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Validity of the distorted-wave approximation (DWA) for inelastic e^-–H_2 scattering

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Abstract. The validity of the distorted-wave approximation for e^-–H_2 scattering is tested through a comparative study with the two-channel Schwinger multichannel method. Calculated differential cross sections are reported for the excitations to $b\,^3\Sigma_u^+$, $a\,^3\Sigma_g^+$ and $c\,^3\Pi_u$ states in the energy range covering from near threshold up to 30 eV. General good agreement is observed between both theories for incident energies above 20 eV.

1. Introduction

Over the past few years, the distorted-wave approximation (DWA) has been widely applied to calculate scattering cross sections for electronic excitations of atoms (Madison and Shelton 1973a, b, Bransden and McDowell 1977, 1978, Sawada *et al* 1971, Machado *et al* 1982, 1984, Padial *et al* 1981, Meneses *et al* 1987) and molecules (Rescigno *et al* 1974, 1976, Fliflet and Mckoy 1980, Lee *et al* 1982, Lee and Mckoy 1982, 1983a, b) by electron impact. For light atomic targets, the range of validity of such a method has been established through systematic comparisons with available experimental results: in the intermediate and high energy region the DWA can generally provide quite satisfactory cross sections. For molecular targets, however, the validity of the DW method in studies of electronic excitations by low-energy electron impact has never been fully tested for several reasons. Firstly, there is a lack of systematic experimental results in the literature. The available experimental cross sections are quite fragmentary (Trajmar *et al* 1983) and sometimes show significant discrepancies (Khakoo *et al* 1987, Nishimura and Danjo 1986, Hall and Andrić 1984) between themselves. In addition, there are very few theoretical studies beyond the DWA level (Chung and Lin 1978, Holley *et al* 1982, Weatherford 1980, Lima *et al* 1985, 1988, Schneider and Collins 1985, Baluja *et al* 1985) in the literature. Most of these studies report only total cross sections (Chung and Lin 1978, Holley *et al* 1982, Weatherford 1980, Schneider and Collins 1985, Baluja *et al* 1985) and therefore, a more meaningful comparison of differential cross sections (DCS) cannot be performed.

In a recent work, Lima *et al* (1988) applied the Schwinger multichannel method (SMC) in a two-channel approximation to calculate the excitation cross sections of H_2 by electron impact. In this approximation, only the coupling between two energetically open electronic states (ground and one excited state) was considered. In their study, they reported the DCS for the excitations $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u$, $X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$ and $X\,^1\Sigma_g^+ \rightarrow c\,^3\Pi_u$

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covering the incident energy range from near the excitation threshold up to 30 eV, and made comparisons with previously reported DW results (Fliflet and Mckoy 1980, Lee *et al* 1982). For some cases, good agreement was observed, but for other cases significant discrepancies remained. Here it should be stressed that the previous DW and SMC studies used different kinds of physical assumptions and this may be the origin of some of those discrepancies.

In general, however, it is expected that the DWA should be valid in the high impact energy range, i.e. away from electronic excitation thresholds, where Feshbach and core-excited shape resonances are known to dominate the cross sections.

In order to access the validity of the DWA through the comparison with a more elaborate method such as SMC in the present work we applied the DWA to calculate the cross sections for excitation of the same electronic states of H_2 ($b\,^3\Sigma_u^+$, $a\,^3\Sigma_g^+$ and $c\,^3\Pi_u$), in the same energy range and under the same physical assumptions (excitation thresholds, static exchange potentials, molecular orbitals, etc) as in the previous study of Lima *et al* (1988). We expect that this study, serving as a check of the DW method, can provide some more concrete information regarding its validity in the e^--H_2 case. It is clear to us, however, that a more general validity condition of this method can only be established when this kind of studies for other molecular systems are carried out in the future. For this purpose, more reliable experimental data are needed as well.

In section 2 we discuss briefly the theory used in this paper and the details of the calculations. The results and discussions will be presented in section 3. In section 4 we summarize our conclusions.

2. Theory and calculations

The basic theory used in the present work has already been described in detail elsewhere (Fliflet and Mckoy 1980). Therefore, only a brief outline will be given in this section.

Using the Born-Oppenheimer and Franck-Condon approximations, and treating the target rotational states as essentially degenerate, the DCS for electronic excitation of the molecule by electron impact can be written as:

$$\frac{d\sigma}{d\Omega}(n \leftarrow 0;\, E, \hat{\boldsymbol{r}}') = SM_n \sum_{\nu'} q_{\nu' o} \frac{k_{\nu'}}{k_o} \frac{1}{8\pi^2} \int d\hat{\boldsymbol{R}}' \, |f_{ko}(n \leftarrow 0, \boldsymbol{R}', \hat{\boldsymbol{r}}')|^2 \qquad (1)$$

where E is the impact energy, k_o and $k_{\nu'}$ are the momenta of the incoming and outgoing electron, respectively, $q_{\nu' o}$ is the Franck-Condon factor for the $\nu = 0$ level of the initial electronic state and the vibrational level ν' of the excited state. The factor S results from summing over final and averaging over initial spin sublevels. For the cases treated in this study, namely the singlet-to-triplet type of excitations, S is equal to $\frac{3}{2}$. For linear molecules, M_n is the orbital angular momentum projection degeneracy factor of the final state (1 for Σ and 2 for Π states). The quantity $f_{ko}(n \leftarrow 0; \boldsymbol{R}', \hat{\boldsymbol{r}}')$ is the laboratory frame scattering amplitude and can be related to the fixed-nuclei dynamical coefficients as follows:

$$f_{ko}(n \leftarrow 0, \boldsymbol{R}', \hat{\boldsymbol{r}}') = \sum_{ll'mm'} a_{ll'mm'}(n \leftarrow 0, k_o, R) D^{(l)*}_{m'm}(\hat{\boldsymbol{R}}) D^{(l')}_{om}(\hat{\boldsymbol{R}}) Y_{lm'}(\hat{\boldsymbol{r}}') \qquad (2)$$

where $D^{(l')}_{m'm}(\hat{\boldsymbol{R}})$ is a rotational harmonic function, and the fixed-nuclei dynamical coefficients $a_{ll'mm'}$ can be written in terms of the fixed-nuclei partial-wave components of the electronic portion of the transition matrix elements as:

$$a_{ll'mm'}(n \leftarrow 0, k_o, R) = -\tfrac{1}{2}\pi[4\pi(2l'+1)]^{1/2} i^{l'-l} \langle k_n lm, n | T_{el} | k_o l'm', o \rangle. \qquad (3)$$

In the DW approximation, $|k_n lm\rangle$ and $|k_o l'm'\rangle$ represent the final and the initial Hartree-Fock continuum partial waves, satisfying incoming-wave and outgoing-wave boundary conditions, respectively, and n and o designate the excited and ground electronic states of the target, respectively.

In the present study, all the calculations are performed within the fixed-nuclei framework, using the ground-state equilibrium distance of 1.4006 au. A SCF wavefunction for the ground state of H_2 was obtained using the same uncontracted Cartesian Gaussian basis set as used by Lima *et al* (1988) in their SMC studies. The same basis set was also used to calculate the wavefunctions of the excited states within the improved virtual orbital (IVO) framework. The calculated vertical excitation energies for the states $b\,^3\Sigma_u^+$, $a\,^3\Sigma_g^+$ and $c\,^3\Pi_u$ are, respectively, 9.975, 12.036 and 12.306 eV. The experimental 'vertical' excitation energies for these transitions are 10.35, 12.28 and 12.60 eV, respectively, from the $v=0$ vibrational level of the ground state. In our approach we used the calculated excitation energies to obtain the DCS in figure 1. In addition, both the final and the initial continuum wavefunctions were obtained in the HF potential field created by the ground-state target. These continuum wavefunctions, required for the computation of the DWT matrix, were calculated using the Schwinger variational iterative method (Lucchese *et al* 1982). To calculate the distorted-wave matrix elements, we made use of single-centre expansions for the continuum wavefunctions, for the initial and the final target orbitals and for the transition potential operator. Sufficient terms are included in these expansions to ensure convergence in each partial-distorted-wave element to three significant figures. In this calculation we included partial-wave matrix elements for l, $l' \leq 8$; m, $m' \leq 2$. We estimate that the contribution from higher-order partial-wave elements to the DCS is less than 1% for the impact energies considered in this work. The radial integrals were evaluated by a Sympson's rule quadrature.

3. Results and discussion

In figures 1-3 we show the DCS for the excitation $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ in H_2 along with the results obtained by SMC at the impact energies 10.5, 20 and 30 eV. The available experimental results are also shown. Generally there is a good qualitative agreement between the two theoretical results. Quantitatively, very good agreement is also seen, particularly at the impact energy of 30 eV. Even for 10.5 eV (less than 1 eV above threshold) there is still a reasonable agreement. The major discrepancies (around 30%) were observed in the backward scattering direction. Discrepancies of the same magnitude are also seen in the forward and in the backward direction for 20 eV impact electrons. Comparing the results of both theories with experimental data (Hall and Andrić 1984, Nishimura and Danjo 1986, Khakoo *et al* 1987), there is a quite satisfactory agreement for the incident energies studied herein, especially if the substantial differences between those data, as reported in the literature, are considered.

Figures 4-6 show the DCS for the excitation $X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$. Here, there is a very good agreement between the results obtained by our theory and by SMC for incident energies above 20 eV. Near threshold (13 eV), there is still a good qualitative agreement. Quantitatively, both theories agree reasonably well at large scattering angles, although substantial disagreement is observed near the forward direction. At 20 eV, one notices from figure 6 that both theories reproduce quite well the experimental data (Khakoo and Trajmar 1986). Nevertheless, this is not repeated for the incident energy of 30 eV

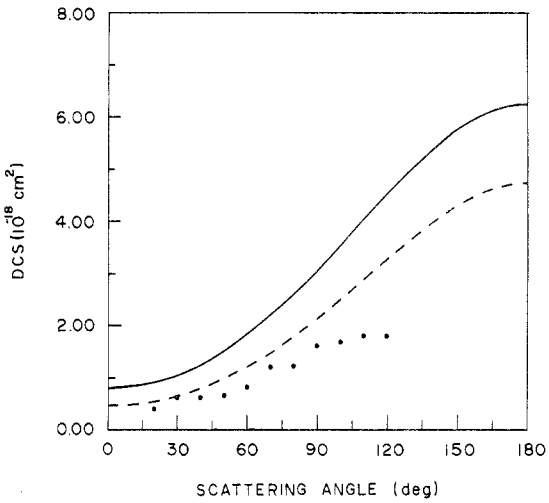

Figure 1. Differential cross section (DCS) for the transition $X\ ^1\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$ of H_2 by electron impact at 10.5 eV. Full curve, present DW results; broken curve, results obtained by SMC (Lima *et al* 1988); full circles, experimental data (Hall and Andrić 1984).

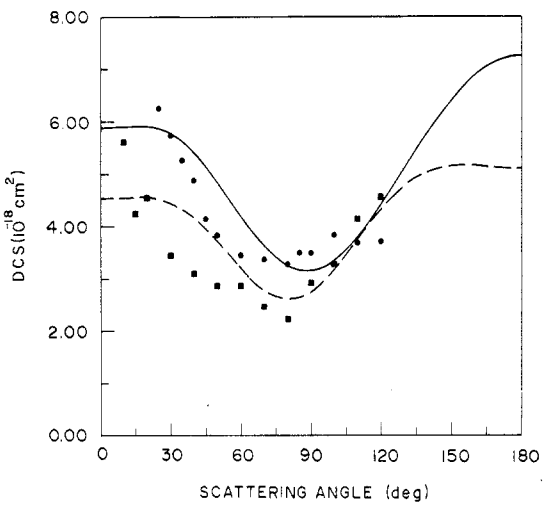

Figure 2. Same as in figure 1 for 20 eV. The experimental data are: full squares, Nishimura and Danjo (1986); full circles, Khakoo *et al* (1987).

(figure 8). In this case both theoretical calculations overestimate the DCS in the angular range between 20° and 80°. The origin of this discrepancy is not well known. In fact, one might attribute it to the multichannel effects in the collisional process and/or electronic correlation effects of the target, which are not included in both calculations. However, it is expected that the influence of those effects will be more significant at lower incident energies. In this sense, the existence of more abundant experimental data will be helpful in clarifying this question.

The DCS for the excitation $X\ ^1\Sigma_g^+ \rightarrow c\ ^3\Pi_u$ in H_2 are shown in figures 7-9 for 13, 20 and 30 eV, respectively. Again, very good agreement is obtained between our DWA results and those of SMC for incident energies above 20 eV. However, at 13 eV, despite

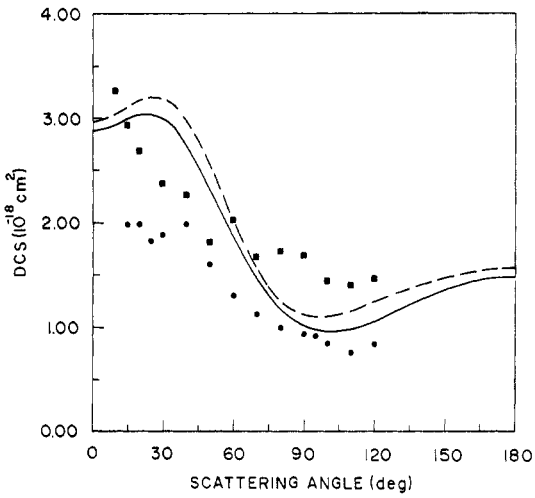

Figure 3. Same as figure 2 for 30 eV.

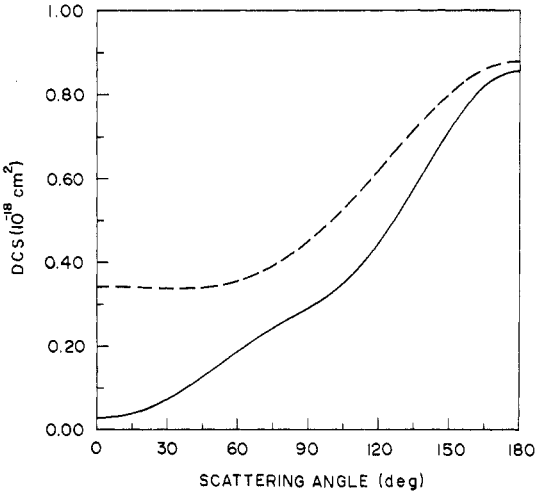

Figure 4. DCS for the transition $X\ ^1\Sigma_g^+ \rightarrow a\ ^3\Sigma_g^+$ of H_2 by electron impact at 13.0 eV. Full curve, present results; broken curve, SMC results (Lima *et al* 1988).

the good qualitative agreement, there is a significant discrepancy between the results of these calculations. At 20 eV, the present DWA results differ significantly from those obtained by Lee *et al* (1982) in a previous study. Actually, the figure shown in that paper is wrong.

For the $X\ ^1\Sigma_g^+ \rightarrow c\ ^3\Pi_u$ transition, comparison with experimental data (Khakoo and Trajmar 1986) is made at 20 and 30 eV for both DWA and SMC. Both calculations overestimate the DCS by a factor of 4 at 20 eV and a factor of 2 at 30 eV. Now, since the results obtained with these two-state level theories agree well between themselves, we suspect that the overestimations may be originated by either the multichannel effects in the collisional process or the electronic correlation effects of the target, or both.

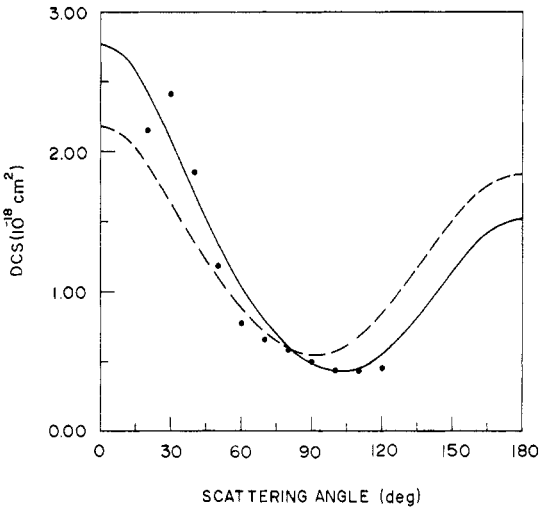

Figure 5. Same as figure 4 for 20 eV; the experimental data (full circles) are from Khakoo *et al* (1987).

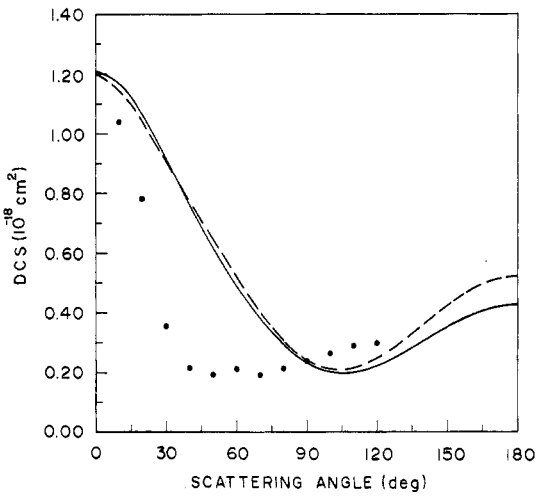

Figure 6. Same as figure 5 for 30 eV.

Tables 1-3 list the DCS and also the integral cross sections (ICS) for the transitions $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$, $X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$ and $X\,^1\Sigma_g^+ \rightarrow c\,^3\Pi_u$, respectively.

4. Conclusions

The DWA has been applied to study the electronic excitations of H_2 by low-energy electron impact. Through a comparative study with the SMC in a two-channel approximation, we have obtained more concrete information regarding the validity of the DWA for e^--H_2 scattering. It has been verified that for the electronic transitions studied herein, the DWA reproduces very well both shape and magnitude of the DCS obtained

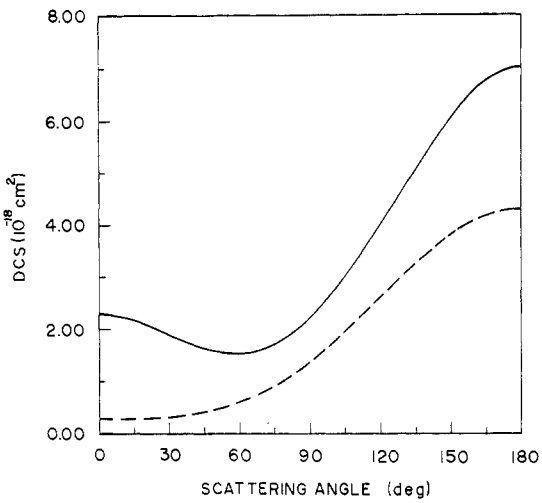

Figure 7. DCS for excitation to the $c\,^3\Pi_u$ state of H_2 by electron impact at 13.0 eV. Full curve, present DW results; broken curve, SMC results (Lima *et al* 1988).

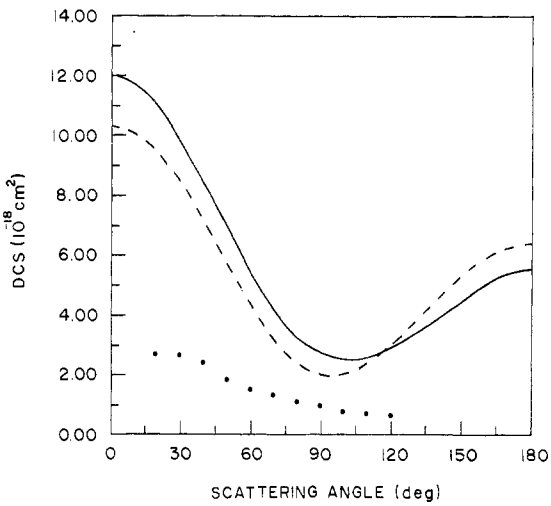

Figure 8. Same as figure 7 for 20 eV; the experimental data (full circles) are from Khakoo *et al* (1987).

by SMC for incident energies above 20 eV. Even near threshold the agreement between these theories is fair.

In addition, the results of both theories compare well with the experimental data for the $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ transition. However, substantial discrepancies are observed for the $X\,^1\Sigma_g^+ \rightarrow c\,^3\Pi_u$ transition, and for the $X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$ transition at 30 eV. Those discrepancies might be attributed to multichannel effects (McConkey *et al* 1988) and/or correlation effects of the target. Multichannel effects cannot be taken into account by the present theory. So, further calculations with more elaborate approximations will be needed in order to better understand the nature of those discrepancies. However, correlation effects of the target can easily be incorporated in the present formalism.

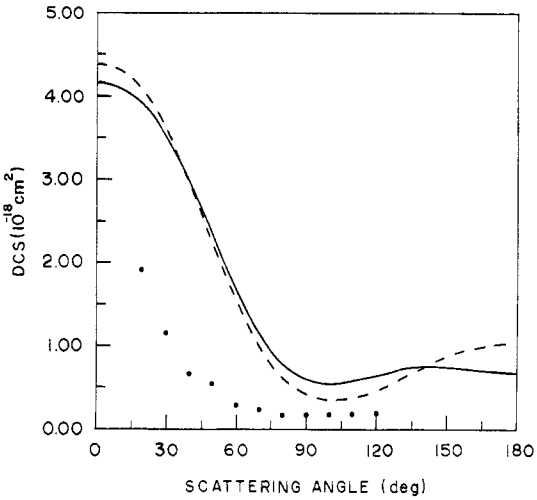

Figure 9. Same as figure 8 for 30 eV.

Table 1. Differential and integral cross sections (in 10^{-18} cm^2) for the transition $X\ ^1\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$ of H_2 by electron impact.

	Energy		
Angle	10.5 eV	20 eV	30 eV
0.0	0.8	5.88	2.87
10.0	0.81	5.90	2.93
20.0	0.923	5.90	3.02
30.0	1.08	5.77	2.99
40.0	1.23	5.41	2.74
50.0	1.49	4.85	2.33
60.0	1.82	4.20	1.87
70.0	2.18	3.63	1.46
80.0	2.59	3.25	1.47
90.0	3.03	3.15	1.01
100.0	3.54	3.35	0.953
110.0	4.05	3.79	0.979
120.0	4.59	4.40	1.05
130.0	4.99	5.10	1.16
140.0	5.46	5.79	1.26
150.0	5.77	6.40	1.35
160.0	5.97	6.87	1.42
170.0	6.15	7.16	1.46
180.0	6.18	7.26	1.47
ICS	40.36	56.81	19.39

Table 2. Same as table 1, for $X\ ^1\Sigma_g^+ \rightarrow a\ ^3\Sigma_g^+$ excitation.

	Energy		
Angle	13 eV	20 eV	30 eV
0.0	0.340	2.18	1.20
10.0	0.341	2.11	1.15
20.0	0.358	1.91	1.04
30.0	0.336	1.64	0.906
40.0	0.337	1.36	0.778
50.0	0.342	1.11	0.650
60.0	0.355	0.887	0.522
70.0	0.377	0.713	0.402
80.0	0.408	0.595	0.305
90.0	0.448	0.547	0.240
100.0	0.497	0.575	0.210
110.0	0.555	0.679	0.215
120.0	0.618	0.846	0.247
130.0	0.683	1.050	0.299
140.0	0.744	1.29	0.361
150.0	0.799	1.51	0.423
160.0	0.842	1.69	0.475
170.0	0.870	1.80	0.509
180.0	0.879	1.85	0.521
ICS	6.292	12.51	5.43

Table 3. Same as table 1, for $X\ ^1\Sigma_g^+ \rightarrow c\ ^3\Pi_u$ excitation.

	Energy		
Angle	13 eV	20 eV	30 eV
0.0	0.29	10.32	4.38
10.0	0.29	10.12	4.32
20.0	0.30	9.53	4.09
30.0	0.33	8.54	3.63
40.0	0.38	7.25	2.96
50.0	0.47	5.79	2.22
60.0	0.61	4.37	1.53
70.0	0.80	3.19	0.99
80.0	1.06	2.37	0.625
90.0	1.39	1.98	0.425
100.0	1.77	1.99	0.359
110.0	2.19	2.34	0.388
120.0	2.63	2.95	0.478
130.0	3.07	3.70	0.600
140.0	3.48	4.49	0.733
150.0	3.83	5.22	0.876
160.0	4.10	5.80	0.953
170.0	4.27	6.18	1.01
180.0	4.32	6.31	1.04
ICS	21.31	52.44	15.30

Indeed, the influence of the electronic correlation effects of the target in the excitation of H_2 has been recently studied (Lee *et al* 1990).

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