice of δ 's which, for any given selection of series terms, will give a lower energy than any other.

But upon adding more terms, the optimum δ 's will in general be found to change, slowly at first, but increasingly erratically as the number of terms becomes greater. On the other hand, the improvement obtainable by varying the δ 's goes rapidly down with increasing number of terms; consequently, although the best δ 's for a very complex function may be quite different from those for a simple function, the error produced by using the latter values instead of the former will be very small. This is, of course, because when many terms are available it is possible to compensate errors in the δ 's by readjustments in the coefficients, C_{mnjkp} .

In practice, it is necessary to use δ 's lying within a certain appropriate range. As set forth in the next paragraph, an unfortunate choice of δ 's results in slow and irregular convergence on the limiting energy. The choice of δ 's may be made through a preliminary investigation with a simple, generally a one-term, function. This need require no great accuracy, as the resulting δ 's will not, in general, be just the best ones for the more complex functions to be used later, but this discrepancy will be of small importance. The one-term function $(10100) = (1/2\pi)(e^{-\delta_1\lambda_1}\lambda_1\mu_1e^{-\delta_2\lambda_2} - e^{-\delta_1\lambda_2}\lambda_2\mu_2e^{-\delta_2\lambda_1})$ evidently represents a model in which the electrons occupy two orbits, an inner "one-quantum" nodeless orbit, and an outer "two-quantum" orbit with a node in the median plane. The effect on the outer electron of promotion and the partial shielding of the nuclei by the inner electron is here represented (with $\delta_1=0.5$, $\delta_2=1$) not only by a diminution in the exponent of the outer orbit, but by the factor λ_1 , which operates to displace the maximum density outwards. The general significance of the δ 's is thus made clear. As a matter of fact, the particular values here used were those which had been found most appropriate for the term $[10000]$ of the state $1\sigma 2s\sigma^3\Sigma_g$. Somewhat different values would doubtless have been chosen if the present calculation had been the first undertaken, but they could hardly have led to a more successful convergence.

ON ESTIMATING CONVERGENCE LIMITS

When the δ 's are favorably chosen convergence has, in all calculations so far undertaken, been quite regular. By this, we mean that the improvement obtained by adding any given term to the function is found to decrease system-

TABLE III. *Energies obtained with various functions.* For each entry, the function used contains the term indicated at the top in addition to the combination indicated at the left. The last figure may be uncertain to several units.

	0	2	3	4	5	6	7	8	9	10
(1)	-0.74788	-0.78307	-0.74886	-0.77013	-0.76224	-0.75723	-0.76968			
(2)	-.78307		-.78350	-.80271	-.79739	-.78392	-.78388			
(3)	-.78350			-.80348	-.79819	-.78481	-.78493			
(4)	-.80348				-.80359	-.80457	-.80458	-0.80442	-0.80364	-0.80525
(5)	-.80359					-.80462	-.80463			
(6)	-.80462						-.80465			
(7)	-.80465									
(7')	-.80458							-.80553	-.80516	-.80526
(8')	-.80553								-.80611	-.80620
(9')	-.80611									-.80642

atically as we increase the number of terms already present in the combination to which it is added. (It must be clearly understood that when we speak of "adding" a term to a function, we mean simply that the given term is added to the list of terms from which the function is formed. The new function will not be the sum of the given term and the previous function, because when the best possible combinations of the two sets of terms are made, the coefficients will not preserve their values, or even their ratios. As a matter of fact, we have not even determined the coefficients except in the case of the best functions found.) This regularity is a great help in estimating the possible improvements from omitted terms. If, at any stage in building up a function, one or more terms are found to be of negligible value, it can be confidently predicted that they will never become more valuable as the complexity of the function increases, and they may be thrown out once for all.

In the present calculation with $\delta_1 = \delta_2 = 0.75$, this regularity of convergence did not appear, a fact which we ascribe to the obvious unsuitability of the choice of δ 's. Table I shows a marked example of "cooperation" between several terms which together give more improvement than the sum of their individual contributions. Considering the first four functions, it will be seen that A is improved by 0.0005 on addition of [00100] to form B , by 0.0016 on addition of [20100] and [21100] to give C , and by 0.0045, more than twice the sum of the individual improvements, when all three terms are put in to give the function D . As a result of this lack of regularity, it was impossible to form any really satisfactory estimate of the convergence limit in this case.

When the δ 's were taken as 0.5 and 1, no such irregularity was noted. As this is a typical case of the application of our method, we shall present a fairly detailed description of the process of determining the best simple function and estimating the allowance for convergence.

The terms not involving ρ were first numbered in the following manner, arbitrarily, except that a few of the terms expected to be most important were put first:

1	[10100]	6	[10010]	11	[11010]
2	[00100]	7	[00010]	12	[02100]
3	[11100]	8	[00300]	13	[01120]
4	[00120]	9	[20100]	14	[11120]
5	[10120]	10	[01100]	15	[01300]

A function containing a set of these terms will be indicated by a sum of the corresponding numbers, and the following abbreviations will be employed:

$$(n) = 1 + \dots + n; (n') = (n) - 5 - 6; (n'') = (n') - 7.$$

In Table III there will be found the energies associated with functions containing such sequences, plus one other term. Examination of this table will show how consistently one finds the importance of a particular term in a function unchanged or decreased on the addition of another term or terms, particularly if several functions are already present. It will be noted that the most essential terms are 1, 2, and 4, and that the function (7') is practically as good as (7). This observation was the basis for omitting further consideration of terms 5 and 6. It will be noted also that 7 seems to be unimportant when 10 is present. It was indeed found that (10'') gave the energy -0.80632 ; this function was accordingly taken as the basis in the further investigations. The negligibility of 9 was also noted, (10'')-9 giving an energy of -0.80619 , but at this stage in the work it was more convenient to retain this term.

The usefulness of the functions 11, 12, 13, 14, and 15 was next tested by adding them singly to (10''). The results:

$$\begin{aligned} (10'') + 11 &\sim -0.80650; & (10'') + 12 &\sim -0.80648; \\ (10'') + 13 &\sim -0.80683; & (10'') + 14 &\sim -0.80632; \\ (10'') + 15 &\sim -0.80632. \end{aligned}$$

The retention of 13 was thus indicated, and the function (4)+8+10+13 ~ -0.80670 was chosen as the basis for further work. In obtaining this function the neglect of eight terms had involved losses totalling $0.00064 \sim 0.017$ ev; the complete

fifteen-term function would thus in all probability have given an energy differing from -0.80670 by less than this amount.

Examination of the relative importance of the terms in the following sets, where just one index varies, will show how rapidly the importance of a term falls with the increase of one of the indices, especially when this rises above 1: 2, 1, 9; 1, 3; 4, 5; 7, 6; 8, 15; 2, 10, 12; 4, 13; 3, 14; 8, 15. A very minor exception seems to be offered by the term 11, which was itself negligible.

Inspection of these results leads us to the following estimates of the improvements available on addition of remaining terms in the indicated sequences:

$[0n100] \sim 0.00005$; $[n1100] + [1n100] \sim 0.00015$;
 $[n0120] \sim 0.00002$; $[mn120] \sim 0.00000$; $[0n120] \sim 0.00010$;
 $[0n300] \sim 0.00000$; $[mn300] \sim 0.00005$;
 $[n1010] + [1n010] \sim 0.00005$; $[n0010] \sim 0.00010$;
 $[m03n0] \sim 0.00000$; $[003n0] \sim 0.00020$; $[00n00] \sim 0.00015$;
 $[mnj00] \sim 0.00005$; $[001n0] \sim 0.00015$; $[011n0] \sim 0.00010$;
 $[mn1j0] \sim 0.00005$.

Adding to these amounts the quantities neglected in the construction of the simple function, we obtain $0.00186 \sim 0.050$ ev. This amount should be a very safe upper limit for the improvement obtainable from the addition of an indefinite number of terms not depending on ρ , and in

view of the usual nonadditivity of small improvements 0.03 ev would appear to be a safe estimate of the change to be expected.

To the seven-term function not involving ρ five terms in ρ were next added: $[00101]$, $[10101]$, $[01101]$, $[11101]$, $[10121]$. Of these only the first two proved to be worth keeping, the resulting nine-term function giving an energy of -0.80906 , while the complete twelve-term function gave -0.80918 . The improvement available from addition of further terms in ρ was estimated to be not more than 0.01 ev.

In the study of the basic state of H_2 it was found that the convergence on addition of terms not involving ρ was much more rapid if there were already present in the function terms which did depend on ρ . (It will be noted that this is not simply a special case of "regular" convergence, since two different limits are involved.) Though in this state the r_{12} terms are much less important than in the basic state, it is to be expected that a similar effect will exist here. In view of this we have estimated that the convergence limit is probably less than 0.03 ev below the energy of our best function, -0.80906 , and can be said to be -0.8100 ± 0.0007 with considerable assurance.

A Study of the Franck-Condon Principle

ALBERT SPRAGUE COOLIDGE, HUBERT M. JAMES AND RICHARD D. PRESENT, *Harvard University and Purdue University*

(Received November 26, 1935)

The validity of the Franck-Condon principle has been investigated in connection with its application to the calculation of spectral intensities in the continuous radiation due to the transitions between the $1s\sigma 2s\sigma^3\Sigma_g$ and the $1s\sigma 2p\sigma^3\Sigma_u$ states of H_2 . For the latter state, a potential curve was constructed on the basis of the authors' theoretical calculations. For the former state, a curve was computed from spectral data by Dunham's method. Accurate wave functions for both states were determined by mechanical integration with the differential analyzer. Transition probabilities from the first four vibrational levels of the stable state were determined by mechanical integration, both for the case that the electric moment matrix element is constant (as assumed in the Franck-Condon method) and for the case that it is a linear function of the nuclear separation. In addition integrals were determined which permitted the calculation of the probability of excitation

of the several vibrational levels by electron impact from the ground state, upon the basis of an extension of the Franck-Condon method. The spectral intensities so obtained are compared with those given by several forms of approximate calculation, and the discrepancies critically discussed. Comparisons are also made with the experimental work of Smith and of Finkelburg and Weizel. It is concluded that the Franck-Condon principle leads to results definitely incompatible with their observations. Indications are found that other transitions than the one treated in this work are contributing appreciably to the radiation observed by Smith. An analysis of the spectrum observed by Finkelburg and Weizel leads to a critical discussion of the method used by them in deducing the potential curve of the repulsive state, from which is drawn the conclusion that this curve is without quantitative significance.