

Relativistic energies of the ground state of the hydrogen molecule

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Relativistic corrections, Born–Oppenheimer energies and adiabatic corrections are computed for $R \leq 12.0$ bohr for the electronic ground state of the hydrogen molecule. The Born–Oppenheimer potential is slightly lower than ever reported. The problem of linear dependencies in the basis set is removed and the same set is used for all internuclear distances which assures continuity of the results. The radiative corrections are evaluated approximately and—for that purpose—the polarizability of the molecule is also computed. Vibrational energies are computed and—corrected for nonadiabatic effects—compared with experiment for several isotopes. It is argued on the basis of the remaining discrepancies that an improvement in the *ab initio* nonadiabatic corrections is necessary.

I. INTRODUCTION

This work was undertaken in order to evaluate the relativistic corrections to the ground state potential energy curve of the hydrogen molecule with an accuracy comparable with that of the Born–Oppenheimer energies and in a wide range of internuclear distances. New results for these corrections are desirable both from the aesthetic and practical points of view. The existing results for the relativistic corrections,¹ used in most comparisons of theoretical and experimental energies of the molecule (see e.g., Refs. 2 and 3), were calculated almost thirty years ago. The wave function employed then was not suitable for larger internuclear distances and the corrections were computed only for internuclear distances $R \leq 3.7$ a.u. and with an accuracy deteriorating with increasing R . Such a situation is certainly very unsatisfactory from the theoretical point of view and there is a demand for new, more reliable results.

The general outline of the computations is given in Sec. III A and more technical details in the appendices.

For the hydrogen molecule the lowest order relativistic corrections to the binding energy¹ are not much larger than the lowest order radiative corrections.⁴ Therefore, for consistency, the latter must also be included in the theoretical energies. They can be estimated fairly accurately^{4,5} on the basis of the relativistic corrections, if some additional information is available. To get this information it is necessary⁵ to compute the adiabatic corrections and also the polarizabilities.

Finally, to compute all the corrections accurately one needs an electronic wave function that is both flexible and continuous with respect to the internuclear distance. In an attempt to find such a function, using the results of Ref. 3, we have constructed an algorithm that is free of discontinuities because the same basis set is used for all internuclear distances. The construction and the results of the Born–Oppenheimer computations are described in the subsequent section.

Atomic units are used throughout unless otherwise stated. When wave numbers are used the conversion factor is 1 hartree = 219 474.631 cm⁻¹.

II. THE BORN–OPPENHEIMER ELECTRONIC ENERGIES AND WAVE FUNCTIONS

The general form of the wave function used in this work is that developed in Ref. 6, 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:

$$\Psi = \sum_i c_i G_i(1,2), \quad (1)$$

where i stands for $\nu_i, r_i, s_i, \bar{r}_i, \bar{s}_i$ and

$$G_i(1,2) = g_i(1,2) + g_i(2,1), \quad (2)$$

$$g_{\nu_i, r_i, s_i, \bar{r}_i, \bar{s}_i}(1,2) = \exp(-\alpha \xi_1 - \bar{\alpha} \xi_2) \rho^{\nu_i} \xi_1^{r_i} \xi_2^{s_i} \xi_1^{\bar{r}_i} \xi_2^{\bar{s}_i} \eta_1^{\nu_i} \eta_2^{\nu_i} \\ \times \{ \exp(\beta \eta_1 + \bar{\beta} \eta_2) + (-1)^{s+\bar{s}} \\ \times \exp(-\beta \eta_1 - \bar{\beta} \eta_2) \}, \quad (3)$$

ξ_j, η_j are the elliptic coordinates of the two electrons, $\rho = 2r_{12}/R$, 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 $\nu_i, r_i, s_i, \bar{r}_i, \bar{s}_i$.

The best energies and wave functions of the ground state published so far are those obtained by Kołos *et al.*³ who used a 249 term expansion of the form Eq. (1), with carefully selected terms, for $0.2 \text{ a.u.} \leq R \leq 4.8 \text{ a.u.}$ and a 72 term expansion for $4.8 \leq R \leq 12.0$. The shorter, 72 term basis contains 30 terms that are not present in the 249 term basis. This results in a slight discontinuity in the vicinity of $R = 4.8$. To avoid this it is only natural to combine the two sets and diagonalize the Hamiltonian for all internuclear distances in the space spanned by the $N = 279$ basis functions. However because of finite computer precision the dimension of the space spanned by the N function is— from the numerical point of view — less than N and therefore the attempt made in Ref. 3 to use the augmented set failed because of numerical instabilities.

The policy adopted in this work is to use the whole space spanned by the 279 functions of Ref. 3, determine at each internuclear distance its dimension, $k(R)$, and then solve the eigenvalue problem in an orthonormal basis. This

goal can be achieved via a singular value decomposition (see, e.g., Ref. 7) of the overlap matrix \mathbf{S} with elements

$$S_{ik} = \langle G_i | G_k \rangle. \quad (4)$$

The decomposition is

$$\mathbf{S} = \mathbf{U} \mathbf{D} \mathbf{U}^T \quad (5)$$

where \mathbf{D} is a diagonal matrix formed by the eigenvalues D_j of \mathbf{S} and \mathbf{U} is an orthogonal matrix whose columns are the eigenvectors of \mathbf{S} . In the following we will assume that the D_j are arranged in a descending order.

If the basis is almost linearly dependent a threshold, ε , must be introduced⁷ and the dimension of the space, k , is defined as the number of eigenvalues, D_j , satisfying $D_j > \varepsilon$. The orthonormal basis is

$$F_s = (1/\sqrt{D_s}) \sum_{i=1}^N G_i U_{is}, \quad s=1, \dots, k \quad (6)$$

with U_{ij} being matrix elements of \mathbf{U} .

Thus for each internuclear distance we perform the singular value decomposition Eq. (5), determine the dimension of the space $k(R)$ and construct a Hamiltonian matrix, \mathbf{H} , in the orthonormal basis Eq. (6). The final eigenvalue problem

$$\mathbf{H} \mathbf{a} = E \mathbf{a} \quad (7)$$

can be solved by any standard library routine to yield the desired eigenvalue and the corresponding eigenfunction

$$\Psi = \sum_s a_s F_s. \quad (8)$$

Eq. (8) can then be transformed to the original basis, Eq. (1), with the aid of Eq. (6). The coefficients c_i are then given by

$$c_i = \sum_{s=1}^k (1/\sqrt{D_s}) U_{is} a_s. \quad (9)$$

The concrete value of the parameter ε depends somewhat on the problem and certainly on the accuracy of the numerical integration of the matrix elements of \mathbf{S} and \mathbf{H} . In this work the integrals were evaluated very accurately by the method described in Ref. 8. Previous experience has shown that too small an ε can result in a spurious eigenvalue of Eq. (7)—below the correct lowest eigenvalue. Therefore in the program a test for the spurious eigenvalue is performed. When a spurious eigenvalue occurs ε is multiplied by 4, the dimension of the problem reduced accordingly, and the Hamiltonian diagonalized again. This process is repeated until the spurious eigenvalue disappears.

For the ground state computations this test was superfluous and all diagonalizations with $\varepsilon = 10^{-12}$ were successful. Test computations performed with $\varepsilon = 10^{-11}$ resulted in energies that were higher by amounts less than 0.001 cm^{-1} .

The exponents $\nu_i, r_i, s_i, \bar{r}_i, \bar{s}_i$ of the 279 different basis functions are given in Ref. 3. These basis functions were used with one exception viz. the parameters $(\nu, r, s, \bar{r}, \bar{s}) = (13111)$ corresponding to the $i=102$ basis function in Ref. 3 were inadvertently replaced by $(\nu, r, s, \bar{r}, \bar{s}) = (03111)$ and this function was used in all computations.

TABLE I. Nonlinear parameters as defined by Eq. (3) optimized for large R .

R	α	$\bar{\alpha}$	β	$\bar{\beta}$
4.8 ^a	3.122	2.962	1.885	-0.121
6.0	3.803	3.456	2.827	-0.955
8.0	4.597	4.293	3.240	-1.949
12.0	5.968	5.971	4.254	-5.590

^aFrom Ref. 3.

The optimized nonlinear parameters for both the 249 and 72 term functions are also listed in Ref. 3 for all relevant internuclear distances. In the present computation we use these parameters for $R \leq 4.8$ a.u. For larger internuclear distances the parameters were reoptimized at $R=6, 8$ and 12 a.u. but not very accurately, because with the full basis set used the optimization had a negligible effect on the energy; the improvement was $0.001 - 0.002 \text{ cm}^{-1}$. In Table 1 the optimized parameters are listed together with the Kołos *et al.*³ values for $R=4.8$. These numbers were used as input for linear interpolation of the parameters for other internuclear distances $R > 4.8$.

The final energies were computed at 670 different internuclear distances in the interval $0.2 \leq R \leq 12.0$ a.u. The complete listing of the results can be found in Ref. 9 and some of them, viz. those for the same internuclear distances as in Ref. 3, are listed in Table II. In column 5 a comparison with Ref. 3 is made and we list the improvement in the binding energy. As expected, the differences are small but systematic and reach the maximum at $R=4.8$, the point of discontinuity of the two functions used in Ref. 3. The irregularities in column 5 are of the order of 0.0001 cm^{-1} which proves high numerical accuracy of both computations.

The dimension of the space spanned by the 279 basis functions, $k(R)$, is also listed in the table. It shows how smoothly the singular value decomposition works. It should be kept in mind, however, that $k(R)$ is not uniquely defined. If a larger threshold, ε were used the resulting dimensions would be less than those given in the table.

When this computation was complete the author became aware of the most recent results obtained by Kołos and Rychlewski¹⁰ with a 155 term basis function for $3.2 \leq R \leq 7.2$ a.u. The present improvement over those results is shown in column 6. The 155 term function used in Ref. 10 contains 66 terms that are not included in our 279 term function. To estimate the accuracy of the present results these terms were added to our basis set yielding a 345 term basis and a few test computations were performed. For $R=1.4$ the energy improvement amounted to 0.0017 cm^{-1} and for $R=4.8$ a.u. to 0.003 cm^{-1} . This shows that at some internuclear distances the present energies are still at least a few thousandths of a wave number above the exact eigenvalues.

The wave function described above was used for the Born-Oppenheimer energy computations only. All corrections to the energy were computed with slightly less accurate functions. Both the relativistic and also the adiabatic corrections require more primitive integrals than the en-

TABLE II. Born–Oppenheimer total, E , and binding, D , energies.

R	E (a.u.)	dE/dR	D (cm $^{-1}$)	Δ_{KSM}	Δ_{KR}	$k(R)^a$
0.20	2.197803500	-24.180197887	-701836.743	0.0018		274
0.30	0.619241793	-10.187637040	-355382.495	0.0011		274
0.40	-0.120230242	-5.305861648	-193087.143	0.0009		276
0.50	-0.526638671	-3.077056097	-103890.803	0.0007		274
0.60	-0.769635353	-1.896166679	-50559.196	0.0009		276
0.80	-1.020056603	-0.783390022	4401.916	0.0011		276
0.90	-1.083643180	-0.507358751	18357.556	0.0009		276
1.00	-1.124539664	-0.322465093	27333.297	0.0009		276
1.10	-1.150057316	-0.195627390	32933.774	0.0009		276
1.20	-1.164935195	-0.107128301	36199.091	0.0009		276
1.30	-1.172347104	-0.044692489	37825.817	0.0009		277
1.35	-1.173963683	-0.020655973	38180.615	0.0011		277
1.40	-1.174475671	-0.000401370	38292.984	0.0007		277
1.45	-1.174057029	0.016657780	38201.102	0.0007		277
1.50	-1.172855038	0.031005965	37937.296	0.0009		277
1.60	-1.168583333	0.053112570	36999.765	0.0007		277
1.70	-1.162458688	0.068410937	35655.561	0.0009		277
1.80	-1.155068699	0.078666877	34033.645	0.0009		277
2.00	-1.138132919	0.088792883	30316.671	0.0013		277
2.20	-1.120132079	0.090118877	26365.944	0.0022		278
2.40	-1.102422568	0.086338578	22479.155	0.0033		278
2.60	-1.085791199	0.079613967	18828.992	0.0050		278
2.80	-1.070683196	0.071281882	15513.168	0.0081		278
3.00	-1.057326233	0.062224970	12581.654	0.0127		278
3.20	-1.045799627	0.053066758	10051.856	0.0184	0.014	278
3.40	-1.036075361	0.044267199	7917.627	0.0270	0.012	278
3.60	-1.028046276	0.036161105	6155.446	0.0364	0.010	278
3.80	-1.021549766	0.028968843	4729.627	0.0481	0.008	278
4.00	-1.016390228	0.022801202	3597.239	0.0608	0.006	278
4.20	-1.012359938	0.017671470	2712.693	0.0724	0.005	278
4.40	-1.009256497	0.013517480	2031.566	0.0856	0.004	278
4.60	-1.006895204	0.010229046	1513.322	0.0996	0.002	278
4.80	-1.005115986	0.007674072	1122.829	0.1126	0.001	278
5.00	-1.003785643	0.005718654	830.853	0.0963	0.002	278
5.20	-1.002796804	0.004239826	613.828	0.0799	0.002	278
5.40	-1.002065047	0.003131734	453.225	0.0658	0.002	278
5.60	-1.001525243	0.002307305	334.752	0.0542	0.003	278
5.80	-1.001127874	0.001697195	247.540	0.0446	0.004	278
6.00	-1.000835702	0.001247477	183.415	0.0367	0.004	277
6.20	-1.000620961	0.000916928	136.285	0.0298	0.005	278
6.40	-1.000463077	0.000674438	101.634	0.0244	0.007	277
6.60	-1.000346878	0.000496757	76.131	0.0198	0.007	277
6.80	-1.000261213	0.000366631	57.330	0.0160	0.008	275
7.00	-1.000197911	0.000271323	43.436	0.0129	0.008	277
7.20	-1.000150992	0.000201473	33.139	0.0105	0.009	275
7.40	-1.000116086	0.000150220	25.478	0.0086		272
7.60	-1.000090001	0.000112546	19.753	0.0068		272
7.80	-1.000070408	0.000084791	15.453	0.0057		271
8.00	-1.000055603	0.000064284	12.203	0.0046		266
8.50	-1.000032170	0.000033217	7.060	0.0029		265
9.00	-1.000019780	0.000018095	4.341	0.0015		253
9.50	-1.000012855	0.000010435	2.821	0.0009		249
10.00	-1.000008754	0.000006370	1.921	0.0002		223
11.00	-1.000004506	0.000002750	0.989	0.0002		216
12.00	-1.000002546	0.000001366	0.559	0.0000		201

^aThe threshold $\epsilon = 10^{-12}$.

ergy computations alone. Therefore to economize some-
how the computations by reducing the number of integrals
the basis set was slightly confined.

The decisive factor that determines the number of in-
tegrals is

$$K_{\text{max}} = \max_j (v_j + \max(r_j, s_j, \bar{r}_j, \bar{s}_j)). \quad (10)$$

In the 279 term basis there are 17 terms giving $K_{\text{max}} = 6$. These terms were omitted which resulted in a 262 term basis. The energies obtained in this basis differ by thousandths of a wave number from those in Table II. Therefore one can claim that the wave function in the 262 term basis is almost as accurate as that in the 279 term basis.

III. CORRECTIONS TO THE BORN-OPPENHEIMER ENERGY

All corrections that we will briefly describe in this section were computed in the 262 term basis described at the end of the preceding section. The relativistic, adiabatic and radiative corrections are related in this work in two ways. First, the integrals necessary for the relativistic corrections allow also the construction of the relevant matrices in the adiabatic correction computations and in the energy computations in the extended, 279 term basis. Next, the approximate radiative corrections can be computed by a method originally given by Garcia⁴ if one uses as input, among others, some terms encountered either in the relativistic or in the adiabatic corrections. This computation can be made more reliable⁵ if one uses in addition the full information that one gets while computing the polarizability of the system. Therefore the polarizability was recomputed in this work.

A. Lowest order relativistic corrections to the electronic energy

The relativistic theory of two electrons in external fields is presented in great detail in Ref. 11, where it is shown that if Ψ and E are the solutions of the nonrelativistic Schrödinger equation

$$(-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + V - E)\Psi = 0 \quad (11)$$

then, for a singlet state and Ψ real, the relativistic corrections can be computed from the formulas

$$E_{\text{rel}} = \epsilon_1 + \epsilon_2 + \epsilon_4 + \epsilon_5 \quad (12)$$

with

$$\epsilon_1 = \alpha^2 \left\{ \int (\Delta_1 \Psi) \Delta_2 \Psi \, d\tau - \frac{1}{2} E^2 + E \int \Psi V \Psi \, d\tau - \frac{1}{2} \int \Psi V^2 \Psi \, d\tau \right\}, \quad (13)$$

$$\epsilon_2 = \frac{1}{2} \alpha^2 \int \Psi r_{12}^{-1} [\nabla_1 \nabla_2 + r_{12}^{-2} \mathbf{r}_{12} (\mathbf{r}_{12} \nabla_1) \nabla_2] \Psi \, d\tau, \quad (14)$$

$$\epsilon_4 = \frac{1}{8} \alpha^2 \int \Psi [\Delta_1 V + \Delta_2 V] \Psi \, d\tau, \quad (15)$$

$$\epsilon_5 = 2\pi\alpha^2 \int \Psi \delta^{(3)}(\mathbf{r}_{12}) \Psi \, d\tau. \quad (16)$$

Above α is the fine structure constant and the indices at the various corrections ϵ_i correspond to the various parts of the Hamiltonian in Ref. 11. For the hydrogen molecule Eq. (15) reads

$$\epsilon_4 = \pi\alpha^2 \int \Psi [2\delta^{(3)}(\mathbf{r}_{1a}) - \delta^{(3)}(\mathbf{r}_{12})] \Psi \, d\tau. \quad (17)$$

The difficult part is the evaluation of ϵ_1 and ϵ_2 . It is seen that the integrand in Eq. (14) behaves like r_{12}^{-1} when $r_{12} \rightarrow 0$ and so, because of the volume element, the region around $r_{12} = 0$ gives no contribution to the integral. Still, with the function defined by Eqs. (1)–(3), Eq. (14) leads to primitive integrals with second and third inverse powers of r_{12} . The first and last terms of Eq. (13) produce also second inverse powers of the interelectronic distance and in these cases the integrand has a r_{12}^{-2} pole. Following Ref. 1 we transform such integrals by using the relation

$$\int r_{12}^{-2} f \, d\tau = \int r_{12}^{-2} \mathbf{r}_{12} \nabla_1 f \, d\tau, \quad \mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1, \quad (18)$$

to a form with an r_{12}^{-1} singularity.

In addition to these integrals the last term in Eq. (13) leads to integrals with r_{1a}^{-2} in the integrand. So in order to evaluate the relativistic corrections we need, beside the integrals needed for the nonrelativistic problem, three new types of integrals. When expressed in elliptic coordinates these integrals have the form

$$I^{-\mu} = \int \exp(-\alpha_1 \xi_1 - \alpha_2 \xi_2 + \beta_1 \eta_1 + \beta_2 \eta_2) \times \rho^{-\mu} W^{\mu-1} d\xi_1 d\xi_2 d\eta_1 d\eta_2 d\varphi_1 d\varphi_2, \quad (19)$$

with $\mu = 2, 3$ and W^μ being polynomials in ξ_i, η_i satisfying

$$\lim_{r_{12} \rightarrow 0} W^\mu r_{12}^{-\mu} < \infty, \quad (20)$$

and

$$L^\mu = \int \exp(-\alpha_1 \xi_1 - \alpha_2 \xi_2 + \beta_1 \eta_1 + \beta_2 \eta_2) \times \frac{\rho^\mu \xi_1^r \eta_1^s \xi_2^{\bar{r}} \eta_2^{\bar{s}}}{\xi_1^2 - \eta_1^2} d\xi_1 d\xi_2 d\eta_1 d\eta_2 d\varphi_1 d\varphi_2, \quad \mu \geq -1. \quad (21)$$

To reduce the dimension of the integrals the generalized Neumann expansion¹² is used

$$\rho^{-2p} = \sum_{l=0}^{\infty} \sum_{m=0}^l d_{lm}(p) [(\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2) \times (1 - \eta_2^2)]^{(m/2)} D_{l-m}^{p+m}(\xi_+) C_{l-m}^{p+m}(\xi_-) C_{l-m}^{p+m}(\eta_1) \times C_{l-m}^{p+m}(\eta_2) C_m^{p-(1/2)}(\cos\varphi), \quad p > 0, \quad (22)$$

where C_l^v are Gegenbauer polynomials (see, e.g., Ref. 13), $\varphi = \varphi_1 - \varphi_2$, $\xi_+ = \max(\xi_1, \xi_2)$, $\xi_- = \min(\xi_1, \xi_2)$,

$$D_n^v(\xi) = C_n^v(\xi) \int_{\infty}^{\xi} (x^2 - 1)^{-v-(1/2)} [C_n^v(x)]^{-2} dx, \quad (23)$$

and

$$d_{lm}(p) = -2^{2m+1} \frac{\Gamma(2p-1) [\Gamma(p+m)]^2 (l-m)! (l+p) (2p+2m-1)}{[\Gamma(p)]^2 \Gamma(2p+l+m)}. \quad (24)$$

Originally this expansion was derived for $p \neq 1/2$ but it is shown in Appendix A that for $p \rightarrow 1/2$ Eq. (22) goes over into the well known (see, e.g., Ref. 14) Neumann expansion and so it can be used for all $p > 0$.

The integrals Eqs. (19) and (21) differ—from the computational point of view—essentially from their counterparts in Ref. 1 by the exponential η_i dependence of the integrands. The evaluation of the I integrals, detailed in Appendix B, is more involved but similar to what was done in Ref. 1. For the L integrals, however, an entirely new algorithm must be used to yield accurate results. It is described in Appendix C.

When the expansion Eq. (22) is used in Eq. (19) one gets a series

$$I = \sum_l I_l. \quad (25)$$

In some cases — depending on the form of W^μ — Eq. (25) is an alternating series and therefore, following Ref. 1, we write

$$s_L = \sum_{l=0}^L I_l, \quad (26)$$

$$I = \lim_{L \rightarrow \infty} s_L \approx \frac{1}{8}(s_{L_{\max}} + 3s_{L_{\max}+1} + 3s_{L_{\max}+2} + s_{L_{\max}+3}) \quad (27)$$

with L_{\max} fixed. In this work we found that $L_{\max}=65$ assures sufficient accuracy. It should be pointed out, however, that the individual integrals Eq. (19) converge slowly with l and for some of them a definitely longer expansion would be required. Fortunately the expectation values Eqs. (13) and (14) are much less sensitive.

For several internuclear distances the corrections were computed additionally with $L_{\max}=85$ and it was found that the final results were affected by less than 0.001 cm^{-1} . However for large R ϵ_2 is sensitive to the expansion length but then it is so small that it has no effect on the final result.

The computed corrections are listed in Table III. A comparison with earlier work¹ is made in column 3 where the differences, the present minus old results, are listed. The differences are indeed very small which shows that the corrections can be computed fairly accurately already with a not very long expansion because in Ref. 1 only 54 terms and one nonlinear parameter were used. This observation might be useful when corrections for other states will be computed.

B. Adiabatic corrections

All relevant formulas for the computation of adiabatic corrections for the hydrogen molecule are given in Ref. 1 and there is no need to repeat them here in any detail. The corrections are

$$E'_1 = -\frac{1}{2\mu} \langle \Delta_R \rangle, \quad E'_2 = -\frac{1}{4\mu} \langle \Delta_1 + \nabla_1 \nabla_2 \rangle, \quad (28)$$

where μ is the reduced mass of the nuclei and the brackets denote expectation values computed with the electronic wave function.

The evaluation of E'_1 requires the first derivatives of the electronic function with respect to the internuclear distance R . As compared with the formulas in Ref. 1 these derivatives are slightly affected by the fact that in consequence of the singular value decomposition the coefficients c_i in Eq. (1) are not independent. It is easiest to compute the derivatives in the orthonormal basis and then transform to the original basis. While doing so we will assume, as in most earlier work, that for the purpose of computing the derivatives — at a given R — one can treat the nonlinear parameters as constants in the neighborhood of R . This is a reasonable assumption because infinitesimal changes in the nonlinear parameters can be absorbed by infinitesimal changes of the linear parameters. This was demonstrated already in Ref. 1 for a 54 term function and when the number of terms increases the absorption becomes even more complete.

With the above assumption the basis, when expressed in elliptic coordinates, is R independent and the only R dependence of the overlap matrix comes from the volume element. The \mathbf{S} and \mathbf{H} matrices can now be written in the neighborhood of R :

$$\mathbf{S} = \left(\frac{R}{2}\right)^6 \mathbf{S}_0, \quad (29)$$

$$\mathbf{H} = \left(\frac{R}{2}\right)^6 \mathbf{H}_0 = \left(\frac{R}{2}\right)^6 \left(\frac{1}{R^2} \mathbf{T}_0 + \frac{1}{R} \mathbf{V}_0\right) \quad (30)$$

with \mathbf{S}_0 , \mathbf{T}_0 , \mathbf{V}_0 —constant matrices. If we omit the $(R/2)^6$ factors in all matrices, the transformation to the orthonormal basis becomes R independent and the eigenvalue problem Eq. (7) now reads

$$(\mathbf{H}_0 - E)\mathbf{a} = 0, \quad (31)$$

$$\mathbf{a} \cdot \mathbf{a} = \left(\frac{2}{R}\right)^6. \quad (32)$$

By differentiating and using Eq. (30) we get the equations for the derivatives:

$$(\mathbf{H}_0 - E) \frac{d\mathbf{a}}{dR} = \left(\frac{2\mathbf{H}_0 - \mathbf{V}_0}{R} + \frac{dE}{dR}\right) \mathbf{a} \quad (33)$$

and

$$\mathbf{a} \cdot \frac{d\mathbf{a}}{dR} = -\frac{3}{R} \left(\frac{2}{R}\right)^6. \quad (34)$$

These equations yield the derivatives in the orthonormal basis. Those in the original basis, Eqs. (1)–(3), are given via the transformation Eq. (9):

$$\frac{dc_i}{dR} = \sum_{s=1}^k (1/\sqrt{D_s}) U_{is} \frac{da_i}{dR}. \quad (35)$$

With the coefficients c_i and their derivatives given the adiabatic corrections can be computed in the original basis exactly as in Ref. 1. The results for the H_2 molecule are

TABLE III. Lowest order relativistic corrections to the total energy, E_{rel} , and to the binding energy, ΔD_{rel} .^a

R	E_{rel}	Δ_{old}	ΔD_{rel}	ϵ_1	ϵ_2	ϵ_4	ϵ_5
0.20	-15.1951		12.2731	-8.639009	-0.128035	6.891930	0.574957
0.30	-11.7233		8.8013	-6.903827	-0.118897	5.517251	0.502379
0.40	-9.1548		6.2328	-5.616234	-0.109180	4.508715	0.433379
0.50	-7.3012		4.3792	-4.656698	-0.100415	3.760294	0.372096
0.60	-5.9559	-0.043	3.0339	-3.932219	-0.091868	3.195053	0.319420
0.80	-4.2463	-0.021	1.3243	-2.944129	-0.077003	2.420760	0.237045
0.90	-3.7027		0.7807	-2.602481	-0.070758	2.151164	0.205255
1.00	-3.2915	-0.014	0.3695	-2.329146	-0.065149	1.934270	0.178395
1.10	-2.9772		0.0552	-2.107976	-0.060099	1.757713	0.155617
1.20	-2.7356	-0.010	-0.1864	-1.927258	-0.055542	1.612498	0.136230
1.30	-2.5490	-0.008	-0.3730	-1.778361	-0.051413	1.492029	0.119645
1.35	-2.4721	-0.007	-0.4499	-1.713768	-0.049496	1.439484	0.112254
1.40	-2.4046	-0.007	-0.5174	-1.654850	-0.047666	1.391376	0.105394
1.45	-2.3452	-0.006	-0.5768	-1.601041	-0.045918	1.347272	0.099019
1.50	-2.2932	-0.005	-0.6288	-1.551848	-0.044247	1.306791	0.093087
1.60	-2.2080	-0.005	-0.7140	-1.465621	-0.041116	1.235406	0.082410
1.70	-2.1438		-0.7782	-1.393279	-0.038240	1.174980	0.073104
1.80	-2.0969	-0.004	-0.8251	-1.332552	-0.035581	1.123761	0.064954
2.00	-2.0436	-0.003	-0.8784	-1.239131	-0.030821	1.043636	0.051459
2.20	-2.0317	-0.003	-0.8903	-1.174835	-0.026669	0.986810	0.040856
2.40	-2.0507	-0.003	-0.8713	-1.132669	-0.022989	0.947786	0.032409
2.60	-2.0932		-0.8288	-1.107720	-0.019684	0.922695	0.025604
2.80	-2.1536		-0.7684	-1.096302	-0.016685	0.908630	0.020085
3.00	-2.2270		-0.6950	-1.095399	-0.013980	0.903224	0.015600
3.20	-2.3083		-0.6137	-1.102360	-0.011533	0.904418	0.011965
3.40	-2.3925		-0.5295	-1.114762	-0.009338	0.910336	0.009049
3.60	-2.4753	0.027	-0.4467	-1.130395	-0.007417	0.919273	0.006740
3.80	-2.5528		-0.3692	-1.147363	-0.005769	0.929755	0.004946
4.00	-2.6225		-0.2995	-1.164166	-0.004395	0.940590	0.003579
4.20	-2.6829		-0.2391	-1.179765	-0.003272	0.950923	0.002557
4.40	-2.7335		-0.1885	-1.193556	-0.002372	0.960233	0.001807
4.60	-2.7749		-0.1471	-1.205300	-0.001673	0.968278	0.001266
4.80	-2.8080		-0.1140	-1.215012	-0.001139	0.975009	0.000881
5.00	-2.8340		-0.0880	-1.222862	-0.000738	0.980498	0.000610
5.20	-2.8543		-0.0677	-1.229099	-0.000445	0.984898	0.000421
5.40	-2.8699		-0.0521	-1.233987	-0.000234	0.988373	0.000289
5.60	-2.8818		-0.0402	-1.237778	-0.000088	0.991084	0.000199
5.80	-2.8910		-0.0310	-1.240695	0.000015	0.993182	0.000136
6.00	-2.8979		-0.0241	-1.242925	0.000082	0.994792	0.000093
6.20	-2.9032		-0.0188	-1.244623	0.000125	0.996026	0.000064
6.40	-2.9072		-0.0148	-1.245912	0.000151	0.996967	0.000044
6.60	-2.9102		-0.0118	-1.246888	0.000166	0.997680	0.000030
6.80	-2.9126		-0.0094	-1.247626	0.000171	0.998224	0.000020
7.00	-2.9143		-0.0077	-1.248184	0.000171	0.998636	0.000014
7.20	-2.9157		-0.0063	-1.248605	0.000167	0.998948	0.000010
7.40	-2.9168		-0.0052	-1.248924	0.000161	0.999186	0.000007
7.60	-2.9176		-0.0044	-1.249165	0.000155	0.999365	0.000004
7.80	-2.9182		-0.0038	-1.249348	0.000148	0.999502	0.000003
8.00	-2.9187		-0.0033	-1.249488	0.000142	0.999606	0.000002
8.50	-2.9196		-0.0024	-1.249710	0.000125	0.999773	0.000001
9.00	-2.9198		-0.0022	-1.249830	0.000129	0.999874	0.000000
9.50	-2.9198		-0.0022	-1.249898	0.000130	0.999934	0.000000
10.00	-2.9201		-0.0019	-1.249928	0.000131	0.999943	0.000000
11.00	-2.9201		-0.0019	-1.249966	0.000137	0.999977	0.000000
12.00	-2.9208		-0.0012	-1.249981	0.000081	0.999988	0.000000
∞	-2.9218			-1.25	0.0	1.0	0.0

^a ϵ_i in $\alpha^2 \times$ (a.u.) = 11.687 15 cm^{-1} . E_{rel} and ΔD_{rel} in cm^{-1} .

given in Table IV. We have also included in the table in column 5 the differences of the energies obtained in the 262 and 279 term bases to support the statement that the shorter basis is almost as accurate as the augmented one. In column 6 we give the difference of the present total correction $\langle H' \rangle$ and the corresponding number, obtained with a less accurate function by Kołos and Rychlewski.¹⁰

In general the differences are smooth and very small. The discontinuities at $R=3.0$ and $R=7.2$ are certainly due to the fact that in Ref. 10 three different wavefunctions were used for small, intermediate and large internuclear distances. The large discrepancy at $R=5.6$ must be due to some typographical error because the inspection of second differences of the total correction in Ref. 10 shows irregu-

TABLE IV. Adiabatic corrections in cm^{-1} for H_2 .^a

R	E_2'	E_1'	$\langle H' \rangle$	$E - E_{279}$	Δ_{KR}	ΔD	S^{-1}
0.20	166.871	18.183	185.054	0.014		-65.524	1.594555
0.30	154.574	25.998	180.572	0.009		-61.042	1.679684
0.40	142.653	31.029	173.682	0.005	-0.022	-54.152	1.778945
0.50	131.748	34.097	165.845	0.004		-46.315	1.887913
0.60	122.018	35.906	157.923	0.003	-0.005	-38.393	2.003853
0.80	105.878	37.498	143.376	0.002	-0.002	-23.847	2.249981
0.90	99.248	37.790	137.037	0.002		-17.507	2.377907
1.00	93.420	37.937	131.357	0.002	-0.001	-11.827	2.507944
1.10	88.291	38.021	126.312	0.003	-0.001	-6.783	2.639395
1.20	83.770	38.095	121.865	0.003	-0.001	-2.336	2.771619
1.30	79.779	38.193	117.973	0.003	-0.001	1.557	2.904004
1.35	77.962	38.259	116.221	0.003	-0.002	3.309	2.970069
1.40	76.253	38.338	114.591	0.003	-0.001	4.938	3.035948
1.45	74.647	38.434	113.080	0.003	-0.002	6.450	3.101564
1.50	73.136	38.546	111.681	0.003	-0.002	7.848	3.166839
1.60	70.379	38.827	109.206	0.002	-0.001	10.323	3.296045
1.70	67.945	39.189	107.134	0.002		12.396	3.422917
1.80	65.799	39.635	105.434	0.002	-0.001	14.096	3.546775
2.00	62.260	40.795	103.055	0.002	-0.001	16.475	3.782599
2.20	59.578	42.313	101.891	0.002	-0.001	17.639	3.997627
2.40	57.616	44.167	101.782	0.002	-0.001	17.747	4.185881
2.60	56.263	46.303	102.566	0.001	-0.001	16.964	4.341801
2.80	55.428	48.627	104.055	0.001	-0.001	15.475	4.460983
3.00	55.023	51.007	106.031	0.002	0.000	13.499	4.541041
3.20	54.967	53.286	108.253	0.002	-0.003	11.276	4.582355
3.40	55.175	55.312	110.487	0.002	-0.003	9.043	4.588380
3.60	55.562	56.975	112.537	0.002	-0.003	6.993	4.565305
3.80	56.054	58.227	114.280	0.002	-0.003	5.249	4.521053
4.00	56.586	59.086	115.672	0.001	-0.002	3.858	4.463919
4.20	57.109	59.619	116.728	0.001	-0.002	2.802	4.401333
4.40	57.590	59.911	117.502	0.001	-0.002	2.028	4.339075
4.60	58.015	60.042	118.057	0.000	-0.002	1.473	4.281023
4.80	58.375	60.078	118.452	0.001	-0.003	1.077	4.229339
5.00	58.672	60.062	118.734	0.000	-0.002	0.795	4.184872
5.20	58.913	60.023	118.937	0.000	-0.001	0.593	4.147580
5.40	59.106	59.978	119.084	0.000	-0.001	0.446	4.116908
5.60	59.257	59.935	119.192	0.000	0.006	0.338	4.092055
5.80	59.375	59.897	119.272	0.000	0.000	0.258	4.072144
6.00	59.465	59.866	119.331	0.000	-0.001	0.198	4.056337
6.20	59.536	59.840	119.376	0.000	0.000	0.153	4.043876
6.40	59.590	59.821	119.410	0.000	0.000	0.119	4.034105
6.60	59.631	59.805	119.436	0.000	0.000	0.093	4.026480
6.80	59.662	59.794	119.456	0.000	0.001	0.074	4.020548
7.00	59.686	59.785	119.471	0.000	0.002	0.058	4.015947
7.20	59.704	59.779	119.483	0.000	0.002	0.047	4.012384
7.40	59.718	59.774	119.492	0.000	-0.002	0.038	4.009629
7.60	59.728	59.771	119.499	0.000	-0.002	0.031	4.007503
7.80	59.736	59.768	119.505	0.000	-0.002	0.025	4.005861
8.00	59.742	59.766	119.509	0.000	-0.001	0.021	4.004593
8.50	59.752	59.764	119.516	0.000	-0.002	0.013	4.002543
9.00	59.757	59.763	119.521	0.000	-0.001	0.009	4.001456
9.50	59.761	59.763	119.524	0.000	-0.002	0.006	4.000869
10.00	59.762	59.763	119.525	0.000	-0.003	0.004	4.000544
11.00	59.763	59.764	119.527	0.000		0.002	4.000245
12.00	59.764	59.764	119.528	0.000	-0.002	0.001	4.000129
∞	59.766	59.766	119.532				4.0

^a S_{-1} in a.u.

larities in the vicinity of $R=5.6$. In the last column of the table the expectation values $S_{-1} = 4/3 \langle x_1 x_2 + z_1 z_2 + r_1^2 \rangle$ are included. These will be used to estimate the radiative corrections.

C. Polarizability

All the relevant formulas concerning the evaluation of the components of the polarizability tensor for the hydro-

gen molecule are given in detail in Refs. 15 and 16. Here we give only the definitions to facilitate the discussion.

If the z axis of the coordinate system coincides with the internuclear axis, $\mu = r_1 + r_2$ is the electronic electric dipole moment operator and H, Ψ and E the clamped nuclei Hamiltonian and solution of the unperturbed Schrödinger equation then the components of the polarizability tensor are given by the equations

TABLE V. Polarizabilities for H₂ in a.u.

R	α_{\perp}	Δ_{Rych}	α_{\parallel}	Δ_{Rych}	S_{-2}	S_{-3}
0.40	1.8517		1.9366		1.8800	2.18038
0.60	2.2823	-0.0023	2.4922	-0.0013	2.3523	3.01615
0.80	2.7823	-0.0045	3.2078	-0.0032	2.9241	4.12321
1.00	3.3405	-0.0018	4.0919	-0.0009	3.5910	5.54390
1.20	3.9430	-0.0035	5.1510	-0.0007	4.3457	7.30593
1.40	4.5764	-0.0022	6.3860	-0.0013	5.1796	9.43114
1.60	5.2260	-0.0031	7.7876	-0.0001	6.0799	11.92720
1.80	5.8760	-0.0034	9.3311	-0.0012	7.0277	14.77537
2.00	6.5095	-0.0038	10.9730	-0.0001	7.9973	17.92420
2.20	7.1088	-0.0040	12.6478	0.0022	8.9551	21.27252
2.40	7.6566	-0.0039	14.2697	0.0035	9.8610	24.67266
2.60	8.1371	-0.0044	15.7374	0.0027	10.6705	27.92882
2.80	8.5377	-0.0053	16.9460	0.0040	11.3405	30.81636
3.00	8.8509	-0.0072	17.8048	0.0052	11.8355	33.11943
3.20	9.0763	-0.0084	18.2563	0.0069	12.1363	34.67830
3.40	9.2194	-0.0094	18.2909	0.0075	12.2432	35.41919
3.60	9.2918	-0.0101	17.9490	0.0085	12.1775	35.37695
3.80	9.3092	-0.0128	17.3124	0.0056	11.9769	34.68572
4.00	9.2878	-0.0159	16.4829	0.0059	11.6862	33.53179
4.50	9.1599	-0.0233	14.1826	-0.0027	10.8341	29.87322
5.00	9.0368	-0.0222	12.2712	-0.0043	10.1149	26.65049
6.00	8.9224	-0.0048	10.2021	0.0046	9.3490	23.13932
7.00	8.9163	0.0038	9.4749	0.0055	9.1025	21.99492
8.00	8.9319	0.0031	9.2262	0.0049	9.0300	21.64863
9.00	8.9485	0.0015	9.1312	0.0012	9.0094	21.54706
10.00	8.9612	0.0001	9.0877	0.0006	9.0034	21.51671
11.00	8.9703		9.0636		9.0014	21.50704
12.00	8.9769		9.0482		9.0007	21.50353
∞	9.0		9.0		9.0	21.5

$$\alpha_i = -\frac{1}{2} \int \Psi' \mu_i \Psi d\tau \quad (36)$$

for $i = x, y, z$ and Ψ' satisfying

$$(H - E)\Psi' = \mu_i \Psi. \quad (37)$$

In this work Ψ was the solution obtained in the 262 term basis as discussed at the end of section II and — as in Ref. 14—the solution of Eq. (36) was sought in the form of an expansion similar to Eq. (1) but of appropriate symmetry: Σ_u and Π_u for the parallel and perpendicular components, respectively. The computation was thus a straightforward extension of Ref. 15. The nonlinear parameters in the expansions for Ψ' were identical with those in Ψ and the basis set was selected at the equilibrium separation $R=1.4$ a.u. To get a reasonably accurate approximation for Ψ' terms were added to the bases used in Ref. 15. For each symmetry about 400 terms were tested and finally 81 terms of Σ_u and 70 of Π_u symmetry were chosen for the final computations. The results are given in Table V. In the last two columns we list

$$S_{-2} = \frac{1}{3}(2\alpha_{\perp} + \alpha_{\parallel}) \quad (38)$$

and

$$S_{-3} = \frac{2}{3}[2\langle \Psi'_{\perp} | \Psi'_{\perp} \rangle + \langle \Psi'_{\parallel} | \Psi'_{\parallel} \rangle]. \quad (39)$$

The parallel and perpendicular components correspond, respectively, to $i=z$ and $i=x$ in Eqs. (36) and (37), and in the third and fifth columns the differences of the present results and those of Ref. 16 are given. The present polar-

izability computations were undertaken in order to get an estimate of S_{-3} and highest accuracy was not required. Therefore it is possible that the bases for Ψ' could be chosen better. However, the convergence of the polarizabilities with the expansion length in Ψ' is rather fast. The best results obtained in this work for $R=1.4$ with 120 and 199 term expansions for Ψ'_{\perp} and Ψ'_{\parallel} , respectively were $\alpha_{\perp} = 4.5765$ and $\alpha_{\parallel} = 6.3874$. Therefore we believe that the discrepancies Δ_{Rych} seen in Table V are mainly due to the fact that in Ref. 16 a less accurate zero order function, Ψ , was used.

D. Radiative corrections

The radiative corrections to the electronic ground state energy of the hydrogen molecule, when expressed in atomic units, read^{11,4}

$$E_{\text{rad}} = E_L + E'_L, \quad (40)$$

$$E_L = \frac{8}{3} \alpha^3 \langle 0 | \delta(\mathbf{r}_{1a}) + \delta(\mathbf{r}_{1b}) | 0 \rangle \left[\ln \frac{c^2}{K_0} + \frac{19}{30} - \ln 2 \right], \quad (41)$$

$$E'_L = \frac{14}{3} \alpha^3 \langle 0 | \delta(\mathbf{r}_{12}) | 0 \rangle \ln \alpha, \quad (42)$$

$\ln(K_0/\text{a.u.})$

$$= \frac{\sum_n |\langle 0 | \mathbf{p} | n \rangle|^2 (E_n - E_0) \ln[(E_n - E_0)/\text{a.u.}]}{\sum_n |\langle 0 | \mathbf{p} | n \rangle|^2 (E_n - E_0)}, \quad (43)$$

where \mathbf{p} is the total momentum operator of the two electrons, α the fine structure constant and c the velocity of

light. Unfortunately, so far no effective method exists for the evaluation of the Bethe logarithm Eq. (43) for the hydrogen molecule and we are forced to use an approximate method following Garcia⁴ and Bishop and Cheung.¹⁷ The method is based on the observation that if one defines

$$S_p = \sum_j f_{0j} (E_j - E_0)^p, \quad (44)$$

$$f_{0j} = \frac{2}{3} (E_j - E_0) |\langle 0 | \mathbf{r} | j \rangle|^2, \quad \mathbf{r} = \mathbf{r}_1 + \mathbf{r}_2, \quad (45)$$

then

$$\ln K_0 = \left[\frac{d}{dp} \ln S_p \right]_{p=2}. \quad (46)$$

Thus if a functional form of S_p is given the logarithm can be readily obtained. This form is determined by fitting an analytical expression to a few known values of the moments S_p . For the ground state of the H_2 molecule these values are

$$\begin{aligned} S_p &\rightarrow \infty \quad \text{for } p \rightarrow 2.5, \\ S_2 &= \frac{16}{3} \pi \langle 0 | \delta(\mathbf{r}_{1a}) | 0 \rangle, \\ S_1 &= -\frac{4}{3} \langle 0 | \Delta_1 + \nabla_1 \nabla_2 | 0 \rangle, \\ S_0 &= 2, \\ S_{-1} &= \frac{4}{3} \langle 0 | 2x_1 x_2 + z_1 z_2 + r_1^2 | 0 \rangle, \end{aligned} \quad (47)$$

and S_{-2} and S_{-3} are given by Eqs. (38) and (39). S_2 is easily obtained from Table III, and S_1 and S_{-1} from Table IV.

To get an analytical expression Garcia⁴ used the form

$$\begin{aligned} S_p &= f_{01} (E_1 - E_0)^p + f_{02} (E_2 - E_0)^p \\ &+ (E_I)^p \left(\sum_{i=0}^k b_i p^i + \frac{d_1}{2.5-p} + \frac{d_2}{3-p} + \frac{d_3}{3.5-p} \right), \end{aligned} \quad (48)$$

with $E_I = 0.5669$ a.u. being the ionization potential, E_1, E_2 — energies of the first excited $B^1\Sigma_u^+$ and $C^1\Pi_u$ states and f_{01}, f_{02} the corresponding oscillator strengths.

Bishop and Cheung¹⁷ advocate the ansatz:

$$\begin{aligned} S_p &= f_{01} (E_1 - E_0)^p + f_{02} (E_2 - E_0)^p + \sum_{i=0}^n b_i p^i \\ &+ \frac{d_0}{(2.5-p)^q}, \quad q \text{ fixed} \end{aligned} \quad (49)$$

and they suggest $q=1.6$ as best suited for the H_2 molecule. The limits of summation, k in Eq. (48) and n in Eq. (49), depend on the number of available moments S_p and the b_i and d_i are determined by requiring that Eqs. (48) and (49) reproduce the given moments.

Since it is difficult to decide *a priori* which form is more reliable, we used both Eq. (48) and Eq. (49) to compute $\ln K_0$ and E_{rad} in the whole range $0.4 \leq R \leq 12.0$. The energies E_1 and E_2 were taken from Ref. 18 and the corresponding transition moments from Ref. 19. Where necessary, the input data were interpolated to 0.4 using in the

interpolation the values for the He atom as the $R=0$ asymptotic. The computations were performed twice. In one computation all six moments for $p=-3, -2, \dots, 2$ were used to yield the correction E_{rad}^1 . Then S_{-3} was omitted and the computation repeated with the remaining five moments as input to get E_{rad}^2 . Thus the effect of using S_{-3} in the fit is

$$\Delta(S_{-3}) = E_{\text{rad}}^1 - E_{\text{rad}}^2. \quad (50)$$

It turns out that $\Delta(S_{-3})$ is definitely smaller if Eq. (48) rather than Eq. (49) is used. This suggests that Eq. (48) provides a better fit of the data. But even in this case $\Delta(S_{-3})$ is not negligible and it is not possible to say which of the two sets E_{rad}^1 or E_{rad}^2 is more reliable. Therefore the final results for the Bethe logarithm were obtained as an average, i.e., we have

$$E_{\text{rad}} = \frac{1}{2} (E_{\text{rad}}^1 + E_{\text{rad}}^2). \quad (51)$$

The final corrections are listed in Table VI. The results obtained with the aid of Eq. (49) are given for comparison in columns 5 and 6.

It is very difficult to give an estimate of the accuracy of the corrections. However, a similar computation for the H_2^+ ion⁵ when compared with the very accurate result of Bukowski *et al.*²⁰ shows that the error in the vibrational levels due to the approximate evaluation of the radiative corrections is less than 0.003 cm^{-1} . One can expect therefore that the present radiative corrections are accurate to about 0.01 cm^{-1} or better and if relative positions of the levels are considered the error should be still smaller.

IV. VIBRATIONAL AND ROTATIONAL LEVELS

A. Adiabatic energies

It has been found during the vibrational computations that if accuracy of better than 0.01 cm^{-1} is required in the vibrational levels then the Born–Oppenheimer energies $E(R)$ and their derivatives dE/dR must be computed at a fine grid. The interpolation of the unperturbed potential needed for the vibrational equation must be accurate to about 9 decimal figures and it is impossible to have such an accuracy if the input energies in the most important region are given at intervals $\Delta R = 0.1$ and 0.2 . Therefore the electronic energies were computed at 670 internuclear separations in the interval $0.2 \leq R \leq 12.0$. For $0.2 \leq R \leq 0.7$ the energies are far above the dissociation limit and therefore $\Delta R = 0.1$ was used. In the most important region, from $R=0.75$ to $R=6.0$ — $\Delta R = 0.01$ was used. Then up to $R=8$ — $\Delta R = 0.02$, up to $R=9$ — $\Delta R = 0.05$ and up to $R=10$ — $\Delta R = 0.1$. Finally for up to $R=12$ — $\Delta R = 0.2$ was used.

The interpolation of the adiabatic, relativistic and radiative corrections creates no such problems because a five figure accuracy is sufficient. So the corrections were interpolated by cubic splines from the data given in Tables III, IV, and VI and extrapolated to $R=0$ using the helium atom data.^{11,5} The Born–Oppenheimer energies were interpolated by cubic polynomials fitted to the energies and their derivatives at two adjacent input points. The correc-

TABLE VI. Radiative corrections in cm^{-1} .

R	$\ln(k_0)$	E_{rad}	$\Delta(S_{-3})$	E_{rad} [Eq. 49]	$\Delta(S_{-3})$
0.400	2.546	2.339	0.006	2.266	0.009
0.500	2.449	1.978	0.001	1.919	0.006
0.600	2.376	1.698	-0.001	1.650	0.005
0.800	2.315	1.298	-0.003	1.269	0.003
0.900	2.308	1.155	-0.003	1.132	0.002
1.000	2.305	1.039	-0.003	1.022	0.003
1.100	2.307	0.944	-0.003	0.931	0.003
1.200	2.310	0.866	-0.003	0.855	0.003
1.300	2.313	0.801	-0.003	0.793	0.004
1.350	2.314	0.773	-0.002	0.765	0.004
1.400	2.314	0.747	-0.002	0.740	0.005
1.450	2.314	0.724	-0.001	0.717	0.005
1.500	2.314	0.702	-0.002	0.697	0.007
1.600	2.312	0.664	-0.001	0.660	0.008
1.700	2.309	0.632	-0.001	0.629	0.010
1.800	2.306	0.605	0.000	0.603	0.012
2.000	2.295	0.563	0.001	0.562	0.014
2.200	2.283	0.534	0.002	0.535	0.019
2.400	2.271	0.514	0.003	0.516	0.021
2.600	2.259	0.501	0.004	0.505	0.024
2.800	2.249	0.494	0.004	0.499	0.026
3.000	2.243	0.492	0.005	0.497	0.026
3.200	2.238	0.493	0.005	0.498	0.027
3.400	2.234	0.497	0.005	0.502	0.027
3.600	2.232	0.502	0.005	0.507	0.027
3.800	2.228	0.508	0.006	0.513	0.028
4.000	2.225	0.514	0.006	0.520	0.030
4.200	2.224	0.520	0.006	0.527	0.032
4.400	2.216	0.526	0.007	0.533	0.033
4.600	2.209	0.530	0.007	0.538	0.035
4.800	2.208	0.534	0.008	0.543	0.037
5.000	2.207	0.537	0.008	0.547	0.039
5.200	2.208	0.540	0.009	0.551	0.041
5.400	2.207	0.542	0.010	0.554	0.044
5.600	2.206	0.543	0.010	0.556	0.045
5.800	2.204	0.544	0.011	0.559	0.048
6.000	2.201	0.546	0.012	0.561	0.050
6.200	2.195	0.547	0.013	0.563	0.052
6.400	2.188	0.548	0.014	0.565	0.054
6.600	2.183	0.548	0.015	0.566	0.055
6.800	2.180	0.549	0.016	0.567	0.057
7.000	2.176	0.549	0.016	0.569	0.059
7.200	2.172	0.550	0.017	0.570	0.060
7.400	2.168	0.550	0.018	0.571	0.062
7.600	2.164	0.551	0.019	0.571	0.062
7.800	2.161	0.551	0.019	0.572	0.063
8.000	2.158	0.551	0.019	0.573	0.064
8.500	2.152	0.552	0.021	0.574	0.066
9.000	2.149	0.552	0.021	0.574	0.066
9.500	2.148	0.552	0.021	0.574	0.066
10.000	2.149	0.552	0.021	0.574	0.065
11.000	2.158	0.552	0.020	0.571	0.061
12.000	2.175	0.550	0.016	0.567	0.054
∞	2.291	0.542			

tions were added to the unperturbed potential and the resulting corrected potential, U , was extrapolated to R_{max} assuming for $R > 12$: $U(R) = U(12) \times (12/R)^6$. In all computations, except the T_2 isotope, $R_{\text{max}} = 20$ was used. For T_2 , in order to get the $v=26$ level, R_{max} was increased to 40. This, however, had no effect on the $v \leq 25$ T_2 levels. The vibrational equation was solved numerically by the Cooley method²¹ for each total angular momentum for all

bound vibrational states. The computations were performed twice with integration steps $h=0.005$ and $h=0.002$ and the energies were then extrapolated to $h=0$ assuming that the truncation error is proportional to h^4 . However, at this fine grid the extrapolation had a very small effect on the results. The nuclear masses for H, D and T were taken as 1836.1527, 3670.4831, and 5496.920, respectively.

On output the program yielded the relativistic, adia-

TABLE VII. Dissociation energies from the $J=0$ levels in cm^{-1} .

ν	H_2	Δ_{KR}	HD	Δ_{KR}	HT	D_2	Δ_{KR}	DT	T_2
0	36118.060	0.011	36405.774	0.011	36512.154	36748.355	0.010	36881.278	37028.489
1	31956.893	0.010	32773.620	0.011	33077.307	33754.746	0.011	34137.953	34563.992
2	28031.051	0.012	29318.903	0.013	29800.542	30880.244	0.012	31494.204	32179.468
3	24335.649	0.009	26038.142	0.011	26678.854	28122.761	0.014	28948.386	29873.694
4	20867.662	0.012	22928.874	0.012	23710.026	25480.643	0.012	26499.149	27645.634
5	17626.087	0.007	19989.722	0.010	20892.691	22952.702	0.014	24145.466	25494.454
6	14612.226	0.010	17220.502	0.009	18226.394	20538.234	0.012	21886.634	23419.524
7	11830.072	0.007	14622.373	0.011	15711.705	18237.070	0.011	19722.310	21420.435
8	9286.866	0.007	12198.044	0.008	13350.350	16049.620	0.012	17652.529	19497.008
9	6993.869	0.000	9952.044	0.009	11145.397	13976.947	0.012	15677.751	17649.316
10	4967.458	-0.003	7891.091	0.004	9101.488	12020.851	0.009	13798.899	15877.703
11	3230.690	-0.002	6024.580	-0.002	7225.159	10183.974	0.010	12017.422	14182.814
12	1815.577	0.007	4365.260	-0.002	5525.255	8469.948	0.005	10335.363	12565.623
13	766.455	0.014	2930.147	0.000	4013.490	6883.562	0.000	8755.451	11027.477
14	144.599	0.017	1741.808	0.007	2705.206	5430.997	-0.001	7281.207	9570.141
15			830.172	0.015	1620.415	4120.114	-0.003	5917.089	8195.858
16			234.923	0.017	785.239	2960.837	0.000	4668.665	6907.421
17			3.588	0.045	233.755	1965.657	0.005	3542.834	5708.259
18					6.514	1150.303	0.012	2548.115	4602.547
19						534.608	0.015	1695.015	3595.339
20						143.381	0.017	996.511	2692.737
21						1.643	0.057	468.643	1902.105
22								131.004	1232.332
23								2.725	694.169
24									300.581
25									66.689
26									0.063

batic vibrational-rotational energies $E_{\nu,j}^{\text{ad}}$ and the expectation values of the vibrational kinetic energy,

$$KE = \left\langle \frac{1}{2\mu} \frac{d^2}{dR^2} \right\rangle. \quad (52)$$

B. Nonadiabatic corrections

At the present time the best estimate of the nonadiabatic corrections to the vibrational-rotational levels for various isotopes is due to Schwartz and LeRoy² who—using the existing *ab initio* results²²—were able to construct a scaling and extrapolation procedure that allows the direct computation of the corrections. The corrections are expressed as simple combinations of the kinetic energy, KE, the rotational quantum number, J, nuclear masses and some coefficients tabulated in Ref. 2. In this work the kinetic energy, KE, was computed for each level and the corrections evaluated exactly as described in Ref. 2. Then the corrections were added to the adiabatic results for all levels except the lowest $\nu=J=0$ levels of H_2 , HD and D_2 . For those three levels the *ab initio*²² results were used because we believe these results to be reliable for the lowest levels. As compared with Ref. 2 the *ab initio* results increase the H_2 , HD and D_2 dissociation energies by 0.018 cm^{-1} , 0.008 cm^{-1} , and 0.001 cm^{-1} , respectively.

The results for the rotationless states are given in Table VII. Tables containing energies for all levels with $J \leq 10$ can be found in Ref. 9. The nonadiabatic corrections used in this work are different from those used by Kołos and Rychlewski¹⁰ who used for all levels the *ab initio* results.²²

Therefore to make the comparison more meaningful as far as the relativistic potential energy curves are concerned in Table VII we list Δ_{KR} which gives the differences of the relativistic, *adiabatic* energies, i.e., energies not corrected for nonadiabatic effects.

V. COMPARISON WITH EXPERIMENT AND CONCLUSIONS

Several very accurate experimental results have been reported in the last decade. Here we will use some of them to estimate the accuracy of the present computations. The relevant results are listed in Tables VII–XV. The discrep-

TABLE VIII. Comparison with experiment of $\Delta G(\nu+1/2)$ for H_2 .

ν	Expt. ^a	Theory	Δ
0	4161.14	4161.167	0.027
1	3925.79	3925.842	0.052
2	3695.43	3695.401	-0.029
3	3467.95	3467.987	0.037
4	3241.61	3241.574	-0.036
5	3013.86	3013.861	0.001
6	2782.13	2782.154	0.024
7	2543.25	2543.207	-0.043
8	2292.93	2292.997	0.067
9	2026.38	2026.410	0.030
10	1736.66	1736.768	0.108
11	1415.07	1415.113	0.043
12	1049.16	1049.122	-0.038
13	622.02	621.856	-0.164

^aFrom Ref. 23.

TABLE IX. H₂ lines. Comparison with experiment.

<i>J</i>	<i>S</i> ₀			<i>O</i> ₁		<i>Q</i> ₁		
	Theory	Δ ^a	Δ ^b	Theory	Δ ^a	Theory	Δ ^a	Δ ^c
0	354.392 ^d	0.027	0.019			4161.167	-0.033	
1	587.032	-0.055	0.000			4155.236	-0.045	-0.013
2	814.425	-0.031	0.000	3806.775	-0.084	4143.449	-0.044	-0.012
3	1034.672	-0.026	0.002	3568.204	-0.035	4125.857	-0.046	-0.011
4	1246.101	0.019	0.003	3329.024	-0.120	4102.568	-0.024	-0.010
5	1447.282	0.035	0.003	3091.185	0.044	4073.719	0.021	-0.020
6	1637.047			2856.467		4039.480	0.029	

<i>J</i>	<i>S</i> ₁			<i>Q</i> ₂		
	Theory	Δ ^a	Δ ^c	Theory	Δ ^a	Δ ^c
0	4497.841	-0.007	0.007	8087.009	-0.021	
1	4712.889	-0.049	-0.011	8075.295	0.012	-0.004
2	4916.993	-0.039	-0.010	8051.977	0.013	-0.003
3	5108.391	-0.024	-0.008	8017.175	0.007	0.000
4	5285.581	-0.051		7971.094		
5	5447.328	-0.709		7914.005		
6	5592.679			7846.232		

^aFrom Ref. 24.^bFrom Ref. 25.^cFrom Ref. 26.^dSee text.TABLE X. 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	179.069	-0.039	0.002			
1	297.534	0.024	0.000			
2	414.648	0.038	0.000	2814.539	-0.031	-0.006
3	529.900	0.090	0.000	2693.963	-0.147	-0.009
4	642.807	0.097	0.001	2572.635	0.135	-0.008
5	752.921	0.011	0.002	2451.079	0.029	
6	859.833	0.073	0.001	2329.798		
7	963.180	0.020		2209.263	0.033	
8	1062.645	0.075		2089.917		
9	1157.958			1972.158		

<i>J</i>	<i>Q</i> ₁			<i>S</i> ₁		
	Theory	Δ ^a	Δ ^c	Theory	Δ ^a	Δ ^c
0	2993.608	0.008		3166.352		-0.008
1	2991.497	-0.003	-0.007	3278.513		-0.009
2	2987.283	0.083	-0.013	3387.253	0.033	-0.008
3	2980.979	-0.021	-0.009	3492.084	0.054	-0.007
4	2972.605	0.105	-0.008	3592.557		
5	2962.184	-0.016		3688.259	-0.101	
6	2949.750	0.050		3778.827		
7	2935.338	0.138		3863.943	0.123	
8	2918.994	0.194		3943.343		
9	2900.763	0.163		4016.812		

^aFrom Ref. 24.^bFrom Ref. 27.^cFrom Ref. 28.

TABLE XI. HT S and Q transitions.

	Expt. ^a	Theory	Δ
$S_0(0)$	237.866	237.871	0.005
$S_0(1)$	394.800	394.840	0.040
$S_0(2)$	549.267	549.426	0.159
$Q_1(0)$	3434.806	3434.846	0.040
$Q_1(1)$	3431.568	3431.609	0.041
$Q_1(2)$	3425.103	3425.147	0.044
$Q_1(3)$	3415.438	3415.487	0.049
$Q_1(4)$	3402.599	3402.668	0.069

^aFrom Ref. 29.TABLE XII. HD $\Delta G(v+1/2)$.

v	Expt.	Theory	Δ
0	3632.152	3632.154	0.002
1	3454.735	3454.717	-0.018
2	3280.721	3280.760	0.039
3	3109.264	3109.268	0.004
4	2939.149	2939.152	0.003
5	2769.199	2769.220	0.021

^aFrom Ref. 29.TABLE XIII. HD and HT $P_v(J)$ and $R_v(J)$ lines.

	HD			HT		
	Expt. ^a	Theory	Δ	Expt. ^a	Theory	Δ
$P_1(3)$	3355.361	3355.368	0.007			
$P_1(2)$	3450.463	3450.460	-0.003	3273.140	3273.201	0.061
$P_1(1)$	3542.932	3542.929	-0.003	3355.355	3355.405	0.050
$R_1(0)$	3717.532	3717.529	-0.003	3511.020	3511.073	0.053
$R_1(1)$	3798.455	3798.449	-0.006	3583.530	3583.577	0.047
$R_1(2)$	3874.357	3874.352	-0.005	3651.870	3651.920	0.050
$R_1(3)$	3944.720	3944.719	-0.001	3715.630	3715.686	0.056
$R_1(4)$	4009.088	4009.088	0.00	3774.450	3774.498	0.048
$P_4(2)$	13283.993	13284.042	0.049			
$P_4(1)$	13387.646	13387.694	0.048	12722.515	12722.707	0.192
$R_4(0)$	13551.065	13551.111	0.046	12868.786	12868.978	0.192
$R_4(1)$	13609.664	13609.712	0.048	12922.534	12922.724	0.190
$R_4(2)$	13652.215	13652.257	0.042	12962.825	12963.019	0.194
$R_4(3)$	13678.322	13678.368	0.046	12989.369	12989.557	0.188
$R_4(4)$				13001.917	13002.098	0.181
$P_5(2)$	16219.473	16219.515	0.042	15445.118	15445.358	0.240
$P_5(1)$	16326.791	16326.840	0.049	15539.796	15540.039	0.243
$R_5(0)$	16486.537	16486.584	0.047	15682.984	15683.230	0.246
$R_5(1)$	16537.816	16537.856	0.040	15730.589	15730.826	0.237
$R_5(2)$	16569.404	16569.441	0.037	15761.691	15761.924	0.233
$R_5(3)$	16581.008	16581.003	-0.005	15776.009	15776.247	0.238

^aFrom Ref. 29.TABLE XIV. Ground state dissociation energies for H_2 , HD, and D_2 in cm^{-1} .

	H_2	HD	D_2
This work	36118.060	36405.774	36748.355
Ref. 10	36118.049	36405.763	36748.345
Present—Ref. 10	0.011	0.011	0.010
Experiment	36118.11 ± 0.08 (Ref. 30)	36406.2 ± 0.4 (Ref. 31)	36748.3 ± 0.1 (Ref. 32)
Expt.—Theory	0.05 ± 0.08	0.4 ± 0.4	-0.1 ± 0.1

TABLE XV. Ionization potentials for H_2 , HD, and D_2 in cm^{-1} .

	H_2	HD	D_2
This work	124417.482	124568.476	124745.387
Ref. 10	124417.471	124568.465	124745.377
Experiment—Ref. 32	124417.484 ± 0.017		124745.353 ± 0.024
Expt.—Theory	0.002 ± 0.017		-0.034 ± 0.024
Experiment—Ref. 33	124417.507 ± 0.012	124568.481 ± 0.012	
Expt.—Theory	0.026 ± 0.012	0.005 ± 0.012	

ancies Δ are always computed as the difference: present result minus experiment.

Let us first discuss the H_2 molecule. Here a comment is needed concerning the $S_0(0)$ theoretical transition in Table X which is somehow inconsistent with other quoted numbers because for the $v=J=0$ level the nonadiabatic correction was computed differently than for other states. If the smoothed correction of Ref. 2 were used, the theoretical number would be smaller by 0.018 cm^{-1} making the agreement with Ref. 25 almost excellent. In general the agreement with Refs. 25 and 26 is much better than with Ref. 24, and all these data are somehow contradictory to Ref. 23. From Table VIII it follows that the theoretical $v=1$ and $v=2$ levels are too high by 0.027 and 0.079 cm^{-1} , respectively, while the data in Table X suggest that the $v=1$ vibrational level is too low and the next higher about right.

For D_2 the comparison is similarly indecisive. The situation is different for the heteronuclear isotopes, Tables XI–XIII. Here the agreement is definitely better for HD than for HT. It seems almost certain that the relatively poor agreement in the case of HT is due to nonadiabatic effects. In Ref. 2 the nonadiabatic corrections for heteronuclear isotopes were extrapolated from the HD data and no other data were available to fit the interpolating polynomial. It is therefore not surprising that the interpolation is less reliable. We fully agree on this point with the conclusions of Chuang and Zare²⁹ that *ab initio* results for the nonadiabatic corrections for HT are necessary for an accurate comparison of theoretical and experimental results.

The dissociation energies of H_2 , HD and D_2 are compared with experiment and Ref. 10 in Table XIV. The present dissociation energies are about 0.01 cm^{-1} larger than those obtained by Kołos and Rychlewski¹⁰ and in consequence the corresponding ionization energies are increased by the same amount. These are listed in Table XV. The agreement with experiment in the case of H_2 and HD is indeed very satisfactory. Nevertheless one should keep in mind that improvement in the accuracy of the theoretical results is still possible. First, as was mentioned in Sec. II, the Born–Oppenheimer energies could still be lowered by a few thousandths of a wave number. Next, as we discussed above, the lowest order radiative corrections estimated in this work may differ slightly from the exact results. Finally, the nonadiabatic corrections are based on *ab initio* results²² obtained a decade ago. A more accurate computation would certainly change these corrections.

The first two sources of inaccuracies in the theoretical energies, viz. the truncation error in the Born–Oppenheimer energies and possible errors in the radiative corrections, can influence the comparisons in Tables XIV and XV, but they can hardly affect Tables VIII–XIII. The improvement in the Born–Oppenheimer curve due to those two effects would certainly be smooth and most probably almost independent of R . Therefore the relative positions of the vibrational levels would be changed by negligible amounts.

The nonadiabatic corrections seem to be the most important source of errors. For homonuclear isotopes and

HD the inaccuracies in the present corrections may be of the order of 0.01 cm^{-1} . For HT and DT the inaccuracies are probably larger. Also, more accurate corrections will influence individual levels independently of each other and therefore all the comparisons in Tables VIII–XV will be affected.

In conclusion we believe—in agreement with Ref. 29—that for the refinement of the theoretical predictions new *ab initio* nonadiabatic corrections are needed in the first place. It would be also desirable to get the radiative corrections more accurately. However, these will have probably little effect on the overall agreement with experiment.

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APPENDIX A: THE $P \rightarrow 1/2$ LIMIT OF THE ρ^{-2P} EXPANSION

To perform the transformation of Eq. (22) for $p \rightarrow 1/2$ we note that one can replace p by $1/2$ everywhere except in the product

$$d_{lm}(p) C_m^{p-(1/2)}(\cos \varphi). \quad (\text{A1})$$

The Gegenbauer polynomials $C_n^\alpha(\cos \varphi)$ satisfy¹³

$$C_0^\alpha = 1 \quad (\text{A2})$$

and

$$\lim_{\alpha \rightarrow 0} \frac{1}{\alpha} C_n^\alpha(\cos \varphi) = C_n^0(\cos \varphi) = \frac{2}{n} \cos(n\varphi), \quad n \neq 0. \quad (\text{A3})$$

Thus, if $m=0$ there is no singularity while for $m \neq 0$ we get

$$\begin{aligned} & \Gamma(2p-1) (2p+2m-1) C_m^{p-(1/2)}(\cos \varphi) \\ &= \frac{\Gamma(2p) (2p+2m-1)}{2[p-(1/2)]} C_m^{p-(1/2)}(\cos \varphi) \rightarrow 2 \cos(m\varphi). \end{aligned} \quad (\text{A4})$$

Hence

$$\begin{aligned} & d_{lm}(p) C_m^{p-(1/2)}(\cos \varphi) \\ & \rightarrow -(2-\delta_{m,0})(2l+1) \\ & \times [(2m-1)!!]^2 \frac{(l-m)!}{(l+m)!} \cos(m\varphi). \end{aligned} \quad (\text{A5})$$

Further we have

$$C_{l-m}^{m+(1/2)}(x) = \frac{1}{(2m-1)!!} \frac{d^m P_l}{dx^m} \quad (\text{A6})$$

and if we use the phases of the associated Legendre functions as in Ref. 14, i.e.,

$$P_l^m(x) = |1-x^2|^{1/2} \frac{d^m P_l}{dx^m}, \quad (\text{A7})$$

$$Q_l^m(\xi) = (-1)^{m+1} \frac{(l+m)!}{(l-m)!} P_l^m(\xi) \times \int_{\infty}^{\xi} (x^2-1)^{-1} [P_l^m(x)]^{-2} dx, \quad (\text{A8})$$

we finally obtain

$$\rho^{-1} = \sum_{l=0}^{\infty} \sum_{m=0}^l (-1)^m (2-\delta_{m,0}) \left[\frac{(l-m)!}{(l+m)!} \right]^2 \times Q_l^m(\xi_+) P_l^m(\xi_-) P_l^m(\eta_1) P_l^m(\eta_2) \cos(m\varphi), \quad (\text{A9})$$

which coincides with the Neumann expansion as given in Ref. 14.

APPENDIX B: EVALUATION OF THE $I^{-\mu}$ INTEGRALS

When Eq. (22) is substituted into Eq. (19) the integral $I^{-\mu}$ is expressed as a sum of terms labeled by l and m :

$$I^{-\mu} = \sum_{l=0}^{\infty} \sum_{m=0}^l I_{l,m}. \quad (\text{B1})$$

Since W^{μ} are polynomials in ξ_i, η_i each $I_{l,m}$ is given as a linear combination of products

$$J_{l,m}^{r,q}(\alpha_1, \alpha_2) B_{l,m}^k(\beta_1) B_{l,m}^s(\beta_2) A_m, \quad (\text{B2})$$

where

$$A_m = \int_0^{2\pi} C_m^{p-(1/2)}(\cos \varphi) d\varphi = \begin{cases} 2\pi \left[\frac{\Gamma[p+(m-1/2)]}{\Gamma[p-(1/2)](m/2)!} \right]^2 & \text{if } m \text{ even,} \\ 0 & \text{if } m \text{ odd,} \end{cases} \quad (\text{B3})$$

$$B_{l,m}^{k,s}(\beta) = \int_{-1}^1 \exp(\beta x) x^k (1-x^2)^{s/2} C_{l-m}^{p+m}(x) dx, \quad (\text{B4})$$

$$J_{l,m}^{r,q}(\alpha_1, \alpha_2) = \int_1^{\infty} \int_1^{\infty} g_1^{r,m}(\xi_1) g_2^{q,m}(\xi_2) \times D_{l-m}^{p+m}(\xi_+) C_{l-m}^{p+m}(\xi_-) d\xi_1 d\xi_2 \quad (\text{B5})$$

and the functions $g_i^{k,m}$ have the form

$$g_i^{k,m}(\xi) = \exp(-\alpha_i \xi) \xi^k (\xi^2 - 1)^{m/2}. \quad (\text{B6})$$

Both the B and J integrals can be computed accurately if use is made of the properties of the Gegenbauer polynomials C_n^{ν} . When applied to $C_{l-m}^{p+m}(x)$, the standard recurrence relation and the differential equation read

$$(l-m+2)C_{l-m+2}^{p+m} - 2(l+p+1)x C_{l-m+1}^{p+m} + (2p+l+m)C_{l-m}^{p+m} = 0, \quad (\text{B7})$$

$$(1-x^2) \frac{d^2}{dx^2} C_{l-m}^{p+m} - (2m+2p+1)x \frac{d}{dx} C_{l-m}^{p+m} + (l-m)(l+m+2p)C_{l-m}^{p+m} = 0. \quad (\text{B8})$$

We also have¹³

$$\frac{d}{dx} C_{l-m}^{p+m} = 2(p+m)C_{l-m-1}^{p+m+1}. \quad (\text{B9})$$

In consequence of Eq. (B3) only even m must be considered and so this will be assumed throughout this section.

In the following subsections we give details of the evaluation of the B and J integrals.

1. Evaluation of $B_{l,m}^{k,m}(\beta)$

Since

$$B_{l,m}^{k,s}(-\beta) = (-1)^{l+k+m} B_{l,m}^{k,s}(\beta) \quad (\text{B10})$$

we assume in the following $\beta > 0$ and expand Eq. (B4) as

$$B_{l,m}^{k,s}(\beta) = \sum_{j=0}^{\infty} \frac{\beta^j}{j!} B_{l,m}^{k,s}(0). \quad (\text{B11})$$

For $s=m$ and with the definition

$$b_{l,m}^k = B_{l,m}^{k,m}(0), \quad (\text{B12})$$

using Eq. (B7) we get the relation

$$b_{l,m}^{k+1} = \frac{l-m+1}{2(l+p)} b_{l+1,m}^k + \frac{2p+l+m+1}{2(l+p)} b_{l-1,m}^k \quad (\text{B13})$$

and with the aid of the above equation all b integrals can be computed from the $b_{n,m}^0$ integrals. To get the latter we note that

$$\int_{-1}^1 (1-x^2)^{m/2} x \frac{d}{dx} C_{l-m}^{p+m} dx = \int_{-1}^1 (1-x^2)^{(m+2)/2} \frac{d^2}{dx^2} C_{l-m}^{p+m} dx, \quad (\text{B14})$$

make use of Eqs. (B8) and (B9) and obtain the recurrence relation

$$b_{l,m-2}^0 = \frac{4(p+m-2)(p+m-1)(2p+m-3)}{m(l-m+2)(l+m+2p-2)} b_{l,m}^0 \quad (\text{B15})$$

$$b_{l,l}^0 = \int_{-1}^1 (1-x^2)^{l/2} dx = \frac{\Gamma[(l+2)/2]\Gamma(1/2)}{\Gamma[(l+3)/2]}. \quad (\text{B16})$$

Thus, since m must be even, starting from Eq. (B16) and using Eq. (B15) we get $b_{l,m}^0$ for $l=0,2,\dots,l_{\max}$ and $m=0,2,\dots,l$ and subsequently $b_{l,m}^k$ from Eq. (B13). Finally, $B_{l,m}^{k,m}(\beta)$ are computed with the aid of Eq. (B11). There is no cancellation of significant figures in this algorithm and the integrals can be computed with—in principle—arbitrary accuracy.

2. Evaluation of $J_{l,m}^{i,q}$

The integral $J_{l,m}^{i,q}$ can be transformed¹² to a simpler form by a method originally given by R udenberg.¹⁴ For that purpose we write

$$J = \int_1^\infty d\xi g_1(\xi) D_n^v(\xi) \int_1^\xi dx g_2(x) C_n^v(x) + \int_1^\infty d\xi g_1(\xi) C_n^v(\xi) \int_\xi^\infty dx g_2(x) D_n^v(x), \quad (\text{B17})$$

where we used the notation $n=l-m$ and $\nu = p+m$ and omitted other indices for simplicity. It is obvious from Eq. (23) that $D_n^v(\xi)$ has a $(\xi-1)^{-\nu+(1/2)}$ singularity for $\xi \rightarrow 1$. Therefore in view of Eq. (B5) it follows that the integrals in Eq. (B13) exist if $p < 5/2$. With this assumption the second term on the right-hand side can be transformed by an integration by parts to yield

$$J = \int_1^\infty d\xi D_n^v(\xi) [C_n^v(\xi)]^{-1} \frac{d}{d\xi} \left\{ \int_1^\xi g_2(x) C_n^v(x) dx \times \int_1^\xi g_1(y) C_n^v(y) dy \right\}. \quad (\text{B18})$$

Now the definition of D_n^v , Eq. (23), gives

$$\frac{d}{d\xi} D_n^v(\xi) [C_n^v(\xi)]^{-1} = (\xi^2 - 1)^{-\nu-(1/2)} [C_n^v(\xi)]^{-2} \quad (\text{B19})$$

and one more integration by parts leads to

$$J = - \int_1^\infty (\xi^2 - 1)^{-\nu-(1/2)} G_1^{r,m}(\xi) G_2^{q,m}(\xi) d\xi, \quad (\text{B20})$$

where, with the indices written explicitly,

$$G_i^{k,s}(\xi) = [C_{l-m}^{p+m}(\xi)]^{-1} \int_1^\xi g_i^{k,s}(x) C_{l-m}^{p+m}(x) dx, \quad i=1,2. \quad (\text{B21})$$

To get the integral J from Eq. (B20) any numerical method can be used if G_i are given. In this work the integral was transformed with the substitution $\xi = t^{-1}$ and the resulting $[0,1]$ interval was divided into up to $N=40$ intervals of equal length. Then in each interval an 8-point Gauss quadrature was used. The functions G_i were computed essentially analytically by the following procedure.

First, we define a slightly more general integral

$$F_{s,k}^{l,m}(\xi, \alpha) = \int_1^\xi (x^2 - 1)^s x^k C_{l-m}^{p+m}(x) \times \exp(-\alpha x) dx, \quad l, m, s, k \geq 0. \quad (\text{B22})$$

The differential equation (B8) together with Eq. (B9) give a recurrence relation

$$C_{l-m}^{p+m}(x) = \frac{2(p+m)}{(l-m)(l+m+2p)} \{ (2m+2p+1) \times x C_{l-m-1}^{p+m+1}(x) + 2(p+m+1) \times (x^2 - 1) C_{l-m-2}^{p+m+2}(x) \}, \quad (\text{B23})$$

i.e., we get

$$F_{s,k}^{l,m} = \frac{2(p+m)}{(l-m)(l+m+2p)} \{ (2m+2p+1) F_{s,k+1}^{l,m+1} + 2(p+m+1) F_{s+1,k}^{l,m+2} \}. \quad (\text{B24})$$

Since $C_0^v = 1$ and $C_1^v(x) = 2vx$,

$$F_{s,k}^{l,l-1} = 2(p+l-1) F_{s,k+1}^{l,l} \quad (\text{B25})$$

and it suffices to find $F_{s,k}^{l,l}$ to start the downward recurrence Eq. (B24). Let us now introduce an auxiliary integral

$$K_{s,r,k} = \int_1^\xi (x-1)^s (x+1)^r x^k \exp(-\alpha x) dx. \quad (\text{B26})$$

We have $F_{s,k}^{l,l} = K_{s,s,k}$ and

$$K_{s,r,k} = K_{s+1,r-1,k} + 2K_{s,r-1,k}, \quad (\text{B27})$$

$$K_{s,0,k} = K_{s+1,0,k-1} + 2K_{s,0,k-1}, \quad (\text{B28})$$

$$K_{k,0,0} = \alpha^{-k-1} \exp(-\alpha) \int_0^{\alpha(\xi-1)} x^k \exp(-x) dx. \quad (\text{B29})$$

The right-hand side of Eq. (B29) can be computed easily by various methods. In this work the integral

$$\int_0^z x^k \exp(-x) dx \quad (\text{B30})$$

was computed for $z \leq 1$ and $k = k_{\max}$ by a Taylor expansion of $\exp(-x)$ and then a downward recurrence for smaller k was performed. For larger z the formula

$$\int_0^{n+\varepsilon} x^k \exp(-x) dx = \int_0^n x^k \exp(-x) dx + \exp(-n) \times \sum_{j=0}^k \binom{k}{j} \int_0^\varepsilon x^j \exp(-x) dx \quad (\text{B31})$$

was used repeatedly. Thus, using Eqs. (B29)–(B24) backwards, we get $F_{s,k}^{l,m}$, and the functions G_i , Eq. (B21), are

$$G_i^{k,m} = F_{(m/2),k}^{l,m}(\alpha_i, \xi) [C_{l-m}^{p+m}(\xi)]^{-1}. \quad (\text{B32})$$

This completes the evaluation of the integrands in Eq. (B20) because for $\xi \geq 1$ the Gegenbauer polynomials $C_n^v(\xi)$ can be readily obtained from Eq. (B23).

APPENDIX C: EVALUATION OF THE L^μ INTEGRALS

When ρ is expressed in elliptic coordinates one gets for even powers:

$$\rho^{2n} = \sum_{k=0}^n w_k [(\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2) \times (1 - \eta_2^2)]^{k/2} \cos(k\varphi), \quad (\text{C1})$$

with w_k being polynomials in ξ_i, η_i . Therefore, for μ – even the only term in Eq. (C1) that contributes to Eq. (21) is w_0 and for μ – odd one can use Eq. (C1) and the expansion

Eq. (22) for ρ^{-1} , i.e., for $p=1/2$. $C_m^{p-(1/2)}(\cos\varphi)$ reduces to $\cos(m\varphi)$ which makes the φ integration trivial and L^{2n-1} is expressed as

$$L^{2n-1} = \sum_{l=0}^{\infty} \sum_{m=0}^n L_{l,m}. \quad (C2)$$

Because of the denominator in Eq. (21) the η_1 integration cannot be factored out and the $L_{l,m}$ integrals are more complex than $I_{l,m}$ in Eq. (B1). However, transformations similar to Eqs. (B17)–(B20) can be carried out and $L_{l,m}$ are expressible as linear combinations of products

$$\bar{J}_{l,m}^{i,j}(\alpha_1, \alpha_2, \beta_1) B_{l,m}^{k,2m}(\beta_2) \quad (C3)$$

with the B integral defined by Eq. (B4) and

$$\bar{J}_{l,m}^{i,j}(\alpha_1, \alpha_2, \beta_1) = - \int_1^{\infty} (\xi^2 - 1)^{-m-1} \bar{G}_1^{i,m}(\xi) G_2^{j,2m}(\xi) d\xi, \quad (C4)$$

$$\begin{aligned} \bar{G}_1^{k,i,s}(\xi) &= [C_{l-m}^{m+(1/2)}(\xi)]^{-1} \int_1^{\xi} g_1^{k,2s}(x) h_{m,i}(x) \\ &\times C_{l-m}^{m+(1/2)}(x) dx, \end{aligned} \quad (C5)$$

$$h_{m,i}(x) = \int_{-1}^1 \frac{f_{m,i}(y) dy}{x^2 - y^2}, \quad (C6)$$

$$f_{m,i}(y) = \exp(\beta_1 y) y^i (1 - y^2)^m C_{l-m}^{m+(1/2)}(y). \quad (C7)$$

The B integrals for $p=1/2$ and $\beta=0$ can be computed analytically³⁴

$$\begin{aligned} B_{l,m}^{k,2m}(0) &= \begin{cases} \frac{2(l+m)!k!}{(l-m)!(k+l+m+1)!!(k-l+m)!!(2m-1)!!} & \text{if } k \geq l-m \text{ and } k+l+m = \text{even,} \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \quad (C8)$$

The \bar{J} integrals must be computed with some care because of the logarithmic singularity of the integrand. In this work the following computational scheme was developed. First, the function $f_{m,i}$, Eq. (C7), was approximated by a Chebyshev expansion, i.e., $h_{m,i}$ was written as

$$\begin{aligned} h_{m,i}(x) &= \sum_n a_{2n}^{m,i} \int_{-1}^1 \frac{T_{2n}(y) dy}{x^2 - y^2} \\ &= \sum_n a_{2n}^{m,i} \frac{1}{x} \int_{-1}^1 \frac{T_{2n}(y) dy}{x - y} \end{aligned} \quad (C9)$$

and then the integrals with the Chebyshev polynomials were evaluated for $x > 2$ by expanding the denominator in the geometric series and for $2 \geq x > 1$ by using the Darboux formula¹³

$$\frac{T_{n+1}(x)T_n(y) - T_n(x)T_{n+1}(y)}{x - y} = 1 + 2 \sum_{k=1}^n T_k(x)T_k(y). \quad (C10)$$

Since only even Chebyshev polynomials need be considered we use Eq. (C10) twice and write

$$\begin{aligned} T_{2n+2}(x) \int_{-1}^1 \frac{T_{2n}(y) dy}{x - y} \\ = T_{2n}(x) \int_{-1}^1 \frac{T_{2n+2}(y) dy}{x - y} \\ + 4x \left[1 - 2 \sum_{k=1}^n \frac{T_{2k}(x)}{4k^2 - 1} \right], \quad x > 1. \end{aligned} \quad (C11)$$

The downward recurrence is always stable but one must start with a high n if x is very close to 1. However, in such a case the forward recurrence is also stable. Therefore for $x < 1.004$ we used Eq. (C11) for increasing n . Otherwise, the downward recurrence was started at $n = n_{\max}$ assuming vanishing of the integral for $n = n_{\max} + 2$.

To avoid inaccuracies due to the logarithmic singularity in \bar{G} , Eq. (C5), we split $h_{m,i}$ in two parts:

$$h_{m,i}(x) = h_{m,i}^0(x) - \frac{1}{x} f_{m,i}(x) \log(x-1). \quad (C12)$$

$h_{m,i}^0$ is regular and the contribution of the second term in Eq. (C12) to the integral in Eq. (C5) can be evaluated according to the scheme:

$$\begin{aligned} \int_1^{\xi} \log(x-1) \Phi(x) dx \\ = \log(x-1) \int_1^{\xi} \Phi(x) dx - \int_1^{\xi} \frac{dy}{y-1} \int_1^y \Phi(x) dx. \end{aligned} \quad (C13)$$

In consequence the integral \bar{J} , Eq. (C4), has the general form

$$\bar{J}_{l,m}^{i,j} = - \int_1^{\infty} \frac{G_2^{j,2m}}{(\xi^2 - 1)^{m+1}} [\log(\xi - 1) G_{11}(\xi) + G_{12}(\xi)] d\xi \quad (C14)$$

with both G_{11} and G_{12} being regular at $\xi=1$. The final integration was performed independently in the $[1, z_0]$ and $[z_0, \infty)$ intervals. In the latter case the transformation $\xi = t^{-1}$ was performed to make the interval finite and all integrals were evaluated by Simpson's rule; for the singular part the quadrature formula contained the appropriate weight.

In the final computations $z_0 \equiv 1.4$ and up to 160 integration points in each interval were used.

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