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Electron scattering from molecules: Applications of the Schwinger multichannel method to e^- -CO and e^- -C₂H₄ collisions

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Abstract. To illustrate our recent efforts to obtain electronic excitation cross sections of molecules by electron impact, we present in this paper results for the X ¹Σ → a ³Π and A ¹Π transitions of CO obtained with the Schwinger multichannel method. Our results are in good agreement with other theoretical calculations, although not so good when compared with experiments. We also discuss the importance of inclusion of polarization effects to obtain electronic excitation cross sections of some molecules through an example using the C₂H₄ molecule, which has a triplet state with a low-energy threshold. Finally, we present a very simple rule to estimate integral electronic excitation cross sections using the differential cross section (DCS) at 90⁰, which can be useful to experimentalists using apparatus with difficulties to measure the DCS's at angles around 0 and 180 degrees. We show its efficiency for the present electronic excitation of the C₂H₄ molecule by electron impact.

1. Introduction

It is a challenge in the electron-molecule scattering field to obtain reliable electronic excitation cross sections of large molecules by electron impact. The study of such system is motivated by the necessity of acquiring collision data for modeling chemical plasmas of industrial importance [1] and for investigating the dissociation processes in molecules of biological interest through vibrational and electronic excitation induced by low-energy electron impact [2]. From a theoretical point of view, methods capable of reproducing, for small molecules, the experimental data and the results of other calculations with the same assumptions but with different theoretical approaches, can be relied on to produce accurate results of electron collisions with large molecular systems.

Recently, we have implemented the CI-singles technique in the computational codes of the Schwinger multichannel (SMC) method [3] for electron-molecule scattering, in order to provide an improved description for the excited states of the target. Such a modification allowed us to perform calculations taking into account the coupling among excited states of different spin multiplicity with a proper description of their spatial wave functions. Since then, we

are investigating in a systematic way the influence of multichannel effects through the coupling between singlet and triplet states with the same spatial symmetry. We have applied this strategy to study the electronic excitation of H₂ [3] and N₂ [4] molecules and obtained a relatively good agreement with the experimental data for many of the electronic transitions studied. As a next step for testing the level of accuracy of our procedure we have considered the electronic excitation by electron impact of CO, a molecule with permanent dipole moment, and of C₂H₄, a small polyatomic target. Among a number of polyatomic molecular systems of interest, we begin with an application for the electronic excitation out of the ground state to the $\tilde{a} \ ^3B_{1u}$ state of the ethylene molecule by electron impact. This transition was previously investigated by Sun *et al.* [5] and by Rescigno and Schneider [6] that carried out, respectively, a two-state calculation with the Schwinger multichannel method and a three-state calculation with the complex-Kohn method. Another motivation for the present investigation is the discrepancy between theory and experiment observed for this transition, that may have its origin in the absence of polarization effects in the theoretical calculations.

2. Theory

The SMC method was discussed in detail elsewhere [7]. Here we only give an outline of the method in order to highlight the most important aspects of its theoretical formulation. In the SMC method the scattering amplitude, calculated in the body-reference frame (as denoted by the label B) is given by:

$$f_B^{SMC}(\vec{k}_f, \vec{k}_i) = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_i} | V | \chi_m \rangle (d^{-1})_{mn} \langle \chi_n | V | S_{\vec{k}_f} \rangle, \quad (1)$$

where the $|\chi_m\rangle$'s are (N+1)-electron Slater determinants, constructed from products of target states, obtained by single-configuration interaction (SCI) with one-particle wave functions, keeping only overall doublet states, if the target is a closed shell system [3]. The d_{mn} matrix elements are given by:

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle \quad (2)$$

and the $A^{(+)}$ operator can be written as:

$$A^{(+)} = \frac{1}{2}(PV + VP) - VG_P^{(+)}V + \frac{1}{N+1} \left[\hat{H} - \frac{N+1}{2}(\hat{H}P + P\hat{H}) \right]. \quad (3)$$

In the above equations $|S_{\vec{k}_i(f)}\rangle$ is an eigenstate of the unperturbed Hamiltonian H_o , given by the product of a target state and a plane wave with momentum $\vec{k}_{i(f)}$; V is the interaction potential between the incident electron and the target; $\hat{H} \equiv E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_o + V$; P is a projection operator onto the open-channel space and $G_P^{(+)}$ is the free-particle Green's function projected on the P -space.

2.1. Numerical Stability Analysis

The analysis for numerical stability of the present calculations is performed through a check procedure developed by Chaudhuri and co-workers to investigate the origin of unphysical resonances appearing in positron-N₂ calculations [8]. Adapted to the case of electron-molecule scattering the analysis begins with the diagonalization of the matrix elements of the \tilde{V} operator:

$$\tilde{V} \equiv \frac{1}{2}(PV + VP) + \frac{\bar{H}}{N+1} - \frac{1}{2}(\bar{H}P + P\bar{H}), \quad (4)$$

where V , P have already been defined and $\bar{H} = \hat{H}$, calculated at a fixed energy, following Refs. [3, 8]. The next step involves the identification and elimination of the configurations weakly coupled by this average potential, that is, the eigenvectors associated to the eigenvalues near zero of the equation $\bar{V} | \tilde{\chi}_m \rangle = v_m | \tilde{\chi}_m \rangle$. The $| \tilde{\chi}_m \rangle$'s are then used as new (N+1)-electron basis functions.

3. Results and discussion

In the present work, the cross sections for triplet states were obtained according to [3], with the partial wave decomposition of the scattering amplitude truncated at the values $\ell_{max} = 7$, $m_{max} = 2$. For singlet \rightarrow singlet transitions we have used the standard Born-closure procedure with $\ell_{max} = 9$ and all possible m values.

3.1. CO molecule

The description of the excited states (a $^3\Pi$ and A $^1\Pi$) and the criteria used for construction of the active space of coupled states were made according to the minimum orbital basis for single configuration interaction (MOB-SCI) strategy [3]. Applied to these transitions, this scheme gives rise to a nine-channel close-coupling calculation. Our calculations were performed within the framework of fixed-nuclei and Frank-Condon approximations [9] at the equilibrium internuclear distance of $2.132 a_0$. The Cartesian Gaussian set of uncontracted functions used for construction of the target states and in the expansion of the trial scattering wave functions is a 11s7p3d for C and O atoms and a 2s3p2d set in the center of mass of the molecule. The calculated ground state SCF energy obtained with this basis set is -135.292 hartree and the calculated vertical excitation energies for the transitions of the ground state to the a $^3\Pi$ and A $^1\Pi$ excited states are 6.0 and 9.5 eV, respectively.

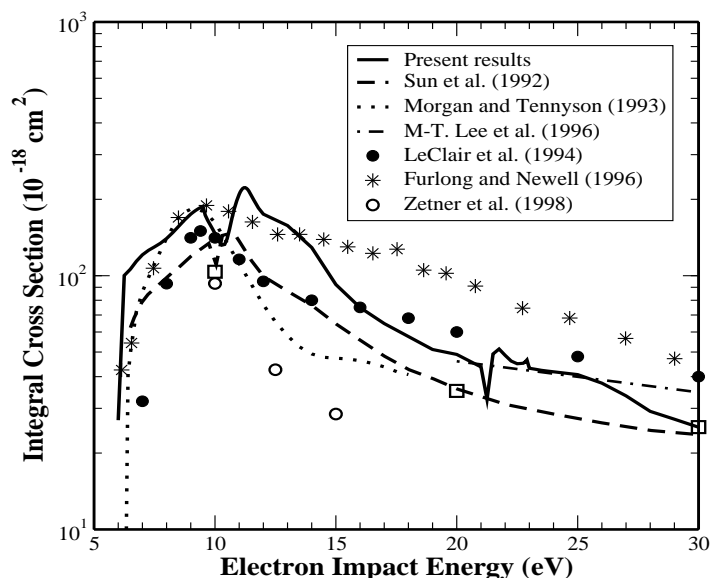


Figure 1. Integral cross sections for the electronic transition $X^1\Sigma \rightarrow a^3\Pi$ of CO.

In Figure 1, we present our integral cross section (ICS) for the electronic excitation of the a $^3\Pi$ state of CO by electron impact. Our results are in general larger than those obtained by other theories, *i.e.* Sun *et al.* [10] (SMC method, 1992), Morgan and Tennyson [11] (R-matrix method, 1993) and M.-T. Lee *et al.* [12] (Distorted-wave method, 1996), but keep the general qualitative shape of the curves. The structures in our cross sections are due to physical (9.5 eV) and pseudo thresholds (21 and 22 eV). There is also disagreement between different experimental data. Our results are in good agreement with the experimental data of Furlong and Newell [13]

at lower energies (below 15 eV) and with LeClair *et al.* [14] above 15 eV. The results of Zetner *et al.* [15] remain below ours at all energies considered.

Figures 2 and 3 present our differential cross sections (DCS) at 15 eV for the $a\ ^3\Pi$ and $A\ ^1\Pi$ states of CO, respectively. For the triplet state we see better agreement with the two-state calculation of Sun *et al.* [10] than with their singlet state results. The agreement with experiment [15, 16] is poor for the triplet state and reasonable for the singlet. A possible reason for the discrepancies between theory and experiment is that the theoretical calculations presented in these figures use Hartree-Fock description of the ground state, that is known to give an inverted permanent dipole moment of CO [17].

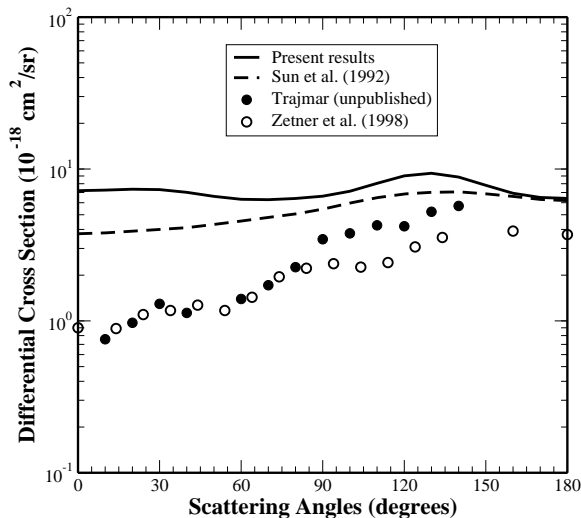


Figure 2. Differential cross sections for the electronic transition $X\ ^1\Sigma \rightarrow a\ ^3\Pi$ of CO at 15 eV.

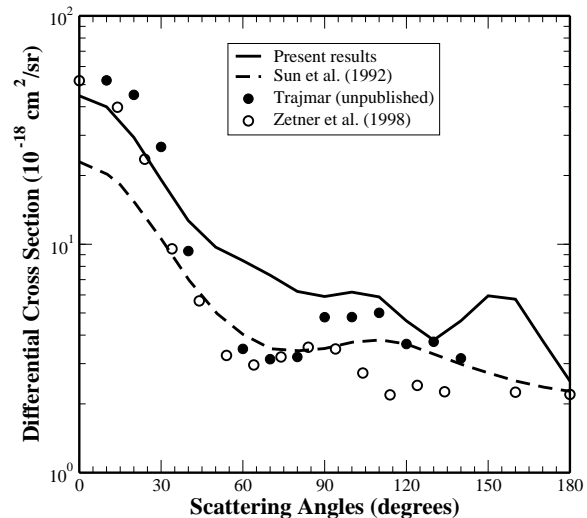


Figure 3. Same as Figure 2 but for the $A\ ^1\Pi$.

3.2. C_2H_4 molecule

In the case of the electronic excitation of the $\tilde{a}\ ^3B_{1u}$ state of the ethylene molecule, we present our two up to five-state coupling results and a study of the influence of polarization effects on the two-channel close-coupling calculation. The scattering amplitudes are calculated using the SMC method to describe the scattering process with the MOB-SCI strategy [3]. The close-coupling results (comparison between the pseudopotential and all-electron approach) will be published elsewhere [18] and here we will only discuss the polarization effects on the electronic excitation process. The $\tilde{a}\ ^3B_{1u}$ state opens at around 3.5 eV and the next electronic channel opens above 7 eV. Therefore eventual discrepancies observed between theory and experiment in this energy interval could not be attributed to multichannel coupling. This discrepancy can be noted in Figures 4 and 5. Figure 4 shows our results with polarization together with our present all-electron calculation (two to five-state calculation), earlier results obtained also with the SMC method (two-state calculation) and results using the Complex Kohn method (two to three-state calculation), and results from the experiment [19]. Figure 5 shows a comparison between the theoretical and experimental DCS. The absolute DCS of Asmis and Allan [20] are much lower than the close-coupling results of the theoretical calculations. Due to this disagreement, we have investigated the role of polarization effects on the excitation process. Polarization effects are known to be important at low-energies. Inclusion of these effects can move a resonance position by more than 2 or 3 eV. By blindly including 1000 configurations per symmetry we have found an enormous change in the excitation cross sections. This is probably a similar effect as the one

observed in furan [21]. In that case, we have found that inclusion of polarization in a proper way places the resonance below the excitation threshold (in agreement with the experimental position). Otherwise the resonance can appear just above this threshold, increasing the cross sections as seen in Figures 4 and 5. Details of this study will be presented elsewhere [22].

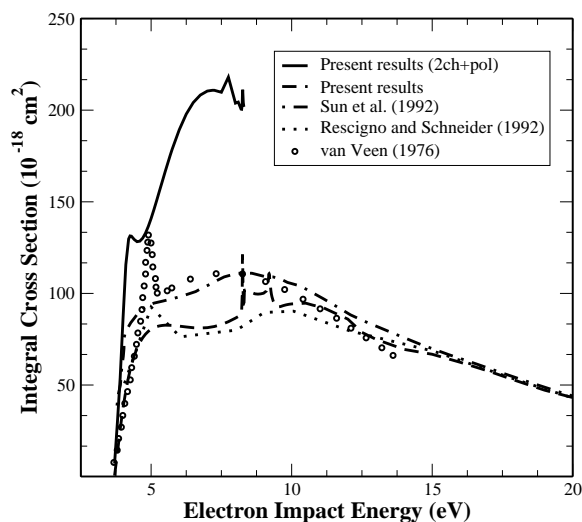


Figure 4. Integral cross sections for electronic excitation of \tilde{a}^3B_{1u} state of C_2H_4 .

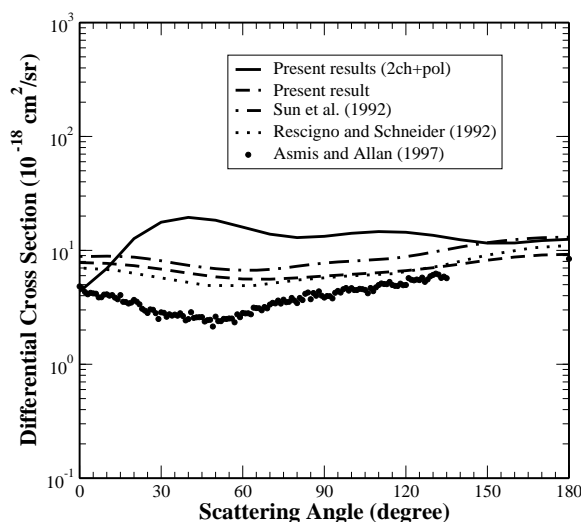


Figure 5. Differential cross sections at 7.1 eV for electronic excitation of \tilde{a}^3B_{1u} state of C_2H_4 .

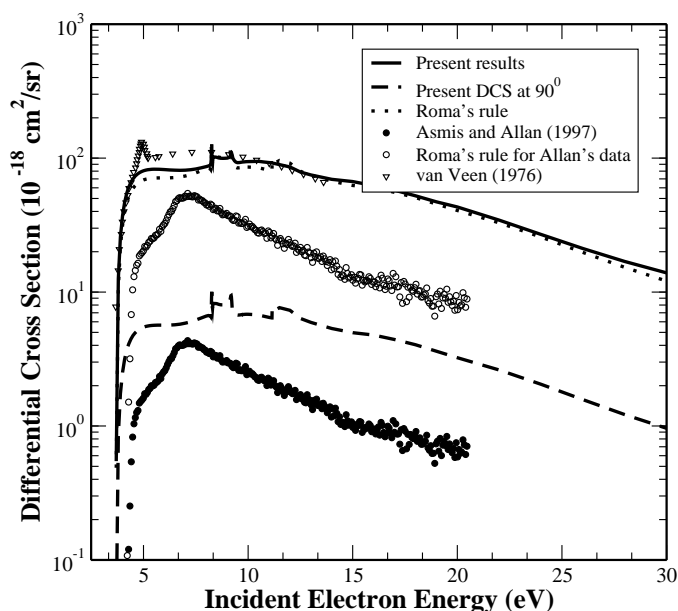


Figure 6. Integral cross sections for electronic excitation of \tilde{a}^3B_{1u} state of C_2H_4 .

3.3. Roma's rule

By comparing the curves of DCS at 90° and ICS of the present electronic excitation of C_2H_4 as a function of energy, we have noted that they were very similar in shape. A quick investigation of Figure 6 has shown that the two curves differs roughly by a factor of 4π . This simple rule allows one to estimate ICS from DCS's measured or calculated at 90° and can be very useful,

especially for experimentalists with difficulties to measure the angles around 0 and 180 degrees. The reason it works is that ICS are obtained from DCS weighted by $\sin \theta$ which gives the largest contribution for 90° and zero contribution for 0° and 180° . The angular region below 90° in general (not always) compensates the angular region above 90° . So, assuming a flat DCS with the 90° value gives a nice estimation (the integral over the solid angle gives the 4π factor). Besides C_2H_4 , we have tested this procedure for H_2 , N_2 , CO , and furan molecules and it worked quite well (below 10% error).

4. Summary and Conclusions

In this paper we have presented applications of the SMC method in the study of the electronic excitation of CO and C_2H_4 molecules by low-energy electron impact. The important finding is that polarization effects play a very important role in electronic excitation of molecules with low-energy thresholds, especially if shape resonances are around these electronic states thresholds. Our results show that a simple n-channel calculation can be meaningless, considering that polarization effects can move shape resonances from above to below the threshold and this can give very different electronic excitation cross sections in shape and in magnitude. We have also presented a very simple rule to estimate ICS from DCS's at 90° .

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