PHYSICAL REVIEW A VOLUME 48, NUMBER 1 JULY 1993

Generalized oscillator-strength calculations for some low-lying excited states of H_2 using a high-accuracy configuration-interaction wave function

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(Received 20 January 1993)

The full configuration-interaction (CI) method using elliptical basis functions has been used to calculate the wave function for a few of the lower $^{1,3}\Sigma_g$ and $^{1,3}\Sigma_u$ excited states. This computational method gives the best wave functions to date for the $GK(3\,^1\Sigma_g)$ and $e(2\,^3\Sigma_u)$ excited states at an internuclear distance $R = 1.5$ a.u., without using explicitly correlated basis functions, i.e., James-Coolidge or Hylleraas-type basis functions. Using these excited-state wave functions, accurate generalized oscillator strengths for excitation to a few of the lower excited states at $R = 1.4$ a.u. are calaculated and given for comparison with other calculations reported elsewhere. It is found that the effect of the ground-state electron correlation is important for excitation to the lowest excited states, but it becomes less significant for excitation to still higher excited states. It is concluded that the CI method and the computation technique presented here is the most practical and accurate one for studying the inelastic scattering by H_2 of fast, charged particles or the electron-impact spectroscopy of H_2.

PACS number(s): 31.20.Di, 34.80.Gs, 34.50.Bw

I. INTRODUCTION

It has been shown [1] that generalized oscillator strengths (GOS) obtained from the inelastic scattering by atoms and molecules of fast charged particles are very important quantities from which many properties of atoms and molecules can be obtained. There have been a number of studies for atoms but very few studies for molecules. So far only one thorough study based on the revised Bethe theory due to Inokuti and Kim [1] has been made for H_2^+ [2]. The hydrogen molecule is a system of fundamental importance for both molecular physics and astronomy and there are a few studies which calculate the GOS for some excitations [3–5]. It is well understood that the accuracy of the calculated GOS depends on the accuracy of the ground- and excited-state wave functions. Only a few accurate studies for the excited states have been reported using James-Coolidge-type or Kolos-Wolniewicz-type wave functions [6] and there has been no report of GOS calculations using those wave functions. Instead of using Kolos-Wolniewicz-type wave functions to calculate the GOS, Kolos, Monkhorst, and Szalewicz [5] calculated the GOS using a wave function expanded in explicitly correlated Gaussian-type functions for excitations to $B(1\,^1\Sigma_u)$ and $EF(2\,^1\Sigma_g)$. Arrighini, Biondi, and Giudotti [4] studied the GOS for a few of the lower excited states calculated using CI wave functions, expanded in Slater-type orbitals. However, their GOS for the excitation to $B(1\,^1\Sigma_u)$ and $EF(2\,^1\Sigma_g)$ are not as accurate as the ones reported by Kolos, Monkhorst, and Szalewicz [5]. Recently Wells and Wilson [7] pointed out that basis set effects are a major and frequently dominant error in molecular structure studies, and they demonstrated that the accuracy of the total energy and other one-electron properties such as quadrupole moments, electronic moments $\langle r^2 \rangle$, etc., for the ground state of the two-electron systems H_2 and HeH^+ obtained using fully numerical self-consistent-field (SCF) procedures can be matched by calculations performed within the algebraic approximation. Furthermore, Presikorn *et al.* [8] have also reported that their configuration-interaction (CI) wave function expanded in Cartesian Gaussian functions for the excited state $e(2\,^3\Sigma_u)$ of H_2 gives a total energy lower than the one obtained using a Kolos-Wolniewicz-type wave function [9]. The basis set effect was also found to be the major source of error in studies of elastic scattering by N_2 at high incident electron energies [10]. This may imply that the CI wave function constructed from quality-type basis sets can be as accurate as one obtained using a Kolos-Wolniewicz-type wave function. The purpose of this work is to demonstrate how an accurate full CI wave function for H_2, expanded in elliptical basis functions, can be used to study GOS and some other one-electron properties. For diatomic molecules [11], elliptical basis functions are known to be very accurate; they are used here to construct various accurate CI wave functions of H_2. It is well known that the accuracy of GOS at small momentum transfers K is very much dependent on the electron correlation of the wave functions while the accuracy of GOS at large K is less dependent on the electron correlation, but is very sensitively dependent on the quality of basis set functions being used. Therefore the study of GOS is a good test for the wave functions obtained here and elsewhere.

The computer program DIREC [12] has been used to evaluate the one- and two-electron molecular integrals for elliptical-type orbitals. The total energy and the full

CI wave function for the ground and excited states of H_2 are computed according to the standard techniques of quantum chemistry described elsewhere [13]. Here the calculated CI wave function is further transformed into natural orbitals (NO's) using the Rothenberg and Davidson scheme [13]. Then the GOS for H_2 is computed in terms of NO's using the computational technique described elsewhere [14,15]. In this work accurate GOS for excitations to a few of the lower excited states of symmetry ${}^1\Sigma_u$ and ${}^1\Sigma_g$ are computed and are compared with other calculations [3–5].

II. THEORETICAL BACKGROUND

According to the Bethe theory [1], the GOS for excitation from the ground state to excited state n of a freely rotating H_2 molecule at a fixed R can be written as

$$f_n(K,R)=[\Delta E_n(R)/\mathcal{R}]\langle|\epsilon_n K,\mathbf{R})|^2\rangle_{\hat{\mathbf{R}}}/(Ka_0)^2 , \quad (1)$$

where a_0 is the Bohr radius, $\mathcal{R}$ is the Rydberg energy (i.e., 13.605 eV), $\Delta E_n(R)$ $[=E_n(R)-E_o(R)]$ is the energy of excitation, $E_o(R)$ and $E_n(R)$ are, respectively, the potential-energy curves of the ground and excited states, $\langle\ \rangle_{\hat{\mathbf{R}}}$ denotes averaging over the orientations of the molecular axis $\mathbf{R}$ with respect to $\mathbf{K}$ (this is equivalent to performing the classical rotational average), $|\epsilon_n(K,\mathbf{R})|^2$ is the first Born electronic transition matrix element squared given by

$$|\epsilon_n(K,\mathbf{R})|^2=|\langle\psi_0(e^{-i\mathbf{K}\cdot\mathbf{r}_1}+e^{-i\mathbf{K}\cdot\mathbf{r}_2}\psi_n)\rangle|^2 . \quad (2)$$

Note that ψ_0 $(\mathbf{r}_1,\mathbf{r}_2,R)$ and ψ_n $(\mathbf{r}_1,\mathbf{r}_2,R)$ are, respectively, the ground- and excited-state wave functions, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of electron 1 and 2 in the center-of-mass system. The electronic wave function $\psi(\mathbf{r}_1,\mathbf{r}_2,R)$ expanded in NO's is written as

$$\psi(\mathbf{r}_1,\mathbf{r}_2,R)=\sum_i c_i f_i(\mathbf{r}_1)g_i(\mathbf{r}_2) , \quad (3)$$

where c_i is the expansion coefficient, and f_i and g_i are the NO's expanded in elliptical basis functions

$$\varphi(\xi,\eta,\phi;\alpha,\beta,n,l,m)=(2\pi)^{-1/2}(2/R)^{-3/2}\xi^n e^{-\alpha\xi}\eta^l e^{\beta\eta} \times[(\xi^2-1)(1-\eta^2)]^{|m|/2}e^{im\phi} . \quad (4)$$

In the present work, we find that basis set functions or molecular orbitals (MO's) with m up to 3, i.e., σ, π, δ, or ϕ, are found to be sufficient to obtain accurate wave functions for the ground and excited states of H_2 [12,13]. MO's used here involve at most two nonlinear parameters (i.e., exponents α). The form factor $\langle|\epsilon_n(K,\mathbf{R})|^2\rangle_{\hat{\mathbf{R}}}$ calculated using the NO's expanded in elliptical basis functions (expressed in confocal spheroidal coordinates) is given in the Appendix. For electron impact, the cross-section dependence on R for the vertical excitation from the ground state to excited state n is given by [1]

$$\sigma_n(R)=\frac{4\pi a_0^2}{T/\mathcal{R}}\int g_n(K,R)d[\ln(Ka_0)^2] , \quad (5)$$

where T is the incident electron energy and $g_n(K,R)=f_n(K,R)/[\Delta E_n(R)/\mathcal{R}]$. It is well known that optical oscillator strengths and their transition moments, respectively, are defined by

$$f_n(R)=f_n(K,R)|_{K=0} \quad (6)$$

and

$$M_n^2(R)=f_n(R)/\Delta E_n(R)\mathcal{R} , \quad (7)$$

where $M_n^2(R)$ for H_2 can be explicitly written as

$$M_n^2(R)=\begin{cases}\frac{2}{3}|\langle\psi_0 z\psi_n\rangle|^2/a_0^2 & \text{for excitation to } \Sigma_u \quad (8a)\\ \frac{4}{3}|\langle\psi_0 x\psi_n\rangle|^2/a_0^2 & \text{for excitation to } \Pi_u . \quad (8b)\end{cases}$$

TABLE I. Ground state of H_2 $X\,{}^1\Sigma_g$ and their electronic moments. $Q_2(R)=[R^2-2(3\langle z^2\rangle-\langle r^2\rangle)]$ (in a.u.) and E is the total energy in hartree for $R=1.4$ a.u., except for item[a] below.

Wave function basis functions	$-E$	$\langle r^2\rangle$	$\langle{}^2\rangle$	$Q_2(R)$
$6\sigma,3\pi,1\delta$[a]	1.173 030 2	2.547 14	1.022 70	0.9205
$9\sigma,5\pi,2\delta$[b]	1.173 70	2.549 39	1.0276	0.8928
$18\sigma,9\pi$[c]	1.174 048 2			
$19\sigma,20\pi,16\delta,8\phi$[d]	1.174 238 0	2.547 05	1.023 69	0.9119
$33\sigma,20\pi,16\delta,8\phi$[d]	1.174 281 2	2.547 15	1.023 66	0.9124
$33\sigma,20\pi,16\delta,16\phi$[d]	1.174 292 0	2.547 08	1.023 63	0.9122
$33\sigma,27\pi,18\delta,16\phi$[d]	1.174 304 3	2.547 24	1.023 66	0.9125
	1.174 434[e]			
	1.174 475[f]	2.546 334 3[f]	1.022 969 8[f]	0.9137[f]

[a] Values at $R=1.4009$ a.u. calculated from E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962).

[b] Unpublished result in 1973 given by Bowen Liu (private communication).

[c] Values given by Arrighini, Biondi, and Giudotti [4].

[d] Present theoretical values.

[e] Values given by Kolos, Monkhorst, and Szalewicz [5].

[f] Values taken from Ref. [6].

Work to calculate the cross section $\sigma_n(R)$ for the optically allowed and forbidden transitions according to Inokuti and Kim [1] is in progress and the results for the excitations including dissociation and ionization will be reported elsewhere [23].

III. CALCULATIONAL RESULTS AND DISCUSSION

A. Wave functions of H_2

In Table I, the total energy and other one-electron properties for the $X\,^1\Sigma_g$ ground state of H_2 computed here are shown to be in good agreement with the most accurate theoretical values [6]. Note that the results in extended precision are in good agreement with the ones in double precision. Atomic units are used throughout this work unless otherwise indicated. We also calculate second and third excited states of symmetry $^1\Sigma_g$ [i.e., $EF(2\,^1\Sigma_g)$ and $GK(3\,^1\Sigma_g)$] in Table II. It is surprising to find that our wave functions for $GK(3\,^1\Sigma_g)$ and H $(4\,^1\Sigma_g)$ at $R=1.5$ a.u. give total energies lower than the ones obtained from a Kolos-Wolniewicz-type wave function [17]. Our H $(4\,^1\Sigma_g)$ state is obtained as the fourth root of the secular equation for the GK state. It is not optimized separately. Our wave function for $EF(2\,^1\Sigma_g)$ at $R=1.4$ a.u. also gives a total energy lower than the one obtained from the wave function expanded in the explicitly correlated Gaussian function reported by Kolos, Monkhorst, and Szalewicz [5]. Total energies for the three excited $^1\Sigma_u$ states are also shown in Table III. Our wave function for $B(1\,^1\Sigma_u)$ also gives a total energy lower than the one reported by Kolos, Monkhorst, and Szalewicz [5]. This implies that the wave function expanded in explicitly correlated Gaussian functions may not be as accurate as the full CI wave function constructed with the quality elliptical basis set presented here. Recently Presikorn *et al.* [8] made a best theoretical study for the $^3\Sigma_u$ triplet states of H_2 using CI and Hylleraas-CI (HCI) methods with Cartesian Gaussian functions. Our total energies for both the *b* and *e* states are lower than their CI values and our total energy for the *e* state at $R=1.5$ a.u. is lower than their HCI value by more than 1 μhartree (see Table IV). Note that both the total energies of our and their CI wave functions for $e\,^3\Sigma_u$ are lower than the ones computed using a Kolos-Wolniewicz-type wave function [9]. This suggests that Kolos-Wolniewicz-type wave functions may not be sufficiently flexible to calculate accurate wave functions for the highly excited states of H_2 mentioned above. We believe that here the CI wave function expanded in elliptical basis functions is very accurate and the CI wave function for the excited states is as accurate as or better than the one expanded in explicitly correlated basis set functions [5,6,8]. All the wave functions for the excited state reported here consist of fewer than 600 symmetry-adapted configurations, which is less than that using the HCI method [8]. Details of the wave-function calculations are available on request from the authors.

TABLE II. Lower $^1\Sigma_g$ excited states of H_2. *E* is the total energy (in hartree) and *R* is in a.u.

$EF\,^1\Sigma_g$		$GK\,^1\Sigma_g$		$H\,^1\Sigma_g$	
R	$-E$	*R*	$-E$	*R*	$-E$
1.4	0.691 894[a]	1.4	0.626 471 483[b]	1.5	0.636 311 036[b]
1.4	0.691 961 8[b]	1.5	0.639 005 780[b]	1.5	0.636 292 973[c]
1.5	0.702 949 025[b]	1.5	0.638 998 978[c]		
1.5	0.702 994 478[c]				

[a]Kolos, Monkhorst, and Szalewicz [5].
[b]Present theoretical values.
[c]Values given by Wolniewicz and Dresser [17].

TABLE III. Lower $^1\Sigma_u$ excited-states of H_2 at $R=1.4$ a.u.

$B\,^1\Sigma_u$ $-E$	$B'\,^1\Sigma_u$ $-E$	$B''\Sigma_u$ $-E$
0.705 678[a]	0.628 649 135[b]	0.602 490 92[b]
0.705 693 8[b]	0.628 688 112[c]	0.601 673[d]
0.705 776 243[c]	0.627 599[d]	0.598 582 86[e]
0.703 953[d]	0.628 662 9[e]	

[a]Values given by Kolos, Monkhorst, and Szalewicz [5].
[b]Present theoretical values.
[c]Values given by Wolniewicz and Dresser [18].
[d]Values given by Branchett and Tennyson [22].
[e]Values given by Kolos [J. Mol. Spectrosc. **62**, 429 (1976)].

B. Generalized oscillator strengths

According to the previous section, we believe that the CI wave functions reported here are very accurate and their GOS and the transition moments for excitations to lower excited states are sufficiently accurate to discriminate against other theoretical values. The values of GOS and transition moments for excitation to the three lowest excited states of symmetry $^1\Sigma_u$ are shown in Table V and VI. Our GOS for excitation to $B(1\,^1\Sigma_u)$ are in good agreement with the values reported by Kolos, Monkhorst, and Szalewicz [5]. Our values of GOS for small *K* should be more accurate than theirs since our wave function for $B(1\,^1\Sigma_u)$ gives a total energy lower than theirs

TABLE IV. Lower $^3\Sigma_u$ excited-state energies (in hartree) of H_2.

$b\,^3\Sigma_u$		$e\,^3\Sigma_u$	
R	$-E$	*R*	$-E$
1.4	0.784 102 96[a]	1.5	0.657 155 74[d]
1.4	0.784 235 38[b]	1.5	0.657 326 74[a]
1.4	0.784 214 11[c]	1.5	0.657 351 16[b]
1.4	0.784 150 1[e]	1.5	0.657 352 29[c]
1.5	0.809 655 64[b]		
1.5	0.809 637 92[c]		
1.5	0.809 609 5[e]		

[a]CI values taken from Presikorn *et al* [8].
[b]HCI values taken from Presikorn *et al.* [8].
[c]Present Theoretical values.
[d]Values given by Rychlewski [9].
[e]Values given by Kolos and Wolniewicz [6].

and our transition moment is the closest to the most accurate value reported by Dresser and Wolniewicz [19]. The GOS for excitation to $B'(2\,^1\Sigma_u)$, the second excited state, reported by Arrighini, Biondi, and Giudotti [4], agrees with our values to at least one decimal place for various values of K and our values are presumably more accurate than their value since both our total energy and transition moment are closest to the most accurate values reported by Wolniewicz and Dresser [18] and Wolniewicz [20], respectively. For the excitation to $B''(3\,^1\Sigma_u)$, the GOS values reported by Arrighini, Biondi, and Giudotti [4] also agree with our values to at least one decimal place. For excitation to $^1\Sigma_u$, we find that the effect of ground-state electron correlation is not as important as the one due to excited-state electron correlation and the effect becomes still less significant for higher excited states. The transition moments for B and $B'\,^1\Sigma_u$ reported by Bauschlicher and Langhoff [21] are in agreement with the present theoretical values. Note that the transition moments for B, B', and $B''\,^1\Sigma_u$ reported recently by Branchett and Tennyson [22] are too large compared with our values and the others shown in Tables V and VI, despite the claim that their values are more accurate than the ones reported by Arrighini, Biordi, and Giudotti [4], since their wave functions were obtained by the R-matrix method using better quality Slater-type basis functions.

In Table VII, the GOS for the excitation to the first and second excited states, i.e., EF and $GK\,^1\Sigma_g$, calculated using our CI wave functions, are shown for comparison with other calculations. The GOS for excitation to $EF(2\,^1\Sigma_g)$ calculated here are shown to be in good agreement with the values reported by Kolos, Monkhorst, and Szalewicz [5] for most K values except at very small K. For this excitation, we found that the effect of ground-state electron correlation on GOS for excitation to the excited states $EF(2\,^1\Sigma_g)$ of H_2 is very important. Our

TABLE V. $g_n(K,R)$ at $R=1.4$ a.u. for excitation to $B\,^1\Sigma_u$ from $X\,^1\Sigma_g$.

K	Present work	Ref. [5]	Ref. [3]	Ref. [4]	Ref. [22]	Ref. [21]	Ref. [19]
0.0	0.642 473	0.6394	0.666	0.6215	0.6447	0.6405	0.6430
0.010	0.6422	0.6393					
0.100	0.6287	0.6259	0.652	0.6082			
0.200	0.5895	0.5873	0.610	0.5697			
0.300	0.5303	0.5289	0.548				
0.400	0.4587	0.4580	0.472	0.4430			
0.500	0.3825	0.3825	0.392				
0.600	0.3086	0.3090	0.315	0.2969			
0.700	0.2417	0.2423	0.246				
0.800	0.1845	0.1851	0.187	0.1761			
0.900	0.1378	0.1383	0.139				
1.000	0.1010	0.1014	0.102	0.9522[−1]			
1.100	0.7287[−1]	0.7325[−1]	0.740[−1]				
1.200	0.5196[−01]	0.5225[−1]	0.532[−1]	0.4851[−1]			
1.300	0.3670[−01]	0.3692[−1]	0.381[−1]				
1.400	0.2574[−01]	0.2590[−1]	0.271[−1]				
1.500	0.1797[−01]	0.1808[−1]	0.193[−1]	0.1665[−1]			
1.600	0.1251[−01]	0.1259[−1]	0.138[−1]				
1.700	0.8693[−02]	0.8751[−2]	0.983[−2]				
1.800	0.6043[−02]	0.6084[−2]	0.702[−2]	0.5599[−2]			
1.900	0.4207[−02]	0.4235[−2]	0.503[−2]				
2.000	0.2935[−02]	0.2956[−2]	0.361[−2]	0.2721[−2]			
3.000	0.1051[−03]	0.1064[−3]	0.170[−3]	0.9346[−4]			
4.000	0.7350[−05]	0.7466[−5]	0.123[−4]	0.6176[−5]			
5.000	0.1023[−05]	0.1034[−5]	0.150[−5]	0.9079[−6]			
6.000	0.2338[−06]	0.2353[−6]	0.319[−6]				
8.000	0.1821[−07]	0.1870[−7]	0.202[−8]				
10.000	0.1903[−08]	0.1856[−8]					
11.000	0.8222[−09]						
12.00	0.3724[−09]	0.3648[−9]					
13.000	0.1635[−09]						
14.000	0.7428[−10]	0.731[−10]					
15.000	0.3834[−10]						
16.000	0.2157[−10]	0.208[−10]					
17.000	0.1196[−10]						
18.000	0.6469[−11]	0.629[−10]					
19.000	0.3695[−11]						
20.000	0.2307[−11]	0.222[−10]					
25.000	0.2566[−12]						

values at small K may not be as accurate as the ones reported by Kolos, Monkhorst, and Szalewicz [5], since our best ground-state wave function is not as accurate as theirs. Fortunately, the contribution to the inelastic cross section due to the error of the GOS at small K is not very significant [23]. The GOS for excitation to $GK(3\,^1\Sigma_g)$ are also shown for comparison with the values reported by Arrighini, Biondi, and Giudotti [4]. Our values should be more accurate then their values since both our wave functions for the ground and excited states are more accurate than theirs.

IV. SUMMARIES AND CONCLUSIONS

This work has demonstrated that full CI wave functions expanded in elliptical basis functions for the ground and excited state of H_2 are very accurate. The wave functions for excited states such as $GK\,^1\Sigma_g$ and $e\,^3\Sigma_u$ are as accurate as or better than the best values obtained from wave functions expanded in explicitly correlated basis functions of Hylleraas-type reported elsewhere [5,8]. A test of the accuracy of the wave function obtained here and elsewhere based on the calculation of GOS for excitation to the lower excited states of H_2 has been carried out. In general, the effect of electron correlation on the GOS for excitation to the lowest excited state is found to be important but it becomes less significant for excitation to still higher excited states. It is encouraging that the method of computation for both wave functions and GOS used here is very accurate. This work provides a practical and accurate method for the study of electron-impact spectroscopy of H_2 and the inelastic scattering processes (including dissociation and ionization) of H_2 colliding with fast charged particles [23].

TABLE VI. $g_n(K,R)$ at $R=1.4$ a.u. for excitation to $^1\Sigma_u$ from $X\,^1\Sigma_g$.

	$X-B'$					$X-B''$		
K	Present work	Ref. [4]	Ref. [22]	Ref. [21]	Ref. [20]	Present work	Ref. [5]	Ref. [4]
0.00	0.105 42	0.1126	0.1116	0.1051	0.1050	0.363 69[−1]	0.3634[−1]	0.6238[−1]
0.01	0.1054					0.3658[−1]		
0.10	0.1043	0.1095				0.3632[−1]	0.3741[−1]	
0.20	0.1011	0.1074				0.3549[−1]	0.3759[−1]	
0.30	0.9569[−1]					0.3404[−1]		
0.40	0.8819[−1]	0.9345[−1]				0.3190[−1]	0.3391[−1]	
0.50	0.7889[−1]					0.2911[−1]		
0.60	0.6840[−1]	0.7040[−1]				0.2577[−1]	0.2730[−1]	
0.70	0.5748[−1]					0.2212[−1]		
0.80	0.4686[−1]	0.4752[−1]				0.1841[−1]	0.1949[−1]	
0.90	0.3716[−1]					0.1488[−1]		
1.00	0.2875[−1]	0.2887[−1]				0.1172[−1]	0.1242[−1]	
1.10	0.2177[−1]					0.9019[−2]		
1.20	0.1620[−1]	0.1610[−1]				0.6806[−2]	0.7157[−2]	
1.30	0.1188[−1]					0.5057[−2]		
1.40	0.8617[−2]					0.3708[−2]		
1.50	0.6197[−2]					0.2693[−2]		
1.60	0.4429[−2]					0.1943[−2]		
1.70	0.3154[−2]					0.1395[−2]		
1.80	0.2241[−2]	0.2194[−2]				0.9983[−3]	0.1038[−2]	
1.90	0.1592[−2]					0.7138[−3]		
2.00	0.1131[−2]	0.1108[−2]				0.5105[−3]	0.5685[−2]	
3.00	0.4576[−4]	0.4352[−4]				0.2137[−4]	0.2408[−4]	
4.00	0.3252[−5]	0.2954[−5]				0.1504[−5]	0.1697[−5]	
5.00	0.4328[−6]	0.4081[−6]				0.1962[−6]	0.2188[−6]	
6.00	0.9681[−7]					0.4368[−7]		
8.00	0.7664[−8]					0.3430[−8]		
10.00	0.7990[−9]					0.3554[−9]		
11.00	0.3440[−9]					0.1531[−9]		
12.00	0.1567[−9]					0.6963[−10]		
13.00	0.6934[−10]					0.3072[−10]		
14.00	0.3153[−10]					0.1395[−10]		
15.00	0.1621[−10]					0.7179[−11]		
16.00	0.9129[−11]					0.4042[−11]		
17.00	0.5086[−11]					0.2249[−11]		
18.00	0.2759[−11]					0.1219[−11]		
19.00	0.1574[−11]					0.6956[−12]		
20.00	0.9812[−12]					0.4337[−12]		
25.00	0.1095[−12]					0.4836[−13]		

ACKNOWLEDGMENTS

The authors would like to thank Dr. Clementi at IBM Corp. for providing us the data on the triplet states of H_2 quoted here. J.W.L. thanks Dr. H. K. Tseng for hospitality at the Department of Physics, National Central University (NCU) and acknowledges support by the National Science Council, Republic of China under Contract No. NSC80-0208-M008-69.

APPENDIX: EVALUATION OF FORM FACTOR $\langle |\epsilon_n(K,\mathbf{R})|^2\rangle_{\hat{\mathbf{R}}}$

According to Eqs. (2)–(4), in order to calculate the form factor, we need to evaluate the integral

$$|\langle f_i(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}}f_j(\mathbf{r})\rangle|^2=4\sum_{n=m}^{\infty}(2-\delta_{om})N_{nm}^{-1}(c)\left[\sum_r{}'\sum_{r'}{}'d_r^{nm}(c)(-1)^{(r'-n-m)^{1/2}}d_{r'}^{nm}(c)\right.$$
$$\times\int_1^{\infty}\int_1^{-1}(\xi^2-\eta^2)\eta^J(1-\eta^2)^{Q+m/2}e^{\beta\eta}P_{r+m}^n(\eta)$$
$$\left.\times d\eta\,\xi^{N-m}(\xi^2-1)^{Q+m/2}e^{-\alpha\xi}j_{r'+m}(\xi)d\xi\right]^2 ,$$

TABLE VII. $g_n(K,R)$ at $R=1.4$ a.u. for excitation to ${}^1\Sigma_g$ from $X\,{}^1\Sigma_g$.

	X-EF			X-GK	
K	Present work	Ref. [15]	Ref. [4]	Present work	Ref. [4]
0.010	0.3260[−2]	0.4247[−4]		0.3076[−4]	
0.100	0.4900[−2]	0.4145[−2]	0.4256[−2]	0.2879[−3]	0.2483[−3]
0.200	0.1602[−1]	0.1542[−1]	0.1550[−1]	0.1029[−2]	0.8532[−3]
0.300	0.3129[−1]	0.3076[−1]		0.1938[−2]	
0.400	0.4680[−1]	0.4637[−1]	0.4585[−1]	0.2705[−2]	0.2082[−2]
0.500	0.5926[−1]	0.5891[−1]		0.3131[−2]	
0.600	0.6667[−1]	0.6639[−1]	0.6594[−1]	0.3174[−2]	0.2473[−2]
0.700	0.6863[−1]	0.6838[−1]		0.2911[−2]	
0.800	0.6581[−1]	0.6562[−1]	0.6588[−1]	0.2471[−2]	0.1958[−2]
0.900	0.5963[−1]	0.5949[−1]		0.1975[−2]	
1.000	0.5159[−1]	0.5150[−1]	0.5181[−1]	0.1506[−2]	0.1148[−2]
1.100	0.4297[−1]	0.4923[−1]		0.1107[−2]	
1.200	0.3470[−1]	0.3469[−1]	0.3468[−1]	0.7924[−3]	0.5722[−3]
1.300	0.2732[−1]	0.2732[−1]		0.5555[−3]	
1.400	0.2106[−1]	0.2107[−1]		0.3838[−3]	
1.500	0.1597[−1]	0.1599[−1]		0.2624[−3]	
1.600	0.1195[−1]	0.1196[−1]		0.1784[−3]	
1.700	0.8849[−2]	0.8858[−2]		0.1208[−3]	
1.800	0.6498[−2]	0.6506[−2]	0.6344[−2]	0.8180[−4]	0.5550[−4]
1.900	0.4743[−2]	0.4749[−2]		0.5544[−4]	
2.000	0.3448[−2]	0.3453[−2]	0.3351[−2]	0.3768[−4]	0.2597[−4]
3.000	0.1486[−3]	0.1488[−3]	0.1483[−3]	0.1072[−5]	0.9205[−6]
4.000	0.1275[−4]	0.1280[−4]	0.1311[−4]	0.5704[−7]	0.6336[−7]
5.000	0.2235[−5]	0.2246[−5]	0.2222[−5]	0.5236[−8]	0.6904[−8]
6.000	0.4689[−6]	0.4695[−6]		0.7941[−9]	
8.000	0.2650[−7]	0.2711[−7]		0.5057[−10]	
10.000	0.3630[−8]	0.3660[−8]		0.5056[−11]	
11.000	0.1404[−8]			0.1824[−11]	
12.000	0.5564[−9]	0.5308[−9]		0.7735[−12]	
13.000	0.2547[−9]			0.3675[−12]	
14.000	0.1317[−9]	0.128[−9]		0.1773[−12]	
15.000	0.6805[−10]			0.8479[−13]	
16.000	0.3419[−10]	0.359[−10]		0.4270[−13]	
17.000	0.1818[−10]			0.2383[−13]	
18.000	0.1073[−10]	0.120[−10]		0.1405[−13]	
19.000	0.6537[−11]			0.8151[−14]	
20.000	0.3853[−11]	0.434[−11]		0.4675[−14]	
25.000	0.7357[−12]			0.1974[−14]	

where $M=m_i-m_j$, $m=|M|$, $N=n_i+n_j$, $J=j_i+j_j$, $\alpha=\alpha_i+\alpha_j$, $\beta=\beta_i+\beta_j$, $c=1/2KR$, $Q=(|m_i|+|m_j|)/2-m/2$, $j_r(c\xi)$ is the spherical Bessel function of order r, $\sum_r{}'$ denotes for the summation over even r if $(r-n-m)$ is even or odd r if $(r-n-m)$ is odd, $d_r^{mn}(c)$ is the expansion coefficient of the angular eigenfunction for spheroidal wave-function equations [16], $N_{nm}(c)$ is the normalization constant for spheroidal wave functions, and $P_{r+m}^{n}(\eta)$ is the associate Legendre polynomial. Note that the basic integrals to be evaluated are

$$B(r,n,m,J,Q;\beta)=\int_1^{-1} d\eta\, \eta^J (1-\eta^2)^{Q+m/2} e^{\beta\eta} P_{r+m}^{n}(\eta)\, d\eta$$

and

$$I(k,r,m;\alpha)=\int_1^{\infty} d\xi\, \xi^{k-m} (\xi^2-1)^m e^{-\alpha\xi} j_{r+m}(\xi) ,$$

which can be accurately calculated according to the computational technique described elsewhere [14,15].

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