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Static-exchange cross sections for electron-collisions with B_2H_6, C_2H_6, Si_2H_6, and Ge_2H_6

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Abstract. We report integral and differential cross sections from 5-30 eV for elastic scattering of electrons by X_2H_6 (X=B, C, Si, Ge) obtained using the Schwinger Multichannel Method with Pseudopotentials [M.H.F. Bettega, L.G. Ferreira, M.A.P. Lima, Phys. Rev. A **47**, 1111 (1993)]. We compare our results with available experimental data and other theoretical results, and also with previous results for XH_4 (X=C, Si, Ge) [M.H.F. Bettega, A.P.P. Natalense, M.A.P. Lima, L.G. Ferreira, J. Chem. Phys. **103**, 10566 (1995)]. To our knowledge this is the first *ab initio* calculation of the B_2H_6 and Ge_2H_6 electron scattering cross sections.

PACS. 34.80.Bm Elastic scattering of electrons by atoms and molecules – 34.80.Gs Molecular excitation and ionization by electron impact

1 Introduction

The development of *ab initio* methods [1,5] to study low-energy electron-molecule collisions made possible calculations of reliable elastic and inelastic cross sections. Several studies involving linear and polyatomic targets were made at different levels of approximations. The simplest is the static-exchange (SE) approximation, where only the Coulomb and the exchange potentials are considered, but they are exactly computed. The SE approximation can be considered as a first step towards calculations that include electronic excitation of the target and target polarization effects. Furthermore, the SE approximation may provide elastic cross section data for a wide range of molecules in the energy range where polarization is not important.

Until recently, even at the SE approximation, the size of the molecular targets was restricted by computer limitations. The reason is simple: the *ab initio* methods combine techniques used in bound-state calculations with those of the scattering equations. In the scattering calculations, the basis set has two roles: 1) to represent the molecular target and 2) to represent the scattered electron. In general, one needs more basis functions in a scattering calculation than in a bound state calculation. When the size of the target grows, more basis functions are needed for a description of both the target and the scattering process, and the computational limit is reached.

To allow studies of scattering by heavier molecules, we implemented soft norm-conserving pseudopotentials [6] in the Schwinger multichannel (SMC) method. The method with pseudopotentials [5] keeps the main features of the SMC method. The difference lies in that now the potential due to the core electrons and the nucleus of each atom in the molecule is replaced by a pseudopotential. The resulting valence wavefunctions are smooth and nodeless and can be represented by smaller Gaussian basis sets than in the all-electron case. We have shown the efficiency of the pseudopotential method in elastic scattering [7], in molecular electronic excitation [5,8] and in molecular rotational excitation [9]. In general, good agreement is found with experimental results and with other theoretical results. Though the pseudopotentials have enormous advantages in computationally heavy problems such as scattering calculations, the literature was slow to realize it. For instance, norm-conserving pseudopotentials (also known as effective potentials) were first proposed by Hamann *et al.* in 1979 [10]. They were included in the Schwinger Multichannel Method in 1993 [5] and only recently they were used together with other scattering calculation methods [11].

In our previous studies [7] of elastic scattering we have focused our attention in molecules belonging to the same family (with the same electronic configuration for the valence, with the same number of valence electrons and geometry). We found that molecules in same family have very similar cross sections. In this study, we apply the method to study low-energy electron scattering by X_2H_6 (X=B, C, Si, Ge) at the SE approximation. We are looking for possible similarities in the cross sections of these

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molecules in the energy range from 5 eV up to 30 eV. B_2H_6 does not belong to this family and has a different geometry, but Boron and Carbon being neighbors in the Periodic Table, it is worth looking for similarities with C_2H_6. To our knowledge, this is the first calculation for B_2H_6 and for Ge_2H_6.

2 Theoretical formulation

The SMC [1,12] method and its version with pseudopotentials [5] have been discussed in earlier works, and we will review it here only to show the approximations being made. The SMC method is a multichannel extension of the Schwinger variational principle. It is a variational approximation for the scattering amplitude, where the scattering wavefunction is expanded in a basis of $(N+1)-$particle Slater determinants. The coefficients of this expansion are then variationally determined. The resulting expression for the scattering amplitude in the body frame is

$$[f_{\boldsymbol{k}_i,\boldsymbol{k}_f}] = -\frac{1}{2\pi}\sum_{m,n} < S_{\boldsymbol{k}_f}|V|\chi_m > (d^{-1})_{mn} < \chi_n|V|S_{\boldsymbol{k}_i} > \tag{1}$$

where

$$d_{mn} = < \chi_m|A^{(+)}|\chi_n > \tag{2}$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP+PV)}{2} - VG_P^{(+)}V. \tag{3}$$

In the above equations $S_{\boldsymbol{k}_i}$, solution of the unperturbed Hamiltonian H_0, is the product of a target state and a plane wave, V is the interaction potential between the incident electron and the target, $|\chi_m\rangle$ is an $(N+1)$-electron Slater determinant used in the expansion of the trial scattering wavefunction, $\hat{H} = E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_0 + V$, P is a projection operator onto the open-channel space defined by target eigenfunctions, and $G_P^{(+)}$ is the free-particle Green's function projected on the P-space.

For elastic scattering at the static-exchange approximation, the P operator is composed only by the ground state of the target $|\Phi_1\rangle$

$$P = |\Phi_1\rangle\langle\Phi_1| \tag{4}$$

and the configuration space $|\chi_m\rangle$ is

$$\{|\chi_m\rangle\} = \mathcal{A}|\Phi_1\rangle|\varphi_i\rangle \tag{5}$$

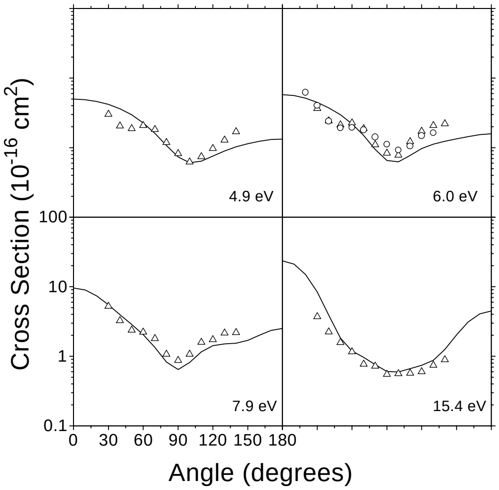

Fig. 1. Differential cross sections for C_2H_6 at 4.9, 6.0, 7.9 and 15.4 eV. Solid line, pseudopotentials-SMC results; triangles, experimental results of reference [15]; circles, experimental results of reference [17].

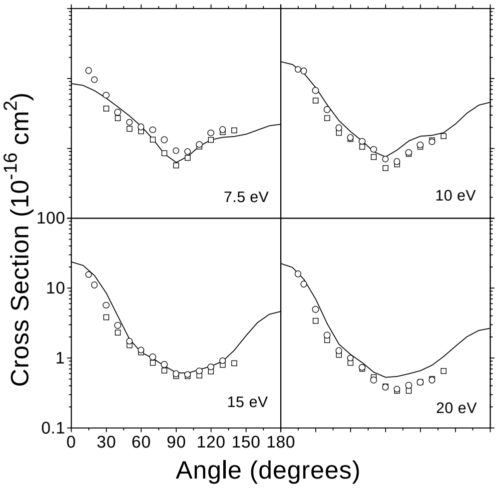

Fig. 2. Differential cross sections for C_2H_6 at 7.5, 10, 15 and 20 eV. Solid line, pseudopotentials-SMC results; squares, experimental results of reference [16]; circles, experimental results of reference [17].

Table 1. Cartesian Gaussian functions[a] for H.

Function Type	Exponent	Coefficient[b]
s	13.3615	0.130844
s	2.0133	0.921539
s	0.4538	1.0
s	0.1233	1.0

[a] Cartesian Gaussian functions are defined by $\varphi_{lmn} = N_{lmn}(x-a_x)^l(y-a_y)^m(z-a_z)^n\exp(-\alpha|\boldsymbol{r}-\boldsymbol{a}|^2)$.

[b] Coefficients different from 1.0 mean contracted functions.

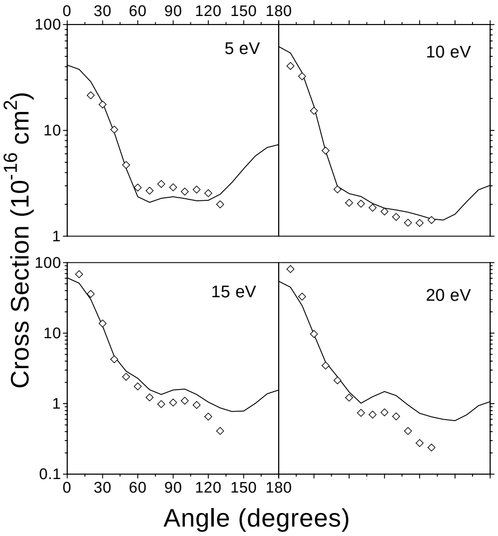

Fig. 3. Differential cross sections for Si_2H_6 at 5, 10, 15 and 20 eV. Solid line, pseudopotentials-SMC results; diamonds, experimental results of reference [18].

where $\mathcal{A}$ is the antissimetrization operator and $|\varphi_i\rangle$ is a 1-particle function represented by one molecular orbital. The interaction V includes the Coulomb pair repulsion between the valence and scattered electron, $1/r_{12}$, and the pseudopotentials replacing the nuclei and cores, whose parameters are tabulated in reference [6]. In this application, the pseudopotential replaces the 1s atomic orbital for B and C, the 1s, 2s and 2p atomic orbitals for Si and the 1s, 2s, 2p, 3s, 3p and 3d atomic orbitals for Ge.

3 Computational procedures

The basis functions we used to describe the valence part of the target state are shown in Table 1, for the hydrogen [13], and in Table 2, for the inner atoms. The Cartesian Gaussian functions for the inner atoms were generated by the procedure described in reference [14]. With these Gaussian sets we constructed, for each molecule, a set of 94 molecular orbitals, solutions of the Hartree-Fock equations. The unoccupied (virtual) orbitals, 88 for B_2H_6 and 87 for the other molecules, were then used to describe the scattered electron $|\varphi_i\rangle$ in equation (5).

All calculations performed on C_2H_6, Si_2H_6 and Ge_2H_6 were made for the staggered conformation, and for all molecules the experimental equilibrium geometries were used.

4 Results and discussion

In Figures 1 and 2 we compare our differential cross sections for C_2H_6 with experimental results of references [15, 17] from 4.9 eV up to 20 eV. In Figure 3 we compare our differential cross section for Si_2 H_6 with experimental data of reference [18]. In both cases we find a good agreement between experiment and the calculated results. Figure 4 compares our integral cross section for C_2H_6 with the experimental total [19] and elastic cross sections [17], and with the calculated results of the all-electron SMC method [20] and the Kohn method [21]. There is good agreement between the calculated results, but some discrepancies are found between theory and experiment for the C_2H_6 integral cross section. Sun *et al.* [21] included polarization effects in their calculations in order to reproduce the Ramsauer-Townsend (RT) minimum for C_2H_6 at very low energies. Their static-exchange results are very

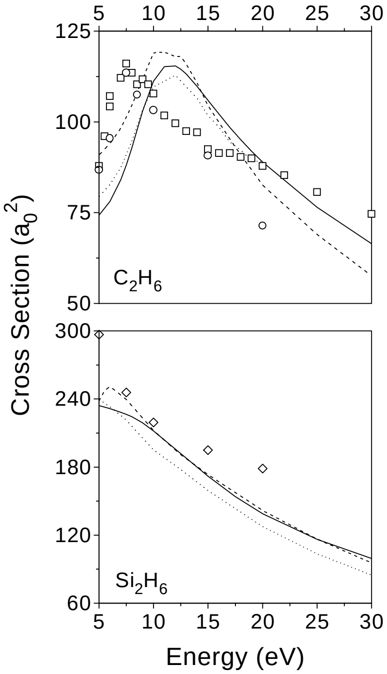

Fig. 4. Integral cross sections for C_2H_6 (upper plot) and for Si_2H_6 (lower plot). For C_2H_6: solid line, pseudopotentials-SMC results; dashed line, all-electron-SMC results; dotted line, complex Kohn results; squares, total cross section of reference [19]; circles, elastic cross section of reference [17]. For Si_2H_6: solid line, present pseudopotentials-SMC results; dashed line, pseudopotentials-SMC results at eclipsed conformation; dotted line, all-electron-SMC results; diamonds, elastic cross section of reference [18].

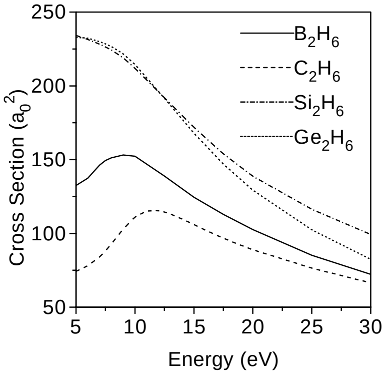

Fig. 5. Integral cross section for X_2H_6.

Table 2. Cartesian Gaussian functions for the inner atoms.

B	C	Si	Ge	
Exponent	Exponent	Exponent	Exponent	Coefficient
s 7.743009	s 12.49627	s 5.289030	s 2.585413	1.0
s 1.588291	s 2.470286	s 0.782819	s 1.142609	1.0
s 0.385169	s 0.614028	s 0.492529	s 0.454205	1.0
s 0.118779	s 0.184028	s 0.127062	s 0.182815	1.0
s 0.026184	s 0.039982	s 0.029528	s 0.049632	1.0
p 3.487316	p 5.228869	p 1.197745	p 1.028430	1.0
p 1.118566	p 1.592058	p 0.436389	p 0.360027	1.0
p 0.398653	p 0.568612	p 0.192503	p 0.125626	1.0
p 0.144251	p 0.210326	p 0.086625	p 0.043080	1.0
p 0.050830	p 0.074450	p 0.036575	p 0.007811	1.0
d 0.717295	d 0.831082	d 1.055806	d 0.475112	1.0
d 0.194907	d 0.229204	d 0.326309	d 0.195662	1.0
d 0.073244	d 0.075095	d 0.050346	d 0.036696	1.0

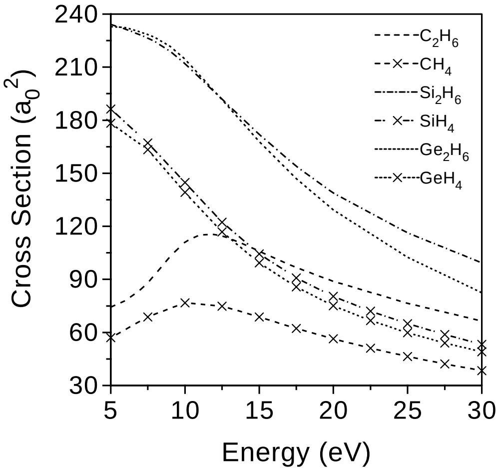

Fig. 6. Integral cross section for X_2H_6 and XH_4.

close to ours. They have shown that polarization effects move the broad maximum (at 12.5 eV) of the integral cross section towards the experimental values (maximum at 7.5 eV). For Si_2H_6, we also show our previous results for the eclipsed conformation [5] and experimental results of reference [18]. We see that the relative positions of the hydrogens have little effect on the cross section.

In Figure 5 we present our results for the entire group of molecules. The cross sections for Si_2H_6 and for Ge_2H_6 are very similar. In Figure 6, we compare the integral cross section for X_2H_6 with previous results for XH_4 (X=C, Si, Ge) [7]. We see that the X_2H_6 cross sections are larger than the corresponding XH_4 cross sections but the curves have similar shapes. The ratio $\sigma_{X_2H_6}/\sigma_{XH_4}$ is about 1.3 for low energies and 1.7 for the higher energies. For a classical collision a factor 5/3 would be expected if the cross section is averaged over the molecular orientations (a factor 1 for collisions along the axis containing the X atoms and a factor 2 for collisions along each one of the two directions perpendicular to this axis).

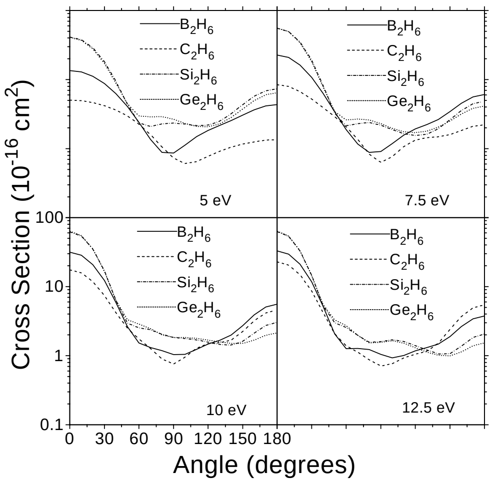

Fig. 7. Differential cross section for X_2H_6 at 5, 7.5, 10 and 12.5 eV.

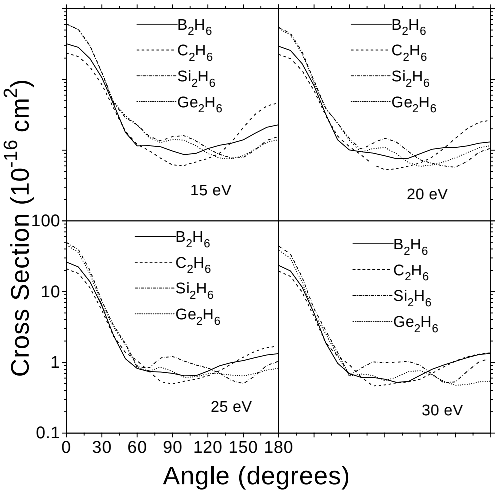

Fig. 8. Differential cross section for X_2H_6 at 15, 20, 25 and 30 eV.

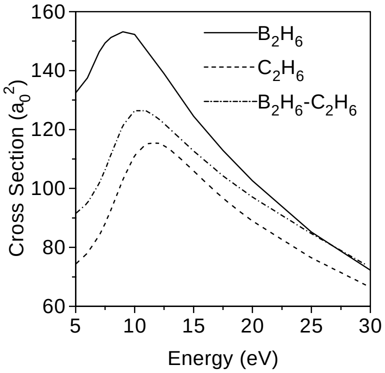

Fig. 9. Integral cross section for B_2H_6 at the geometry of C_2H_6. Solid line: our results for B_2H_6, dashed line: our results for C_2H_6, dotted-dashed line: our results for B_2H_6 at the geometry of C_2H_6.

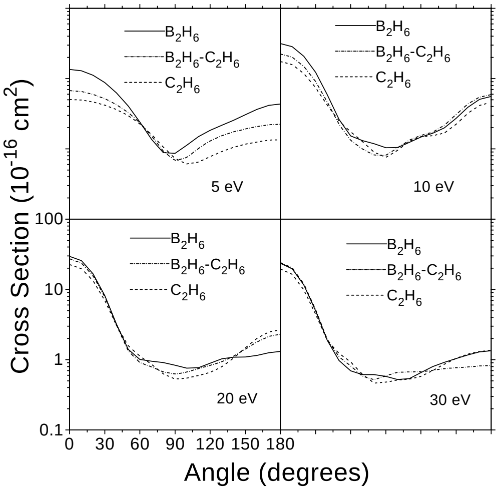

Fig. 10. Differential cross sections for B_2H_6 at the geometry of C_2H_6 at 5, 10, 20 and 30 eV. Solid line: our results for B_2H_6, dashed line: our results for C_2H_6, dotted-dashed line: our results for B_2H_6 at the geometry of C_2H_6.

Differential cross sections for X_2H_6 (X=B, C, Si, Ge) are presented in Figures 7 and 8. For lower energies, the differential cross sections for Si_2H_6 and Ge_2H_6 are very close. For higher energies this pattern is no longer observed. In the entire energy range, the differential cross sections for Si_2H_6 and Ge_2H_6 present an oscillatory behavior. For B_2H_6 and C_2H_6 these oscillations are not seen. As expected, heavier inner atoms couple higher angular momenta in the scattering process as in the case of XH_4 [7]. This coupling is responsible for the oscillatory behavior in the differential cross sections plots for the heavier molecules.

B_2H_6 and C_2H_6 are close neighbors but their chemical bonds are different. Geometrically borane has 6 atoms in a same plane (H_2B+BH_2) and 2 other hydrogens lying symmetrically above and below this plane (the bridging hydrogens) while C_2H_6 is formed by two pyramidal CH_3 molecules connected by a single bond C–C. In order to find any similarity in their cross sections, we calculated integral and differential cross sections for B_2H_6 at the geometry of C_2H_6. Such an arrangement corresponds to two BH_3 molecules placed together with no chemical bonds between them. At the new geometry, the hydrogen bonds of B_2H_6 are similar to those of C_2H_6 but the B–B is an empty bond while the C–C is a single bond. The results are shown in Figures 9 and 10. The integral cross section for B_2H_6 remains above that for C_2H_6, but the shapes are now similar. There are small differences in the differential cross section plots.

5 Summary

We report integral and differential cross sections calculations for X_2H_6 (X=B, C, Si, Ge) searching for possible similarities between them. For Si_2H_6 and Ge_2H_6 the integral and differential cross sections are similar, while for C_2H_6 and B_2H_6 they present distinct behaviors. Comparing the integral cross sections for C_2H_6 with that obtained for B_2H_6 at the geometry of C_2H_6, we see that the shapes of the curves are similar but the cross sections differ in magnitude. This suggests that the differences in the chemical bonds (and in the electronic charge densities) of these molecules at their experimental geometry are responsible for the differences in the cross sections. We also compare our integral cross sections for X_2H_6 with previous results for XH_4 (X=C, Si, Ge) and find that, as expected, $\sigma_{X_2H_6} > \sigma_{XH_4}$. In general we find good agreement between our calculated cross sections and the available experimental data or other theoretical results.

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