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Elastic scattering of low-energy electrons by N_2 including the effect of target electronic correlation

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Abstract

A procedure to use configuration-interaction (CI) target wave-functions in the electron–molecule collision theory is applied to study the elastic e^-–N_2 scattering in the (5–20) eV incident energy range. Correlated static and exchange contributions to the interaction potential are presented. Two different atomic basis sets are used. Differential cross sections (DCS) obtained by using Hartree–Fock or CI wave-functions are presented and compared. In the CI case, single and double, and single, double and triple excitations are considered. The effect of electron correlation is analyzed in all the cases. The continuum wave-functions were obtained via the Schwinger variational iterative method. The influence on the DCS of both the size of the atomic basis set and the inclusion of higher-order excitations in the CI calculation is discussed.
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1. Introduction

Over the last few years, there has been a significant progress in the development of both theoretical and experimental methods to study electron–molecule collision processes [1–6]. On the theoretical side these methods are in general founded on very firm theoretical bases and require an accurate representation of the full electron–target interaction potential. In the framework of single-channel calculations, the potential is primarily divided into four contributions: static (S), exchange (E), polarization (P) and absorption (A) [7–9]. Nevertheless, when such methods are used to study

elastic differential cross sections (DCS) they present, in some cases, quantitative and/or qualitative discrepancies when compared to the measured data [10]. A reason for these discrepancies can be the well-known electronic correlation effects in the target, which are not taken into account since the electron–molecule interaction potential is in general derived from the Hartree–Fock (HF) wave-function of the target [11,12].

It is known from modern atomic and molecular electronic structure theory that the HF approximation, while remarkably successful in many cases, has some limitations and problems [13–15]. In particular, in more recent molecular calculations the HF approximation is frequently used as a starting point for more accurate approximations such as the configuration interaction (CI) method, the multireference CI (MRCI) procedure

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and the many-body perturbation theory (MBPT), that include correlation effects [16,17].

A CI calculation, in principle, provides an exact solution of the many-electron problem. The ideal CI calculation would be the "full CI" (FCI), in which the full many-electron function space of the appropriate spin and symmetry generated by the adopted basis set is used in the wave-function expansion. The FCI, however, is rarely feasible because the number of configuration state functions (CSF) goes up factorially with the basis set size [18]. As far as one goes to larger basis sets this can quickly require the accounting of thousands or even millions of determinantal functions, thus making unfeasible, in principle, a direct derivation of the interaction potential for electron–molecule collision. Therefore in most applications it is necessary in some way to truncate the CI expansion space. In practice, such calculations are usually limited to single and double (SDCI), single, double and triple (SDTCI) or single, double, triple and quadruple (SDTQCI) excitations. To the authors' knowledge only a few works have been published that include target correlation in low-energy electron–molecule scattering [10,19–22] or molecular photoionization [23,24].

Recently we have developed a theoretical procedure [25] to treat elastic electron–molecule collisions using the CI method to determine the target wave-function. By this procedure both the static and the exchange potentials are all given by analytical expressions written as a sum of m^2 terms where m is the number of atomic spin–orbitals used in the linear combination of atomic orbitals, LCAO [26] basis set. As a consequence, in the determination of the interaction potential for electron–molecule collision we can use CI expansions with arbitrary number of CSF. Besides, our procedure differs from that of the previous ones [10,19,20,23] since we use an interaction potential that is obtained directly from the total Hamiltonian of the electron–target system. In a previous work we have applied this procedure [25] to calculate DCS for elastic e^-–H_2 and e^-–CH_4 scattering in the (0.5–20) eV incident energy range and compared our results to those obtained using HF target wave-function and to the available experimental data. Elastic e^-–H_2 and e^-–CH_4 scattering have probably been the most studied, both theoretically and experimentally, electron–molecule collision processes [11,12,27–29]. However, the number of electrons in both systems is not great. Furthermore, a general validity of our method for studying e^-–molecule scattering processes is still to be confirmed via more extensive investigations. We therefore think it is important and interesting to use our methodology in more detail and test it for other physical systems, like N_2, CO and H_2O. Here we will consider the elastic e^-–N_2 process, with the target wave-function being obtained from different LCAO basis sets [30] and CI expansions. Our objective with these calculations is to analyze the influence of the LCAO basis set and the different CI expansions on the determination, by our procedure, of DCS in the SE level.

From a theoretical viewpoint the nitrogen molecule has become almost a standard test case for low energy electron collision calculations. Molecular nitrogen is sufficiently spherical and has an electronic structure which is sufficiently complicated to make it typical of small molecules with closed shells, while still remaining a computationally tractable target for electron scattering calculations [31,32]. In many aspects nitrogen is a better test case for scattering processes than the next simplest commonly occurring molecule, hydrogen. The presence of a well-known resonance in the elastic e^-–N_2 scattering at low energies (2–3 eV) and nitrogen's 14 electrons make it more suitable for analysis such as the importance of the electronic correlation. Also, it is expected that the similarity on the electronic configurations of N_2 and CO can lead to similar DCS for electron scattering by both systems. On the other hand, the presence of a moderate dipole moment in CO is responsible for different forward-scattering behaviors of these two molecules; we plan to investigate, with our CI procedure, the influence of the target electronic correlation on the e^-–N_2 scattering in the resonance region and on the elastic e^-–CO scattering in different papers.

The organization of the paper is as follows. In Section 2 we present some theoretical details. The Schwinger variational iterative method (SVIM) [23] is briefly discussed in Section 3 and we summarize the procedure to use CI wave-function in the scattering theory. In Section 4 some computational details of our calculation are presented. In Section 5 we present our calculated results for the DCS of elastic e^-–N_2 scattering using HF and different CI target wave-functions, with the continuum electron wave-function being calculated in the static-exchange (SE) approximation. Here our interest is primarily to show how the static and exchange contributions calculated with the inclusion of target electron-correlation (i.e. static correlation) modify the DCS obtained with HF approach. Finally, in Section 6 we present our concluding remarks.

2. Theoretical details

The electron–molecule collision is described by the Lippmann–Schwinger equation

$$|\Theta\rangle = |\theta\rangle + G_0^{\pm} U |\Theta\rangle, \tag{1}$$

where $|\Theta\rangle$ is the state function of the interacting electron–molecule system, $|\theta\rangle$ is the corresponding state function without interaction, $G_0^{\pm} = \lim_{\epsilon \to 0} (\nabla^2 + k_0^2 \pm i\epsilon)^{-1}$ is the free-particle Green's operator and $U = 2V$ is the reduced potential operator. The superscript $+$ $(-)$ denotes the

outgoing (incoming) traveling-wave boundary condition of the scattering function.

In the present communication, we will consider the single-channel theory. We have in the coordinate representation the wave-function

$$\Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \ \vec{r}) = \hat{A}(\Phi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\xi(\vec{r})) \qquad (2)$$

with $\Phi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ a many-electron wave-function, $\xi(\vec{r})$ the state function of the scattering electron and $\hat{A}$ an antisymmetrizer operator. The wave-function $\Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \ \vec{r})$ satisfies the Schrödinger equation $(\hat{H}_T - E)\Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \ \vec{r}) = 0$, i.e.,

$$\left(\hat{H} - \frac{1}{2}\nabla^2 + \sum_A V(|\vec{r} - \vec{r}_A|) + \sum_j V(|\vec{r} - \vec{r}_j|) - E \right)$$
$$\times \Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \ \vec{r}) = 0, \qquad (3)$$

where $V(|\vec{r} - \vec{r}_A|)$ is the interaction potential between the scattering electron and the nucleus at $\vec{r}_A$, $V(|\vec{r} - \vec{r}_j|)$ is the interaction potential between the jth electron and the scattering electron, $-\frac{1}{2}\nabla^2$ refers to the kinetic operator of the scattering electron and $\hat{H}$ is the N–electron molecular Hamiltonian given (in atomic units) by

$$\hat{H} = \sum_i^N \hat{h}(i) + \sum_{j<\ell}^N \frac{1}{r_{j\ell}}. \qquad (4)$$

In Eq. (4) $\hat{h}(i)$ is the Hamiltonian operator for the ith electron moving in the potential of the nuclei A, B, ... alone and $r_{j\ell}$ is the distance between the jth and ℓth electron. By projecting Eq. (3) on $\Phi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$, we have

$$(\nabla^2 + k_0^2)\xi(\vec{r}) = U_0\xi(\vec{r}). \qquad (5)$$

In Eq. (5) the kinetic energy of the incident electron satisfies the relation $\frac{1}{2}k_0^2 = E - \mathscr{E}_0$ with $\mathscr{E}_0$ being the target energy. As a vector state in the continuum part of the spectrum, $\xi(\vec{r})$ can be calculated by imposing either outgoing (+) or incoming (−) wave-function boundary conditions. In this work we have used the Schwinger variational iterative method (SVIM) [23] for the calculation of $\xi(\vec{r})$. The interaction potential U_0 is obtained from a target CI wave-function.

3. SVIM procedure

In this section we will briefly discuss the method used to determine $\xi(\vec{r})$; details can be found elsewhere [23]. The DCS for elastic electron–molecule scattering is given by

$$\frac{d\sigma}{d\Omega} = \frac{1}{8\pi^2} \int d\alpha \sin\beta \, d\beta \, d\gamma |f(\vec{k}', \vec{k}_0')|^2, \qquad (6)$$

where $f(\vec{k}', \vec{k}_0')$ is the laboratory-frame (LF) scattering amplitude, $\vec{k}_0'$ and $\vec{k}'$ are the incident and scattered electron linear momenta, respectively, and (α, β, γ) are the Euler angles [33] which define the direction of the molec-

ular principal axis. The LF scattering amplitude is related to the LF T-matrix by the well-known formula

$$f(\vec{k}', \vec{k}_0') = -2\pi^2 T_{\vec{k}', \vec{k}_0'}. \qquad (7)$$

This LF T-matrix can be obtained from the corresponding body-frame (BF) T-matrix $T_{\vec{k}, \vec{k}_0}$ by the usual BF–LF transformation. The Schwinger variational expression for the BF T-matrix can be written in the bilinear form:

$$T_{\vec{k}, \vec{k}_0} = \langle \zeta_{\vec{k}}^{(\mp)} | U_0 | \xi_{\vec{k}_0}^{(\pm)} \rangle + \langle \xi_{\vec{k}}^{(\mp)} | U_0 | \zeta_{\vec{k}_0}^{(\pm)} \rangle - \langle \xi_{\vec{k}}^{(\mp)} | U_0$$
$$- U_0 G_0^{(\pm)} | \xi_{\vec{k}_0}^{(\pm)} \rangle, \qquad (8)$$

where $\xi_{\vec{k}}^{(\pm)}$ and $\zeta_{\vec{k}}^{(\mp)}$ denote the trial scattering and the free-particle wave-functions, respectively, with outgoing (+) or incoming (−) boundary conditions.

The trial scattering wave-functions can be partial-wave expanded as

$$\xi_{\vec{k}}^{(\pm)}(\vec{r}) = \left(\frac{2}{\pi}\right)^{1/2} \frac{1}{k} \sum_{\ell m} i^\ell \xi_{k\ell m}^{(\pm)}(\vec{r}) Y_{\ell m}^*(\hat{k}). \qquad (9)$$

In practice the summation in ℓ, m is truncated to some cutoff values ℓ_c, m_c. To proceed, a set of $\mathscr{L}^2$ functions is used to represent the initial trial scattering wave-function. In our work, a set of Cartesian Gaussian basis functions, R_0, is chosen for this purpose. Improvement of the scattering wave-functions can be achieved via an iterative procedure, that consists basically of augmenting the basis set R_0 by the set S of the partial-wave components $\xi_{k\ell m}^{(\pm)}(\vec{r})$. The new augmented set, $R_1 = R_0 \cup S$, is used as a new basis for obtaining a new set S' of improved wave-functions $\xi_{\vec{k}}^{(\pm)}(\vec{r})$. In the sequence $R_2 = R_0 \cup S'$ is now used as a new basis set and a set S'' is determined. Hence we consider $R_3 = R_0 \cup S''$ and this procedure is continued until converged $\xi_{k\ell m}^{(\pm)}(\vec{r})$ are obtained [23]. These converged scattering wave-functions correspond, in fact, to exact solutions of the truncated Lippmann–Schwinger equation with SE potential.

In the static-exchange (SE) level of approximation the potential U_0 in Eq. (5) can be written as

$$U_0 = 2V^S + 2V^E, \qquad (10)$$

where $V^S(V^E)$ is the static (exchange) operator. In the usual formulation U_0 is constructed from a HF wave-function of the ground state of the target [23], i.e., one has for U_0

$$U_{HF} = 2V_{HF}^S + 2V_{HF}^E, \qquad (11)$$

which is obtained (we consider that the target has an even number $N = 2n$ of electrons) from Eq. (3) with $\Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \ \vec{r}) = \hat{A}(\psi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\xi(\vec{r}))$, where $\psi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ is a Slater determinant.

In the present paper we consider a configuration interaction (CI) target many-electron function $|\Phi_0\rangle$, i.e., in usual notation

$$|\Phi_0\rangle = C_0|\psi_0\rangle + \sum_{a,r} C_a^r|\psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} C_{ab}^{rs}|\psi_{ab}^{rs}\rangle + \cdots, \qquad (12)$$

where $|\psi_0\rangle$ is the HF Slater determinant taken as reference function. The other determinants $|\psi_{ab...}^{rs...}\rangle$ are obtained from $|\psi_0\rangle$ by considering excitations from the occupied molecular spin–orbitals (MSO) $\chi_a, \chi_b, \ldots$ to virtual MSOs $\chi_r, \chi_s, \ldots$; the coefficients $C_a^r, C_{ab}^{rs}, \ldots$ are determined by diagonalizing the target Hamiltonian $\hat{H}$ given in Eq. (4). Specifically, in the case where we have a finite basis set of $2K \geqslant N$ MSOs we can construct $M = \binom{2K}{N}$ different $N-$electron Slater determinants and use these determinants as a basis set to expand the exact many-electron function $|\Phi_0\rangle$. In this case we have for the potential U_0 (for details see previous work [25])

$$U_{CI} = 2V_{CI}^S + 2V_{CI}^E \qquad (13)$$

with

$$V_{CI}^S \xi(\vec{r}) = \sum_{i,j=1}^{2K} f(i,j)\langle\chi_i| \frac{1}{|\vec{r}' - \vec{r}|} |\chi_j\rangle \xi(\vec{r}) + \sum_A \frac{Z_A}{|\vec{r} - \vec{r}_A|} \xi(\vec{r}) \qquad (14)$$

and

$$V_{CI}^E \xi(\vec{r}) = \sum_{i,j=1}^{2K} g(i,j)\langle\chi_i| \frac{1}{|\vec{r}' - \vec{r}|} |\xi\rangle \varphi_j(\vec{r})\eta_j, \qquad (15)$$

where $\chi_j(\vec{r}) = \varphi_j(\vec{r})\eta_j$ are MSOs, $\chi_{2i-1} = \varphi_i\alpha_i$, $\chi_{2i} = \varphi_i\beta_i$, $(i = 1, 2, \ldots, n)$; α, β are spin functions and φ_i are molecular spatial orbitals.

In Eqs. (14) and (15) a numerical integration with respect to the $\vec{r}'$ coordinates is performed and the numerical factors $f(i,j)$ and $g(i,j)$ depend on the CI coefficients $C_0, C_a^r, \ldots$ We have implemented a set of computational algorithm to evaluate all factors $f(i,j)$ and $g(i,j)$; they are calculated after the CI equations have been solved.

In order to analyse the importance of the electronic correlation of the target in the determination of the DCS, in the present work we have performed calculations with U_0 given by Eq. (11) and by Eq. (13). Besides we have considered two different atomic basis set (DZV and DZV-d) and two CI calculations, that is, SDCI (CI with single and double excitations) and SDTCI (CI with single, double and triple excitations). Our results are presented and discussed in Section 5.

4. Computational procedures

Here, the SE potential used in Eq. (5) is constructed from a HF and from a CI wave-function $|\Phi_0\rangle$ of the ground state of N_2. We used in the HF and CI calculations two Double Zeta basis sets, namely, (10s5p)/[3s2p] (DZV) and (10s5p1d)/[3s2p1d] (DZVd). The HF and CI wave-functions were determined by the standard quantum chemistry code GAMESS [34] and the numerical factors $f(i,j)$ and $g(i,j)$ by our computer codes. The bound orbitals as well as the wave-functions of the scattering electron, $\xi(\vec{r})$, were all determined using par-

Table 1
Basis set for the calculation of initial trial scattering functions

Symmetry	Basis functions	Exponents
σ	s	8.0, 4.0, 2.0, 1.0, 0.5, 0.2, 0.05
	z	4.0, 2.0, 1.0, 0.3
π	x	8.0, 4.0, 2.0, 1.0, 0.5, 0.2
	xz	4.0, 2.0, 1.0, 0.3
δ and higher	xy	8.0, 4.0, 2.0, 1.0, 0.5, 0.2

tial-wave expansions, with the radial functions being calculated on a grid sufficiently extended to ensure reaching the asymptotic region. The partial-wave expansions were truncated at $\ell_{max} = 40$ for the static potential and at $\ell_{max} = 25$ and $m_{max} = 20$ for the scattering functions. Our results shown below were all converged within 5 iterations. The normalization of all bound orbitals were better than 0.999. In Table 1 we show the basis sets R_0 used for the calculation of the initial trial scattering functions.

The molecule N_2 belongs to $D_{\infty h}$ symmetry and is a non-polar target. With the atomic basis set DZV we have done HF-SCF, SDCI and SDTCI calculations. The resulting SDCI (SDTCI) wave-function was composed by 508 (7760) CSFs with 1928 (67168) determinants. At the experimental equilibrium geometry (1.037 au) the energies of the CI wave-functions resulted −109.082 au in the SDCI case and −109.087 au in the SDTCI one, to be compared with the HF-SCF energy of −108.878 au and the HF limit of −108.997 au [35]; the corresponding DCS were noted by HF-DZV, SDCI-DZV and SDTCI-DZV. With the DZVd atomic basis set both SDCI and HF-SCF calculations were performed; in this case the SDCI wave-function was composed by 1996 CSFs and 8270 determinants; the resulting energy value was of −109.242 au, to be compared to the corresponding HF-SCF value of −108.959 au. The corresponding DCS were noted as SDCI-DZVd and HF-DZVd, respectively.

5. Results and discussions

In Figs. 1–5 we show our calculated DCS for elastic $e^- - N_2$ scattering in the (5.0–20.0) eV incident energy range, along with the experimental data of Brennan et al. [36], Srivastava et al. [37], Shyn and Carignan [38], Nickel et al. [39], Zubek et al. [1], and Rolles et al. [40], for comparison. We also show the theoretical results of Siegel et al. [41], Huo et al.[42], Gillan et al. [43], Sun et al. [44] and Rolles et al. [40], who used the multiple scattering method (MSM), the Schwinger multichannel variational method (SMC), the R-matrix method, the converged vibrational close-coupling method (CVCC) and a numerical method for the solution of Schrödinger equation, respectively. Although the latter
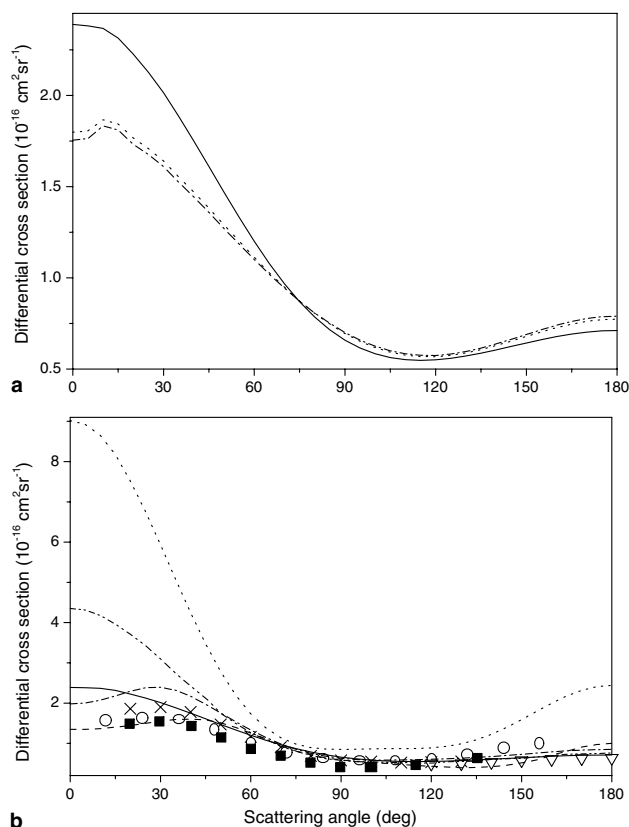
Fig. 1. DCS for elastic electron –N_2 scattering at 5.0 eV. (a) ——, present SDCI-DZVd results; ······, present SDCI-DZV results; – · –, present SDTCI-DZV results. (b) ——, present SDCI-DZVd results; ······, present HF-DZVd results; – – –, theoretical results of Huo et al. [42]; – · –, theoretical results of Sun et al. [44]; – · · –, theoretical results of Gillan et al. [43]; ○, experimental data of Shyn and Carignan [38]; ■, experimental data of Srivastava et al. [37]; ▽, experimental data of Zubek et al. [1] and ×, experimental data of Brennan et al. [36].

Fig. 2. DCS for elastic electron –N_2 scattering at 7.0 eV. (a) ——, present SDCI-DZVd results; ······, present SDCI-DZV results; – · –, present SDTCI-DZV results. (b) ——, present SDCI-DZVd results; ······, present HF-DZVd results; – · –, theoretical results of Sun et al. [44]; ○, experimental data of Shyn and Carignan [38]; ■, experimental data of Srivastava et al. [37].

two calculations [40,44] report vibrational excitation cross sections, we compare our elastic DCS with their vibrationally elastic $v = 0 \rightarrow v' = 0$ results, since is expected that this process is dominant.

In Figs. 1(a)–5(a) we compare our calculated DCS from the three different calculations we have done, i.e. SDCI-DZV, SDTCI-DZV and SDCI-DZVd. The comparison among corresponding DCS and experimental results shows that the SDCI-DZVd calculation provides a better description of both angular and energy dependence of the DCS, thus indicating the improvement of the atomic basis set is probably more relevant than the inclusion of higher-order excitations in the configuration-space CI expansion with a poorer atomic basis set.

In Figs. 1(b)–5(b) we compare both our HF-DZVd and SDCI-DZVd results to experimental and theoretical results available in the literature. A generally good agreement is observed among our SDCI-DZVd results and all of the experimental data, for all of the chosen energies, in the (10–13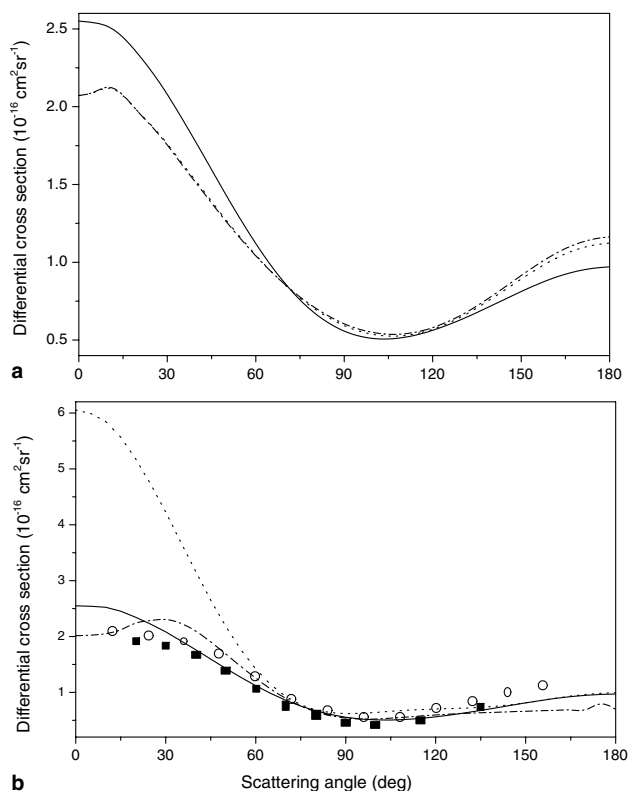0°) angular range. For scattering angles above 130° there is still a good agreement among our SDCI-DZVd results and experiment, except at 5.0 eV incident energy, where a discrepancy is observed between ours and Shyn and Carignan's data [38]. However, even in this case our results are in good agreement with the more recent experimental data of Zubek et al. [1]. In particular at 10.0 eV there is an excellent agreement among our SDCI-DZVd results and those Srivastava et al. [37], in the entire angular range.

The comparison of our CI results with the available theoretical data show a good agreement with those of Sun et al. [44] (at 5.0, 7.0 and 10.0 eV) in the entire angular range and a very good agreement with the results of Huo et al. [42] (at 5.0 eV) for $\theta > 35°$; in the angular range $0 \leqslant \theta \leqslant 35°$ the Huo's results are better than ours. Sun et. al. and Huo et al. results are the only theoretical calculations that include target correlation (i.e. static correlation) effects. It is interesting to notice that Huo et al. calculation includes both target-correlation and polarization effects (e.g. dynamical correlation) by using the Schwinger multichannel formulation through single particle-hole excitations. This can explain the discrepancies observed between Huo et al. results and ours for $\theta < 35°$, since our procedure
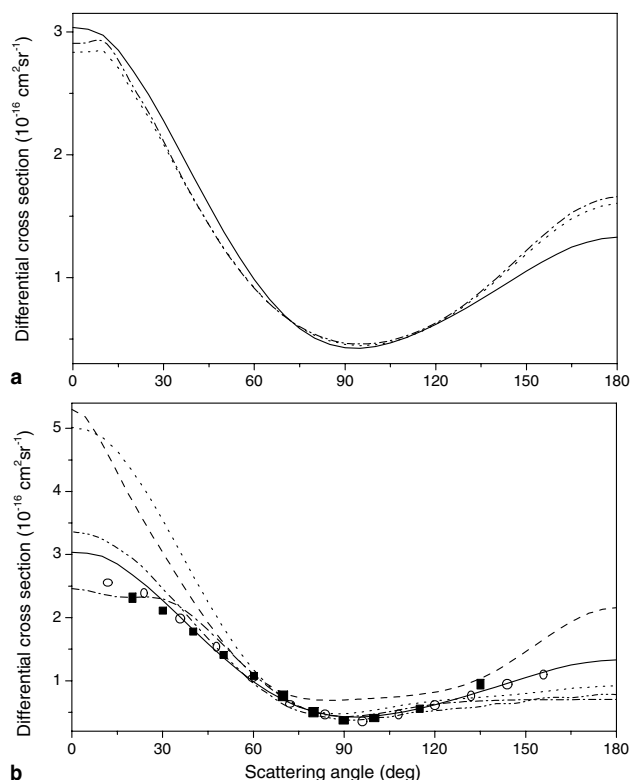
Fig. 3. DCS for elastic electron –N_2 scattering at 10.0 eV. (a) ——, present SDCI-DZVd results; ······, present SDCI-DZV results; – · –, present SDTCI-DZV results. (b) ——, present SDCI-DZVd results; ······, present HF-DZVd results; – – –, theoretical results of Siegel and Dehmer [41]; – · –, theoretical results of Sun et al. [44]; – · · –, theoretical results of Gillan et al. [43]; ○, experimental data of Shyn and Carignan [38]; ■, experimental data of Srivastava et al. [37].

Fig. 4. DCS for elastic electron –N_2 scattering at 15.0 eV. (a) ——, present SDCI-DZVd results; ······, present SDCI-DZV results; – · –, present SDTCI-DZV results. (b) ——, present SDCI-DZVd results; ······, present HF-DZVd results; – · –, theoretical results of Rolles et al. [40]; – · · –, theoretical results of Siegel et al. [41]; ○, experimental data of Shyn and Carignan [38]; ■, experimental data of Srivastava et al. [37].

is based on a monochannel theory and does not include the dynamical correlation. In fact our results are based on an improved static-exchange potential determined directly from the Hamiltonian $\hat{H}_T$ in Eq. (3). On the other hand, although the comparison of our CI results with those of Gillan et al. [43] (at 10.0 eV) and Rolles et al. [40] (at 15.0 eV) is still good in the intermediate-angle region ($\theta > 30°$), discrepancies are observed between the small-angle data of Gillan et al. and ours at 5.0 eV, as well as between those of Siegel et al. [41] (at 10.0 and 15.0 eV) and ours in the entire angular range. These discrepancies can possibly be due to the lack of target correlation effects in their calculations.

The comparison of our SDCI-DZVd and HF-DZVd results shows that all the calculated DCS in the former calculation are in better agreement, both in shape and magnitude with the available experimental data, than those obtained from HF wave-function. These results are particularly meaningful since they confirm the validity of our description via correlated static-exchange potential. In particular for energy $\varepsilon = 10.0$ eV the comparison of our DCS with existing experimental data
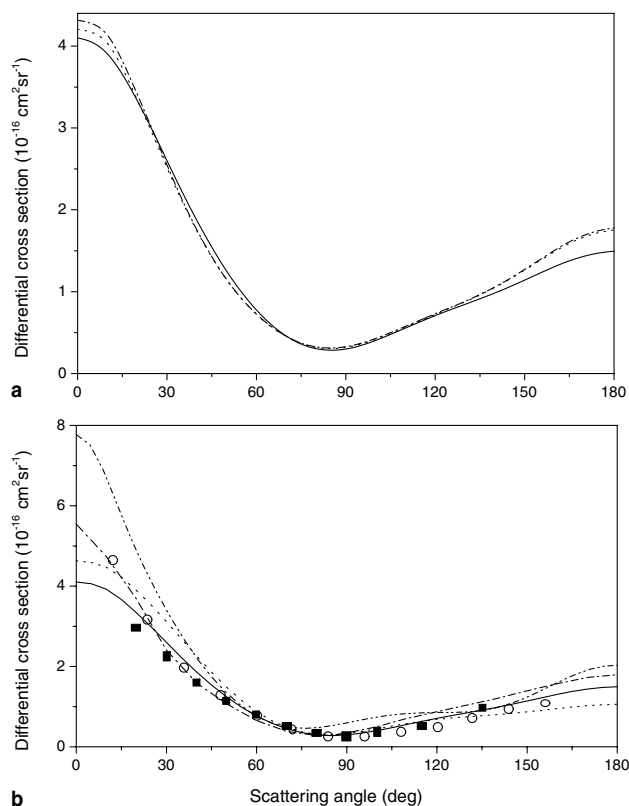
shows excellent agreement, both qualitatively and quantitatively. For energies $\varepsilon > 10.0$ eV we note that the difference between CI-DCS and HF-DCS are less pronounced; this confirms that the electronic correlation of the target are more important for lower energies. In fact for $\varepsilon = 7.0$ and 5.0 eV the DCS obtained using HF wave-functions are overestimated at small ($\theta < 60°$) scattering angles, underestimated for $\theta > 130°$ and very different if compared to experimental data; our CI-DCS results, however, are in very good agreement with these experimental values.

Concluding this section we remark that in their study on the N_2 shape resonance Meyer et al. [20] have done calculations using both CI and algebraic diagrammatic construction (ADC) methods [45–47]. In their work they have shown that, for the used basis set, very extensive multi-reference CI (MRCI) calculations are need in order to correctly describe the target correlation in the energy range (2–5) eV. On the contrary, in the present work we investigate a different quantity, the DCS, in a different energy range, i.e. (5–20) eV. Besides, the expression we use to obtain the static and exchange potentials is different from that
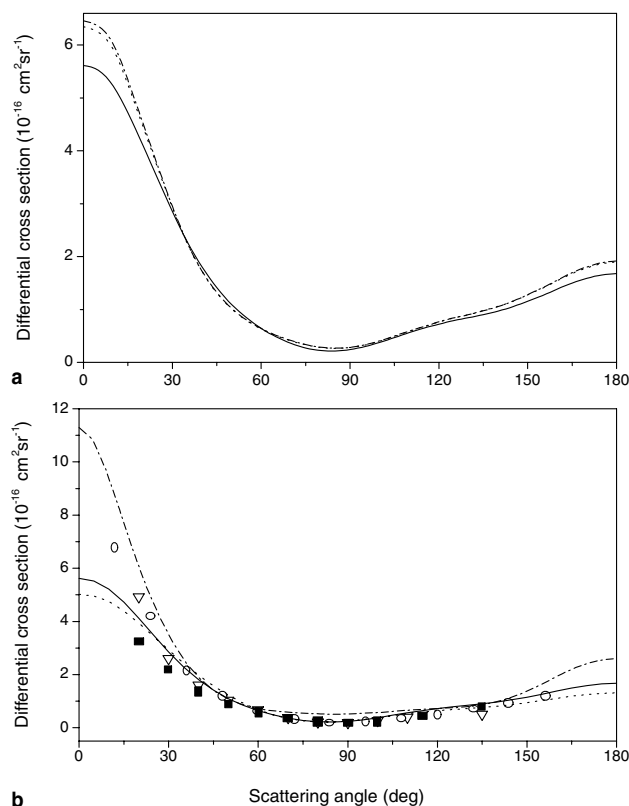
Fig. 5. DCS for elastic electron –N₂ scattering at 20.0 eV. (a) ——, present SDCI-DZVd results; ······, present SDCI-DZV results; – ·–, present SDTCI-DZV results. (b) ——, present SDCI-DZVd results; ······, present HF-DZVd results; – ·–, theoretical results of Siegel et al. [41]; ○, experimental data of Shyn and Carignan [38]; ■, experimental data of Srivastava et al. [37]; ▽, experimental data of Nickel et al. [39].

of Meyer et al. (for example, in Eqs. (14,15) $g(i,j)$ and $f(i,j)$ are different factors while in Eq. (2.5) of [20] the same factor ρ_{ij} is used to determine both V^S and V^E contributions). This can explain why a conventional SDCI calculation with a DZVd basis set is sufficient to our present calculation.

Another point to comment is the role played by the dynamical correlation. It is known that for low-energy electron scattering its contribution to the cross section can result very important, mainly at or near multi-channel resonant structures. In a previous work [25] we have reported a procedure to account for this contribution via a local correlation-polarization potential that uses the exact one-particle density ρ (see [25] for details). However, for the sake of clearing the discussion, we have chosen do not include this contribution in our present work. As a matter of fact, for the energy range we have considered here the dynamical correlation becomes much less important. This explains why we have found a good agreement with experiment using only the static correlation and also why this agreement is much better for 15 eV than for 5 eV.

6. Conclusions

In this work we have used a general method previously developed by Vianna et al. [25] for the use of correlated CI-type target wave-functions in the calculation of differential cross sections for elastic electron–molecule scattering. In our procedure the static and exchange contributions to the interaction potential are obtained from correlated target wave-functions. Although the polarization contribution to the scattering potential can be determined using our procedure [25], we have not considered this contribution in the present study because our interest was to analyze the DCS in an exact SE level. One of the advantages of our method is that the static and exchange contributions to the interaction potential can be written in terms of the molecular spin–orbitals using different numerical factors $f(i,j)$ and $g(i,j)$, respectively. As a consequence, our procedure allows that an arbitrary number of CSF be used in the CI calculation, always demanding the same computational effort in the scattering calculation. In the present work we have studied the elastic e⁻–N₂ collision with the scattering electron wave-function calculated at the SE level of approximation. We have used two different atomic basis set and performed both HF and CI calculations for the ground-state target wave-function. In the CI case, single and double (SD) and single, double and triple (SDT) excitations were considered; all the DCS obtained with a CI-expansion truncated up to single excitations resulted practically equal to the HF-DCS.

We would like to comment that the main goal of the present work is to show the importance of static correlation (isolated target) for a reliable description of elastic e⁻–N₂ scattering. This could be hardly done at the resonance region, where both static and dynamical correlation (polarization) are known to be very important since an undesirable superposition of effects then occurs. Hence we looked for energies above the resonance region in order to avoid this superposition and so to determine clearly the role played by the static correlation in the calculation of DCS.

Our results for the elastic e⁻–N₂ scattering in the (5–20) eV energy range using a static-exchange potential obtained from CI wave-functions show that, at these energies: (i) for a given atomic basis set (DZV or DZVd in our case), higher-than-double excitations are not needed to be included in the CI expansion since, differently of the resonance energy region [20], a conventional SDCI calculation is capable of providing theoretical results of DCS in good agreement with experimental values; (ii) it is by far more relevant for the calculation of CI-DCS for elastic e⁻–N₂ scattering, to improve the used atomic basis set than include such higher-order excitations using a poorer atomic basis set.

A systematic investigation on the influence of both the size of the atomic basis set and of the inclusion of higher-order excitations on other physical processes than e^-–N_2 scattering is needed and is underway by the authors. Another point to investigate is the analysis of the scattering potential in the N_2 resonance energy using our procedure for the determination of the static, exchange and polarization contributions and the determination of DCS. This is now under study.

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