Cross sections for collisions of lowenergy electrons with the hydrides PH3, AsH3, SbH3, SnH4, TeH2, and HI

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Cross sections for collisions of low-energy electrons with the hydrides PH$_3$, AsH$_3$, SbH$_3$, SnH$_4$, TeH$_2$, and HI

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We calculated integral and differential cross sections for scattering of low-energy electrons by two groups of hydrides from 10 to 30 eV. The first group is composed by the hydrides of elements in the same column of the Periodic Table and includes PH$_3$, AsH$_3$, and SbH$_3$. The second group is formed by hydrides in the same row and includes SnH$_4$, SbH$_3$, TeH$_2$, and HI. The calculations employed the Schwinger multichannel method with norm-conserving pseudopotentials [M.H.F. Bettega, L.G. Ferreira, and M.A.P. Lima, Phys. Rev. A **47**, 1111 (1993)]. Our goal is to find similarities and differences in the cross sections in these two groups. © *1996 American Institute of Physics.* [S0021-9606(96)02327-6]

I. INTRODUCTION

The processes of scattering of low-energy electrons by molecules play an important role in the description of cold plasmas, that are currently used in technological applications.[1] For example, the dissociation cross sections of the neutral molecules of the gas are fundamental in plasma etching and plasma enhanced vapor deposition. It follows that the knowledge of elastic and inelastic cross sections for a wide range of molecular systems is a very important subject. To calculate cross sections some *ab initio* methods have been developed, of which two are currently in use: the Schwinger multichannel (SMC) method[2] and the complex Kohn variational method (CKVM).[3] We can also cite the *R* matrix method.[4] Most applications of this method are restricted to linear molecules.

The SMC and CKVM methods make use of L^2 functions to describe the scattering wave function (the SMC uses only L^2 functions) and were designed to study electron scattering by molecules with arbitrary geometry. Due to the use of L^2 functions, the techniques for bound-state calculations could be incorporated by both methods.

Specially in the case of molecules with many electrons, the amount of computational work severely hinders the *ab initio* calculation of electron cross sections. To remedy this problem we introduced the pseudopotentials (PP) in the SMC method.[5] In this approach, only the valence electrons are taken into account, the core electrons being replaced by the pseudopotential. We chose the norm-conserving PP generated by Bachelet, Hamann and Schlüter.[6] These PP are soft and produce smooth, nodeless valence atomic wave functions. The fact that only the valence electrons are taken into account is a general property of PP, but soft wave functions is an exclusive property of the norm-conserving PP. This softness of the pseudo wave functions permits the expansion of the scattering wave function in smaller basis sets and leads to a great simplification in the whole process of calculation, broadening the range of molecular sizes that can be calculated.[7,8] Furthermore, these PP incorporate relativistic corrections that are important for heavier atoms.

In this paper, we present results of a systematical study of low-energy electron scattering by two families of hydrides. We have used the SMC method with PP (SMCPP). The first family includes PH$_3$, AsH$_3$, SbH$_3$, which are made of atoms in the same column. The second family, formed by SnH$_4$, SbH$_3$, TeH$_2$, and HI, are hydrides of atoms in the same row. We aim at verifying similarities and differences in the integral and differential elastic cross sections between these two series of molecules in the energy range from 10 eV up to 30 eV. In our previous investigation of electron-scattering by XH$_4$ (X = C,Si,Ge,Sn,Pb), we found similarities in their integral and differential cross sections.[8] We then concluded that, aside from yielding the electrons that close the atomic shell of the heavier atom, the Hydrogens played only a small part in the scattering process. In the energy range being considered, scattering was mainly determined by the atomic size of X. In the present paper, the calculation for the vertical family (column) may be considered a continuation of the work on the XH$_4$ hydrides, though the geometry of the molecule is now different. The question then is how the geometry change affects the cross section. In the horizontal family (row) the atoms have approximately the same size but the numbers and configurations of the Hydrogens are very different, and we aim at verifying to what extent the conclusions of the previous work prevail.

Except for SnH$_4$, all these molecules have small permanent dipole moments. A calculation of differential cross sections for molecules having a permanent dipole moment in the fixed-nuclei approximation is well known to lead to a logarithmic divergence in the forward direction and, therefore, to a divergent integral elastic cross section.[9] The solution for this problem is to use a treatment that combines a variational calculation (SMC or CKVM, for example) and the first Born approximation.[9–11] In this procedure, the lower partial waves

are obtained from a variational calculation made in a fixed-nuclei approximation, and the higher partial waves, that diverge in this approximation, are obtained from the first Born approximation. However, Winstead *et al.*[12] have shown that for molecules with small dipole moment, the Born correction is also small, and meaningful cross sections can be extracted by truncating the fixed-nuclei partial waves at some finite angular momentum ℓ. This idea was successfully applied in electron scattering by C_3H_8,[12] PH_3, and AsH_3.[13] Even if the dipole is not too small, the SMC method leads to meaningful results. Earlier studies using the SMC method on H_2O (Ref. 14) and NH_3 (Ref. 15) (with much larger dipole moments than the molecules we are considering here) have not included the Born corrections, but the results agree with those obtained with the CKVM method plus Born[10] above 6 eV and 30°.

In the present work, all calculations were performed with the SMCPP method in a fixed-nuclei static-exchange approximation, and no Born corrections are included. It is well known that the static-exchange approximation is valid in the energy range considered here, where polarization effects do not play an important role. The truncation of the higher partial waves mentioned above is made by the SMC (SMCPP) method itself, with the use of both L^2 functions and appropriate quadratures in numerical calculations. The angles above which the differential cross sections are valid are discussed elsewhere.[12,13]

The theoretical formulation of SMC method is presented in Sec. II. Section III presents the computational procedures. The results and discussion are presented in Sec. IV. Section V ends with a brief summary.

II. THEORETICAL FORMULATION

The SMC[2] and SMCPP[5] methods are well discussed in the literature and we will review here only the key steps of the methods. The SMC method is based on a variational approximation for the scattering amplitude, whose working expression is written as

$$[f_{\vec{k}_i,\vec{k}_f}] = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_f}|V|\chi_m\rangle (A^{(+)-1})_{mn} \langle\chi_n|V|S_{\vec{k}_i}\rangle,$$
(1)

where

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

In the equations above, $S_{\vec{k}_i}$, 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, χ_m are (N+1)-electron Slater determinants 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 the target eigenfunctions, and $G_P^{(+)}$ is the free-particle Green's function projected on the P space.

With the choice of Cartesian Gaussians functions to represent the molecular and scattering orbitals, all the matrix elements arising in Eq. (1) can be computed analytically, except those from $\langle\chi_m|VG_P^{(+)}V|\chi_n\rangle$ (VGV), that are evaluated by numerical quadrature.[16]

The calculation of the VGV term presents the more expensive step in the SMC code and demands almost the entire computational time of the scattering calculation. These matrix elements are expressed as a sum of primitives two-electron integrals involving a plane wave and three Cartesian Gaussians

$$\langle\alpha\beta|V|\gamma\vec{k}\rangle = \int \int d\vec{r}_1 d\vec{r}_2 \alpha(\vec{r}_1)\beta(\vec{r}_1)\frac{1}{r_{12}}\gamma(\vec{r}_2)e^{i\vec{k}\cdot\vec{r}_2}$$
(3)

and must be evaluated for all possible combinations of α, β and γ and for several directions and moduli of $\vec{k}$. Even for small molecules, a large number of these integrals must be evaluated. This limits the size of molecules in scattering calculations. In the SMCPP method we need shorter basis set to describe the target and scattering and consequently the number of two electron integrals is smaller than in the all-electron case. The reduction in the number of these integrals allows the study of bigger molecules than those reachable by all-electron techniques.

III. COMPUTATIONAL PROCEDURES

In our calculations the valence part of the target state was described by a single configuration wave function, obtained at the Hartree-Fock level of approximation, where no correlation effects are included. However, by construction, the PP includes core-core and core-valence correlation.[6] The Cartesian Gaussian basis sets employed in the target and in the scattering calculations for the heavier atoms were generated by a variational method,[17] by fitting linear combinations of Cartesian Gaussian functions to the atomic wavefunctions. Table I presents the Cartesian Gaussian functions for the heavier atoms. For the Hydrogens, the calculations on SnH_4, PH_3, AsH_3, and SbH_3 used three contracted s functions given by Dunning.[18] For SnH_4, the Hydrogen basis was augmented by one p function (exponent 0.75) and for PH_3, AsH_3, and SbH_3 the Hydrogen basis was augmented by two p functions (exponents 0.75 and 0.1875). We also generated by our procedure the Hydrogen basis used on TeH_2 and HI. Table II shows the Hydrogen basis used on TeH_2 (basis 1) and HI (basis 2).

For all molecules, we have tested the convergence of our results with respect to basis set by repeating the calculations using larger basis. The results for the many basis sets were not different by more than 3%. The results presented here are those obtained with the larger basis sets for each case.

IV. RESULTS AND DISCUSSION

A. PH_3, AsH_3, and SbH_3

Just for illustration, in Figs. 1 and 2 we compare our results with other available theoretical results. Figures 1(a)

TABLE I. Cartesian Gaussian functions[a] for the heavier atoms.

	P Exponent		As Exponent		Sb Exponent		Sn Exponent		Te Exponent		I Exponent
s	12.524 06	s	14.375 40	s	10.013 55	s	3.297 555	s	4.155 929	s	4.640 454
s	3.745 793	s	5.479 020	s	3.825 364	s	0.793 987	s	2.903 283	s	3.917 617
s	1.446 075	s	0.865 623	s	0.849 370	s	0.533 845	s	0.966 967	s	0.956 240
s	0.594 791	s	0.524 922	s	0.564 441	s	0.148 310	s	0.657 771	s	0.649 274
s	0.240 327	s	0.137 104	s	0.175 107	s	0.039 620	s	0.199 320	s	0.259 286
s	0.073 944	s	0.023 814	s	0.016 717			s	0.059 653	s	0.088 879
										s	0.048 025
p	2.643 781	p	4.929 918	p	3.047 568	p	2.606 823	p	3.841 243	p	4.312 091
p	1.064 158	p	1.266 223	p	0.838 121	p	0.533 912	p	1.075 123	p	1.128 504
p	0.410 957	p	0.441 445	p	0.675 204	p	0.378 668	p	0.578 687	p	0.918 164
p	0.201 602	p	0.156 902	p	0.267 415	p	0.114 711	p	0.275 698	p	0.335 619
p	0.119 230	p	0.096 300	p	0.084 885	p	0.039 775	p	0.138 669	p	0.105 330
p	0.027 344	p	0.054 391	p	0.018 684			p	0.083 686	p	0.020 812
d	1.377 912	d	0.576 857	d	0.301 095	d	0.32	d	0.292 602	d	2.534 312
d	0.453 777	d	0.268 374	d	0.185 051	d	0.128	d	0.083 725	d	0.927 190
d	0.083 955	d	0.063 640	d	0.052 629	d	0.051 2	d	0.012 687	d	0.375 876
d	0.038 998	d	0.014 222	d	0.012 745					d	0.074 225
										d	0.016 770

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

and 1(b) show that the integral cross section for PH$_3$ and AsH$_3$ obtained with the SMCPP method is in excellent agreement with those obtained by Winstead *et al.* using the all-electron SMC method (SMCAE).[13] Figure 1(a) also compares our results for PH$_3$ with those of Jain and Baluja[19] and of Yuan and Zhang.[20] Jain and Baluja[19] employed a spherical complex optical potential composed of static, exchange (local approximation), polarization (parameter free model potential of Padial and Norcross,[21]) and absorption terms. The results of Yuan and Zhang[20] shown in this figure were obtained at the static-exchange level of approximation (with a spherical molecular wave function).

Above 15 eV, there is good agreement between our results and those of Yuan and Zhang. The results of Jain and Baluja are somewhat above ours. Figure 2 compares the differential cross section at 20 eV for PH$_3$ (a) and AsH$_3$ (b)

obtained with SMCPP to that obtained with SMCAE.[13] Although Fig. 1 shows good agreement between SMCPP and SMCAE results, we obtained an even better agreement when we used a shorter, therefore less precise basis.

The integral cross section for SbH$_3$ is shown in Fig. 3, together with results of PH$_3$ and AsH$_3$. The curve for SbH$_3$ crosses the other two. The crossing can be understood

TABLE II. Cartesian Gaussian functions for hydrogen.

	Basis 1 Exponent		Basis 2 Exponent
s	13.236 80	s	117.063 7
s	1.972 460	s	17.848 79
s	0.435 714	s	3.809 654
s	0.109 852	s	0.976 260
		s	0.278 295
		s	0.084 038
p	0.341 264	p	5.784 606
p	0.080 694	p	1.167 081
p	0.026 822	p	0.314 454
		p	0.107 633
		p	0.044 984
		p	0.019 918
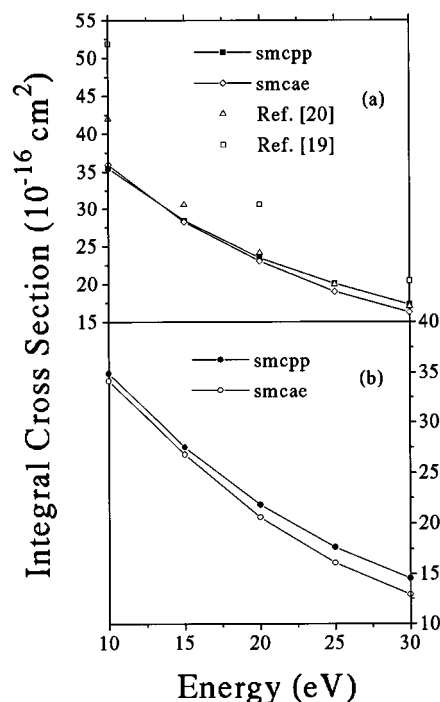
FIG. 1. Integral cross section for (a) PH$_3$, (b) AsH$_3$.
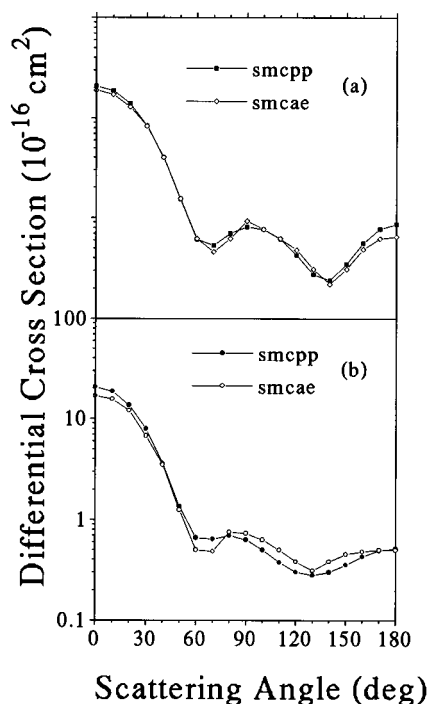
FIG. 2. Differential cross section at 20 eV for (a) PH_3, (b) AsH_3.

FIG. 4. Normalized integral cross section for PH_3, AsH_3, and SbH_3.

in terms of the different atomic sizes of P, As and Sb. Dividing the cross section by the squared interatomic distance and multiplying the energy (k^2) by the same number, we obtain the normalized cross section versus normalized wave vector plot of Fig. 4. There one sees the total similarity between AsH_3 and SbH_3 and that PH_3 has slightly larger cross sections. Figure 5 presents differential cross sections for XH_3 (X=P, As, Sb) for 10 (a), 15(b), 20 (c), and 30 (d) eV. These curves present two minima, a feature of *d*-scattering. The oscillatory behavior is more accentuated for PH_3 than for the other two molecules. For all energies considered, the
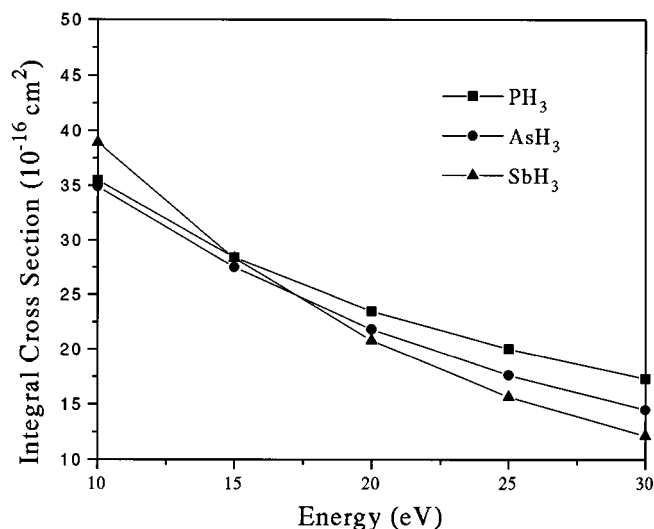
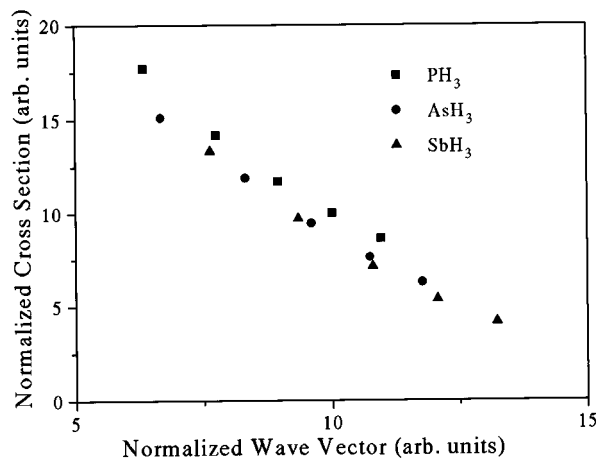shapes of differential cross sections for AsH_3 and SbH_3 are quite similar. Then, for the vertical series XH_3 the conclusions are similar to those of the series XH_4: The cross section depends primarily on the size of the molecule, determined mainly by the atomic size of the heavy atom, and only for the lighter molecule of the series one can detect a small non standard behavior.

B. SnH_4, SbH_3, TeH_2, and HI

Figure 6 shows the integral cross section for SnH_4, SbH_3, TeH_2 and HI. The integral cross sections for these molecules are almost similar in the energy range of interest. The number of Hydrogens and their arrangement in space is not contributing to the cross section. However, these molecules present small differences in their differential cross
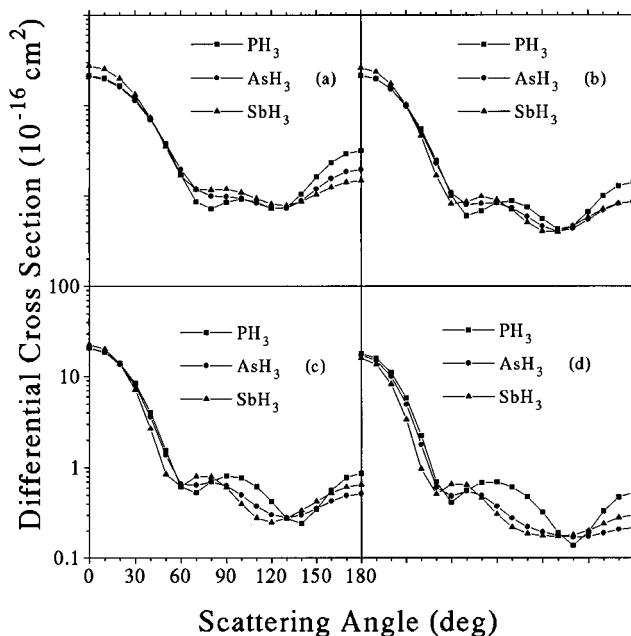

FIG. 3. Integral cross section for PH_3, AsH_3, and SbH_3.

FIG. 5. Differential cross section for PH_3, AsH_3 and SbH_3 at (a) 10 eV, (b) 15 eV, (c) 20 eV, and (d) 30 eV.
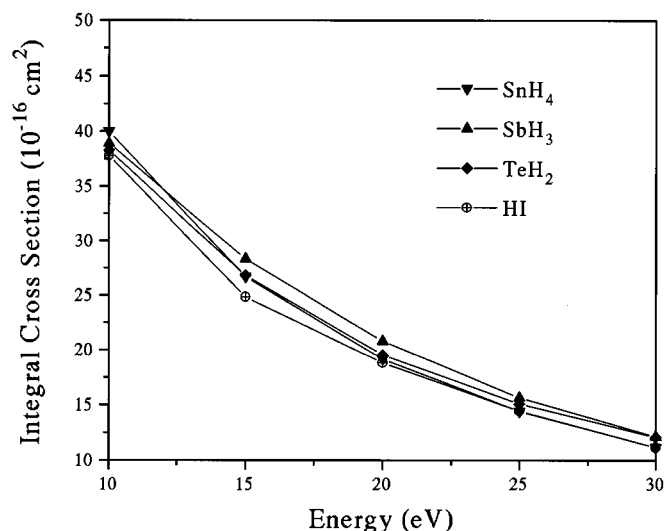
FIG. 6. Integral cross section for SnH_4, SbH_3, TeH_2, and HI.

sections plots for 10, 15, 20, and 30 eV, shown in Fig. 7(a)–7(d) respectively. A *d*-scattering character appears in all plots of differential cross sections for all molecules and *f*-scattering appears mildly only for SnH_4 at 25 and 30 eV. The backward scattering for 10 and 15 eV shows a pattern. The backward scattering decreases with the number of Hydrogens present in the molecule.
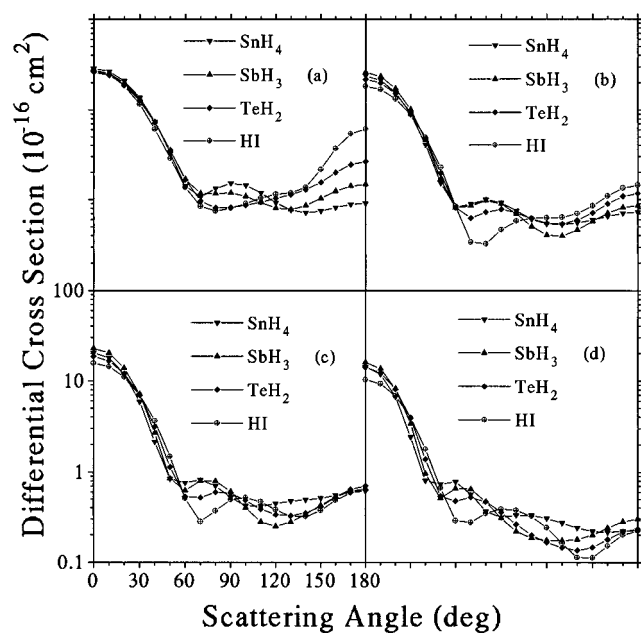

FIG. 7. Differential cross section for SnH_4, SbH_3, TeH_2, and HI at (a) 10 eV, (b) 15 eV, (c) 20 eV, and (d) 30 eV.

V. CONCLUSIONS

Calculated elastic integral and differential cross sections were presented for two families of molecules namely, PH_3, AsH_3 and SbH_3; TeH_2, SnH_4, SbH_3 and HI, from 10 to 30 eV. To our knowledge there is only previous results for PH_3 and AsH_3. Good agreement between our results and those of Refs. 13, 20 were found. These two families, together with our results for the XH_4 (Ref. 8) form a massive body of information on the scattering of electrons by the hydrides in the energy range where polarization is not important.

Aside from yielding the electrons that close the shell of the heavier atoms, the Hydrogens of the hydrides have a small and barely noticeable role in the electron scattering. The cross section is mainly determined by the size of the heavy atom. The presence of Hydrogens, their number and space arrangement, are felt mainly in the backward scattering and specially in the hydrides of lighter atoms.

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