Studies of Elastic $e^-\text{NH}_3$ Collisions

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We report on the elastic differential cross sections (DCS) for the scattering of electrons by \text{NH}_3 for several energies. These cross sections were obtained using the Schwinger variational principle. In our procedure 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; all results are obtained at the static level of approximation. Our calculated DCS agree reasonably well with available experimental data and with other theoretical results (obtained at the static-exchange level of approximation).

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I. INTRODUCTION

The cross sections of $e^-\text{NH}_3$ scattering are very important in many fields of research, including space science, radiation physics, gas lasers, and even fundamental chemistry. The scattering of electrons by \text{NH}_3 has been studied both theoretically and experimentally, but only a few studies have been done. Some experiments have been carried out in recent years. The total cross sections were measured by Sueoka et al. \cite{1} and the differential cross sections by Danjo and Nishimura \cite{2}. In fact, the available experimental differential cross section data do not provide a definitive test capable of judging the efficiency of the theoretical methods used for $e^-\text{NH}_3$ \cite{3, 4}. Obtaining accurate differential cross sections for collisions still remains an important endeavour. As a step toward addressing this need, we have recently described the Schwinger variational principle (SVP) with plane waves as a trial basis set \cite{5, 6}. The main limitation of the SVP method resides in what makes it a general method: the expansion of the scattering function is done in an $L^2$ basis (Cartesian Gaussian functions), but this is very effective only for short-range potentials. An important development of the method would be to allow for the inclusion of plane waves (PW) in the scattering basis, which is the motivation for the present paper. In order to do this, we have developed computer codes involving matrix elements of the second-Born term type with no restrictions on the molecular geometries \cite{7}. In this paper we present results for $e^-\text{NH}_3$ scattering in the static approximation. Although the correct treatment of exchange and of polarization effects is known to be important, we surprisingly found that the present static results are in good agreement with experimental data. The present study has several goals: first, to our knowledge, no theoretical study using the Schwinger
variational principle with plane waves as a trial basis set has yet been published for e\textsuperscript{-}-NH\textsubscript{3}; second, the present work serves, in addition, as a necessary prelude to planned low energy scattering studies; third, our results are useful for establishing benchmark calculations at the static approximation level, which is indispensable in the development of a more complete formalism, including exchange plus polarization effects; and fourth, our study of e\textsuperscript{-}-NH\textsubscript{3} collisions may be regarded as a good test regarding usefulness. Our main interest is to check whether the SVP using plane waves is capable, for instance, of describing correctly the structures in the DCS. Hereafter, we will refer to the SVP using plane waves as the SVP-PW.

The organization of this paper is as follows. In Sec. 2 the theory is briefly described. Our calculated results and a discussion are presented in Sec. 3. Section 4 summarizes our conclusions.

II. THEORETICAL FORMULATION

Details of the Schwinger variational principle (SVP) of electron-molecule collisions have been discussed elsewhere [8] and only a brief outline will be given here. The Hamiltonian for the collision can be written as

\[ H = (H_N + T_{N+1}) + V = H_0 + V, \]

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

\[ (E - H)\Psi_{k_f}^{(\pm)} = 0. \]

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

\[ [f(\vec{k}_f, \vec{k}_i)] = -\frac{1}{2\pi} \left\{ \langle S_{k_i}^- | V | \Psi_{k_f}^{(+)\dagger} \rangle - \langle S_{k_i}^+ | V | \Psi_{k_f}^{(-)} \rangle - \langle S_{k_f}^- | V | G_P^{(+)} V | \Psi_{k_i}^{(-)} \rangle \right\}. \]

Here \( | S_{k_i}^- \rangle \) 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. \( | S_{k_f}^+ \rangle \) 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. [8]:

\[ G_P^{(+)} = \int d^3k \frac{| \Phi_0 \vec{k} \rangle \langle \vec{k} \Phi_0 |}{(E - H_0 + i\epsilon)}, \]

\( H_0 \) 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 $| \Psi_{k_i}^{(+)} \rangle$ and $| \Psi_{k_f}^{(-)} \rangle$ are products of the target wave function $| \Phi_o \rangle$ and the 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. Thus, in the static approximation, for elastic scattering, the expansion of the scattering wave function is done in a discrete form as

$$
| \Psi_{k_i}^{(+)} \rangle = \sum_m a_m(k_m) | \Phi_0 k_m \rangle ,
$$

and

$$
| \Psi_{k_f}^{(-)} \rangle = \sum_n b_n(k_n) | \Phi_0 k_n \rangle .
$$

The inclusion of these definitions in Eq. (3), and the application of a stationarity condition [7] with respect to the coefficients, gives the working form of the scattering amplitude:

$$
[f(k_f, k_i)] = -\frac{1}{2\pi} (\sum_{mn} S_{k_f}^{(+)}, V | \Phi_0 k_m \rangle (d^{-1})_{mn} (k_n | \Phi_0 \rangle | V | S_{k_i}^{(-)})) ,
$$

where

$$
d_{mn} = (\Phi_0 k_m | V - V G_P^{(+)} V | \Phi_0 k_n) .
$$

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

$$
P = \sum_{\ell} | \Phi_\ell \rangle \langle \Phi_\ell | = 1 ,
$$

where $P$ is truncated and carries only energetically open bound state channels. With the help of the linear momentum representation [7, 8] of the one-particle unit operator, the matrix element

$$
\langle \Phi_0 k_m | V G_P^{(+)} V | \Phi_0 k_n \rangle
$$

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

$$
\sum_{\ell} \int_0^{\infty} dk \frac{2k^2}{k^2 - k^2} g_{k_m k_n}^{(\ell)} (k) ,
$$

where

$$
g_{k_m k_n}^{(\ell)} (k) = \int d\Omega_k \langle \Phi_0 k_m | V | \Phi_\ell \rangle \langle \Phi_\ell | V | \Phi_0 k_n \rangle ;
$$
the function $g_{k_m k_n}^L (k)$ is essentially an angular integration of the first Born terms with different magnitudes of $k$ (off-shell terms). The difficulty in evaluating Eq. (10), associated with possible discontinuities, has been examined and was treated in a way similar to the subtraction method [7, 8]. We simply add and subtract the expression $\frac{2k^2}{k^2 - k^2} g_{k_m k_n}^L (k)$ 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 $k$) and the added term is evaluated analytically. In our implementation we use two different quadratures for $k_m$ and $k_n$ to avoid situations where $|k_m - k_n|$ is too small [9]. For example, to obtain the differential cross section we just evaluate the square modulus of this amplitude, summing over all $k_m$ directions and averaging over the $k_n$'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 $\theta$ and $\phi$ 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 $f(k_m, k_n)$ in a partial-wave series and make the requisite transformation 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 the initial spin states and a sum over the final spin states [9-11]. The calculation is carried out via a Gauss-Legendre quadrature.

III. RESULTS AND DISCUSSION

To illustrate, we present the results of applications of the present method for the elastic scattering of electrons by NH$_3$ using the fixed-nuclei approximation [12]. We have used Hartree-Fock calculations to represent the ground state of the target with the same Cartesian Gaussian basis set used in Ref. [4]. The experimental geometry of R(N-H)=1.92\,a_o and \( \theta(\text{H-N-H})=106.7^\circ \) is assumed here.

Figure 1(a) shows our DCS for NH$_3$ at 8.5 eV. Our results were compared with experimental data [2]. As noted, although the SVP-PW does not include exchange plus polarization effects, the results are, in general, in quite satisfactory agreement with the experimental data.

In Figure 1(b) we show the elastic differential cross sections (DCS) for e$^-$-NH$_3$ scattering at 15 eV. Our results are compared with the Schwinger multichannel method (using the static-exchange approximation) [4] and the experimental data [2, 10]. Again, the comparison between our SVP-PW and the experimental data and theoretical results are, in general, satisfactory.

Figure 1(c) shows the elastic differential cross sections at 20 eV. As noted, at 20 eV our calculated cross section agree well with the experimental data [2].

Figure 1(d) shows the elastic differential cross sections at 30 eV. As noted, our calculated cross section are in good agreement with the experimental data [2].
FIG. 1: (a)-(d). Elastic differential cross sections for $e^-$-NH$_3$ scattering. (a) At 8.5 eV, solid line: our SVP-PW, black triangle: experimental data of Ref. [2]. (b) At 15 eV, solid line: our SVP-PW, dashed line: Schwinger multichannel method (Ref. [4]), black triangle: experimental data of Ref. [2], open circle: experimental data of Ref. [10]. (c) At 20 eV, solid line: our SVP-PW, dashed line: Schwinger multichannel method (Ref. [4]), black triangle: experimental data of Ref. [2], open triangle: experimental data of Ref. [10]. (d) At 30 eV, solid line: our SVP-PW, black triangle: experimental data of Ref. [2].

IV. CONCLUSION

Although the exchange potential and polarization effects are not taken into account in our calculations, our results are, in general, in good agreement with both the experimental observations and the results of other theoretical methods for elastic electron scattering of NH$_3$ over the range of approximately 8.5 to 30 eV. These results give an indication that our scheme may be used to investigate polar targets such as NH$_3$.

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