

*International Winter School on Electronic
Structure Calculations, Paderborn, Feb 10, 2020*

Introduction to Quantum Chemical Methods

Frank Neese

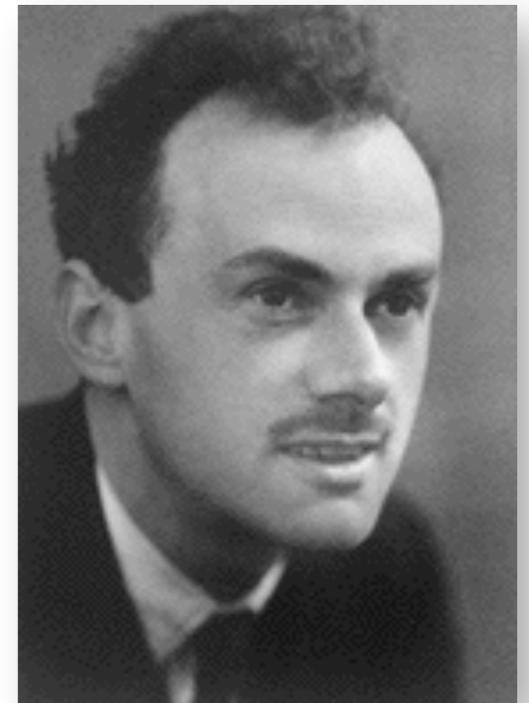
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MAX-PLANCK-GESELLSCHAFT

The Big Promise

*The fundamental laws necessary for the mathematical treatment of large part of physics **and the whole of chemistry** are thus completely known, and the difficulty lies only in the fact that applications of these laws leads to equations that are too complex to be solved “*



Paul Adrien Maurice
Dirac
(1902-1984)

„... hence it would be desirable to develop practical approximation schemes for the application of quantum mechanics“

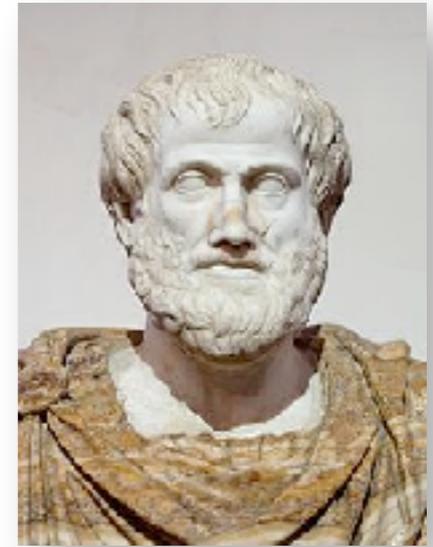
.. but not like this please!

We can calculate everything!
(1975)



Enrico Clementi
(born 1931)

„All science begins by wondering why the things are as they are“



Aristotle
(384 BC - 322 BC)

„Science starts by being curious“

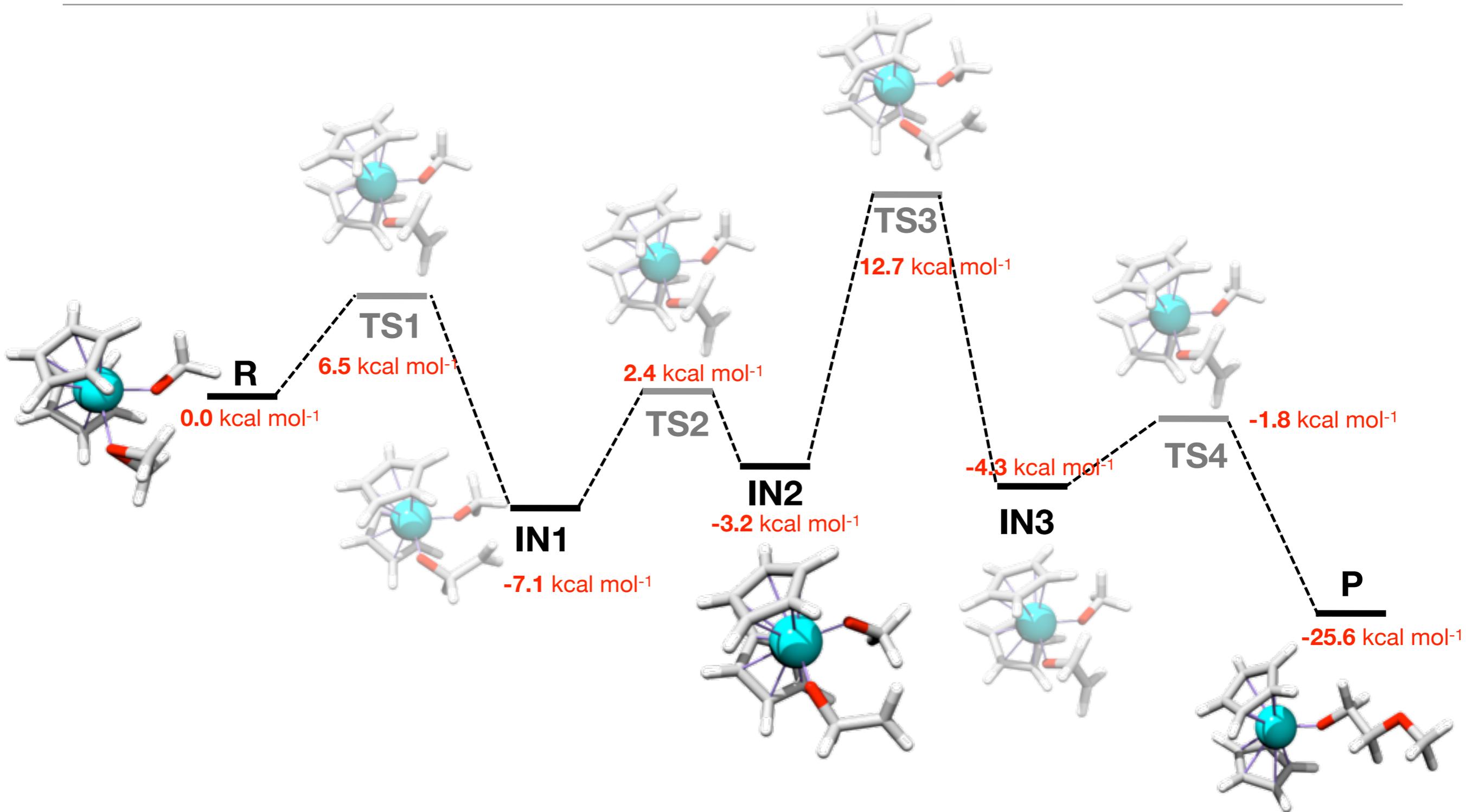


Linus Pauling
(1901-1994)

Why Quantum Chemistry ?

- In order to predict quantities that can not be measured (example: short lived intermediates that never accumulate enough for experimental studies)
- In order to interpret the outcome of experiments (example: complex NMR or EPR spectra)
- In order to obtain insight in the regularities of data (example: understand the key factors that contribute to reactivity trends in a series of related molecules)
- In order to predict the outcome of future experiments (example: Design of materials - how do i have to change the molecule in order to optimize a given property)
- Have fun with computers, study algorithms, approximations and other „inner theoretical reasons to do it“, ...

... but not like this please

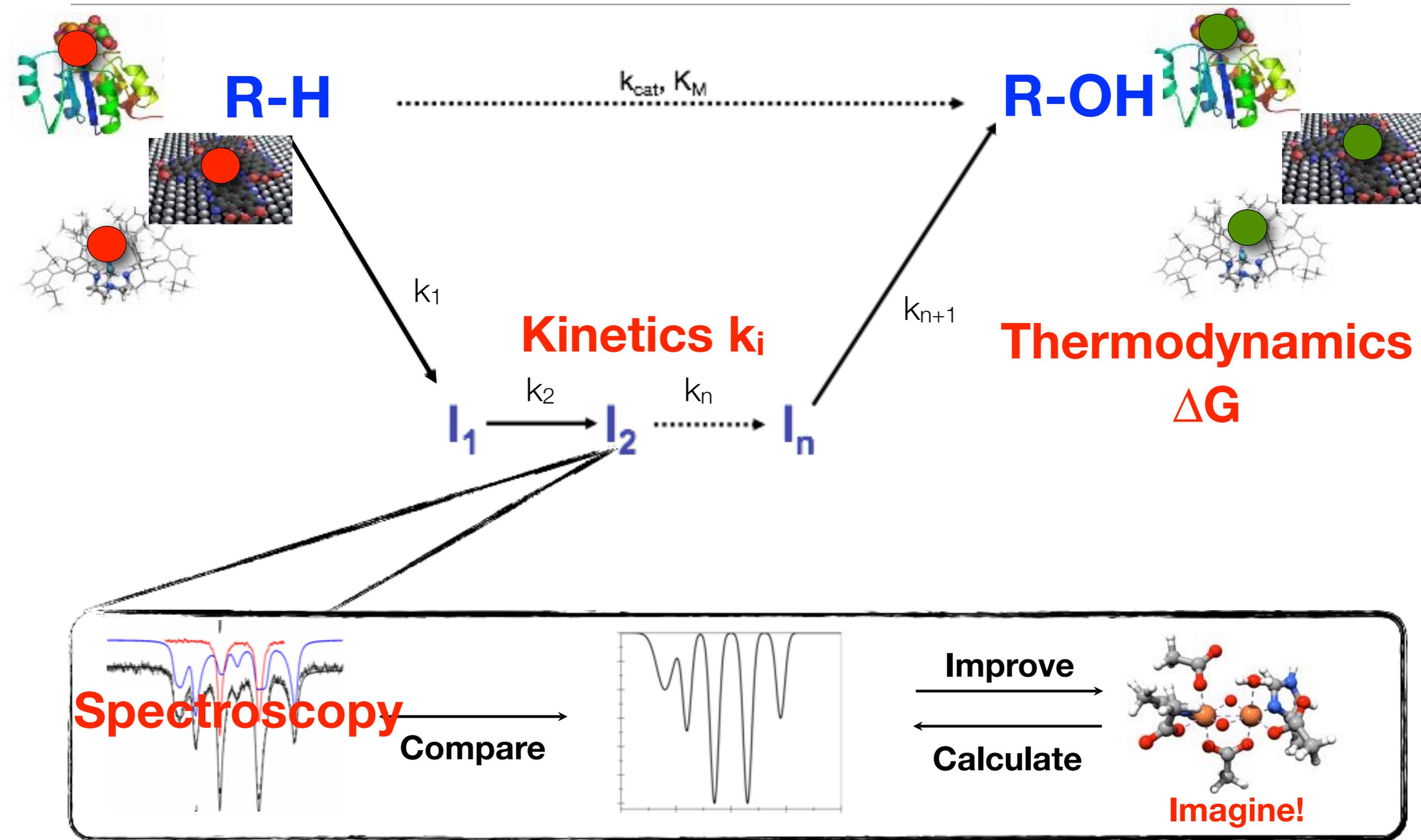


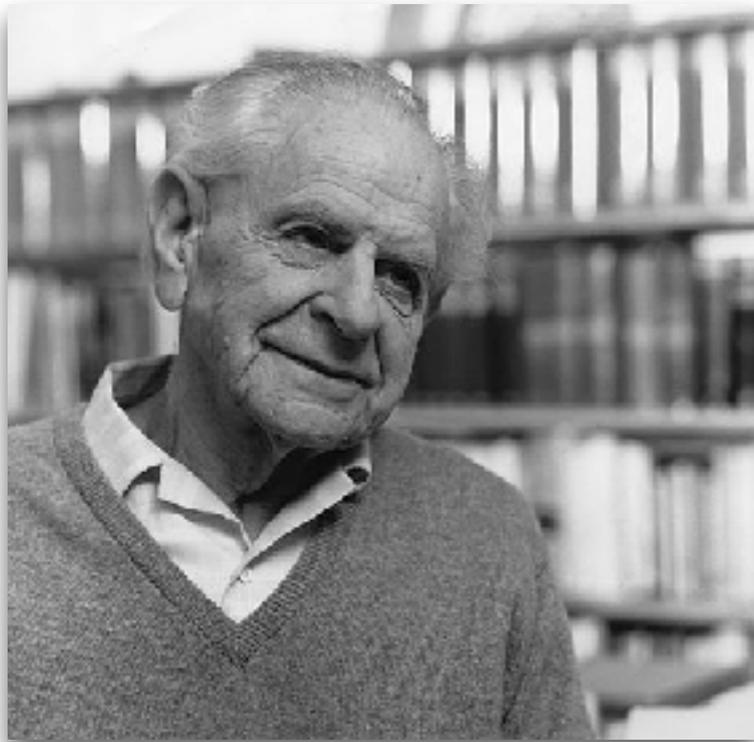
Note: 1.a.u. = 27.21 eV

1eV = 8065 cm⁻¹ = 23.06 kcal/mol

1 cm⁻¹ = 29979 MHz

Seeking Feedback from Experiment





Karl Raimund Popper
(1902-1994)

*... but I shall certainly admit a system as empirical or scientific only if it is capable of being tested by experience. These considerations suggest that **not verifiability but the falsifiability** of a system is to be taken as a criterion of demarcation.*

The logic of scientific discovery (1959)

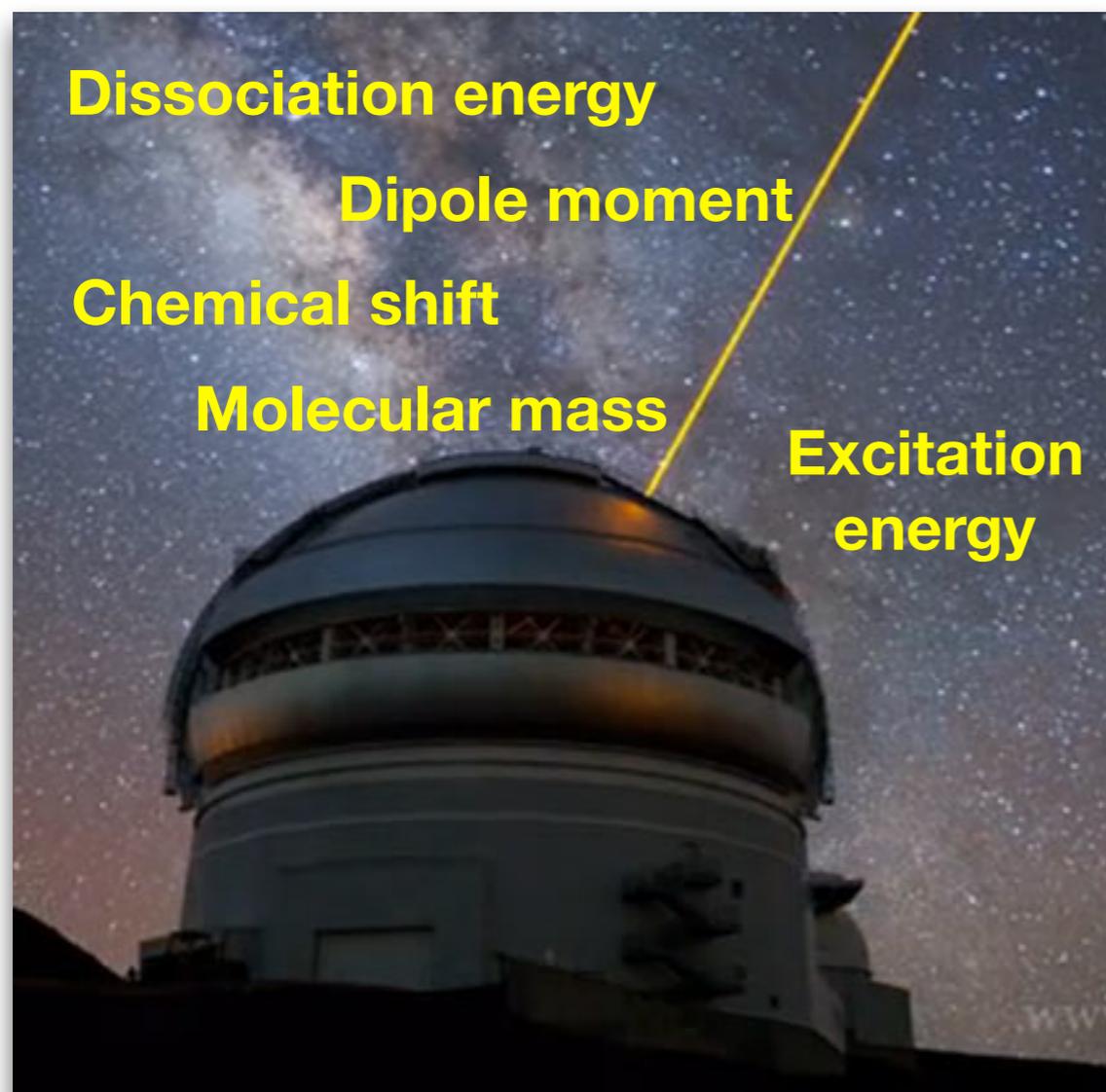
„Experiments are the only source of knowledge at our disposal. The rest is poetry, imagination“

quoted in Adv. Biochem. Psychopharm., **1980**, 25, 3

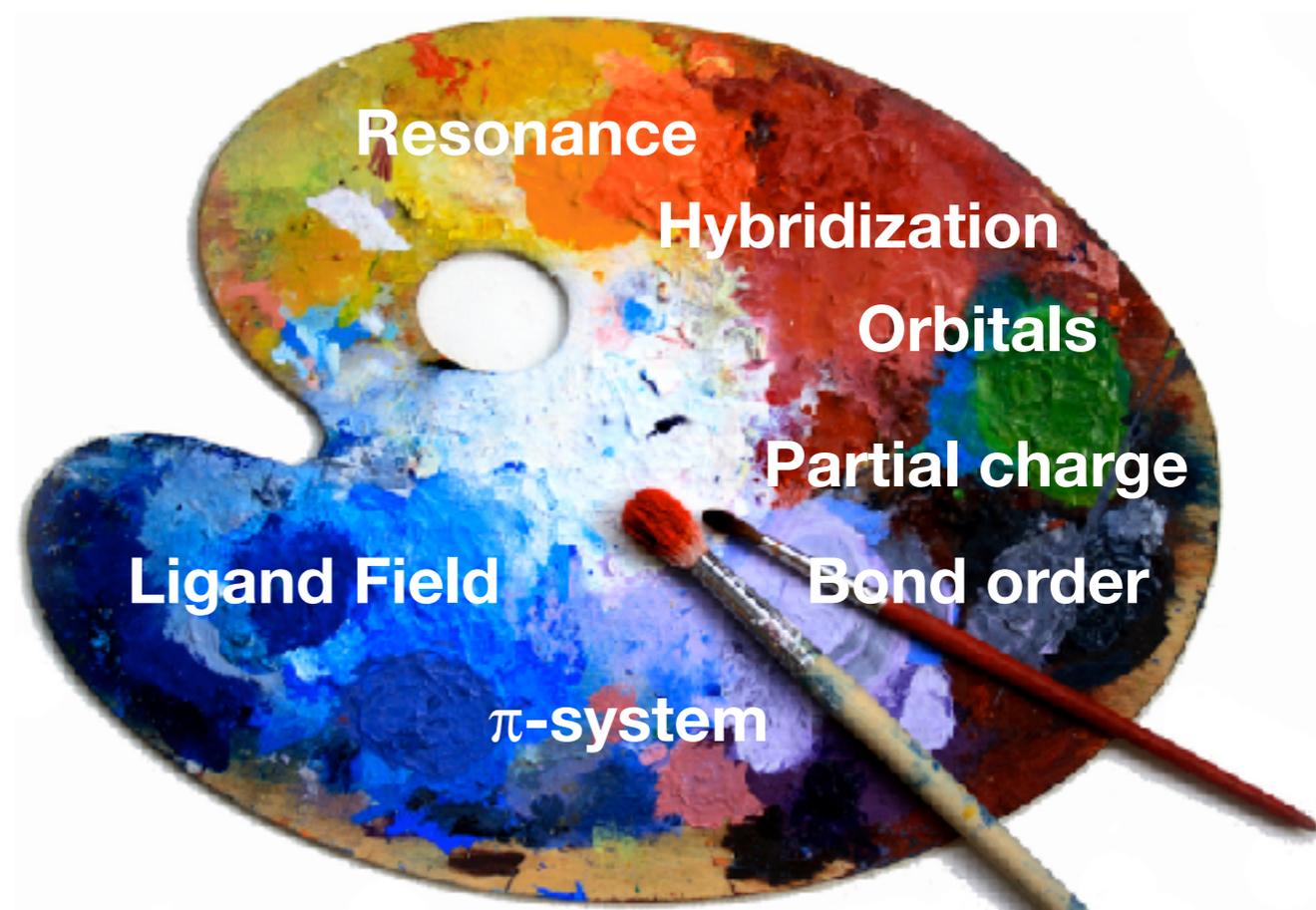


Max Planck
(1858-1947)

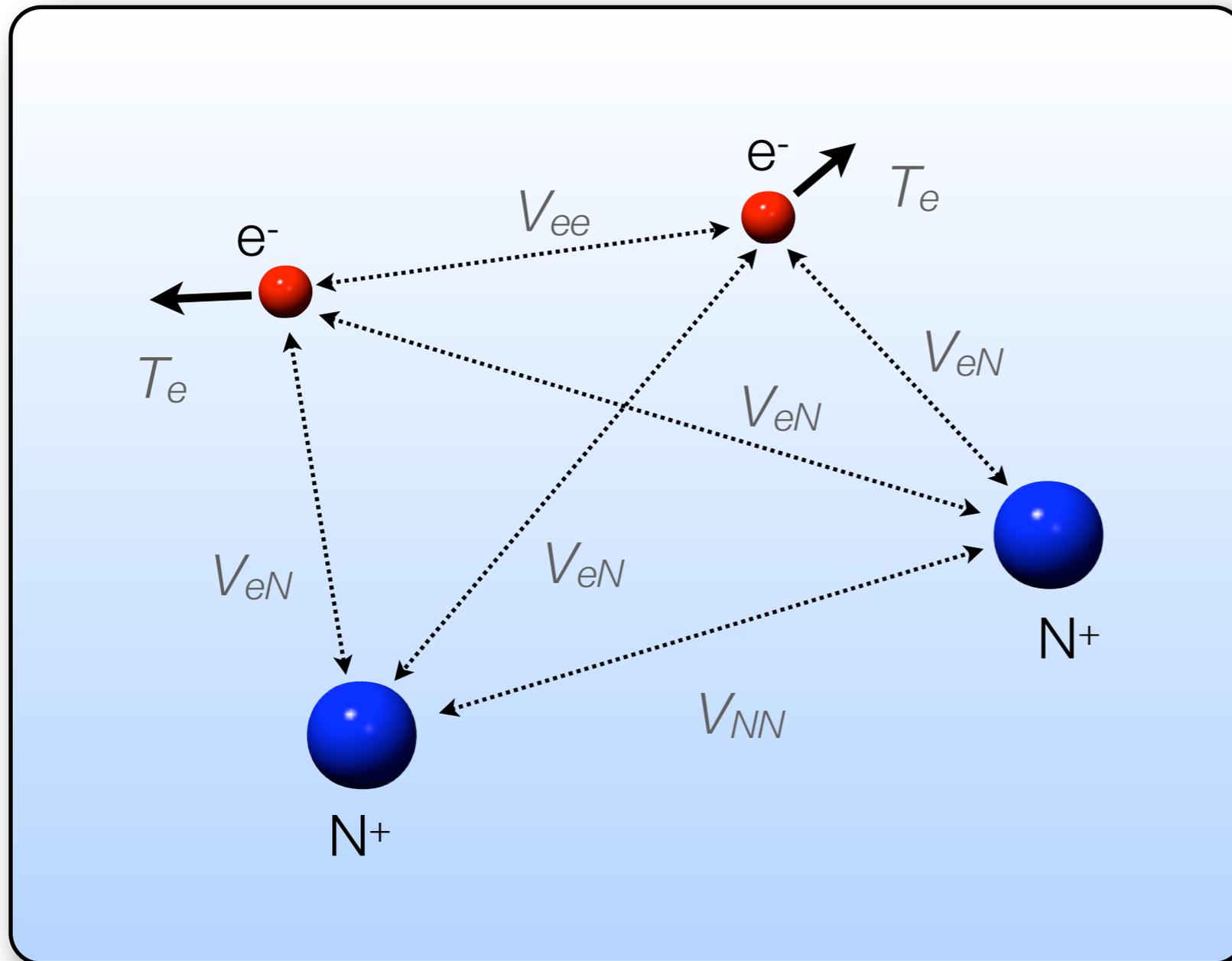
Observables



Interpretation Aids

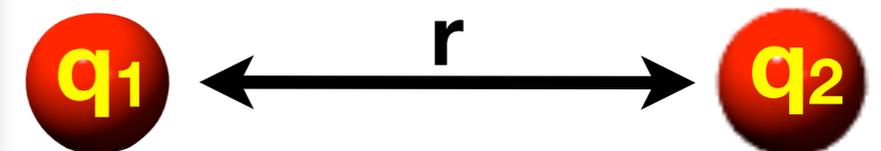


Fundamental Interactions in Molecules



Just 2 Laws:

1. Coulomb's Law



$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

2. Kinetic Energy



$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

$$E = T_e + T_N + V_{eN} + V_{NN} + V_{ee}$$

The Schrödinger Equation

- ★ In order to go to quantum mechanics we move over to **atomic units** in which

$$\hbar = 4\pi\epsilon_0 = e_0 = m_e = 1 \quad c = 137.06$$

- ★ And replace the **momentum** by its quantum mechanical analogue:

$$\mathbf{p}_i \rightarrow -\hat{i}\vec{\nabla}_i \quad \vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \quad \hat{i} = \text{imaginary unit } \hat{i}^2 = -1$$

- ★ We finally need to introduce the **spin of each electron** σ_i that can only assume the two values α and β . The three space and one spin variable for each electron are collected in the vector \mathbf{x} .

- ★ **Schrödinger's equation** for the many particle wavefunction $\Psi(x_1, \dots, x_N, R_1, \dots, R_M, t) \equiv \Psi(\mathbf{x}, \mathbf{R}, t)$ is:

$$\hat{i} \frac{\partial}{\partial t} \Psi(\mathbf{x}, \mathbf{R}, t) = \hat{H}(\mathbf{x}, \mathbf{R}, t) \Psi(\mathbf{x}, \mathbf{R}, t)$$

- ★ But if the Hamiltonian does not depend on time (which is assumed henceforth), we obtain the **time-independent Schrödinger eigenvalue equation**

$$\hat{H}(\mathbf{x}, \mathbf{R}) \Psi(\mathbf{x}, \mathbf{R}) = E \Psi(\mathbf{x}, \mathbf{R}) \quad E = \text{Total Energy}$$

The Born-Oppenheimer Approximation

- ★ As a final step, we need the **Born-Oppenheimer approximation** which amounts to the neglect of the kinetic energy of the nuclei.

$$\hat{H}(\mathbf{r}, \mathbf{R}) \rightarrow \hat{H}_{BO}(\mathbf{r}, \mathbf{R}) = T_e + V_{eN} + V_{ee} + \underbrace{V_{NN}}_{\text{constant for given } \mathbf{R}}$$

- ★ **Justification (heuristic):** Nuclei are much heavier and move much slower than electrons. hence, electrons adjust themselves immediately to any nuclear configuration.
- ★ **Consequence 1:** The concepts of chemical structures and potential energy surfaces (Energy as function of nuclear coordinates) emerges!
- ★ **Consequence 2:** The Schrödinger equation separates into two equations. One of the electrons for any given arrangement of the nuclei and one for the nuclei on a given potential energy surface!

$$\hat{H}_{BO} \Psi(\mathbf{x} | \mathbf{R}) = E(\mathbf{R}) \Psi(\mathbf{x} | \mathbf{R})$$

$$\left\{ \hat{T}_N + E(\mathbf{R}) \right\} \Theta(\mathbf{R}) = \mathcal{E} \Theta(\mathbf{R})$$

The total wavefunction would be the product of the electronic wavefunction and the nuclear wavefunction but here we are mainly concerned with the electronic part.

Is the Born-Oppenheimer Approximation Good?

The BO Hamiltonian - despite its (apparent) simplicity - is a great achievement: it describes 99% of all chemistry correctly. Exceptions are:

- ★ The BO Hamiltonian does not contain terms that describe the interactions of nuclei and electrons with **external electric and magnetic fields**
- ★ The BO Hamiltonian misses many small terms that are associated with the **electron and nuclear spins**
- ★ The BO Hamiltonian does assume a **point like nucleus**
- ★ The BO Hamiltonian breaks down in situations where the separation of **nuclear and electronic movements** is no longer well separated. For example in **Jahn-Teller systems**.
- ★ The Born-Oppenheimer Hamiltonian needs to be partly replaced or supplemented with **relativistic terms** if heavy elements are involved.

Only for the description of more advanced spectroscopies, such as EPR spectroscopy, do we need to proceed beyond the Born-Oppenheimer approximation.

The Many Particle Wavefunction

Born-Interpretation:

$$|\Psi(\mathbf{x} | \mathbf{R})|^2 = \Psi^*(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N | \mathbf{R}) \Psi(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N | \mathbf{R})$$

Given the nuclear configuration \mathbf{R} , the square of Ψ gives the **conditional probability** for finding electron 1 at r_1 with spin σ_1 , electron 2 at r_2 with spin σ_2 , ...

Pauli-Principle:

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N | \mathbf{R}) = -\Psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N | \mathbf{R})$$

Antisymmetry with respect to particle interchanges (electrons are Fermions)

How do I picture the many electron wavefunction?



You don't

- ➔ Nobody can intuitively picture a function of $4N$ variables.
- ➔ Insight has to come from elsewhere

Important NOTE: NO ORBITALS YET! Orbitals are not fundamental objects

The Total Energy

What is the total energy $E(\mathbf{R})$?

The energy that is required to separate the molecule into noninteracting protons and electrons.

Is this observable?

In principle: YES

in practice: NO

What is its relevance?

In chemistry and spectroscopy we measure **energy differences!** This will be elaborated below

How large is it?

Quite typically, for a transition metal complex, it is, say, 10,000-100,000 eV

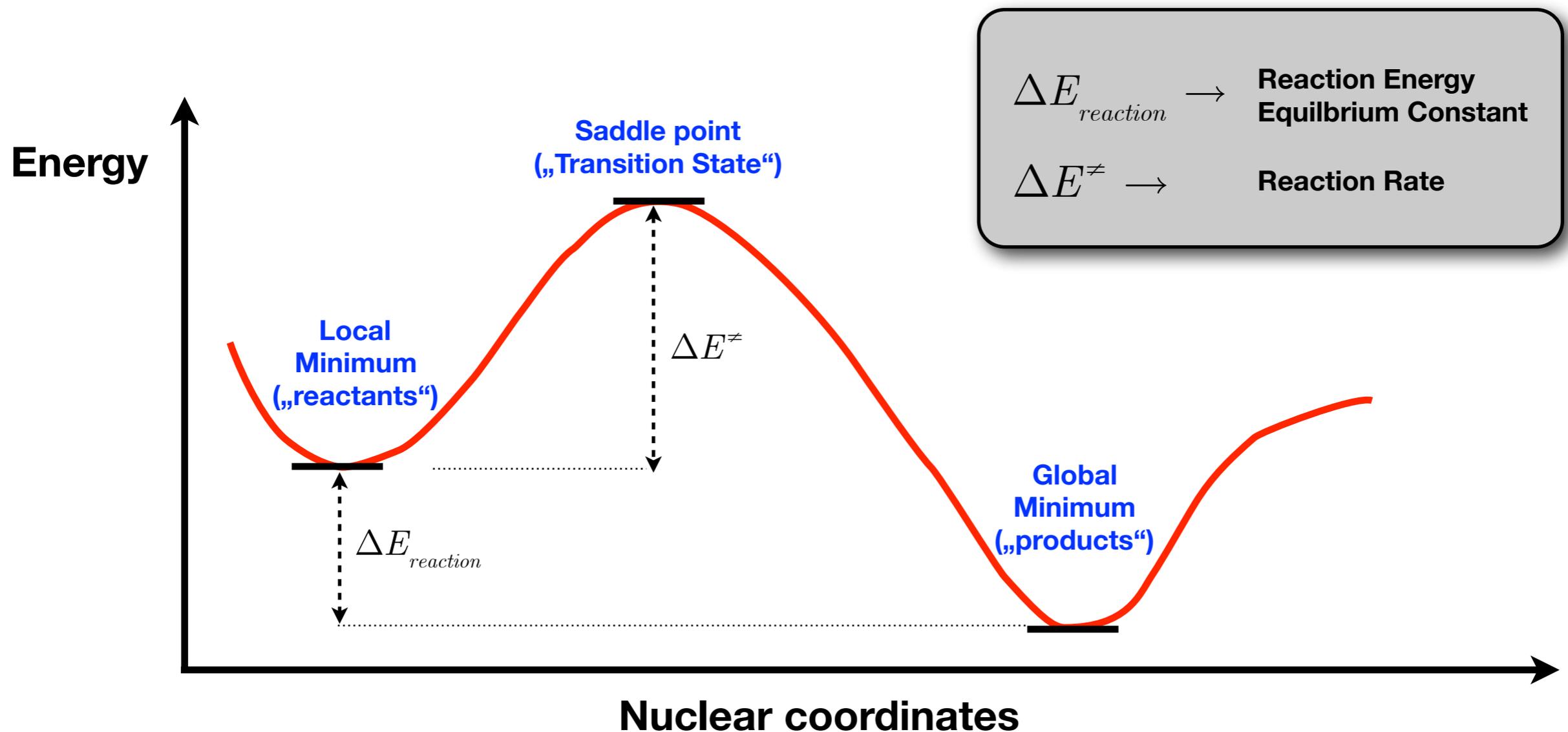
How accurate do we need it?

If we want to have energy differences accurate to ~ 1 kcal/mol then we need to have it accurate to 0.05 eV or in other words: better than 1 ppm!

Note: 1 atomic unit (a.u.) ~ 27.21 eV ~ 627 kcal/mol

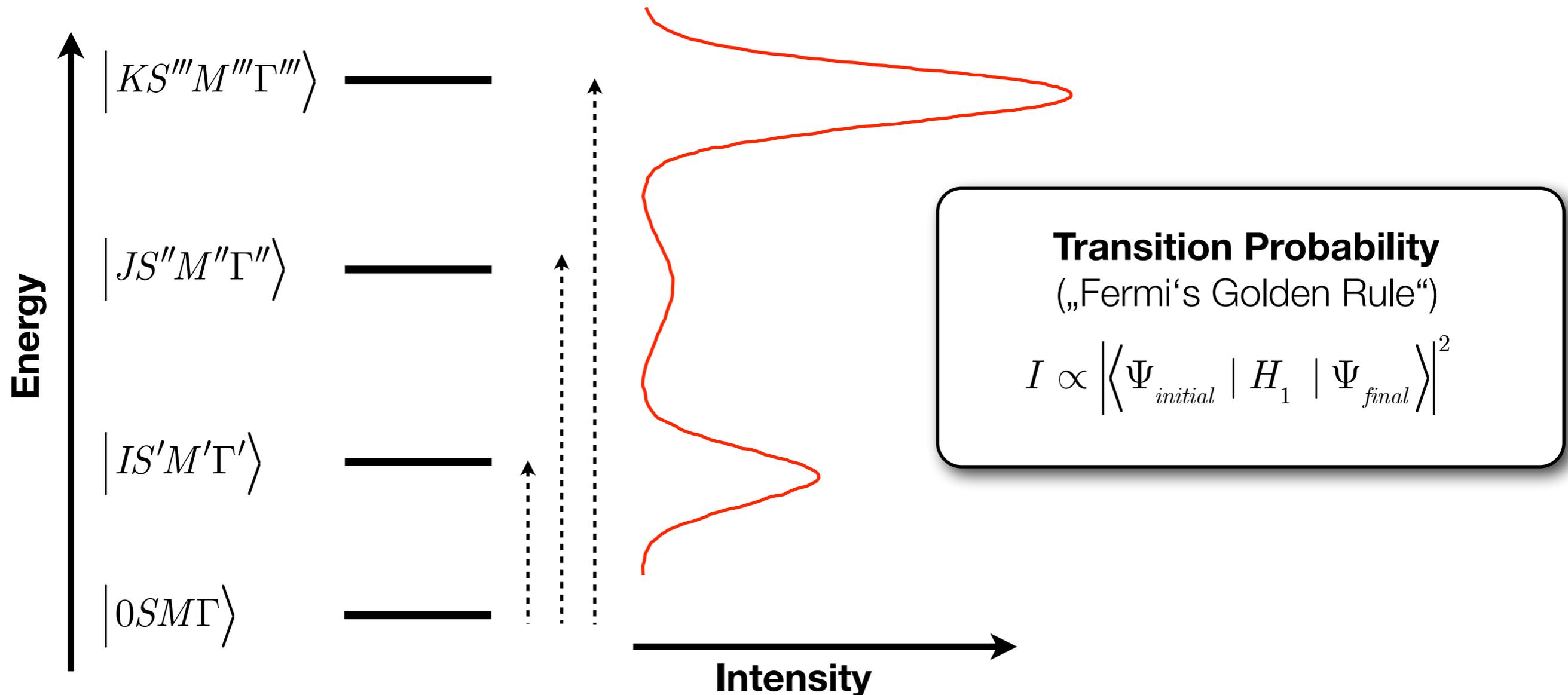
Chemistry and Potential Energy Surfaces

Chemistry (reactions) occur typically only on the ground or at most on a few low-lying potential energy surfaces. Thus, the most important feature is the variation of the total energy with changes in the nuclear coordinates:



Spectroscopy and States

Apply some kind of oscillating perturbing field with Hamiltonian $H_1(\omega)$ in order to induce transitions between different **states** of the system



Spectroscopic Techniques

Gamma

X-Ray

UV/vis

Infrared

Microwave

Radiowave

eV

14000

8000

2000

4 - 1

0.1-0.01

10^{-4} - 10^{-5}

10^{-6} - 10^{-7}

Mössbauer

XAS
EXAFS

ABS

MCD

CD

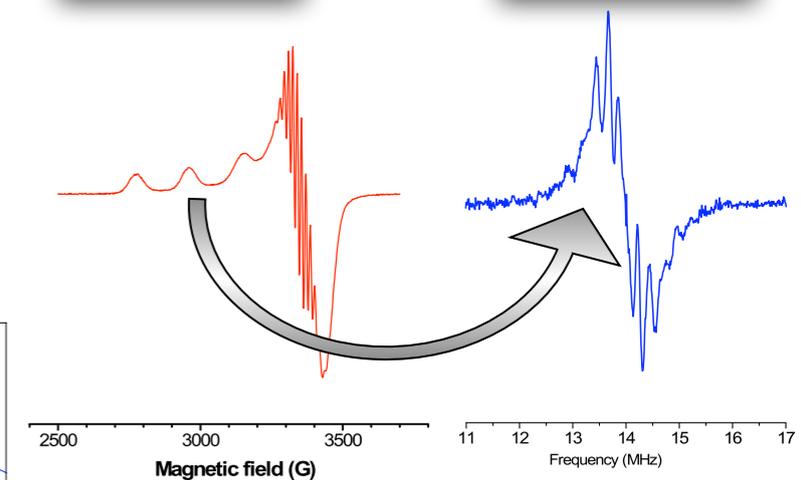
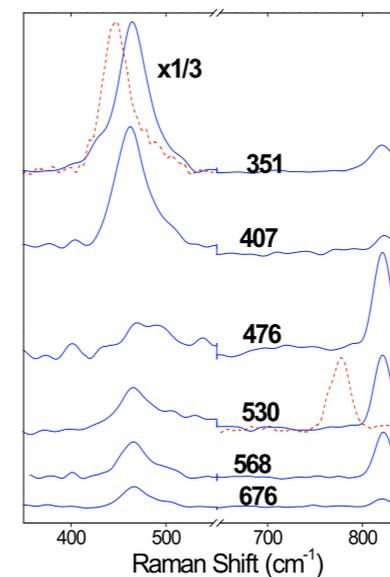
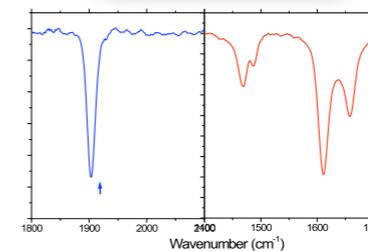
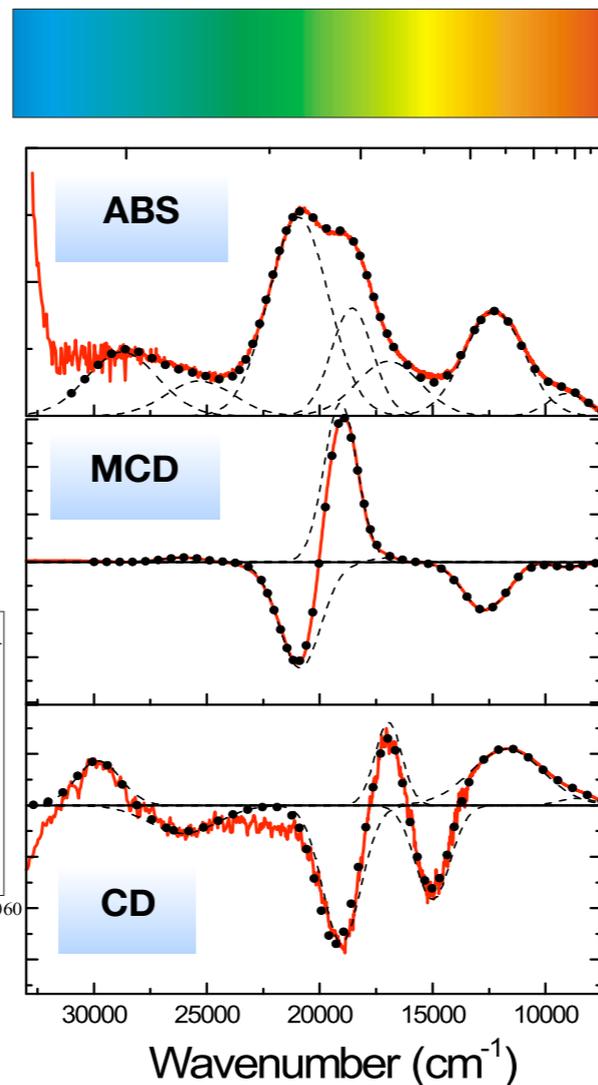
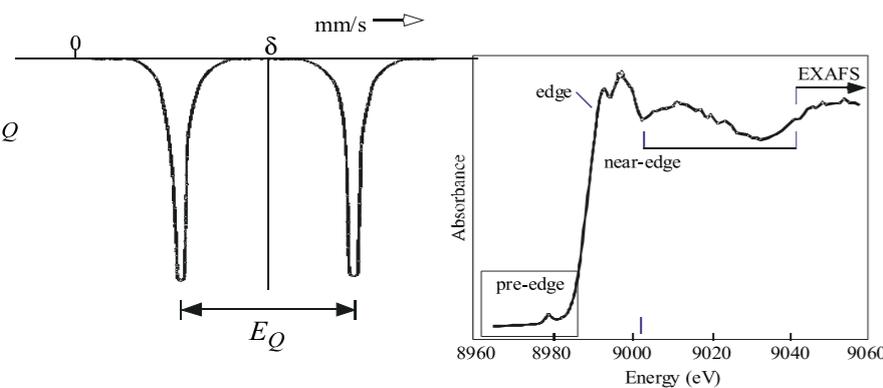
IR

EPR

ENDOR

Raman

NMR



Note: 1.a.u. = 27.21 eV

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1 cm^{-1} = 29979 MHz

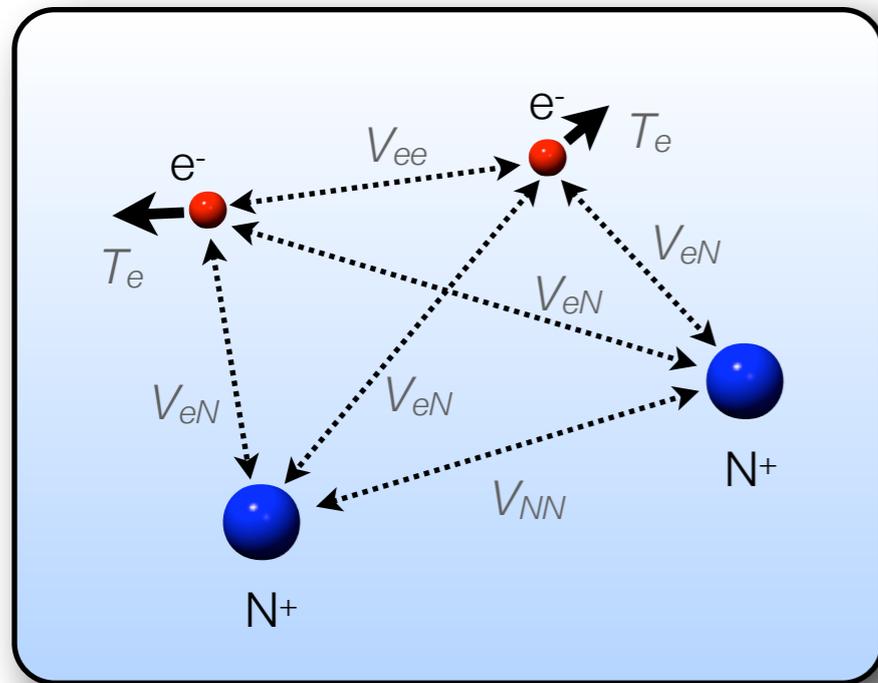
Solving the Born-Oppenheimer Equation

★ How do we solve the many-particle Born-Oppenheimer equation?

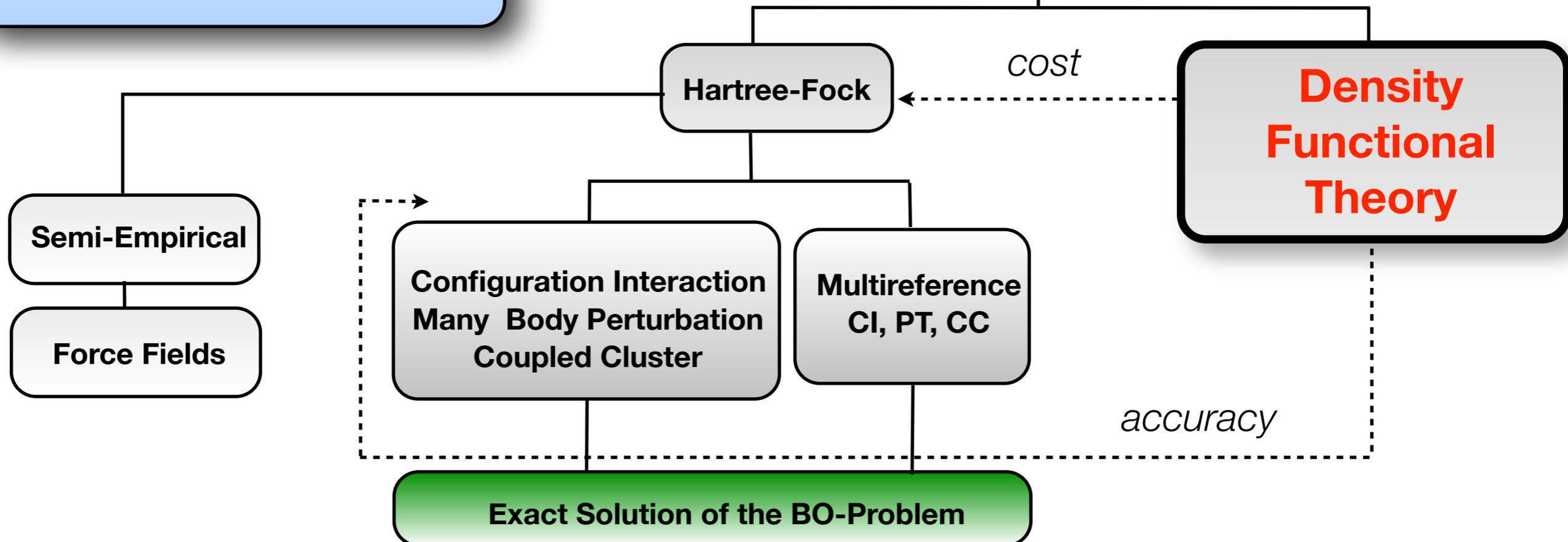
NOT AT ALL!

- ➔ The Born-Oppenheimer Schrödinger equation can not be solved in closed form for more than one electron. Not even for the simplest two electron cases.
- ➔ We need approximation methods

Approximate Quantum Mechanical Methods



$$\hat{H}(\mathbf{x}, \mathbf{R})\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N | \mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N | \mathbf{R})$$



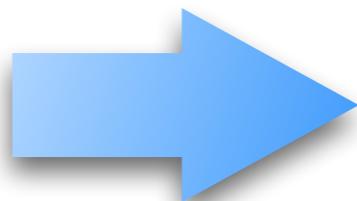
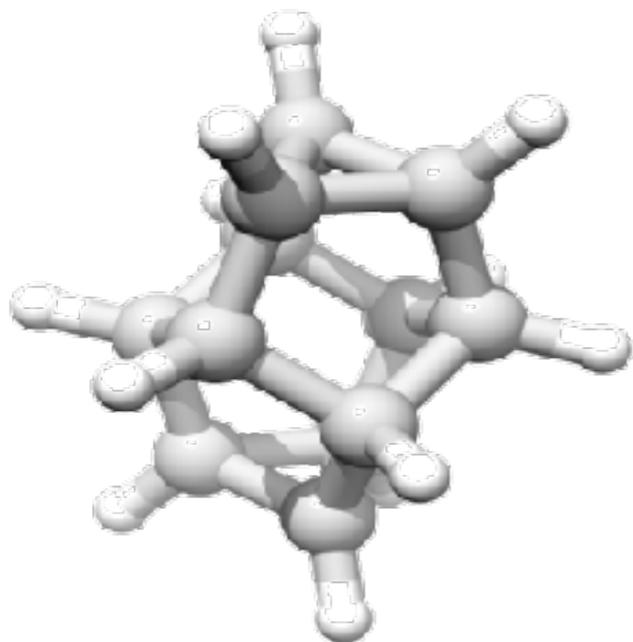
✓ Ideally we would always solve the relativistic many particle Schrödinger equation combined with quantum dynamics for a the entire system including its environment at finite temperature and inclusion of radiative corrections ...

.... but we cannot do that

.... **neither do we *need* that to answer many useful chemical questions**

➔ **Be accurate where it matters!**

➔ **Be interested in your error sources!**



An error of only **1.3 kcal/mol** (=0.056 eV =450 cm⁻¹) is equivalent to:

- pK_a-value : **One log-unit**
- Redox Potential : **56 mV**
- Reaction Rate : **Factor 10**

Total Energy ~ 290 668 kcal/mol



Queen Mary 2:
ca. 56 400 000 kg

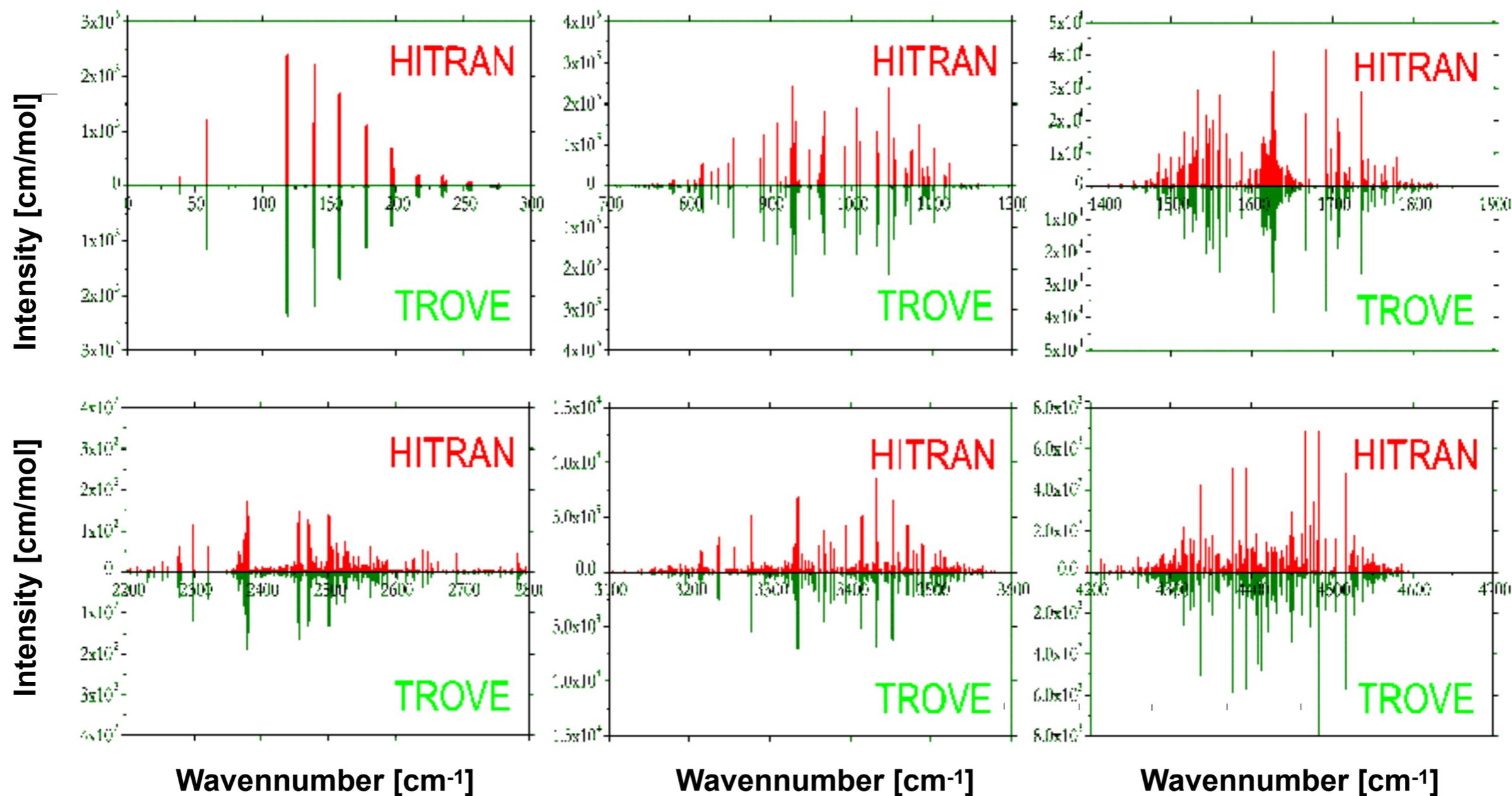


Frank Neese
ca. 80 kg

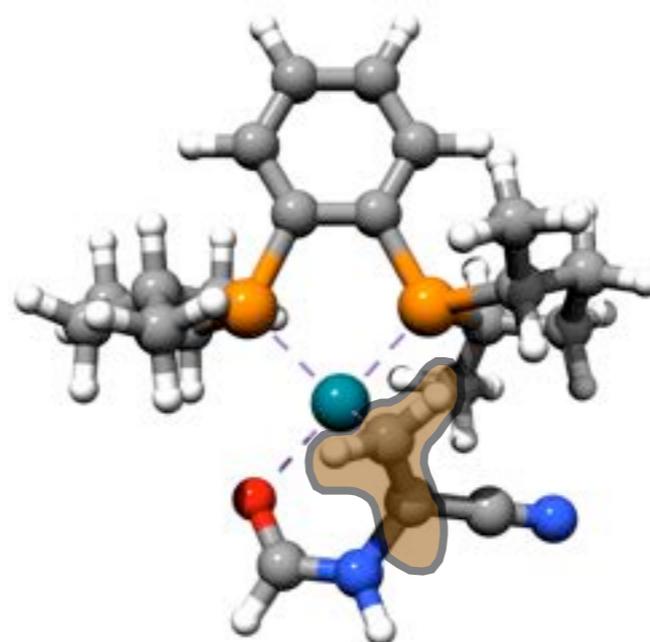
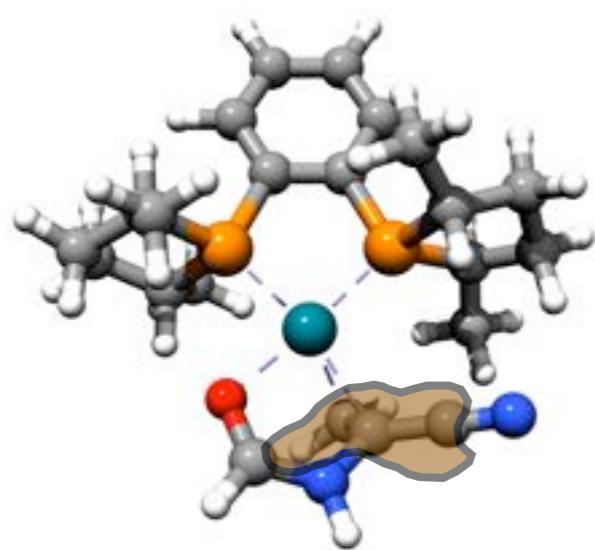
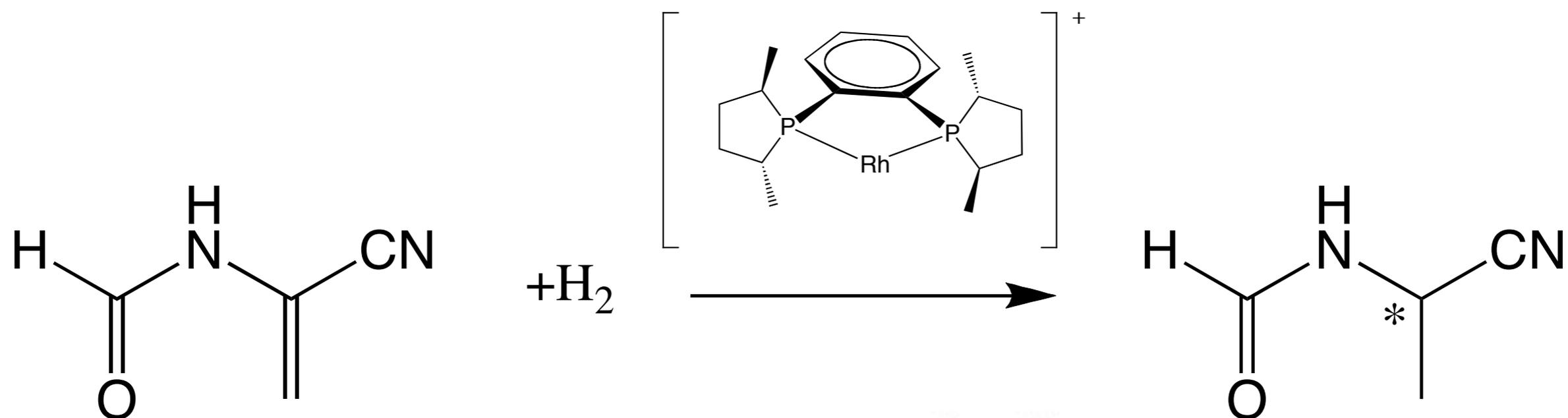
Possible Consequences:

- Need extremely accurate theory**
- Need very good error compensation
- Care about properties other than E_{tot}**

Where it matters NH₃: rovibrational bands at T=300 K

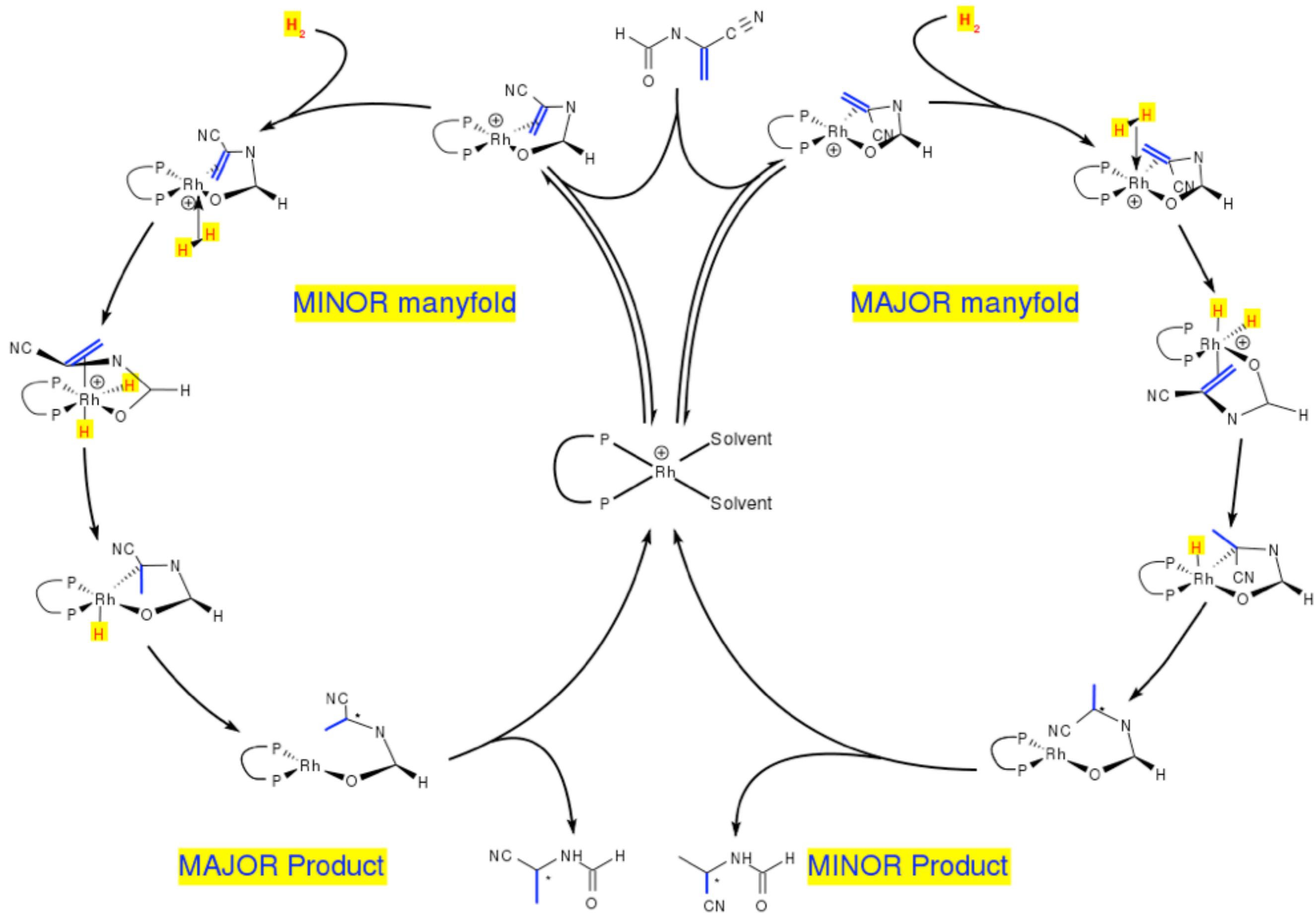


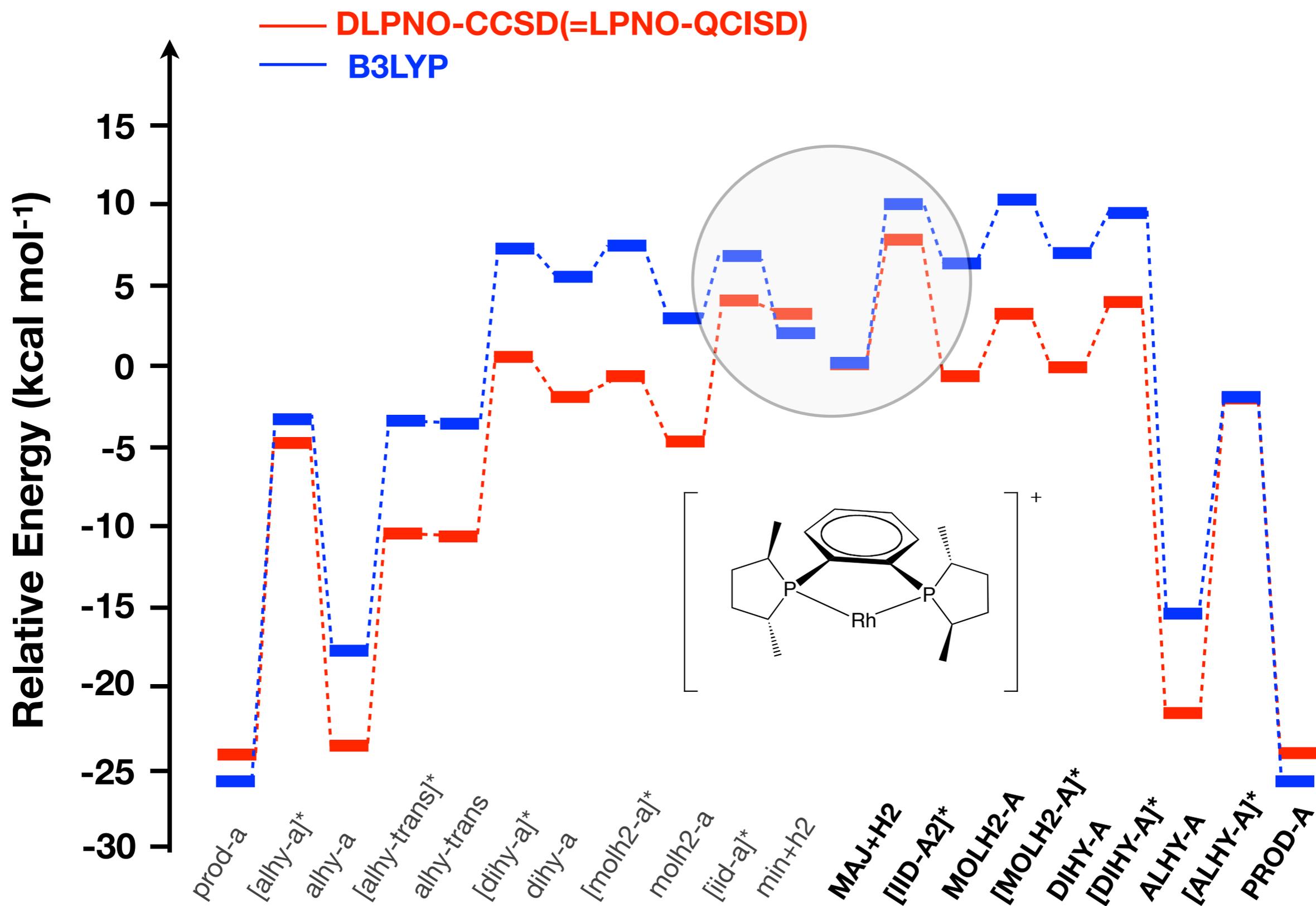
Where it matters: Enantioselective Hydrogenation of Prochiral Enamides



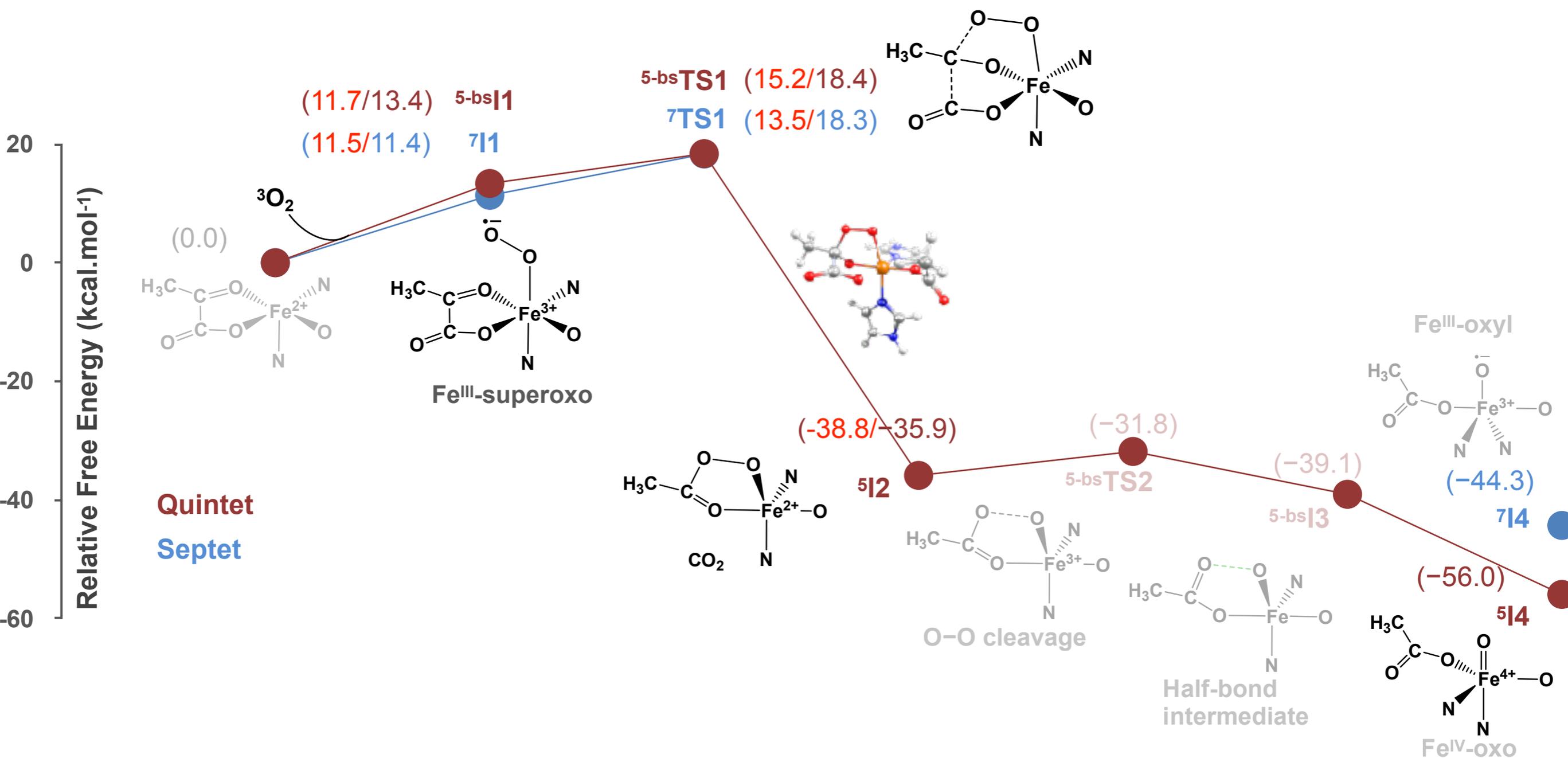
Minor conformer

Major conformer





How accurate is accurate enough?

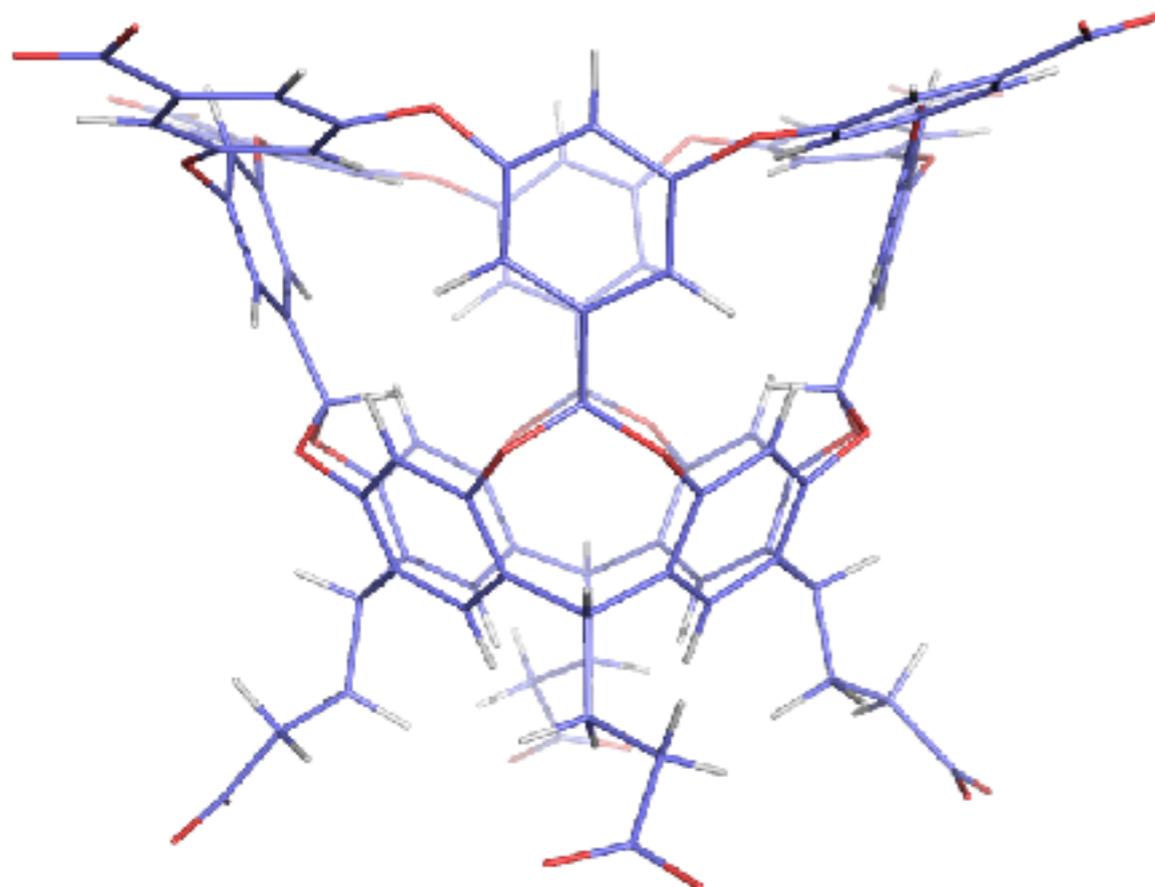


DLPNO-CCSD(T)/def2-TZVPP // B3LYP-D3/def2-TZVP/CPCM

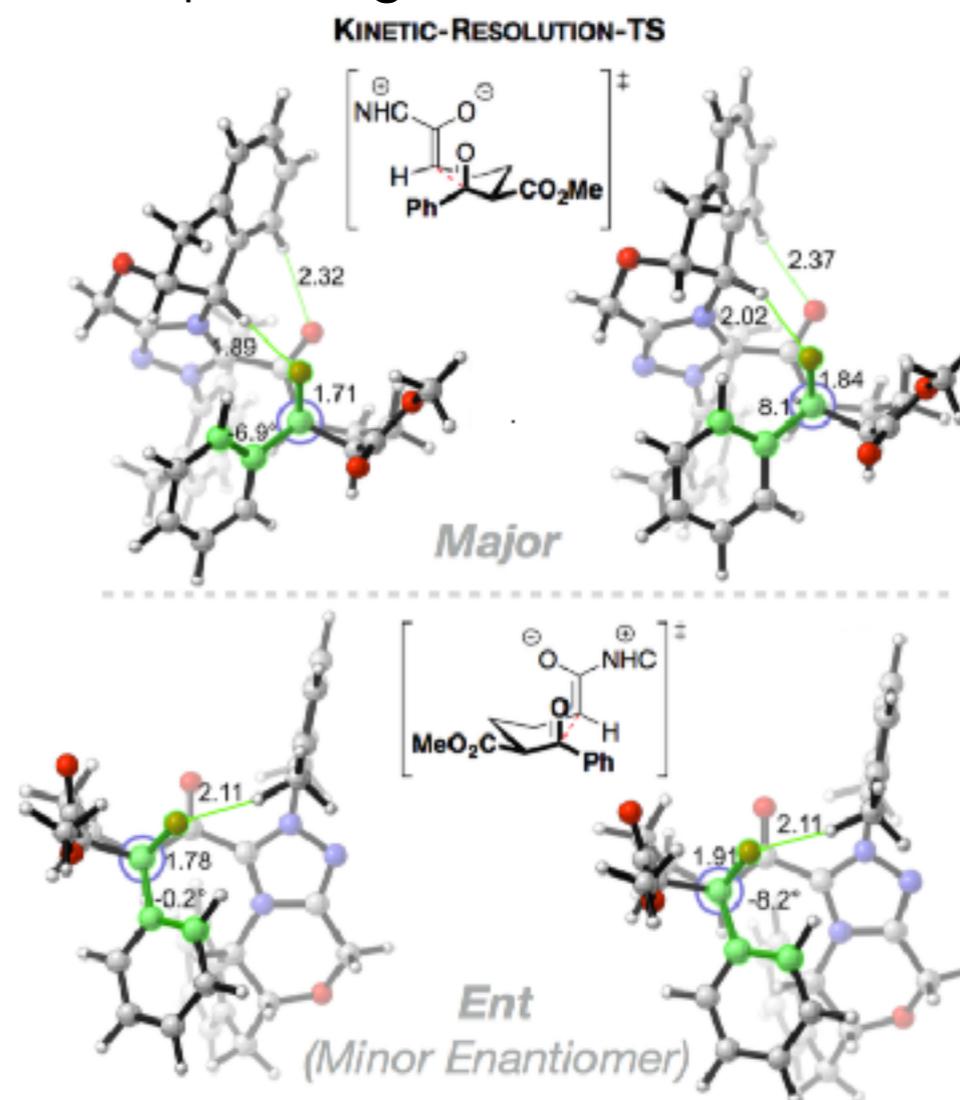
B3LYP-D3/def2-TZVPP // B3LYP-D3/def2-TZVP/CPCM

Where efforts may not be well spent

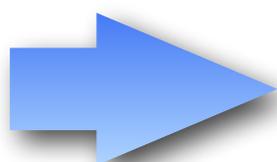
Example: Host/guest or Drug/Receptor complexes: Complex organic reaction mechanisms



O Caldararu, MA Olsson, C Riplinger, FN, U Ryde *Comp. Aid. Molec. Design.*, **2017**, 31, 87



D Walden, O Ogba, P Cheong, C Riplinger, FN *JCTC*, **2017**, to be submitted



In both cases, overall not much *overall* improvement over DFT due to limitations in entropy and solvation contributions

Approximations: The Variational Principle

Given a trial wavefunction that depends on some parameters \mathbf{p} : $\Psi_{trial}(\mathbf{x} | \mathbf{R}, \mathbf{p})$

The „**Ritz-functional**“ is:

$$E[\Psi] = \frac{\langle \Psi_{trial} | H | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle}$$

For the **exact wavefunction** $E[\Psi]$ is the **exact energy**. For any other wavefunction it is readily shown that:

$$E[\Psi] \geq E_{exact}$$

Hence, we can search for a minimum of $E[\Psi]$ with respect to the parameters \mathbf{p} to obtain the best possible approximation within the given Ansatz. The condition for a **stationary point** is:

$$\frac{\partial E[\Psi]}{\partial p_I} = 0 \quad (all I)$$

Ansatz: The Hartree-Fock Method

The **Hartree-Fock** (HF) method is obtained by a specific Ansatz for the trial wavefunction. It is inspired by the form the wavefunction would have, if the electron-electron interaction would not be there („**independent particle model**“)

In this case, the wavefunction would be a simple product of one-electron functions. However, the overall wavefunction needs to fulfil the Pauli principle. Hence, one employs a „**Slater determinant**“

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & \cdots & \psi_1(\mathbf{x}_N) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & \cdots & \psi_2(\mathbf{x}_N) \\ \vdots & \vdots & & \vdots \\ \psi_N(\mathbf{x}_1) & \psi_N(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix} \equiv | \psi_1 \psi_2 \cdots \psi_N |$$

The „auxiliary“ one-electron functions that have been introduced are called „orbitals“. They are the objects to be varied in order to find the best possible approximation to the true wavefunction.

The Hartree-Fock Roothaan Method

It is difficult to vary the orbitals themselves. Rather what one does is to expand the orbitals in another set of auxiliary functions, the „**basis set**“

$$\psi_i(\mathbf{x}) = \sum_{\mu} c_{\mu i} \varphi_{\mu}(\mathbf{x})$$

If the basis set $\{\phi\}$ would be mathematically „complete“, the expansion would be exact. In practice, we have to live with less than complete basis set expansions.

Carrying out the variation now with respect to the unknown „**MO coefficients**“ \mathbf{c} leads to the famous **Hartree-Fock Roothaan** equations. The MO coefficients must satisfy the following coupled set of nonlinear equations:

$$F\psi_i = \varepsilon_i \psi_i \quad \Leftrightarrow \quad \sum_{\nu} F_{\mu\nu}(\mathbf{c})c_{\nu i} = \varepsilon_i \sum_{\nu} c_{\nu i} S_{\mu\nu} \quad (\text{all } \mu, i)$$

ε_i = *Orbital Energy of Orbital i*

F = *Fock Operator*

S = *Overlap Matrix*

The Fock Operator

The orbital energy is the expectation value over the Fock operator and describes the average energy of the electron in orbital i :

$$\varepsilon_i = \langle \psi_i | F | \psi_i \rangle = \left\langle \psi_i \left| \underbrace{T_e + V_{eN}}_h \right| \psi_i \right\rangle + \sum_j \langle \psi_i \psi_j || \psi_i \psi_j \rangle$$

Where the „two-electron integral“ is:

$$\begin{aligned} \langle \psi_i \psi_j || \psi_i \psi_j \rangle &= \langle \psi_i \psi_j | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \psi_j \psi_i \rangle \\ &= \underbrace{\int \int \frac{|\psi_i(\mathbf{x}_1)|^2 |\psi_j(\mathbf{x}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2}_{\text{Coulomb integral}} - \underbrace{\int \int \frac{\psi_i(\mathbf{x}_1) \psi_j(\mathbf{x}_1) \psi_i(\mathbf{x}_2) \psi_j(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2}_{\text{Exchange integral}} \end{aligned}$$

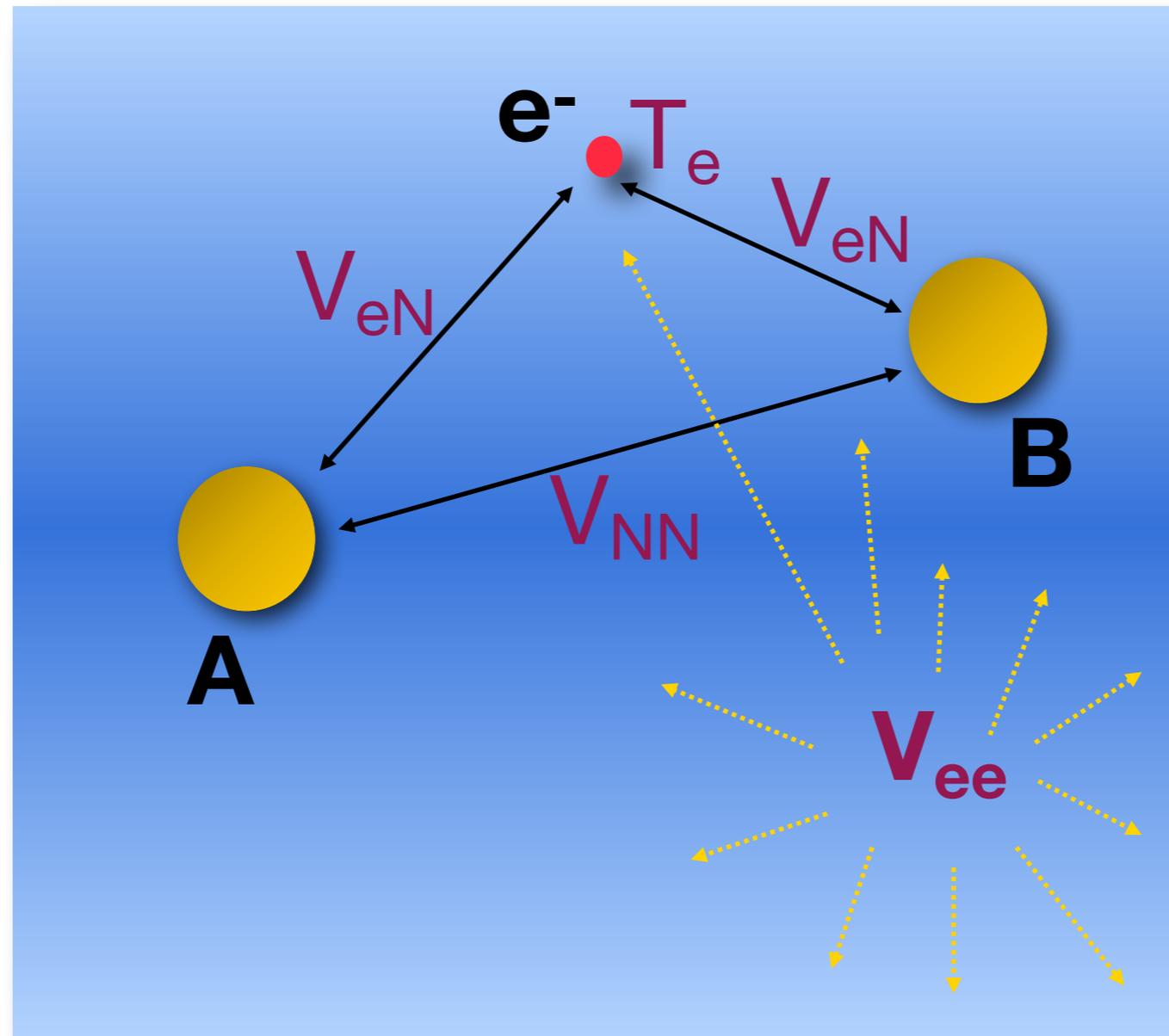
Coulomb integral

- Electrostatic interaction between „smeared“ out charge distributions $|\psi_i|^2$ and $|\psi_j|^2$
- „classical“ interaction
- Always positive

Exchange integral

- Electrostatic self-interaction of the „smeared“ out „interference density“ $\psi_i \psi_j$
- Purely quantum mechanical
- Arises from the Pauli principle
- Always positive (not trivial)
- Does NOT describe a genuine „exchange interaction“

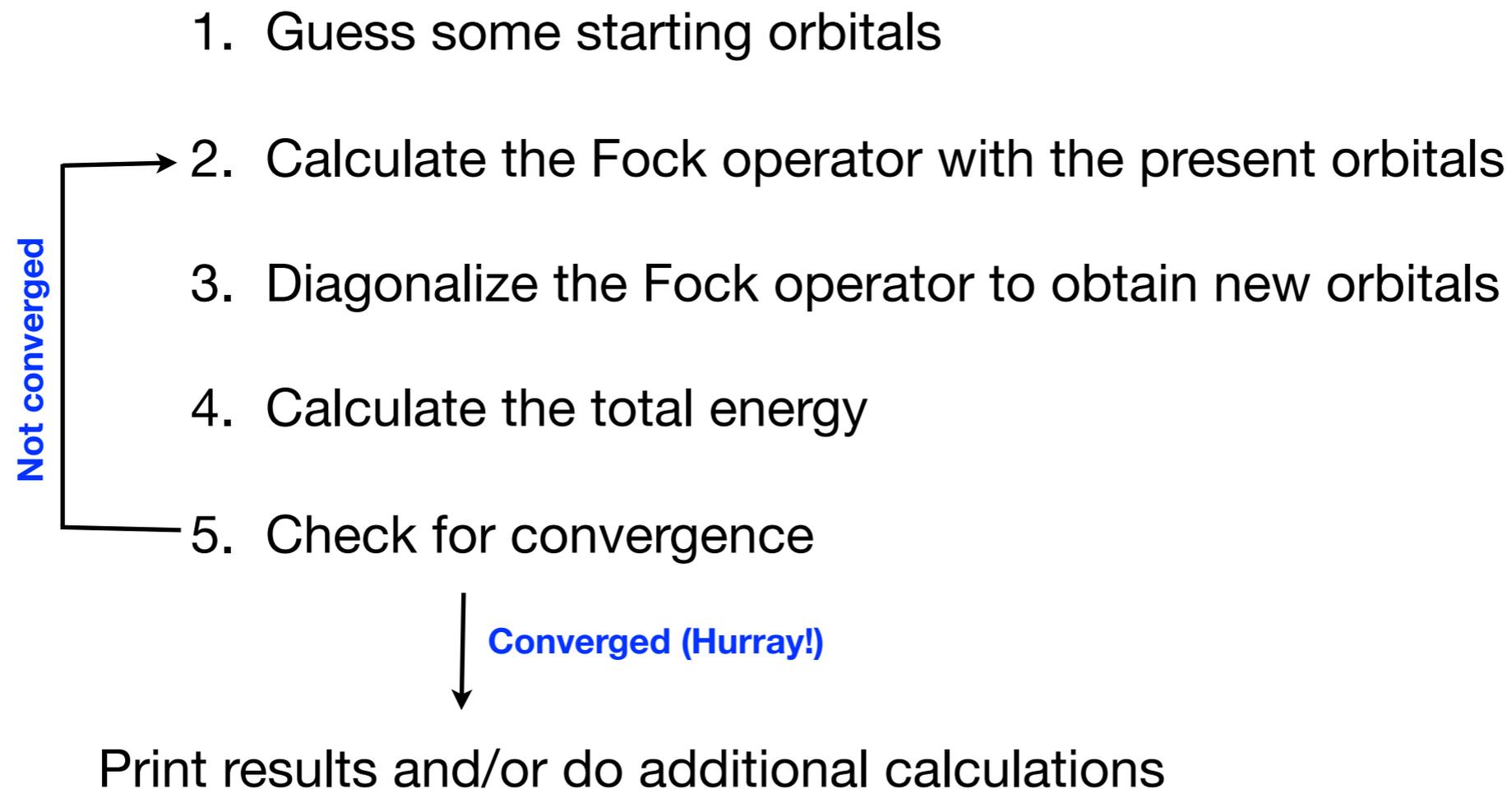
Interpretation of the Hartree-Fock Model



Each electron moves in the field created by the nuclei and the average field created by the other electrons („**mean field model**“) - this also called the „**Hartree-Fock sea**“

Solving the Hartree-Fock Equations

The Fock operator depends on its own eigenfunctions! Hence, the Hartree-Fock equations are highly nonlinear and can only be solved by an iterative process:



Disclaimer

Convergence may be slow, may not occur at all or may occur to a high energy solution that may or may not be physically sensible! Special techniques are often required to reach convergence

How Good is Hartree-Fock Theory?

Consider a Hartree-Fock calculation on the Neon atom (10 electrons)

```
Exact HF Energy           : -128.547 Eh
Exact Experimental Energy : -129.056 Eh
```

(NOTE: exact experimental energy= sum of the ten ionization potentials)

Good News: HF recovers 99.6% of the exact energy (after subtraction of relativistic effects ~99.8%)

Bad News: The conversion factors work against us!

```
1 Eh = 27.21 eV
1 eV = 23.06 kcal/mol
      = 8065 cm-1
```

Thus, the small HF error amounts to the huge number of 319 kcal/mol error! In chemistry one aims at 1 kcal/mol accuracy.

✓ Very hard to achieve for *absolute* energies

✓ We usually want relative energies (much easier but still hard)

Interpretation of the Hartree-Fock Solutions

The primary result of Hartree-Fock calculation (once converged) is the **Total energy**

$$E = V_{NN} + \sum_i \langle \psi_i | h | \psi_i \rangle + \frac{1}{2} \sum_{i,j} \langle \psi_i \psi_j || \psi_i \psi_j \rangle$$

And the approximate **many-electron wavefunction**

$$\Psi_{HF}(\mathbf{x}_1, \dots, \mathbf{x}_N) = |\psi_1 \dots \psi_N|$$

But what about the „secondary quantities“, the **orbital energies**

ε_i = roughly the energy it takes to remove the electron from the molecule (‘ionization potential’) (**Koopman’s Theorem**)

And the **orbitals** themselves:

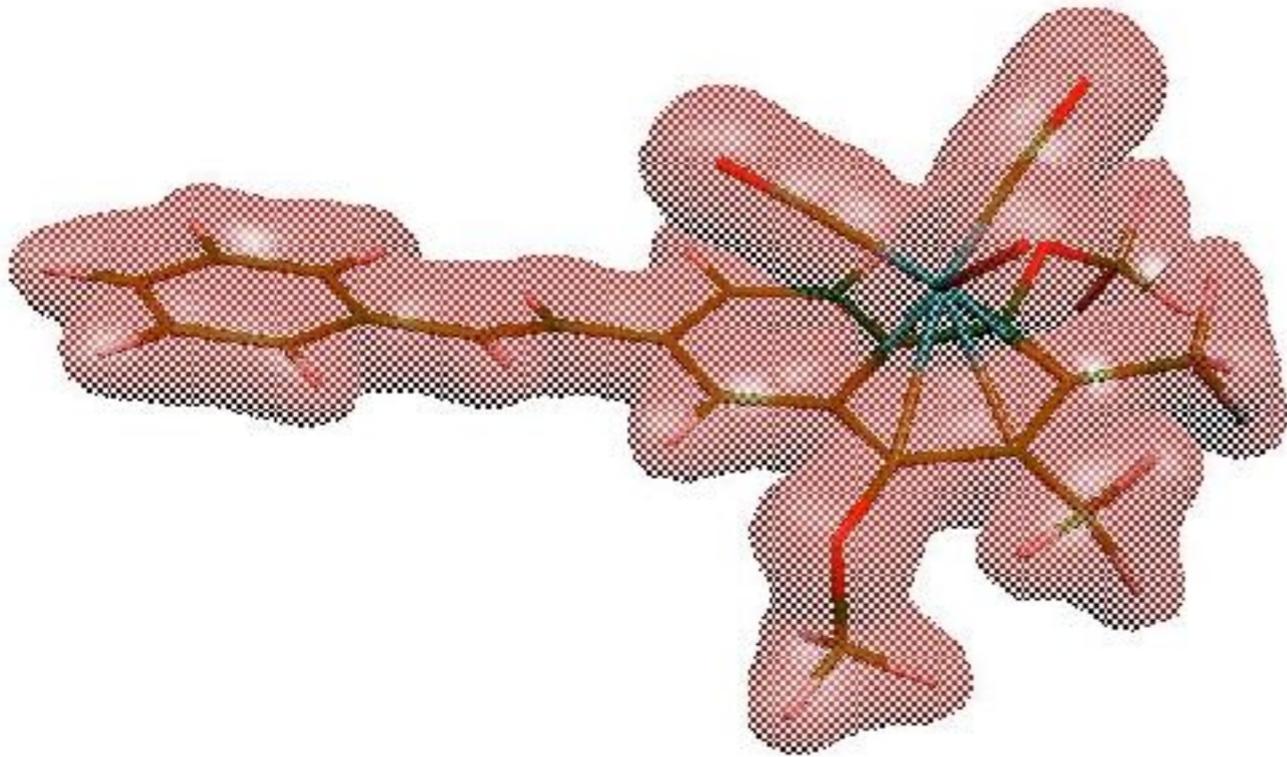
$$\psi_i(\mathbf{x}) = \sum_{\mu} c_{\mu i} \varphi_{\mu}(\mathbf{x})$$

Rigorous: No fundamental importance despite frequent use of HOMO/LUMO and related arguments

In practice: Describes the „electronic structure“ of the molecule in terms of bonding orbitals, antibonding orbitals or lone pairs.

→ Subject of endless fights and debates. However, please remember: **Orbitals are NOT observable.**

The Electron Density



- ✓ Weakly structured
- ✓ Always positive
- ✓ Insensitive to bonding

In HF Theory:

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_i |\psi_i^\alpha(\mathbf{r})|^2 + \sum_i |\psi_i^\beta(\mathbf{r})|^2 \\ &= \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \\ &= \sum_{\mu\nu} \underbrace{(P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta)}_{P_{\mu\nu}} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r})\end{aligned}$$

Partial Charges and Bond Orders

As (bio)chemists we want to think of „polar groups“ and „partial charges“ and „ionic character“ and all that. Hence, we have a desire to divide the total electron density such that parts of it are „assigned“ to individual atoms.

This is the subject of „**population analysis**“. It is never unique and hence very many different schemes exist.

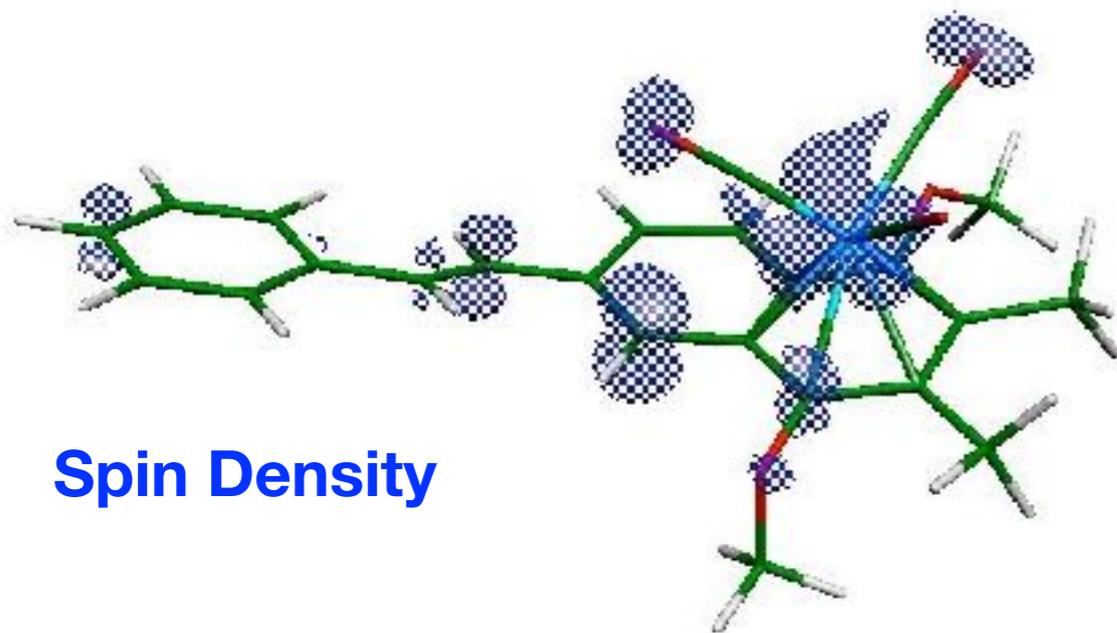
The easiest is due to Mulliken:

$$N_A = \sum_{\mu\nu \in A} P_{\mu\nu}^{AA} S_{\mu\nu}^{AA} + \sum_{B \neq A} \sum_{\mu \in A, \nu \in B} P_{\mu\nu}^{AB} S_{\mu\nu}^{AB}$$
$$Q_A = Z_A - N_A$$

Refined Schemes are the „**Natural Population Analysis**“ (NPA) and the „**Atoms in Molecules** (Bader)“ Analysis.

NOTE: Since partial charges are NOT observables there is no „best“ charge. One should stick to one scheme and then look at trends.

The Spin Density



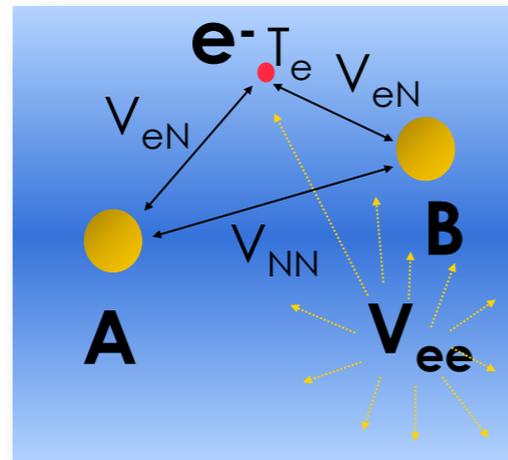
- ✓ Strongly structured
- ✓ Positive or negative
- ✓ Highly sensitive to bonding

In HF Theory:

$$\begin{aligned}\rho^{\alpha-\beta}(\mathbf{r}) &= \sum_i |\psi_i^\alpha(\mathbf{r})|^2 - \sum_i |\psi_i^\beta(\mathbf{r})|^2 \\ &= \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \\ &= \sum_{\mu\nu} \underbrace{(P_{\mu\nu}^\alpha - P_{\mu\nu}^\beta)}_{P_{\mu\nu}^{\alpha-\beta}} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r})\end{aligned}$$

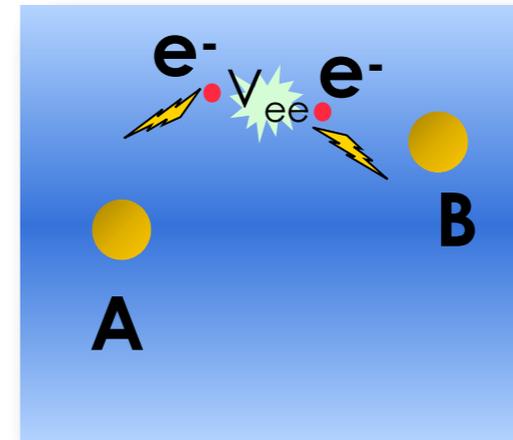
What is missing from Hartree-Fock Theory?

Exact Energy =



“Mean Field”
Hartree-Fock

+



Instantaneous electron-
electron interaction

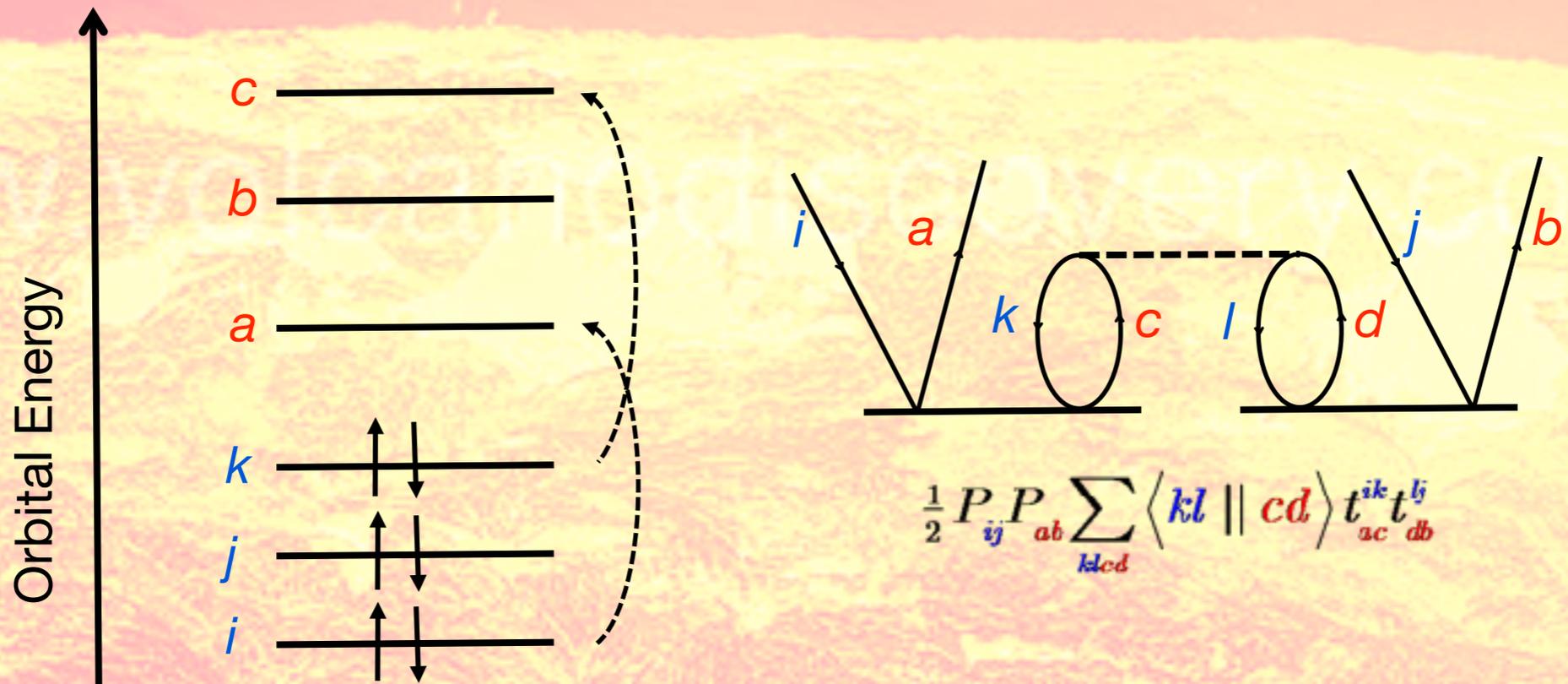
$$\text{Correlation energy} = \frac{1}{2} \sum_{i,j \text{ Electron pairs}} \mathcal{E}_{ij}(\uparrow\uparrow) + \mathcal{E}_{ij}(\uparrow\downarrow)$$

Fermi-Correlation
Coulomb-correlation



*Relatively easy due to
“Fermi hole” in the
mean-field*

*Extremely hard to
calculate due to
interelectronic cusp at
the coalescence point
 $r_1=r_2$*



$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ia} C_a^i |\Psi_i^a\rangle + \frac{1}{4} \sum_{ijab} C_{ab}^{ij} |\Psi_{ij}^{ab}\rangle + \frac{1}{36} \sum_{ijkabc} C_{abc}^{ijk} |\Psi_{ijk}^{abc}\rangle + \dots$$

Coupled Cluster Theory in a Nutshell

$$\Psi = \exp(T) \Psi_0 \quad \Psi_0 = |\phi_1 \dots \phi_N| \quad \phi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \varphi_{\mu}(\mathbf{r})$$

Ansatz
(Coester & Kuemmel)
Reference determinant
MOs
 μ
MO coeffs
BFs

Cluster Operator $T = T_1 + T_2 + T_3 + \dots$

$$T_1 = \sum_{ia} t_a^i a_a^+ a_i \quad T_2 = \frac{1}{4} \sum_{ijab} t_{ab}^{ij} a_{ab}^+ a_b^+ a_a a_j$$

Cluster Amplitudes

CC wavefunction $\Psi = \left(1 + (T_1 + T_2 + \dots) + \frac{1}{2} (T_1 + T_2 + \dots)^2 + \dots \right) \Psi_0$

$$= \left(1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{2} T_2^2 + \dots \right) \Psi_0$$

Conncted excitations
like CI, linear

disconnected excitations
(statistically uncorrelated)

Determination of the energy and the cluster amplitudes

$$E_{CC} = \langle \Psi_0 | e^{-T} \hat{H} e^T | \Psi_0 \rangle$$

$$R_K = \langle t_K \Psi_0 | e^{-T} \hat{H} e^T | \Psi_0 \rangle = 0$$

Nonlinear equation set,
not hard to solve;
up to 4th power of amplitudes

**Gold Standard:
CCSD(T)**

Accurate Solutions

THE JOURNAL OF CHEMICAL PHYSICS **125**, 144108 (2006)

W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions

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(Received 7 July 2006; accepted 10 August 2006; published online 12 October 2006)

... group systems, ... theory, is proposed. Computational cost is not insurmountably higher than that of the earlier W3 theory, while performance is markedly superior.

Our W4 atomization energies for a number of key species are in excellent agreement (better than 0.1 kcal/mol on average, 95% confidence intervals narrower than 1 kJ/mol) with the latest experimental data obtained from Active Thermochemical Tables. Lower-cost variants are proposed:

... meaning the (non-relativistic) Schrödinger equation is solved to an accuracy of $0.0001 E_h$ which is $\sim 99.9999\%$ or ~ 1 part in 10^6 !

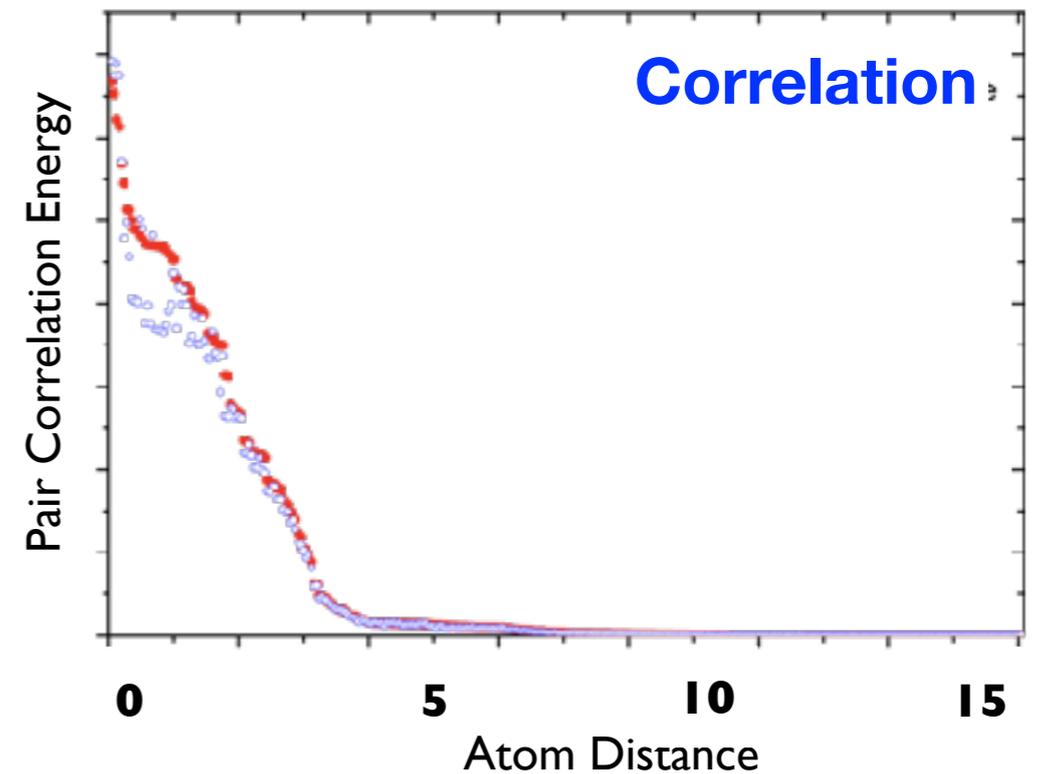
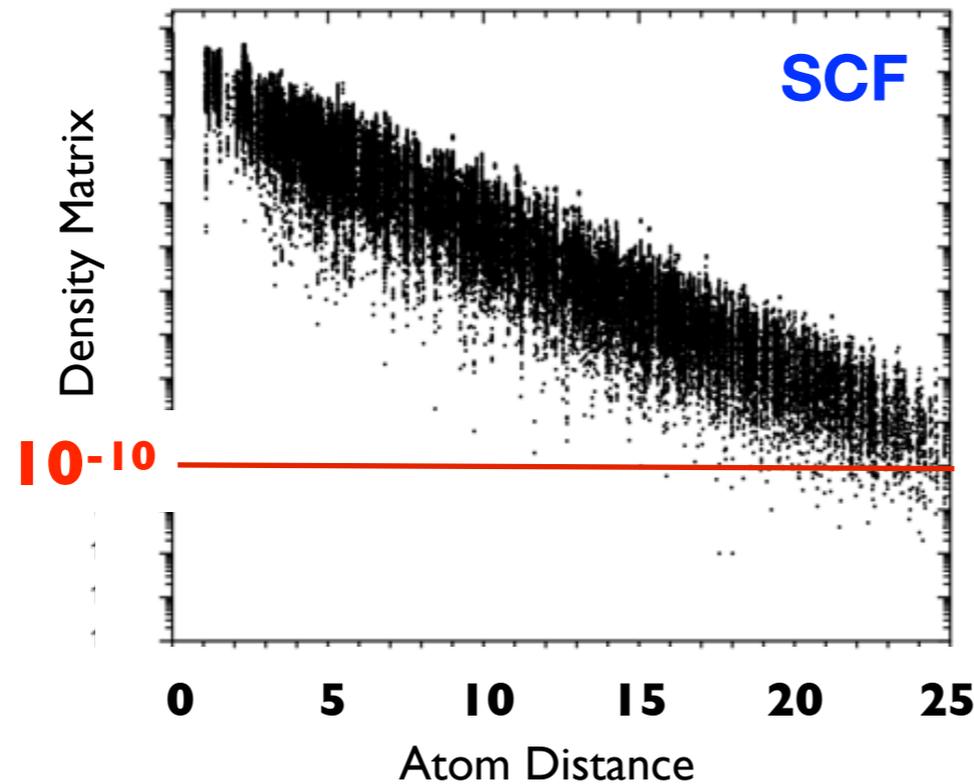
... For **really** small systems (1-6 *electrons*), we can today reach „crazy accuracy“, e.g. Nakatsuji calculated the H_2^- ground state energy to be **-0.597 139 063 123 405 074 834 134 096 025 974 142 a.u.** (36 significant digits!)

Problems with Coupled Cluster Theory



Saving Time in Electronic Structure Calculations

Exploit Sparsity!

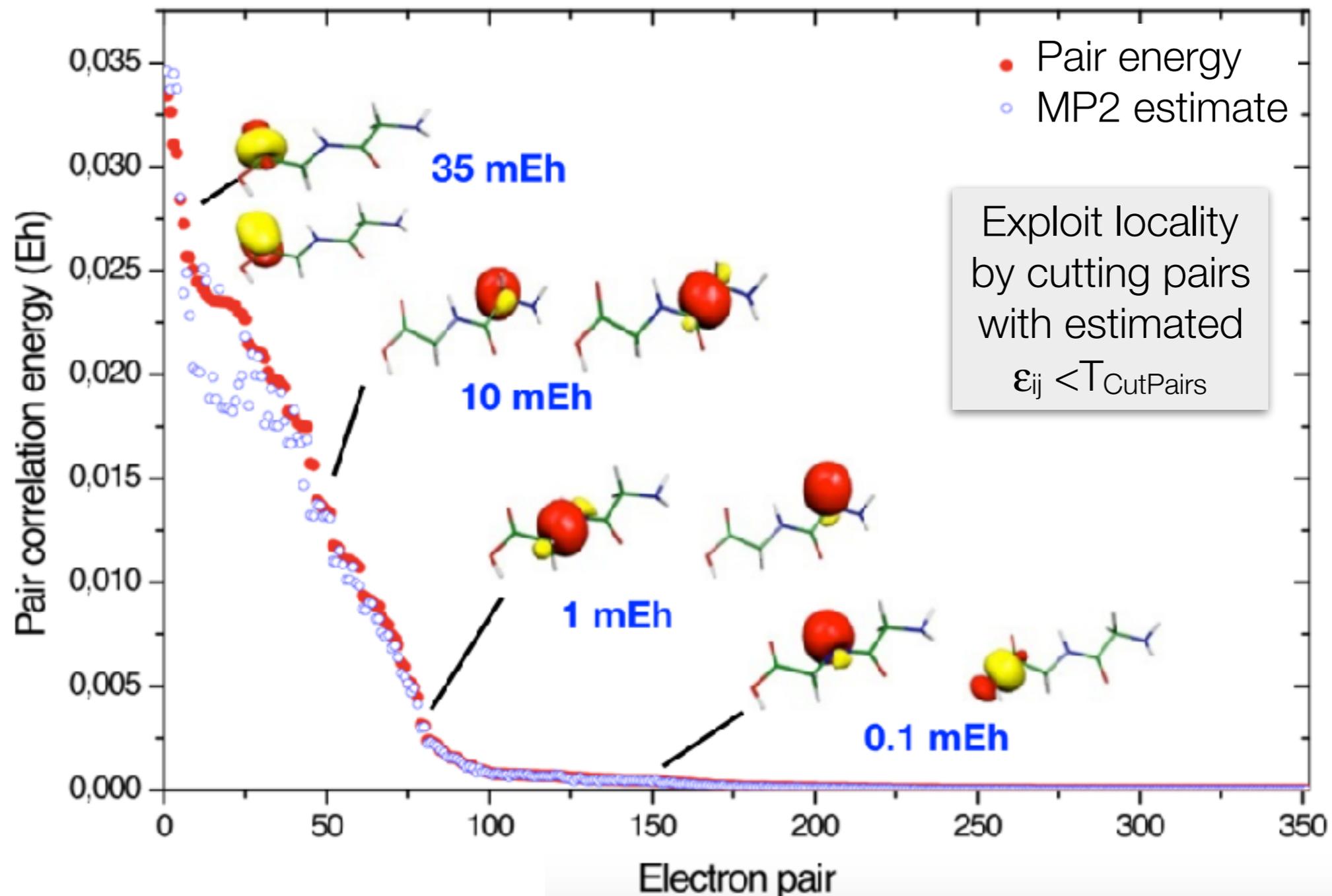


Compress Data!

$$M = \left(\begin{array}{c} \text{Large gray square} \end{array} \right) \xrightarrow{M' = U^\dagger M U} M' = \left(\begin{array}{cc} \text{Small gray square} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{array} \right)$$

Approximation 1: Pair Approximation

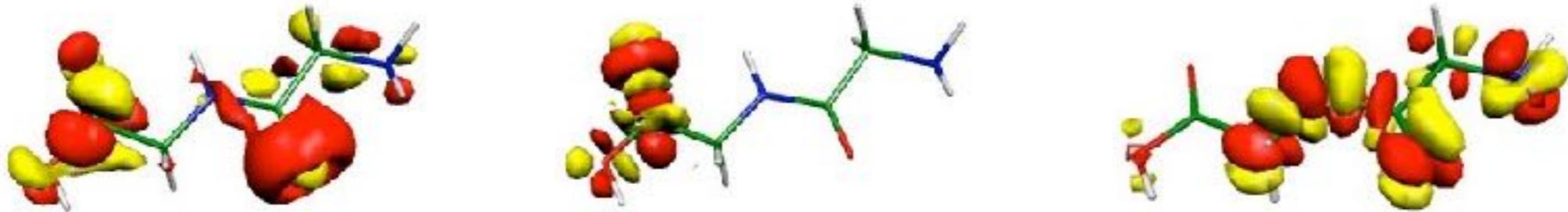
$$E_{corr} = \frac{1}{4} \sum_{ijab} C_{ab}^{ij} \langle ij || ab \rangle = \frac{1}{2} \sum_{ij} \epsilon_{ij}$$



Approximation 2: Virtual Space truncation

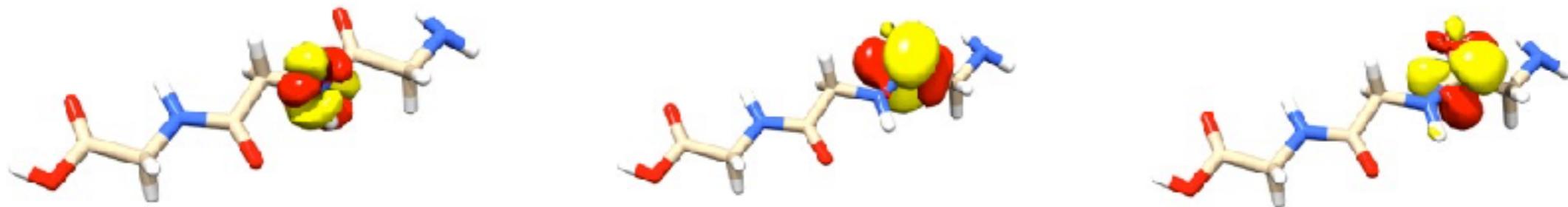
$$\varepsilon_{ij} \approx \frac{1}{2} \sum_{a,b \in \text{pair-domain } ij} C_{ab}^{ij} \langle ij || ab \rangle$$

- ✓ Truncated canonical virtual orbitals?



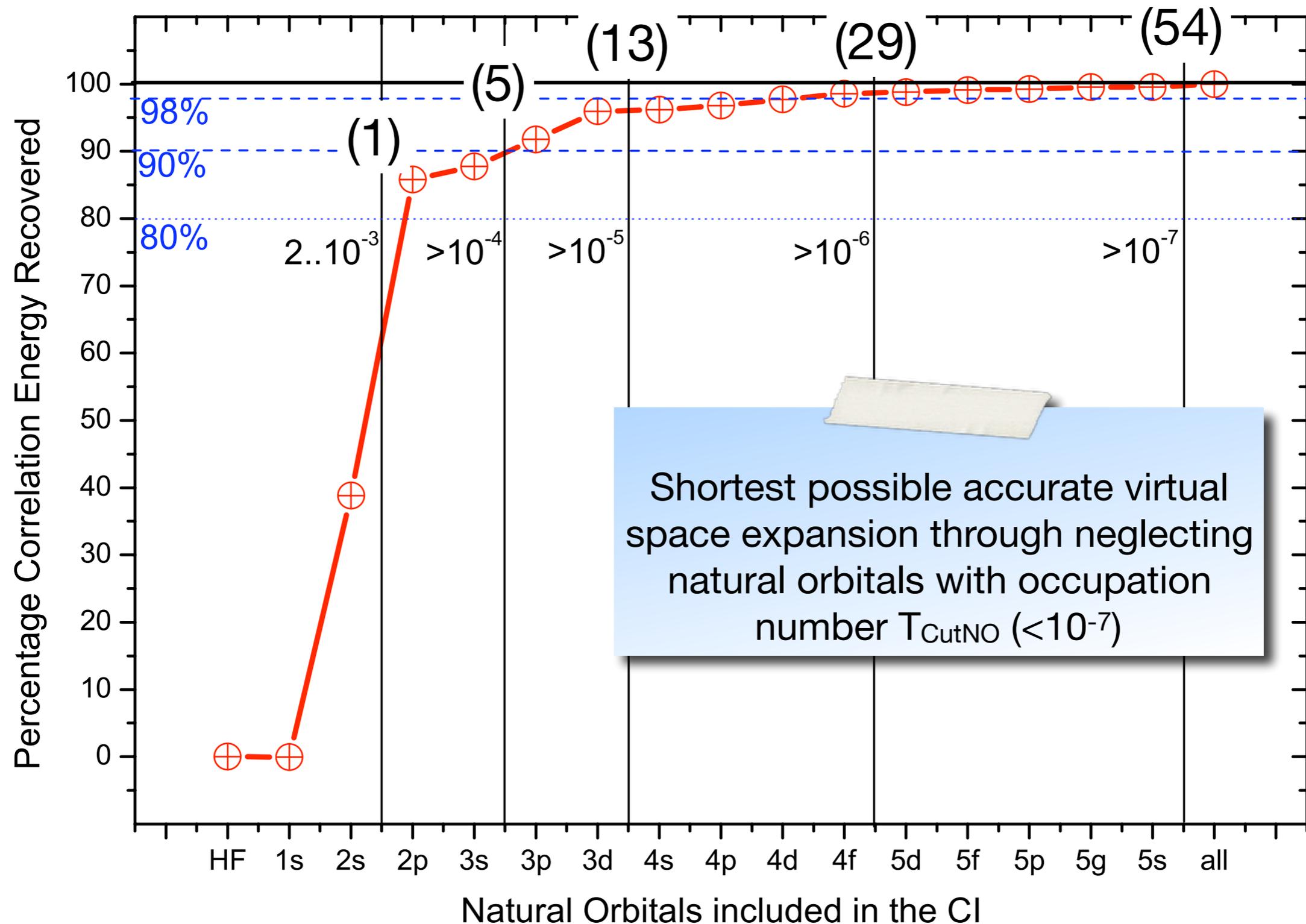
➔ BAD idea!

- ✓ Projected atomic orbitals (Pulay, Werner, Schütz), localized virtual orbitals (Förner, Jørgensen, ...)

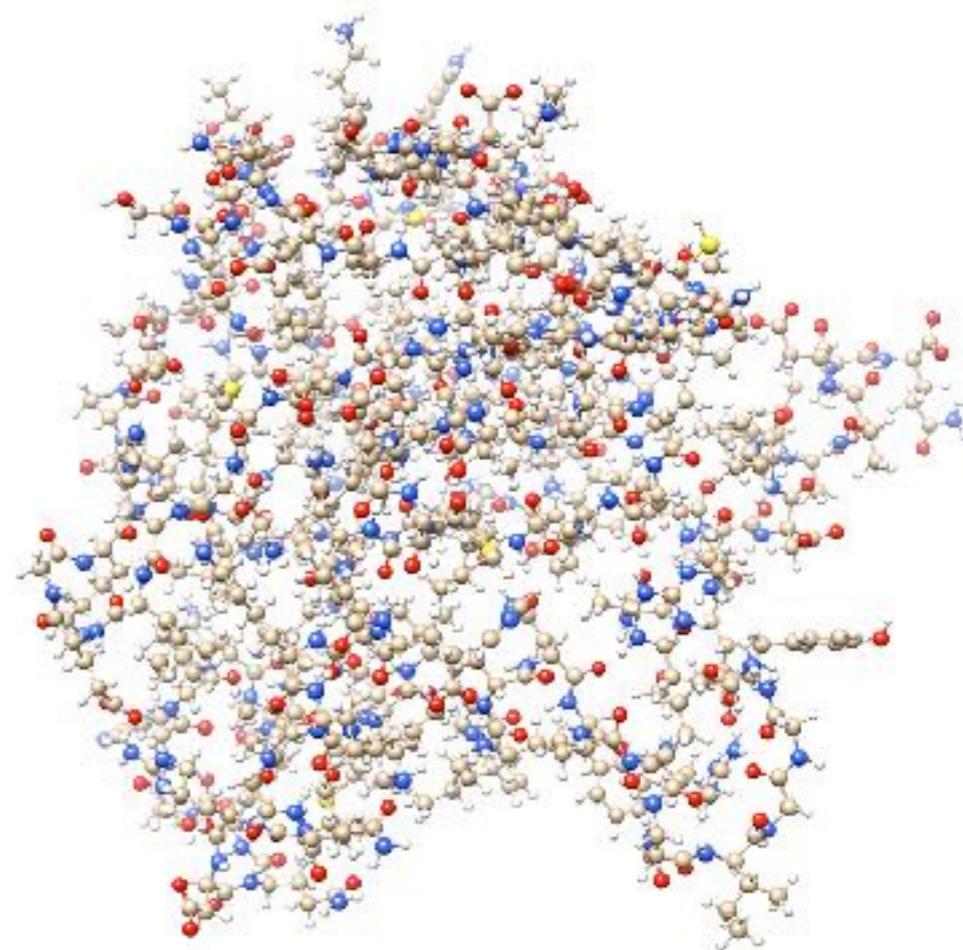
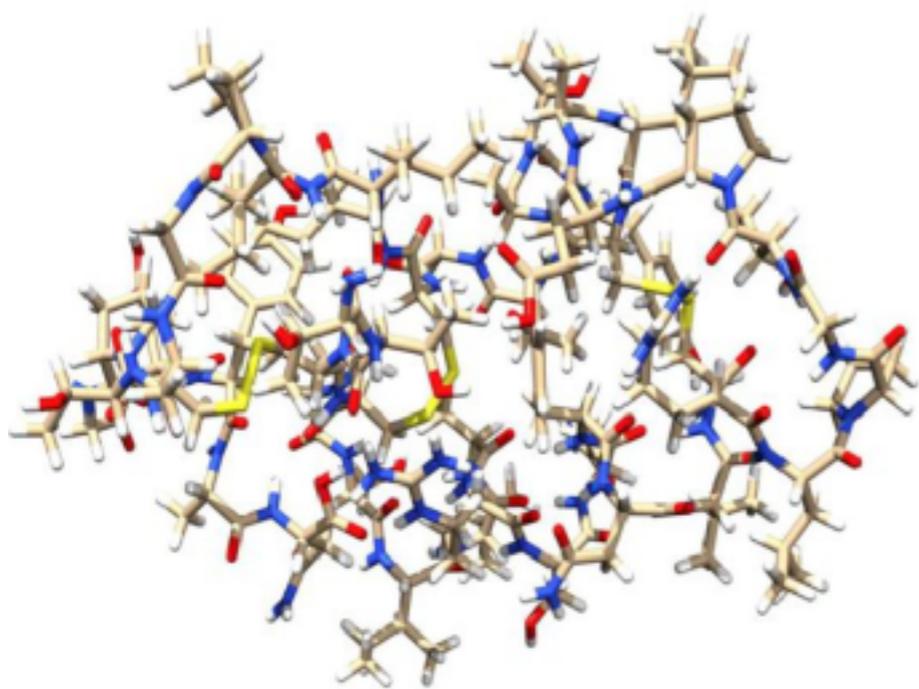


- ➔ It works, but for high accuracy (99.9%) the domains become impractically large
- ➔ Need „compaction“ of the space

Most Compact Expansion: Natural Orbitals



Huge Calculations with linear DLPNO-CCSD(T)



Crambin/def2-TZVP

644 atoms

12705 Basis functions

10 d/4 cores

$C_{350}H_{702}$ /def2-TZVP

1052 atoms

15062 Basis functions

18h/4 cores

Integrase/cc-pVDZ

2380 atoms

22621 Basis functions

62h/64 cores

(CIM-DLPNO-CCSD(T))

Y. Guo, FN, 2017, in preparation

DFT: Basis for the Hohenberg-Kohn Theorems

$$\lim_{r \rightarrow 0} \left[\frac{\partial}{\partial r} + 2Z_A \right] \bar{\rho}(r) = 0$$

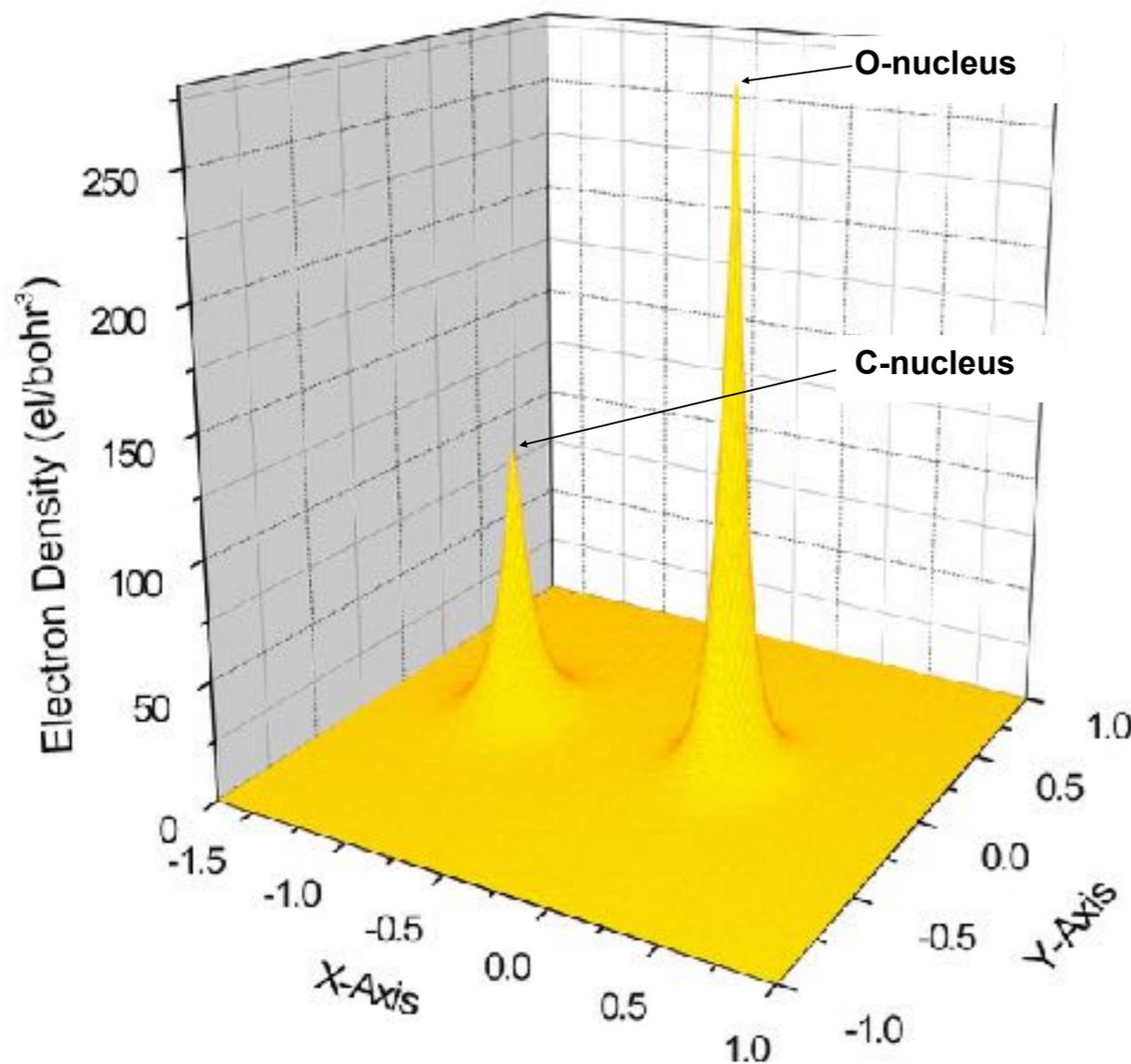
$$\int \rho(\mathbf{r}) d\mathbf{r} = N$$



We can reconstruct the nuclear positions and charges from the electron density



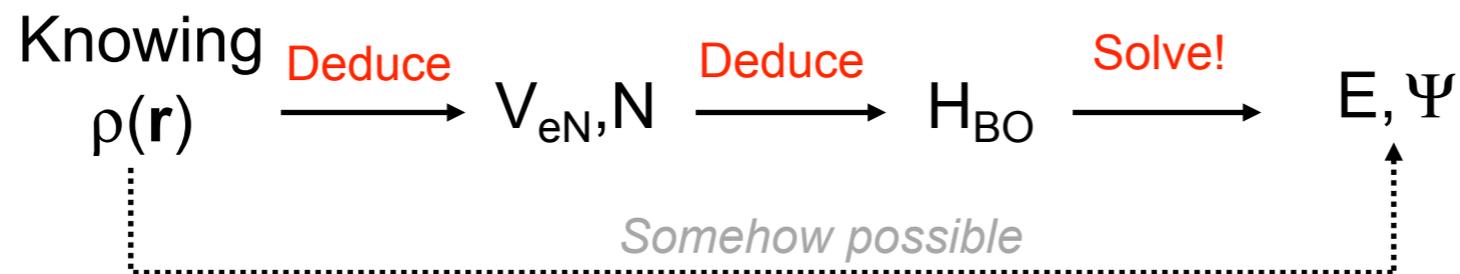
This means, we can reconstruct the BO Hamiltonian of the molecule from $\rho(r)$ alone



Electron Density of the CO molecule

The Hohenberg Kohn-Theorems

If we know the BO Hamiltonian of the molecule we could (in principle) solve the Schrödinger equation. Hence, the exact N -particle wavefunction, the exact energy and all expectation values are **functionals** of the electron density!



The “**big dream**” is to go directly from the electron density to the exact energy. From the DFT logics this must be “somehow” possible, but we don’t know how!

- 1) The existence of the “universal” functional $E[\rho]$ is guaranteed by the **first Hohenberg-Kohn** (HK) theorem.
- 2) The **second HK theorem** establishes a variational principle that states that $E[\rho']$ (ρ' being a test density) $\geq E[\rho]$

The DFT Functional

We can start to approach the functional by separating the parts inspired by HF theory that we know we can write exclusively in terms of the density:

$$E[\rho] = V_{NN} + V_{eN}[\rho] + J[\rho] + T[\rho] + E'_{XC}[\rho]$$

$$V_{NN}$$

Nuclear Repulsion (trivial):

$$V_{eN}[\rho] = -\sum_A Z_A \int \rho(\mathbf{r}) r_{iA}^{-1} d\mathbf{r}$$

Electron-Nuclear Attraction (ok)

$$J[\rho] = \frac{1}{2} \sum_{ij} \langle ij | ij \rangle = \frac{1}{2} \int \int \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$$

Coulomb Energy (ok)

$$T[\rho]$$

Kinetic Energy (unknown)

$$E'_{XC}[\rho] = K[\rho] + C[\rho]$$

Exchange and Correlation (unknown)

The Kohn-Sham Construction (I)

DFT only became a practical tool after an ingenious trick of Kohn-Sham. They have considered a **fictitious model system** of independent particles that share the exact electron density with the real system.

The wavefunction for such a system is a single Slater determinant (Kohn-Sham determinant)

$$\rho_{KS}(\mathbf{r}) = \sum_i \int |\psi_i(\mathbf{x})|^2 ds \equiv \rho_{exact}(\mathbf{r})$$

Re-inserting $\rho(\mathbf{r})$ into the energy expression yields the exact E.

$$E[\rho] = V_{NN} + T_s[\rho] + V_{eN}[\rho] + J[\rho] + E_{XC}[\rho]$$

The “noninteracting” kinetic energy is:

$$T_s[\rho] = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle$$

But now the exchange correlation contains the missing part of the kinetic energy:

$$E_{XC}[\rho] = E'_{XC}[\rho] + T[\rho] - T_s[\rho]$$

The Kohn-Sham Construction (II)

The Kohn-Sham orbitals are found from the **Kohn-Sham equations**:

$$\left\{ -\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r}) \right\} \psi_i(\mathbf{x}) = \varepsilon_i \psi_i(\mathbf{x})$$

The **effective Kohn-Sham potential** is defined by:

$$v_{eff}(\mathbf{r}_1) = -\sum_A Z_A r_{A1}^{-1} + \int \rho(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_2 + V_{XC}(\mathbf{r})$$

And the XC contribution is defined by a “**functional derivative**”:

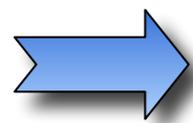
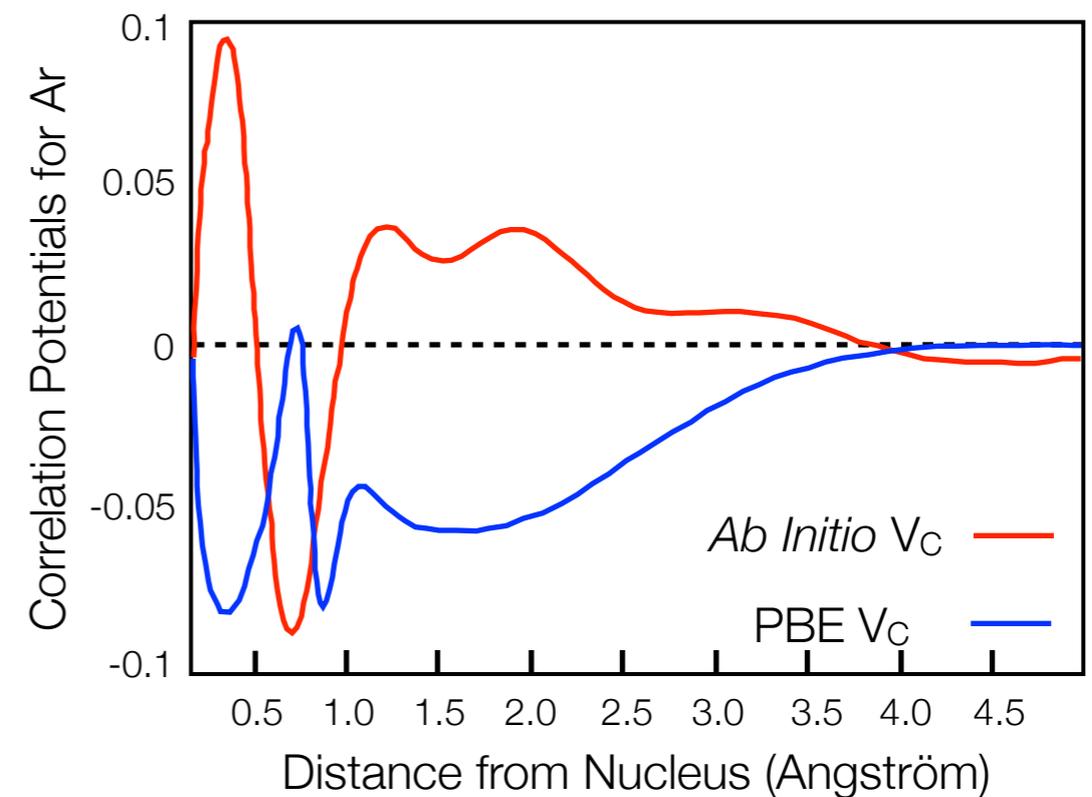
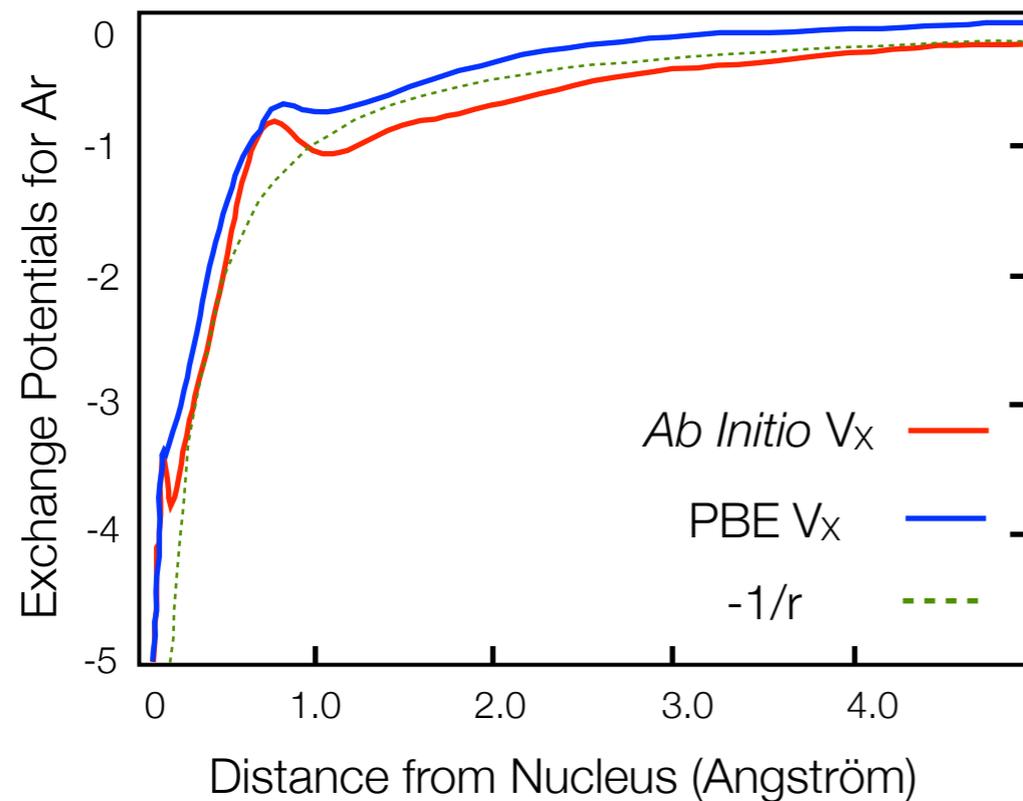
$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta \rho(\mathbf{r})}$$

This is the celebrated formal apparatus of DFT! If we would know E_{XC} , these equations would constitute an *exact* framework. But we don't (and likely never will)!

However, much progress has been made by **guessing** approximate $E_{XC}[\rho]$ and inserting them into the Hohenberg-Kohn-Sham machinery.

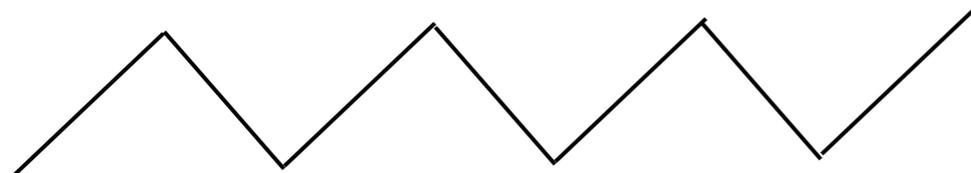
Ab Initio DFT Potentials

There are (expensive!) ways to construct very good KS potentials from accurate densities (red). These can be compared with “typical” present day potentials (blue).



The presently used potentials are far from being correct and all present day DFT results rely on cancellation of large errors.

Big Problems may still exist ...



ΔE	=	$+1.9 \pm 0.5$	kcal/mol	Exp.
		+1.4	kcal/mol	SCS-MP2
		-11.5	kcal/mol	HF
		-8.4	kcal/mol	B3LYP
		-9.9	kcal/mol	BLYP

Numerical Results

Total, correlation and exchange energies of the Neon atom using the *ab initio* CCSD(T) method and various standard functionals (deviations from the wavefunction results in mEh).

	E_{tot}	E_{corr}	E_{x}
CCSD(T)	-128.9260	-0.379	-12.098
	-129.0640 (rel)		
BP86	-128.9776 (-52)	-0.388 (- 9)	-12.104 (-6)
PBE	-128.8664 (+60)	-0.347 (+32)	-12.028 (+70)
BLYP	-128.9730 (-47)	-0.383 (- 4)	-12.099 (-1)
TPSS	-128.9811 (-55)	-0.351 (+28)	-12.152 (-54)
B3LYP	-128.9426 (-17)	-0.452 (-73)	-12.134 (-36)
B2PLYP	-128.9555 (-30)	-0.392 (-13)	-12.103 (- 5)
Exp	-129.056		



Wavefunction theory is very accurate (but also very expensive). DFT results vary widely among different functionals and either over- or undershoot. However, total energies are not important in chemistry – relative energies matter.