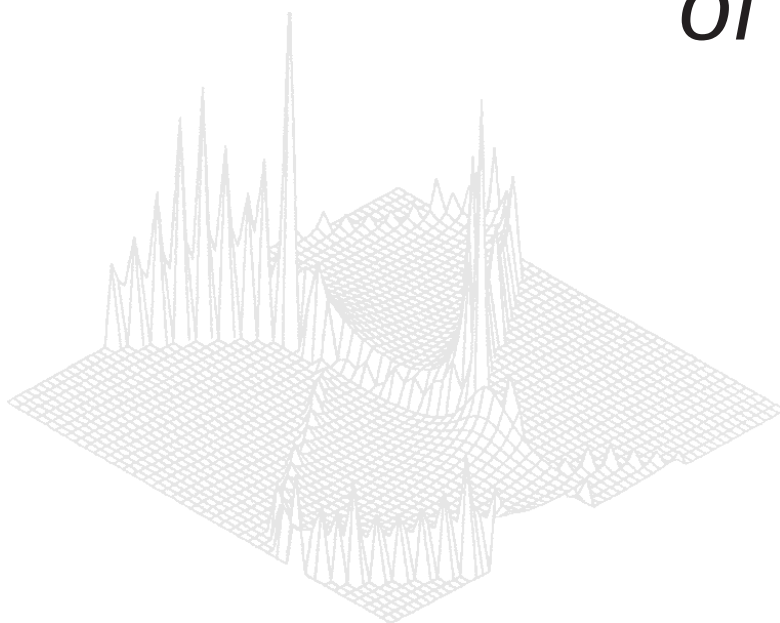

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Low-Energy Electron Scattering by CS₂ Molecules

Márcio H. F. Bettega

Departamento de Física, Universidade Federal do Paraná,
Caixa Postal 19044, 81531-990, Curitiba, Paraná, Brazil.

Abstract

We report the integral elastic cross section for low-energy electron scattering by CS₂ molecules. To perform our calculations we used the Schwinger multichannel method with pseudopotentials. We have found, in a static-exchange calculation, a shape resonance around 1 eV that belongs to the Π_u symmetry. With the inclusion of polarisation effects only in that symmetry, we show that the resonance becomes a bound state. This result is in agreement with other results available in the literature.

Scattering of low-energy electrons by CS₂ has been the subject of recent theoretical and experimental studies. Lee *et al.* (1999a) calculated elastic differential, integral and grand total (elastic + inelastic) cross sections by means of the Schwinger iterative method combined with the distorted-wave approximation. To describe the e[−]–molecule interaction they used a complex potential consisting of static, exchange, correlation-polarisation and absorption terms, obtained from a fully molecular wave function. Bettega *et al.* (2000a) calculated elastic integral, differential and momentum transfer cross sections for energies from 5 to 50 eV, using the Schwinger multichannel (SMC) method with pseudopotentials (SMCPP). Sakamoto *et al.* (1999) measured elastic differential cross sections at selected energies. There are also the experimental studies of Szmytkowski (1987) and Sohn *et al.* (1987) and the calculations of Lynch and Dill (1979) and Raj and Tomar (1997). Lynch and Dill used in their calculations the continuum multiple-scattering model (CMSM), along with the Hara potential for the exchange interaction, to study elastic scattering of electrons by CO₂, OCS and CS₂. They found a relative insensitivity of their results to the polarisation potential, but they did not report whether they included the polarisation interaction in their e[−]–CS₂ scattering calculations, in order to check the insensitivity of this particular molecule to this interaction. They chose to present their results for these molecules without including polarisation. In particular, the CS₂ cross section of Lynch and Dill shows a low-energy shape resonance around 2 eV, associated with the Π_u symmetry. However, there is no indication of such a resonance in the theoretical results of Lee *et al.* which take polarisation effects into account, or in the experimental data of Szmytkowski and Sohn *et al.*. In our previous study on e[−]–CS₂ collisions we have avoided energies lower than 5 eV, and therefore we were not able to investigate the existence of this low-energy resonance.

Polarisation effects come from the distortion of the electronic cloud of the target due to the presence of the incoming electron, and are known to be important in giving a correct description of the scattering process at low impact energies (usually below 5 eV). In particular, the position of a shape resonance is very sensitive to the polarisation of the target and it moves, when polarisation is considered, to an energy lower than that obtained at the static-exchange approximation. Sometimes a shape resonance that is found in a static-exchange calculation becomes a bound state when polarisation effects are included (Bettega 2000b).

In this work we present cross sections for electron scattering by CS₂ molecules at energies lower than 5 eV, obtained with the Schwinger multichannel method (Takatsuka and McKoy 1981, 1984; Lima *et al.* 1990) with pseudopotentials (Bettega *et al.* 1993). In our applications of this method (see e.g. Natalense *et al.* 1999; Varella *et al.* 1999; Bettega 2000a; Bettega *et al.* 2000c), we have employed the norm-conserving pseudopotentials of Bachelet *et al.* (1982). The basis set we used in this study is the same set used in our previous calculations on e[−]–CS₂ collisions (Bettega *et al.* 2000a), and was obtained as described by Bettega *et al.* (1996). In order to investigate the low-energy Π_u shape resonance found in the static-exchange approximation calculations, we included polarisation effects only in this symmetry. Our calculations were performed at the fixed-nuclei approximation at the equilibrium geometry of the ground state of the neutral molecule (CRC 1998).

The SMC method (Takatsuka and McKoy 1981, 1984; Lima *et al.* 1990) has been described in detail in several publications, and we will review here only the steps which are important to this work. The SMC method is a variational approximation to the scattering amplitude, where the scattering wave function is expanded in a basis set consisting of $(N + 1)$ -electron Slater determinants $\{|\chi_m\rangle\}$ as follows:

$$|\Psi_{\vec{k}}^{(\pm)}\rangle = \sum_m a_m^{(\pm)}(\vec{k}) |\chi_m\rangle, \quad (1)$$

and the coefficients $\{a_m^{(\pm)}(\vec{k})\}$ of this expansion are determined through a variational approach. The resulting expression for the scattering amplitude is

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

where

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle, \quad (3)$$

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP + PV)}{2} - VG_P^{(+)}V. \quad (4)$$

In the above equations $|S_{\vec{k}_i}\rangle$ is a solution of the unperturbed Hamiltonian H_0 and is given by the product of a target state and a plane wave, V is the interaction potential between the incident electron and the target, $\{|\chi_m\rangle\}$ is a set of $(N + 1)$ -electron Slater determinants used in the expansion of the trial scattering wave function, $\hat{H} = E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_0 + V$. Further, P is a projection operator onto the open-channel space defined in terms of target eigenfunctions $|\Phi_l\rangle$:

$$P = \sum_l^{open} |\Phi_l\rangle \langle \Phi_l|, \quad (5)$$

and $G_P^{(+)}$ is the free-particle Green function projected on the P -space.

In a static-exchange approximation calculation, where the target polarisation is completely neglected, the configuration space $\{|\chi_m\rangle\}$ is constructed as

$$|\chi_m\rangle = \mathcal{A}\{|\Phi_1\rangle |\varphi_t\rangle\}, \quad (6)$$

where $|\Phi_1\rangle$ is the target ground state wave function, described at the Hartree–Fock level of approximation, $|\varphi_i\rangle$ is a one-electron function, and $\mathcal{A}$ is the antisymmetriser. To take polarisation into account, the configuration space is enlarged by including configurations of the type

$$|\chi_m\rangle = \mathcal{A}\{|\Phi_j\rangle |\varphi_u\rangle\}; \quad j \geq 2, \quad (7)$$

where $|\Phi_j\rangle$ are virtual states of the target obtained from the ground state by single excitations, and $|\varphi_u\rangle$, as before, is a one-electron function.

Polarisation can be separated into two different classes: (i) radial correlation where the excitations do not destroy the symmetry of the ground state of the molecule, and (ii) angular correlation where the excitations destroy the symmetry of the ground state of the molecule. In their study on e^- –N₂ scattering, Schneider and Collins (1984) noted that the background scattering, associated with the Σ_g^+ symmetry, is sensitive to long-range polarisation, which is mostly related to angular correlations. They also noted that the resonant scattering associated with the Π_g symmetry is critically dependent on the short-range polarisation, which is related to radial correlations. There are several approaches to polarisation treated in the literature (Huo *et al.* 1987a, 1987b; Rescigno and Lengsfeld 1992; Azevedo *et al.* 2000; Beyer *et al.* 2000). To account for polarisation effects in the Π_u symmetry, which in principle is a resonant symmetry, we followed the procedure developed by Winstead and McKoy (1998) on e^- –N₂O collision calculations, that is based on the conclusions of Schneider and Collins (1984). This procedure was also used on e^- –CO₂ (Lee *et al.* 1999b) and e^- –C₆H₆ (Bettega *et al.* 2000b) collision calculations. We have recently used this procedure with our codes to study scattering of electrons by N₂O and by the boron trihalides (Bettega 2000b). This procedure is as follows: we constructed a valence-like ‘modified virtual orbital’ (MVO) $|\tilde{\varphi}\rangle$ from a +4 cation Fock operator according to the recipe given by Bauschlicher (1990). The $(N + 1)$ -particle configuration space, given by equations (6) and (7), is then built considering only single excitations that preserved the symmetry of the target ground state, i.e. symmetry- and spin-preserving excitations of the type $[|p_\gamma\rangle \rightarrow |q_\gamma\rangle]|\tilde{\varphi}\rangle$ (radial correlation). Here $|p_\gamma\rangle$ is an occupied orbital and $|q_\gamma\rangle$ a virtual orbital, and both orbitals belong to the same representation γ . In the present calculation the $|p_\gamma\rangle$ and $|q_\gamma\rangle$ orbitals belong to the Σ_g , Σ_u , Π_g and Π_u representations and the $|\tilde{\varphi}\rangle$ orbital belongs to the Π_u representation. As a result, the target and the temporary-anion wave functions are described in a balanced way, avoiding overcorrelation of the anion. Single excitations from the eight valence orbitals were included, giving a total of 264 configurations for the Π_u symmetry.

In Fig. 1 we present our integral cross section for energies up to 15 eV, obtained at the static-exchange approximation. We also show, for purposes of comparison, the theoretical results of Lynch and Dill and Lee *et al.*, the total cross section measurements of Szmytkowski, and the elastic cross section measurements of Sohn *et al.* Our cross section and that of Lynch and Dill show a shape resonance at energies below 2 eV. This structure was not seen in the results of Lee *et al.*, where polarisation was included, or those of Szmytkowski and Sohn *et al.* The origin of the resonance seen in the cross section of Lynch and Dill is probably due to an inadequate description of the polarisation interaction, once they found a relative insensitivity of their results to this potential. It could also be due to a lack of polarisation, because as discussed above Lynch and Dill have not reported whether they computed the cross sections for CS₂ by including polarisation, as a check to that insensitivity.

In Fig. 2 we show our cross section for the Π_u symmetry obtained with the static-exchange and static-exchange plus polarisation approximations. We also show the Π_u cross

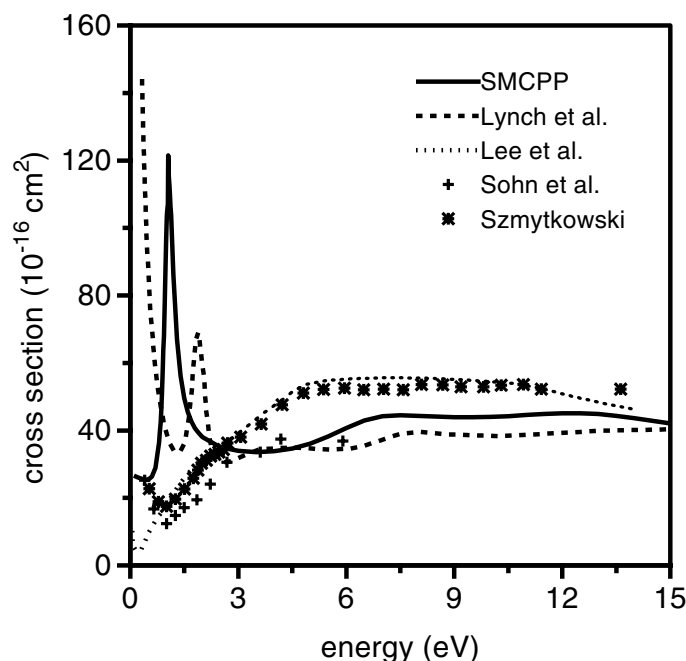


Fig. 1. Integral cross section for CS_2 , showing our pseudopotential results at the static-exchange approximation (SMCPP), the theoretical results of Lynch *et al.* (1979) and Lee *et al.* (1999a), plus the experimental elastic cross section of Sohn *et al.* (1997) and the experimental total cross section of Szmytkowski (1987).

section of Lynch and Dill. With the inclusion of polarisation effects the resonance becomes a bound state, which agrees with the results of Lee *et al.*, Szmytkowski, and Sohn *et al.* In order to further investigate this result, we have diagonalised the $(N + 1)$ -particle Hamiltonian, and calculated the vertical electron affinity (VEA) of CS_2 . Once our N - and $(N + 1)$ -particle Hamiltonians are balanced by construction, this procedure indicates whether the anion is stable. We obtained for the VEA the value of $+0.96$ eV, which indicates that the anion CS_2^- is stable at the vertical geometry, that is, at the geometry of the neutral molecule. We show in Fig. 3 the eigenphase sum for the Π_u symmetry, obtained with the static-exchange plus polarisation approximation. Again, there is no indication of a resonance.

As discussed above, our calculations were performed at the fixed-nuclei approximation, that is, with the nuclei of the molecule fixed at their equilibrium bond lengths. This approximation is no longer valid in the presence of a resonance, and to obtain a correct description of that resonance, e.g. its magnitude and width, the vibrational motion should also be included (McCurdy and Mowrey 1982; Huo *et al.* 1987a, 1987b; Gully *et al.* 1998; Rescigno *et al.* 1999). Sohn *et al.* have studied the effects of vibration on the cross section of CS_2 and OCS molecules (OCS has a Π shape resonance around 1.2 eV). They did not find in their results any indication of the Π_u resonance seen in the results of Lynch *et al.* in the CS_2 cross section, although they have confirmed the existence of the Π resonance for OCS also seen in the results of Lynch *et al.* McCurdy and Mowrey found in their study of the Σ_u^+ resonance in H_2 that this resonance became a bound state at the internuclear distance of 2.85 Å. In their study on the $\text{e}^- - \text{CO}_2$ collision,

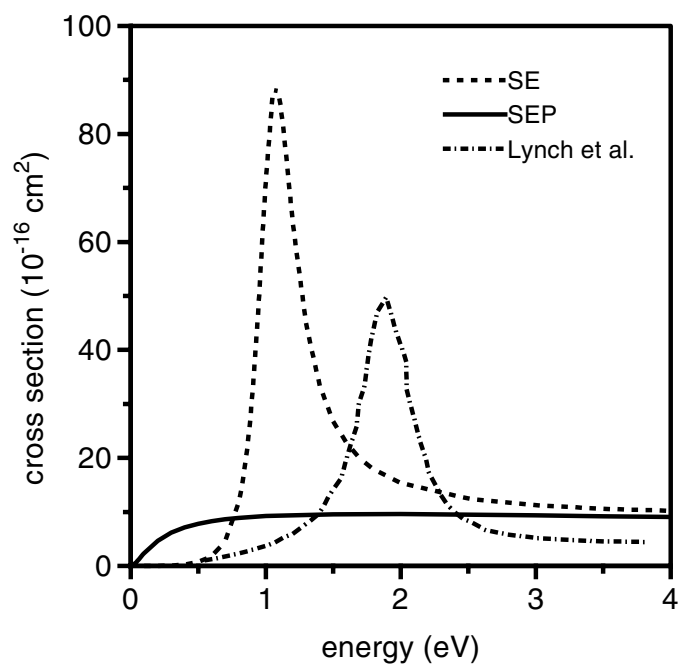


Fig. 2. Integral cross section for the Π_u symmetry, showing our static-exchange plus polarisation (SEP) results, our static-exchange (SE) results, and the theoretical results of Lynch *et al.* (1979).

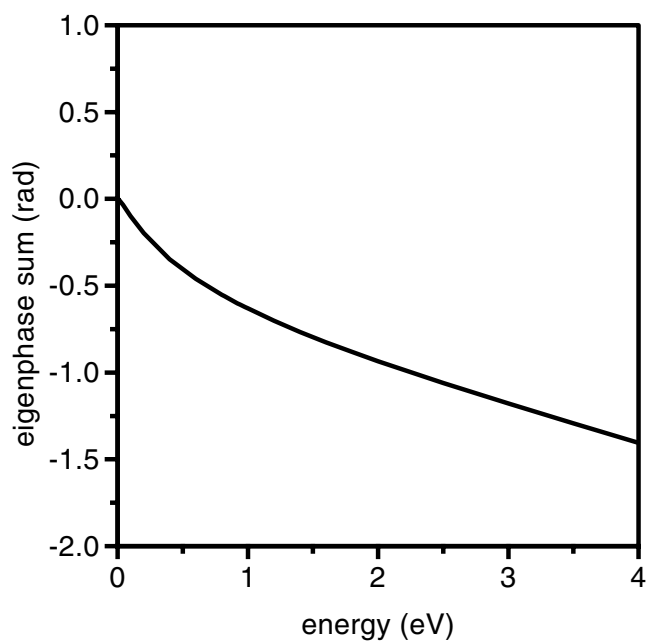


Fig. 3. Eigenphase sum for the Π_u symmetry with the static-exchange plus polarisation approximation.

Rescigno *et al.* (1999) included the vibrational motion of the nuclei considering only the effect of the CO symmetric-stretch motion on the Π_u resonance. They calculated the Π_u cross section at different CO internuclear distances and found that the resonance energy is lowered with increasing CO distance. When the integration of the T -matrix over the vibrational wave functions was performed, they found that the effect of the nuclear motion was to broaden and lower the resonance, keeping its position unchanged, which agreed with experiment. Based on the above results, we can conjecture that for CS₂ the resonance may become unbound if we calculate the Π_u cross section at different CS internuclear distances, but it will remain bound when the integration over the vibrational wave functions is performed.

We have presented elastic cross sections for electron scattering by CS₂ molecules. We found a shape resonance at the Π_u symmetry around 1 eV in a static-exchange calculation. This resonance becomes a bound state when polarisation effects are taken into account. This result agrees with the experimental results of Szmytkowski and Sohn *et al.* and the theoretical results of Lee *et al.*

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