Novel theory of the HD dipole moment. II. Computations

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In the preceding paper we derived a new theory of the dipole moments of homopolar but *isotopically* asymmetric molecules (such as HD, HT, and DT) in which the electrical asymmetry appears directly in the electronic Hamiltonian (in an appropriate Born-Oppenheimer separation) and the dipole moment may be computed as a purely electronic property. In the present paper we describe variation-perturbation calculations and convergence studies on the dipole moment for HD, which is found to have the value 8.51×10^{-4} debye at 1.40 a.u. Using the two alternative formulations of the electronic problem, we can provide a test of basis-set adequacy and convergence of the results, and such convergence studies are reported here. We have also computed vibration-rotation transition matrix elements and these are compared with experimental and other theoretical results.

I. INTRODUCTION

In the preceding paper[1] we presented a new formulation of the theory of electric dipole moments in HD and other homopolar but *isotopically* asymmetric molecules. A canonical transformation to new electronic and heavy particle coordinates was made, such that the isotopically induced asymmetry all appears directly in the *electronic Hamiltonian*—specifically, the potential energy no longer has $D_{\infty h}$ symmetry, but contains a small *ungerade* term proportional to the parameter $\alpha_0 = \frac{1}{2} \lambda m / \mu$, where $\lambda = (M_A - M_B)/(M_A + M_B)$ is the nuclear mass asymmetry and m/μ is the ratio of electronic and nuclear reduced masses (for HD, $\alpha_0 = 1.36 \times 10^{-4}$). It follows that the dipole moment of HD may be derived as a purely electronic property within the Born-Oppenheimer approximation, and the intensities of vibration-rotation and pure rotation transitions computed in the usual way for a diatomic molecule. Nonadiabatic couplings (which are responsible for these dipole moments in the conventional theory) play no part in the new theory; their inclusion would affect the dipole moment calculation by terms of order α_0^3 at most.

Using this new theory, in this paper we carry out calculations of variational type for the $X^1\Sigma^+$ electronic ground state of HD, and study the convergence of the dipole moment function in the neighborhood of the equilibrium separation R_e, as a function of the basis size. Since the dipole moment is an *odd* and therefore essentially linear function of α_0, the variation-perturbation scheme is most convenient, and moreover the dipole moment functions for the other isotopically asymmetric hydrogens HT and DT may be obtained merely by rescaling the HD result.

Figure 1 of the preceding paper shows the resulting dipole moment function for HD (solid curve) and for comparison the function calculated by Browne and Ford[2] using nonadiabatic perturbation theory (dashed curve). The two are in good general agreement (1.6% at $R = R_e$) but there are systematic differences between them at both large and small internuclear distances.

We have used this dipole moment function (rescaled for HT and DT) to compute matrix elements for vibration-rotation and pure rotation transitions arising from the ground vibrational level for all these molecules; these are listed (and compared with experimental and other theoretical results, where available) in Tables III and IV.

General features of the electronic problem and its formulation have been discussed in Sec. III of the preceding paper. We showed in particular that there are two distinct ways of setting up the electronic Hamiltonian, which differ slightly in the choice of electronic coordinates, the form of the perturbation term in the Hamiltonian, and the formal expression for the dipole moment function, and we denoted these as "Scheme 1" and "Scheme 2." However, we also showed, using the variation-perturbation framework, that the numerical value for the dipole moment obtained from each scheme must be the same provided the odd-symmetry *(ungerade)* part of the Hilbert space used for expansion is complete. We have turned this fact to good advantage by using the agreement of results from the two schemes as a test of basis quality. The dipole moments reported here are identical for the two schemes to within 1.1% at all R values computed, and to better than 0.05% for $1.0 \lesssim R \lesssim 1.8$ a.u.

Our trial wave functions were based on James-Coolidge-type expansions,[3] including up to second-power terms in the interelectronic coordinate to represent electron correlation. Certain new molecular integrals in prolate spheroidal coordinates then arise and we have developed new methods for doing these.

Section II of this paper is concerned with basis set description and the molecular integral computations which arise for our variation-perturbation calculation. Section III presents the results of the electronic calculations, with particular attention to convergence and stability of the dipole moment as function of basis size. In Sec. IV the vibration-rotation and pure rotation matrix elements are presented and discussed.

II. BASIS SET AND COMPUTATION METHOD

For computational purposes an adequate starting point is outlined in Sec. III B of Ref. 1 and the equations found there, to which we here refer. As indicated, the Schemes 1 and 2 are to be solved independently but in parallel for each basis set used and the difference between the dipole moments found for each provides a test of basis adequacy. This is easy to do since both schemes involve the same molecular integrals.

A. Basis set description

As given in Eq. (3.22) the variation-perturbation wave function has a zeroth-order even *(gerade)* component $|\psi_g^0\rangle$ and a first-order odd *(ungerade)* component $|\psi_u\rangle$; each of these is expanded in basis functions of the proper symmetry (denoted $\{g_k\}, \{u_n\}$, respectively in Ref. 1). We have used James-Coolidge-type[3] basis functions for both components; these employ prolate spheroidal coordinates for each electron $(i = 1,2)$,

$$\xi_i = (r_{Ai} + r_{Bi})/R, \quad 1 \leq \xi_i < \infty$$

$$\eta_i = (r_{Ai} - r_{Bi})/R, \quad -1 \leq \eta_i \leq +1 \qquad (2.1)$$

$$\varphi_i = \text{azimuth angle}, \quad 0 \leq \varphi_i < 2\pi$$

and the scaled interelectronic coordinate $\rho = 2r_{12}/R$, and they have the form (here α is an orbital exponent, not α_0)

$$|mnjks;\alpha\rangle \equiv \exp[-\alpha(\xi_1+\xi_2)]\xi_1^m\xi_2^n\eta_1^j\eta_2^k\rho^s . \qquad (2.2)$$

A basis ket $|mnjks\rangle$ is even *(gerade)* if $(j + k)$ is even and odd *(ungerade)* if it is odd. Since spin and Pauli symmetry require that the coefficients for $|nmkjs\rangle$ and $|mnjks\rangle$ are equal, they are not counted as distinct kets.

We included basis functions with $s = 0$, 1, and 2. In our convergence studies, we found that the selection of basis sets by the prescription of Bishop and Cheung[4] is appropriate and efficient for both g and u subspace components. In their notation a basis set denoted by $(G$ or $U):(a_0a_1a_2 \mid b)$ consists of all basis kets (of g or u symmetry) such that $a_s = \max(j + m) = \max(k + n)$ for the kets of the given s, $s = 0,1,2$ and $b = \max(j + k + m + n)$ in any case. As indicated by Bishop and Cheung the rationale for this prescription is the inclusion of all functions capable of simulating a given maximum number of nodes.

In principle the orbital exponent α may be varied versus R and also may be different for the g and u components. We did some limited calculations with $\alpha = 0.75$ to test the sensitivity of the even *(ungerade)* component to changes in α, but we found this had no significant effect on the results. Accordingly we did all the computations reported here with the value $\alpha = 0.95$ which is an appropriate choice for $R = R_e = 1.40$ a.u., and used the same value for both subspaces for maximum computational efficiency in evaluating the molecular integrals. As noted below, this limits the quality of the results at internuclear distances R significantly different from R_e.

B. Molecular integrals

A new type of molecular integral arises in this problem and we had to go to some trouble to compute it accurately. Except for the matrix elements of h_e' in Eq. (3.25b), all matrix elements in the determining Eqs. (3.25a), (3.25b), and (3.26) lead to integrals done by standard methods or whose evaluation is well known and is done by widely available computer routines. A new type of integral however arises from the correlated gradient terms in Eqs. (3.28a) and (3.28b), and unfortunately it is impervious to the upward recursion type of approach used by the existing programs for the functions $H_\tau^\nu(m,n;\alpha)$ defined by James and Coolidge.[3] We therefore had to develop an alternate procedure for the new integral, and to test its accuracy and speed we also used it to generate the related but simpler functions $H_\tau^\nu(m,n;\alpha)$. The resulting package yields values for $H_\tau^\nu(m,n;\alpha)$ which are more accurate and allows a substantially wider range of indices than the conventional packages. An account of our evaluation method is given in the Appendix.

III. DIPOLE MOMENT CALCULATIONS

All the convergence studies reported here are for basis sets including terms in the interelectronic coordinate ρ with powers $s = 0$, 1, and 2. We performed a large number of preliminary calculations for basis sets limited to $s = 0,1$ only, but these showed no definite stability or convergence in the dipole moment behavior and the difference between the results for Schemes 1 and 2 remained large (1% or more even for $R \approx R_e$). When terms with $s = 2$ are included, immediate improvement is found in convergence of results, both for a given scheme versus basis size and in comparison of the two schemes.

We made extensive studies of convergence vs. basis size only near the equilibrium separation, $R_e \simeq 1.40$ a.u. Having established from these studies the general trend of results and the basis sizes needed to achieve stability and convergence of the dipole moment, we then studied the behavior of dipole moment for both schemes as function of internuclear distance R for a selected subset of bases.

Energies reported in the tables are the zeroth-order values associated with the even *(gerade)* basis component $|\psi_g^0\rangle$. Corrections to this energy are of second order in α_0, i.e., smaller than 5×10^{-8} a.u.—less than the last significant digit reported in the energy; as is well known the first-order perturbation wave function minimizes the second-order energy.

We have not reported specific information on the structure of the first-order wave function $|\psi_u\rangle$, on the grounds that this has less direct physical significance than the measurables or near-measurables we do report.

Table I summarizes our convergence studies at $R = 1.40$ a.u.: for each g,u basis-set pair indicated by Bishop-Cheung indices in the first column, we have tabulated the total number of basis functions, the dipole moments (in units of 10^{-4} debye) for Schemes 1 and 2, and the zeroth-order energy (a.u.). As expected, since the agreement of Schemes 1 and 2 is a test of completeness in the u portion of the Hilbert space, changes in the u basis set have a marked effect on this agreement. Changes in the u basis set, especially changes in the number of func-

TABLE I. Dipole moment vs basis set at $R = 1.40$ a.u. Basis sets (g, u) (notation of Bishop and Cheung); dipole moments μ (10^{-4} debye) for Schemes 1 and 2.

| Basis set | | Number of | Dipole moment ($\times 10^4$) | | Energy |
(g)	(u)	functions	Scheme 1	Scheme 2	ϵ_g^0 (a.u.)
(666 | 6)	(666 | 6)	180,150	8.5086	8.5085	$-1.174\,475$
(666 | 6)	(666 | 5)	180,90	8.5049	8.5049	$-1.174\,475$
(555 | 5)	(666 | 6)	108,150	8.5084	8.5086	$-1.174\,474$
(555 | 5)	(555 | 5)	108,90	8.5049	8.5050	$-1.174\,474$
(555 | 5)	(444 | 4)	108,48	8.5121	8.5176	$-1.174\,474$
(444 | 4)	(555 | 5)	66,90	8.4994	8.4982	$-1.174\,471$
(444 | 4)	(444 | 4)	66,48	8.5066	8.5109	$-1.174\,471$
(444 | 4)	(333 | 3)	66,24	8.5568	8.4797	$-1.174\,471$
(434 | 4)	(434 | 4)	63,46	8.5006	8.5087	$-1.174\,471$
(434 | 4)	(333 | 4)	63,42	8.4315	8.4328	$-1.174\,471$
(333 | 4)	(434 | 4)	57,46	8.4952	8.4968	$-1.174\,456$
(333 | 4)	(333 | 4)	57,42	8.4274	8.4210	$-1.174\,456$
(333 | 3)	(444 | 4)	33,48	8.4951	8.4934	$-1.174\,364$
(333 | 3)	(333 | 4)	33,42	8.4225	8.4181	$-1.174\,364$
(333 | 3)	(333 | 3)	33,24	8.5501	8.4681	$-1.174\,364$
(323 | 3)	(333 | 4)	31,42	8.4226	8.4175	$-1.174\,363$
(323 | 3)	(323 | 4)	31,36	8.4366	8.4043	$-1.174\,363$
(323 | 3)	(332 | 4)	31,36	8.3886	8.4062	$-1.174\,363$
(323 | 3)	(323 | 3)	31,22	8.5588	8.4682	$-1.174\,363$
(332 | 3)	(332 | 4)	31,36	8.3895	8.4089	$-1.174\,363$
(332 | 3)	(332 | 3)	31,22	8.5478	8.4741	$-1.174\,363$

tions with $s = 2$, also affect the value of the dipole moment strongly, until a u basis size of about 90 is reached. Changes in the g basis size, on the other hand, have little or no effect on the value or convergence of the results for bases larger than (444/4) (66 g functions).

From these studies we conclude that the dipole moment of HD at 1.400 a.u. is $(8.5086 \pm 0.004) \times 10^{-4}$ debye. This value is in sufficiently good agreement with the results of Ford and Browne[2] (8.371×10^{-4}) to establish the general validity of the theoretical results obtained by either their method or ours, but the difference (1.6%) is significantly larger than the probable uncertainty in our result. We note that in all the nonadiabatic perturbation calculations certain rovibronic energy denominators were replaced by average electronic term-difference values, in order to use closure in sums over vibration-rotation levels and reduce these to simpler matrix elements. This procedure may perhaps have introduced errors of the magnitude of the discrepancy with our variational result.

Table II shows the behavior of the dipole moment $\mu_e(R)$ vs R for three reasonably large basis sets. Both the energy and the discrepancy between the values for Schemes 1 and 2 show that at the extreme ends ($R = 0.50$, $R = 3.00$) even the largest basis used is not really adequate to achieve satisfactory convergence, but the situation is much better for $0.75 \lesssim R \lesssim 2.50$.

There are certain limitations to the validity of the theory and calculations at both small and large internuclear distances. For $R \to 0$, the formulation of the electronic model Hamiltonians given in Sec. III of Ref. 1 breaks down because the condition $|\vec{r}_i| \ll R/\alpha_0$ is not satisfied for all regions covered by the bound-state wave function, so that even in principle we cannot use the present theory to discuss that limit. In our actual calculations however the major limitations arise from our use of James-Coolidge[3] expansions, and from the use of a fixed orbital exponent appropriate to $R \simeq R_e$. At the smallest R studied (0.5 a.u.), our use of the orbital exponent $\alpha = 0.95$, which is the value appropriate to $R = R_e$, has a noticeable effect on the convergence of the expansions, and there is correspondingly a 0.25% discrepancy between the dipole moments from Schemes 1 and 2. On the other end, for $R > 2.0$ a.u. the James-Coolidge expansion's explicit use of ρ to describe electron correlation becomes inadequate to simulate interatomic correlation which would be more properly represented by a valence-bond type of expansion; there is a 1.1% discrepancy between results of the two schemes at $R = 3.00$ a.u. (basis set A). Nevertheless the results should be good enough to provide accurate transition matrix elements for the vibrating rotor spectra.

TABLE II. HD dipole moment μ (10^{-4} debye) vs distance R, for three different basis sets.

R (a.u.)	μ, Scheme 1	μ, Scheme 2	Ford and Browne	Energy (a.u.)
	Basis set A :g, (666 | 6), 180 functions; u, (666 | 6), 150 functions			
0.50	23.876	23.830	27.390	−0.525 084
1.40	8.5086	8.5085	8.371	−1.174 475
2.50	6.6771	6.6855	6.375	−1.093 933
3.00	5.5690	5.6112	5.271	−1.057 307

Basis set B :g, (555 | 5), 108 functions; u, (666 | 6), 150 functions

R (a.u.)	μ, Scheme 1	μ, Scheme 2	Ford and Browne	Energy (a.u.)
0.50	22.913	22.856	27.390	−0.521 719
0.75	15.305	15.303	15.350	−0.976 310
0.80	14.174	14.173		−1.020 046
0.90	12.395	12.395		−1.083 640
1.00	11.107	11.108	10.926	−1.124 538
1.10	10.161	10.161		−1.150 056
1.20	9.4533	9.4536	9.305	−1.164 933
1.30	8.9180	8.9183	8.762	−1.172 345
1.35	8.6998	8.7001	8.556	−1.173 962
1.40	8.5084	8.5086	8.371	−1.174 474
1.45	8.3400	8.3403	8.172	−1.174 055
1.50	8.1915	8.1918	8.050	−1.172 853
1.60	7.9734	7.9738	7.763	−1.168 581
1.80	7.5840	7.5849	7.392	−1.155 065
2.00	7.3237	7.3259	7.091	−1.138 127
2.25	7.0282	7.0346		−1.115 628
2.50	6.6730	6.6883	6.375	−1.093 916
2.75	6.1924	6.2249		−1.074 249
3.00	5.5606	5.6212	5.271	−1.057 191

Basis set C :g (444 | 4), 66 functions; u, (555 | 5), 90 functions

R (a.u.)	μ, Scheme 1	μ, Scheme 2	Ford and Browne	Energy (a.u.)
0.50	19.536	19.414	27.390	−0.511 55
0.75	15.017	15.004	15.350	−0.976 16
1.00	11.075	11.071	10.926	−1.124 53
1.20	9.437	9.434	9.305	−1.164 93
1.30	8.906	8.904	8.762	−1.172 34
1.35	8.689	8.688	8.556	−1.173 96
1.40	8.4994	8.4982	8.371	−1.174 474
1.45	8.333	8.332	8.172	−1.174 05
1.50	8.186	8.186	8.050	−1.172 85
1.60	7.940	7.942	7.763	−1.168 58
1.80	7.584	7.590	7.392	−1.155 06
2.00	7.325	7.336	7.091	−1.138 11
2.50	6.653	6.710	6.375	−1.093 74
3.00	5.498	5.686	5.271	−1.056 17

IV. VIBRATION-ROTATION TRANSITION MATRIX ELEMENTS

We can use the dipole moment function computed for HD (and displayed in Fig. 1 of Ref. 1) to compute vibration-rotation and pure rotation transition matrix elements for all three isotopic species HD, HT, and DT, since the functions for HT and DT are merely rescaled by the corresponding value of the parameter α_0. For the three species, the values for α_0 are as follows: $\alpha_0(\text{HD}) = 1.359\,94 \times 10^{-4}$; $\alpha_0(\text{HT}) = 1.807\,79 \times 10^{-4}$; $\alpha_0(\text{DT}) = 0.451\,668 \times 10^{-4}$. The data used to generate the dipole moment function for HD are the averages of the values from Schemes 1 and 2 given in Table II, basis set B [g, (555 | 5); u, (666 | 6)], except for the value at 0.50 a.u., where we took the result from basis set A, and the value at 3.00 a.u., where we averaged the results from basis set

A with those from B; we have used a smooth interpolating device to generate data at any desired R.

Given the electronic dipole moment functions $\mu_e(R)$ for the $X^1\Sigma^+$ ground states of these molecules, we need not use electronic potential functions computed with the present theory to generate the vibrational eigenstates and transition matrix elements. The vibrational eigenstates $R^{-1}F_{vJ}$ satisfy the equation

$$\left[-\left[\frac{\hbar^2}{2\mu'} \right] \frac{d^2}{dR^2} + \frac{J(J+1)\hbar^2}{2\mu'R^2} + U(X^1\Sigma^+;R) \right] F_{vJ}(R)$$

$$= E_{vJ}F_{vJ} \quad (4.1)$$

and it is easily proved that our effective potential $U(X^1\Sigma^+;R)$ is given by

TABLE III. Dipole vibration-rotation transition moments for HD, HT, and DT (10^{-4} debye; each entry lists, in order, the values for HD, HT, DT).

Band	P(4)	P(3)	P(2)	P(1)	R(0)	R(1)	R(2)	R(3)
					Line			
0-0	8.420	8.440	8.455	8.463	8.463	8.455	8.440	8.420
	11.232	11.256	11.273	11.283	11.283	11.273	11.256	11.232
	2.812	2.816	2.819	2.820	2.820	2.819	2.816	2.812
1-0	0.326	0.374	0.421	0.466	0.552	0.592	0.630	0.665
	0.439	0.497	0.554	0.609	0.715	0.764	0.810	0.853
	0.110	0.120	0.130	0.140	0.158	0.167	0.176	0.184
2-0	0.144	0.156	0.167	0.179	0.200	0.210	0.219	0.228
	0.187	0.200	0.214	0.227	0.253	0.265	0.276	0.286
	0.040 4	0.042 6	0.044 8	0.046 9	0.051 0	0.052 9	0.054 7	0.056 5
3-0	0.065 4	0.069 8	0.074 2	0.078 6	0.087 0	0.090 9	0.094 5	0.097 9
	0.082 0	0.087 1	0.092 3	0.097 4	0.107	0.112	0.116	0.120
	0.015 8	0.016 5	0.017 3	0.018 0	0.019 4	0.020 1	0.020 8	0.021 4
4-0	0.030 3	0.032 4	0.034 5	0.036 5	0.040 5	0.042 4	0.044 2	0.045 8
	0.037 1	0.039 4	0.041 8	0.044 2	0.048 7	0.050 9	0.052 9	0.054 8
	0.006 45	0.006 77	0.007 08	0.007 40	0.007 99	0.008 27	0.008 55	0.008 82
5-0	0.015 2	0.016 3	0.017 3	0.018 4	0.020 5	0.021 5	0.022 5	0.023 3
	0.018 1	0.019 3	0.020 5	0.021 7	0.024 1	0.025 2	0.026 2	0.027 2
	0.002 85	0.003 00	0.003 15	0.003 29	0.003 57	0.003 70	0.003 83	0.003 96
6-0	0.008 15	0.008 75	0.009 35	0.009 96	0.011 2	0.011 7	0.012 3	0.012 8
	0.009 47	0.010 1	0.010 8	0.011 5	0.012 7	0.013 4	0.013 9	0.014 5
	0.001 35	0.001 42	0.001 50	0.001 57	0.001 71	0.001 78	0.001 84	0.001 90

$$U(X^1\Sigma^+;R)=V_0(X^1\Sigma_g^+;R)+(2\mu)^{-1}\langle X^1\Sigma^+ \mid [\vec{P}_R^2 + \tfrac{1}{4}(\vec{p}_1^2+\vec{p}_2^2)+\tfrac{1}{2}(\vec{p}_1\cdot\vec{p}_2)] \mid X^1\Sigma^+ \rangle \qquad (4.2)$$

to within terms of order α_0^2, where $V_0(X^1\Sigma^+;R)$ is the Born-Oppenheimer potential for the $X^1\Sigma_g^+$ state of H_2 (computed using m_0 as electron mass) and is independent of isotopic mass. Both terms in Eq. (4.2) have been computed by Kolos and Wolniewicz;[5] $V_0(X^1\Sigma_g^+;R)$ is the entry labeled E in their Table III, and the second term in (4.2) is the entry labeled E_{nucl} (for the case of H_2), and need only be rescaled for the appropriate isotopic mass.

The resulting vibrational transition matrix elements, defined by

$$R(v,J)= \int_0^\infty dR\, F_{vJ+1}(R)\mu_e(R)F_{0J}(R)$$

and   (4.3)

$$P(v,J)= \int_0^R dR\, F_{vJ-1}(R)\mu_e(R)F_{0J}(R)\ ,$$

are presented for all three isotopes in Table III, for $v=0,1,\ldots,6$ and $J=(0),1,2,\ldots$. In each box the top entry is for HD, the second one for HT, and third for DT.

In Table IV we present a comparison for HD between our results, those of Ford and Browne,[2] and some available experimental values,[6-14] similar to Table VIII given

by Ford and Browne.[2] Our results appear to be in slightly better agreement with most of the vibration-rotation transition matrix elements measured by McKellar and co-workers[9,10] than do previous theoretical values, but we do not think this improvement is very significant. It is likely that a more elaborate calculation on the lines presented here, especially with optimized orbital exponents and allowing explicitly for valence-bond-type interatomic electron correlation at larger R values, would lead to small but significant changes in the curve for $\mu_e(R)$ and appreciable changes in the transition matrix elements.

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APPENDIX: EVALUATION OF NEW MOLECULAR INTEGRALS

Nontrivial two-electron integrals in this problem may all be expressed in terms of two fundamental molecular integrals defined as follows:

TABLE IV. Comparison of experimental and theoretical dipole transition moments for HD in units of 10^{-4} debye.

Band/line	Experimental results								Wolniewicz (Ref. 15)	Theoretical values Ford and Browne (Ref. 2)	This work
	Nelson and Tabisz (Ref. 7)	Essenwanger and Gush (Ref. 14)	McKellar, Johns, Majewski, and Rich (Ref. 13)	Bejar and Gush (Ref. 8)	McKellar (Ref. 9)	Rich, Johns, and McKellar (Ref. 11)	McKellar, Goetz, and Ramsay (Ref. 10)	Trauger and Mickelson (Ref. 12)			
0-0											
R(0)	8.78 ±0.20		8.18 ±0.26						8.36	8.31	8.463
R(1)	8.47 ±0.20		7.9 ±0.4						8.38	8.30	8.455
R(2)	10.21 ±0.20								8.39	8.29	8.440
R(3)		8.47 ±0.09							8.41	8.26	8.420
R(5)		8.1 ±0.8									
R(6)		9.9 ±0.3									
1-0											
P(3)				0.330 ±0.04		0.340 ±0.022				0.401	0.374
P(2)				0.405 ±0.03		0.379 ±0.012				0.445	0.421
P(1)				0.450 ±0.03		0.435 ±0.011				0.485	0.466
R(0)				0.515 ±0.02	0.42 ±0.08	0.504 ±0.012			0.598	0.560	0.552
R(1)				0.550 ±0.03	0.68 ±0.12	0.533 ±0.014			0.628	0.594	0.592
R(2)				0.615 ±0.03					0.656	0.623	0.630
R(3)				0.655 ±0.03	0.72 ±0.14	0.609 ±0.013			0.685	0.650	0.665
R(4)					0.70 ±0.14	0.642 ±0.026					
R(5)						0.664 ±0.080					
2-0											
P(1)					0.17 ±0.02					0.176	0.179
R(0)					0.19 ±0.02				0.160	0.192	0.200
R(1)					0.20 ±0.02				0.166	0.199	0.210
3-0											
R(0)					0.0795±0.0035				0.100	0.082	0.0870
R(1)					0.0800±0.005				0.102	0.084	0.0909
4-0											
P(2)							0.0397±0.0026	0.0329±0.0003		0.035	0.0344
P(1)					0.0465±0.003		0.0417±0.0024	0.0349±0.0003		0.038	0.0365
R(0)							0.0425±0.0021	0.0386±0.0004	0.056	0.039	0.0405
R(1)							0.0459±0.0026	0.0410±0.0004	0.056	0.040	0.0424
R(2)							0.0514±0.0053	0.0425±0.0004	0.055	0.042	0.0442
R(3)									0.053	0.042	0.0458
5-0											
R(0)							0.0207±0.0020	0.0195±0.0002		0.023	0.0205
R(1)							0.0214±0.0014	0.0207±0.0002		0.023	0.0215
R(2)							0.0231±0.0021			0.024	0.0224
6-0											
R(1)								0.0110±0.004		0.014	0.0117

$$Y^{\mathrm{T}}(M;N_1,N_2,K_1,K_2;A)$$

$$\equiv (4\pi^2)^{-1}\int_1^\infty d\xi_1 \int_1^\infty d\xi_2 \int_{-1}^{+1} d\eta_1 \int_{-1}^{+1} d\eta_2 \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2 (1/\rho)\cos M(\varphi_2-\varphi_1)$$

$$\times [(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{M/2}$$

$$\times \exp[-A(\xi_1+\xi_2)]\xi_1^{N_1}\xi_2^{N_2}\eta_1^{K_1}\eta_2^{K_2} \tag{A1}$$

and

$$X^{\mathrm{T}}(M;N_1,N_2,K_1,K_2;A)$$

$$\equiv (4\pi^2)^{-1}\int_1^\infty d\xi_1 \int_1^\infty d\xi_2 \int_{-1}^{+1} d\eta_1 \int_{-1}^{+1} d\eta_2 \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2 (1/\rho)\cos M(\varphi_2-\varphi_1)(\xi_1^2-\eta_1^2)^{-1}$$

$$\times [(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{M/2}$$

$$\times \exp[-A(\xi_1+\xi_2)]\xi_1^{N_1}\xi_2^{N_2}\eta_1^{K_1}\eta_2^{K_2} . \tag{A2}$$

The integrals Y^{T} are well known and arise from matrix elements of both h_e^0 and h_e'; the integrals X^{T} are the new ones, arising from matrix elements of h_e'. Using the well-known Neumann[16] expansion for $(1/\rho)$, they may both be reduced to sums over certain basic radial integrals G_{11},G_{21}:

$$Y^{\mathrm{T}}(M;N_1,N_2,K_1,K_2;A)=\sum_{L=M}^{(K_<+M)}(2L+1)\left[\frac{(L-M)!}{(L+M)!}\right]^2 C^P(K_1;L,M)C^P(K_2;L,M)G_{11}(L,M;N_1,N_2;A) \tag{A3a}$$

(where $K_<$ is the lesser of K_1,K_2), and

$$X^{\mathrm{T}}(M;N_1,N_2,K_1,K_2;A)=\sum_{L=M}^{K_2+M}(2L+1)\left[\frac{(L-M)!}{(L+M)!}\right]^2 C^P(K_2;L,M)G_{21}(L,M;K_1;N_1,N_2;A) . \tag{A3b}$$

The coefficients $C^P(K;L,M)$ are just the integrals defined

$$C^P(K;L,M)\equiv \int_{-1}^{+1} d\eta\, \eta^K(1-\eta^2)^{M/2}P_L^M(\eta) ;$$

they vanish if $(L-M)>K$, or if $(L-M),K$ have different parity, and their nonvanishing values are

$$C^P(K;L,M)=\phi_m(K+L)\left[\frac{(L+M)!2^{L-M+2}K!\left[\dfrac{K+L-M}{2}+1\right]!}{(L-M)!(K+L-M+2)!\left[\dfrac{K-L+M}{2}\right]!}\right] \tag{A4a}$$

where

$$\phi_0(J)=1, \quad \phi_1(J)=1/(J+2), \quad \phi_2(J)=1/(J+1)(J+3) ,$$

$$\phi_3(J)=1/[(J)(J+2)(J+4)], \quad \text{etc.} \tag{A4b}$$

(we only need to compute $M=0,1,2,3$ for the bases we use). The basic radial integrals G_{11},G_{21} are defined

$$G_{11}(L,M;N_1,N_2,;A)\equiv \int_1^\infty d\xi_1 \int_1^\infty d\xi_2 \xi_1^{N_1}\xi_2^{N_2}e^{-A(\xi_1+\xi_2)}q_L^M(\xi_>)p_L^M(\xi_<) \tag{A5a}$$

and

$$G_{21}(L,M;K;N_1,N_2;A)\equiv \int_1^\infty d\xi_1 \int_1^\infty d\xi_2 \xi_1^{N_1}\xi_2^{N_2}e^{-A(\xi_1+\xi_2)}q_L^M(\xi_>)p_L^M(\xi_<)C^{PQ}(K;L,M;\xi_1) , \tag{A5b}$$

where $(\xi_>,\xi_<)$ are, respectively, the greater and lesser of ξ_1,ξ_2; the functions $p_L^M(x),q_L^M(x)$ are related to the associated Legendre functions $P_L^M(x),Q_L^M(x)$ of first and second kind[17] by

$$p_L^M(x)\equiv (x^2-1)^{M/2}P_L^M(x), \quad q_L^M(x)\equiv (-1)^M(x^2-1)^{M/2}Q_L^M(x) \tag{A6}$$

and the function $C^{PQ}(K;L,M;x)$ is defined

$$C^{PQ}(K;L,M,x)\equiv x^{-1}\{\tfrac{1}{2}[1+(-1)^{K-L+M}]\}\int_{-1}^{+1}\frac{\eta^K(1-\eta^2)^{M/2}p_L^M(\eta)}{x-\eta} . \tag{A7}$$

$G_{11}(L,M;N_1,N_2;A)$ is just equal to the function $H_L^M(N_1,N_2;A)$ defined by James and Coolidge.[3]

The functions $C^{PQ}(K;L,M;x)$ may be generated efficiently using the recursion relation

$$C^{PQ}(K+1;L,M;x)=(2L+1)^{-1}[(L-M+1)C^{PQ}(K;L+1,M;x)+(L+M)C^{PQ}(K;L-1,M;x)] \tag{A8a}$$

and the easily proved formula

$$C^{PQ}(0;L,M;x)=(2/x)q_L^M(x) . \tag{A8b}$$

The radial integrals G_{11},G_{21} may be written in the forms

$$G_{11}(L,M;N_1,N_2;A)=\int_1^\infty dx\, x^{N_1}e^{-Ax}F^{PQI}(N_2;L,M;A,x) \tag{A9a}$$

and

$$G_{21}(L,M;K;N_1,N_2;A)=\int_1^\infty dx\, x^{N_1}e^{-Ax}F^{PQI}(N_2;L,M;A,x)C^{PQ}(K;L,M;x) , \tag{A9b}$$

where the functions F^{PQI} are defined

$$F^{PQI}(N_2;L,M;A,x)\equiv \left[q_L^M(x)\int_0^x dy\, y^{N_2}e^{-Ay}p_L^M(y)+p_L^M(x)\int_x^\infty dy\, y^{N_2}e^{-Ay}q_L^M(y)\right] . \tag{A10}$$

The final integrations [Eqs. (A9)] are performed numerically, but to do so accurately we must take into account the logarithmic character of the integrand factors $F^{PQI}(x)$ and $C^{PQ}(x)$ near $x=1$: Defining $z=x-1$, we break the integrals into two pieces, $0\leq z\leq z_0$ and $z_0\leq z<\infty$; the outer piece ($z_0\leq z<\infty$) is done by direct Gauss-Laguerre quadrature in the scaled variable $t=A(z-z_0)$, and for the inner piece we make the mapping transform $z=z_0e^{-u}$, $dz=-z_0e^{-u}$, $0\leq u<\infty$, and use Gauss-Laguerre quadrature in u. Provided tables of the integrand factors $F^{PQI}(x)$ and $C^{PQ}(x)$ are computed efficiently and accurately at the required quadrature points, both sets of integrals (A9a) and (A9b) may be accurately evaluated with 24- to 32-point quadratures for each range; the results, depending on the indices for F^{PQI} and C^{PQ} and the power N_1, are stable and precise to 8−10 significant figures for break points z_0 in the range $0.75\lesssim z\lesssim 2.00$.

$F^{PQI}(N_2,L,M;A,x)$ is computed most efficiently by direct assembly from its four components for $z=(x-1)\gtrsim 0.015-0.020$. $p_L^M(x)$ and the indefinite integral containing it are computed with suitable recursion relations, standard methods and the convenient polynomial expansion[18]

$$p_L^M(1+z)=z^m\left[\frac{(L+M)!}{(L-M)!}\right]\sum_{J=0}^L \frac{(L+J)!}{(L-J)!J!(J+M)!}\left[\frac{z}{2}\right]^J . \tag{A11}$$

$q_L^M(x)$ is generated using downward recursion relations and the hypergeometric series expansion[19]

$$q_L^M(x)=\frac{2^L L!(L+M)!(x^2-1)^M}{(2L+1)!x^{L+M+1}}\left[1+\frac{(L+M+2)(L+M+1)}{(2L+3)}(2x^2)^{-1}\right.$$
$$\left.+\frac{(L+M+4)(L+M+3)(L+M+2)(L+M+1)}{(2L+5)(2L+3)2!}(2x^2)^{-2}+\cdots\right] . \tag{A12}$$

The incomplete integrals

$$F^{QI}(N_2;L,M;A,x)\equiv \int_y^\infty dy\, y^{N_2}e^{-Ay}q_L^M(y) \tag{A13}$$

are computed by recursion relations from tables of $F^{QI}(N;0,0;A,x)$ and $F^{QI}(0;L,0;A,x)$, and these in turn are expressed by term-by-term integration using the expansion (A12) in terms of the standard functions $E_n(Ax)$ and $\alpha_n(Ax)$ defined by Abramowitz and Stegun.[17]

For $z\lesssim 0.015-0.020$, direct computation of F^{PQI} from its components is not accurate; instead we write

$$F^{PQI}(N_2,L,M;A,x)=p_L^M(x)\int_1^\infty dy\, y^{N_2}e^{-Ay}q_L^M(y)-S^{PQI}(N_2;L,M;A,z) , \tag{A14}$$

where $z=x-1$ and

$$S^{PQI}(N_2;L,M;A,z)\equiv e^{-A}\int_0^z du\,(1+u)^{N_2}e^{-Au}[q_L^M(1+u)p_L^M(1+z)-q_L^M(1+z)p_L^M(1+u)] \tag{A15}$$

and we compute S^{PQI} directly, using expressions for $q_L^M(1+z)$ valid for small z, and performing certain cancellations in the series obtained for S^{PQI} analytically. The relevant expression for $q_L^M(1+z)$ at small z is[20]

$$q_L^M(1+z)=(-1)^M\left[\tfrac{1}{2}p_L^M(1+z)\ln\left[\frac{2+z}{z}\right]-\omega_L^M(1+z)\right] \tag{A16}$$

where $p_L^M(1+z)$ is given by (A11) and ω_L^M is a polynomial in z of order $(L+M-1)$,

$$\omega_L^M(1+z)=(1-\delta_{M0})\sum_{I=0}^{M-1}\left[\frac{(-1)^{M-I-1}2^{M-1}(L+M)!(L+I-M)!(M-I-1)!}{(L-M)!(L+M-I)!I!}\right]\left[\frac{z}{2}\right]^I$$

$$+z^M\sum_{J=0}^{L-1}\left[\frac{(L+M)!(L+J)!}{(L-M)!(L-J)!J!(J+M)!}\right]\Delta(L,M;J)\left[\frac{z}{2}\right]^J,\tag{A17}$$

where the coefficients $\Delta(L,M;J)$ are computed by the relations

$$\Delta(L,M;L-1)=\frac{1}{L+M},\tag{A18a}$$

$$\Delta(L,M+1;J)=[2(J+1)(2L+1)]^{-1}[(L+J+2)(L+J+1)\Delta(L+1,M;J+1)-(L-J-1)(L-J)\Delta(L-1,M;J+1)];\tag{A18b}$$

$$\Delta(L,0;J)=\zeta_L-\zeta_J,\tag{A18c}$$

where

$$\zeta_n=\sum_{k=1}^{n}(1/k).$$

Since cancellations in the resulting expressions for S^{PQI} can still occur to 9—12 decimal places, it is necessary to use quadruple-precision arithmetic at certain points to ensure the accuracy required (our routines otherwise use only double-precision arithmetic throughout). To evaluate the first term in Eq. (A14), we compute F^{PQI} near the limiting region ($z\approx0.015-0.020$) by direct computation methods and then add to it the value for S^{PQI} at the same point.

Using the above techniques we have been able to compute both G_{11} and G_{21} to somewhat higher precision (8—10 significant figures) and for a wider range of indices ($L-M\lesssim30$, $N_1,N_2\lesssim20$) than is achieved by the usual routines for G_{11} (based on upward recursion relations given by James and Coolidge,[3] and using quadruple-precision arithmetic throughout). For computation of G_{11} alone, our procedure is probably about a factor of 10 more costly since it has large core storage requirements and involves recursion of integrand functions rather than only of the final integrals.

[1]W. R. Thorson, J. H. Choi, and S. K. Knudson, preceding paper [Phys. Rev. A 31, 22 (1984)].

[2]A. L. Ford and J. C. Browne, Phys. Rev. A 16, 1992 (1977).

[3]H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933); 3, 129 (1935).

[4]D. M. Bishop and L. M. Cheung, Phys. Rev. A 18, 1846 (1978).

[5]W. Kolos and L. Wolniewicz, J. Chem. Phys. 41, 3663 (1964); cf. especially Table III.

[6]M. Trefler and H. P. Gush, Phys. Rev. Lett. 20, 703 (1968).

[7]J. B. Nelson and G. C. Tabisz, Phys. Rev. A 28, 2157 (1983); see also Phys. Rev. Lett. 48, 1393 (1982).

[8]J. Bejar and H. P. Gush, Can. J. Phys. 52, 1669 (1974).

[9]A. R. W. McKellar, Can. J. Phys. 51, 389 (1973); Astrophys. J. 185, L53 (1973); Can. J. Phys. 52, 1144 (1974).

[10]A. R. W. McKellar, W. Goetz, and D. A. Ramsay, Astrophys. J. 207, 663 (1976).

[11]N. H. Rich, J. W. C. Johns, and A. R. W. McKellar, J. Mol. Spectrosc. 95, 432 (1982).

[12]J. T. Trauger and M. E. Mickelson, Icarus 56, 176 (1983).

[13]A. R. W. McKellar, J. W. C. Johns, W. Majewski, and N. H. Rich, Can. J. Phys. (to be published).

[14]P. Essenwanger and H. P. Gush, Can. J. Phys. (to be published).

[15]L. Wolniewicz, Can. J. Phys. 53, 1207 (1975); 54, 672 (1976).

[16]See, for example, E. W. Hobson, The Theory of Spherical and Ellipsoidal Harmonics (Cambridge University, Cambridge, England, 1931), Chap. X, Sec. 245 (reprinted by Chelsea, New York, 1955).

[17]M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, Natl. Bur. Stand. (U.S.) Appl. Math. Ser. Circ. No. 55 (U.S. GPO, Washington, D.C., 1964), Chap. 8.

[18]This result is a generalization for nonzero M of the expansion given by E. W. Hobson, The Theory of Spherical and Ellipsoidal Harmonics, Ref. 16, Chap. II, p. 22, for $M=0$.

[19]M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, Ref. 17, Chap. 8, No. 8.1.3.

[20]This and its related formulas are generalizations of the expression given by E. W. Hobson, The Theory of Spherical and Ellipsoidal Harmonics, Ref. 16, Chap. II, Sec. 34, pp. 54 and 55, for $M=0$. Note, however, that Hobson denotes our ω_L^0 as W_{L-1}.