Theoretical study of electron - SiH_4 collisions using the Schwinger variational principle with plane waves as a trial basis set

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We report an application of the Schwinger variational principle with plane waves as a trial basis set. Differential cross sections are obtained for electron-SiH_4 collisions from 7.5-40 eV. Our differential cross sections are found to be in reasonable agreement with experimental data.

Keywords: Electron scattering; Schwinger variational principle.

Se analiza una aplicación del principio variacional de Schwinger desde la perspectiva de ondas planas para un conjunto base. El propósito de este trabajo es mostrar la sección eficaz diferencial para electron-SiH_4 en el intervalo de 7.5-40 eV Los resultados se comparan con los experimentos.

Descriptores: Dispersión electrónica; principio variacional de Schwinger.

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1. Introduction

The cross sections of e^- - SiH_4 scattering are very important in many fields of research, including space science, radiation physics, gas laser, and even fundamental chemistry. SiH_4 is of theoretical interest as an analog of CH_4, which has served as a prototypical polyatomic molecule for electron-scattering calculations. There have been several experimental or experimentally based studies of e^- - SiH_4 collisions. Sueoka and Mori have measured total cross sections for electron-SiH_4 scattering in a wide energy range (1-400 eV) using a straight type retarding-potential time-of-flight apparatus [1]. Hayashi analyzed electron-SiH_4 swarm data to extract cross section from very low to the one hundred eV energy region [2]. Also other investigations using electron-transmission-spectroscopy type experiments (which give information particularly on the resonances and negative ion formation) have been used [3]. Theoretical studies of electron-SiH_4 scattering have appeared, beginning with the multiple scattering calculation of Tossel and Davenport [4], Jain [5], Jain and Thompson [6, 7], Gianturco *et al.* [8], Yuan [9], and Winstead and McKoy [10] have studied electron-SiH_4 collisions using a variety of approximate treatments involving exchange and polarization with some agreement with experiment data. In fact, the avaliable experimental data of differential cross section still do not provide a definitive test capable of judging the efficiency of the theoretical methods used for e^- - SiH_4 scattering. Obtaining accurate differential cross sections collisions remains an important endeavour. As a step toward addressing this need, we have recently described the Schwinger variational principle with plane waves as a trial basis set (SVP-PW) [11, 12]. The main limitation of the method (SVP) resides in what makes it a general method: the expansion of the scattering function is done on a L^2 basis (Cartesian Gaussian functions), 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 $< \vec{k}_f \mid VG_0^{(+)}V \mid \vec{k}_i >$ second-Born term with no restrictions on molecular geometries [13]. We have considered the effect of including exchange in the SVP-PW by replaning the first Born approximation (FBA) by FBA + g where g is the Born-Ochkur exchange amplitude [14]. The present study has several goals; first, to the best of our knowledge, no theoretical study using the SVP-PW with Born-Ochkur model has been tested for the system e^- - SiH_4; second, to test the relevance of the exchange effects (Born-Ochkur level of approximation) at intermediate energies; and third, as SiH_4 is heavier and more polarizable [15] than CH_4 [16], our results can provide an indication of the reliability of SVP-PW and serve as a necessary prelude to studies planned at low energy scattering (we are concerned here only with the intermediate enery region 7.5 eV - 40 e eV).

The remainder of this paper is organized into three sections. Section 2 gives some relevant theoretical details. In Sec. 3 we present our results and compare them with experimental and other calculations. Sec. 4 contains a brief discussion and concluding remarks.

2. Theoretical formulation

Details of the Schwinger variational principle (SVP) of electron-molecule collisions have been discussed elsewhere [17] and only a brief outline will be given here. The Hamiltonian for the collision can be written as

$$H = (H_N + T_{N+1}) + V = H_o + V \qquad (1)$$

where H_N is the target Hamiltonian, T_{N+1} is the kinetic energy operator of the incident electron, and V is the interaction potential between the incident electron and the target. The

total scattering wave function satisfies the Schrodinger equation

$$(E-H)\Psi_{\vec{k}}^{(\pm)}=0 \tag{2}$$

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

$$[f(\vec{k}_f,\vec{k}_i)]=-\frac{1}{2\pi}\{\langle S_{\vec{k}_f}\mid V\mid\Psi_{\vec{k}_i}^{(+)}\rangle+\langle\Psi_{\vec{k}_f}^{(-)}\mid V\mid S_{\vec{k}_i}\rangle - \langle\Psi_{\vec{k}_f}^{(-)}\mid V-VG_P^{(+)}V\mid\Psi_{\vec{k}_i}^{(+)}\rangle\} \tag{3}$$

Here $\mid S_{\vec{k}_i}\rangle$ is the input channel state represented by the product of a plane wave $\vec{k}_i$ times $\mid\Phi_0\rangle$, the initial (ground) target state. $\mid S_{\vec{k}_f}\rangle$ has an analogous definition, except that the plane wave points to $\vec{k}_f$, V is the interaction between the incident electron and the target, $G_P^{(+)}$ is the projected Green's function, written as in Ref. 17:

$$G_P^{(+)}=\int d^3k\frac{\mid\Phi_0\vec{k}\rangle\langle\vec{k}\Phi_0\mid}{(E-H_0+i\epsilon)} \tag{4}$$

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

$$\mid\Psi_{\vec{k}_i}^{(+)}\rangle=\sum_m a_m(\vec{k}_m)\mid\Phi_0\vec{k}_m\rangle \tag{5}$$

$$\mid\Psi_{\vec{k}_f}^{(-)}\rangle=\sum_n b_n(\vec{k}_n)\mid\Phi_0\vec{k}_n\rangle \tag{6}$$

The inclusion of these definitions in Eq. (3) and the application of a stationarity condition [13], with respect to the coefficients gives the working form of the scattering amplitude:

$$[f(\vec{k}_f,\vec{k}_i)]=-\frac{1}{2\pi}\left(\sum_{mn}\langle S_{\vec{k}_f}\mid V\mid\Phi_0\vec{k}_m\rangle(d^{-1})_{mn}\times\langle\vec{k}_n\Phi_0\mid V\mid S_{\vec{k}_i}\rangle\right), \tag{7}$$

where

$$d_{mn}=\langle\Phi_0\vec{k}_m\mid V-VG_P^{(+)}V\mid\Phi_0\vec{k}_n\rangle \tag{8}$$

We have implemented a set of computational codes to evaluate all matrix elements of Eq. (7). The $G_P^{(+)}$ is the projected outgoing-wave Green's function and P is the target-space unit operator

$$P=\sum_\ell\int\mid\Phi_\ell\rangle\langle\Phi_\ell\mid=1, \tag{9}$$

where P is truncated and carries only energetically open bound state channels. The calculation of the VGV term presents the more expensive step in the SVP-PW code and demands almost the entire computational time of the scattering calculation. With the help of the linear momentum representation [13,17] of the one-particle unit operator, the matrix element

$$\langle\Phi_0\vec{k}_m\mid VG_P^{(+)}V\mid\Phi_0\vec{k}_n\rangle \tag{10}$$

used in Eq.(8) is found by direct numerical quadrature and can be rewritten as

$$\sum_\ell^{open}\int_o^\infty dk\frac{2k^2}{k_\ell^2-k^2}g^\ell_{\vec{k}_m\vec{k}_n}(k), \tag{11}$$

where

$$g^\ell_{\vec{k}_m\vec{k}_n}(k)=\int d\Omega_{\vec{k}}\langle\Phi_o\vec{k}_m\mid V\mid\Phi_o\vec{k}\rangle\langle\vec{k}\Phi_o\mid V\mid\Phi_o\vec{k}_n\rangle, \tag{12}$$

and the function $g^\ell_{\vec{k}_m\vec{k}_n}(k)$ is essentially an angular integration of first Born terms with different magnitude of $\vec{k}$'s (off-shell terms). The difficulty in evaluating Eq.(10), associated with possible discontinuities, has been examined and treated in a similar to in the subtraction method [13, 17]. We just add and subtract the expression $2k^2/(k_\ell^2-k^2)g^\ell_{\vec{k}_m\vec{k}_n}(k_\ell)$ in Eq. (11), where the subtracted term makes the integration smoother (since the numerator and the denominator of the composed expression will vanish simultaneuosly for k's around k_ℓ), and the added term is evaluated analytically. In our implementation we use two different quadratures for $\vec{k}_m$ and $\vec{k}_n$ to avoid situations where $\mid\vec{k}_m-\vec{k}_n\mid$ are too small [18]. For example, to obtain a differential cross section, we simply evaluate the square modulus of this amplitude, summing over all $\vec{k}_m$ directions and averaging over the $\vec{k}_n$'s. Our discrete representation of the scattering wave function (given by Eqs. (5) and (6)) 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). The present formulation allows us to calculate an analytical approximation to the body-frame fixed nuclei scattering amplitude for molecules of arbitrary geometry. We then expand f($\vec{k}_m$,$\vec{k}_n$) in a partial-wave series and make the requisite transformation into the laboratory frame. After accounting for the randon orientation of the target, the differential cross section is obtained in the usual manner by performing the appropriate average over initial spin states and summing over final spin states [18]. The calculation is carried out via a Gauss-Legendre quadrature. When exchange effects are to be considered in electron scattering, the first Born approximation (FBA) used in Eq.(7) is replaced by

$$f^{exchange}=FBA+g, \tag{13}$$

where g is the exchange amplitude in the Born-Ochkur approximation [14].

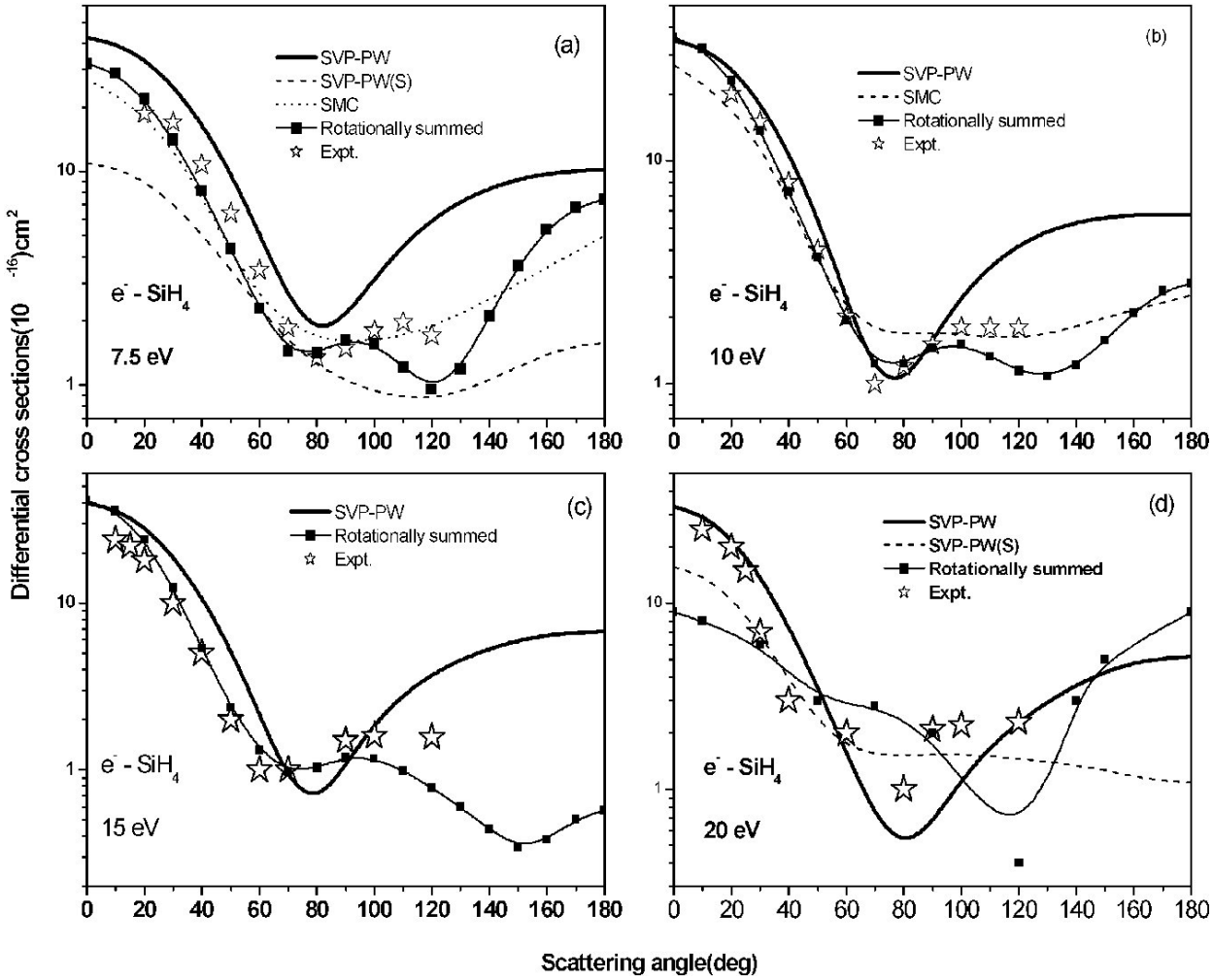

FIGURE 1. (a) Elastic DCS for e^- - SiH_4 scattering at 7.5 eV. Present results SVP-PW: solid line; Present results SVP-PW(S) level static only: dashed line; SMC method of Ref. 10: dott line; elastic rotationally summed results of Jain and Thompson of Ref. 15; solid line with square: experimental results of Ref. 19; star. (b) Elastic DCS for e^- - SiH_4 scattering at 10 eV. Present results SVP-PW: solid line; SMC method of Ref. 18: dott line; elastic rotationally summed results of Jain and Thompson of Ref. 6; solid line with square: experimental results of Ref. 19; star. (c) Elastic DCS for e^- - SiH_4 scattering at 15 eV. Present results SVP-PW: solid line; elastic rotationally summed results of Jain and Thompson of Ref. 6; solid line with square: experimental results of Ref. 15; star. (d) Elastic DCS for e^- - SiH_4 scattering at 20 eV. Present results SVP-PW: solid line; Present results SVP-PW(S) level static only: dashed line; elastic rotationally summed results of Jain and Thompson of Ref. 6; solid line with square: experimental results of Ref. 15; star.

3. Results and discussion

To illustrate, we present the results of applications of the present method for elastic scattering of electrons by SiH_4 using the fixed-nuclei approximation. We have used Hartree-Fock calculations to represent the ground state of the target with the same Cartesian Gaussian basis set used in Ref. 10.

In Fig.1(a) we show our differential cross sections at 7.5 eV compared with the Schwinger multichannel method (SMC) of Winstead and McKoy [10], the elastic rotationally summed calculation of Jain and Thompson [6], and experimental data of Tanaka and co-workers (the measured values are not available above a 130° angle) [15]. For comparison we also included the SVP-PW results in the static field only (we refer to this case as SVP-PW(S)). As observed, the SVP-PW curve shows clearly that our exchange model plays an important role at 7.5 eV. On the other hand, although the shape of our SVP-PW calculation can be seen to agree quite well with experimental data, the results of Jain and Thompson [6] are more realistic than our SVP-PW calculation (in our calculations we do not include polarization and elastic rotationally summed effects).

In Fig.1(b), we show our elastic differential cross sections (DCS) at 10 eV compared with the Schwinger multichannel method (SMC) calculation of Winstead and McKoy [10], and experimental data of Tanaka and co-workers [15]. Our results agree at 10 eV with the experimental data [15], and also with the SMC method [10] at smaller scattering angles. In particular, our curve clearly exhibits a minimum (around 80°) consistent with experimental data and theoretical results of Jain and Thompson using elastic rotationally summed [6]. In

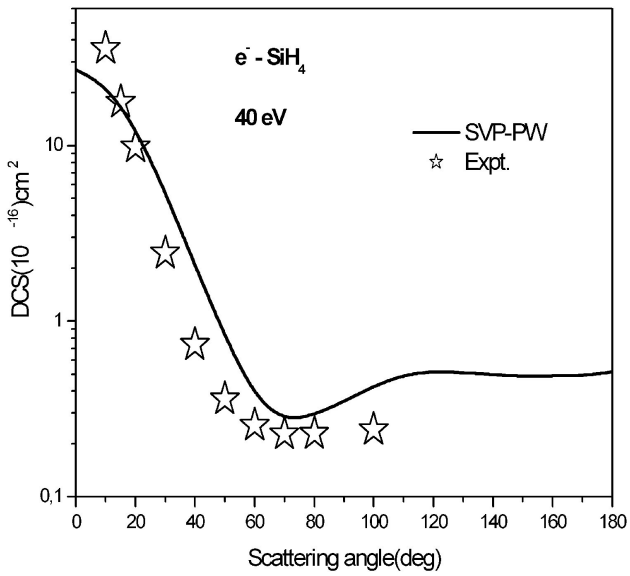

FIGURE 2. Elastic DCS for e^- - SiH_4 scattering at 40 eV. Present results SVP-PW: solid line; experimental results of Ref. 15; star.

fact, our DCS using SVP-PW are highly encouraging also at 10 eV.

In Fig.1(c) we show our elastic differential cross sections (DCS) at 15 eV compared with experimental data [15]. For comparison we also included the results of Jain and Thompson using elastic rotationally summed [6]. Our present SVP-PW calculation agree well with experimental data.

Next we show in Fig.1(d) our elastic differential cross sections (DCS) at 20 eV compared with the elastic rotationally summed calculation of Jain and Thompson [6], and experimental data of Tanaka and co-workers [15]. For comparison again, we included the SVP-PW results in the static field only (SVP-PW(S)). Our calculation reproduces well the measurements of Tanaka [15]. Note that again our SVP-PW calculation introduces qualitative changes in the DCS when compared with SVP-PW(S) at 20 eV.

Finally, Fig. 2 illustrates our differential cross sections at 40 eV compared with experimental data of Tanaka and co-workers [15]. As noted, the agreement with experimental data is very reasonable.

4. Conclusion

In this paper we have reported an application of the Schwinger variational principle with plane waves as a trial basis set to electron collisions with SiH_4. The exchange interaction is included via a Born-Ochkur model. We have compared our results with available measurements and theoretical studies, and the agreement is encouraging for intermediate energies and serve as an indispensable prelude to the development of new ingredients such as polarization and absorption.

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