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Introduction to Quantum Chemical Methods

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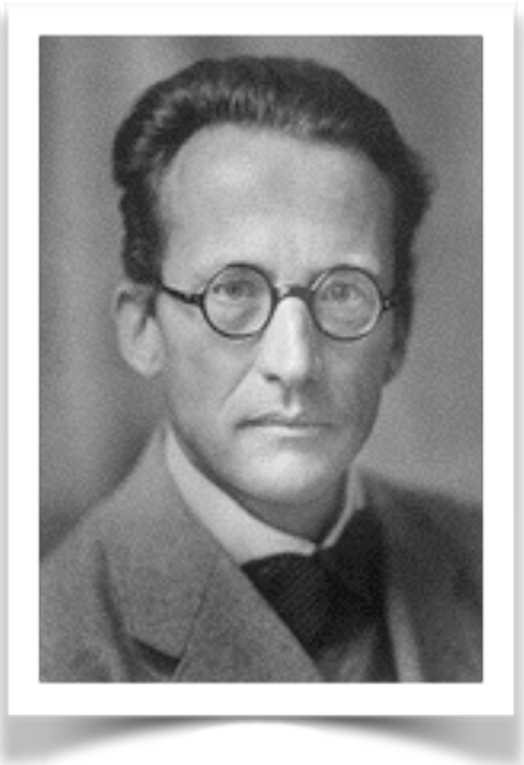
How Theoretical Chemistry almost didn‘t Start

„Any attempt to use mathematical methods for the investigation of chemical questions must be considered as completely irrational and is strongly opposing the spirit of chemistry. If mathematics will ever occupy a prominent place in chemistry - an absurd idea that fortunately is completely unrealistic - this would lead to a rapid and irreversible decay of this scientific discipline“

Isidore Marie Auguste François Xavier Comte (1798-1857)

Comte, IMAFX *Cours der philosophie positive,* Schleicher, Paris, **1838**, p- 28-29

... but then



Erwin Schrödinger

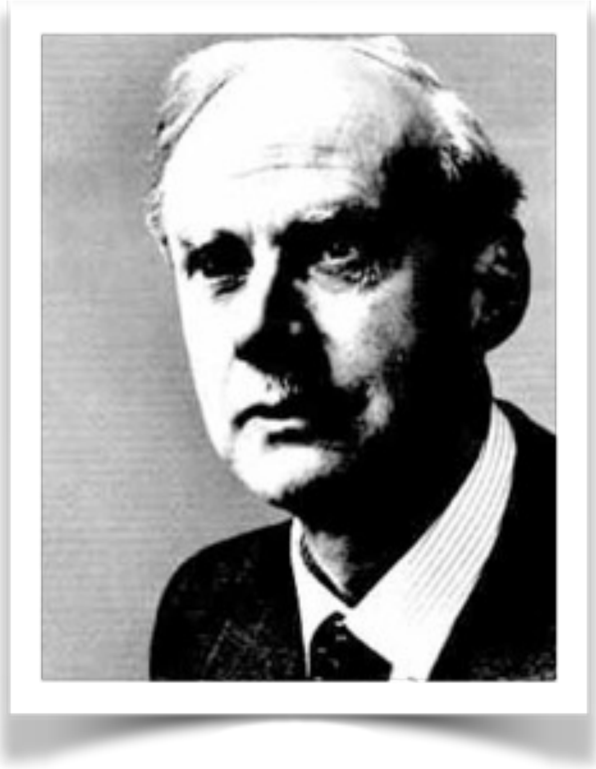
$$\left\{-\tfrac{1}{2}\nabla^2 + V(\mathbf{r})\right\}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Wave Mechanics (1926)

Werner Heisenberg

$$\left\{\mathbf{T} + \mathbf{V}\right\}\mathbf{C} = E\mathbf{C}$$

Matrix Mechanics (1926)



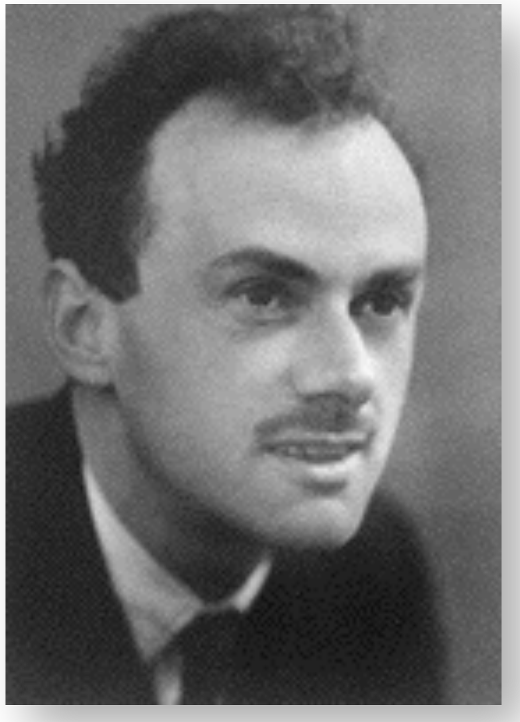
Paul A.M. Dirac

$$\begin{pmatrix} V(\mathbf{r}) & c\vec{\sigma}\mathbf{p} \\ c\vec{\sigma}\mathbf{p} & V(\mathbf{r}) - 2c \end{pmatrix}\begin{pmatrix} \psi_{L}(\mathbf{r}) \\ \psi_{L}(\mathbf{r}) \end{pmatrix} = E\begin{pmatrix} \psi_{L}(\mathbf{r}) \\ \psi_{L}(\mathbf{r}) \end{pmatrix}$$

Relativistic Quantum Mechanics (1928)

... and shortly after

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 Adrian Maurice Dirac
(1902-1984)

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

Dirac, PAM Proc. Roy. Soc.Ser. A, **1929**, 123, 714

.. up to

We can calculate everything!

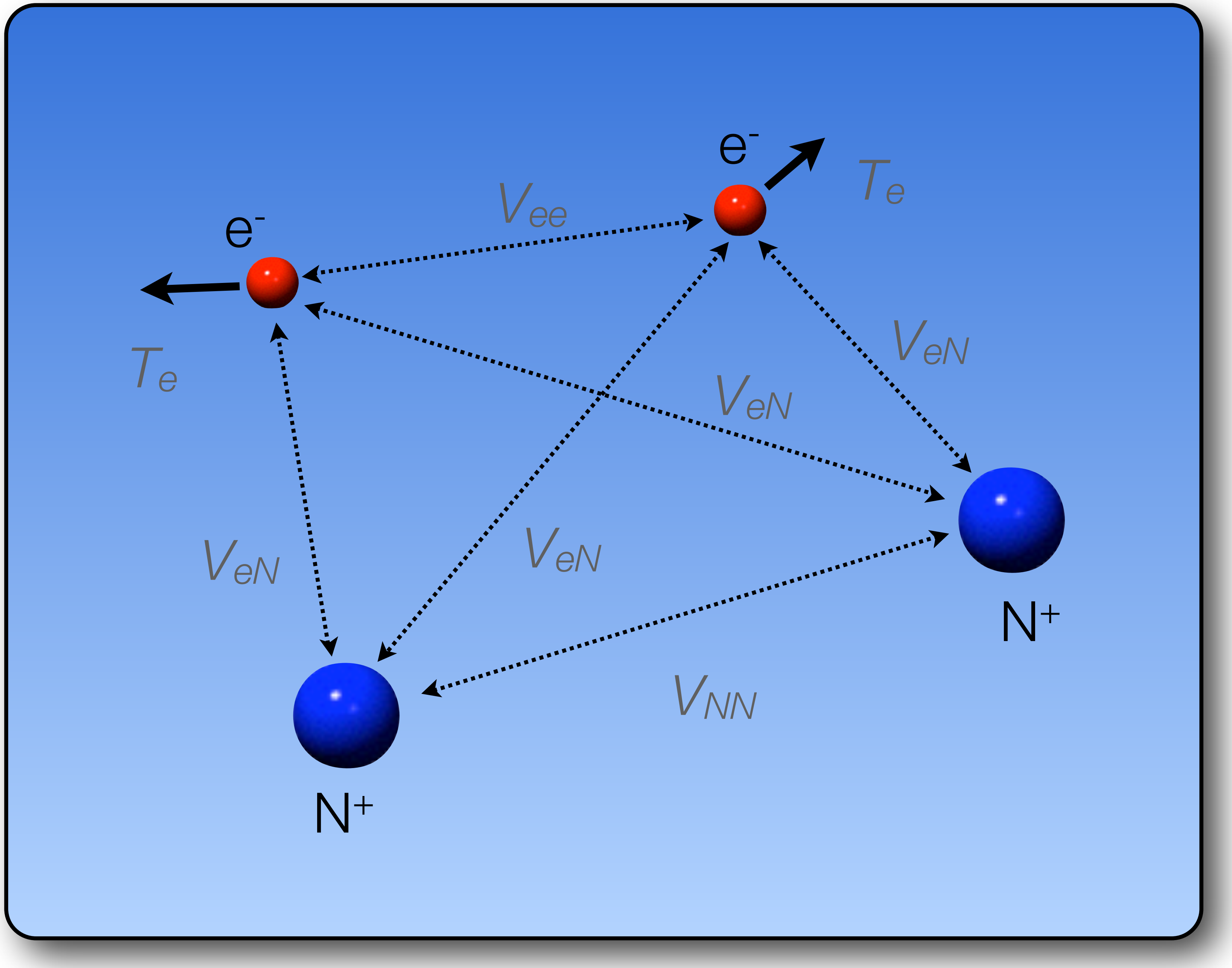
(1975)

Enrico Clementi
(born 1931)

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)
- ... many other reasons why the synergy between theory and experiment is greatly enhancing the efficieny and the depths of the scientific analysis

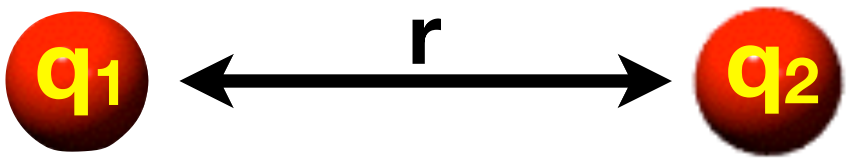
Fundamental Interactions in Molecules



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

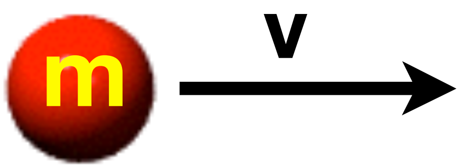
Just 2 Laws:

1. Coulomb's Law



$$E = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}$$

2. Kinetic Energy



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

From Classical to Quantum Mechanics

- In classical mechanics **Newton‘s equations** are solved that contain the positions (**r**) and momenta **p** (recall **p**=m**v**) as unknown variables. The solutions are **r**(t) and **p**(t) (the „trajectory“ of the particles).
- In quantum mechanics the **uncertainty principle** forbids us to know **r**(t) and **p**(t) simultaneously. Instead we are aiming for the „wavefunction“ that provides us with the probability of finding the particles at given points in space with given velocities (a more detailed definition follows).
- In order to calculate the wavefunction, a special form of the equations of motion are used - the **Hamiltonian formalism** that is most readily transferred from classical to quantum mechanics.
- The „**Hamiltonian**“ of the system corresponds to the total energy. Thus, it is the sum of all terms that contribute to the total energy

$$\hat{H}(\mathbf{r},\mathbf{R}) = T_e + T_N + V_{eN} + V_{ee} + V_{NN}$$

$$T_e = \sum_i p_i^2 / 2m_{el}$$

$$T_N = \sum_A p_A^2 / 2m_A$$

$$V_{ee} = \frac{e_0^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

$$V_{NN} = \frac{e_0^2}{4\pi\varepsilon_0} \sum_{A<B} \frac{Z_A Z_B}{\left|\mathbf{R}_A - \mathbf{R}_B\right|}$$

$$V_{eN} = -\frac{e_0^2}{4\pi\varepsilon_0} \sum_{A,i} \frac{Z_A}{\left|\mathbf{r}_i - \mathbf{R}_A\right|}$$

Note: i ,j sum over electrons, A,B sum over nuclei, Z_A,M_A- Charge and Mass of Nucleus ‚A‘

The Schrödinger Equation

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

$$\hbar = 4\pi\varepsilon_0 = e_0 = m_e = 1 \quad c = 137.06$$

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

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

- ★ 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 **x**.
- ★ **Schrödinger's equation** for the many particle wavefunction Ψ(x$_1$,...,x$_N$,R$_1$,...,R$_M$,t) ≡ Ψ(x,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**

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

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.

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

- ★ **Justification (heuristic):** Nuclei are much heavier and move much slower than electrons. hence, electrons adjust themselves immediatly 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!

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

$$\left\{\hat{T}_{N} + E(\mathbf{R})\right\}\Theta(\mathbf{R}) = \mathfrak{E}\Theta(\mathbf{R})$$

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 party 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:

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

Given the nuclear configuration **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:

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

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(**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

Ground and Excited States

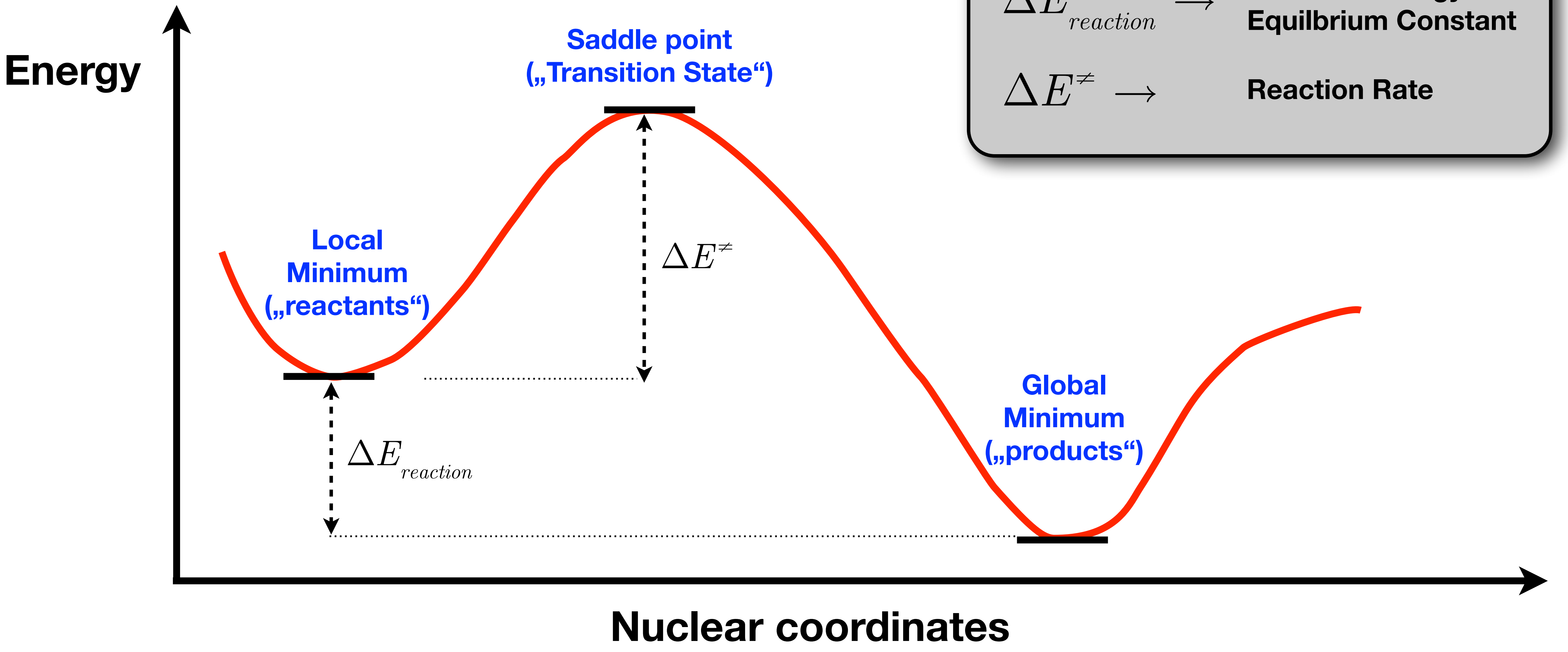
The BO eigenvalue equation (like any other eigenvalue equation) has an infinite number of solutions. If we order, the solutions according to incraesing energy and start labelling by ‚0‘:

- ★ $E_0(\mathbf{R})$ is the **ground state** total energy of the system
- ★ $E_I(\mathbf{R})$ for I>0 are the **excited states** of the system
- ★ NOTE: Each state has its own eigenfunction $\Psi_I(\mathbf{x}|\mathbf{R})$
- ★ If two or several eigenvalues are identical (say *n*), we say that the state is *n*-fold **degenerate.** The eigenfunctions belonging to the same degenerate eigenvalue are only determined up to an arbitrary unitary transformation.
- ★ The eigenfunctions can be classified at least according to three criteria:
  - ✓ Their **total spin *S*** (to be discussed later)
  - ✓ Their **spin-projection quantum number *M*** (to be discussed later)
  - ✓ Their overall **spatial symmetry** with irreducible representation Γ (not disucssed here)

$$\left.\begin{matrix} \\ \\ \\ \end{matrix}\right\} \Psi_I^{SM\Gamma} \equiv \left| ISM\Gamma \right\rangle$$

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:

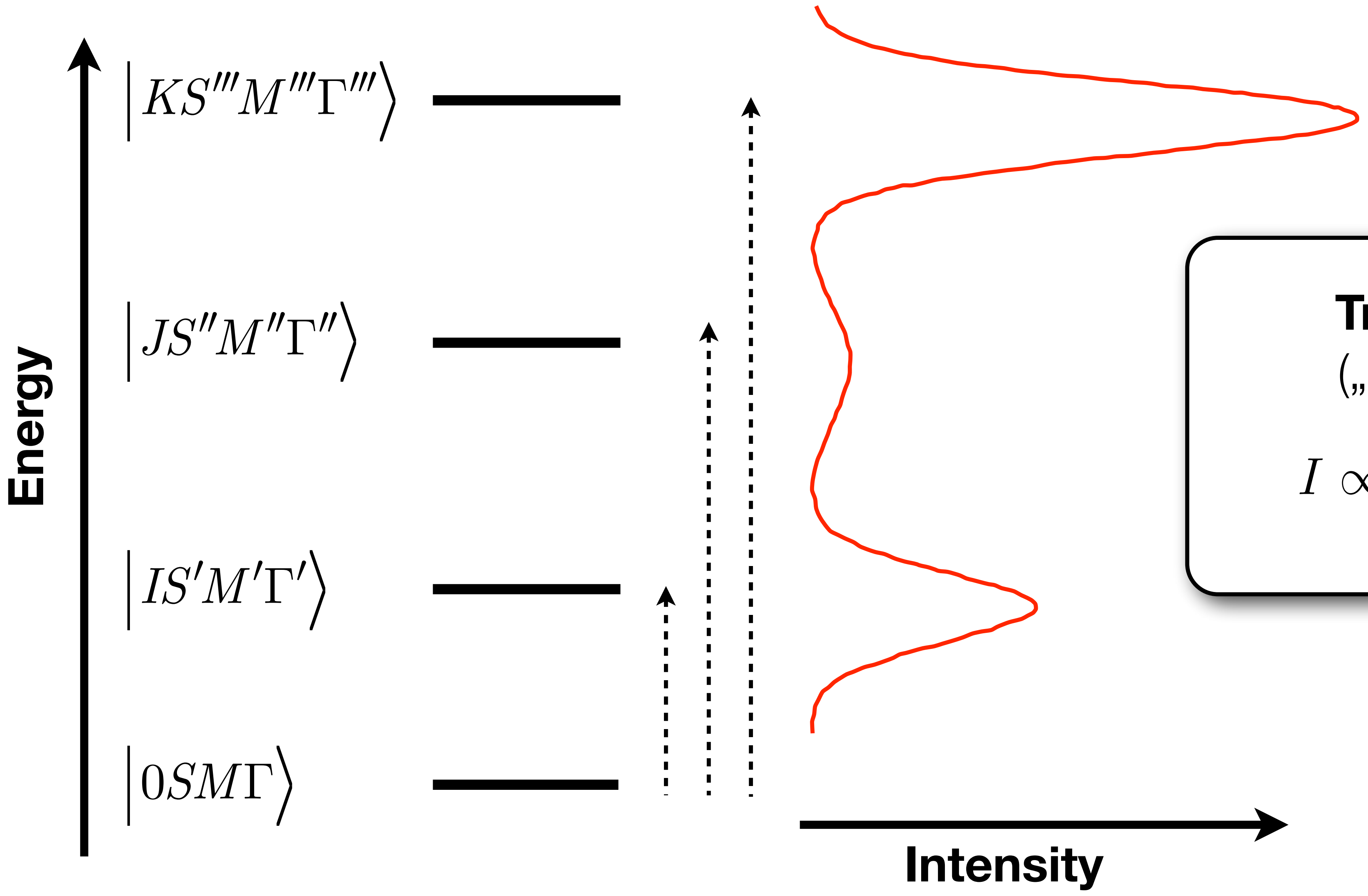


$\Delta E_{reaction} \longrightarrow$ **Reaction Energy**
Equilbrium Constant

$\Delta E^{\neq} \longrightarrow$ **Reaction Rate**

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



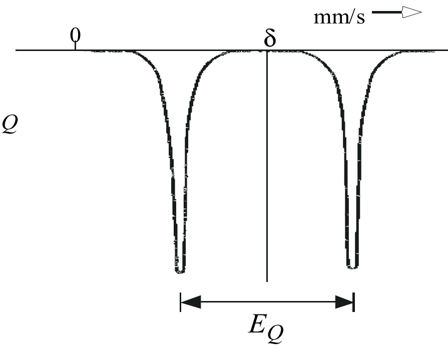
Transition Probability
(„Fermi‘s Golden Rule“)

$$I \propto \left| \langle \Psi_{initial} \mid H_1 \mid \Psi_{final} \rangle \right|^2$$

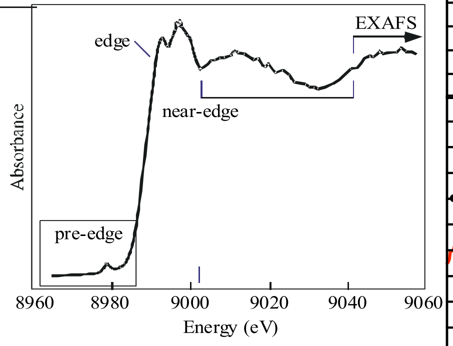
Spectroscopic Techniques

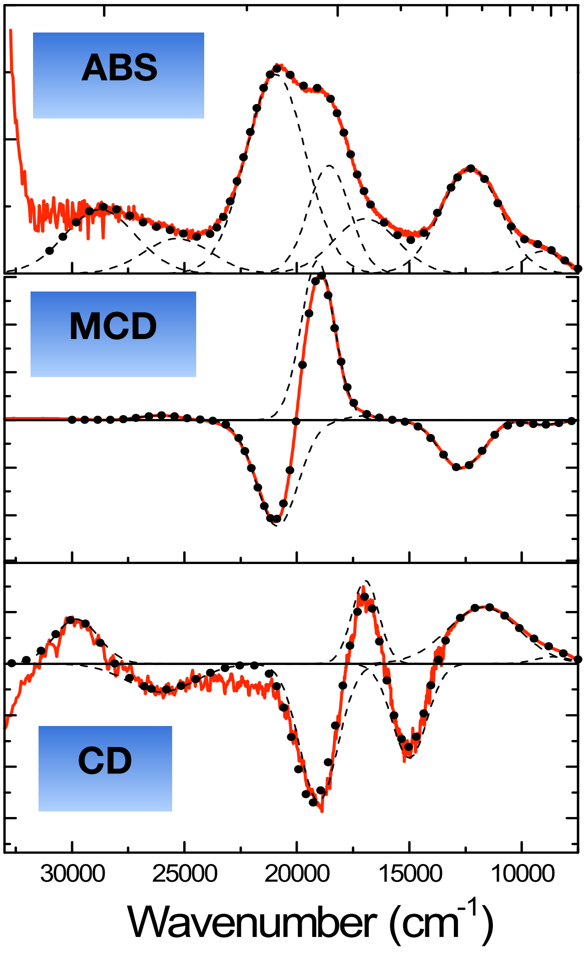
	Gamma	X-Ray		UV/vis	Infrared	Microwave	Radiowave
eV	14000	8000	2000	4 - 1	0.1-0.01	10^{-4} -10^{-5}	10^{-6} -10^{-7}

Möss-bauer

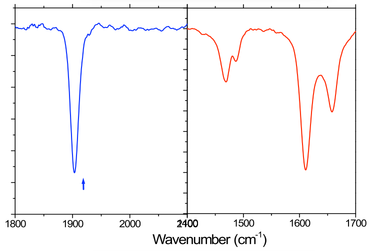


XAS
EXAFS

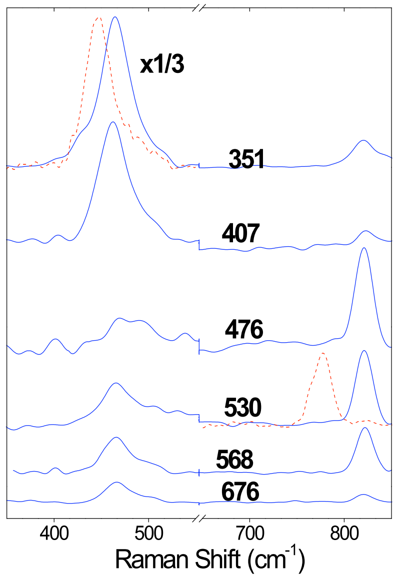




IR

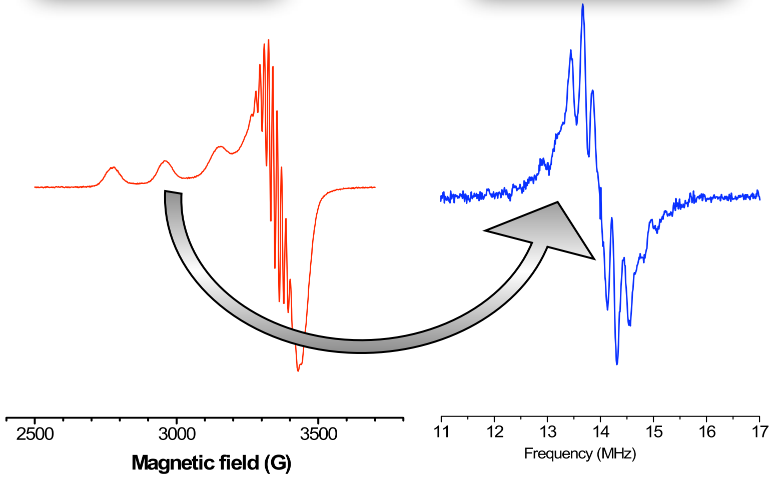


Raman



EPR

ENDOR



NMR

Note: 1.au. = 27.21 eV 1eV = 8095 cm^{-1} = 23.06 kcal/mol 1 cm^{-1}=29979 MHz

Solving the Born-Oppenheimer Equation

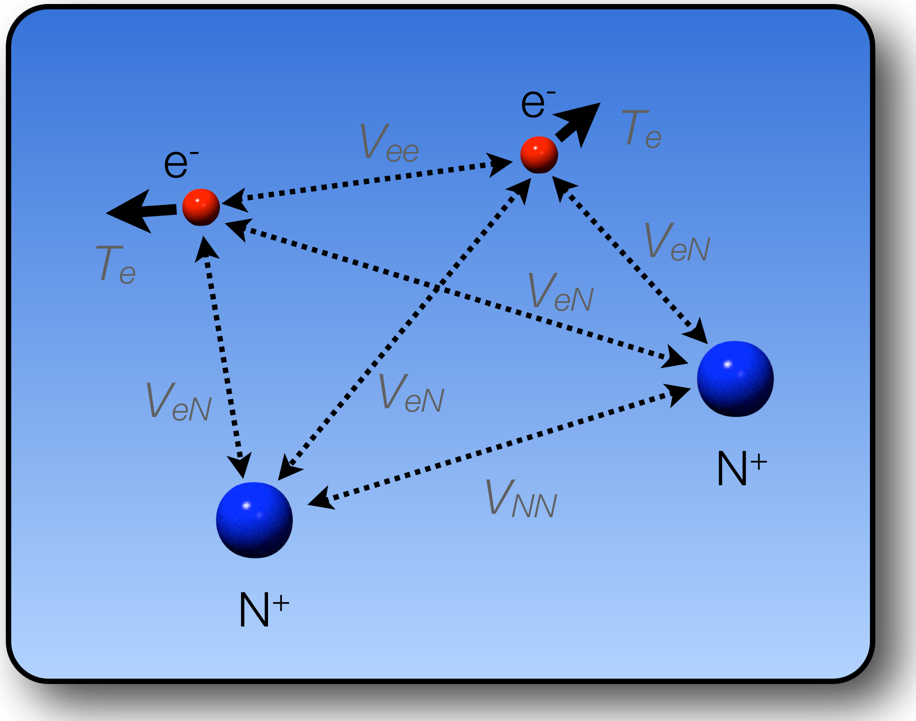
★ How do we solve the many-particle Born-Oppenheimer equation?

NOT AT ALL!

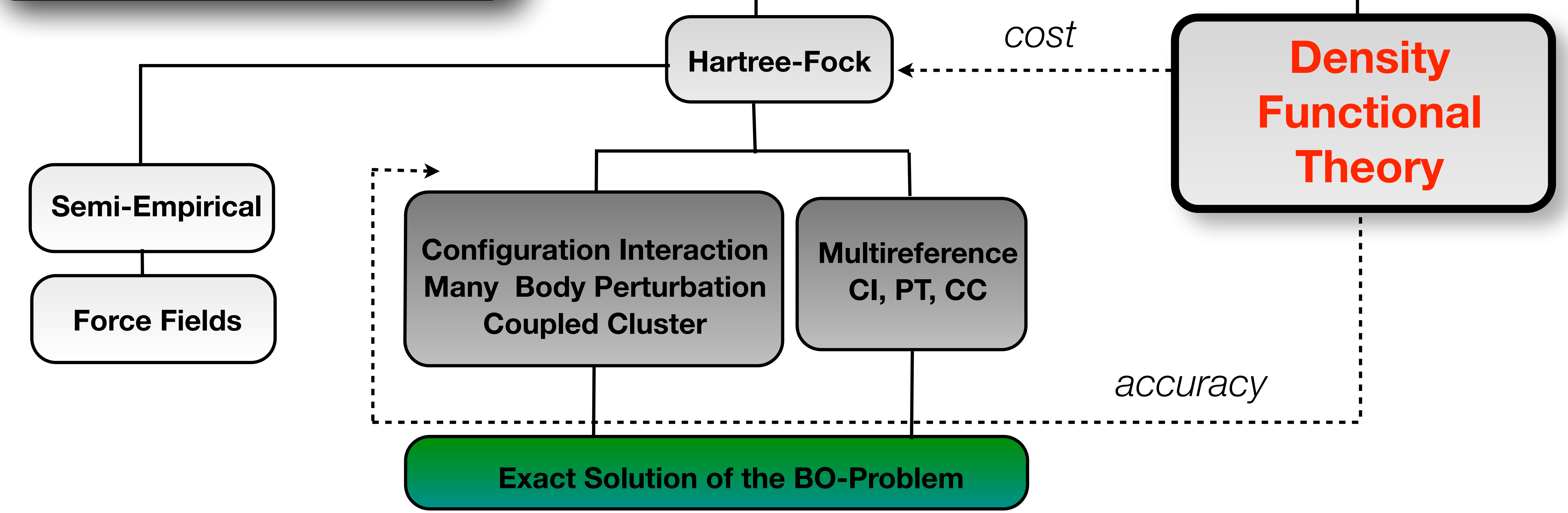
➡ The Born-Oppenheimer Schrödinger equation can not be solved in closed form for more than one electron. Not even for the simplest two electron cases.

➡ We need approximation methods

Approximate Quantum Mechanical Methods



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



Hartree-Fock

cost

Density Functional Theory

Semi-Empirical

Force Fields

Configuration Interaction
Many Body Perturbation
Coupled Cluster

Multireference
CI, PT, CC

accuracy

Exact Solution of the BO-Problem

Approximations: The Variational Principle

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

The „**Ritz-functional**“ is:

$$E[\Psi] = \frac{\left\langle \Psi_{trial} \mid H \mid \Psi_{trial} \right\rangle}{\left\langle \Psi_{trial} \mid \Psi_{trial} \right\rangle}$$

For the **exact wavefunction** E[Ψ] 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[Ψ] with respect to the parameters **p** to obtain the best possible approximation within the given Ansatz. The condition for a **stationary point** is:

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

Ansatz: The Hartree-Fock Method

The **Hartree-Fock** (HF) method is obtain by a specific Ansatz for the trail wavefunction. It is inspired by the form the wavefunction would have, if the electron-electron interation 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**“

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

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 {ϕ} would be mathmatically „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**“ **c** leads to the famous **Hartree-Fock Roothaan** equations. The MO coefficients must satisfy the following coupled set of nonlinear equations:

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

$$\varepsilon_i = Orbital\ Energy\,of\ Orbital\ i$$

$$F = Fock\,Operator$$

$$S = Overlap\,Matrix$$

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*:

$$\varepsilon_i = \left\langle \psi_i \mid F \mid \psi_i \right\rangle = \left\langle \psi_i \mid \underbrace{T_e + V_{eN}}_{h} \mid \psi_i \right\rangle + \sum_j \left\langle \psi_i \psi_j \parallel \psi_i \psi_j \right\rangle$$

Where the „**two-electron integral**“ is:

$$\left\langle \psi_i \psi_j \parallel \psi_i \psi_j \right\rangle = \left\langle \psi_i \psi_j \mid \psi_i \psi_j \right\rangle - \left\langle \psi_i \psi_j \mid \psi_j \psi_i \right\rangle$$

$$= \underbrace{\int\int \frac{\left|\psi_i(\mathbf{x}_1)\right|^2 \left|\psi_j(\mathbf{x}_2)\right|^2}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} d\mathbf{x}_1\, d\mathbf{x}_2}_{} - \underbrace{\int\int \frac{\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\psi_j(\mathbf{x}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} d\mathbf{x}_1\, d\mathbf{x}_2}_{}$$

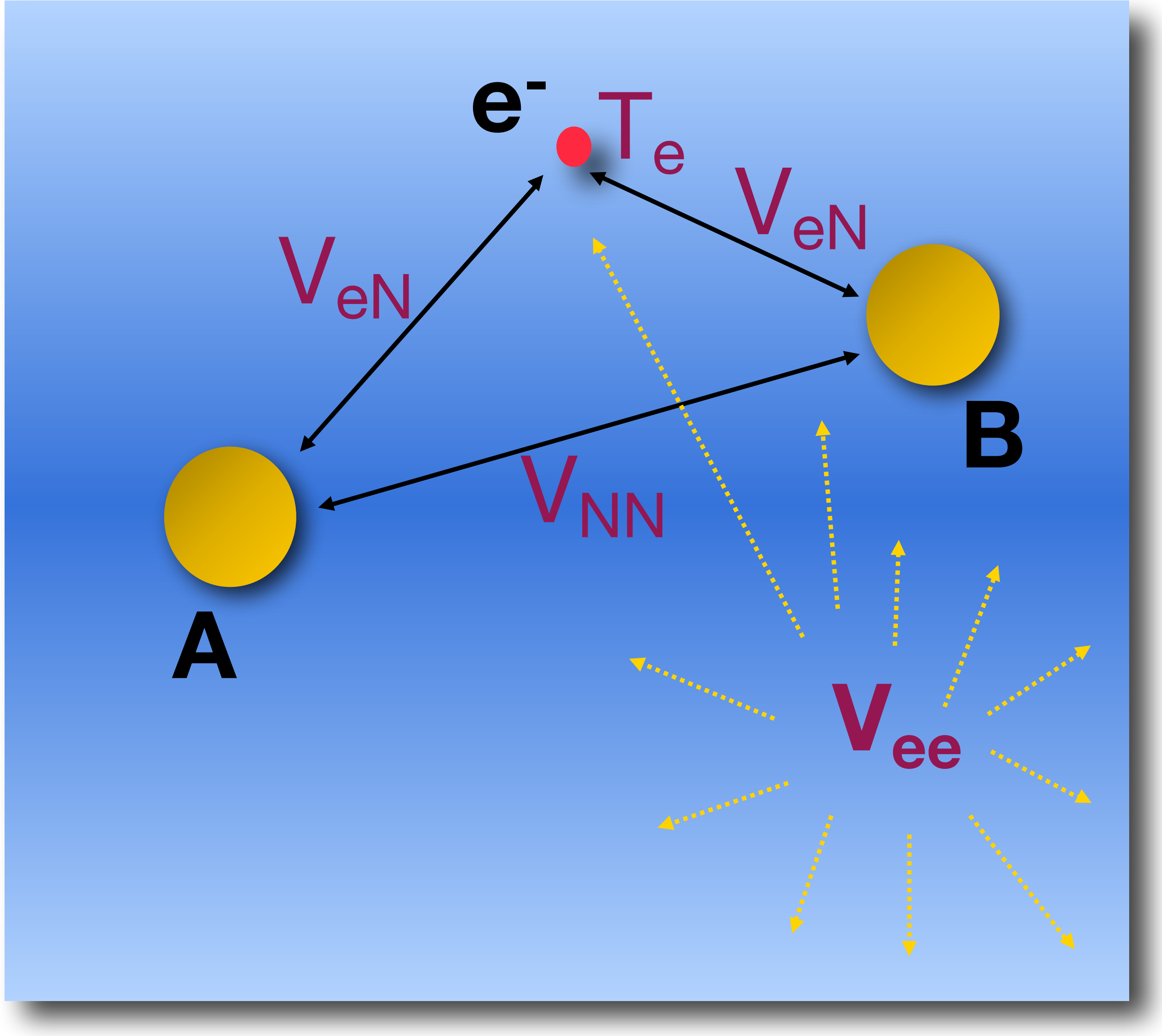
Coulomb integral

- 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“

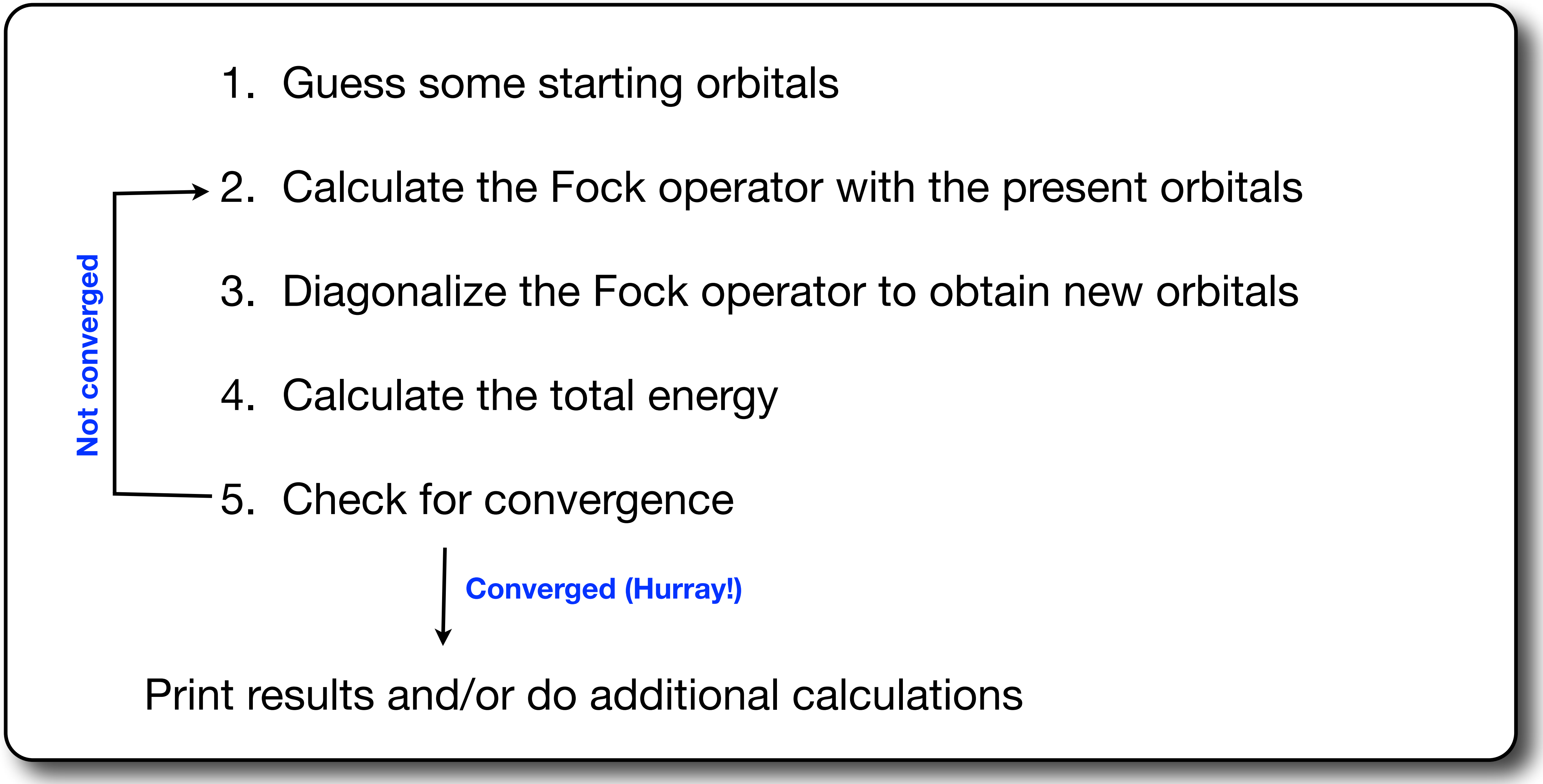
Interpretation of the Hartree-Fock Model



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:



1. Guess some starting orbitals
2. Calculate the Fock operator with the present orbitals
3. Diagonalize the Fock operator to obtain new orbitals
4. Calculate the total energy
5. Check for convergence

Not converged

Converged (Hurray!)

Print results and/or do additional calculations

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}

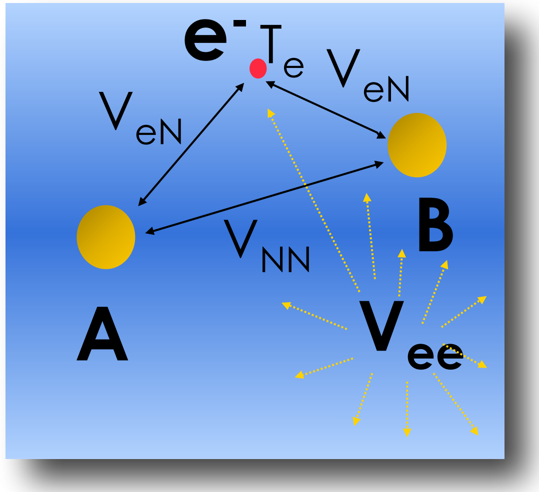
Thus, the small HF error amounts to the huge number of 319 kcal/mol error! In chemistry one aims at 1 kcal/mol accuracy.

✓ Very hard to achieve for *absolute* energies

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

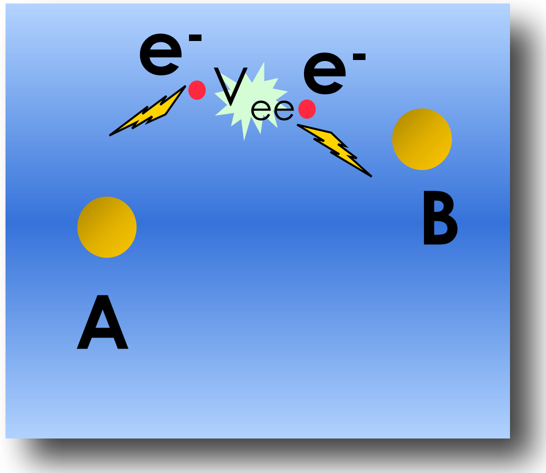
What is missing from Hartree-Fock Theory?

Exact Energy =



"Mean Field"
Hartree-Fock

+



Instantaneous electron-electron interaction

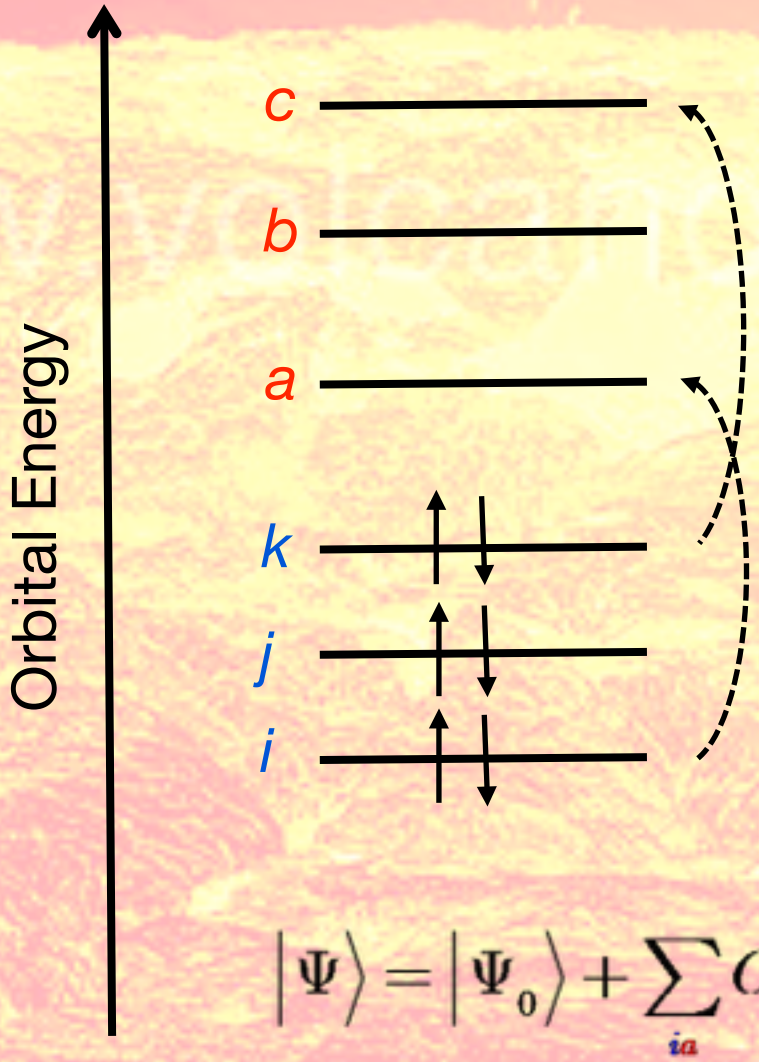
Correlation energy= $\frac{1}{2}\sum_{i,j \text{ Electron pairs}} \varepsilon_{ij}(\uparrow\uparrow) + \varepsilon_{ij}(\uparrow\downarrow)$

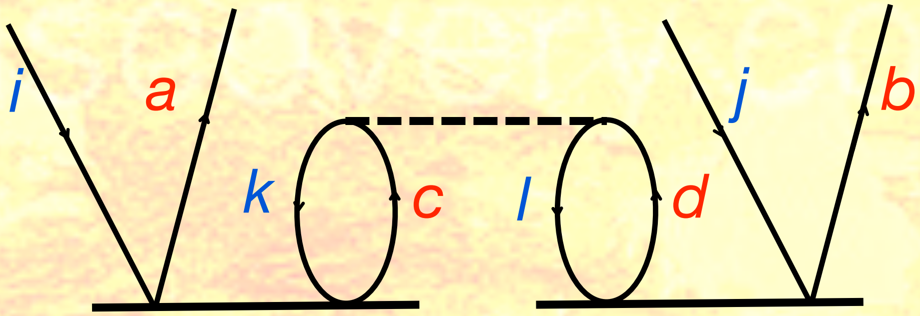
Fermi-Correlation ↑

Relatively easy due to "Fermi hole" in the mean-field

Coulomb-correlation ↑

Extremely hard to calculate due to interelectronic cusp at the coalescence point $\mathbf{r}_1=\mathbf{r}_2$





$$\frac{1}{2}P_{ij}P_{ab}\sum_{klcd}\langle kl\,\|\,cd\rangle\, t^{ik}_{ac}t^{lj}_{db}$$

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ia} C^{i}_{a}|\Psi^{a}_{i}\rangle + \frac{1}{4}\sum_{ijab} C^{ij}_{ab}|\Psi^{ab}_{ij}\rangle + \frac{1}{36}\sum_{ijkabc} C^{ijk}_{abc}|\Psi^{abc}_{ijk}\rangle + \ldots$$

Interpretation of the Hartree-Fock Solutions

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

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

And the approximate **many-electron wavefunction**

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

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:

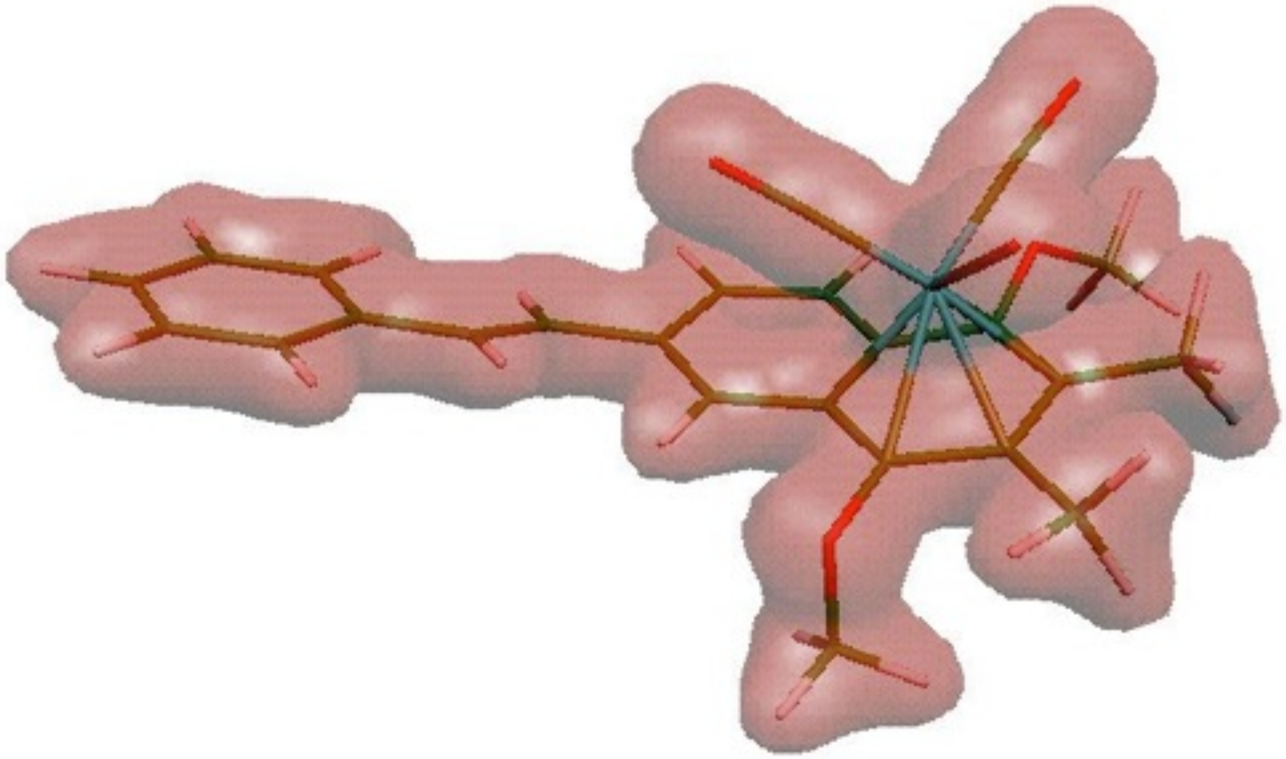
$$\psi_i(\mathbf{x}) = \sum_\mu c_{\mu i} \varphi_\mu(\mathbf{x})$$

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:

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

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:

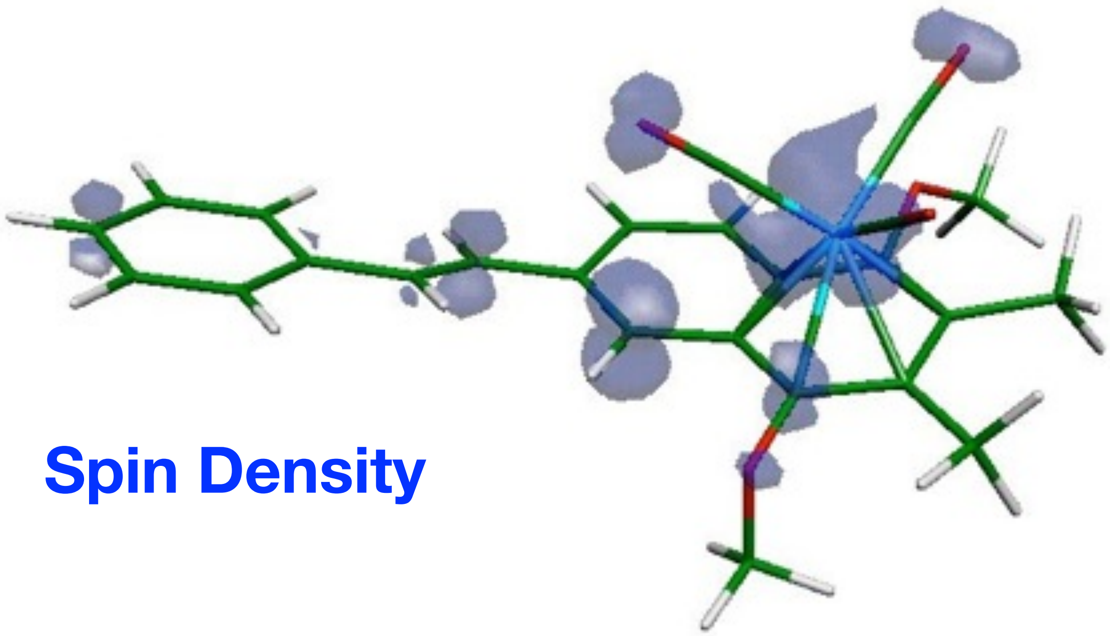
$$N_A = \sum_{\mu\nu \in A} P_{\mu\nu}^{AA} S_{\mu\nu}^{AA} + \sum_{B \neq A} \sum_{\mu \in A \nu \in B} P_{\mu\nu}^{AB} S_{\mu\nu}^{AB}$$

$$Q_A = Z_A - N_A$$

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



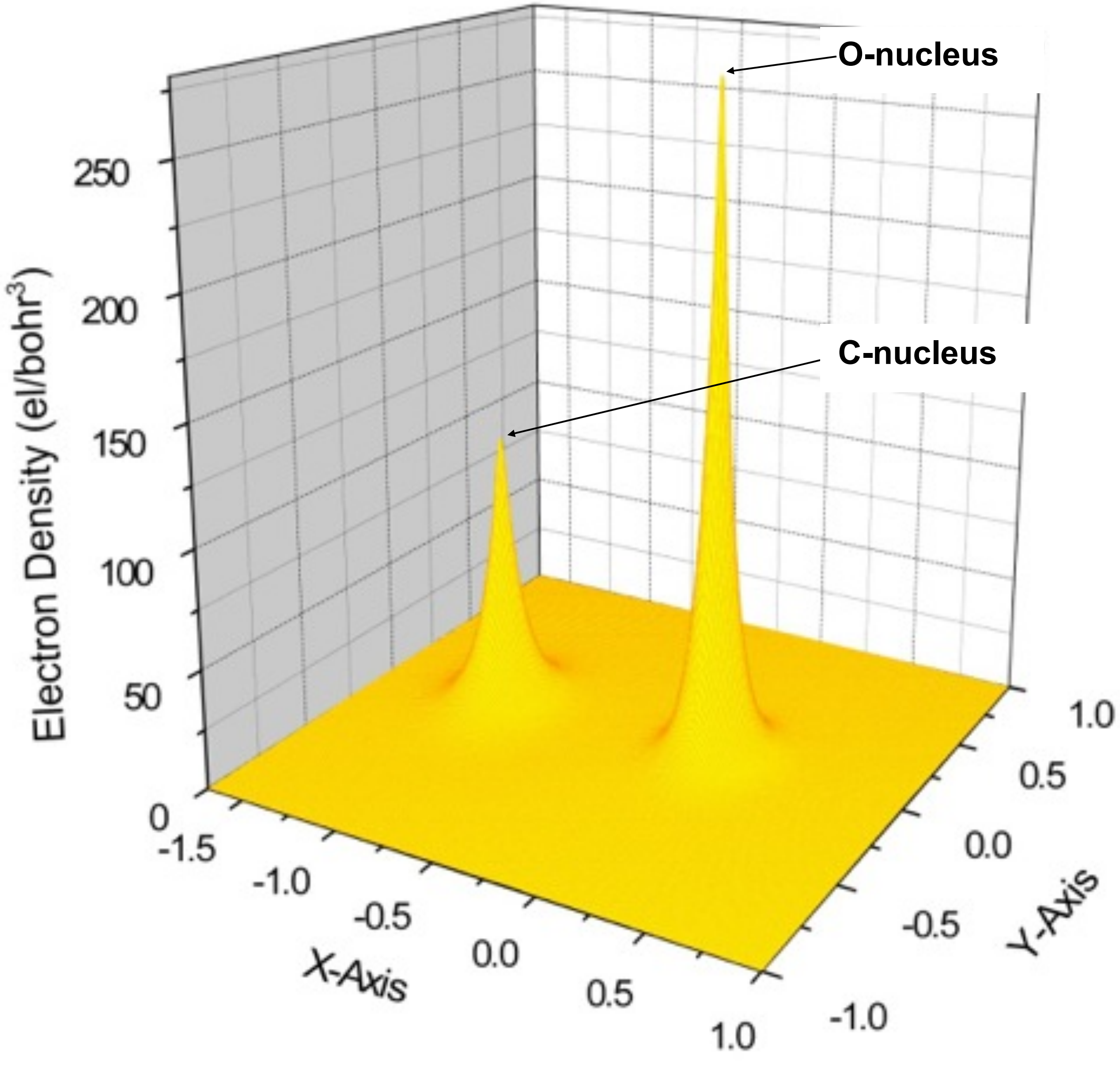
Spin Density

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

In HF Theory:

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

The Basis for the Hohenberg-Kohn Theorems



Electron Density of the CO molecule

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

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

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

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

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!

$$\begin{tikzcd}
\text{Knowing}\ \rho(\mathbf{r}) \arrow[r, "\text{Deduce}"] \arrow[rrr, dotted, bend right, "\text{Somehow possible}"'] & V_{eN},N \arrow[r, "\text{Deduce}"] & H_{BO} \arrow[r, "\text{Solve!}"] & E,\Psi
\end{tikzcd}$$

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 existance of the "universal" functional E[ρ] is guaranteed by the **first Hohenberg-Kohn** (HK) theorem.
2) The **second HK theorem** establishes a variational principle that states that E[ρ'] (ρ' being a test density) ≥ E[ρ]

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:

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

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

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

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**:

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

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

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

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

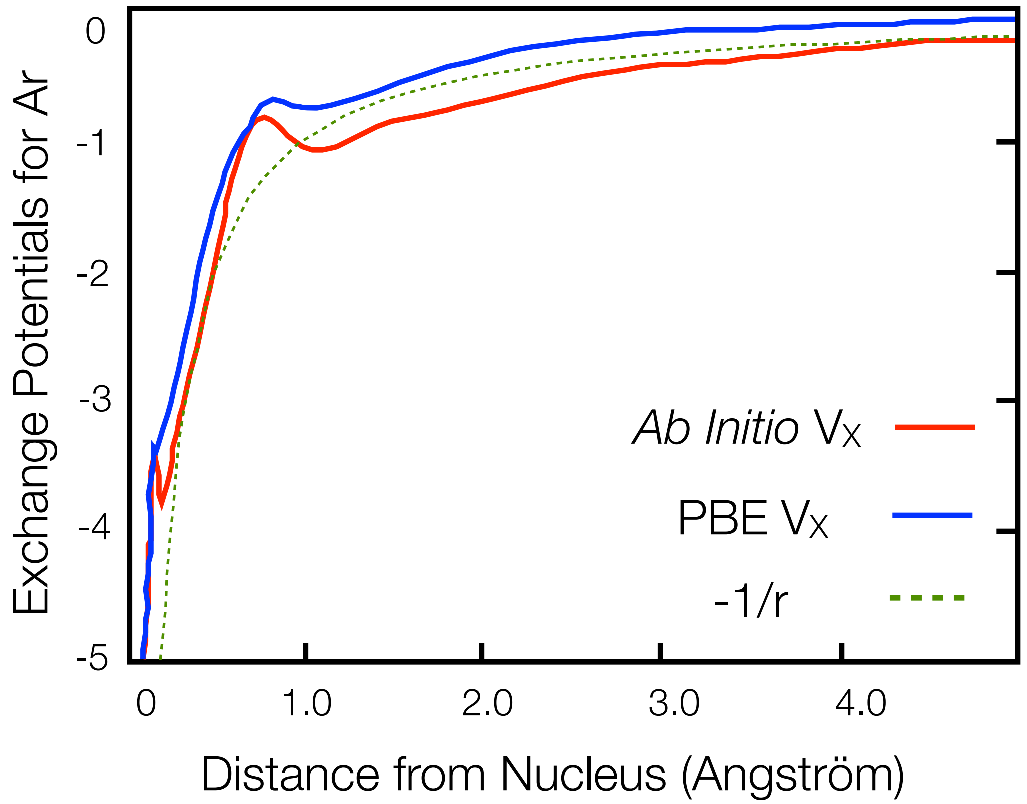
$$V_{XC}\left(\mathbf{r}\right) = \frac{\delta E_{XC}}{\delta\rho\left(\mathbf{r}\right)}$$

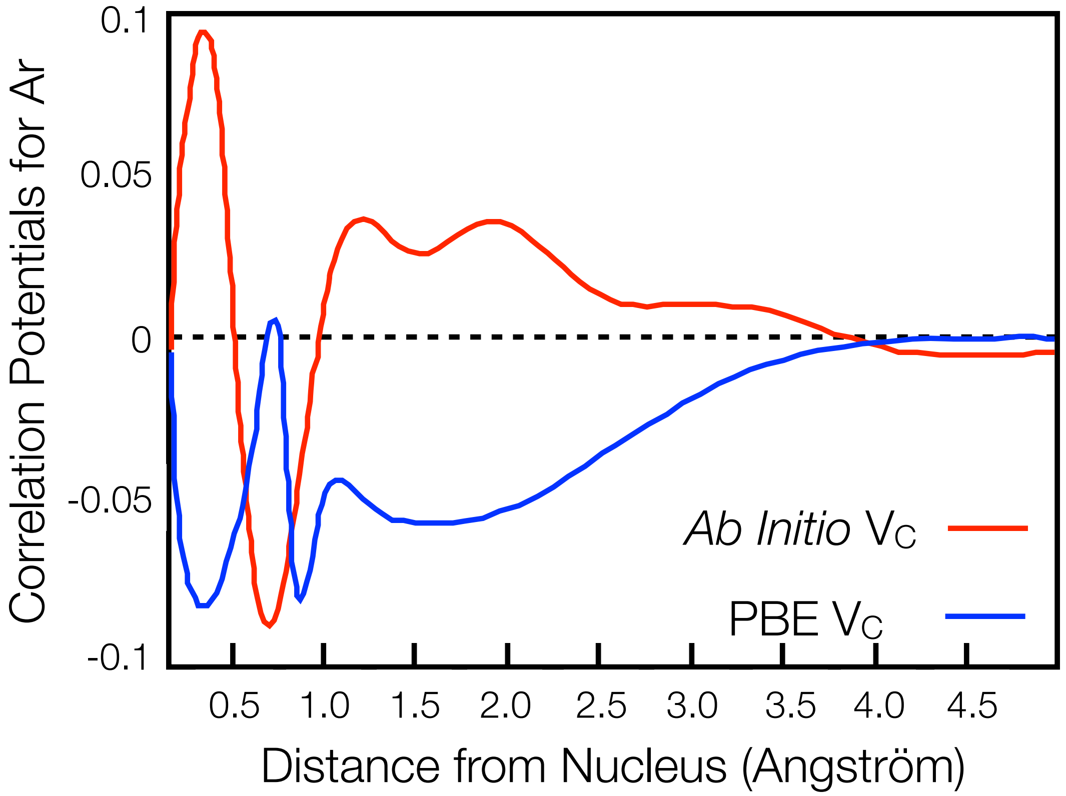
This is the celebrated formal apparatous of DFT! If we would know E_{XC}, these equations would constitute an *exact* framework. But we don’t (and likely never will)!

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

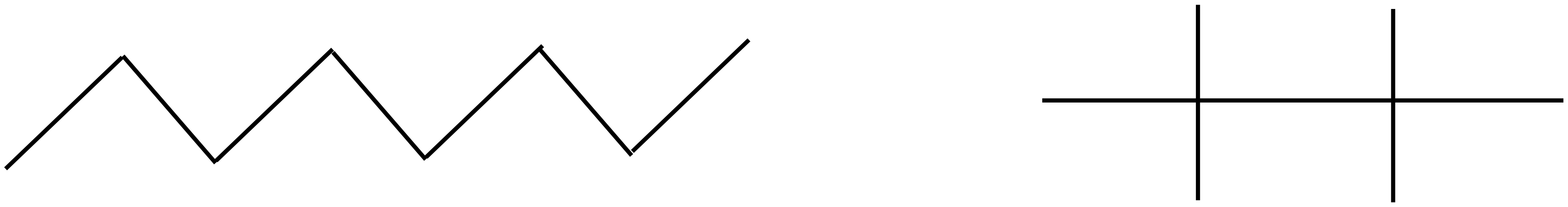
There are (expensive!) ways to construct very good KS potentials from accurate densities (red). These can be compared with “typical” present day potentials (blue).





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±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).

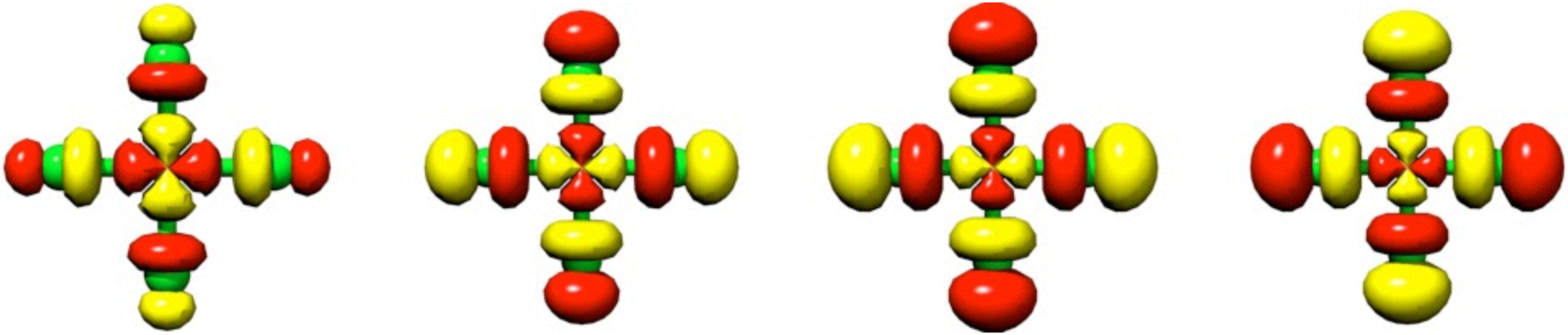
	E_{tot}	E_{corr}	E_x
CCSD(T)	-128.9260	-0.379	-12.098
	-129.0640 (rel)		
BP86	-128.9776 (-52)	-0.388 (- 9)	-12.104 (-6)
PBE	-128.8664 (+60)	-0.347 (+32)	-12.028 (+70)
BLYP	-128.9730 (-47)	-0.383 (- 4)	-12.099 (-1)
TPSS	-128.9811 (-55)	-0.351 (+28)	-12.152 (-54)
B3LYP	-128.9426 (-17)	-0.452 (-73)	-12.134 (-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.

Back to Covalency from a Computational Chemist’s Point of View

Are all Theories Equal? $CuCl_4^{2-}$

Straightforward d^9 system with d_{x2-y2} based SOMO:



UHF	**BHLYP**	**B3LYP**	**BLYP**
100% HF-X	50% HF-X	20% HF-X	0% HF-X
86% Cu	71% Cu	54% Cu	47% Cu

„Dramatic“ dependence on HF exchange. The more is in the functional the more ionic the bonds get

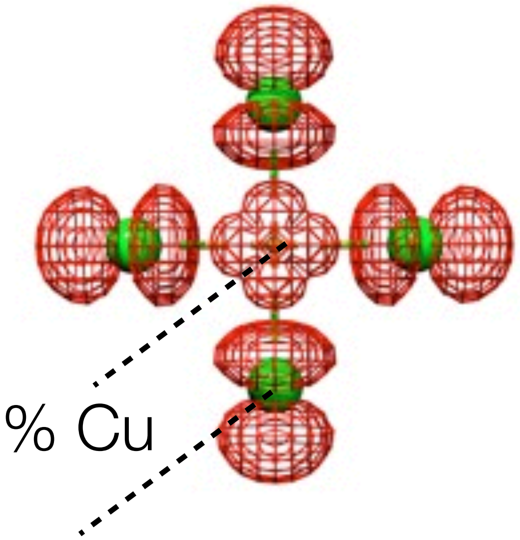
Pure HF is always too ionic while pure DFT is always too covalent (e.g. has a tendency to over-delocalize)

Covalency and Spin-Density

Since the singly occupied MO also dominates the spin-density which can be analyzed experimentally:

DFT

(BP86)

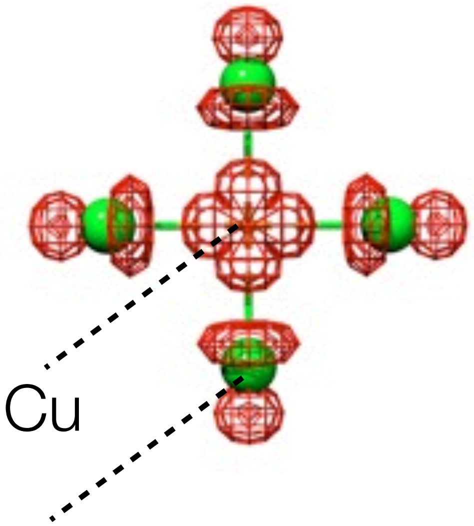


47% Cu

13% Cl

much too covalent

UHF

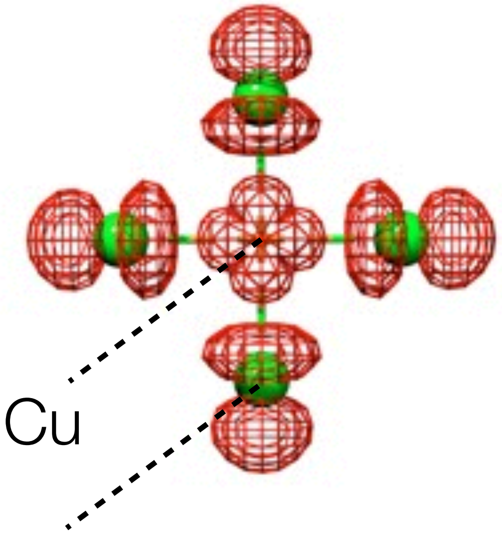


86% Cu

3% Cl

much too ionic

ACPF



58% Cu

10.5% Cl

about right

Best „experimental“ estimate: **61%Cu 9.7% Cl**

Dynamic correlation effects are HUGE in TM chemistry

Assignment of Oxidation States

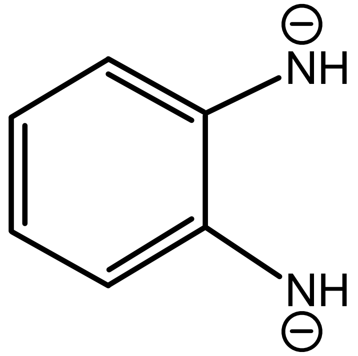
- ★ We can take the analysis of covalency one step further in order to „recover“ the concept of an oxidation state from our calculations.
- ★ This is even more approximate since it must be based on a subjective criterion
- ★ **Proposed procedure:**

- Analyze the occupied orbitals of the compound and determine the orbital covalencies (covalency is *anisotropic*!)
- In ***ORCA*** this is possible via the `NormalPrint, Localize` or `UNO` keywords (see next slide)
- Orbitals that are centered more than, say, 70% on the metal are counted as pure metal orbitals
- Count the number of electrons in such metal based orbitals. This gives you the d^N configuration
- The local spin state on the metal follows from the singly occupied metal-based orbitals
- This fails, if there are some orbitals that are heavily shared with the ligands (metal character < 70%). In this case the oxidation state is ambiguous. Typically, experiments are ambiguous as well in these cases.

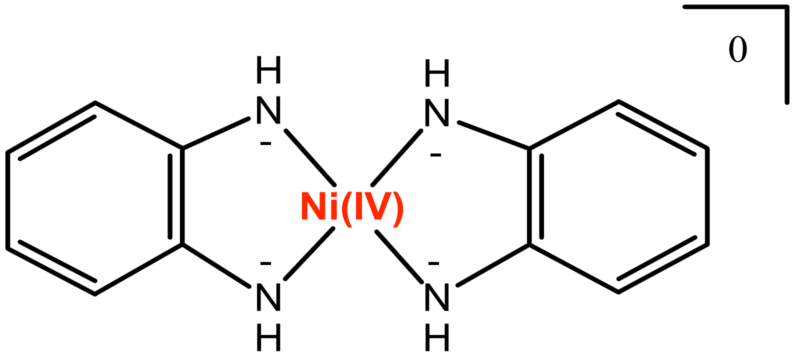
Which Orbitals to Look at?

- What do we mean by „the orbitals“ of the complex?
- There are several sets of orbitals that may be looked at:
  - **Canonical orbitals** (the straightforward ones that come out of the calculation and are accessed by `NormalPrint`)
    - Frequently these orbital are not fun to look at. They may be amiguous or the metal character is smeared out through many MOs.
    - In UKS/UHF calculations spin-up and spin-down orbitals need to be looked at separately
  - **Localized orbitals** (accesssed through the `%localize` block)
    - Localized orbitals display bonds and „lone pairs“.
    - They will never show a bond that is not there.
    - A good set of orbitals! Spin-up and spin-down still need to be treated separately
    - They do not have a well defined orbital energy
  - **Quasi-restricted orbitals** (A special set of orbitals accessed by the `UNO` keyword)
    - Extracted from the natural orbitals of a UKS calculation.
    - Often they are „quite nice“ and in accord with intuition
    - They have well defined energy
  - **Natural orbitals** (e.g. from a correlated CI type calculation)
    - More advanced set of orbitals with non-integer occupation numbers. Typically good to look at

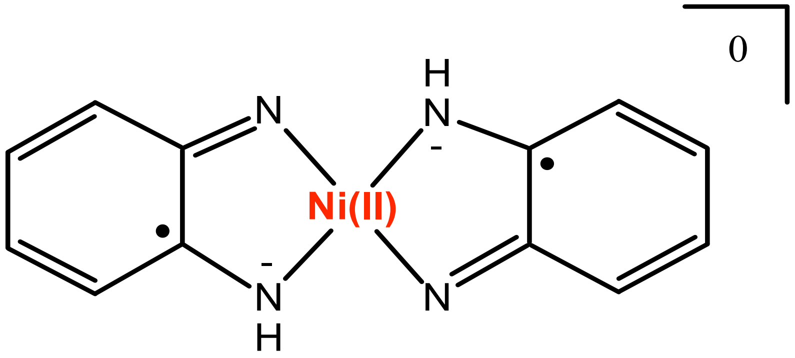
An Example

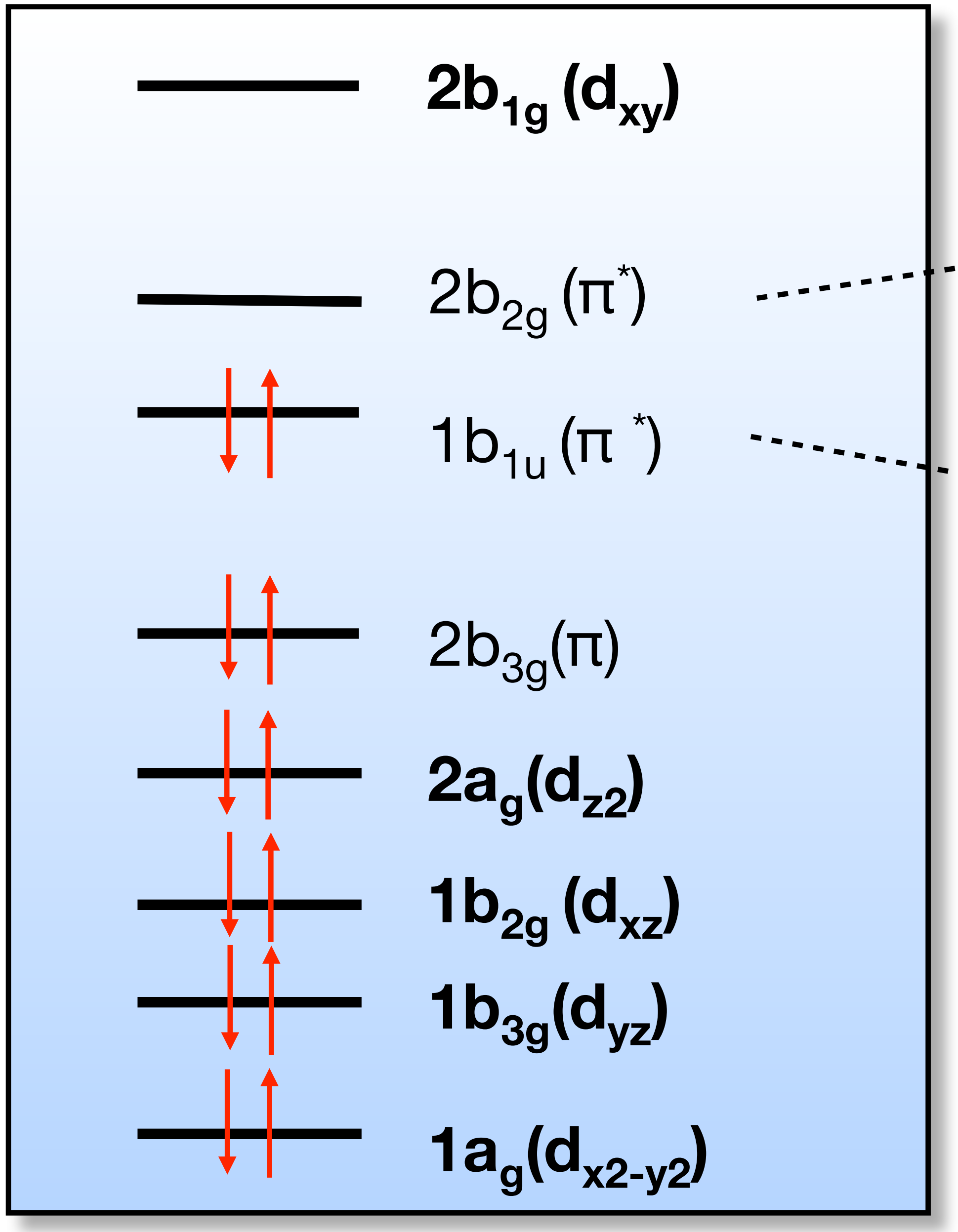


$+Ni^{2+}$



OR





$2b_{1g}$ (d_{xy})

$2b_{2g}$ (π^*)

$1b_{1u}$ (π^*)

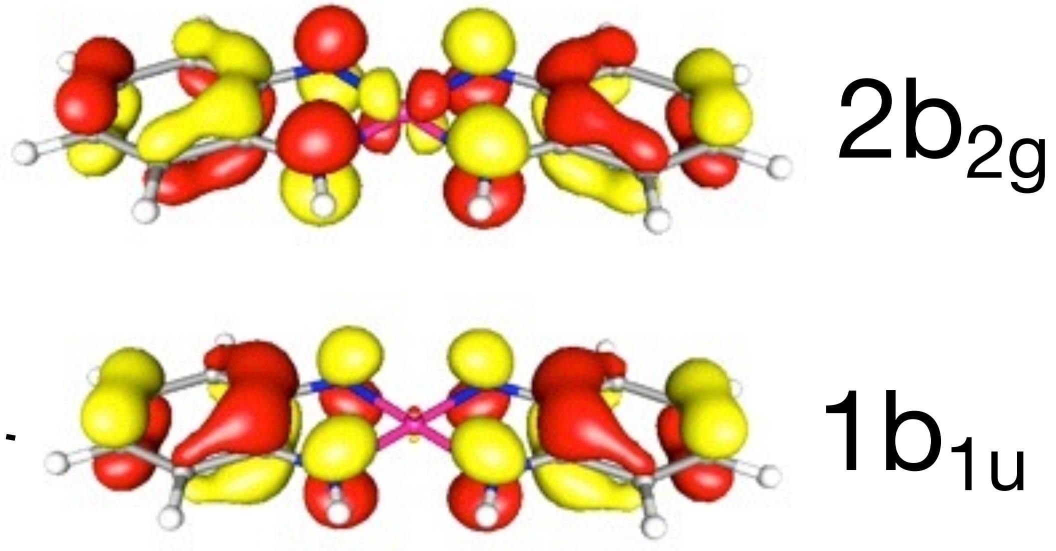
$2b_{3g}$(π)

$2a_g$(d_{z2})

$1b_{2g}$ (d_{xz})

$1b_{3g}$(d_{yz})

$1a_g$(d_{x2-y2})



4 doubly occupied and one empty metal based orbitals

- Ni(II) oxidation state
- Ligand must be oxidized and has diradical character

This is evidenced by close lying HOMO and LUMO that are symmetric and antisymmetric combinations

Herebian et al. *J. Am. Chem. Soc.*, **2003**, 125, 10997

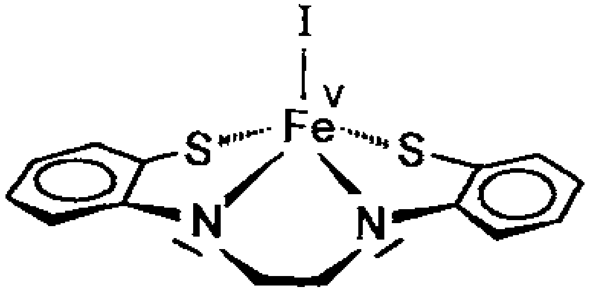
Physical versus Formal Oxidation States

The **formal oxidation state** of a metal ion in a complex is the d^N configuration that arises upon dissociating all ligands in their closed shell „standard“ states taking into account the total charge of the complex

The **physical oxidation state** of a metal ion in a complex is the d^N configuration that arises from an analysis of its electronic structure by means of spectroscopic measurements and molecular orbital calculations

Chaudhuri, P.; Verani, C.N.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.,* **2001**, 123, 2213 *„The Art of Establishing Physical Oxidation States in Transition-Metal Complexes Containing Radical Ligands “***.** However, The concept goes back to CK Jörgensen

- ★ The two often coincide but may well be different! In the example before, the formal oxidation state is Ni(IV) but the physical oxidation state is Ni(II)



2

This complex has first been described by its formal oxidation state of Fe(V) but has a physical oxidation of Fe(III)

Chlopek, C. *et al. Chem. Eur. J.* **2007**, 13, 8390

Assignment of Oxidation States

- ★ We can take the analysis of covalency one step further in order to „recover“ the concept of an oxidation state from our calculations.
- ★ This is even more approximate since it must be based on a subjective criterion
- ★ Proposed procedure:
  - Analyze the **occupied orbitals** of the compound and determine the orbital covalencies
  - Orbitals that are centered more than, say, **70-80%** on the metal are counted as pure **metal orbitals**
  - **Count the number of electrons in such metal based orbitals**. This gives you the **d^N configuration**
  - The **local spin state** on the metal follows from the singly occupied metal-based orbitals
  - *This fails, if there are some orbitals that are heavily shared with the ligands (metal character < 70%). In this case the oxidation state is ambiguous. Typically, experimens are ambiguous as well in these cases*.

➡ **BUT: Make sure that your calculated electronic structure makes sense by correlating with spectroscopy! Spectroscopy is the experimental way to study electronic structure!**

Physical versus Formal Oxidation States

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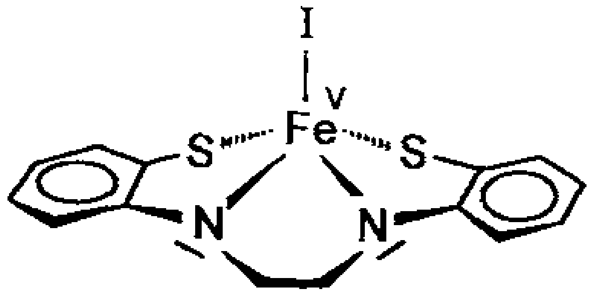
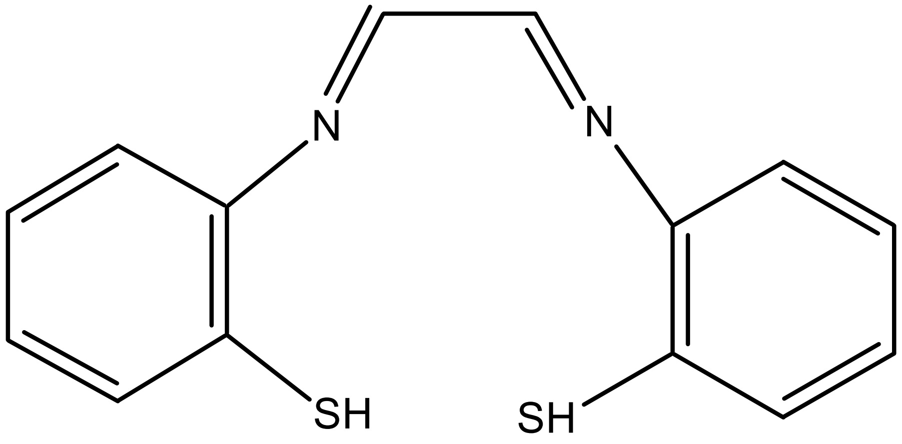


2

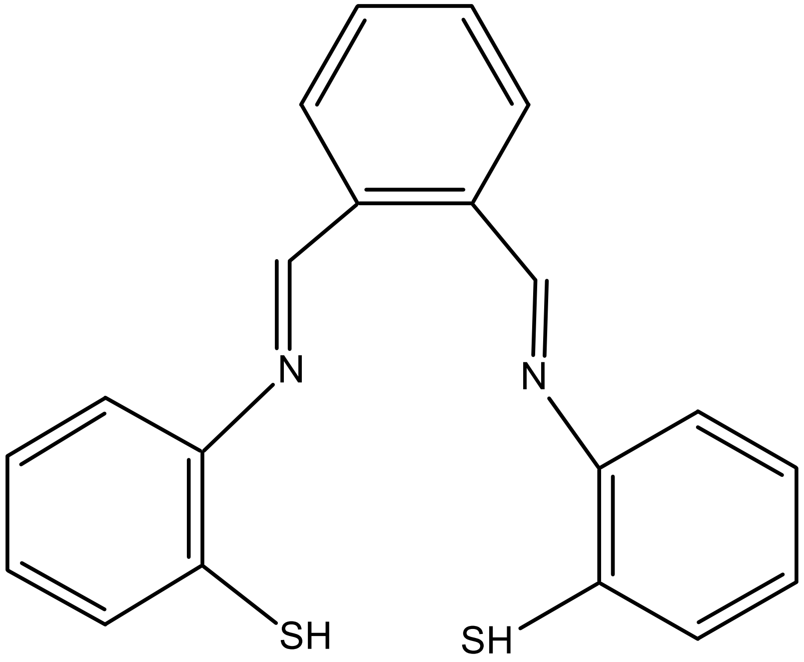
This complex has first been described by its formal oxidation state of Fe(V) but has a physical oxidation of Fe(III)

Chlopek, C. *et al. Chem. Eur. J.* **2007**, 13, 8390

An Example for an ‚Exciting‘ Oxidation State



gma



PhBMA

[Zn(gma)] S=0 (Holm,Gray)

$[Zn(gma)]^-$ S=1/2 (Holm,Gray)

[Ni(gma)] S=0 (Holm,Gray)

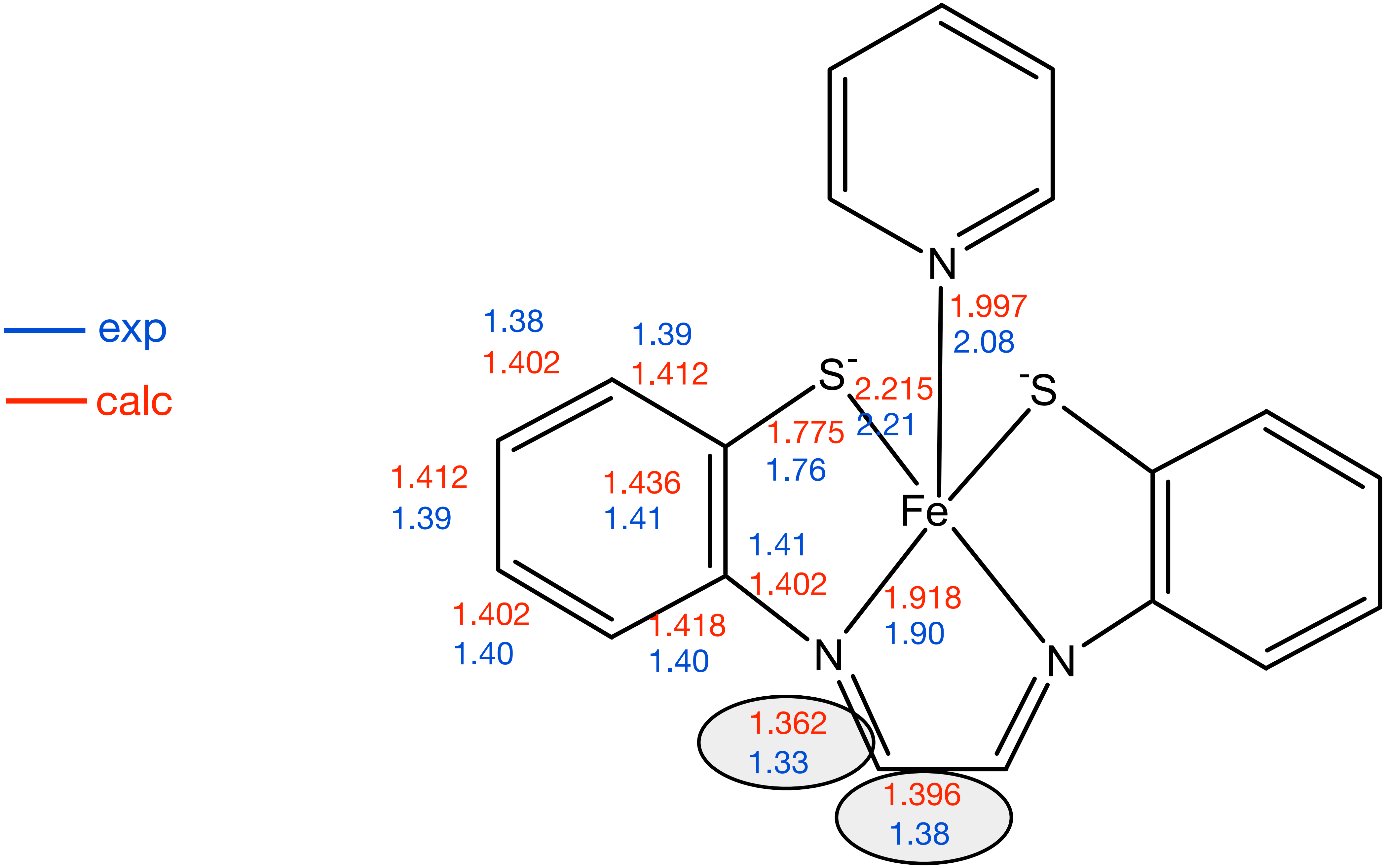
$[Ni(gma)]^-$ S=1/2 (Holm,Gray)

[Fe(gma)(py)]
$[Fe(gma)(PR_3)]$
$[Fe(gma)(CN)]^-$
S=1 (Strähle, Sellmann, Wieghardt)

[Fe(PhBMA)] S=1
$[Fe(gma)(PR_3)_2]$ S=0
$[Fe(gma)(py)]^+$ S=1/2
(Wieghardt)

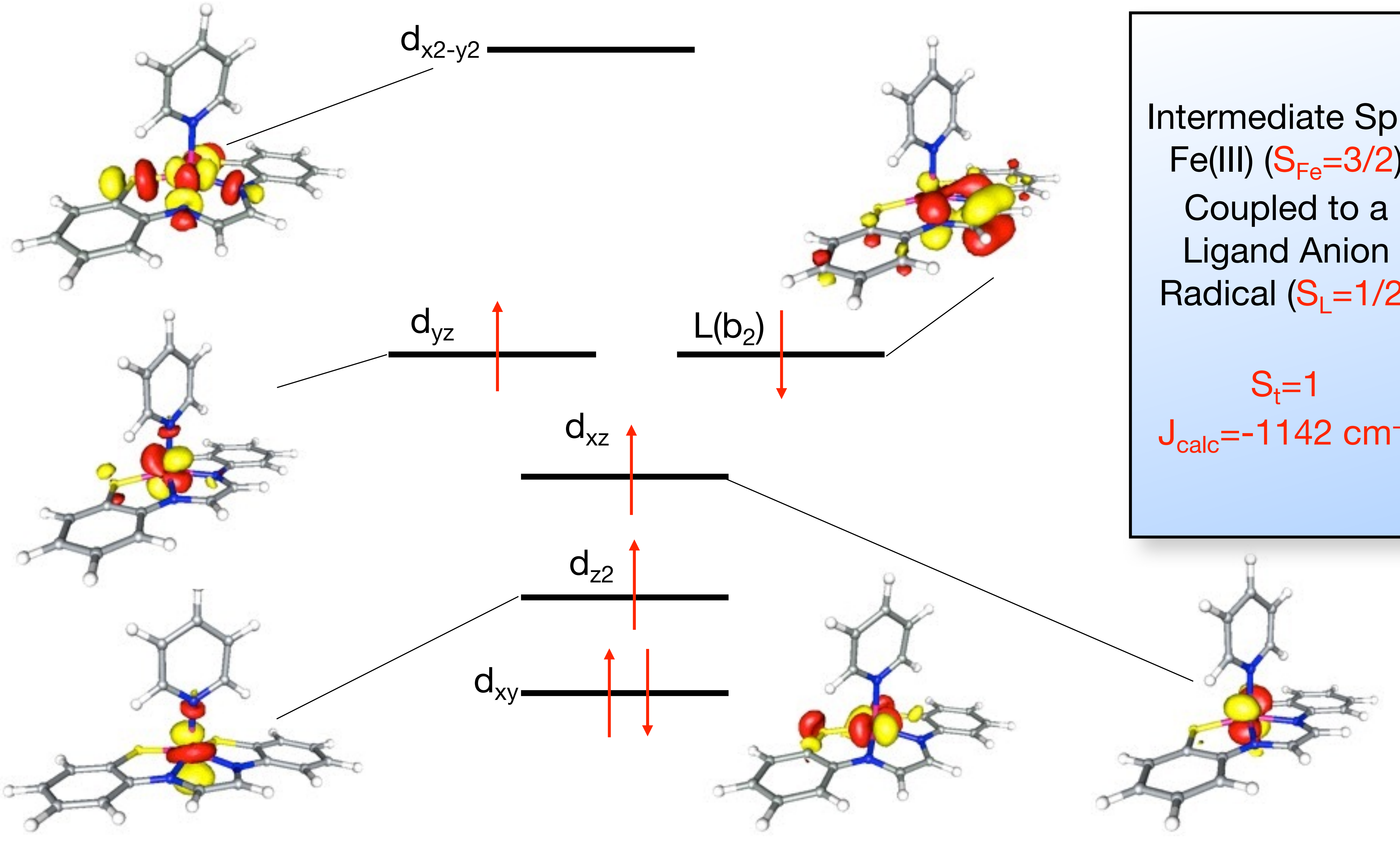
All described as ordinary metal(II) chelates

Optimized Structure of [Fe(L)(py)]



		δ_{MB}	ΔE_Q	η
[Fe(L)(py)]	Calc.	0.205	+2.371	0.084
	Exp.	0.270	+2.33	small

Electronic Structure of [Fe(gma)(py)]



Intermediate Spin Fe(III) ($S_{Fe}=3/2$) Coupled to a Ligand Anion Radical ($S_L=1/2$)

$S_t=1$

$J_{calc}=-1142\ cm^{-1}$

Ghosh, P.; Bill, E.; Weyhermüller, T.; FN; Wieghardt, K. *J. Am. Chem. Soc.*, **2003**, 125, 1293

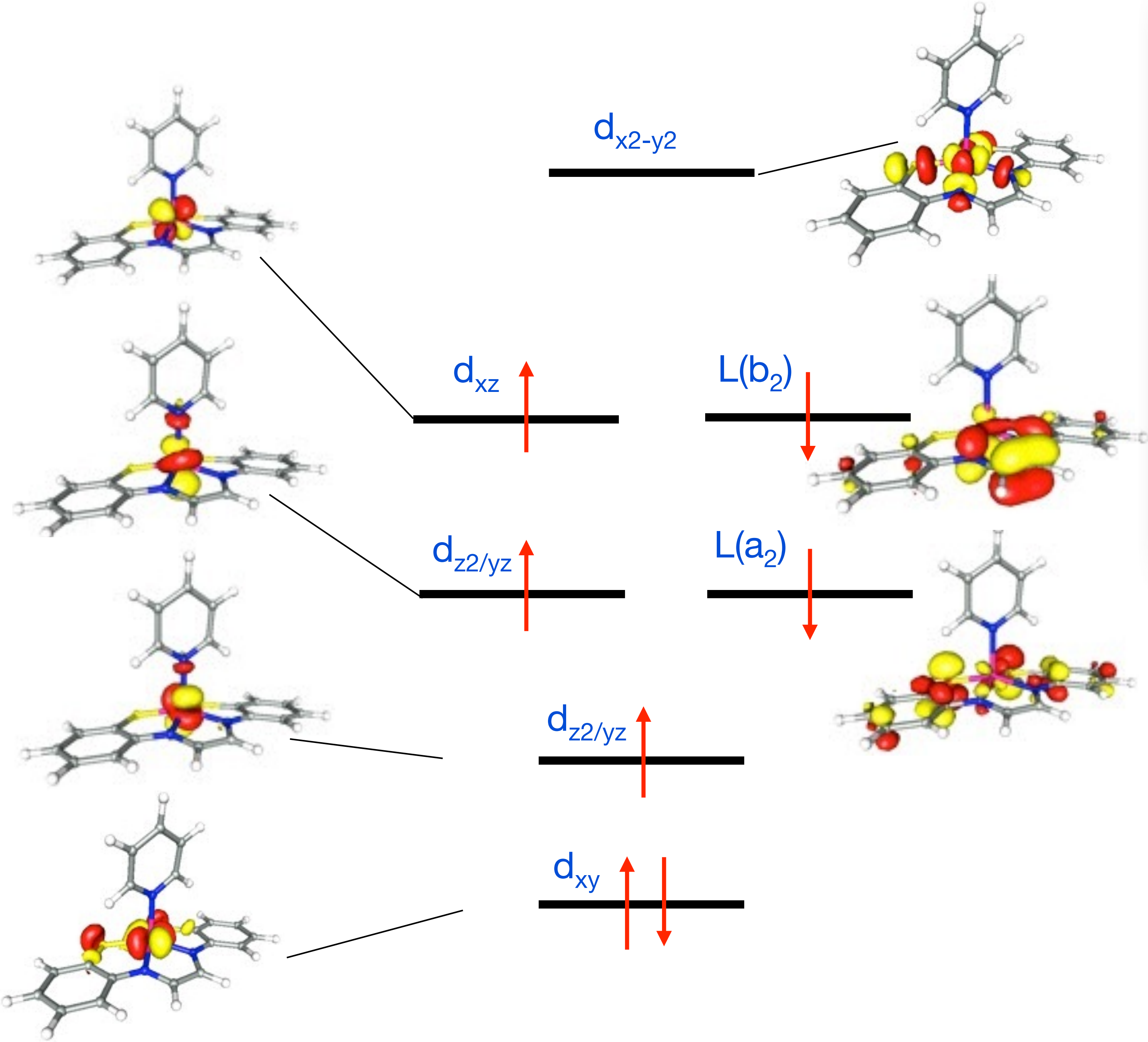
Electronic Structure of [Fe(gma)(py)]$^+$

Observation: Oxidation leaves the Mössbauer parameters invariant

Dilemma:

- ★ [Fe(gma)(py)] has a spin of 1
  - Intermediate Spin Fe(III)/Ligand Radical
- ★ Taking the Electron out of the ligand LUMO
  - Intermediate Spin Fe(III)/Closed Shell Ligand
  - S=3/2 Expected but S=1/2 Observed
- ★ Taking the Electron out of the Ligand but Changing the Spin at Fe
  - Would have been Detected in MB Experiments
- ★ Taking the Electron from the Iron gives Fe(IV)
  - Would have been Detected in MB Experiments

Electronic Structure of [Fe(gma)(py)]$^+$



Mössbauer Parameters

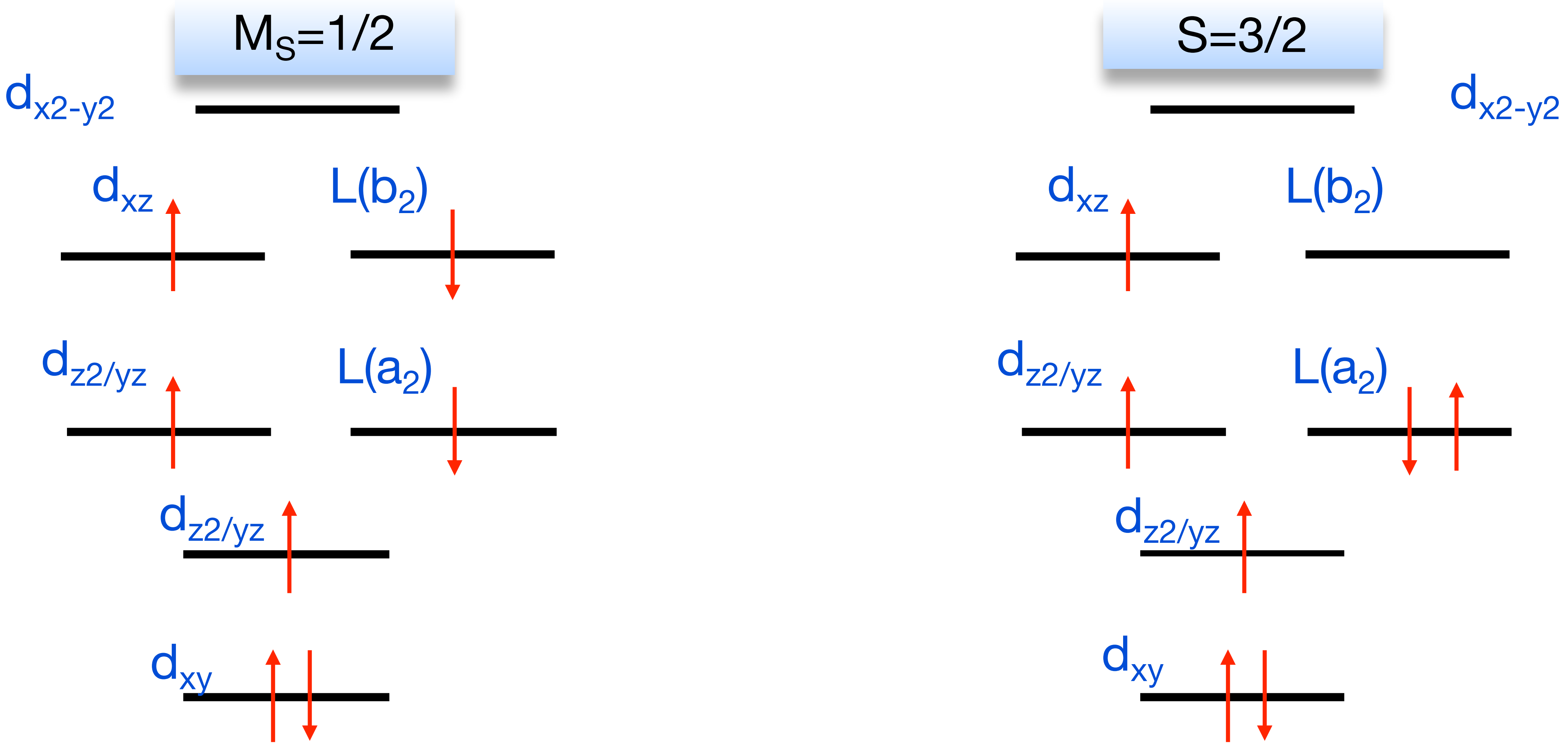
	δ (mm/s)	ΔE_Q (mm/s)	η
Neutral	0.205	2.371	0.084
Cation	0.246	2.430	0.023
Exp.	(0.27)	(2.33)	?

Intermediate Spin Fe(III) ($S_{Fe}=3/2$) Coupled to a Ligand Triplet State ($S_L=1$)

$S_t=1/2$ $J_{calc}=-845$ cm^{-1}

Ghosh, P.; Bill, E.; Weyhermüller, T.; FN; Wieghardt, K. *J. Am. Chem. Soc.*, **2003**, 125, 1293

Electronic Structure of $[Fe(gma)(py)]^+$



$E(M_S=1/2)$ =-0.6 kcal/mol

E(S=1/2) ~ -5.4 kcal/mol

E(S=3/2) =0.0 kcal/mol

Large Exchange Coupling Drives Ligand Triplet State Coordination
Basis for a „Metal Field Theory“ rather than „Ligand Field Theory“

(Guihery, N.; Robert, V.; FN *J. Phys. Chem.*, 2008, 112, 12975)

Ghosh, P.; Bill, E.; Weyhermüller, T.; FN; Wieghardt, K. *J. Am. Chem. Soc.*, **2003**, 125, 1293

Back to Spin States and Exchange Coupling

„Exchange Coupling“: Anderson Model

2e$^-$ in 2 orbitals problem: $\left|{}^1\Psi_1\right\rangle = \left|\psi_1\bar{\psi}_1\right|$ $\left|{}^1\Psi_2\right\rangle = \left|\psi_2\bar{\psi}_2\right|$ $\left|{}^1\Psi_3\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_1\bar{\psi}_2\right| - \left|\bar{\psi}_1\psi_2\right|\right)$ 3-Singlets

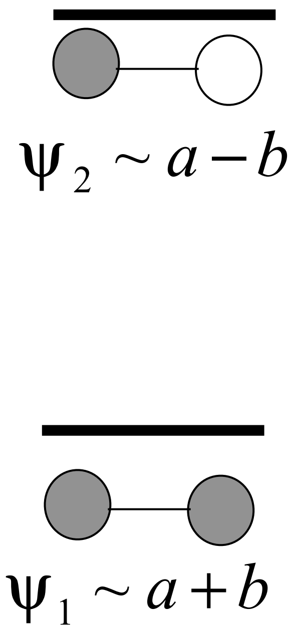
$\psi_{1,2} = \frac{1}{\sqrt{2}}\left(a \pm b\right)$ $\left|{}^3\Psi_1\right\rangle = \left|\psi_1\psi_2\right|$ 1-Triplet

Neglect overlap for a moment

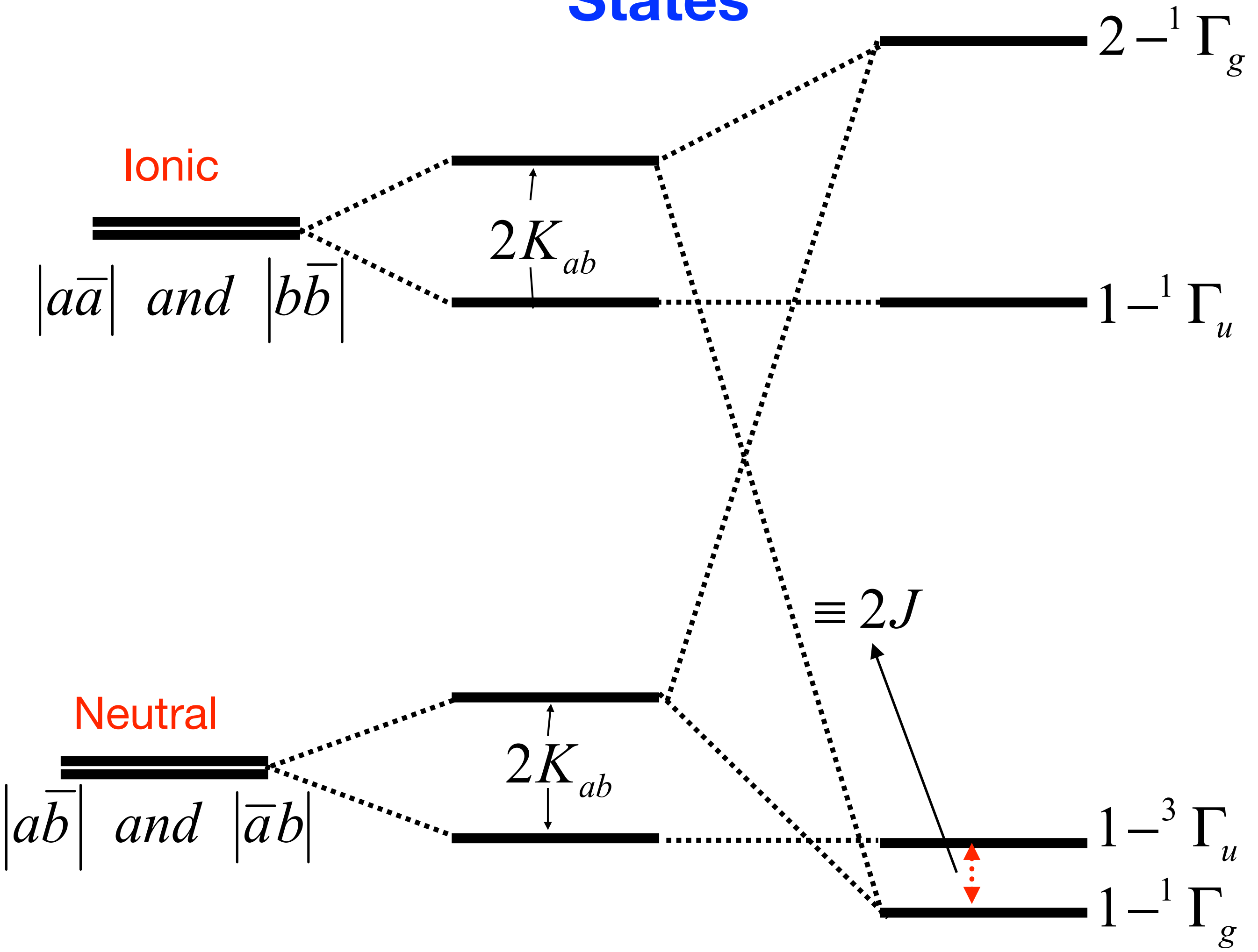
After-CI: $E\left(\left|{}^1\Psi\right\rangle\right) - E\left(\left|{}^3\Psi\right\rangle\right) \approx 2K_{ab} - \frac{4F_{ab}^2}{J_{aa} - J_{ab}} \equiv 2J_{HDvV}$

Heisenberg-Dirac-van Vleck „effective“ Exchange ($H=-2JS_AS_B$)

Orbitals



States



Integrals

$J_{aa} = J_{bb} = \left(a(1)a(1)\,|\,r_{12}^{-1}\,|\,a(2)a(2)\right)$

On-Site Coulomb Integral

$J_{ab} = \left(a(1)a(1)\,|\,r_{12}^{-1}\,|\,b(2)b(2)\right) \propto R_{ab}^{-1}$

Inter-Site Coulomb Integral

$K_{ab} = \left(a(1)b(1)\,|\,r_{12}^{-1}\,|\,a(2)b(2)\right) \propto \mathrm{e}^{-\alpha R_{ab}}$

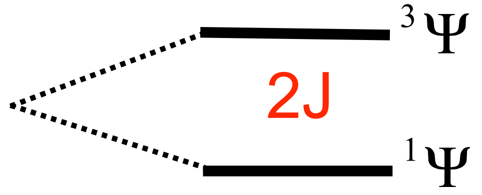
Inter-Site Exchange Integral

$$F_{ab} = h_{ab} + \left(a(1)a(1)\,|\,r_{12}^{-1}\,|\,a(2)b(2)\right) + \left(b(1)b(1)\,|\,r_{12}^{-1}\,|\,a(2)b(2)\right)$$

Fock Like „Transfer“ Integral

„Exchange Coupling“

$\hat{H} = -2J\hat{S}_A\hat{S}_B$



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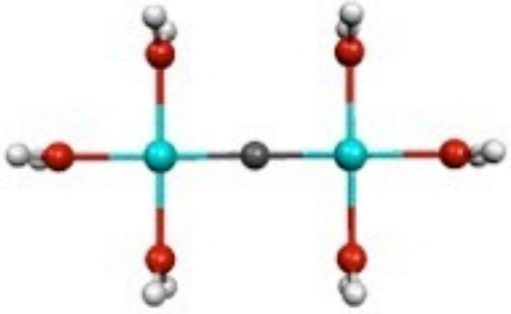
1. The „Exchange Hamiltonian“ does NOT follow from magnetic interactions (there is no such thing as an „exchange interaction“ in nature)
2. The Born-Oppenheimer Hamiltonian is enough to describe the splitting of states of the same configuration (unlike spin-crossover!) but different multiplicity
3. The splitting is related to the electron-electron interaction and the antisymmetry of the N-particle wavefunction
4. The simplest (Anderson) model leads to two contributions:
    a) The „**Direct Exchange**“ : $K_{ab} = \left(a(1)b(1) \mid r_{12}^{-1} \mid a(2)b(2)\right) > 0$ (Ferromagnetic)
    b) The „**Kinetic Exchange**“ : $-\dfrac{F_{ab}^2}{J_{aa} - J_{ab}} \equiv -\dfrac{\beta}{U} < 0$ (Antiferromagnetic)

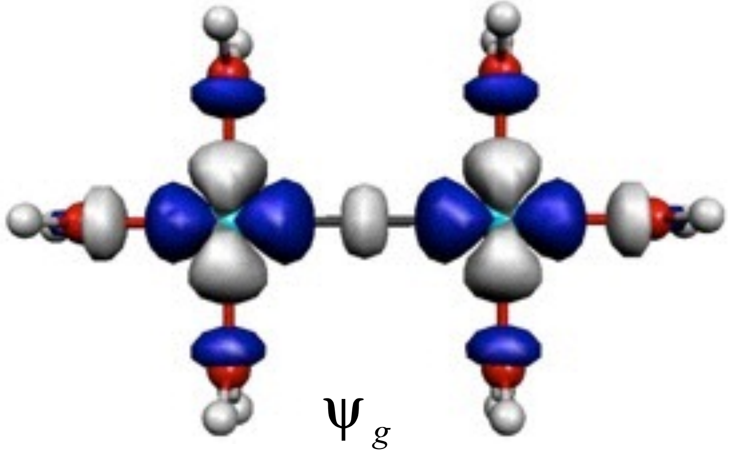
We can talk and argue this way, but how do we calculate it ?

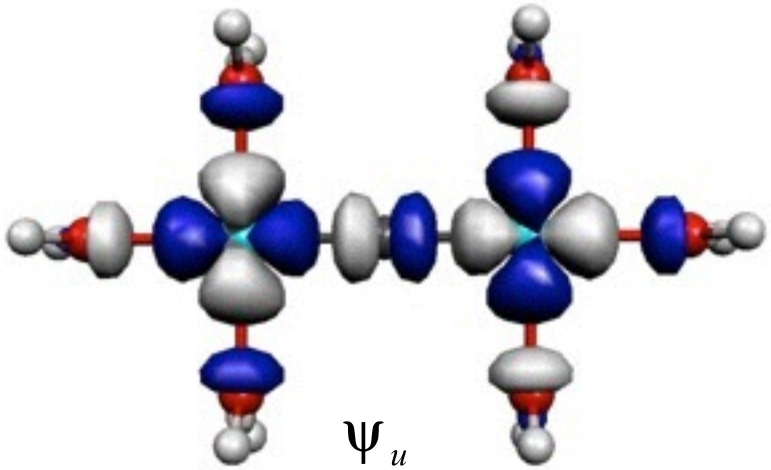
A model calculation: $[Cu_2(\mu\text{-}F)(H_2O)_6]^{3+}$

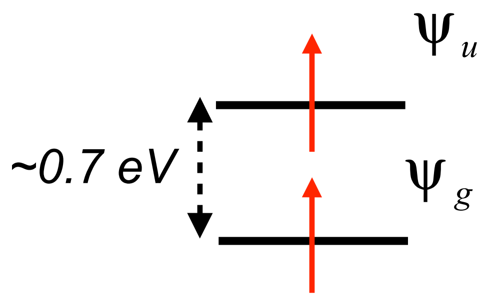


A Model Calculation: $[Cu_2(\mu\text{-}F)(H_2O)_6]^{3+}$

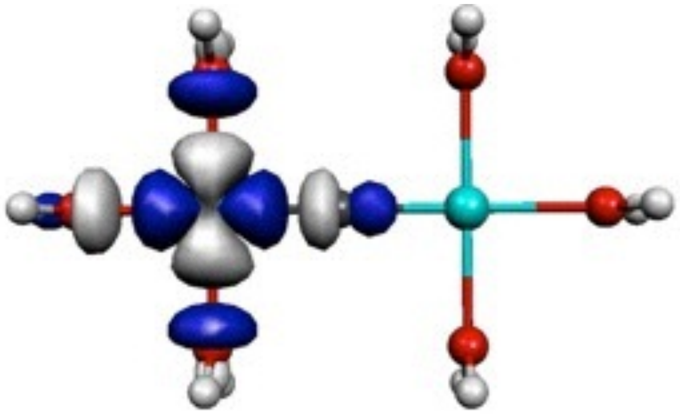
The Hartree-Fock SOMOs of the triplet state („active“ orbitals)



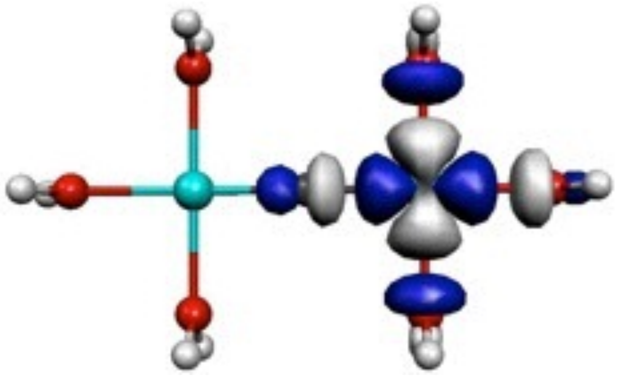




The pseudo-localized „magnetic orbitals“



$a = 2^{-1/2}(\psi_g + \psi_u)$



$b = 2^{-1/2}(\psi_g - \psi_u)$

Notes:

- ‚a‘ and ‚b‘ have **tails** on the bridge (and on the other side)
- ‚a‘ and ‚b‘ are **orthogonal** and **normalized**
- ‚a‘ and ‚b‘ do **not** have a **definite energy**
- THE orbitals of a compound are not well defined! (ROHF, MC-SCF, DFT, Singlet or Triplet Optimized, ...)

Values of Model Parameters:

$$\hat{H} = -2J\hat{S}_A\hat{S}_B$$

„Direct“ (Potential) exchange term:

$$K_{ab} = \left(a(1)b(1) \mid r_{12}^{-1} \mid a(2)b(2) \right) = 17\ cm^{-1}$$

Exactly calculated „kinetic“ exchange term:

$$\underline{-2\beta^2 / U = -57\ cm^{-1}}$$

$$J = -40\ cm^{-1}$$

Is that accurate? Look at the singlet wavefunction:

$$\left| {}^1\Psi_0 \right\rangle = 99.94\% \left| neutral \right\rangle + 0.06\% \left| ionic \right\rangle$$

BUT:

- The ionic parts are too high in energy and mix too little with the neutral configuration (electronic relaxation)
- What about charge transfer states?

➢ Need a more rigorous electronic structure method:

a) Difference Dedicated CI (DDCI): Malrieu, Caballol et al.
b) CASPT2: Roos, Pierloot
c) MC-CEPA: Staemmler

Recommended Literature:

Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, *116*, 2728
Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys* **2002**, *116*, 3985
Fink, K.; Fink, R.; Staemmler, V. *Inorg. Chem.* **1994**, *33*, 6219
Ceulemans, A.; et al., L. *Chem. Rev.* **2000**, *100*, 787

Refined *Ab Initio* Calculation

Include relaxation and LMCT/MLCT states via the Difference Dedicated CI procedure:

(~10^5 Configurations)

$$\begin{aligned} K_{ab} &= 17\ cm^{-1} \\ -2\beta^2/U &= -57\ cm^{-1} \\ all\ others &= -166\ cm^{-1} \\ \hline J &= -206\, cm^{-1} \end{aligned}$$

Look at the singlet wavefunction

$$\left|{}^1\Psi_0\right\rangle = 92.3\% \left|neutral\right\rangle + 3.3\% \left|ionic\right\rangle + 4.4\% \left|LMCT\right\rangle$$

Reduced **Increased!** **NEW+IMPORTANT**

The Anderson model is not really realistic and should not be taken literally even though its CI ideas are reasonable.

- Relaxation of ionic configurations are important („dressing“ by dynamic correlation: (DDCI, CASPT2,MC-CEPA,...)
- LMCT states are important

Treatment of LMCT States in Model Calculations: VBCI Model: Tuczek, F.; Solomon, E. I. Coord. Chem. Rev. 2001, 219, 1075

Exchange Coupling by DFT

The dominant part of the triplet wavefunction is:

$$\left|{}^{3}neutral\right\rangle = \left|core\, a_{\alpha} b_{\alpha}\right|$$

The dominant part of the singlet wavefunction is:

$$\left|{}^{1}neutral\right\rangle = \frac{1}{\sqrt{2}}\left(\left|core\, a_{\alpha} b_{\beta}\right| - \left|core\, a_{\beta} b_{\alpha}\right|\right)$$

This is a Wavefunction that Can NOT be Represented by a Single Slater Determinant!

➡ BIG Problem – DFT can only do single determinants (Triplet: fine; Singlet: :-( )

Noodleman (*J. Chem. Phys.*, (1981), 74, 5737)

- Use only either $\left|core\ a_{\alpha} b_{\beta}\right|$ or $\left|core\ a_{\beta} b_{\alpha}\right|$ as starting point BUT reoptimize orbitals $\left|core\ a_{\alpha} b_{\beta}\right| \xrightarrow{Minimize\ Energy!!!} \left|core\ \tau_{\alpha}^{A} \tau_{\beta}^{B}\right| \equiv \left|BS\right\rangle$
- NOTE: $\tau_{\alpha}^{A}, \tau_{\beta}^{B}$ are no longer orthogonal in their space parts
- ASSUME: $\left|BS\right\rangle \sim$ 50% Singlet, 50% Triplet

$$J = -\frac{E_{HS} - E_{BS}}{(S_A + S_B)^2}$$

Better:

$$J = -\frac{E_{HS} - E_{BS}}{\left\langle S^2 \right\rangle_{HS} - \left\langle S^2 \right\rangle_{BS}}$$

(Yamaguchi)

Broken Symmetry Limits

Weak-Limit: $\left|BS\right\rangle \rightarrow \left|core\ a_{\alpha} b_{\beta}\right| \rightarrow \frac{1}{\sqrt{2}}\left(\left|S_0\right\rangle + \left|T_0\right\rangle\right) \longrightarrow E\left(S_0\right) - E\left(T_0\right) = 2\left(E\left(BS\right) - E\left(T_0\right)\right)$

Strong-Limit: $\left|BS\right\rangle \rightarrow \left|core\ \psi_1^{\alpha}\psi_1^{\beta}\right| \rightarrow \left|CS\right\rangle \longrightarrow E\left(S_0\right) - E\left(T_0\right) = 2\left(E\left(CS\right) - E\left(T_0\right)\right)$

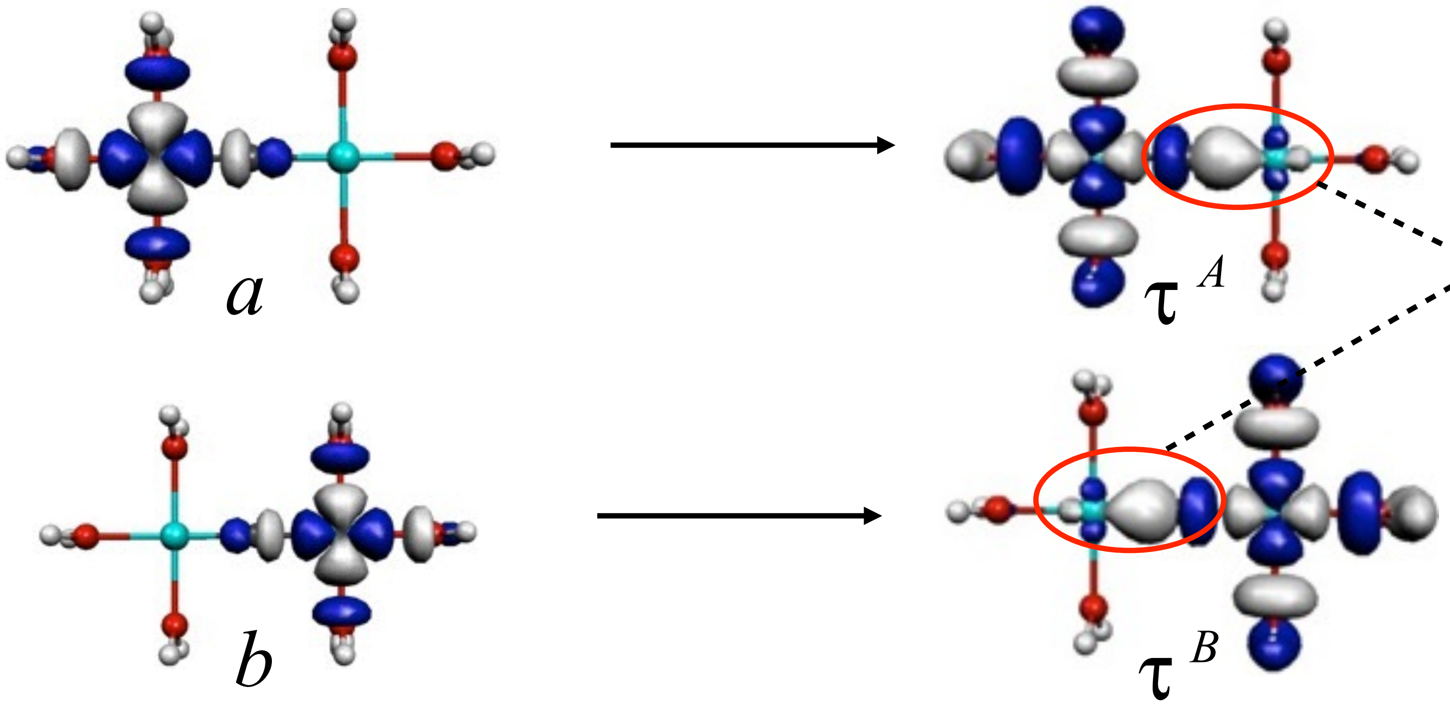
Intermediate-Region: $\left|BS\right\rangle \rightarrow mixture \longrightarrow E\left(S_0\right) - E\left(T_0\right) = -2\frac{E\left(BS\right) - E\left(T_0\right)}{\left\langle S^2\right\rangle_{BS} - \left\langle S^2\right\rangle_{T}}$

Yamaguchi

Soda, T.; et al. *Chem. Phys. Lett.* **2000**, *319*, 223

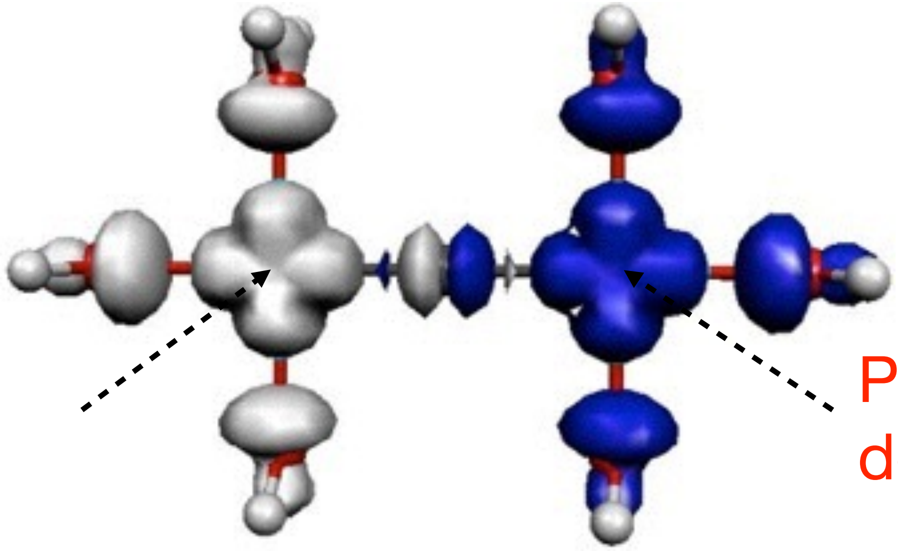
The Broken Symmetry Wavefunction

Relaxation of Orbitals ‚a‘ and ‚b‘:



Energy gain through partial delocalization gives nonorthogonality of space parts (S~0.16 here)

Terrible mistake:



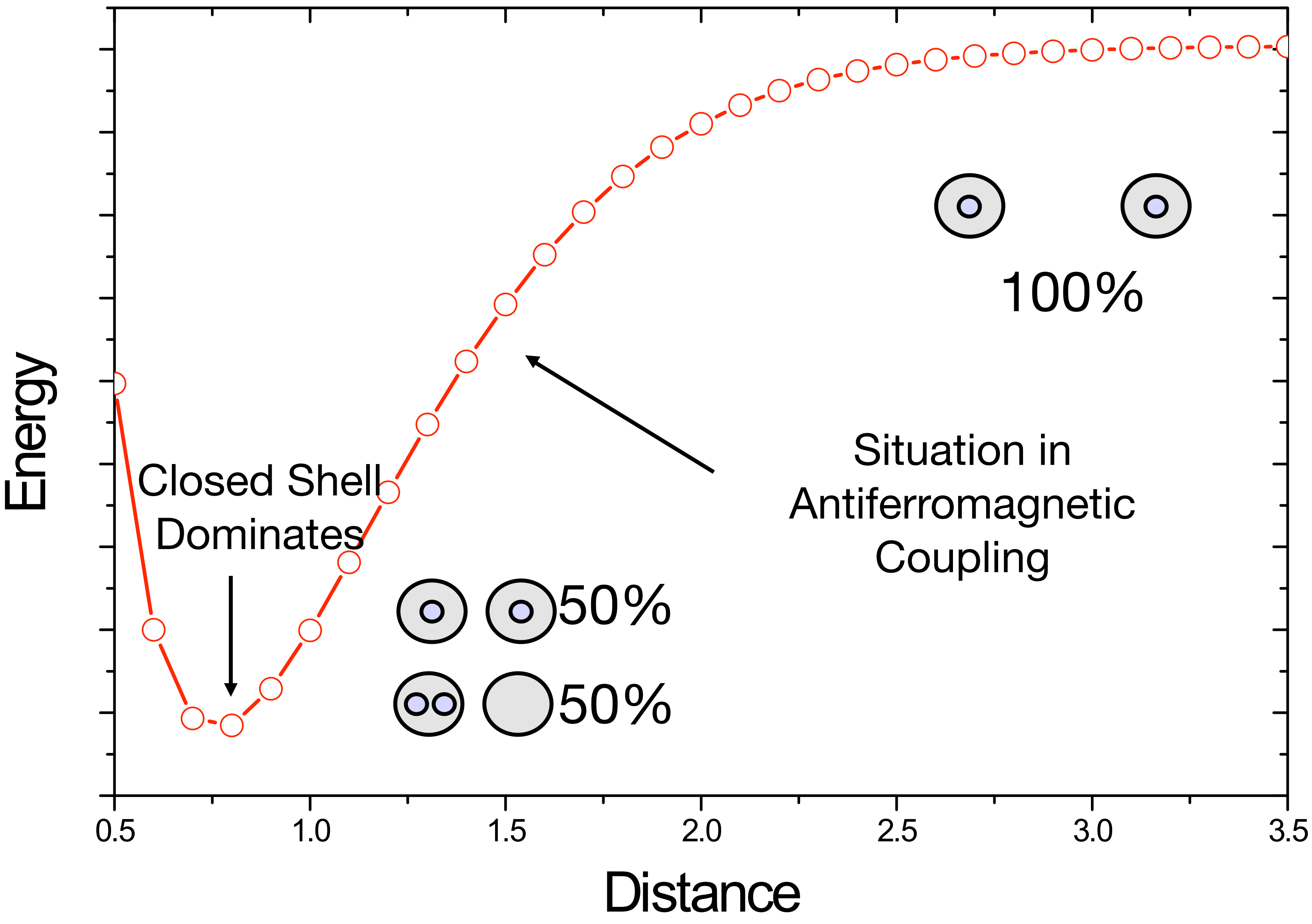
Negative spin density

Positive spin density

In the real world everywhere zero for a singlet state!!!

My View:
FN (**2003**) *J. Phys. Chem. Solids*, 65, 781

Interpretation of the BS Wavefunction



Diradical Index:

200 x Percentage Neutral Character on Top of the Closed Shell Wavefunction (=50%)

BS-DFT

$\%d=100x(1+|S|)x(1-|S|)$

Ab Initio CI

$\%d=200x(c_0^2c_d^2/(c_0^2+c_d^2))^{1/2}$

My View:
FN (**2003**) *J. Phys. Chem. Solids*, 65, 781

Corresponding Orbitals

How to calculate the overlap of the relaxed magnetic orbitals ? (Problem: how to find and define them in the many MOs composing the BS determinant?)

Our suggestion: Use the **corresponding orbitals**

$$\psi_i^\alpha \rightarrow \sum_j U_{ji}^\alpha \psi_j^\alpha$$

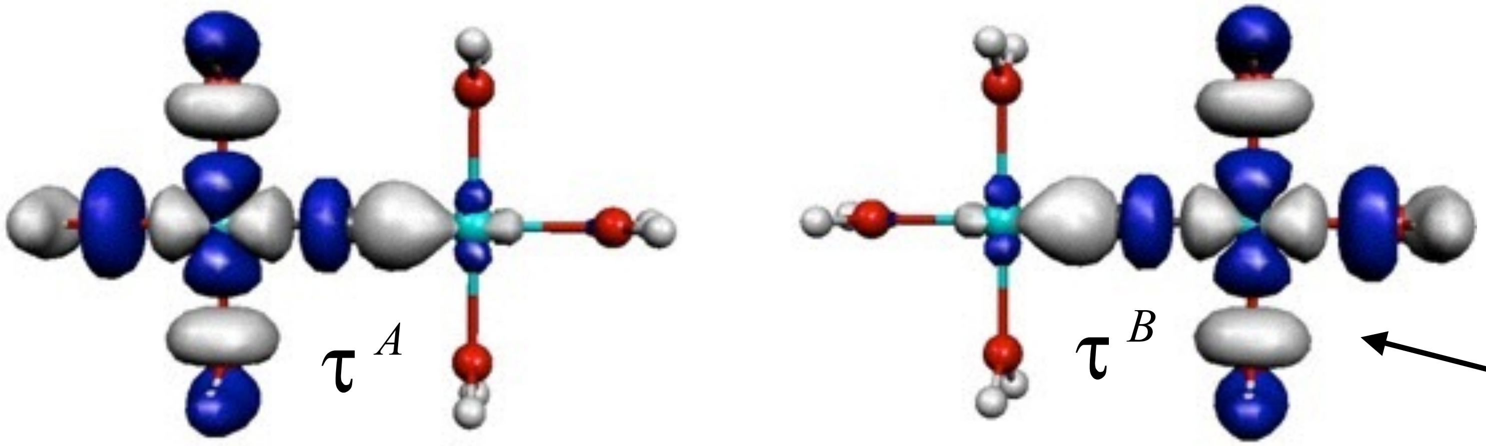
$$\psi_i^\beta \rightarrow \sum_j U_{ji}^\beta \psi_j^\beta$$

such that $\left\langle \psi_i^\alpha \mid \psi_j^\beta \right\rangle \neq 0$ For at most 1 j

$$\boxed{\left\langle S^2 \right\rangle_{BS} = \left(\frac{N^\alpha - N^\beta}{2}\right)\left(\frac{N^\alpha - N^\beta}{2} + 1\right) + N_\beta - \sum_i n_i^\alpha n_i^\beta \left| S_{ii}^{\alpha\beta} \right|^2}$$

Overlap

```
120:        1.00000
121:        1.00000
122:        0.99999
123:        0.99999
          ...
146:        0.99475
147:        0.99267
148:        0.16195...
```



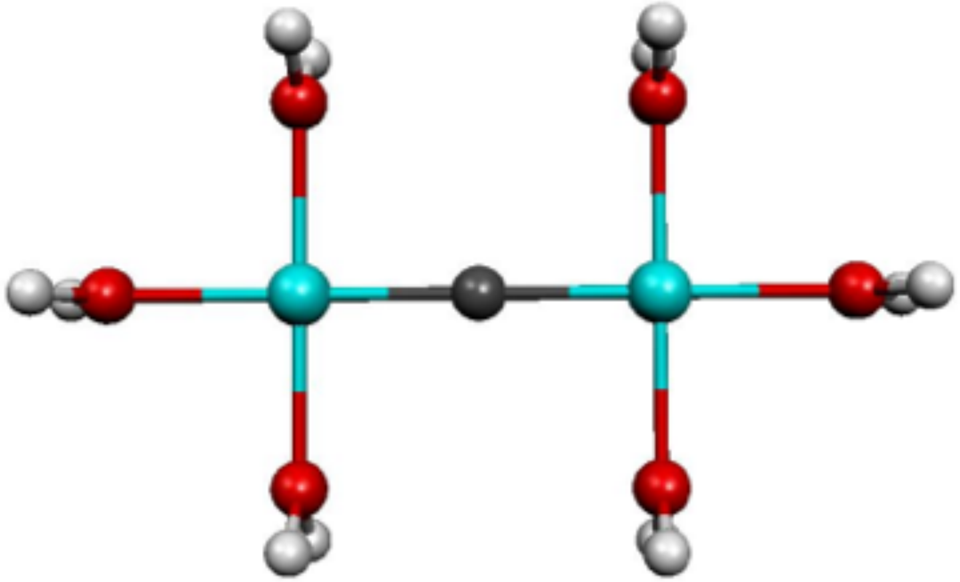
‚Magnetic Pair‘

NOTE : Larger overlap → Stronger AF coupling

BUT : Overlap is result of variational calculation NOT of intuition

Ghosh et al. (**2003**) *JACS*, 125, 1293;
Herebian et al. (**2003**) *JACS*, 125, 10997
FN (**2003**) *J. Phys. Chem. Solids*, 65, 781

Numerical Comparison



Singlet-Triplet Gap

Difference Dedicated CI : -411 cm^{-1}

B3LYP : -434 cm^{-1}

BP : -1035 cm^{-1}

Conclusion:

- ➡ *Ab Initio* Methods accurate, reliable, (beautiful ☺) but expensive
- ➡ BS-DFT can be used with caution and insight BUT depends rather strongly on the functional (GGA: ☹, hybrid: ☺) and can have substantial errors

Summary of Lecture 1

- ✓ Chemistry is described by the many particle **Schrödinger equation**
- ✓ The **Born-Oppenheimer approximation** is a cornerstone of molecular theory and is (most of the time) accurate enough
- ✓ The many particle Schrödinger equation cannot be solved exactly
- ✓ **Hartree-Fock theory** is a useful first step and recovers more than 99.8% of the exact energy. The remaining error is still too large for chemistry!
- ✓ „**Post-HF**“ methods can approach chemical accuracy but are computationally still too expensive for widespread application
- ✓ **Density functional theory** offers an efficient and pragmatic route towards usefully accurate chemical results but the presently available models are semi-empirical in nature and all involve the cancellation of very large errors.