European Summer School of Quantum Chemistry
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Lecture 2: Magnetic Properties, Quantum Chemistry & experiment

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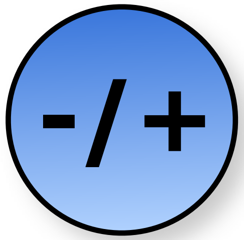
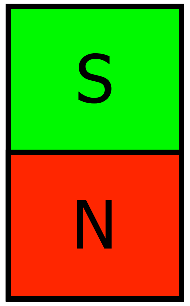
Elementary Properties of Electrons & Nuclei

	Electron	Nuclei
Mass	m_e	M_A
Charge	$-e_0$	$Z_A e_0$
Spin → Magnetic Dipole Moment	μ_e	μ_N



Electric monopole



Magnetic Dipole (Electrons, Nuclei with Spin I>0)

$$\mu_e = -\underbrace{g_e}_{2.002319\ldots}\ \underbrace{\beta_e}_{\text{Bohr‘s Magneton}=9.274010\text{x}10^{-24}\ \text{J/T}}$$

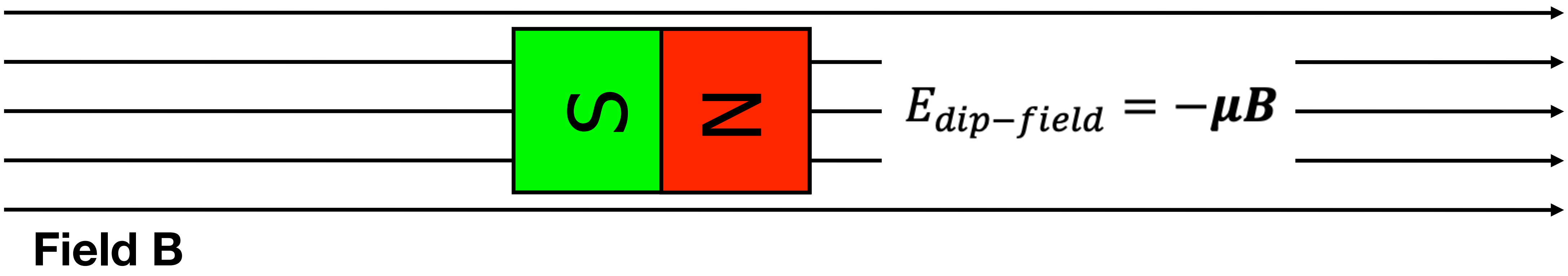
$$\mu_N = g_N\ \underbrace{\beta_N}_{\text{Nuclear Magneton}=5.050783\text{x}10^{-27}\text{J/T}}$$

The electron is intrinsically a 1836 times stronger magnet than nuclei

NOTE - atomic units: $\beta_e = \frac{\alpha}{2} = \frac{1}{2c} \approx \frac{1}{2x137} \approx O(10^{-2});\ \frac{\alpha^2}{2} \approx O(10^{-4})Eh \approx 0.01\frac{kcal}{mol}$

Interactions Between Fields & Magnetic Dipoles

Interaction with a uniform magnetic field



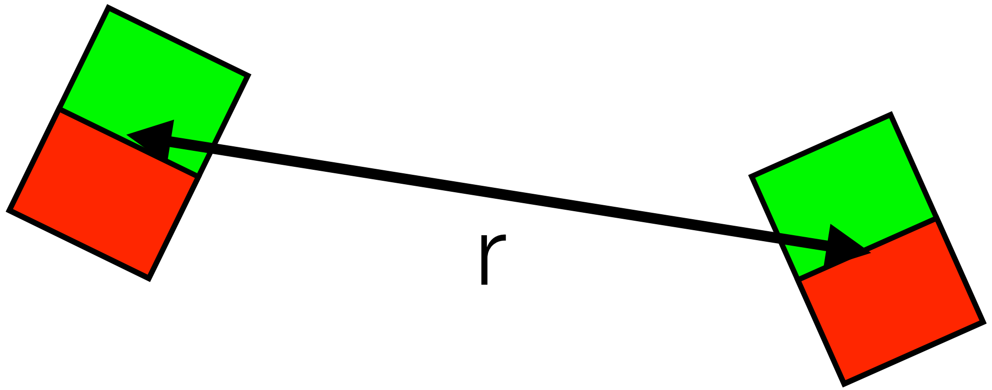
$$E_{dip-field} = -\boldsymbol{\mu}\boldsymbol{B}$$

✓ The interaction is quantized: $|SM_S\rangle \quad M_S = S, S-1, \dots, -S$

$|IM_I\rangle \quad M_I = I, I-1, \dots, -I$

✓ Spin-space: $|SM_SIM_I\rangle = |SM_S\rangle \otimes |IM_I\rangle$ dim=(2S+1)(2I+1)

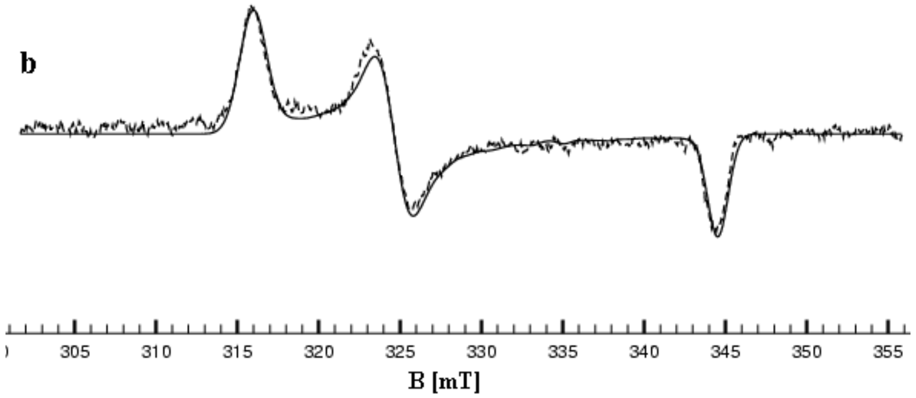
Interaction between dipoles



$$E_{dip-dip} = r^{-5}\{r^2\boldsymbol{\mu}_1\boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1\boldsymbol{r})(\boldsymbol{\mu}_2\boldsymbol{r})\} \propto r^{-3}$$

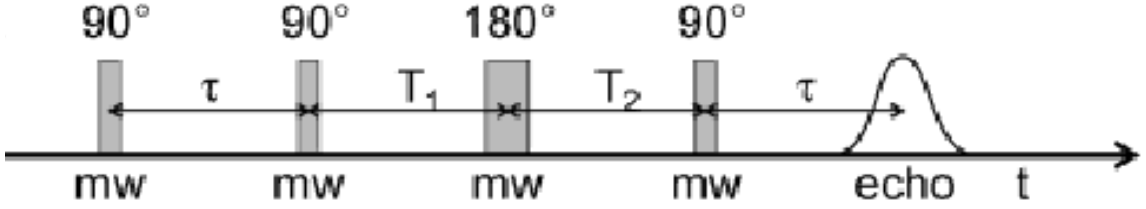
Introduction: The Phenomenological Spin Hamiltonian

„Magnetic Resonance Business“

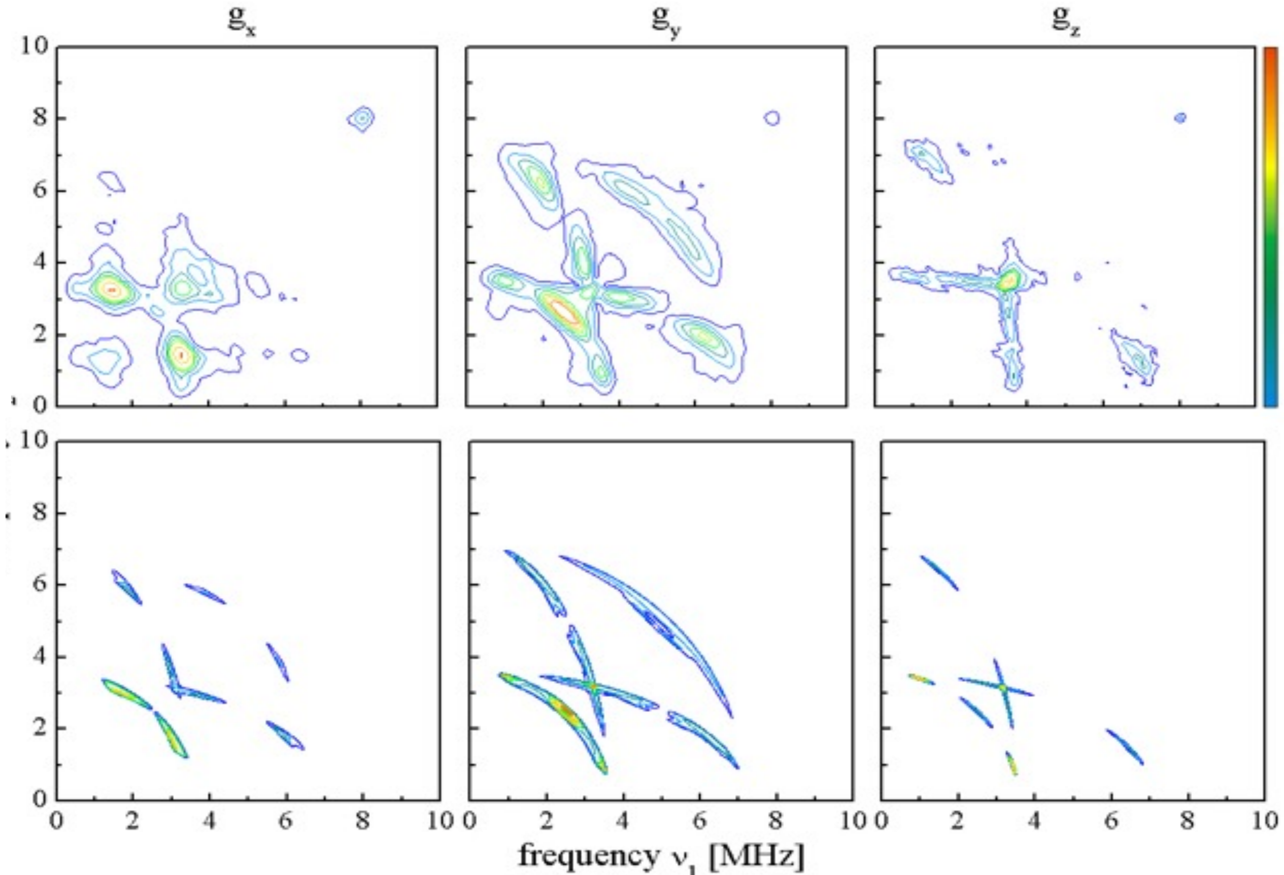


Spectrum

Design an experiment



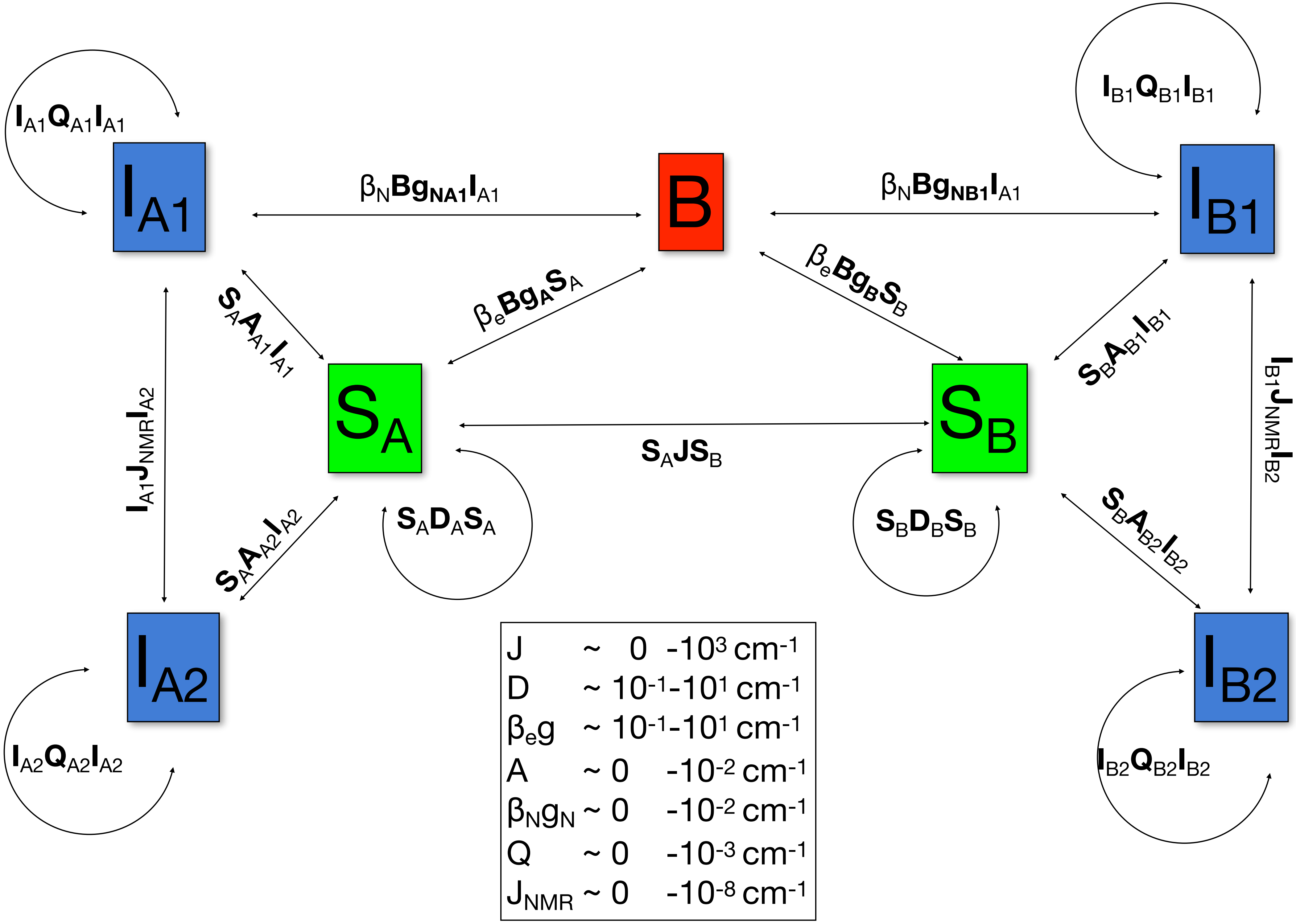
Obtain High Resolution Data



Simulate the Data

And now ?

Magnetic Interactions: Summary



J	~ 0 -10^{3} cm^{-1}
D	~ 10^{-1}-10^{1} cm^{-1}
$\beta_e g$	~ 10^{-1}-10^{1} cm^{-1}
A	~ 0 -10^{-2} cm^{-1}
$\beta_N g_N$	~ 0 -10^{-2} cm^{-1}
Q	~ 0 -10^{-3} cm^{-1}
J_{NMR}	~ 0 -10^{-8} cm^{-1}

The Spin Hamiltonian: Summary

$\hat{H}_{Spin} = \vec{S}\mathbf{D}\vec{S} \qquad (= D(S_z^2 - \frac{1}{3}S(S+1)) + \frac{E}{D}(S_x^2 - S_y^2))$	**Zero-Field Splitting**
$+ \beta\vec{B}\mathbf{g}\vec{S}$	**Zeeman Term (g-Tensor)**
$+ \sum_{A} \vec{S}\mathbf{A}^{(A)}\vec{I}^{(A)}$	**Hyperfine Interaction**
$+ \sum_{A} \vec{I}^{(A)}\mathbf{Q}^{(A)}\vec{I}^{(A)}$	**Quadrupole Interaction**
$- \beta_N \sum_{A} \vec{B}\mathbf{g}_N^{(A)}\vec{I}^{(A)}$	**Nuclear Zeeman**
$+ \sum_{A<B} \vec{I}^{(A)}\mathbf{J}^{(A,B)}\vec{I}^{(B)}$	**Spin-Spin Coupling**

$\vec{S}$	Fictitous Electron Spin	β	Bohr‘s Magneton
$\vec{I}^{(A)}$	Nuclear Spin	β_N	Nuclear Magneton

(Apologies offered for using μ and β interchangeable for the magnetons - literature does that too 😬)

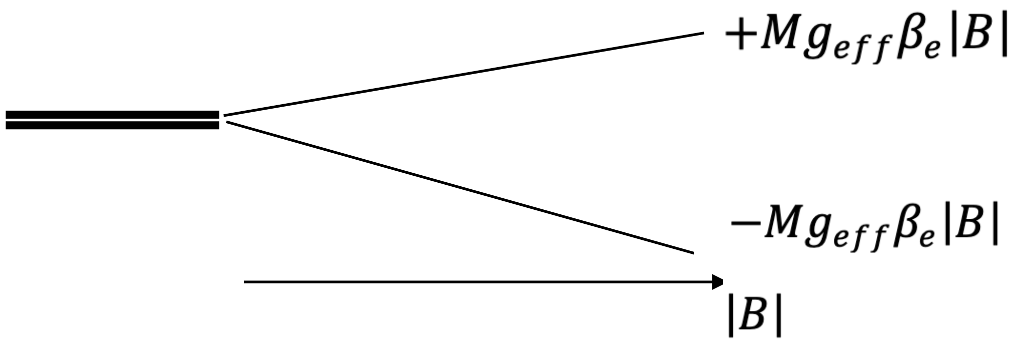
What do these Terms describe (I)?

Consider a multiplet |S,M>

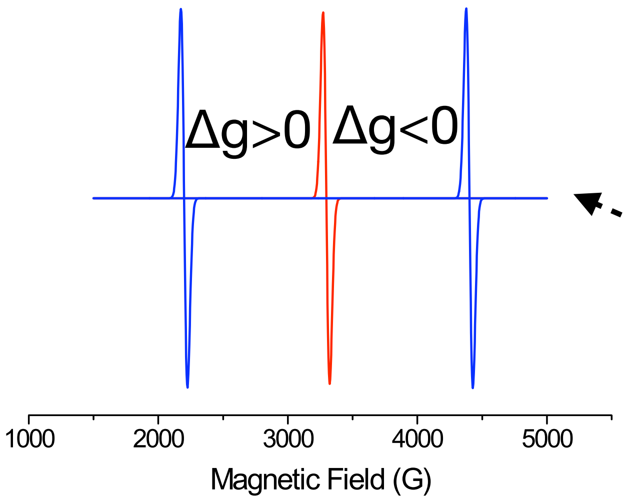
No interaction

All 2S+1 sublevels are degenerate

Electron Zeeman:



✓ Linear divergence



$\Delta E = h\nu = \beta|B|\, g_{eff}$

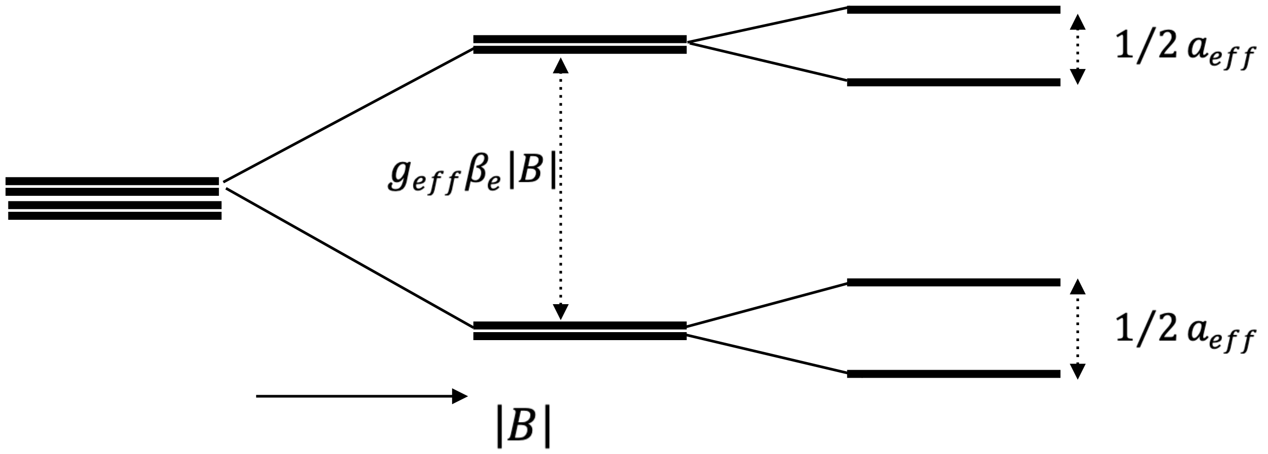
MOLECULAR Quantity=$g_e + \Delta g$

Analogous: NMR chemical shift

What do these Terms describe (II)?

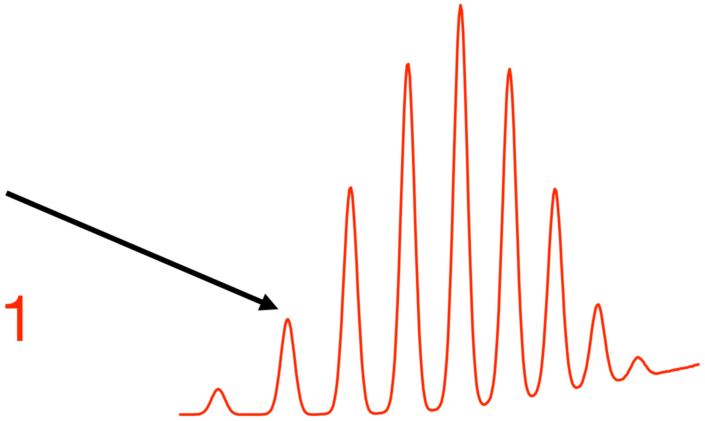
Consider a multiplet |S,MS,I,MI>

Hyperfine



- ✓ Field independent
- ✓ Usually << Zeeman

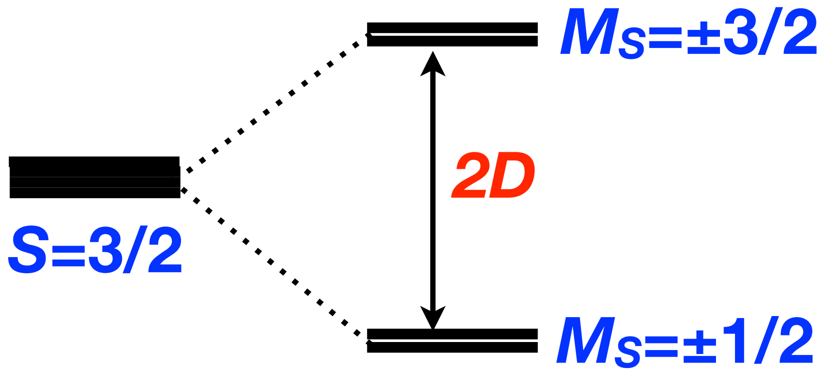
	I=1/2	I=1
	1:1	1:1:1
	1:2:1	1:2:3:2:1
	1:3:3:1	1:2:3:4:3:2:1
	1:2:3:2:1	1:2:3:4:5:4:3:2:1



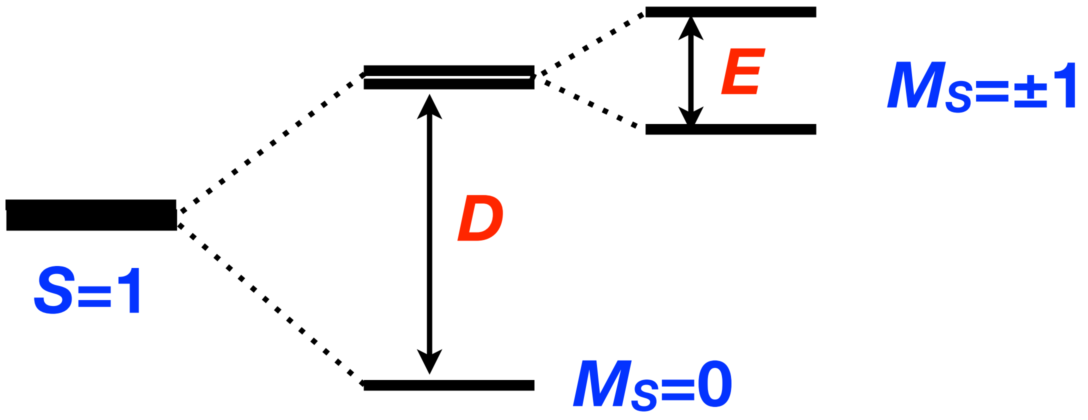
Hyperfine coupling: Analogous NMR Spin-Spin Coupling

What do these Terms describe (III)?

Zero-Field Splitting:



Kramers System



Non Kramers System

- ✓ Only for S>1/2
- ✓ Kramers pairs (non-integer S)
- ✓ Any splitting (integer S)

- ✓ Can be positive or negative
- ✓ Can be <<,= or >> Zeeman
- ✓ THE quantity for single molecule magnets

Analogous: NMR Quadrupole Coupling (I>1/2)

Quick Comment: EPR vs NMR Conventions

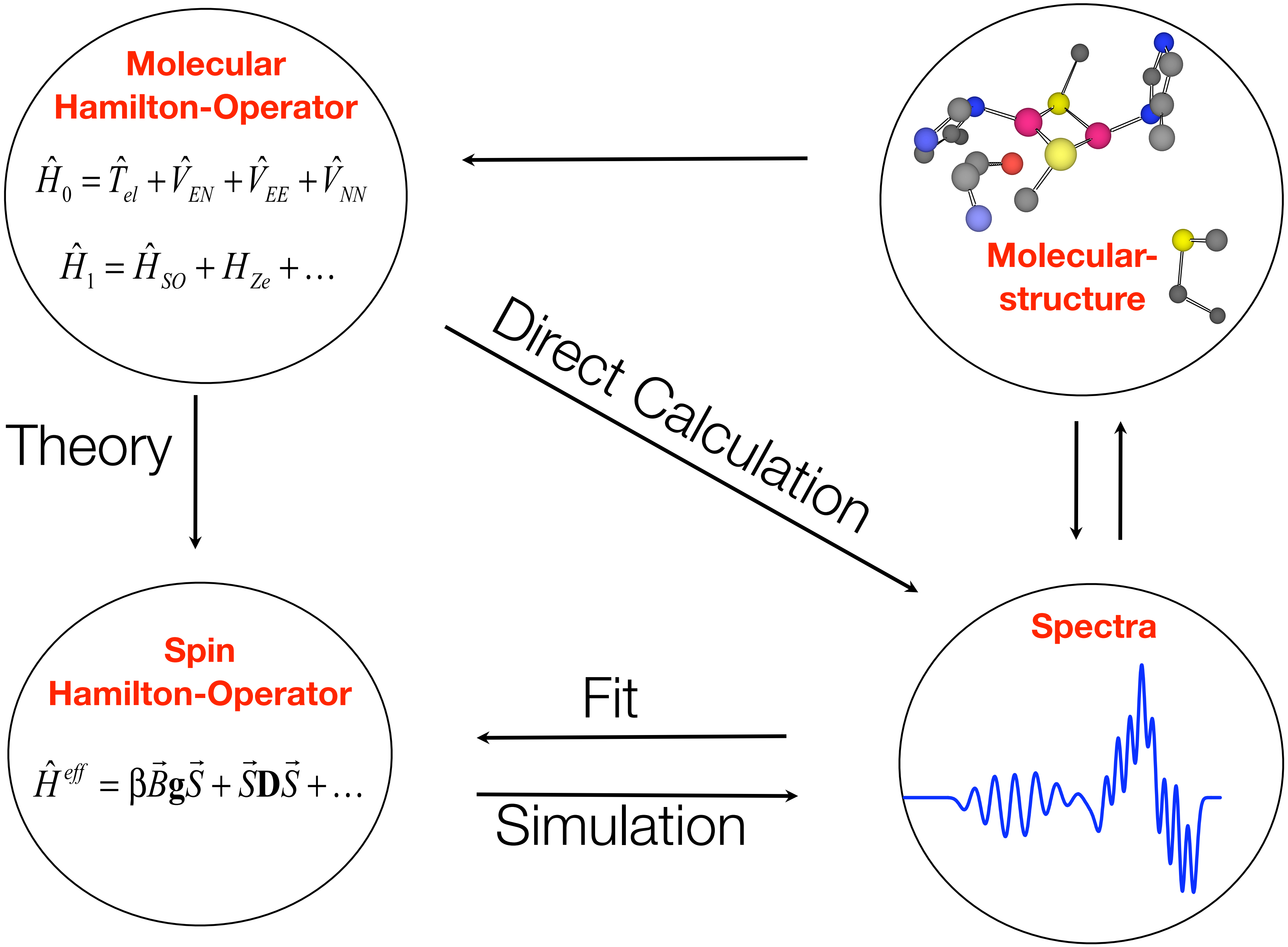
In **EPR** spectroscopy, people like to thing of deviations from the free-electron g-value as the **molecular g-shift**

$$\hat{H}_{ZE-E} = \mu_e \boldsymbol{B} \boldsymbol{g} \hat{\boldsymbol{S}} = \mu_e \boldsymbol{B}\left(\hat{\boldsymbol{1}} g_e + \boxed{\Delta \boldsymbol{g}}\right)\hat{\boldsymbol{S}}$$

In practice nobody in the **NMR** field uses „nuclear g-tensors“, but the NMR culture consists of thinking about the **chemical shift** as a modification of the external field

$$\hat{H}_{ZE-N} = -\mu_N \boldsymbol{B} \sum_A \boldsymbol{g}_N^{(A)} \hat{\boldsymbol{I}}^{(A)} = -\mu_N \boldsymbol{B} \sum_A g_N^{(A)} \left(\hat{\boldsymbol{1}} - \boxed{\boldsymbol{\sigma}}\right)\hat{\boldsymbol{I}}^{(A)}$$

Theoretical Magnetic Spectroscopy



Molecular Hamilton-Operator

$$\hat{H}_0 = \hat{T}_{el} + \hat{V}_{EN} + \hat{V}_{EE} + \hat{V}_{NN}$$

$$\hat{H}_1 = \hat{H}_{SO} + H_{Ze} + \ldots$$

Molecular-structure

Direct Calculation

Theory

Spin Hamilton-Operator

$$\hat{H}^{eff} = \beta \vec{B}\mathbf{g}\vec{S} + \vec{S}\mathbf{D}\vec{S} + \ldots$$

Fit

Simulation

Spectra

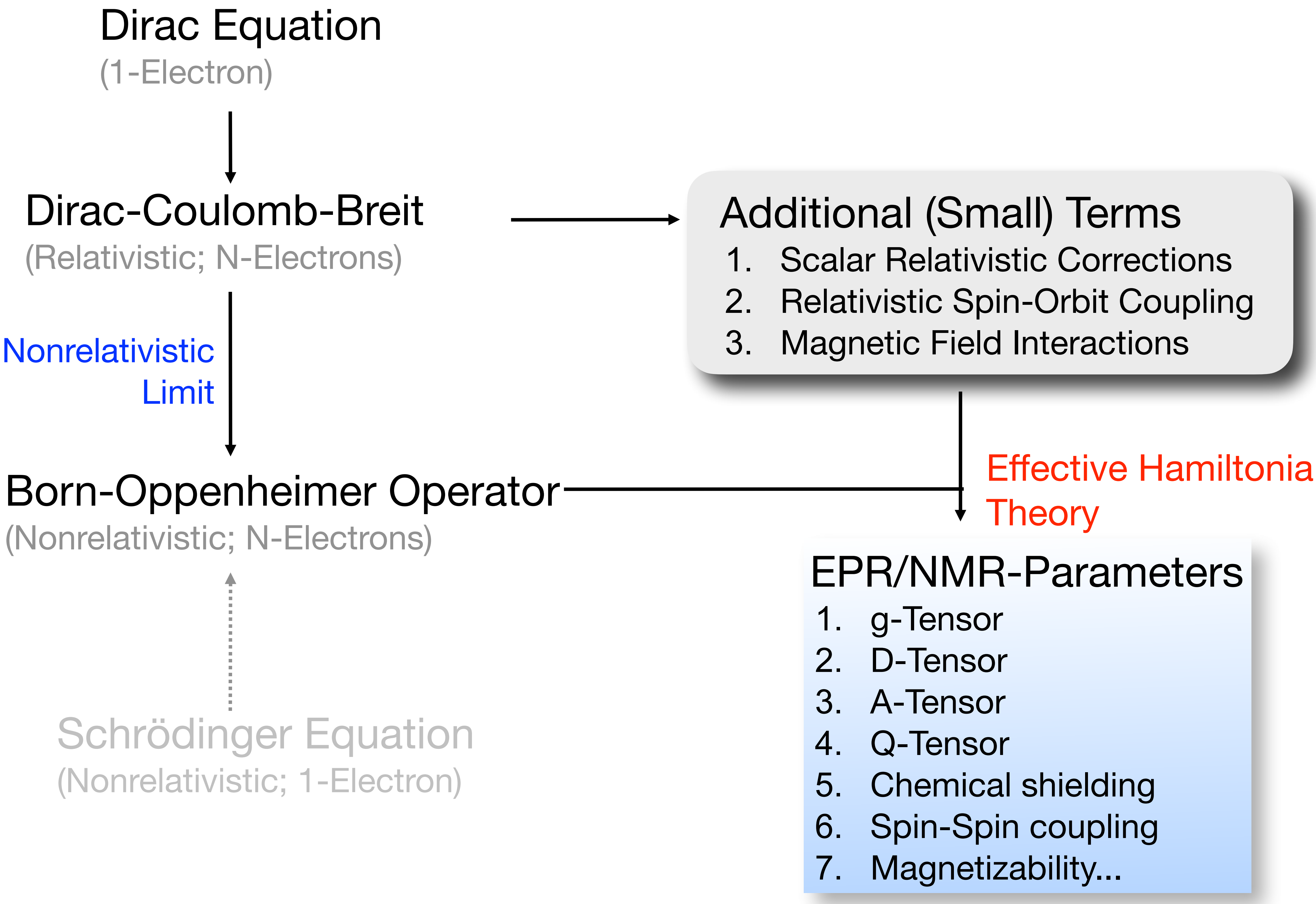
Neese, F. Quantum Chemistry and EPR Parameters *eMagRes* **2017**, *6*, 1.
(and many other reviews since 2001)

Chapter 1:

Additional Terms in the Hamiltonian

Where do the Extra Terms come From?

See relativity &
Magnetic
Properties
lectures!



Dirac Equation
(1-Electron)

Dirac-Coulomb-Breit
(Relativistic; N-Electrons)

Nonrelativistic
Limit

Born-Oppenheimer Operator
(Nonrelativistic; N-Electrons)

Schrödinger Equation
(Nonrelativistic; 1-Electron)

Additional (Small) Terms

1. Scalar Relativistic Corrections
2. Relativistic Spin-Orbit Coupling
3. Magnetic Field Interactions

Effective Hamiltonian
Theory

EPR/NMR-Parameters

1. g-Tensor
2. D-Tensor
3. A-Tensor
4. Q-Tensor
5. Chemical shielding
6. Spin-Spin coupling
7. Magnetizability...

Additional Terms 0: units, notations constants

$$\alpha = c^{-1} \approx 1/137 = Fine\ structure\ constant$$

$$g_e = Free - electron\ g - value = 2.002319\ \ldots$$

$$\beta_e = Bohr\ Magneton = 9.274\ \ldots \times 10^{-24}\frac{J}{T} = \frac{\alpha}{2}$$

$$\beta_N = Nuclear\ Magneton = 5.050\ \ldots \times 10^{-27}\frac{J}{T}$$

$$\boldsymbol{l}_i = (\boldsymbol{r}_i - \boldsymbol{Origin}) \times \boldsymbol{p}_i$$

➡ Angular momenta are relative to a reference point

$$\boldsymbol{l}_i^{(A)} = (\boldsymbol{r}_i - \boldsymbol{R}_A) \times \boldsymbol{p}_i$$

$$\boldsymbol{l}_i^{(j)} = (\boldsymbol{r}_i - \boldsymbol{r}_j) \times \boldsymbol{p}_i$$

$$r_{iA} = |\boldsymbol{r}_i - \boldsymbol{R}_A|$$

➡ Interparticle distances

$$r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$$

Additional Terms 1: Scalar Relativistic Terms

In Breit-Pauli Approximation

$$\hat{H}_{Darwin} = \frac{\pi}{2}\alpha^2 \sum_{A,i} Z_A \delta\left(r_{iA}\right)$$

$$\hat{H}_{MV} = -\frac{1}{8}\alpha^2 \sum_{i} \nabla_i^4$$

- ➡ The Breit-Pauli expansion is divergent and practical never used anymore
- ➡ Almost all calculations use some form of spin-free scalar relativistic treatment such as X2C, ZORA. DKH, NESC
- ➡ Consensus for X2C seems to be emerging
- ➡ These terms are NOT treated as a perturbation but are included in the 0th order Hamiltonian (and hence in the SCF and post SCF treatment)

Additional Terms 2: Spin-Orbit Coupling

In Breit-Pauli Approximation

$$\hat{H}_{SOC-1el} = \frac{1}{2}\alpha^2 \sum_{A,i} Z_A r_{iA}^{-3} \boldsymbol{l}_i^{(A)} \hat{\boldsymbol{s}}_i$$

$$\hat{H}_{SOC-2el} = -\frac{1}{2}\alpha^2 \sum_{i} \hat{\boldsymbol{s}}_i \sum_{j \neq i} r_{ij}^{-3} \left\{ \boldsymbol{l}_i^{(j)} + 2\boldsymbol{l}_j^{(i)} \right\}$$

Breit-Pauli forms (frequently used)
In practice: Needs picture change

➡ This operator is frequently used

➡ In a X2C, ZORA,… treatment, a picture change correction is required

Practice: Spin-Orbit Mean Field Operator

Note: $\hat{H}_{SOC} \neq \lambda \boldsymbol{LS}$

$$\langle p|\hat{H}_{SOMF}|q\rangle = \frac{1}{2}\alpha^2 \sum_{i} \hat{\boldsymbol{s}}_i \left\{ \sum_{A} Z_A \langle p|r_A^{-3} \boldsymbol{l}_i^{(A)}|q\rangle \right.$$
$$\left. - \sum_{rs} P_{rs} \left[\left(pq|r_{ij}^{-3}(\boldsymbol{l}_2^{(2)} + 2\boldsymbol{l}_2^{(1)})|rs\right) - \left(pr|r_{ij}^{-3}(\boldsymbol{l}_1^{(2)} + 2\boldsymbol{l}_2^{(1)})|qs\right) \right] \right\}$$

➡ Effective 1-particle operator, captures >99% of all SOC effects

AMFI: BA Hess, CM Marian, U Wahlgren, O Gropen, *CPL* (**1996**), 251, 365; Full: FN (**2005**), *JCP*, 122, 034107

Additional Terms 3: Spin/Magnetic Field

Straightforward

$$\hat{H}_{ZE-Spin} = g_e \beta_e \boldsymbol{B} \sum_i \hat{\boldsymbol{s}}_i$$

➡ No orbital part; spin only

$$\hat{H}_{ZE-Orbital} = \beta_e \boldsymbol{B} \sum_i \hat{\boldsymbol{l}}_i$$

➡ Diagonal in spin

$$\hat{H}_{ZE-Nuc} = \beta_N \boldsymbol{B} \sum_A g_N^{(A)} \hat{\boldsymbol{I}}^{(A)}$$

➡ No orbital part; Diagonal in spin

Additional Terms 4: Spin-Spin Interactions

These are dipole-dipole and contact interactions

$$\hat{H}_{SS} = \frac{1}{2}\alpha^2 \sum_{i} \sum_{j \neq i} r_{ij}^{-5}\left\{r_{ij}^2 \hat{\boldsymbol{s}}_i \hat{\boldsymbol{s}}_j - 3\left(\hat{\boldsymbol{s}}_i \boldsymbol{r}_{ij}\right)\left(\hat{\boldsymbol{s}}_j \boldsymbol{r}_{ij}\right)\right\}$$

➡ Electron/electron

$$\hat{H}_{SI} = g_e \beta_e \beta_N \sum_{A} g_N^{(A)} \sum_{i} r_{iA}^{-5}\left\{r_{iA}^2 \hat{\boldsymbol{s}}_i \hat{\boldsymbol{I}}^{(A)} - 3\left(\hat{\boldsymbol{s}}_i \boldsymbol{r}_{iA}\right)\left(\hat{\boldsymbol{I}}^{(A)} \boldsymbol{r}_{iA}\right)\right\}$$

➡ Electron/Nucleus spin

$$\hat{H}_{LI} = g_e \beta_e \beta_N \sum_{A} g_N^{(A)} \sum_{i} r_{iA}^{-3} \hat{\boldsymbol{s}}_i \boldsymbol{l}_i^{(A)}$$

➡ Electron/Nucleus orbital

$$\hat{H}_{FC} = \frac{8\pi}{3} g_e \beta_e \beta_N \sum_{A} g_N^{(A)} \sum_{i} \delta(r_{iA}) \hat{\boldsymbol{s}}_i \boldsymbol{l}_i^{(A)}$$

➡ Fermi contact

Total Spin vs Individual Spin

Note carefully:

$$\hat{\boldsymbol{S}} = \sum_i \hat{\boldsymbol{s}}_i$$

$$\hat{\boldsymbol{L}} = \sum_i \hat{\boldsymbol{l}}_i$$

➡ The relativistic/field operators act on individual spin **s**$_i$ but the Spin-Hamiltonian is formualted in terms of the total spin **S**.

➡ NEVER EVER confuse those two!

$$\hat{S}_z|SM\rangle = M|SM\rangle$$

$$\hat{S}^2|SM\rangle = S(S+1)|SM\rangle$$

➡ Only true for the total spin!

$$[\hat{S}_i, \hat{S}_j] = \varepsilon_{ijk} i \frac{h}{2\pi} \hat{S}_k$$

➡ True for the total +individual spins/ mixtures

➡ Basis for applying the Wigner-Eckart theorem later to relate s and S

ε_{ijk} =1 for an even permutation of x,y,z, -1 for odd permutation (Levi-Civitta)

Chapter 2:

The Concept of Effective Hamiltonians

Hamiltonians and Eigensystems

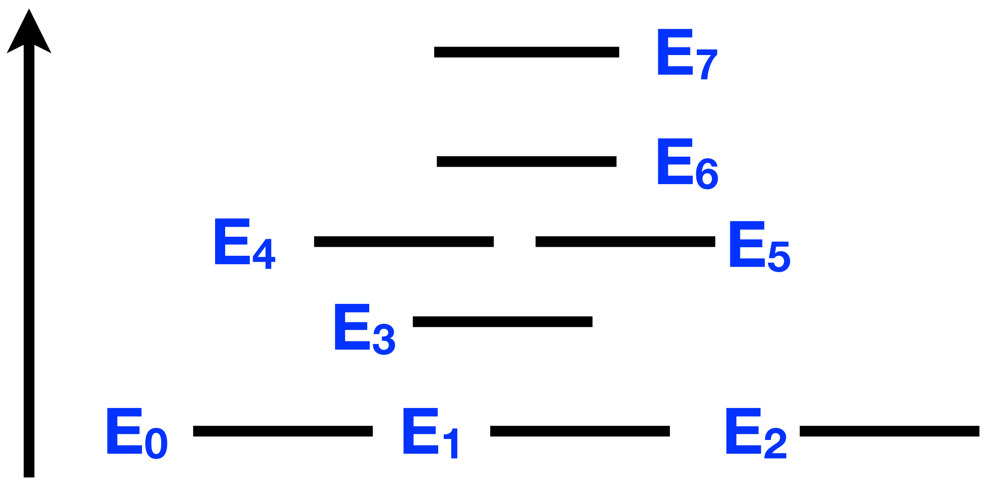
- Let us assume that we have a Hamiltonian that works on a set of variables x_1 .. x_N.

$$H\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right)$$

- Then its eigenfunctions (time-independent) are also functions of x_1 ... x_N.

$$H\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right)\Psi_I\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right) = E_I\Psi_I\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right)$$

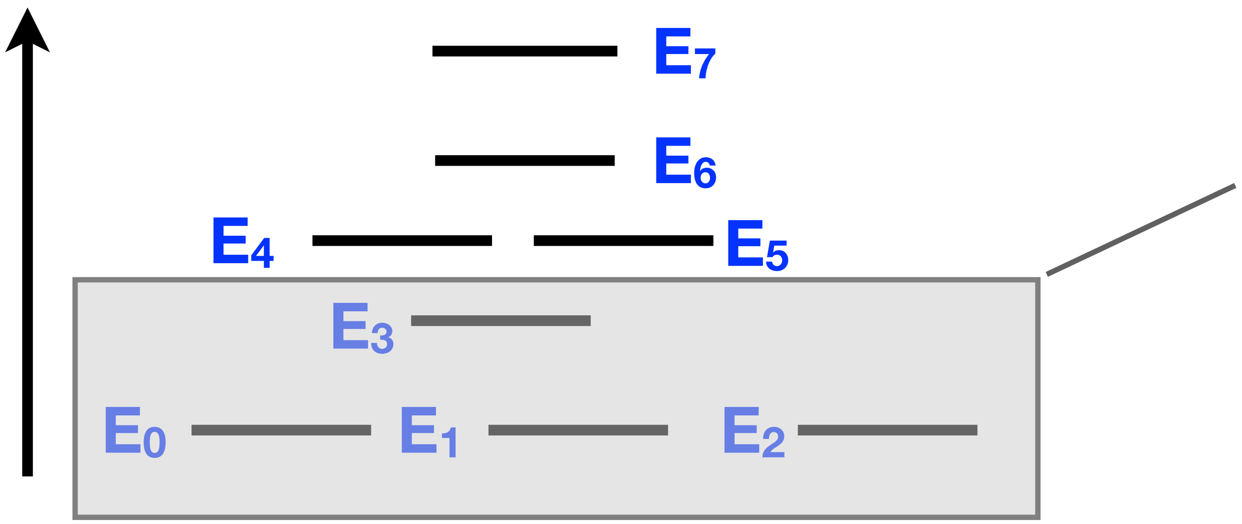
- The eigenvalues of the Hamiltonian form a „spectrum“ of eigenstates that is characteristic for the Hamiltonian



There may be multiple systematic or accidental degeneracies among the eigenvalues

Effective Hamiltonians

- An „effective Hamiltonian“ is a Hamiltonian that acts in a reduced space and only describes a part of the eigenvalue spectrum of the true (more complete) Hamiltonian



Part that we want to describe

TRUE $H\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right)\Psi_I\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right) = E_I\Psi_I\left(\mathbf{x}_1,\ldots,\mathbf{x}_N\right)$ (I=0...infinity)

(nearly) identical eigenvalues wanted!

EFFECTIVE $H_{eff}\Phi_I = E_I\Phi_I$ (I=0...3)

Expansion of the Wavefunction

- ✓ Assume that we have defined our „Complete Hamiltonian“. Assume that we can (or should) divide it into a part H_0 and a part H_1

$$H\Psi_I = (H^{(0)} + H^{(1)})\Psi_I = E_I \Psi_I$$

- ✓ The solutions to $H^{(0)}\Psi_I^{(0)} = E_I^{(0)}\Psi_I^{(0)}$
- ✓ are assumed to be known (**BOLD** assumption!)
- ✓ Then we can always expand the eigenfunctions of the full Hamiltonian in terms of the eigenfunctions of the 0th order Hamiltonian:

$$\Psi_I = \sum_J C_{JI} \Psi_J^{(0)}$$

- ✓ Hence, the Schrödinger equation turns into a matrix eigenvalue problem

$$\mathbf{HC} = E\mathbf{C}$$

The Partitioning Approach

✓ Critical step: divide the 0th order states into the **‚a‘ set** that (=**model space**; the functions that dominate the final states of interest - very small!)

✓ The **b-space** or ‚**outer space**‘. The outer space can be very large!

✓ Partitioned eigenvalue problem:

$$\begin{pmatrix} \mathbf{H}^{AA} & \mathbf{H}^{AB} \\ \mathbf{H}^{BA} & \mathbf{H}^{BB} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{A} \\ \mathbf{C}^{B} \end{pmatrix} = E \begin{pmatrix} \mathbf{C}^{A} \\ \mathbf{C}^{B} \end{pmatrix}$$

✓ The equation for the ‚b‘ space coefficients can be formally solved:

$$\mathbf{C}^{B} = -(\mathbf{H}^{BB} - \mathbf{1}E)^{-1}\mathbf{H}^{BA}\mathbf{C}^{A}$$

✓ Hence:

$$\mathbf{H}^{AA}\mathbf{C}^{A} - \mathbf{H}^{AB}(\mathbf{H}^{BB} - \mathbf{1}E)^{-1}\mathbf{H}^{BA}\mathbf{C}^{A} = E\mathbf{C}^{A}$$

Expansion of the Partitioned Eigenvalue Problem

- ✓ Hence: $\mathbf{H}^{eff}(E)\mathbf{C}^{A} = E\mathbf{C}^{A}$

- ✓ With the effective Hamiltonian:

$$\mathbf{H}^{eff}(E) = \mathbf{H}^{AA} - \mathbf{H}^{AB}(\mathbf{H}^{BB} - \mathbf{1}E)^{-1}\mathbf{H}^{BA}$$

dimension=dim(A)xdim(A)

- ✓ Exact equation!

- ✓ However, since the desired energy E is contained in the effective Hamiltonian, the equation is nonlinear and difficult to solve.

- ✓ We will pursue a simple approach here that exposes the nature of the reasoning. First let us look at the Hamiltonian in b-space:

$$\begin{aligned}(\mathbf{H}^{BB})_{IJ} &= \left\langle \Psi_I^{(0)} \mid H^{(0)} \mid \Psi_J^{(0)} \right\rangle + \left\langle \Psi_I^{(0)} \mid H^{(1)} \mid \Psi_J^{(0)} \right\rangle \\ &= \delta_{IJ} E_I^{(0)} + \left\langle \Psi_I^{(0)} \mid H^{(1)} \mid \Psi_J^{(0)} \right\rangle \\ &\approx \delta_{IJ} E_I^{(0)}\end{aligned}$$

Coupling among the b-space eigenfunctions can be neglected if H_1 is much smaller than H_0

Simplification of the Effective Hamiltonian

✓ Realize that we seek solutions in the vicinity of the eigenvalues of H^{AA} - possible if the coupling to the b-space is not too large.

✓ Dropping this restriction leads to the reasoning of Malrieu‘s ***intermediate Hamiltonians*** that contain a ‚**buffer space**‘ to ‚protect‘ the model space against strong perturbers.

✓ With that assumption, we can replace:

$$(\mathbf{1}E)_{IJ} \approx \delta_{IJ} E_{a}$$

$$E_{a} = \frac{1}{\dim(A)} \sum_{I \in 'a'} E_{I}^{(0)}$$

again neglecting the ‚small‘ coupling of the ‚a‘ states via H_1 (but we could have taken eigenvalues of H_0+H_1 in ‚a‘ space equally well

✓ Then we are done

$$\mathbf{H}^{eff} = \mathbf{H}^{AA} - \mathbf{H}^{AB}(\mathbf{E}^{BB} - \mathbf{1}E)^{-1}\mathbf{H}^{BA}$$

Matrix Elements of the Effective Hamiltonian

$$\begin{aligned}(\mathbf{H}^{\mathit{eff}})_{IJ} &= \delta_{IJ}E_I^{(0)} + \left\langle \Psi_I^{(0)} \mid H^{(1)} \mid \Psi_j^{(0)} \right\rangle \\ &\quad - \sum_{K\in 'b'} \frac{\left\langle \Psi_I^{(0)} \mid H^{(1)} \mid \Psi_K^{(0)} \right\rangle \left\langle \Psi_K^{(0)} \mid H^{(1)} \mid \Psi_J^{(0)} \right\rangle}{E_K^{(0)} - E_a}\end{aligned}$$

- ✓ This looks like second order perturbation theory but is more general since the coupling of the ‚a‘ space functions via the perturbing operator H_1 is taken into account.

- ✓ We could have arrived at this result as well by a formal series expansion of the inverse matrix that would then also define higher order corrections to the effective Hamiltonian but for most intents and purposes the second order H^{eff} is the desired one.

Summary

✓ In order to apply the effective Hamiltonin theory in the proposed form the following conditions have to be met:

1. There must be a sensible division of the ‚Complete Hamiltonian‘ into H_0 and H_1.
2. We must know the complete set of eigenfunctions of H_0
3. There must be a large enough energy gap between the model space and the outer space (Hence, the matrix elements of H_1 should not be so large as to induce a crossing or near crossing of the b-space eigenfunctions with the ‚a‘ space eigenfunctions).

✓ All three assumptions may or may not be critical. In particular (2)+(3) are sometimes hard to meet and then one has to look into an alternative approach (→**linear response theory**)

The Value of Effective Hamiltonians

✓ EH’s are **MUCH simpler** than the ‚parent‘ Hamiltonians

- Treat their eigensystems analytically or with little effort numerically
- Help to Identify the minimum number of physically sensible empirical parameters to effectively describe the physical situation at hand.

✓ EH’s have a great **imaginative power**:

- They create **pictures** in which we can think
- They provide a **language** in which we can talk
- They provide insights into **classes of substances** rather than numbers for individual systems

➡ **GOOD** effective Hamiltonians have parameters that have an unambiguous definition in terms of first principle physics

➡ **LESS GOOD** effective Hamiltonians have parameters with a cloudy of ill defined connection to first principle physics

Following this logic, the Spin Hamiltonian is a GOOD effective Hamiltonian while the Hückel Hamiltonian is a less good effective Hamiltonian.

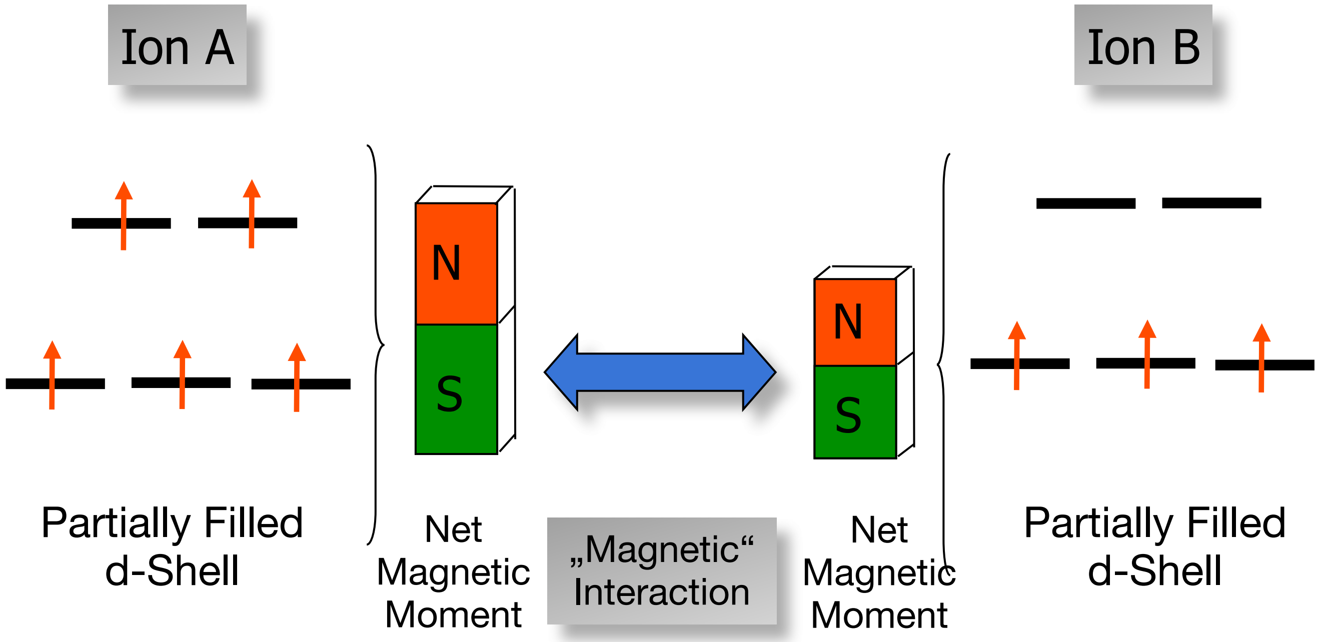
Chapter 3:

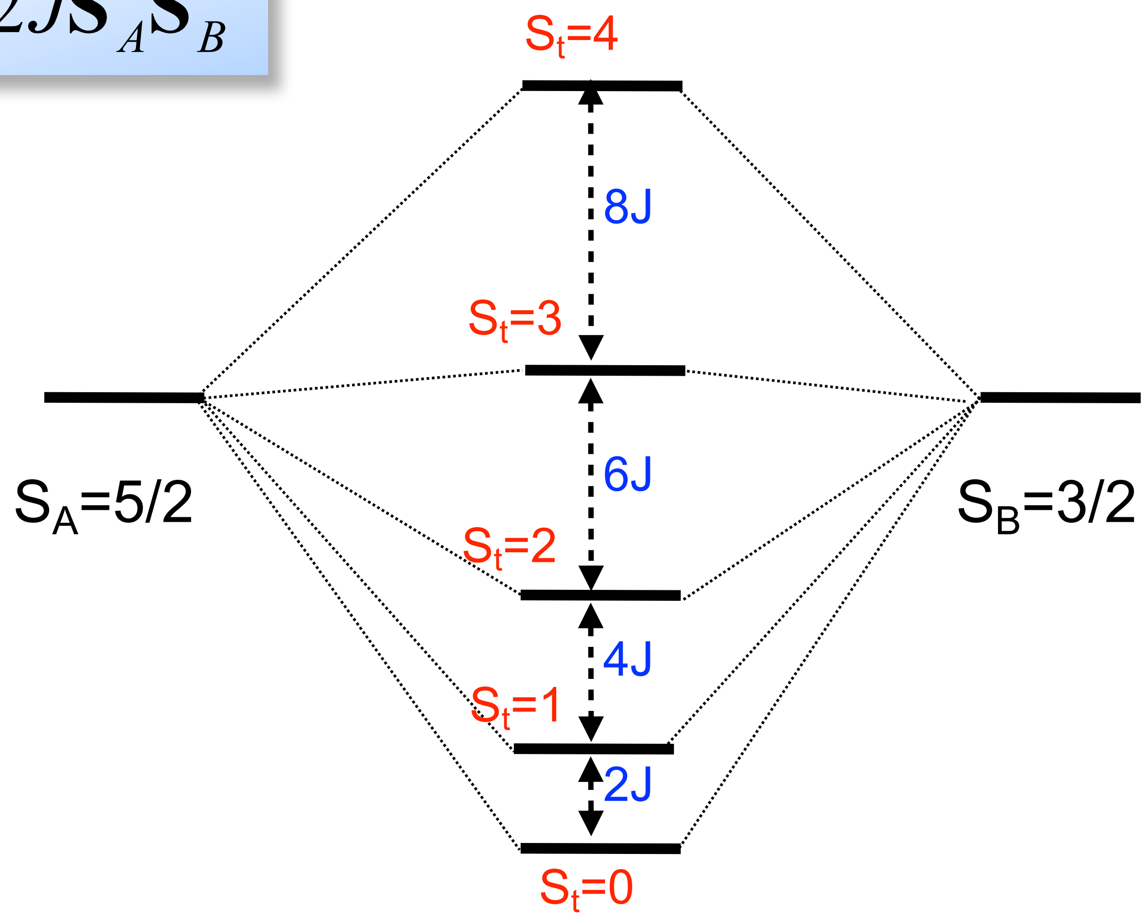
First Application: Exchange Couplings

What is Exchange ?

The interaction of two paramagnetic ions (or more generally fragments) leads to a „ladder“ of total spin states which are described phenomenologically by the Heisenberg-Dirac-VanVleck Hamiltonian

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





What is the origin of this „magnetic“ interaction and how do we calculate it?

With no other magnetic interactions, the energy of a given spin-state is simply: $E(J,S,S_A,S_B) = -J[S(S+1) - S_A(S_A+1) - S_B(S_B+1)]$

Effective Hamiltonian Treatment of the Heisenberg Model

✓ In order to derive the Heisenberg Hamiltonian in the simplest case (the Anderson model). we make the following specification of the general second-order effective Hamiltonian

1. **H_0** is the **Epstein-Nesbet Hamiltonian** (diagonal of the CI matrix) and $H_1 = H - H_0$. Thus, the complete Hamiltonian is the Born-Oppenheimer Hamiltonian.
2. This means, we *do* know the eigenfunctions of the 0th order Hamiltonian exactly (Slater determinants).
3. Our **model space** for the most elementary case of two interacting S=1/2 systems consists of two ‚neutral' determinants $|\mathrm{core}(a_\alpha b_\beta)>$ and $|\mathrm{core}(a_\beta b_\alpha)>$.
4. We assume that we know the **quasi-localized orbitals** ‚a' and ‚b'.
5. The **outer-space** consists of all other Slater determinants including the ionic ones $|\mathrm{core}(a_\alpha a_\beta)>$ and $|\mathrm{core}(b_\alpha b_\beta)>$ and we restrict attention to those

Evaluation of the Effective Hamiltonian

- Assuming two (semi) localized orbitals ‚a‘ and ‚b’, then the **model space** is:

$$|(core)a_\alpha b_\beta\rangle \qquad |(core)a_\beta b_\alpha\rangle$$

- The ‚+‘ and ‚-‘ combination of these determinants are the M=0 components of the lowest singlet and the lowest triplet respectively.
- The diagonal elements of the effective Hamiltonian are equal for both model functions and hence may be put to 0.
- The **off-diagonal first order term** is:

$$\langle a_\alpha b_\beta | H_1 | a_\beta b_\alpha \rangle = (a_\alpha b_\alpha | a_\beta b_\beta) = K_{ab}$$

- And the **off-diagonal second-order term** is:

$$-\frac{\langle a_\alpha b_\beta | H_1 \boxed{| a_\alpha a_\beta \rangle \langle a_\alpha a_\beta |} H_1 | a_\beta b_\alpha \rangle}{\langle a_\alpha a_\beta | H_0 | a_\alpha a_\beta \rangle - \langle a_\alpha b_\beta | H_0 | a_\alpha b_\beta \rangle} - \frac{\langle a_\alpha b_\beta | H_1 \boxed{| b_\alpha b_\beta \rangle \langle b_\alpha b_\beta |} H_1 | a_\beta b_\alpha \rangle}{\langle b_\alpha b_\beta | H_0 | b_\alpha b_\beta \rangle - \langle a_\alpha b_\beta | H_0 | a_\alpha b_\beta \rangle}$$

Extraction of the Exchange Coupling Constant

✓ Since: $\left\langle a_{\alpha} b_{\beta} \mid H_{1} \mid a_{\alpha} a_{\beta} \right\rangle = \left\langle a_{\alpha} b_{\beta} \mid H_{1} \mid b_{\alpha} b_{\beta} \right\rangle = F_{ab}$

$$\left\langle a_{\alpha} a_{\beta} \mid H_{0} \mid a_{\alpha} a_{\beta} \right\rangle - \left\langle a_{\alpha} b_{\beta} \mid H_{0} \mid a_{\alpha} b_{\beta} \right\rangle = (a_{\alpha} a_{\alpha} \mid a_{\beta} a_{\beta}) - (a_{\alpha} a_{\alpha} \mid b_{\beta} b_{\beta}) = J_{aa} - J_{ab} \equiv U$$

✓ We obtain the effective Hamiltonian:

$$H^{eff} = \begin{pmatrix} 0 & K_{ab} - 2\dfrac{F_{ab}^{2}}{U} \\ cc & 0 \end{pmatrix}$$

✓ And the splitting:

$$E(S=0) - E(S=1) = 2K_{ab} - 4\frac{F_{ab}^{2}}{U}$$

✓ And from the Spin-Hamiltonian

$$\begin{aligned} H_{HDvV} &= -2JS_{A}S_{B} \\ &= -J(S^{2} - S_{A}^{2} - S_{B}^{2}) \end{aligned}$$

✓ Hence

$$E(S=0) - E(S=1) = 2J$$

$$\boxed{J = K_{ab} - 2\frac{F_{ab}^{2}}{U}}$$

„Exchange Coupling“: Anderson Model

$2e^-$ in 2 orbitals problem:

$$\psi_{1,2} = 2^{-1/2}\{a \pm b\}$$

Neglect overlap for a moment

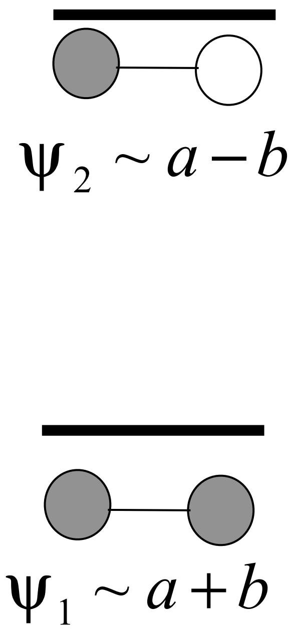
$$|\psi_1\overline{\psi}_1| \quad |\psi_2\overline{\psi}_2| \quad 2^{-1/2}\left(|\psi_1\overline{\psi}_2| - |\overline{\psi}_1\psi_2|\right)$$ 3-Singlets

$$|\psi_1\psi_2|$$ 1-Triplet

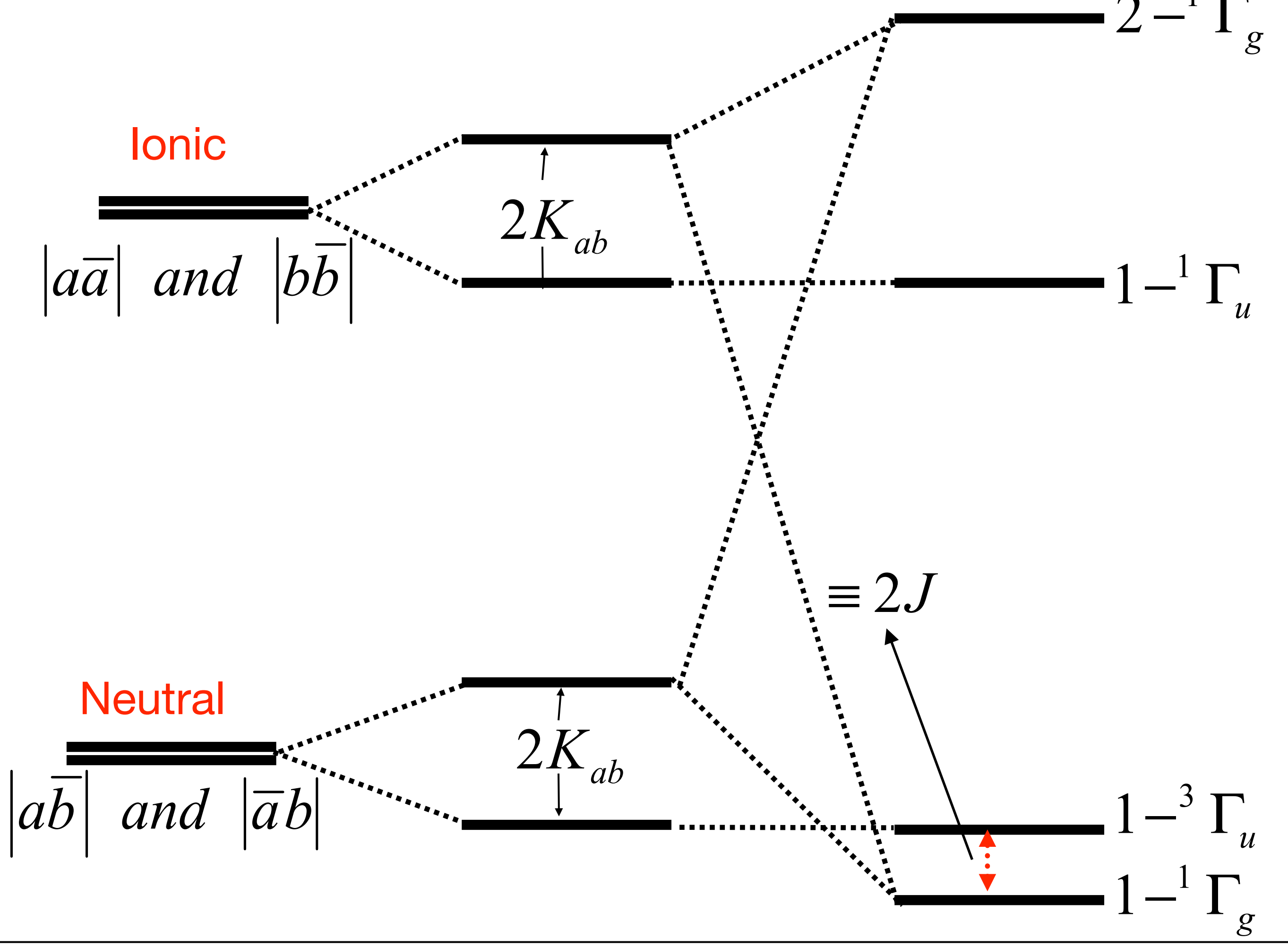
After-CI: $$E(1-{}^1\Gamma_g) - E(1-{}^3\Gamma_g) \approx 2K_{ab} - \frac{4F_{ab}^2}{J_{aa} - J_{ab}} \equiv 2J_{HDvV}$$

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

Orbitals



States



Integrals

$$J_{aa} = J_{bb} = \langle a(1)a(1)|r_{12}^{-1}|a(2)a(2)\rangle$$

On-Site Coulomb Integral

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

Inter-Site Coulomb Integral

$$K_{ab} = \langle a(1)b(2)|r_{12}^{-1}|a(1)b(2)\rangle \propto \exp^{-\alpha R_{ab}}$$

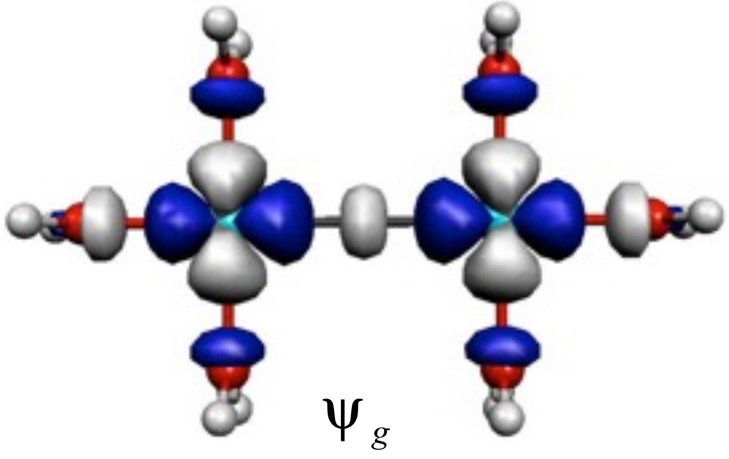
Inter-Site Exchange Integral

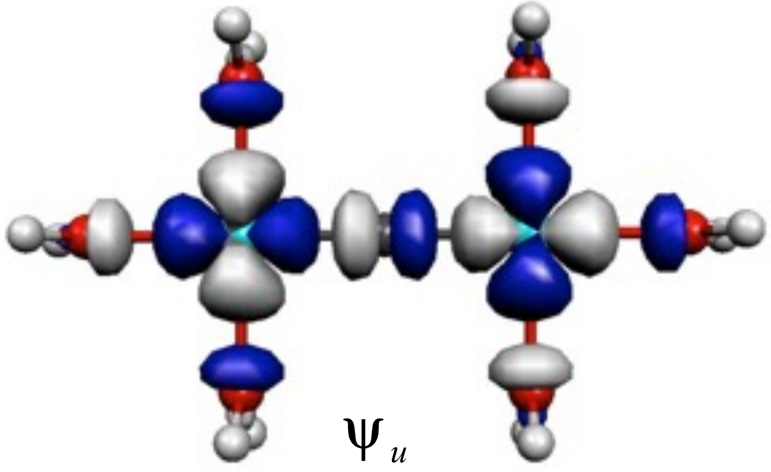
$$F_{ab} = h_{ab} + \langle a(1)a(1)|r_{12}^{-1}|a(2)b(2)\rangle + \langle b(1)b(1)|r_{12}^{-1}|a(2)b(2)\rangle$$

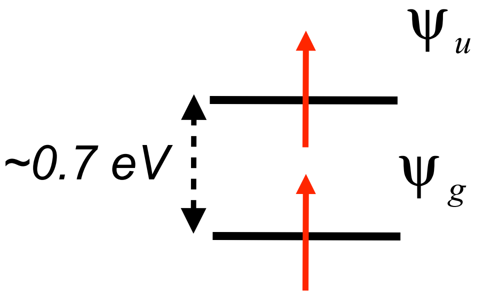
Fock Like „Transfer“ Integral

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

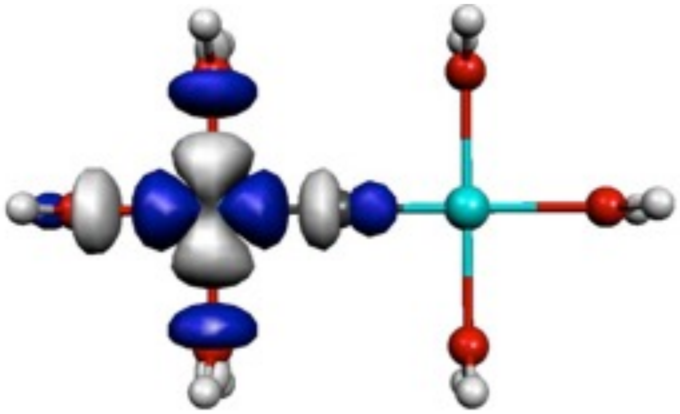
The Hartree-Fock SOMOs of the triplet state („active“ orbitals)



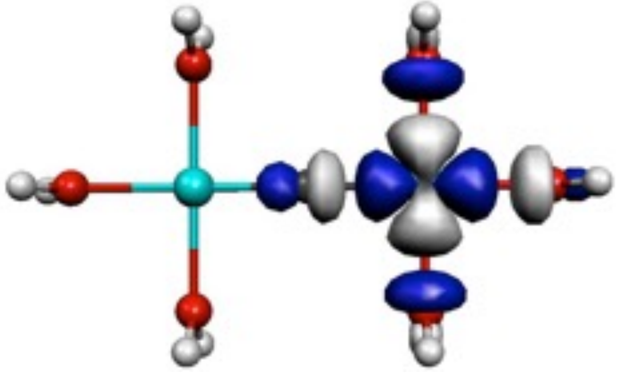




The pseudo-localized „magnetic orbitals“



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



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

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: $\langle ab|r_{12}^{-1}|ab\rangle = 17\ cm^{-1}$

Exactly calculated „kinetic“ exchange term: $-\frac{2\beta^2}{U} = -57\ cm^{-1}$

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

Is that accurate? Look at the singlet wavefunction: **Far off**

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

BUT:

- The ionic parts are too high in energy and mix too little with the neutral configuration (electronic relaxation)
- Need to include dynamic correlation into the calculation

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 Difference Dedicated CI:

(~10^5 Configurations)

$$\begin{array}{r}
\langle ab|r_{12}^{-1}|ab\rangle = 17\ cm^{-1} \\
-\dfrac{2\beta^2}{U} = -57\ cm^{-1} \\
all\ others = -166\ cm^{-1} \\
\hline
J = -206\ cm^{-1}
\end{array}$$

Look at the singlet wavefunction

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

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)
- LMCT states are important

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

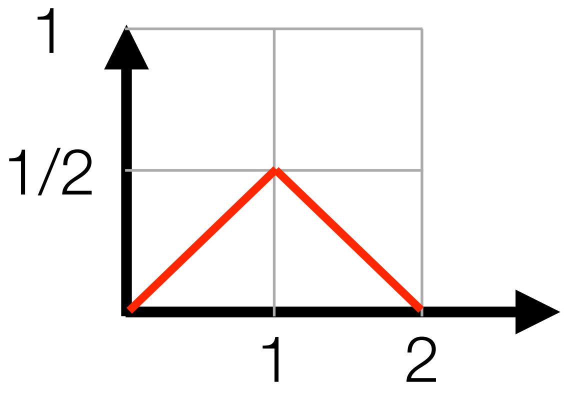
Comments

- ✓ K_{ab} is always positive (*ferromagnetic*). „**Potential Exchange**“
- ✓ $-F^2/U$ is always negative since $J_{aa} > J_{ab}$ (*antiferromagnetic*). „**Kinetic Exchange**“
- ✓ This effective Hamiltonian is **too simple** and upon *ab initio* evaluation of the integrals one recovers only a fraction of J.
- ✓ The reason is that the **‚bare‘ U is much too large** since the ionic configurations relax a lot in the dynamic correlation field.
- ✓ The **dynamic correlation contributions** can - again - be calculated through an effective Hamiltonian.

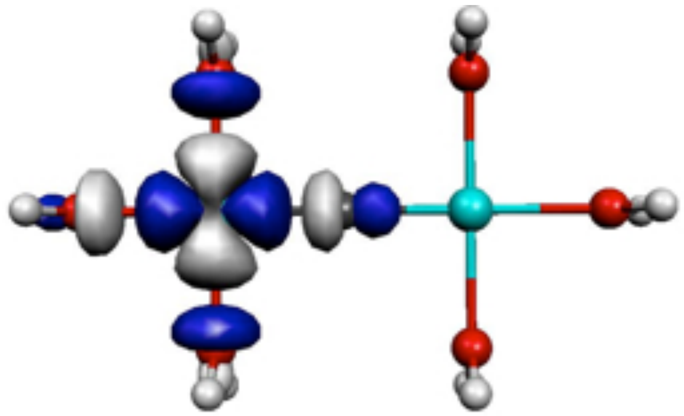
de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, 103, 4007; Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, 116, 3985; Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, 116, 2728. Miralles, J.; Caballol, R.; Malrieu, J. P. *Chem. Phys.* **1991**, 153, 25; Miralles, J.; Daudey, J. P.; Caballol, R. *Chem. Phys. Lett.* **1992**, 198, 555.

A quick Comment on Broken Symmetry DFT

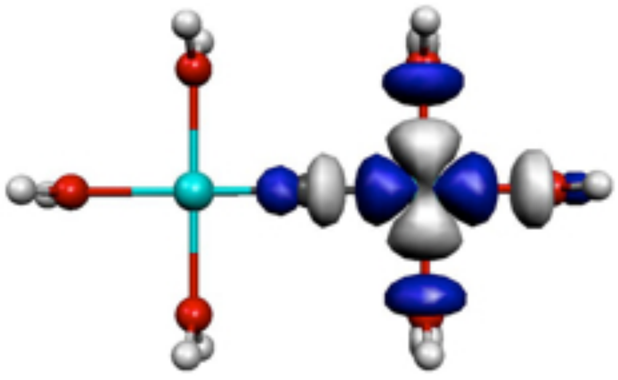
Simplest possible case



$$|\Psi^{00}\rangle = \frac{1}{\sqrt{2}}\left(|a\bar{b}\rangle - |\bar{a}b\rangle\right)$$



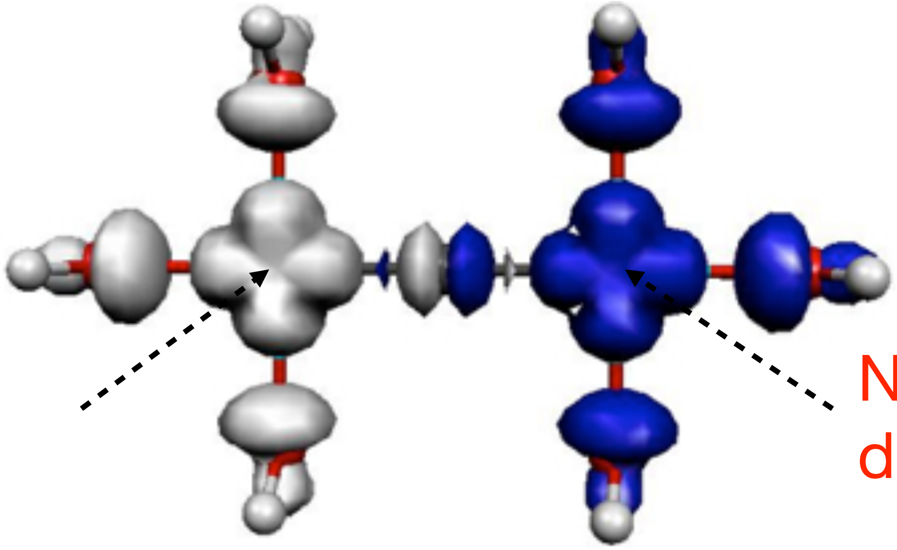
$$|a\rangle = \frac{1}{\sqrt{2}}\left(|\psi_g\rangle + |\psi_u\rangle\right)$$



$$|b\rangle = \frac{1}{\sqrt{2}}\left(|\psi_g\rangle - |\psi_u\rangle\right)$$

✓ **tails** on the bridge, **orthogonal**

Terrible mistake:



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

Positive spin density

Negative spin density

My View: FN (**2003**) *J. Phys. Chem. Solids*, 65, 781; FN *Coord. Chem. Rev.*, **2009**, 253,526

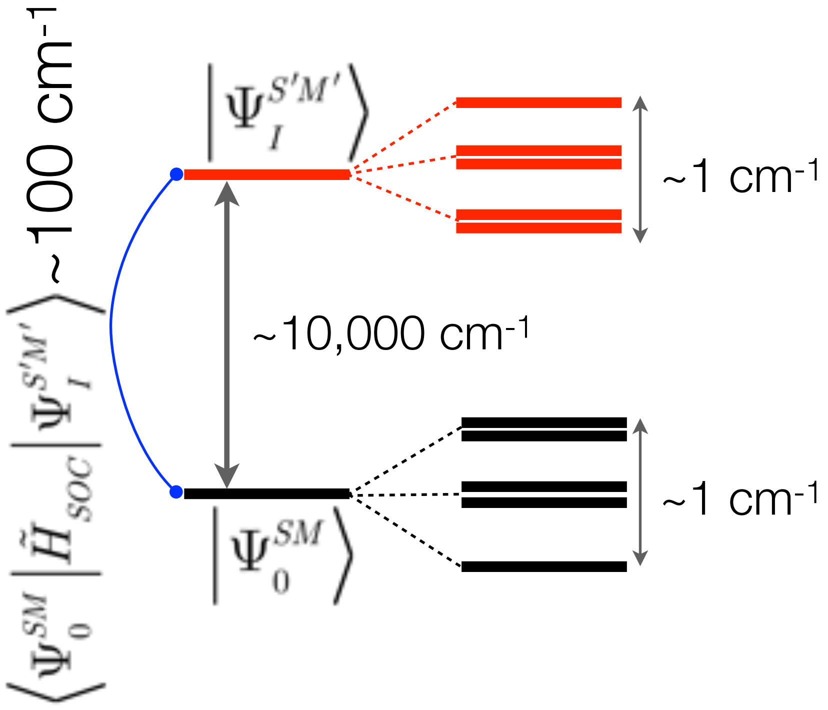
Chapter 4:

Second Application: Spin Hamiltonians

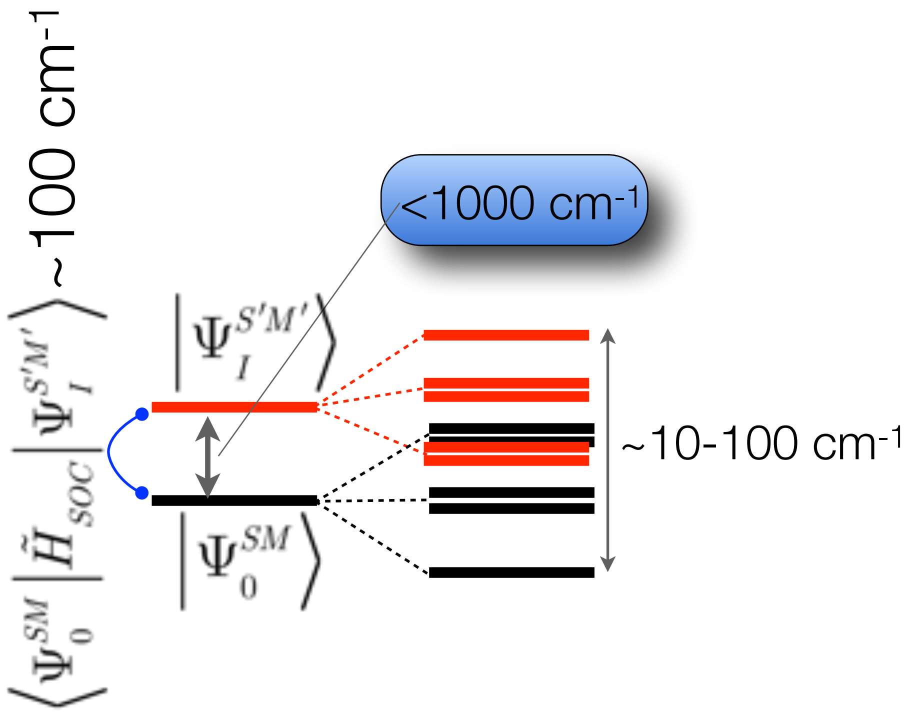
Spin-Hamiltonians and their Limitations

Standard: $\hat{H} = \underbrace{\hat{H}_{BO}}_{\hat{H}_0} + \underbrace{\hat{H}_{rel} + \hat{H}_{Fields}}_{\hat{H}_1}$

Normal:



Special:



✓ Separation between multiplets is much larger than SOC

➡ Spin-Hamiltonian **is** valid

✓ Separation between multiplets is **not** much larger than SOC

➡ Spin Hamiltonian **not** valid

FN (**2001**) *J. Chem. Phys.*, 115, 11080

Perturbation Theory of SH Parameters

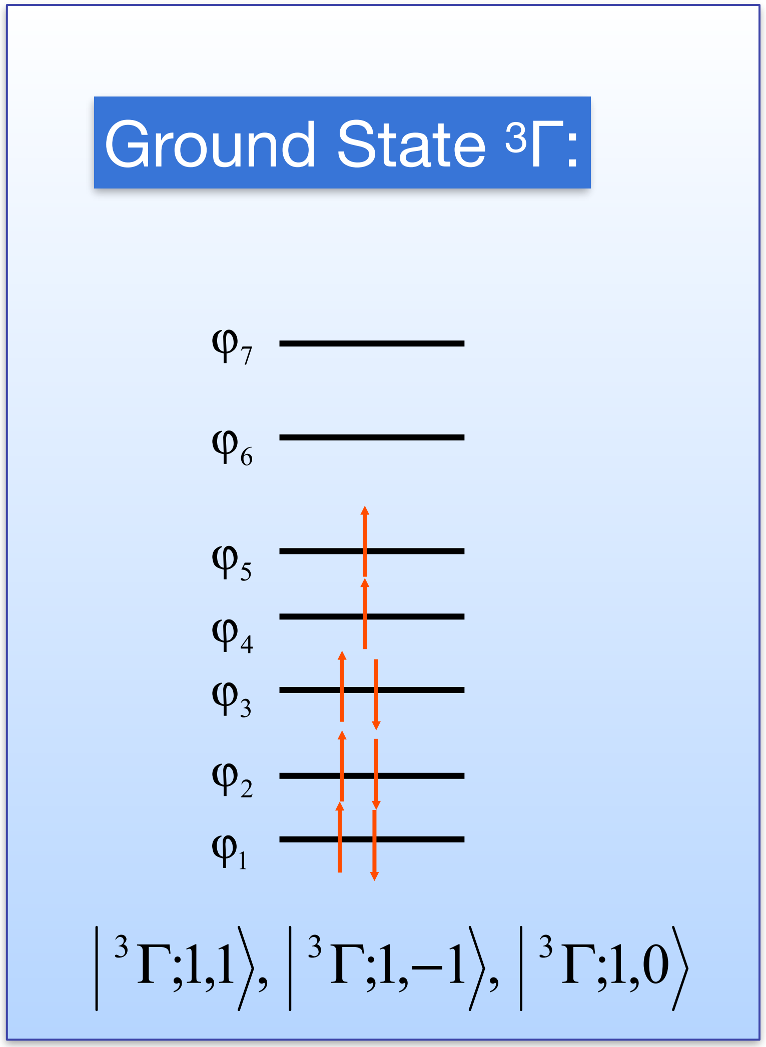
Divide the Complete Set of Many Electron States into Two Sets

1. „**Model Space**“: $|aS_0M\rangle$ $M = S, S-1, \dots, -S$

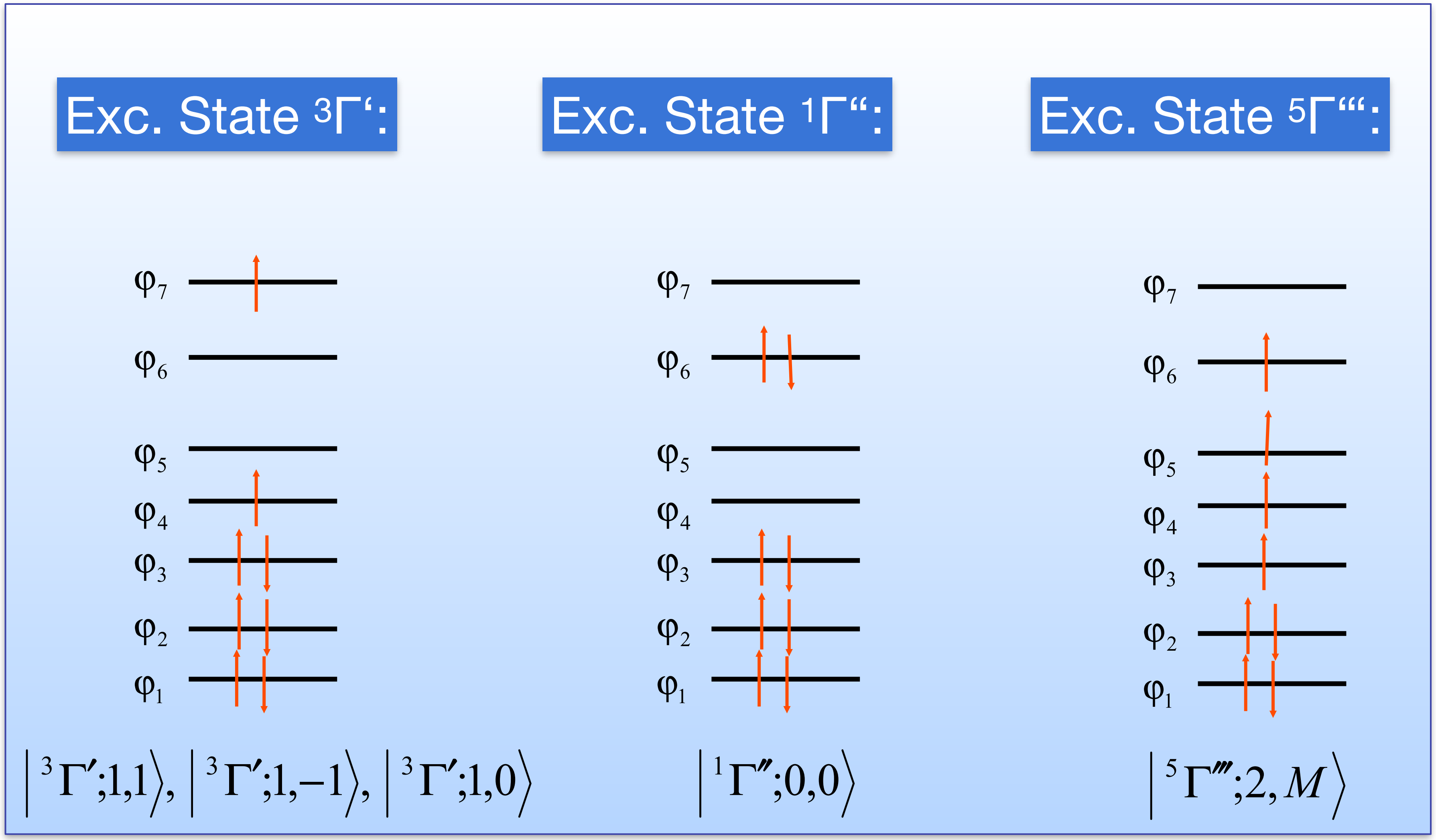
   The 2S+1 components of the orbitally nondegenerate ground state

2. „**Outer Space**“: $|bS_bM\rangle$

Example: *All other states of any multiplicity and symmetry*


Ground State $^3\Gamma$:

$|^3\Gamma;1,1\rangle, |^3\Gamma;1,-1\rangle, |^3\Gamma;1,0\rangle$


Exc. State $^3\Gamma$‘: Exc. State $^1\Gamma$“: Exc. State $^5\Gamma$“‘:

$|^3\Gamma';1,1\rangle, |^3\Gamma';1,-1\rangle, |^3\Gamma';1,0\rangle$ $|^1\Gamma'';0,0\rangle$ $|^5\Gamma''';2,M\rangle$

Defining the Spin-Hamiltonian

- We arrive at the effective Hamiltonian:

$$(\boldsymbol{H}^{eff})_{MM'} = E_0\delta_{MM'} + \langle aS_0M|H^{(1)}|aS_0M'\rangle - \sum_{bS'M''} \frac{\langle aS_0M|H^{(1)}|bS_bM''\rangle\langle bS_bM''|H^{(1)}|aS_0M'\rangle}{E_b - E_0}$$

The 0^{th} order ground state energy can obviously be dropped since it does not add anything to the splitting of the magnetic sublevels.

- But there is a deep symmetry that relates the components with different M for each state ‚a‘ or ‚b‘ - we have to make use of this with the powerful **Wigner-Eckart theorem** in the next step.
- But let us first be more specific on the perturbing Hamiltonian and derive the g-Tensor. Let:

$$H^{(1)} = \beta\boldsymbol{B}\sum_i \boldsymbol{l}_i + g_e\hat{\boldsymbol{s}}_i + \sum_i \boldsymbol{h}_i^{SOC}\hat{\boldsymbol{s}}_i$$

l_i = Angular momentum of electron i relative to the ‚global‘ origin (whatever this means ...)
s_i = Spin angular momentum of electron i
h^{SOC} = Effective one-electron spin-orbit Hamiltonian (e.g. SOMF)

Derivation of the g-Tensor

- First of all, the first order terms are zero since the expectation value over the purely complex operators **l** or **h**^{SOC} vanish:

$$\langle aS_0M|H^{(1)}|aS_0M'\rangle = 0$$

- Hence we are interested in the second-order terms - but only those terms that are linear in the magnetic field since the g-Tensor *describes a linear coupling to* **B**. This immediatly gives:

$$\begin{aligned}(\boldsymbol{H}^{eff})_{MM'} = -\beta\boldsymbol{B}\sum_{bS'M''}\frac{\langle aS_0M|\sum_i \boldsymbol{l}_i + g_e\hat{\boldsymbol{s}}_i|bS_bM''\rangle\langle bS_bM''|\sum_i \boldsymbol{h}_i^{SOC}\hat{\boldsymbol{s}}_i|aS_0M'\rangle}{E_b - E_0}\\ -\beta\boldsymbol{B}\sum_{bS'M''}\frac{\langle aS_0M|\sum_i \boldsymbol{h}_i^{SOC}\hat{\boldsymbol{s}}_i|bS_bM''\rangle\langle bS_bM''|\sum_i \boldsymbol{l}_i + g_e\hat{\boldsymbol{s}}_i|aS_0M'\rangle}{E_b - E_0}\end{aligned}$$

  - The LS matrix element reduces easily since the orbital angular momentum part is diagonal in spin and the spin angular momentum part vanishes since it is diagonal in the spatial part;

$$\langle aS_0M\left|\sum\nolimits_i \boldsymbol{l}_i + g_e\hat{\boldsymbol{s}}_i\right|bS_bM''\rangle = \delta_{S_0S_b}\langle aS_0M\left|\sum\nolimits_i \boldsymbol{l}_i\right|bS_bM''\rangle$$

The Spin-Orbit Coupling Matrix Elements

★ The SOC matrix elements are more subtle. Here one has to make use of the Wigner-Eckart theorem that tells us that for any operator of the form:

$$\hat{O} = \sum_i f_i \hat{\boldsymbol{s}}_i^{(m)}$$

★ where *m* is a ‚spherical tensor component‘ (*m* = 0, ±1):

$$\left\langle \Psi_I^{SM} \middle| \sum_i f_i \; s_i^{(m)} \middle| \Psi_J^{S'M'} \right\rangle = \underbrace{\left(\begin{array}{cc|c} S' & 1 & S \\ M' & m & M \end{array} \right)}_{Clebsch\_Gordon\,Coefficient} \underbrace{\left\langle \Psi_I^{S} \, \| \sum_i f_i \; \| \, \Psi_J^{S'} \right\rangle}_{\mathrm{Re}\,duced\,Matrix\,Element\,Y_{IJ}^{SS'}}$$

★ This fairly esoteric looking equation says that all the M-dependence of the SOC matrix elements is in the **‚Clebsch-Gordon coefficient‘** and that the rest (the hard part!) comes from the **‚reduced matrix element‘**. Hence, we only need the **‚standard components‘** *M* = *S* of each multiplet to calculate the entire (2*S*‘+1)(2*S*+1) block.

★ Note also that this equation tells us that a general operator that depends on the individual electron spins couples states of different multiplicity!

Reduced Matrix Elements

- ★ Without proof: the reduced matrix elements are calculated from the standard states as:

$$\left\langle \Psi_I^S \,||\, \sum_i f_i \,||\, \Psi_J^S \right\rangle = \frac{\sqrt{S\left(S+1\right)}}{S} \left\langle \Psi_I^{SS} \,|\, \sum_i f_i \; s_{0,i} \,|\, \Psi_J^{SS} \right\rangle$$

$$\left\langle \Psi_I^S \,||\, \sum_i f_i \,||\, \Psi_J^{S+1} \right\rangle = \sqrt{\frac{2S+3}{2S+1}} \left\langle \Psi_I^{SS} \,|\, \sum_i f_i \; s_{-1,i} \,|\, \Psi_J^{S+1S+1} \right\rangle$$

$$\left\langle \Psi_I^S \,||\, \sum_i f_i \,||\, \Psi_J^{S+1} \right\rangle = \left\langle \Psi_I^{SS} \,|\, \sum_i f_i \; s_{+1,i} \,|\, \Psi_J^{S-1S-1} \right\rangle$$

- ★ With the ‚spherical tensor components‘ of the spin operators being given by:

$$s_{0,i} = s_{z,i}$$

$$s_{+1,i} = -\frac{1}{\sqrt{2}}\left(s_{x,i} + i s_{y,i}\right)$$

$$s_{-1,i} = \frac{1}{\sqrt{2}}\left(s_{x,i} - i s_{y,i}\right)$$

FN, El Solomon *Inorg. Chem.*, **1998**. 37,6568

The Second Order g-Tensor

- After this significant detour we can now evaluate the sums over the intermediate M-components exactly and arrive at the second-order expression for the g-Tensor

- Let us first look at an element of the Spin-Hamiltonian:

$$\beta B_z g_{zz} \left\langle SS \mid S_z \mid SS \right\rangle = \beta B_z g_{zz} S$$

- Now the same for our perturbation sum:

compare to find the expression for g!

$$\begin{aligned}\left(\mathbf{H}^{eff}\right)_{SS} = &-\beta B_z \sum_{bS} \Delta_b^{-1} \left\langle aSS \mid \sum\nolimits_i l_{iz} \mid bSS \right\rangle \left\langle bSS \mid \sum\nolimits_i h_z^{SOC} \hat{s}_{0,i} \mid aSS \right\rangle \\ &-\beta B_z \sum_{bS} \Delta_b^{-1} \left\langle aSS \mid \sum\nolimits_i h_z^{SOC} \hat{s}_{0,i} \mid bSS \right\rangle \left\langle bSS \mid \sum\nolimits_i l_{iz} \mid aSS \right\rangle\end{aligned}$$

- Thus (and generalizing to all components):

$$\boxed{\begin{aligned}g_{KL} = &-\frac{1}{S} \sum_{bS} \Delta_b^{-1} \left\langle aSS \mid \sum\nolimits_i l_{iK} \mid bSS \right\rangle \left\langle bSS \mid \sum\nolimits_i h_L^{SOC} \hat{s}_{0,i} \mid aSS \right\rangle \\ &-\frac{1}{S} \sum_{bS'} \Delta_b^{-1} \left\langle aSS \mid \sum\nolimits_i h_K^{SOC} \hat{s}_{0,i} \mid bSS \right\rangle \left\langle bSS \mid \sum\nolimits_i l_{iL} \mid aSS \right\rangle\end{aligned}}$$

- **Note**: Only excited states of the same spin as the ground state
- **Note**: Only standard components M=S

First Order g-Tensor Contributions

- ★ For completeness, we notice that there are also a few relativistic operators that are bilinear in spin and field and hence give rise to **first order contributions**. They read:

$$
\begin{aligned}
g_{KL}^{(first-order)} = \; & \underbrace{\delta_{KL} g_e}_{Spin-Zeeman} \\
& \underbrace{+\,\delta_{KL} \frac{\alpha^2}{S} \left\langle aSS \,\middle|\, \sum_i \vec{\nabla}_i^2 s_{zi} \,\middle|\, aSS \right\rangle}_{\mathrm{Re}\,duced-Mass} \\
& + \underbrace{\frac{\alpha^2}{2S} \left\langle aSS \,\middle|\, \sum_{iA} \frac{Z_A^{eff}}{r_{iA}^3} \left\{ (\mathbf{r}_{iA}\mathbf{r}_i) - (\mathbf{r}_{iA})_K (\mathbf{r}_i)_L \right\} s_{zi} \,\middle|\, aSS \right\rangle}_{Diamagnetic\,Spin-Orbit\;(Gauge\;correction)}
\end{aligned}
$$

- ★ Except for the trivial **g_e=2.002319...** the first order terms are typically much smaller than the second order term.
- ★ α≈1/137 is the **fine structure constant** and Z^{eff} is an *effective nuclear charge* that is semiempirical and has been introduced to avoid expensive (and small) two-electron gauge terms.

From EPR g-Tensors to to NMR Chemcial Shifts

Electrons

$$\hat{H}_{\mathrm{el-Ze}} = \mu_{\mathrm{B}}\mathbf{B}\sum_{\mathrm{i}}\hat{l}_{\mathrm{i}} + g_{\mathrm{e}}\hat{s}_{\mathrm{i}}$$

Electron Zeeman

$$\hat{H}_{\mathrm{SOC}} = \sum_{\mathrm{i}}\hat{\mathbf{h}}_{\mathrm{i}}^{\mathrm{SOC}}\hat{s}_{\mathrm{i}} = \frac{\alpha^2}{2}\sum_{\mathrm{i,A}} Z_{\mathrm{A}}^{\mathrm{eff}}\frac{\hat{l}_{\mathrm{i}}^{(\mathrm{A})}\hat{s}_{\mathrm{i}}}{r_{\mathrm{iA}}^3}$$

Spin-orbit coupling

Nuclei

$$\hat{H}_{\mathrm{Nuc-Ze}} = \mu_{\mathrm{N}}\mathbf{B}\sum_{\mathrm{A}}\hat{I}_{\mathrm{A}}$$

Nuclear Zeeman

$$\hat{H}_{\mathrm{NOC}} = \frac{\alpha}{2}\mu_{\mathrm{N}}\sum_{\mathrm{i,A}} g_{\mathrm{N}}^{(\mathrm{A})}\frac{\hat{l}_{\mathrm{i}}^{(\mathrm{A})}\hat{I}_{\mathrm{A}}}{r_{\mathrm{iA}}^3}$$

Nucleus-orbit coupling

The g-Tensor vs the Chemical Shift Tensor

First-order (diagmagnetic term)

EPR

$$g_{ZZ}^{(D,SB)} = \frac{1}{S}\langle \Psi_0^{SS} \mid \sum_A \sum_i \left(\frac{\alpha^2 Z_A^{eff}}{2}\right) r_{iA}^{-3} (\mathbf{r}_i \mathbf{r}_{iA} - z_i z_{iA}) \hat{s}_{zi} \mid \Psi_0^{SS} \rangle$$

(property of the entire system)

NMR

$$g_{ZZ}^{(D,SB;A)} = \left\langle \Psi_0^{SS} \mid \sum_i r_{iA}^{-3} (\mathbf{r}_i \mathbf{r}_{iA} - z_i^T z_{iA}) \mid \Psi_0^{SS} \right\rangle$$

(property of nucleus A)

Second-order (paramagnetic term)

EPR

$$g_{ZZ}^{(LB,LS)} = \frac{1}{S} \sum_{\substack{I>0 \\ (S''=S)}} \Delta_I^{-1} \left(\left\langle \Psi_0^{SS} \middle| \sum\nolimits_i \hat{l}_{zi} \middle| \Psi_I^{S''S''} \right\rangle \left\langle \Psi_I^{S''S''} \middle| \sum\nolimits_i h_z^{SOC} \hat{s}_{0i} \middle| \Psi_0^{SS} \right\rangle + cc \right)$$

(property of the entire system)

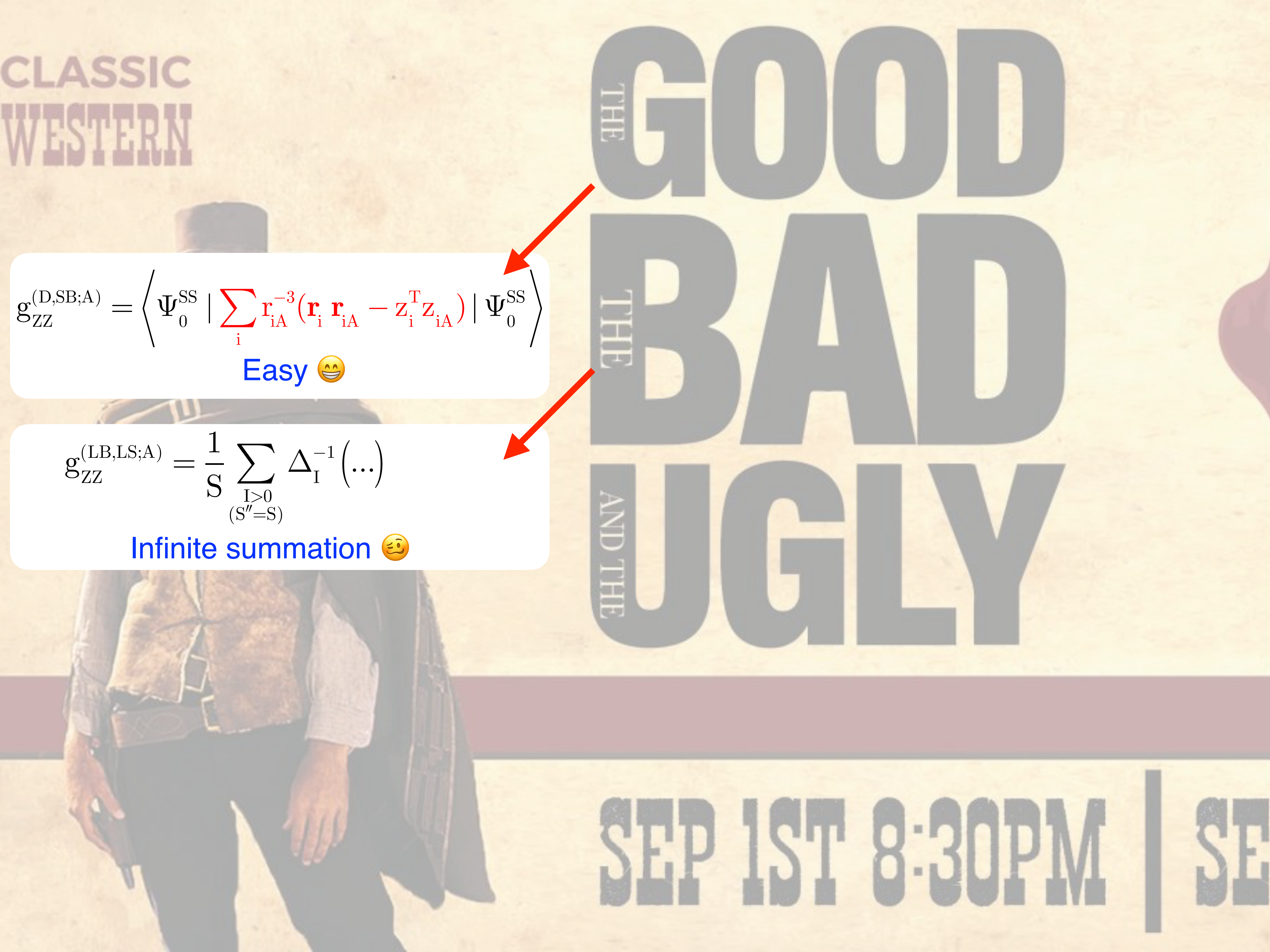
NMR

$$g_{ZZ}^{(LB,LS;A)} = \frac{1}{S} \sum_{\substack{I>0 \\ (S''=S)}} \Delta_I^{-1} \left(\left\langle \Psi_0^{SS} \middle| \sum\nolimits_i \hat{l}_{zi} \middle| \Psi_I^{S''S''} \right\rangle \left\langle \Psi_I^{S''S''} \middle| \sum\nolimits_i r_{iA}^{-3} \hat{l}_{zi}^{(A)} \middle| \Psi_0^{SS} \right\rangle + cc \right)$$

(property of nucleus A)

Chapter 5:

Connection of Response and Analytic Derivatives



$$g_{\mathrm{ZZ}}^{(\mathrm{D,SB;A})} = \left\langle \Psi_0^{\mathrm{SS}} \,\middle|\, \sum_{\mathrm{i}} r_{\mathrm{iA}}^{-3} \left(\mathbf{r}_{\mathrm{i}} \mathbf{r}_{\mathrm{iA}} - z_{\mathrm{i}}^{\mathrm{T}} z_{\mathrm{iA}} \right) \,\middle|\, \Psi_0^{\mathrm{SS}} \right\rangle$$

Easy 😁

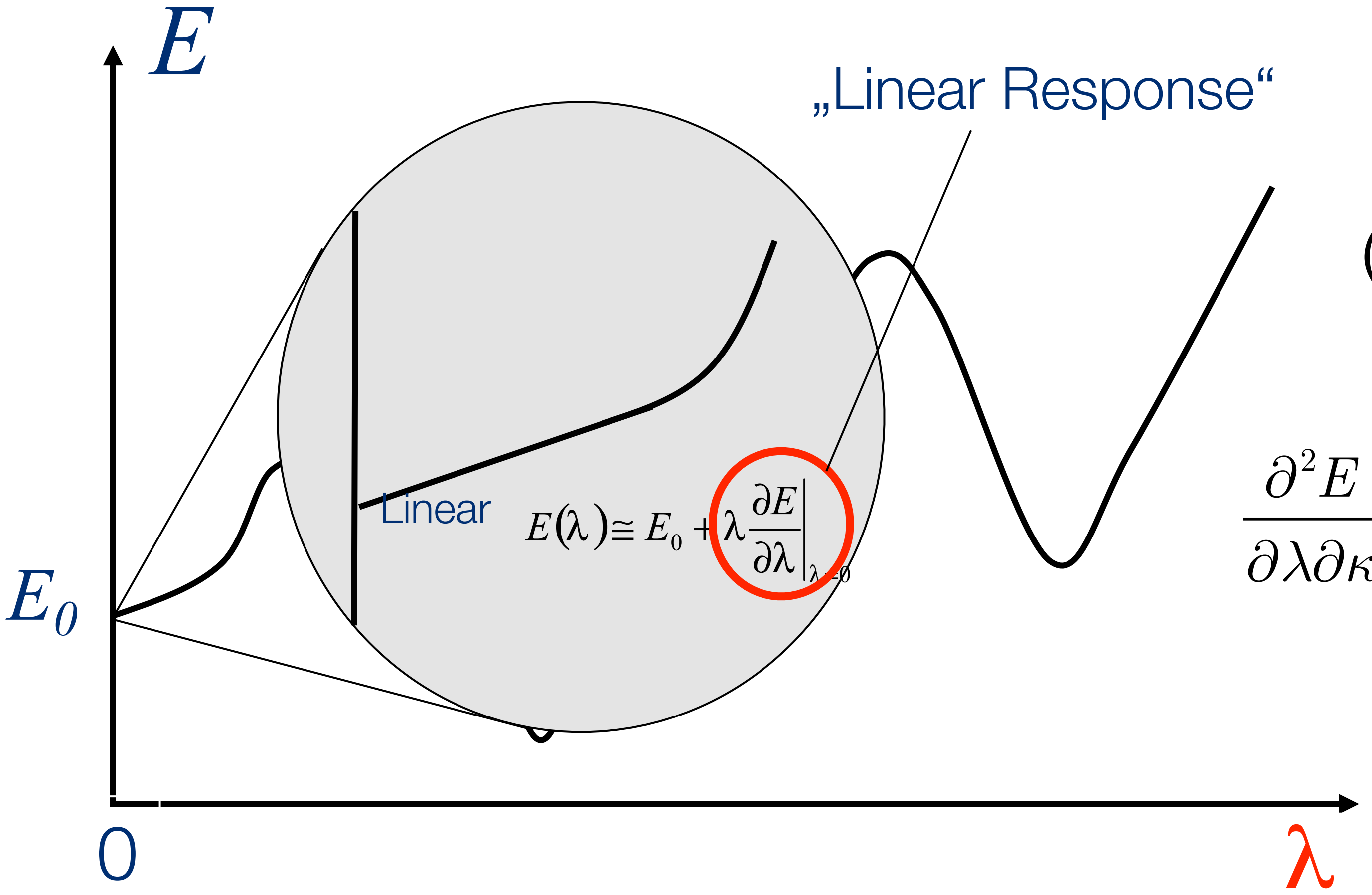
$$g_{\mathrm{ZZ}}^{(\mathrm{LB,LS;A})} = \frac{1}{\mathrm{S}} \sum_{\substack{\mathrm{I}>0 \\ (\mathrm{S}''=\mathrm{S})}} \Delta_{\mathrm{I}}^{-1} \left(\ldots \right)$$

Infinite summation 🥴

Linear Response Approach

Search for approximate solutions of: $\hat{H}\Psi = E\Psi$

Explicitly: $$E\Psi(\mathbf{x}_1 \ldots, \mathbf{x}_N) = \left(\underbrace{T_e + V_{eN} + V_{NN} + V_{ee}}_{H_{BO}} + \underbrace{\lambda V_{magnetic} + \mu V_{electric} + \kappa V_{relativistic}}_{small\ \ corrections} \right) \Psi(\mathbf{x}_1 \ldots, \mathbf{x}_N)$$



(Almost) all molecular properties

$$\left.\frac{\partial^2 E}{\partial\lambda\partial\kappa}\right|_{\lambda=\kappa=0} = \sum_{\mu\nu} \frac{\partial P^{\pm}_{\mu\nu}}{\partial\kappa} \left\langle \varphi_\mu \left| \frac{\partial h}{\partial\lambda} \right| \varphi_\nu \right\rangle + P^{\pm}_{\mu\nu} \left\langle \varphi_\mu \left| \frac{\partial^2 h}{\partial\lambda\partial\kappa} \right| \varphi_\nu \right\rangle$$

FN (**2001**) *J. Chem. Phys.*, 115, 11080

Sum-over-States versus Linear Response

- ★ So far we had formulated our second order terms in the Spin-Hamiltonian as infinite sums over many electron eigenfunctions of the Born-Oppenheimer Hamiltonian
- ★ For two reasons this is unrealistic: (a) we don‘t know exact solutions to the BO Hamiltonia and (b) we never know an infinite number of eigenfunctions. Thus, we need to come up with something else.
- ★ To make the connection with SOS fomulations we will first find a formulation that is exactly equivalent to SOS in the case of exact solutions and then apply this to the various approximate schemes like HF, DFT, CASSCF, MRCI,...
- ★ Let us start from the BO Hamiltonian in second quantization:

$$H_{BO} = \sum_{pq} h_{pq} p^{+} q + \frac{1}{4} \sum_{pqrs} \left\langle pq \,||\, rs \right\rangle p^{+} q^{+} s r$$

- ★ and some perturbation

$$H^{\lambda} = \lambda \sum_{pq} h_{pq}^{(\lambda)} p^{+} q \qquad\qquad h_{pq}^{(\lambda)} = \frac{\partial h}{\partial \lambda}$$

Exact Equivalence of SOS and LRT

- Assume that we know the exact eigenspectrum of the BO Hamiltonian as our basis. Then the **Hellmann-Feynman theorem** tells us that

$$E_0^{(0)} = \left\langle 0 \,|\, H_{BO} \,|\, 0 \right\rangle$$

Ground state energy

$$E(\lambda) = E_0^{(0)} + \lambda \left. \frac{\partial E_0}{\partial \lambda} \right|_{\lambda=0} + \ldots$$

Taylor expansion of the perturbed energy

$$\left. \frac{\partial E_0}{\partial \lambda} \right|_{\lambda=0} = \left\langle 0 \,|\, H^{(\lambda)} \,|\, 0 \right\rangle = \sum_{pq} D_{pq} \frac{\partial h_{pq}}{\partial \lambda}$$

First Derivative

$$D_{pq} = \left\langle 0 \,|\, p^{+} q \,|\, 0 \right\rangle$$

One particle density

- This result is exactly equivalent with the first order perturbation theory. Can we do the same thing for the second derivative?

$$\left. \frac{\partial^2 E_0}{\partial \lambda \partial \mu} \right|_{\lambda=\mu=0} = \sum_{pq} \frac{\partial D_{pq}}{\partial \mu} h_{pq} + \sum_{pq} D_{pq} \frac{\partial^2 h_{pq}}{\partial \lambda \partial \mu} \qquad \left(\frac{\partial D_{pq}}{\partial \mu} = \left\langle \frac{\partial \Psi}{\partial \mu} \,|\, p^{+} q \,|\, \Psi \right\rangle + cc \right)$$

Second Derivative and SOS

- ★ We take the derivative with respect to another perturbation h$^{(\mu)}$

$$\left.\frac{\partial^2 E_0}{\partial\lambda\partial\mu}\right|_{\lambda=\mu=0} = \sum_{pq}\frac{\partial D_{pq}}{\partial\mu}h_{pq}^{(\lambda)} + \sum_{pq} D_{pq}\frac{\partial^2 h_{pq}}{\partial\lambda\partial\mu}$$

- ★ Since: $\sum_{pq} D_{pq}\frac{\partial^2 h_{pq}}{\partial\lambda\partial\mu} = \left\langle 0 \mid h^{(\mu,\lambda)} \mid 0\right\rangle$

- ★ This term is already exactly equivalent to the first-order term in **H**^{eff}

- ★ For the „response term“ involving the derivative of the density we have:

$$\frac{\partial D_{pq}}{\partial\mu} = \left\langle \frac{\partial\Psi_0}{\partial\mu} \mid p^+ q \mid \Psi_0 \right\rangle + \left\langle \Psi_0 \mid p^+ q \mid \frac{\partial\Psi_0}{\partial\mu}\right\rangle$$

- ★ But we are certainly allowed to expand the first derivative in terms of the unperturbed eigenstates of the BO Hamiltonian:

$$\left|\frac{\partial\Psi_0}{\partial\mu}\right\rangle = \sum_n d_n \left|n\right\rangle$$

Second Derivative and SOS (ctd.)

- But first-order perturbation theory tells us that:

$$\left|\frac{\partial\Psi_0}{\partial\mu}\right\rangle = -\sum_n \frac{\left\langle 0 \mid H^{(\mu)} \mid n\right\rangle}{E_n - E_0}\left|n\right\rangle$$

- Hence:

$$\frac{\partial D_{pq}}{\partial\mu} = -\sum_n \frac{\left\langle 0 \mid H^{(\mu)} \mid n\right\rangle\left\langle n \mid p^+q \mid \Psi_0\right\rangle}{E_n - E_0} - \sum_n \frac{\left\langle 0 \mid p^+q \mid n\right\rangle\left\langle n \mid H^{(\mu)} \mid 0\right\rangle}{E_n - E_0}$$

- So:

$$\left.\frac{\partial^2 E_0}{\partial\lambda\partial\mu}\right|_{\lambda=\mu=0} = \sum_{pq}\frac{\partial D_{pq}}{\partial\mu}h^{(\lambda)}_{pq} + \sum_{pq} D_{pq}\frac{\partial^2 h_{pq}}{\partial\lambda\partial\mu}$$

$$= -2\sum_n \frac{\left\langle 0 \mid H^{(\mu)} \mid n\right\rangle\left\langle n \mid H^{(\lambda)} \mid \Psi_0\right\rangle}{E_n - E_0} + \left\langle 0 \mid H^{(\mu,\lambda)} \mid 0\right\rangle$$

- Thus, *second derivatives are exactly equivalent to the H^{eff} to second order!* (there is some Wigner-Eckart trickery involved for nondiagonal components but this should not distract from the beauty of the argument)

*see FN Mol. Phys, **2007**, 105, 2507* *FN J. Chem. Phys.*, ***2007***, *127*, 164112

Chapter 6:

Spin-Hamiltonian Parameters as Analytic Derivatives

Explicit Expressions from Response Theory

$$
\begin{aligned}
\hat{H}_{Spin} &= \underbrace{\beta\mathbf{BgS}}_{Zeeman} + \underbrace{\mathbf{SDS}}_{Zero-Field-Splitting} + \sum_K \underbrace{\mathbf{SA}^{(K)}\mathbf{I}^{(K)}}_{Hyperfine} - \underbrace{g_N^{(K)}\beta_N\mathbf{BI}^{(K)}}_{Nuclear-Zeeman} + \underbrace{\mathbf{I}^{(K)}\mathbf{Q}^{(K)}\mathbf{I}^{(K)}}_{Quadrupole} \\
&= \beta\mathbf{B}\Bigg\{-\frac{\alpha^2}{S}\sum_{\mu,\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \phi_\mu \middle| \hat{T} \middle| \phi_\nu \right\rangle + \frac{1}{2S}\sum_{\mu,\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \varphi_\mu \middle| \sum_A \xi\left(r_A\right)(\mathbf{r}_A\mathbf{r} - \mathbf{r}_{A,k}\mathbf{r}_l) \middle| \varphi_\nu \right\rangle + \frac{1}{2S}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{(\alpha-\beta)}}{\partial B_k}\left\langle \varphi_\mu \middle| \hat{z}_l^{SOMF} \middle| \varphi_\nu \right\rangle\Bigg\}\mathbf{S} \\
&\quad + \mathbf{S}\Bigg\{-\frac{g_e^2}{16}\frac{\alpha^2}{S\left(2S-1\right)}\sum_{\mu\nu}\sum_{\kappa\tau}\left\{P_{\mu\nu}^{\alpha-\beta}P_{\kappa\tau}^{\alpha-\beta} - P_{\mu\kappa}^{\alpha-\beta}P_{\nu\tau}^{\alpha-\beta}\right\}\left\langle \mu\nu \middle| r_{12}^{-5}\left\{3r_{12,k}r_{12,l} - \delta_{kl}r_{12}^2\right\} \middle| \kappa\tau \right\rangle \\
&\quad - \frac{1}{4S^2}\sum_{\mu\nu}\left\langle \mu \mid h_k^{SOC} \mid \nu \right\rangle\frac{\partial P_{\mu\nu}^{(0)}}{\partial S_l^{(0)}} + \frac{1}{2\left(S+1\right)\left(2S+1\right)}\sum_{\mu\nu}\left\langle \mu \mid h_k^{SOC} \mid \nu \right\rangle\frac{\partial P_{\mu\nu}^{(-1)}}{\partial S_l^{(+1)}} + \frac{1}{2S\left(2S-1\right)}\sum_{\mu\nu}\left\langle \mu \mid h_k^{SOC} \mid \nu \right\rangle\frac{\partial P_{\mu\nu}^{(+1)}}{\partial S_l^{(-1)}}\Bigg\}\mathbf{S} \\
&\quad + \sum_K \mathbf{S}\Bigg\{\delta_{kl}\frac{8\pi}{3}\frac{P^{(K)}}{2S}\rho^{\alpha-\beta}\left(\mathbf{R}_K\right) + \frac{P^{(K)}}{2S}\sum_{\mu\nu} P_{\mu\nu}^{\alpha-\beta}\left\langle \varphi_\kappa \middle| r_K^{-5}\left(r_K^2\delta_{\mu\nu} - 3r_{K;\mu}r_{A;\nu}\right) \middle| \varphi_\tau \right\rangle - \frac{P_A}{S}\sum_{\mu\nu}\frac{\partial P_{\mu\nu}^{\alpha-\beta}}{\partial \hat{I}_k^{(A)}}\left\langle \varphi_\mu \mid z_l^{SOMF} \mid \varphi_\nu \right\rangle\Bigg\}\mathbf{I}^{(K)} \\
&\quad - g_N^{(K)}\beta_N\mathbf{BI}^{(K)} + \mathbf{I}^{(K)}\Bigg\{\frac{e^2Q^{(K)}}{4I\left(2I-1\right)}\sum_{\kappa,\tau} P_{\kappa\tau}^{\alpha+\beta}\left\langle \varphi_\kappa \middle| r_K^{-5}\left(r_K^2\delta_{\mu\nu} - 3r_{K;\mu}r_{A;\nu}\right) \middle| \varphi_\tau \right\rangle\Bigg\}\mathbf{I}^{(K)}
\end{aligned}
$$

First-order one-electron terms First-order two-electron terms Second-order one-electron terms

How to Calculate the SH Parameters in Practice?

Let us assume that we have the (one-electron) perturbating operators: $\hat{h}^{KL}, \hat{h}^{K}, \hat{h}^{L}$

Then the first order contribution to the response property is:

$$Q_{KL}^{(1)} = \frac{\partial^2 E}{\partial K \partial L} = \sum_{\mu\nu} P_{\mu\nu}^{\pm} \langle \mu | \hat{h}^{KL} | \nu \rangle$$

With $\{\mu\}$ being the basis set and $P_{\mu\nu}^{\pm} = P_{\mu\nu}^{\alpha} \pm P_{\mu\nu}^{\beta}$ Is the electron or spin density

What would you program (DFT or HF will be our example)?

```
Solve SCF equations for the orbitals and the density P
Call integral package to make all HKL(p,q)
For all p,q add BLAS_Trace(P,HKL) to the tensor Q(K,L)
```

➡ If there are too many HKL to hold in memory, the integral package could contract batches of HKL with P on the fly

Calculating the Second-Order Terms

Let us start from the SCF conditions (I=occupied, a=empty):

$$F_{ai}^{(0)} = \langle a|\hat{F}|i\rangle = 0$$

With: $|i\rangle = \sum_{\mu} c_{\mu i}|\mu\rangle$ $\quad P_{\mu\nu} = \sum_{i} c_{\mu i}^{*} c_{\nu i}$ $\quad \hat{F}|i\rangle = \varepsilon_i|i\rangle$

$$F_{\mu\nu}^{(0)} = h_{\mu\nu} + \sum_{\kappa\tau} P_{\kappa\tau}\{(\mu\nu|\kappa\tau) - c_x(\mu\kappa|\nu\tau)\} + V_{\mu\nu}^{XC}$$

c_x =Fraction HF exchange

$V_{\mu\nu}^{XC}$ =XC potential

Let us expand the orbitals in the order of the pertubation (either K or L is fine):

$$|i\rangle = |i_0\rangle + |i_1\rangle = |i_0\rangle + \sum_{a} \boxed{U_{ia}^{(K)}}|a_0\rangle$$

$$P_{\mu\nu} = P_{\mu\nu}^{(0)} + P_{\mu\nu}^{(1)} = P_{\mu\nu}^{(0)} + \sum_{i,a} U_{ai}^{K*} c_{\mu a}^{*} c_{\nu i} + U_{ai}^{K} c_{\mu i}^{*} c_{\nu a}$$

Inserting this and solving for **U** gives the coupled-perturbed SCF (CP-SCF) equations:

The CP-SCF equations

U$^{(K)}$ is the solution of the linear CP-SCF equations:

$$\boldsymbol{A}\boldsymbol{U}^{(K)} = \boldsymbol{b}^{(K)}$$

A is dependent on the type E=electric(real) or M=magnetic(imaginery) of the pertubation:

$$A_{ia,jb}^{(E/M)} = (\varepsilon_a - \varepsilon_i)\delta_{ia,jb} + \delta_E\{2(ia|jb) + 2f_{ia,jb}^{XC}\} - c_x\{(ib|ja) \pm (ij|ab)\}$$

=XC „Kernel“

Special properties of **magnetic perturbations:**

- ➡ The Coulomb term and all local potentials give 0
- ➡ If there is no HF exchange, the A matrix is diagonal
- ➡ The perturbed (response) density is antisymmetric
- ➡ There is no first order change in the total electron density $\rho(\boldsymbol{r})$

The right-hand side **b** is defined by the perturbation

$$b_{ia}^{(K)} = h_{ia}^{(K)} - \varepsilon_i S_{ia}^{(K)} - \frac{1}{2}F(S^K) \qquad S_{pq}^{(K)} = \langle p \left| \frac{\partial S_{\mu\nu}}{\partial K} \right| q \rangle$$

=Response Fock with overlap derivative as density

Solving the CP-SCF equations

The **A**-matrix is of dimension $(n_{occ} * n_{virt})^2$ and thus *O*(N^4).

- ➡ Too big to keep in memory and solve equations by inversion of A

Solution:

- ➡ Transform everything to the **AO basis**
- ➡ Solve the equations **iteratively** using any solver (DIIS, Davidson, Pople,…)
- ➡ Transform back to the **MO basis**
- ➡ Calculate **perturbed (response) densities**

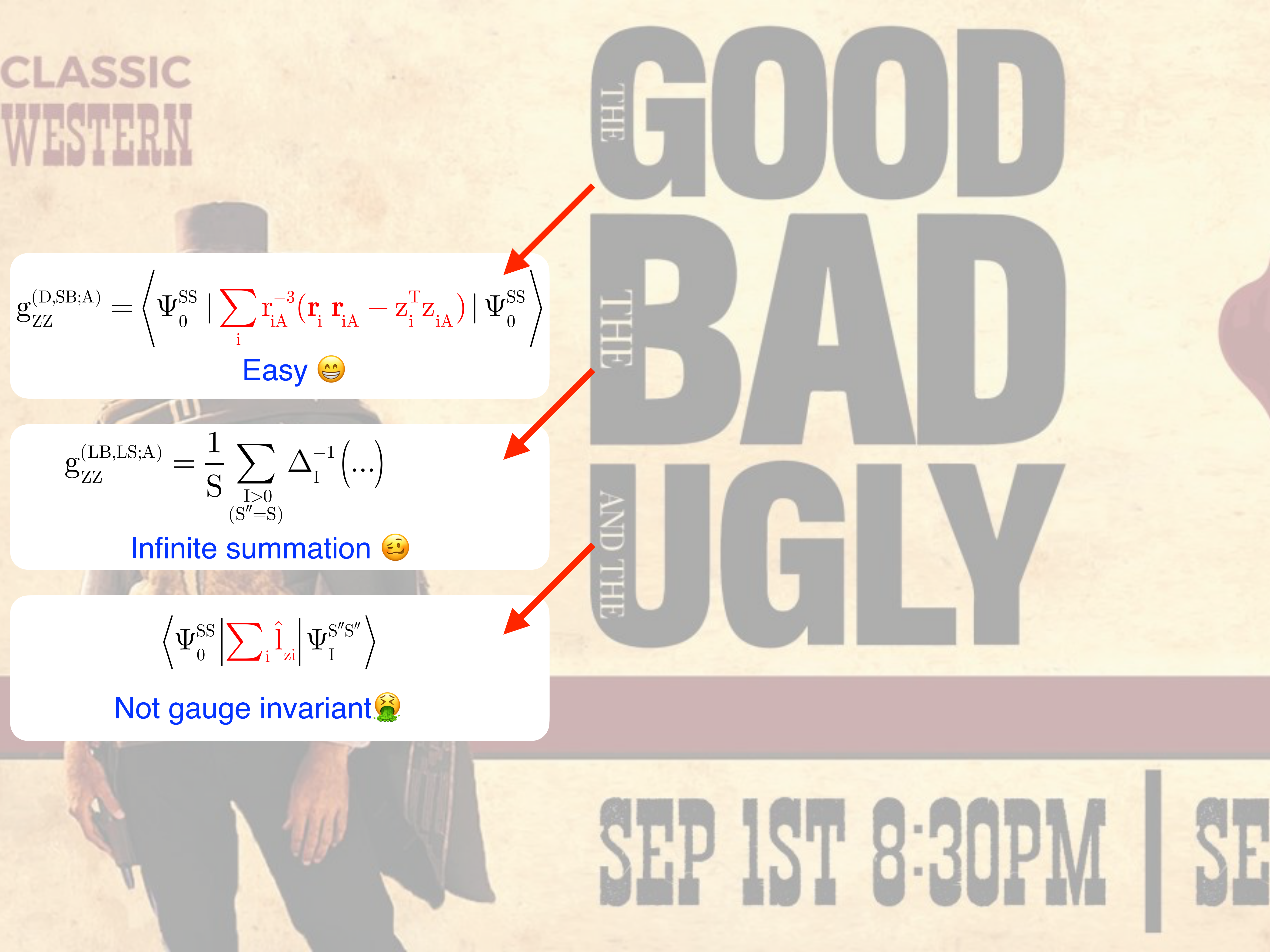
Response term:

$$Q_{KL}^{(2)} = \frac{\partial^2 E}{\partial K \partial L} = \sum_{\mu\nu} \frac{\partial P_{\mu\nu}^{\pm}}{\partial K} \langle \mu | \hat{h}^L | \nu \rangle$$

In each step of the iteration cycle, one calculates a **Fock-like matrix** using the same techniques already available from the SCF code of your program

The cost for one perturbation is roughly the same as for one full SCF, but treating many perturbations together can bring major advantages

Detailed equations & derivation for example in: FN, „Prediction of molecular properties and molecular spectroscopy with density functional theory: From fundamental theory to exchange-coupling“ *Coord. Chem. Rev.*, **2009**, 253, 526-563



$$g_{ZZ}^{(D,SB;A)} = \left\langle \Psi_0^{SS} \,\middle|\, \sum_i r_{iA}^{-3}(\mathbf{r}_i \, \mathbf{r}_{iA} - z_i^T z_{iA}) \,\middle|\, \Psi_0^{SS} \right\rangle$$

Easy 😁

$$g_{ZZ}^{(LB,LS;A)} = \frac{1}{S} \sum_{\substack{I>0 \\ (S''=S)}} \Delta_I^{-1} \left(\dots \right)$$

Infinite summation 🥴

$$\left\langle \Psi_0^{SS} \middle| \sum_i \hat{l}_{zi} \middle| \Psi_I^{S''S''} \right\rangle$$

Not gauge invariant🤮

Dealing with the Ugly: GIAO's

A lack of Gauge invariance is not acceptable. Cure:

Gauge including Atomic Orbitals:

Normal basis function: $$\varphi_{\mu}^{(A)}(\mathbf{r}) = S_{lm}^{(\mu)}(\theta,\phi)\sum_{k} d_{k}^{(\mu)} \exp\left(-\alpha_{k}^{(\mu)} r_{A}^{2}\right)$$

GIAO: $$\tilde{\varphi}_{\mu}^{(A)}(\mathbf{r},\mathbf{B}) = e^{\frac{i}{2c}(\mathbf{B}\times\mathbf{R}_{A})\mathbf{r}}\varphi_{\mu}^{(A)}(\mathbf{r})$$

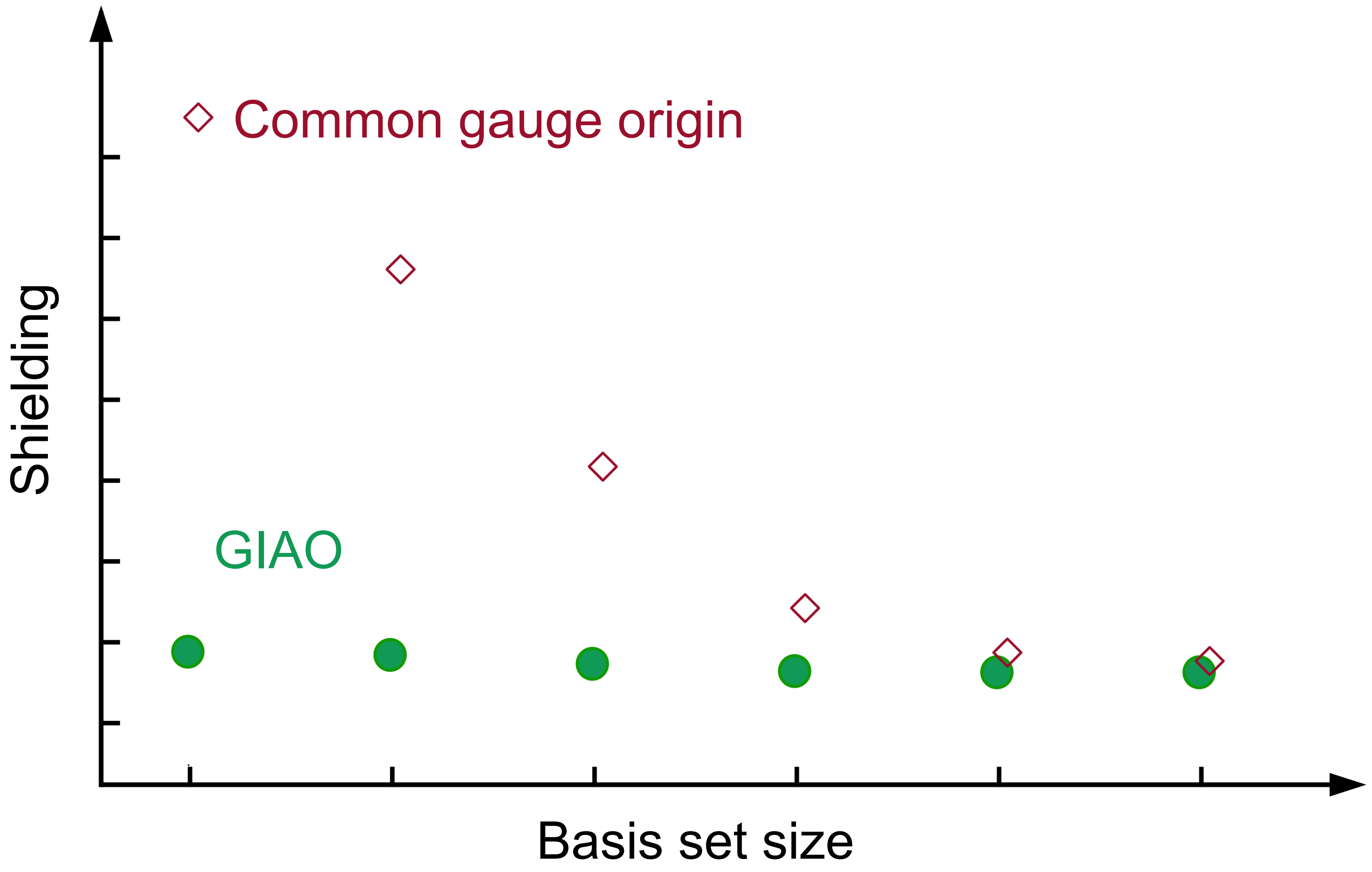
Consequence:

$$\frac{\partial(\mu\nu\,|\,\kappa\tau)}{\partial\mathbf{B}} = 0 \quad \Rightarrow \quad \frac{\partial(\tilde{\mu}\tilde{\nu}\,|\,\tilde{\kappa}\tilde{\tau})}{\partial\mathbf{B}} = \frac{i}{2}\left(\mu^{C}\nu^{D}\,\middle|\,\frac{Q_{CD}\mathbf{r}_{1} + Q_{EF}\mathbf{r}_{2}}{r_{12}}\,\middle|\,\kappa^{E}\tau^{F}\right)$$

etc. …about a dozen different types of new integrals

$$\boldsymbol{Q}^{AB} = \begin{pmatrix} 0 & -Z_{AB} & Y_{AB} \\ Z_{AB} & 0 & -X_{AB} \\ -Y_{AB} & X_{AB} & 0 \end{pmatrix}$$

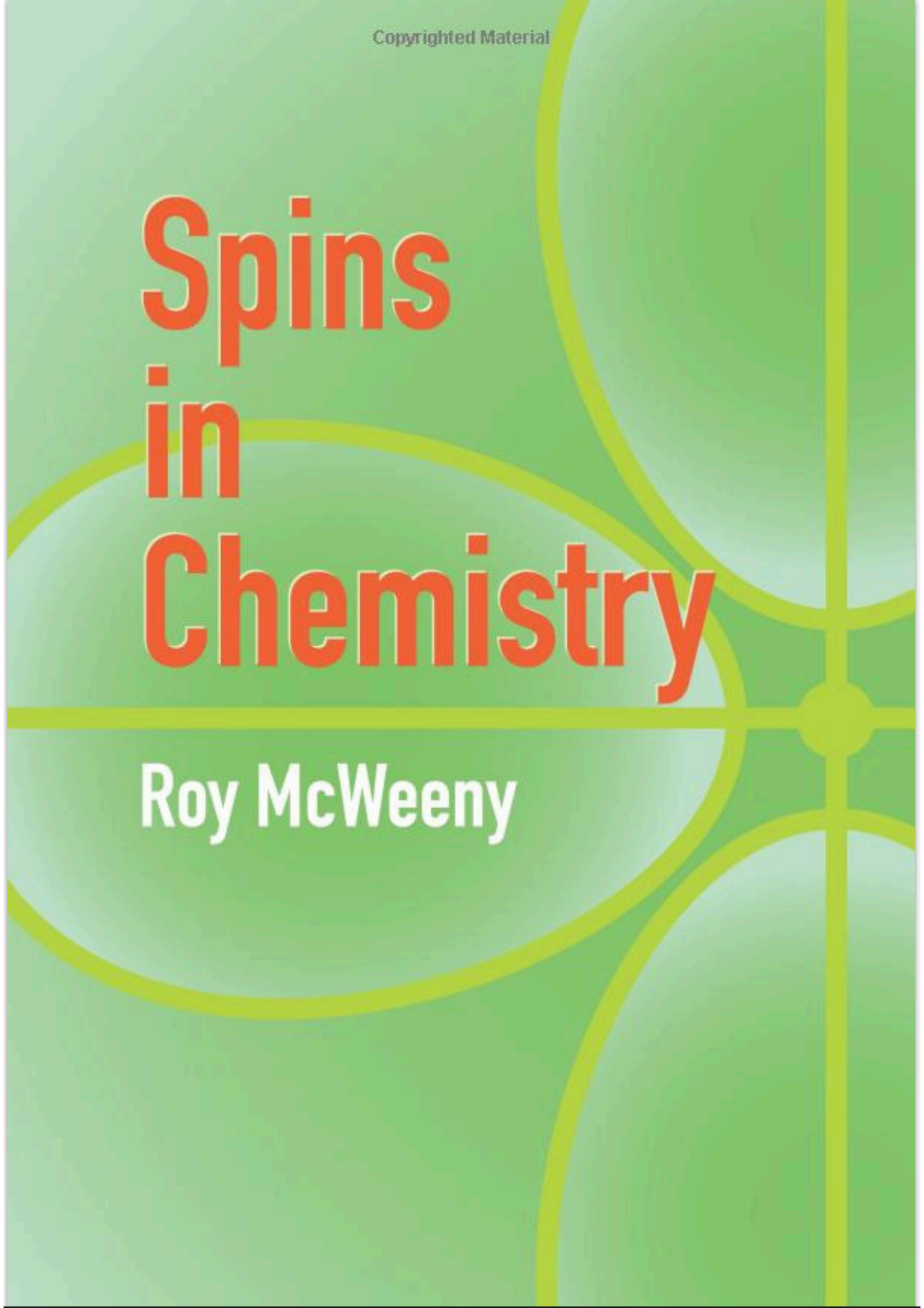
Convergence to the Basis Set Limit



➡ Convergence to the basis set limit is very slow and in practice calculations with GIAOs are mandatory

Magnetic Properties: Conclusions

- ✓ **EPR and NMR spectroscopy** are major analytical tools in chemistry.
  - They allow for fine finger printing.
  - They carry very detailed electronic structure information and hence they are a great target for validating electronic structure calculations.
- ✓ **Effective Hamiltonian theory** connects electronic structure with phenomenological treatments
  - Exchange coupling / Heisenberg Hamiltonian (NOT a magnetic interaction)
  - Spin Hamiltonians for EPR and NMR spectroscopy
- ✓ **Linear response theory** connects cleanly to the Spin-Hamiltonian
  - Most common tool used in practice
- ✓ When excited states come close in energy to the ground state multiplet, LRT breaks down and one is best advised treating magnetic fields and relativity (SOC) to infinite order using **Quasi-Degenerate Perturbation Theory** (QDPT)
  - Crucial for treating single molecule magnets.



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Lecture Notes

https://www.cond-mat.de/events/correl20/manuscripts/neese.pdf

The lecture notes have been published as an OpenAccess book:

Eva Pavarini and Erik Koch (eds.)
Topology, Entanglement, and Strong Correlations
Modeling and Simulation, Vol. 10
Verlag des Forschungszentrum Jülich, 2020
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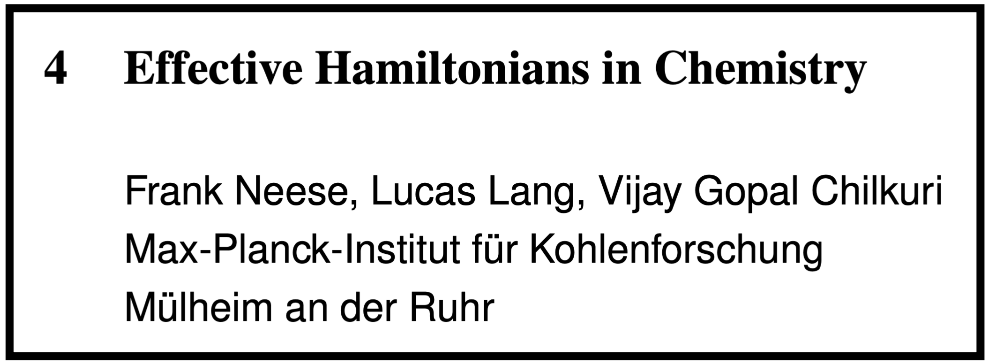

4 Effective Hamiltonians in Chemistry

Frank Neese, Lucas Lang, Vijay Gopal Chilkuri
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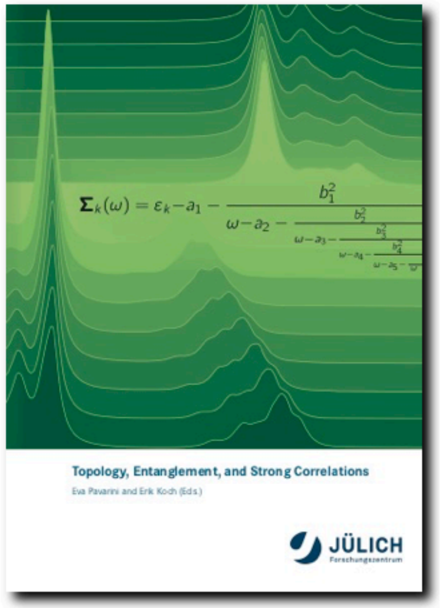

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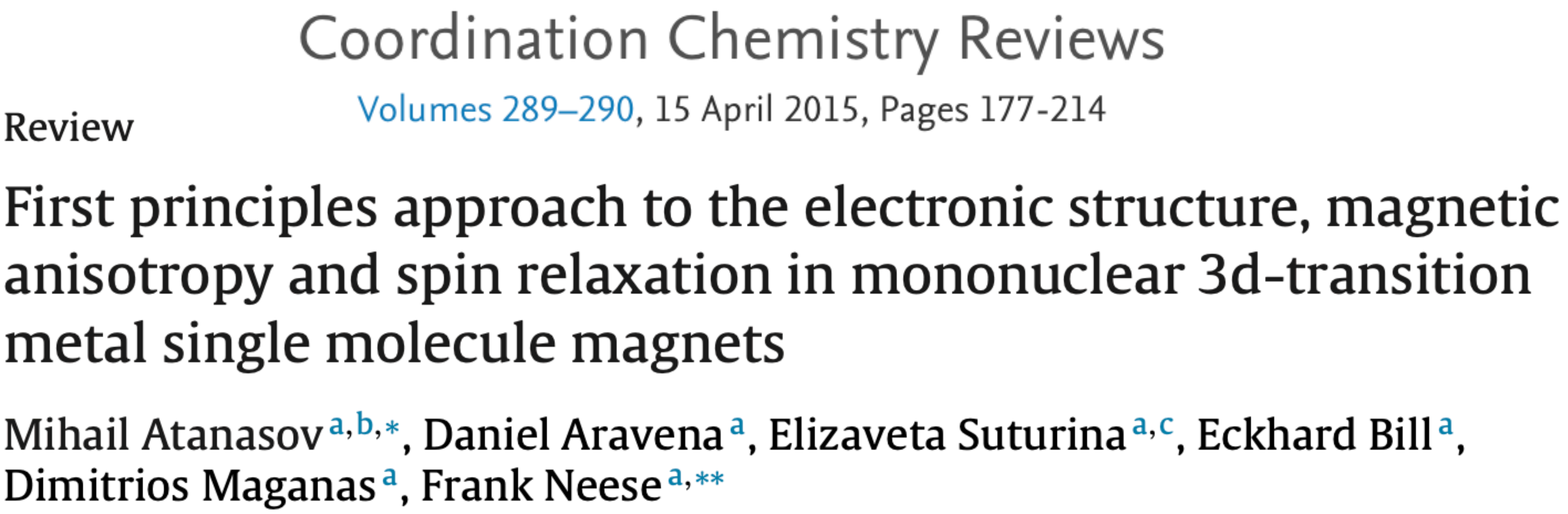

Coordination Chemistry Reviews

Review

Volumes 289–290, 15 April 2015, Pages 177-214

First principles approach to the electronic structure, magnetic anisotropy and spin relaxation in mononuclear 3d-transition metal single molecule magnets

Mihail Atanasov[a,b,*], Daniel Aravena[a], Elizaveta Suturina[a,c], Eckhard Bill[a], Dimitrios Maganas[a], Frank Neese[a,**]