Studies of Electron-Molecule Collisions Using the Schwinger Variational Principle with Plane Waves as a Trial Basis Set

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We report elastic differential cross sections (DCS) for the scattering of electron by H_2, CH_4, C_2H_4, SiH_4, and H_2O in the 5 to 20 eV energy range. These cross sections were obtained using the Schwinger variational principle. In our procedures the scattering wave function is expanded as a combination of plane waves. In the present implementation the exchange potential and polarization effects are not considered and all results are obtained at the static level of approximation. For all molecules, except H_2, our calculated DCS agree reasonably well with avaliable experimental data and with other theoretical results (obtained at the static-exchange level of approximation). Our study suggests that the Schwinger variational principle with plane wave expansion may become an efficient method for studying electron-molecule scattering.

Among the first-principle methods, the Schwinger variational principle (SVP) [1] has received special attention in the last couple of decades. The first calculations using the SVP for electron-molecule scattering were presented by McKoy and co-workers using a separable form for the Green's function [2]. To account for polarization effects and multichannel coupling (due to inelastic processes involving energetically open electronic excited states), Takatsuka and McKoy introduced modifications into the SVP and created the so called Schwinger Multichannel Method (SMC)[3]. Several applications of this method are reported in the literature [4]. Later on, studies using the SMC method with norm conserving pseudopotentials [5] were shown to be very useful for molecules containing heavy atoms [6]. In addition to applications of Schwinger Variational type of methods, several other studies using iterative procedures (ISVP) to solve the Lippmann-Schwinger equation have also been applied to electron-molecule scattering calculations [7-11]. The main limitation of the method (SVP or SMC) resides on what makes it a general method: the expansion of the scattering function is done in a L^2 basis (Cartesian Gaussian func-

tions) and this is very effective only for short-range potentials. An important development of the method would be to allow inclusion of plane waves (PW) in the scattering basis and this is the motivation of the present paper. In order to do this, we have developed computer codes involving matrix elements of the type $< \vec{k}_f \mid V G_0^{(+)} V \mid \vec{k}_i >$ (second-Born type of terms) with no restrictions on molecular geometries [12, 13]. In this paper we present results for e^- - H_2, CH_4, C_2H_4, SiH_4, and H_2O scattering in the static approximation in the (5-20)-eV energy range. Although the correct treatment of exchange and of polarization effects is known to be important for low-energy scattering, we surprisingly found that the present static results are in very good agreement with experimental data for all molecules of the above list, except for H_2 at 5 and 10 eV, and for CH_4 at 5 eV. Our results are also useful to establish benchmark calculations at the static level of approximation, indispensable in the development of a more complete formalism including exchange and polarization effects. Other particular interest is to check if the SVP using plane waves is capable, for instance, of describing correctly the structures in the DCS. Here after, we will

refer the SVP using plane waves as SVP-PW.

In the SVP for electron-molecule elastic scattering, the bilinear variational form of the scattering is

$$f(\vec{k}_f, \vec{k}_i)] = -\frac{1}{2\pi}\{< S_{\vec{k}_f} \mid V \mid \Psi_{\vec{k}_i}^{(+)} > + < \Psi_{\vec{k}_f}^{(-)} \mid V \mid S_{\vec{k}_i} > - < \Psi_{\vec{k}_f}^{(-)} \mid V - VG_0^{(+)}V \mid \Psi_{\vec{k}_i}^{(+)} >\} \tag{1}$$

Here $\mid S_{\vec{k}_i} >$ is the input channel state represented by the product of a plane wave $\vec{k}_i$ times $\mid \Phi_0 >$, the initial (ground) target state. $\mid S_{\vec{k}_f} >$ has analogous definition, except that the plane wave points to $\vec{k}_f$, V is the interaction between the incident electron and the target, $G_0^{(+)}$ is the projected Green's function, written as in the SMC method [14]:

$$G_0^{(+)} = \int d^3k \frac{\mid \Phi_0\vec{k} >< \vec{k}\Phi_0 \mid}{(E - H_0 + i\epsilon)} \tag{2}$$

H_0 is the Hamiltonian for the N electrons of the target plus the kinectic energy of the incident electron and E is total energy of the system (target + electron). The scattering states $\mid \Psi_{\vec{k}_i}^{(+)} >$ and $< \Psi_{\vec{k}_f}^{(-)} \mid$ are products of the target wave function $\mid \Phi_o >$ and one-particle scat-

tering wave function. The initial step in our SVP calculations is to expand the one-particle scattering wave functions as a combination of plane waves. So, in the static approximation, for elastic scattering, the expansion of the scattering wave function is done in a discrete form as

$$\mid \Psi_{\vec{k}_i}^{(+)} > = \sum_m a_m(\vec{k}_m) \mid \Phi_0\vec{k}_m > \tag{3}$$

$$\mid \Psi_{\vec{k}_f}^{(-)} > = \sum_n b_n(\vec{k}_n) \mid \Phi_0\vec{k}_n > \tag{4}$$

The inclusion of these definitions in Eq. (1) and the application of a stationarity condition [1, 13] with respect to the coefficients, gives the working form of the scattering amplitude:

$$[f(\vec{k}_f, \vec{k}_i)] = -\frac{1}{2\pi}(\sum_{mn} < S_{\vec{k}_f} \mid V \mid \Phi_0\vec{k}_m >)(d^{-1})_{mn} < \vec{k}_n\Phi_0 \mid V \mid S_{\vec{k}_i} >) \tag{5}$$

where

$$d_{mn} = < \Phi_0\vec{k}_m \mid V - VG_0^{(+)}V \mid \Phi_0\vec{k}_n > \tag{6}$$

We have implemented a set of computational programs to evaluate all matrix elements of Eq. (5). The Green's function given in Eq. (2) and its associated discontinuities have been examined and treated in a similar way as in the subtraction method [15, 14, 13]. Our discrete representation of the scattering wave function (given by Eqs. (3) and (4)) is made only in two dimensional space (spherical coordinates, using Gaussian quadratures for θ and ϕ and the on-shell k value for the radial coordinate). To illustrate, we present results of applications of the present method for elastic scattering of electrons by H_2, CH_4, C_2H_4, SiH_4 and H_2O, for several impact energies (from 5 to 20 eV). For all molecules we used Hartree-Fock calculations to rep-

resent the ground state of the targets with the same Cartesian Gaussian basis set expansion that have been used in previous calculations with the SMC method (Ref. [16] for H_2, Ref. [17] for CH_4, Ref. [18] for C_2H_4, Ref. [19] for SiH_4, and Ref. [20] for H_2O).

Fig. 1 shows our DCS for H_2 along with selected experimental data ([21, 22]). As noted, at 5 eV the absence of exchange and polarization contributions causes an overall underestimation of the calculated cross section. Above 10 eV, the SVP-PW generally agree well with the experimental data, except at near forward direction, where the long-range polarization potential plays a special role.
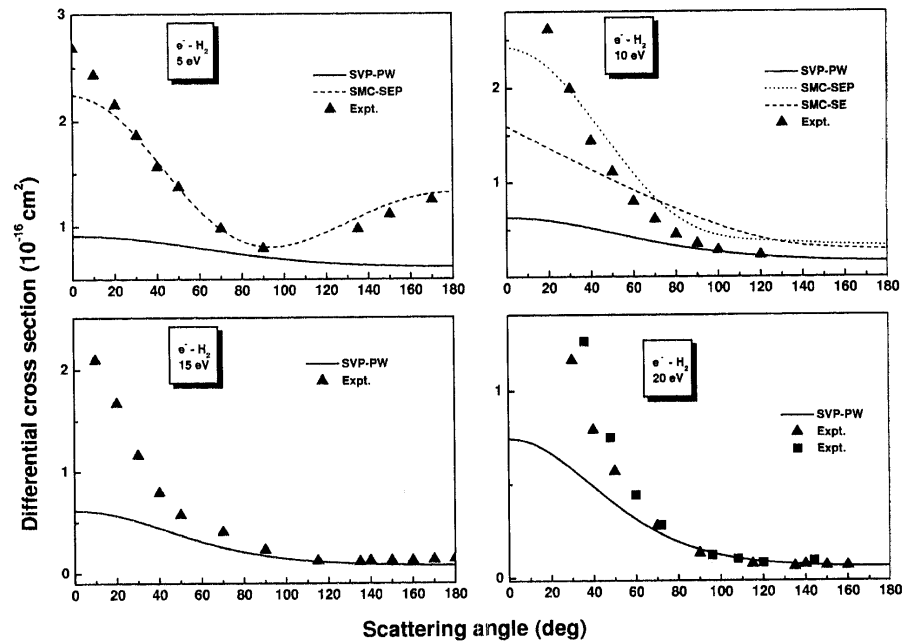
Figure 1. Elastic DCS for e⁻ - H_2 scattering at 5, 10, 15 and 20 eV. Present results SVP-PW: solid line; experimental data of Refs. [21, 22]: full triangule and square symbols, respectively.
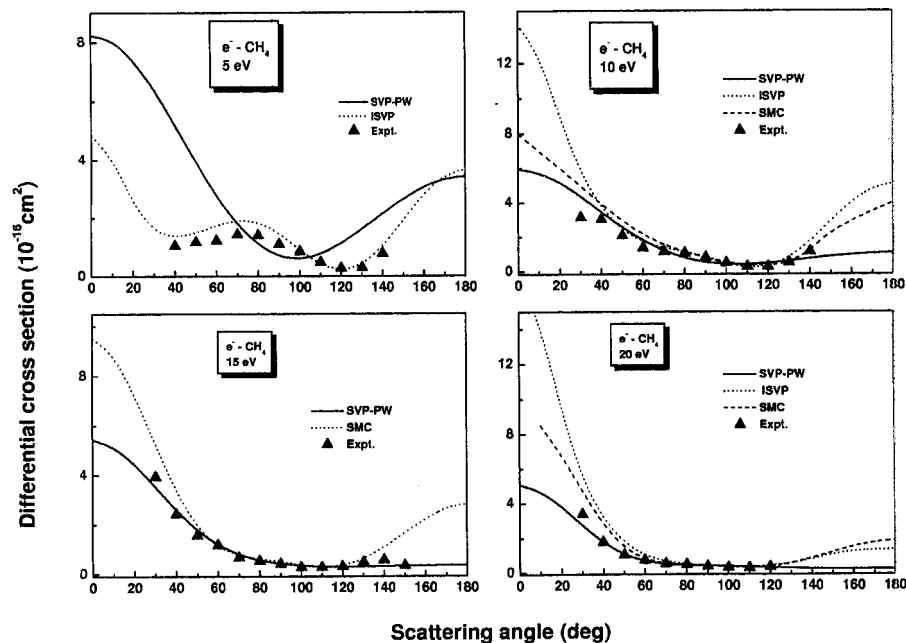

Figure 2. Elastic DCS for e⁻ - CH_4 scattering at 5, 10, 15 and 20 eV. Present results SVP-PW: solid line; experimental data of Ref. [23]: full triangule; results of the SMC method using static-exachange approximation of Ref. [24]: dashed line; results of the ISVP in static-exchange-plus-polarization approximation of Ref. [25]: dotted line.

Fig. 2 shows our DCS for CH_4 with experimental data of Tanaka *et al.* [23]. Theoretical cross sections using static-exchange (SE) approximation with the Schwinger Multichannel Method [24] and iterative Schwinger Method [25] are also included for compari-

son. Again, the differences at 5 eV are expected, due to the fact that we are neglecting exchange and polarization effects. Above 5 eV, however, the comparison between our results and theoretical results [24, 25] is in general quite satisfactory.
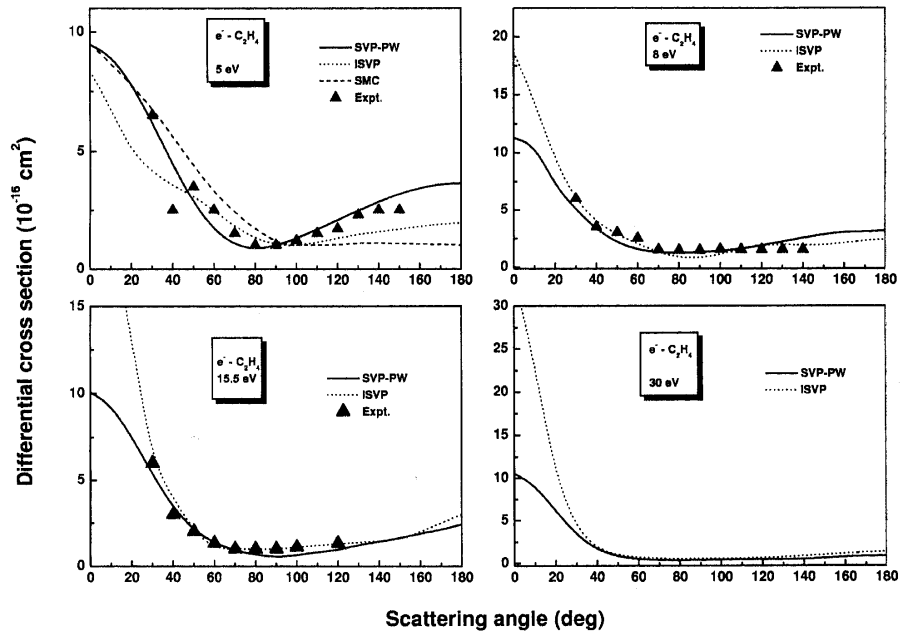
Figure 3. Elastic DCS for e⁻ - C_2H_4 scattering at 5, 8, 15.5 and 30 eV. Present results SVP-PW: solid line; experimental data of Ref. [26]: full triangule; results of the ISVP using static-exchange-plus-polarization of Ref. [27]: dotted line; results of SMC method using static-exchange of Ref. [18]: dashed line.

Fig. 3 shows our DCS for C_2H_4 along with experimental data ([26]) and theoretical results obtained with the Schwinger Multichannel Method [18] and iterative Schwinger Method [27], both at the static-exchange plus polarization (SEP) level of approximation. As noted, for all energies, our DCS are reasonably close to the experimental and theoretical results.
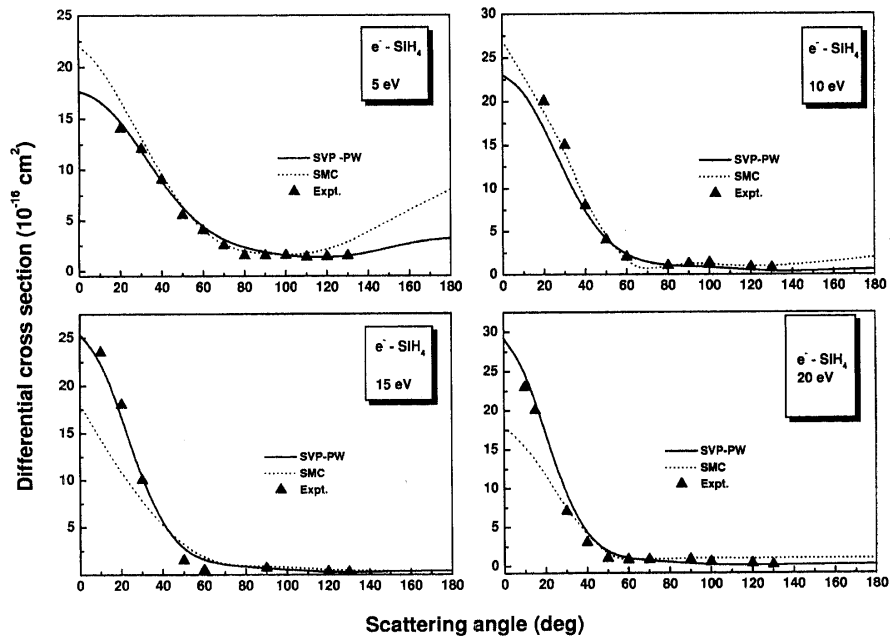

Figure 4. Elastic DCS for e⁻ - SiH_4 scattering at 5, 10, 15 and 20 eV. Present results SVP-PW: solid line; experimental data of Ref. [29]: full triangule; results of the SMC method using static-exchange approximation of Ref. [19]: dotted line.

Fig. 4 shows DCS for SiH_4. Again, for all energies, our results using the SVP-PW at the static level of approximation are very close to experimental

results [29] and to theoretical results obtained at the static-exchange level of approximation with the SMC method [19].
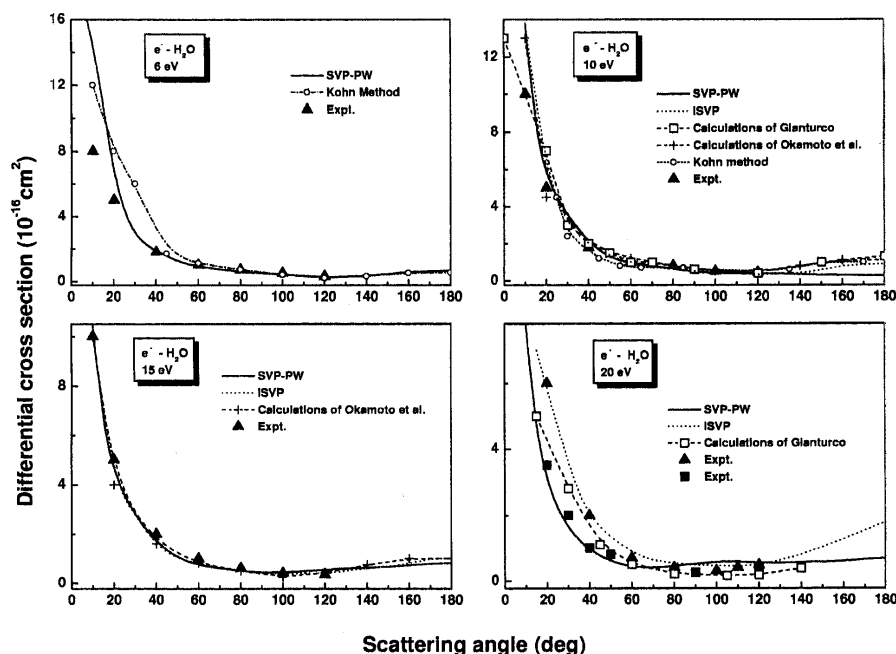

Figure 5. Elastic DCS for e^- - H_2O scattering at 6, 10, 15, and 20 eV. Present results SVP-PW: solid line; experimental data of Ref. [34, 35]: full triangle and full square symbols, respectively; results of the ISVP using static-exchange of Ref. [30]: dotted line; calculations of Okamoto *et al.* using static-exchange-polarization [31]: plus-dashed line; calculations of Gianturco [32]: dashed line with open square.

Finally, Fig. 5 shows DCS for H_2O. Theoretical studies [30-33] are also included for comparison whenever available. As expected for H_2O, due to the permanent dipole moment, our cross sections show very strong forward-peaking. Agreement between our calculated cross sections and available experimental data is generally good. Our results also agree quite well with other theoretical studies over the angular and energy regions covered here.

In summary, although exchange potential and polarization effects are not taken into account in our calculations, our results are, in general, in good agreement with experimental and other theoretical methods for elastic electron scattering of H_2, CH_4, C_2H_4, SiH_4, and H_2O over the range of aproximately 5 to 20 eV. In the future, we plan to extend the present method to investigate the the lower-energy scattering range from 0 to 5 eV. This will be done by implementing the plane wave expansion in the SMC method, where exchange and polarization effects can be treated in an *ab-initio* form.

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