Elastic scattering of low-energy electrons from ammonia

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We report an application of the Schwinger variational principle with plane waves as a trial basis set [J.L.S. Lino, M.A.P. Lima, Braz. *J. Phys.* **32**, 432 (2000)]. Differential cross sections are obtained for electron-NH_3 collisions from 8.5 to 30 eV. Differential cross sections are found to be in reasonable agreement with existing measurements.

Keywords: Elastic scattering of electrons; molecular excitation.

Se analiza una aplicacion del principio variacional de Schwinger desde la perspectiva de ondas planas para un cunjunto base [J.L.S. Lino, M.A.P. Lima, Braz. *J. Phys.* **32**, 432 (2000)]. El proposito de este trabajo es mostrar la seccions eficaces diferenciales para las colisiones electron-NH_3 entre 8.5 - 30 eV. Los resultados obtenidos se comparan con los experimentos.

Descriptores: Retrodispersión elástica de electrones; excitación molecular.

PACS: 34.80.Bm; 34.80.Gs; 34.80.-i

1. Introduction

Studies of low-energy electron-molecule collisions by *ab initio* methods, although fundamental and practical interest, have proven to be much more difficult and proceeded more slowly than corresponding studies of bound-state electronic structure. In recent years, there has been considerable progress both in the application of existing methods and in the developments of promising new approaches [1–4]. The demand for data on the collision cross sections of low-energy electrons by polyatomic targets has continued to grow, due to the expanding use of cold plasma in the process and fabrication of materials [5, 6]. In the present study differential cross sections for elastic e^- - NH_3 scattering are reported. Such cross sections for e^- - NH_3 scattering are very important in many fields of research, as space science, radioastronomy in the interstellar medium, laser gas, synthetic chemistry and even fundamental chemistry. The scattering of electrons by NH_3 has been studied by theory and experimentation, but only few studies have been carried out. The total cross sections were measured by Sueoka *et al.* [7], and the differential cross sections by Danjo and Nishimura [8–10]. From a theortical perspective, there exist some calculations for the elastic scattering of electrons from NH_3. For example, the Schwinger multichannel method used by Pritchard *et al.* [11], the parameter-free model calculations by Gianturco [12], Jain and Thompson [13], and the Kohn variational method (KVM) by Jain [14] too. In fact, the avaliable experimental data of differential cross sections do not provide a definitive test to the efficiency of the theoretical methods used for e^- - NH_3. In this paper, I present cross sections for elastic scattering of electrons by NH_3 for incident energies, from 8.5 to 30 eV. These cross sections were obtained through the fixed-nuclei approximation, and with the Born-Ochkur exchange model [15]. A fixed-nuclei treatment of electron scattering by polar molecules is well known to lead to divergent cross sections due to the slow fallow of the T-matrix elements for large ℓ (this is an essential property of the dipole potential). The usual remedy for the dilemmas caused by the electron-dipole interaction is by using a hybrid treatment, through which only the low order partial-wave components of the T-matrix are determined from variational calculations, and the higher order terms are included by the Born approximation via a closure formula. As a step toward addressing this need, Lino and Lima [16, 17] recently described the Schwinger variational principle with plane waves as a trial basis set. The main limitation of the method (SVP) resides on what makes it a general method: the expansion of the scattering function is done on a L^2 basis (Cartesian Gaussian functions), which is very effective only for short-range potentials. An important development of the method is to allow the inclusion of plane waves (PW) within scattering basis, which in fact is the motivation of the present paper [18]. The present study has several goals: firstly, no theoretical study for SVP-PW using the Born-Ochkur model has been published before for e^--NH_3; secondly, the present study can be regarded as a good test for a polar target (the essential point is that the SVP-PW contains typically the first Born approximation, which can be an adequate strategy for polar targets). From here on contains, we will refer to SVP using plane waves as SVP-PW.

This paper is organized as follows. In Sec. 2 the theory is briefly described. Calculated results and discussions are present in Sec. 3. Section 4 summarizes the conclusions.

2. Theoretical formulation

Details of the Schwinger variational principle (SVP) of electron-molecule collisions have been discussed elsewhere [19], so only a brief outline will be given here. The

hamiltonian for the collision can be written as

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

where H_N is the target hamiltonian, and T_{N+1} is the kinetic energy operator of the incident electron. 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

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

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 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. 19:

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

H_0 is the Hamiltonian for the N electrons of the target plus the kinetic energy of the incident electron, and E is the 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, in the static approximation, for elastic scattering, the expansion of the scattering wave function is done in a discrete form as

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

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

The inclusion of these definitions in Eq. (3), and the application of a stationarity condition [18] with respect to the coefficients, give 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 programs to evaluate all matrix elements of Eq. (7). The $G_P^{(+)}$ is the projeted 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 bounded state channels. With the help of the linear momentum representation [18, 19] 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 done 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

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

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 to evaluate Eq.(10), associated with possible discontinuities, has been examined and treated as in the subtraction method [18, 19]. I just add and subtract the expression

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

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. In the present study the effect of including an exchange is considered by replacing the first Born approximation (FBA) used in the SVP-PW by FBA + g, where "g" is the Ochkur amplitude [15]. In the actual implementation two different quadratures are used for $\vec{k}_m$ and $\vec{k}_n$ to avoid situations where $\mid \vec{k}_m - \vec{k}_n \mid$ are too small [20]. For example, to obtain a differential cross section, we just evaluate the square modulus of this amplitude, summing over all $\vec{k}_m$ directions and averaging them 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 enables to calculate an analytical approximation of the body-frame fixed nuclei scattering amplitude for molecules of arbitrary geometry. The amplitude is then expanded f($\vec{k}_m$,$\vec{k}_n$) in a partial-wave series, and make the requisite transformations into the laboratory frame. After accounting for the random orientation of the target, the differential cross section is obtained in the usual manner by performing the appropriate average over initial spin states, and sum over final spin states. The calculation is carried out via a Gauss-Legendre quadrature.

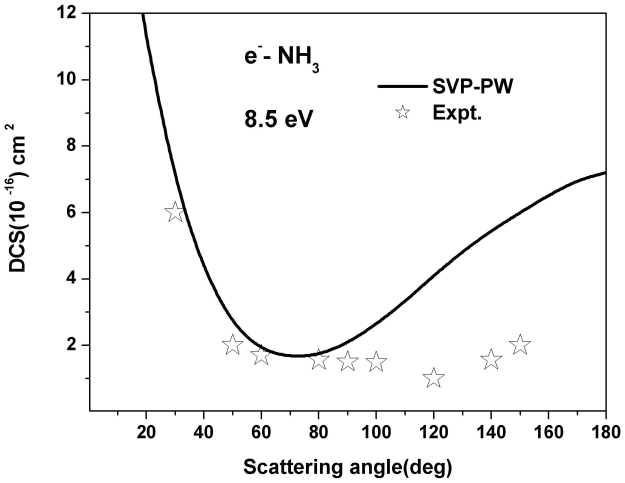

FIGURE 1. Elastic DCS for e^- - NH_3 scattering at 8.5 eV. Present results SVP-PW: solid line; Experimental results of Ref. 8; star.

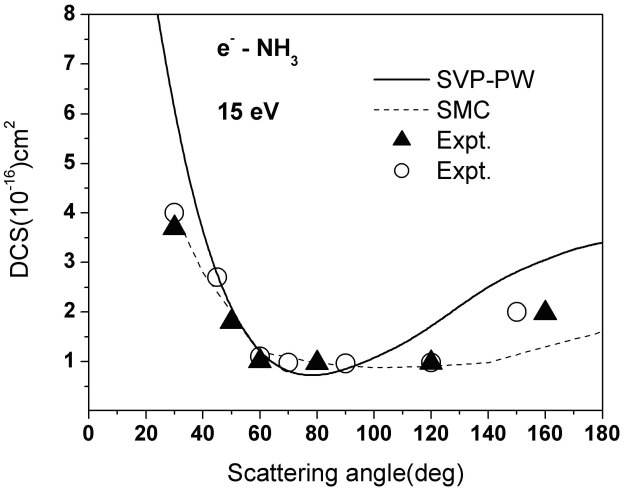

FIGURE 2. Elastic DCS for e^- - NH_3 scattering at 15 eV. Present results SVP-PW: solid line; Schwinger multichannel method Ref. 10: dashed line; Experimental results of Ref. 8: black triangle; Experimental results of Ref. 9: circle.

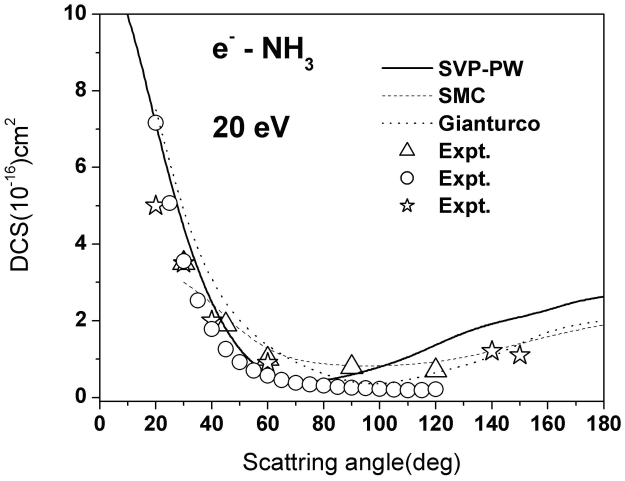

FIGURE 3. Elastic DCS for e^- - NH_3 scattering at 20 eV. Present results SVP-PW: solid line; Schwinger multichannel method Ref. 10: dashed line; Theoretical results of Gianturco [11]: dott line; Experimental data of Ref. 8.

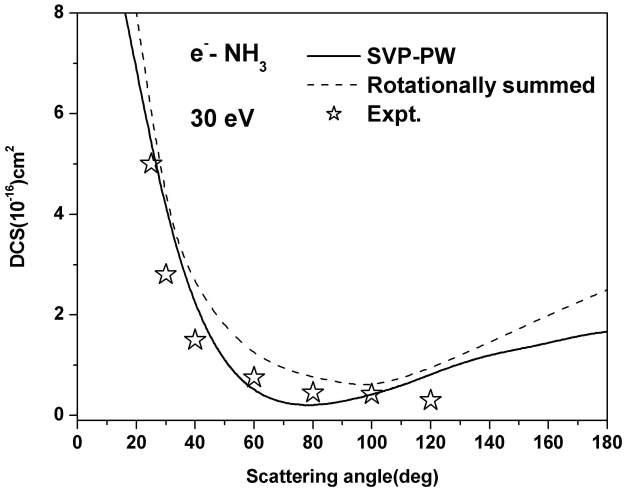

FIGURE 4. Elasic DCS for e^- - NH_3 scattering at 30 eV. Present results SVP-PW: solid line; Theoretical results of Gianturco of Ref. 11: dashed line; Experimental data of Ref. 8: star.

3. Results and discussion

To illustrate what already been mentioned, we present the results of present method applications the for elastic scattering of electrons by NH_3 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. [11]. At the experimental geometry of $R_(N-H)$= 1.92a_o, and θ(H-N-H)= 106.7° assumed here.

Figure 1 shows elastic differential cross sections DCS for NH_3 at 8.5 eV. The SVP-PW results are compared with experimental data [8] as expected for a polar molecule, and the cross sections show very strong forward-peaking (there is an agreement between SVP-PW calculated cross sections and available experimental data). At 8.5 eV, our calculations clearly underestimate the measured DCS at large scattering angle. The discrepancies between the results indicate the sensitivity of the exchange model adopted.

Figure 2 presents elastic differential cross sections (DCS) for e^- - NH_3 scattering at 15 eV. The SVP-PW results are compared with Schwinger multichannel method-SMC (using static-exchange approximation) [11], and experimental data [8, 10]. SVP-PW results also agree with experimental data. As observed, the SMC using a L^2 basis clearly underestimate the measured DCS at a small scattering angle (character of the dipole potential).

Figure 3 shows elastic differential cross sections at 20 eV. As noted at 20 eV, the SVP-PW calculated cross section agree with the experimental data [8], the Schwinger multichannel method [11], and the results of Gianturco [12]. Particularly

the SVP-PW agree well with the static-exchange plus polarization (also rotationally summed) model of Gianturco [12].

Figure 4 shows elastic differential cross sections at 30 eV. As in Fig. 3, the SVP-PW calculated cross sections agree with experimental data [8], the SMC method [11], and results of Gianturco [12].

4. Conclusion

In this paper, I present an application of the Schwinger variational principle using plane waves and a set basis trial (SVP-PW) for low-energy electron impact collision with NH_3. Differential cross sections were found agree with experimental data and more complete theoretical studies including polarization effects (at larger scattering angles, our results indicate the sensitivity of the exchange model adopted). These results show that the SVP-PW scheme can be used to investigate polar targets as well as the NH_3.

Acknowledgments

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