



Electronic transitions of molecular fragments obtained by the Frozen Localized MO scheme

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Motivation

Some properties of molecules may be determined by just a small fragment, e.g. spectroscopic transitions of chromophore.

- It is appealing to describe such transitions by treating only the chromophore.
- If heteroatom effects are of interest, a model molecule just for the chromophore may not suffice. Including the surrounding of the chromophore may prohibit high level calculations due to size limits.

Frozen Localized MO (FLMO) scheme [1]

- The entire molecule is treated at the self-consistent-field (SCF) level.
- Localized MOs are determined and classified as 'fragment' or 'out-of-fragment'.
- Out-of-fragment MOs are frozen at the SCF level. Interaction of fragment electrons with those out-of-fragment are incorporated into an effective Hamiltonian formulated in terms of solely fragment MOs.
- Electronic structure, e.g. excitation energies are calculated by correlation methods, treating only fragment electrons and MOs.

Previous FLMO applications

- Localized orbitals are obtained by projection of AOs into the occupied/virtual subspace [1].

Aim of the present study

- Investigate the performance of the so-called extremely localized MOs [2] within the FLMO scheme.
- Introduce a numerical measure of the localized character of an excitation.

Extremely localized MOs [2]

Take the Hartree-Fock (HF) MOs expressed with AOs

$$\phi_i = \sum_{\mu} \chi_{\mu} c_{\mu i}$$

The projector of the occupied space reads

$$\hat{P}_{\text{occ}} = \sum_{\mu\nu} |\chi_{\mu}\rangle P_{\mu\nu} \langle\chi_{\nu}|$$

Select the atoms constituting the fragment. Fragment atom centered AOs form subspace X . The projector of the fragment reads

$$\hat{P}_X = \sum_{\mu,\lambda \in X} |\chi_{\mu}\rangle (S_{XX})_{\mu\lambda}^{-1} \langle\chi_{\lambda}|$$

where $(S_{XX})_{\mu\lambda}^{-1}$ are elements of the inverse of the fragment AO overlap. Extremely localized MOs ψ_i are expanded over fragment AOs as

$$\psi_i = \sum_{\lambda \in X} \chi_{\lambda} d_{\lambda i} \quad (1)$$

Coefficients $d_{\lambda i}$ arise from a variational principle (by solving the generalized eigenvalue equation of $\hat{P}_X \hat{P}_{\text{occ}} \hat{P}_X$):

$$\frac{\langle \hat{P}_{\text{occ}} \psi_i | \hat{P}_{\text{occ}} \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \frac{\langle \psi_i | \hat{P}_X \hat{P}_{\text{occ}} \hat{P}_X | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \text{max} \rightarrow$$

$$(SPS)_{XX} d_X^i = S_{XX} d_X^i \nu_i$$

where $(SPS)_{XX}$ is the fragment block of SPS .

Properties of extremely localized MOs of Eq.(1):

- strictly localized on fragment AOs;
- exhibit maximal projection in the occupied HF space;
- eigenvalues $\nu_i \in [0, 1]$ can be interpreted as occupation numbers;
- orthogonality is conserved if projected by $\hat{P}_{\text{occ}}$: $\langle \varphi_i | \varphi_j \rangle = \nu_i \delta_{ij}$ where $\varphi_i = \hat{P}_{\text{occ}} \psi_i$
- simultaneously eigenvectors to $\hat{P}_X \hat{P}_{\text{virt}} \hat{P}_X$

Freezing localized MOs [1]

The SCF energy formula reads

$$E_{\text{SCF}} = \frac{1}{2} \text{Tr} [(h + F) P]$$

with the RHF definitions for F and P , e.g.

$$P_{\mu\nu} = \sum_i^{\text{occ}} c_{\mu i} c_{\nu i}^*$$

Introducing the active density matrix as

$$P_{\mu\nu}^{\text{active}} = \sum_i^{\text{occ active}} c_{\mu i} c_{\nu i}^*$$

the total density matrix is partitioned for an active and a frozen component

$$P = P^{\text{frozen}} + P^{\text{active}} \quad (2)$$

This gives rise to a partitioning of the SCF energy as

$$E_{\text{SCF}} = E^{\text{frozen}} + E_{\text{SCF}}^{\text{active}}$$

where the SCF energy of the frozen part reads

$$E^{\text{frozen}} = \frac{1}{2} \text{Tr} [(h + h^{\text{eff}}) P^{\text{frozen}}]$$

and the SCF energy of the fragment looks

$$E_{\text{SCF}}^{\text{active}} = \frac{1}{2} \text{Tr} [(h^{\text{eff}} + F) P^{\text{active}}]$$

with

$$h_{\mu\nu}^{\text{eff}} = h_{\mu\nu} + \sum_{\lambda\rho} (\langle \mu\lambda | \nu\rho \rangle - \langle \mu\lambda | \rho\nu \rangle) P_{\lambda\rho}^{\text{frozen}}$$

Once h^{eff} and E^{frozen} is constructed, the frozen MOs are not needed any more. A fragment Hamiltonian is formulated in terms of fragment MOs ψ_i as

$$\hat{H}^{\text{eff}} = \sum_{i,j}^{\text{active}} h_{ij}^{\text{eff}} \psi_i^+ \psi_j^- + \frac{1}{2} \sum_{i,j,k,l}^{\text{active}} \langle ij | kl \rangle \psi_i^+ \psi_j^+ \psi_l^- \psi_k^-$$

Note, that the use of h_{ij}^{eff} and $\langle ij | kl \rangle$ implies an integral transformation to the basis of fragment MOs. Correlation calculations characterizing the fragment are based on the Hamiltonian $\hat{H}^{\text{eff}}$.

Measure of locality

Change in electron density brought about by an excitation:

$$\Delta \hat{\rho} = \sum_{\mu\nu} (D_{\mu\nu}^e - D_{\mu\nu}^g) |\chi_{\mu}\rangle \langle\chi_{\nu}|$$

where $D^{g/e}$ is the spinless density matrix of the ground/excited state. Project $\Delta \hat{\rho}$ into the fragment space:

$$\Delta \hat{\rho}_X = \hat{P}_X \Delta \hat{\rho} \hat{P}_X$$

Matrix representation of $\Delta \hat{\rho}$ and $\Delta \hat{\rho}_X$ in the AO basis:

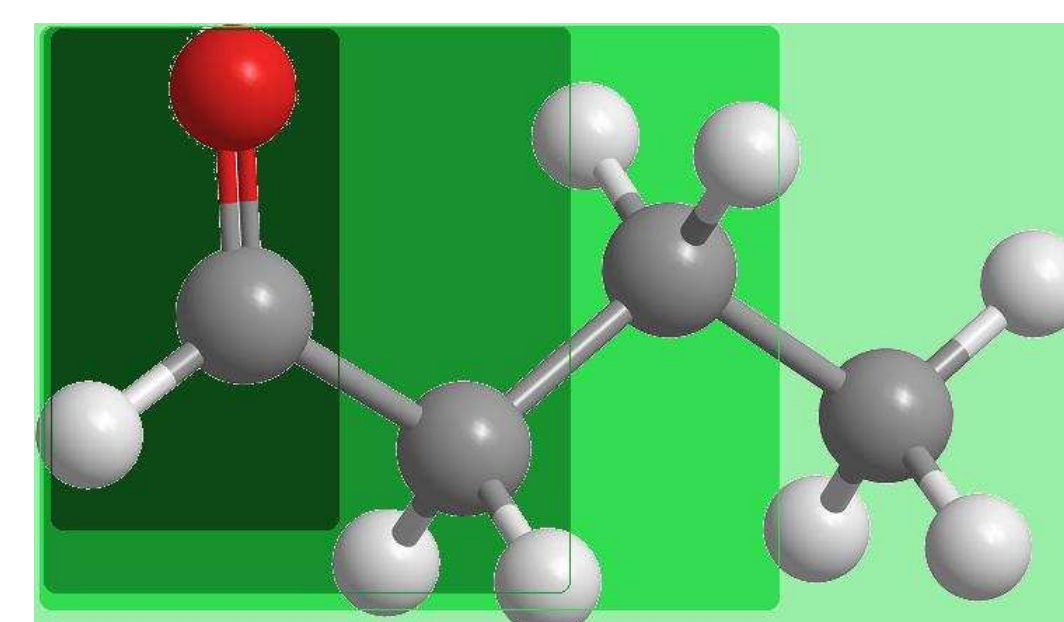
$$\Delta \rho = \Delta D S, \quad \Delta \rho_X = S_{XX}^{-1} S \Delta D S L_X$$

where L_X is a cutoff matrix. Locality is measured by the Frobenius norm of $\Delta \rho_X$ in proportion to the norm of $\Delta \rho$:

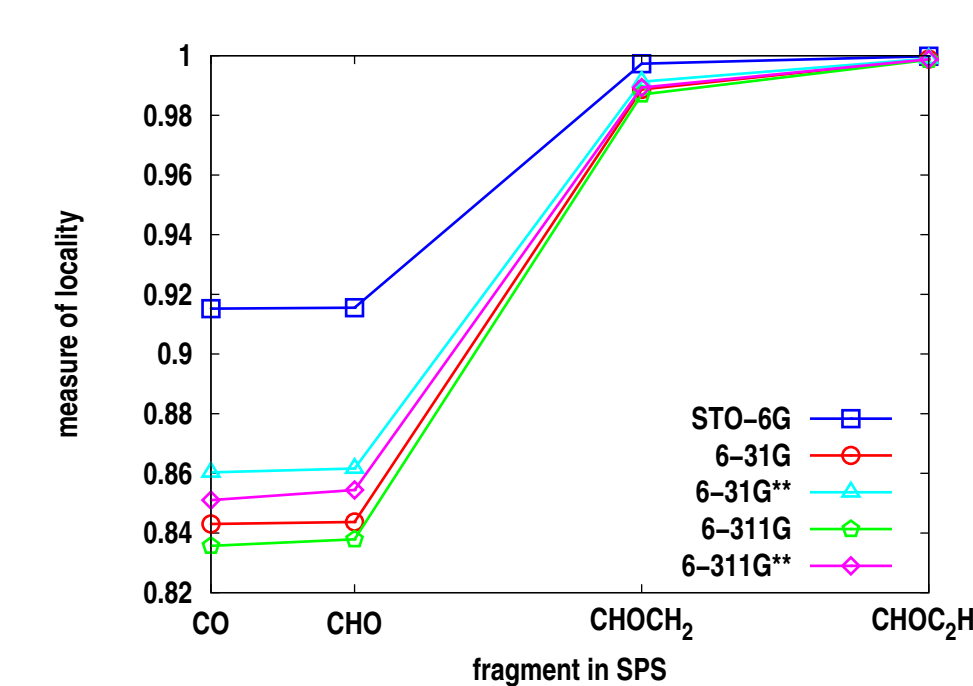
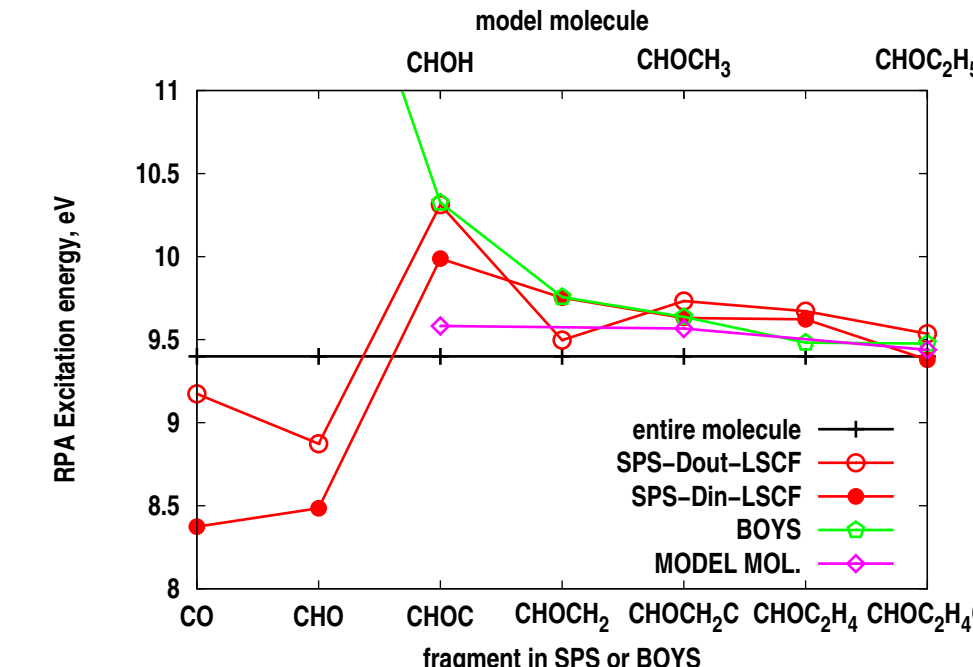
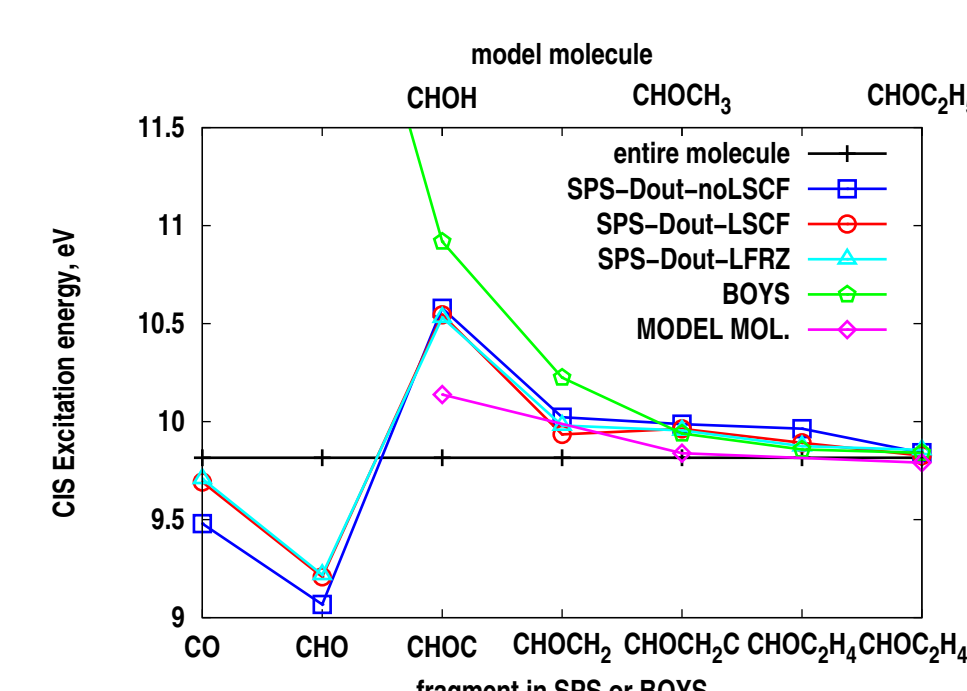
$$\eta = \left(\frac{\text{Tr}(\Delta \rho_X^\dagger \Delta \rho_X)}{\text{Tr}(\Delta \rho^\dagger \Delta \rho)} \right)^{1/2}$$

Pilot applications

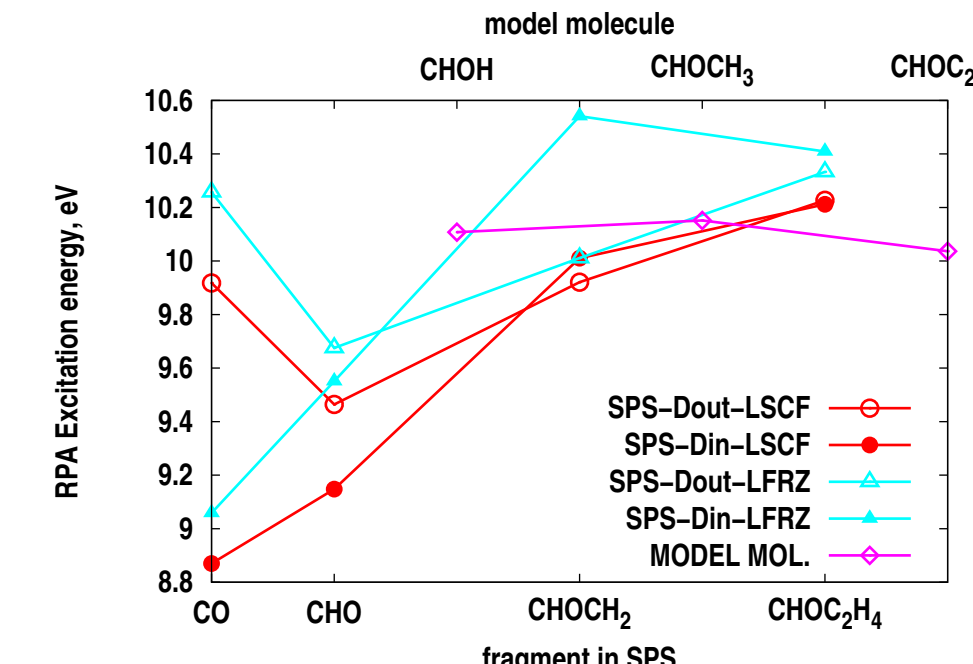
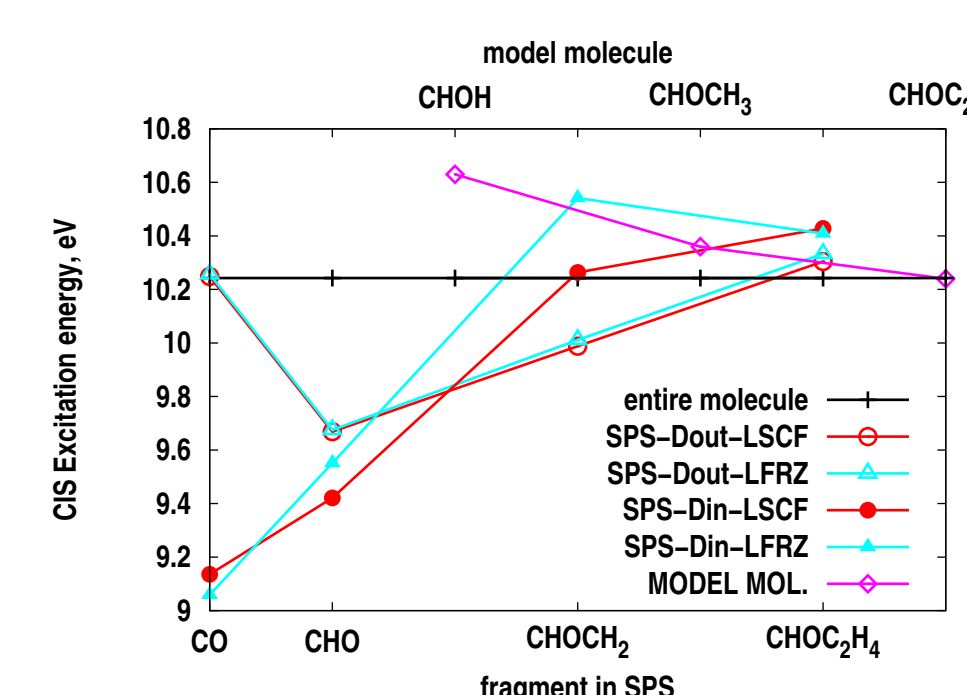
$\pi \rightarrow \pi^*$ transition of the carbonyl group by CIS and RPA in 6-31G** basis



OCH-CH₂-CH₂-CH₃



OCH-CH₂-CH₂-CH₂F



Some technical issues

- Selection of active occupied MOs is based on ν_i . Occupied: $0.965 < \nu_i$, dangling: $0.65 < \nu_i \leq 0.965$, virtual: $\nu_i \leq 0.65$.
- For freezing, P^{active} can either be built with φ_i or with ψ_i (LFRZ).
- Advantage of extremely localized MOs: strict locality. Hence the integral transformation scales as $\sim N_{\text{active}}^5$.
- Drawback of extremely localized MOs: though they are the closest to the "true" occupied/virtual space, they have some contamination. Hence the Fockian built with ψ_i is not block diagonal. If canonical MOs are needed, a local SCF procedure may be carried out (LSCF, noLSCF).

Work still in progress...

[1] P. R. Surján, D. Kóhalmi, Z. Rolik, Á. Szabados, Chemical Physics Letters 450 (2007) 400.

[2] T. Zoboki, I. Mayer, Journal of Computational Chemistry 32 (2011) 689.

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