Effective Hamiltonian Theory

Frank Neese
Hamiltonians and Eigensystems

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

$$H(x_1, \ldots, x_N)$$

★ Then its eigenfunctions are also functions of $x_1 \ldots x_N$.

$$H(x_1, \ldots, x_N)\Psi_I(x_1, \ldots, x_N) = E_I \Psi_I(x_1, \ldots, x_N)$$

★ 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.

**TRUE**

\[
H \left(x_1, \ldots, x_N\right) \Psi_I \left(x_1, \ldots, x_N\right) = E_I \Psi_I \left(x_1, \ldots, x_N\right) \quad (I=0\ldots\text{infinity})
\]

(nearly) identical eigenvalues wanted!

**EFFECTIVE**

\[
H_{\text{eff}} \Phi_I = E_I \Phi_I 
\]

(I=0\ldots3)
Examples of Effective Hamiltonians

★ The **Spin-Hamiltonian** in EPR and NMR Spectroscopy.
  ‣ It works only on fictitious effective electron and nuclear spin variables
  ‣ It only describes the \((2S+1)(2I+1)\) magnetic sublevels of the spectrum of the complete Hamiltonian

★ The **Heisenberg-Dirac-van Vleck Hamiltonian** of Molecular Magnetism
  ‣ It works on fictitious electron spin variables of magnetic subsystems
  ‣ It only describes a few low-lying multiplets of the complete spectrum

★ The **Hubbard Hamiltonian** of Molecular Magnetism
  ‣ refinement of the HDvV Hamiltonian with on-site electron repulsion

★ The **‘Double Exchange‘ Hamiltonian** of mixed valence systems and the **‘Electron transfer‘ Hamiltonian** of electron transfer theory
  ‣ It describes only a two site system with localized electrons

★ The **Hückel Hamiltonian** for aromatic systems
  ‣ it only describes π-Electron excited states

★ The **Ligand Field Hamiltonian** of coordination chemistry
  ‣ it only describes d-d excited states

★ The **quasi-relativistic ZORA Hamiltonian**
  ‣ it only describes the large component of the spinor

★ ... many others throughout chemistry and physics!
The Value of Effective Hamiltonians

- Effective Hamiltonians are central to chemistry
  - Effective Hamiltonians are **MUCH simpler** than the true Hamiltonias and hence their eigensystems can often be determined analytically or with little effort numerically
  - Effective Hamiltonians have a great **imaginative power**: they create pictures in which we can think and provide a language in which we can talk
  - Effective Hamiltonians typically 'hide' the underlying complexity in a **small set of parameters** that can be determined by fitting to experiments
  - Effective Hamiltonians **provide insight** into the behavior of **classes of compounds** rather than providing results for individual molecules (like quantum chemical calculations!)
  - **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 is the „Complete Hamiltonian“?

★ What is regarded as the „Complete Hamiltonian“ depends to some extent on the context of the discussion.

♦ 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‘; this is true if degeneracies between the magnetic sublevels (Ms-levels) play no role: 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 or the Hubbard Hamiltonian that serves as basis for many effective Hamiltonians in physics)
Effective Hamiltonians through Partitioning Theory
Expansion of the Wavefunction

★ Let us assume that we have defined what we want to regard as our „Complete Hamiltonian“. Let us 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 \( 0^{\text{th}} \) order Hamiltonian:

\[
\Psi_I = \sum_j C_{ji} \Psi_j^{(0)}
\]

★ Hence, the Schrödinger equation turns into a matrix eigenvalue problem

\[
HC = EC
\]
The Partitioning Approach

★ Now comes the critical step: we have to divide our basis of 0th order states into two sets: the \textbf{a} set that we call the \textit{model space}. It contains the functions that dominate the final states of interest. The model space is typically very small!
★ The remaining 0th order functions constitute the \textbf{b-space} or \textit{outer space}. The outer space can be very large!
★ Our job consists of estimating the effect of the outer space on the eigenfunctions that are dominant by the model space.
★ We start from the partitioned eigenvalue problem:

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

★ The equation for the \textbf{b} space coefficients can be formally solved:

\[
C^B = -(H^{BB} - 1E)^{-1}H^{BA}C^A
\]
★ Hence:

\[
H^{AA}C^A - H^{AB}(H^{BB} - 1E)^{-1}H^{BA}C^A = EC^A
\]
Expansion of the Partitioned Eigenvalue Problem

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

★ With the effective Hamiltonian:

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

★ Dimension = \text{dim}(A) \times \text{dim}(A)

★ This equation is still exact since we have not made any approximation! It is simply a reformulation of the original Schrödinger 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:

\[
(\mathbf{H}^{BB})_{IJ} = \langle \Psi_I^{(0)} | H^{(0)} | \Psi_J^{(0)} \rangle + \langle \Psi_I^{(0)} | H^{(1)} | \Psi_J^{(0)} \rangle
\]

\[
= \delta_{IJ} E_I^{(0)} + \langle \Psi_I^{(0)} | H^{(1)} | \Psi_J^{(0)} \rangle
\]

\[
\approx \delta_{IJ} E_I^{(0)}
\]
Simplification of the Effective Hamiltonian

★ Next, we have to realize that we seek solutions in the vicinity of the eigenvalues of $H^{AA}$ - If the coupling of the 'a' set with the 'b' set is very large, then the partitioning approach becomes questionable and a perturbative expansion is no longer possible.

★ 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. But we cannot go into details here.

★ If the final eigenvalues of the effective Hamiltonian are in the vicinity of the 'a' space eigenvalues we can replace:

\[
(1E')_{ij} \approx \delta_{ij} E_a
\]

\[
E_a = \frac{1}{\dim(A)} \sum_{I \in \alpha'} E_I^{(0)}
\]

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

\[
H^{eff} = H^{AA} - H^{AB}(E^{BB} - 1E)^{-1} H^{BA}
\]
Matrix Elements of the Effective Hamiltonian

★ The no longer nonlinear effective Hamiltonian has no difficult term any more and reads explicitly:

\[
(H_{\text{eff}})_{IJ} = \delta_{IJ} E_I^{(0)} + \left\langle \Psi_I^{(0)} | H^{(1)} | \Psi_j^{(0)} \right\rangle \\
- \sum_{K \in \alpha} \frac{\left\langle \Psi_I^{(0)} | H^{(1)} | \Psi_K^{(0)} \right\rangle \left\langle \Psi_K^{(0)} | H^{(1)} | \Psi_J^{(0)} \right\rangle}{E_K^{(0)} - E_a}
\]

★ 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 \(H_{\text{eff}}\) is the desired one.
In order to apply the effective Hamiltonian 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)
Sum over States vs Linear Response
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 Hamiltonian 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 formulations 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:

\[ H_{BO} = \sum_{pq} h_{pq} p^+ q + \frac{1}{4} \sum_{pqrs} \langle pq \mid rs \rangle p^+ q^+ s r \]

★ and some perturbation

\[ H^\lambda = \lambda \sum_{pq} h_{pq}^{(\lambda)} p^+ q \]

\[ h_{pq}^{(\lambda)} = \frac{\partial h}{\partial \lambda} \]
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

\[
E^{(0)}_0 = \left\langle 0 \middle| H_{BO} \middle| 0 \right\rangle
\]

\[
E(\lambda) = E^{(0)}_0 + \lambda \frac{\partial E^{(0)}_0}{\partial \lambda} \bigg|_{\lambda=0} + \ldots
\]

\[
\frac{\partial E^{(0)}_0}{\partial \lambda} \bigg|_{\lambda=0} = \left\langle 0 \middle| H^{(\lambda)} \middle| 0 \right\rangle = \sum_{pq} D_{pq} h_{pq}
\]

\[
D_{pq} = \left\langle 0 \middle| p^+ q \middle| 0 \right\rangle
\]

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

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

\[
\frac{\partial^2 E_0}{\partial \lambda \partial \mu} \bigg|_{\lambda=\mu=0} = \sum_{pq} \frac{\partial D_{pq}}{\partial \mu} h^{(\lambda)}_{pq} + \sum_{pq} D_{pq} \frac{\partial^2 h_{pq}}{\partial \lambda \partial \mu}
\]

★ Since:

\[
\sum_{pq} D_{pq} \frac{\partial^2 h_{pq}}{\partial \lambda \partial \mu} = \langle 0 | h^{(\mu, \lambda)} | 0 \rangle
\]

★ This term is already exactly equivalent to the first-order term in \( H^{\text{eff}} \)

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

\[
\frac{\partial D_{pq}}{\partial \mu} = \left\langle \frac{\partial \Psi_0}{\partial \mu} | p^+ q | \Psi_0 \right\rangle + \left\langle \Psi_0 | p^+ q | \frac{\partial \Psi_0}{\partial \mu} \right\rangle
\]

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

\[
\left| \frac{\partial \Psi_0}{\partial \mu} \right\rangle = \sum_n d_n | n \rangle
\]
But first-order perturbation theory tells us that:

\[ \frac{\partial \Psi_0}{\partial \mu} = -\sum_n \frac{\langle 0 \mid H^{(\mu)} \mid n \rangle \langle n \mid \Psi_0 \rangle}{E_n - E_0} \]

Hence:

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

So:

\[ \frac{\partial^2 E_0}{\partial \lambda \partial \mu} \bigg|_{\lambda = \mu = 0} = \sum_{pq} \frac{\partial D_{pq}}{\partial \mu} h^{(\lambda)}_{pq} + \sum_{pq} D_{pq} \frac{\partial^2 h_{pq}}{\partial \lambda \partial \mu} \]

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

Thus, second derivatives are exactly equivalent to the $H^{\text{eff}}$ 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  
This equality brings us a new powerful approach if we do NOT know the exact eigenstates of the BO Hamiltonian.

For any approximate method that we come up with: take the mixed second derivative with respect to two perturbations.

Taking derivatives is MUCH more feasible than taking infinite sums over states. Truncated SOS expansions are ALWAYS ambiguous.

Hence, the linear response is an elegant, powerful and well defined concept that underlies most present day property calculations.

For exact wavefunctions the $H^{\text{eff}} / \text{SOS}$ approach and the LRT approach are exactly equivalent. For approximate methods they differ and then the derivative approach is the preferred one since it doesn‘t suffer from truncation errors.

Intellectually, it is of course much more efficient to just calculate the change of the wavefunction in the presence of the perturbation rather than making a brute force expansion of the N-particle wavefunction.
Example 1: The Spin-Hamiltonian
Example 1: the Spin Hamiltonian

1. \( H_0 \) is the **Born-Oppenheimer Hamiltonian** and \( H_1 \) contains all spin dependent (relativistic) and all magnetic field dependent terms.
2. We assume that we know the spectrum of eigenfunctions of the BO problem (which will never be true - this makes effective Hamiltonian theory academic in this field - progress comes from linear response to be discussed later).
3. Our **model space** consists of the \( 2S+1 \) functions \( \psi^{SM} \) with \( M=S, S-1,...,-S \) (‘magnetic sublevels’) that belong to the lowest eigenvalue, \( E_0 \), of the BO Hamiltonian. These functions are all degenerate within the BO approach.
4. This procedure is usually well defined: the matrix elements of \( H_1 \) 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 0\textsuperscript{th} order functions as: \[ |\alpha S M\rangle \quad (\alpha = a \ or \ b) \]

★ We arrive at the effective Hamiltonian:

\[
(H^{\text{eff}})_{MM'}^{MK} = E_0^{(0)} + \left\langle aSM \left| H^{(1)} \right| aSM' \right\rangle \\
- \sum_{bS'M''} \left\langle aSM \left| H^{(1)} \right| bS'M' \right\rangle \left\langle bS'M' \left| H^{(1)} \right| aSM' \right\rangle \frac{E_b^{(0)} - E_0^{(0)}}
\]

The 0\textsuperscript{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 \textbf{Wigner-Eckart theorem} in the next step.

★ But let us first be more specific on the perturbing Hamiltonian and derive the \textbf{g-Tensor}. Let:

\[ H^{(1)} = H_{LS} + H_{SOC} \]

\[ = \beta B \sum_i (\hat{I}_i + g_e \hat{s}_i) + \sum_i h_i^{SOC} \hat{s}_i \]

- \( i \) = Angular momentum of electron i relative to the ‘global’ origin (whatever this means …)
- \( s_i \) = Spin angular momentum of electron i
- \( h^{\text{SOC}} \) = 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:

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

★ 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:

$$(H_{eff})_{MM'} = -\beta \sum_{bS'M''} \Delta^{-1}_b \left\langle aSM \mid B \sum_i l_i + 2\mathbf{s}_i \mid bS'M'' \right\rangle \left\langle bS'M'' \mid \sum_i h^{SOC} \mathbf{s}_i \mid aSM' \right\rangle$$

$$- \beta \sum_{bS'M''} \Delta^{-1}_b \left\langle aSM \mid \sum_i h^{SOC} \mathbf{s}_i \mid bS'M'' \right\rangle \left\langle bS'M'' \mid B \sum_i l_i + 2\mathbf{s}_i \mid aSM' \right\rangle$$

★ 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;

$$\left\langle aSM \mid B \sum_i l_i + 2\mathbf{s}_i \mid bS'M' \right\rangle = \delta_{SS'} \left\langle aSM \mid \sum_i l_i B \mid bS'M' \right\rangle$$
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:

\[ \hat{O} = \sum_{i} f_i s_i^{(m)} \]

- where m is a *spherical tensor* component \((m=0, \pm 1)\):

\[
\left\langle \Psi_I^S M \left| \sum_i f_i s_i^{(m)} \right| \Psi_J^{S' M'} \right\rangle = \begin{pmatrix} S' & 1 \\ M' & m \end{pmatrix} \begin{pmatrix} S \\ M \end{pmatrix} \left\langle \Psi_I^S \left| \sum_i f_i \right| \Psi_J^{S'} \right\rangle
\]

- 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 \((2S'+1)(2S+1)\) 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:

\[
\langle \Psi_I^S \mid \sum_i f_i \mid \Psi_J^S \rangle = \sqrt{\frac{S(S+1)}{2S}} \langle \Psi_I^{SS} \mid \sum_i f_i s_{0,i} \mid \Psi_J^{SS} \rangle
\]

\[
\langle \Psi_I^S \mid \sum_i f_i \mid \Psi_J^{S+1} \rangle = \sqrt{\frac{2S+3}{2S+1}} \langle \Psi_I^{SS} \mid \sum_i f_i s_{-1,i} \mid \Psi_J^{S+1S+1} \rangle
\]

\[
\langle \Psi_I^S \mid \sum_i f_i \mid \Psi_J^{S-1} \rangle = \langle \Psi_I^{SS} \mid \sum_i f_i s_{+1,i} \mid \Psi_J^{S-1S-1} \rangle
\]

★ With the 'spherical tensor components' of the spin operators being given by:

\[
s_{0,i} = s_{z,i}
\]

\[
s_{+1,i} = -\frac{1}{\sqrt{2}}(s_{x,i} + is_{y,i})
\]

\[
s_{-1,i} = \frac{1}{\sqrt{2}}(s_{x,i} - is_{y,i})
\]

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:

\[ \beta B_z g_{zz} \langle SS | S_z | SS \rangle = \beta B_z g_{zz} \]

★ Now the same for our perturbation sum:

\[ \left( H^{\text{eff}} \right)_{SS} = -\beta B_z \sum_{b_S} \Delta_b^{-1} \left\langle aSS | \sum_i l_{iz} | bSS \right\rangle \left\langle bSS | \sum_i h_{z}^{\text{SOC}} \hat{s}_{0,i} | aSS \right\rangle \]

\[ -\beta B_z \sum_{b_{S'}} \Delta_{b}^{-1} \left\langle aSS | \sum_i h_{z}^{\text{SOC}} \hat{s}_{0,i} | bSS \right\rangle \left\langle bSS | \sum_i l_{iz} | aSS \right\rangle \]

★ Thus (and generalizing to all components):

\[ g_{KL} = -\frac{1}{S} \sum_{b_S} \Delta_b^{-1} \left\langle aSS | \sum_i l_{iK} | bSS \right\rangle \left\langle bSS | \sum_i h_{L}^{\text{SOC}} \hat{s}_{0,i} | aSS \right\rangle \]

\[ -\frac{1}{S} \sum_{b_{S'}} \Delta_{b}^{-1} \left\langle aSS | \sum_i h_{K}^{\text{SOC}} \hat{s}_{0,i} | bSS \right\rangle \left\langle bSS | \sum_i l_{iL} | aSS \right\rangle \]

★ Note: Only excited states of the same spin as the ground state

★ Note: Only standard components M=S
Example 2: The Heisenberg Hamiltonian
Example 2: The Heisenberg 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 0\(^{th}\) 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

\( \star \) 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.
Evaluation of the Effective Hamiltonian

★ Assuming the existence of some (semi) localized orbitals \(a\) and \(b\), our model space consists of the two determinants:

\[
\begin{align*}
\left| \text{core} a_\alpha b_\beta \right> & \quad \left| \text{core} a_\beta b_\alpha \right> \\
\end{align*}
\]

★ 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:

\[
\left< a_\alpha b_\beta | H_1 | a_\beta b_\alpha \right> = (a_\alpha b_\alpha | a_\beta b_\beta) = K_{ab}
\]

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

\[
\begin{align*}
- 
\frac{
\left< a_\alpha b_\beta | H_1 | a_\alpha b_\beta \right> \left< a_\alpha a_\beta | H_1 | a_\beta \alpha \right> - \left< a_\alpha b_\beta | H_0 | a_\alpha b_\beta \right> \left< a_\alpha a_\beta | H_0 | a_\beta \alpha \right>}{
\left< a_\alpha a_\beta | H_0 | a_\alpha a_\beta \right> - \left< a_\alpha b_\beta | H_0 | a_\alpha b_\beta \right> - \left< a_\alpha a_\beta | H_0 | a_\alpha a_\beta \right>}
\end{align*}
\]
Extraction of the Exchange Coupling Constant

Since:

\[
\begin{align*}
\langle a_\alpha b_\beta | H_1 | a_\alpha a_\beta \rangle &= \langle a_\alpha b_\beta | H_1 | b_\alpha b_\beta \rangle = F_{ab} \\
\langle a_\alpha a_\beta | H_0 | a_\alpha a_\beta \rangle - \langle a_\alpha b_\beta | H_0 | a_\alpha b_\beta \rangle &= (a_\alpha a_\alpha | a_\beta a_\beta) - (a_\alpha a_\alpha | b_\beta b_\beta) = J_{aa} - J_{ab} \equiv U
\end{align*}
\]

We obtain the effective Hamiltonian:

\[
H^{\text{eff}} = \begin{pmatrix}
0 & K_{ab} - 2 \frac{F_{ab}^2}{U} \\
cc & 0
\end{pmatrix}
\]

And the splitting:

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

And from the Spin-Hamiltonian

\[
H_{DvV} = -2JS_A S_B
\]

\[
E(S = 0) - E(S = 1) = 2J = -J(S^2 - S_A^2 - S_B^2)
\]

Hence

\[
J = K_{ab} - 2 \frac{F_{ab}^2}{U}
\]
The direct exchange integral $K_{ab}$ is always positive and hence ferromagnetic. It is also called "Potential Exchange".

The term $-F^2/U$ is always negative since $J_{aa} > J_{ab}$ and hence the contribution is always antiferromagnetic. It is also called "Kinetic Exchange".

As discussed beautifully in great detail by Malrieu and co-workers, 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 as done in the pioneering studies of Malrieu and co-workers.

However, the perturbative expansion converges slowly and therefore it is more accurate to only obtain insight into which excitation contribute to $J$ and treat those to all order variationally → Difference Dedicated CI.
Example 3: Ligand Field Theory
Ligand Field Theory as an Effective Hamiltonian

FeO$_4^{2-}$ doped in K$_2$SeO$_4$

Brunold, T.C.; Hauser, A.; Güdel, H.U.
*J.Luminescence*, **1994**, *59*, 321-332

LMCT
NOT Covered by Ligand Field Theory

d-d
Covered by Ligand Field Theory

Tanabe-Sugano Diagrams

\[ \text{[V(H}_2\text{O)}_6]^{3+} \]
A complete LFT calculation in the strong field scheme proceeds as:

1. Build the one-electron matrix:

   \[ h_{\mu\nu} = f(e_{\sigma}^L, e_{\pi}^L), \quad \mu, \nu = d - orbitals \]

2. Build all configurations

3. Build all Slater determinants: \( \Phi_I(x_1, \ldots, x_N) \)

   \[ \Phi_1 = | d_{xy}^{\alpha} d_{xz}^{\alpha} d_{z}^{\beta} | \ldots \quad \Phi_{65} = | d_{xz}^{\beta} d_{yz}^{\alpha} d_{x^2-y^2}^{\alpha} |. \ldots \]

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

   \[ H_{IJ}^{\text{LFT}}(e, B, C) = \left< \Theta_I | \hat{H}_{\text{LFT}} + H_{SB} + H_{ZE} | \Theta_J \right> \]

6. Diagonalize the ligand field Hamiltonian

   \[ \hat{H}_{\text{LFT}} \mathbf{C} = E \mathbf{C}_{\text{LFT}} \]

   \( \rightarrow \) 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:

\[ h_{ab} = \sum_L \sum_\lambda F_{\lambda a}(\theta_L, \phi_L, \psi_L) F_{\lambda b}(\theta_L, \phi_L, \psi_L) \]

\[ L = \text{sum over ligands} \]

\[ F = \text{angular factor (symmetry!)} \]

\[ e_{\sigma,\pi} = \text{Interaction parameter (ligand specific, transferrable)} \]

Two-electron part of the ligand field

\[ \langle d_\sigma d_\sigma | r_{12}^{-1} | d_\pi d_\pi \rangle = \langle d_\sigma d_\sigma | r_{12}^{-1} | d_\pi d_\pi \rangle = F_{dd}^{0} + \frac{49}{49} F_{dd}^{2} - \frac{24}{441} F_{dd}^{4} \]

\[ \langle d_i d_i | r_{12}^{-1} | d_i d_i \rangle = F_{dd}^{0} + \frac{49}{49} F_{dd}^{2} + \frac{36}{441} F_{dd}^{4} \]

\[ \langle d_\delta d_\delta | r_{12}^{-1} | d_\delta d_\delta \rangle = F_{dd}^{0} + \frac{49}{49} F_{dd}^{2} - \frac{34}{441} F_{dd}^{4} \]

\[ \text{etc.} \]

\[ \begin{align*}
A &= F_{dd}^{0} - \frac{49}{441} F_{dd}^{4} \\
B &= \frac{1}{49} F_{dd}^{2} - \frac{5}{441} F_{dd}^{4} \\
C &= \frac{35}{441} F_{dd}^{4} \approx 4B
\end{align*} \]

Racah parameters.

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

<table>
<thead>
<tr>
<th>Ligand</th>
<th>e</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>7530</td>
<td>-930</td>
</tr>
<tr>
<td>F</td>
<td>7390</td>
<td>1690</td>
</tr>
<tr>
<td>Cl</td>
<td>5540</td>
<td>1160</td>
</tr>
<tr>
<td>Br</td>
<td>4920</td>
<td>830</td>
</tr>
<tr>
<td>I⁻</td>
<td>4100</td>
<td>670</td>
</tr>
<tr>
<td>NH</td>
<td>7030</td>
<td>0</td>
</tr>
<tr>
<td>en</td>
<td>7260</td>
<td>0</td>
</tr>
<tr>
<td>py</td>
<td>5850</td>
<td>-670</td>
</tr>
<tr>
<td>H</td>
<td>7900</td>
<td>1850</td>
</tr>
<tr>
<td>OH</td>
<td>8670</td>
<td>3000</td>
</tr>
</tbody>
</table>

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.

\[
H_{IJ}^{\text{eff}} = H_{IJ}^{aa} - \sum_{K \in b} \frac{\langle I^a | H | K^b \rangle \langle K^b | H | J^a \rangle}{H_K^{bb} - E_0}
\]

- **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.

\[
H_{IJ}^{aa}
\]

**An element of CAS-CI matrix**

\[
\langle I^a | H - H_0 | K^b \rangle
\]

**Interaction of CAS-CSFs with NEV outer space**

\[
H_K^{bb} = \langle K^b | H_0 | K^b \rangle
\]

**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.**

\[
\Theta^\text{LFT}_I = | d_x^\alpha d_y^\beta \cdots d_z^\alpha | \quad \Theta^\text{CASSCF}_I = | \psi_x^\alpha \psi_y^\beta \cdots \psi_z^\alpha |
\]

**Ligand field pure d-orbital**

**Ab initio** molecular orbital with metal d-parentage

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

\[
| H^\text{LFT}_{IJ} - H^\text{eff}_{IJ} | = \min \quad \text{For each matrix element!}
\]

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!

\[
H^{LFT}(e, B, C) = H^{LFT}(0) + \frac{\partial H^{LFT}}{\partial B} B + \frac{\partial H^{LFT}}{\partial C} C + \sum_{L} \frac{\partial H^{LFT}}{\partial e_L} e_L
\]

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

\[
Ap = -b \iff p = -A^{-1}b
\]

\[p_K = \text{The } k^{th} \text{ ligand field parameter}
\]

\[A_{KL} = \sum_{IJ} \frac{\partial H^{LFT}_{IJ}}{\partial p_K} \frac{\partial H^{LFT}_{IJ}}{\partial p_L}
\]

\[b_K = \sum_{IJ} \frac{\partial H^{LFT}_{IJ}}{\partial p_K} H^{eff}_{IJ}
\]

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 CrX$_6^{3-}$ (X=F,Cl,Br,I)**

<table>
<thead>
<tr>
<th>Calculated states</th>
<th>CrF</th>
<th>CASSCF</th>
<th>NEVPT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4T$</td>
<td>-20</td>
<td>-111</td>
<td></td>
</tr>
<tr>
<td>$^4T$</td>
<td>-42</td>
<td>-533</td>
<td></td>
</tr>
<tr>
<td>$^4T$</td>
<td>-16</td>
<td>439</td>
<td></td>
</tr>
<tr>
<td>$^2E(1)$</td>
<td>-64</td>
<td>-283</td>
<td></td>
</tr>
<tr>
<td>$^2T$</td>
<td>-38</td>
<td>-575</td>
<td></td>
</tr>
<tr>
<td>$^2T$</td>
<td>-85</td>
<td>-119</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Extracted parameters</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>10Dq</td>
<td>13359</td>
<td>13414</td>
<td>13257</td>
</tr>
<tr>
<td>B</td>
<td>1071</td>
<td>1071</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>4018</td>
<td>4020</td>
<td></td>
</tr>
<tr>
<td>C/B</td>
<td>3.75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Deviations from Ligand field fit and ab initio calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very good agreement between <em>ab initio</em> values and empirical values for 10Dq</td>
</tr>
<tr>
<td>Still slight overestimation of electron repulsion (basis set incompleteness + 2$^{nd}$ order perturbation theory)</td>
</tr>
<tr>
<td>Ligand field fit to CASSCF near perfect, to NEVPT2 within 1000 cm$^{-1}$</td>
</tr>
</tbody>
</table>

The End