Electron collisions with OCS and CS_2 molecules

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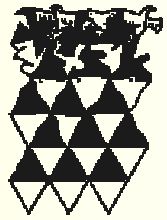


Motivation

- Experimental studies on electron collisions with CO_2, OCS and CS_2 suggested the existence of an s-wave virtual state in the elastic cross section of these molecules. [Sohn *et al.*, J. Phys. B: At. Mol. Phys. **20**, 3217 (1987); Szmytkowski *et al.*, Chem. Phys. Lett. **107**, 481 (1984); Sueoka *et al.*, J. Chem. Phys. **111**, 245 (1999); Kawada *et al.*, J. Chem. Phys. **112**, 7057 (2000); C. Szmytkowski, J. Phys. B: At. Mol. Phys. **20**, 6613 (1987); Jones *et al.*, Phys. Rev. Lett. **89**, 093201 (2002)]
- Previous theoretical studies (R-Matrix (UK), SMC, Kohn) focused their attention on electron collisions with CO_2. [M. A. Morrison, Phys. Rev. A **25**, 1445 (1982); L. A. Morgan, Phys. Rev. Lett. **80**, 1873 (1998); Lee *et al.* J. Chem. Phys. **111**, 5056 (1999); Rescigno *et al.*, Phys. Rev. A **60**, 2186 (1999)]
- Our goal is to investigate the existence of a virtual state for OCS and CS_2.
- OCS: Π shape-resonance, s-wave virtual state, and Ramsauer-Townsend minimum.
- CS_2: s-wave virtual state and Ramsauer-Townsend minimum (Π_u shape-resonance at the static-exchange approximation).

SMC method

Takatsuka and McKoy, Phys. Rev. A **24**; 2473 (1981)
Takatsuka and McKoy, Phys. Rev. A **30**; 1734 (1984)

- Variational approach;
- Formulated for applications to low-energy electron-molecule collisions;
- Capable of addressing important aspects of these collisions as:
  - molecular targets of general geometry;
  - exchange interactions (*ab initio*);
  - effects arising from the polarization of the target by the incident electron (*ab initio*);
  - electronic excitation.
- Pseudopotentials from Bachelet, Hamann and Schlüter (LDA/norm-conserving).

Bettega, Ferreira and Lima, Phys. Rev. A **47**, 1111 (1993)

SMC method

- The Hamiltonian:

$$H = (H_N + T_{N+1}) + V = H_0 + V$$

- We know how to solve the target (Hartree-Fock):

$$H_N \Phi_\ell = E_\ell \Phi_\ell$$

- The Lippmann-Schwinger equation:

$$A^{(\pm)} \Psi_m^{(\pm)} = V S_m; \; S_m = \Phi_m \exp(i\vec{k}_m.\vec{r}_{N+1})$$

- Variational stability: $A^{(+)^\dagger} = A^{(-)}$

- The $A^{(+)}$ operator:

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

SMC method

- $\hat{H} = E - H$. P is a projection operator onto the open-channel space defined by the target eigenfunctions

$$P = \sum_{\ell \in \text{open}} |\Phi_\ell(1, 2, \ldots, N)\rangle\langle\Phi_\ell(1, 2, \ldots, N)|$$

- $G_P^{(+)}$ is the free-particle Green's function projected on the P-space.
- The SMC method is a multichannel extension of the Schwinger variational principle. It is a variational approximation for the scattering amplitude, where the scattering wave function is expanded in a basis of (N+1)-particle Slater determinants

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

The coefficients $a_m^{\pm}(\vec{k})$ of this expansion are then variationally determined.

SMC method

- The “working” expression for the scattering amplitude is

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

  where

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

- Because of practical limitations on the sum over the configuration space

$$\sum_n |\chi_n\rangle\langle\chi_n| \approx \mathbb{1}$$

  a SMC calculation depends on physical intuition.

SMC method

- The direct configuration space is constructed as follows:

$$\{|\chi_i\rangle\} = \{\mathcal{A}\left(|\Phi_1\rangle \otimes |\varphi_i\rangle\right)\}$$

- To take polarization into account, the configuration space is enlarged by including configuration state functions of the type:

$$\{|\chi_m\rangle\} = \{\mathcal{A}\left(|\Phi_j\rangle \otimes |\varphi_u\rangle\right)\} \; ; \; j \geq 2$$

- Polarized orbitals:

$$|\varphi_{i,\mu}\rangle = \sum_{j \in \text{virtuals}} \frac{\langle\varphi_j|x_\mu|\varphi_i\rangle}{E_j - E_i}|\varphi_j\rangle; \; \mu = 1,2,3; \; \varphi_i = \text{occupied orbital}$$

Ramsauer-Townsend minimum

- Potential scattering:

$$\sigma(k) = \sum_{\ell=0}^{\infty} \sigma_\ell(k);\ \sigma_\ell(k) = \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell(k)$$

- For $k \to 0$ it may happens that δ_0 goes through π and $\delta_{\ell\neq 0} \approx 0$: Ramsauer-Townsend minimum.
- Attractive V: $\delta_l > 0$
- Repulsive V: $\delta_l < 0$
- Our potential: $V = V_{\text{static}} + V_{\text{exchange}} + V_{\text{polarization}}$
- When δ_0 changes sign, V also changes sign, going through zero. In that case there is no scattering (Ramsauer-Townsend minimum).

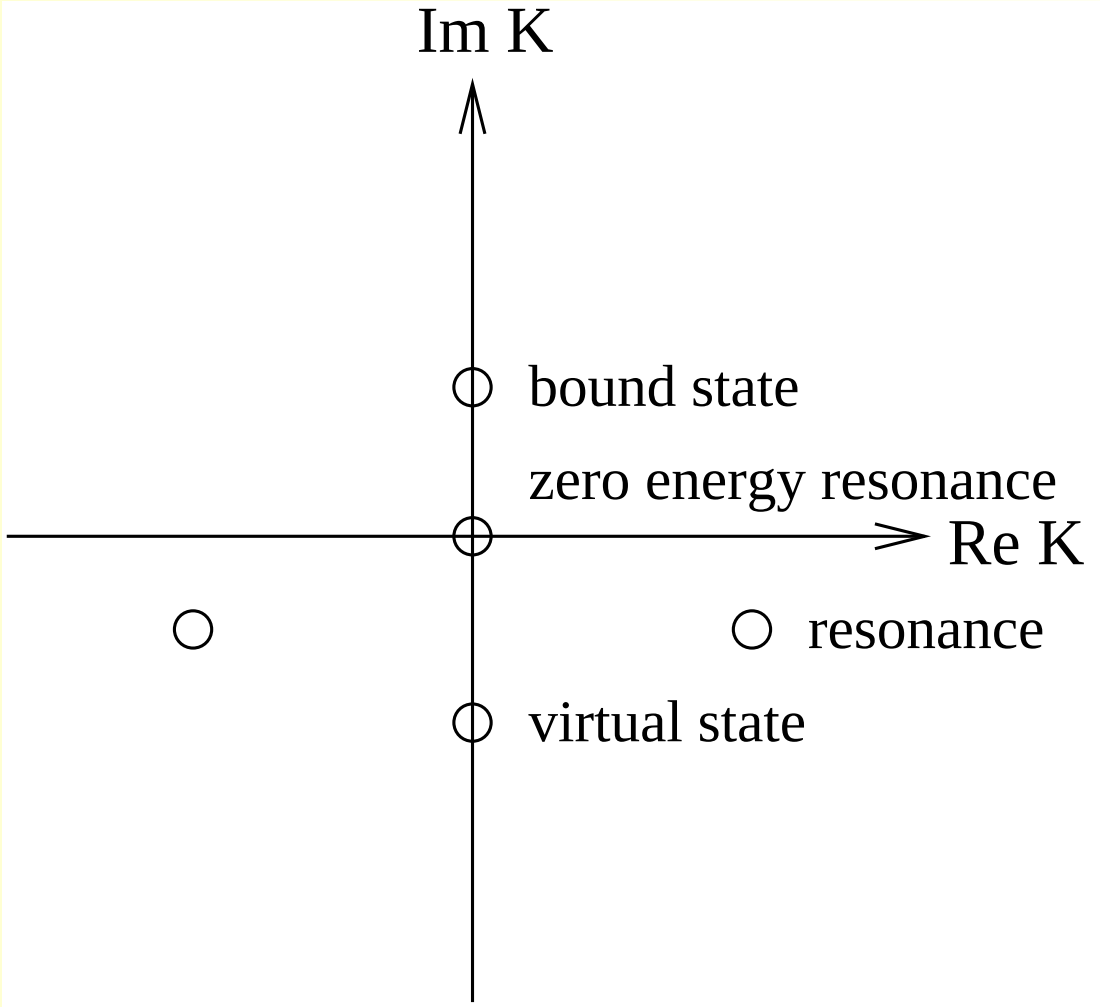
Virtual state

- The virtual state is not a true bound state neither a resonance. It is related to a zero of the s-wave Jost function on the negative imaginary k axis
- It appears when the potential is *nearly* strong enough to support an s-wave bound state.
- Potential scattering: $\delta_0 \to \pi/2, \alpha \to -\infty, \sigma \to \infty$ as $k \to 0$: (zero energy resonance)
- Consequences:
  - the scattering lenght α is “large” and negative;
  - the cross section is “large” for $k \to 0$.

$$\alpha = -\lim_{k\to 0} \frac{\tan\delta_0(k)}{k}\,; \sigma(k=0) = 4\pi\alpha^2$$

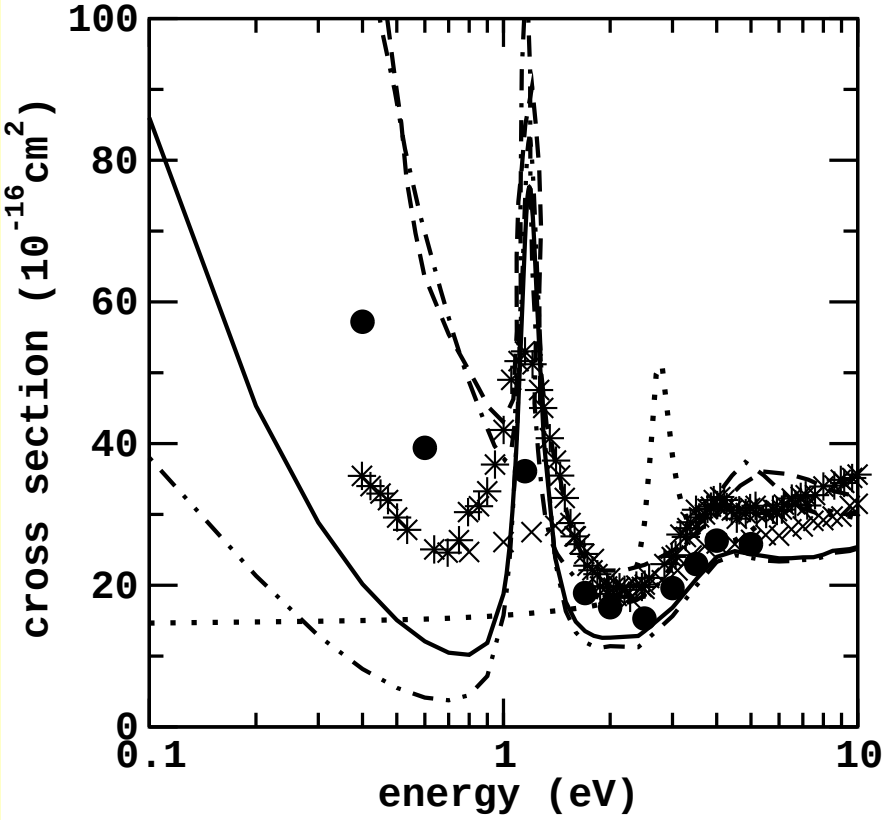
- OCS: $\alpha = -4.63a_0$, CS_2: $\alpha = -7.17a_0$

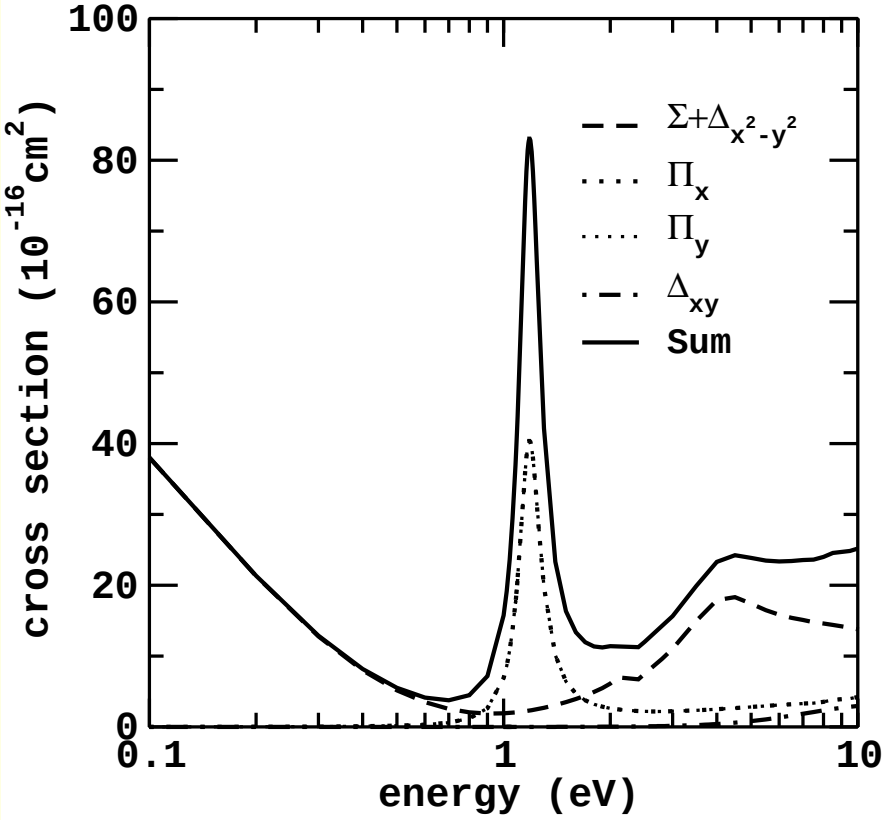
Virtual state



Zeros of the Jost function (poles of the S matrix).

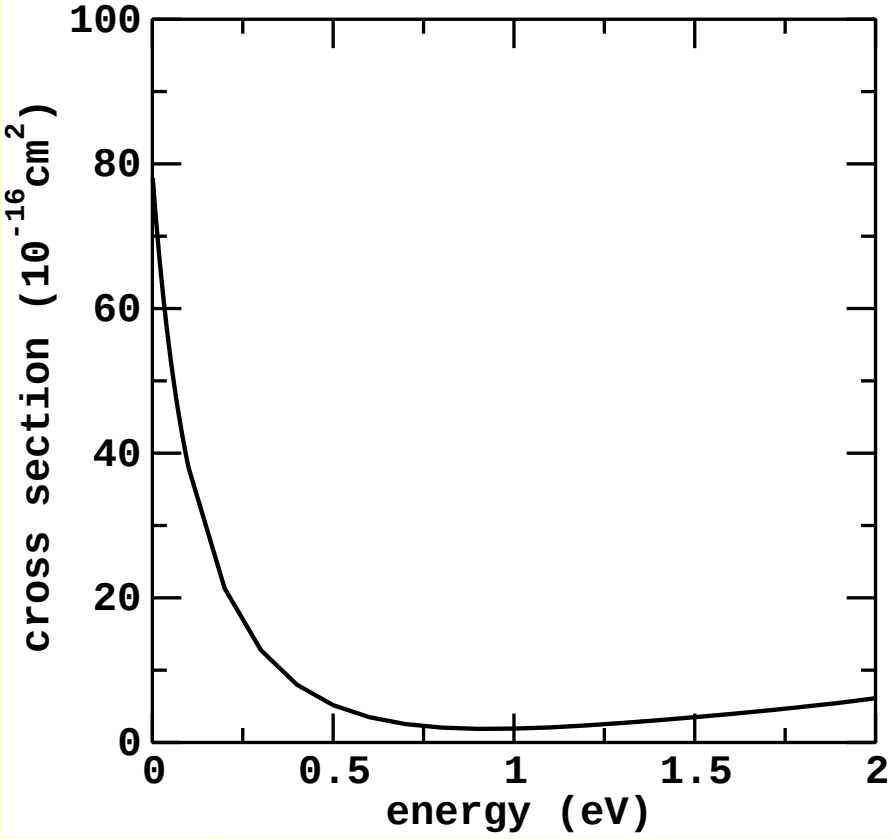
Results: OCS

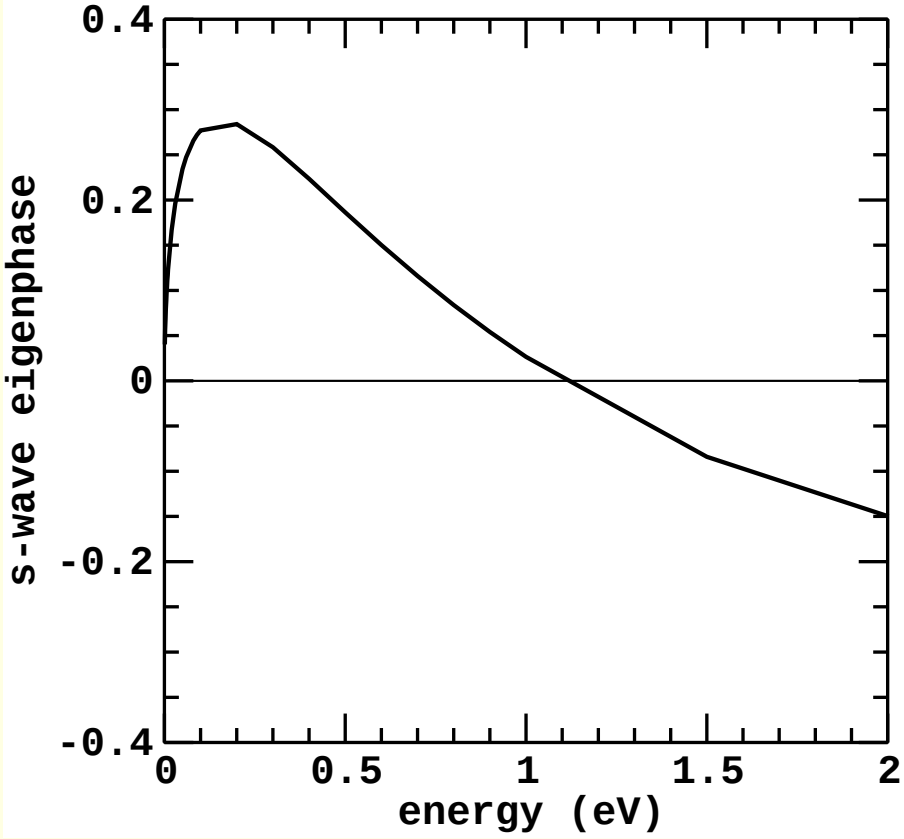




Integral cross section for OCS.

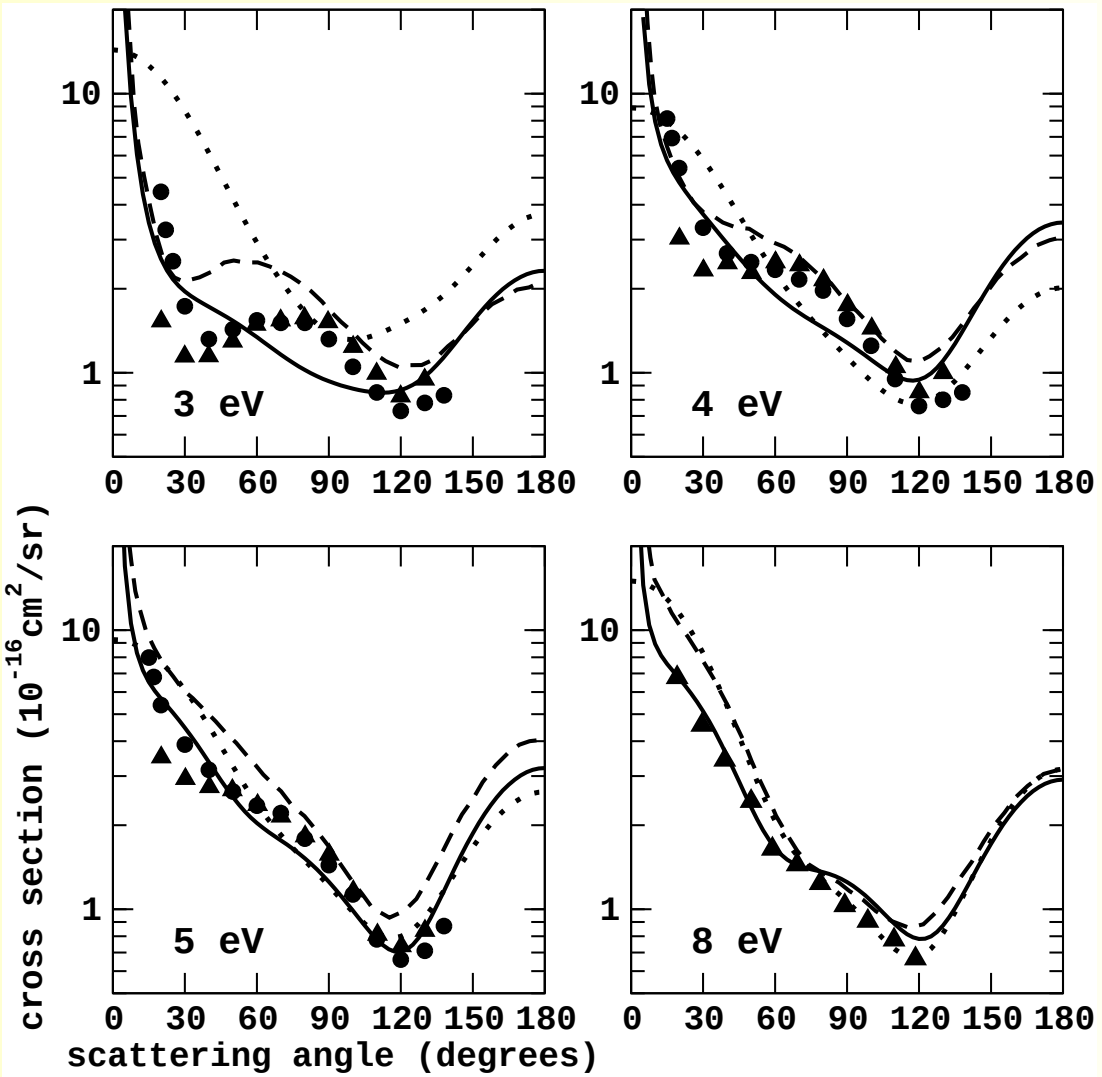
Results: OCS





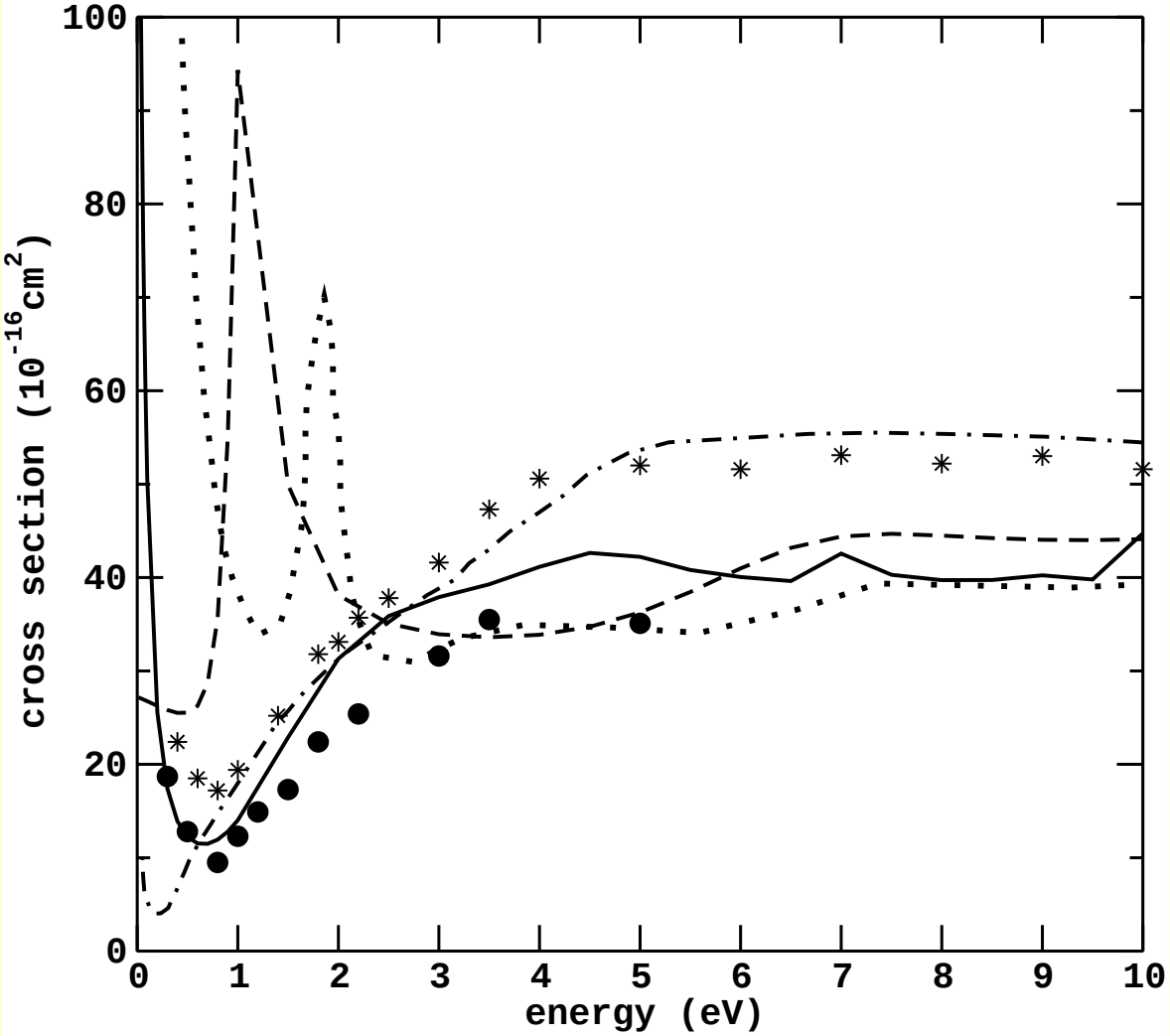
Σ cross section and s-wave eigenphase for OCS.

Results: OCS



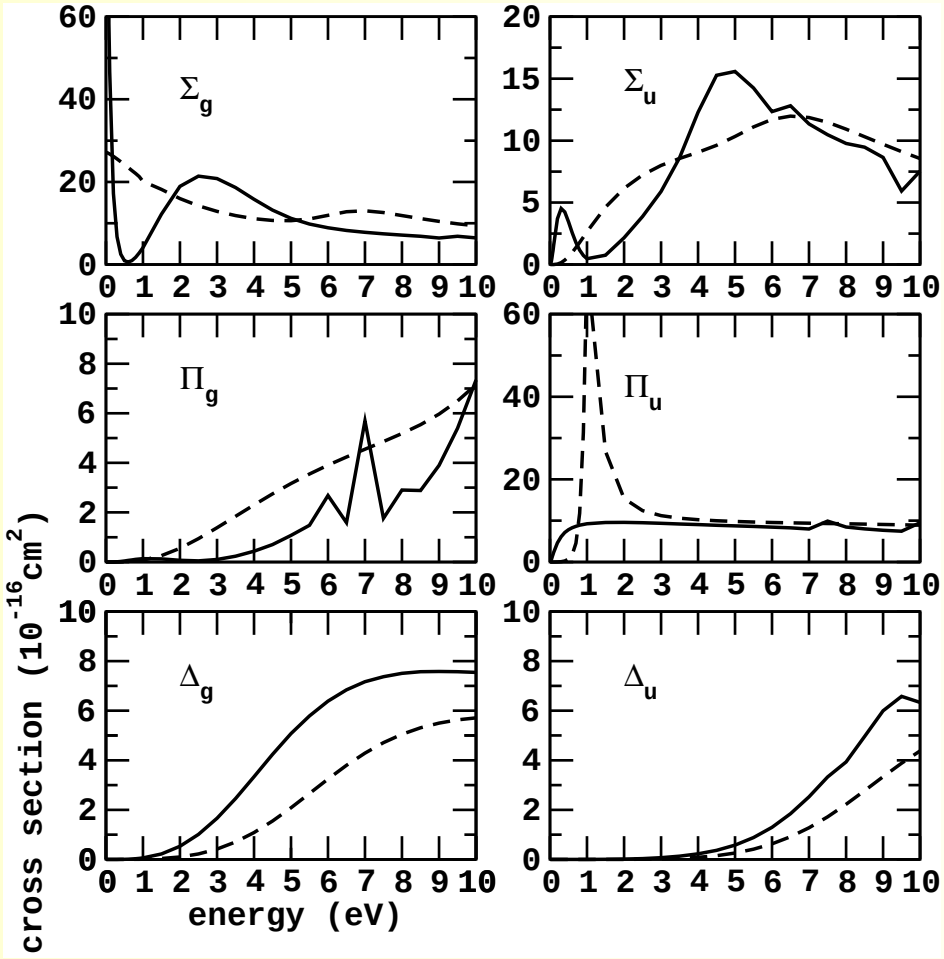
Differential cross sections for OCS.

Results: CS_2



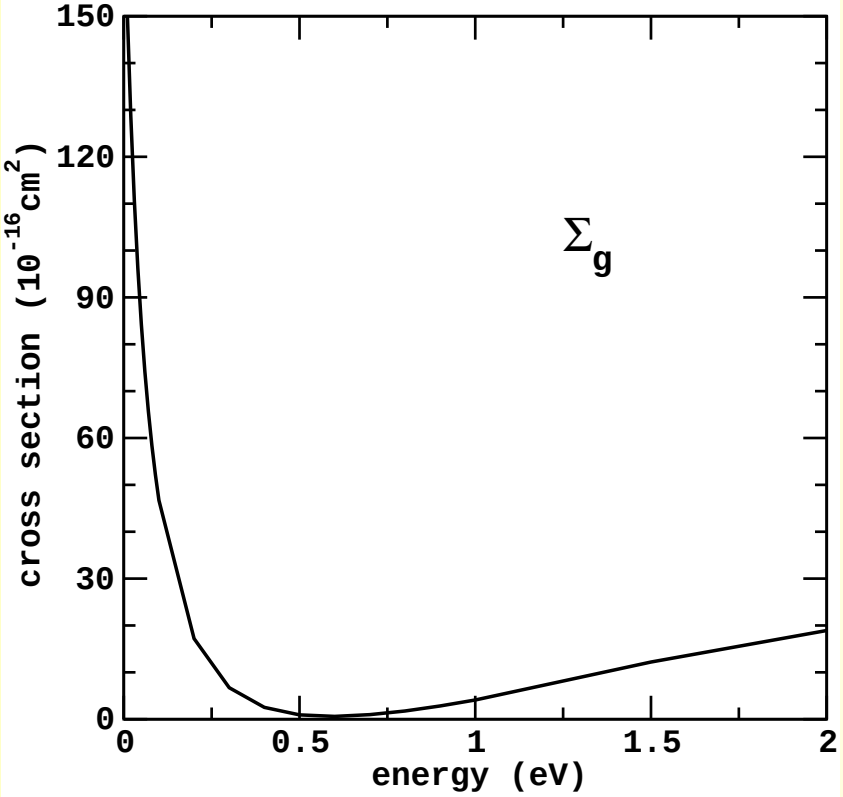
Cross section for CS_2.

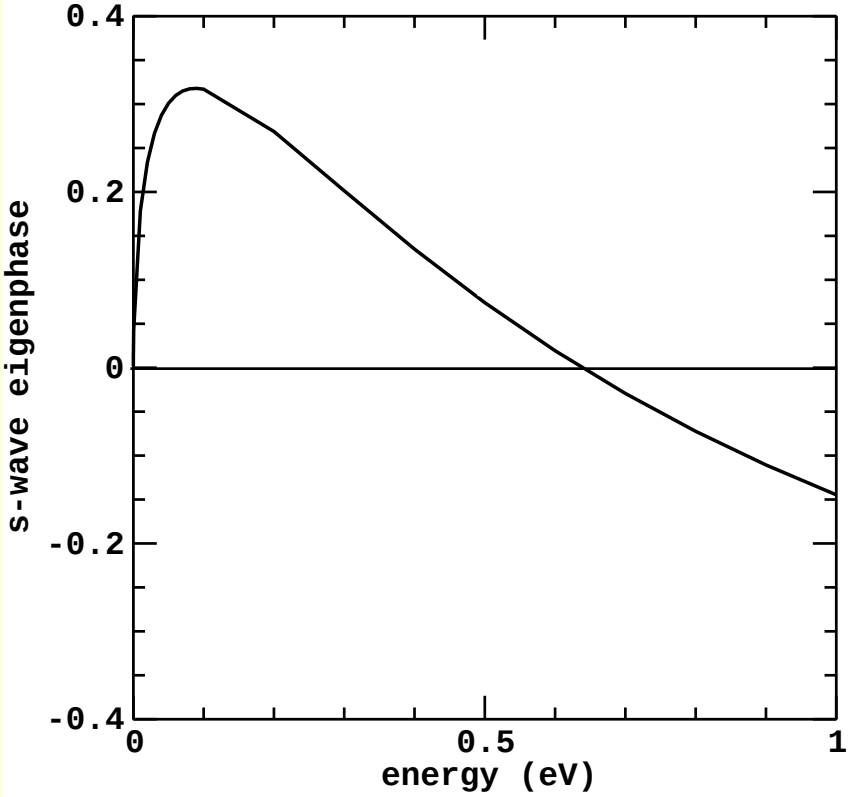
Results: CS_2



Symmetry decomposition of the integral cross section for CS_2.

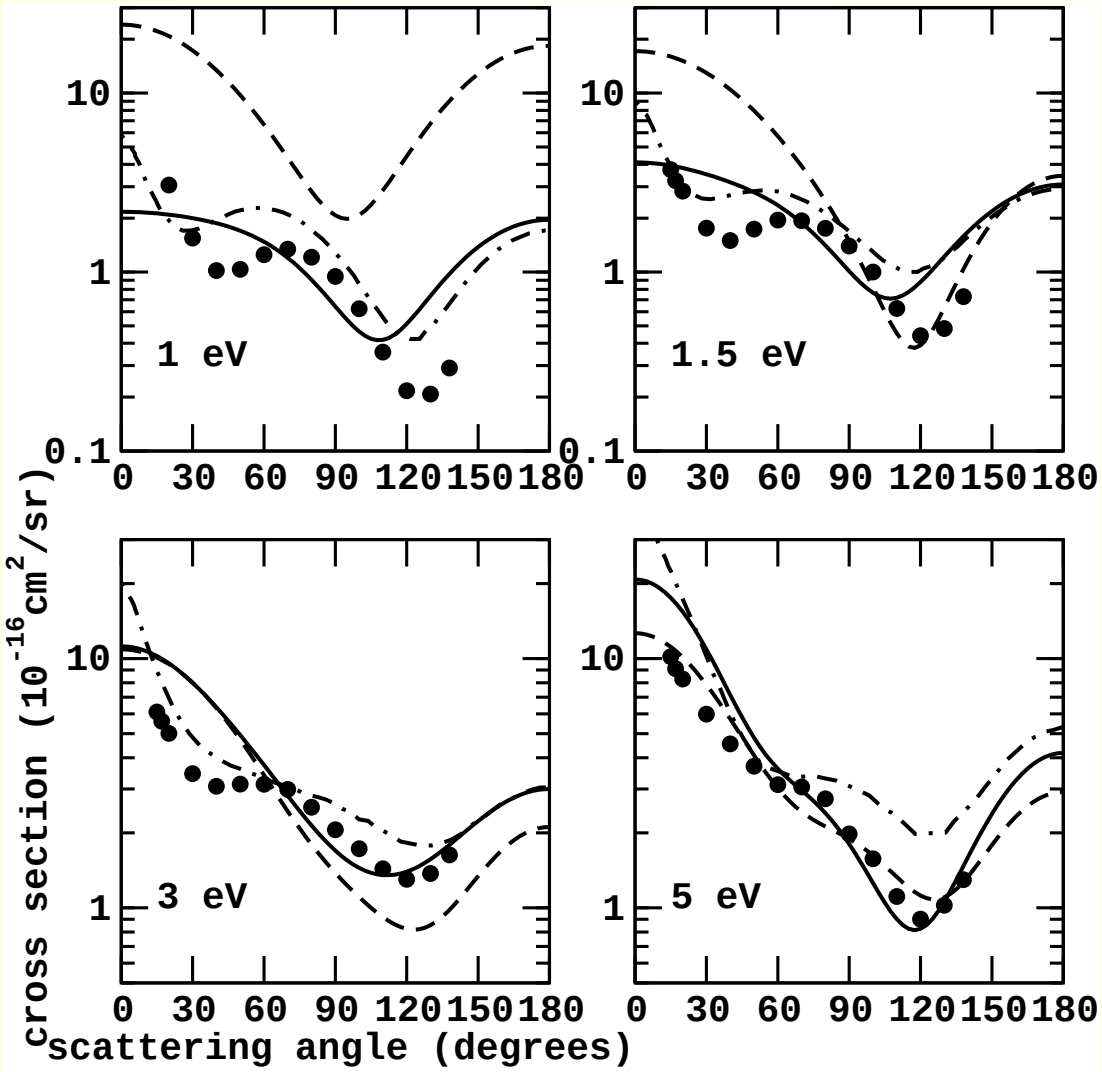
Results: CS_2





s-wave cross section and eigenphase for CS_2.

Results: CS_2



Differential cross sections for CS_2.

Acknowledgements

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  `http://fisica.ufpr.br/jk/prog/srctex/texprog.html`
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