Wave Functions and Potential Curves for Excited H2

Albert Sprague Coolidge and Hubert M. James

Additional information on J. Chem. Phys.

Wave Functions and Potential Curves for Excited H₂

ALBERT SPRAGUE COOLIDGE AND HUBERT M. JAMES
Harvard University, Cambridge, Massachusetts, and Purdue University, Lafayette, Indiana
(Received August 29, 1938)

Results on wave functions and energy values for the $1s\sigma 2p\sigma^3\Sigma_u$ and $1s\sigma 2s\sigma^3\Sigma_g$ states of H₂, obtained by a variational method, are given. The nuclear separations considered range from $1.3a_H$ to $2.9a_H$. The errors in the computed energies for the $^3\Sigma_u$ state are of the order of 0.001 atomic unit, while the computed energies for the $^3\Sigma_g$ state are in general more accurate. Root-mean-square errors in the wave functions are of the order of 2 percent.

IN order to carry out a calculation of the energy distribution in that continuous spectrum of H₂ which is produced by transitions from the stable $1s\sigma 2s\sigma^3\Sigma_g$ state to the repulsive state $1s\sigma 2p\sigma^3\Sigma_u$, we have required reasonably accurate approximations to the electronic wave functions of these states, and knowledge of the respective potential curves, over a considerable range of nuclear separation. To determine the electronic functions and the repulsive potential curve the only available method of adequate accuracy is that applied by us to the treatment of the ground state[1] and extended by Present and ourselves[2, 3] to various two-quantum excited states of this molecule. In these latter papers will be found computed wave functions and energies for one nuclear separation in the case of the $^3\Sigma_g$ state,[2] and three in the case of the $^3\Sigma_u$ state.[3] We here report on extensive calculations on both states by this method, of high accuracy and covering the range from $R=1.3a_H$ to $R=2.9a_H$. A complete description of the method will be found in the references given, the notation of which will be used in the present report.

Before presenting our numerical results, a discussion of their theoretical significance may be in order. It is well understood that the familiar two-stage method of treating molecular problems in quantum mechanics is based upon a forced separation of variables, whereby certain small terms are ignored. The resulting errors in the wave functions are undoubtedly negligible in comparison with those which are introduced by the further approximations (such as the use of a finite number of terms in a series) upon which it is necessary to fall back in order to treat the electronic motion in the separated problem. On the other hand, the energy values are more accurate than the wave functions with which they are obtained, and in comparing them with experiment the separation errors should be considered.

Van Vleck[4] has discussed the corrections to be applied to computations of energy levels based on the separation of nuclear and electronic co-ordinates, assembling formulas for the first- and second-order perturbations arising from all terms neglected in such treatments. He omits from consideration spin terms in the energy, negligible in H₂. According to Van Vleck, all diagonal perturbation terms (i.e., terms arising between states having the same electronic quantum numbers) may be accounted for by using a potential curve corrected at each value of R (the nuclear separation) by adding to the energy of the corresponding fixed-nuclei problem three small terms $P_{nn}(R)+Q_{nn}(R)+S_{nn}(R)$. (For infinite separation, this correction becomes just that required to convert the fixed- into the free-nuclei problem, and we may call it the correction for nuclear motion.) Insofar as nondiagonal perturbations can be neglected, this corrected potential curve should agree with the empirical potential curve which reproduces observed energy levels (to the degree to which such an empirical curve is defined). It is such a comparison that we make in this paper. Nondiagonal perturbations cannot be expressed as corrections to a computed potential curve, and prevent the exact representation of observed energy levels by any empirical potential curve. Our comparison of theory with experi-

[1] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[2] R. D. Present, J. Chem. Phys. **3**, 122 (1935).
[3] H. M. James, A. S. Coolidge and R. D. Present, J. Chem. Phys. **4**, 187 (1936).
[4] J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936).

ment thus depends for its validity on the absence of such perturbations, which fortunately seem to be safely negligible in the present cases.

THE REPULSIVE STATE $1s\sigma 2p\sigma\,^3\Sigma_u$

Wave functions for this state have already been given for $R = 1.5$, 1.6, and 1.87.[3] (R is the internuclear distance in Bohr radii.) Of these, the first, which was based upon a careful selection of terms, was retained for the present work. The second was not used, as the difference in R was too small, while the third was discarded because it seemed likely (and proved true) that a better function could be constructed by including some terms which had proved to be useless at the smaller R. New functions were computed for $R = 1.3$, 1.7, 1.87, and 2, using 12 terms of a series with the same form:

$$\psi = \sum_{mnjkp} C_{mnjkp}[mnjkp],$$

where

$$[mnjkp] = \frac{1}{2\pi}\{e^{-\delta_1\lambda_1-\delta_2\lambda_2}\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k$$
$$- e^{-\delta_2\lambda_1-\delta_1\lambda_2}\lambda_1{}^n\lambda_2{}^m\mu_1{}^k\mu_2{}^j\}\,\rho^p,$$

with $j+k$ odd, $\delta_1 = 0.5$, and $\delta_2 = 1$. (We wish to acknowledge our indebtedness to Dr. Present for the use of his tables of matrix elements in this part of our work.)

For larger separations it was clearly necessary to work with larger values of the exponential parameters, and, indeed, it seemed probable that a series of a different form might be found to converge more rapidly. The series previously used may be regarded as developed from a leading term which describes a $1s\sigma$ and a $2p\sigma$ molecular orbital, and is thus adapted to the "united atom" or Hund-Mulliken point of view. At a large enough distance, we know that the "separated atom" or Heitler-London point of view must be correct; it therefore seemed promising to explore the possitilities of a series with the Heitler-London (or the Wang) function as its leading term. Such a series (which we may call the H-L series) is that having the typical term

$$[mnjkp] = \frac{1}{2\pi}e^{-\delta(\lambda_1+\lambda_2)}\rho^p$$
$$\times[\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k(e^{\delta(\mu_1-\mu_2)} - (-1)^{j+k}e^{-\delta(\mu_1-\mu_2)})$$
$$- \lambda_1{}^n\lambda_2{}^m\mu_1{}^k\mu_2{}^j(e^{\delta(\mu_2-\mu_1)} - (-1)^{j+k}e^{-\delta(\mu_2-\mu_1)})].$$

TABLE I.

SERIES	NUMBER OF TERMS (NONE INVOLVING r_{12})	ENERGY (ATOMIC UNITS)	NUMBER OF TERMS (SOME INVOLVING r_{12})	ENERGY
H-L	8	−0.9430		
One-parameter	13	−0.9440	14	−0.9450
Two-parameter	14	−0.9430	16	−0.9446

A third possibility is the "one-parameter" series in which δ_1 and δ_2 of the two-parameter series are taken equal to each other, thus dropping the distinction between the normal and the excited electron, but retaining the molecular, rather than the atomic character of the orbitals.

For an orienting calculation, the distance $R = 2.5$ was selected, using $\delta = 1.25$ in the H-L and one-parameter series, and $\delta_1 = \frac{5}{6}$, $\delta_2 = \frac{5}{3}$ in the two-parameter series, so that (for the second and third series) the values of the δ's might bear to each other and to R the same ratio as in Present's corresponding exploration at $R = 1.5$. The results of this calculation are given in Table I. Except with the one-parameter series, no careful search was made for the best possible selection of terms. It appears that, in agreement with expectation, the H-L series is the most rapidly converging, and, contrary to the case when $R = 1.5$, the one-parameter series is somewhat superior to the two-parameter one. The latter fact may be referred to the slightness of the promotion effect upon the $2p\sigma$ electron at this distance.

In spite of its slight inferiority to the others, the two-parameter series was selected for the final computations, since, on the one hand, it seemed good enough for our purposes if sufficient terms were taken, and, on the other, it was found to be suitable for the $^3\Sigma_g$ state, and a great saving of labor could be secured by using the same series for both states. Doubtless the H-L series could also have been made to serve for both states, but the computations with this series were much complicated by the exponentials in the μ's, and it was therefore rejected. Functions using 16 terms of the two-parameter series were calculated for $R = 2.1$, 2.3, 2.5, 2.7, and 2.9.

In Table II are shown the coefficients of all functions for the repulsive state, the energies actually computed, and the estimated convergence limits. In stating the extrapolated energy

TABLE II. *The* $1s\sigma2p\sigma\,^3\Sigma_u$ *state.*

R IN a_H	$\delta_1=1/2,\ \delta_2=1$					$\delta_1=5/6,\ \delta_2=5/3$				
	1.3	1.5	1.7	1.87	2.0	2.1	2.3	2.5	2.7	2.9
Energy values										
Calc. (at. units)	−0.75406	−0.80906	−0.85021	−0.87781	−0.89492	−0.90849	−0.92870	−0.94460	−0.95687	−0.96587
Extrap. (at. units)	−0.756	−0.810	−0.851	−0.879	−0.896	−0.910	−0.930	−0.946	−0.958	−0.967
Repulsion (ev)	6.61	5.14	4.03	3.28	2.82	2.44	1.90	1.46	1.14	0.89
Coefficients of terms in wave functions										
[00100]	0.979050	1.548772	2.239678	2.599628	2.659882	1.936894	2.234818	2.941302	3.575884	4.041758
[01100]	0.170157	−0.027247	−0.321723	−0.515224	−0.590717	0.633018	0.832691	0.426836	−0.143139	−0.714533
[02100]	0.006601	——	0.011082	0.023675	0.029833	0.423497	0.164173	0.067069	0.048085	0.072247
[10100]	0.472356	0.204526	−0.188502	−0.459722	−0.571635	0.827257	0.011657	−0.869994	−1.555611	−2.019773
[11100]	−0.013866	−0.048833	−0.010614	0.026871	0.046351	−0.247715	−0.247237	−0.081591	0.113698	0.287866
[20100]	−0.000468	——	0.014215	0.032764	0.040667	−0.139321	−0.030849	0.083321	0.168937	0.223823
[00120]	0.130312	0.683718	0.942823	1.089500	1.138531	0.972096	2.067164	2.828300	3.311904	3.555939
[01120]	0.138519	0.039157	−0.048175	−0.089747	−0.109526	1.786428	1.279151	0.847516	0.499280	0.232730
[10120]	0.145136	——	−0.062575	−0.108259	−0.128555	−0.072024	−0.420895	−0.657306	−0.805350	−0.882633
[00300]	0.183226	0.205257	0.213798	0.212291	0.206694	1.096518	1.256921	1.368414	1.426851	1.425551
[10300]						−0.047583	−0.160486	−0.253337	−0.320530	−0.358368
[00320]						0.661987	0.762547	0.834345	0.880178	0.909575
[00010]						−0.170930	−0.195044	−0.214049	−0.230343	−0.235046
[00101]	0.192528	0.248869	0.224885	0.197417	0.170286	0.318177	0.625430	0.809566	0.895080	0.924795
[10101]	0.020854	−0.017416	−0.023218	−0.025499	−0.024072	0.051059	−0.036792	−0.086760	−0.110019	−0.118585
[01101]						0.199616	0.032409	−0.085467	−0.161526	−0.209103

no correction for nuclear motion has been made, since there is in this case no possibility of a correspondingly accurate comparison with experimental evidence. The extrapolated energies may be expected to be correct to within 0.001 atomic unit; comparison with the corresponding computations on the $1s\sigma2s\sigma\,^3\Sigma_g$ state indicates that for the intermediate values of R corresponding to either choice of δ_1 and δ_2 the allowance for convergence may well be too great. Upon converting to electron volts and referring to the energy of the separate normal atoms as zero, we obtain a potential curve which lies within the limits suggested in a previous paper,[5] somewhat nearer the lower than the upper limit.

The coefficients are given to sufficient places to ensure that the function is accurately normalized, but it is not to be imagined that the minimum problem has been solved with corresponding accuracy. We have found that, in general, properly related variations of several percent in the coefficients can be made without appreciably affecting the energy. Thus, a recalculation at $R=1.5$ in order to supply the coefficients of the

three missing terms would not be worth while, since we already knew that those terms were useless at this distance. A rough interpolation from the table shows that they must all be small. On the other hand, at $R=1.87$ these coefficients have all increased (in absolute magnitude), and by including them we improve the energy from −0.87472 to −0.87781. The root-mean-square errors of the wave functions can be estimated by a method applied in reference 1, and further discussed in a separate paper.[6] The computations on He to be found in this latter paper indicates to us that in reference 1 the values estimated for ϵ_z (there called ΔE) are somewhat too low, the estimated root-mean-square errors in the functions somewhat too high. For the best functions in reference 1 we now believe a better estimate of the root-mean-square error would be 1–2 percent, an estimate which applies also to the functions of Table II.

THE STABLE STATE $1s\sigma2s\sigma\,^3\Sigma_g$

For this state, Present's wave function was available for the equilibrium distance $R=1.87$.[2]

[5] A. S. Coolidge, H. M. James and R. D. Present, J. Chem. Phys. 4, 193 (1936), (Fig. 2).

[6] H. M. James and A. S. Coolidge, Phys. Rev. 51, 860 (1937).

TABLE III. *The $1s\sigma 2s\sigma\,{}^3\Sigma_g$ state.*

R IN a_H	$\delta_1=1/2,\ \delta_2=1$					$\delta_1=5/6,\ \delta_2=5/3$				
	1.3	1.5	1.7	1.87	2.0	2.1	2.3	2.5	2.7	2.9
Energy values (Binding energy includes correction for nuclear motion)										
Calc. (at. units)	−0.69730	−0.72350	−0.73427	−0.73609	−0.73449	−0.73115	−0.72702	−0.72001	−0.71164	−0.70275
Binding (ev)	1.957	2.667	2.958	3.007	2.964	2.874	2.762	2.572	2.345	2.105
Experiment	1.988	2.683	2.975	3.035	3.006	2.954	2.794	2.589	2.362	2.126
Coefficients of terms in wave functions										
[00000]	7.334504	2.676890	0.000000	−1.161959	−0.834000	15.648688	9.068104	5.624794	3.077609	1.674374
[01000]	1.585267	0.905995	0.334730	——	−0.027924	3.367721	2.038518	1.798262	1.293116	0.981765
[10000]	−2.258956	−0.700890	0.143395	0.499368	0.376281	−8.589064	−5.007215	−3.035991	−1.642966	−0.871511
[11000]	−0.260871	−0.172787	−0.112603	−0.077834	−0.079971	−0.999031	−0.533742	−0.442045	−0.316694	−0.259331
[20000]	0.304102	0.129032	0.039516	——	0.007870	1.681193	1.015974	0.648982	0.399628	0.258872
[00200]						0.794005	0.312874	−0.029954	−0.258188	−0.424428
[10200]	0.053391	0.049071	0.042381	0.034815	0.028552	0.024387	0.124910	0.186825	0.219285	0.233503
[00020]						1.926092	0.922516	0.128024	−0.475760	−0.957345
[10020]	−0.033654	0.013360	0.049868	0.071975	0.082826	−1.984110	−1.185013	−0.518044	0.012731	0.455800
[20020]						0.500301	0.371342	0.258578	0.169435	0.091070
[11020]	−0.000037	−0.008961	−0.015106	−0.018709	−0.020754	0.233960	0.139793	0.059715	−0.005355	−0.060504
[10110]	−0.009887	−0.008209	−0.011727	−0.014422	−0.016033					
[11110]						−0.168156	−0.157347	−0.148075	−0.142058	−0.133054
[00001]	0.169002	0.090723	0.092908	0.091777	0.153050	0.898820	0.406936	0.223444	0.162129	0.196296
[10001]	−0.032174	−0.001510	−0.001499	−0.004742	−0.019470	−0.443052	−0.159783	−0.045550	0.008296	0.011954
[11001]	0.013321	0.001016	−0.001149	−0.000503	0.001138	0.247307	0.111747	0.047792	0.009993	−0.006960
[10021]	0.028654	0.020566	0.013686	0.009030	0.006414	0.020252	0.026095	0.031614	0.035153	0.038348

We have made new computations for all nuclear separations for which the repulsive state was treated, employing series of the same form, with the same values for the parameters δ_1 and δ_2, but differing in that the terms employed had $j+k$ even, in keeping with the *gerade* symmetry of this state. Since this state, in contrast to the repulsive one, gives an excited atom upon dissociation, it is to be expected that the best values of δ_1 and δ_2 will remain different as R increases; as we have mentioned, the values employed were chosen as appropriate for this state rather than the repulsive one, though no extensive investigation was made in selecting these values. Our experience has always been that moderate deviations from the best choice of parameters can be compensated by increasing the number of terms in the series, which, for the larger values of R, is 16 in the present investigation.

Since our main purpose was connected with the wave functions rather than with the computed energy we have not attempted to attain the maximum accuracy for all values of R, nor have we attempted any careful estimate of the convergence limits at the different distances. It was clear that the computations at $R=1.5$ and $R=2.5$ were of high accuracy, apparently being about 0.01 ev from the convergence limit, while for the extreme values of R associated with either choice of δ_1 and δ_2 the error was rather greater. In particular, extrapolations of the two sets of computations to intermediate values of R do not join smoothly, because of the increasing error in either curve in this region.

In Table III will be found, together with the wave functions for the various nuclear separations, values of the energy as computed, values for this energy corrected for nuclear motion, but not for imperfect convergence, and, finally, empirical values for the correct energy.

The estimate for the correction due to nuclear motion was made as follows. For the ground state, Van Vleck estimates that at the equilibrium distance the correction is 114 cm^{-1} or 0.014 ev, and this is also its value for infinite separation. For our state, the value at infinite separation is $\frac{5}{8}$ of this amount, 0.009 ev. Van Vleck estimates that in the two-quantum states $^1\Sigma$ and $^1\Pi$ at the equilibrium distances the inner electron is responsible for a correction of 0.007 ev. If we raise

this by 0.002 ev to allow for the effect of the outer electron we obtain, as in the ground state, the same correction as at complete separation. We have, therefore, taken this correction as 0.009 ev at all values of R.

The empirical results are taken from a paper[7] in which we have discussed methods of obtaining empirical potential curves of high accuracy, using as illustrative material computations on this state. The relation of our theoretical results to our best empirical determination is precisely what

[7] A. S. Coolidge, H. M. James, and E. L. Vernon, Phys. Rev. 54, 726 (1938).

our experience with the theoretical computations has led us to expect. It will be noted, however, that these theoretical results are definitely incompatible with some of the empirical curves set up by less accurate and more usual methods, lying below rather than above the presumptive "observed" curve.

From the varying energy errors of the several functions it will be clear that there is also a considerable variation in the root-mean-square error of these functions. An estimate of 1 percent for this quantity for the best functions, 3 percent for the worst, should not be far from the mark.

The Negative Bands of $N^{14} - N^{15}$

R. W. WOOD AND G. H. DIEKE
Johns Hopkins University, Baltimore, Maryland
(Received August 8, 1938)

The negative bands of nitrogen were photographed with a mixture which contained about 15 percent of N^{15}. The $0\rightarrow0$, $1\rightarrow0$ and $0\rightarrow1$ bands of the $N^{14} - N^{15}$ molecule were analyzed. Their position is within the limits of experimental errors where the elementary theory of the isotopic shifts predicts them. The bands do not show any intensity alternations and there are no perturbations at the places where the corresponding bands of ordinary nitrogen have them.

INTRODUCTION

THE availability of mixtures with a considerable percentage of the heavy nitrogen isotope N^{15} now makes possible a study of the molecules which contain one or more atoms of N^{15}. The most interesting of these molecules would be $N^{15} - N^{15}$ because with its help the spin of the N^{15} atom can be determined. With the determination of the spin as chief aim we have begun the investigation of some bands of the nitrogen molecule. This research was made possible through the courtesy of Professor H. C. Urey, who supplied us with a small amount of ammonium nitrate prepared in his laboratory which yielded nitrogen with a concentration of about 15 percent of the heavy isotope.

The present communication gives some of the preliminary results. Although we have photographed several $N^{15} - N^{15}$ bands, they are, with the available sample, relatively weak compared to the $N^{14} - N^{15}$ and the $N^{14} - N^{14}$ bands, so that

reliable intensity measurements necessary for the determination of the spin would be difficult. The $N^{14} - N^{14}$ bands are naturally by far the strongest bands. Therefore we hope to repeat the experiments with more concentrated samples in order to obtain the spin. In this paper we report on some bands of $N^{14} - N^{15}$.

The nitrogen molecule has many band systems in the ultraviolet and visible. Most of these, e.g., the first and second positive groups, are of a rather complicated structure, and can be completely resolved only with difficulties. It is obvious that weak bands of $N^{14} - N^{15}$ or $N^{15} - N^{15}$ partly overlapped by the much stronger $N^{14} - N^{14}$ bands would represent rather unfavorable objects for analysis. However, the so-called negative bands due to the N_2^+ ion have a relatively simple structure and therefore we have chosen them for a first study. The present paper contains the three bands $0\rightarrow0$, $1\rightarrow0$ and $0\rightarrow1$ of the positive $N^{14} - N^{15}$ ion.