Autumn School on Correlated Electrons

Effective Hamiltonians: Theory and Application

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What is and why care about effective Hamiltonians?

Hamiltonians and Eigensystems

 \star Let us assume that we have a Hamiltonian that works on a set of variables $x_1 \dots x_N$.

$$H(\mathbf{x}_1,...,\mathbf{x}_N)$$

\star Then its eigenfunctions (time-independent) are also functions of $x_1 \dots x_N$.

$$H\left(\mathbf{x}_{1},...,\mathbf{x}_{N}\right)\Psi_{I}\left(\mathbf{x}_{1},...,\mathbf{x}_{N}\right)=E_{I}\Psi_{I}\left(\mathbf{x}_{1},...,\mathbf{x}_{N}\right)$$

★ The eigenvalues of the Hamiltonian form a "spectrum" of eigenstates that is characteristic for the Hamiltonian



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



Examples of Effective Hamiltonians treated here

1. The Self-Consistent Size-Consistent CI Method to treat electron correlation

- Pure ab initio method.
- Work in the basis of singly- and doubly-excited determinants
- Describes the effect of higher excitations

2. The **Spin-Hamiltonian** in EPR and NMR Spectroscopy.

- Leads to empirical parameters
- Works on fictitous effective electron (S) and nuclear (I) spins
- Describe the (2S+1)(2I+1) ,magnetic sublevels' of the electronic ground state

3. The Heisenberg-Dirac-van Vleck Hamiltonian of Molecular Magnetism

- Empirical, parameterized model
- Works on fictitious electron spin variables of ,magnetic subsystems';
- Describes a few low-lying multiplets

4. The Ligand Field Hamiltonian of coordination chemistry

- Empirical, parameterized model
- Works on a fictitious set of n-electrons in the d- or f-orbitals of a d- or f-element
- Describes d-d excited states in transition metal complexes

Other Examples of Effective Hamiltonians

1. The Hubbard Hamiltonian of Molecular Magnetism

- Works on fictitious single sites
- Refinement of the HDvV Hamiltonian with ,on-site' electron repulsion

2. The **,Double Exchange** Hamiltonian of mixed valence systems and the **,Electron**

transfer' Hamiltonian of electron transfer theory

Describes only a two site system with localized electrons

3. The Hückel Hamiltonian for aromatic systems

Describes π-Electron excited states

4. The Quasi-Relativistic ZORA Hamiltonian

Describes the ,large component' of the spinor

5.... (hundreds of uses throughout chemistry and physics)

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.

What do we mean by the "Complete Hamiltonian"?

(with a short excursion into Quantum Chemistry)

What is the "Complete Hamiltonian"?

- One could always take the many particle four component relativistic
 Hamiltonian with inclusion of external electric and magnetic fields as complete
 Hamiltonian as it describes, to the best of our knowledge, all chemical phenomena
- For EPR (in particular!) and NMR (to some extent) theory this is essentially the case. Hence, the EPR physics is a very complete one!
- For many other effective Hamiltonians it is enough to regard the Born Oppenheimer Hamiltonian as ,the complete Hamiltonian'; for example in the H-D vV Hamiltonian.
- Sometimes even an effective Hamiltonian at one level may serve as the basis for an effective Hamiltonian at another level (e.g. the full spin Hamiltonian in relation to the description of only a nuclear spin manifold)

The Molecular Hamiltonian



$$\begin{split} H(\mathbf{r},\mathbf{R}) &= T_e^{-} + T_N^{-} + V_{eN}^{-} + V_{ee}^{-} + V_{NN}^{-} \\ T_e^{-} &= \sum_i p_i^2 / 2m_{el}^{-} V_{NN}^{-} = \frac{e_0^2}{4\pi\varepsilon_0} \sum_{A < B} \frac{Z_A Z_B^{-}}{\left|\mathbf{R}_A^{-} - \mathbf{R}_B^{-}\right|} & V_{eN}^{-} = -\frac{e_0^2}{4\pi\varepsilon_0} \sum_{A,i} \frac{Z_A^{-}}{\left|\mathbf{r}_i^{-} - \mathbf{R}_A^{-}\right|} \\ T_N^{-} &= \sum_A p_A^2 / 2m_A^{-} & V_{ee}^{-} = \frac{e_0^2}{4\pi\varepsilon_0} \sum_{i < j} \frac{1}{\left|\mathbf{r}_i^{-} - \mathbf{r}_j^{-}\right|} \end{split}$$

Note: i ,j sum over electrons, A,B sum over nuclei, ZA,MA- Charge and Mass of Nucleus ,A'

Molecules are Many Particle Systems





chemistry

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Low-energy spectrum of iron-sulfur clusters directly from many-particle quantum mechanics

Sandeep Sharma¹, Kantharuban Sivalingam³, Frank Neese² and Garnet Kin-Lic Chan^{1*}



The particle/hole spectrum is very far from the real spectrum!

Extreme Example: L-Edge X-Ray Absorption

L-edge excitations lead to final states with a (n-1)p core hole, e.g.:



Numerical Data: The Mn²⁺ Ion (⁶S, high-spin d⁵)



Effective Hamiltonians through Partitioning Theory

Expansion of the Wavefunction

Assume that we have defined our "Complete Hamiltonian". Assume that we can (or should) divide it into a part H₀ and a part H₁

$$H\Psi_{I} = (H^{(0)} + H^{(1)})\Psi_{I} = E_{I}\Psi_{I}$$

✓ The solutions to $H^{(0)}\Psi_{I}^{(0)} = E_{I}^{(0)}\Psi_{I}^{(0)}$

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:

$$\begin{array}{ccc} \mathbf{H}^{AA} & \mathbf{H}^{AB} \\ \mathbf{H}^{BA} & \mathbf{H}^{BB} \end{array} \right) \left(\begin{array}{c} \mathbf{C}^{A} \\ \mathbf{C}^{B} \end{array} \right) = E \left(\begin{array}{c} \mathbf{C}^{A} \\ \mathbf{C}^{B} \end{array} \right)$$

✓ 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

$$\checkmark \text{ Hence:} \qquad \mathbf{H}^{eff}(E)\mathbf{C}^{A} = E\mathbf{C}^{A}$$

✓ With the effective Hamiltonian:

 $\mathbf{H}^{eff}(E) = \mathbf{H}^{AA} - \mathbf{H}^{AB}(\mathbf{H}^{BB} - \mathbf{1}E)^{-1}\mathbf{H}^{BA} \qquad \text{dimension} = \dim(A) \times \dim(A)$

- 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:

$$\begin{split} \left(\mathbf{H}^{BB}\right)_{IJ} &= \left\langle \Psi_{I}^{(0)} \mid H^{(0)} \mid \Psi_{J}^{(0)} \right\rangle + \left\langle \Psi_{I}^{(0)} \mid H^{(1)} \mid \Psi_{J}^{(0)} \right\rangle \\ &= \delta_{IJ} E_{I}^{(0)} + \left\langle \Psi_{I}^{(0)} \mid H^{(1)} \mid \Psi_{J}^{(0)} \right\rangle & \underset{\text{eige}}{\text{eige}} \\ &\approx \delta_{IJ} E_{I}^{(0)} & \text{H}_{1} \text{ is } \end{split}$$

Coupling among the b-space eigenfunctions can be neglected if H₁ is much smaller than H₀

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

$$\begin{split} \left(\mathbf{H}^{e\!f\!f} \right)_{IJ} &= \delta_{IJ} E_{I}^{(0)} + \left\langle \Psi_{I}^{(0)} \mid H^{(1)} \mid \Psi_{j}^{(0)} \right\rangle \\ &\quad - \sum_{K \in 'b'} \frac{\left\langle \Psi_{I}^{(0)} \mid H^{(1)} \mid \Psi_{K}^{(0)} \right\rangle \left\langle \Psi_{K}^{(0)} \mid H^{(1)} \mid \Psi_{J}^{(0)} \right\rangle}{E_{K}^{(0)} - E_{a}} \end{split}$$

- This looks like second order perturbation theory but is more general since the coupling of the ,a' space functions via the perturbing operator H₁ 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 H₀ and H₁.
 - 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 H₁ 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 asusmptions 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)

Example 1: The Heisenberg Hamiltonian

"Parameterizing a few low-lying electronic states"

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



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
 - H₀ is the Epstein-Nesbet Hamiltonian (diagonal of the CI matrix) and H₁ = H - H₀. 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 $|core(a_{\alpha}b_{\beta})\rangle$ and $|core(a_{\beta}b_{\alpha})\rangle$.
 - 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 $|core(a_{\alpha}a_{\beta})\rangle$ and $|core(b_{\alpha}b_{\beta})\rangle$ and we restrict attention to those

Evaluation of the Effective Hamiltonian

* Assuming two (semi) localized orbitals ,a' and ,b', then the model space is:



- ★ 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:

$$\left\langle a_{\alpha}b_{\beta} \mid H_{1} \mid a_{\beta}b_{\alpha} \right\rangle = \left(a_{\alpha}b_{\alpha} \mid a_{\beta}b_{\beta}\right) = K_{ab}$$

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

$$-\frac{\left\langle a_{\alpha}b_{\beta}\mid H_{1}\mid a_{\alpha}a_{\beta}\right\rangle\left\langle a_{\alpha}a_{\beta}\right\rangle H_{1}\mid a_{\beta}b_{\alpha}\right\rangle}{\left\langle a_{\alpha}a_{\beta}\mid H_{0}\mid a_{\alpha}a_{\beta}\right\rangle-\left\langle a_{\alpha}b_{\beta}\mid H_{0}\mid a_{\alpha}b_{\beta}\right\rangle}-\frac{\left\langle a_{\alpha}b_{\beta}\mid H_{1}\mid b_{\alpha}b_{\beta}\right\rangle\left\langle b_{\alpha}b_{\beta}\mid H_{1}\mid a_{\beta}b_{\alpha}\right\rangle}{\left\langle b_{\alpha}b_{\beta}\mid H_{0}\mid b_{\alpha}b_{\beta}\right\rangle-\left\langle a_{\alpha}b_{\beta}\mid H_{0}\mid a_{\alpha}b_{\beta}\right\rangle}$$

Extraction of the Exchange Coupling Constant

$$\checkmark \text{ Since: } \left\langle a_{\alpha}b_{\beta} \mid H_{1} \mid a_{\alpha}a_{\beta} \right\rangle = \left\langle a_{\alpha}b_{\beta} \mid H_{1} \mid b_{\alpha}b_{\beta} \right\rangle = F_{ab}$$
$$\left\langle a_{\alpha}a_{\beta} \mid H_{0} \mid a_{\alpha}a_{\beta} \right\rangle - \left\langle a_{\alpha}b_{\beta} \mid H_{0} \mid a_{\alpha}b_{\beta} \right\rangle = (a_{\alpha}a_{\alpha} \mid a_{\beta}a_{\beta}) - (a_{\alpha}a_{\alpha} \mid b_{\beta}b_{\beta}) = J_{aa} - J_{ab} \equiv U$$

✓ We obtain the effective Hamiltonian:

$$H^{e\!f\!f} = \left(egin{array}{ccc} 0 & K_{ab} - 2 rac{F_{ab}^2}{U} \ cc & 0 \end{array}
ight)$$

And the splitting:

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

✓ And from the Spin-Hamiltonian $H_{HDvV} = -2JS_AS_B$ $= -J(S^2 - S_A^2 - S_B^2)$ ✓ Hence $J = K_{ab} - 2\frac{F_{ab}^2}{U}$

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

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



 $b = 2^{-1/2} (\Psi_g - \Psi_u)$

Notes:

- ,a' and ,b' have tails on the bridge (and on the other side)
- ,a' and ,b' are orthogonal and normalized

 $a = 2^{-1/2} (\Psi_{o} + \Psi_{u})$

- ,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:

Exactly calculated "kinetic" exchange term:

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

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

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

Is that accurate? Look at the singlet wavefunction:

 $|_{\square}^{1}\Psi_{0}\rangle = 99.94\% |neutral\rangle + 0.06\% |ionic\rangle$

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: (~10⁵ Configurations)

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

 $-\frac{2\beta^2}{U} = -57 \ cm^{-1}$
all others = -166 $\ cm^{-1}$
 $J = -206 \ cm^{-1}$

Look at the singlet wavefunction

$$\left| \mathbb{I} \Psi_{0} \right\rangle = 92.3\% |neutral\rangle + 3.3\% |ionic\rangle + 4.4\% |LMCT\rangle$$

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"

✓ -F²/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**, <u>103</u>, 4007; Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, <u>116</u>, 3985; Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, <u>116</u>, 2728. Miralles, J.; Caballol, R.; Malrieu, J. P. *Chem. Phys.* **1991**, <u>153</u>, 25; Miralles, J.; Daudey, J. P.; Caballol, R. *Chem. Phys. Lett.* **1992**, <u>198</u>, 555.

A Comment on Broken Symmetry

Simplest possible case







tails on the bridge, orthogonal \checkmark



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

Example 2: The Spin-Hamiltonian

"Incorporating additional small effects (here relativistic and external field effects)"

Magnetic Interactions



The Spin Hamiltonian: Summary

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

 $\beta_{_N}$

Nuclear Magneton

 $\vec{I}^{(A)}$ Nuclear Spin

Theoretical Magnetic Spectroscopy



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

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Effective Hamiltonian Treatment of the Spin Hamiltonian

- ★ In order to arrive at the effective Hamiltonian of EPR (and NMR) spectroscopy, we take the point of view
 - 1. H₀ is the **Born-Oppenheimer Hamiltonian** and H₁ contains all spin dependent (relativistic) and all magnetic field dependent terms.
 - We assume that we know the spectrum of eigenfunctions of the BO problem (which will never be true - this makes effectiveHamiltonian theory academic in this field - progress comes from linear response to be discussed later).
 - Our model space consists of the 2S+1 functions ψSM with M=S, S-1,...,-S (,magnetic sublevels') that belong to the lowest eigenvalue, E₀, of the BO Hamiltonian. These functions are all degenerate within the BO approach.
 - 4. This procedure is usually well defined: the matrix elements of H₁ are much smaller than those of the BO Hamiltonian and typically the outer ,b' space is well removed from the ,a' space - only for orbitally (nearly) degenerate states (such as Jahn- Teller systems the treatment breaks down)

Defining the Spin-Hamiltonian

★ Now that we can write our 0th order functions as: $|\alpha SM\rangle$ ($\alpha = a \text{ or } b$)

★ We arrive at the effective Hamiltonian:

$$\begin{aligned} \left(\mathbf{H}^{e\!f\!f} \right)_{MM'} &= E_0^{(0)} + \left\langle aSM \mid H^{(1)} \mid aSM' \right\rangle \\ &- \sum_{bS'M''} \frac{\left\langle aSM \mid H^{(1)} \mid bS'M' \right\rangle \left\langle bS'M' \mid H^{(1)} \mid aSM' \right\rangle}{E_b^{(0)} - E_0^{(0)}} \end{aligned}$$

The 0th 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:

li -

Si

$$\begin{split} H^{(1)} &= H_{_{LS}} + H_{_{SOC}} \\ &= \beta \mathbf{B} {\sum_i} (\hat{\mathbf{l}}_i + g_{_e} \hat{\mathbf{s}}_i) + {\sum_i} \mathbf{h}_i^{_{SOC}} \hat{\mathbf{s}}_i \end{split}$$

- Angular momentum of electron i relative to the ,global' origin (whatever this means ...)
- = 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 I or h^{SOC} vanish:

$$\left\langle aSM \mid H^{(1)} \mid aSM' \right\rangle = 0$$

★ 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 immediately gives:

$$\begin{split} \left(\mathbf{H}^{e\!f\!f}\right)_{\!M\!M'} &= -\beta \sum_{\!bS'\!M''} \Delta_{\!b}^{-1} \left\langle aSM \,|\, \mathbf{B}\!\sum_{i} \mathbf{l}_{i} + 2\hat{\mathbf{s}}_{i} \,|\, bS'M'' \right\rangle \! \left\langle bS'M'' \,|\, \sum_{i} \mathbf{h}^{SOC} \hat{\mathbf{s}}_{i} \,|\, aSM' \right\rangle \\ &- \beta \sum_{\!bS'\!M''} \Delta_{\!b}^{-1} \left\langle aSM \,|\, \sum_{i} \mathbf{h}^{SOC} \hat{\mathbf{s}}_{i} \,|\, bS'M'' \right\rangle \! \left\langle bS'M'' \,|\, \mathbf{B}\!\sum_{i} \mathbf{l}_{i} + 2\hat{\mathbf{s}}_{i} \,|\, aSM' \right\rangle \end{split}$$

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;

$$\left\langle aSM \mid \mathbf{B}\sum_{i} \mathbf{l}_{i} + 2\hat{\mathbf{s}}_{i} \mid bS'M' \right\rangle = \delta_{SS'} \left\langle aSM \mid \sum_{i} \mathbf{l}_{i} \mathbf{B} \mid bS'M' \right\rangle$$

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:

$$\beta B_{z} g_{zz} \left\langle SS \mid S_{z} \mid SS \right\rangle = \beta B_{z} g_{zz} S$$

 \star Now the same for our perturbation sum:

$$\begin{split} \left(\mathbf{H}^{e\!f\!f}\right)_{\!S\!S} &= -\beta B_z \sum_{bS} \Delta_b^{-1} \left\langle aSS \mid \sum_i l_{iz} \mid bSS \right\rangle \! \left\langle bSS \mid \sum_i h_z^{SOC} \hat{s}_{0,i} \mid aSS \right\rangle \\ &- \beta B_z \sum_{bS'} \Delta_b^{-1} \left\langle aSS \mid \sum_i h_z^{SOC} \hat{s}_{0,i} \mid bSS \right\rangle \! \left\langle bSS \mid \sum_i l_{iz} \mid aSS \right\rangle \end{split}$$

★ Thus (and generalizing to all components):

$$\begin{split} g_{_{KL}} &= -\frac{1}{S} \sum_{_{bS}} \Delta_{_{b}}^{^{-1}} \left\langle aSS \mid \sum_{i} l_{_{iK}} \mid bSS \right\rangle \left\langle bSS \mid \sum_{i} h_{_{L}}^{^{SOC}} \hat{s}_{_{0,i}} \mid aSS \right\rangle \\ &- \frac{1}{S} \sum_{_{bS'}} \Delta_{_{b}}^{^{-1}} \left\langle aSS \mid \sum_{i} h_{_{K}}^{^{SOC}} \hat{s}_{_{0,i}} \mid bSS \right\rangle \left\langle bSS \mid \sum_{i} l_{_{iL}} \mid aSS \right\rangle \end{split}$$

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

Example 3: Size Consistent-Self Consistent Cl

"Deriving approximations to the many particle electron correlation problem"

Definition of the Correlation Energy

The Hartree-Fock model is characterized by:

- The use of a single Slater determinant which describes a system of N quasi-independent electrons (independent particle or mean field model!)
- \checkmark The orbitals are optimized to achieve the lowest possible energies.
- ✓ The method is variational. It provides an upper bound to the exact solution of the Born-Oppenheimer hamiltonian (usually >99% of the exact nonrelativistic energy is recovered).
- The remaining energy error is called correlation error and arises from "instantaneous" electron-electron interactions (as opposed to the mean-field interaction present in HF theory).
- ✓ Define the **correlation energy** as (Löwdin):

$$E_{corr} = E_{excact} - E_{HF}$$

Ansatz for the Many Particle Wave Function



Size of the Full CI space

n	Number of Determinants	
1 2 3 4 5 6 7 8 9 10	400 35100 1185600 19191900 16581806 806059800 2237227200 3460710825 2734388800 847660528	Example: 10 electrons 50 orbitals (e.g. H ₂ O)
Σ	10272278170 ~ 10 ¹⁰	

The size of the full CI matrix is HUGE even for moderately sized systems!

Model System: Minimal Basis H₂

For a single minimal basis H_2 molecule we found that the CID matrix was of the form:

$$\mathbf{H} = \begin{pmatrix} 0 & V \\ V & \Delta \end{pmatrix} \qquad \qquad \Delta = \left\langle \Psi_D \mid \hat{H} \mid \Psi_D \right\rangle - \left\langle \Psi_{HF} \mid \hat{H} \mid \Psi_{HF} \right\rangle \qquad \qquad \mathbf{\sigma}^* \qquad \mathbf{\Phi} \quad \mathbf{\Phi}$$

With the lowest eigenvalue:

$$E_{0} = \frac{1}{2} \left(\Delta - \sqrt{\Delta^2 + 4V^2} \right)$$



By contrast, for N noninteracting H₂ molecules CID gave:

$$E_{0} = \frac{1}{2} \left(\Delta - \sqrt{\Delta^{2} + 4NV^{2}} \right)$$

Which is not size consistent. We return to N=2 and study what is missing from CID.

Refinement of the CID treatment

One step beyond CID is to include higher excitations. In the minimal basis $2x H_2$ model system this would be a "simultaneous pair excitation" in which both H₂'s are put in their excited state.



Matrix-elements: $\langle D_A | \hat{H} | D_A \rangle = \langle D_B | \hat{H} | D_B \rangle = \langle 0 | \hat{H} | 0 \rangle + \Delta$ **Diagonal doubles** $\left\langle Q | \hat{H} | Q \right\rangle = \left\langle 0 | \hat{H} | 0 \right\rangle + 2\Delta$ **Diagonal quadruple** $\langle 0 | \hat{H} | D_A \rangle = \langle 0 | \hat{H} | D_B \rangle = \langle \sigma \sigma \| \sigma^* \sigma^* \rangle = V$ Doubles/ground state $\langle 0 | \hat{H} | Q \rangle = 0$ Quadruple/ground state $\langle D_A | \hat{H} | Q \rangle = \langle D_B | \hat{H} | Q \rangle = V$ Quadruple/doubles =Doubles/ground state!

In order to solve the problem we form again the symmetry adapted linear combination of the two doubles: $|D\rangle = \frac{1}{\sqrt{2}} \left(D_A \rangle + |D_B \rangle \right)$

The variational principle leads us then to the CI matrix (the configurations are in the order |0>, |D>, |Q>):

$$\mathbf{H} = \left(\begin{array}{ccc} 0 & \sqrt{2}V & 0\\ \sqrt{2}V & \Delta & \sqrt{2}V\\ 0 & \sqrt{2}V & 2\Delta \end{array} \right)$$

The lowest root is (without proof; look in a formula collection or use a computer algebra system):

$$E_0 = \Delta - \sqrt{\Delta^2 + 4V^2}$$

This is **twice the energy of a single H**₂. Thus, the **inclusion of the quadruple excitation restores the size consistency**!

Furthermore:

$$C_{Q} = \frac{\sqrt{2}V}{\underbrace{E-2\Delta}_{C_{D}/2C_{0}}}C_{D} = \frac{1}{2C_{0}}C_{D}^{2}$$



For noninteracting subsystems, the coefficients of the quadruples are exactly products of doubles coefficients!

Conclusions

We had 3 key results in studying the $2xH_2$ problem:

- 1. Inclusion of the simultaneous pair excitation exactly restores the size consistency.
- The product of the simultaneous pair excitation was exactly proportional to the square of the coefficients of the double excitations (as predicted less rigorously but more generally by perturbation theory).
- The matrix elements of the quadruple excitation with the doubles was equal to the matrix elements of the doubles with the ground state. Both sets of determinants differ by a double substitution from each other.

Now we want to generalize these findings and restart from the full-CI equations which are written in intermediate normalization (we neglect odd excitations at the moment):

$$\left|\Psi\right\rangle = \left|\Psi_{HF}\right\rangle + \left|\Psi_{D}\right\rangle + \left|\Psi_{Q}\right\rangle + \dots$$

Effective (Intermediate) Hamiltonian Treatment of Higher Excitations

- 1. H_0 is the **Möller-Plesset Hamiltonian** (The Fock 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** is the HF determinant
- 4. Our intermediate space is the space of single and double substitutions
- 5. The **outer-space** consists of the triple-, quadruple, substituted determinants

$$\hat{H} |\Psi_0\rangle + \hat{H} |\Psi_D\rangle + \hat{H} |\Psi_Q\rangle = E(|\Psi_0\rangle + |\Psi_D\rangle + |\Psi_Q\rangle).$$

$$\tilde{\mathbf{H}} = \mathbf{P} \cdot \mathbf{H} \cdot \mathbf{P} + \tilde{\mathbf{V}},$$

"Dressing" that incorporates the effects of higher excitations

Resulting equations

Working through the algebra, we find the following intermediate effective Hamiltonian:

$$\begin{split} \left\langle \Psi_{ij}^{ab} \mid \hat{H} \mid \Psi_{HF} \right\rangle + \frac{1}{4} \sum_{klcd} C_{cd}^{kl} \left\langle \Psi_{ij}^{ab} \mid \hat{H} \mid \Psi_{kl}^{cd} \right\rangle + C_{ab}^{ij} \underbrace{\left(E_{corr} - \Delta_{ijab}^{(EPV)} \right)}_{Diagonal \ Shift} = C_{ab}^{ij} \underbrace{\left(E_{HF} + E_{corr} \right)}_{Normal \ CID \ RHS} \\ \Delta_{ijab}^{(EPV)} &= \frac{1}{4} \sum_{klcd \subset ijab} C_{kl}^{cd} \left\langle \Psi_{kl}^{cd} \mid \hat{H} \mid \Phi_{HF} \right\rangle \qquad \text{Rigorous: (SC)}^2\text{-CISD} \\ \Delta_{ijab}^{(EPV)} &= \frac{1}{4} \sum_{klcd \subset ijab} C_{cd}^{kl} \left\langle \Psi_{kl}^{cd} \mid \hat{H} \mid \Phi_{HF} \right\rangle \qquad \text{Approximate: CEPA/1} \\ &= \frac{1}{4} \sum_{klcd \subset ijab} C_{cd}^{kl} \left\langle kl \mid | \ cd \right\rangle \\ &\approx \frac{1}{2} \sum_{kl \subset ij} \varepsilon_{kl} \\ &= \sum_{k} (\varepsilon_{ik} + \varepsilon_{jk}) - \varepsilon_{ij} \end{split}$$
(EPV=, Exclusion Principle Violating")

Generalization: Coupled Cluster Theory

$$\Psi = \exp(T)\Psi_0 \qquad \Psi_0 = \left|\phi_1 \right|.$$

Ansatz (Coester & Kuemmel) Reference determinant

 $.\phi_{N}$

Cluster Operator $T = T_1 + T_2 + T_3 + \dots$ Cluster Amplitudes $T_{1} = \sum_{ia} t_{a}^{i} a_{a}^{+} a_{i} \qquad T_{2} = \frac{1}{4} \sum_{ijab} t_{ab}^{ij} a_{b}^{+} a_{a}^{+} a_{i} a_{j}$ $\Psi = \left(1 + (T_1 + T_2 + ...) + \frac{1}{2}(T_1 + T_2 + ...)^2 + ...\right)\Psi_0$ CC wavefucntion $= \left(1 + T_{1} + T_{2} + \frac{1}{2}T_{1}^{2} + T_{1}T_{2} + \frac{1}{2}T_{2}^{2} + \dots\right)\Psi_{0}$ disconnected excitations **Connected excitations** like CI. linear (statistically uncorrelated motion)

CCS

Determination of the energy and the cluster amplitudes

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

$$R_K = \left\langle t_K \Psi_0 \mid e^{-T} \hat{H} e^T \mid \Psi_0 \right\rangle = 0$$
Nonlinear equation set,
not hard to solve;
up to 4th power of amplitudes

Gold Standard:
CCSD(T)

Summary

- Effective Hamiltonians are an extremely versatile and powerful tools in electronic structure theory
- Effective Hamiltonians can be used as powerful numerical tools.
- Effective Hamiltonians can be used to derive new approximations to the many body problem that are firmly grounded in fundmental physics.
- Effective Hamiltonians can be used to find parameterizations for groups of low-lying states.
- Effective Hamiltonians can be used to connect phenomenological models to fundamental physics.
- Effective Hamiltonians bring structure and order into complex problems
- Effective Hamiltonians help to create a simple language in which we can talk about complex problems

The End

Example 4: Ligand Field Theory

Ligand Field Theory as an Effective Hamiltonian



Tanabe-Sugano Diagrams



"Complete" Ligand Field Theory

A complete LFT calculation in the strong field scheme proceeds as:

1. Build the one-electron matrix:

$$h_{_{\!\mu\nu}}=f(e_{_{\!\sigma}}^{^{\scriptscriptstyle L}},e_{_{\!\pi}}^{^{\scriptscriptstyle L}})\qquad \quad \mu,\nu=d-orbitals$$

2. Build all configurations



3. Build all Slater determinants: $\Phi_{l}(\mathbf{x}_{1},...,\mathbf{x}_{N}) = \Phi_{1} = |d_{xy}^{\alpha}d_{xz}^{\alpha}d_{z^{2}}^{\beta} | ... = |d_{xz}^{\beta}d_{yz}^{\alpha}d_{x^{2}-y^{2}}^{\alpha} |....$

4. Build all Configuration State functions for total spin S and Irrep $\Gamma = \Theta_I = \sqrt{\frac{1}{3}} \Phi_{23} - \sqrt{\frac{2}{3}} \Phi_{51}$

5. Calculate Hamiltonian matrix elements

$$H_{IJ}^{LFT}(\mathbf{e}, B, C) = \left\langle \Theta_{I} \mid \hat{H}_{LFT} + H_{SB} + H_{ZE} \mid \Theta_{J} \right\rangle$$

6. Diagonalize the ligand field Hamiltonian \mathbf{H}^{Li}

 $\mathbf{H}^{LFT}\mathbf{C}^{LFT} = E\mathbf{C}^{LFT}$

→ Yields all ligand field multiplets as a function of the LFT parameters.
Order them in the Tanabe-Sugano diagrams

The Angular Overlap Parameterization

In the AOM the one-electron part of the ligand field is written as:

$$h_{ab} = \sum_{L} \sum_{\lambda} F_{\lambda a}(\theta_{L}, \varphi_{L}, \psi_{L}) F_{\lambda b}(\theta_{L}, \varphi_{L}, \psi_{L})$$

- L= sum over ligands
- F= angular factor (symmetry!)
- $e_{\sigma,\pi}$ = Interaction parameter (ligand specific, transferrable)

Two-electron part of the ligand field

$$\left\langle d_{\sigma}d_{\sigma} \middle| r_{12}^{-1} \middle| d_{\pi}d_{\pi} \right\rangle = \left\langle d_{\sigma}d_{\sigma} \middle| r_{12}^{-1} \middle| d_{\pi'}d_{\pi'} \right\rangle = F_{dd}^{0} + \frac{2}{49}F_{dd}^{2} - \frac{24}{441}F_{dd}^{4}$$

$$\left\langle d_{i}d_{i} \middle| r_{12}^{-1} \middle| d_{i}d_{i} \right\rangle = F_{dd}^{0} + \frac{4}{49}F_{dd}^{2} + \frac{36}{441}F_{dd}^{4}$$

$$\left\langle d_{\delta}d_{\delta} \middle| r_{12}^{-1} \middle| d_{\delta'}d_{\delta'} \right\rangle = F_{dd}^{0} + \frac{4}{49}F_{dd}^{2} - \frac{34}{441}F_{dd}^{4}$$

$$\left\langle d_{\delta}d_{\delta} \middle| r_{12}^{-1} \middle| d_{\delta'}d_{\delta'} \right\rangle = F_{dd}^{0} + \frac{4}{49}F_{dd}^{2} - \frac{34}{441}F_{dd}^{4}$$

$$etc.$$

$$A = F_{dd}^{0} - \frac{49}{441}F_{dd}^{4}$$

$$B = \frac{1}{49}F_{dd}^{2} - \frac{5}{441}F_{dd}^{4}$$

$$C = \frac{35}{441}F_{dd}^{4} \approx 4B$$

$$Bacah parameters.$$

Just two (one) parameter describes the electron-electron repulsion, 1-3 parameters for each ligand.

Examples of AOM parameters

Ligand	e _σ (cm ⁻¹)	e _π (cm ⁻¹)
CN-	7530	-930
F-	7390	1690
CI-	5540	1160
Br-	4920	830
-	4100	670
NH ₃	7030	0
en	7260	0
ру	5850	-670
H ₂ O	7900	1850
OH-	8670	3000

Note: $10Dq = \Delta = 3e_{\sigma}-4e_{\pi}$

.... The task at hand is to construct an effective Hamiltonian that yields the ligand field states (and *only* those!)

.... This effective Hamiltonian will be identified with the complete ligand field CI matrix

.... It will turn out that this match will allow for an unambiguous determination of the ligand field parameters

The *ab initio* Intermediate Hamiltonian

- 1. We have a **"model space**" that contains all the essential physics that we want to describe. This is the **CAS(n,5)** space of N-particle wavefunctions that cleanly maps onto the ligand field manifold
- 2. We have a **"outer space**" that brings in all the remaining effects of dynamic correlation

$$H_{IJ}^{e\!f\!f} = H_{IJ}^{aa} - \sum_{K \in b} \frac{\left\langle I^a \mid H \mid K^b \right\rangle \left\langle K^b \mid H \mid J^a \right\rangle}{H_K^{bb} - E_0}$$

- *intermediate* Hamiltonian in the model space. Same dimension as ligand field CI matrix Completely *ab initio*. No parameters! Yields a near exact eigenvalue spectrum

If this concept is realized in the CASSCF/NEVPT2 framework we obtain the QD-**NEVPT2** method

$$\begin{split} H^{aa}_{IJ} \\ \left\langle I^{a} \mid H - H_{0} \mid K^{b} \right\rangle \\ H^{bb}_{K} = \left\langle K^{b} \mid H_{0} \mid K^{b} \right\rangle \end{split}$$

An element of CAS-CI matrix

Interaction of CAS-CSFs with NEV outer space

Energy of outer space functions using the Dyall Hamiltonian

Unambiguous Match between NEVPT2 and LFT

Overwhelming importance:

There is a 1:1 correspondence between the ligand field CSFs and the CAS-CI CSFs.



Thus, all we have to ensure is that ligand field d-orbitals and CASSCF molecular orbitals of the same parentage are ordered in the same way and that CSFs are constructed in the same way.

The condition is then that the ligand field CI matrix should resemble the *ab initio* effective Hamiltonian as closely as possible

$$\left| H_{IJ}^{LFT} - H_{IJ}^{eff} \right| = \min$$
 For each matrix element!

While this looks at first sight to be a nonlinear optimization problem, in reality things are easy **because the ligand field matrix is linear in each and every ligand field parameter!**

$$\mathbf{H}^{\scriptscriptstyle LFT}(e,B,C) = \mathbf{H}^{\scriptscriptstyle LFT}(0) + \frac{\partial \mathbf{H}^{\scriptscriptstyle LFT}}{\partial B}B + \frac{\partial \mathbf{H}^{\scriptscriptstyle LFT}}{\partial C}C + \sum_{\scriptscriptstyle L} \frac{\partial \mathbf{H}^{\scriptscriptstyle LFT}}{\partial e_{\scriptscriptstyle L}}e_{\scriptscriptstyle L}$$

This ensures that there is a **unique least squares solution** that provides the <u>unambiguous</u> best fit of the ligand field and effective Hamiltonian matrices:

$$\mathbf{A}\mathbf{p} = -\mathbf{b} \;\; \Leftrightarrow \; \mathbf{p} = -\mathbf{A}^{-1}\mathbf{b}$$

 $p_{_K} =$ The k'th ligand field parameter

$$\begin{split} A_{\rm KL} &= \sum_{\rm IJ} \frac{\partial H_{\rm IJ}^{\rm LFT}}{\partial p_{\rm K}} \frac{\partial H_{\rm IJ}^{\rm LFT}}{\partial p_{\rm L}} \\ b_{\rm K} &= \sum_{\rm IJ} \frac{\partial H_{\rm IJ}^{\rm LFT}}{\partial p_{\rm K}} H_{\rm IJ}^{\rm eff} \end{split}$$

This implies the strategy:

- 1. Choose your AOM scheme
- 2. Perform a QD-NEVPT2 calculation to obtain H^{eff}
- 3. Solve linear equation system to obtain the ligand field parameters

Application to CrX₆³⁻ (X=F,CI,Br,I)

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Calculated s CrF63-		CASSCF	NEVPT2	Deviations from Ligand field fit						
		4 T 2	-20	-111		and a	ab initio c		ons	
⁴ T ₂ ⁴ T ₁ (1)		4T1(1)	-42	-533	0	Extracted parameters				
⁴ T ₁ (1) ⁴ T ₁ (2)		-16	439	0						
		² E(1)	-64	-283			CrBrc ³⁻		Crlc ³⁻	
CASSCF	CASSCF	² T ₁ (1)	-38	-575	Exp.	CASSCF	NEVPT2	Exp.	CASSCF	NEVPT2
		² T ₂ (1)	-85	-119						
0Dq	13359	1 ² A1	25	-156	12630	9876	13542	13089	9258	13533
В	1071	⁸ 2T ₂ (2)	88	-527	632	972	729	471	943	699
С	4018	3 ² T ₁ (2)	20	-678	3180	3886	3631	3249	3841	3627
C/B	3.75	² E(2)	10	-151	5	4.00	4.98	6.90	4,07	5.18
- 12	(J)	² T ₁ (3)	90	-694						
2 T 1	(4)	² T ₂ (3)	-24	-797		 Very good agreement between all values and empirical values for 10 Still slight overestimation of electric 		ween <i>ab i.</i> es for 100	nitio	
² A ₂		² T ₁ (4)	89	-767				of electror	⁷ 4 1	
² T ₂ (4) ² E(3)		² A ₂	-4	-480		repulsion (basis set incompleteness + 2 nd order perturbation theory) ✓ Ligand field fit to CASSCF near perfect, to				
		² T ₂ (4)	-11	762]					
		² E(3) -166 -1017 NEVPT2 within 1000 cm ⁻¹			1	,				