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Accurate Adiabatic Treatment of the Ground State of the Hydrogen Molecule*

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Accurate ground-state energies of the hydrogen molecule have been computed using wavefunctions in the form of expansions in elliptic coordinates and including explicitly the interelectronic distance. The computations have been made with 54-term expansions ($0.4 \leq R \leq 3.7$) and with 80-term expansions ($0.5 \leq R \leq 2.0$). For the equilibrium internuclear distance, the best total energies obtained in the two cases are -1.1744701 a.u. and -1.1744746 a.u., respectively, the corresponding binding energies being 38 291.8 and 38 292.7 cm^{-1}. Employing the 54-term wavefunctions, the relativistic corrections and the diagonal corrections for nuclear motion have been computed for several internuclear distances. For equilibrium their contributions to the binding energy have been found to be -0.526 and 4.947 cm^{-1}, respectively. Thus the final theoretical binding energy for H_2 amounts to 38 297.1 cm^{-1} and is a little larger than the experimental value 38 292.9±0.5 cm^{-1}. The discrepancy may be due to the adiabatic approximation.

In recent years the hydrogen molecule has been studied extensively and with great accuracy by experimental and theoretical methods. The most accurate theoretical binding energy to date, computed for clamped nuclei[1] using a nonrelativistic Hamiltonian, differed by 4.6 cm^{-1} from the most accurate experimental value obtained recently by Herzberg and Monfils.[2] However, if the diagonal corrections for nuclear motion as computed by Van Vleck[3] are employed to extrapolate the experimental binding energy to the case of infinitely heavy nuclei, the disagreement between theory and experiment decreases[2] to only 0.1 cm^{-1}, which is five times smaller than the experimental error.

There are, however, good reasons to believe that this excellent agreement between theory and experiment is fortuitous: (1) It is not known whether the 50-term wavefunction which was used[1] yielded the limiting value of the energy. It is possible that, by using in the variational wavefunction more terms with higher powers of the variables, one would get a still lower energy. (2) No relativistic effects were included in the theoretical results, and later estimations suggest[4] that the relativistic contribution to the binding energy may be of the order of -1 cm^{-1}, or even[5] $+7$ cm^{-1}. (3) The diagonal corrections are sensitive to the form of the wavefunction, and a contribution of -5.1 cm^{-1} has also been reported[4] in contrast to Van Vleck's value of 4.5 cm^{-1}. Thus the Van Vleck corrections, computed with a relatively poor wavefunction, may differ from accurate values. (4) Even if the above-mentioned objections are taken care of, the resulting theoretical binding energy may still differ from the experimental value due to the neglect of the nondiagonal terms coupling the electronic and nuclear motion.

The computations reported in this paper were undertaken to clarify these points and to compute an accurate binding energy of the hydrogen molecule within the framework of the adiabatic approach.

ADIABATIC APPROXIMATION

The separation of electronic and nuclear motion in diatomic molecules can be performed using a method of Born,[6] which is somewhat different from the earlier

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[1] W. Kołos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).

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

[3] J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936).

[4] W. Kołos and L. Wolniewicz, Acta Phys. Polon. **20**, 129 (1961).

[5] A. Fröman, Rev. Mod. Phys. **32**, 317 (1960).

[6] M. Born, Nachr. Akad. Wiss. Göttingen **1** (1951); M. Born and K. Huang, *Dynamical Theory of Crystal Lattice* (Oxford University Press, New York, 1956) pp. 406–407.

Born–Oppenheimer[7] approach. The exact nonrelativistic Hamiltonian of the symmetrical H_2 molecule in the center-of-mass system is separated into two parts:

$$\mathcal{H}=\mathcal{H}^0+\mathcal{H}', \tag{1}$$

where $\mathcal{H}^0$ denotes the Hamiltonian in the clamped nuclei approximation including the nuclear repulsion, and $\mathcal{H}'$ describes the kinetic energy of the relative motion of the two nuclei as well as the coupling between electronic and nuclear motions:

$$\mathcal{H}'=\mathcal{H}_1+\mathcal{H}_2, \tag{2}$$

where

$$\mathcal{H}_1=-(1/M)\Delta_{\mathbf{R}},$$

$$\mathcal{H}_2=-(1/4M)(\Delta_{r_1}+\Delta_{r_2}+2\nabla_{r_1}\nabla_{r_2}). \tag{3}$$

The electronic problem

$$\mathcal{H}^0\psi_n(x,R)=E_n{}^0(R)\psi_n(x,R) \tag{4}$$

is assumed to be solved. In (4), x represents the coordinates of all electrons in the molecule $R=|\mathbf{R}|$, and $\mathbf{R}$ is the relative position vector of the nuclei. The electronic wavefunctions $\psi_n(x,R)$ are chosen to be real and normalized for all values of the parameter R. Obviously they from a complete set in the space of x. Next one looks for the solution of the problem

$$(\mathcal{H}^0+\mathcal{H}')\Psi(x,\mathbf{R})=E\Psi(x,\mathbf{R}), \tag{5}$$

in the form of the expansion

$$\Psi(x,\mathbf{R})=\sum_n\chi_n(\mathbf{R})\psi_n(x,R), \tag{6}$$

which gives the following rigorous set of equations for the functions $\chi_n(\mathbf{R})$:

$$[-(1/2\mu)\Delta_{\mathbf{R}}+E_n{}^0(R)+\mathcal{H}'_{nn}(R)-E]\chi_n(\mathbf{R})$$
$$=-\sum_{m\neq n}\mathcal{H}'_{mn}(R)\chi_m(\mathbf{R}), \tag{7}$$

where

$$\mathcal{H}'_{mn}=\int\psi_m(x,R)\mathcal{H}'\psi_n(x,R)dx, \tag{8}$$

and μ is the reduced mass of the two nuclei.

By neglecting the right-hand side of Eq. (7), one gets the adiabatic approximation $\Psi=\chi_n\psi_n$ and a Schrödinger-type equation for the nuclear motion

$$[-(1/2\mu)\Delta_{\mathbf{R}}+U_n(R)-E]\chi_n(\mathbf{R})=0. \tag{9}$$

The potential energy in this equation,

$$U_n(R)=E_n{}^0(R)+\mathcal{H}'_{nn}(R), \tag{10}$$

takes partly into account the coupling between electronic and nuclear motion and is sometimes called "the best potential-energy curve" for the given nth electronic state of the diatomic molecule.

CLAMPED NUCLEI COMPUTATION

The clamped nuclei computation was a straightforward extension of the variational treatment of H_2 carried out by Kolos and Roothaan,[1] i.e., the following wavefunction was employed:

$$\Phi=\sum_i c_i\Phi_i, \tag{11}$$

where

$$\Phi_i=\Psi_{r_is_i\bar{r}_i\bar{s}_i\mu_i}+\Psi_{\bar{r}_i\bar{s}_ir_is_i\mu_i} \tag{12}$$

and

$$\Psi_{rs\bar{r}\bar{s}\mu}=(1/2\pi)\exp[-\alpha(\xi_1+\xi_2)]\xi_1{}^r\eta_1{}^s\xi_2{}^{\bar{r}}\eta_2{}^{\bar{s}}\rho^\mu. \tag{13}$$

ξ and η denote the elliptic coordinates, and $\rho=2r_{12}/R$, where r_{12} and R are the interelectronic and internuclear distances, respectively. The symmetry restriction that $s+\bar{s}$ be even must be fulfilled.

Since the expansion coefficients c_i satisfy

$$\sum_j(\mathcal{H}_{ij}{}^0-E^0S_{ij})c_j=0, \tag{14}$$

the energy is the lowest root of

$$\det(\mathbf{\mathcal{H}}^0-E^0\mathbf{S})=0 \tag{15}$$

and was computed using the Ostrowski[8] iterative method:

$$(\mathbf{\mathcal{H}}^0-E^{0(n)}\mathbf{S})\mathbf{c}^{(n+1)}=\mathbf{S}\mathbf{c}^{(n)}, \tag{16}$$

where $\mathbf{c}^{(n)}$ denotes the eigenvector in the nth approximation, and

$$E^{0(n)}=\mathbf{c}^{(n)}\mathbf{\mathcal{H}}^0\mathbf{c}^{(n)}/\mathbf{c}^{(n)}\mathbf{S}\mathbf{c}^{(n)}. \tag{17}$$

In most cases, starting with $c_1{}^{(0)}=1$ and $c_i{}^{(0)}=0$ for $i\neq1$, only three or four iterations were needed to get satisfactory results.

DIAGONAL CORRECTIONS FOR NUCLEAR MOTION

The computation of the diagonal elements $\mathcal{H}'_{nn}$, defined by Eqs. (2) and (8), can be carried out using a method published previously by the present authors.[4,9] For the matrix elements of $\mathcal{H}_2$, with respect to the functions Ψ_i, one obtains

$$(\mathcal{H}_2)_{ij}=-\frac{1}{8M}\int\rho^{\mu_i+\mu_j}[\Psi'_i\nabla_1\nabla_2\Psi'_j+\Psi'_j\nabla_1\nabla_2\Psi'_i-\nabla_1\Psi'_i\nabla_2\Psi'_j-\nabla_1\Psi'_j\nabla_2\Psi'_i$$
$$+\Psi'_i\Delta_1\Psi'_j+\Psi'_j\Delta_2\Psi'_i-\nabla_1\Psi'_i\nabla_1\Psi'_j-\nabla_2\Psi'_i\nabla_2\Psi'_j]d\tau_1d\tau_2, \tag{18}$$

where $\Psi'_k=\rho^{-\mu_k}\Psi_k$.

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[7] M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).

[8] A. M. Ostrowski, Arch. Rational Mech. Anal. **1**, 233 (1958); Math. Rev. **21**, 80 (1960).

[9] W. Kołos and L. Wolniewicz, Rev. Mod. Phys. **35**, 473 (1963).

To compute the expectation value of Δ_{R}, one can use the relation

$$\int \Phi\Delta_{\mathrm{R}}\Phi d\tau_1 d\tau_2=\sum_i\int (R\rho)^{\mu_i}\Phi\Delta_{\mathrm{R}}c_i(R\rho)^{-\mu_i}\Phi_i d\tau_1 d\tau_2, \tag{19}$$

and in Eq. (19), the operator Δ_{R} can be shown[4,9] to be equivalent to

$$\begin{aligned}\Delta_{\mathrm{R}}=&\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}+\frac{2(\xi_1^2+\eta_1^2-1)}{R^2(\xi_1^2-\eta_1^2)}\left[\frac{\partial}{\partial\xi_1}(\xi_1^2-1)\frac{\partial}{\partial\xi_1}+\frac{\partial}{\partial\eta_1}(1-\eta_1^2)\frac{\partial}{\partial\eta_1}\right]\\
&-\frac{4}{R^2(\xi_1^2-\eta_1^2)}\left[\xi_1(\xi_1^2-1)\frac{\partial}{\partial\xi_1}+\eta_1(1-\eta_1^2)\frac{\partial}{\partial\eta_1}\right]\left[1+R\frac{\partial}{\partial R}\right]+\frac{2}{R^2(\xi_1^2-\eta_1^2)(\xi_2^2-\eta_2^2)}\\
&\times\left[\xi_1(\xi_1^2-1)\frac{\partial}{\partial\xi_1}+\eta_1(1-\eta_1^2)\frac{\partial}{\partial\eta_1}\right]\left[\xi_2(\xi_2^2-1)\frac{\partial}{\partial\xi_2}+\eta_2(1-\eta_2^2)\frac{\partial}{\partial\eta_2}\right]\\
&+\frac{2[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}}{R^2(\xi_1^2-\eta_1^2)(\xi_2^2-\eta_2^2)}\cos(\varphi_1-\varphi_2)\left[\eta_1\frac{\partial}{\partial\xi_1}-\xi_1\frac{\partial}{\partial\eta_1}\right]\left[\eta_2\frac{\partial}{\partial\xi_2}-\xi_2\frac{\partial}{\partial\eta_2}\right]\equiv\frac{\partial^2}{\partial R^2}+D_1\frac{\partial}{\partial R}+D_2.\end{aligned} \tag{20}$$

Thus the expectation value of Δ_{R} can readily be computed if the derivative of the wavefunction with respect to the internuclear distance is known. The differentiation has been carried out assuming that in the wavefunction not only the coefficients c_i, but also the exponent α, is a function of R. With these assumptions, a simple manipulation gives for the expectation value of Δ_{R} the equation

$$\begin{aligned}\langle\Delta_{\mathrm{R}}\rangle=&\frac{21}{R^2}-\int\left(\frac{\partial\Phi}{\partial R}\right)^2 d\tau_1 d\tau_2+\sum_i\int\rho^{\mu_i}\Phi\left[\frac{(\mu_i+1)\mu_i}{R^2}-\frac{\mu_i}{R}D_1+D_2\right]c_i\Phi_i\rho^{-\mu_i}d\tau_1 d\tau_2\\
&+\sum_i\int\rho^{\mu_i}\Phi\left(-\frac{2\mu_i}{R}+D_1\right)\Phi_i\rho^{-\mu_i}\frac{dc_i}{dR}d\tau_1 d\tau_2+\frac{d\alpha}{dR}\sum_i\int\rho^{\mu_i}\Phi(\xi_1+\xi_2)\left(\frac{2\mu_i}{R}-D_1\right)\Phi_i\rho^{-\mu_i}c_i d\tau_1 d\tau_2.\end{aligned} \tag{21}$$

Since

$$-\int\left(\frac{\partial\Phi}{\partial R}\right)^2 d\tau_1 d\tau_2=-\sum_{ik}\frac{dc_i}{dR}\frac{dc_k}{dR}S_{ik}+2\frac{d\alpha}{dR}\sum_{ik}c_i\frac{dc_k}{dR}\int\Phi_i(\xi_1+\xi_2)\Phi_k d\tau_1 d\tau_2-\left(\frac{d\alpha}{dR}\right)^2\sum_{ik}c_i c_k\int\Phi_i(\xi_1+\xi_2)^2\Phi_k d\tau_1 d\tau_2, \tag{22}$$

Eq. (21) may be written in the following final form:

$$\begin{aligned}\langle\Delta_{\mathrm{R}}\rangle=&\frac{21}{R^2}-\sum_{ik}\frac{dc_i}{dR}\frac{dc_k}{dR}S_{ik}+\sum_i\int\Phi\rho^{\mu_i}D_2 c_i\Phi_i\rho^{-\mu_i}d\tau_1 d\tau_2+\sum_i\int\Phi b_i''\Phi_i d\tau_1 d\tau_2\\
&+\sum_i\int\rho^{\mu_i}\Phi D_1 b_i'\Phi_i\rho^{-\mu_i}d\tau_1 d\tau_2+2\frac{d\alpha}{dR}\sum_i\int\Phi(\xi_1+\xi_2)b_i'''\Phi_i d\tau_1 d\tau_2\\
&-\left(\frac{d\alpha}{dR}\right)^2\int\Phi(\xi_1+\xi_2)^2\Phi d\tau_1 d\tau_2-\frac{d\alpha}{dR}\sum_i\int\rho^{\mu_i}\Phi(\xi_1+\xi_2)D_1 c_i\Phi_i\rho^{-\mu_i}d\tau_1 d\tau_2,\end{aligned} \tag{23}$$

where

$$b_i'=\frac{dc_i}{dR}-\frac{\mu_i}{R}c_i,\qquad b_i''=\frac{\mu_i}{R}\left(\frac{\mu_i+1}{R}c_i-2\frac{dc_i}{dR}\right),\qquad b_i'''=\frac{\mu_i}{R}c_i+\frac{dc_i}{dR}. \tag{24}$$

The derivative dc_i/dR, appearing in Eq. (23), can easily be found. The coefficients c_i obviously satisfy the set of equations

$$\sum_i c_i(R)[\mathcal{H}_{ik}(R)-E^0 S_{ik}(R)]=0 \tag{25}$$

and

$$\sum_i c_i(R)c_k(R)S_{ik}(R)=1. \tag{26}$$

By differentiating Eq. (25) with respect to R and employing the virial theorem, one obtains

$$\sum_i(\mathcal{H}_{ik}-E^0 S_{ik})\frac{dc_i}{dR}=\sum_i\left(\frac{2\mathcal{H}_{ik}-V_{ik}}{R}-\frac{2E^0-\langle V\rangle}{R}S_{ik}\right)c_i+\frac{d\alpha}{dR}\sum_i\{\xi_1+\xi_2,\mathcal{H}-E^0\}_{ik}c_i, \tag{27}$$

where the curly brackets denote the anticommutator. Making use of the wave equation, one easily gets

$$\sum_k \{\xi_1+\xi_2, \mathcal{H}-E^0\}_{ik}c_k = -\frac{8}{R^2}\sum_k \left\{\frac{1}{\xi_1^2-\eta_1^2}\left[\xi_1^2+(\xi_1^2-1)\frac{\partial}{\partial\xi_1}\right]\right\}_{ik} c_k. \tag{28}$$

Similarly, a differentiation of Eq. (26) with respect to R gives

$$\sum_{ik} c_k S_{ki}\frac{dc_i}{dR} = -\frac{3}{R}+\frac{d\alpha}{dR}\sum_{ik} c_i(\xi_1+\xi_2)_{ik}c_k. \tag{29}$$

By solving the set of inhomogeneous linear equations (27) with the auxiliary condition (29), one gets the derivatives dc_i/dR.

To perform integrations in the matrix elements of $\mathcal{H}^0$, $\mathcal{H}_1$, and $\mathcal{H}_2$, one has to evaluate integrals of the type

$$I^{\mu}{}_{rs\bar{r}\bar{s}} = \frac{1}{4\pi^2}\int \exp[-2\alpha(\xi_1+\xi_2)]\xi_1^r\eta_1^s\xi_2^{\bar{r}}\eta_2^{\bar{s}}\rho^{\mu}d\xi_1 d\xi_2 d\eta_1 d\eta_2 d\varphi_1 d\varphi_2$$

and

$$M^{\mu}{}_{rs\bar{r}\bar{s}} = \frac{1}{4\pi^2}\int \exp[-2\alpha(\xi_1+\xi_2)]\xi_1^r\eta_1^s\xi_2^{\bar{r}}\eta_2^{\bar{s}}\rho^{\mu}[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}\cos(\varphi_1-\varphi_2)d\xi_1 d\xi_2 d\eta_1 d\eta_2 d\varphi_1 d\varphi_2, \tag{30}$$

where $\mu \geq -1$. The integrals have been computed using the method given by Kolos and Roothaan,[10] which is based on Ruedenberg's[11] analysis for the exchange integrals. The auxilary integrals $\Phi_{n\bar{n}}{}^{Ml}$ were computed by a 110-point numerical integration, which has been found to be satisfactory for single precision computations.

RELATIVISTIC CORRECTIONS

The relativistic corrections for H_2 have been computed using the two-electron relativistic Hamiltonian which can be derived from the Breit equation in the Pauli approximation.[12] In the absence of external fields, it reads

$$\mathcal{H} = \mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_3+\mathcal{H}_4+\mathcal{H}_5, \tag{31}$$

where $\mathcal{H}_0$ is the Schrödinger Hamiltonian of the molecule, and

$$\begin{aligned}
\mathcal{H}_1 &= -\tfrac{1}{8}\alpha^2(\Delta_1^2+\Delta_2^2),\\
\mathcal{H}_2 &= \tfrac{1}{2}\alpha^2(1/r_{12})[\nabla_1\nabla_2+(1/r_{12}^2)\mathbf{r}_{12}(\mathbf{r}_{12}\nabla_1)\nabla_2],\\
\mathcal{H}_3 &= -i\tfrac{1}{2}\alpha^2\{[\mathbf{F}_1\times\nabla_1+(2/r_{12}^3)\mathbf{r}_{12}\times\nabla_2]\mathbf{s}_1+[\mathbf{F}_2\times\nabla_2+(2/r_{12}^3)\mathbf{r}_{21}\times\nabla_1]\mathbf{s}_2\},\\
\mathcal{H}_4 &= \tfrac{1}{4}\alpha^2\{\nabla_1\mathbf{F}_1+\nabla_2\mathbf{F}_2\},\\
\mathcal{H}_5 &= \alpha^2\{-\tfrac{8}{3}\pi(\mathbf{s}_1\mathbf{s}_2)\delta^{(3)}(\mathbf{r}_{12})+(1/r_{12}^3)[\mathbf{s}_1\mathbf{s}_2-(3/r_{12}^3)(\mathbf{s}_1\mathbf{r}_{12})(\mathbf{s}_2\mathbf{r}_{12})]'\}, \qquad \mathbf{F}_i = -\nabla_i V.
\end{aligned} \tag{32}$$

A perturbation treatment can now be employed to compute the relativistic corrections. In the case of the ground state of H_2, which is a $^1\Sigma_g{}^+$ state, the expectation value of $\mathcal{H}_3$ and of the second term in $\mathcal{H}_5$ vanish, and the corrections $\epsilon_i = \int\Phi\mathcal{H}_i\Phi d\tau_1 d\tau_2$ to be computed can be expressed as follows[13]:

$$\begin{aligned}
\epsilon_1 &= \alpha^2\left\{\frac{1}{4}\int(\Delta_1\Phi)\Delta_2\Phi d\tau_1 d\tau_2-\tfrac{1}{2}E^2+E\int\Phi V\Phi d\tau_1 d\tau_2-\frac{1}{2}\int\Phi V^2\Phi d\tau_1 d\tau_2\right\},\\
\epsilon_2 &= \tfrac{1}{2}\alpha^2\int\Phi(r_{12})^{-1}[\nabla_1\nabla_2+(r_{12}^2)^{-1}\mathbf{r}_{12}(\mathbf{r}_{12}\nabla_1)\nabla_2]\Phi d\tau_1 d\tau_2,\\
\epsilon_4 &= \pi\alpha^2\int\Phi[2\delta^{(3)}(\mathbf{r}_{1a})-\delta^{(3)}(\mathbf{r}_{12})]\Phi d\tau_1 d\tau_2,\\
\epsilon_5 &= 2\pi\alpha^2\int\Phi\delta^{(3)}(\mathbf{r}_{12})\Phi d\tau_1 d\tau_2.
\end{aligned} \tag{33}$$

In the derivation of (33) use has been made of the wave equation in order to simplify the evaluation of ϵ_1.

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[10] W. Kołos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 205 (1960).

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

[12] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35/1, p. 267.

[13] Note that in Eqs. (32) and (33) α denotes the fine structure constant and not the parameter used in the wavefunction.

In the numerical computation, the wavefunction (11) was used and the matrix elements of the corrections (33) were expressed in terms of integrals in elliptic coordinates. In addition to the integrals (30), the following new types of integrals are needed for the relativistic case:

$$I^{-3}=\int \exp[-2\alpha(\xi_1+\xi_2)]\rho^{-3}W^{(2)}(\xi_1\eta_1\xi_2\eta_2)\,d\xi_1 d\xi_2 d\eta_1 d\eta_2 d\varphi_1 d\varphi_2, \tag{34}$$

$$I^{-2}=\int \exp[-2\alpha(\xi_1+\xi_2)]\rho^{-2}W^{(1)}(\xi_1\eta_1\xi_2\eta_2)\,d\xi_1 d\xi_2 d\eta_1 d\eta_2 d\varphi_1 d\varphi_2, \tag{34'}$$

and

$$L=\int \exp[-2\alpha(\xi_1+\xi_2)]\rho^{m}\xi_1^{r}\eta_1^{s}\xi_2^{\bar{r}}\eta_2^{\bar{s}}(\xi_1^2-\eta_1^2)^{-1}d\xi_1 d\xi_2 d\eta_1 d\eta_2 d\varphi_1 d\varphi_2, \tag{35}$$

where $m\geq -1$, and $W^{(i)}$ may be expressed in terms of

$$P_1=(2/R)(z_1-z_2) \quad\text{and}\quad P_2=(2/R)^2(r_1^2-r_2^2) \tag{36}$$

as follows: $W^{(1)}\propto P_1$ or P_2, and $W^{(2)}$ is equal to one of the three products: P_1P_1, P_1P_2, or P_2P_2, multiplied by powers of ξ_1, η_1, ξ_2, η_2.

It is obvious that each $W^{(i)}$ is a polynomial in ξ_1, η_1, ξ_2, η_2 having a zero of at least the ith order, if $\xi_1=\xi_2$ and $\eta_1=\eta_2$ simultaneously.

In the numerical integration of (35), use has been made of the Neumann expansion for r_{12}^{-1}, and for the higher inverse powers of r_{12} in (34) the following series was used[14]:

$$\rho^{-2p}=\sum_{l=0}^{\infty}\sum_{m=0}^{l}d_{lm}(p)[(1-\eta_1^2)(1-\eta_2^2)(\xi_1^2-1)(\xi_2^2-1)]^{m/2}$$
$$\times D_{l-m}^{p+m}(\xi_+)C_{l-m}^{p+m}(\xi_-)C_{l-m}^{p+m}(\eta_1)C_{l-m}^{p+m}(\eta_2)C_m^{p-\frac{1}{2}}(\cos\varphi) \qquad p\rangle 0, \qquad p\neq\tfrac{1}{2}, \tag{37}$$

where C_l^m are the Gegenbauer polynomials, $\varphi=\varphi_1-\varphi_2$,

$$D_n^{\nu}(\xi)=C_n^{\nu}(\xi)\int_{\infty}^{\xi}(x^2-1)^{-\nu-\frac{1}{2}}[C_n^{\nu}(x)]^{-2}dx,$$

$$d_{lm}(p)=-2^{2m+1}\frac{\Gamma(2p-1)[\Gamma(p+m)]^2(l-m)!(l+p)(2p+2m-1)}{[\Gamma(p)]^2\Gamma(2p+l+m)}. \tag{38}$$

It will be noticed that the integrands in (34) behave like r_{12}^{-1} if $r_{12}\to 0$, and for the existence of (34) the behavior $\propto r_{12}^{-2}$ would be sufficient. There are, however, two difficulties if (37) is used in an integrand that goes like r_{12}^{-2}: (1) the convergence of the series is very poor; (2) the integration of the right-hand side of (37) over the region $r_{12}=0$ always produces zero, while the left-hand side gives a nonvanishing contribution. As a consequence, this region has to be considered separately. However, both these difficulties disappear if the integrand behaves like r_{12}^{-1} near $r_{12}=0$, and this is just the case in (34) and (34′).

From (32) it is readily seen that $H_2\propto r_{12}^{-1}$ if $r_{12}\to 0$. Thus the evaluation of ϵ_2 in terms of (34) and (34′) is straightforward, though tedious. In ϵ_1, however, the integrand goes like r_{12}^{-2}. Nevertheless, the use of the integrals (34′) is still possible due to the identity

$$\int r_{12}^{-2}f d\tau_1 d\tau_2=\int r_{12}^{-2}(\mathbf{r}_{12}\nabla_1)f d\tau_1 d\tau_2, \quad \mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1, \tag{39}$$

which is always satisfied if both integrals exist. Equation (39) was used to achieve the proper behavior of the integrals in ϵ_1.

There is one more point concerning the final summation in (37) to be mentioned. If we denote by I_l the contribution to a given integral (34) due to the one value of l (and all corresponding m values), the integral reads either

$$I=\sum_{l=0}^{\infty}I_l \tag{40}$$

or

$$I=\lim_{L\to\infty}s_L, \qquad s_L=\sum_{l=0}^{L}I_l. \tag{41}$$

In some cases it happens that (40) represents an alternating series and the partial sums s_L have alternating signs, unless L is very large. This makes the convergence of (41) prohibitively slow. To avoid this difficulty, use has been made of the property of sequences

$$\lim_{L\to\infty}s_L=\lim_{L\to\infty}s_{L+k}, \tag{42}$$

and the summation has been performed in an equivalent

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TABLE I. Convergence of the ground-state energy.

P	No. of terms	E (a.u.)	D (cm^{-1})
	($\alpha=1.0$, $R=1.4$ a.u.)		
1	3	−1.1520288	33 366.6
2	9	−1.1733127	38 037.7
3	20	−1.1743389	38 263.0
4	40	−1.1744663	38 290.9
5	67	−1.1744728	38 292.4
>5	80	−1.1744742	38 292.7

but more rapidly converging way

$$I=\lim_{L\to\infty} S_L, \tag{43}$$

where

$$S_L=\tfrac{1}{8}(s_L+3s_{L+1}+3s_{L+2}+s_{L+3}). \tag{44}$$

In the final computation, the summation to $L=40$ was used, i.e., we replaced (43) by $I\approx S_{40}$, since it has been found that a further increase of L did not change the results. The numerical integrations were carried out using Simpson's rule with 80 integration points. An increase of the number of integration points up to 160 did not change the values of the corrections.

RESULTS AND DISCUSSION

The computations were carried out on the IBM 7094 computer at the Computation Center of the University of Chicago. Keeping fixed values of $\alpha=1.0$ and $R=1.4$ a.u., numerous test runs were made to select the most important terms in the wavefunction (11). The expansion length was gradually increased with the following limitations for the powers of the variables: $r+s$ (and $\bar{r}+\bar{s}$) ≤ 5 for $\mu=0$ and $r+s$ (and $\bar{r}+\bar{s}$) ≤ 3 for $\mu=1$, 2, 3. The terms which did not significantly improve the total energy were rejected in subsequent runs. In this way a 80-term wavefunction has been selected, and the wavefunction was also used for other values of the internuclear distance. The convergence of the energy is shown in Table I, where $p_{\max}$ denotes the maximum value of $p=r+s+\bar{r}+\bar{s}+\mu$.

TABLE II. Total, binding, and potential energies computed with 80-term wavefunctions.

R (a.u.)	α	E (a.u.)	V (a.u.)	D (cm^{-1})
0.55	0.536	−0.6627707	−2.6465751	−74 013.3
0.60	0.562	−0.7696341	−2.6769660	−50 559.5
0.65	0.597	−0.8543614	−2.6899810	−31 964.0
0.70	0.636	−0.9220261	−2.6904771	−17 113.3
0.75	0.662	−0.9763357	−2.6819180	−5 193.7
0.80	0.698	−1.0200556	−2.6668205	4 401.7
0.90	0.765	−1.0836422	−2.6239059	18 357.2
1.00	0.837	−1.1245385	−2.5715404	27 333.0
1.10	0.892	−1.1500562	−2.5152997	32 933.5
1.20	0.959	−1.1649342	−2.4584207	36 198.9
1.30	1.014	−1.1723459	−2.4027901	37 825.6
1.35	1.043	−1.1739627	−2.3758101	38 180.4
1.39	1.066	−1.1744517	−2.3547115	38 287.7
1.40	1.072	−1.1744744	−2.3495093	38 292.7
1.401	1.072	−1.1744746	−2.3489908	38 292.7
1.4011	1.072	−1.1744746	−2.3489392	38 292.7
1.41	1.077	−1.1744599	−2.3443366	38 289.5
1.45	1.100	−1.1740558	−2.3239571	38 200.8
1.50	1.121	−1.1728537	−2.2991984	37 937.0
1.60	1.165	−1.1685799	−2.2521884	36 999.0
1.70	1.210	−1.1624570	−2.2086130	35 655.2
1.80	1.258	−1.1550670	−2.1685307	34 033.3
1.90	1.295	−1.1468496	−2.1319110	32 229.8
2.00	1.342	−1.1381312	−2.0986802	30 316.3

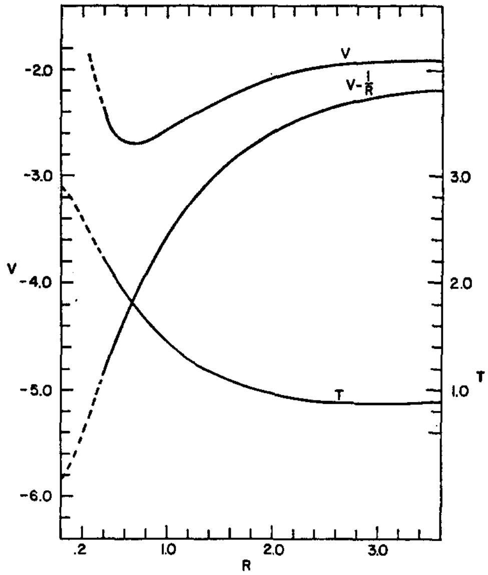

FIG. 1. Energies (in atomic units) for the ground state of H_2(54-term wavefunction).

Similar test runs were also made with more restricted expansions. Thus, with $r+s\leq 4$ for $\mu=0$ and $r+s\leq 2$ for $\mu=1$, 2, 3, the best energy obtained was $E^0=-1.1744720$ a.u., which gives the binding energy $D_e=38\,292.3\ \mathrm{cm}^{-1}$. This is only by 0.1 cm^{-1} worse than the 67-term result given in Table I, obtained with higher powers of ξ and η. With $r+s\leq 4$ for $\mu=0$ and $r+s\leq 2$ for $\mu=1$, 2, the best energy obtained using a 54-term expansion was $E^0=-1.744699$ a.u., which gives the binding energy $D_e=38\,291.7\ \mathrm{cm}^{-1}$. These

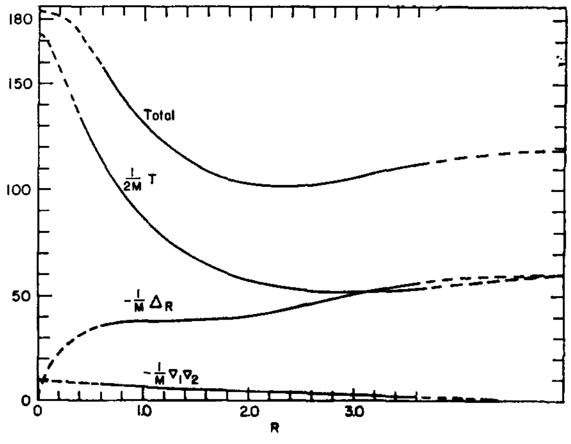

FIG. 2. Diagonal corrections for nuclear motion for the ground state of H_2(in reciprocal centimeters).

TABLE III. Energies and diagonal corrections for nuclear motion computed with 54-term wavefunctions.[a]

R	α	E	V	D	$-(2M)^{-1} \times\langle\Delta_{r_1}\rangle$	$-(2M)^{-1} \times\langle\nabla_{r_1}\nabla_{r_2}\rangle$	$-M^{-1} \times\langle\Delta_R\rangle$	E_{nucl}	ΔD_{nucl}
0.40	0.407	−0.1202028	−2.3630289	−193 093.2					
0.45	0.416	−0.3509282	−2.5024310	−142 454.8					
0.50	0.442	−0.5266270	−2.5917873	−103 893.4					
0.55	0.4836	−0.6627583	−2.6465583	−74 016.0					
0.60	0.5223	−0.7696253	−2.6769600	−50 561.4	113.994	8.026	36.084	158.104	−38.572
0.65	0.5601	−0.8543531	−2.6899756	−31 965.8	109.708	7.880	36.654	154.242	−34.710
0.70	0.5966	−0.9220185	−2.6904717	−17 115.0	105.693	7.736	37.076	150.505	−30.973
0.75	0.6314	−0.9763287	−2.6819152	−5 195.2	101.936	7.596	37.382	146.914	−27.382
0.80	0.6745	−1.0200487	−2.6668265	4 400.2	98.421	7.459	37.615	143.495	−23.963
0.90	0.7334	−1.0836362	−2.6239031	18 356.0	92.055	7.193	37.871	137.119	−17.587
1.00	0.8025	−1.1245331	−2.5715414	27 331.9	86.482	6.940	38.005	131.427	−11.895
1.10	0.8560	−1.1500512	−2.5152963	32 932.4	81.595	6.697	38.072	126.364	−6.832
1.20	0.9148	−1.1649294	−2.4584158	36 197.8	77.306	6.465	38.136	121.907	−2.375
1.30	0.9723	−1.1723414	−2.4027857	37 824.6	73.539	6.242	38.226	118.007	1.525
1.35	1.000	−1.1739581	−2.3758036	38 179.4	71.829	6.134	38.289	116.252	3.280
1.39	1.021	−1.1744472	−2.3547044	38 286.7	70.539	6.049	38.348	114.936	4.596
1.40	1.027	−1.1744699	−2.3495022	38 291.7	70.227	6.028	38.365	114.620	4.912
1.401	1.027	−1.1744701	−2.3489835	38 291.8	70.196	6.026	38.366	114.588	4.944
1.4011	1.027	−1.1744701	−2.3489315	38 291.8	70.193	6.025	38.367	114.585	4.947
1.41	1.031	−1.1744556	−2.3443296	38 288.6	69.919	6.007	38.382	114.308	5.224
1.45	1.054	−1.1740513	−2.3239486	38 199.8	68.725	5.923	38.457	113.105	6.427
1.50	1.078	−1.1728492	−2.2991869	37 936.0	67.317	5.821	38.566	111.704	7.828
1.60	1.132	−1.1685773	−2.2521693	36 998.4	64.762	5.619	38.843	109.224	10.308
1.70	1.187	−1.1624521	−2.2085964	35 654.1	62.524	5.424	39.201	107.149	12.383
1.80	1.249	−1.1550616	−2.1685117	34 032.1	60.570	5.232	39.644	105.446	14.086
1.90	1.308	−1.1468425	−2.1318795	32 228.2	58.872	5.043	40.176	104.091	15.441
2.00	1.362	−1.1381236	−2.0986316	30 314.6	57.406	4.857	40.794	103.057	16.475
2.10	1.427	−1.1291528	−2.0686852	28 345.8	56.152	4.673	41.505	102.330	17.202
2.20	1.486	−1.1201190	−2.0419222	26 363.1	55.092	4.489	42.301	101.882	17.650
2.30	1.554	−1.1111659	−2.0182412	24 398.1	54.212	4.306	43.184	101.702	17.830
2.40	1.614	−1.1024035	−1.9975034	22 475.0	53.496	4.123	44.140	101.759	17.773
2.50	1.676	−1.0939149	−1.9795924	20 611.9	52.933	3.939	45.168	102.040	17.492
2.60	1.747	−1.0857627	−1.9643862	18 822.7	52.512	3.754	46.255	102.521	17.011
2.70	1.806	−1.0779927	−1.9517054	17 117.4	52.218	3.570	47.385	103.173	16.359
2.80	1.863	−1.0706404	−1.9414292	15 503.8	52.043	3.383	48.538	103.964	15.568
2.90	1.926	−1.0637259	−1.9334036	13 986.2	51.977	3.197	49.709	104.883	14.649
3.00	2.000	−1.0572607	−1.9274598	12 567.3	52.008	3.012	50.875	105.895	13.637
3.10	2.067	−1.0512547	−1.9234024	11 249.1	52.125	2.826	52.013	106.964	12.568
3.20	2.126	−1.0457057	−1.9210074	10 031.2	52.313	2.642	53.253	108.208	11.324
3.30	2.192	−1.0406020	−1.9201199	8 911.1	52.565	2.461	54.102	109.128	10.404
3.40	2.262	−1.0359419	−1.9205494	7 888.3	52.869	2.285	54.989	110.143	9.389
3.60	2.382	−1.0278471	−1.9242625	6 111.7	53.575	1.948	56.588	112.111	7.421
3.70	2.517	−1.0243742	−1.9276723	5 349.5	53.986	1.786	57.276	113.048	6.484
∞		−1.0	−2.0	0	59.766	0	59.766	119.532	0

[a] R, E, and V in atomic units; D and all corrections in reciprocal centimeters; $E_{\text{nucl}} \equiv \langle\mathcal{H}\rangle$, Eq. (8); $\Delta D_{\text{nucl}} = E_{\text{nucl}}(R=\infty) - E_{\text{nucl}}(R)$.

results clearly show that the energy has converged, and that probably our best energy differs from the accurate eigenvalue of the nonrelativistic clamped nuclei Hamiltonian by not more than a fraction of a reciprocal centimeter.

The energy for several internuclear distances was computed using three different values of α for each R. The final energies are shown in Table II, and they were computed for interpolated exponents α assuming that E versus α is a parabola. Our best results $E^0 = -1.1744744$ a.u. and $D_e = 38\,292.7$ cm^{-1} are significantly better than the best previously reported values[1]: $E^0 = -1.174444$ a.u. and $D_e = 38\,286.9$ cm^{-1}.

Similar computations were carried out with the 54-term wavefunction mentioned above. The exponents α in this case were obtained by five-point interpolations, and the eigenvectors computed for interpolated α's were employed to compute the diagonal corrections for nuclear motion (8) and the relativistic corrections (33). The results are shown in Tables III and IV, where the last columns contain the contributions to the binding energy.

The computed clamped nuclei kinetic and potential energies are also shown in Fig. 1, where the scale on the left-hand side applies to the potential energy and on the right-hand side to the kinetic energy. The corrections for nuclear motion and the relativistic corrections are shown graphically in Figs. 2 and 3. It is seen that the form of the $E_{\text{nucl}}(R)$ function is determined mainly by the term proportional to the kinetic energy of the electrons.

For $\alpha = 1.0$ and $R = 1.4$ a.u., the corrections were also computed using a smaller number of terms in the wavefunction. The relativistic corrections for $3 \leq N \leq 54$ are presented in Table V. For a given number of terms the results on the corresponding horizontal line apply to a

TABLE IV. Relativistic corrections computed with 54-term wavefunctions.[a]

R	ϵ_1	ϵ_2	ϵ_4	ϵ_5	E_{rel}	ΔD_{rel}
0	−13.52204	−0.13910	11.04099	0.66856	−22.810	19.888
0.6	−3.93452	−0.09186	3.19829	0.32219	−5.913	2.991
0.8	−2.94627	−0.07723	2.42283	0.23913	−4.225	1.303
1.0	−2.33091	−0.06536	1.93580	0.17998	−3.278	0.356
1.2	−1.92873	−0.05572	1.61369	0.13748	−2.726	−0.196
1.3	−1.77973	−0.05159	1.49314	0.12076	−2.541	−0.381
1.35	−1.71510	−0.04967	1.44055	0.11332	−2.465	−0.457
1.40	−1.65613	−0.04783	1.39240	0.10640	−2.398	−0.524
1.401	−1.65500	−0.04779	1.39147	0.10626	−2.397	−0.525
1.4011	−1.65489	−0.04779	1.39138	0.10625	−2.396	−0.526
1.45	−1.60227	−0.04607	1.34825	0.09996	−2.339	−0.583
1.5	−1.55304	−0.04440	1.30771	0.09399	−2.288	−0.634
1.6	−1.46673	−0.04126	1.23625	0.08322	−2.203	−0.719
1.8	−1.33351	−0.03571	1.12454	0.06559	−2.093	−0.829
2.0	−1.23992	−0.03094	1.04427	0.05198	−2.041	−0.881
2.1	−1.20459	−0.02879	1.01335	0.04632	−2.030	−0.892
2.2	−1.17548	−0.02678	0.98737	0.04128	−2.029	−0.893
2.3	−1.15192	−0.02488	0.96592	0.03679	−2.035	−0.887
2.4	−1.13313	−0.02309	0.94822	0.03276	−2.048	−0.874
2.7	−1.10056	−0.01850	0.91429	0.02307	−2.123	−0.799
3.1	−1.09697	−0.01315	0.90141	0.01402	−2.275	−0.647
3.6	−1.12606	−0.00788	0.91277	0.00708	−2.502	−0.420
∞	−1.25	0	1.0	0	−2.922	0

[a] R in atomic units, ϵ_i in $\alpha^2 \times (\mathrm{a.u.}) = 11.68715\ \mathrm{cm}^{-1}$, E_{rel} and ΔD_{rel} in reciprocal centimeters.

wavefunction containing terms defined in the second column on and above the horizontal line. The last column contains the relativistic contribution to the binding energy.

To compute the expectation value of $-(1/M)\Delta_R$ we had to assume certain functional dependence of α on R. The interpolated values of α for the 54-term wavefunction are shown in Fig. 4 as function of R. It is seen that α is an almost linear function of the internuclear distance; therefore, we assumed that

$$\alpha = a + bR. \tag{45}$$

To see how sensitive are the results of the particular choice of the function $\alpha(R)$, the correction $-(1/M)\langle\Delta_R\rangle$ was computed for three different cases: (1) assuming a constant value of α, i.e., $b=0$; (2) assuming $a=0$ and an average value of b; (3) assuming average values of a and b. The resulting values of $-(1/M)\langle\Delta_R\rangle$ for the three cases and the two other corrections for nuclear motion are shown in Table VI for various expansion lengths. The order of terms in the wavefunction was the same as that defined in Column 2 of Table V. The last three columns of Table VI give the contributions to the binding energy, in reciprocal centimeters, for the three cases (1)–(3), respectively. It is seen that for short expansions, the best and most consistent results were obtained in Case (3). However, for the 54-term wavefunction, the differences between the three cases are negligibly small. In Table VII we give in addition the values of the various contributions to the expectation value of $-(1/M)\Delta_R$ which were obtained in the three cases with a 54-term wavefunction. The good agreement served as a check for our analysis as well as of the numerical computations.

To obtain an accurate value of the equilibrium internuclear distance R_e, we employed the virial theorem $V/2E=1$ for $R=R_e$. Using this relation and the values of the total and potential energies listed in Tables II and III, one gets $R_e = 1.401080$ a.u. $= 0.74141$ Å, and $R_e = 1.401083$ a.u. $= 0.74141$ Å for the 80- and 54-term functions, respectively. The experimental value[15] obtained from the extrapolated rotational constant B_e is $R_e = 0.74158$ Å; however, if this is corrected to include the effects of (1) interaction of

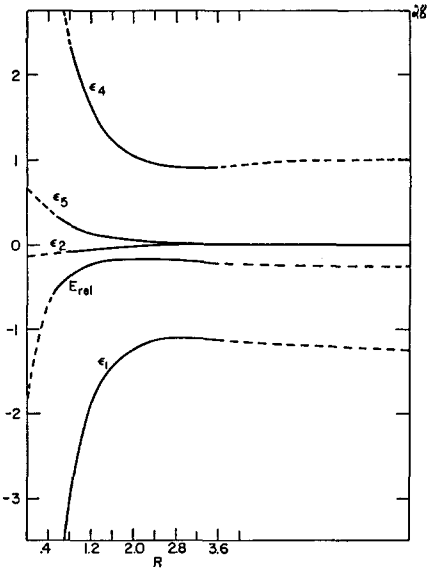

FIG. 3. Relativistic corrections for the ground state of H_2(in $\alpha^2 \times$a.u.).

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[15] G. Herzberg and L. L. Howe, Can. J. Phys. **37**, 636 (1959).

TABLE V. Total energy, binding energy, and relativistic corrections computed with three- to 54-term wavefunctions ($\alpha=1.0$, $R=1.4$ a.u.).

No. of terms	μ	rs	$\bar{r}\bar{s}$	E	D	ϵ_1	ϵ_2	ϵ_4	ϵ_5	E_{rel}	ΔD_{rel}
1	0	00	00								
2	0	00	10								
3	1	00	00	−1.1520289	33 366.5	−1.393345	−0.060102	0.989831	0.103734	−4.206	1.284
4	0	00	20	−1.1532352	33 631.2	−1.403043	−0.058171	1.008506	0.104538	−4.069	1.147
5	0	00	02	−1.1706537	37 454.2	−1.624057	−0.054415	1.350343	0.118755	−2.447	−0.475
6	0	10	10	−1.1709694	37 523.4	−1.633545	−0.051878	1.359490	0.118301	−2.427	−0.495
7	0	01	01	−1.1730119	37 971.7	−1.668260	−0.049631	1.388933	0.117999	−2.466	−0.456
8	1	00	10	−1.1730849	37 987.7	−1.664700	−0.051123	1.381735	0.120848	−2.492	−0.430
9	2	00	00	−1.1733128	38 037.8	−1.659255	−0.048181	1.382452	0.114337	−2.462	−0.460
10	0	00	30	−1.1733564	38 047.3	−1.656333	−0.048112	1.376982	0.113891	−2.496	−0.426
11	0	00	12	−1.1734197	38 061.2	−1.649021	−0.048025	1.361529	0.113681	−2.593	−0.329
12	0	10	20	−1.1734210	38 061.5	−1.648854	−0.048060	1.361346	0.113673	−2.593	−0.329
13	0	10	02	−1.1739949	38 187.5	−1.652355	−0.048220	1.371383	0.111275	−2.547	−0.375
14	0	01	11	−1.1740369	38 196.7	−1.650639	−0.048309	1.369738	0.110923	−2.551	−0.371
15	1	00	20	−1.1740489	38 199.3	−1.650387	−0.048498	1.368074	0.111858	−2.559	−0.363
16	1	00	02	−1.1742383	38 240.9	−1.654642	−0.049158	1.379096	0.110272	−2.506	−0.416
17	1	10	10	−1.1743025	38 255.0	−1.653760	−0.048793	1.378502	0.109863	−2.503	−0.419
18	1	01	01	−1.1743067	38 255.9	−1.653808	−0.048812	1.378784	0.109692	−2.503	−0.419
19	2	00	10	−1.1743325	38 261.6	−1.652445	−0.048381	1.379209	0.107570	−2.502	−0.420
20	0	00	22	−1.1743423	38 263.7	−1.654091	−0.048359	1.383978	0.107559	−2.465	−0.457
21	0	00	04	−1.1743526	38 266.0	−1.655798	−0.048335	1.390141	0.107587	−2.412	−0.510
22	0	10	30	−1.1743531	38 266.1	−1.655727	−0.048340	1.390077	0.107570	−2.412	−0.510
23	0	10	12	−1.1743655	38 268.8	−1.656405	−0.048251	1.391580	0.107401	−2.404	−0.518
24	0	01	21	−1.1743703	38 269.9	−1.656191	−0.048240	1.391397	0.107309	−2.404	−0.518
25	0	20	20	−1.1743719	38 270.2	−1.656151	−0.048221	1.391357	0.107311	−2.404	−0.518
26	0	20	02	−1.1744006	38 276.5	−1.656451	−0.048140	1.391636	0.107466	−2.402	−0.520
27	0	02	02	−1.1744338	38 283.8	−1.656925	−0.048161	1.392092	0.107605	−2.400	−0.522
28	0	11	11	−1.1744376	38 284.6	−1.656940	−0.048156	1.392076	0.107618	−2.401	−0.521
29	1	10	20	−1.1744397	38 285.1	−1.656902	−0.048108	1.392163	0.107512	−2.400	−0.522
30	1	10	02	−1.1744405	38 285.3	−1.656924	−0.048097	1.392278	0.107444	−2.399	−0.523
31	1	01	11	−1.1744420	38 285.6	−1.656988	−0.048084	1.392546	0.107393	−2.397	−0.525
32	2	00	20	−1.1744432	38 285.9	−1.657223	−0.048115	1.392714	0.107681	−2.395	−0.527
33	2	10	10	−1.1744508	38 287.5	−1.656706	−0.047946	1.392894	0.106928	−2.394	−0.528
34	2	01	01	−1.1744577	38 289.0	−1.656327	−0.047880	1.392517	0.106604	−2.397	−0.525
35	0	10	40	−1.1744589	38 289.3	−1.656142	−0.047896	1.391814	0.106716	−2.402	−0.520
36	0	10	04	−1.1744598	38 289.5	−1.656252	−0.047898	1.392223	0.106710	−2.398	−0.524
37	0	01	13	−1.1744652	38 290.7	−1.656511	−0.047912	1.392328	0.106911	−2.398	−0.524
38	0	01	31	−1.1744652	38 290.7	−1.656487	−0.047913	1.392270	0.106908	−2.398	−0.524
39	0	20	30	−1.1744653	38 290.7	−1.656488	−0.047911	1.392259	0.106913	−2.399	−0.523
40	0	02	30	−1.1744659	38 290.8	−1.656478	−0.047913	1.392263	0.106894	−2.399	−0.523
41	0	02	12	−1.1744667	38 291.0	−1.656434	−0.047912	1.392076	0.106910	−2.400	−0.522
42	2	10	20	−1.1744672	38 291.1	−1.656392	−0.047893	1.392052	0.106861	−2.400	−0.522
43	2	10	02	−1.1744674	38 291.2	−1.656365	−0.047894	1.392000	0.106855	−2.401	−0.521
44	2	01	11	−1.1744682	38 291.3	−1.656341	−0.047882	1.392162	0.106730	−2.400	−0.522
45	0	20	22	−1.1744681	38 291.3	−1.656332	−0.047885	1.392116	0.106745	−2.400	−0.522
46	0	02	22	−1.1744682	38 291.3	−1.656346	−0.047886	1.392149	0.106748	−2.400	−0.522
47	0	11	13	−1.1744682	38 291.3	−1.656335	−0.047886	1.392138	0.106740	−2.400	−0.522
48	0	11	31	−1.1744685	38 291.4	−1.656338	−0.047880	1.392243	0.106698	−2.399	−0.523
49	0	30	30	−1.1744684	38 291.4	−1.656336	−0.047880	1.392243	0.106693	−2.399	−0.523
50	0	12	30	−1.1744685	38 291.4	−1.656325	−0.047880	1.392211	0.106698	−2.399	−0.523
51	2	20	20	−1.1744686	38 291.4	−1.656308	−0.047878	1.392174	0.106692	−2.400	−0.522
52	2	02	02	−1.1744692	38 291.6	−1.656198	−0.047854	1.392146	0.106562	−2.400	−0.522
53	2	20	02	−1.1744692	38 291.6	−1.656174	−0.047856	1.392092	0.106566	−2.400	−0.522
54	2	11	11	−1.1744698	38 291.7	−1.656099	−0.047836	1.392194	0.106425	−2.400	−0.522

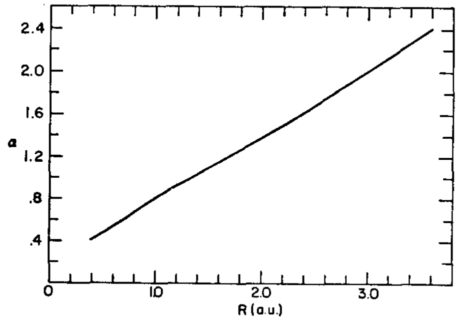

FIG. 4. The optimum exponent α as function of the internuclear distance.

rotation and vibration, (2) interaction of electronic and nuclear motion, and (3) L uncoupling, one gets[15] $R_e=0.74116$ Å. The discrepancy between this value and our result may be partly due to inaccurate values of the corrections and partly to the adiabatic approximation.

In Table VIII we list our final results for the binding energies of H_2, HD, and D_2. In the first row the clamped nuclei binding energies are given; the next two rows show the contributions to the binding energies due to the diagonal corrections for nuclear motion and to the relativistic effects. The subsequent row shows the final theoretical binding energies, and it is followed by experi-

TABLE VI. Diagonal corrections for nuclear motion computed with three- to 54-term wavefunctions in reciprocal centimeters ($\alpha=1.0$, $R=1.4$ a.u.).

No. of terms	$-(1/2M)\langle\Delta_1\rangle$	$-(1/2M)\langle\nabla_1\nabla_2\rangle$	$-(1/M)\langle\Delta_R\rangle$ 1	2	3	ΔD_{nucl} 1	2	3
1								
2								
3	66.897	7.747	47.174	23.510	25.463	−2.286	21.378	19.425
4	65.962	7.392	32.384	19.919	20.995	13.793	26.259	25.182
5	69.469	6.748	45.332	30.831	32.160	−2.017	12.484	11.155
6	69.880	6.503	43.464	34.446	35.343	−0.315	8.703	7.806
7	70.622	6.226	45.798	35.959	36.956	−3.114	6.724	5.727
8	70.438	6.419	41.094	37.493	37.890	1.581	5.182	4.785
9	70.425	5.947	41.174	37.502	37.906	1.986	5.658	5.254
10	70.379	5.940	39.968	36.763	37.133	3.244	6.449	6.080
11	70.332	5.921	39.090	37.643	37.798	4.189	5.636	5.482
12	70.331	5.920	39.156	37.762	37.910	4.124	5.518	5.370
13	70.173	5.944	38.411	37.670	37.754	5.005	5.745	5.661
14	70.152	5.940	38.216	37.944	37.973	5.224	5.495	5.466
15	70.156	5.934	38.291	38.180	38.186	5.151	5.262	5.256
16	70.208	6.017	38.663	38.516	38.527	4.644	4.792	4.781
17	70.197	6.029	38.464	38.144	38.178	4.842	5.162	5.128
18	70.200	6.037	38.503	38.185	38.220	4.791	5.109	5.075
19	70.210	6.056	38.488	38.172	38.208	4.778	5.094	5.058
20	70.208	6.053	38.408	38.062	38.102	4.863	5.209	5.169
21	70.212	6.050	38.440	38.091	38.131	4.830	5.178	5.138
22	70.212	6.050	38.432	38.073	38.114	4.838	5.197	5.156
23	70.221	6.041	38.485	38.269	38.293	4.785	5.000	4.977
24	70.223	6.039	38.504	38.315	38.335	4.765	4.955	4.935
25	70.222	6.039	38.511	38.323	38.343	4.760	4.948	4.928
26	70.210	6.031	38.366	38.250	38.262	4.925	5.041	5.029
27	70.221	6.022	38.456	38.316	38.331	4.833	4.973	4.958
28	70.220	6.024	38.424	38.281	38.296	4.865	5.007	4.992
29	70.221	6.024	38.431	38.315	38.327	4.856	4.972	4.960
30	70.222	6.022	38.423	38.323	38.333	4.865	4.696	4.954
31	70.222	6.024	38.424	38.323	38.333	4.861	4.963	4.953
32	70.221	6.024	38.383	38.282	38.293	4.904	5.004	4.993
33	70.222	6.025	38.378	38.265	38.278	4.907	5.019	5.007
34	70.222	6.028	38.379	38.267	38.279	4.903	5.015	5.002
35	70.223	6.029	38.367	38.310	38.316	4.913	4.970	4.963
36	70.224	6.029	38.368	38.311	38.318	4.911	4.968	4.962
37	70.226	6.026	38.397	38.338	38.345	4.882	4.942	4.935
38	70.226	6.026	38.393	38.340	38.346	4.886	4.939	4.933
39	70.226	6.026	38.393	38.341	38.347	4.886	4.939	4.933
40	70.225	6.026	38.379	38.334	38.339	4.901	4.946	4.941
41	70.225	6.026	38.378	38.344	38.347	4.903	4.937	4.933
42	70.226	6.026	38.376	38.352	38.354	4.904	4.928	4.925
43	70.226	6.027	38.371	38.348	38.350	4.907	4.931	4.929
44	70.226	6.028	38.370	38.355	38.357	4.907	4.922	4.921
45	70.226	6.028	38.370	38.359	38.360	4.907	4.919	4.918
46	70.226	6.028	38.371	38.360	38.361	4.906	4.918	4.917
47	70.226	6.028	38.371	38.360	38.361	4.907	4.917	4.916
48	70.226	6.028	38.369	38.358	38.359	4.909	4.919	4.919
49	70.226	6.028	38.368	38.358	38.359	4.909	4.920	4.919
50	70.226	6.028	38.368	38.358	38.359	4.909	4.920	4.919
51	70.226	6.028	38.368	38.360	38.360	4.909	4.918	4.917
52	70.226	6.027	38.368	38.359	38.360	4.911	4.920	4.919
53	70.226	6.027	38.367	38.359	38.360	4.911	4.919	4.919
54	70.226	6.028	38.367	38.358	38.359	4.911	4.920	4.919

mental results.[2] When Herzberg and Monfils[2] measured the binding energies of H_2, HD, and D_2, they could not unambiguously conclude whether $B'\,{}^1\Sigma_u$ or $C\,{}^1\Pi_u$ was the upper state of the continuum, and they gave two sets of binding energies, one set being shifted with respect to another by 0.6 cm^{-1}. The experimental binding energies listed in Table VIII are the larger values obtained by assuming that $B'\,{}^1\Sigma_u$ is the upper state of the continuum. However, even in this case the theoretical binding energies are slightly larger than the corresponding experimental values. If one assumes that both the theoretical and experimental values are correct, the discrepancy can only be attributed to the adiabatic approximation. But, if this is the case, the results show that the contribution to the binding energy due to the nondiagonal terms, neglected in the adiabatic approximation, is of the same order as the contribution due to the diagonal terms.

The accuracy of our results was tested in several different ways. There are two most significant possible sources of inaccuracy: the first, resulting from numerical integration of the I and M integrals (30) for odd powers

TABLE VII. Contributions to $-(1/M)\Delta_R$ computed with a 54-term wavefunction ($\alpha=1$, $R=1.4$ a.u.).

	$\alpha=$const.	$\alpha=bR$	$\alpha=a+bR$
$-M^{-1}(21/R^2)$	-0.00583529	-0.00583529	-0.00583529
$M^{-1}\langle c' \mid S \mid c' \rangle$	0.00272445	0.00062968	0.00021184
$-M^{-1}\langle c \mid D_2 \mid c \rangle$	-0.00335248	-0.00335248	-0.00335248
$-M^{-1}\langle c \mid S \mid b'' \rangle$	-0.00060920	-0.00016953	0.00006128
$-M^{-1}\langle c \mid D_1/\vert/b' \rangle$	0.00724733	-0.00235916	-0.00102385
$-(2/M)(d\alpha/dR)\langle c \mid \xi_1+\xi_2 \mid b''' \rangle$	0	-0.00460948	-0.00255074
$-M^{-1}(d\alpha/dR)^2\langle c \mid (\xi_1+\xi_2)^2 \mid c \rangle$	0	$+0.00592422$	$+0.00439175$
$+M^{-1}(d\alpha/dR)\langle c \mid (\xi_1+\xi_2)D_1 \mid c \rangle$	0	$+0.00960775$	0.00827227
$-M^{-1}\Delta_R$ a.u.	0.00017481	0.00017477	0.00017478

of r_{12}, and the second due to rounding off errors in the diagonalization. The first possibility has been eliminated by testing the convergence of the matrix elements and of the total energy with increasing number of integration points. In addition, independent tests have been made for some of our integrals. For instance, the integral

$$I=\frac{1}{2\pi^2}\left(\frac{2}{R}\right)^3\int \exp[-\alpha(\xi_1+\xi_2)]r_{12}^{-1}\nabla_1\nabla_2 \times \exp[-\alpha(\xi_1+\xi_2)]d\tau_1 d\tau_2 \quad (46)$$

can be evaluated in terms of our $I^{\mu}{}_{rs\bar{r}\bar{s}}$ integrals

$$I=\alpha^2(-I_{1010}{}^1-2I_{1010}{}^{-1}+2I_{3010}{}^{-1}+2I_{1210}{}^{-1} +2I_{0101}{}^{-1}-4I_{2101}{}^{-1}), \quad (47)$$

or analytically

$$I=2A_2-\tfrac{2}{3}A_0, \quad (48)$$

where

$$A_n=\int \exp(-4\alpha\xi)\xi^n d\xi. \quad (49)$$

Using (47) and (48), we obtained, for $\alpha=1$, $I=0.011828848$ and $I=0.011828840$, respectively. Since the most important elements of the $\mathcal{H}^0$ matrix were computed with a still better accuracy, we are convinced that our matrix elements used in the computation of the clamped nuclei energy are sufficiently accurate to yield the energy with at least seven figures of accuracy.

TABLE VIII. Binding energies of the isotopic hydrogen molecules (reciprocal centimeters).

	H_2	HD	D_2
$D_e{}^0$	38 292.7	38 292.7	38 292.7
ΔD_{nucl}	4.9	3.3	2.5
ΔD_{rel}	-0.5	-0.5	-0.5
D_e(theoret.)	38 297.1	38 295.5	38 294.7
D_e(exptl.)	38 292.9±0.5	38 290.9±1.5	38 291.4±0.7

We are also convinced that the diagonalization procedure employed in this computation yielded reliable results. For instance, when we increased the number of iterations, or changed a little the value of one of the nonlinear parameters α or R, the energy fluctuations did never exceed 4 in the eighth significant figure for the energy. In most cases they were smaller. The rounding off errors were larger for large internuclear distances ($R>3.5$ for the 54-term expansion and $R>2$ for the 80-term expansion); however, in this region, our wavefunction becomes poor anyway. We may also add that for the equilibrium internuclear distance, we have noticed larger rounding off errors when we had almost redundant terms in the wavefunction. It is possible that our wavefunctions, which were selected and tested for the equilibrium internuclear distance, contained almost-redundant terms for large values of R, and this may account for the increased rounding off errors in that region.

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