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Citation: *The Journal of Chemical Physics* **103**, 1792 (1995); doi: 10.1063/1.469753

View online: <http://dx.doi.org/10.1063/1.469753>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/103/5?ver=pdfcov>

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Nonadiabatic energies of the ground state of the hydrogen molecule

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(Received 17 March 1995; accepted 27 April 1995)

Possible sources of residual errors in the theoretical energies of the hydrogen molecule are investigated. Nonadiabatic corrections are computed for all bound, $J \leq 10$ $X^1\Sigma_g^+$ ro-vibrational states of the six isotopic hydrogen molecules. The new results improve significantly the overall agreement with accurate experimental transition frequencies. In order to estimate the convergence errors of the Born–Oppenheimer energies generalized James–Coolidge functions with powers of the interelectronic distance, r_{12} , up to 6 are used and the precision of the computations is increased. Except for the equilibrium separation, $R = 1.4011$ bohr, the obtained potential energy curve is lower by a few thousandths of a wave number than any other reported variational result. This lowers the $v=0$ vibrational levels by 0.009 cm^{-1} and results in a dissociation energy of H_2 , $D_0 = 36118.069\text{ cm}^{-1}$. © 1995 American Institute of Physics.

I. INTRODUCTION

In a recent work¹ we have investigated numerically the electronic ground state of the hydrogen molecule and many transition frequencies have been compared with very accurate experimental results published for different isotopic molecules by various authors. An inspection of the remaining discrepancies definitely suggests that nonadiabatic effects must be responsible — at least partly — for the inaccuracies in the theoretical energy levels. A similar conclusion was drawn earlier by Chuang and Zare.² For H_2 , HD and D_2 nonadiabatic corrections were computed some time ago by the present writer.³ However, the accuracy of those corrections decreases with increasing vibrational and rotational excitation. On the basis of the computed corrections Schwartz and LeRoy⁴ were able to derive simple formulas that allow extrapolation of the *ab initio* results to HT, DT and T_2 and to higher rotational states. Corrections obtained by this method were used both by Chuang and Zare² and in Ref. 1 and it has been found that agreement with experiment is not very satisfactory especially in the cases of HD and HT. Therefore this work was undertaken in order to get possibly accurate *ab initio* nonadiabatic corrections to the ground state vibrational-rotational energy levels of all six isotopic hydrogen molecules. This is the main aim of the present paper and in this sense it is a natural continuation of Ref. 1. However, very recently Kołos — by using an extrapolation procedure — estimated⁵ the convergence error of the Born–Oppenheimer energy at the equilibrium separation and came to the conclusion that the results in Ref. 1 have a systematic error of 0.01 cm^{-1} due to the neglect of some terms in the wave function. Since the extrapolation used by Kołos is not quite unambiguous we decided to study this problem in some more detail which lead to Section II of this paper.

Atomic units are used throughout unless otherwise stated. When wave numbers are used the conversion factor is: $1\text{ hartree} = 219474.631\text{ cm}^{-1}$.

II. THE BORN–OPPENHEIMER ELECTRONIC ENERGY

The general form of the electronic wave function used in this work and in Refs. 1 and 5 is that developed in Refs. 6 and 7, i.e., the function is assumed in the form of an expansion in elliptic coordinates of the two electrons denoted below by 1 and 2:

$$\Psi = \sum_k c_k G_k(1,2), \quad (1)$$

where k stands for $\nu_k, r_k, s_k, \bar{r}_k, \bar{s}_k$ and

$$G_k(1,2) = (x_1 + iy_1)^\Lambda g_k(1,2) \pm (x_2 + iy_2)^\Lambda g_k(2,1) \quad (2)$$

$$g_{\nu, r, s, \bar{r}, \bar{s}}(1,2) = \exp(-\alpha \xi_1 - \bar{\alpha} \xi_2) \rho^\nu \xi_1^r \eta_1^s \xi_2^{\bar{r}} \eta_2^{\bar{s}} \\ \times \{\exp(\beta \eta_1 + \bar{\beta} \eta_2) + (-1)^{s+\bar{s}+\Lambda+p} \\ \times \exp(-\beta \eta_1 - \bar{\beta} \eta_2)\}. \quad (3)$$

The \pm in Eq. (2) refers to singlet and triplet states, respectively, Λ is the familiar angular momentum projection quantum number and $p=0,1$ for g and u symmetry, respectively. ξ_j, η_j are the elliptic, and x_j, y_j the Cartesian coordinates of the two electrons with the z axis coinciding with the internuclear axis. $\rho = 2r_{12}/R$, r_{12} is the interelectronic distance and $c_i, \alpha, \bar{\alpha}, \beta, \bar{\beta}$ are variational parameters. Thus the basis set is defined by the set of exponents $\nu_i, r_i, s_i, \bar{r}_i, \bar{s}_i$.

In all previous ground state computations with the expansion Eqs. (1)–(3) the power of ρ was limited to $\nu \leq 3$. Kołos in a recent study⁵ came to the conclusion that the neglect of higher powers of ρ introduces a systematic error of about 0.01 cm^{-1} in the Born–Oppenheimer energies. Therefore in order to shed some light on this question the precision of the electronic energy computations in this work was increased to 16 bytes and powers of ρ up to $\nu=6$ were included in the wave function. We started with the 279 term expansion of, Ref. 1, reoptimized the nonlinear parameters and then performed a selection of additional terms in a way similar to the approach of Kołos,⁵ i.e., new terms were added—one at a time—and the energy improvements recorded. Then the individual energy improvements were serialized and 500 new terms, corresponding to the largest im-

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TABLE I. Total and binding Born–Oppenheimer energies at equilibrium.

R	$E(\text{a.u.})$	$D(\text{cm}^{-1})$	Δ^a	N^b	ν_{max}
1.4	−1.174475686 ^c	38292.9868 ^d		370	3
	−1.1744756881	38292.9873	0.0005	376	3
	−1.174475698067	38292.989452	0.0022	657	3
	−1.174475712020	38292.992514	0.00306	738	4
	−1.174475713172	38292.992767	0.00025	819	5
	−1.174475713565	38292.992853	0.00009	883	6
1.4011	−1.174475931 ^e	38293.0406 ^d		700	
	−1.174475930742	38293.040518	−0.000057±0.0001	883	6

^aImprovement over previous line in cm^{-1} .^bNumber of terms.^cKołos, Ref. 5—computed value.^dHere the accuracy is $\pm 0.0001 \text{ cm}^{-1}$ due to limited precision of E .^eRychlewski, Cencek and Komasa, Ref. 8.

provements, were added to the initial 279 terms to yield a 779 term expansion. In the selections all terms were considered that fulfilled: $\nu \leq 6$, $\nu + r + s \leq 8$ and — if $\nu \leq 4$ — $\nu + \max(r, s) \leq 7$. The selection was repeated independently for several internuclear distances. For test purposes, at the equilibrium separation the energy was computed as described above, and then again with a modified wave function: all selected $\nu > 3$ terms were skipped and replaced with 226 terms satisfying $r, s \leq 2$ for $\nu = 4, 5$ and for $\nu = 6$ in addition $r + s \leq 3$. This resulted in an 883 term expansion and an energy improvement of 0.0002 cm^{-1} over the 779 term result. A summary of the new and a comparison with earlier results is given in Tables I and II.

The 779 and 883 term results at equilibrium mentioned above show clearly that the obtained energies cannot be treated as final. A further enlargement of the basis set would undoubtedly further improve the energies by an amount of the order of 0.0001 cm^{-1} or more. Also it is seen from Table I that the contribution to the energy of the $\nu = 4, 5$ and 6 powers of ρ amounts to 0.003 cm^{-1} only which is one third

of Kołos⁵ estimate. It should also be stressed that the selection of terms in the wave function—in this work and in Ref. 5—is by no means unique. Since the basis is not orthogonal different sets of terms lead to the same energy and therefore the convergence rate of the binding energy with increasing ν_{max} as seen in Table I cannot be used for a reliable extrapolation.

Our results given in Table II are markedly better than the most recent results of Rychlewski *et al.*⁸ obtained with a 300 term expansion in a correlated Gaussian basis. However, their $R = 1.4011$, 700 term result listed in Table I coincides within the accuracy given in Ref. 8 with our result.

The improvements of the energies over those obtained with the 279 term function of Ref. 1 are given in the third column of Table II. These are rather irregular. This is due partly to the reoptimization of the nonlinear exponents but mainly to the fact that different sets of terms were used at different internuclear distances. Numerous tests have convinced the present writer that there are no accidental numerical inaccuracies in the reported results. On the other hand it is impossible to give a reliable estimate of the remaining convergence error. We believe, however, that the energies in Table II are to within a few 0.0001 cm^{-1} the best results that can be obtained with a variational function in the form of Eqs. (1)–(3) and with an expansion length of about 1000 terms. The results of Ref. 8 suggest that the same conclusion can be drawn in the case of correlated Gaussian functions. Thus we conclude that the convergence errors in the Born–Oppenheimer energies in Table II amount to at least several ten-thousandths of a wave number and we only *believe* that these errors are below 0.01 cm^{-1} .

III. NONADIABATIC RO-VIBRATIONAL ENERGIES

The method that is used in this work was described in detail before.^{3,9} Here we will recall only these equations that we will need in the discussion.

A. The variation-perturbation method

If H is the total nonrelativistic Hamiltonian of the molecule in the center of mass system and ψ_k^0 , E_k^0 —approximate solutions of the Schrödinger equation

TABLE II. Born–Oppenheimer energy.

R	$E(\text{a.u.})$	Δ_{BO}^a	Δ_{RCK}^b
0.6	−0.769635427887	−0.0164	
0.8	−1.020056664330	−0.0135	−0.0080
1.0	−1.124539718008	−0.0119	−0.0081
1.2	−1.164935241876	−0.0103	−0.0081
1.4	−1.174475713565	−0.0093	−0.0074
1.6	−1.168583371916	−0.0085	−0.0068
1.8	−1.155068736046	−0.0081	−0.0068
2.0	−1.138132955488	−0.0080	−0.0076
2.2	−1.120132112181	−0.0073	−0.0066
2.4	−1.102422601703	−0.0074	−0.0067
2.6	−1.085791233366	−0.0075	−0.0067
2.8	−1.070683223812	−0.0061	−0.0057
3.0	−1.057326265285	−0.0071	−0.0062
3.2	−1.045799653502	−0.0058	−0.0041
4.0	−1.016390251364	−0.0051	
4.5	−1.007993728135	−0.0040	
5.0	−1.003785657939	−0.0033	
6.0	−1.000835707231	−0.0011	
8.0	−1.000055604837	−0.0004	

^aImprovement over Ref. 1 in cm^{-1} ^bImprovement over 300 term results of Ref. 8.

$$H\psi = E\psi, \quad (4)$$

we write

$$\psi = \psi_k^0 + \psi'_k \quad (5)$$

and we split the Hamiltonian into the zeroth order part and a perturbation:

$$H = H_0 + H' \quad (6)$$

in such a way that

$$H_0\psi_k^0 = E_k^0\psi_k^0 \quad (7)$$

with

$$E_k^0 = \langle \psi_k^0 | H | \psi_k^0 \rangle. \quad (8)$$

Thus the first order energy correction vanishes but — in general — H_0 is not a differential operator and we cannot use the standard perturbation equations to get ψ'_k . Therefore in order to get the second order energy correction we solve an auxiliary problem:⁹

$$(H - E_i^0 - \delta)\phi'_\delta = -(H - E_i^0)\psi_i^0, \quad (9)$$

$$\epsilon''(\delta) = \langle \phi'_\delta | H - E_i^0 | \psi_i^0 \rangle, \quad (10)$$

with δ being a parameter.

Obviously ψ_i^0 has a definite symmetry, say S_0 , and due to H' it may interact with other symmetries S , giving rise to different functions $\phi'_{\delta,S}$. Eqs. (9) and (10) must be solved separately for each symmetry S , and the total second order energy correction E'' is a sum of contributions, $E''(S)$, for all allowed S :

$$E'' = \sum_S E''(S). \quad (11)$$

The evaluation of $E''(S)$ depends on whether S equals to S_0 or not. In the latter case we have

$$E''(S) = \epsilon''_S(0). \quad (12)$$

If $S = S_0$ however, H has an eigenvalue, E_i , close to E_i^0 and $\epsilon''(\delta)$ has a singularity:

$$\epsilon''(\delta) \approx -\frac{a}{\Delta E - \delta} + b \quad \text{for } \delta \approx \Delta E = E_i - E_i^0. \quad (13)$$

The three constants a, b and ΔE can be determined from Eqs. (13) if $\epsilon''(\delta)$ is evaluated for three different values of δ in the vicinity of the pole. The energy correction is then⁹

$$E''(S_0) = \epsilon''(0) + \frac{a}{\Delta E}. \quad (14)$$

We also get an estimate of the eigenvalue

$$E_i = E_i^0 + \Delta E. \quad (15)$$

Obviously, both Eqs. (14) and (15) give good approximations to the nonadiabatic eigenvalue if ΔE is small.

In practice we solve Eq. (9) by a variational procedure, i.e., a finite basis set of electronic functions, $\{f_i\}$, is assumed and ϕ'_δ is expanded as

$$\phi'_\delta = \frac{1}{R} \sum f_i(x) F_i(R), \quad (16)$$

where x represents the electronic coordinates.

A substitution of Eq. (16) into Eq. (9) and a projection onto the basis $\{f_i\}$ leads to a set of ordinary differential equations for $F_i(R)$ which we collect to a column vector \mathbf{F} . If we choose an orthonormal basis $\{f_{ij}\}$, which might be R -dependent, the general form of the equations is

$$\left\{ \frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{1}{\mu} \mathbf{B} \frac{d}{dR} - \mathbf{C} + \lambda_i \right\} \mathbf{F} = \mathbf{P}^i, \quad (17)$$

where μ is the reduced mass of the nuclei, $\lambda_i = E_i^0 + \delta$, \mathbf{P}^i is a column vector and \mathbf{B}, \mathbf{C} — R -dependent matrices with components:

$$P_k^i = (f_k | H - E_i^0 | \psi_i^0), \quad (18)$$

$$B_{k,l} = (f_k | d/dR | f_l), \quad (19)$$

$$C_{k,l} = (f_k | H | f_l) + \frac{J(J+1)}{2\mu} \delta_{kl}. \quad (20)$$

Above the parentheses denote integration over the electronic coordinates only, and the boundary conditions are: $\mathbf{F}(0) = \lim_{R \rightarrow \infty} \mathbf{F}(R) = 0$. Eq. (10) reads now

$$\epsilon''(\delta) = \int_0^\infty \mathbf{F}^+ \mathbf{P} dR. \quad (21)$$

It should be noted, however, that — if we use Eqs. (16) and (17) — the eigenvalue of H , E_i , in Eq. (13) will be replaced by the eigenvalue \tilde{E}_i of the homogeneous set corresponding to Eq. (17) which makes the estimate Eq. (15) less accurate than Eq. (14).

B. Numerical realization and tests

In this work the symmetry is $S_0 = {}^1\Sigma_g^+$, and the zeroth order functions, ψ_i^0 , and energies, E_i^0 , are the nonrelativistic adiabatic ro-vibronic solutions for the $X^1\Sigma_g^+$ ground state obtained in Ref. 1, i.e., they are products of the electronic, ψ^{el} , and vibrational-rotational, χ_i , functions:

$$\psi_i^0 = \psi^{\text{el}} \chi_i(R). \quad (22)$$

For homonuclear hydrogen molecules the permissible symmetries of ϕ'_δ are ${}^1\Sigma_g^+$ and ${}^1\Pi_g$. In the heteronuclear case ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ must also be considered. Thus for each of those symmetries a basis $\{f_i\}$ must be defined and we construct it from the primitive functions G_k , Eq. (2), of proper symmetry as follows:

- (1) The same nonlinear parameters and the same set of indices $\{\nu, r, s, \bar{r}, \bar{s}\}$ defining the basis are used as in the 261 term function of Ref. 1. (In Ref. 1 this number was given erroneously as 262.)
- (2) At the equilibrium separation, $R = 1.4$, a singular value decomposition of the overlap matrix $S, S_{ik} = (G_i | G_k)$, is performed to yield an 80×261 transformation matrix, \mathbf{U} , transforming the original basis $\{G_k\}$ to an orthonormal basis of $N = 80$ eigenvectors of S corresponding to the largest eigenvalues.
- (3) The constant matrix \mathbf{U} is then used at all internuclear distances to contract the basis $\{G_k\}$ to an — in general nonorthogonal — basis $\{\tilde{f}_i\}$: $\tilde{f}_i = \sum U_{ij} G_j$.

TABLE III. $E''_{v,0}(^1\Sigma_g^+)$ convergence with the basis length for H_2 .

N	$E''_{1,0}$	Δ	$E''_{4,0}$	Δ	$E''_{10,0}$	Δ
21	-1.3078		-3.3159		-5.0736	
41	-1.3303	-0.0225	-3.3722	-0.0562	-5.1652	-0.0916
51	-1.3332	-0.0028	-3.3786	-0.0064	-5.1729	-0.0077
61	-1.3347	-0.0015	-3.3818	-0.0032	-5.1766	-0.0037
71	-1.3350	-0.0003	-3.3824	-0.0006	-5.1772	-0.0006
81	-1.3352	-0.0001	-3.3829	-0.0005	-5.1776	-0.0004

^aNumber of terms in ϕ' .^b Δ is the improvement over the previous line.

- (4) For symmetries other than $^1\Sigma_g^+$ — $\{\tilde{f}_i\}$ is orthonormalized to yield $\{f_{ij}\}$.
- (5) For the $^1\Sigma_g^+$ symmetry ψ^{el} is added to the basis and $\{\tilde{f}_i, \psi^{\text{el}}\}$ orthonormalized to $\{f_{ij}\}$.

One can argue with good reason that the bases are not optimal. However, only a few digits accuracy is needed to get the energy correction Eq. (10) and therefore the accuracy required in ϕ'_δ is much less than in the case of ψ_i^0 . We believe therefore that the bases chosen are flexible enough for our purposes.

The inclusion of ψ^{el} into the basis is essential for an accurate evaluation of the $^1\Sigma_g^+$ contribution of the energy correction because it assures that the eigenvalues, \tilde{E}_i , of the total Hamiltonian in the subspace spanned by $\{f_{ij}\}$ are bounded from above by the corresponding adiabatic energies: $\tilde{E}_i \leq E_i^0$. This has the consequence that ΔE is small and therefore finding and removing the proper pole in Eq. (13) presents no difficulties.

In the final computations the boundary conditions were approximated by $F(0.2)=F(12.0)=0$ and the matrices \mathbf{B} , \mathbf{C} and the vector \mathbf{P} evaluated at 226 internuclear distances in the interval $[0.2, 12.0]$. In the most important region, $0.9 \leq R \leq 3.0$ the matrices were computed at intervals $\Delta R = 0.025$. To get the matrices at a uniform grid we used cubic splines to interpolate the matrix elements. Then Eqs. (17) were integrated and ϵ'' , Eq. (21) was computed by the method described in Ref. 10. In the final computations 71

TABLE IV. $J=0$, $^1\Sigma_g^+$ corrections for H_2 in cm^{-1} . Comparison with earlier results.

v	Ref. 3	Present	Diff.
0	-0.4980	-0.4988	-0.0008
1	-1.3343	-1.3350	-0.0007
2	-2.0884	-2.0913	-0.0029
3	-2.7654	-2.7728	-0.0074
4	-3.3669	-3.3824	-0.0155
5	-3.8908	-3.9208	-0.0300
6	-4.3346	-4.3847	-0.0501
7	-4.6913	-4.7654	-0.0741
8	-4.9442	-5.0459	-0.1017
9	-5.0606	-5.1980	-0.1374
10	-4.9916	-5.1772	-0.1856
11	-4.5806	-4.9176	-0.3370
12	-4.0694	-4.3270	-0.2576
13	-2.9107	-3.2844	-0.3737
14	-1.4335	-1.6482	-0.2147

TABLE V. Expansion coefficients of $E''_{v,J}$, Eq. (25), for H_2 .

v	a_0	a_1	a_2	a_3	$\Delta\epsilon$
0	-0.4988	-0.3339	0.0033	-0.0007	0.0000
1	-1.3350	-0.2835	-0.0007	-0.0004	0.0001
2	-2.0913	-0.2390	-0.0034	-0.0003	0.0001
3	-2.7728	-0.1980	-0.0063	0.0002	0.0001
4	-3.3824	-0.1592	-0.0079	0.0006	0.0001
5	-3.9208	-0.1187	-0.0091	0.0020	0.0002
6	-4.3847	-0.0728	-0.0067	0.0030	0.0002
7	-4.7654	-0.0136	-0.0005	0.0047	0.0002
8	-5.0459	0.0702	0.0112	0.0082	0.0003
9	-5.1980	0.1955	0.0327	0.0145	0.0003
10	-5.1772	0.3879	0.0686	0.0274	0.0004
11	-4.9178	0.6871	0.1182	0.0660	0.0005
12	-4.3287	1.1845	0.0630	0.2981	0.0042
13	-3.2850	1.8759	0.2435	0.9266	0.0011 ^a
14	-1.6486	3.1408	-0.4361	18.2778	0.0006 ^b

^a $J \leq 7$.^b $J \leq 4$.

(for $^1\Sigma_g^+$ corrections) or 70 coupled equations were integrated. An integration step $h=0.01$ was found to be sufficiently small for our purposes.

The dependence of the final results on the dimension of the basis, N , is illustrated in Table III for some vibrational levels of H_2 . It is clear that a larger basis would still lower the energy. The remaining error is of the same order of magnitude as the truncation error of the Born–Oppenheimer energy and our final 71 term energy corrections are probably too small in absolute value by about 0.001 cm^{-1} .

We have also investigated the sensitivity of the results to the interpolation of \mathbf{B} , \mathbf{C} and \mathbf{P} . We omitted some of the 226 input points and performed the computations for the $J=0$ levels of H_2 with an interpolation based on 130, 162, 186 and 226 points. The results obtained differed by a maximum of

TABLE VI. Expansion coefficients of $E''_{v,J}$, Eq. (25), for HD.

v	a_0	a_1	a_2	a_3	$\Delta\epsilon$
0	-0.3714	-0.3894	0.0245	-0.0025	0.0001
1	-1.0001	-0.3497	0.0190	-0.0008	0.0002
2	-1.5747	-0.3162	0.0201	-0.0022	0.0001
3	-2.0989	-0.2831	0.0180	-0.0018	0.0000
4	-2.5744	-0.2512	0.0159	-0.0012	0.0001
5	-3.0023	-0.2198	0.0149	-0.0011	0.0001
6	-3.3821	-0.1871	0.0146	-0.0009	0.0001
7	-3.7116	-0.1514	0.0150	-0.0004	0.0001
8	-3.9858	-0.1095	0.0168	0.0002	0.0002
9	-4.1964	-0.0570	0.0209	0.0010	0.0003
10	-4.3299	0.0125	0.0274	0.0027	0.0003
11	-4.3663	0.1076	0.0383	0.0056	0.0003
12	-4.2769	0.2398	0.0579	0.0093	0.0003
13	-4.0224	0.4281	0.0834	0.0223	0.0003
14	-3.5511	0.7010	0.1105	0.0687	0.0005
15	-2.7964	1.0916	0.1707	0.2328	0.0005 ^a
16	-1.6825	1.6961	0.3925	1.4970	0.0002 ^b
17	-0.2241 ^c	-0.1440 ^d			

^a $J \leq 8$.^b $J \leq 5$.^cTotal correction for $J=0$.^dTotal correction for $J=1$.

TABLE VII. Expansion coefficients of $E''_{v,J}$, Eq. (25), for HT.

v	a_0	a_1	a_2	a_3	$\Delta\epsilon$
0	-0.3626	-0.5056	0.0368	-0.0030	0.0000
1	-0.9741	-0.4655	0.0355	-0.0034	0.0002
2	-1.5354	-0.4271	0.0329	-0.0029	0.0000
3	-2.0487	-0.3905	0.0311	-0.0029	0.0000
4	-2.5157	-0.3550	0.0288	-0.0021	0.0001
5	-2.9375	-0.3201	0.0277	-0.0022	0.0001
6	-3.3138	-0.2847	0.0273	-0.0024	0.0001
7	-3.6435	-0.2470	0.0264	-0.0017	0.0001
8	-3.9234	-0.2055	0.0270	-0.0014	0.0001
9	-4.1479	-0.1577	0.0293	-0.0013	0.0001
10	-4.3083	-0.0994	0.0324	-0.0004	0.0001
11	-4.3918	-0.0256	0.0387	0.0006	0.0002
12	-4.3798	0.0710	0.0480	0.0028	0.0002
13	-4.2466	0.1999	0.0638	0.0061	0.0002
14	-3.9584	0.3768	0.0844	0.0161	0.0001
15	-3.4706	0.6223	0.1097	0.0495	0.0004
16	-2.7285	0.9838	0.0875	0.2409	0.0016 ^a
17	-1.6677	1.5300	-0.0872	1.9867	0.0012 ^b
18	-0.2911 ^c	-0.2340 ^d			

^a $J \leq 9$.^b $J \leq 6$.^cTotal correction for $J=0$.^dTotal correction for $J=1$.

0.0007 if the number of points was increased from 130 to 162, by 0.0001 if it was further increased to 186, and by less than 0.00005 cm^{-1} when the full set was used. This supports our earlier statement that lower precision is required in the computations of ϕ'_δ than in the case of the Born–Oppenheimer computations.

TABLE VIII. Expansion coefficients of $E''_{v,J}$, Eq. (25), for D_2 .

v	a_0	a_1	a_2	a_3	$\Delta\epsilon$
0	-0.1725	-0.0853	0.0003	0.0001	0.0001
1	-0.4769	-0.0762	0.0002	0.0000	0.0000
2	-0.7605	-0.0677	-0.0002	-0.0001	0.0001
3	-1.0246	-0.0598	-0.0006	0.0001	0.0001
4	-1.2698	-0.0525	-0.0004	-0.0002	0.0001
5	-1.4970	-0.0453	-0.0012	0.0002	0.0001
6	-1.7062	-0.0386	-0.0011	0.0001	0.0001
7	-1.8977	-0.0316	-0.0008	-0.0001	0.0001
8	-2.0709	-0.0238	-0.0014	0.0005	0.0000
9	-2.2246	-0.0150	-0.0011	0.0005	0.0001
10	-2.3568	-0.0044	-0.0004	0.0005	0.0001
11	-2.4646	0.0090	0.0010	0.0003	0.0001
12	-2.5434	0.0268	0.0022	0.0008	0.0001
13	-2.5869	0.0507	0.0044	0.0010	0.0001
14	-2.5868	0.0831	0.0079	0.0013	0.0001
15	-2.5316	0.1271	0.0128	0.0019	0.0001
16	-2.4071	0.1869	0.0196	0.0032	0.0001
17	-2.1951	0.2681	0.0293	0.0067	0.0001
18	-1.8742	0.3794	0.0418	0.0189	0.0001
19	-1.4196	0.5414	0.0365	0.0963	0.0005 ^a
20	-0.8055	0.7699	0.1587	0.4707	0.0000 ^b
21	-0.0860 ^c	-0.0529 ^d			

^a $J \leq 9$.^b $J \leq 5$.^cTotal correction for $J=0$.^dTotal correction for $J=1$.TABLE IX. Expansion coefficients of $E''_{v,J}$, Eq. (25), for DT.

v	a_0	a_1	a_2	a_3	$\Delta\epsilon$
0	-0.1380	-0.0818	0.0014	0.0001	0.0000
1	-0.3830	-0.0748	0.0010	0.0003	0.0000
2	-0.6127	-0.0685	0.0016	-0.0003	0.0001
3	-0.8276	-0.0626	0.0021	-0.0008	0.0001
4	-1.0286	-0.0564	0.0005	0.0002	0.0001
5	-1.2159	-0.0509	0.0007	0.0000	0.0000
6	-1.3899	-0.0456	0.0008	-0.0002	0.0001
7	-1.5507	-0.0400	0.0002	0.0002	0.0000
8	-1.6982	-0.0346	0.0010	-0.0003	0.0001
9	-1.8319	-0.0286	0.0010	-0.0003	0.0001
10	-1.9509	-0.0215	0.0003	0.0003	0.0001
11	-2.0540	-0.0137	0.0011	0.0001	0.0000
12	-2.1390	-0.0039	0.0014	0.0002	0.0000
13	-2.2031	0.0083	0.0022	0.0003	0.0001
14	-2.2424	0.0239	0.0036	0.0002	0.0001
15	-2.2517	0.0444	0.0047	0.0006	0.0000
16	-2.2243	0.0707	0.0078	0.0003	0.0001
17	-2.1515	0.1056	0.0108	0.0009	0.0001
18	-2.0229	0.1516	0.0146	0.0021	0.0000
19	-1.8256	0.2117	0.0211	0.0040	0.0001
20	-1.5449	0.2918	0.0299	0.0110	0.0001
21	-1.1638	0.4037	0.0362	0.0481	0.0003 ^a
22	-0.6663	0.5715	0.0354	0.4142	0.0002 ^b
23	-0.0913 ^c	-0.0717 ^d			

^a $J \leq 9$.^b $J \leq 6$.^cTotal correction for $J=0$.^dTotal correction for $J=1$.TABLE X. Expansion coefficients of $E''_{v,J}$, Eq. (25), for T_2 .

v	a_0	a_1	a_2	a_3	$\Delta\epsilon$
0	-0.0932	-0.0384	-0.0001	0.0002	0.0001
1	-0.2614	-0.0350	-0.0002	0.0002	0.0001
2	-0.4201	-0.0319	0.0003	-0.0002	0.0001
3	-0.5700	-0.0288	-0.0002	0.0001	0.0000
4	-0.7112	-0.0262	0.0002	-0.0003	0.0001
5	-0.8441	-0.0232	-0.0009	0.0005	0.0000
6	-0.9689	-0.0210	0.0001	-0.0002	0.0000
7	-1.0858	-0.0183	-0.0001	-0.0002	0.0000
8	-1.1947	-0.0157	-0.0004	0.0000	0.0000
9	-1.2957	-0.0131	-0.0004	0.0000	0.0001
10	-1.3883	-0.0103	-0.0003	0.0000	0.0000
11	-1.4723	-0.0071	-0.0003	0.0000	0.0001
12	-1.5468	-0.0035	-0.0001	0.0001	0.0001
13	-1.6108	0.0010	0.0004	-0.0001	0.0001
14	-1.6630	0.0065	0.0004	0.0001	0.0001
15	-1.7014	0.0134	0.0011	0.0000	0.0001
16	-1.7236	0.0224	0.0013	0.0002	0.0001
17	-1.7265	0.0336	0.0026	-0.0001	0.0001
18	-1.7059	0.0485	0.0030	0.0004	0.0001
19	-1.6571	0.0672	0.0047	0.0004	0.0002
20	-1.5740	0.0915	0.0065	0.0008	0.0001
21	-1.4498	0.1225	0.0091	0.0014	0.0001
22	-1.2762	0.1625	0.0127	0.0029	0.0001
23	-1.0442	0.2146	0.0191	0.0070	0.0001
24	-0.7444	0.2891	0.0169	0.0418	0.0003 ^a
25	-0.3701	0.3976	0.0543	0.3539	0.0001 ^b

^a $J \leq 9$.^b $J \leq 5$.

TABLE XI. Ground state, $v=0, J=0$ dissociation energies of the hydrogen molecule in cm^{-1} .

H ₂	HD	HT	D ₂	DT	T ₂
36118.069	36405.787	36512.207	36748.364	36881.283	37028.498

Finally we compare in Table IV the present $^1\Sigma_g^+$ corrections with those obtained earlier³ with a very limited basis and less accurate zero order solutions. As expected, the differences increase significantly with the vibrational excitation. However, for the lowest vibrational levels the accuracy of the old results is remarkable.

C. Results

The nonadiabatic energy corrections were computed for all bound vibration-rotational levels with $J \leq 10$ with one exception, viz. the $v=26$ vibrational level of T₂. This particular level was omitted because it is very weakly bound — 0.06 cm^{-1} in the adiabatic approximation — and therefore our assumption that the wave function is negligibly small for $R > 12.0$ does not hold.

For all levels the computations were performed independently for each J and each symmetry to yield the final correction. For the heteronuclear molecules the correction is thus

$$E''_{v,J} = E''_{v,J}(\Sigma_g) + E''_{v,J}(\Pi_g) + E''_{v,J}(\Sigma_u) + E''_{v,J}(\Pi_u). \quad (23)$$

For homonuclear molecules the last two terms are omitted, because the corresponding corrections vanish.

In an attempt to reduce the number of data — following Schwartz and LeRoy⁴ — we tried to describe the mass dependence of the corrections by a scaling procedure. However we were not able to find a satisfactory scaling method. Nev-

TABLE XII. $\Delta G(v+1/2)$ for H₂ and HD in cm^{-1} .

	ν	Theory	Δ^a		ν	Theory	Δ^a
H ₂	0	4161.167	0.027	7	2543.175	−0.075	
	1	3925.836	0.046	8	2292.950	0.020	
	2	3695.389	−0.041	9	2026.351	−0.029	
	3	3467.976	0.026	10	1736.707	0.047	
	4	3241.564	−0.046	11	1415.076	0.006	
	5	3013.851	−0.009	12	1049.139	−0.021	
	6	2782.136	0.006	13	621.956	−0.064	
HD	0	3632.161	0.009	3	3109.259	−0.005	
	1	3454.717	−0.018	4	2939.144	−0.005	
	2	3280.754	0.033	5	2769.214	0.015	

^aTheory—Experiment. For H₂ exp. from Dabrowski (Ref. 17) for HD from Chuang and Zare (Ref. 2).

ertheless, for each individual isotope, the J dependence of $E''_{v,J}$ is regular and so a least squares fit to a polynomial $W_v(J)$ represents quite well the computed second order energies:

$$E''_{v,J} \approx W_v(J), \quad (24)$$

$$W_v(J) = \sum_{k=0}^3 a_k(v) [J(J+1)/100]^k. \quad (25)$$

The coefficients $a_k(v)$ are given in Tables V–X. For some vibrational levels not all rotational levels are bound. This is indicated in the tables. Also we have included the maximum error, $\Delta\epsilon$, of the fit

$$\Delta\epsilon_v = \max_J |W_v(J) - E''_{v,J}|. \quad (26)$$

It is seen—that except in the case of the highest levels of H₂ and HT—the fit reproduces the computed values almost perfectly.

TABLE XIII. H₂ lines. Comparison with experiment.

J	S_0			O_1		Q_1		
	Theory	Δ^a	Δ^b	Theory	Δ^a	Theory	Δ^a	Δ^c
0	354.373	0.008	0.000			4161.167	−0.033	
1	587.032	−0.055	0.000			4155.255	−0.026	0.006
2	814.424	−0.032	−0.001	3806.794	−0.065	4143.466	−0.027	0.005
3	1034.671	−0.027	0.001	3568.223	−0.016	4125.873	−0.030	0.005
4	1246.099	0.017	0.001	3329.042	−0.102	4102.583	−0.009	0.005
5	1447.281	0.034	0.002	3091.203	0.062	4073.733	0.035	−0.006
6	1637.046			2856.483		4039.493	0.042	
J	S_1			Q_2				
	Theory	Δ^a	Δ^c					
0	4497.839	−0.009	0.005	8087.004				
1	4712.905	−0.033	0.005	8075.309				
2	4917.007	−0.025	0.004	8051.989				
3	5108.404	−0.011	0.005	8017.184				
4	5285.592	−0.040		7971.101				
5	5447.337	−0.700		7914.009				
6	5592.686			7846.232				

^aTheory—experiment. Exp. from Veirs and Rosenblatt (Ref. 15).

^bExp. from Jennings and Brault (Ref. 12).

^cExp. from Bragg *et al.* (Ref. 18).

TABLE XIV. D₂ lines. Comparison with experiment.

<i>J</i>	<i>S</i> ₀			<i>O</i> ₁		
	Theory	Δ ^a	Δ ^b	Theory	Δ ^a	Δ ^b
0	179.067	−0.041	0.000			
1	297.534	0.024	0.000			
2	414.648	0.038	0.000	2814.550	−0.020	0.005
3	529.900	0.090	0.000	2693.974	−0.136	0.002
4	642.807	0.097	0.001	2572.645	0.145	0.002
5	752.920	0.010	0.001	2451.089	0.039	
6	859.832	0.072	0.000	2329.808		
7	963.180	0.020		2209.274	0.044	
8	1062.645	0.075		2089.927		

<i>J</i>	<i>Q</i> ₁			<i>S</i> ₁		
	Theory	Δ ^a	Δ ^c	Theory	Δ ^a	Δ ^c
0	2993.617	0.017		3166.361		0.001
1	2991.507	0.007	0.003	3278.523		0.001
2	2987.294	0.094	−0.002	3387.263	0.043	0.002
3	2980.990	−0.010	0.002	3492.094	0.064	0.003
4	2972.615	0.115	0.002	3592.566		
5	2962.194	−0.006		3688.268	−0.092	
6	2949.759	0.059		3778.835		
7	2935.348	0.148		3863.952	0.132	
8	2919.003	0.203		3943.351		
9	2900.772	0.172				

^aTheory—experiment. Exp. from Veirs and Rosenblatt (Ref. 15).
^bExp. from Jennings *et al.* (Ref. 13).
^cExp. from McKellar and Oka (Ref. 14).

To get the final energies we have first computed the adiabatic, relativistic energy levels using the internuclear potential of Ref. 1 and then corrected them for the directly computed nonadiabatic corrections, $E''_{v,J}$. Finally, to take into account the new Born–Oppenheimer energies given in Table II we have treated the correction Δ_{BO} as a perturbation, i.e., $\Delta_{\text{BO}}(R)$ was interpolated and the correction, $\Delta E^{\text{BO}}_{v,J}$, computed for each level as an expectation value of Δ_{BO} . Finally, the dissociation energies for all bound $J \leq 10$ vibrational levels of the six isotopic molecules were computed relative to the theoretical atomic energies of the dissociation products. These are given in Ref. 11 and when corrected for the recent value of the Rydberg constant they are: -109678.7717 , -109708.6145 and $-109718.5439 \text{ cm}^{-1}$ for the H, D and T atom, respectively. In Table XI we list the $v=0$, $J=0$ results.

TABLE XV. *S* and *Q* lines in HT.

	Theory	Δ ^a
<i>S</i> ₀ (0)	237.871	0.005
<i>S</i> ₀ (1)	394.840	0.040
<i>S</i> ₀ (2)	549.427	0.160
<i>Q</i> ₁ (0)	3434.814	0.008
<i>Q</i> ₁ (1)	3431.576	0.008
<i>Q</i> ₁ (2)	3425.114	0.011
<i>Q</i> ₁ (3)	3415.454	0.016
<i>Q</i> ₁ (4)	3402.635	0.036

^aTheory—Experiment. Exp. from Chuang and Zare (Ref. 2).

The full set of the dissociation energies can be obtained either by electronic mail from the author or directly through anonymous ftp. (Ftp to ftp.phys.uni.torun.pl. The file name is /pub/publications/ifiz/luwo/x_state.95.)

TABLE XVI. HD and HT *P_v*(*J*) and *R_v*(*J*) lines.

	HD		HT	
	Theory	Δ ^a	Theory	Δ ^a
<i>P</i> ₁ (3)	3355.371	0.010		
<i>P</i> ₁ (2)	3450.463	0.000	3273.158	0.018
<i>P</i> ₁ (1)	3542.933	0.001	3355.361	0.006
<i>R</i> ₁ (0)	3717.533	0.001	3511.029	0.009
<i>R</i> ₁ (1)	3798.452	−0.003	3583.533	0.003
<i>R</i> ₁ (2)	3874.354	−0.003	3651.875	0.005
<i>R</i> ₁ (3)	3944.720	0.000	3715.640	0.010
<i>R</i> ₁ (4)	4009.088	0.000	3774.452	0.002
<i>P</i> ₄ (2)	13284.010	0.017		
<i>P</i> ₄ (1)	13387.663	0.017	12722.511	−0.004
<i>R</i> ₄ (0)	13551.079	0.014	12868.781	−0.005
<i>R</i> ₄ (1)	13609.678	0.014	12922.526	−0.008
<i>R</i> ₄ (2)	13652.220	0.005	12962.821	−0.004
<i>R</i> ₄ (3)	13678.328	0.006	12989.356	−0.013
<i>R</i> ₄ (4)			13001.896	−0.021
<i>P</i> ₅ (2)	16219.482	0.009	15445.127	0.009
<i>P</i> ₅ (1)	16326.807	0.016	15539.809	0.013
<i>R</i> ₅ (0)	16486.551	0.014	15682.999	0.015
<i>R</i> ₅ (1)	16537.820	0.004	15730.594	0.005
<i>R</i> ₅ (2)	16569.402	−0.002	15761.691	0.000
<i>R</i> ₅ (3)	16580.961	−0.047	15776.012	0.003

^aTheory—experiment. Exp. from Chuang and Zare (Ref. 2).

TABLE XVII. Ionization potentials for H₂, HD and D₂ in cm⁻¹.

	H ₂	HD	D ₂
This work	124417.491	124568.489	124745.395
Experiment ^{a,c}	124417.488 ± 0.017		124745.362 ± 0.024
Exp. - Theory	-0.003 ± 0.017		-0.033 ± 0.024
Experiment ^b	124417.507 ± 0.012	124568.481 ± 0.012	
Exp. - Theory	0.016 ± 0.012	-0.008 ± 0.012	

^aReference 19.^bReference 20.^cRevised values (Ref. 21).

IV. COMPARISON WITH EXPERIMENT

To compare the present results with experiment we use the same experimental data as in Ref. 1 and we quote in Tables XII–XVI the theoretical results and the remaining discrepancies $\Delta = \text{theory} - \text{experiment}$. In general, the agreement of the present results with experiment is quite satisfactory and in the case of some experiments, viz. Refs. 12–14 — excellent. There are discrepancies, however, that are difficult to explain in terms of theoretical inaccuracies. For instance, in view of the overall fair agreement with the results of Veirs and Rosenblatt¹⁵ the large error in the $S_1(5)$ line of H₂ is quite unexpected. Also it is very surprising that the computed $S_0(2)$ line frequency of HT differs so much from the experimental result because for the $S_0(J)$ transitions the theory is expected to be more reliable than otherwise. Thus it would seem that some of the experimental results have errors markedly larger than the average.

The present dissociation energies of H₂, HD and D₂ differ from those of Ref. 1 by amounts smaller than the experimental accuracy and these differences do not influence the agreement with experiment. Therefore, we list in Table XVII the ionization potentials only because the experimental uncertainties are much smaller in this case.

The accuracy of the theoretical dissociation energies and ionization potentials is about the same for all isotopic molecules although the uncertainty in the nonadiabatic corrections decreases with increasing mass. As was already mentioned in the preceding sections both the Born–Oppenheimer potential and the nonadiabatic corrections converged probably to about 0.001 cm⁻¹ and thus full convergence would shift down all energy levels, independently of v, J , and thus increase the theoretical results in Table XVII by this order of magnitude. However, there is one other source of uncertainty, viz. the radiative corrections to the internuclear potential, and the sign of this error is not known. The radiative corrections were computed in Ref. 1 in an approximate way which is believed to reproduce correctly the R dependence of the corrections but may introduce errors of some thousandths of a wave number or more in the total energies. So, similarly as the convergence errors discussed above, the radiative corrections introduce a constant error that affects the ionization potentials but not the transition frequencies. We believe therefore that the differences of the energies given in this paper are accurate to about 0.001 cm⁻¹ but the error in the ionization potentials might be larger. Thus the discrepancies between experiment and theory visualized in Table XVII are still within the combined uncertainties. It should be stressed,

however, that the theoretical error is not due to numerical noise, i.e., the theoretical ionization potentials in Table XVII might be shifted but all three by the same amount. Therefore one should not expect that the theoretical value of the D₂ ionization potential will be decreased and the remaining two remain unchanged.

After the paper had been submitted for publication Chen and Anderson¹⁶ reported results of an extensive Monte Carlo calculation of the nonrelativistic nonadiabatic H₂ ground state energy. Their result, E (Ref. 16) = -1.1640239 ± 0.0000009 hartree, is directly comparable with our nonrelativistic nonadiabatic result. The main uncertainties in the present dissociation energies discussed above are due to radiative effects. Our nonrelativistic energy, $E = -1.164025018$, is free from those uncertainties and represents an upper bound to the exact eigenvalue. Thus it follows that the Monte Carlo result is still too high by at least 0.25 ± 0.2 cm⁻¹ i.e. the actual error is larger than the error bar given in Ref. 16.

ACKNOWLEDGMENTS

I am very much indebted to K. Dressler for many valuable comments and discussions. I am also indebted to W. Kołos and J. Rychlewski for making their results available prior to publication. This work was supported by a Polish KBN Grant No. 2 P03B 021 08 and by a Guest appointment at the Swiss Federal Institute of Technology (ETH Zurich).

¹L. Wolniewicz, J. Chem. Phys. **99**, 1851 (1993).²M.-C. Chuang and R. N. Zare, J. Mol. Spectrosc. **121**, 380 (1987).³L. Wolniewicz, J. Chem. Phys. **78**, 6173 (1983).⁴C. Schwartz and R. J. Le Roy, J. Mol. Spectrosc. **121**, 420 (1987).⁵W. Kołos, J. Chem. Phys. **101**, 1330 (1994).⁶W. Kołos and L. Wolniewicz, J. Chem. Phys. **45**, 509 (1966).⁷L. Wolniewicz, Can. J. Phys. **54**, 672 (1976).⁸J. Rychlewski, W. Cencek, and J. Komasa, Chem. Phys. Lett. **229**, 657 (1994).⁹L. Wolniewicz and K. Dressler, J. Chem. Phys. **96**, 6053 (1992).¹⁰L. Wolniewicz, J. Comput. Phys. **40**, 440 (1981).¹¹G. W. Erickson, J. Phys. Chem. Ref. Data **6**, 831 (1977).¹²D. E. Jennings and J. W. Brault, J. Mol. Spectrosc. **102**, 265 (1983).¹³D.E. Jennings, A. Weber, and J. W. Brault, Appl. Opt. **25**, 284 (1986).¹⁴A. R. W. McKellar and T. Oka, Can. J. Phys. **56**, 1315 (1978).¹⁵D. K. Veirs and G. M. Rosenblatt, J. Mol. Spectrosc. **121**, 401 (1987).¹⁶B. Chen and J. B. Anderson J. Chem. Phys. **102**, 2802 (1995).¹⁷I. Dabrowski, Can. J. Phys. **62**, 1639 (1984).¹⁸S. L. Bragg, J. W. Brault, and W. H. Smith, Astrophys. J. **263**, 999 (1982).¹⁹C. Jungen, I. Dabrowski, G. Herzberg, and M. Vervloet, J. Mol. Spectrosc. **153**, 11 (1992).²⁰J. M. Gilligan and E. E. Eyler, Phys. Rev. **46**, 3676 (1992).²¹C. Jungen (private communication, 1994).