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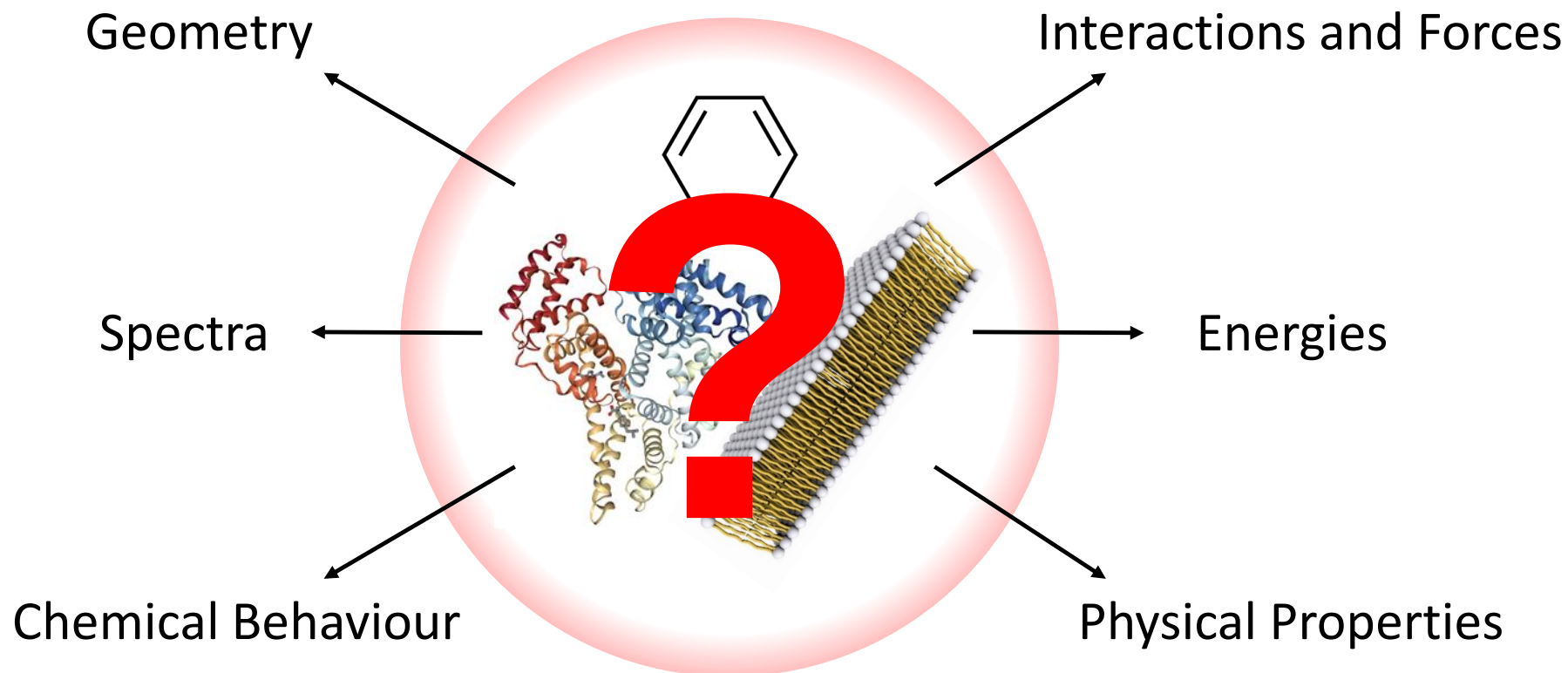
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JUSTUS-LIEBIG-
 UNIVERSITÄT
GIESSEN

Computational Chemistry- Review of Methods and Applications

Aileen Rebecca Raab – AG Schreiner – 04/12/2020

Of Problems and Solutions...



<http://www.chemspider.com/Chemical-Structure.236.html>; retrieved on 10.2.2020, 16:05

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Ab Initio Methods: Hartree-Fock

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

- Self-Consistent Field
- Born-Oppenheimer Approximation and Mean Field Approach
 - Little consideration of correlation and no dispersive interactions

$$\psi^{\text{HP}} = \prod_{i=1}^N \psi_i$$



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Ab Initio Methods: Hartree-Fock

- Slater determinant
 - Fulfills the antisymmetry principle
 - indistinguishability of electrons



$$\psi^{\text{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\beta(1) & \cdots & \psi_{N/2(1)}\beta(1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N)\alpha(N) & \psi_2(N)\beta(N) & \cdots & \psi_{N/2(N)}\beta(N) \end{vmatrix}$$

<https://deacademic.com/dic.nsf/dewiki/1470334>; retrieved on 2.10.2020, 20:50

<https://history.aip.org/phn/11406001.html>; retrieved on 30.11.2020, 19:49

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Roothaan-Hall

$$FC = SCE$$

$$F_{\mu\nu} = H_{core} + 2 J_{\mu\nu} - K_{\mu\nu}$$

- Self-Consistent Field

$$E_{HF} \geq E$$

- High computational cost
 - Small molecules, systematic errors
- Improvement: Post-HF methods



<http://www.quantum-chemistry-history.com/Roothaa1.htm>; retrieved on 2.10.2020, 21:25

<http://www.quantum-chemistry-history.com/Hall1.htm>; retrieved on 2.10.2020, 21:25

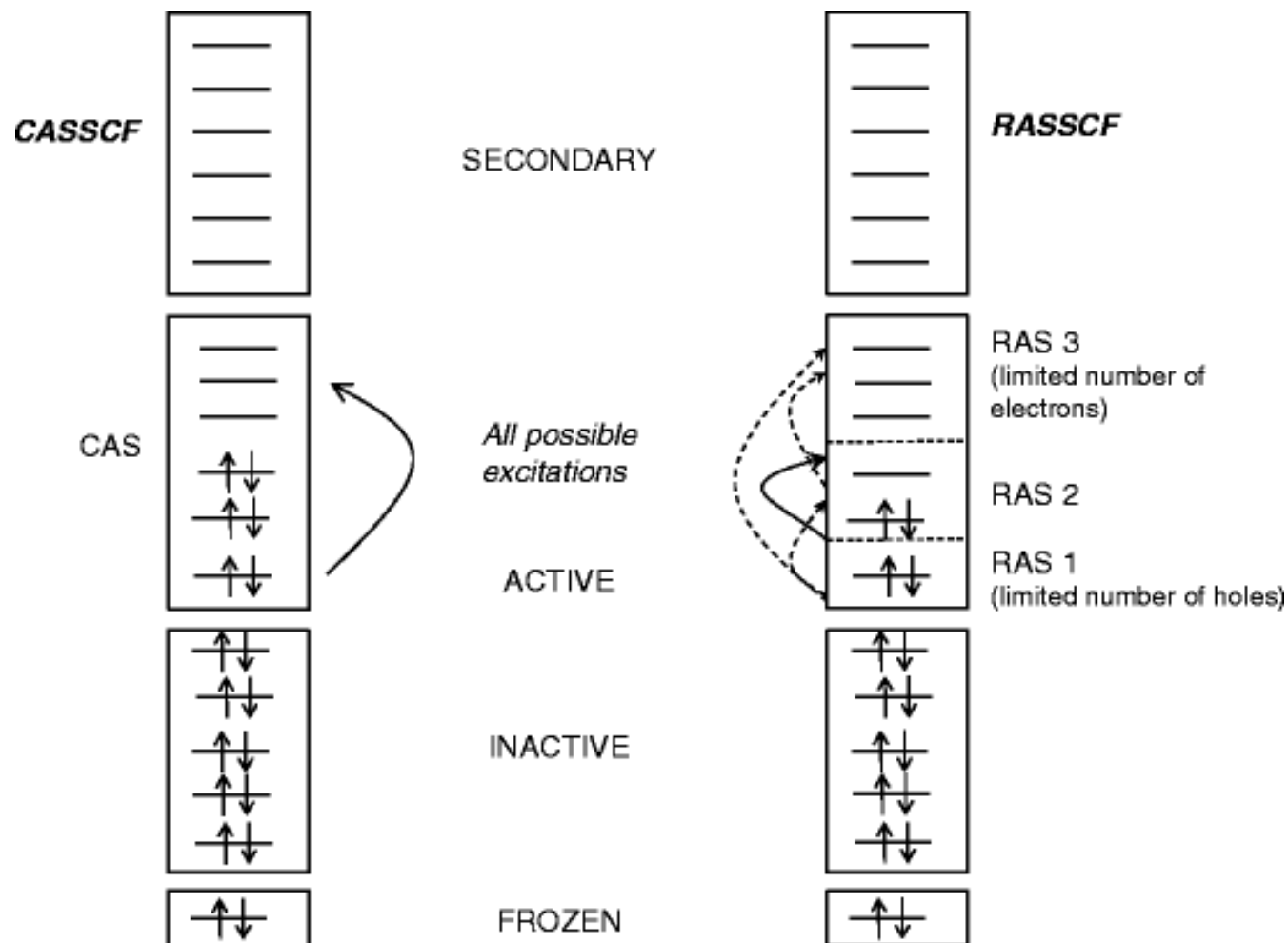
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The Active Space



Perturbation Theory

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

- Taylor expansion for the eigenvalues and eigenfunctions
- Solving the corresponding eigenvalue equations
- MP1: No improvement over HF

$$\left\langle \psi_0^{(0)} \right| \hat{V} \left| \psi_0^{(0)} \right\rangle = a^{(1)} \quad E_{\text{HF}} = E_{\text{MP0}} + E_{\text{MP1}}$$

- MP2, MP3, MP4, CASPTn, NEVPT

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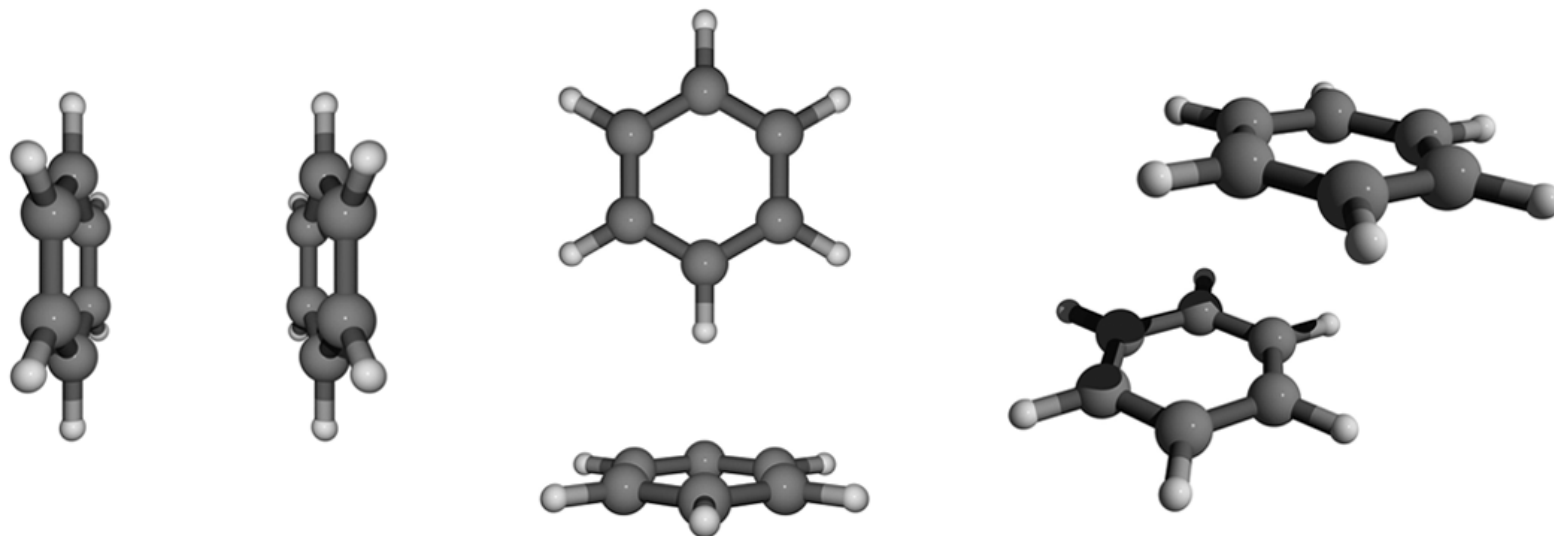
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Perturbation theory: Dispersion



Sandwich	T-Shaped	Parallel Displaced	Geometry
4.50	1.48	5.59	$dE^{\text{SCF}}/\text{kcal} \cdot \text{mol}^{-1}$
-2.13	-2.84	-3.33	$dE^{\text{MP2}}/\text{kcal} \cdot \text{mol}^{-1}$
-1.48	-2.46	-2.48	$dE^{\text{CCSD(T)}}/\text{kcal} \cdot \text{mol}^{-1}$

P. Hobza, H. L. Selzle, E. W. Schlag, *J. Am. Chem. Soc.* **1994**, *116*, 3500-3506.

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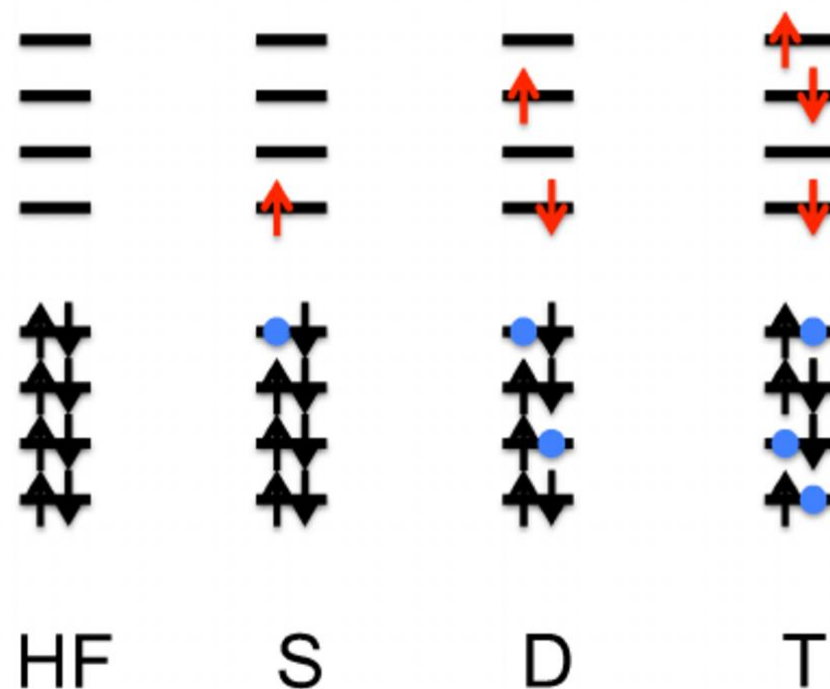
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M. O. Sinnokrat, E. F. Valeev, C. D. Sherril, *J. Am. Chem. Soc.* **2002**, *124*, 10887-10893.

Configurational Interaction (CI)

$$\Psi = c_0 \Psi_{\text{HF}} + \sum_i^{\text{occ}} \sum_r^{\text{vir}} c_i^r \Psi_i^r + \sum_{i<j}^{\text{occ}} \sum_{r<s}^{\text{vir}} c_{ij}^{rs} \Psi_{ij}^{rs}$$

- Full CI
 - exact solution of Schrödinger equation at CBS limit
 - High computational cost
- CISD, CID, CISDT
- MRCI-methods



C. D. Sherrill, H. F. Schaefer, *Adv. Quantum Chem.* **1999**, 34, 143-269.

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Coupled Cluster (CC)

$$\psi_{\text{CC}} = e^{\hat{T}} \psi_{\text{HF}}$$

$$\hat{T}_i = \frac{1}{i!} \sum_{\substack{\alpha_1, \dots, \alpha_i \\ r_1, \dots, r_i}} t_{\alpha_1, \dots, \alpha_i}^{r_1, \dots, r_i} \prod_{j=1}^i \hat{c}_{r_j}^{\dagger} \hat{c}_{\alpha_j}$$

- All excitations considered
 - Exact solution of Schrödinger equation
- Truncation: Singles, Doubles, Triples, Quadruples...
 - Higher excitations are approximated due to exponential ansatz
- State of the art: CCSD(T)
- MRCC-methods

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M. Kállay, J. Gauss, *J. Chem. Phys.* **2005**, 123, 214105.

Density functional theory (DFT)

$$E[\rho(r)]$$

- Thomas-Fermi
 - Uniformal electron gas
- Hohenberg Kohn theorems
 - properties of a molecular system unambiguously can be traced back to ρ
 - $E_0[\rho_0(r)]$
- Kohn-Sham
 - No simplification of solving the Schrödinger equation
 - Calculation for non-interactive system with same density

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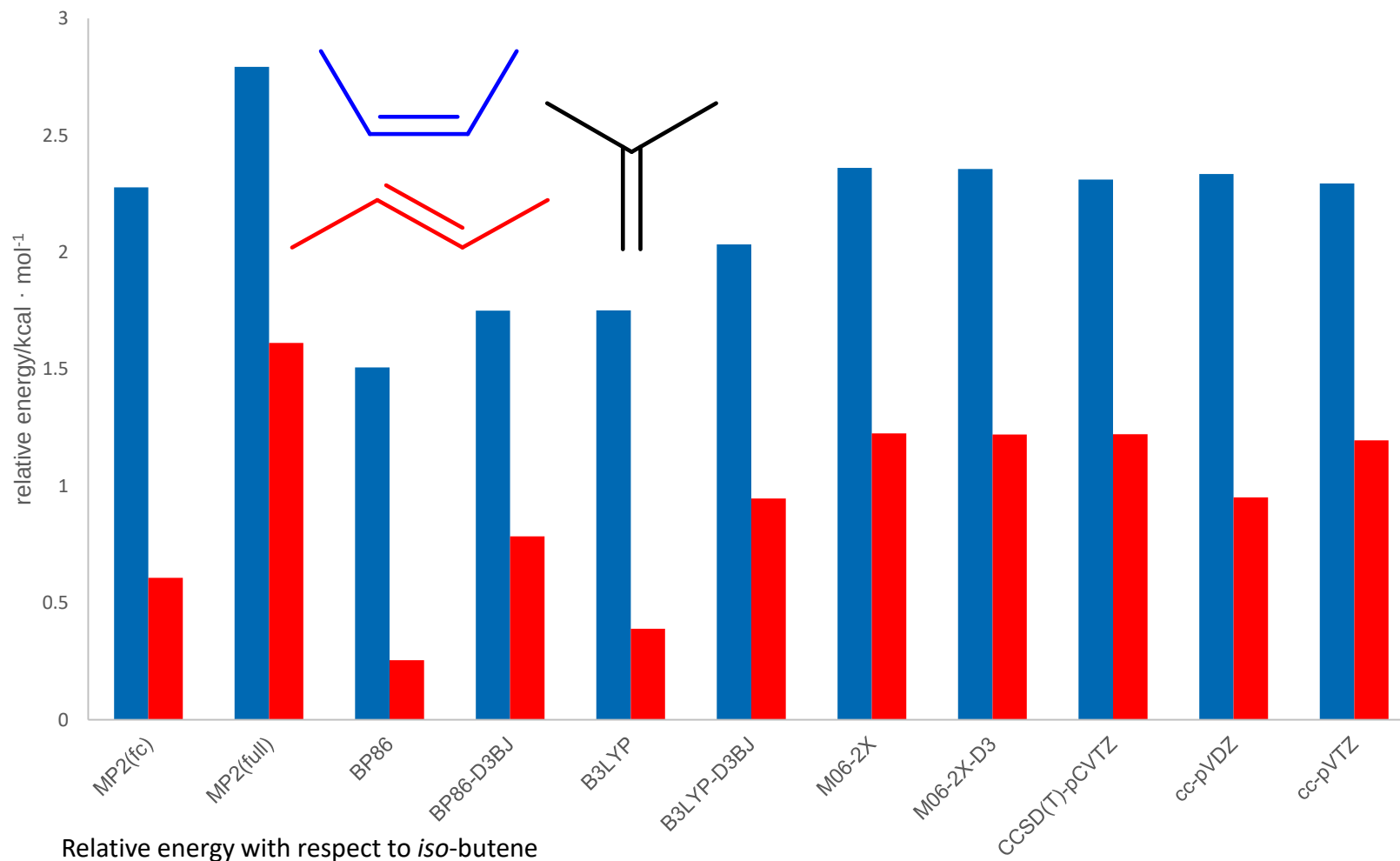
W. Kohn, L. J. Sham, Phys. Rev. **1965**, 140, A1133-A1138.

DFT: Exchange-correlation energy

$$E[\rho(r)] = \sum_i^N \left(\langle \chi_i | -\frac{1}{2} \nabla_i^2 | \chi_i \rangle - \langle \chi_i | \sum_k \frac{Z_k}{|r - r_k|} | \chi_i \rangle \right) + \sum_i^N \langle \chi_i | \frac{1}{2} \int \frac{\rho(r)}{|r - r'|} dr' | \chi_i \rangle + \text{EXC}[\rho(r)]$$

- Local density approximation (LDA)
 - VWN, PZ81, PW92...
- Generalized Gradient Approximation (GGA)
 - B, PBE, PW91, LYP, P86, PBE, PW91...
- *meta*-GGA
 - B88, PKZB, TPSS, M06...
- Hybrid Functionals: B3LYP, B3PW91, B3P86...

Benchmark



Conclusion

Interacting orbitals			Stabilization energy (D21VD-D21D)/kcal · mol ⁻¹			Stabilization energy (D21VC-D21D)/kcal · mol ⁻¹		
			Natural Population					

			Core	Valence	Rydberg	Total		

<i>cis</i> -Butene: σ C(<i>sp</i> ²)-H →	Atom No	Natural Charge						
<i>trans</i> -Butene σ C(<i>sp</i> ²)-H →	C 1	0.02058	1.99998	3.96742	0.01201	5.97942	.4	
	C 2	-0.42222	1.99998	4.40858	0.01366	6.42222		
<i>iso</i> -Butene: σ C(<i>sp</i> ²)-H →	C 3	-0.65734	1.99998	4.64807	0.00929	6.65734	.9	
	C 4	-0.65734	1.99998	4.64807	0.00929	6.65734		
	H 5	0.21976	0.00000	0.77857	0.00167	0.78024	.5	
	H 6	0.21976	0.00000	0.77857	0.00167	0.78024		
	H 7	0.22115	0.00000	0.77749	0.00136	0.77885		
	H 8	0.21976	0.00000	0.77857	0.00167	0.78024		
	H 9	0.22115	0.00000	0.77749	0.00136	0.77885		
	H 10	0.21976	0.00000	0.77857	0.00167	0.78024		
	H 11	0.19750	0.00000	0.80091	0.00159	0.80250		
	H 12	0.19750	0.00000	0.80091	0.00159	0.80250		
=====								
* Total *		0.00000	7.99992	23.94322	0.05686	32.00000		

Thanks to...

