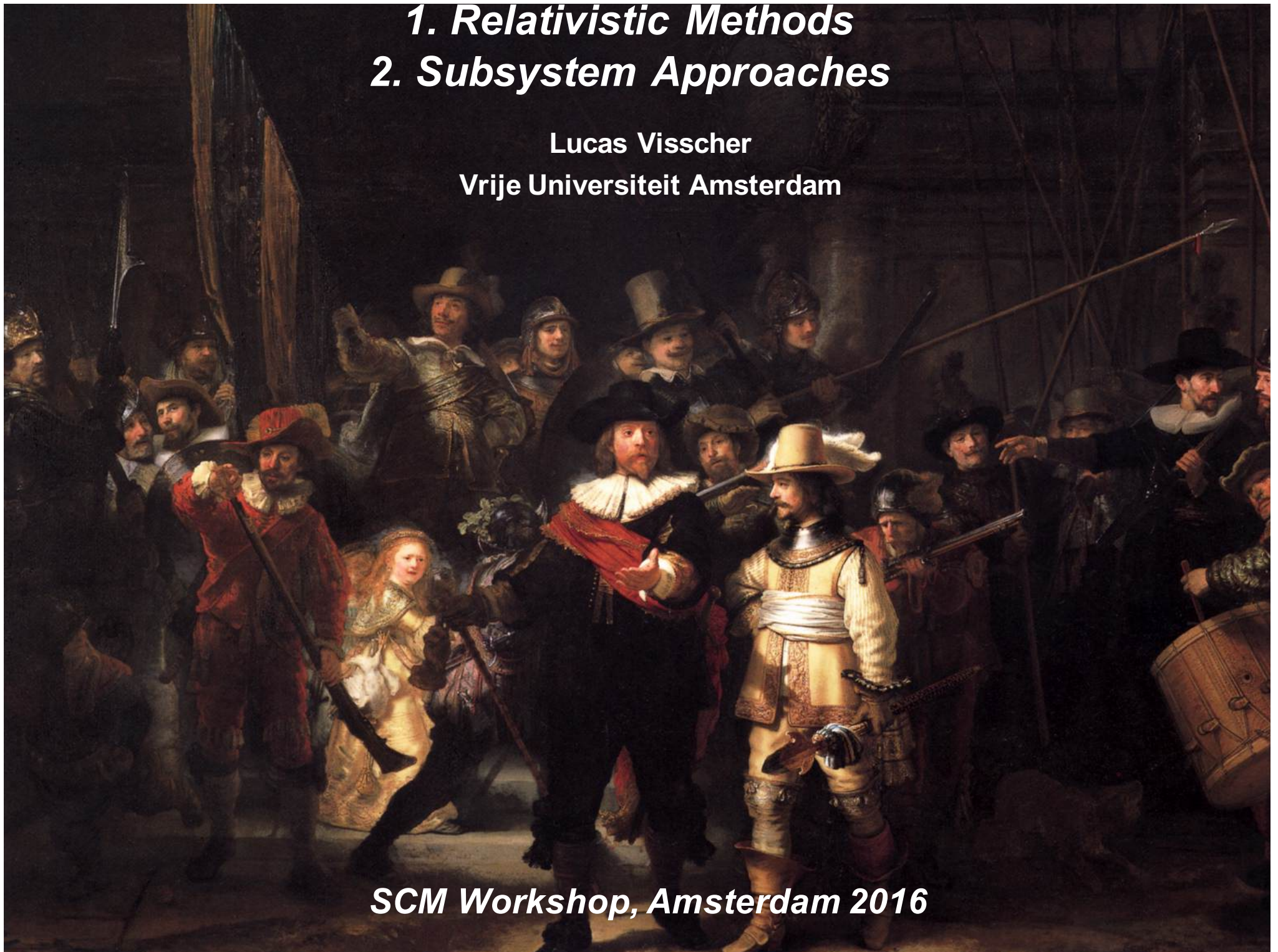


1. Relativistic Methods

2. Subsystem Approaches

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SCM Workshop, Amsterdam 2016

Assumptions in Quantum Chemistry

- Born-Oppenheimer approximation
 - Electronic and nuclear motion can be **decoupled**
 - Electronic energies for motion around clamped nuclei provide *potential energy surfaces* for nuclear motion
 - Coupling between surfaces can be studied by **perturbation theory**
- Nuclear charge distribution
 - **Point nucleus** approximation
 - Nuclear deformations are treated in **perturbation theory**
- Relativity
 - The speed of electrons is always **far below the speed of light**
 - Goal is to find **time-independent** wave functions (stationary states)
 - Magnetic effects are neglected or **treated in perturbation theory**

Dirac's view



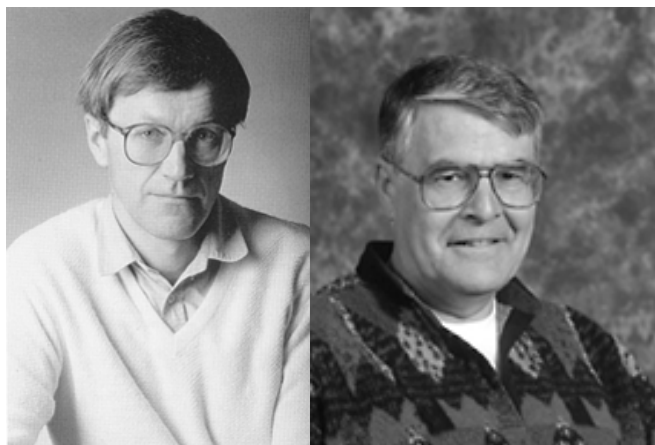
Dirac (1929)

- The general theory of quantum mechanics is now almost complete, the imperfection that still remain being in connection with the exact fitting in of the theory with relativistic ideas. These give rise to difficulties only when high speed particles are involved, and **are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions** in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei.
- The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and **the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.**

Later insights



- Pekka Pyykkö and Jean-Paul Desclaux (1979)
 - The chemical difference between the fifth row and the sixth row seems to contain **large, if not dominant, relativistic contributions** which, however, enter in an individualistic manner for the various columns and their various oxidation states, explaining, for example, both the inertness of Hg and the stability of Hg_2^{2+} . These relativistic effects are particularly strong around gold. A detailed understanding of **the interplay between relativistic and shell-structure effects** will form the impact of relativity on chemistry.



- Jan Almlöf & Odd Gropen (1996)
 - While the incorporation of these effects sometimes increases the computation labor, **the increase is generally reasonable**, and certainly much less than in, e.g. the transition from semiempirical to ab initio methods for routine quantum chemistry applications. We predict, therefore, that relativistic corrections in one form or another **will be included in the majority** of all quantum chemistry calculations before the end of this decade.

Special relativity

Postulate 1: All inertial frames are equivalent

Postulate 2: The laws of physics have the same form in all inertial frames

Lorentz coordinate transformations mix time and space

Postulates hold for electromagnetism (Maxwell relations)

Postulates do not hold for Newtonian mechanics

Develop quantum theory from classical relativistic equations and make sure electron spin is described

The Dirac equation

$$(\beta mc^2 + c \boldsymbol{\alpha} \cdot \boldsymbol{\pi} + q\phi)\psi(r,t) = i\hbar \frac{\partial \psi(r,t)}{\partial t}$$

- ☺ First derivatives with respect to time and position
- ☺ Linear in scalar and vector potentials
- ☺ Lorentz invariant

α and β are 4-component matrices

$$\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \quad \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \quad \alpha_z = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

The Dirac Hamiltonian

$$\hat{H} = \beta mc^2 + c \boldsymbol{\alpha} \cdot \hat{\boldsymbol{\pi}} + q\phi$$
$$= \begin{pmatrix} mc^2 + q\phi & 0 & c\pi_z & c(\pi_x - i\pi_y) \\ 0 & mc^2 + q\phi & c(\pi_x + i\pi_y) & -c\pi_z \\ c\pi_z & c(\pi_x - i\pi_y) & -mc^2 + q\phi & 0 \\ c(\pi_x + i\pi_y) & -c\pi_z & 0 & -mc^2 + q\phi \end{pmatrix}$$

Four component wave function

- 1) Spin doubles the number of components
- 2) Relativity doubles the number of components again

Charge and current density

- Charge density

$$\rho(\mathbf{r}, t) = q\psi^\dagger(\mathbf{r}, t)\psi(\mathbf{r}, t)$$

- Current density

$$\mathbf{j}(\mathbf{r}, t) = q\psi^\dagger(\mathbf{r}, t) c\boldsymbol{\alpha} \psi(\mathbf{r}, t) \quad \longleftarrow c\boldsymbol{\alpha} \text{ is the relativistic velocity operator}$$

- Continuity relation

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0$$

Free particle Dirac equation

- Take simplest case : $\phi = 0$ and $\mathbf{A} = 0$
- Use plane wave trial function

$$\Psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix}$$

← Non-relativistic functional form with constants a_i that are to be determined

$$(E - mc^2)a_1 - c\hbar k_z a_3 - c\hbar k_- a_4 = 0$$

$$(E - mc^2)a_2 - c\hbar k_+ a_3 + c\hbar k_z a_4 = 0$$

$$-c\hbar k_z a_1 - c\hbar k_- a_2 + (E + mc^2)a_3 = 0$$

$$-c\hbar k_+ a_1 + c\hbar k_z a_2 + (E + mc^2)a_4 = 0$$

← After insertion into time-independent Dirac equation

$$k_{\pm} = k_x \pm ik_y$$

Free particle Dirac equation

- Two doubly degenerate solutions

$$(E^2 - m^2 c^4 - c^2 \hbar^2 k^2) = 0$$

$$E_+ = +\sqrt{m^2 c^4 + c^2 \hbar^2 k^2}$$

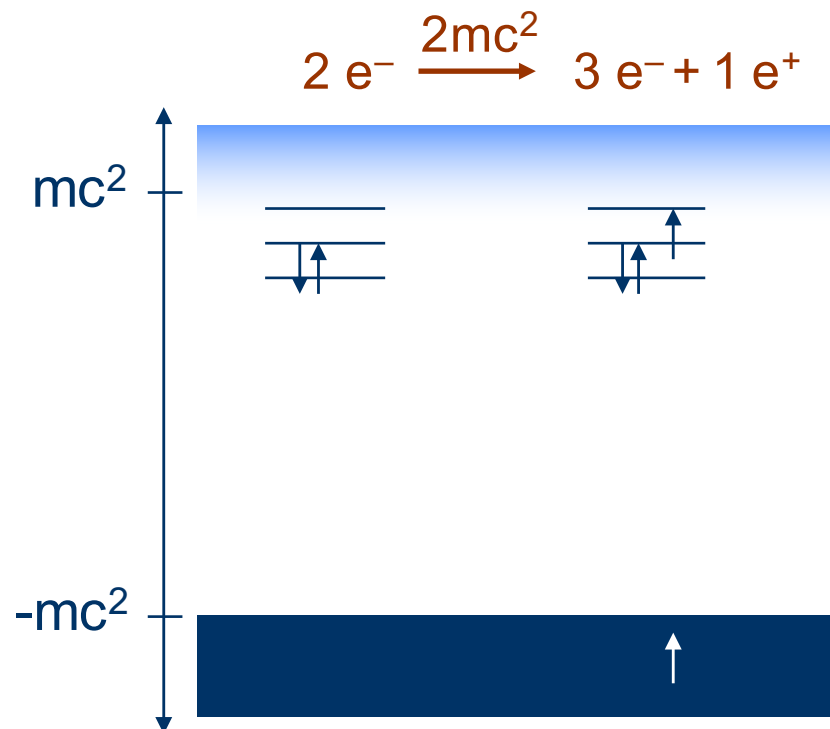
$$E_- = -\sqrt{m^2 c^4 + c^2 \hbar^2 k^2}$$

- Compare to classical energy expression

$$E = \sqrt{m^2 c^4 + c^2 p^2}$$

- Quantization (for particles in a box) and prediction of negative energy solutions

Dirac sea of electrons



- Negative energy solutions are all occupied
- Pauli principle applies
- ☺ Holes in this sea of electrons are seen as particles with positive charge: positrons (1933)
- ☹ Infinite background charge
- ⊙ QED (Quantum Electrodynamics) to properly account for contribution of negative energy states
- ⊙ **No-pair approximation**

The hydrogenic atom: Energies

- The exact non-relativistic energy

$$E^{NR} = -\frac{Z^2}{2n^2}$$

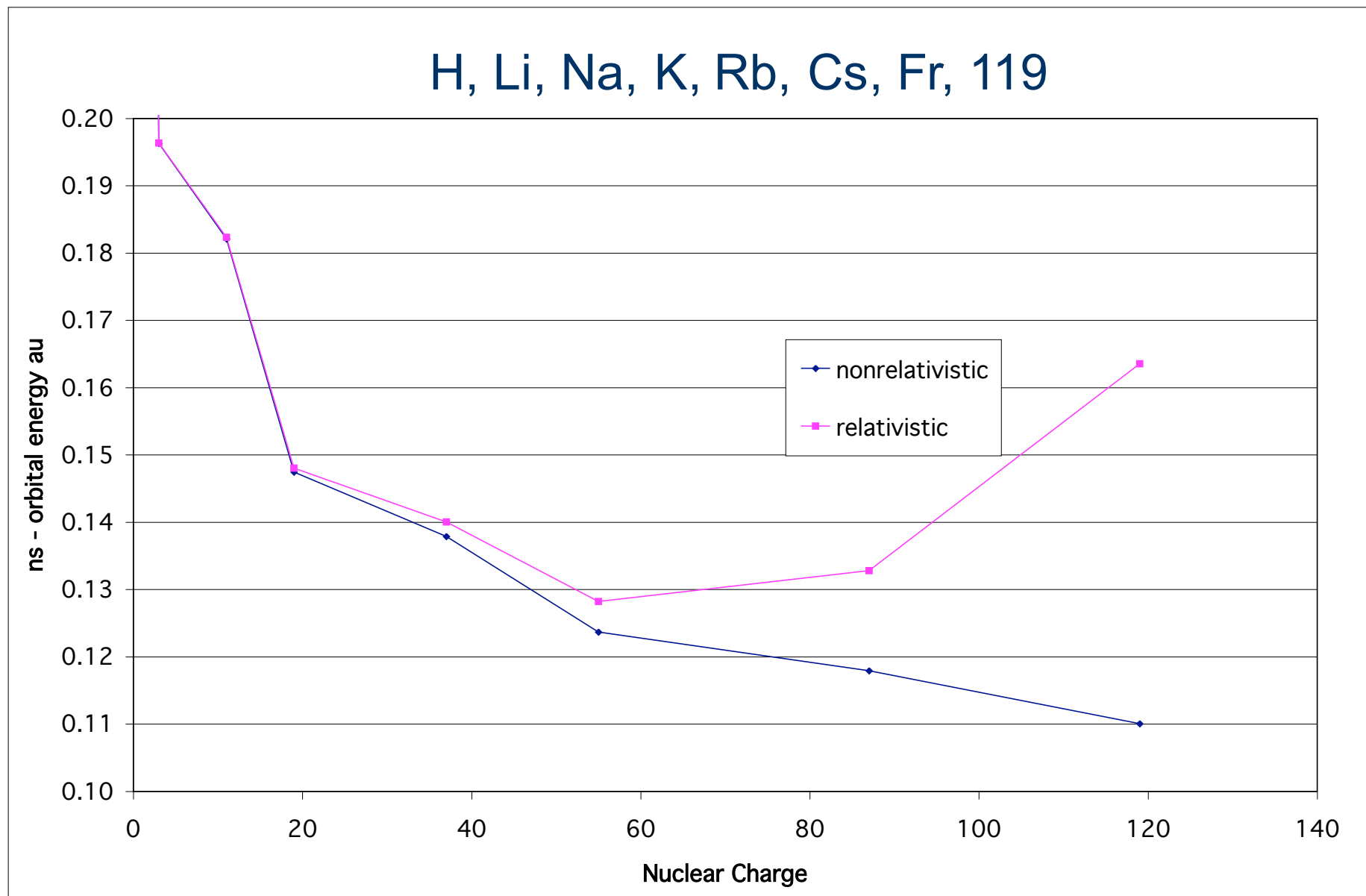
- The exact relativistic energy

$$E = mc^2 / \sqrt{1 + \left\{ \frac{Z/c}{n - j - \frac{1}{2} + \sqrt{(j + 1/2)^2 - \frac{Z^2}{c^2}}} \right\}^2}$$

- Spin-orbit coupling : $j = l \pm s$

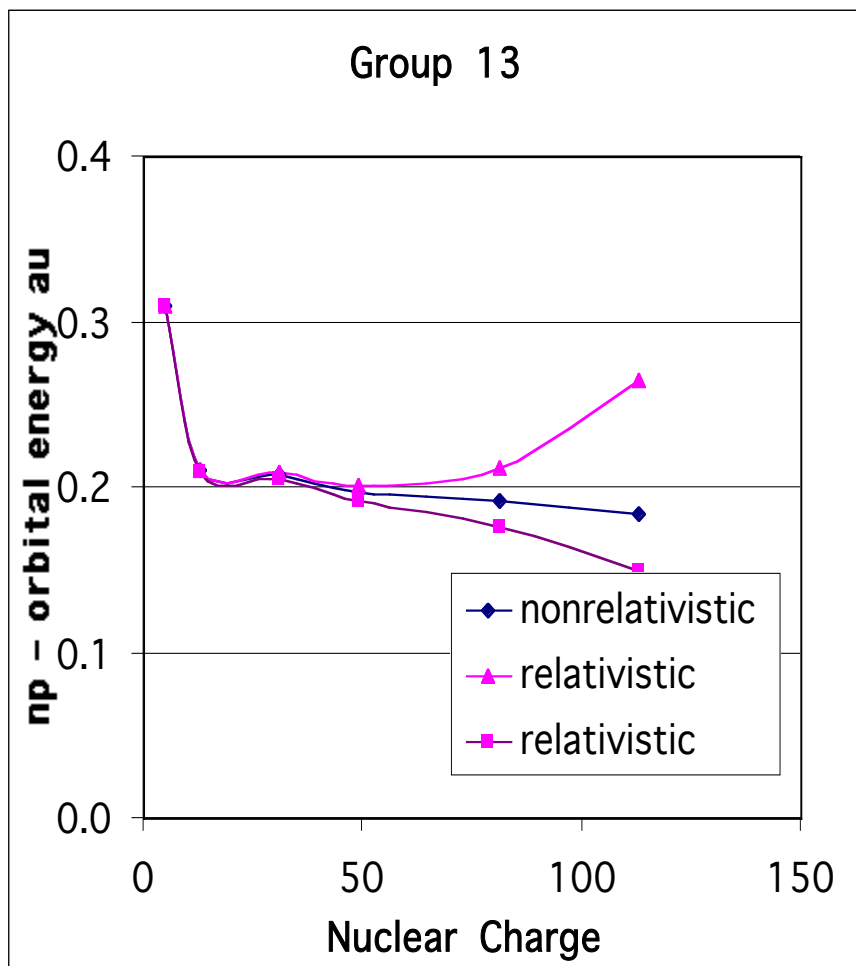
Energy depends on orbital and spin variables

Orbital stabilization: increase in ionization energy

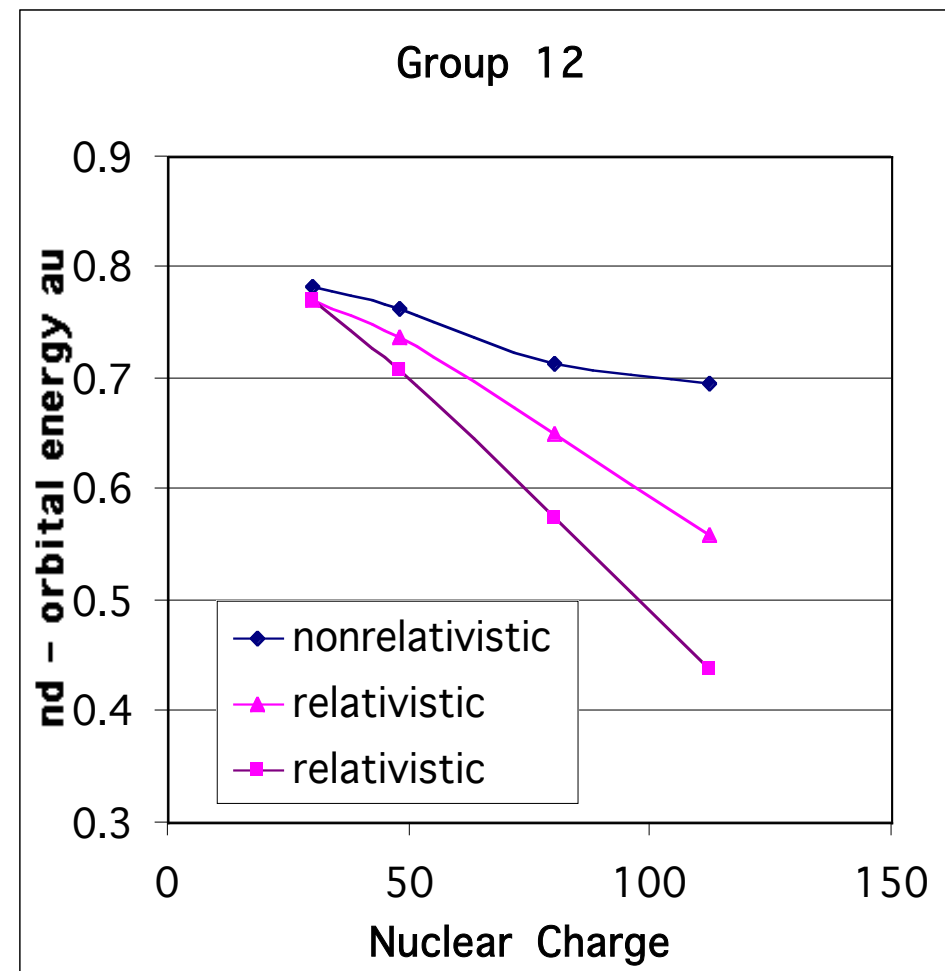


Orbital destabilization and spin-orbit splitting

B, Al, Ga, In, Tl, 113

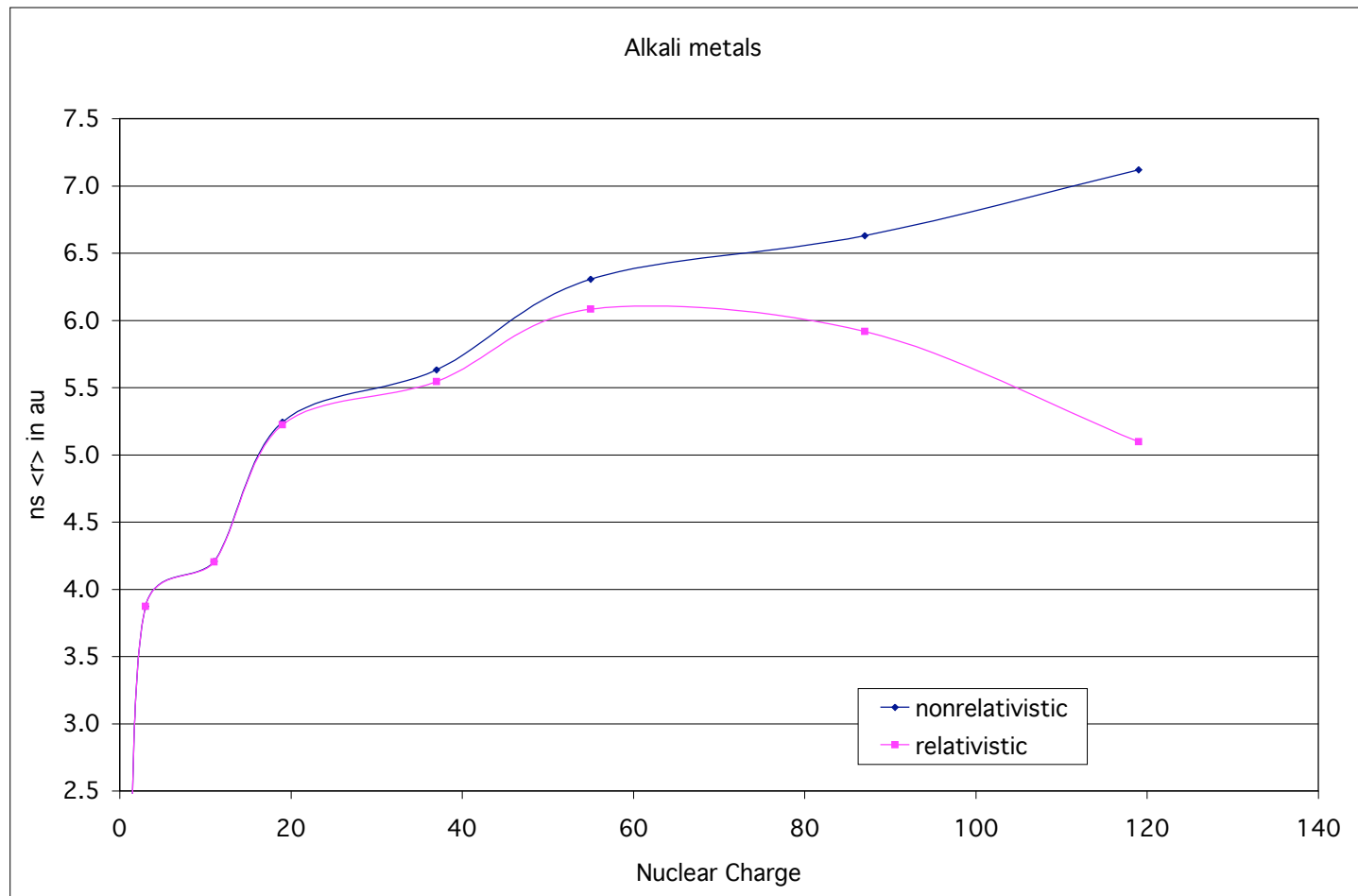


Zn, Cd, Hg, Cn



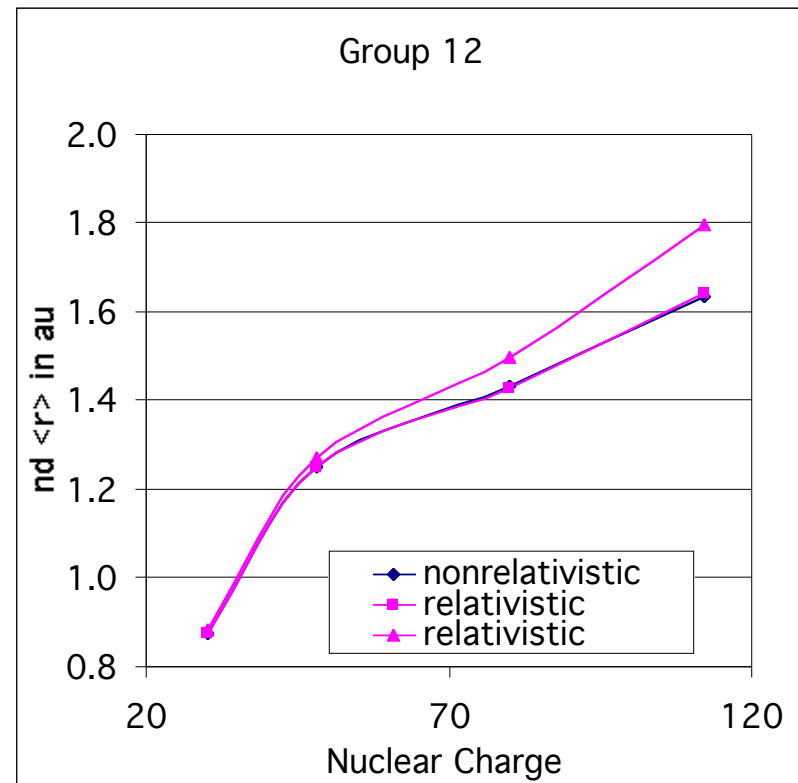
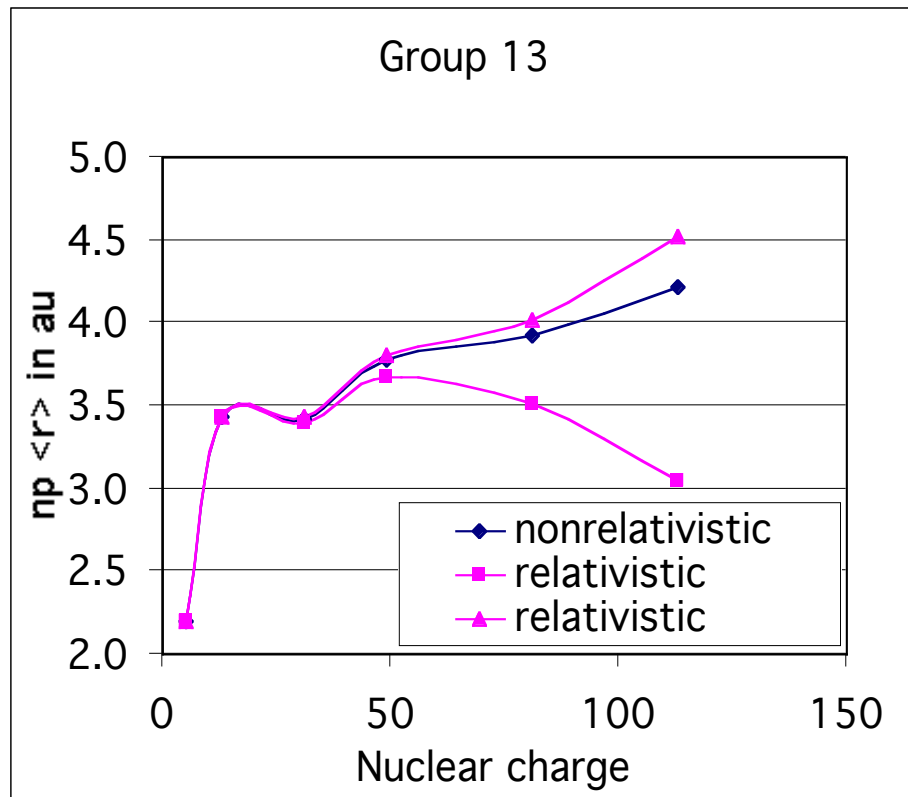
Orbital contraction

- The outermost s-orbital becomes more compact

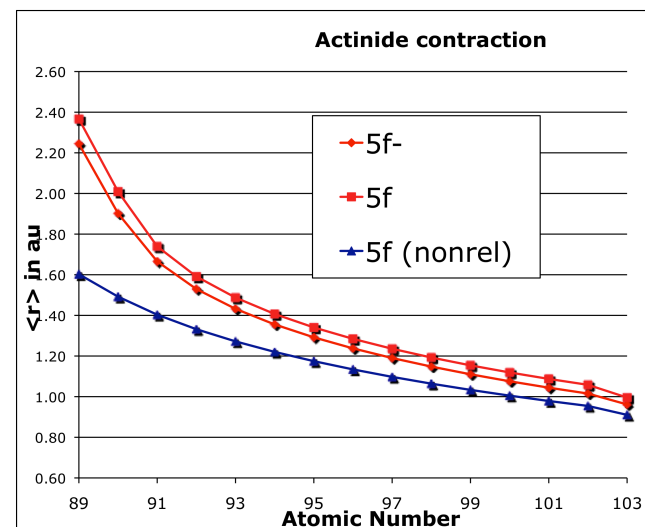
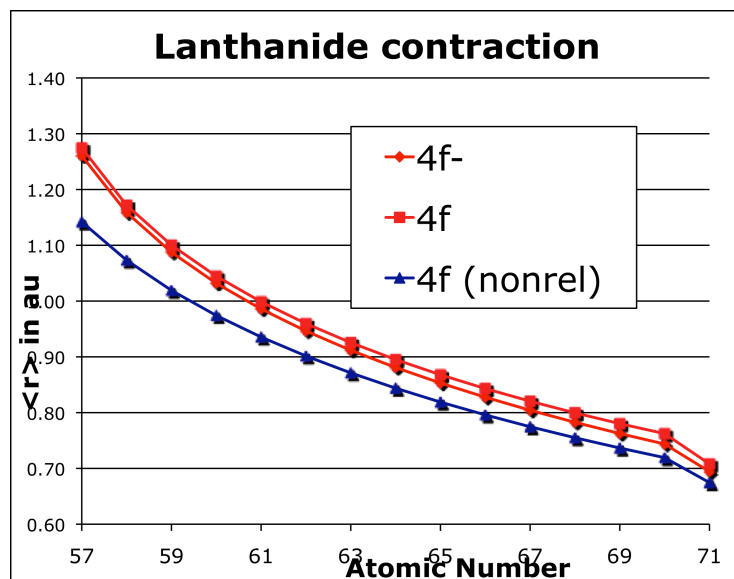


Orbital expansion

- The outermost p- and d-orbitals expand



Ln-An contraction



- Ln-An contraction is partly caused by relativistic effects
- Trend expected from the atomic calculations is confirmed by calculations on LnF , AnF , LnH_3 and AnH_3 molecules.

Expansion of the energy expression

- The exact Hydrogenic energy expression

$$E = mc^2 / \sqrt{1 + \left\{ \frac{Z/c}{n - j - \frac{1}{2} + \sqrt{(j + 1/2)^2 - \frac{Z^2}{c^2}}} \right\}^2}$$

- Can be expanded to

$$(1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^2 - \dots$$

$$E = mc^2 - \frac{Z^2}{2n^2} + \frac{Z^4}{2n^4 c^2} \left\{ \frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right\} + O\left(\frac{Z^6}{c^4}\right)$$

Approximate Hamiltonians

- Find 2-component operators that describe these scalar relativistic and spin-orbit coupling energy corrections in molecular systems
- Start by decoupling the large and small component equations

$$V\psi^L + c \boldsymbol{\sigma} \cdot \mathbf{p} \psi^S = E\psi^L$$

$$c \boldsymbol{\sigma} \cdot \mathbf{p} \psi^L + (V - 2mc^2)\psi^S = E\psi^S$$

- Rewrite the lower equation as

$$\psi^S(\mathbf{r}) = \left(1 + \frac{E - V}{2mc^2}\right)^{-1} \frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc} \psi^L(\mathbf{r})$$

$$= K(E, \mathbf{r}) \frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc} \psi^L(\mathbf{r})$$

$$K(E, \mathbf{r}) = \left(1 + \frac{E - V}{2mc^2}\right)^{-1}$$

Approximate Hamiltonians

- Substitute in the upper equation

$$\left\{ \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) K(E, \mathbf{r}) (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \right\} \psi^L(\mathbf{r}) = E \psi^L(\mathbf{r})$$

- Unnormalized Elimination of the Small Component (UESC)
 - The full spinor is normalized to 1, so the large component only must have a norm < 1
 - Large component spinors are not orthogonal to each other (only the full spinors are orthogonal)
- The UESC equation is exact: is used as starting point for approximations

Regular Approximation

- What can go wrong ? Check the expansion parameter

$$K(E, \mathbf{r}) = \left[1 + \frac{(E - V)}{2mc^2} \right]^{-1} = 1 - \frac{(E - V)}{2mc^2} + O(c^{-4})$$

- E should be small relative to $2mc^2$
 - Orbital energies vary over a range of -0.1 to 5,000 au
 - Twice the rest mass energy is 37,558 au
 - This difference should be large enough
- V should be small relative to $2mc^2$
 - The potential is dominated by the nuclear attraction close to the nuclei

$$V \approx -\frac{Z}{r}$$

- Take $r = 10^{-4}$ au and $Z=6$ (carbon): $V = 60,000$ au
- Is this inside the nucleus ? No : the nuclear radius is $4.7 \cdot 10^{-5}$ au for C.

0th order regular approximation: ZORA

- Can we find a good expansion parameter ? Yes !

$$K(E, \mathbf{r}) = \left[1 + \frac{(E - V)}{2mc^2} \right]^{-1} = \left(1 - \frac{V}{2mc^2} \right)^{-1} \left(1 + \frac{E}{2mc^2 - V} \right)^{-1}$$

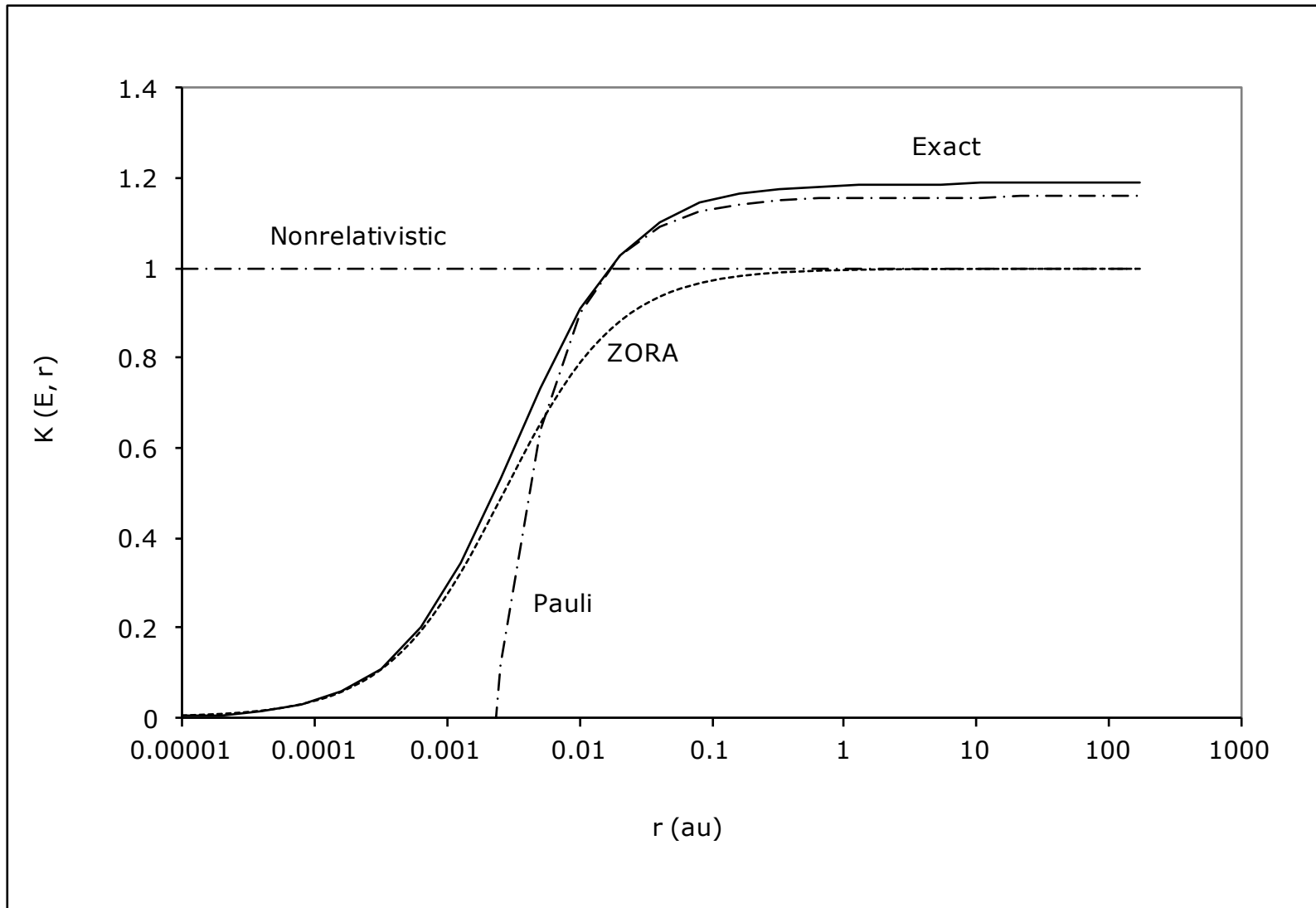
- E should be small relative to $2mc^2 - V$
 - V is negative which *improves* the expansion close to the nuclei
- Zeroth order in this expansion

$$\left\{ \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) \left(1 - \frac{V}{2mc^2} \right)^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \right\} \psi^{\text{ZORA}}(\mathbf{r}) = E \psi^{\text{ZORA}}(\mathbf{r})$$

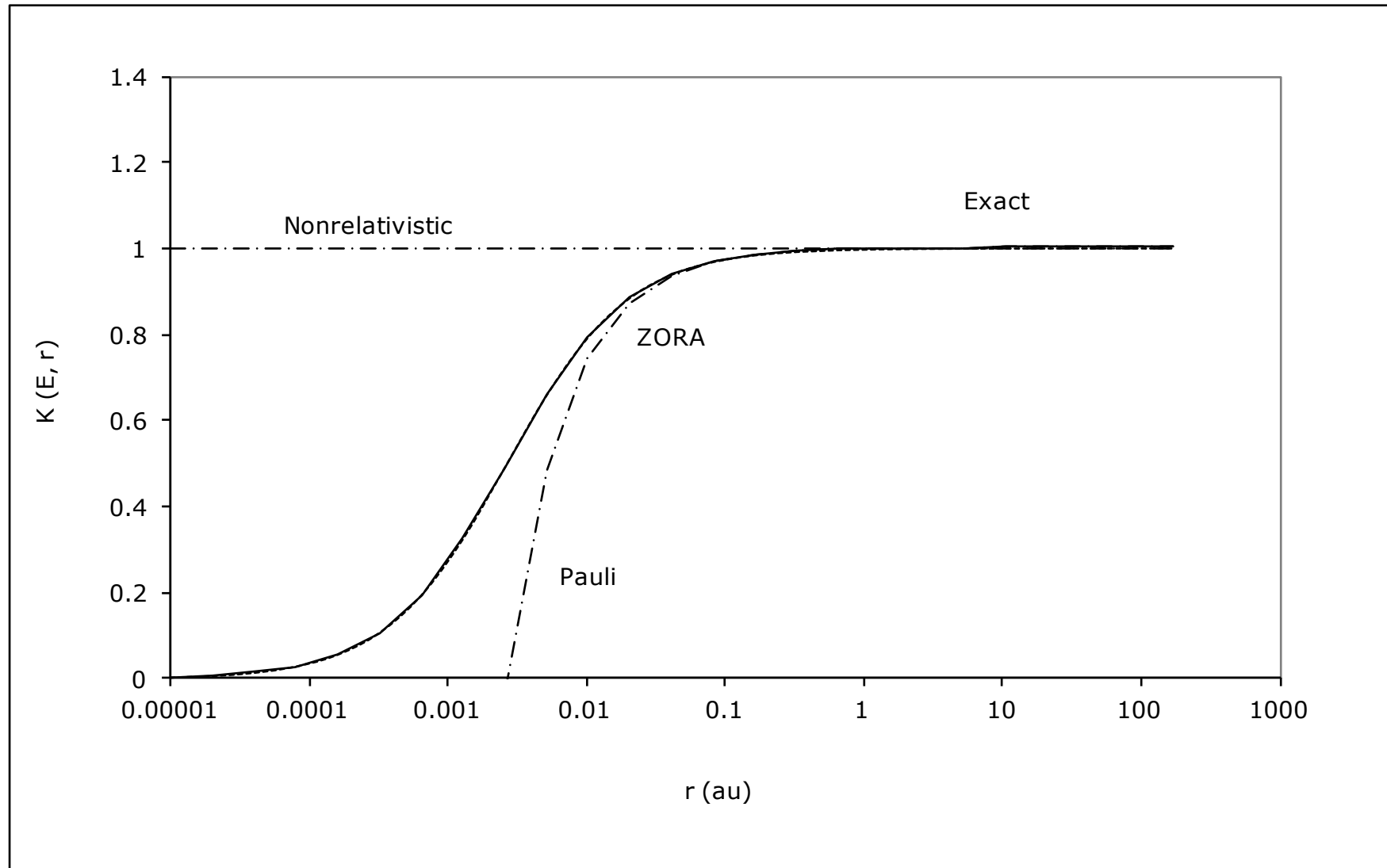
- ☺ Zeroth order equation does describe SO-coupling and scalar relativistic corrections
- ☹ Gauge dependence of the energy
 - Affects ionization energies, structures
 - Is avoided by keeping potential in the denominator fixed

$$V \rightarrow V + C \quad E \rightarrow E + C - \frac{EC}{2mc^2}$$

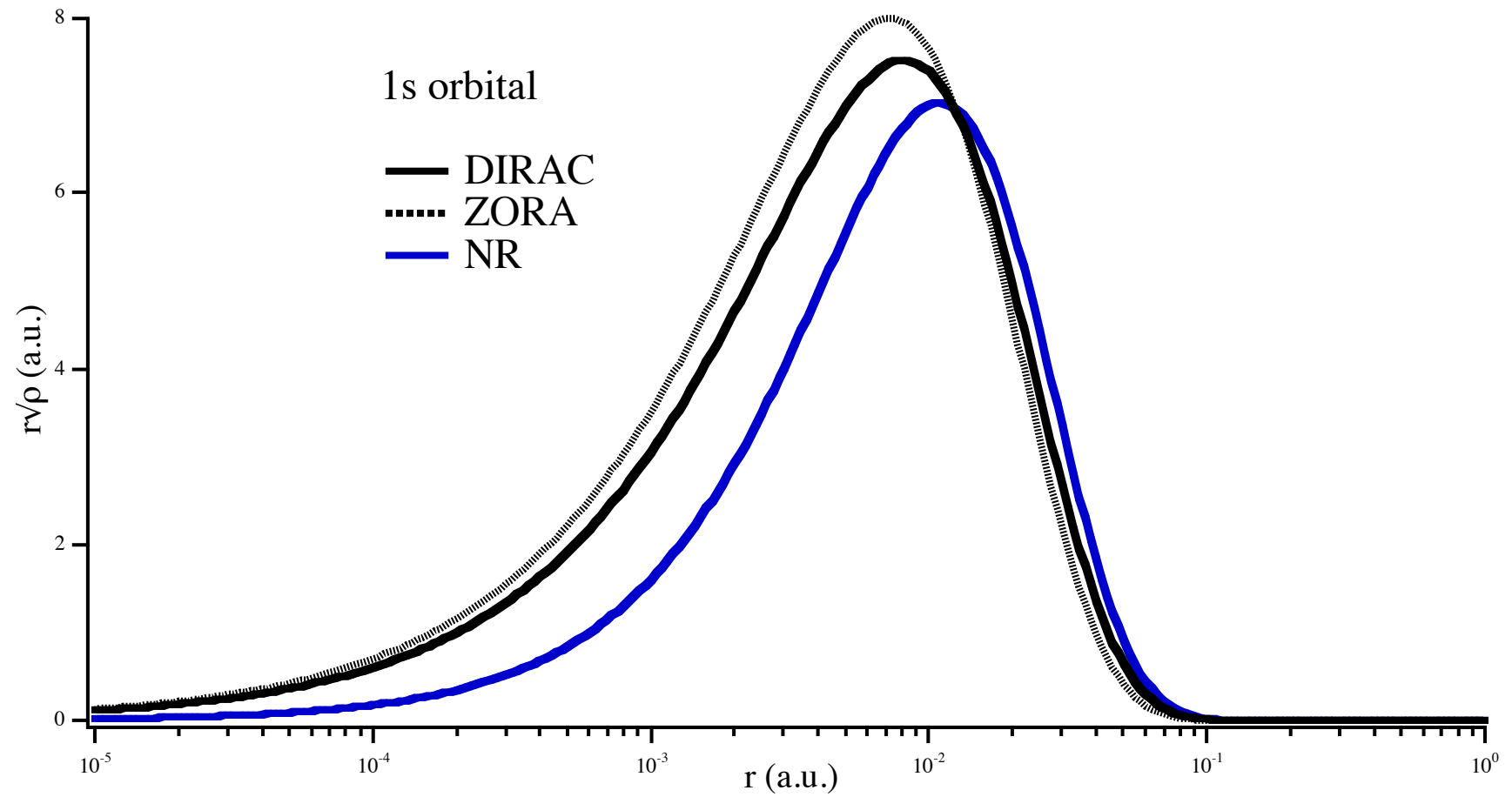
Approximations to $K(E,r)$ for the 1s orbital of Fm^{99+}



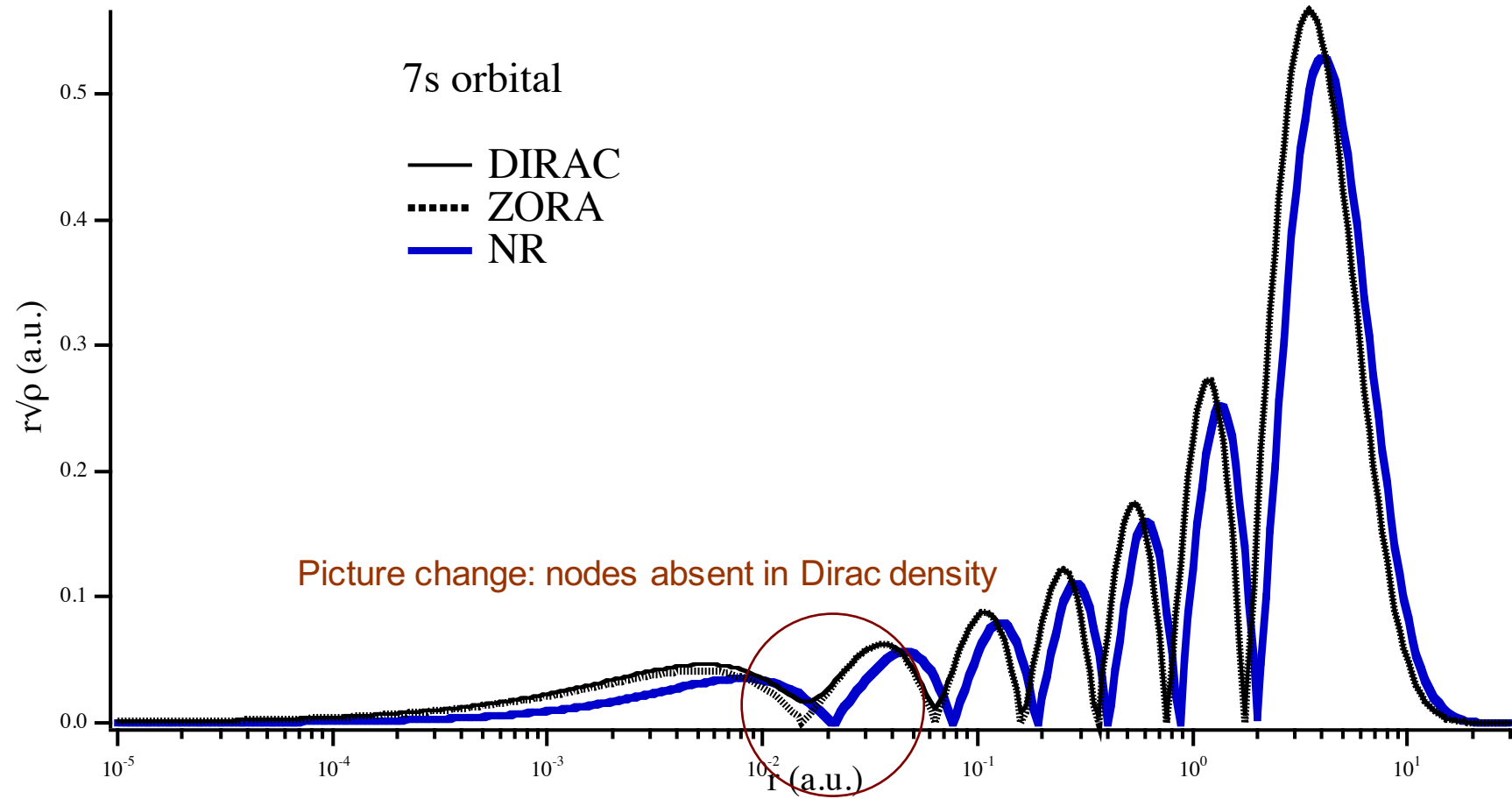
Approximations to $K(E,r)$ for the 7s orbital of Fm^{99+}



Uranium atom

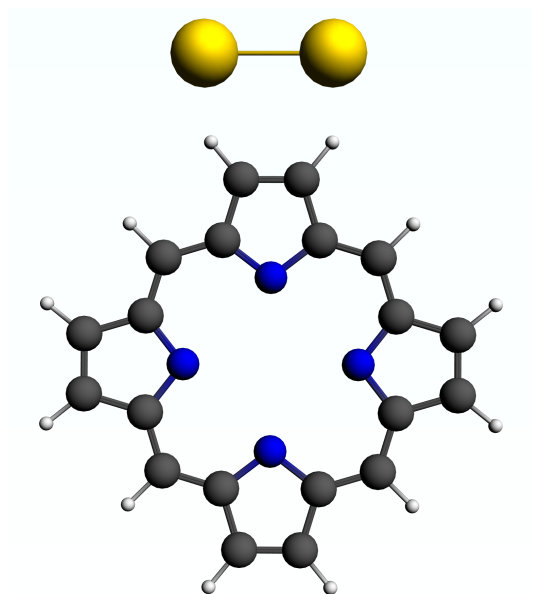


Uranium atom



Chemistry of heavy elements

- A different world....

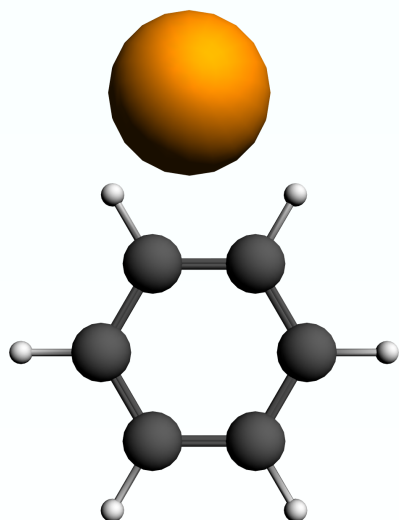


	Au ₂	C ₂₀ N ₂₀ H ₁₂
electrons	178	160
total energy	-36,870 Hartree	-987 Hartree
basis functions	48s38p24d18f2g 426 functions	240s108p24d 684 functions
chemical bonds	1	40
Bond energy	0.1 Hartree 2.3 eV	10 Hartree 272 eV

- Possible to use **frozen core** approximation

f-elements

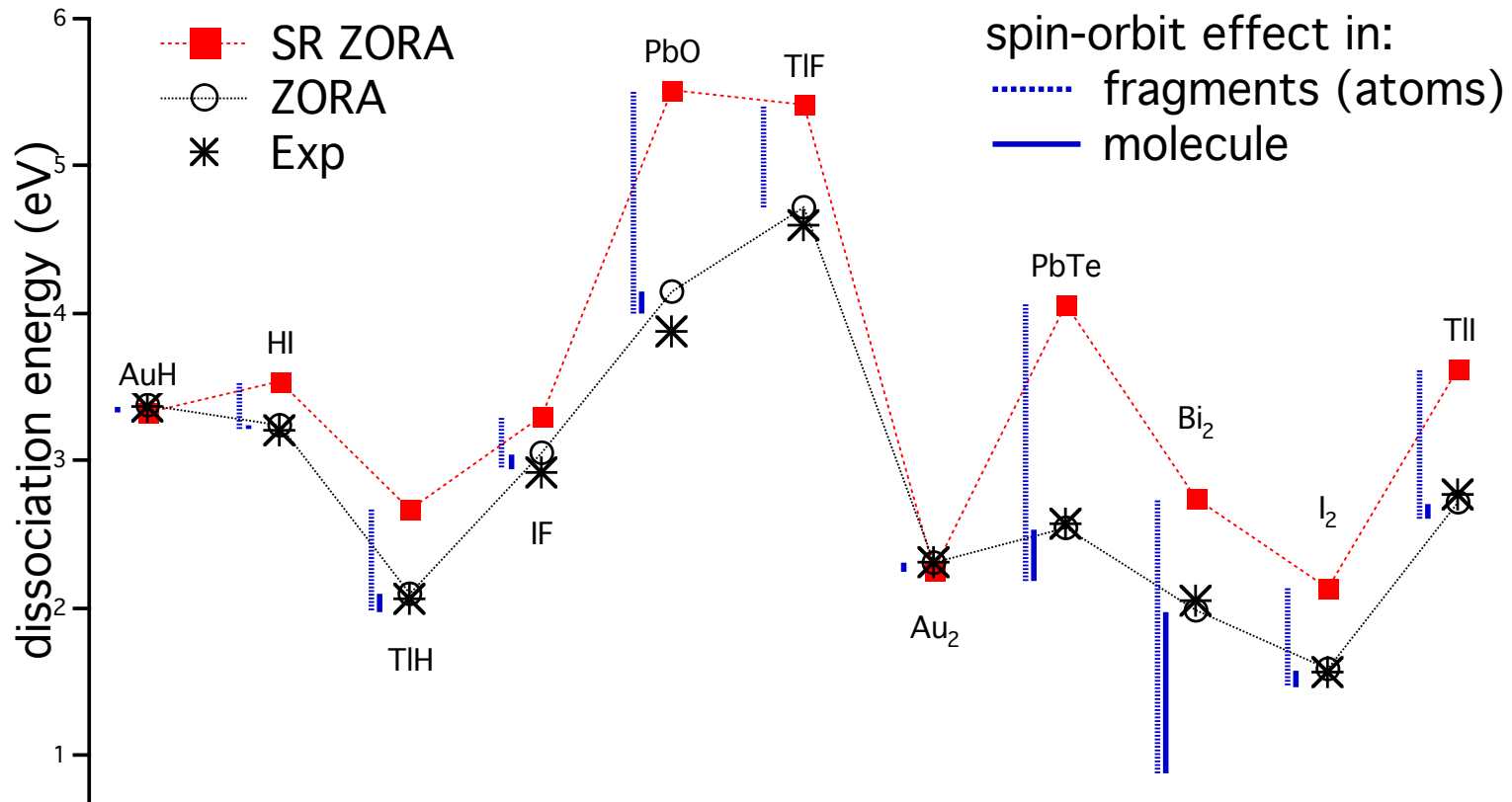
- Many low-lying electronic states



	Eu ³⁺	C ₆ H ₆
electrons	6 f-electrons	6 π -electrons
orbitals	7	6
energies < 0.125 Hartree	3 (with SOC: 8)	1
states < 0.125 Hartree	159 (with SOC:58)	1

- Lanthanides: 4f is shielded from environment
- Actinides: 5f can participate in chemical bonding
- SOC is very important in open shell molecules

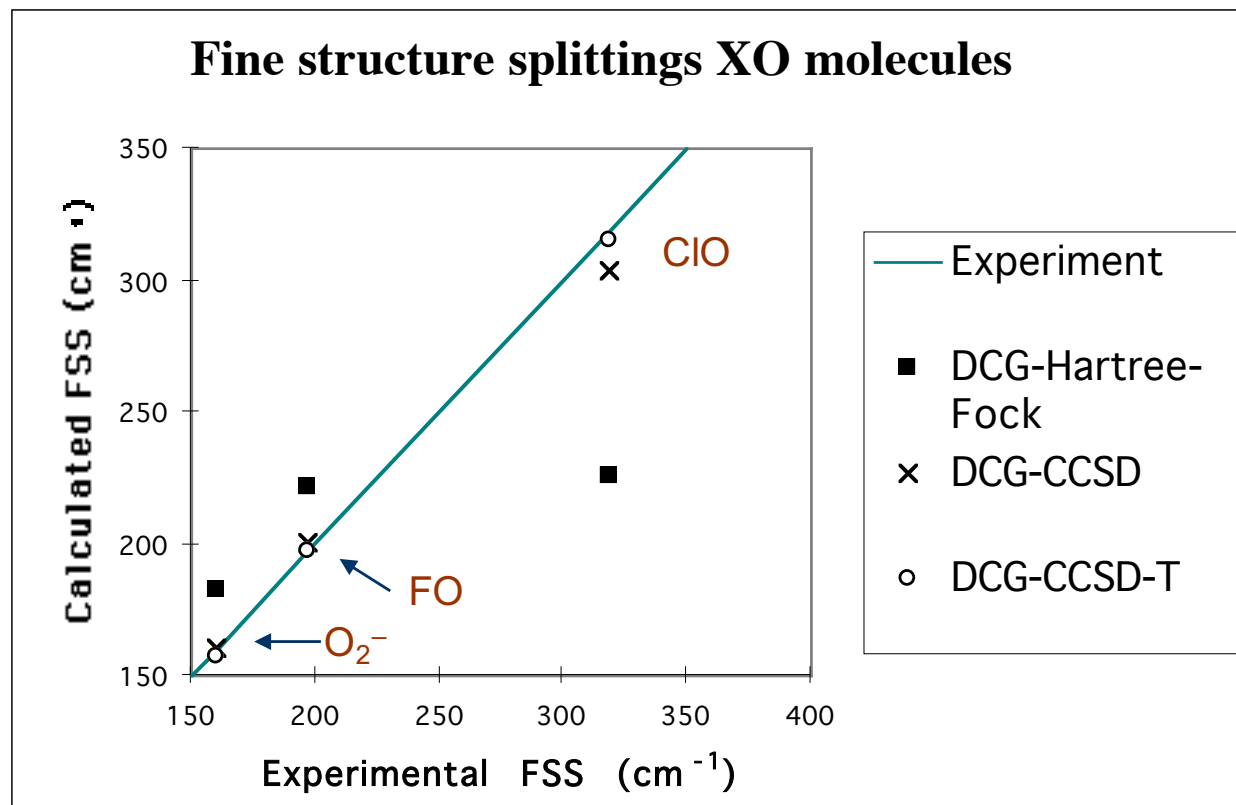
SOC in simple molecules



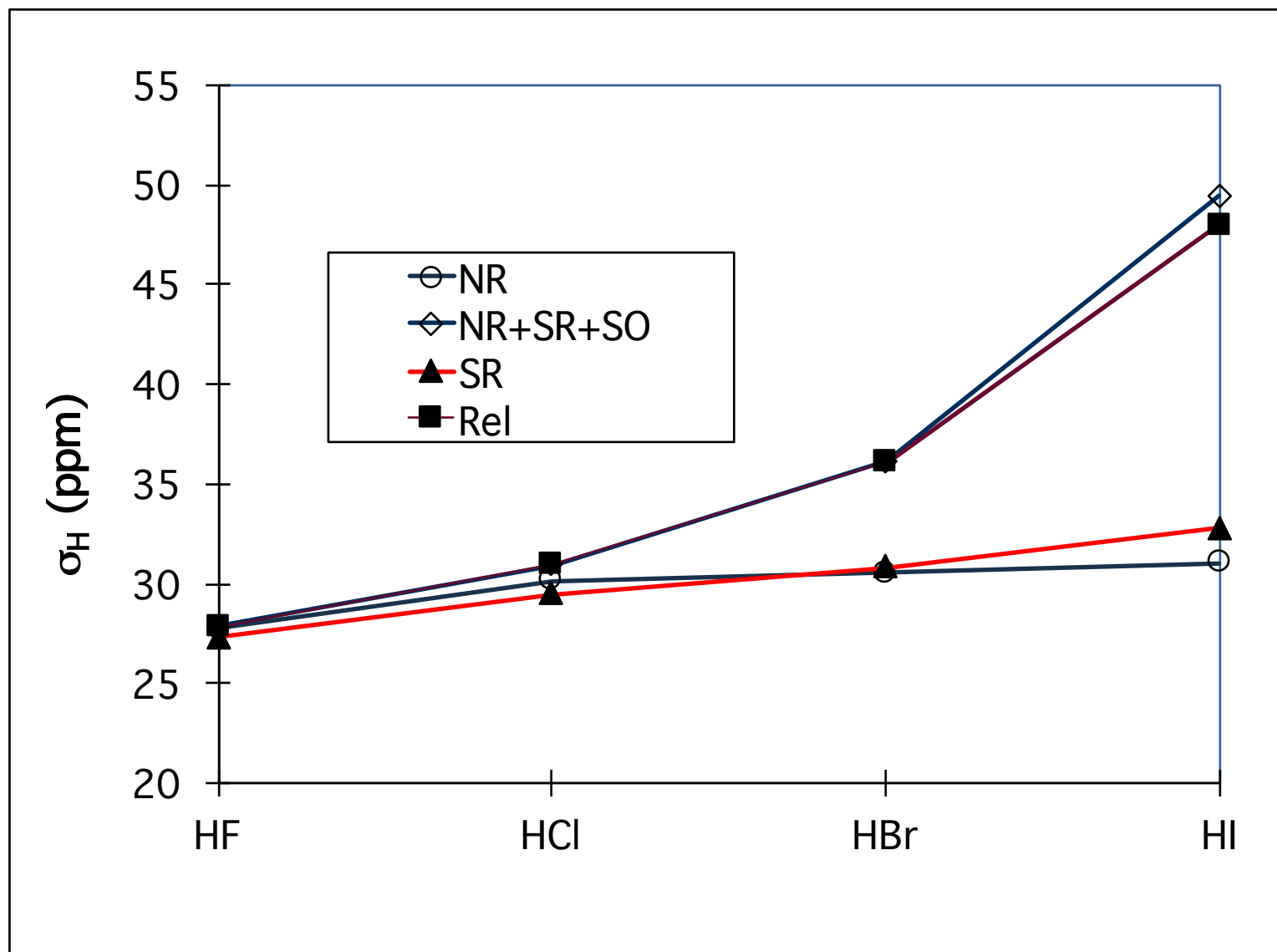
Make orbital diagram and identify possible SOC effects. Always include scalar effects.

Fine structure splitting in radicals

- Valence iso-electronic systems O_2^- , FO, ClO
- Breit interaction and correlation should be included for accurate results

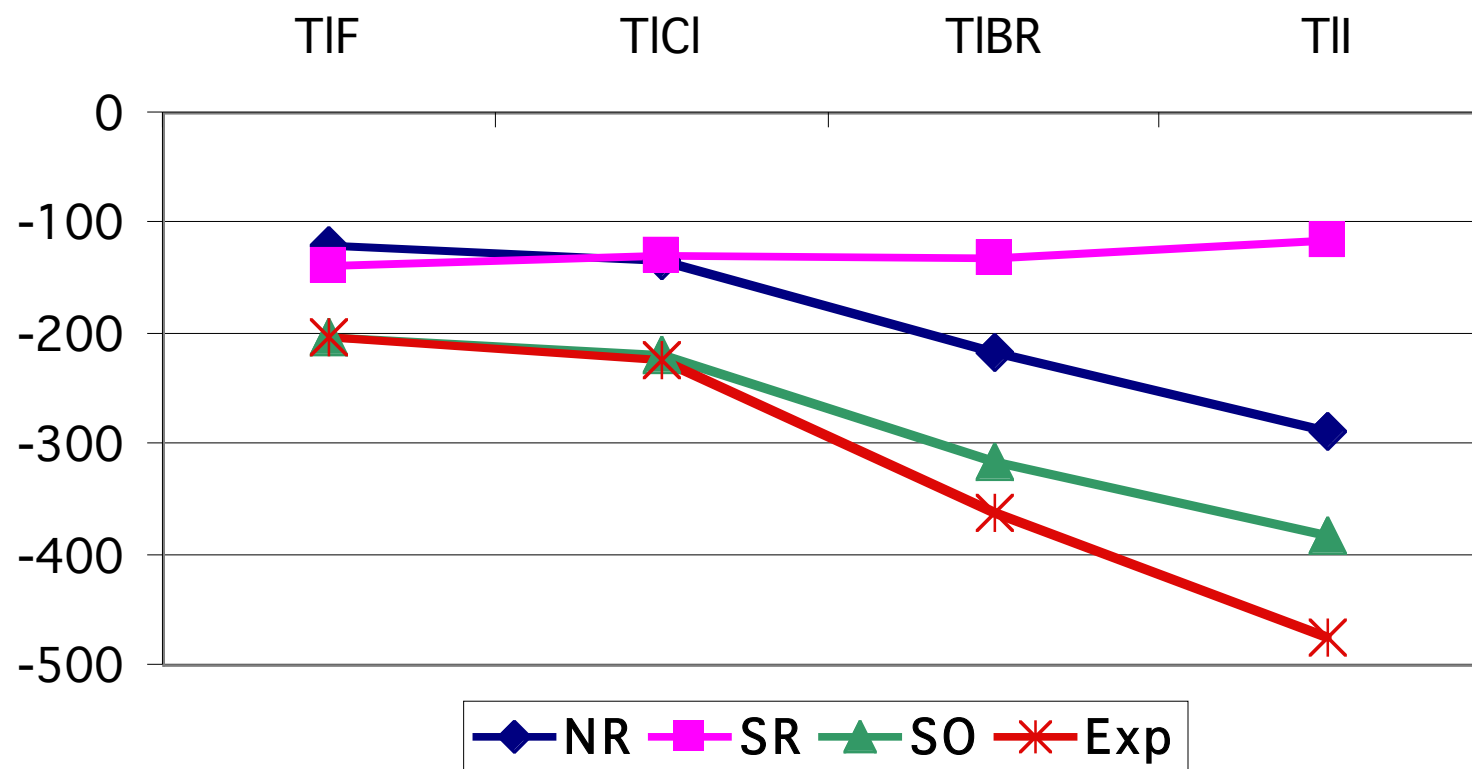


NMR: ^1H shielding trends



NMR spin-spin couplings

ZORA-DFT : J. Autschbach, T. Ziegler, J. Chem. Phys. 113 (2001) 9410.



Why are SOC effects so important for NMR

- Shielding and spin-spin couplings can be written as a second derivative of the energy relative to the internal/external magnetic fields

$$E_K^{(11)} = \frac{d^2 E}{d\mathbf{M}_K d\mathbf{B}} = -\mathbf{I}_3 + \sigma_K \quad \text{Shielding}$$

$$E_{KL}^{(02)} = \frac{d^2 E}{d\mathbf{M}_K d\mathbf{M}_L} = \frac{\mu_0}{4\pi} \frac{R_{KL}^2 \mathbf{I}_3 - 3\mathbf{R}_{KL} \mathbf{R}_{KL}^T}{R_{KL}^5} + \mathbf{K}_{KL} \quad \text{Indirect nuclear spin-spin coupling}$$

$$E_K^{(11)} = \langle 0 | H^{(11)} | 0 \rangle + \sum_S \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_0 - E_S} + \sum_S \sum_T \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{SO} | T \rangle \langle T | H^{(01)} | 0 \rangle}{(E_0 - E_S)(E_0 - E_T)}$$

$$E_{KL}^{(02)} = \langle 0 | H^{(02)} | 0 \rangle + \sum_S \frac{\langle 0 | H^{(01)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_0 - E_S} + \sum_T \sum_S \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | T \rangle \langle T | H^{SO} | 0 \rangle}{E_0 - E_T} + \sum_T \sum_S \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | T \rangle \langle T | H^{SO} | 0 \rangle}{E_0 - E_T}$$

- Can either be handled perturbatively (like in the above analysis) or in a more rigorous approach by including SOC from the start

Further reading

Relativistic Quantum Mechanics

- M. Reiher and A. Wolf, *Relativistic Quantum Chemistry*, (Wiley, 2009)
- K. G. Dyall and K. Faegri Jr, *Relativistic Quantum Chemistry*, (Oxford University Press, 2007)
- R. E. Moss, *Advanced molecular quantum mechanics*. (Chapman & Hall, London, 1973).
- P. Strange, *Relativistic Quantum Mechanics*. (Cambridge University Press, Cambridge, 1998).

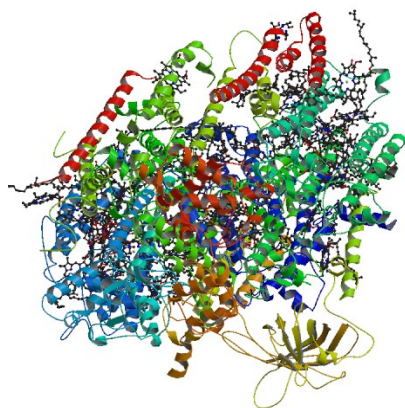
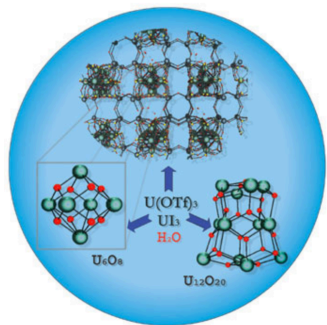
Relativistic Quantum Chemical methods

- *Relativistic Electronic Structure Theory - Part 1 : Fundamentals*, ed. P. Schwerdtfeger (Elsevier, Amsterdam, 2002).
- *Theoretical chemistry and physics of heavy and superheavy elements*, ed. U. Kaldor and S. Wilson (Kluwer, Dordrecht, 2003).

Applications

- *Relativistic Electronic Structure Theory - Part 2 : Applications*, ed. P. Schwerdtfeger (Elsevier, Amsterdam, 2004).

Subsystem approaches



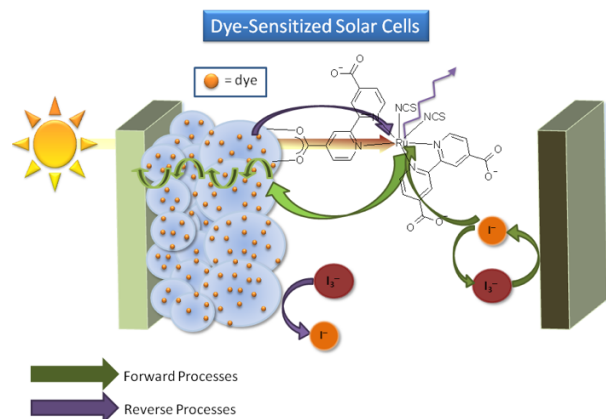
Common element in chemical drawings

- Complexity is reduced by **defining subunits**
- Function of subunits is explained **separately**

Models should reflect this way of thinking !

Requirements for models:

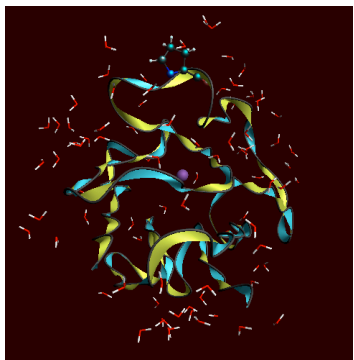
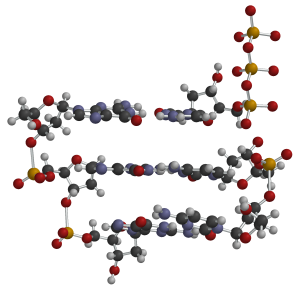
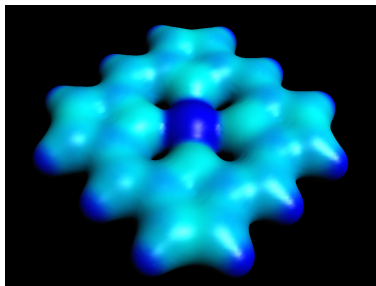
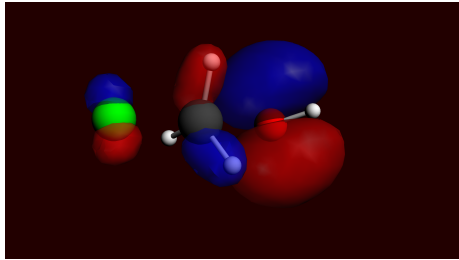
- Reliability: Model should give **correct answers**
- Mapping: Model should be **representative**
- Feasible: Model construction should be **easy**
- Speed: Calculations should be **fast**
- Interpretation: Model should provide **insights**



Criteria are often not fulfilled

- Reliable but too slow
- Fast but too inaccurate
- Impossible to use by non-specialists
- Calculations answer other questions than asked
- Relevant data from calculations is ignored

Toolbox for multiscale modeling



- (Relativistic) Wave Function Theory (WFT)
 - Precise, adjustable, description of electronic structure
 - Small systems (< 100 atoms).
 - No dynamics.
- Density Functional Theory (DFT)
 - Adequate but non-adjustable description of electronic structure
 - Medium size systems (< 1000 atoms)
 - AIMD on small systems, short times (ps)
- Density Functional Theory Tight-Binding (DFTB)
 - Simplest description of electronic structure
 - Large size systems (1000s atoms)
 - AIMD routinely possible
- Atomistic Modelling or Molecular Mechanics (MM)
 - No explicit description of electrons
 - Large systems (up to 1,000,000 atoms)
 - Molecular dynamics, medium times (ns)
- Coarse Grain Modeling
 - Fuse individual atoms to larger units
 - Mesoscopic systems (polymers, membranes, solids)
 - Dynamics for widely varying time scales
- Continuum Models
 - Atomic structure of matter suppressed
 - Macroscopic systems (hydro and aerodynamics)

$$\Psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N)$$



$$\rho_e(\mathbf{r})$$



$$q_i(\mathbf{R}, t)$$



$$M(\mathbf{R}, t)$$



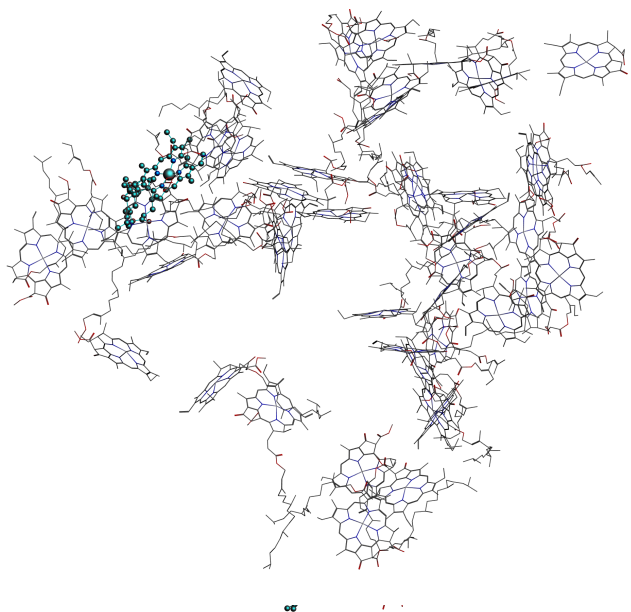
$$\rho(\mathbf{R}, t)$$

Subsystem DFT

Partitioning of density by **subsystems**

$$\rho(\mathbf{r}) = \rho^I(\mathbf{r}) + \sum_{J \neq I}^{\text{subsystems}} \rho^J(\mathbf{r})$$

$$E[\rho^I + \rho^{II}] = E^I[\rho^I] + E^{\text{int}}[\rho^I, \rho^{II}] + E^{II}[\rho^{II}]$$



- Focus on density of subsystem(s) of interest
 - Optimize only active part of the density
 - Tune calculation for each subsystem
- Interactions between adjacent subsystems
 - Use 3-FDE for covalent bonds
 - Use FDE for H- and non-bonded interactions
- Polarization and charge transfer
 - Relaxation (“freeze & thaw”) to correct density close to the active center
 - Charge-transfer under development
- Response Theory
 - Provides access to spectroscopy
- WFT in DFT
 - Communication via density, not via orbitals
 - Full CI provides exact density
 - Approximate WFT provides approx. density

G. Senatore and K. R. Subbaswamy, Phys. Rev. B **34** (1986) 5754. P. Cortona, Phys. Rev. B **44** (1991) 8454.

T. A. Wesolowski and A. Warshel, J. Phys. Chem. **97** (1993) 8050-8053.

N. Govind, Y. A. Wang, A. J. R. da Silva and E. A. Carter, Chem. Phys. Lett., 1998, 295, 129.

sDFT energy

$$E^{\text{tot}}[\rho_{\text{tot}}] = E^{\text{I}}[\rho_{\text{I}}] + E^{\text{int}}[\rho_{\text{I}}, \rho_{\text{II}}] + E^{\text{II}}[\rho_{\text{II}}]$$

- Electrostatic interaction: Exact

$$E_{\text{el-st}}^{\text{int}}[\rho_{\text{I}}, \rho_{\text{II}}] = E_{\text{el-st}}[\rho_{\text{tot}}] - E_{\text{el-st}}[\rho_{\text{I}}] - E_{\text{el-st}}[\rho_{\text{II}}]$$

- Exchange-correlation energy: Functionals used in KS-DFT

$$E_{\text{xc}}^{\text{int}}[\rho_{\text{I}}, \rho_{\text{II}}] = E_{\text{xc}}[\rho_{\text{tot}}] - E_{\text{xc}}[\rho_{\text{I}}] - E_{\text{xc}}[\rho_{\text{II}}]$$

- Kinetic energy: **Non-additive** part of K. E. Density Functional

$$T_{\text{s}}^{\text{int}}[\rho_{\text{I}}, \rho_{\text{II}}] = T_{\text{s}}[\rho_{\text{tot}}] - T_{\text{s}}[\rho_{\text{I}}] - T_{\text{s}}[\rho_{\text{II}}]$$

Embedding potential (FDE)

$$V^{emb}[\rho_I, \rho_{II}] = \left. \frac{\delta E[\rho]}{\delta \rho} \right|_{\rho=\rho_{tot}=\rho_I+\rho_{II}} - \left. \frac{\delta E[\rho]}{\delta \rho} \right|_{\rho=\rho_I}$$

$$V^{emb} = V^{emb:el.st.} + V^{emb:xc} + V^{emb:kin}$$

- “Classical” contribution: screened nuclear potential

$$V^{emb:el.st.}(\mathbf{r}) = \sum_A -\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + \int \frac{\rho_{II}(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 \quad \leftarrow \text{Standard, long range}$$

- XC potential: difference between full and sub system

$$V^{emb:xc}(\mathbf{r}) = V^{xc}[\rho_{tot}, \mathbf{r}] - V^{xc}[\rho_I, \mathbf{r}] \quad \leftarrow \text{Standard, short range}$$

- Kinetic potential: difference between full and sub system

$$V^{emb:kin}(\mathbf{r}) = \left. \frac{\delta T_S[\rho]}{\delta \rho} \right|_{\rho=\rho_{tot}} - \left. \frac{\delta T_S[\rho]}{\delta \rho} \right|_{\rho=\rho_I} \quad \leftarrow \text{KEDF, short range}$$

Embedding kernel

$$f^{emb}[\rho_I, \rho_{II}] = \left. \frac{\delta^2 E[\rho]}{\delta \rho^2} \right|_{\rho=\rho_{tot}=\rho_I+\rho_{II}} - \left. \frac{\delta^2 E[\rho]}{\delta \rho^2} \right|_{\rho=\rho_I}$$

Uncoupled formalism

- “Classical” contribution: Coulomb interaction

$$f^{el.st.}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad f^{emb:el.st.}(\mathbf{r}, \mathbf{r}') = 0 \quad \leftarrow \text{No changes necessary}$$

- XC kernel: adjust for difference between full and sub system

$$f^{emb:xc}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta^2 E_{xc}[\rho]}{\delta \rho^2} \right|_{\rho=\rho_{tot}} - \left. \frac{\delta^2 E_{xc}[\rho]}{\delta \rho^2} \right|_{\rho=\rho_I} \quad \leftarrow \text{Change input density, density variation only in I}$$

- Kinetic kernel: extra ingredient in TD-DFT

$$f^{emb:kin}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta^2 T_s[\rho]}{\delta \rho^2} \right|_{\rho=\rho_{tot}} - \left. \frac{\delta^2 T_s[\rho]}{\delta \rho^2} \right|_{\rho=\rho_I} \quad \leftarrow \text{Like XC term, can also be combined}$$

Magnetic fields in FDE: NMR shieldings

$$E[\rho, \mathbf{j}_p] = E[\rho^I + \rho^{II}, \mathbf{j}_p^I + \mathbf{j}_p^{II}] = E^I[\rho^I, \mathbf{j}_p^I] + E^{II}[\rho^{II}, \mathbf{j}_p^{II}] + E^{\text{int}}[\rho^I + \rho^{II}, \mathbf{j}_p^I + \mathbf{j}_p^{II}]$$

$$E^{\text{int}} = E^{\text{int:el.st.}} + E^{\text{int:xc}} + E^{\text{int:kin}}$$

- Electrostatic interaction: Does not depend on the current
- XC contribution: Current dependency is usually ignored anyway

$$E^{\text{xc}}[\rho, \mathbf{j}_p] \approx E^{\text{xc}}[\rho] \Rightarrow E^{\text{int,xc}}[\rho^I, \rho^{II}, \mathbf{j}_p^I, \mathbf{j}_p^{II}] \approx E^{\text{int,xc}}[\rho^I, \rho^{II}]$$

- Kinetic contribution: Use the same approximation

$$E^{\text{int,kin}}[\rho^I, \rho^{II}, \mathbf{j}_p^I, \mathbf{j}_p^{II}] \approx E^{\text{int,kin}}[\rho^I, \rho^{II}]$$

- Resulting formalism
 - Decoupling of induced currents in the subsystems
 - Chemical shielding reduces to a sum of subsystem contributions
 - Shielding calculation is similar to NMR + NICS evaluation

Magnetic fields in FDE: NMR couplings

$$\begin{aligned} E[\rho, \mathbf{j}_p, \mathbf{m}] &= E[\rho^I + \rho^{II}, \mathbf{j}_p^I + \mathbf{j}_p^{II}, \mathbf{m}^I + \mathbf{m}^{II}] \\ &= E^I[\rho^I, \mathbf{j}_p^I, \mathbf{m}^I] + E^{II}[\rho^{II}, \mathbf{j}_p^{II}, \mathbf{m}^{II}] + E^{\text{int}}[\rho^I + \rho^{II}, \mathbf{j}_p^I + \mathbf{j}_p^{II}, \mathbf{m}^I + \mathbf{m}^{II}] \end{aligned}$$

$$E^{\text{int}} = E^{\text{int:el.st.}} + E^{\text{int:xc}} + E^{\text{int:kin}}$$

- Electrostatic interaction: not affected
- XC and Kinetic contributions: write in spin-density form

$$E^{\text{int,xc}}[\rho^I, \rho^{II}, \mathbf{m}^I, \mathbf{m}^{II}] \approx E^{\text{int,xc}}[\rho_{\uparrow}^I, \rho_{\downarrow}^I, \rho_{\uparrow}^{II}, \rho_{\downarrow}^{II}]$$

- Use collinear or non-collinear approach similar to XC evaluation with spin-polarization
- Resulting formalism
 - Consider spin-spin couplings *within* a subsystem
 - Neglect induced currents in other subsystems
 - Account for indirect effect of other subsystem in kernel
 - Cost of NMR calculation does only depend on active subsystem

sDFT: fundamental aspects

- Arbitrariness of density partitioning

- Infinite number of **valid ways** to split the density
- Infinite number of **invalid ways** to split the density
- Partition DFT: allow for **fractional occupation** to equilibrate chemical potentials

P. Elliott, M.H. Cohen, A. Wasserman, K. Burke, JCTC **5** (2009) 827–833.

- Freeze and Thaw

- **Only needed for approximate** (non-universal) functionals
- Does in practice improve results

T. Wesolowski, J. Weber, Chem Phys Lett. **248** (1996) 71–76.

O. Gritsenko, in Recent Advances in Orbital-Free Density Functional Theory, ed. A. Wang and T. A. Wesolowski, (World Scientific, Singapore, 2013).

- External Orthogonality

- In principle **not necessary to have orbitals** for the frozen system (FDE)
- Orthogonality can be enforced by **projectors**: brings theory **outside domain** of FDE

F.R. Manby, M. Stella, J.D. Goodpaster, T.F. Miller III, J Chem Theory Comput. **8** (2012) 2564–2568.

Y.G. Khait, M.R. Hoffmann, Ann. Rep. in Comp. Chem. **8** (2012) 53-70.

- Excited states / Response

- **State-specific** environment polarization or **frequency-dependent response**
- Uncoupled: Localized excitations perturbed by environment
- Coupled: Delocalization possible, but no (or limited) charge-transfer possibilities

C. Daday, C. König, O. Valsson, J. Neugebauer, C. Filippi, J Chem Theory Comput. **9** (2013) 2355–2367.

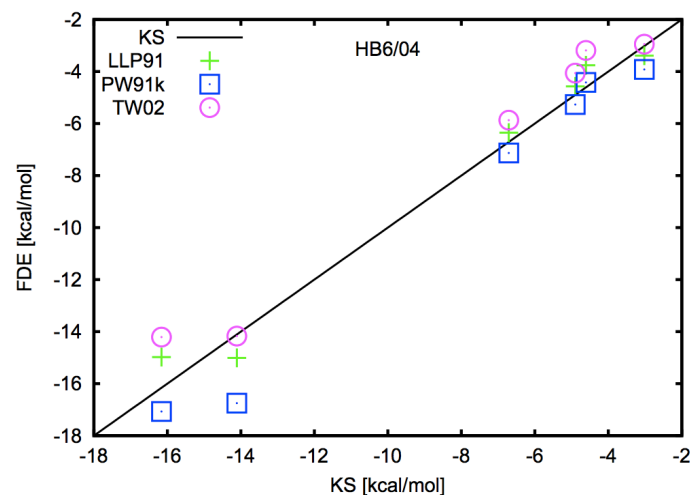
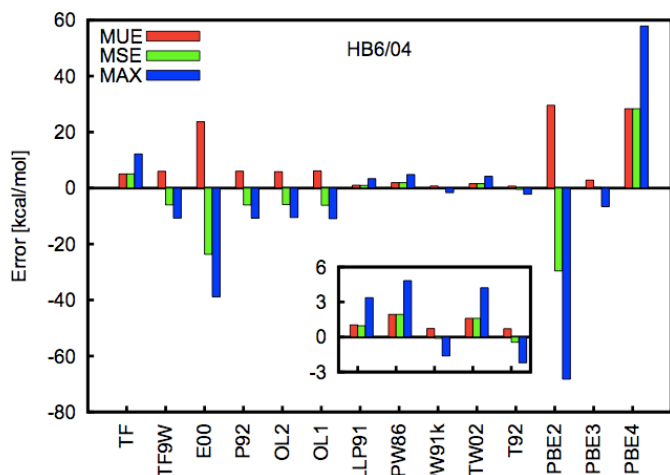
S. Höfener, A.S.P. Gomes, L. Visscher, J Chem. Phys. **136** (2012) 044104.

sDFT: practical aspects

- Basis set expansion
 - Only economical if basis set is restricted to the monomer (FDE(m))
 - Conventional basis sets can be used in unmodified form
- Self-consistency
 - Full self consistency for freeze-thaw is usually not pursued
 - Freeze-thaw (“polarization”) iterations are often done with DFT
- Implementation
 - Calculate Coulomb potential for frozen density on a numerical integration grid appropriate for the active density
 - Calculate non-additive kinetic energy contributions on the same grid, preferably by a dedicated library
 - Use of a scripting framework (pyADF) is helpful to automatize sampling and partitioning in biomolecular systems

sDFT: Interaction energies

H-Bonded systems

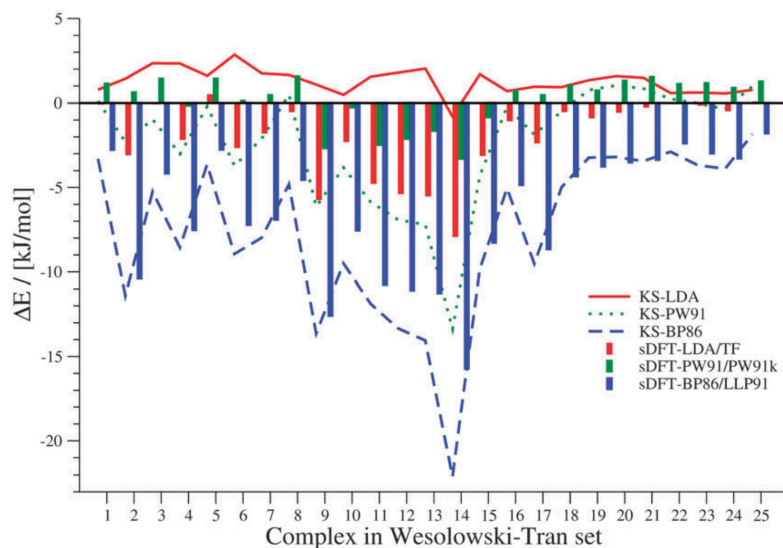


- ADF implementation
 - Slater-type orbitals
 - Coulomb interaction via fitted density
- Tests with available functionals
 - Truhlers¹ test sets
 - Kohn-Sham energy as reference value (judge quality of T_s)
- Monomer/supermolecular expansion
 - Supermolecular (s): benchmark results
 - Monomer (m): practical application
- Freeze-Thaw optimization
 - SCF convergence
 - FT convergence

1) Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. 1 (3), 415–432 (2005). Y. Zhao and D. G. Truhlar, J. Phys. Chem. A. 109(25), 5656–5667 (2005).

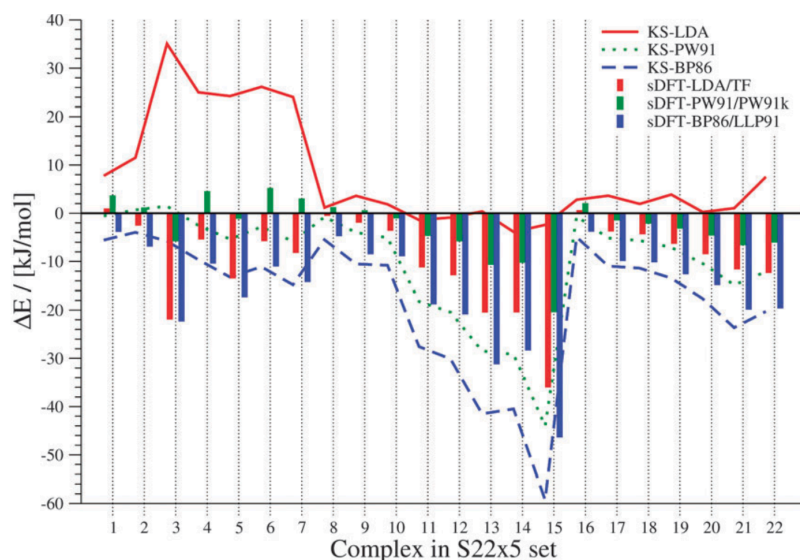
sDFT: Better than DFT ?

Wesolowski-Tran test set: weak interactions



- sDFT-PW91/PW91K functional has best overall performance
- Underbinding for sDFT-LDA/TF whereas DFT-LDA overbinds
- BP86/LLP91 most consistent with DFT-BP86 results

Hobza: S22 test set

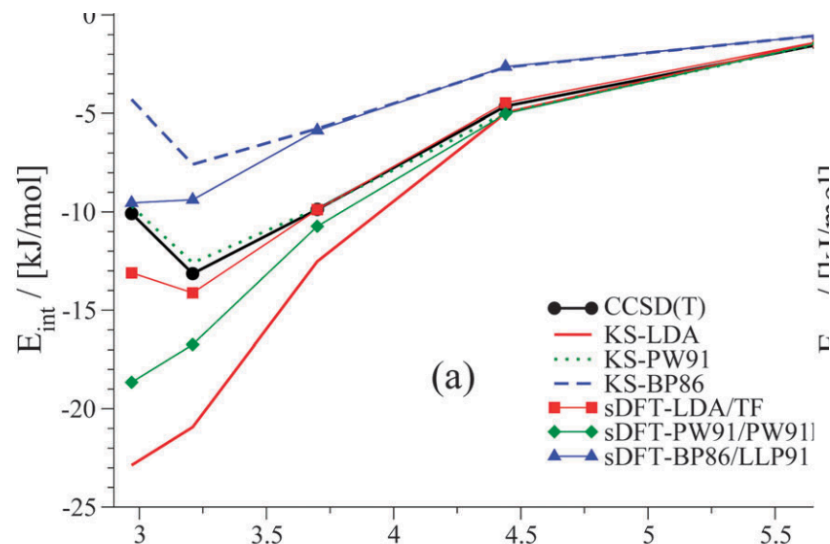


- Largely confirms earlier benchmarks for sDFT

D. Schlüns, K. Klahr, C. Mück-Lichtenfeld, LV, J. Neugebauer, Phys. Chem. Chem. Phys. **17** (2015) 14323–14341.

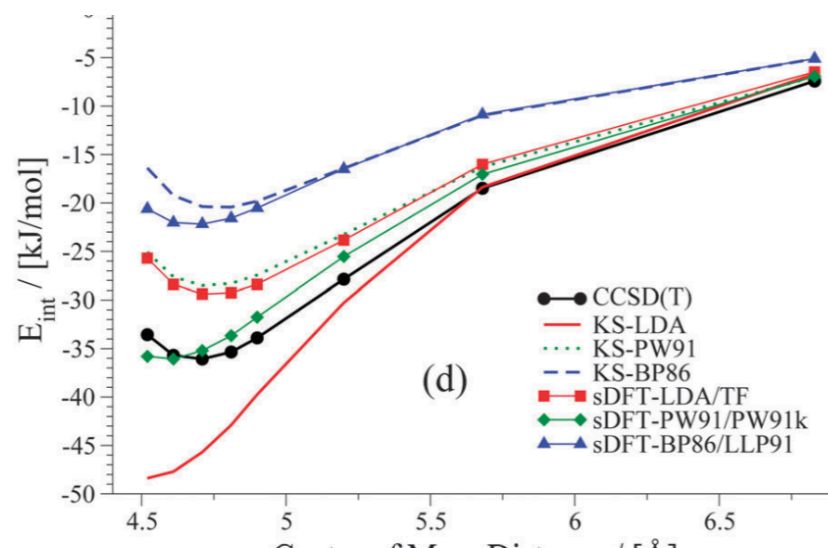
sDFT: Better than DFT ?

S22x5: Ammonia dimer



- sDFT-PW91/PW91K is quite good at equilibrium but too attractive at short distance
- Can possibly be improved by also including empirical repulsive correction (van-der-Waals correction with both dispersion and repulsion)

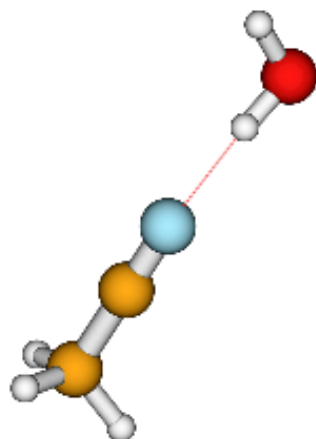
S66x8: Peptide dimer



- Not yet suitable as black-box method for geometry optimization

D. Schlüns, K. Klahr, C. Mück-Lichtenfeld, LV, J. Neugebauer, Phys. Chem. Chem. Phys. **17** (2015) 14323–14341.

FDE: NMR shieldings



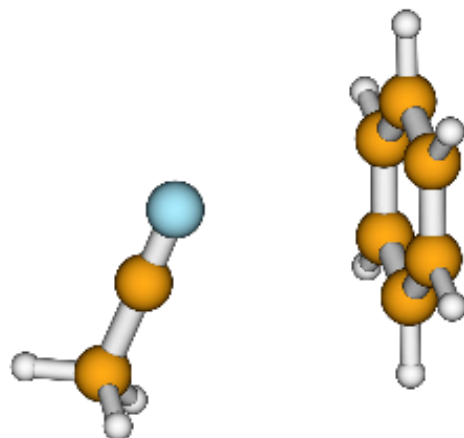
Solvent shifts of nitrogen shielding

	BP86	SAOP
supermolecule	15.05	16.99
FDE($m,0$)	12.04	11.89
FDE($m,1$)	16.41	15.63
FDE(m,∞)	16.64	15.79
FDE(s,∞)	16.44	15.40

- simplest approximation FDE($m,0$) qualitatively correct
- one freeze-and-thaw cycle is sufficient
- inclusion of basis functions of the frozen system is not needed
- accuracy of FDE ca. 2 ppm (N shielding scale: 600 ppm)

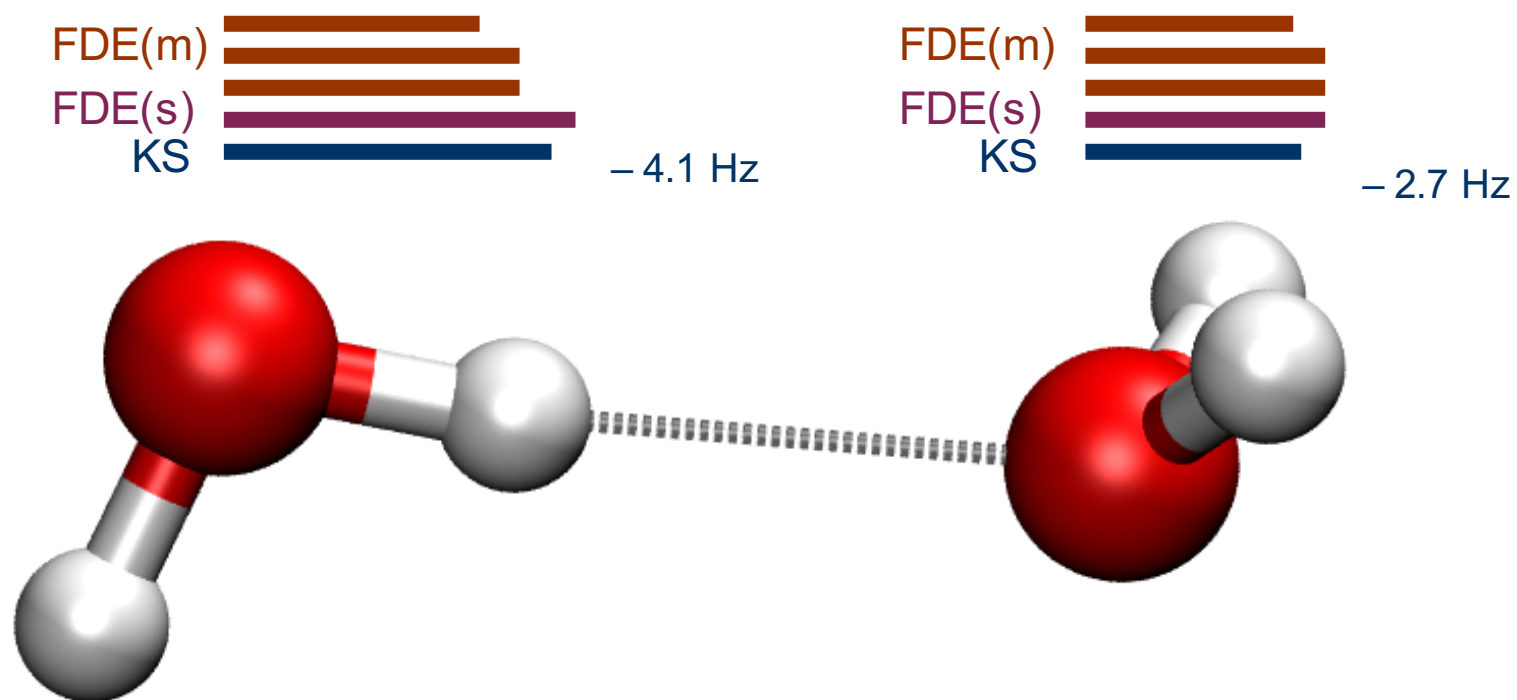
FDE: NMR shieldings

Solvent shifts of nitrogen shielding



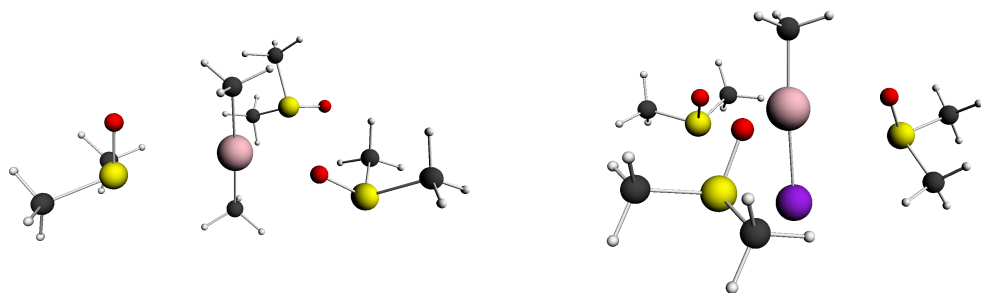
	BP86	SAOP
supermolecule	−0.29	2.42
FDE($m,0$)	−2.53	−2.10
FDE($m,1$)	−1.20	−0.95
FDE(m,∞)	−1.18	−0.97
FDE(s,∞)	−1.04	−1.10
env(m,∞)	+1.37	+1.39
FDE+env(m,∞)	0.19	0.42
FDE+env(s,∞)	0.31	0.24

- contribution of the frozen subsystem significant (ca. 1.4 ppm)

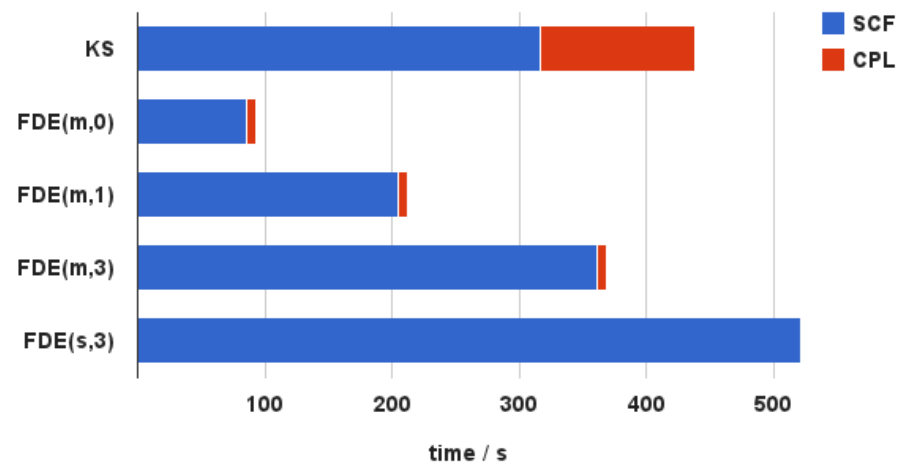
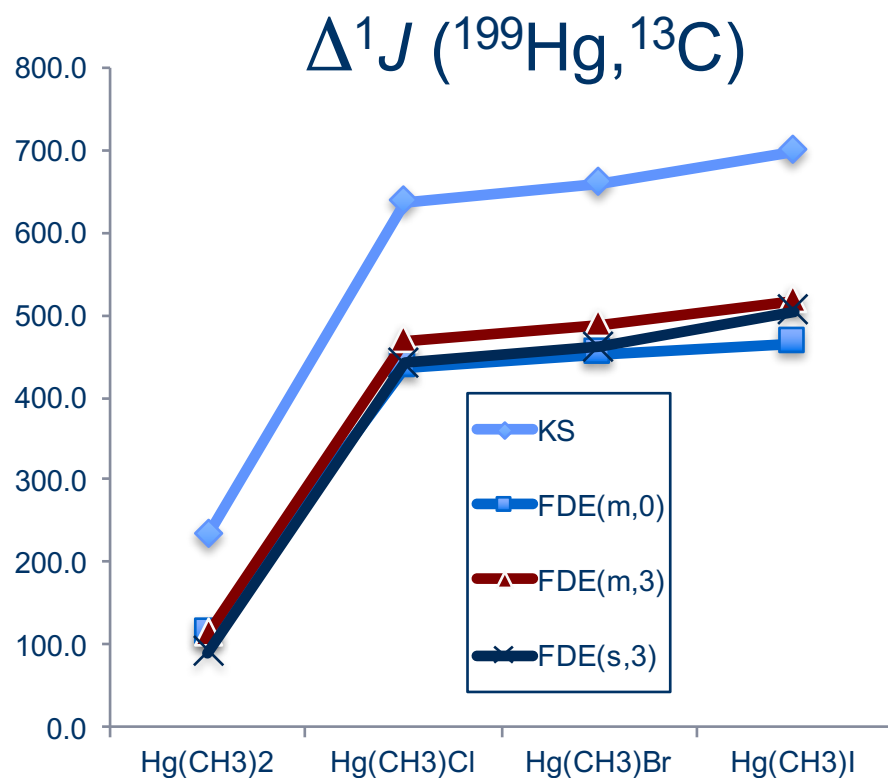
$\Delta^1J(\text{O},\text{H})$ $\Delta^1J(\text{O},\text{H})$ 

A.W. Götz, J. Autschbach, LV, J Chem Phys. **140** (2014) 104107.

Mercury complexes in DMSO



- Environment shift of same magnitude as coupling itself
- Fast convergence with FT-cycles
- Qualitative agreement
- Efficient: FDE(m)

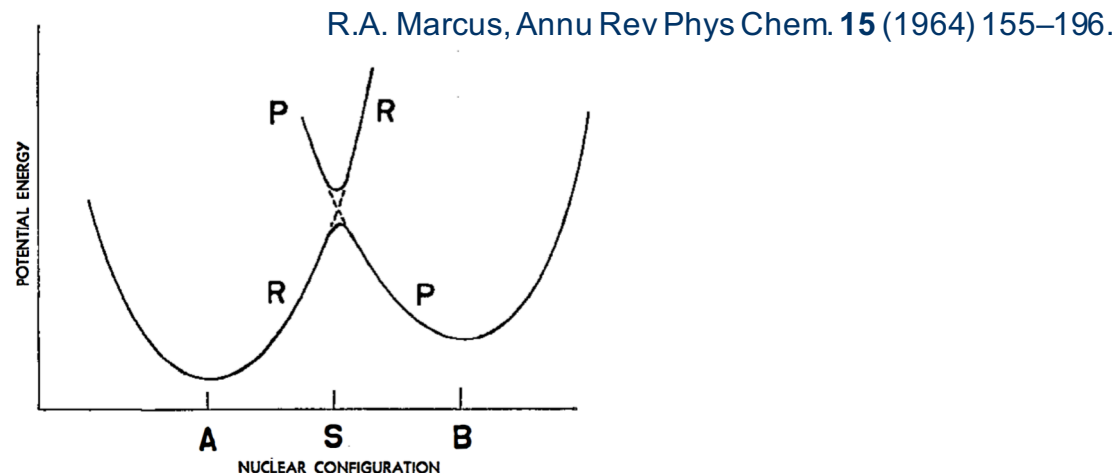


sDFT: Electron Transfer

Hole transport



Electron transport



- sDFT partitioning can be used to define (quasi)-diabatic states
 - $\Phi_A^{D^+ A} = \mathcal{A}(\|\phi_{D^+}^1 \dots \phi_{D^+}^{N_D-1}\| \otimes \|\phi_A^1 \dots \phi_A^{N_A}\|)$
 - $\Phi_B^{DA^+} = \mathcal{A}(\|\phi_D^1 \dots \phi_D^{N_D}\| \otimes \|\phi_{A^+}^1 \dots \phi_{A^+}^{N_A-1}\|)$
 - Four sets of non-orthogonal orbitals obtained from two freeze-thaw calculations
- $$H_{AB} = \langle \Phi_A | \hat{H} | \Phi_B \rangle = E[\rho^{(AB)}] S_{AB}$$
- With further approximation (no polarization) Frozen Orbital DFT (**FODFT**)

M. Pavanello, J. Neugebauer, J Chem Phys. **135** (2011) 234103–14; M. Pavanello, T. Van Voorhis, LV, J. Neugebauer, J Chem Phys. **138** (2013) 054101–13.

FDE-ET / FODFT: Porphyrin dimers

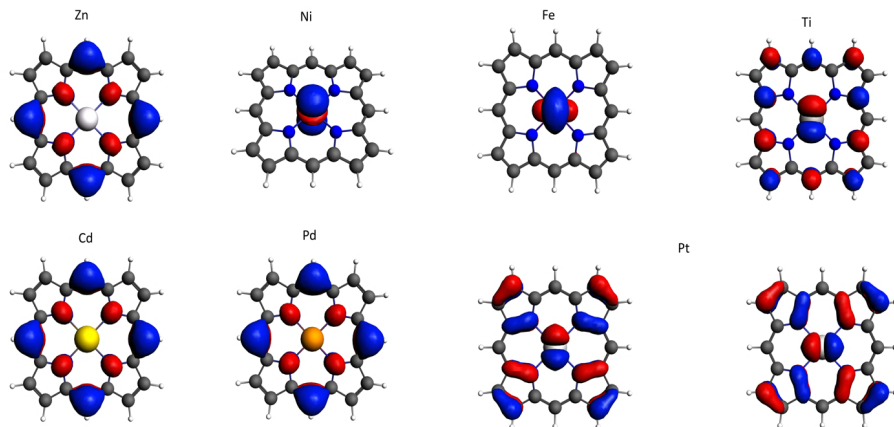


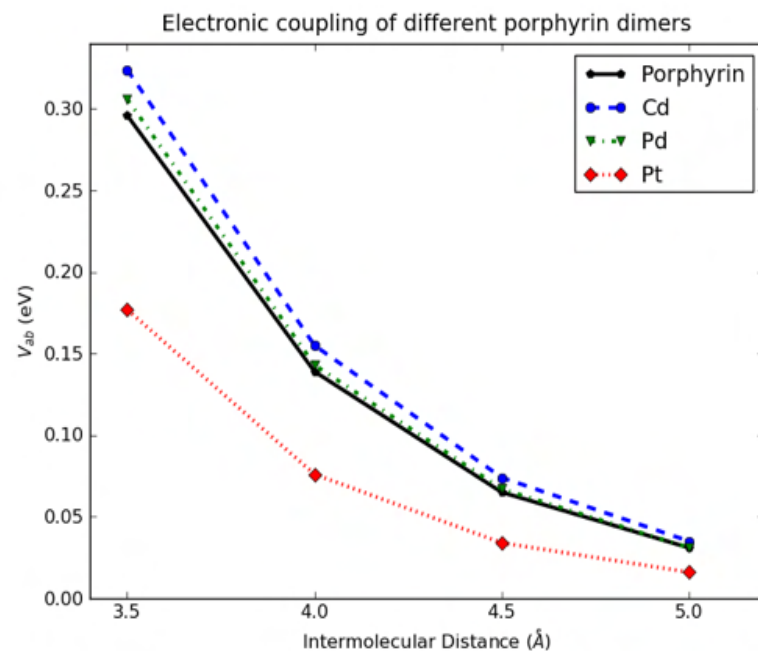
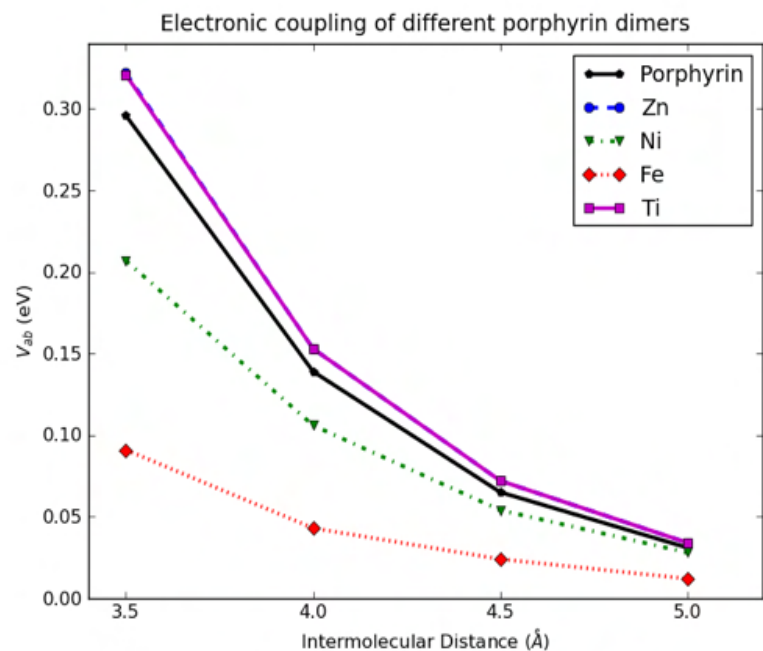
Figure 5. HOMO orbitals for a series of metalated porphyrin rings. The orbitals are obtained from a single point DFT calculation on the isolated structure, using ADF. For the case of Pt, the HOMO orbital is two-fold degenerated, and both orbitals are given.

Polarization effects are modest
(~20% for coupling parameter)

Consideration of overlap sufficient to
explain trends

Choice of metal is crucial for transfer
properties

F. Hernández-Fernández, M. Pavanello, LV, PCCP, online (2016)



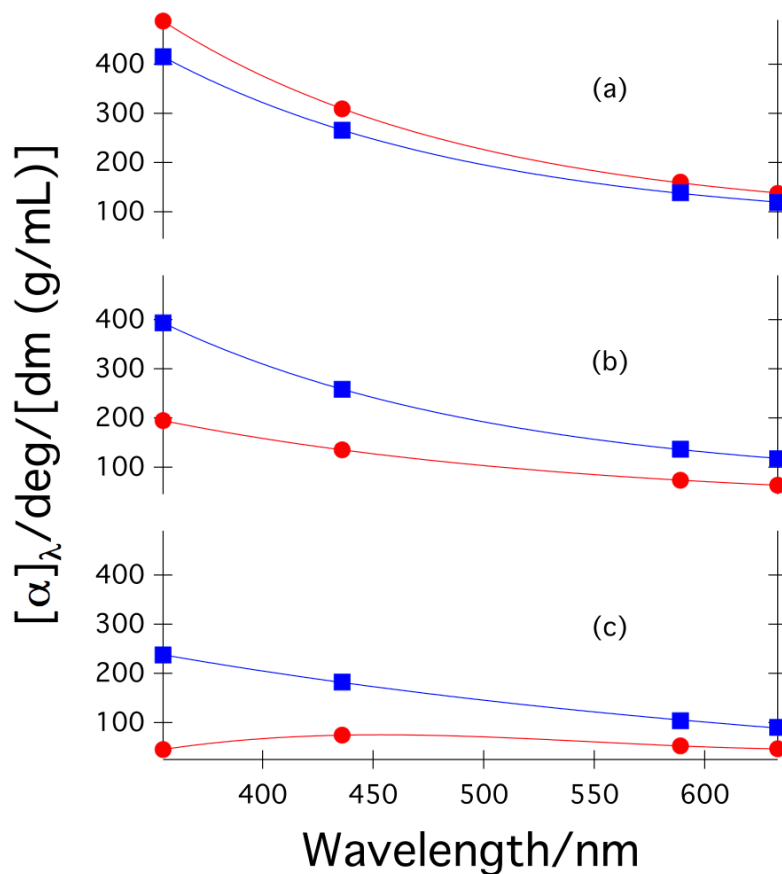
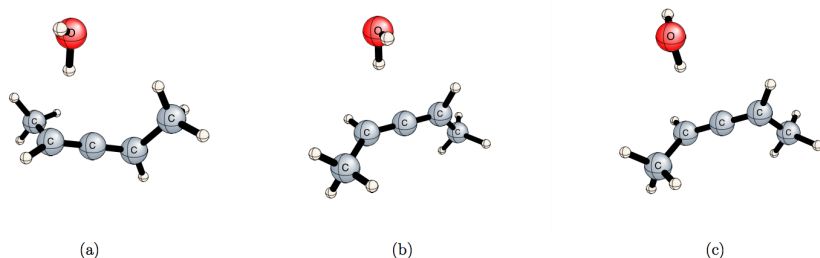
Chiroptical properties with FDE: ORD and ECD

- Motivation
 - Investigate solvent effect on ORD of methyloxirane
 - M. C. Tam, N. J. Russ, T. D. Crawford, J Chem. Phys. **121** (2004) 3550.
 - FDE should capture “cavity” effect of surrounding solvent
 - Solvent excitations in ECD can be studied via subsystem TD-DFT
 - J. Neugebauer, J. Chem. Phys. **126** (2007) 134116.
- Pure embedding application: environment frozen
- Simplest WFT-in-DFT formalism: **fixed embedding potential** made after DFT freeze-thaw iterations
- Communicate numerical representation of embedding potential

$$V_{pq}^{emb} = \int \chi_p(\mathbf{r}) V^{emb}(\mathbf{r}) \chi_q(\mathbf{r}) d\mathbf{r} \approx \sum_g w_g V^{emb}(\mathbf{r}_g) \chi_p(\mathbf{r}_g) \chi_q(\mathbf{r}_g)$$

- Study also other simple systems: dimethylallene

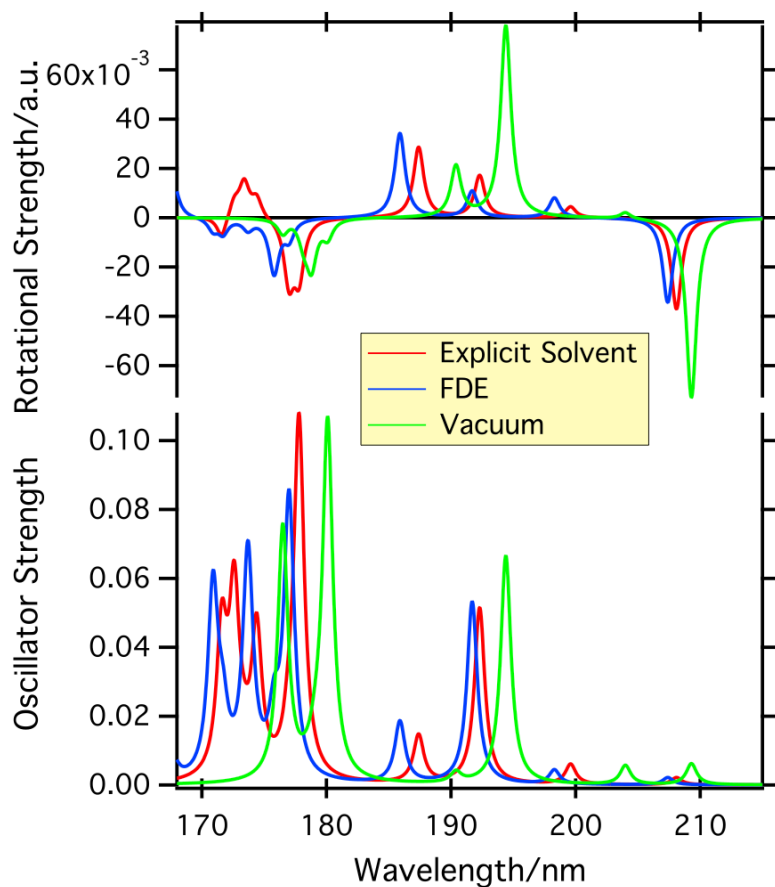
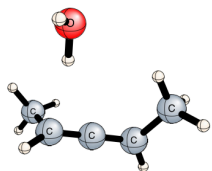
ORD: Dimethylallene



- Different microsolvated environments (1, 2, 3 waters)
- ADF: PBE, TZP basis
- PSI4: CC2, aug-cc-pVDZ
- FDE gives **too small shift** relative to vacuum calculation
- In some cases: qualitatively wrong description
- Similar picture for methyloxirane
- **What is missing ?**

T.D. Crawford, A. Kumar, K.P. Hannon, S. Höfener, LV, J Chem Theory Comput. (2016) doi:10.1021/acs.jctc.5b00845.

Dimethylallene analysis



- Calculate UV and ECD spectrum to understand errors
- FDE does shift peaks in the correct direction, reduces magnitude of rotational strengths
- Some shifts are too large, but not dramatic
- Slow convergence in sum over states expression, higher (charge-transfer) excitations to blame

T.D. Crawford, A. Kumar, K.P. Hannon, S. Höfener, LV, J Chem Theory Comput. (2016) doi:10.1021/acs.jctc.5b00845.

sDFT and Wave Function Theory

Consider the embedding potential defined in FDE

$$\begin{aligned} v_I^{emb}[\rho_I; \rho_{II}] &= v_s[\rho_{tot}] - v_s[\rho_I] + \left. \frac{\delta T_s}{\delta \rho} \right|_{\rho=\rho_{tot}} - \left. \frac{\delta T_s}{\delta \rho} \right|_{\rho=\rho_I} \\ &= v_s[\rho_{tot}] - v_s[\rho_I] + v^{na-kin}[\rho_I; \rho_{II}] \end{aligned}$$

Minimization of the energy of a full CI wave function for this **local potential**

$$E_I^{FCI,emb} = \min_{\Psi_I} \langle \Psi_I | \sum_i v_I^{ext+emb}(\mathbf{r}_i) + T + V^{ee} | \Psi_I \rangle$$

is equivalent to minimizing the Hohenberg-Kohn energy of the embedded system

$$E_I^{HK,emb}[\rho_I] = \min_{\rho_I} \left\{ F[\rho_I] + \int d\mathbf{r} v_I^{ext+emb}(\mathbf{r}) \rho_I(\mathbf{r}) \right\}$$

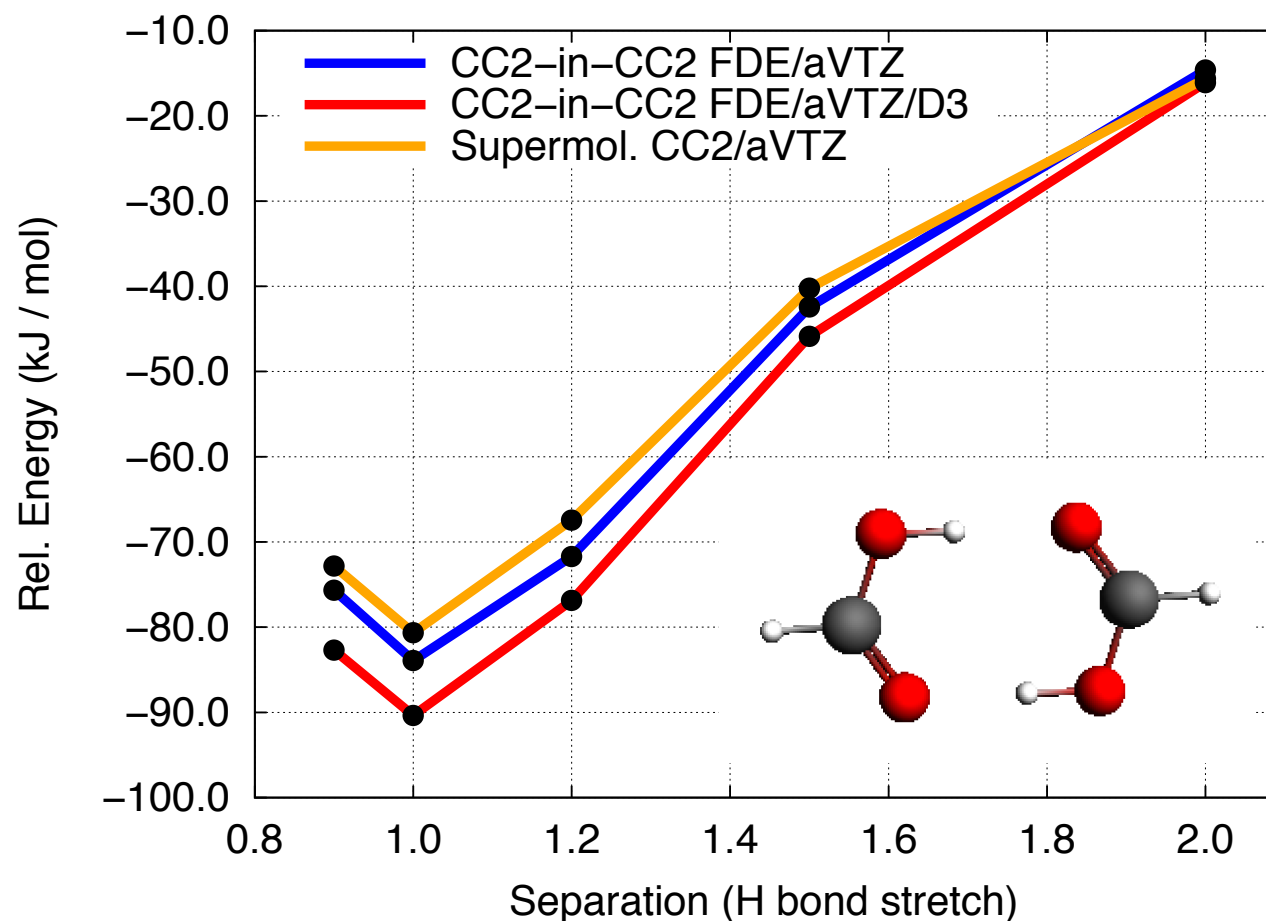
$$\text{because } F(\rho_I) = \min_{\Psi_I \rightarrow \rho_I} \langle \Psi_I | T + V^{ee} | \Psi_I \rangle \quad (\text{Levy constrained search})$$

Conditions to be fulfilled

$$\rho_{II}(\mathbf{r}) \leq \rho_{tot}(\mathbf{r}) \quad \rho_I \text{ should be } v\text{-representable}$$

References: N. Govind, Y. A. Wang, A. J. R. da Silva and E. A. Carter, Chem. Phys. Lett., 1998, 295, 129–134.
T. A. Wesolowski, PRA 012504 (2008), A. S. P. Gomes, C. R. Jacob, LV, PCCP 10 (2008) 5353 - 5362.

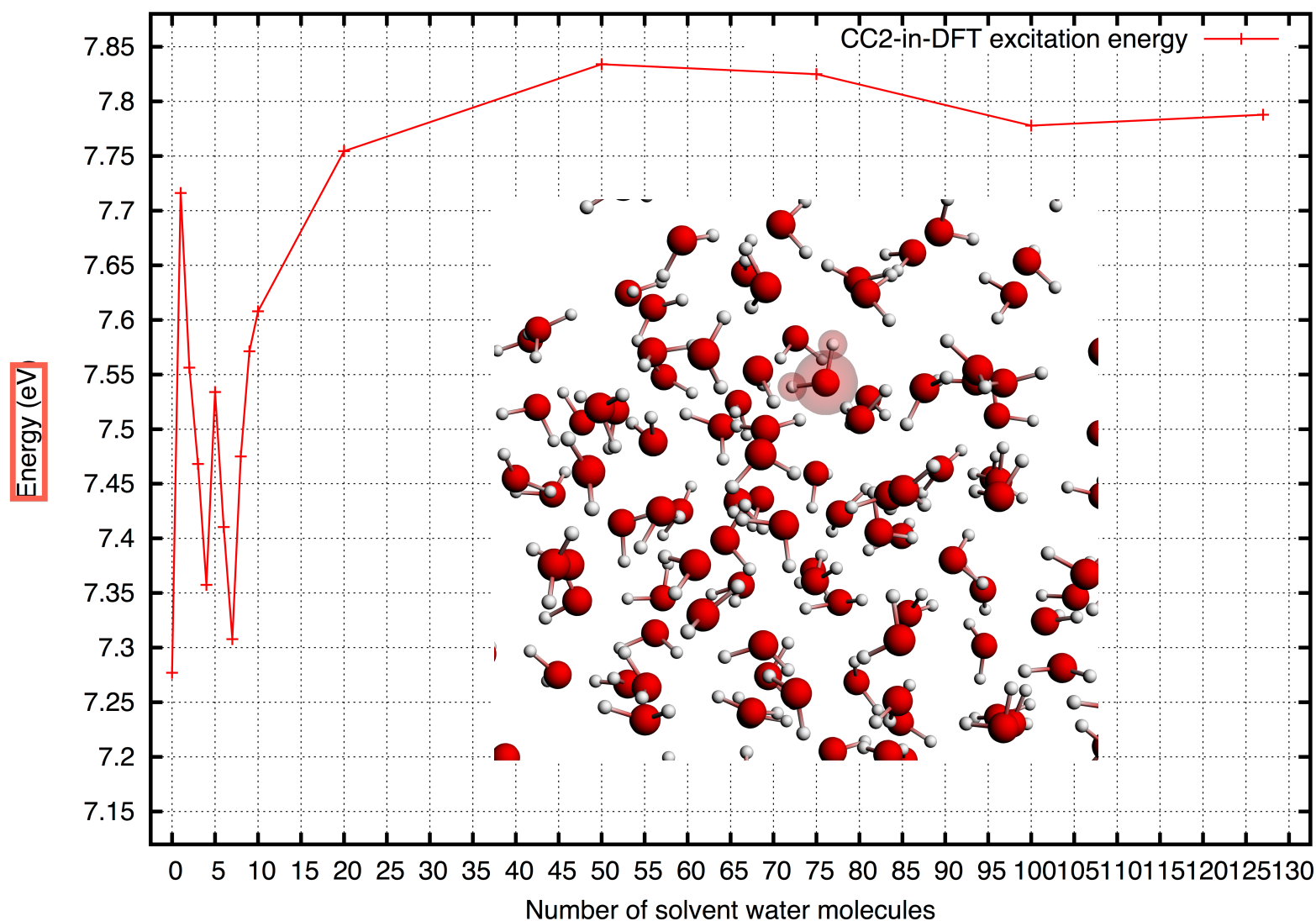
WFT-in-WFT: formic acid dimer



- Good description of strong intermolecular hydrogen bonds
 - Addition of explicit dispersion interactions leads to overestimation of bond strength
 - PW91k kinetic energy functional does probably underestimate Pauli repulsion
- Computationally efficient when using density fitting of Coulomb terms

WFT-in-DFT: water in water

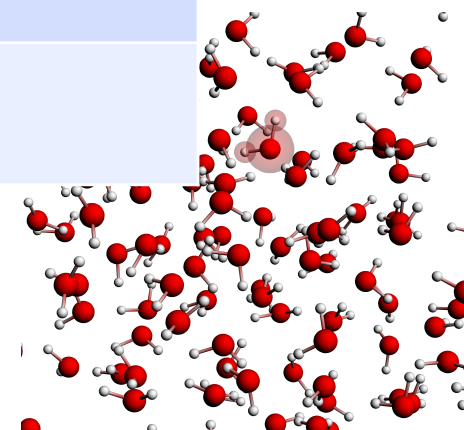
Convergence of explicit solvation model for CC2



WFT-in-DFT: water in 127 water

WFT Method	Embedding choices	Excitation Energy (eV)	Shift w.r.t. vacuum
HF	LDA-p-r-no	9.55	0.90
CC2	LDA-p-r-no	8.14	0.86
CCSD	LDA-p-r-no	8.52	0.88
HF	GGA-p-r-no	9.25	0.60
CC2	GGA-p-r-no	7.78	0.50
CCSD	GGA-p-r-no	8.20	0.56

- 1) **LDA/GGA** embedding potential
- 2) perturbed / unperturbed HF orbitals
- 3) relaxed / static embedding potential
- 4) kernel: **none**, LDA, GGA

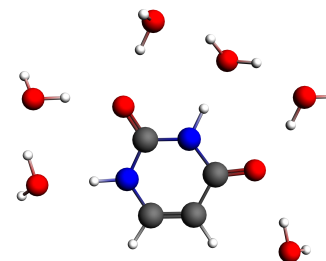


WFT-in-DFT: uracil in 6 water

WFT Method	Embedding choices	$n \rightarrow \pi^*$ (eV)	$\pi \rightarrow \pi^*$ (eV)
CC2	vacuum	4.65	5.48
CC2	GGA-p-s-no	5.42	5.46
CC2	GGA-p-r-no	5.42	5.46
CC2	GGA-p-r-LDA	5.42	5.46
CC2	Supermolecule	5.31	5.36

Structures: M. Etinski and C. M. Marian, Phys. Chem. Chem. Phys. **12**, 4915 (2010).

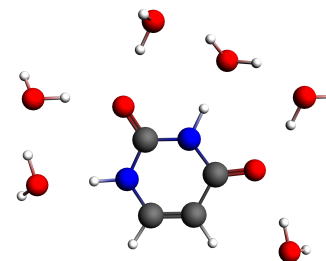
- 1) **LDA/GGA** embedding potential
- 2) **perturbed / unperturbed** HF orbitals
- 3) **relaxed / static** embedding potential
- 4) **kernel: none, LDA, (GGA)**



WFT-in-WFT: uracil in 6 water

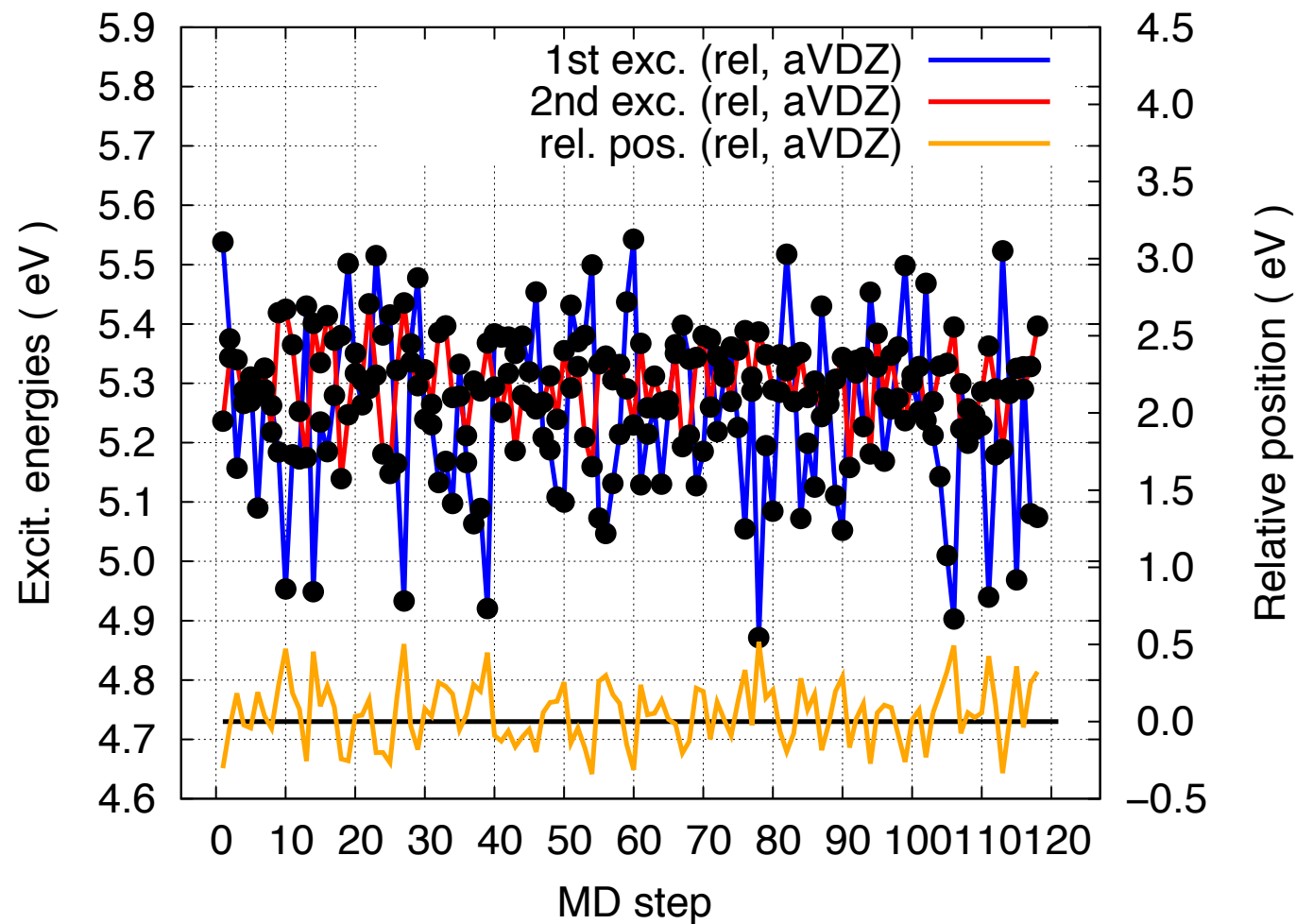
WFT Method	Environment	$n \rightarrow \pi^*$ (eV)	$\pi \rightarrow \pi^*$ (eV)
CC2	vacuum	4.65	5.48
CC2	DFT	5.42	5.46
CC2	CC2	5.36	5.45
CC2	Supermolecule	5.31	5.36

- 1) **GGA** embedding potential
- 2) **perturbed** HF orbitals
- 3) **relaxed** embedding potential
- 4) **kernel: none**



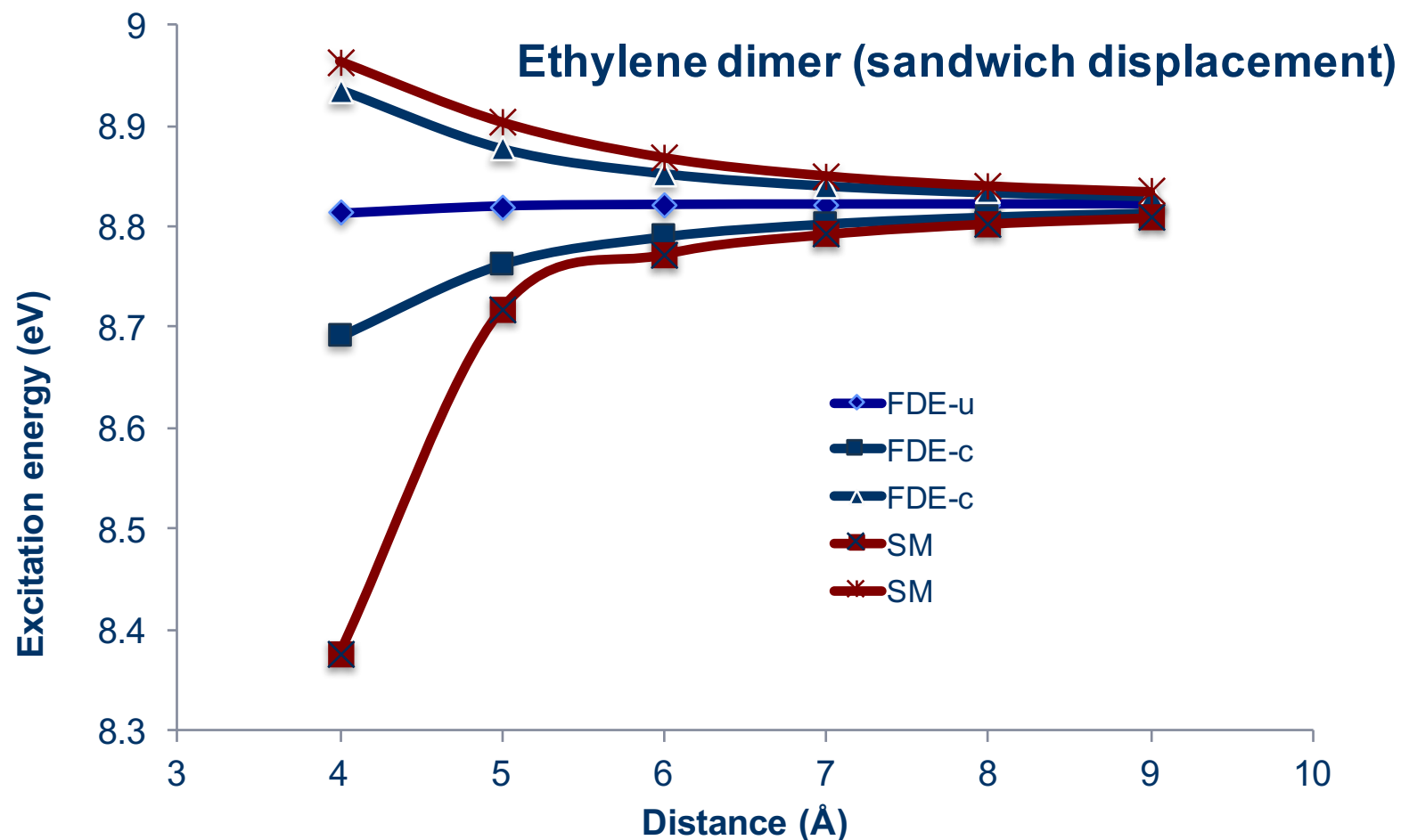
- Slight improvement by using CC2 environment densities

WFT-in-DFT: uracil in water box



- States become almost degenerate on average
- Individual snapshots show relatively large variations

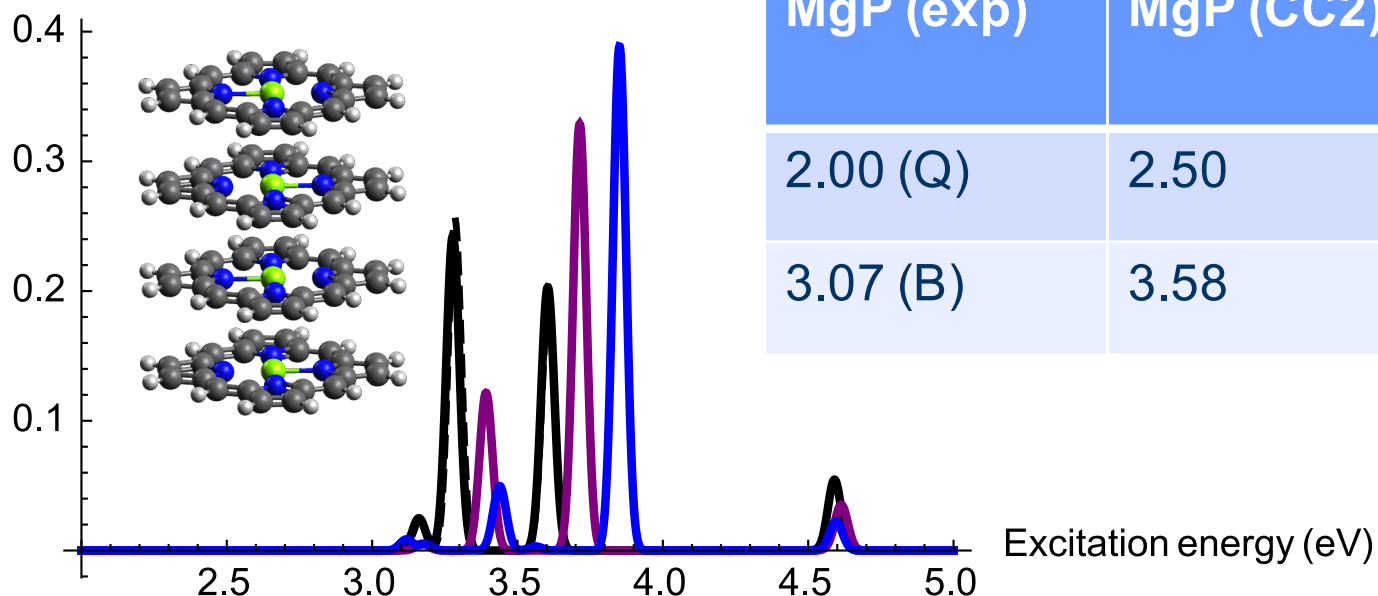
Coupled excitations: ethylene dimer



- Subsystem approach breaks down at short distance for lowest state
 - Deficiencies of the kinetic energy functionals
 - Omission of charge-transfer states
- At longer distance agreement with supermolecular splittings

Coupled excitations: 4 Mg Porphyrins

Oscillator strength (arb.units)



- General formalism for WFT, DFT, approximate DFT
 - Splitting slightly larger than with DFT-in-DFT
 - Computational effort mainly in embedded monomer calculations
 - Long-range approximations (e.g Förster dipoles) can be readily applied in the calculation of coupling elements
- Interpretation similar to well-known parametric models for exciton coupling

Summary

Subsystem density functional theory

- Facile inclusion of many explicit molecules / ions in the environment
- Very general: subsystems can be treated with DFT or WFT
- All interaction terms are expressed in terms of (current) density functionals
- Easy interpretation: can be used to connect to qualitative (semi-empirical) models

Technical details

- Modular implementation (ADF, Dalton, Dirac, NWChem, Psi3, ...)
- Organization of calculations via the PyADF python scripting framework

Outlook

- Standardization for response: “model spectroscopies”
- Larger chromophores with more efficient WFT codes
- Inclusion of charge-transfer excitations

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- Johannes Neugebauer (Münster)
- Michele Pavanello (Newark)
- Andre Gomes (Lille)
- Jochen Autschbach (Buffalo)
- Daniel Crawford (Virginia)

- DIRAC: www.diracprogram.org
- ADF: www.scm.com
- PyADF: www.pyadf.org

- Financial & other support

- Netherlands Organization for Scientific Research
- European Union
- DAAD, DFG

