

## Electronic excitation of $H_2$ by electron impact using soft norm-conserving pseudopotentials

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We calculate electronic excitation cross sections for the  $b^3\Sigma_u^+$ ,  $a^3\Sigma_g^+$ ,  $c^3\Pi_u$ , and  $d^3\Pi_u$  states of  $H_2$  by electron impact. Our results were obtained with the Schwinger multichannel method with pseudopotentials and real potentials at the two-channel level of approximation. Pseudo-H atoms are used to generate  $H_2$  molecules with almost the same low-energy spectrum as the real molecules. We show that the dynamics of the electronic excitation process of the pseudomolecules by electron impact is very similar to the real case. Our results support the idea that pseudopotentials can be used to obtain reliable molecular electronic excitation cross sections by low-energy electron impact, confirming the expectations of previous studies with  $CH_2O$  [Bettega *et al.*, Phys. Rev. A **25**, 1111 (1993)] and  $HBr$  [Rescigno, J. Chem. Phys. **104**, 125 (1996)]. [S1050-2947(96)02412-2]

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In this paper, we calculate electronic excitation cross sections by electron impact for the  $b^3\Sigma_u^+$ ,  $a^3\Sigma_g^+$ ,  $c^3\Pi_u$ , and  $d^3\Pi_u$  states of the  $H_2$  molecule using the Schwinger multichannel method [1] with pseudopotentials (SMCPP) [2] and real potentials (SMC). The basic idea in the SMCPP method is to replace the real target by a pseudotarget where the core electrons and the nucleus of each atom in the molecule are replaced by the corresponding soft norm conserving pseudopotentials and the valence electrons (in the present implementation) are described in the Hartree-Fock approximation. The method keeps the many-body character of the scattering wave function and allows studies where this feature is of fundamental importance as in molecular electronic excitation by electron impact. In most of our applications of the SMCPP method we studied the elastic scattering of electrons by molecules described by pseudopotentials and in general we obtained very good results [3]. We have also studied the inelastic scattering of electrons by  $CH_2O$  [2] molecules. For this molecule, we have found very good agreement between the electronic excitation cross sections obtained with pseudo- and real potentials. More recently Rescigno and McCurdy [4] implemented norm-conserving pseudopotentials in the complex Kohn method. Rescigno [5] has shown the efficiency of their procedures in a study of electronic excitation of  $HBr$  by electron impact. In the present application, we have chosen to study the  $H_2$  molecule because the hydrogen atom has no core electrons. Thus the pseudopotential, which is designed to be regular at the origin, replaces only the real potential  $1/r$  of the nucleus. We can then compare the pseudopotential to the real potential of the nucleus and study the influence of removing the cusp of the  $1/r$  potential on the excitation cross sections of  $H_2$ . Besides, although the H atom has no core electrons, its pseudopotential has general properties equivalent to those of any other atom, i.e., the pseudopotential bounds no core orbitals, it is soft, and it generates soft wave functions.

The so-called norm-conserving pseudopotentials [6,7] were derived from all-electron calculations and were designed to produce nodeless pseudo-wave-functions which, when normalized, are equal to the true valence wave functions beyond some core radius  $R_c$ . The integrals from 0 to

$R$  of the real charge densities and pseudo-charge-densities are then the same for  $R > R_c$  (norm conservation). They are also constructed to be identical to the real potential beyond  $R_c$ . The most relevant consequence of the norm conservation property can be expressed by the following equation (in atomic units—derived in Ref. [8]):

$$-2\pi \left[ (r\phi)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln\phi \right]_R = 4\pi \int_0^R \phi^2 r^2 dr, \quad (1)$$

where  $\phi$  is a solution of the radial Schrödinger equation which is regular at the origin. The logarithmic derivative of  $\phi$  is related to the scattering phase shift. Thus since the integral that appears in the right hand side of Eq. (1) is the same for both cases, the scattering properties of the pseudopotential have the same variation with energy as the scattering properties of the real potential.

In this calculation we use, for each hydrogen atom, the pseudopotential of Bachelet, Hamann, and Schlüter [9], which is an extension of the pseudopotentials of Ref. [6] to include relativistic effects. It is decomposed into a long-range Coulomb part which is  $l$  independent [ $\hat{V}_{core}(r)$ ], and a short-range  $l$ -dependent part [ $\hat{V}_{ion}(r)$ ]:

$$\hat{V}_{pp}(r) = \hat{V}_{core}(r) + \hat{V}_{ion}(r), \quad (2)$$

with

$$\hat{V}_{core}(r) = -\frac{Z_v}{r} \left[ \sum_{i=1}^2 c_i^{core} \operatorname{erf}[(\alpha_i^{core})^{1/2} r] \right], \quad (3)$$

and

$$\hat{V}_{ion}(r) = \sum_{n=0}^1 \sum_{j=1}^3 \sum_{l=0}^2 A_{njl} r^{2n} e^{-\alpha_{jl} r^2} \sum_{m=-l}^{+l} |lm\rangle \langle lm|, \quad (4)$$

where  $Z_v$  is the valence charge of the atom and in this application it is equal to 1. The coefficients  $c_i^{core}$ ,  $A_{njl}$ , and the decay constants  $\alpha_i^{core}$  and  $\alpha_{jl}$  are tabulated in Ref. [9].

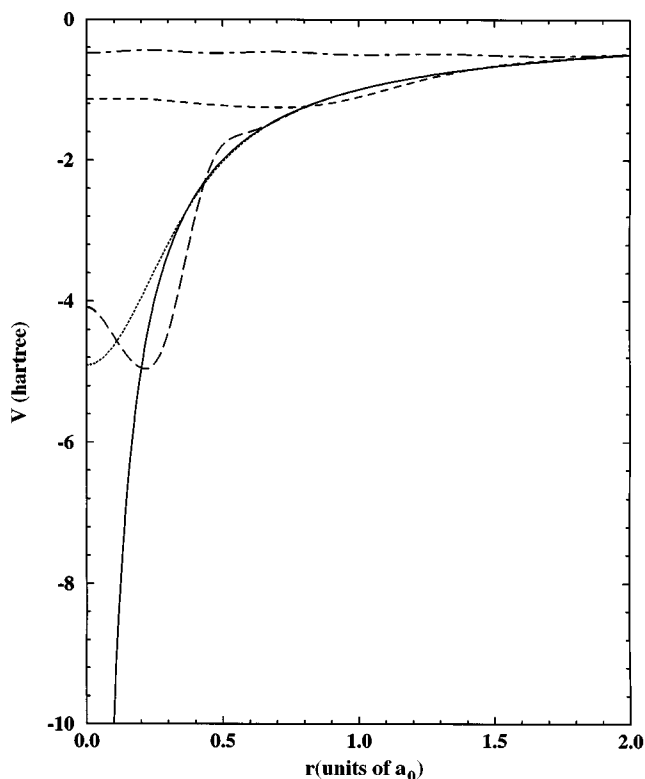


FIG. 1. Real potential and pseudopotentials for the hydrogen atom. Full line: real potential; long dashed line: pseudopotential for  $l=0$ ; short dashed line: pseudopotential for  $l=1$ ; dot-dashed line: pseudopotential for  $l=2$ ; dotted line:  $\hat{V}_{pp}(r)$  potential for  $l \geq 3$ .

The  $\hat{V}_{core}(r)$  potential smoothly approaches a finite value for  $r \rightarrow 0$ . That is also the case for the  $l$ -dependent part, which goes to a different but finite value for each  $l$ . Figure 1 shows the real potential for the hydrogen atom compared to the corresponding pseudopotential  $\hat{V}_{pp}(r)$ . The core radius  $R_c$  depends on  $l$  and was chosen in Ref. [9] by an empirical rule. Note that the pseudopotentials for different partial waves are very different from each other and from the real potential inside the core region ( $r < R_c$ ), but they all converge to the same curve ( $1/r$ ) for large  $r$ 's. For  $l \geq 3$  we have  $\hat{V}_{pp}(r) = \hat{V}_{core}(r)$ , which is  $l$  independent and accounts for the coupling of all partial waves with  $l$  higher than 2. In Fig. 1 we can clearly see that the net result of describing a hydrogen atom with pseudopotentials is to replace the cusp of the real potential  $1/r$  at the origin by a set of pseudopotentials that are all finite. One should also note that a particle with a fixed value for its total energy would have lower kinetic energy when under the action of the pseudopotential than if it moves in the presence of the real potential. Therefore a particle in the pseudopotential would have, on average, a larger wavelength. Its pseudo-wave-function would be smoother than the real one, and therefore easier to describe.

As a first test of the H pseudopotential we have numerically solved the Schrödinger equation for the pseudo-H-atom up to the  $n=5$  level. We have found an energy spectrum almost identical to the real one (the largest difference is 0.2% for the  $1s$  level). Since all energies beyond the  $n=5$  level are very close to each other, Eq. (1) indicates that the pseudopotential is, in fact, good for the whole bound state spectrum of the H atom.

TABLE I. Excitation thresholds (eV).

	$b^3\Sigma_u^+$	$a^3\Sigma_g^+$	$c^3\Pi_u$	$d^3\Pi_u$
Real potential	9.98	12.03	12.31	14.55
Pseudopotential	10.08	12.02	12.29	14.52
Other calculations	10.62 <sup>a</sup>	12.54 <sup>b</sup>	12.93 <sup>c</sup>	14.56 <sup>d</sup>

<sup>a</sup>Reference [12].

<sup>b</sup>Reference [13].

<sup>c</sup>Reference [14].

<sup>d</sup>Reference [15].

The self-consistent field wave function of the  $X^1\Sigma_g^+(1\sigma_g^2)$  state of the  $H_2$  molecule was calculated using an uncontracted  $9s6p$  Cartesian Gaussian basis set [10] ( $s$ : 39.186 359, 6.567 8062, 1.774 5375, 0.623 416 84, 0.235 659 27, 0.089 189 09, 0.036 337 81, 0.015 303 56, 0.005 615 93 and  $p$ : 1.475 4747, 0.339 955 51, 0.109 565 38, 0.042 477 76, 0.017 663 03, 0.006 933 56). The same basis set was used to represent the  $b^3\Sigma_u^+$ ,  $a^3\Sigma_g^+$ ,  $c^3\Pi_u$ , and  $d^3\Pi_u$  states through a frozen core approximation [improved virtual orbitals [11] (IVO)]. We completed this basis set with 1  $d$  function (exponent: 0.3) and used the whole set as scattering basis. Table I compares the excitation thresholds of the  $b^3\Sigma_u^+$ ,  $a^3\Sigma_g^+$ ,  $c^3\Pi_u$ , and  $d^3\Pi_u$  states of the  $H_2$  molecule calculated with the real potential and pseudopotentials with some precise results of the literature [12–14] and with the IVO result of Ref. [15] for the  $d^3\Pi_u$  state. The spectra of the  $H_2$  molecule are almost identical in the two cases (real and pseudopotential), indicating that even pseudopotentials generated for hydrogen atoms in the local-density approxi-

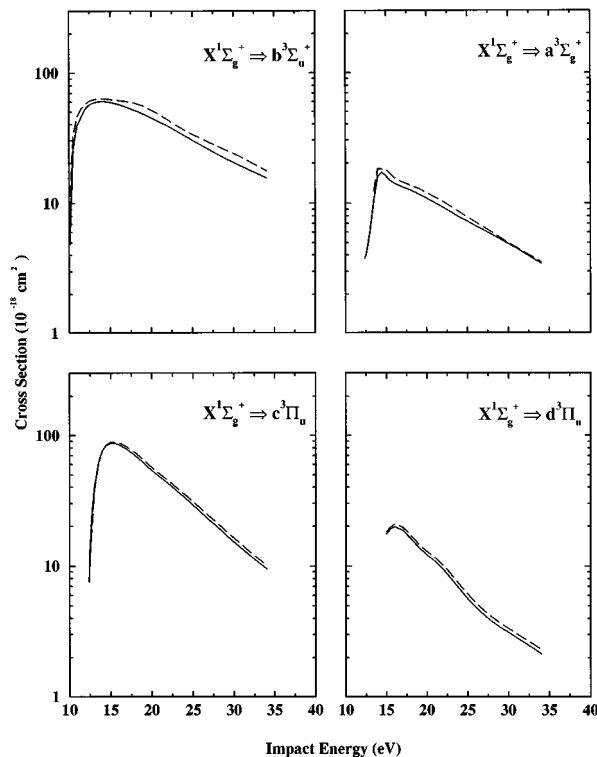


FIG. 2. Electronic excitation of the  $H_2$  molecule by electron impact. Full lines: pseudopotential calculations; dashed lines: real potential calculations.

TABLE II. Integral cross sections calculated with pseudopotentials ( $10^{-18}$  cm<sup>2</sup>).

Energy (eV)	$b^3\Sigma_u^+$	$a^3\Sigma_g^+$	$c^3\Pi_u$	$d^3\Pi_u$
10.1	4.820			
10.5	25.534			
11.0	39.005			
12.0	53.145			
12.5	56.733	3.926	12.819	
13.0	58.897	5.971	39.248	
14.0	60.372	15.876	76.073	
15.0	59.399	15.862	86.517	17.412
16.0	57.236	14.058	84.315	19.772
17.0	54.518	13.171	77.988	18.598
18.0	51.461	12.467	70.064	16.114
19.0	48.211	11.703	61.514	13.690
20.0	44.918	10.881	54.031	12.097
22.0	38.556	9.268	42.529	9.410
24.0	32.693	7.871	33.176	6.674
26.0	27.596	6.721	25.500	4.844
28.0	23.483	5.750	19.584	3.779
30.0	20.262	4.889	15.157	3.106
32.0	17.673	4.112	11.895	2.594
34.0	15.512	3.434	9.505	2.149

mation are transferrable to Hartree-Fock calculations.

Figure 2 shows electronic excitation cross sections for the  $b^3\Sigma_u^+$ ,  $a^3\Sigma_g^+$ ,  $c^3\Pi_u$ , and  $d^3\Pi_u$  states of the H<sub>2</sub> molecule. Table II shows the pseudopotential results. All calculations were carried out in the two-channel static-exchange approxi-

mation. The excitation cross sections calculated with pseudopotentials agree perfectly well with those obtained with the real potential. Although not shown, the cross sections for the  $b^3\Sigma_u^+$ ,  $a^3\Sigma_g^+$  and  $c^3\Pi_u$  states reproduce well those of Ref. [16], which are all-electron calculations using the SMC method. Therefore all comparisons with other theoretical calculations and experimental results made in that reference are appropriate for the present results. For the  $d^3\Pi_u$  state our results do not agree with those of Ref. [15] obtained with a distorted wave approximation and the reason remains to be explained.

Our results show that the replacement of the real potential by these sets of soft norm-conserving pseudopotentials keeps the electronic excitation cross sections for the four studied states unchanged. Our conclusions may be summarized as follows: (1) Pseudo-H-atoms generate a pseudomolecule very similar to the real one (same electronic spectrum); (2) the scattering of electrons against this pseudomolecule (continuum states of the H<sub>2</sub><sup>-</sup> system) is also equivalent to the real case, and as seen in Fig. 2, it gives rise to the same dynamics of electronic excitation by electron impact (the real molecules and pseudomolecules have the same electronic transition properties); (3) since the general properties of the H pseudopotential are the same as those of any other atom, the present work strongly supports the transferability of norm-conserving pseudopotentials to studies of electronic excitation of molecules by electron impact.

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