PHYSICAL REVIEW A VOLUME 36, NUMBER 11 DECEMBER 1, 1987

Moments of the Bethe surface and total inelastic x-ray scattering cross sections for H_2

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(Received 10 June 1987; revised manuscript received 17 August 1987)

Moments, $S(j,K)$, of the generalized oscillator strength distribution are global properties of the Bethe surface. Apart from $S(-1,K)$ which is related to the Waller-Hartree incoherent scattering factor, little is known about these moments for nonzero K. This paper describes high-accuracy calculations of $S(1,K)$ and $S(2,K)$ for molecular hydrogen. Comparison with experiment is made, and the utility of simple asymptotic approximations is confirmed. The moments are used to calculate differential cross sections for the inelastic scattering of x rays using the constant-momentum-transfer and constant-angle theories of Bonham. These cross sections differ from the Waller-Hartree cross sections at large angles thus demonstrating the importance of making corrections to the Waller-Hartree theory if the incoherent scattering factor $S(K)$ is to be extracted from experimental inelastic cross sections. Total cross sections for scattering of 6- and 7-keV photons from H_2 are compared with synchrotron radiation scattering experiments. The calculations suggest that the Bonham constant-angle cross sections agree best with experiment. However, further experimental and theoretical work is needed to obtain firm conclusions about the limitations of Waller-Hartree theory.

I. INTRODUCTION

The target dependence of the Bethe-Born differential cross section for the inelastic scattering of fast charged structureless particles from atoms and molecules is governed by the generalized oscillator strength (GOS) of the target.[1] A plot of the GOS as a function of the energy loss E and the momentum transfer K (or $\ln K^2$) defines the Bethe surface which contains all the information necessary to predict, within the framework of the first Born approximation, the behavior of matter under charged-particle impact.

The energy moments of the GOS are defined by

$$S(j,K)=\sum_n E_n^j f_n(K)+\int E^j[df(K,E)/dE]dE, \quad j<5/2 \quad (1)$$

where $f_n(K)$ is the GOS for bound-state transitions and $df(K,E)/dE$ is the density of the GOS for transitions into the continuum. These moments are global properties of the Bethe surface and have been studied extensively[2] in the optical limit ($K\rightarrow 0$). However, the only[3] familiar moment for nonzero K is

$$S(-1,K)=S(K)/K^2 , \quad (2)$$

where $S(K)$ is the usual incoherent scattering factor.[4,5] Very little is known about the other moments for nonzero K. In particular, the exact $S(1,K)$ and $S(2,K)$ are known for atomic hydrogen[6] and we recently reported[7] high-accuracy calculations for atomic helium. On the experimental side, there are the early measurements of the energy moments for atomic helium[8] and molecular hydrogen[9] made by Wellenstein, Bonham, and Ulsh. More recently, measurements have been made for ammonia by Lahmam-Bennani *et al.*[10(a)] and for atomic helium by Ketkar and Bonham.[10(b)]

The purpose of this paper is to report high-accuracy calculations of $S(1,K)$ and $S(2,K)$ for molecular hydrogen. Section II contains an outline of the methods used to obtain the moments which are tabulated and compared with experiment in Sec. III. X-ray inelastic cross sections computed by Bonham's methods,[11] which require knowledge of $S(1,K)$ and $S(2,K)$, are presented, discussed, and compared with experiment and the usual Waller-Hartree cross sections in Sec. IV. Concluding remarks are made in Sec. V. Rydberg atomic units ($h=2\pi$, $a_0=1$, $e=\sqrt{2}$, $m_e=\frac{1}{2}$, $c=2/\alpha$ in which α is the fine-structure constant) are used throughout this paper.

II. METHODOLOGY

A. Theory

It is known that $S(1,K)$ and $S(2,K)$ can be expressed as ground-state expectation values and explicit formulas are available for atoms.[1] The extension of the $S(2,K)$ expression to the molecular case is also known. However, a tedious derivation along well-known lines was necessary to obtain the $S(1,K)$ formula in the molecular case. The final expressions, within the framework of the Born-Oppenheimer fixed nuclei approximation, are

$$S(1,K)=K^2[S(K)+\sigma_{ee}(K)]-a(K)+4T/3 \quad (3)$$

and

$$S(2,K)=NK^4+4TK^2+b(K)+(16\pi/3)\sum_A Z_A\rho(\mathbf{R}_A) \quad (4)$$

in which T is the electronic kinetic energy, $\rho(\mathbf{r})$ is the ground-state electronic charge density normalized to the number of electrons N, the sum in Eq. (4) is over nuclei with charges $Z_A e$ and position vectors $\mathbf{R}_A$, and

$$S(K)=(4\pi)^{-1}\int d\Omega_K G(\mathbf{K})\ , \tag{5a}$$

$$G(\mathbf{K})=N+\int[2\Gamma(\mathbf{r}_1,\mathbf{r}_2)-\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)]\times\exp[i\mathbf{K}\cdot(\mathbf{r}_1-\mathbf{r}_2)]d\mathbf{r}_1 d\mathbf{r}_2\ , \tag{5b}$$

$$\sigma_{ee}(K)=(4\pi)^{-1}\int d\Omega_K\,|F(\mathbf{K})|^2\ , \tag{6a}$$

$$F(\mathbf{K})=\int\exp(i\mathbf{K}\cdot\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\ , \tag{6b}$$

$$a(K)=(4\pi)^{-1}\int d\Omega_K g(\mathbf{K})\ , \tag{7a}$$

$$g(\mathbf{K})=-(2/K^2)\sum_m\sum_{\substack{n\\(n\neq m)}}\langle\exp[i\mathbf{K}\cdot(\mathbf{r}_m-\mathbf{r}_n)]\times(\mathbf{K}\cdot\mathbf{p}_m)(\mathbf{K}\cdot\mathbf{p}_n)\rangle\ , \tag{7b}$$

$$b(K)=16\int_0^\infty P(u)u^{-3}j_2(Ku)du\ , \tag{8a}$$

$$P(u)=\int\Gamma(\mathbf{r}_1,\mathbf{r}_2)\delta(u-|\mathbf{r}_1-\mathbf{r}_2|)d\mathbf{r}_1 d\mathbf{r}_2\ . \tag{8b}$$

In the above, $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is the ground-state electron pair density[12] normalized to the number of electron pairs $N(N-1)/2$, $P(u)$ is the radial intracule density,[12] $\mathbf{r}_m$ and $\mathbf{p}_m$, respectively, are position and momentum vectors of electron m in Eq. (7b) where the expectation value is taken with respect to the ground-state wave function, j_2 in Eq. (8a) is a spherical Bessel function, and δ in Eq. (8b) is the Dirac δ function. In the case that all $\mathbf{K}$-dependent functions are spherically symmetric, Eqs. (5)–(7) reduce to the well-known atomic expressions.[1]

Each of the above quantities depends on the internuclear separation R, and can be denoted as $Q(R)$. The effects of molecular vibration can be taken into account by computing the average

$$\bar{Q}=\int_0^\infty|\phi_{vJ}(R)|^2 Q(R)R^2dR \tag{9}$$

in which ϕ_{vJ} is the vibration-rotation wave function corresponding to the state labeled by the vibrational and rotational quantum numbers v and J, respectively. In this paper, attention will be restricted to the ground $v=J=0$ state. It is possible to derive expressions for the moments $S(j,K)$ without invoking the Born-Oppenheimer approximation. Such expressions for $S(0,K)$ and $S(-1,K)$ have been studied previously[13] but, to our knowledge, are not known for $S(1,K)$ and $S(2,K)$. We have not attempted to examine such expressions because (i) we felt that the Born-Oppenheimer approximation is adequately accurate for our purposes and (ii) suitable nonadiabatic wave functions for H_2 are not available.

B. Wave-function and computational details

The various quantities defined in Eqs. (3)–(8) were computed for the ground ${}^1\Sigma_g^+$ state of H_2 at five bond lengths corresponding to $R/a_0=1.350$, 1.375, 1.400, 1.425, and 1.450 from 36-term, explicitly correlated, Gaussian geminal, spin-free wave functions of the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=(1+P_{12})(1+P_{ab})\sum_j C_j\phi_j(\mathbf{r}_1,\mathbf{r}_2)\ , \tag{10a}$$

where

$$\phi_j(\mathbf{r}_1,\mathbf{r}_2)=\exp(-\alpha_j r_{a1}^2-\beta_j r_{b1}^2-\xi_j r_{a2}^2-\eta_j r_{b2}^2-\gamma_j r_{12}^2) \tag{10b}$$

and P_{12} is an operator which interchanges the coordinates of electrons 1 and 2, P_{ab} is an operator that interchanges the coordinates of protons a and b, the r_{mn} are distances between particles m and n, $(\alpha_j,\beta_j,\xi_j,\eta_j,\gamma_j)$ are nonlinear variational parameters optimized[14,15] for $R=1.4a_0$, and the linear coefficients C_j were optimized by us for each R. These wave functions yield variational energies which differ from the exact[16] nonrelativistic Born-Oppenheimer values by 9.2, 9.0, and 9.5 cm^{-1} at $R/a_0=1.35$, 1.40, and 1.45, respectively.

Closed formulas can be obtained for all quantities of interest in Eqs. (3)–(8) for wave functions of the form (10) and were used by us with the following exceptions. The spherical averages of Eqs. (5a) and (6a) were performed numerically, as was the Hankel transform of Eq. (8a). For the latter, $P(u)$ was already available from our previous work on Coulomb holes[17] and correlation potentials.[18] Maclaurin and asymptotic expansions of $b(K)$ were not found useful in contrast with our calculations[7] for atomic helium. Note that we used values of T and $\sum_A Z_A\rho(\mathbf{R}_A)$ obtained[19] from the work of Kolos and Wolniewicz[20,21] because they are more accurate than those predicted by our wave functions.

The average over the vibrational motion was carried out by representing each property $Q(R)$ by a quartic interpolating polynomial as follows:

$$Q(R)=a_0+a_1R+a_2R^2+a_3R^3+a_4R^4\ , \tag{9'}$$

which upon combination with Eq. (9) yields

$$\bar{Q}=a_0+a_1\langle R\rangle+a_2\langle R^2\rangle+a_3\langle R^3\rangle+a_4\langle R^4\rangle\ , \tag{9''}$$

where $\langle R^n\rangle$ stands for $\langle v=0, J=0\,|\,R^n\,|\,v=0, J=0\rangle$. The requisite values of the matrix elements $\langle R^n\rangle$ were obtained from a recent compilation[22,23] which is based on the most accurate potential curves available.

III. MOMENTS OF THE BETHE SURFACE

Table I contains values of $S(1,K)$, $S(2,K)$, and all their components for ${}^1\Sigma_g^+$ H_2 at $R=1.4a_0$ and Table II contains the vibrationally averaged values. Accurate values for $R=1.4a_0$ in the optical limit are[24] $a(0)=-0.268\,96$ and $S(1,0)=3.4024$. The good agreement between the accurate values and those in Table I is reassuring.[25]

Ulsh *et al.*[9] have mapped out the Bethe surface for H_2 using 25-keV electrons. A comparison with their experimental moments is presented in Table III and Fig. 1. The theoretical values are within the experimental error bars[26] for $Ka_0>2$. The discrepancies between the experimental and theoretical moments are due partly to difficulties in extrapolating the missing tail[8–10] of the experimental GOS and partly to the neglect of nonadiabatic effects in our calculations.

Two simple approximations to the moments are also of interest. The first is the asymptotic approximation[7] for large K whereby

$$S(1,K) \sim NK^2 + 4T/3 + O(K^{-1}) \ , \qquad (11a)$$

$$S(2,K) \sim NK^4 + 4TK^2 + C + O(K^{-1}) \ , \qquad (11b)$$

in which

$$C = (16\pi/3)\left[\sum_A Z_A \rho(\mathbf{R}_A) + 4h(0)\right] \ , \qquad (11c)$$

where

$$h(u) = P(u)/(4\pi u^2) \qquad (11d)$$

is the spherical average of the intracule density.[12] The other approximation to the moments of H_2 is to simply

TABLE I. Calculated energy moments and their components for ground-state H_2 at $R = 1.4$. Note that $T = 2.350\,065\,431\,4$ and $\sum_A Z_A \rho(\mathbf{R}_A) = 0.920\,30$. All quantities are in Rydberg atomic units as defined in Sec. I.

K	$S(K)$	σ_{ee}	$a(K)$	$b(K)$	$S(1,K)$	$S(2,K)$
0.0	0.000 00	4.000 00	−0.267 95	0.000 00	3.4014	15.420
0.1	0.015 10	3.966 22	−0.251 33	0.006 25	3.4246	15.520
0.2	0.059 50	3.866 94	−0.203 36	0.024 80	3.4938	15.824
0.3	0.130 60	3.708 01	−0.129 39	0.055 08	3.6083	16.337
0.4	0.224 40	3.498 48	−0.037 42	0.096 16	3.7665	17.071
0.5	0.335 98	3.249 58	0.062 98	0.146 84	3.9668	18.042
0.6	0.460 01	2.973 59	0.162 00	0.205 70	4.2075	19.269
0.7	0.591 20	2.682 77	0.250 78	0.271 18	4.4869	20.777
0.8	0.724 75	2.388 40	0.322 27	0.341 65	4.8036	22.597
0.9	0.856 56	2.100 14	0.371 85	0.415 50	5.1565	24.762
1.0	0.983 40	1.825 64	0.397 43	0.491 21	5.5450	27.311
1.1	1.102 92	1.570 43	0.399 25	0.567 37	5.9689	30.290
1.2	1.213 57	1.338 03	0.379 52	0.642 73	6.4282	33.746
1.3	1.314 53	1.130 18	0.341 77	0.716 25	6.9232	37.735
1.4	1.405 51	0.947 21	0.290 32	0.787 07	7.4544	42.315
1.5	1.486 65	0.788 36	0.229 72	0.854 50	8.0225	47.550
1.6	1.558 38	0.652 12	0.164 32	0.918 06	8.6280	53.510
1.7	1.621 31	0.536 51	0.097 99	0.977 42	9.2715	60.268
1.8	1.676 19	0.439 32	0.033 91	1.032 39	9.9537	67.904
1.9	1.723 77	0.358 28	−0.025 51	1.082 92	10.675	76.502
2.0	1.764 83	0.291 19	−0.078 58	1.129 04	11.436	86.150
2.2	1.830 34	0.190 85	−0.162 31	1.208 56	13.078	108.98
2.4	1.878 10	0.124 27	−0.215 58	1.272 49	14.883	137.19
2.6	1.912 53	0.080 75	−0.242 32	1.322 81	16.850	171.68
2.8	1.937 16	0.052 61	−0.248 80	1.361 65	18.982	213.41
3.0	1.954 68	0.034 53	−0.241 50	1.391 02	21.278	263.41
3.2	1.967 10	0.022 94	−0.225 93	1.412 73	23.737	322.81
3.4	1.975 92	0.015 51	−0.206 24	1.428 34	26.361	392.78
3.6	1.982 19	0.010 70	−0.185 30	1.439 13	29.147	474.61
3.8	1.986 67	0.007 56	−0.164 93	1.446 15	32.095	569.63
4.0	1.989 91	0.005 47	−0.146 18	1.450 26	35.206	679.27
4.4	1.993 98	0.003 06	−0.115 17	1.452 25	41.911	948.48
4.8	1.996 23	0.001 82	−0.092 71	1.448 89	49.261	1295.1
5.2	1.997 52	0.001 12	−0.076 89	1.442 47	57.254	1733.4
5.6	1.998 31	0.000 70	−0.065 46	1.434 37	65.888	2278.5
6.0	1.998 81	0.000 44	−0.056 69	1.425 41	75.163	2947.3
7.0	1.999 47	0.000 13	−0.040 69	1.402 11	101.15	5279.4
8.0	1.999 73	0.000 04	−0.029 86	1.379 97	131.15	8810.4
9.0	1.999 84	0.000 02	−0.022 87	1.360 08	165.15	13 900
10.0	1.999 90	0.000 01	−0.018 27	1.342 54	203.14	20 957
11.0	1.999 94	0.000 00	−0.014 97	1.327 16	245.14	30 436
12.0	1.999 96	0.000 00	−0.012 49	1.313 65	291.14	42 842
13.0	1.999 97	0.000 00	−0.010 65	1.301 74	341.14	58 727
14.0	1.999 98	0.000 00	−0.009 31	1.291 19	395.14	78 691
15.0	1.999 98	0.000 00	−0.008 32	1.281 79	453.14	103 382

use twice the moments for atomic hydrogen.[6] Thus,

$$S(1,K) \simeq 2K^2 + \tfrac{8}{3}\,, \tag{12a}$$

$$S(2,K) \simeq 2K^4 + 8K^2 + \tfrac{32}{3}\,. \tag{12b}$$

These two approximations are also compared with the complete calculations in Table III and Fig. 1. Both approximations underestimate the exact values with the exception of the asymptotic approximation (11b) to $S(2,K)$ at small K. The noninteracting atom approximations (12) are inferior to the asymptotic approximations (11) even at small K. The good agreement between the latter and the exact values confirms our earlier suggestion[7] that the asymptotic approximations are useful ones.

IV. INELASTIC SCATTERING

A. Comparison of various theories

Bonham[11] has developed corrections to the usual Waller-Hartree approximation for the total inelastic scattering cross-section σ differential with respect to the solid angle Ω for detection of scattered x rays from

TABLE II. Vibrationally averaged moments and their components for H_2. Vibrationally averaged $T=2.318\,912$, and $\sum_A Z_A \rho(\mathbf{R}_A)=0.907\,31$. All quantities are in Rydberg atomic units.

K	$S(K)$	σ_{ee}	$a(K)$	$b(K)$	$S(1,K)$	$S(2,K)$
0.0	0.000 00	4.000 00	−0.264 17	0.000 00	3.3561	15.202
0.1	0.015 40	3.965 37	−0.247 58	0.006 17	3.3793	15.301
0.2	0.060 66	3.863 64	−0.199 76	0.024 47	3.4486	15.601
0.3	0.133 06	3.700 97	−0.126 18	0.054 32	3.5631	16.107
0.4	0.228 47	3.486 84	−0.035 05	0.094 79	3.7214	16.832
0.5	0.341 78	3.233 01	0.063 91	0.144 66	3.9217	17.791
0.6	0.467 49	2.952 25	0.160 80	0.202 49	4.1622	19.003
0.7	0.600 18	2.657 26	0.246 75	0.266 72	4.4413	20.494
0.8	0.734 94	2.359 63	0.314 88	0.335 72	4.7575	22.293
0.9	0.867 62	2.069 19	0.360 79	0.407 89	5.1099	24.435
1.0	0.994 98	1.793 65	0.382 70	0.481 72	5.4978	26.959
1.1	1.114 69	1.538 45	0.381 18	0.555 82	5.9210	29.910
1.2	1.225 26	1.306 99	0.358 73	0.628 97	6.3796	33.335
1.3	1.325 89	1.100 82	0.319 09	0.700 16	6.8739	37.290
1.4	1.416 35	0.920 08	0.266 73	0.768 57	7.4046	41.834
1.5	1.496 85	0.763 79	0.206 23	0.833 54	7.9721	47.031
1.6	1.567 84	0.630 29	0.141 89	0.894 64	8.5772	52.950
1.7	1.629 99	0.517 44	0.077 46	0.951 56	9.2205	59.664
1.8	1.684 07	0.422 92	0.015 95	1.004 15	9.9026	67.255
1.9	1.730 85	0.344 40	−0.040 40	1.052 39	10.624	75.804
2.0	1.771 15	0.279 61	−0.090 12	1.096 31	11.385	85.401
2.2	1.835 25	0.183 13	−0.166 94	1.171 83	13.028	108.12
2.4	1.881 81	0.119 41	−0.213 99	1.232 31	14.833	136.22
2.6	1.915 27	0.077 89	−0.235 86	1.279 78	16.801	170.58
2.8	1.939 13	0.051 06	−0.239 07	1.316 32	18.934	212.17
3.0	1.956 08	0.033 80	−0.230 01	1.343 91	21.231	262.03
3.2	1.968 08	0.022 68	−0.213 92	1.364 27	23.691	321.26
3.4	1.976 60	0.015 48	−0.194 63	1.378 91	26.315	391.07
3.6	1.982 66	0.010 78	−0.174 69	1.389 01	29.102	472.73
3.8	1.987 01	0.007 66	−0.155 63	1.395 59	32.051	567.57
4.0	1.990 15	0.005 56	−0.138 31	1.399 43	35.161	677.01
4.4	1.994 12	0.003 09	−0.109 95	1.401 25	41.868	945.80
4.8	1.996 32	0.001 81	−0.089 40	1.398 03	49.218	1292.0
5.2	1.997 59	0.001 09	−0.074 69	1.391 88	57.211	1729.7
5.6	1.998 36	0.000 67	−0.063 77	1.384 10	65.845	2274.4
6.0	1.998 85	0.000 41	−0.055 17	1.375 49	75.121	2942.5
7.0	1.999 48	0.000 13	−0.039 25	1.353 04	101.11	5273.1
8.0	1.999 74	0.000 05	−0.028 69	1.331 69	131.11	8802.2
9.0	1.999 85	0.000 02	−0.021 99	1.312 51	165.10	13 890
10.0	1.999 91	0.000 01	−0.017 58	1.295 61	203.10	20 944
11.0	1.999 94	0.000 00	−0.014 41	1.280 80	245.10	30 421
12.0	1.999 96	0.000 00	−0.012 03	1.267 78	291.10	42 824
13.0	1.999 97	0.000 00	−0.010 27	1.256 30	341.10	58 706
14.0	1.999 98	0.000 00	−0.008 99	1.246 13	395.10	78 666
15.0	1.999 98	0.000 00	−0.008 03	1.237 08	453.10	103 354

TABLE III. Comparison of calculated moments for ground-state H_2 with experimental, asymptotic, and 2H values. The numbers in parentheses are uncertainties in the experimental values. All quantities are in Rydberg atomic units.

	$S(1,K)$				$S(2,K)$			
K	2H[a]	Asym.[b]	Theory[c]	Experiment[d]	2H[a]	Asym.[b]	Theory[c]	Experiment[d]
0.795	3.9317	4.3984	4.7879 4.7418	4.32(0.13)	16.527	23.340	22.504 22.201	13.5(0.07)
1.174	5.4232	5.8900	6.3054 6.2569	5.98(0.18)	25.492	33.350	32.798 32.396	25.3(1.0)
1.552	7.4841	7.9508	8.3326 8.2820	7.91(0.40)	41.540	50.841	50.554 50.014	40.4(4.0)
2.309	13.330	13.796	14.041 13.991	13.8(0.70)	110.17	123.56	123.63 122.71	113(11.0)
3.064	21.443	21.910	22.047 22.000	22.5(1.4)	262.04	281.12	281.34 279.91	290(14)
3.819	31.836	32.303	32.384 32.339	31.8(2.0)	552.78	579.13	579.40 577.31	552(66)
5.325	59.378	59.845	59.883 59.840	59.7(4.8)	1845.6	1891.2	1891.5 1887.7	1870(280)
7.572	117.34	117.80	117.82 117.78	121.0(9.7)	7044.0	7130.2	7130.4 7123.0	7430(1100)

[a] Approximation of Eqs. (12) based on noninteracting hydrogen atoms.

[b] Asymptotic approximation ($R=1.4$), Eqs. (11), using $h(0)=0.0175$ as computed for wave function (10) in Ref. 17.

[c] Calculated from the explicitly correlated wave functions. See Sec. II B. The upper values correspond to $R=1.4a_0$ and the lower values are the vibrationally averaged values for the $v=0$, $J=0$ state.

[d] Experiment involving impact by 25-keV electrons (Ref. 9). See also Ref. 26.

atomic and molecular targets. For data collected at *constant momentum transfer K,* he finds

$$(d\sigma/d\Omega)_i=(\sigma_T/2)[S(K)f_0-NK^2E_0^{-1}f_1+K^2S(1,K)E_0^{-2}f_2-K^2S(2,K)E_0^{-3}f_3+O(E_m^{-7/2})]\ , \tag{13}$$

where $f_0=1+x^2$, $f_1=1+2x-x^2$, $f_2=1-x+x^2$, $f_3=x-x^2$ with $x=\cos(2\theta_B)$ in which θ_B is defined by $\cos2\theta_B=1-2K^2/\alpha^2E_0^2$, σ_T is the Thompson constant, α is the fine-structure constant, E_0 is the energy of the incident x ray, and E_m is the maximum observable energy loss. For data collected at *fixed scattering angle* θ_B, the correct[27] expression is

$$(d\sigma/d\Omega)_i=(\sigma_T f_0/2)\{S(K_e)-2K_e^2NE_0^{-1}+(\alpha^2/4)[(3-2x)S(1,K_e)+(5-4x)T(1,K_e)]-(\alpha^2/4E_0)[S(2,K_e)+(5-2x)T(2,K_e)]+O(E_m^{-7/2})\}\ , \tag{14a}$$

in which

$$T(j,K)=K^2[dS(j,K)/dK^2]\quad \text{for } j=1,2\ , \tag{14b}$$

and K_e is the elastic momentum transfer defined by

$$K_e^2=\alpha^2E_0^2(1-x)/2\ . \tag{14c}$$

Note well that Eqs. (13) and (14) are expressed in Rydberg atomic units as defined[28] in Sec. I. The first term in both Eqs. (13) and (14a) is the familiar Waller-Hartree result. The constant-momentum formula (13) should[11] be more accurate but the constant-angle formula (14) corresponds to the data collection mode employed in all experiments reported so far. Bonham also gave a quasirelativistic formula for the constant-momentum-transfer case but it will not be considered further because its predictions have been found[7] to be rather similar to that of the corresponding nonrelativistic formula (13).

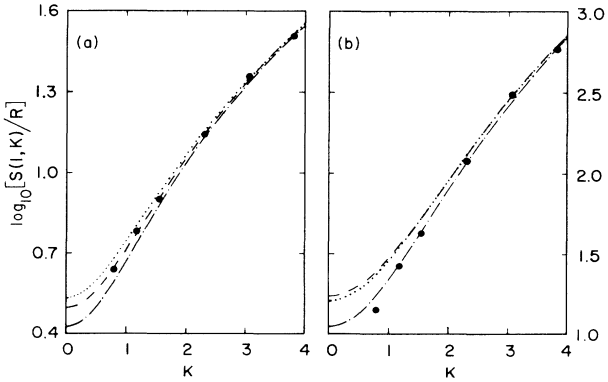

FIG. 1. Moments of the Bethe surface for H_2. (a) $S(1,K)$, (b) $S(2,K)$. Note the logarithmic scale. ●, experiment (Ref. 9); · · · ·, theory ($R=1.4a_0$) using correlated wave function; — — —, asymptotic estimates, Eqs. (11); —·—·—, noninteracting hydrogen atoms, Eqs. (12).

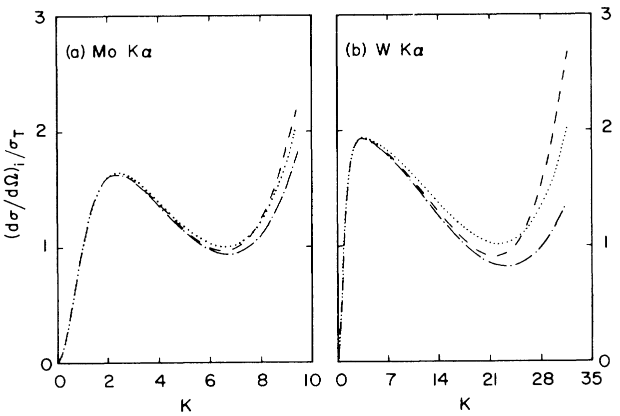

FIG. 2. Total differential cross sections for inelastic scattering of x rays from H_2 ($R=1.4a_0$). (a) Mo $K\alpha$ (17.441 keV) x rays, (b) W $K\alpha$ (58.856 keV) x rays. — — —, Bonham constant-K formula, Eq. (13); —·—·—·, Bonham constant-angle formula, Eq. (14). For this case K is defined by Eq. (14c). · · · ·, Waller-Hartree theory.

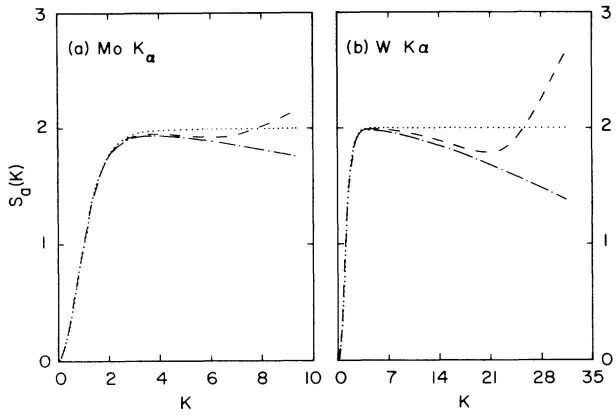

FIG. 3. Apparent incoherent scattering factors for H_2 ($R=1.4a_0$) as defined in Eq. (15). (a) Mo $K\alpha$ (17.441 keV) x rays, (b) W $K\alpha$ (58.856 keV) x rays. — — —, using Bonham constant-K cross sections; —·—·—·, using Bonham constant-angle cross sections; · · · ·, Waller-Hartree theory.

In Fig. 2 the Bonham cross sections (13) and (14) are compared with the Waller-Hartree cross section for inelastic scattering of Mo $K\alpha$ and W $K\alpha$ radiation from H_2 molecules. For the constant-angle cross section, K in Fig. 2 corresponds to K_e as given by Eq. (14c). The Bonham cross sections are virtually indistinguishable from the Waller-Hartree cross section at small K but substantial differences can be seen at large angles (larger K). Consider scattering of W $K\alpha$ x rays as in Fig. 2(b). All three cross sections are essentially identical for $Ka_0 < 7$ or $\theta_B < 13°$. For $7 < Ka_0 < 20$ (or $13° < \theta_B < 39°$) the Bonham cross sections agree well with each other but are lower than the Waller-Hartree cross section. For even larger K or θ_B, all three cross sections differ from one another. For back scattering ($\theta_B = \pi/2$, $Ka_0 \simeq 31.57$) the constant-angle cross section, the Waller-Hartree cross section, and the constant-K cross section, respectively, are in the ratio 1.36 to 2.00 to 2.64. These differences are less than those reported earlier for helium. Unfortunately, the latter are in error;[29] the correct results for helium are very similar to those shown for H_2 in this paper.

Frequently, the purpose of an x-ray experiment is to extract $S(K)$ which can be inverted to obtain information about the effects of electron correlation on electron pair densities.[12] Define an apparent incoherent scattering factor by

$$S_a(K) = (2/\sigma_T f_0)(d\sigma/d\Omega)_i \ . \tag{15}$$

Note that $S_a(K) = S(K)$ within Waller-Hartree theory. However, $S_a(K)$ will differ from $S(K)$ if the true cross section is inserted into Eq. (15). This is illustrated in Fig. 3 which displays $S(K)$ and $S_a(K)$ for H_2 calculated from both Bonham cross sections (13) and (14). The differences are substantial at large K and increase in magnitude with the frequency of the incident x ray.

TABLE IV. Comparison of theoretical total scattering cross sections for H_2 with experiment at photon energies of 6.00 and 7.00 keV. The numbers in parentheses are uncertainties in the experimental values. The upper values correspond to $R = 1.4a_0$ and the lower values to the $v=0$, $J=0$ state.

		$2(d\sigma/d\Omega)_t/\sigma_T f_0$			
$2\theta_B$ (deg)	Ka_0	Waller-Hartree[a]	Bonham constant-K[b]	Bonham constant-angle[c]	Experiment[d]
60.9	1.6309	2.1930	2.1762	2.1694	2.03(+0.13, −0.10)
		2.1813	2.1644	2.1576	
60.9	1.9027	2.0813	2.0616	2.0537	1.99(+0.13, −0.10)
		2.0745	2.0548	2.0469	
135.6	2.9795	1.9892	2.0157	1.9117	1.87(+0.12, −0.09)
		1.9898	2.0163	1.9123	

[a] Equation (16) with Waller-Hartree inelastic cross sections.
[b] Equation (16) with inelastic cross sections from Eq. (13).
[c] Equation (16) with inelastic cross sections from Eq. (14).
[d] Reference 30.

TABLE V. Comparison of theoretical total scattering cross sections for He with experiment at a photon energy of 6.00 keV. The numbers in parentheses are uncertainties in the experimental values.

		$2(d\sigma/d\Omega)_t/\sigma_T f_0$			
$2\theta_B$ (deg)	Ka_0	Waller-Hartree[a]	Bonham constant-K[b]	Bonham constant-angle[c]	Experiment[d]
60.9	1.6309	2.7388	2.7220	2.7152	2.60(+0.18, −0.13)
135.6	2.9795	2.1281	2.1549	2.0508	2.04(+0.13, −0.10)

[a]Equation (16) with Waller-Hartree inelastic cross sections. These values are the same as in Ref. 7.
[b]Equation (16) with inelastic cross sections from Eq. (13). These values are corrections to the ones given in Table 4 of Ref. 7.
[c]Equation (16) with inelastic cross sections from Eq. (14) and energy moments of Ref. 7.
[d]Reference 30.

B. Comparison with experiment

Total (elastic + inelastic) differential cross sections $(d\sigma/d\Omega)_t$ have been measured for the scattering of synchrotron radiation from atomic helium and molecular hydrogen.[30] These can be computed from the inelastic cross sections by adding the elastic contributions. Thus,

$$(d\sigma/d\Omega)_t=(d\sigma/d\Omega)_e+(d\sigma/d\Omega)_i \ , \tag{16a}$$

in which

$$(d\sigma/d\Omega)_e=(\sigma_T f_0/2)\sigma_{ee} \ , \tag{16b}$$

where σ_{ee} is defined by Eq. (6) and σ_T and f_0 are the same as in Eq. (13).

Tables IV and V present a comparison between the experimental values of Ice *et al.*[30] and theoretical cross sections based on Eq. (16) with inelastic contributions computed from (a) Waller-Hartree theory, (b) the constant-K formula, and (c) the constant-angle formula. In all cases, the theoretical values based on inelastic cross sections from the constant-angle formula lie closest to the experimental ones. However, it is not clear what conclusions can be drawn from this comparison because (i) in most cases, the experimental error bars are not sharp enough to distinguish among the different theoretical results, (ii) the experimental values were obtained[30] by a process which involves determination of a scale factor by comparison with Waller-Hartree theory at one angle and incident energy, and (iii) in the case of H_2, the theoretical cross sections have not been corrected for nonadiabatic effects.

V. CONCLUDING REMARKS

Our high-accuracy calculations of the GOS moments $S(1,K)$ and $S(2,K)$ for H_2 are the first ever for a molecule. The results in this paper along with our previous results[7] for He show that the asymptotic estimates of Eqs. (11) are reasonably accurate; they should be useful for other systems as well since they can be computed quite easily.

Our calculations of apparent incoherent scattering factors demonstrate the importance of using corrections to the Waller-Hartree theory if $S(K)$ is to be extracted from measured inelastic cross sections.

Further work is needed to help clarify the regions of validity and accuracy of the constant-K formula (13) and the constant-angle formula (14). On the experimental side, new measurements with higher-energy x rays would be helpful as would a reanalysis of the older experiments[30] using the Bonham cross sections in Tables IV and V to determine the scale factor for conversion between relative and absolute cross sections. On the theoretical side, a calculation of the nonadiabatic effects on the moments of the Bethe surface and cross sections for H_2 would be helpful. Such a calculation is being planned in our laboratory.

ACKNOWLEDGMENTS

We are grateful to Krzysztof Szalewicz for providing us with the exponents of his explicitly correlated wave function, Robert J. LeRoy for providing us unpublished values of his matrix elements, and Hermann F. Wellenstein and Russell A. Bonham for helpful comments. The continuing support of the Natural Sciences and Engineering Research Council of Canada helped make this work possible. One of us (A.J.T.) thanks the Alfred P. Sloan Foundation for their support. The other (B.S.S.) thanks the Manager and Principal of D. J. College, Baraut, India for granting leave for absence.

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[24] $a(0)$ was computed from the diagonal correction for nuclear motion given in column 7, Table III of Ref. 21 for H_2. $S(1,0)$ then follows from Eq. (3). See also Ref. 19.

[25] The $S(2,0)$ value in Table I is in perfect agreement with the accurate one because we use the accurate value of $\sum_A Z_A \rho(\mathbf{R}_A)$. See Sec. II B.

[26] Their error limit for $S(1,K)$ at $Ka_0 = 2.309$ is listed in Ref. 9 as 0.07 but this is likely to be a typographical mistake since the errors should increase with K. We have therefore guessed the true error limit to be 0.70.

[27] Equations (19), (21), and (22) of the original Ref. 11 are in error. The equations in this paper are the correct ones as reported in the erratum to Ref. 11.

[28] We caution the reader not to confuse the Rydberg atomic units defined in Sec. I with a *different* set of Rydberg atomic units ($h/2\pi = \sqrt{2}$, $a_0 = 1$, $e = \sqrt{2}$, $m_e = 1$, $c = \sqrt{2}/\alpha$) employed in condensed matter physics. The set we use is employed in the literature on scattering from atomic and molecular targets. Both sets have in common $a_0 = 1$, $e = \sqrt{2}$, $h^2/m_e = 8\pi^2$, and hence also the Rydberg as the unit of energy.

[29] The numerical results in Sec. 4 of Ref. 7 are in error because an incorrect value of c was used due to a mixup between two sets of Rydberg atomic units (see Ref. 28 above). Figures 2 and 3 of Ref. 7 are qualitatively correct but the Bonham cross sections at large K (large angle) are overestimated, especially for W $K\alpha$ radiation. The correct diagrams for helium are very similar to the H_2 results shown in Figs. 2 and 3 of this paper. Corrections to Table 4 of Ref. 7 may be found in Table V of this paper.

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