

# Coupled-cluster approach for studying the optical properties of charged $\pi$ -conjugated oligomers

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## Abstract

We have developed a size-consistent correlated quantum-chemical approach, the coupled-cluster equation of motion (CC-EOM) method, to describe the charged excited states of conjugated materials. We apply this formalism to study a variety of conjugated oligomers: polyenes, oligophenylenevinyls, oligothiophenes, and oligophenylenes. The transition energies and absorption intensities of the positively charged species are calculated. In all cases, two subgap absorption features are found to dominate the optical spectrum, which are the characteristic optical signatures for polarons in conjugated materials. The relative intensity of these two bands and the dependence on chain length and chemical structure are analyzed. Excellent agreement is found with experimental data.

*Keywords:* Semi-empirical models and model calculations, optical absorption and emission spectroscopy.

## 1. Introduction

Conjugated polymers and oligomers have attracted much interest due to their remarkable electronic and optical properties, including photo- and electroluminescence. Electron correlation effects have been shown to be essential to understand theoretically the photophysics of these systems.

Our aim is to develop a size-consistent and effective method, which can provide accurate descriptions of electron correlation both for the ground state and the excited states in many-body systems. We then apply this method to investigate the nature of the optical transitions in positively singly charged oligomers.

Upon formation of positive charges, new electronic states are created, that couple to local lattice distortions of the backbone. In terms of condensed-matter physics, such charges are described as positive polarons. The formation of polarons induces a strong modification of the electronic structure of the polymer: two new localized one-electron levels appear within the original gap, as shown in Fig. 1. Two subgap optical transitions are expected: HOMO  $\rightarrow$  POL1 and POL1  $\rightarrow$  POL2 [1]. We note that for the systems we investigated, the HOMO  $\rightarrow$  POL2, or POL1  $\rightarrow$  LUMO transitions are forbidden by symmetry.

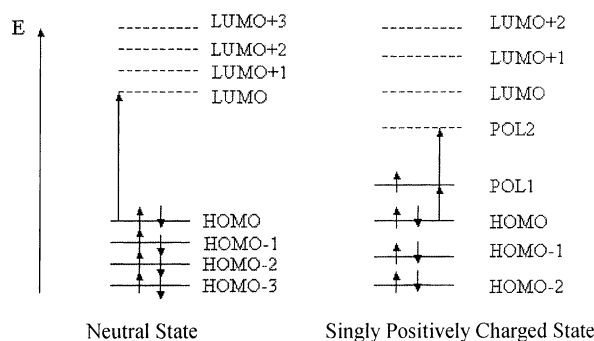


Fig. 1. Schematic single particle representation of the absorption process in neutral and singly positive charged conjugated molecules.

## 2. Methodology

In this work, we simulate the transition energies and absorption intensity of the positively charged species by combining the semiempirical intermediate neglect of differential overlap (INDO) method [2,3] to the CC-EOM technique including single and double (SD) excitations [4]. The CCSD-EOM approach is used to describe the ground state, positively and negatively charged states, and exciton states of a conjugated polymer chain [5,6]. We have shown

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that this approach can accurately determine the electronic structure and optical properties.

When an electron is extracted from a molecule, we can form the positively charged basis as:

$$|\sigma\rangle = \{k, c^+kl, c^+d^+klm\}, \quad (1)$$

where indices  $k, l, m$  refer to occupied MOs and  $c, d$  refer to a virtual MO. The CCSD/EOM excited states can be expressed as:

$$|p\rangle = \sum_{\sigma} X_{\sigma} \exp(T)|\sigma\rangle \quad (2)$$

$$\langle p| = \sum_{\sigma} \langle\sigma|Y_{\sigma} \exp(-T) \quad (3)$$

The eigen-equation is

$$\sum_{\rho} (\bar{H}_{\sigma\rho} - E_{CC}\delta_{\sigma\rho})X_{\rho} = \Delta EX_{\sigma} \quad (4)$$

$$\sum_{\sigma} Y_{\sigma} (\bar{H}_{\sigma\rho} - E_{CC}\delta_{\sigma\rho}) = \Delta EY_{\rho} \quad (5)$$

where  $\Delta E = E - E_{CC}$  is the ionization potential (IP),  $E_{CC}$  is the CCSD ground state energy. Diagonalizing the Jacobian matrix  $A_{\sigma\rho} = \bar{H}_{\sigma\rho} - E_{CC}\delta_{\sigma\rho}$  gives rise to the positively charged states.

The expectation value of the transition moment between the lowest charged state (*i.e.*, charged ground state, which corresponds to the right-hand side panel in Fig. 1) and  $m$ th charged state is:

$$\begin{aligned} \langle p_1 | \hat{\mu} | p_m \rangle &= \sum_{\sigma\rho} Y_{\rho} X_{\sigma} \langle \rho | \exp(-T) \mu \exp(T) | \sigma \rangle \\ &= \sum_{\sigma\rho} Y_{\rho} X_{\sigma} \bar{\mu}_{\sigma\rho} \end{aligned} \quad (6)$$

After obtaining the eigenstates and the transition moment, we can calculate the intensity of absorption spectrum by the following expression:

$$I(\omega) \sim \frac{\omega}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (7)$$

where

$$\begin{aligned} \alpha_{xx} &= \sum_{m \neq 1} \text{Im} \left[ \frac{\langle p_1 | \hat{\mu}_x | p_m \rangle \langle p_m | \hat{\mu}_x | p_1 \rangle}{\langle p_1 | p_1 \rangle \langle p_m | p_m \rangle} \right] \\ &\left( \frac{1}{E_m - E_1 - \hbar\omega - i\Gamma} + \frac{1}{E_m - E_1 + \hbar\omega - i\Gamma} \right) \end{aligned} \quad (8)$$

### 3. Result and Discussion

We have applied CCSD-EOM to study of a variety of conjugated oligomers: polyenes, oligothiophenes, oligophenylenes, and oligophenylenevinylenes. Here, we only present the results for oligophenylenevinylenes (OPVs).

The INDO/CCSD-EOM simulated absorption spectra of singly positively charged OPVs are illustrated in Fig. 2. The first peak mainly originates from the electron transition  $H \rightarrow \text{POL}1$  and the second peak mainly originates from the electron transition  $\text{POL}1 \rightarrow \text{POL}2$ . Evolution of the two

lowest energy transitions are illustrated in Fig. 3. Our results are in good agreement with the experimental data of Schenk *et al.* [7] as illustrated in Fig. 3. Even when only considering single excitations (CCS) in our approach, the results are good, and sometimes better than CCSD. This is due to the fact that the INDO parameters are based on single excitation, even though CCSD is more accurate. In general, our method is effective and reliable for charged systems.

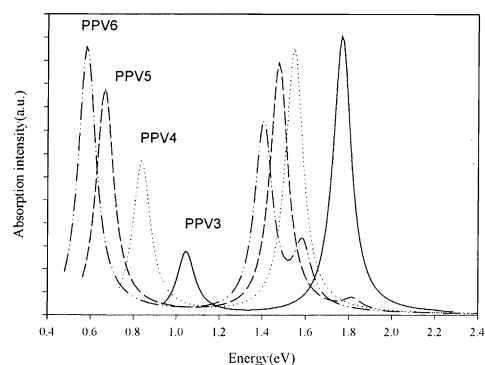


Fig. 2. INDO/CCSD-EOM simulated absorption spectra of singly positively charged OPVs.

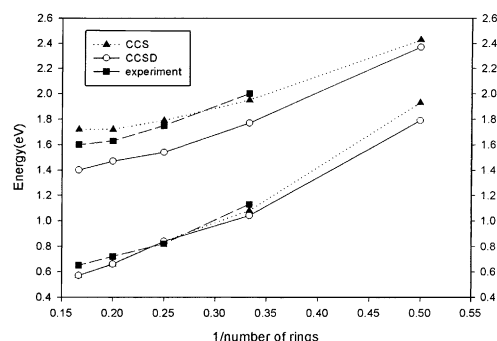


Fig. 3. Evolution of the two lowest energy transitions calculated by CCS and CCSD in singly positively charged OPVs as a function of inverse number of rings.

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