

Elastic electron scattering by water molecules

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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 $e^- - \text{H}_2\text{O}$ from 10 to 50 eV. In these studies the exchange potential is evaluated by the Born-Ochkur model and our results are found to be in reasonable agreement with experimental data and theoretical studies.

Keywords: Molecular excitation; elastic scattering of electrons; variational principle.

Se analiza una aplicación del principio variacional de Schwinger desde la perspectiva de ondas planas para un conjunto base usando un modelo Born-Ochkur. El propósito de este trabajo es mostrar la sección eficaz para $e^- - \text{H}_2\text{O}$ en el intervalo de 10 - 50 eV. Los resultados se comparan con los experimentos.

Descriptores: Excitación molecular; dispersión elástica de electrones; principio variacional.

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1. Introduction

An electron collision with a water molecule is a fundamental process in various fields such as radiation physics and available chemistry, atmospheric physics and astrophysics [1]. A water molecule can be used as a representative target in the theory of electron collision with polyatomic molecules, which are characterized by a multicentred nature and a long-range force due to a dipole or other multipole moment. In addition to the pioneering work of Bruche [2], measurements of total cross sections have been reported by several groups such as Sokolov and Sokolova [3], Sueoka *et al.* [4], Szmytkovski [5], Zecca *et al.* [6], and Nishimura and Yano [7]. Differential cross sections for elastic scattering and vibrational excitation were reported by Jung *et al.* [8], Danjo and Nishimura [9], Shyn and Cho [10] and Johnstone and Newell [11]. On the theoretical side, there are several studies using more sophisticated treatments, including the static-exchange-polarization model potential approach of Jain and Thompson [12], the static-exchange Schwinger multichannel method (SMC) of Brescansin *et al.* [13], the local modified semi-classical exchange of Gianturco and Scialla [14], the complex Kohn variational method of Rescigno and Lengsfeld [15], and the iterative Schwinger variational method used by Machado *et al.* [16]. In the present paper, elastic electron scattering by H_2O is studied using the Schwinger variational principle with plane waves as a trial basis set (SVP-PW) [17]. Recently, we have shown that the SVP-PW for scattering theory is an effective approach to electron-molecule collisions [18, 19]. The main limitation of the Schwinger variational principle lies in what makes it a general method: the expansion of the scattering function is done in an L^2 basis (Cartesian Gaussian functions) and this is very effective only for short-range potentials (the Schwinger method requires a good description of the scattering wavefunction only in the region where the potential is non-zero and, as most nonlinear molecules have dipole moments, the

long range of such potentials can make it difficult to adequately represent the trial function in an L^2 basis only). Our implementation of plane waves as a trial basis set can be desirable to adequately represent, for example, the long range regions (the attempt to deal with long range potentials using a Schwinger-type method was originally proposed by Kolsrud [20] and subsequently discussed more fully by Takatsuka and McKoy [21] and Tao *et al.* [22] for electron scattering, and by Lino for positron scattering [23, 24]).

In the present study we have investigated the SVP-PW to $e^- - \text{H}_2\text{O}$ in the region of collision below 50 eV. In addition to the static interaction, we have here considered the effect of including exchange by replacing the first Born approximation (FBA) used in the SVP-PW by FBA + g where “g” is the Ochkur amplitude [25]. The present study has several goals: first, to our knowledge, no theoretical study using the SVP-PW with the Born-Ochkur approximation for $e^- - \text{H}_2\text{O}$, has been presented; second, a fixed-nuclei treatment of electron scattering by polar molecules is well known to lead to divergent cross sections. This is an essential property of the dipole potential and can usually be remedied by introducing the rotational motion of the target molecule [15]. The usual strategy for the dilemmas caused by the electron-target (polar) is to use a hybrid treatment in which only the low order partial-wave components of the T-matrix are determined from variational calculations, and the higher order terms are included in the Born approximation via a closure formula [15]. As we have recently shown [19], the SVP-PW typically uses the first Born approximation (FBA) and this fact has evidently been appreciated. We shall see that our conclusion regarding the use of SVP-PW to the calculation of scattering cross sections $e^- - \text{H}_2\text{O}$ is encouraging.

The organization of this paper is the following. In Sec. 2 the theory is described, our calculated results and discussions are presented in Sec. 3, and Sec. 4 summarizes our conclusions.

2. Theoretical formulation

Details of the Schwinger variational principle (SVP) of electron-molecule collisions have been discussed elsewhere [26], and only a brief outline will be given here. The Hamiltonian for the collision can be written as

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

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 Schrödinger equation

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

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

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

Here $|S_{\vec{k}_i}\rangle$ is the input channel state represented by the product of a plane wave \vec{k}_i times $|\Phi_0\rangle$, the initial (ground) target state. $|S_{\vec{k}_f}\rangle$ 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. 26:

$$G_P^{(+)} = \int d^3k \frac{|\Phi_0\vec{k}\rangle\langle\vec{k}\Phi_0|}{(E - H_o + i\epsilon)}, \quad (4)$$

H_o 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 $|\Psi_{\vec{k}_i}^{(+)}\rangle$ and $\langle\Psi_{\vec{k}_f}^{(-)}|$ are products of the target wave function $|\Phi_o\rangle$ 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

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

$$\langle\Psi_{\vec{k}_f}^{(-)}| = \sum_n b_n(\vec{k}_n) \langle\Phi_0\vec{k}_n|. \quad (6)$$

The inclusion of these definitions in Eq. (3), and the application of a stationarity condition [27] with respect to the coefficients gives the working form of the scattering amplitude:

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

where

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

We have implemented a set of computational programs 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

$$P = \sum_{\ell} |\Phi_{\ell}\rangle\langle\Phi_{\ell}| = 1, \quad (9)$$

where P is truncated and carries only energetically open bound state channels [26]. The importance of the accurate determination of Green's function matrix elements in molecular collision physics has been felt over the years. 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 calculations. As prescribed by Lima *et al.* [26], the evaluation of the remaining terms involving the Green's functions can be done numerically in the linear-momentum space as [26, 27] of the one-particle unit operator; however, the matrix element

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

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

$$\sum_{\ell}^{open} \int_0^{\infty} dk \frac{2k^2}{k_{\ell}^2 - k^2} g_{\vec{k}_m\vec{k}_n}^{\ell}(k), \quad (11)$$

where

$$g_{\vec{k}_m\vec{k}_n}^{\ell}(k) = \int d\Omega_{\vec{k}} \langle \Phi_o\vec{k}_m | V | \Phi_o\vec{k} \rangle \langle \vec{k}\Phi_o | V | \Phi_o\vec{k}_n \rangle, \quad (12)$$

and the function $g_{\vec{k}_m\vec{k}_n}^{\ell}(k)$ is essentially an angular integration of first Born terms with different magnitude of \vec{k} 's (off-shell terms). The difficulty in evaluating the Eq. (10), associated with possible discontinuities, has been examined and treated in a similar way to the subtraction method [26]. We just add and subtract the expression

$$\frac{2k^2}{k_{\ell}^2 - k^2} g_{\vec{k}_m\vec{k}_n}^{\ell}(k_{\ell})$$

to Eq. (11) where the subtracted term makes the integration smoother (since the numerator and the denominator of the composed expression will vanish simultaneously for k 's around k_{ℓ}) and the added term is evaluated analytically. The convergence of this procedure could also be assessed by numerical quadrature. In our implementation we use two different quadratures for \vec{k}_m and \vec{k}_n to avoid situations where $|\vec{k}_m - \vec{k}_n|$ are too small [28]. 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). When exchange effects are to be considered in electron scattering, the first Born approximation (FBA) used is replaced by

$$f^{Born-Ochkur} = f_{FBA} + g, \quad (13)$$

where g is the exchange amplitude in the Ochkur approximation [25].

3. Applications

In this section, we test the SVP-PW procedure for the H_2O molecule. In the present work for the self consistent-field (SCF), we have a chosen basis set as in Ref. 13. This basis gives an SCF energy of -76.05 a.u. and a calculated dipole

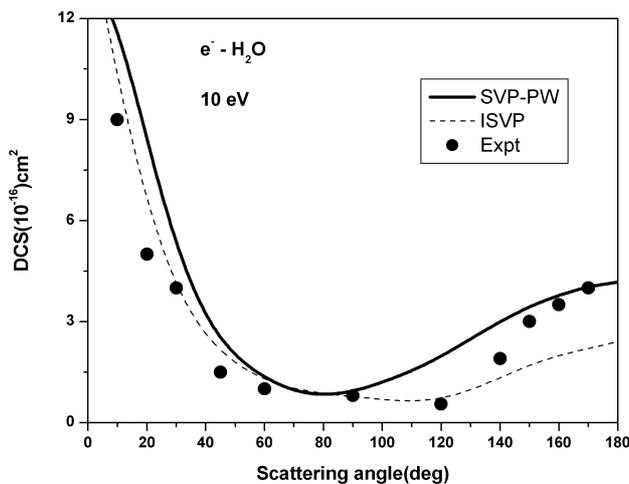


FIGURE 1. Elastic DCS for $e^- - H_2O$ scattering at 10 eV. Present results (SVP-PW): solid line; iterative Schwinger variational method used by Machado *et al.* [16]: dashed line; experimental data [9,10]: black circle.

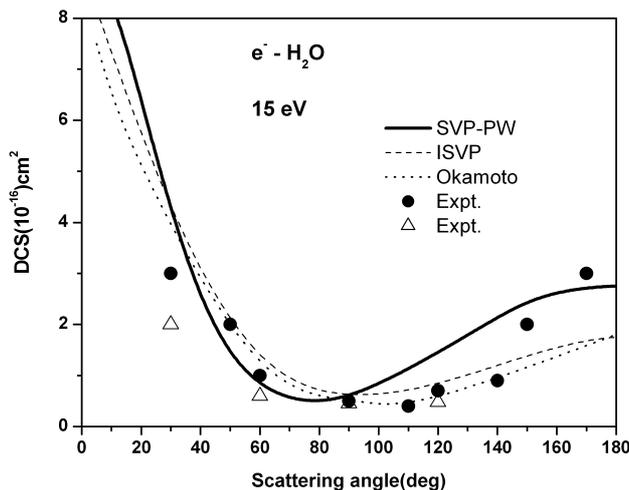


FIGURE 2. Elastic DCS for $e^- - H_2O$ scattering at 15 eV. Present results (SVP-PW): solid line; iterative Schwinger variational method used by Machado *et al.* [16]: dashed line; theoretical studies of Okamoto *et al.* [30]: dotted line; experimental data [9,10]: black circle; experimental data of Danjo and Nishimura [9]: triangle.

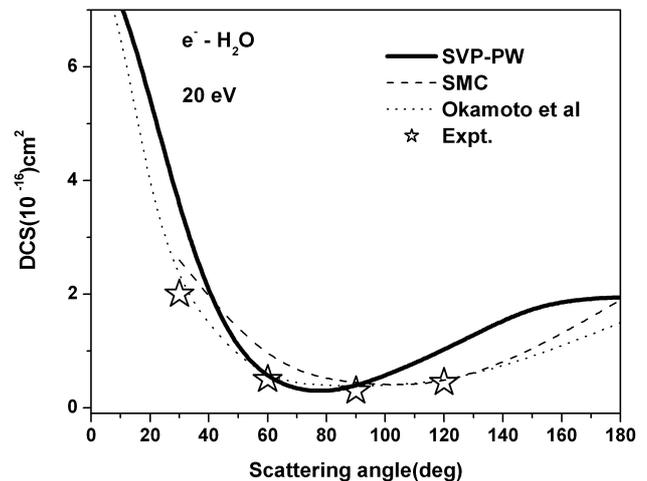


FIGURE 3. Elastic DCS for $e^- - H_2O$ scattering at 20 eV. Present results (SVP-PW): solid line; Schwinger multichannel method used by Brescansin *et al.* [13]: dashed line; theoretical studies of Okamoto *et al.* [30]: dotted line; experimental data [9,10]: triangle.

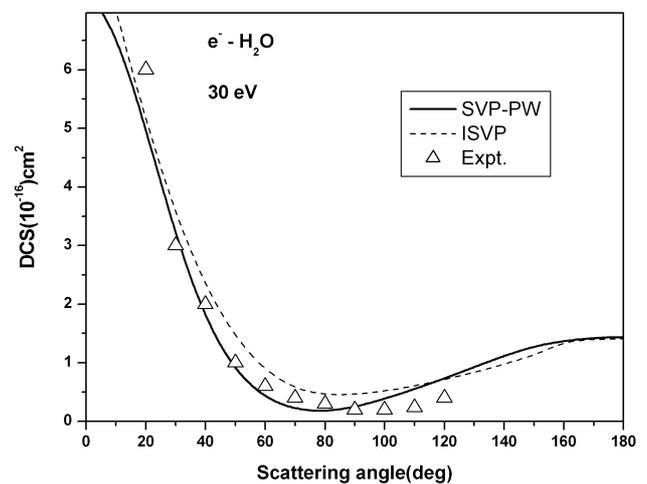


FIGURE 4. Elastic DCS for $e^- - H_2O$ scattering at 30 eV. Present results (SVP-PW): solid line; iterative Schwinger variational method used by Machado *et al.* [16]: dashed line; experimental data of Danjo and Nishimura [9]: triangle.

moment of 0.78 a.u. compared with the experimental value of 0.72 [29]. We have selected representative results on differential cross sections, mostly where experimental data and/or other calculations are available for comparison and our calculations are performed within the framework of the fixed-nuclei approximation.

In Fig. 1 we compare our calculated differential cross sections (DCS) for elastic $e^- - H_2O$ scattering at 10 eV with the measurements of Shyn and Cho [9], and the theoretical results of Machado *et al.* [16], using the iterative Schwinger variational method. As expected for a polar molecule, our cross sections show very strong forward-peaking (our results also show the backward enhancement in the DCS). Agreement between our calculated cross sections and available experimental data is generally good. On the other hand, it

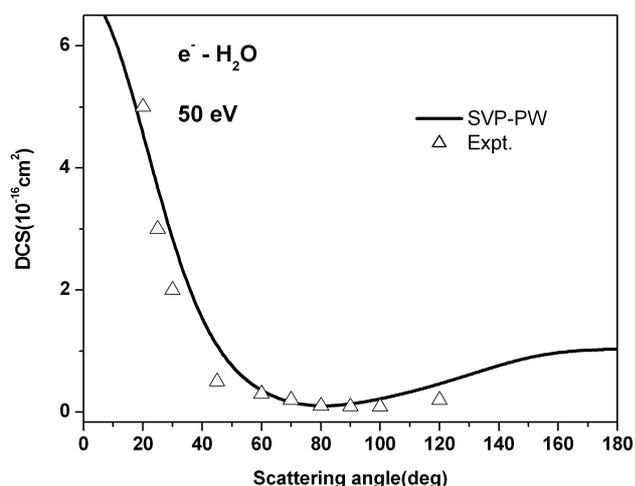


FIGURE 5. Elastic DCS for e^- - H_2O scattering at 50 eV. Present results (SVP-PW): solid line; experimental data of Danjo and Nishimura [9]: triangle.

should be noted that, although the method used by Machado *et al.* [16] is essentially equivalent to our SVP-PW, the discrepancies between the two calculations at large scattering angles can possibly be attributed to our Born-Ockur model (sensitivity of exchange model potential). In Fig. 2 we compare our calculated differential cross sections (DCS) for elastic e^- - H_2O scattering at 15 eV with the measurements of Danjo and Nishimura [9], Shyn and Cho [10] and theoretical results of Okamoto, and Itikawa *et al.*, using the combined free-gas plus correlation- polarization [9, 30], and Machado *et al.* [16]. As in Fig. 1, our results agree well with experimental data [9] and theoretical studies of Okamoto, and Itikawa *et al.* [9, 30], and Machado *et al.*, using the iterative Schwinger variational principle [16]. Again, we can see some discrepancies at an intermediate angle. In Fig. 3 we

compare our calculated differential cross sections (DCS) for elastic e^- - H_2O scattering at 20 eV with the measurements of Danjo and Nishimura [9], the theoretical results of Brescansin [13] using the Schwinger multichannel method, and the studies of Okamoto *et al.* [9, 30]. Also, our results are in good agreement with the experimental data of Danjo and Nishimura [9] and results of Brescansin *et al.* [13] at intermediate angles, and studies of Okamoto *et al.* [9, 30]. In Fig. 4 we compare our calculated differential cross sections (DCS) for elastic e^- - H_2O scattering at 30 eV with experimental data [9], and the theoretical results of Machado *et al.* [16], using the iterative Schwinger variational method. Again, our results are in good agreement with experimental data and theoretical results. The discrepancies at intermediate angles is less significant at 30 eV. In Fig. 5 we compare our calculated differential cross sections (DCS) for elastic e^- - H_2O scattering at 50 eV with experimental data [9]. As observed, our results are in good agreement with experimental data [9].

4. Summary

We have used the Schwinger variational principle with plane waves as a trial basis set to study elastic scattering of electrons by H_2O in the 10-50 eV energy range. Comparison between our calculated differential cross sections with selected experimental and other theoretical results is encouraging and shows that our formalism can be used for studying elastic electron-polar-molecule collisions.

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