Elastic cross sections for intermediate-energy e^- - CH_4 collisions

J.L.S. Lino
Núcleo de Pesquisas em Matemática e Matemática Aplicada, Universidade Braz Cubas UBC, Campus I, 08773-380, Mogi das Cruzes, São Paulo, Brazil.

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We report an application of the Schwinger variational principle with plane waves as trial basis set. Elastic differential cross sections (DCS) for the scattering of electrons by CH_4 in the 10 to 100 eV energy range are available and our differential cross sections are found to be in reasonable agreement with existing measurements.

Keywords: Schwinger, electron, methane.

Se analiza una aplicación del principio variacional de Schwinger desde la perspectiva de ondas planas para un conjunto base y sección eficaz diferencial para e^- - CH_4 en el intervalo de 10-100 eV, y se encuentra que los resultados obtenidos están en razonable acuerdo con los datos existentes.

Descriptores: Schwinger, electrón, metano.

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1. Introduction

Over the last years the Schwinger variational principle (SVP) [1] has been widely used for calculations on elastic electron-molecule scattering [1]. Besides its capability of treating electron scattering by polyatomic targets, the Schwinger method has very solid theoretical grounds. The first calculations using the Schwinger variational principle (SVP) for electron-molecule scattering were presented 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), was introduced modifications into the SVP and created the so called Schwinger Multichannel Method (SMC) and several applications of this method are reported in the literature [3]. The main limitation of the method type Schwinger resides on what makes it a general method: the expansion of the scattering function is done in a L^2 basis (Cartesian Gaussian functions) and this is very effective only for short-range potentials. Recently we have presented a study of the Schwinger variational principle with plane waves as a trial basis set (SVP-PW) [4, 5]. In one paper we report results for the e^- - H_2, CH_4, C_2H_4, SiH_4, and H_2O elastic scattering in the static approximation [4]. In second paper [5] we present elastic cross sections for e^- - Ne using the SVP-PW where we have tested the Born-Ochkur approximation to include the effect of electron exchange. In present paper we report a application of the SVP-PW plus Born-Ochkur approximation to elastic e^- - CH_4 scattering and theoretical and experimental results are avaliable for comparison. The present study has several goals; first, the system e^- - CH_4 represent a good study of electron-polyatomic molecule scattering using the SVP-PW plus Born-OchKur approximation; second, to test the relevance of the exchange effects (Born-Ochkur level) at intermediate energies and large scattering angles; third, our study is adequate for establish benchmark calculations as an sort of calculations indispensable in the development of new methodologies. We compare our results with other theoretical developments using exchange plus polarization effects in a form ab-initio which is important to check if the SVP-PW is capable of descrebing correctly the structures in the DCS.

A brief review of our theoretical formulation is provided in Sec. 2. In Sec. 3 we report differential cross sections for e-CH_4 scattering in the (10 - 100) eV energy range. These results are compared with available experimental data. We summarize our results and conclusions in Sec. 4.

2. Theoretical formulation

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

$$[f(\vec{k}_f,\vec{k}_i)] = -\frac{1}{2\pi} \times\{< S_{\vec{k}_f} \mid V \mid \Psi^{(+)}_{\vec{k}_i} > + < \Psi^{(-)}_{\vec{k}_f} \mid V \mid S_{\vec{k}_i} > - < \Psi^{(-)}_{\vec{k}_f} \mid V - VG_0^{(+)}V \mid \Psi^{(+)}_{\vec{k}_i} >\} \quad (1)$$

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 Ref 6:

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

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 scattering 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, 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, 3] with respect to the coefficients, gives the working form of the scattering amplitude:

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

where

$$d_{mn} = < \Phi_0 \vec{k}_m \mid V - V G_0^{(+)} V \mid \Phi_0 \vec{k}_n > . \tag{6}$$

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 [4, 6–8]. 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). We have considered the effect of including exchange in the SVP-PW by replaning first Born approximation f_{FBA} by f_{FBA} + g where "g" is the Born-Ochkur exchange amplitude [9] and our main interest is to check if the SVP-PW plus Born-Ochkur approximation is capable of describing the structures in the DCS.

3. Results

As a application of our formulation we have calculated elastic differential cross sections (DCS) for electron-impact energies of 10, 15, 20, 30, 50, and 100 eV. We have used Hartree-Fock calculations to represent the ground state of the target CH_4 with the same Cartesian Gaussian basis set expansion that have been used in previous calculations [4, 10, 11]. Figure 1 shows our DCS at 10, 15, 20, and 30 eV for e^- - CH_4. Expe-

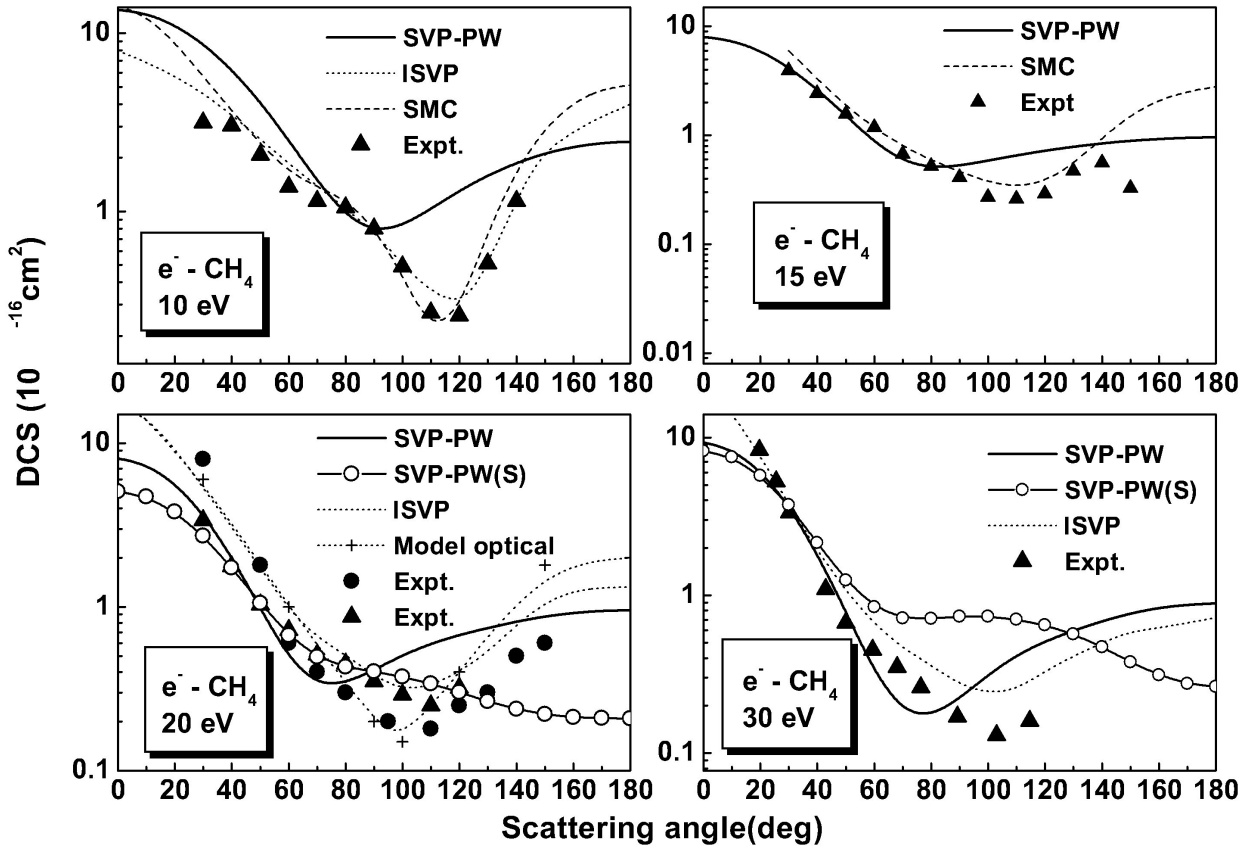

FIGURE 1. Elastic DCS for e^- - CH_4 scattering at 10 eV, 15 eV, 20 eV, and 30 eV. Present results SVP-PW: solid line; SVP-PW(S) Ref. [4]: dashed line with open circle; Experimental results of Ref. 12: circle; results of the ISVP in static-exchange-plus-polarization approximation of Ref. 13: dotted line; results of the SMC method using static-exchange approximation [10]: dashed line.

rimental data [12] and theoretical cross sections as the iterative Schwinger Method (ISV) [13] (using exchange plus polarization effects) and model potential (using exchange plus polarization) [14] are also included for comparison. As noted, at 10 eV the SVP-PW plus Born-Ochkur approximation have a shape similar with experimental and theoretical results. Above 10 eV, our method generally agree well with experimental data. The comparison between our results and theoretical methods [13, 14] are in general quite satisfactory. In Fig. 1 at 20 eV and 30 eV for comparison we have also included the SVP-PW results in the static field only (we refer to this case as SVP-PW(S)). As noted, when the SVP-PW include the Born-Ochkur approximation our results agree well with each other at large-angle scattering. Figure 2 shows DCS for CH_4 at 50 eV along with experimental data [12] and theoretical results obtained with the iterative Schwinger variational principle [13]. As noted, our DCS is reasonably close to the experimental and theoretical results. Figure 3 shows our DCS at 100 eV for e^- - CH_4 with experimental data of Ref [12]. The comparison between our results and theoretical [13] and experimental results [12] are very similar.

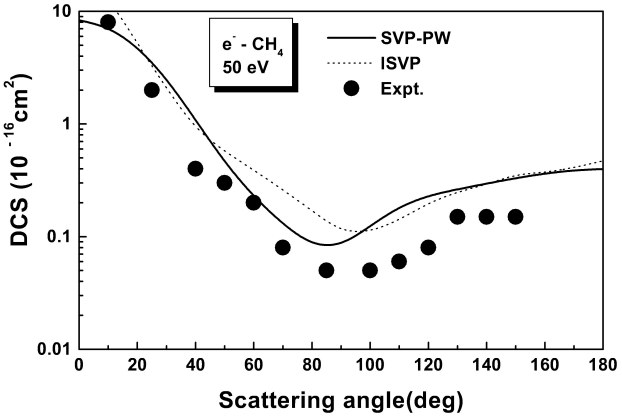

FIGURE 2. Elastic DCS for e^- - CH_4 scattering at 50 eV. Present results SVP-PW: solid line; results of the ISVP in static-exchange-plus-polarization approximation of Ref. 13: dotted line; Experimental results of Ref. 12: circle.

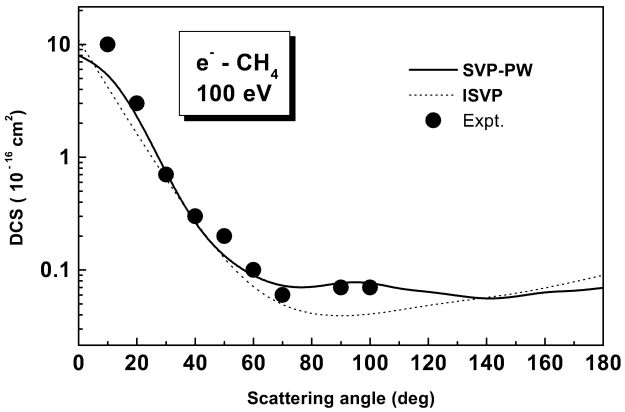

FIGURE 3. Elastic DCS for e^- - CH_4 scattering at 100 eV. As in Fig. 2.

4. Conclusion

In this paper we have reported an application of the Schwinger variational principle with plane waves to electron collisions with CH_4. Using this system we have tested the Born-Ochkur model for the description of exchange potential. Our study has reveled that, in general, the cross sections calculated are in good agreement when compared with experimental data. The present study helps to demonstrate the utility of SVP-PW in the region of intermediate energies. Applications of these codes to other molecular systems are underway.

Acknowledgments

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