Mikroskopowe wyprowadzenie H_{spin} (MSH) dla orbitalnego singletu ze spinem S

Prezentuje:
Grzegorz Leniec

Prezentacja na podstawie publikacji:

Czeslaw Rudowicz and Sushil K. Misra, „SPIN-HAMILTONIAN FORMALISMS INELECTRON MAGNETIC RESONANCE (EMR) AND RELATED SPECTROSCOPIES", *APPLIED SPECTROSCOPY REVIEWS*, 36(1), 11–63 (**2001**)

W prezentacji użyto 6 slajdów z wykładu Prof. Cz. Rudowicza

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Concept map: *SH theory for transition ions in crystals*

Phenomenological SH (PSH)

✧No clear definition

✧Postulated on ad hoc basis

SH used to describe EMR spectra

Group Theory (GT) & Symmetry & Operators

- Spin ($S \geq 1$) ⇔ ZFS ranks
- Local site structure ⇔ Point symmetry group (PSG) ⇔ ZFS terms

Derivational SH approach

$H_{physical}$ (FI + CF) ⇨ Perturbation Theory (PT) ⇨ *effective* (spin) $\mathcal{H}$

≡ *Microscopic SH (MSH):*

MSH ∝ (*physical parameters*)

✧ Form of SH *and* values of ZFSPs & g-factors can be predicted

Methods:

- Conventional method (*Pryce*)
- Tensor method (*Rudowicz*)
- S-state $3d^N$ & $4f^N$ ions

Constructional SH approach

PSG ⇨ GT ⇨ *Invariant* combinations of spin (S) & other operators (B, I)

⇨ *Generalized SH (GSH):*

GSH ∝ (*ZFS, Ze & HO terms*)

✧Form of SH including higher-order (HO) terms can be predicted *but* no information about ZFSP (HOP) values

Methods:

- Matrix method (*Koster & Statz*)
- Method of invariants

Elements of perturbation theory [PT]

PT has many applications in QM and theoretical physics ⇨ two methods:

- **time – independent PT ≡ Rayleigh – Schrödinger PT**

  In PT one considers an unperturbed Hamiltonian operator $\hat{\mathbf{H}}_0$ to which is added a small /often external/ perturbation $\tilde{\mathbf{V}}$

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

  where λ is an arbitrary real parameter.

- time – dependent PT

Standard textbook QM derivations of PT expressions are a bit cumbersome

An elegant version of time – independent PT in application to the spin Hamiltonian was given by

C.E. Soliverez: J. Phys. C2, 2161 (1969).

Definition of the problem:

$$\hat{H} | \psi >= E | \psi >$$

$|\psi> \in \Omega$ space of finite dimension g.

In most cases we cannot solve Eq. (1) BUT we can split:

$$\hat{H} = \hat{H}_o + \hat{V}$$

where $\hat{H}_o | j >= \varepsilon_j | j >$ $\qquad \langle j | k \rangle = \delta_{jk}$

i.e. we can exactly solve the **zero-order** Hamiltonian $\hat{\mathbf{H}}_0$. Then the effect of the **perturbation** $\tilde{V}$ on a particular eigenvalue ε_o of can be obtained as a series expansion.

Definition of the problem:

Assumption required: the effect of $\tilde{V}$ on the energy levels of must be small. The set {| j >} (j = 1, 2, … , g) is g-fold degenerate and forms the complete orthonormal basis for the space Ω. In PT we want to study the effect of on a particular eigenvalue ε_o of $\hat{H}_0$.

Ω is split into ($\Omega_o + \Omega'$), where the manifold Ω_o is spanned by the eigenvectors belonging to the specified eigenvalue ε_o of $\hat{H}_0$ and Ω' comprises all other states:

$$\left(\hat{H}_0 - \varepsilon_0\right)\left|a\right\rangle = 0 \qquad a = 1, 2, \ldots, g_o$$

$$\left(\hat{H}_0 - \varepsilon_\alpha\right)\left|\alpha\right\rangle = 0 \qquad \alpha = g_o + 1, \ldots, g$$

Solivarez method in perturbation theory [PT]

Defining the operators (so-called 'projection' operators):

$$P_o = \sum_a | a >< a |$$

{| a >} – the states belonging to the ground energy level ε_0 of $\hat{H}_{0.}$

$$K = \sum_\alpha \frac{| \alpha >< \alpha |}{\varepsilon_\alpha - \varepsilon_o}$$

{| α >} – the excited states, i.e. all states above the 'ground' one

Solivarez has shown that the PT expressions can be derived in a simple form for each k-th order in the series expansion as follows:

Solivarez method in perturbation theory [PT]

Solivarez has shown that the PT expressions can be derived in a simple form for each k-th order in the series expansion as follows:

$$\tilde{H}_1 = P_o \hat{V} P_o$$

$$\tilde{H}_2 = -P_o \hat{V} K \hat{V} P_o$$

$$\tilde{H}_3 = P_o \hat{V} K \hat{V} K \hat{V} P_o - \frac{1}{2}[P_o \hat{V} K^2 \hat{V} P_o \hat{V} P_o + P_o \hat{V} P_o \hat{V} K^2 \hat{V} P_o]$$

$$\tilde{H}_4 = \{\text{nine terms involving } \hat{V} - \hat{V} - \hat{V} - \hat{V} \}$$

$\tilde{H}_n$ = the ***effective*** (~) Hamiltonian describing the n-th order perturbation theory contribution to the energy level ε_o of $\hat{H}_0$

Microscopic spin Hamiltonian [MSH] derivation of the conventional zero-field splitting [ZFS] term S·D·S

The concept of effective Hamiltonian

We consider application of PT to an orbital singlet ground state [OSGS] denoted in general as $|\Gamma_o>$.

In an explicit form, an OSGS comprises (**orbital** x **spin** part): $\{|\Gamma_0> |SM_S>\}$ using Soliverez PT:

$$P_0 = \left|\Gamma_0\right\rangle\left\langle\Gamma_0\right|$$

;

$$K = \sum_\alpha \frac{|\Gamma_\alpha><\Gamma_\alpha|}{\varepsilon_\alpha - \varepsilon_o} = \sum_\alpha \frac{|\Gamma_\alpha><\Gamma_\alpha|}{\Delta_\alpha}$$

e.g. $\hat{H}_0 = \hat{H}_{orb} + \hat{H}_{CF}$ & $\hat{V} = \lambda \vec{L} \cdot \vec{S} = \hat{H}_{SO}$

Microscopic spin Hamiltonian [MSH] derivation of the conventional zero-field splitting [ZFS] term S·D·S

Example:

d^4 configuration ⇨ ^5D term

the ground state = any of the possible orbital singlets: $\left\{\left|\Gamma_0\right\rangle\left|SM_s\right\rangle\right\} = \left|\Gamma_0\right\rangle, S = 2$

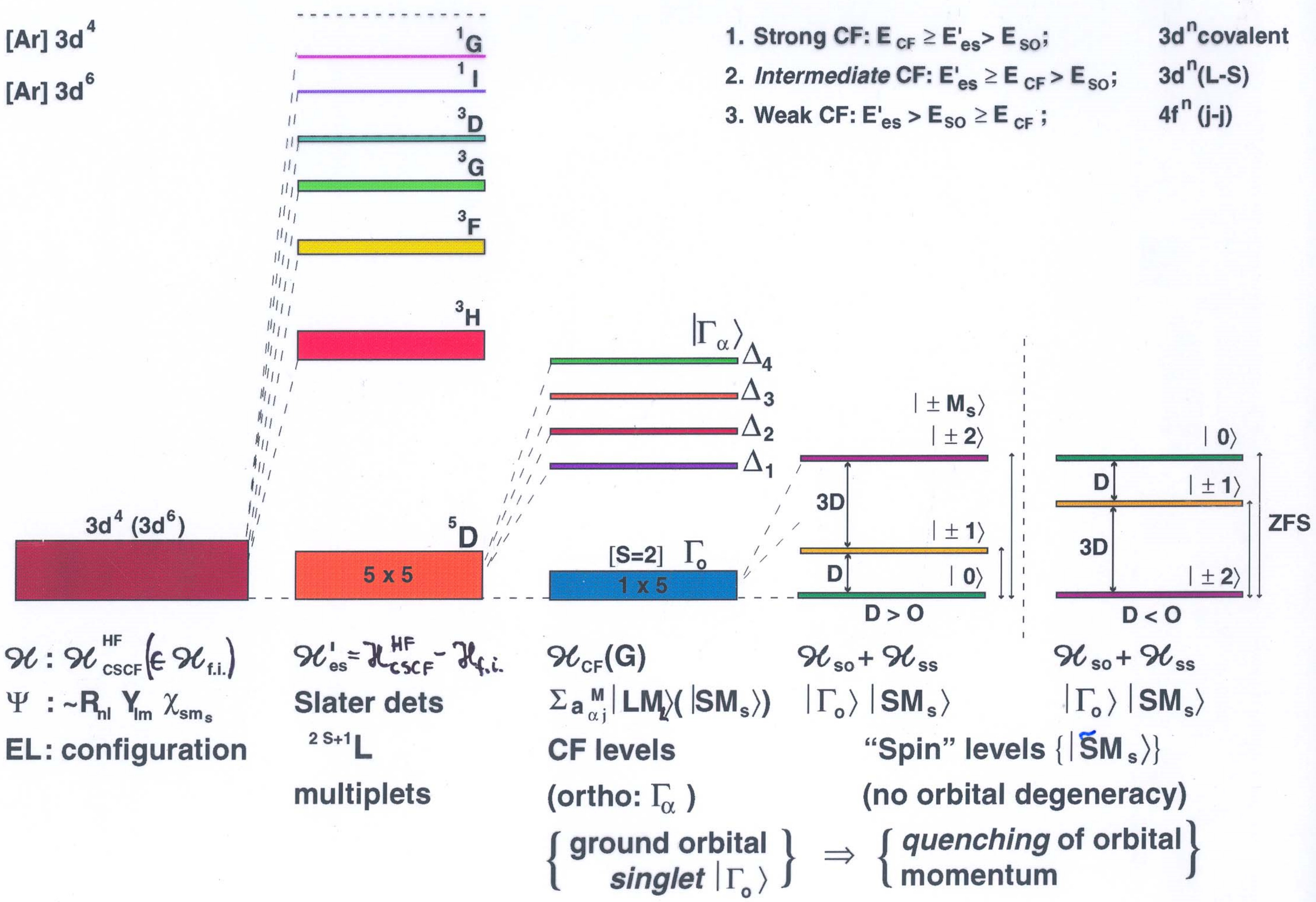
the excited states within the ^5D term Γ_α : $\{(\sum_M a_{\alpha j}^M \mid LM_L >) \mid SM_S >\}$

Definition:

the effective $\tilde{\mathrm{H}}$ yields the (*approximate*) eigenvalues of $\hat{\mathrm{H}}$ in the limited subspace of the eigenstates of $\hat{\mathrm{H}}_0$ and represents **the effect of** $\tilde{\mathrm{V}}$ as a perturbation on the energies of $\hat{\mathrm{H}}_0$.

Up to the 2nd order in PT we obtain: $$\tilde{\mathrm{H}} = \varepsilon_o + \tilde{\mathrm{H}}_1 + \tilde{\mathrm{H}}_2$$

This definition is general; the **spin Hamiltonian**, including the ZFS and the Zeeman terms discussed below, is a *special case* of an effective H.


[Ar] 3d4
[Ar] 3d6
1. Strong CF: E CF ≥ E'es > E SO; 3dn covalent
2. Intermediate CF: E'es ≥ E CF > E SO; 3dn(L-S)
3. Weak CF: E'es > E SO ≥ E CF ; 4fn (j-j)
1G
1I
3D
3G
3F
3H
5D
3d4 (3d6)
5 x 5
|Γα⟩
Δ4
Δ3
Δ2
Δ1
[S=2] Γo
1 x 5
| ± Ms⟩
| ± 2⟩
| ± 1⟩
| 0⟩
3D
D
D > O
| 0⟩
| ± 1⟩
| ± 2⟩
D < O
ZFS
ℋ : ℋ HF CSCF (∈ ℋ f.i.)
Ψ : ~Rnl Ylm χsms
EL: configuration
ℋ'es = ℋ HF CSCF − ℋ f.i.
Slater dets
2S+1L
multiplets
ℋCF(G)
Σ a M αj |LML⟩(|SMs⟩)
CF levels
(ortho: Γα)
{ ground orbital singlet |Γo⟩ } ⇒ { quenching of orbital momentum }
ℋso + ℋss
|Γo⟩ |SMs⟩
ℋso + ℋss
|Γo⟩ |SMs⟩
"Spin" levels {|SMs⟩}
(no orbital degeneracy)

Important points in the derivation of the ZFS term:

S·D·S

➢ **The integration in the PT expressions is carried out only over the orbital variables:**

e.g. $$< \Gamma_\alpha | \vec{L} \cdot \vec{S} | \Gamma_0 > = \vec{S} \cdot (< \Gamma_\alpha | \vec{L} | \Gamma_0 >)$$

$$< \Gamma_o | \vec{L} \cdot \vec{S} | \Gamma_\alpha > = (< \Gamma_o | \vec{L} | \Gamma_\alpha >) \cdot \vec{S}$$

here: $(< \Gamma_o | \vec{L} | \Gamma_\alpha >)$ is an orbital 'vector' $\sim L_{o\alpha}$ $\vec{S}$ - the spin operator

⇨ the final Hamiltonian = the ***effective*** $\widetilde{H}$ involves, apart from the numerical constants (arising from $L_{o\alpha}$ and $\frac{1}{\Delta_\alpha}$), only the **SPIN** operator variables: $\vec{S}$ or its components / powers $\hat{S}_\alpha^n$

⇨ Hence the name: **the (*effective*) <u>spin Hamiltonian</u> [SH].**

Important points in the derivation of the ZFS term: S·D·S

➢**Derivation for an orbital singlet ground state:**

First order PT: $<\Gamma_o|\vec{L}|\Gamma_o>\cdot\vec{S}\equiv 0$

But $<\Gamma_o|\vec{L}|\Gamma_o>\equiv 0$ due to the **quenching of the orbital angular momentum** $\vec{L}$ **.** Hence, there is **no first order contribution**: $\tilde{H}_1 \rightarrow 0$ and some terms in the higher orders PT vanish.

Second order PT:

$\tilde{H}_2$ with $\hat{V}=\lambda\vec{L}\cdot\vec{S}$ yields:

$$\tilde{H}_2^{SO}=-\lambda^2\sum_{ij}\hat{S}_i\left(\sum_\alpha\frac{<\Gamma_o|\hat{L}_i|\Gamma_\alpha><\Gamma_\alpha|\hat{L}_j|\Gamma_o>}{\Delta_\alpha}\right)\hat{S}_j\equiv\vec{\mathbf{S}}\cdot\vec{\mathbf{D}}\cdot\vec{\mathbf{S}}$$

where $\sum_\alpha\frac{<\Gamma_o|\hat{L}_i|\Gamma_\alpha><\Gamma_\alpha|\hat{L}_j|\Gamma_o>}{\Delta_\alpha}$ is the Λ_{ij} tensor;

⇨ **The zero-field splitting [ZFS] 'tensor' D** is obtained as: $D_{ij} = -\lambda^2\Lambda_{ij}$

NOTE: D – 'tensor' *(not actually a real tensor, but a 3 by 3 matrix)* is **traceless**: $\sum D_{ii}\equiv 0$.

Contributions from other interactions

- In similar way $\hat{H}_{SS}$ yields a non-zero **first order contribution**: $\hat{H}_1^{SS}$
- ⇨ the spin-spin coupling contribution to the ZFS D-tensor.

- For $\hat{H}_{Ze}$ - the mixed terms $\hat{V} = \hat{H}_{Ze}$ and $\hat{V} = \hat{H}_{SO}$ yield the ***effective g-tensor*** for TM ions in crystals:

$$\tilde{\mathrm{H}}_{\mathrm{Ze}} = \mu_{\mathrm{B}} \vec{\mathrm{B}} \cdot \overleftrightarrow{\mathrm{g}} \cdot \vec{\mathrm{S}}$$

where $g_{ij} \equiv g_e(\delta_{ij} - \lambda\Lambda_{ij})$

$\lambda\Lambda_{ij}$ - orbital contribution to the g-factor appears only in the second order

$g_{ij} \neq 2.0023 = g_e$

Forms of orthorhombic SH - important points

- When referred to the ***principal axes,*** the ZFS 'tensor' D, regardless of the contributions included, takes the form:

$$D_x\hat{S}_x^2 + D_y\hat{S}_y^2 + D_z\hat{S}_z^2 \equiv D(\hat{S}_z^2 - \frac{1}{3}S(S+1)) + E(\hat{S}_x^2 - \hat{S}_y^2)$$

where $(\hat{S}_z^2 - \frac{1}{3}S(S+1)) \sim O_2^0(\vec{S})$, $(\hat{S}_x^2 - \hat{S}_y^2) \sim O_2^2(\hat{S})$ - the Stevens operators

- **Conversion relations:** D = 3/2D$_z$, E = 1/2(D$_x$ – D$_y$)

in terms of the Stevens operators - mSH takes the following form:

$$\vec{H}_{ZFS} = B_2^0 O_2^0 + B_2^2 O_2^2 \quad \Rightarrow \quad B_2^0 = \frac{1}{3}D, B_2^2 = E$$

- $\vec{H}_{ZFS} = \hat{S}\cdot\hat{D}\cdot\hat{S}$ represents the **fine structure** or the **zero-field splitting** of the ground orbital singlet of a TM ion in the absence of external magnetic field.

<u>Origin of spin Hamiltonian - microscopic SH [MSH]</u>

- The original Pryce (1950) derivation of $\hat{H}_{ZFS}$ **for TM ($3d^N$) ions is known as the "conventional <u>microscopic" SH</u>.** In this method SH originates basically from $\hat{H}_{SO}$ (& $\hat{H}_{SS}$) taken as a perturbation on the crystal field states within a ground term ^{2S+1}L.

- **The microscopic <u>origin</u>** of SH including $\hat{H}_{ZFS}$ and $\hat{H}_{Ze}$ for other cases:
  (I) RE $4f^N$ ions as well as
  (II) $3d^5$ (S-state) ions with no orbital degeneracy and
  (III) $3d^N$ ions with orbital degeneracy

is basically the same as for $3d^N$ ions with an orbital singlet ground state (*discussed above*), but the microscopic SH expressions for the **D & g 'tensors'** are much more complicated to derive, since we need to consider higher-orders in PT.

Origin of spin Hamiltonian - microscopic SH [MSH]

- MSH theory yields for (D, E) or equivalently B_k^q and g_{ij} the expressions:

SHPs $\propto (\lambda, \Delta_\alpha; \rho)$

i.e. the microscopic theory of SH (ZFS & Ze) parameters enables:

(I) theoretical estimates of ZFS parameters [ZFSPs] using, e.g. $D_{ij} = -\lambda^2\Lambda_{ij}$

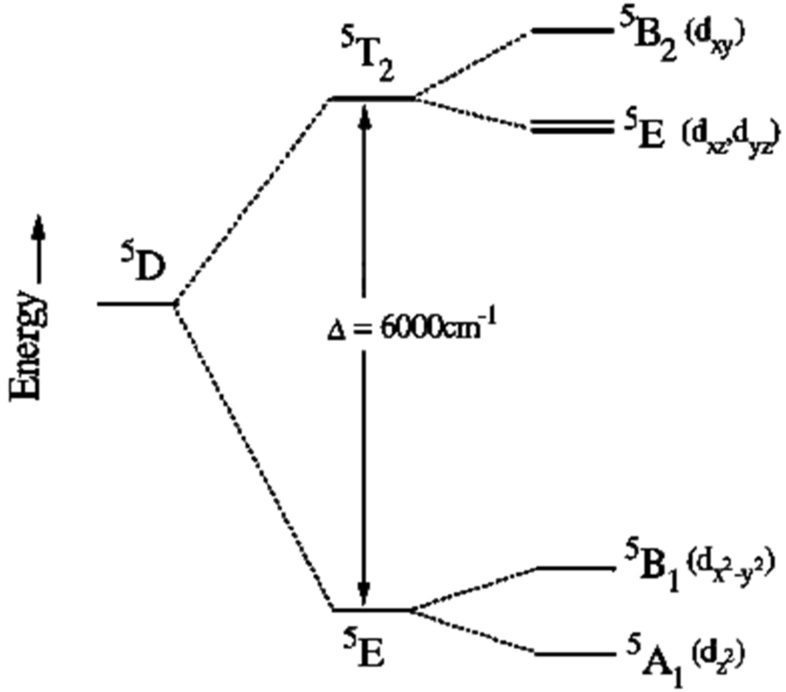
(II) correlation of the optical data (related to CF parameters) with EPR data (related to ZFSPs).

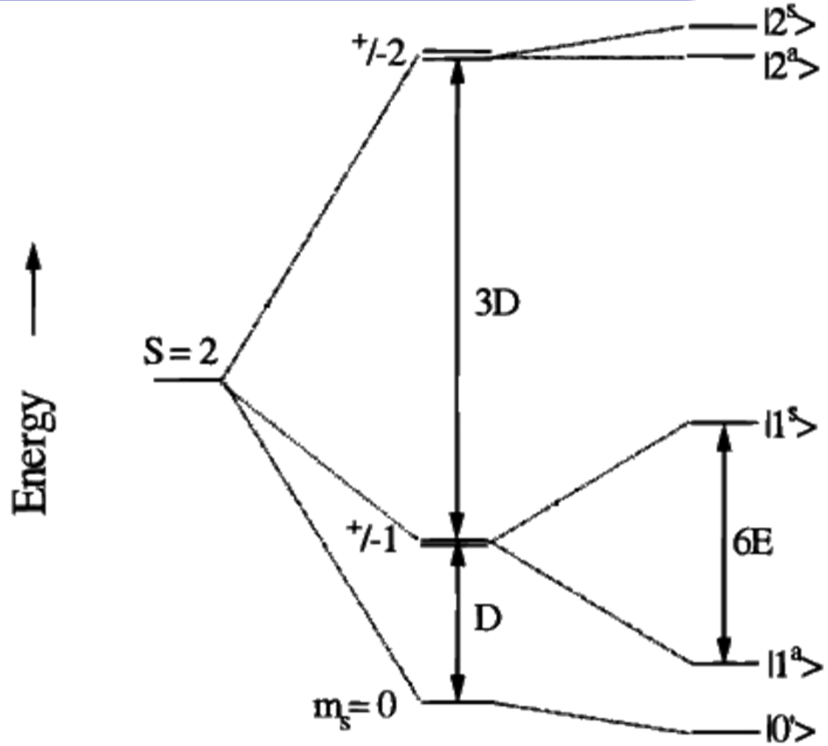
- Various PT approaches to MSH theory for transition ions and for various symmetry cases exist in the literature. Comprehensive reviews have been provided by CZR: MRR 1987 & ASR 2001.

MRR 1987 = C. Rudowicz, *"Concept of spin Hamiltonian, forms of zero-field splitting and electronic Zeeman Hamiltonians and relations between parameters used in EPR. A critical review",* Magn. Res. Rev. 13, 1-89, 1987; Erratum, ibidem 13, 335, 1988.

ASR 2001 = C. Rudowicz and S. K. Misra, *"Spin-Hamiltonian Formalisms in Electron Magnetic Resonance (EMR) & Related Spectroscopies",* Applied Spectroscopy Reviews 36/1, 11-63, 2001.

Examples for the 3d^4 and 3d^6 (S = 2) ions





$$g_x = g_y = g_e - 2(\lambda/\Delta)\left(\cos\delta - 3^{1/2}\sin\delta\right)^2 \qquad D = -3\left(\rho + \lambda^2/\Delta\right)\cos 2\delta$$

$$g_z = g_e - 8(\lambda/\Delta)\cos^2\delta \qquad E = -3^{1/2}\left(\rho + \lambda^2/\Delta\right)\sin 2\delta$$

Inorganic Chemistry, Vol. 39, No. 2, 2000

MSH relations for the ZFS parameters

➢ Sample MSH results for the four cases of the ground state of the $3d^4$ and $3d^6$ (S = 2) ions:

(α): $$D = -\lambda^2 \left(\frac{4}{\Delta_2} - \frac{1}{\Delta_1}\right)$$

(β): $$D = +3\lambda^2 \frac{1}{\Delta_3}$$

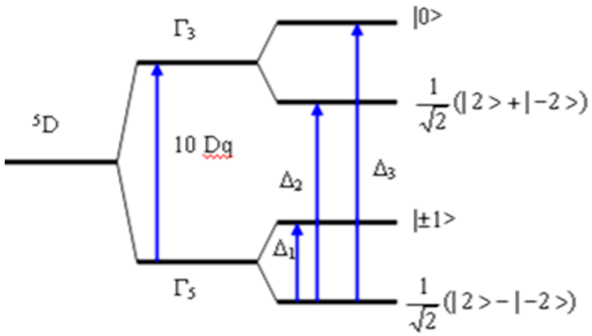
(γ): $$D = -\lambda^2 \left(\frac{4}{\Delta_2} - \frac{1}{\Delta_3}\right)$$

(δ): $$D = +3\lambda^2 \left(\frac{\sin^2\theta}{\Delta_1} - \frac{\cos^2\theta}{\Delta_2}\right)$$

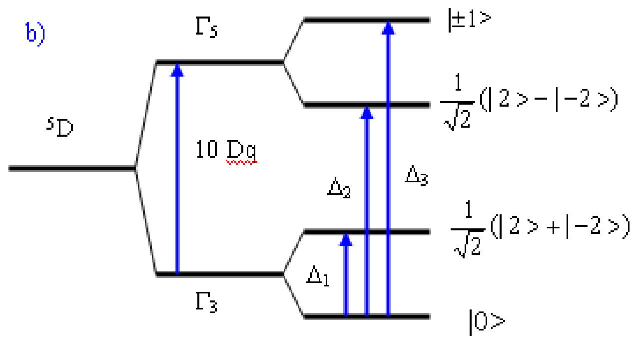
⇨ **From experimental value of D we can determine the ground state, i.e. the "case"!**

Examples for the $3d^4$ and $3d^6$ (S = 2) ions

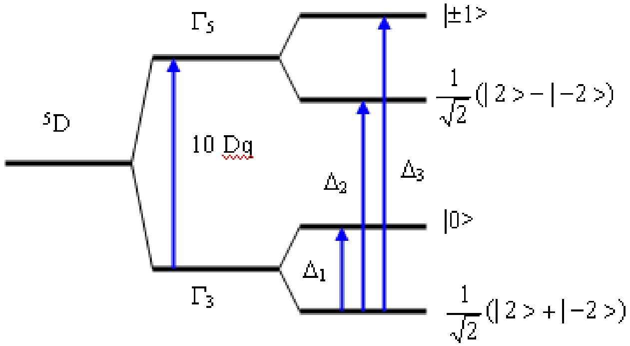
(α):



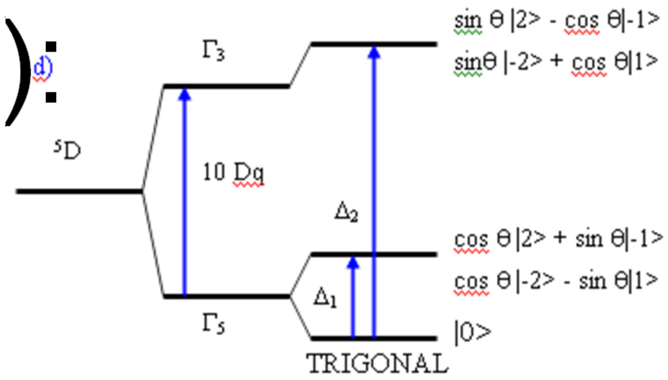
(β):



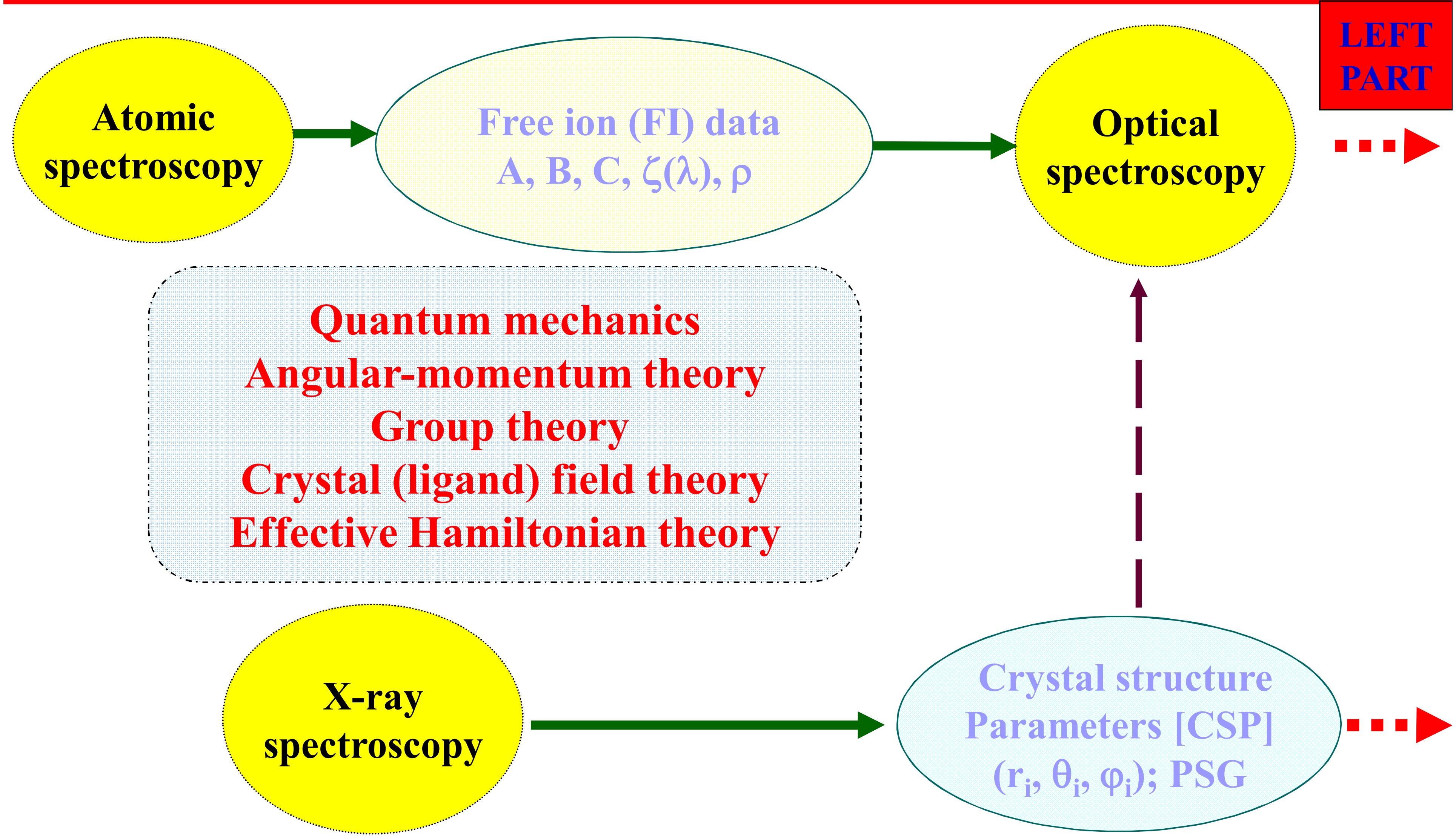
(γ):



(δ):



Modeling = interplay: Experiment ⇔ Theory ⇔ Computation



Underlying concept: ***free ion*** + ***crystal field Hamiltonian*** = ($H_{FI} + H_{CF}$)

Modelling = interplay: Experiment ⇔ Theory ⇔ Computation

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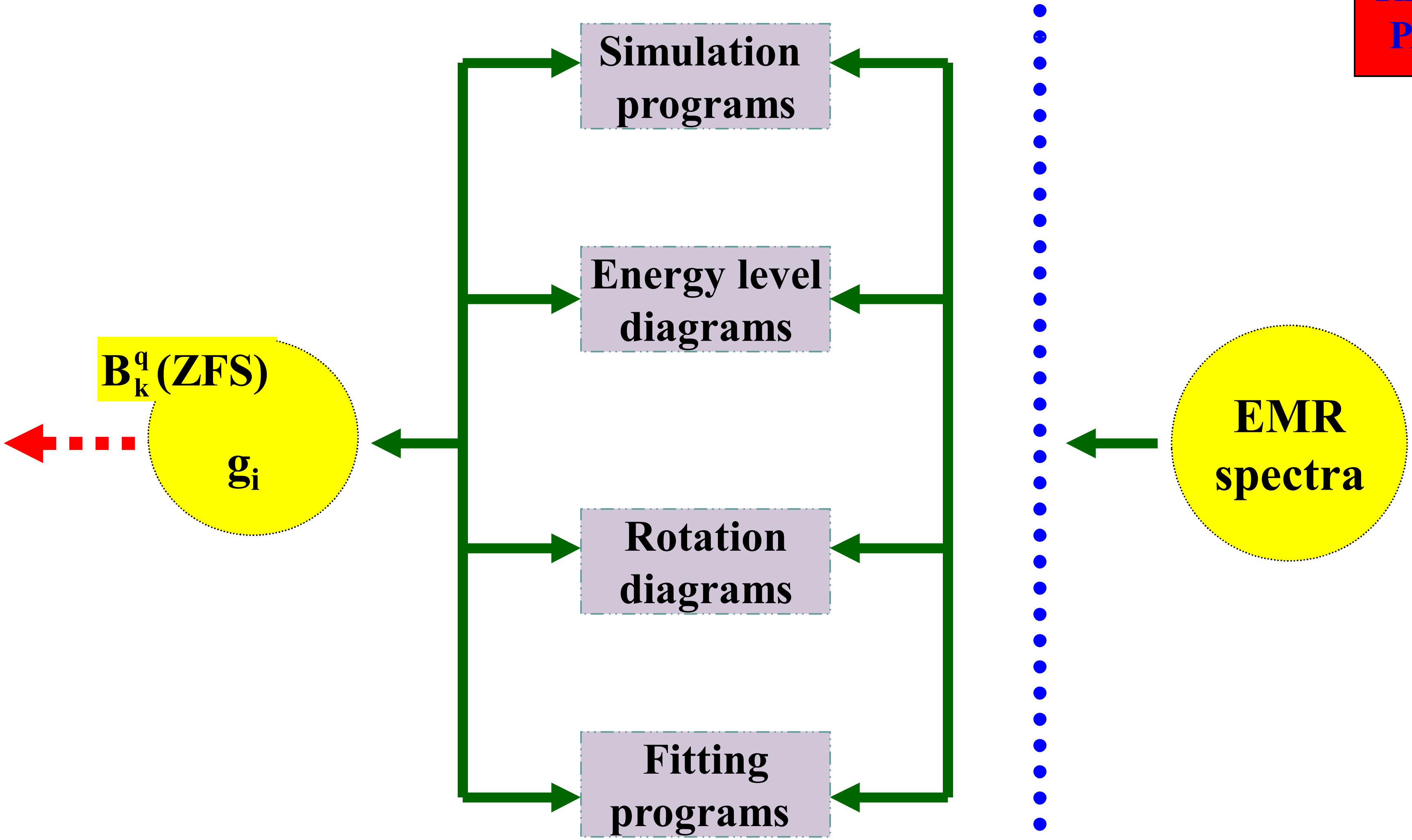
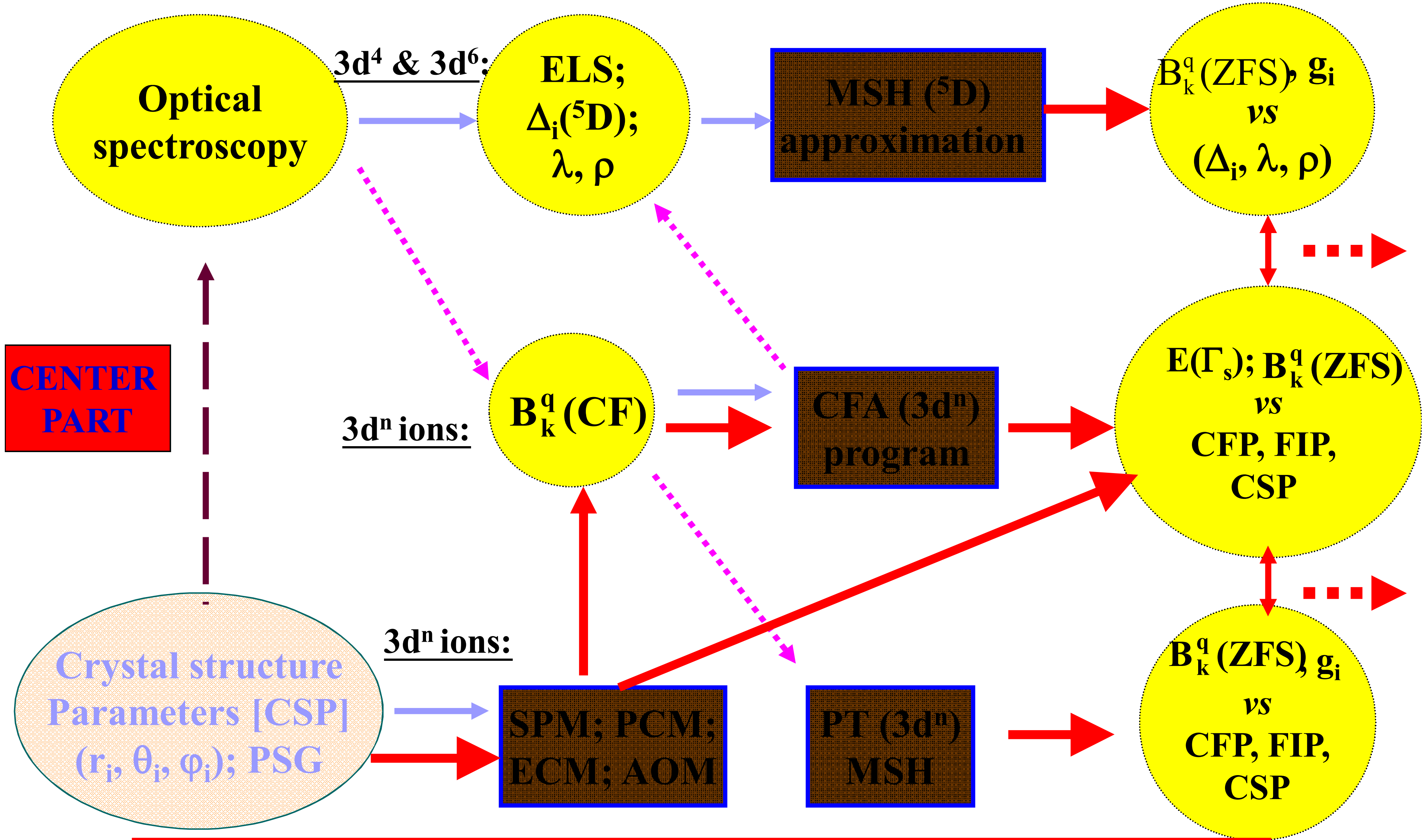


Underlying concept: *effective* spin Hamiltonian (SH) = $(H_{ZFS} + H_{Ze})$

Modelling = interplay: Experiment ⇔ Theory ⇔ Computation

→ *Modelling experimental data via theory & computation*



CONCEPT MAPS illustrating MODELING METHODOLOGY

Distinction between the actual physical Hamiltonians and the effective spin Hamiltonians

- the first observation of the EPR spectrum by Zavoisky in 1944.
- the idea of spin Hamiltonian preceded the discovery of EPR, since a precursor SH can be traced to Van Vleck's papers in 1939–40. Emergence of the spin-Hamiltonian concept, however, may be credited to Pryce, who in 1950 introduced the idea of an '*effective* Hamiltonian involving only the spin variables', which was later abbreviated *'spin Hamiltonian'*. Thus, the SH concept arose out of studies in paramagnetism. Note that there was no mention of 'paramagnetic resonance', nor equivalent terms, nor references in Pryce M.H.L., 1950, *Proc*. *Phys*. *Soc*. A63, 25., the article being entitled *'A modified perturbation procedure for a problem in paramagnetism'*.

To describe succinctly the role of SH concept as used in EMR one may quote Griffith:

"The spin-Hamiltonian is a convenient resting place during the long trek from fundamental theory to the squiggles on an oscilloscope which are the primary result of electron resonance experiments."

Concept map: *SH theory for transition ions in crystals*

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