Efficient Multi-reference DMC and Insight from QMC

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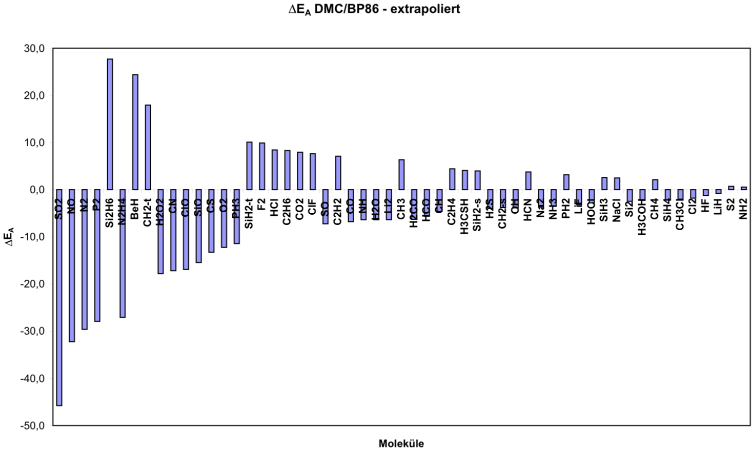
Benchmark calculations

- experimental atomization energies of 55 small molecules (G2 set)
- previous DMC benchmark calculations by J. C. Grossman and Nemec/Towler/Needs
- Grossman: natural orbitals, SBK PP, FN-DMC
- Nemec/Towler/Needs: HF orbitals from GTO and STO basis, all electron, cusp correction, FN-DMC

Our benchmark methodology

- standard FN-DMC code with drift-diffusion propagator, Metropolis step, local energy, and drift cut-off
- Slater-Jastrow one determinant guide function with standard Schmidt-Moskowitz Jastrow
- cc-pVTZ-f basis set (standard TZP GTO basis set without f functions)
- 1s and 2s Cusp correction (Manten/Lüchow, JCP 115, 5362 (2001))
- Comparison of KS (BP86, B3LYP) and HF orbitals.
- Time step extrapolation
- experimental geometries

benchmark results: details



benchmark results: conclusions

errors of FN-DMC atomization energies in kJ/mol for 55 molecules of G2 set using different MOs

	R(O)HF	UHF	B3LYP	BP86
MAD	13.4	12.2	10.4	9.4
MD	–6.7	–3.7	–4.8	–3.5
RMS	19.2	18.6	15.1	13.4

- Grossman: MAD=11.6, MD=-7.8, RMS=16.4 kJ/mol
- Nemec/Towler/Needs: MAD for STOs is 13.4, for GTOs 21.3 kJ/mol

Conclusion

No obvious advantage of STO compared with cusp-corrected GTOs, but significant gain from GGA MOs.

further results on second row molecules

- all-electron calculations on 50 molecules with second row atoms Na – Ar
- time-step needs to decrease with nuclear charge Z
- calculations with time-step down to 0.00025 a.u.

all-electron FN-DMC for second-row molecules

No loss in accuracy for all-electron FN-DMC calculations using GTO with cusp-correction.

Do we really need accurate energies?

- Why are traditional ab initio methods so successful in spite of lousy total energies?

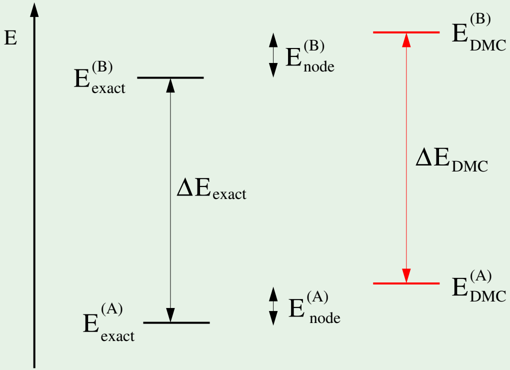
systematic error cancellation

- Traditional ab initio method have a systematic basis set error
- wave function based method have a systematic higher-level correlation error
- DFT methods have a systematic E_{XC} functional bias

Error cancellation in DMC

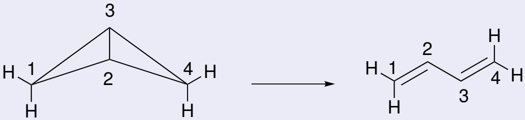
- FN-DMC accuracy of 10 kJ/mol for atomization energies
- errors in total energies often 100 kJ/mol
- goal: how to improve error cancellation of
  - node location error
  - time-step error

visualization of error cancellation in FN-DMC



Example: ring opening of bicyclo[1.1.0]butane

isomerization of bicyclo[1.1.0]butane to *trans*-1,3-butadiene



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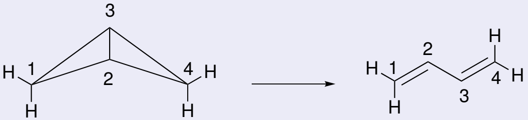
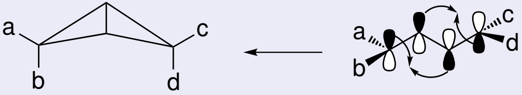


↓

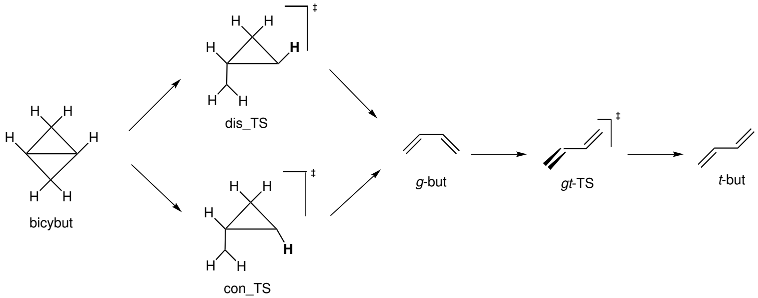
Woodward-Hoffmann rules

↓

conrotatory ring closure



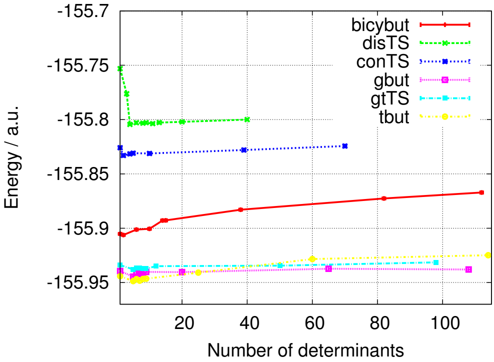
reaction path



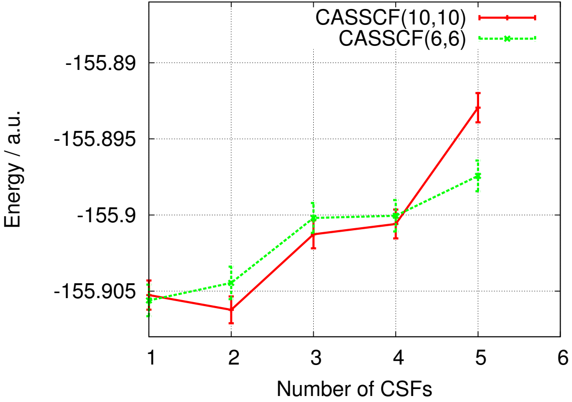
- two possible transition state: conrotatory and disrotatory
- rearrangement of gauche-butadiene to trans-butadiene

Multireference-DMC

- To account for non-dynamical correlation CASSCF guide functions are calculated
- truncated CASSCF functions are employed (with optimized Jastrow) in FN-DMC

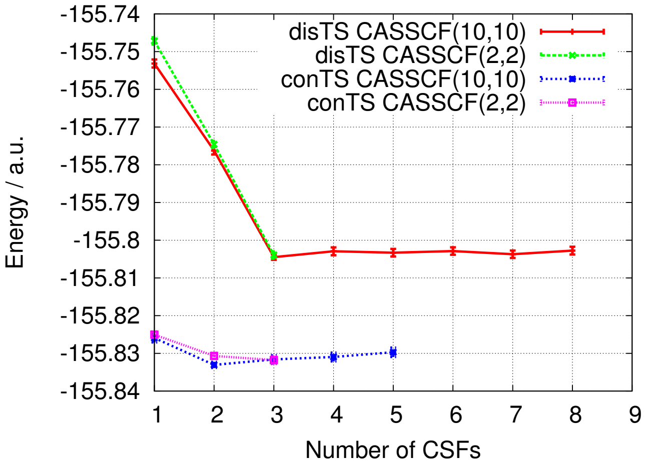


MR-DMC: bicylcobutane



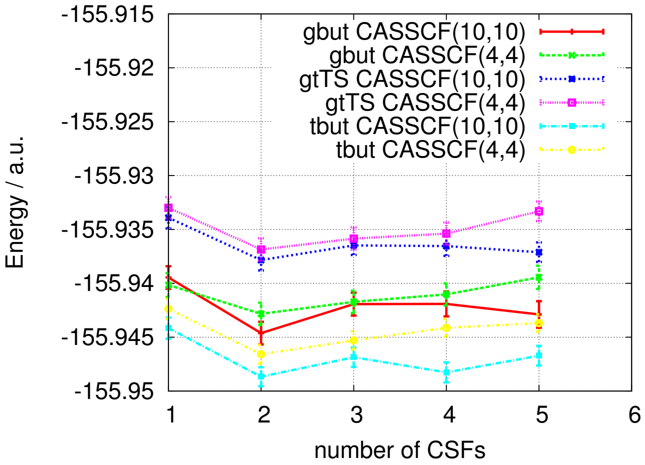
- FN-DMC *increases as CASSCF wave function improves!*

MR-DMC: transition states



- only initial decrease then increase of energy, mostly in dis_TS

MR-DMC: products



- significant decrease only with second CSF

Optimal Multi-Reference (OMR-)DMC

- Well known fact: FN-DMC increases with improving MCSCF (Flad, Lüchow, Caffarel,...)

Why?

- CASSCF accounts for non-dynamical as well as partially for the dynamical electron correlation
- The dynamical correlation is accounted for by Jastrow: CASSCF deteriorates nodes
- The non-dynamical correlation contribution improves nodes and FN-DMC

Best compromise: Use minimum of FN-DMC vs # CSF curve

- in this example: only 3 CSFs in the dis_TS system, 1 CSF in educt, 2 CSFs in rest

Alternative: reoptimize CI coefficients (Umrigar, Toulouse, Sorella, Filippi, Hennig...). Cost?

Results for OMR-DMC

in kcal/mol relative to bicyclobutane

	con_TS	dis_TS	g-but	gt_TS	t-but
experiment	40(2.5)	-	-	-	-25.9(4)
DFT/B3LYP	41.5	49.8	-26.3	-22.8	-29.9
CCSD(T)	40.6	21.8	-25.1	-22.3	-28.0
CR-CCSD(T)	42.8	68.8	-24.8	-22.1	-27.7
CR-CC(2,3)	41.1	66.1	-24.9	-22.1	-27.9
OMR1-DMC	43.4(6)	59.1(5)	-25.8(5)	-22.8(5)	-27.0(5)
OMR2-DMC	42.6(6)	59.4(5)	-24.2(5)	-22.3(5)	-27.5(5)
OMR3-DMC	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)
DMC/HF	51(1)	95.2(1)	-22.8(9)	-20.1(9)	-25.8(1)
DMC/B3LYP	54(1)	85.1(8)	-23.1(9)	-21.1(8)	-27.4(1)
DMC/CASSCF	47(1)	91.7(9)	-22.5(9)	-19.4(9)	-25.5(9)

CC: A. Kinal, P. Piecuch, JPCA 111, 734 (2007)

OMR1: small CAS; OMR2: CAS(10,10); OMR3: DMC-optimized

DMC/CASSCF: first det from CAS(10,10)

Discussion of OMR-DMC

- CCSD(T) fails to predict a conrotatory TS
- B3LYP has too small difference between conrotatory and disrotatory TS
- SR-DMC overestimates both TS
- OMR-DMC has excellent agreement with sophisticated CR-CC calculation (and experiment)
- OMR-DMC also improves significantly for small non-dynamical contributions (products)
- Reoptimization of CI coefficients (with DMC!) does not yield significant improvements
- OMR-DMC is very efficient in accounting for dynamical and non-dynamical electron correlation

Insight from QMC

- QMC produces samples from accurate many-body wave functions
    - $|\Psi_G|^2$ in VMC and $|\Psi_G \Psi_0^{(FN)}|$ in FN-DMC
    - $3n$ dimensional probabilites
    - contain information about antisymmetry (Fermi hole, “Pauli repulsion”) and electron correlation
- insight from simple model or *a posteriori* from accurate wave functions?
- binding energies, lone pair energies, orbitals, etc.: no observables

How to visualize many-body effects like antisymmetry?

- QMC emphasizes “real space” analysis (rather than “orbital space”)

Most probable electron arrangement

Most probable electron arrangement

The maximum of $|\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n)|^2$ yields the *most probable electron arrangement of all n electrons simultaneously*. The arrangement contains considerable information about the bonding in the molecule.

- Due to antisymmetry, same spin electrons avoid each other more than unlike spin electrons
- For eight electrons (4α, 4β) around an atom, the most probable arrangement consists of two tetrahedra
    - Linnett's double quartet theory (1960), Artmann (1940)

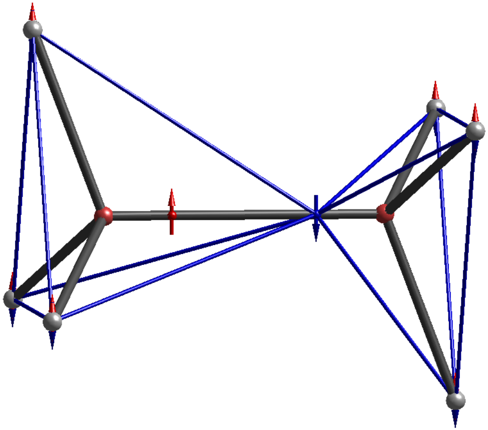
Determination of the maximum of $|\Psi|^2$ is a global optimization problem: today easy

- Metropolis-Monte Carlo random walk combined with local gradient optimization.

Ethane

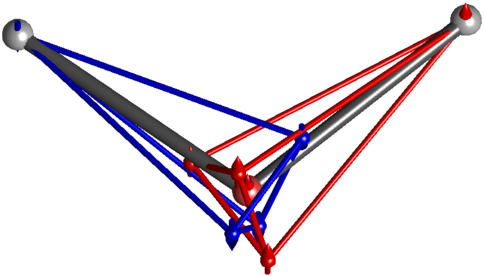
Most probable electron arrangement for ethane (HF/cc-pVTZ):

- connected tetrahedra
- symmetry breaking!

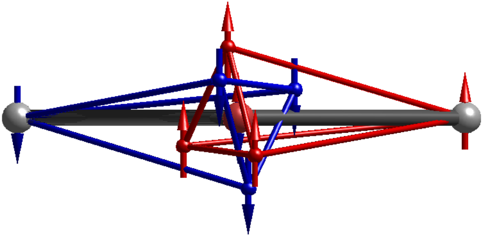


Water

Maximum with correlated wave function (Slater-Jastrow):



Water II



Single electron densities

- Electrons are mostly not at the maximum position
- Partition the total density $\rho(\mathbf{r})$ into *single electron densities* that are obtained by assigning electrons from the many-body distribution $|\Psi|^2$ to the maximum.

$$\rho(\mathbf{r}) = \sum_{i=1}^{n} \rho_i^{SED}(\mathbf{r})$$

Single electron densities (SED)

Assign electrons of many-body distribution $|\Psi|^2$ to a reference arrangement by finding the permutation that minimizes the distance (in $\mathbb{R}^{3n}$) to the reference. Single electron densities are the densities of the assigned electrons.

Single electron densities (SED)

Compare:

- electron density (integrating to electron number n)

$$\rho(\mathbf{r}_1) = n \int |\Psi(\mathbf{R})|^2 d\mathbf{r}_2 \dots d\mathbf{r}_n, \qquad \mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

- single electron density for electron 1:

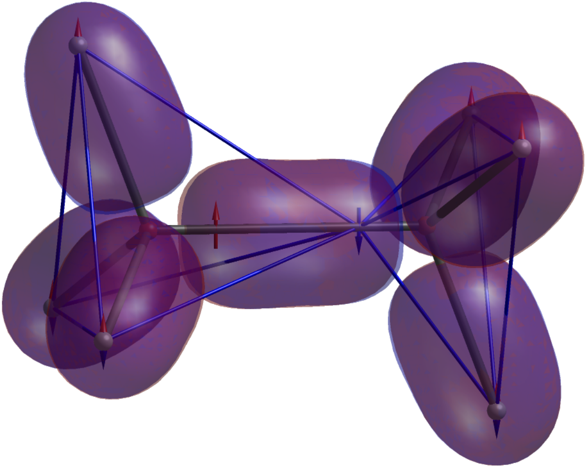
$$\rho_1^{SED}(\mathbf{r}_1) = \int |\Psi(\mathcal{P}\mathbf{R})|^2 d\mathbf{r}_2 \dots d\mathbf{r}_n, \qquad \mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

  where the permutation $\mathcal{P}$ depends on $\mathbf{R}$ and a reference arrangement $\mathbf{R}_{ref}$

    - Currently we require: $|\mathcal{P}\mathbf{R} - \mathbf{R}_{ref}| \overset{!}{=} \min$

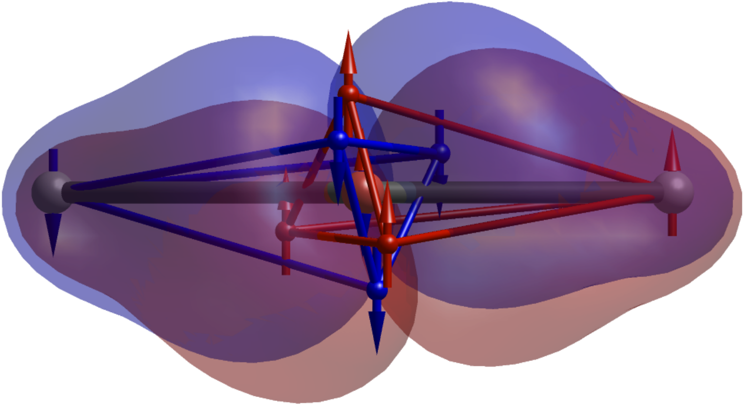
Ethane

- uncorrelated wave function

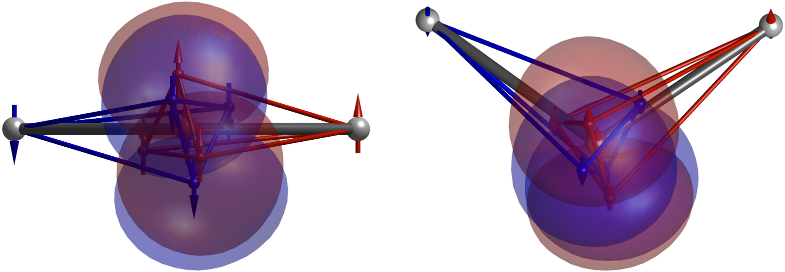


Water

- correlated wave function

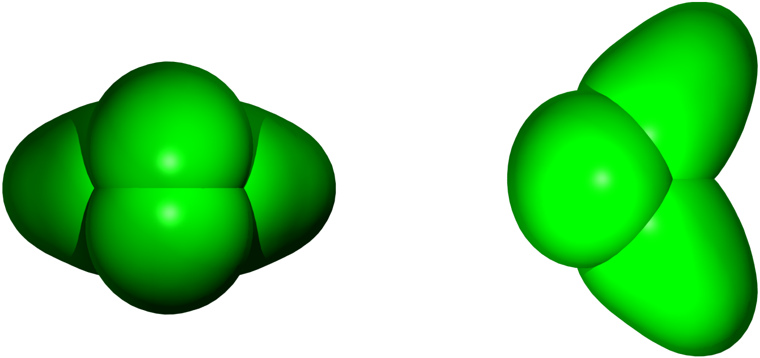


Water



Water: “electron pairs”

- add SEDs to pairs, use symmetry (invariant maxima)
- obvious relation to VSEPR model

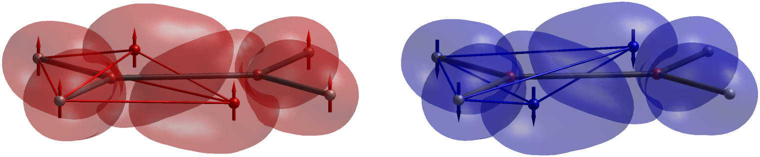


Comparison to ELF

- Electron structure is mostly determined by antisymmetry of electronic wave function – and by attraction from the nuclei.
- Antisymmetry is an inherently many-body effect – difficult to visualize
- ELF measures the *excess kinetic energy* due to antisymmetry
- SEDs contain the many-body information because the assignment to a SED *depends on all electrons*
- ELF and SED show similar spatial topology (?!)

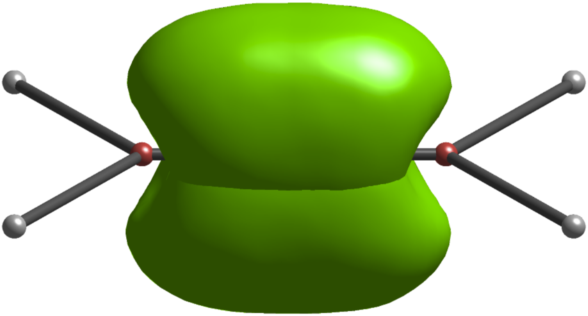
double bond: ethene

- splitting of α and β maximum already at uncorrelated level
- “banana” type bonds with distorted tetrahedral arrangement

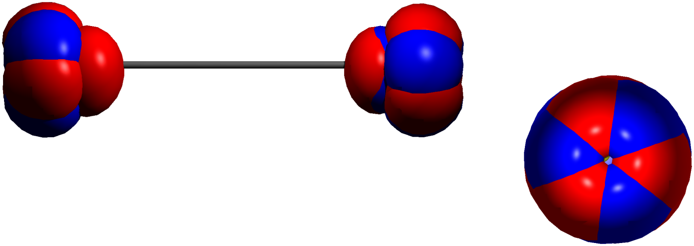


double bond: ethene

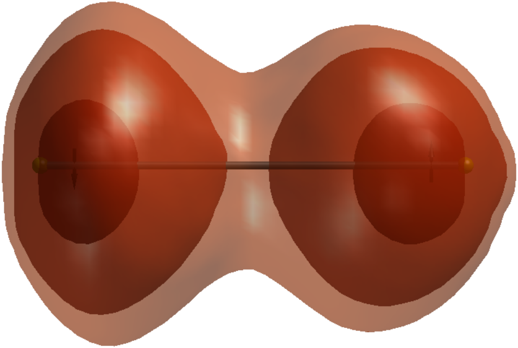
- double bond "electron pairs" after adding upper and lower SEDs (of all invariant maxima)



fluorine dimer F_2



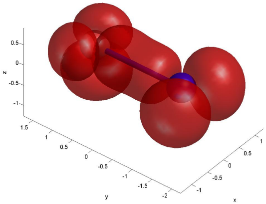
fluorine dimer bond

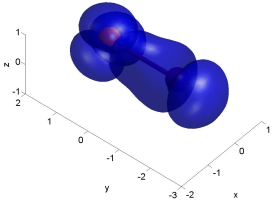


- strong left-right correlation (55 % LR vs. 52% in H_2O_2, N_2H_4, C_2H_6)

nitrogen monoxide NO

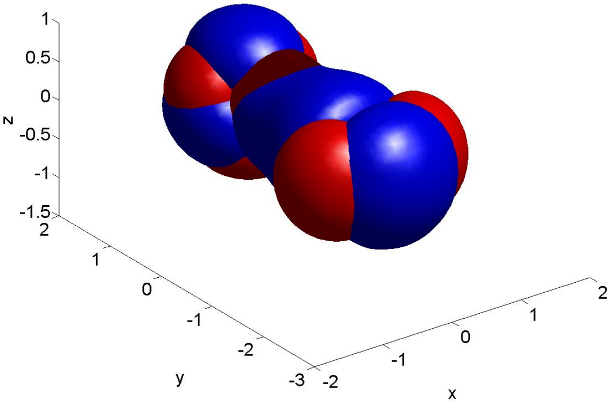
- regular tetrahedral, triangular or linear arrangement for 6α and 5β electrons





NO

- α, β systems avoid building electron pairs due to Coulomb interaction



Benzene

Conclusions

- partitioning of density based on physically meaningful max of $|\Psi|^2$
- like ELF role of antisymmetry in electron structure is visualized
- structure of SEDs easily understood in terms of Fermi holes and Coulomb interaction
- electrons of *unlike* spin *separate* rather than unite if possible (ethene, benzene, etc.)
- energy partitioning based on SEDs is intuitive and simple: SED pair energies
- many-body real space analysis independent of models (MO, VB)