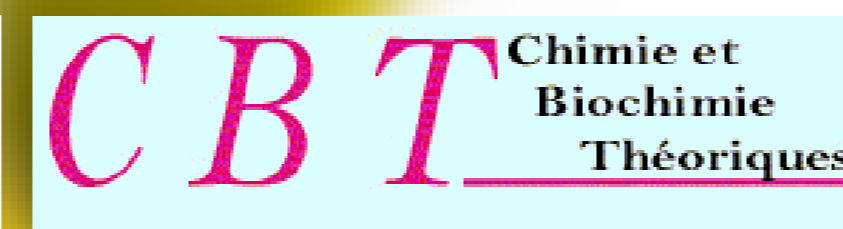


Self-Consistent Strictly Localized Bond Orbital within the Local Self-Consistent Field Method

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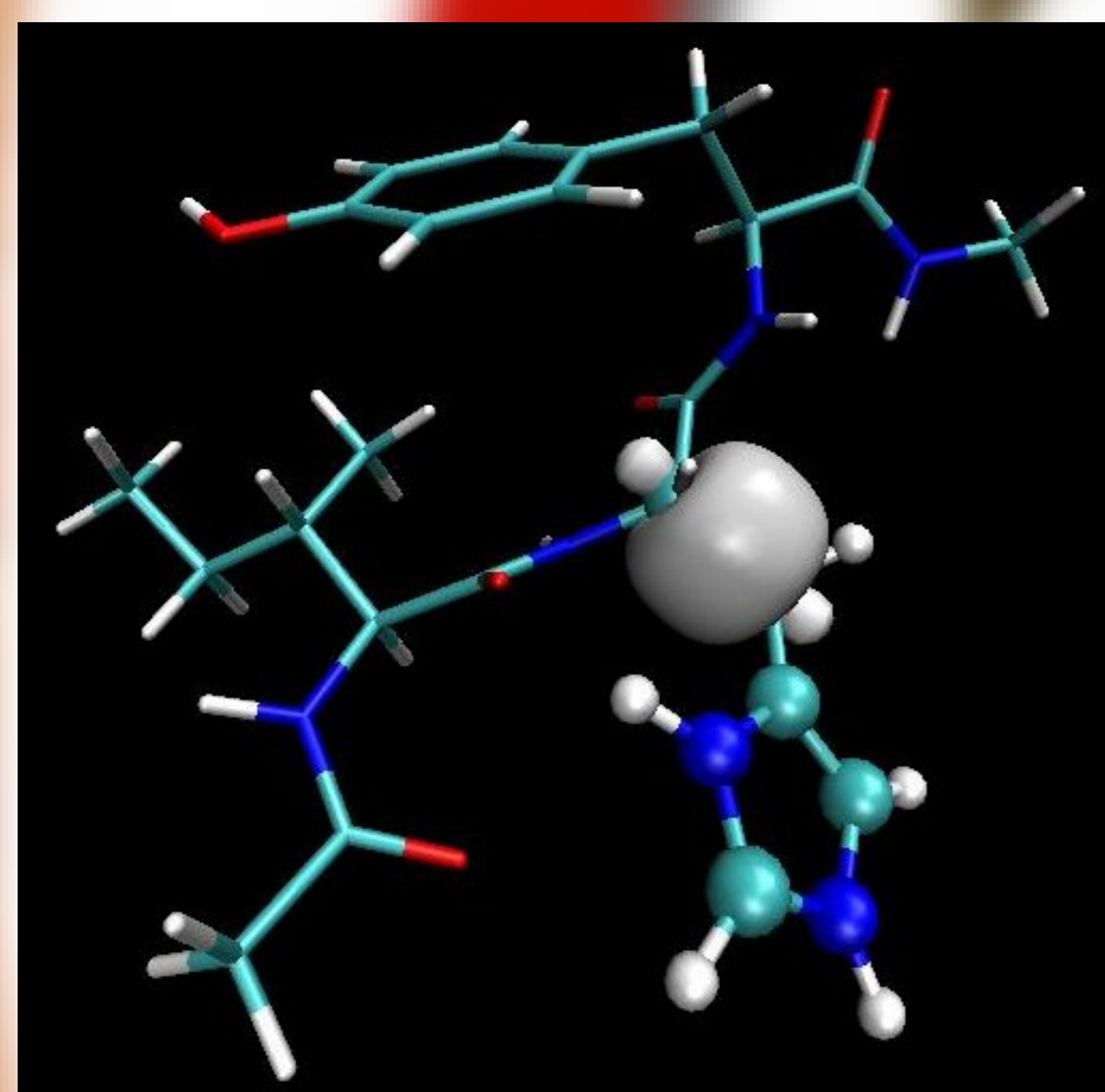
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I. Introduction

To deal with large macromolecular systems one generally takes advantage of the QM/MM philosophy. A small part is treated with the help of Quantum Mechanics (QM) and the remaining by means of classical Molecular Mechanics force fields (MM). Many QM/MM methods exist, differing by the levels of theory (QM and/or MM) and by the way they handle the connection between the two parts[1, 2]. In this poster we focus our attention on the Local Self-Consistent Field (LSCF) method[3, 4] which represents the frontier bond, the one connecting the QM piece to the MM one, by means of a frozen Strictly Localized Bond Orbital (SLBO). Here frozen means that the expansion the SLBO over the basis functions is kept fixed during the wave function optimization. This implies that the QM part must have a significant size to minimize the effect of the SLBO on the total wave function. This is a critical issue when one is willing to perform Molecular Dynamics (MD) calculations. To keep the size of the QM region as small as possible, one has to allow the SLBOs to readjust themselves according to the density variations of the whole wave function.



We propose a modification of the LSCF method, called Optimized Local Self-Consistent Field (OLSCF), which allows the SLBO to relax by simple linear combination with their corresponding Strictly Localized Anti-Bonding Orbital (SLABO).

II. Choice of SLBO and SLABO

- For small basis set :
 - SLBO and SLABO obtained by localization algorithm (Boys-Foster[5], Pipeck-Mezey[6],...)
- For larger basis set (more than DZ) :
 - SLBO obtained from usual localization procedures
 - SLABO build with the projection of the one obtained with a small basis set on the large basis set [7]

$$|\psi_i^{LB}\rangle = \sum_{\mu\nu} |\mu\rangle (\mathbf{S}^{-1})_{\mu\nu} \langle \nu | \psi_i^{SB}\rangle$$

III. Modification of the LSCF method

- Projection of the initial basis $\{|\mu\rangle\}_{1 \leq \mu \leq N}$

$$|\tilde{\mu}\rangle = \left(1 - \sum_{i,j} S_{\mu i} (\mathbf{D}^{-1})_{ji} S_{\mu j}\right)^{-1/2} \left(|\mu\rangle - \sum_{i,j} |i\rangle (\mathbf{D}^{-1})_{ji} \langle j | \mu\rangle\right)$$

- Mutual orthogonalization : canonical method $\{|\tilde{\mu}\rangle\}_{1 \leq \mu \leq N} \Rightarrow \{|\mu'\rangle\}_{1 \leq \mu \leq N}$

$$\mathbf{X} = \mathbf{U} \cdot \tilde{\mathbf{s}}^{-1/2}$$

- Composition of the two transformations $\{|\mu\rangle\}_{1 \leq \mu \leq N} \Rightarrow \{|\mu'\rangle\}_{1 \leq \mu \leq N}$

$$\mathbf{B} = \mathbf{M} \cdot \mathbf{X}$$

- Density matrix with non-orthogonal orbitals

$$P_{\mu\nu}^T = P_{\mu\nu}^Q + P_{\mu\nu}^L = 2 \sum_i^{n-L} c_{\mu i} c_{\nu i} + 2 \sum_j^L a_{\mu j} \tilde{a}_{\nu j}$$

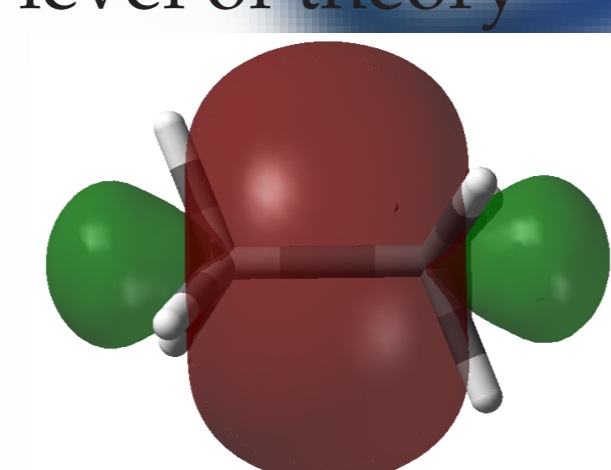
- Duals orbitals

$$\tilde{a}_{\mu i} = \sum_j a_{\mu j} (\mathbf{D}^{-1})_{ji}$$

- Definition of the Fock operator

$$F_{\mu\nu} = H_{\mu\nu}^C + \sum_{\lambda\sigma} P_{\lambda\sigma}^T \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\lambda\nu) \right]$$

SLBO obtained on the ethane molecule at the 6-31G* level of theory



IV. Optimization of the SLBO

Optimization by linear combination between the SLBO and its SLABO

$$\mathbf{F}^i = \begin{pmatrix} \langle l_i | \hat{F} | l_i \rangle & \langle l_i^* | \hat{F} | l_i \rangle \\ \langle l_i | \hat{F} | l_i^* \rangle & \langle l_i^* | \hat{F} | l_i^* \rangle \end{pmatrix}$$
$$\mathbf{F}^i \begin{pmatrix} C_1^i & -C_2^i \\ C_2^i & C_1^i \end{pmatrix} = \begin{pmatrix} \kappa_1^i & 0 \\ 0 & \kappa_2^i \end{pmatrix} \begin{pmatrix} C_1^i & -C_2^i \\ C_2^i & C_1^i \end{pmatrix}$$

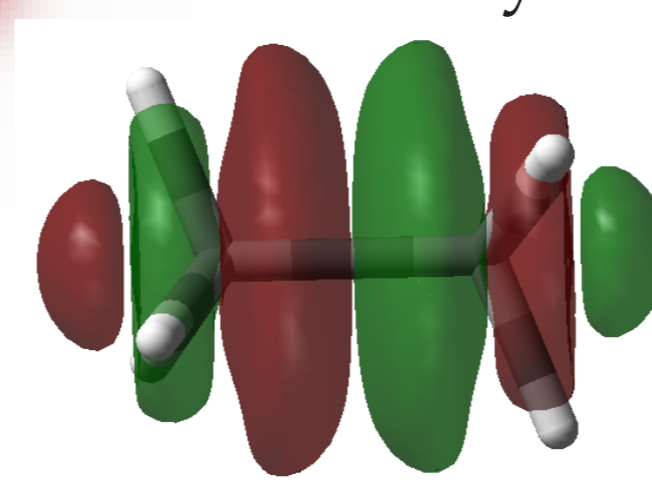
the new set of localized orbitals is :

$$\begin{cases} |l_i\rangle_{new} = C_1^i \cdot |l_i\rangle_{old} + C_2^i \cdot |l_i^*\rangle_{old} \\ |l_i^*\rangle_{new} = -C_2^i \cdot |l_i\rangle_{old} + C_1^i \cdot |l_i^*\rangle_{old} \end{cases}$$

V. Algorithm

- Determine SLBOs and SLABOs on a model molecule
- Build the M matrix. Orthogonalize the AOs basis set to the SLBOs
- Build the X matrix. Transform the functions obtained in 2. into an orthogonal and linearly independent set
- Compute $\mathbf{B} = \mathbf{M} \cdot \mathbf{X}$
- Define the Fock matrix \mathbf{F} on the original basis set and take into account the density matrix in non-orthogonal basis set
- Compute $\mathbf{F}' = \mathbf{B}^\dagger \cdot \mathbf{F} \cdot \mathbf{B}$
- Diagonalize $\mathbf{F}' : \epsilon = \mathbf{C}'^\dagger \cdot \mathbf{F}' \cdot \mathbf{C}'$ where ϵ is the diagonal (eigenvalues) matrix
- Transform the eigenvectors in the original basis set : $\mathbf{C} = \mathbf{B} \cdot \mathbf{C}'$
- Compute \mathbf{P}^Q
- For each (SLBO, SLABO) pair, diagonalize the (2×2) Fockian to determine the new pair
- Compute \mathbf{P}^L and \mathbf{P}^T
- Exit test. If not satisfied, go back to 5

SLABO obtained on the ethane molecule at the 6-31G* level of theory



VI. Polarization of the SLBO

Mulliken charge on atom A due to $|l_i\rangle$

$$q_i^A = \sum_{\mu \in A} \sum_{\nu} a_{\mu i} S_{\mu\nu} a_{\nu i}$$

Mulliken charge of the SLBO (in electron) Pipeck-Mezey HF/6-311G** on the CH_3CX_3 molecules

X	$q^C(\text{SCF})$	$q^C(\text{OLSCF})$	Δ
H	0.50	0.50	0.00
Li	0.54	0.52	-0.02
BH ₂	0.46	0.48	0.03
CH ₃	0.47	0.48	0.01
NH ₂	0.42	0.45	0.03
OH	0.42	0.42	0.00
F	0.44	0.41	-0.03
RMSD			0.01

Mulliken charge of the SLBO (in electron) Boys-Foster HF/6-311G** SLABO projected from HF/6-31G* on the CH_3CX_3 molecules

X	$q^C(\text{SCF})$	$q^C(\text{OLSCF})$	Δ
H	0.50	0.50	0.00
Li	0.52	0.52	0.00
BH ₂	0.45	0.49	0.04
CH ₃	0.47	0.48	0.01
NH ₂	0.43	0.46	0.03
OH	0.43	0.44	0.01
F	0.45	0.43	-0.02
RMSD			0.01

Solvation of $\text{CF}_3\text{CH}_2\text{OH}$

SLBO (from ethane) on the CC bond Pipeck-Mezey HF/6-311++G** and HF(PCM)/6-311++G**

	SCF	LSCF	OLSCF
Vacuum (a.u.)	-450.8013	-450.7679	-450.5887
Solvent (a.u.)	-450.8174	-450.7826	-450.6039
Solvation (kcal/mol)	10.10	9.20	9.52

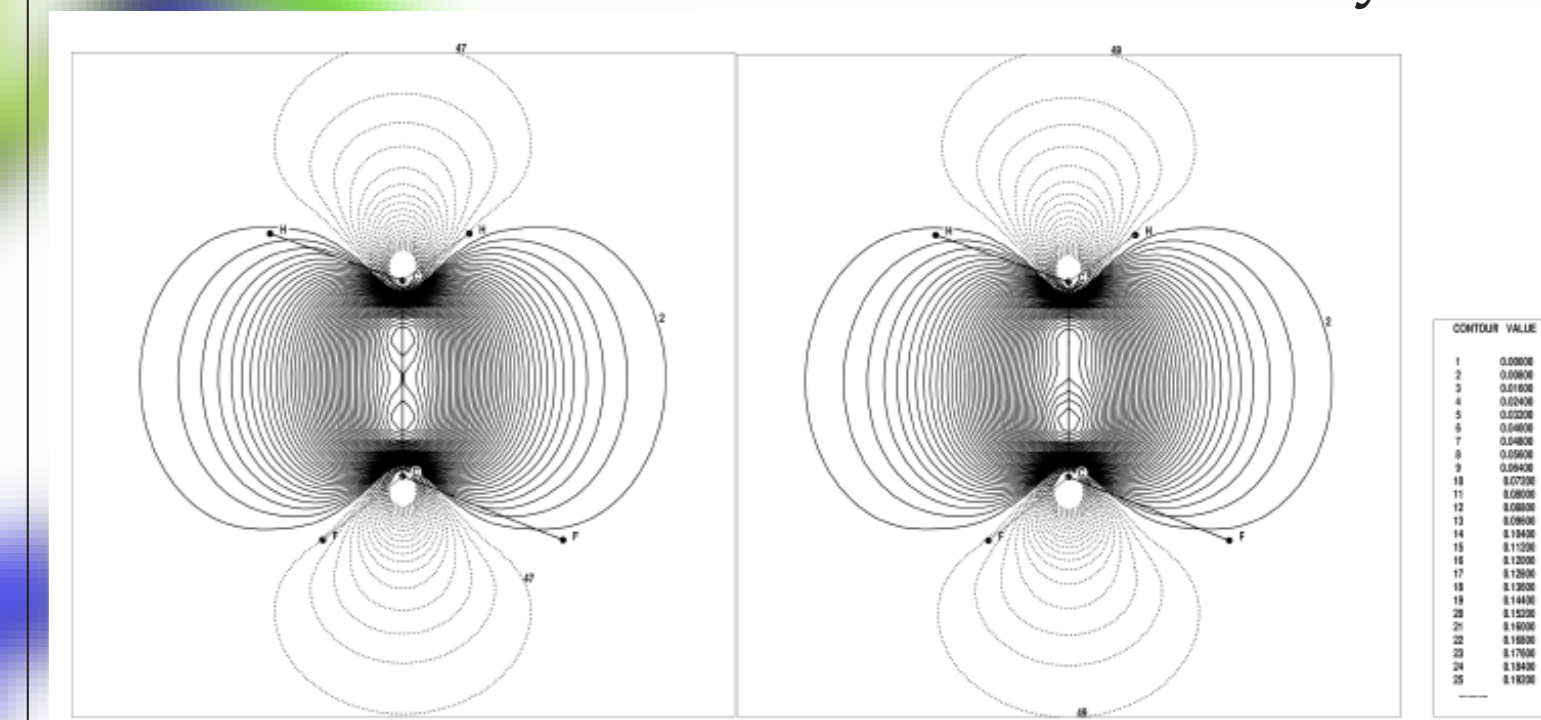
Solvation of $\text{CF}_3\text{CH}_2\text{OH}$

SLBO (from ethane) on the CC bond Pipeck-Mezey B3LYP/6-311++G** and B3LYP(PCM)/6-311++G**

	SCF	LSCF	OLSCF
Vacuum (a.u.)	-452.9155	-452.8874	-452.7484
Solvent (a.u.)	-452.9313	-452.9018	-452.7648
Solvation (kcal/mol)	9.89	9.08	10.28

VII. SLBO Map

Polarization of the SLBO on the trifluoroethane at the HF/6-31G* level of theory



VIII. Conclusions

- Implementation in our modified GAUSSIAN03 package[8] for restricted and unrestricted HF, DFT or post-SCF calculations
- Validation of the method on target systems
- Polarization of the optimized SLBO is correctly handled

IX. Outlooks

- Adaptation of the new method to the QM/MM framework
- First derivatives of the energy with respect to nuclear displacement is under progress

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