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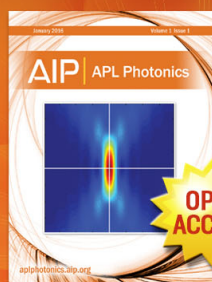
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# Accurate Compton profiles for $H_2$ and $D_2$ including the effects of electron correlation and molecular vibration and rotation<sup>a)</sup>

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Accurate isotropic Compton profiles  $J(q, R)$  for  $H_2(X^1\Sigma_g^+)$  are calculated for 22 internuclear separations from the 126 configuration wavefunctions of Liu. These profiles, supplemented by the united atom and separated atom profiles, are then rigorously averaged over vibration-rotation wavefunctions computed by direct numerical solution of the radial Schrödinger equation using nearly exact potential energy curves including adiabatic and relativistic corrections. These averages are performed for a large number of vibration-rotation states of  $H_2$  and the ground vibration-rotation state of  $D_2$ . It is shown that the effects of averaging Compton profiles over vibration-rotation states are significant and cannot be neglected. The isotope effect is shown to be smaller than the vibration-rotation effect. The peak of the calculated  $H_2$  Compton profile for the ground vibration-rotation state is found to be in excellent agreement with the very recent high energy electron impact measurements of Lee. A number of expansion techniques for vibration-rotation averaging, including a new, very simple, and reasonably accurate delta approximation, are presented.

## I. INTRODUCTION

Compton scattering offers a useful approach to the study of electron momentum distributions in atomic and molecular systems. There is now a rapidly growing literature on the subject. A recent book<sup>1</sup> contains an excellent set of review articles on various aspects of Compton scattering.

It is of obvious importance to calculate highly accurate Compton profiles for small systems. Such calculations provide a reference for experimental work and also serve to probe the validity of the theory—in particular, the impulse approximation (IPA).

The hydrogen molecule is an excellent system for such studies since both accurate theoretical and experimental work is feasible. Unfortunately, a discrepancy between theory and experiment has persisted to date. Eisenberger<sup>2</sup> made experimental x-ray studies of the Compton profile of molecular hydrogen in its ground electronic state ( $X^1\Sigma_g^+$ ). There was however a substan-

tial discrepancy between his results and the calculated results of Henneker.<sup>3</sup> The latter reported profiles calculated from a self-consistent-field (SCF) wavefunction due to Cade and Wahl<sup>4</sup> and a multiconfiguration self-consistent-field (MCSCF) wavefunction constructed by Das and Wahl.<sup>5</sup> The SCF profile was well outside Eisenberger's error bounds and the MCSCF profile was in even greater disagreement with the experimental results in the vicinity of the profile peak. Brown and Smith<sup>6</sup> then computed a profile from a 39 natural-configuration wavefunction built by Liu.<sup>7</sup> This profile gave better agreement with Eisenberger's experimental results than the SCF and Das-Wahl functions. Nevertheless, the peak of the Brown-Smith profile was still 1% larger than Eisenberger's result which had been estimated to have an experimental error of no more than 0.7%.

All the theoretical calculations mentioned above had been made from electronic wavefunctions appropriate to an internuclear separation  $R$  equal to the equilibrium one  $R = R_e = 1.4$  bohr. Ulsh *et al.*<sup>8</sup> pointed out the importance of vibrational effects on the Compton profile. They made a rough calculation based on the Wang<sup>9</sup> electronic wavefunction, and used a Taylor series expansion to estimate the vibrational correction. Their conclusion was that the vibrational correction to the theoretic-

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cal Compton profile raises it by approximately 1% in the low-momentum region and thereby *increases* the disagreement between theory and experiment. The Compton profile was then remeasured using high energy electron impact techniques by Ulsh, Wellenstein, and Bonham.<sup>10</sup> Their results were in essential agreement with Eisenberger's x-ray work.<sup>2</sup>

Braun-Keller and Epstein<sup>11</sup> have recently made another study of vibrational effects again using the Wang<sup>9</sup> electronic wavefunction, and harmonic oscillator and Morse vibrational wavefunctions. They conclude that the vibrational effect on the Compton profile is much smaller than that found by Ulsh *et al.*<sup>8</sup> and that "it will probably not contribute significantly to any discrepancy between theory and experiment." However, Whangbo *et al.*<sup>12</sup> have recently shown that the Braun-Keller and Epstein parameterization of the Morse potential for H<sub>2</sub> does not properly reflect the anharmonicities of the true potential. The latter property of the potential had been shown<sup>8,12</sup> to be primarily responsible for the vibrational contribution to the peak of the Compton profile. Hence, Braun-Keller and Epstein's results<sup>11</sup> have been considered<sup>12</sup> to be unreliable.

Very recently, Lee<sup>13,14</sup> has repeated the electron impact experiments of Ulsh, Wellenstein, and Bonham.<sup>10</sup> He reports a Compton profile that differs from the Eisenberger<sup>2</sup> and the Ulsh, Wellenstein, and Bonham<sup>10</sup> profiles.

In this paper we compute the Compton profile of H<sub>2</sub> from the 126 configuration wavefunctions of Liu.<sup>15</sup> The calculations are made at 22 different values of the internuclear separation. The resulting profiles  $J(q, R)$  are then rigorously averaged over vibrational and rotational wavefunctions computed by direct numerical solution of the radial Schrödinger equation using the nearly exact potential curve including adiabatic and relativistic corrections that was compiled by Bishop and Shih<sup>16</sup> from the calculations of Kolos and Wolniewicz.<sup>17</sup> Our calculated Compton profile peak for the ground vibrational and rotational state of H<sub>2</sub> is in excellent agreement with Lee's experimental results.<sup>13,14</sup> Thus, the long-standing discrepancy between theory and experiment seems to have been resolved in part. We also present results for D<sub>2</sub>.

In Sec. II the electronic wavefunctions of Liu,<sup>15</sup> the calculation of the profiles, and the averaging over the vibrational and rotational wavefunctions is described. The results are presented in Sec. III. Comparison with experiment, analysis of vibrational and rotational effects, and a development of various expansion techniques including a new delta approximation for rough vibration-rotation averaging are presented in Sec. IV. Section V contains summarizing remarks.

## II. METHOD OF CALCULATIONS

In order to calculate the Compton profile we make the usual impulse approximation (IPA). The IPA assumes that the binding energy of the electron in the target atom or molecule is insignificant in comparison with the energy imparted to it during the scattering process. With-

in the IPA the isotropic Compton profile is given by

$$J(q) = \frac{1}{2} \int_{|q|}^{\infty} I_0(p) p^{-1} dp, \quad (1)$$

where  $q$  is the projection of the initial electron momentum  $p$  on the scattering vector of the incident particle, and  $I_0(p)$  is the radial momentum distribution. To obtain  $I_0(p)$  from an electronic wavefunction we use the prescription suggested and developed by Benesch and Smith.<sup>18</sup> Thus,

$$I_0(p) = \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi p^2 \rho(\mathbf{p} | \mathbf{p}), \quad (2)$$

$$\rho(\mathbf{p} | \mathbf{p}') = (2\pi)^{-3} \int e^{-i\mathbf{p} \cdot \mathbf{r} + i\mathbf{p}' \cdot \mathbf{r}} \gamma(\mathbf{r} | \mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (3)$$

$\rho(\mathbf{p} | \mathbf{p}')$  is the Fourier transform of the spin-traced one-electron density matrix  $\gamma(\mathbf{r} | \mathbf{r}')$ , which is defined as

$$\gamma(\mathbf{r}_1 | \mathbf{r}_1') = N \int \psi(X_1, X_2, \dots, X_N) \times \psi^*(X_1', X_2', \dots, X_N') d\xi_1 dX_2 \dots dX_N. \quad (4)$$

$X_i$  denotes the combined space and spin coordinates of the  $i$ th electron ( $\mathbf{r}_i, \zeta_i$ ). In the case of H<sub>2</sub> the electronic wavefunctions  $\psi(X_1, \dots, X_N)$  are parametrically dependent on the internuclear separation  $R$  and hence  $I_0(p)$  and  $J(q)$  are also parametrically dependent on  $R$ . Therefore, the notation we use in this paper for the Compton profile is  $J(q, R)$ . Note that<sup>18</sup>

$$\int_0^{\infty} J(q, R) q^n dq = \frac{1}{2(n+1)} \langle p^n \rangle (R), \quad \text{for } 0 \leq n \leq 4, \quad (5)$$

and that  $J(0) = \frac{1}{2} \langle p^{-1} \rangle (R)$ , where  $\langle R \rangle$  denotes that the expectation values  $\langle p^n \rangle$  are parametrically dependent on  $R$ .

The electronic wavefunctions we use are the configuration-interaction (CI) wavefunctions constructed by Liu<sup>15</sup> for 22 different values of  $R$  ranging from 0.8 to 8.0 a.u. Note that the wavefunction for  $R = R_e = 1.4$  a.u. is different from that<sup>7</sup> used by Brown and Smith.<sup>6</sup> The one-particle space for the Liu CI wavefunctions is that spanned by an extended basis set of Slater-type functions (STF) centered on the hydrogen nuclei. The basis set for each hydrogen atom consists of two sets of  $s$  functions ( $1s, 2s; 1s', 2s'$ ), two sets of  $p$  functions ( $2p; 2p', 3p'$ ), and one set of  $d$  functions ( $3d, 4d$ ). This leads to a set of nine  $\sigma_g$ , nine  $\sigma_u$ , five  $\pi_u$ , five  $\pi_g$ , two  $\delta_g$ , and two  $\delta_u$  molecular orbitals (MO) which are orthonormal and adapted to  $D_{\infty h}$  symmetry. The wavefunctions contain all possible configurations of  ${}^1\Sigma_g^+$  symmetry that can be constructed from these MO's. The total number of configurations is 126. Details about the choice of exponents for the STF's are given elsewhere.<sup>15</sup> Liu<sup>15</sup> has compared his results in detail with the very accurate Born-Oppenheimer results of Kolos and Wolniewicz.<sup>17</sup> Here we merely note that the deviation of Liu's results from the near-exact potential energy curve increases monotonically from  $1.5 \times 10^{-5}$  a.u. at  $R = 8.0$  a.u. to  $9.1 \times 10^{-4}$  a.u. at  $R = 0.9$  a.u. The CI potential curve is very nearly parallel to the exact one near the equilibrium internuclear separation  $R_e$ .

The Compton profiles calculated as described above

were then supplemented with the profile at  $R=0$  a.u. (i.e., the  $1^1S$  state of He, the united atom) computed by Benesch<sup>19</sup> from the explicitly correlated wavefunctions of Bonham and Kohl,<sup>20</sup> and with the exact nonrelativistic separated atom (H+H) profile given by

$$J(q, \infty) = 16/[3\pi(1+q^2)^3]. \quad (6)$$

The averaging of  $J(q, R)$  over the vibrational and rotational motion was performed as follows: Numerical wavefunctions for the vibration-rotation states were calculated by direct numerical solution of the radial Schrödinger equation for the nuclear motion. The numerical solution was carried out by the Numerov technique as described by Cooley<sup>21</sup> and Cashion<sup>22</sup> using 1921 mesh points equally spaced between  $R=0.4$  and  $R=10.0$  a.u. with a step size of 0.005 a.u. The potential curves for H<sub>2</sub> and D<sub>2</sub> used in the radial equation were obtained on the above mesh by seven-point Lagrangian interpolation of the 157 data points (between  $R=0.4$  and  $R=10.0$  a.u.) given by Bishop and Shih.<sup>16</sup> The latter authors compiled their nearly exact curves from the Born-Oppenheimer results of Kolos and Wolniewicz (KW)<sup>17</sup> and the adiabatic and relativistic corrections computed by KW.<sup>17</sup> The profiles were then averaged by simple numerical integration

$$J(q)_{v,J} = \langle vJ | J(q, R) | vJ \rangle, \quad (7)$$

where  $v$  and  $J$  are the vibrational and rotational quantum numbers, respectively, and  $\langle R | vJ \rangle = \phi_{v,J}(R)$  is the vibration-rotation wavefunction. This integration was done with the trapezoidal rule on the same 1921 point mesh described above.  $J(q, R)$  values were generated on this mesh as follows: The available values of  $J(q, R)$  at the 24 values, including the united-atom and separated-atom limit, of  $R$  were fit to a cubic spline under tension<sup>23</sup> (tension parameter = 1) approximating  $R = \infty$  by  $R = 500$  a.u. The spline was then used to generate  $J(q, R)$  values at the same 157  $R$  values at which the Bishop-Shih<sup>16</sup> potential curves were given. Finally five-point Lagrangian interpolation was used on this 157 point mesh to generate a tabulation on the 1921 point mesh.

### III. RESULTS

The Compton profiles  $J(q, R)$  for the 22  $R$  values and a range of  $q$  values are presented in Table I. The united atom profile  $J(q, 0)$  may be found in Benesch's paper.<sup>19</sup> The separated atom profile  $J(q, \infty)$  may be trivially calculated from Eq. (6) and is included in Table I. Within the IPA  $J(q, R)$  is an even function of  $q$ , so only nonnegative values of  $q$  are included in the table. Since we are working within the Born-Oppenheimer approximation, differences between H<sub>2</sub> and D<sub>2</sub> show up only in the vibrationally averaged values.

The vibrationally and rotationally averaged Compton profiles  $J(q)_{v,J}$  for H<sub>2</sub> are listed in Table II for a range of  $q$  values and for  $(v, J) = (0, J)$ ,  $J = 0, 1, \dots, 7$  and for  $(v, J) = (v, 0)$   $v = 0, 1, \dots, 14$ .  $J(q)_{00}$  for D<sub>2</sub> is listed in Table III.

The computed vibration-rotation energy eigenvalues  $E_{v,J}$  for the above mentioned  $(v, J)$  states are listed in Table IV. The data presented in the table have been

rounded to six decimals. More accurate values are available on request.

Note that all values quoted in this paper are in atomic units. Liberal use is made of standard computer notation as exemplified by

$$0.827852E-01 = 0.827852 \times 10^{-1}. \quad (8)$$

### IV. DISCUSSION

Examination of Table I shows a number of interesting trends. The profile peak  $J(0, R)$  increases monotonically from 1.32 at  $R=0.8$  to 1.87 at  $R=3.0$  a.u. and decreases monotonically from 1.868 at  $R=3.5$  a.u. to 1.698 at  $R=\infty$ . Inverse interpolation shows that the maximum of  $J(0, R)$  is 1.8722 at  $R=3.275$  a.u.  $J(0.5, R)$  shows different behavior. It is essentially flat from  $R=0.8$  to  $R=8.0$  a.u.; starting from 0.8614 at  $R=0.8$  a.u., it increases to a local maximum of 0.8864 at  $R=1.525$  a.u., decreases to a local minimum of 0.8294 at  $R=3.75$  a.u., and then increases to 0.8692 at  $R=\infty$ . It should be noted that  $J(q, 8.0) \approx J(q, \infty)$  for all  $q$ .

Comparison of  $J(q, R_e) = (J(q, 1.4))$  in Table I with  $J(q)_{00}$  in Table II shows that averaging over the ground vibration-rotation wavefunction raises the profile peak by 0.95%. This is in very good agreement with the prediction of Ulsh *et al.*,<sup>8</sup> and confirms the contention of Whangbo *et al.*<sup>12</sup> that the Braun-Keller and Epstein<sup>11</sup> results are not reliable. It can be seen that the  $J(q, R_e)$  and  $J(q)_{00}$  curves cross<sup>24</sup> at some  $q$  value between 0.4 and 0.5. Table II shows that as the rotational quantum number increases for the  $v=0$  vibrational state the peak of the averaged profile is steadily raised.  $J(0)_{03}$  is 0.27% larger than  $J(0)_{00}$  and  $J(0)_{07}$  is 1.94% higher than  $J(0)_{00}$ . We also see that as  $v$  increases from 0 to 12 for the rotationless states  $J(0)_{v,0}$  increases, and then it decreases for  $v=13$  and 14.  $J(0)_{10}$  is 1.79% larger than  $J(0)_{00}$ ,  $J(0)_{50}$  is 8.46% larger than  $J(0)_{00}$ ,  $J(0)_{90}$  is 13.6% larger than  $J(0)_{00}$ ,  $J(0)_{12,0}$  is 15.0% larger than  $J(0)_{00}$ , and  $J(0)_{14,0}$  is 12.4% larger than  $J(0)_{00}$ . The obvious conclusion here is that averaging over the ground vibration-rotation wavefunction raises the profile peak as compared with that at the equilibrium internuclear distance  $R_e$ . Further, as one increases the rotational quantum number the averaged profile peak is raised. Similarly, the averaged profile peak is raised as the vibrational quantum number is increased until the vibrational quantum number gets quite large ( $v=12$ ) and then starts to decrease. The magnitudes of these shifts show that *vibrational and rotational averaging is significant and cannot be neglected*. The large shifts for high vibrational levels show that averaging is very important if theory is to be compared with experiment at high temperatures.

Comparison of  $J(q)_{00}$  for H<sub>2</sub> (see Table II) and  $J(q)_{00}$  for D<sub>2</sub> (see Table III) shows that *the isotope effect is smaller than the effect of vibrational and rotational averaging*. The D<sub>2</sub> profile peak is 0.27% lower than the H<sub>2</sub> profile peak in the ground vibration-rotation state. This difference seems to be somewhat smaller than present day experimental uncertainties ( $\sim 0.5\%$  at the peak).<sup>1,25</sup>

TABLE I. Compton profiles  $J(q, R)$  for H<sub>2</sub> and D<sub>2</sub>

$q/R$	0.80	1.00	1.10	1.20
0.0	1.31591	1.39100	1.42762	1.46340
0.1	1.29235	1.36353	1.39809	1.43176
0.2	1.22485	1.28522	1.31413	1.34202
0.3	1.12220	1.16726	1.18826	1.20811
0.4	0.996714	1.02492	1.03734	1.04858
0.5	0.861429	0.873849	0.878403	0.881860
0.6	0.727649	0.727017	0.725241	0.722560
0.7	0.603472	0.593192	0.586911	0.579979
0.8	0.493517	0.476905	0.467828	0.458376
0.9	0.399499	0.379348	0.368872	0.358273
1.0	0.321129	0.299565	0.288712	0.277950
1.2	0.205125	0.184650	0.174818	0.165365
1.4	0.130422	0.113337	0.105444	0.980487E-01
1.6	0.831792E-01	0.698315E-01	0.638835E-01	0.584469E-01
1.8	0.534280E-01	0.433764E-01	0.390544E-01	0.352017E-01
2.0	0.346361E-01	0.272280E-01	0.241570E-01	0.214905E-01
2.5	0.122760E-01	0.898031E-02	0.774477E-02	0.674916E-02
3.0	0.466894E-02	0.324775E-02	0.277573E-02	0.242935E-02
4.0	0.846810E-03	0.598340E-03	0.539030E-03	0.504590E-03
5.0	0.215410E-03	0.176100E-03	0.168350E-03	0.161960E-03
	1.30	1.35	1.40	1.45
0.0	1.49831	1.51539	1.53221	1.54876
0.1	1.46451	1.48049	1.49621	1.51165
0.2	1.36887	1.38189	1.39461	1.40704
0.3	1.22683	1.23575	1.24438	1.25272
0.4	1.05869	1.06333	1.06768	1.07176
0.5	0.884305	0.885161	0.885785	0.886185
0.6	0.719085	0.717072	0.714892	0.712556
0.7	0.572524	0.568628	0.564638	0.560565
0.8	0.448675	0.443761	0.438822	0.433871
0.9	0.347674	0.342402	0.337165	0.331972
1.0	0.267389	0.262207	0.257104	0.252090
1.2	0.156359	0.152038	0.147846	0.143788
1.4	0.911860E-01	0.879596E-01	0.848725E-01	0.819250E-01
1.6	0.535298E-01	0.512645E-01	0.491271E-01	0.471155E-01
1.8	0.318087E-01	0.302786E-01	0.288562E-01	0.275383E-01
2.0	0.192079E-01	0.182021E-01	0.172825E-01	0.164449E-01
2.5	0.596506E-02	0.564303E-02	0.536317E-02	0.512163E-02
3.0	0.218444E-02	0.209279E-02	0.201843E-02	0.195858E-02
4.0	0.484570E-03	0.477380E-03	0.471180E-03	0.465240E-03
5.0	0.154710E-03	0.150480E-03	0.145900E-03	0.141000E-03
	1.50	1.60	1.70	1.80
0.0	1.56503	1.59667	1.62704	1.65604
0.1	1.52681	1.55620	1.58432	1.61109
0.2	1.41918	1.44252	1.46460	1.48538
0.3	1.26076	1.27594	1.28994	1.30276
0.4	1.07558	1.08241	1.08824	1.09310
0.5	0.886372	0.886128	0.885139	0.883478
0.6	0.710077	0.704723	0.698933	0.692799
0.7	0.556425	0.547977	0.539402	0.530790
0.8	0.428921	0.419058	0.409333	0.399827
0.9	0.326836	0.316765	0.307035	0.297713
1.0	0.247174	0.237657	0.228618	0.220107
1.2	0.139869	0.132453	0.125626	0.119405
1.4	0.791198E-01	0.739261E-01	0.692932E-01	0.652113E-01
1.6	0.452299E-01	0.418184E-01	0.388772E-01	0.363822E-01
1.8	0.263233E-01	0.241802E-01	0.224027E-01	0.209600E-01
2.0	0.156871E-01	0.143884E-01	0.138578E-01	0.125662E-01
2.5	0.491609E-02	0.459422E-02	0.437506E-02	0.423526E-02
3.0	0.191196E-02	0.184549E-02	0.180679E-02	0.178381E-02
4.0	0.459580E-03	0.445830E-03	0.429850E-03	0.411470E-03
5.0	0.136010E-03	0.125570E-03	0.115930E-03	0.107720E-03
	2.00	2.20	2.50	3.00
0.0	1.70959	1.75655	1.81303	1.86561
0.1	1.66025	1.70303	1.75392	1.80001
0.2	1.52285	1.55459	1.59087	1.62033
0.3	1.32486	1.34232	1.36009	1.36938
0.4	1.10012	1.10391	1.10456	1.09662
0.5	0.878466	0.871758	0.859977	0.841309
0.6	0.679875	0.666708	0.648091	0.625385
0.7	0.513832	0.497828	0.477052	0.455333
0.8	0.381802	0.365594	0.345822	0.377870
0.9	0.280546	0.265724	0.248654	0.235411
1.0	0.204845	0.192169	0.178412	0.169659
1.2	0.108813	0.100705	0.930496E-01	0.907539E-01
1.4	0.586440E-01	0.540787E-01	0.505344E-01	0.512317E-01
1.6	0.326235E-01	0.303151E-01	0.290207E-01	0.304977E-01
1.8	0.189545E-01	0.179168E-01	0.176474E-01	0.188965E-01
2.0	0.115708E-01	0.111732E-01	0.112580E-01	0.120022E-01

TABLE I (Continued)

$q/R$	2.00	2.20	2.50	3.00
2.5	0.411496E-02	0.410633E-02	0.412988E-02	0.406028E-02
3.0	0.175217E-02	0.171123E-02	0.161803E-02	0.148834E-02
4.0	0.371580E-03	0.336820E-03	0.308930E-03	0.311650E-03
5.0	0.969700E-04	0.928900E-04	0.912900E-04	0.866900E-04
	3.50	4.00	4.50	5.00
0.0	1.86778	1.83656	1.79592	1.76125
0.1	1.80012	1.77062	1.73346	1.70233
0.2	1.61559	1.59102	1.56320	1.54135
0.3	1.35991	1.34276	1.32735	1.31731
0.4	1.08495	1.07644	1.07334	1.07422
0.5	0.830652	0.830448	0.837135	0.845815
0.6	0.618091	0.624582	0.637464	0.650193
0.7	0.452309	0.463219	0.478798	0.492376
0.8	0.328797	0.341829	0.357404	0.369707
0.9	0.239289	0.252562	0.266436	0.276416
1.0	0.175301	0.187525	0.198891	0.206313
1.2	0.970112E-01	0.105438	0.111718	0.115013
1.4	0.560192E-01	0.607149E-01	0.634899E-01	0.646276E-01
1.6	0.334132E-01	0.355642E-01	0.365699E-01	0.369533E-01
1.8	0.203326E-01	0.211260E-01	0.214789E-01	0.217230E-01
2.0	0.125317E-01	0.127685E-01	0.129760E-01	0.132181E-01
2.5	0.399685E-02	0.410212E-02	0.427284E-02	0.437975E-02
3.0	0.150997E-02	0.159540E-02	0.164292E-02	0.166190E-02
4.0	0.316980E-03	0.322460E-03	0.333930E-03	0.339710E-03
5.0	0.882900E-04	0.914500E-04	0.931700E-04	0.950500E-04
	6.00	8.00	$\infty(H+H)$	
0.0	1.72096	1.70032	1.69765	
0.1	1.66694	1.64967	1.64773	
0.2	1.51855	1.50955	1.50921	
0.3	1.30981	1.30992	1.31090	
0.4	1.07974	1.08627	1.08761	
0.5	0.859335	0.868254	0.869198	
0.6	0.666468	0.674549	0.674889	
0.7	0.507564	0.513257	0.513204	
0.8	0.381811	0.385025	0.384873	
0.9	0.284954	0.286373	0.286295	
1.0	0.211725	0.212182	0.212207	
1.2	0.116651	0.116784	0.116864	
1.4	0.651142E-01	0.654381E-01	0.654597E-01	
1.6	0.373407E-01	0.376274E-01	0.376296E-01	
1.8	0.221262E-01	0.222656E-01	0.222716E-01	
2.0	0.135251E-01	0.135744E-01	0.135812E-01	
2.5	0.443017E-02	0.445412E-02	0.445487E-02	
3.0	0.169019E-02	0.169724E-02	0.169765E-02	
4.0	0.344030E-03	0.345480E-03	0.345543E-03	
5.0	0.961800E-04	0.965700E-04	0.965893E-04	

Comparison of our computed vibration-rotation eigenenergies in Table IV with the results of Bishop and Shih<sup>16</sup> confirms the accuracy of our numerical integration scheme for the solution of the radial Schrödinger equation.

In Table V we reproduce the average experimental profile of Lee.<sup>13,14</sup> It should be noted that his profile is not normalized (his  $\langle p^0 \rangle = 1.993$  instead of 2). His analysis of the experimental techniques and data indicates that his values are most accurate at and near the peak. It also indicates that the experimental profile should not be renormalized. Comparing his profile with  $J(q)_{00}$  of Table II we see that the experimental and theoretical profile peaks are in excellent agreement. Lee's results are somewhat ( $\sim 1\%$ ) lower than  $J(q)_{00}$  for small values of  $q$  away from the peak. The curves cross between  $q = 0.7$  and  $0.8$  and again between  $q = 0.8$  and  $0.9$ . Clearly, it would be of great interest if photon scattering measurements could be repeated for the profile in order to see if Eisenberger's x-ray data<sup>2</sup> can be brought into agreement with Lee's electron-impact data and our

TABLE II. Vibrationally and rotationally averaged Compton profiles  $J(q)_{vj}$  for H<sub>2</sub>.

$q^-(v, J)$	(0, 0)	(0, 1)	(0, 2)	(0, 3)
0.0	1.54674	1.54745	1.54886	1.55097
0.1	1.50963	1.51029	1.51161	1.51357
0.2	1.40504	1.40557	1.40663	1.40821
0.3	1.25084	1.25120	1.25190	1.25295
0.4	1.07016	1.07033	1.07067	1.07117
0.5	0.884977	0.884990	0.885015	0.885049
0.6	0.711814	0.711710	0.711503	0.711192
0.7	0.560288	0.560111	0.559758	0.559231
0.8	0.434001	0.433788	0.433363	0.432728
0.9	0.332421	0.332198	0.331755	0.331094
1.0	0.252762	0.252548	0.252122	0.251488
1.2	0.144663	0.144491	0.144148	0.143639
1.4	0.827852E-01	0.826609E-01	0.824138E-01	0.820468E-01
1.6	0.478602E-01	0.477577E-01	0.476079E-01	0.473589E-01
1.8	0.281372E-01	0.280820E-01	0.279724E-01	0.278101E-01
2.0	0.169035E-01	0.168684E-01	0.167988E-01	0.166961E-01
2.5	0.532331E-02	0.531302E-02	0.529270E-02	0.526284E-02
3.0	0.203058E-02	0.202784E-02	0.202244E-02	0.201455E-02
4.0	0.466430E-03	0.466080E-03	0.465390E-03	0.464380E-03
5.0	0.140370E-03	0.140170E-03	0.139780E-03	0.139180E-03
$q^-(v, J)$	(0, 4)	(0, 5)	(0, 6)	(0, 7)
0.0	1.55376	1.55721	1.56129	1.56599
0.1	1.51617	1.51938	1.52318	1.52755
0.2	1.41029	1.41286	1.41590	1.41939
0.3	1.25433	1.25604	1.25805	1.26034
0.4	1.07183	1.07264	1.07359	1.07466
0.5	0.885090	0.885131	0.885168	0.885195
0.6	0.710776	0.710254	0.709626	0.708889
0.7	0.558529	0.557657	0.556616	0.555409
0.8	0.431887	0.430844	0.429603	0.428172
0.9	0.330220	0.329137	0.327859	0.326376
1.0	0.250649	0.249612	0.248386	0.246977
1.2	0.142968	0.142141	0.141165	0.140050
1.4	0.815639E-01	0.809705E-01	0.802730E-01	0.794785E-01
1.6	0.470322E-01	0.466318E-01	0.461628E-01	0.456308E-01
1.8	0.275976E-01	0.273381E-01	0.270351E-01	0.266930E-01
2.0	0.165618E-01	0.163984E-01	0.162084E-01	0.159950E-01
2.5	0.522414E-02	0.517750E-02	0.512396E-02	0.506467E-02
3.0	0.200441E-02	0.199231E-02	0.197861E-02	0.196366E-02
4.0	0.463030E-03	0.461380E-03	0.459430E-03	0.457180E-03
5.0	0.138400E-03	0.137420E-03	0.136250E-03	0.134910E-03
$q^-(v, J)$	(1, 0)	(2, 0)	(3, 0)	(4, 0)
0.0	1.57436	1.60140	1.62772	1.65318
0.1	1.53507	1.55988	1.58396	1.60716
0.2	1.42465	1.44355	1.46168	0.47891
0.3	1.26272	1.27386	1.28421	1.29374
0.4	1.07435	1.07786	1.08068	1.08282
0.5	0.882924	0.880341	0.877264	0.873737
0.6	0.705538	0.698950	0.692109	0.685090
0.7	0.551740	0.543111	0.534472	0.525909
0.8	0.424712	0.415547	0.406575	0.397884
0.9	0.323418	0.314693	0.306310	0.298344
1.0	0.244632	0.236879	0.229556	0.222725
1.2	0.138852	0.133482	0.128577	0.124169
1.4	0.790777E-01	0.785760E-01	0.780372E-01	0.774610E-01
1.6	0.456786E-01	0.453752E-01	0.451284E-01	0.448761E-01
1.8	0.269451E-01	0.269564E-01	0.251528E-01	0.245155E-01
2.0	0.163056E-01	0.158318E-01	0.154629E-01	0.151797E-01
2.5	0.527950E-02	0.524749E-02	0.521728E-02	0.518119E-02
3.0	0.205101E-02	0.205575E-02	0.204477E-02	0.202005E-02
4.0	0.453260E-03	0.437930E-03	0.422900E-03	0.409920E-03
5.0	0.131350E-03	0.125210E-03	0.121050E-03	0.117960E-03
$q^-(v, J)$	(5, 0)	(6, 0)	(7, 0)	(8, 0)
0.0	1.67737	1.70064	1.72205	1.74132
0.1	1.62930	1.65015	1.66940	1.68662
0.2	1.49513	1.51016	1.52378	1.53569
0.3	1.30236	1.30999	1.31654	1.32186
0.4	1.08428	1.08505	1.08515	1.08459
0.5	0.869815	0.865566	0.861083	0.856502
0.6	0.677980	0.670894	0.663972	0.657420
0.7	0.517528	0.509457	0.501856	0.494952
0.8	0.389577	0.381781	0.374647	0.368388
0.9	0.290889	0.284055	0.277967	0.272807
1.0	0.216460	0.210848	0.205985	0.202007
1.2	0.120289	0.116979	0.114274	0.112228

TABLE II (Continued)

$q^-(v, J)$	(5, 0)	(6, 0)	(7, 0)	(8, 0)
1.4	0.681850E-01	0.664617E-01	0.651396E-01	0.642161E-01
1.6	0.398134E-01	0.389936E-01	0.383966E-01	0.379966E-01
1.8	0.240230E-01	0.236529E-01	0.233824E-01	0.231837E-01
2.0	0.149617E-01	0.147895E-01	0.146459E-01	0.145112E-01
2.5	0.513341E-02	0.507060E-02	0.499326E-02	0.490393E-02
3.0	0.198493E-02	0.194334E-02	0.189954E-02	0.185842E-02
4.0	0.399570E-03	0.391690E-03	0.385490E-03	0.379760E-03
5.0	0.115170E-03	0.112230E-03	0.109520E-03	0.107020E-03
$q^-(v, J)$	(9, 0)	(10, 0)	(11, 0)	(12, 0)
0.0	1.75780	1.77057	1.77821	1.77852
0.1	1.70122	1.71239	1.71886	1.71871
0.2	1.54547	1.55258	1.55615	1.55497
0.3	1.32577	1.32803	1.32833	1.32630
0.4	1.08340	1.08165	1.07952	1.07735
0.5	0.852912	0.847904	0.844671	0.843140
0.6	0.651514	0.646655	0.643481	0.642997
0.7	0.489044	0.484547	0.482099	0.482650
0.8	0.363279	0.359688	0.358158	0.359448
0.9	0.268797	0.266225	0.265498	0.267140
1.0	0.199079	0.197400	0.197235	0.198886
1.2	0.110898	0.110339	0.110602	0.111698
1.4	0.636849E-01	0.635257E-01	0.636941E-01	0.641091E-01
1.6	0.377635E-01	0.376589E-01	0.376271E-01	0.376060E-01
1.8	0.230279E-01	0.228876E-01	0.227310E-01	0.225421E-01
2.0	0.143683E-01	0.142075E-01	0.140231E-01	0.138301E-01
2.5	0.480713E-02	0.471196E-02	0.463019E-02	0.457047E-02
3.0	0.182358E-02	0.179609E-02	0.177504E-02	0.175543E-02
4.0	0.373660E-03	0.367260E-03	0.361070E-03	0.356230E-03
5.0	0.104980E-03	0.103270E-03	0.101710E-03	0.100140E-03
$q^-(v, J)$	(13, 0)	(14, 0)	(15, 0)	(16, 0)
0.0	1.76775	1.73871	1.68279	1.68279
0.1	1.70870	1.68279	1.62938	1.52938
0.2	1.54709	1.52938	1.31423	1.31423
0.3	1.32154	1.31423	1.07607	1.07825
0.4	1.07607	1.07825	0.844946	0.853718
0.5	0.844946	0.853718	0.646997	0.658889
0.6	0.646997	0.658889	0.487751	0.499867
0.7	0.487751	0.499867	0.364673	0.375181
0.8	0.364673	0.375181	0.271805	0.279908
0.9	0.271805	0.279908	0.202630	0.208287
1.0	0.202630	0.208287	0.113499	0.115545
1.2	0.113499	0.115545	0.646087E-01	0.650108E-01
1.4	0.646087E-01	0.650108E-01	0.375324E-01	0.374730E-01
1.6	0.375324E-01	0.374730E-01	0.223402E-01	0.222473E-01
1.8	0.223402E-01	0.222473E-01	0.136724E-01	0.136137E-01
2.0	0.136724E-01	0.136137E-01	0.453122E-02	0.448636E-02
2.5	0.453122E-02	0.448636E-02	0.173179E-02	0.171061E-02
3.0	0.173179E-02	0.171061E-02	0.352510E-03	0.348320E-03
4.0	0.352510E-03	0.348320E-03	0.987400E-04	0.975500E-04

calculations. Lee<sup>13,14</sup> has also measured the Compton profile of D<sub>2</sub>. However, due to the difficulty of obtaining D<sub>2</sub> he performed only a single experiment at 8°. Therefore, we do not make any detailed comparison with his D<sub>2</sub> profile. We merely note that no significant isotope shift was observed by Lee.

We now consider vibrational and rotational averaging schemes based upon expansion techniques. Suppose that a property  $P(R)$ , for example  $J(q_0, R)$ , where  $q_0$  is some fixed value of  $q$ , is expanded in a Taylor series about  $R = R^*$ . Thus,

$$P(R) = \sum_{k=0}^{\infty} (\partial^k P / \partial R^k)_R (R - R^*)^k / k! \quad (8)$$

Now average Eq. (8) over the vibration-rotation state  $|vJ\rangle$  to obtain

TABLE III. The vibrationally averaged Compton profile for D<sub>2</sub>.

$q$	$J(q)_{00}$
0.0	1.54257
0.1	1.50578
0.2	1.40206
0.3	1.24901
0.4	1.06947
0.5	0.885232
0.6	0.712716
0.7	0.561548
0.8	0.435389
0.9	0.333780
1.0	0.254002
1.2	0.145565
1.4	0.833721E-01
1.6	0.482134E-01
1.8	0.283358E-01
2.0	0.170070E-01
2.5	0.533366E-02
3.0	0.202743E-02
4.0	0.467940E-03
5.0	0.141840E-03

$$\begin{aligned} \langle vJ|P(R)|vJ\rangle &= \sum_{k=0}^{\infty} (\partial^k P/\partial R^k)_{R^*} \langle vJ|(R-R^*)^k|vJ\rangle/k! \\ &= P(R^*) + (\partial P/\partial R)_{R^*} \langle vJ|(R-R^*)|vJ\rangle \\ &\quad + (\partial^2 P/\partial R^2)_{R^*} \langle vJ|(R-R^*)^2|vJ\rangle/2 + \dots \end{aligned} \quad (9)$$

The usual choice for  $R^*$  is  $R_e$ —the equilibrium internuclear separation.<sup>26</sup> Presumably, this choice is made in analogy with Dunham's expansion of the potential energy.<sup>27</sup> Ulsh *et al.*<sup>8</sup> and Whangbo *et al.*<sup>12</sup> have shown that, in such a case, the linear term must be retained

TABLE IV. Vibrational and rotational eigenenergies for H<sub>2</sub> and D<sub>2</sub>.

$v$	$J$	$-E_{vJ}$
H <sub>2</sub>		
0	0	1.164032
0	1	1.163492
0	2	1.162418
0	3	1.160817
0	4	1.158706
0	5	1.156103
0	6	1.153028
0	7	1.149508
1	0	1.145068
2	0	1.127177
3	0	1.110336
4	0	1.094532
5	0	1.079759
6	0	1.066025
7	0	1.053347
8	0	1.041758
9	0	1.031310
10	0	1.022078
11	0	1.014166
12	0	1.007722
13	0	1.002947
14	0	1.000121
D <sub>2</sub>		
0	0	1.167178

TABLE V. The average experimental Compton profile of H<sub>2</sub> taken from the work of Lee.<sup>13,14</sup>

$q$	$J(q)$
0.0	1.5453
0.1	1.4935
0.2	1.3881
0.3	1.2300
0.4	1.0488
0.5	0.8708
0.6	0.7016
0.7	0.5617
0.8	0.4338
0.9	0.3402
1.0	0.2600
1.2	0.1482
1.4	0.0853
1.6	0.0519
1.8	0.0307
2.0	0.0215
2.4	0.0070
2.6	0.0053
3.0	0.0030
4.0	0.0004

in order to obtain useful results. However, a better choice of  $R^*$  is possible. Let

$$R^* = \langle vJ|R|vJ\rangle \equiv R_{vJ}. \quad (10)$$

Then we see from Eq. (9) that

$$\begin{aligned} \langle vJ|P(R)|vJ\rangle &= P(R_{vJ}) + (\partial^2 P/\partial R^2)_{R_{vJ}} \\ &\quad \times \{\langle vJ|R^2|vJ\rangle - \langle vJ|R|vJ\rangle^2\}/2 + \dots \end{aligned} \quad (11)$$

Clearly, the choice of  $R^*$  given by Eq. (10) forces the linear term to vanish. The expansion (11) converges faster than the expansion (9) with  $R^* = R_e$ . This is most clearly seen from Tables I and II. Note that<sup>17</sup>  $R_e = 1.40$  and that  $R_{00} = 1.45$  a.u. Compare  $J(q, R_e)$  and  $J(q, R_{00})$  with  $J(q)_{00}$ . Clearly,  $J(q, R_e)$  differs much more from  $J(q)_{00}$  than  $J(q, R_{00})$  differs from  $J(q)_{00}$ . This shows that a very simple way of obtaining a quick and reasonably accurate estimate of  $\langle vJ|P(R)|vJ\rangle$  is to truncate the expansion (11) after the leading term obtaining

$$\langle vJ|P(R)|vJ\rangle \approx P(R_{vJ}). \quad (12)$$

We call the approximation (12) the delta approximation since it is equivalent to the approximation

$$|\phi_{vJ}(R)|^2 \approx \delta(R - R_{vJ}), \quad (13a)$$

where  $\delta(R - R_{vJ})$  is the Dirac delta function. It should be noted that this approximation implies the so-called "R-centroid" approximation

$$\langle vJ|R^k|vJ\rangle \approx \langle vJ|R|vJ\rangle^k. \quad (13b)$$

More sophisticated expansions than Eq. (8) are also possible. Thus, we may write

$$P(R) = \sum_{k=0}^{\infty} (\partial^k P/\partial \lambda^k)_{\lambda=0} (\lambda)^k/k!, \quad (14)$$

where  $\lambda$  is some function of  $R$ . Equation (8) is a special case of Eq. (14) with

$$\lambda(R) = R. \quad (15)$$

In analogy with the Simons, Parr, and Finlan<sup>28</sup> expansion of the potential energy we could choose

$$\lambda(R) = (R - R^*)/R. \quad (16)$$

More generally, as suggested by Thakkar<sup>29</sup> we could utilize

$$\lambda(R) = \text{sgn}(p)[1 - R^*/R]^p, \quad (17)$$

where  $p$  is an adjustable and, in general, nonintegral parameter and

$$\text{sgn}(p) = \begin{cases} +1, & p \geq 0, \\ -1, & p < 0. \end{cases} \quad (18)$$

Two special cases of Eq. (17) are rather familiar. The special case  $p = -1$  gives Eq. (15) apart from a constant, and the special case  $p = +1$  gives precisely Eq. (16).

Averaging Eq. (14) over  $|vJ\rangle$  we obtain

$$\langle vJ | P(R) | vJ \rangle = \sum_{k=0}^{\infty} (\partial^k P / \partial \lambda^k)_{\lambda=0} \langle vJ | (\lambda)^k | vJ \rangle / k!. \quad (19)$$

The delta approximation for Eq. (19) is given by

$$\langle vJ | P(R) | vJ \rangle \approx P(R^*), \quad (20)$$

where  $R^*$  is chosen so that

$$\langle vJ | \lambda | vJ \rangle = 0. \quad (21)$$

It seems that a study of Thakkar's general expansion (14) with  $\lambda$  given by the expression (17) carried out in order to determine optimal values of  $p$  and  $R^*$  for various properties would be of interest.<sup>30</sup>

Finally, we note that at temperatures at which vibration-rotation states other than the ground state are significantly populated the correct theoretical average of the Compton profile is given by

$$\langle J(q) \rangle_T = \sum_{vJ} e^{-E_{vJ}/kT} (2J+1) J(q)_{vJ} / Q, \quad (22)$$

where the partition function  $Q$  is given by

$$Q = \sum_{vJ} e^{-E_{vJ}/kT} (2J+1). \quad (23)$$

In the above  $k$  is Boltzmann's constant,  $T$  the absolute temperature, and  $(2J+1)$  is the degeneracy of  $|vJ\rangle$ . Note also that for D<sub>2</sub> only even values of  $J$  occur in Eq. (22) and (23).

## V. SUMMARIZING REMARKS

An accurate calculation of the isotropic Compton profiles  $J(q, R)$  has been presented for the ground state ( $X^1\Sigma_g^+$ ) of the hydrogen molecule. The calculated profiles have then been rigorously averaged over a large number of vibration-rotation states for H<sub>2</sub>, and the ground vibration-rotation state of D<sub>2</sub>. The computed profile peak for the ground vibration-rotation state of H<sub>2</sub> is in excellent agreement with the very recent measurements of Lee.<sup>13,14</sup> It has been shown that vibrational and rotational averaging cannot be neglected in theoretical studies of  $J(q, R)$  for H<sub>2</sub> and its isotopes. It has also been shown that the isotope effect is smaller than the vibrational and rotational averaging effect. A variety of

expansion techniques for such averaging have been presented. The latter include the very simple and reasonably accurate delta approximation.

Suggestions for further research include measurement of the H<sub>2</sub> Compton profile using photon scattering techniques, and a study of Eq. (14) with a view to determining optimal values of  $p$  and  $R^*$  for various properties.

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