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Potential-Energy Curves for the $X\ {}^1\Sigma_g{}^+$, $b\,{}^3\Sigma_u{}^+$, and $C\ {}^1\Pi_u$ States of the Hydrogen Molecule*

W. Kołos† and L. Wolniewicz‡

Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago, Illinois

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Previous calculation of the ground-state energy of H_2 has been extended to include large internuclear distances and accurate potential-energy curve for $0.4 \leq R \leq 10.0$ a.u. is presented. For $0.4 \leq R \leq 4.0$ a.u. expectation values of several operators have also been calculated. The calculation was made using a wavefunction in the form of an expansion in elliptic coordinates. The wavefunction depends on the interelectronic distance but, in contrast to the James–Coolidge expansion, is flexible enough to describe properly the dissociation of the molecule. Extensive calculations have also been made for the repulsive ${}^3\Sigma_u{}^+$ state ($1.0 \leq R \leq 10.0$) and for the ${}^1\Pi_u$ state ($1.0 \leq R \leq 10.0$). In the former case a van der Waals minimum has been found at $R = 7.85$ a.u. and 4.3 cm^{-1} below the dissociation limit. For the ${}^1\Pi_u$ state the computed binding energy $D_e = 20\,490.0$ cm^{-1} and the equilibrium internuclear distance $R_e = 1.0330$ Å are in a satisfactory agreement with the experimental values $D_e = 20\,488.5$ cm^{-1} and $R_e = 1.0327$ Å. In this case a van der Waals potential maximum has been found to occur at $R = 9.0$ a.u. and 105.5 cm^{-1} above the dissociation limit. Preliminary results for the ${}^1\Sigma_u{}^+$ state at $R \approx R_e$ are also given.

INTRODUCTION

ACCURATE ground-state energy of the hydrogen molecule has been computed recently by the present authors,[1] in the adiabatic approximation, for several values of the internuclear distance R. In that calculation the wavefunction was represented by an expansion in elliptic coordinates first used by James and Coolidge.[2] It is, however, well known that the expansion converges more and more slowly with increasing value of R, and therefore the most accurate calculations have been carried out only for $R \leq 2.0$ a.u.

For very large distances it is natural to use the perturbation theory to compute the energy of interaction between two atoms. A special perturbation method has been suggested for this purpose by Dalgarno and Lynn,[3] and their numerical results for the interaction energy of two hydrogen atoms in the lowest ${}^1\Sigma_g{}^+$ and ${}^3\Sigma_u{}^+$ states are believed to be of high accuracy. Undoubtedly the perturbation theory is superior to the variational method for large distances between the interacting atoms. In the variational method one computes the total energy of the system and not the interaction energy alone. Therefore it is difficult to get an accurate value of the latter if it is several orders of magnitude smaller than the former. However, for smaller internuclear separations a finite-order perturbation theory fails to give accurate results, while the variational approach has the important advantage of giving always an upper limit of the energy.

The most accurate variational calculations for large distances between the hydrogen atoms are probably those carried out by Hirschfelder and Linnett.[4] Their energies for both the ${}^1\Sigma_g{}^+$ and ${}^3\Sigma_u{}^+$ states are significantly higher than those of Dalgarno and Lynn[3]; it is however not known whether the latter lie higher or lower than the true energies, and a more accurate variational treatment of the problem is certainly desirable. For the ground state, results of such calculations could be compared with the so called experimental potential-energy curve obtained recently by Weissman *et al.*[5] from the experimental vibrational energies[6] by using the Rydberg–Klein–Rees method. However, the "experimental" ground-state potential-energy curve can only be determined up to $R = 6.16$ a.u. which is the classical turning point for the highest (14th) vibrational level. For still larger internuclear distances, including the important van der Waals region, no experimental data are available. Thus, accurate theoretical results for this region would represent a valuable contribution to the theory of the long-range interatomic and intermolecular forces.

For the same reason it would be interesting to compute an accurate potential-energy curve for the lowest ${}^3\Sigma_u{}^+$ state which is known to be repulsive and to have only a shallow van der Waals minimum at a large value of R. The repulsive section of this potential-energy curve is of importance for scattering problems and to account for the well-known extensive continuous spectrum of H_2.

Among other states of H_2 which are of interest there is the lowest ${}^1\Pi_u$ state. The van der Waals interaction in this case gives rise to a maximum of the potential energy, first considered in detail by King and Van Vleck,[7] and computed recently by Browne,[8] and Sales.[9]

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† Permanent address: Institute of Nuclear Research, Polish Academy of Sciences, Warsaw, Poland.

‡ Permanent address: Department of Theoretical Physics, Nicholas Copernicus University, Torun, Poland.

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[7] G. W. King and J. H. Van Vleck, Phys. Rev. **55**, 1165 (1939).

[8] J. C. Browne, J. Chem. Phys. **40**, 43 (1964).

[9] K. D. Sales (private communication).

Since in the experimental determination of the dissociation energy of H_2 the molecule may be supposed[10] to dissociate via this state, the problem of existence of the potential hump and of its height is of great interest.

In the present work we have extended to large internuclear distances the previous calculation of the ground-state energy of H_2 using a generalized James-and-Coolidge-type wavefunction. In addition, expectation values of several operators have been computed as functions of the internuclear distance. For the excited states ${}^3\Sigma_u^+$ and ${}^1\Pi_u$, the potential-energy curves have also been calculated, and the results are reported below. The accuracy of the ${}^3\Sigma_u^+$ curve is believed to be comparable to that of the ground-state curve. For the ${}^1\Pi_u$ state the results are somewhat inferior and are, perhaps, by a few reciprocal centimeters higher than the accurate eigenvalues of the nonrelativistic clamped nuclei Hamiltonian. The energy of the lowest ${}^1\Sigma_u^+$ state for the equilibrium internuclear distance has also been computed and an unexpected disagreement with the experimental value has been found. The reason of the discrepancy is unclear.

METHOD OF CALCULATION

For infinite distance between two hydrogen atoms the Heitler–London wavefunction

$$\Psi=\psi_a(1)\psi_b(2)+\psi_b(1)\psi_a(2) \qquad (1)$$

represents the exact solution of the electronic Schrödinger equation for the ground state of the system. However, even for large but finite distances (1) does not represent an accurate wavefunction, since, without additional terms which take into account the electron correlation, it is unable to account for the long-range dispersion forces between the two atoms.

The James and Coolidge wavefunction is certainly adequate for small and intermediate distances. It is therefore reasonable to expect that, if this wavefunction is generalized to have the asymptotic form (1) for $R\rightarrow\infty$, the generalized wavefunction will be flexible enough to give accurate energies, with a finite number of terms, also for large values of R.

For the ground state of H_2 the James and Coolidge wavefunction is defined by

$$\Psi=\sum_i c_i[\Phi_i(1,2)+\Phi_i(2,1)], \qquad (2)$$

$$\Phi_i(1,2)=\exp[-\alpha(\xi_1+\xi_2)]\xi_1^{r_i}\eta_1^{s_i}\xi_2^{\bar{r}_i}\eta_2^{\bar{s}_i}\rho^{\mu_i}, \qquad (3)$$

where ξ and η are elliptic coordinates, $\rho=2r_{12}/R$, and r_{12} denotes the interelectronic distance. The exponent α as well as the linear coefficients c_i are variational parameters.

In elliptic coordinates the asymptotic wavefunction (1) has the form

$$\Psi=\exp[-\tfrac{1}{2}R(\xi_1+\xi_2)]\cosh[-\tfrac{1}{2}R(\eta_1-\eta_2)]. \qquad (4)$$

Therefore it is natural to generalize the James and Coolidge wavefunction by using instead of (3) the following basis set:

$$\Phi_i=\exp[-\alpha\xi_1-\bar{\alpha}\xi_2]\cosh(\beta\eta_1+\bar{\beta}\eta_2)\xi_1^{r_i}\eta_1^{s_i}\xi_2^{\bar{r}_i}\eta_2^{\bar{s}_i}\rho^{\mu_i}, \qquad (5)$$

where α, $\bar{\alpha}$, β, $\bar{\beta}$ are variational parameters. The same basis set can be used not only for the ground state but also for states of a different symmetry. If the total wavefunction is assumed in the form

$$\Psi=\sum_i c_i[\Phi_i(1,2)x_1^l\pm\Phi_i(2,1)x_2^l], \qquad (6)$$

where x_i denotes the Cartesian coordinate of the ith electron perpendicular to the molecular axis, then for $l=0$ and $l=1$, Eq. (6) represents wavefunctions for Σ and Π states, respectively. The $+$ or $-$ sign in (6) results in a singlet or triplet state.[11] The g or u character of the wavefunction is determined by the parity of $s_i+\bar{s}_i+l$ in (5) and (6). For the lowest ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states the asymptotic values of the exponents are $\alpha=\bar{\alpha}=\beta=-\bar{\beta}=\frac{1}{2}R$ and for the lowest ${}^1\Pi_u$ state $\alpha=-\beta=\frac{1}{4}R$, $\bar{\alpha}=\bar{\beta}=\frac{1}{2}R$. Wavefunctions (6) with the basis set (5) were used in the present calculation. If, however, in the functions (5) $\cosh(\beta\eta_1+\bar{\beta}\eta_2)$ is replaced by $\exp(\beta\eta_1+\bar{\beta}\eta_2)$, the wavefunction (6) has neither g nor u symmetry and therefore can be employed to the heteropolar two-electron diatomic molecules, e.g., to the helium hydride ion HeH^+.[12]

The numerical procedure adopted in this work was different from that used previously[1] in the case of $\alpha=\bar{\alpha}$ and $\beta=\bar{\beta}=0$. Because of the relative complexity of the wavefunction (6), we had to write an entirely new computer program for the numerical integration and for the computation of the required matrix elements. If the Φ_i functions defined by (5) are used in (6), any matrix element needed in our computations can be expressed in terms of the integrals

$$\begin{aligned}\mathcal{J}_{rs\bar{r}\bar{s}}^{\mu k}=\int &\exp(-\alpha_1\xi_1-\alpha_2\xi_2+\beta_1\eta_1+\beta_2\eta_2)\xi_1^r\eta_1^s\xi_2^{\bar{r}}\eta_2^{\bar{s}}\rho^\mu\\ &\times[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{k/2}\\ &\times[\cos(\phi_1-\phi_2)]^k d\xi_1\cdots d\phi_2, \qquad (7)\end{aligned}$$

where r, s, $\bar{r}$, $\bar{s}\geqslant 0$, $\mu=-1$, 0, $k\geqslant 0$, and α_1, α_2, β_1, β_2 are simple linear combinations of the α, $\bar{\alpha}$ and β, $\bar{\beta}$, respectively, from Eq. (5).

For $\mu=0$ all integrations in (7) are elementary, as each of the J integrals in this case is simply a product of two one-electron integrals. For $\mu=-1$ the J integrals resemble very closely the familiar exchange integrals and the integrations can be performed by making

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[10] G. Herzberg and A. Monfils, J. Mol. Spectry. 5, 482 (1960).

[11] Note that for the ${}^3\Sigma_u^+$ state $\cosh(\beta\eta_1+\bar{\beta}\eta_2)$ in the asymptotic form (4) should be replaced by $\sinh(\beta\eta_1+\bar{\beta}\eta_2)$ and, e.g., for the ${}^1\Sigma_u^+$ state by a combination of $\cosh(\beta\eta_1+\bar{\beta}\eta_2)$ and $\sinh(\beta\eta_1+\bar{\beta}\eta_2)$. However, it may be shown that for the ${}^3\Sigma_u^+$ state the basis set (5) results in the correct asymptotic energy and therefore this basis set was used in the present calculation.

[12] L. Wolniewicz, "Variational Treatment of the HeH^+ ion and the β Decay in HT," J. Chem. Phys. (to be published).

use of the Neumann expansion for r_{12}^{-1}. If $\beta_1=0$ or $\beta_2=0$ the integrations over η_i leave a finite number of terms in the sum over l from the Neumann expansion. If, however, β_1 and β_2 are both different from zero, the sum over l remains infinite and this introduces some computational problems. Since, in general, different J integrals entering a matrix element can differ by several orders of magnitude, not all of them need be computed with the same accuracy. For this reason and because of the large number of required J integrals, it has proved to be more convenient and more economical to apply the Neuman expansion to the whole matrix elements, rather than to express them in terms of the J integrals.

Each matrix element is composed of contributions with different α_1, α_2, β_1, β_2 values, corresponding to different combinations of α, $\bar{\alpha}$, β, $\bar{\beta}$ from Eq. (5). For given α_1, α_2, β_1, β_2 the contribution $M_{ik}(\alpha_1, \cdots, \beta_2)$ to a matrix element $M_{ik}(\alpha, \bar{\alpha}, \beta, \bar{\beta})$ was expressed as

$$M_{ik}(\alpha_1, \alpha_2, \beta_1, \beta_2)=\sum_l\sum_m M_{ik}^{(ml)}(\alpha_1, \alpha_2, \beta_1, \beta_2), \quad (8)$$

where $M_{ik}^{(ml)}$ denotes the term due to a pair of l, m indices in the Neumann expansion. Each $M_{ik}^{(ml)}(\alpha_1, \alpha_2, \beta_1, \beta_2)$ was built up from Ruedenberg's[13] $\Phi_{n\bar{n}}^{ml}(\alpha_1, \alpha_2)$ and $B_j^{ml}(\beta)$ integrals. The $\Phi_{n\bar{n}}^{ml}$ integrals with $m=0$, for each pair of α_1, α_2, have been computed numerically by employing the Simpson rule. For $m\neq0$ the Ruedenberg recursion formula was used. To compute the B_j^{ml} functions we have used a program written by Wahl[14] who has kindly provided us with the program and with all the necessary information.

The sum over m in (8) truncates in any case when the integration over ϕ is carried out. However, the sum over l remains infinite, unless $\beta=0$. The convergence threshold for this summation was in our case 10^{-8}, i.e., the summation for each matrix element was continued until the relative magnitudes of M_{ik}^{ml}/M_{ik} for two consecutive l values were smaller in absolute value than 10^{-8}.

The accuracy of the computed matrix elements has been checked in various ways. First, a great number of hand calculations have been carried out to check the program step by step. Next, the matrices have been computed for the special case $\alpha=\bar{\alpha}$, $\beta=\bar{\beta}=0$ and compared with our previous results obtained with the earlier program.[1] The equality of the matrix elements computed in two different ways was a check for both programs and increased our confidence in the correctness of the obtained results. Finally, many test runs have been made for $\alpha\neq\bar{\alpha}$ and $\beta\neq0$, $\bar{\beta}\neq0$. As each term of the wavefunction consists of a sum

$$\Phi_i(1, 2)\pm\Phi_i(2, 1),$$

the matrix elements of an operator $\hat{M}$ are sums of four terms of the form

$$M=\int \exp(-\alpha\xi_1-\bar{\alpha}\xi_2)\cosh(\beta\eta_1+\bar{\beta}\eta_2)\xi_1^r\eta_1^s\xi_2^{\bar{r}}\eta_2^{\bar{s}}\rho^\mu\hat{M}$$
$$\times\exp(-\alpha^1\xi_1-\bar{\alpha}^1\xi_2)$$
$$\times\cosh(\beta^1\eta_1+\bar{\beta}^1\eta_2)\xi_1^p\eta_1^q\xi_2^{\bar{p}}\eta_2^{\bar{q}}\rho^\nu d\xi_1\cdots d\phi_2, \quad (9)$$

where $\alpha^1=\alpha$ and $\bar{\alpha}^1=\bar{\alpha}$ or $\alpha^1=\bar{\alpha}$ and $\bar{\alpha}^1=\alpha$, and similar relations hold for β. From symmetry considerations one can replace one of the hyperbolic functions, say, $\cosh(\beta\eta_1+\bar{\beta}\eta_2)$, by a single exponential function $\exp(\beta\eta_1+\bar{\beta}\eta_2)$, thus getting

$$M=\tfrac{1}{2}(M_++M_-) \quad (10)$$

with

$$M_\pm=\int \exp(-\alpha\xi_1-\bar{\alpha}\xi_2+\beta\eta_1+\bar{\beta}\eta_2)\xi_1^r\eta_1^s\xi_2^{\bar{r}}\eta_2^{\bar{s}}\rho^\mu\hat{M}$$
$$\times\exp(-\alpha^1\xi_1-\bar{\alpha}^1\xi\pm\beta^1\eta_1\pm\bar{\beta}^1\eta_2)\xi_1^p\eta_1^q\xi_2^{\bar{p}}\eta_2^{\bar{q}}\rho^\nu d\xi_1\cdots d\phi_2. \quad (11)$$

The $M_\pm$ elements have been checked stepwise. First the $\alpha\neq\bar{\alpha}$, $\beta=\bar{\beta}=0$ case was considered. The matrix elements in this case depend only on two parameters: α, $\bar{\alpha}$. By making use of the obvious expansion

$$\exp(-\bar{\alpha}\xi)=\exp(-\alpha\xi)\sum_n[(\bar{\alpha}-\alpha)^n/n!]\xi^n, \quad (12)$$

the $M_\pm(\alpha, \bar{\alpha})$ elements, for small differences $|\bar{\alpha}-\alpha|$, can be easily expressed in terms of $M_\pm(\alpha, \alpha)$. Thus the first test of the program consisted in computing the matrix elements with $\alpha=\bar{\alpha}$, employing (12) to get the elements with $\alpha\neq\bar{\alpha}$, and comparing these numbers with those resulting from a direct application of our program for $\alpha\neq\bar{\alpha}$. In all tested cases we had an excellent agreement; the differences between the corresponding numbers never exceeded 2 in the last (eighth) significant figure. In the next step, we expanded the $\exp(\beta\eta)$ functions in power series and thus the $M_\pm(\alpha, \bar{\alpha}, \beta, \bar{\beta})$ matrix elements could be expressed in terms of the already checked elements with $\beta=\bar{\beta}=0$. Again the two sets of numbers were in complete agreement. Finally the total matrix elements have been tested in a similar way. If we denote the terms in the wavefunction (6) as

$$\{\alpha, \bar{\alpha}, \beta, \bar{\beta}; r, s, \bar{r}, \bar{s}, \mu\}\equiv\Phi(1, 2)\pm\Phi(2, 1),$$

where Φ is given by (5), we get the following relations:

$$(\partial/\partial\alpha)^n\{\alpha, \bar{\alpha}, \beta, \bar{\beta}; r, s, \bar{r}, \bar{s}, \mu\}$$
$$=(-1)^n\{\alpha, \bar{\alpha}, \beta, \bar{\beta}; r+n, s, \bar{r}, \bar{s}, \mu\},$$

$$(\partial/\partial\alpha)^n\{\alpha, \bar{\alpha}, \beta, \bar{\beta}; r, s, \bar{r}, \bar{s}, \mu\}_{\beta=\bar{\beta}=0}$$
$$=\begin{cases}\{\alpha, \alpha, 0, 0; r, s+n, \bar{r}, \bar{s}, \mu\} & \text{for even } n\\ 0 & \text{for odd } n.\end{cases}$$

Similar relations hold for the derivatives with respect to $\bar{\alpha}$ and $\bar{\beta}$, and for the cross derivatives. Hence, the

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[13] K. Ruedenberg, J. Chem. Phys. **19**, 1459 (1951).

[14] A. C. Wahl (private communication).

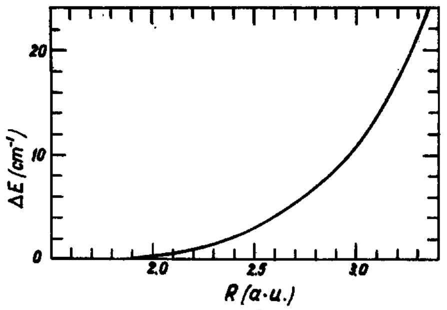

FIG. 1. Improvement of the ground-state energy of H_2 due to the β variation in the 54-term wavefunction.

total matrix elements consisting of eight $M_\pm$ integrals may be easily expressed as a power series in $(\bar{\alpha}-\alpha)$, β and $\bar{\beta}$ and can be computed for any set of the exponents α, $\bar{\alpha}$, β, $\bar{\beta}$ if the matrix elements for $\alpha=\bar{\alpha}$ and $\beta=\bar{\beta}=0$ are known. This method, different from that used by the program, was employed in the hand computations. The full agreement of the results confirmed the correctness of the analysis and the accuracy of the computations.

Note that the $M_\pm$ integrals defined by (11) are identical with the complete matrix elements in the heteropolar case,[12] i.e., when the basis functions (5) need not be symmetrical or antisymmetrical with respect to the inversion and $\cosh(\beta\eta_1+\bar{\beta}\eta_2)$ in (5) is replaced by $\exp(\beta\eta_1+\bar{\beta}\eta_2)$.

RESULTS AND DISCUSSION

The numerical computations were carried out on the IBM 7094 computer at the Computation Center of the University of Chicago. The computation of the ground-state energy was started by reproducing the previously reported[1] results obtained with $\alpha=\bar{\alpha}$ and $\beta=\bar{\beta}=0$. Since the present program was more general, we have made some additional test runs in which the number of integration points in the numerical integration was gradually increased up to the maximum number of 250 points and for shorter expansion of the wavefunction up to 500 points. The results were completely satisfactory; the small oscillations of the total energy which appeared in the last (eighth) significant figure could be attributed to rounding errors.

In the next step the exponents α, $\bar{\alpha}$, β, $\bar{\beta}$ were varied. It has been found that for $R\approx R_e$ the independent variation of all four nonlinear parameters did not improve our previous results obtained with $\alpha=\bar{\alpha}$ and $\beta=\bar{\beta}=0$. For the ground state the variation has been found to be effective only for short expansions or for large internuclear distances. However, even for large R it turned out to be completely sufficient to put $\beta=-\bar{\beta}$ and $\alpha=\bar{\alpha}$, and to vary only two nonlinear parameters. In Fig. 1 we show graphically the energy improvement resulting from introducing the variational parameter β to our previously used 54-term wavefunction of James and Coolidge type. It is seen that even for $R=2.0$ a.u. the energy improvement amounts only to 0.4 cm^{-1}, and vanishes at about $R=1.6$ a.u. Since for the previously used 80-term wavefunction the energy improvement due to β variation must be still smaller, we decided to accept the previous 80-term results for $R\leq 2.0$ a.u. and to vary β only for larger values of the internuclear distance.

The final electronic energies for the ground state of H_2 are listed in Table I where in addition to the total and potential energies E and V we give the binding energy (in cm^{-1}) and the ratio $V/2E$ which, by invoking the virial theorem, enabled us to calculate the derivative dE/dR given in the last column of Table I. The total energy is plotted in Fig. 2 which also shows the energy curves for other states to be discussed below.

As has already been mentioned we could not use the same expansion of the wavefunction for all internuclear distances. To get reliable results, one has to avoid cancellation of significant figures in the final computation of the energy $E=\sum c_i c_k h_{ik}$. In consequence of $H_{00}/S_{00}\approx E$ it is obvious that the cancellation must occur when $|c_0|^2>10$. Because of this difficulty we had to exclude from the wavefunction all "almost linearly dependent" terms. In practice we adopted the following procedure: having chosen an expansion for a given internuclear distance, we used it for larger R until we arrived at a point, say R_1, where the condition $|c_0|^2<10$ was not fulfilled. At that point we made a new selection of terms which resulted as a rule in a shorter expansion for the wavefunction. The new function was then used for $R\geq R_1$ and also for $R\lesssim R_1$ if it improved the energy in the latter region. When the next point was reached where $|c_0|^2\approx 10$, the whole process was repeated.

The computed potential-energy curve can be compared with the curve constructed from the observed vibrational and rotational energies by using the Rydberg–Klein–Rees (RKR) method. The RKR method,

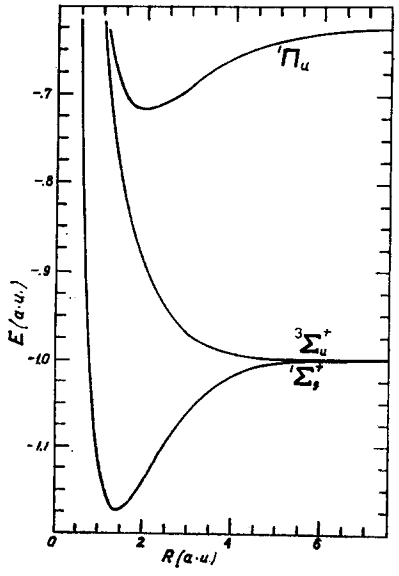

FIG. 2. Computed potential-energy curves for H_2.

Table I. Theoretical ground-state energies for the hydrogen molecule computed in the Born–Oppenheimer approximation.[a]

R	N	α	β	D	E	V	$V/2E$	dE/dR
.4000	54	.407	.0	-193093.2	-.1202028	-2.3630289	9.8293421	-5.3065581
.4500	54	.416	.0	-142454.8	-.3509282	-2.5024310	3.5654456	-4.0012768
.5000	54	.442	.0	-103893.4	-.5266270	-2.5917873	2.4607429	-3.0770665
.5500	80	.536	.0	-74013.3	-.6627707	-2.6465751	1.9965993	-2.4018794
.6000	80	.562	.0	-50559.5	-.7696341	-2.6769660	1.7391160	-1.8961623
.6500	80	.597	.0	-31964.0	-.8543614	-2.6899810	1.5742641	-1.5096280
.7000	80	.636	.0	-17113.3	-.9220261	-2.6904771	1.4590027	-1.2091784
.7500	80	.662	.0	-5193.7	-.9763357	-2.6819180	1.3734610	-.9723288
.8000	80	.698	.0	4401.7	-1.0200556	-2.6668205	1.3071937	-.7833866
.9000	80	.765	.0	18357.3	-1.0836422	-2.6239059	1.2106883	-.5073572
1.0000	80	.837	.0	27333.0	-1.1245385	-2.5715404	1.1433759	-.3224634
1.1000	80	.892	.0	32933.5	-1.1500562	-2.5152997	1.0935551	-.1956248
1.2000	80	.959	.0	36198.9	-1.1649342	-2.4584207	1.0551758	-.1071269
1.3000	80	1.014	.0	37825.6	-1.1723459	-2.4027901	1.0247786	-.0446910
1.3500	80	1.043	.0	38180.4	-1.1739627	-2.3758101	1.0118763	-.0206553
1.3900	80	1.066	.0	38287.7	-1.1744517	-2.3547115	1.0024727	-.0041785
1.4000	80	1.072	.0	38292.7	-1.1744744	-2.3495093	1.0002386	-.0004003
1.4010	80	1.072	.0	38292.7	-1.1744746	-2.3489908	1.0000177	-.0000297
1.4011	80	1.072	.0	38292.7	-1.1744746	-2.3489392	.9999957	.0000071
1.4100	80	1.077	.0	38289.5	-1.1744599	-2.3443366	.9980488	.0032505
1.4500	80	1.100	.0	38200.8	-1.1740558	-2.3239571	.9897132	.0166583
1.5000	80	1.121	.0	37937.0	-1.1728537	-2.2991984	.9801727	.0310060
1.6000	80	1.165	.0	36999.0	-1.1685799	-2.2521884	.9636433	.0531071
1.7000	80	1.210	.0	35655.2	-1.1624570	-2.2086130	.9499762	.0684124
1.8000	80	1.258	.0	34033.3	-1.1550670	-2.1685307	.9387034	.0786685
1.9000	80	1.295	.0	32229.8	-1.1468496	-2.1319110	.9294641	.0851517
2.0000	80	1.342	.0	30316.3	-1.1381312	-2.0986802	.9219852	.0887911
2.1000	54	1.360	.232	28346.5	-1.1291562	-2.0687129	.9160437	.0902855
2.2000	54	1.406	.263	26364.0	-1.1201233	-2.0419623	.9114900	.0901292
2.3000	54	1.453	.296	24399.5	-1.1111725	-2.0182976	.9081837	.0887163
2.4000	54	1.499	.328	22477.0	-1.1024127	-1.9975905	.9060085	.0863479
2.5000	54	1.546	.360	20614.7	-1.0939273	-1.9797159	.9048663	.0832555
2.6000	54	1.575	.375	18826.8	-1.0857810	-1.9645346	.9046643	.0796259
2.7000	54	1.640	.423	17122.6	-1.0780164	-1.9519321	.9053351	.0755929
2.8000	54	1.680	.450	15510.3	-1.0706700	-1.9417264	.9067810	.0712906
2.9000	54	1.733	.487	13994.6	-1.0637641	-1.9337932	.9089389	.0668052
3.0000	54	1.780	.519	12578.5	-1.0573118	-1.9279398	.9117177	.0622279
3.1000	54	1.834	.549	11263.1	-1.0513185	-1.9239862	.9150349	.0576293
3.2000	54	1.888	.578	10048.3	-1.0457832	-1.9217428	.9188055	.0530699
3.3000	54	1.942	.610	8932.7	-1.0407003	-1.9210189	.9229453	.0486005
3.4000	54	2.000	.640	7913.8	-1.0360578	-1.9216012	.9273620	.0442689
3.5000	54	2.050	.670	6988.1	-1.0318402	-1.9232798	.9319659	.0401145
3.6000	54	2.100	.706	6151.3	-1.0280272	-1.9258641	.9366795	.0361640
3.7000	54	2.150	.741	5398.6	-1.0245978	-1.9291385	.9414126	.0324479
3.8000	54	2.200	775	4725.2	-1.0215297	-1.9329636	.9461123	.0289726
3.9000	54	2.250	.812	4125.4	-1.0187967	-1.9371441	.9507020	.0257562
4.0000	54	2.300	.848	3592.6	-1.0163689	-1.9415062	.9551189	.0228079
4.1000	54	2.350	.889	3122.0	-1.0142247	-1.9459930	.9593500	.0201113
4.2000	54	2.400	.930	2707.7	-1.0123371	-1.9504301	.9633303	.0176772
4.3000	54	2.450	.971	2344.2	-1.0106810	-1.9547796	.9670607	.0154842
4.4000	35	2.441	1.054	2025.8	-1.0092303	-1.9590288	.9705559	.0135072
4.5000	35	2.496	1.087	1748.8	-1.0079682	-1.9629989	.9737405	.0117639
4.6000	35	2.551	1.120	1507.9	-1.0068703	-1.9667247	.9766525	.0102208
4.7000	35	2.606	1.152	1298.8	-1.0059176	-1.9701804	.9792949	.0088628
4.8000	35	2.662	1.185	1117.6	-1.0050923	-1.9733754	.9816886	.0076686
4.9000	35	2.717	1.217	960.9	-1.0043782	-1.9762917	.9838384	.0066254
5.0000	35	2.772	1.250	825.8	-1.0037626	-1.9789434	.9857627	.0057164
5.1000	35	2.817	1.295	709.1	-1.0032309	-1.9813473	.9874832	.0049244
5.2000	35	2.861	1.339	608.8	-1.0027740	-1.9835202	.9890166	.0042361
5.3000	35	2.906	1.384	522.3	-1.0023800	-1.9854763	.9903810	.0036384
5.4000	35	2.951	1.429	448.2	-1.0020423	-1.9872066	.9915782	.0031256
5.5000	35	2.989	1.464	384.5	-1.0017521	-1.9887490	.9926353	.0026828
5.6000	35	3.033	1.517	329.9	-1.0015030	-1.9901214	.9935674	.0023008
5.7000	35	3.076	1.569	283.1	-1.0012899	-1.9913336	.9943841	.0019730
5.8000	35	3.120	1.622	242.9	-1.0011069	-1.9924043	.9951007	.0016913
5.9000	35	3.164	1.675	208.5	-1.0009498	-1.9933786	.9957435	.0014442
6.0000	35	3.207	1.727	178.9	-1.0008150	-1.9942168	.9962964	.0012355
6.1000	35	3.251	1.780	153.7	-1.0007002	-1.9949376	.9967709	.0010595
6.2000	35	3.295	1.833	132.3	-1.0006030	-1.9955517	.9971745	.0009120
6.3000	25	3.190	2.930	113.3	-1.0005162	-1.9962159	.9975930	.0007645
6.4000	25	3.250	3.000	98.0	-1.0004466	-1.9966965	.9979026	.0006557
6.5000	25	3.310	3.070	84.8	-1.0003864	-1.9971259	.9981773	.0005611
6.6000	25	3.370	3.150	73.0	-1.0003328	-1.9975166	.9984260	.0004771
6.7000	25	3.410	3.230	63.8	-1.0002906	-1.9978183	.9986189	.0004124
6.8000	25	3.460	3.310	54.6	-1.0002466	-1.9981429	.9988232	.0003462
6.9000	25	3.500	3.390	47.3	-1.0002154	-1.9983950	.9989823	.0002950
7.0000	25	3.550	3.470	41.5	-1.0001889	-1.9986055	.9991140	.0002532
7.2000	23	3.650	3.580	31.5	-1.0001434	-1.9989473	.9993303	.0001860
7.4000	23	3.750	3.690	23.8	-1.0001086	-1.9992067	.9994948	.0001366
7.6000	23	3.825	3.800	19.1	-1.0000868	-1.9993928	.9996096	.0001027
7.8000	23	3.900	3.900	15.0	-1.0000682	-1.9995334	.9996985	.0000773
8.0000	23	4.000	4.000	11.6	-1.0000526	-1.9996605	.9997775	.0000556
8.2500	19	4.125	4.125	8.9	-1.0000404	-1.9997821	.9998507	.0000362
8.5000	17	4.250	4.250	6.9	-1.0000314	-1.9998516	.9998945	.0000248
9.0000	17	4.500	4.500	4.1	-1.0000185	-1.9998794	.9999212	.0000175
9.5000	14	4.750	4.750	2.7	-1.0000121	-1.9999437	.9999598	.0000085
10.0000	14	5.000	5.000	2.0	-1.0000091	-1.9999596	.9999707	.0000059

[a] N denotes the number of terms in the wavefunction; R, E, and V are in atomic units, D in cm^{-1}. The results for $0.4 \leq R \leq 2.0$ are from Ref. 1.

TABLE II. Comparison of the computed potential-energy curves for the ground state of H_2 with the classical turning points $R_{\min}$ and $R_{\max}$ for the vth vibrational level obtained by using the RKR method.[a]

v	$R_{\min}$[b]	ΔR_1	ΔR_2	ΔR_3	$R_{\max}$[b]	ΔR_1	ΔR_2	ΔR_3
0	0.633	0	0	0	0.883	0	0	0
1	0.571	0	0	0	1.013	0	0	1
2	0.535	−1	−1	0	1.120	0	0	0
3	0.509	0	0	0	1.219	0	0	0
4	0.489	0	0	0	1.316	0	0	0
5	0.473	0	0	0	1.413	0	0	0
6	0.460	0	0	0	1.513	0	0	0
7	0.449	0	0	0	1.618	−1	−1	0
8	0.439	0	0	0	1.730	−1	−1	0
9	0.432	0	0	0	1.853	−1	−1	0
10	0.425	0	0	0	1.992	−1	−1	0
11	0.420	0	0	0	2.158	−1	−1	0
12	0.416	0	0	0	2.370	−1	−1	···
13	0.413	0	0	0	2.675	−2	−1	···
14	0.411	0	0	0	3.260	0	−1	···

[a] R in angstroms, ΔR_i in 10^{-3} Å. [b] See Ref. 5.

based on the WKB approximation, gives the classical turning points for the rotationless vibrational energy levels, and these points are believed to determine the most probable potential-energy curve. The reference point for the energy in the RKR method, is fixed at the bottom of the energy curve rather than at the dissociation limit. However, to compare different energy curves, it seems more natural to use the dissociation limit as the reference energy, for this is the only really well established point of such curves. This point of view was adopted in the present calculation, i.e., the lowest vibrational level in the electronic ground state was assumed to lie, according to the most recent data,[10] 36 113.6 cm^{-1} below the dissociation limit.

Having computed the potential-energy curve $E(R)$ one can use the experimental values[6] of the vibrational levels, E_v, to find the corresponding classical turning points to be compared with those obtained in the RKR approach. The turning points for the vth vibrational level are solutions of the equation

$$E(R)=E_v \qquad (v=0,\, 1,\, \cdots 14). \tag{13}$$

For each v the two roots of this equation $R_{\min}$ and $R_{\max}$ have been found by approximating the $E(R)$ curve piecewise by polynomials. The results are presented in Table II. In Columns 2 and 6 we give the most accurate RKR results obtained by Weissman *et al.*[5] By ΔR_i we denote the differences (in 10^{-3} Å) between our results obtained from Eq. (13) and the corresponding RKR values. The first two sets, ΔR_1 and ΔR_2, were computed by using the energies from Table I and approximating the $E(R)$ curve, for the region under consideration, by the second and fifth degree polynomials, respectively. In the computation of ΔR_3 the diagonal corrections for nuclear motion computed previously[1] were added to the total energy, interpolation being made by using the second-degree polynomials. Unfortunately, the corrections had been computed only for internuclear distances up to $R\approx 2$ Å. For this reason the corrected turning points could not be calculated for larger values of R.

TABLE III. The changes of the energy due to a shift by 5.10^{-4} Å of the classical turning points from Table II.

	$E(\text{cm}^{-1})$			$E(\text{cm}^{-1})$	
v	at $R_{\min}$	at $R_{\max}$	v	at $R_{\min}$	at $R_{\max}$
0	22.9	13.2	8	139.7	10.4
1	46.3	17.7	9	152.3	8.3
2	62.2	18.7	10	159.0	6.3
3	78.6	18.3	11	166.0	4.3
4	94.3	17.3	12	173.3	2.5
5	107.6	15.9	13	181.0	1.1
6	122.6	14.3	14	181.0	0.2
7	133.7	12.4			

It is seen from Table II that by taking into account the corrections for nuclear motion, we obtained a very good agreement with the RKR results. The slight disagreement for the $v=1$ level may be due to the WBK approximation and/or to the fact that, in the Weissman *et al.* calculations, a zero-point energy was used that is by 8 cm^{-1} smaller than the most recent experimental value.[10] In the RKR procedure the differences $R_{\max}-R_{\min}$ and $1/R_{\min}-1/R_{\max}$ are given by integrals over the energy extended from the minimum of the energy curve to the respective vibrational level. Hence, the turning points of the lowest levels may be expected to be sensitive to the assumed value of the zero-point vibration energy.

It must be pointed out, however, that one should not overestimate the significance of the agreement seen in Table II; an accuracy of 5×10^{-4} Å is not sufficient for a precise comparison of the energies. This is best seen from Table III where the changes in the energy, $\Delta E=(dE/dR)\Delta R$, resulting from a shift of the turning points by $\Delta R=5\times10^{-4}$ Å are given.

It is well known that energy is not a good criterion to judge the accuracy of an approximate wavefunction. The root-mean-square error in the wavefunction is known[15] to be roughly equal to the square root of the relative error in the energy. However, the accuracy of the expectation values of other operators may be quite

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[15] C. Eckhart, Phys. Rev. **36**, 878 (1930).

TABLE IV. Convergence of various expectation values (in atomic units) with increasing number of terms in the wavefunction for the ground state of H_2 ($R=1.4$ a.u., $\alpha=1.0$).

N	r_{12}^{-1}	r_{12}	r_{12}^2	x_1x_2	z_1z_2	x_1^2	z_1^2
3	.59362929	.21344626+1	.54303682+1	-.85479393-1	-.11731880	.77130383	.88429883
4	.58675049	.21733954+1	.56586955+1	-.84670779-1	-.11573395	.81056153	.92314918
5	.59323335	.21563071+1	.55756360+1	-.74076626-1	-.11475130	.76824885	.98841577
6	.59325589	.21520873+1	.55444906+1	-.71582015-1	-.11127432	.76589057	.98602582
7	.59051903	.21560938+1	.55541124+1	-.59616121-1	-.14791937	.75998549	.98993361
8	.58963352	.21630391+1	.55948549+1	-.62749395-1	-.15390254	.76224474	.99353667
9	.58978286	.21583179+1	.55666148+1	-.58070142-1	-.15030859	.76186388	.99313079
10	.58948506	.21613656+1	.55903657+1	-.58004440-1	-.14989334	.76604208	.99719652
11	.58931394	.21620144+1	.55936858+1	-.57611389-1	-.15088866	.76164982	.10074318+1
12	.58930283	.21620015+1	.55930877+1	-.57565821-1	-.15072635	.76164372	.10073984+1
13	.58806045	.21661674+1	.56146476+1	-.57221144-1	-.15023551	.76516978	.10123065+1
14	.58786829	.21671589+1	.56195879+1	-.54884664-1	-.15666240	.76475856	.10138451+1
15	.58788525	.21664599+1	.56125720+1	-.54423004-1	-.15564285	.76434486	.10131074+1
16	.58763646	.21670479+1	.56159426+1	-.54655546-1	-.15588867	.76317602	.10164195+1
17	.58754618	.21677201+1	.56219731+1	-.54770852-1	-.15809507	.76309744	.10171549+1
18	.58754817	.21677496+1	.56220956+1	-.54726542-1	-.15824364	.76307214	.10172068+1
19	.58756222	.21679889+1	.56261192+1	-.55443109-1	-.15913821	.76294740	.10171404+1
20	.58752695	.21682127+1	.56275524+1	-.55385573-1	-.15935714	.76131093	.10210261+1
21	.58753619	.21681872+1	.56274265+1	-.55375639-1	-.15934260	.76129057	.10210382+1
22	.58753601	.21681828+1	.56274811+1	-.55385580-1	-.15934990	.76129135	.10210368+1
23	.58752304	.21681781+1	.56273359+1	-.55461119-1	-.15910576	.76133481	.10209704+1
24	.58752733	.21680776+1	.56266212+1	-.55703891-1	-.15836629	.76135800	.10208205+1
25	.58752389	.21680801+1	.56265319+1	-.55735955-1	-.15823569	.76137958	.10207992+1
26	.58737695	.21689470+1	.56318333+1	-.55742672-1	-.15821574	.76221369	.10217882+1
27	.58738029	.21689529+1	.56318398+1	-.55448448-1	-.15877550	.76195989	.10223277+1
28	.58737145	.21690072+1	.56322284+1	-.55046279-1	-.15968845	.76189336	.10225464+1
29	.58737301	.21689613+1	.56316111+1	-.55055405-1	-.15951297	.76187273	.10224363+1
30	.58737612	.21689313+1	.56314435+1	-.55037074-1	-.15951120	.76188041	.10223756+1
31	.58737788	.21689265+1	.56314738+1	-.55008707-1	-.15961099	.76186062	.10223873+1
32	.58736761	.21690462+1	.56328659+1	-.55037761-1	-.15965079	.76205164	.10226034+1
33	.58736932	.21690148+1	.56327126+1	-.55031102-1	-.15946519	.76203754	.10227538+1
34	.58737240	.21689839+1	.56328026+1	-.55106864-1	-.15940975	.76189879	.10229803+1
35	.58738133	.21688863+1	.56320240+1	-.55130024-1	-.15944921	.76174130	.10228202+1
36	.58737957	.21688900+1	.56320378+1	-.55129054-1	-.15944993	.76174476	.10228213+1
37	.58736748	.21689427+1	.56323242+1	-.55081207-1	-.15962445	.76168618	.10230029+1
38	.58736825	.21689381+1	.56323014+1	-.55076625-1	-.15964694	.76168016	.10229902+1
39	.58736826	.21689361+1	.56322863+1	-.55073197-1	-.15965407	.76167708	.10229885+1
40	.58736356	.21689829+1	.56326523+1	-.55076174-1	-.15964385	.76173756	.10230549+1
41	.58736096	.21689948+1	.56327058+1	-.55062420-1	-.15967242	.76167231	.10232110+1
42	.58736326	.21689716+1	.56325473+1	-.55081576-1	-.15965473	.76164722	.10231613+1
43	.58736280	.21689797+1	.56326210+1	-.55085555-1	-.15967499	.76163205	.10232003+1
44	.58736264	.21689814+1	.56325783+1	-.55116683-1	-.15956994	.76168495	.10231159+1
45	.58736226	.21689834+1	.56325880+1	-.55118125-1	-.15956932	.76168182	.10231248+1
46	.58736214	.21689837+1	.56325862+1	-.55119311-1	-.15956535	.76167652	.10231361+1
47	.58736165	.21689857+1	.56325980+1	-.55112451-1	-.15958289	.76167277	.10231457+1
48	.58736162	.21689877+1	.56326143+1	-.55090310-1	-.15962605	.76168289	.10231347+1
49	.58736170	.21689878+1	.56326135+1	-.55090400-1	-.15962606	.76168273	.10231344+1
50	.58736167	.21689872+1	.56326089+1	-.55090400-1	-.15962392	.76168142	.10231369+1
51	.58736210	.21689835+1	.56325815+1	-.55095220-1	-.15962366	.76167119	.10231343+1
52	.58736255	.21689806+1	.56325857+1	-.55100506-1	-.15961510	.76166516	.10231464+1
53	.58736247	.21689817+1	.56325785+1	-.55104210-1	-.15961312	.76165169	.10231643+1
54	.58736278	.21689824+1	.56326246+1	-.55099727-1	-.15963913	.76166105	.10231516+1

different due to the fact that, if the approximate wavefunction is particularly poor in a certain region of configurational space, different operators may weigh this region differently. To test the accuracy of our 54-term wavefunction, we have computed expectation values of several operators starting with a three-term expansion and then gradually increasing the expansion length. Some of our results are shown in Table IV. It seems that most of the expectation values have converged to five–six figures. In some cases, however, e.g., in $\langle x_1x_2\rangle$, $\langle z_1z_2\rangle$, and $\langle 3z^2-r^2\rangle$, only four figures seem to be constant. It may be also pointed out that for these operators, as many as 20 terms in the wavefunction were needed to get 99% accuracy. Obviously, if the wavefunction is known, it may be expressed in terms of the natural spin orbitals and in this representation the 99% accuracy could probably be achieved with a few terms only.

The absolute accuracy of the computed expectation values are, unfortunately, not known. The convergence seen in Table IV means only that we have obtained limiting values for our particular limited set of basis functions. It is possible that the apparent accuracy of our expectation values will decrease by, say, one order of magnitude if a larger basis set is used in the computation.

Expectation values of several operators have been computed as functions of the internuclear distance. The results are listed in Table V and some are also shown graphically in Fig. 3. The dependence of the expectation values on the internuclear distance is of two main types. In the case of an operator which depends explicitly or implicitly on the internuclear distance, the R dependence of the operator determines the R dependence of the expectation value. Thus, e.g., $\langle r^2\rangle$, and $\langle z^2\rangle$ increase approximately as R^2 with in-

TABLE V. Expectation values (in atomic units) for the ground state of H_2 computed with 54-term wavefunction.

R	α	β	$D(\text{cm}^{-1})$	E	r_{12}^{-1}	r_{12}	r_{12}^2
.40	.407	.0	-193093.0	-.1202034	.84847655	.15640188+1	.30157642+1
.60	.522	.0	-50561.5	-.7696250	.78455209	.16764754+1	.34449086+1
.80	.675	.0	4400.2	-1.0200486	.72620851	.17953810+1	.39266022+1
1.00	.803	.0	27331.8	-1.1245329	.67431513	.19177557+1	.44535560+1
1.20	.915	.0	36197.8	-1.1649292	.62833072	.20423423+1	.50220534+1
1.35	1.000	.0	38179.4	-1.1739580	.59718645	.21370934+1	.54757333+1
1.40	1.027	.0	38291.7	-1.1744699	.58736591	.21689528+1	.56323895+1
1.45	1.054	.0	38199.8	-1.1740511	.57780323	.22009628+1	.57918526+1
1.60	1.132	.0	36998.4	-1.1685773	.55053774	.22979959+1	.62878147+1
1.80	1.249	.0	34032.0	-1.1550612	.51707286	.24301993+1	.69935660+1
2.00	1.313	.200	30315.1	-1.1381257	.48631379	.25666243+1	.77577478+1
2.20	1.400	.250	26364.0	-1.1201234	.45773359	.27083678+1	.85892101+1
2.40	1.490	.325	22477.0	-1.1024129	.43090991	.28566722+1	.94991159+1
2.60	1.575	.375	18826.8	-1.0857810	.40553347	.30127200+1	.10499792+2
2.80	1.680	.450	15510.3	-1.0706700	.38140426	.31773835+1	.11601357+2
3.00	1.780	.519	12578.5	-1.0573118	.35843488	.33511496+1	.12814635+2
3.20	1.888	.578	10048.2	-1.0457832	.33663534	.35337753+1	.14144345+2
3.40	2.000	.640	7913.8	-1.0360578	.31608606	.37243859+1	.15591382+2
3.60	2.100	.706	6151.3	-1.0280272	.29690237	.39214527+1	.17150991+2
3.80	2.200	.775	4725.2	-1.0215297	.27919251	.41230326+1	.18813963+2
4.00	2.300	.848	3592.6	-1.0163689	.26301818	.43271482+1	.20569042+2

R	r_a	r_a^{-1}	r_a^2	r_ar_b	$r_{1a}r_{2a}$	$r_{1a}r_{2b}$
.40	.10420740+1	.14278761+1	.14598111+1	.14335621+1	.10455717+1	.10476812+1
.60	.11347286+1	.12820443+1	.17023414+1	.16435054+1	.12435786+1	.12492023+1
.80	.12345082+1	.11607586+1	.19850480+1	.18802535+1	.14752170+1	.14871885+1
1.00	.13379287+1	.10614637+1	.23035795+1	.21386554+1	.17346916+1	.17571585+1
1.20	.14430520+1	.98001988	.26546327+1	.24142949+1	.20178711+1	.20567266+1
1.35	.15223452+1	.92843267	.29381047+1	.26303422+1	.22437877+1	.23001529+1
1.40	.15488034+1	.91278856	.30363543+1	.27039128+1	.23214145+1	.23848370+1
1.45	.15752600+1	.89785163	.31364572+1	.27781883+1	.24001180+1	.24712894+1
1.60	.16545502+1	.85692682	.34477576+1	.30048090+1	.26421868+1	.27413053+1
1.80	.17598739+1	.81028477	.38881903+1	.33143041+1	.29768785+1	.31265632+1
2.00	.18645390+1	.77124029	.43577311+1	.36300731+1	.33220315+1	.35417884+1
2.20	.19683306+1	.73855836	.48562358+1	.39492498+1	.36736159+1	.39885454+1
2.40	.20711512+1	.71129077	.53842799+1	.42693485+1	.40274499+1	.44690893+1
2.60	.21729643+1	.68867087	.59429316+1	.45880707+1	.43792547+1	.49861841+1
2.80	.22737490+1	.67006838	.65329049+1	.49028446+1	.47246049+1	.55424766+1
3.00	.23736039+1	.65492700	.71562219+1	.52123918+1	.50601877+1	.61410187+1
3.20	.24725921+1	.64271952	.78140058+1	.55151633+1	.53832312+1	.67837660+1
3.40	.25708751+1	.63295122	.85079159+1	.58109975+1	.56927618+1	.74720730+1
3.60	.26686027+1	.62513607	.92391088+1	.61002236+1	.59892226+1	.82059861+1
3.80	.27659114+1	.61882851	.10008187+2	.63836840+1	.62743695+1	.89844150+1
4.00	.28629362+1	.61363109	.10815469+2	.66626900+1	.65508834+1	.98055585+1

R	x_1x_2	z_1z_2	x^2	z^2	r^2	$Q=R^2-2(3z^2-r^2)$
.40	-.27999162-1	-.32072652-1	.46763929	.48453253	.14198111+1	.92427077-1
.60	-.33128824-1	-.43855265-1	.52410166	.56413807	.16123414+1	.19985436
.80	-.38714378-1	-.60824308-1	.58358550	.65787705	.18250480+1	.34283379
1.00	-.44393779-1	-.84410927-1	.64403591	.76550773	.20535795+1	.51411271
1.20	-.49929223-1	-.11653551	.70380435	.88702406	.22946328+1	.70712121
1.35	-.53855458-1	-.14767606	.74745379	.98757210	.24824797+1	.86202675
1.40	-.55102913-1	-.15963461	.76169285	.10229686+1	.25463543+1	.91489695
1.45	-.56314342-1	-.17246538	.77575380	.10593246+1	.26108322+1	.96821672
1.60	-.59706252-1	-.21673721	.81668533	.11743870+1	.28077576+1	.11291934+1
1.80	-.63545180-1	-.29150237	.86789586	.13423986+1	.30781903+1	.13419891+1
2.00	-.66445408-1	-.38825198	.91432311	.15290749+1	.33577311+1	.15410130+1
2.20	-.68244742-1	-.51187977	.95535625	.17355233+1	.36462358+1	.17193319+1
2.40	-.68836678-1	-.66760465	.99026628	.19637474+1	.39442799+1	.18660756+1
2.60	-.68149118-1	-.86066628	.10185136+1	.22159045+1	.42529316+1	.19704363+1
2.80	-.66185155-1	-.10954034+1	.10400471+1	.24928108+1	.45729049+1	.20289451+1
3.00	-.63045871-1	-.13750038+1	.10547499+1	.27967221+1	.49062219+1	.20321115+1
3.20	-.58946528-1	-.17002736+1	.10631311+1	.31277437+1	.52540058+1	.19815495+1
3.40	-.54124776-1	-.20695253+1	.10660457+1	.34858246+1	.56179160+1	.18808843+1
3.60	-.48888463-1	-.24786097+1	.10646085+1	.38698917+1	.59991088+1	.17388674+1
3.80	-.43560157-1	-.29216739+1	.10600672+1	.42780529+1	.63981873+1	.15680574+1
4.00	-.38407540-1	-.33922365+1	.10536475+1	.47081743+1	.68154694+1	.13818932+1

creasing R, $\langle r_{12}\rangle$ is an almost linear function of R, and $\langle \xi \rangle$ goes to infinity with decreasing R. On the other hand if the operator does not depend on R, a different effect determines the R dependence of its expectation value. It is known that when two hydrogen atoms approach each other, there is first a slight expansion of the electronic charges around each of the atoms and then, for smaller distances, a contraction. This has been first shown by Rosen,[16] who employed a Heitler–London wavefunction with a variable orbital

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[16] N. Rosen, Phys. Rev. 38, 2099 (1931).

exponent α. He found the value of the orbital exponent to be $\alpha<1$ for $R>R^*$ and $1<\alpha\leq 1.675$ for $R^*>R\geq 0$, R^* being approximately equal to 2.7 a.u. These changes in the wavefunction seem to be mainly responsible for the R dependence of $\langle x^2\rangle$, $\langle x_1x_2\rangle$, etc.

Some of the expectation values are related to the experimentally measurable quantities. However, accurate comparison with experimental values requires averaging of our results over vibrations and rotations of the molecule. Results of computations of the vibrational and rotational energies as well as the averaged expectation values of various operators will be published shortly.

An approximate comparison of the expectation values with experiment can be made by using the theoretical values for $R=\langle R\rangle$ rather than those for $R=R_e$. In Table VI we give the experimental values[17] of r^2 and $3z^2-r^2$, the values computed with an accurate vibronic wavefunction[18] and those obtained from Table V for $R=1.449$ a.u. which is the expectation value of R for the vibronic ground state.[18] The good agreement of the results listed in the two last columns obtained in two different approaches and using different and independently written programs increases our confidence in the theoretical results.

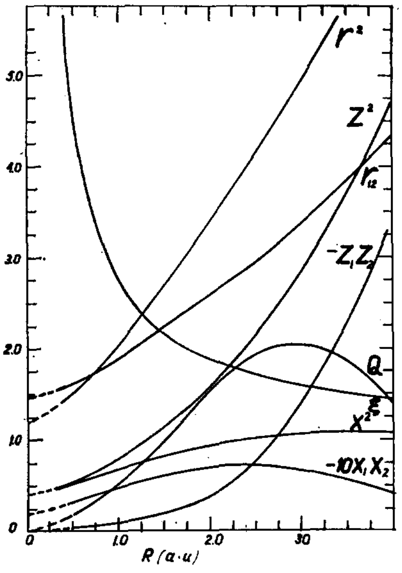

FIG. 3. Expectation values for the ground state of H_2.

For the $^3\Sigma_u{}^+$ state the energy calculation was similar to that for the ground state. Only two nonlinear parameters were varied assuming $\alpha=\bar{\alpha}$ and $\beta=-\bar{\beta}$. For small values of R similarily as for the ground state it has proved sufficient to put $\beta=\bar{\beta}=0$. The results are given in Table VII and the energy curve is also shown in Fig. 2.

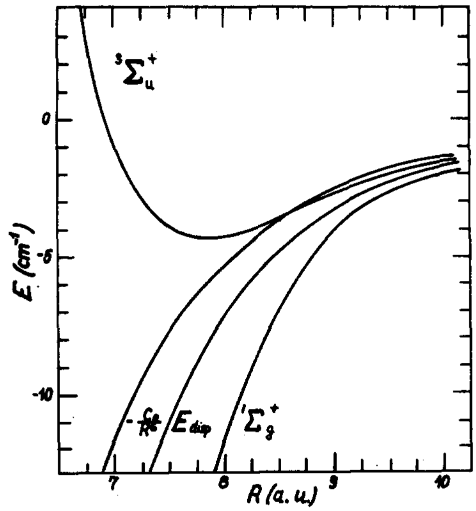

FIG. 4. Computed potential-energy curves for large internuclear distances in H_2.

The computed energies for all values of R are lower than any previous results obtained by the variational method for the $^3\Sigma_u{}^+$ state. The van der Waals minimum has been found to appear at $R=7.85$ a.u. and to be only 4.3 cm^{-1} deep. Estimation shows that for H_2 this is not sufficient to accomodate even the zeroth vibrational level, although for D_2 and T_2 the zero-point energy may be smaller than 4.3 cm^{-1}. A significantly deeper minimum has been obtained by Dalgarno and Lynn,[3] however, since this was an approximate perturbation calculation, it provides neither an upper nor a lower limit and it is impossible to decide whether their results are more accurate than those given in Table VII.

For the $^3\Sigma_u{}^+$ state, similarily as for the ground state, we had to reduce the number of terms for large values of R. This was indispensible for avoiding significant rounding errors resulting from near redundancy which appears in the wavefunction for large R. For the finally chosen wavefunction, the errors in the energy are believed not to exceed 0.1 cm^{-1}. The significant oscillations of V and dE/dR seen in Table VII for $R>8.0$ a.u., are due to the fact that for this region we were not able to determine accurately the optimum values of the exponents; the total energy was very insensitive to the changes of the exponents thus making an accurate interpolation impossible. This hardly affected the

TABLE VI. Comparison of some expectation values (in square angstroms) for the ground state of H_2.

		Theoretical	
	Experimental[a]	Vibronic[b]	for $R=\langle R\rangle$
$\langle r^2\rangle$	0.726±0.002	0.732	0.731
$\langle 3z^2-r^2\rangle$	0.167±0.010	0.160	0.159

[a] See Ref. 17.
[b] See Ref. 18.

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[17] N. F. Ramsay, Science 117, 470 (1953); R. G. Barnes, P. J. Bray, and N. F. Ramsey, Phys. Rev. 94, 893 (1954).
[18] W. Kołos and L. Wolniewicz, J. Chem. Phys. 41, 3674 (1963).

Table VII. Theoretical energies computed in the Born–Oppenheimer approximation for the $^3\Sigma_u^+$ state of H_2.[a]

R	N	α	β	D	E	V	$V/2E$	dE/dR
1.0000	53	.536	.0	-83066.2	-.6215227	-1.8543878	1.4918101	-.6113423
1.1000	53	.586	.0	-71169.7	-.6757268	-1.8804968	1.3914624	-.4809484
1.2000	53	.636	.0	-61680.3	-.7189640	-1.9049860	1.3248132	-.3892150
1.3000	53	.687	.0	-53902.2	-.7544033	-1.9289081	1.2784329	-.3231549
1.4000	53	.738	.0	-47373.6	-.7841501	-1.9521286	1.2447417	-.2741632
1.5000	53	.790	.0	-41785.9	-.8096095	-1.9741300	1.2191865	-.2366073
1.6000	53	.843	.0	-36932.4	-.8317238	-1.9942686	1.1988768	-.2067632
1.7000	53	.895	.0	-32672.2	-.8511347	-2.0120447	1.1819779	-.1822208
1.8000	53	.948	.0	-28906.7	-.8682913	-2.0272111	1.1673565	-.1614603
1.9000	53	1.000	.0	-25564.7	-.8835186	-2.0396922	1.1543006	-.1435026
2.0000	53	1.053	.0	-22591.9	-.8970636	-2.0495843	1.1423852	-.1277286
2.1000	53	1.106	.0	-19945.2	-.9091230	-2.0570807	1.1313545	-.1137309
2.2000	53	1.155	.0	-17588.9	-.9198593	-2.0624268	1.1210556	-.1012310
2.3000	53	1.206	.0	-15492.2	-.9294123	-2.0659098	1.1114066	-.0900371
2.4000	53	1.243	.235	-13628.3	-.9379051	-2.0677969	1.1023487	-.0799944
2.5000	53	1.300	.300	-11973.2	-.9454463	-2.0683706	1.0938594	-.0709912
2.6000	53	1.357	.365	-10505.2	-.9521346	-2.0678612	1.0859080	-.0629200
2.7000	53	1.415	.430	-9205.1	-.9580585	-2.0664862	1.0784760	-.0556923
2.8000	53	1.463	.495	-8055.0	-.9632985	-2.0644339	1.0715442	-.0492275
2.9000	53	1.511	.560	-7039.2	-.9679271	-2.0618709	1.0650961	-.0434540
3.0000	53	1.559	.625	-6143.0	-.9720104	-2.0589384	1.0591133	-.0383059
3.1000	53	1.600	.638	-5353.6	-.9756071	-2.0557534	1.0535765	-.0337223
3.2000	53	1.640	.650	-4659.1	-.9787717	-2.0524120	1.0484630	-.0296464
3.3000	53	1.680	.663	-4048.9	-.9815517	-2.0489952	1.0437530	-.0260278
3.4000	53	1.720	.675	-3513.6	-.9839910	-2.0455687	1.0394245	-.0228196
3.5000	53	1.760	.688	-3044.6	-.9861279	-2.0421809	1.0354543	-.0199786
3.6000	53	1.801	.701	-2634.2	-.9879977	-2.0388792	1.0318239	-.0174677
3.7000	53	1.843	.714	-2275.7	-.9896312	-2.0356899	1.0285094	-.0152507
3.8000	53	1.884	.726	-1962.9	-.9910564	-2.0326374	1.0254903	-.0132959
3.9000	53	1.925	.739	-1690.4	-.9922979	-2.0297374	1.0227459	-.0115747
4.0000	53	1.967	.752	-1453.3	-.9933781	-2.0270065	1.0202592	-.0100625
4.1000	53	2.014	.785	-1247.4	-.9943164	-2.0244439	1.0180079	-.0087344
4.2000	53	2.061	.817	-1068.8	-.9951304	-2.0220571	1.0159759	-.0075706
4.3000	53	2.109	.850	-914.0	-.9958355	-2.0198438	1.0141453	-.0065518
4.4000	53	2.156	.882	-780.1	-.9964456	-2.0178050	1.0125013	-.0056622
4.5000	53	2.203	.915	-664.7	-.9969715	-2.0159252	1.0110244	-.0048849
4.6000	53	2.250	.948	-565.1	-.9974252	-2.0142059	1.0097027	-.0042077
4.7000	53	2.297	.980	-479.4	-.9978159	-2.0126397	1.0085226	-.0036187
4.8000	35	2.358	1.002	-406.0	-.9981500	-2.0112257	1.0074766	-.0031095
4.9000	35	2.404	1.036	-342.8	-.9984382	-2.0099357	1.0065399	-.0026652
5.0000	35	2.450	1.070	-288.6	-.9986849	-2.0087720	1.0057086	-.0022804
5.1000	35	2.496	1.104	-242.3	-.9988960	-2.0077277	1.0049734	-.0019482
5.2000	35	2.542	1.138	-202.7	-.9990763	-2.0067905	1.0043229	-.0016611
5.3000	35	2.588	1.172	-169.2	-.9992292	-2.0059471	1.0037473	-.0014130
5.4000	35	2.634	1.206	-140.5	-.9993597	-2.0051946	1.0032397	-.0011991
5.5000	35	2.680	1.240	-116.3	-.9994703	-2.0045320	1.0027972	-.0010166
5.6000	35	2.740	1.292	-95.8	-.9995635	-2.0039368	1.0024060	-.0008589
5.7000	35	2.800	1.344	-78.3	-.9996432	-2.0034242	1.0020696	-.0007259
5.8000	35	2.860	1.396	-63.8	-.9997094	-2.0029613	1.0017717	-.0006108
5.9000	35	2.920	1.448	-51.5	-.9997655	-2.0025563	1.0015130	-.0005128
6.0000	35	2.980	1.500	-41.1	-.9998125	-2.0022055	1.0012904	-.0004301
6.1000	35	3.035	1.520	-32.6	-.9998515	-2.0018892	1.0010933	-.0003584
6.2000	35	3.090	1.540	-25.4	-.9998842	-2.0016168	1.0009243	-.0002981
6.3000	35	3.145	1.560	-19.5	-.9999112	-2.0013738	1.0007758	-.0002463
6.4000	35	3.200	1.580	-14.6	-.9999337	-2.0011655	1.0006491	-.0002028
6.5000	35	3.255	1.600	-10.5	-.9999521	-2.0009870	1.0005414	-.0001666
6.6000	35	3.310	1.620	-7.2	-.9999670	-2.0008311	1.0004486	-.0001359
6.7000	35	3.365	1.640	-4.5	-.9999795	-2.0006929	1.0003670	-.0001095
6.8000	25	3.274	1.720	-2.5	-.9999887	-2.0005656	1.0002940	-.0000865
6.9000	25	3.342	1.760	-.7	-.9999966	-2.0004703	1.0002386	-.0000691
7.0000	25	3.410	1.800	.7	-1.0000030	-2.0003923	1.0001931	-.0000552
7.1000	25	3.478	1.840	1.7	-1.0000076	-2.0003175	1.0001511	-.0000426
7.2000	25	3.546	1.880	2.6	-1.0000117	-2.0002569	1.0001167	-.0000324
7.3000	25	3.614	1.920	3.1	-1.0000143	-2.0002055	1.0000885	-.0000242
7.4000	25	3.682	1.960	3.7	-1.0000167	-2.0001649	1.0000658	-.0000178
7.5000	25	3.750	2.000	3.9	-1.0000180	-2.0001247	1.0000444	-.0000118
7.6000	25	3.770	2.050	4.2	-1.0000191	-2.0000956	1.0000287	-.0000076
7.7000	25	3.790	2.100	4.3	-1.0000195	-2.0000710	1.0000160	-.0000041
7.8000	25	3.805	2.150	4.3	-1.0000197	-2.0000524	1.0000065	-.0000017
7.9000	25	3.820	2.200	4.3	-1.0000194	-2.0000268	.9999940	.0000015
8.0000	25	3.840	2.250	4.3	-1.0000196	-2.0000076	.9999842	.0000040
8.1000	25	3.892	2.300	4.2	-1.0000192	-1.9999923	.9999770	.0000057
8.2000	25	3.944	2.350	4.2	-1.0000191	-1.9999975	.9999796	.0000050
8.3000	25	3.996	2.400	3.9	-1.0000180	-1.9999924	.9999783	.0000052
8.4000	25	4.048	2.450	3.8	-1.0000173	-1.9999841	.9999748	.0000060
8.5000	25	4.150	2.500	3.6	-1.0000164	-1.9999733	.9999702	.0000070
8.6000	25	4.220	2.540	3.5	-1.0000158	-1.9999805	.9999745	.0000059
8.7000	25	4.290	2.580	3.3	-1.0000152	-1.9999582	.9999640	.0000083
8.8000	25	4.360	2.620	3.1	-1.0000143	-1.9999769	.9999741	.0000059
8.9000	25	4.430	2.660	3.1	-1.0000143	-1.9999899	.9999807	.0000043
9.0000	25	4.500	2.700	2.8	-1.0000127	-1.9999599	.9999672	.0000073
9.2500	18	4.625	2.837	2.4	-1.0000109	-1.9999805	.9999794	.0000045
9.5000	18	4.750	2.975	2.1	-1.0000095	-1.9999751	.9999781	.0000046
9.7500	18	4.875	3.112	1.7	-1.0000076	-1.9999672	.9999760	.0000049
10.0000	18	5.000	3.250	1.5	-1.0000067	-1.9999722	.9999794	.0000041

[a] R, E, and V in atomic units, D in cm^{-1}.

total energy, however, the separation of the total energy into the kinetic and potential parts was found to be critically dependent on the value of α and β.

Let us now consider the energy curves for both the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states at large internuclear separations shown in Fig. 4. Long-range interaction due to the dispersion forces between two hydrogen atoms has been studied by several authors.[3,4,19,20] The usual procedure consists in expanding the interaction potential in terms of inverse powers of the internuclear distance. This series, which represents all multipole–multipole interactions, is employed to compute the second and higher-order corrections to the energy. The dispersion energy in the second-order perturbation theory is then given by the formula

$$E_{\text{disp}} = -\sum_{i=0} (C_i/R^{6+2i}). \tag{14}$$

The first three C_i coefficients have been computed by Pauling and Beach[19] who obtained $C_0=6.49903$, $C_1=124.399$, and $C_2=1135.21$ (in atomic units). More recent values of the first two coefficients calculated by Hirschfelder and Löwdin[20] are $C_0=6.499026$ and $C_1=144.8497$. Unfortunately, there is some disagreement between the two C_1 values and the reason for the discrepancy is not clear.

The energy resulting from Eq. (14) as well as the energy resulting from the first term in (14) is also shown in Fig. 4.

Since the exchange or valence interaction energy decreases roughly exponentially with R, it is not necessary for large internuclear distances to symmetrize or antisymmetrize the wavefunction. Thus, in the case of very large R the wavefunction

$$\Psi = \psi_a(1)\psi_b(2)$$

may be used in the zeroth approximation for both the $^1\Sigma_g^+$ and the $^3\Sigma_u^+$ state, and this type of wavefunction was employed in the derivation of (14). The differences between accurate $^1\Sigma_g^+$ and $^3\Sigma_u^+$ energies and those calculated from (14) represent the magnitude of the valence interaction at large values of R. Our results for the two states show that even for $R=10.0$ a.u. the exchange interaction is not negligible. Therefore for $R\leq 10$ the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ energies are not directly comparable with those obtained from the formula (14). However, since the exchange interactions in the two states have approximately the same absolute value and opposite signs, the average of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ energies, for given R, may be compared with the value obtained from Eq. (14). This comparison is made in Table VIII. One can see that for $R\leq 8.5$ a.u. the exchange repulsion in the $^3\Sigma_u^+$ state seems to become stronger than the exchange attraction in the $^1\Sigma_g^+$ state.

The form of the van der Waals minimum calculated for the $^3\Sigma_u^+$ state is also of considerable interest. It is well known that, with the exception of a few cases, the calculated dispersion energies disagree with the so-called experimental values.[21] The latter were obtained from the viscosity measurements assuming the intermolecular interaction to be correctly represented by the Lennard-Jones potential

$$V = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$$

and determining from the experimental results the two parameters ϵ and σ. The value of $4\epsilon\sigma^6$ may then be said to represent the experimental dispersion energy (multiplied by R^6) for the system under consideration and can be compared with a mean value of the C's defined in Eq. (14). In most cases the two values disagree by a factor of 2.0–2.5, and the reason for this discrepancy is not clear. To some extent the method can be tested by using our results for the $^3\Sigma_u^+$ state and fitting the Lennard-Jones potential to the computed van der Waals minimum. If the two parameters of the Lennard-Jones potential are determined by requiring the minimum of this potential to coincide with the minimum of the variational potential, one gets $4\epsilon\sigma^6=9.17$. The mean value of C_0, C_1, and C_2 can be calculated from the formula[21]

$$\bar{C} = C_0 + (C_1/\sigma^2) + (C_2/\sigma^4).$$

By using the Hirschfelder and Löwdin[20] values of C_0 and C_1, one gets $\bar{C}=9.461$, whereas the Pauling and Beach[19] values of C_0, C_1, and C_2 give $\bar{C}=9.517$. The relatively good agreement between these results and the corresponding value obtained by fitting the Lennard-Jones potential to the variationally determined minimum suggests that at least for two H atoms, the Lennard-Jones potential may be used to represent the long-range interaction due to the dispersion forces.

TABLE VIII. Average energies for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2 at large internuclear separations.[a]

		$-E_{\text{disp}}$ from Eq. (14)	
R	$-\frac{1}{2}[E(^1\Sigma_g^+)+E(^3\Sigma_u^+)]$	b	c
10.0	1.7_6	1.744	1.724
9.5	2.4	2.419	2.393
9.0	3.4_6	3.423	3.390
8.5	5.2_6	4.949	4.911
8.0	7.9_6	7.336	7.300

[a] R in atomic units, energies in reciprocal centimeters with respect to the energy of two separated H atoms.

[b] Calculated with C_i values from Ref. 20.

[c] Calculated with C_i values from Ref. 19.

As the last potential-energy curve we computed the curve for the lowest $^1\Pi_u$ state of H_2. Since this is a $1s\sigma 2p\pi$ state, we could not assume $\alpha=\bar{\alpha}$, $\beta=-\bar{\beta}$, and all four exponents had to be varied independently for each internuclear distance. This made the computa-

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[19] L. Pauling and J. Y. Beach, Phys. Rev. **47**, 685 (1935).

[20] J. O. Hirschfelder and P.-O. Löwdin, Mol. Phys. **2**, 229 (1959).

[21] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 966.

TABLE IX. Theoretical energies computed in the Born–Oppenheimer approximation for the $^1\Pi_u$ state of H_2.[a]

R	N	α	$\bar{\alpha}$	β	$\bar{\beta}$	D	E	V	dE/dR
1.000	27	.330	.830	-.100	.360	-11524.4	-.5724911	-1.6610400	-.5160579
1.125	27	.370	.911	-.530	.429	117.9	-.6255371	-1.6407573	-.3463850
1.250	27	.410	.992	-.098	.498	7954.1	-.6612415	-1.6119309	-.2315583
1.375	27	.450	1.072	-.540	.567	13137.7	-.6848598	-1.5812100	-.1538112
1.500	27	.490	1.153	-.095	.636	16562.4	-.7004638	-1.5477238	-.0978642
1.625	27	.520	1.210	-.111	.665	18678.0	-.7101032	-1.5153688	-.0585615
1.750	27	.546	1.267	-.128	.693	19874.8	-.7155565	-1.4840439	-.0302463
1.850	27	.568	1.314	-.141	.715	20345.0	-.7176989	-1.4600595	-.0133307
1.900	27	.579	1.340	-.147	.726	20452.2	-.7181873	-1.4484701	-.0063661
1.950	27	.590	1.360	-.154	.738	20487.7	-.7183489	-1.4371620	-.0002381
1.951	27	.590	1.360	-.154	.738	20487.8	-.7183492	-1.4369386	-.0001231
1.952	27	.590	1.360	-.154	.738	20487.8	-.7183492	-1.4367147	-.0000084
1.953	27	.590	1.360	-.154	.738	20487.8	-.7183491	-1.4364909	.0001062
1.954	27	.590	1.360	-.154	.738	20487.7	-.7183490	-1.4362669	.0002206
1.960	27	.595	1.364	-.152	.744	20487.1	-.7183460	-1.4349465	.0008906
1.970	27	.600	1.368	-.150	.750	20483.8	-.7183310	-1.4327296	.0019962
2.000	27	.614	1.380	-.140	.770	20460.1	-.7182230	-1.4261640	.0051410
2.100	27	.637	1.430	-.150	.820	20245.2	-.7172439	-1.4050377	.0140238
2.250	27	.672	1.500	-.170	.895	19614.5	-.7143703	-1.3756404	.0236001
2.500	27	.730	1.620	-.200	1.020	18036.1	-.7071783	-1.3326864	.0326681
2.750	27	.780	1.710	-.170	1.050	16121.8	-.6984564	-1.2968287	.0363942
3.000	27	.830	1.800	-.150	1.080	14098.4	-.6892372	-1.2676921	.0369274
3.500	27	.930	2.010	-.268	1.285	10216.2	-.6715486	-1.2274129	.0330527
4.000	27	1.033	2.225	-.387	1.490	6937.7	-.6566106	-1.2073402	.0264702
4.500	27	1.134	2.430	-.506	1.700	4418.4	-.6451316	-1.2025252	.0194973
5.000	27	1.236	2.650	-.625	1.900	2631.3	-.6369889	-1.2074744	.0133007
5.500	27	1.337	2.860	-.744	2.100	1456.1	-.6316345	-1.2167615	.0084559
6.000	27	1.439	3.070	-.863	2.310	733.6	-.6283423	-1.2262515	.0050722
6.500	24	1.804	3.150	-1.020	2.880	305.6	-.6263925	-1.2348501	.0027592
7.000	24	1.967	3.474	-1.260	3.125	88.0	-.6254011	-1.2405282	.0014677
7.500	24	2.110	3.800	-1.500	3.370	-24.4	-.6248886	-1.2442544	.0007364
7.750	24	2.176	3.989	-1.663	3.498	-56.3	-.6247433	-1.2456047	.0005009
8.000	24	2.233	4.126	-1.742	3.615	-78.7	-.6246415	-1.2466319	.0003314
8.250	24	2.290	4.263	-1.821	3.732	-92.7	-.6245775	-1.2474455	.0002072
8.500	24	2.350	4.400	-1.900	3.850	-101.0	-.6245398	-1.2480877	.0001167
8.750	24	2.525	4.640	-1.980	4.030	-104.5	-.6245240	-1.2486229	.0000486
9.000	24	2.700	4.870	-2.060	4.200	-105.5	-.6245195	-1.2490412	-.0000002
9.250	24	2.875	5.100	-2.140	4.370	-104.8	-.6245223	-1.2493712	-.0000353
9.500	24	3.050	5.330	-2.220	4.540	-102.5	-.6245331	-1.2496404	-.0000604
10.000	24	3.225	5.560	-2.300	4.700	-95.3	-.6245660	-1.2498371	-.0000705

[a] R, E, and V in atomic units, D in cm^{-1}.

tions a very time-consuming procedure and therefore the calculations have been carried out with a relatively small number of terms in the wavefunction.

The results of the energy computations are collected in Table IX. The equilibrium internuclear distance, calculated from the virial theorem, is $R_e = 1.9521$ a.u. $=$ 1.0330 Å which is in a very good agreement with the experimental value[22] $R_e = 1.0327$ Å. The experimental binding energy for the $^1\Pi_u$ state, according to Namioka,[22] is[23] $D_e = 20\,488.5\ \text{cm}^{-1}$, whereas the older term values[24] and spectroscopic constants give $D_e = 20\,509\ \text{cm}^{-1}$. The theoretical binging energy from Table IX is $D_e = 20\,487.8\ \text{cm}^{-1}$. To check the accuracy of the theoretical value, we have made an additional calculation for $R = R_e$. Namely, the expansion of the wavefunction was extended to include all terms which in the test runs improved the energy by at least $0.1\ \text{cm}^{-1}$. Thus, the expansion length was increased from 27 to 58 terms and this resulted in an energy improvement of $2.2\ \text{cm}^{-1}$, the final theoretical binding energy being $D_e = 20\,490.0\ \text{cm}^{-1}$. This is in very good agreement with Namioka's experimental value. The small discrepancy between theory and experiment amounting to $1.5\ \text{cm}^{-1}$ is certainly not larger than the probable values of the nuclear motion and relativistic corrections which have not been calculated for the $^1\Pi_u$ state.

Similarly, to check the accuracy of our results for larger internuclear distances, we have made some additional test runs for $R = 8.0$ a.u. Having tested many terms not included in the 24-term expansion used in the final computation of this section of the potential-energy curve, we selected the next six most important terms. The energy improvement achieved by adding the six terms to the 24-term wavefunction and reoptimizing all parameters was only $1.5\ \text{cm}^{-1}$. Hence, it seems that for the $^1\Pi_u$ state, our energies are already quite close to the corresponding accurate eigenvalues of the nonrelativistic clamped nuclei Hamiltonian.

The results also show that the van der Waals maximum in the $C\,^1\Pi_u$ state definitely exists. In comparison with the results of Browne[8] the maximum has been flattened out by about $40\ \text{cm}^{-1}$ and shifted to larger internuclear distance of 9.0 a.u. in perfect agreement with Mulliken's prediction[25] that the repulsive dispersion forces in the $C\,^1\Pi_u$ state should lose their dominance over attractive valence forces at $R = 9$ a.u. The existence of the maximum seems to eliminate definitely the $C\,^1\Pi_u$ state as the possible upper state of the far-

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[22] T. Namioka (private communication).

[23] Not corrected for rotation–vibration interaction (Y_{00}).

[24] From G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1950), Vol. 1.

[25] R. S. Mulliken, Phys. Rev. **120**, 1674 (1960).

ultraviolet absorption continuum which plays crucial role in the experimental determination[10] of the ground-state dissociation energy. The results are also in agreement with the conclusion of Namioka[26] who from his recent experimental study of the $C\,^1\Pi_u$ state predicts the height of the maximum to be at least 50 cm^{-1}.

Namioka[22] has also employed the RKR method to calculate the classical turning points R_{min} and R_{max} for vibrations in the $C\,^1\Pi_u$ state. His results are shown in Table X. Similarly, as for the ground state we have used the energy values from Table IX and the experimental energies of the vibrational levels to find the classical turning points for vibrations for all vibrational states. The differences, ΔR, between our results obtained by quadratic interpolation from Eq. (13) and Namioka's RKR results are also given in Table X.

The relatively poor agreement may be due to several factors: (a) to the lack of the corrections for nuclear motion, (b) to the error in the RKR results which is believed[22] to be about 1% due to inaccuracy of the B_v values, (c) to the errors introduced by interpolation of our results for the energy which are certainly larger than in the case of the ground state, (d) to the inaccuracies of our variational energies, (e) to possible inaccuracies of the WKB method used in the RKR procedure.

Time did not permit us to extend the present investigation to still other excited states. However, we were able to make a calculation for the $B\,^1\Sigma_u^+$ state which is of considerable interest. For the internuclear distance $R=2.5$ a.u., we selected a 49-term wavefunction and computed the optimum exponents $\alpha=1.37$, $\bar{\alpha}=0.815$, $\beta=0.98$, and $\bar{\beta}=-0.20$. The 49-term wavefunction with these values of the nonlinear parameters was then employed in a calculation in which the internuclear distance was varied. The numerical results are shown in Table XI. The theoretical internuclear distance $R_e=2.431$ a.u. $=1.286$ Å is only in a fair agreement with the experimental value[6] $R_e=1.2925$ Å.

TABLE X. Comparison of the computed potential-energy curve for the $^1\Pi_u$ state of H_2 with the classical turning points, R_{min} and R_{max}, for the vth vibrational level obtained by using the RKR method.[a]

v	R_{min}[b]	ΔR	R_{max}[b]	ΔR
0	0.888	−1	1.223	−2
1	0.805	0	1.399	0
2	0.756	0	1.543	−1
3	0.721	1	1.677	−2
4	0.694	1	1.808	−1
5	0.673	1	1.940	0
6	0.655	0	2.076	0
7	0.641	0	2.219	−1
8	0.629	−1	2.374	−2
9	0.619	−1	2.545	−4
10	0.611	−1	2.742	−3
11	0.604	−1	2.981	−9
12	0.599	−1	3.303	−10
13	0.596	−1	3.843	−44

[a] R in angstroms, ΔR in 10^{-3} Å.
[b] See Ref. 22.

TABLE XI. Energies of the lowest $^1\Sigma_u^+$ state computed with a 49-term wavefunction.

R(a.u.)	$-E$(a.u.)	D(cm^{-1})	$-V$(a.u.)	$V/2E$
2.40	0.75662269	28 887.8	1.5160211	1.0018343
2.41	0.75663223	28 889.9	1.5151357	1.0012366
2.42	0.75663821	28 891.3	1.5142538	1.0006458
2.43	0.75664034	28 891.7	1.5133747	1.0000621
2.44	0.75663894	28 891.4	1.5124994	0.9994855
2.45	0.75663401	28 890.3	1.5116271	0.9989157
2.46	0.75662547	28 888.5	1.5107578	0.9983524
2.47	0.75661374	28 885.9	1.5098915	0.9977954
2.48	0.75659848	28 882.5	1.5090274	0.9972445
2.49	0.75658003	28 878.5	1.5081669	0.9967002
2.50	0.75655841	28 873.7	1.5073085	0.9961614

The experimental binding energy for the $B\,^1\Sigma^+$ state can be easily found from the published data[6,10] as the difference between the energy of the dissociation products in the $^1\Sigma_u^+$ state (120 551.9 cm^{-1}) and the energy of the potential minimum for the $^1\Sigma_u^+$ state (91 699.1 cm^{-1}), both energies being measured with respect to the minimum of the ground-state potential-energy curve. In this way one gets $D_e=28\,852.8$ cm^{-1}, which is by 38.9 cm^{-1} smaller than the theoretical value. Since, in view of the other results obtained with the present program, it does not seem likely that there are errors in our calculation, we are more inclined to attribute the existing discrepancy between theory and experiment mostly to the neglected coupling between electronic and nuclear motion, though the small value of these corrections obtained for the ground state[1] does not seem to justify this point of view.

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[26] T. Namioka, J. Chem. Phys. **41**, 2141 (1964).