Basics of multi-reference
many-body perturbation theories

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General considerations on perturbation theory

The key formulas in perturbation theory are:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}$$

$$\hat{\mathcal{H}}_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)}$$

The first equation defines the "partition" of $\hat{\mathcal{H}}$, that is the identification of what can be solved exactly ($\hat{\mathcal{H}}_0$) and of what can be considered a "perturbations" ($\hat{\mathcal{V}}$).

In PT the ambition is to include in $\hat{\mathcal{H}}_0$ as much "physics" as possible, so that $\hat{\mathcal{V}}$ represents a "small" perturbation.

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Working equations:

$$\Psi_m^{(1)} = -\sum_{i \neq m} \frac{\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{V}} \right| \Psi_i^{(0)} \right\rangle}{E_i^{(0)} - E_m^{(0)}} \Psi_i^{(0)}$$

$$E_m^{(1)} = \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{V}} \right| \Psi_m^{(0)} \right\rangle$$

$$E_m^{(2)} = -\sum_{i \neq m} \frac{\left| \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{V}} \right| \Psi_i^{(0)} \right\rangle \right|^2}{E_i^{(0)} - E_m^{(0)}}$$

General considerations on perturbation theory

Two simple (but often taken for granted!!) relevant relations:

$$
\begin{aligned}
\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{V}} \right| \Psi_i^{(0)} \right\rangle &= \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} - \hat{\mathcal{H}}_0 \right| \Psi_i^{(0)} \right\rangle \\
&= \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_i^{(0)} \right\rangle
\end{aligned}
$$

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\begin{aligned}
E_m^{(0)} + E_m^{(1)} &= \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}}_0 \right| \Psi_m^{(0)} \right\rangle + \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{V}} \right| \Psi_m^{(0)} \right\rangle \\
&= \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle
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General considerations on perturbation theory

Given that $\Psi_m^{(1)}$ and $E_m^{(2)}$ (but also $E_m^{(3)}$) depend on $\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_i^{(0)} \right\rangle$, to computed these quantities the sum over i can be restricted to the set of $\Psi_i^{(0)}$ directly interacting with $\Psi_m^{(0)}$

$$\Downarrow$$

one needs to know only these eigenfunctions (and the associated eigenenergies) of $\hat{\mathcal{H}}_0$!!

Actually, in different MRPT methods, $\hat{\mathcal{H}}_0$ is even not defined outside the space of the functions interacting with $\Psi_m^{(0)}$ (called First Order Interacting Space).

The calculation of $\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_i^{(0)} \right\rangle$ is complex in MRPT methods, given that both $\Psi_m^{(0)}$ and $\Psi_i^{(0)}$ are in general MR wfs.

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Another important quantity is

$$E_i^{(0)} - E_m^{(0)}$$

It appears at the denominator: if it is "small", PT methods show instabilities and possibly divergences.

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- Quasi degenerate states must be treated carefully (Quasi Degenerate Perturbation Theory).
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The electron correlation

In practical *ab-initio* studies of the GS of a molecule close to its equilibrium geometry, HF-SCF is the simplest description.
In HF-SCF one can intuitively say that each electron is moving in the mean-field of the other electrons $\Rightarrow$ the motion of the electrons is "uncorrelated".

Warning! This is not strictly true: the antisymmetry of the wave function imposes a correlation of the motion of electrons with the same spin ("Fermi hole", Fermi correlation).

The difference between the exact and the HF energy with a given basis set is called "electron correlation energy":

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Electron correlation in single reference methods

In single reference systems, a single Slater determinant plays a central role: it has a very large coefficient (> 0.9) in "correlated" wave functions (e.g. FCI). The electronic structure is qualitatively well described by this determinant, which is normally computed at the HF level.

If a quantitative description is required, one considers "single reference" based correlated methods, such as those of the Coupled Cluster family (CCSD, CCSDT), those of the CI family (CISD, CISDTQ,DDCI), or those of the PT family (MP2, MP4). We focus here on the perturbation approach.

A very successful SR method is the Møller-Plesset perturbation theory (MP2) (other are possible, *e.g.* Epstein-Nesbet): it gives normally very good results and it is rather cheap.

The Møller-Plesset PT

In MP2 the zero order Hamiltonian is

$$\hat{\mathcal{H}}_0 = \hat{\mathcal{F}} = \sum_i \hat{f}(i) = \sum_i \varepsilon_i a_i^\dagger a_i$$

The eigenfunctions of $\hat{\mathcal{H}}_0$ are the determinants (or CSFs). For the HF wave function

$$\hat{\mathcal{H}}_0 \Phi_{\mathrm{HF}} = \sum_i^{\mathrm{occ}} \varepsilon_i \ \Phi_{\mathrm{HF}} = E_{\mathrm{HF}}^{(0)}(\mathrm{MP}) \ \Phi_{\mathrm{HF}}$$

The perturbation operator $\hat{\mathcal{V}} = \hat{\mathcal{H}} - \hat{\mathcal{F}}$ is know also as the "fluctuation potential".

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Any other determinant can be seen as the result of the application an excitation string to Φ_{HF}

$$\Phi_\mu = \tau_\mu \Phi_{\text{HF}}$$

where $\tau_\mu = a_r^\dagger a_i$ for single excitations, $\tau_\mu = a_r^\dagger a_s^\dagger a_i a_j$ for doubles, etc. One has

$$
\begin{aligned}
\hat{\mathcal{H}}_0 \tau_\mu \Phi_{\text{HF}} &= \left[\hat{\mathcal{H}}_0, \tau_\mu\right] \Phi_{\text{HF}} + \tau_\mu \hat{\mathcal{H}}_0 \Phi_{\text{HF}} \\
&= \left[\Delta\varepsilon_\mu + E_{\text{HF}}^{(0)}(\text{MP})\right] \tau_\mu \Phi_{\text{HF}}
\end{aligned}
$$

where $\Delta\varepsilon_\mu$ is the sum of the orbital energies of the creators in τ_μ minus the orbital energies of the annihilators ($\Delta\varepsilon_\mu = \varepsilon_r - \varepsilon_i$ for singles, $\Delta\varepsilon_\mu = \varepsilon_r + \varepsilon_s - \varepsilon_i - \varepsilon_j$ for doubles, etc.).

The Møller-Plesset PT

Noticing that

$$\left\langle \Phi_{\mathrm{HF}} \left| \hat{\mathcal{H}} \right| a_r^\dagger a_i \Phi_{\mathrm{HF}} \right\rangle = 0$$

(Brillouin' theorem), the second order contribution to the energy is

$$E_{\mathrm{MP}}^{(2)} = -\sum_{r>s} \sum_{i>j} \frac{|\langle rs\|ij\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_i - \varepsilon_j}$$

This approach gives very stable results (no divergences in the PT expansion at second order). It brings a clear improvement on the HF description.

The Møller-Plesset PT

The key point in MP2 is in the denominator of the perturbation sum: the quantities ε can be seen as energies associated to a physical process (Koopmans' theorem).

For occupied orbitals $-\varepsilon_i$ represents an approximation to an ionization energy, while for virtual orbitals ε_r represents an approximation to an electron affinity.

Note: for this reason the denominator is always large and positive!!

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Møller-Plesset and Koopmans' theorem

The role in MP2 of the "orbital energies" as energies associated to well defined processes is relevant for MRPT methods.

Koopmans' theorem (for IPs) is usually presented showing that

$$IP \simeq \left\langle a_i\,\Phi_{\mathrm{HF}} \left| \hat{\mathcal{H}} \right| a_i\,\Phi_{\mathrm{HF}} \right\rangle - \left\langle \Phi_{\mathrm{HF}} \left| \hat{\mathcal{H}} \right| \Phi_{\mathrm{HF}} \right\rangle = -F_{ii}$$

where F_{ii} is the diagonal element of the Fock matrix associated to Φ_{HF}. If this matrix is diagonal (canonical orbitals), then $F_{ii} = \varepsilon_i \Rightarrow -\varepsilon_i$ are approximations for the IPs.

Actually this relation is general: it is valid for any determinant even different from Φ_{HF} and for any choice of the orbitals on which the determinant is written.

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Koopmans' theorem

Among the identities indicated by Eq. (21) are the well-known results

$$D^a - D_0 = (a|\mathscr{H}_0|a)\,; \quad D_i - D_0 = -(i|\mathscr{H}_0|i) \qquad (24)$$

sometimes referred to (misleadingly) as Koopmans' theorem. The contribution of Koopmans' paper[16] was not these identities, which have no physical content, but a theorem to the effect that if the reference state Φ_0 has stationary energy and if the orbitals ϕ_a or ϕ_i are eigenfunctions of the operator $\mathscr{H}_0$, then the determinants Φ^a, Φ_i formed from Φ_0 by adding ϕ_a to the occupied set or by removing ϕ_i, respectively, also have stationary energy with respect to further variations involving these orbitals. It follows that all these determinants are approximations to eigenfunctions of the $N+1$, N, and $N-1$ particle systems, and the energy differences given by the identities of Eq. (24) can be interpreted as electron affinities or ionization potentials, respectively.

R. K. Nesbet, Adv. Chem. Phys., 9, 321 1965

Koopmans' theorem

What is the role of the canonical orbitals?
To answer this question, one can expand the wave function of the
ion ($N-1$ electrons) on the various $a_i \Phi_{\mathrm{HF}}$

$$\Psi^{N-1} = \sum_i c_i a_i \Phi_{\mathrm{HF}}$$

The c_i are found by diagonalization of the Hamiltonian matrix

$$
\begin{aligned}
H_{ij} &= \left\langle a_i \Phi_{\mathrm{HF}} \left| \hat{\mathcal{H}} \right| a_j \Phi_{\mathrm{HF}} \right\rangle = \left\langle \Phi_{\mathrm{HF}} \left| a_i^\dagger \hat{\mathcal{H}} a_j \right| \Phi_{\mathrm{HF}} \right\rangle \\
&= \left\langle \Phi_{\mathrm{HF}} \left| a_i^\dagger a_j \hat{\mathcal{H}} \right| \Phi_{\mathrm{HF}} \right\rangle + \left\langle \Phi_{\mathrm{HF}} \left| a_i^\dagger \left[\hat{\mathcal{H}}, a_j \right] \right| \Phi_{\mathrm{HF}} \right\rangle \\
&= \delta_{ij} E_{\mathrm{HF}} - \mathrm{F}_{ij}
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$\Rightarrow$ the $\mathbf{H}$ matrix is, apart from a diagonal shift and a sign change,
equal to the $\mathbf{F}$ matrix.

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Koopmans' theorem

Therefore, the use of the canonical orbitals, making the $\mathbf{F}$ matrix diagonal, makes also diagonal the Hamiltonian in the space $\left\{ a_i \Phi_{\mathrm{HF}} \right\}$.

The canonical orbitals satisfy a constrained variational optimization for the ion (wave function based only on the occupied MOs of the neutral molecule).

A similar derivation can be reported for the EAs.

These considerations will help us to extend the MP2 method to multireference problems.

The Møller-Plesset approach

Koopmans' theorem allows to consider the ε as approximations to the energies required for well defined physical processes: ionization potentials and electron affinities.

For this reason the denominator (EAs + IPs) is expected to be never vanishing (EAs can be zero with diffuse basis set, but IPs are in general large and positive).

This is the strong point for MP2 but it becomes a big problem for higher order! For instance the energy for the removal of six electrons from the $2p$ orbitals in Ne is $6 \times$IP $\rightarrow$ the energy of this process is largely underestimated (6×21.6 eV versus 503 eV)! J. P. Malrieu, C. Angeli, *Mol. Phys.*, **111**, *1092*, 2013.

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The Møller-Plesset approach

This error leads to the "strange" behavior of MPn: very good results for low n (2-10) and possible divergences for large n.
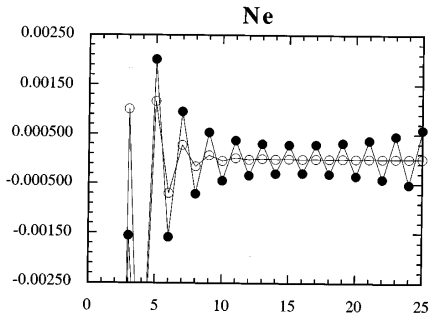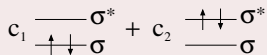

FIG. 1. Correlation contributions for Ne in the cc-pVTZ-(f/d) ($\bigcirc$) and aug-cc-pVDZ ($\bullet$) basis sets.

J. Olsen, O. Christiansen, H. Kock, P. Jørgensen, *J. Chem. Phys.*, **105**, *5082*, 1996.

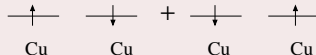## Multireference Chemical Systems

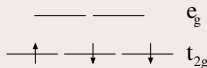### Why multi reference approaches are required?

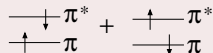Different chemical systems require a multireference description

$c_1 \underset{\underset{\sigma}{\uparrow\downarrow}}{\overline{}\sigma^*} + c_2 \underset{\underset{\sigma}{}}{\overline{\uparrow\downarrow}\sigma^*}$

Bond breaking

$\underset{Cu}{\overline{\uparrow}} \quad \underset{Cu}{\overline{\downarrow}} + \underset{Cu}{\overline{\downarrow}} \quad \underset{Cu}{\overline{\uparrow}}$

Magnetic systems

$\overline{} \quad \overline{} \quad e_g$

$\overline{\uparrow} \quad \overline{\downarrow} \quad \overline{\downarrow} \quad t_{2g}$

Transition metal
complexes

$\underset{\underset{\pi}{\uparrow}}{\overline{\uparrow}\pi^*} + \underset{\underset{\pi}{\downarrow}}{\overline{\uparrow}\pi^*}$

Excited states

Many "interesting" chemical processes need a multireference
description!!

General considerations on MR methods

In MR approaches one usually considers a first approximation to the wave function where

$$\Psi = \sum_{I \in S} c_I |I\rangle \qquad |I\rangle = \text{dets or CSFs}$$

In many approaches Ψ is of CASSCF type ($\Psi_m^{(0)}$):

$$\hat{\mathcal{P}}_{\text{CAS}} \hat{\mathcal{H}} \hat{\mathcal{P}}_{\text{CAS}} \Psi_m^{(0)} = E_m^{(0)} \Psi_m^{(0)}$$

where both the CI coefficients (c_I) and the orbitals are variationally optimized.

General considerations on MR methods

The first step is normally followed by a treatment which improves the description (*e.g.* CAS+CI, CAS+PT2, MRCC) where

$$\Psi = \sum_{I \in S} \tilde{c}_I |I\rangle + \sum_{K \in P} \tilde{c}_K |K\rangle$$

S and P are called "reference" and "outer" spaces.

From a general point of view, one can say that

- the reference space accounts for the static ("strong") correlation
- the outer space introduces the dynamic ("weak") correlation

A few key aspects of MR methods

In multireference methods there are some key aspects:

- the "contraction";
- the quasi-degeneracy;
- the intruder state problem (PT);
- the first order interacting space;
- the partition of the Hamiltonian (PT).

In the following the last two of these aspects are shortly described (PT in particular). They are strongly connected!

The partition of $\hat{\mathcal{H}}$

$\hat{\mathcal{H}}_0$ is normally defined using three different approaches:

1) Explicit definition in second quantization.

Example MP2:

$$\hat{\mathcal{H}}_0 = \sum_i^{\text{occ}} \varepsilon_i a_i^\dagger a_i + \sum_r^{\text{virt}} \varepsilon_r a_r^\dagger a_r$$

Apart from the simple case of MP2, this approach is not very practicable.

The partition of $\hat{\mathcal{H}}$

2) Definition by spectral decomposition.

$$\hat{\mathcal{H}}_0 = \sum_i |\Psi_i^{(0)}\rangle E_i^{(0)} \langle \Psi_i^{(0)}|$$

This approach is used for instance in the Epstein-Nesbet partition where the $\Psi_i^{(0)}$ are simple determinants and $E_i^{(0)}$ their energies ($\hat{\mathcal{H}}_0$ is the diagonal part of $\hat{\mathcal{H}}$ in a determinant basis).

Note: we know the eigenfunctions and eigenvalues of $\hat{\mathcal{H}}_0$ without the knowledge of its explicit form! Actually, we first identify the eigenfunctions and the eigenvalues and this define $\hat{\mathcal{H}}_0$.

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The partition of $\hat{\mathcal{H}}$

3) Definition by means of a model Hamiltonian.
Example CASPT2

$$\hat{\mathcal{H}}_0 = \hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}} \hat{\mathcal{F}} \hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}} + \hat{\mathcal{P}}_{\mathrm{SD}} \hat{\mathcal{F}} \hat{\mathcal{P}}_{\mathrm{SD}} + \hat{\mathcal{P}}_x \hat{\mathcal{F}} \hat{\mathcal{P}}_x$$

The partition of $\hat{\mathcal{H}}$

The SD space generically indicated with "the interacting space", is not unique!.

To be clear from a formal point of view, it is better to say that $\hat{\mathcal{H}}_0$ is defined in two steps:

- identification of the "interacting space" (First Order Interacting Space, FOIS);
- projection of the model Hamiltonian in this space.

First Order Interacting Space: preliminary considerations

As said, in *ab initio* methods one usually considers a first approximation to the wave function, $\Psi_m^{(0)}$, for a state m (for instance HF, CASSCF, CI) followed by a treatment which improves the description (*e.g.* CISD, MP2, CAS+CI or CAS+PT2) where

$$\Psi = c_m^{(0)}\Psi_m^{(0)} + \sum_{K \in \mathcal{R}} c_K |K\rangle$$

where $\mathcal{R}$ is the space complementary to space spanned by $\Psi_m^{(0)}$

$$\left\{ \Psi_m^{(0)} \right\} \oplus \mathcal{R} = \text{FCI}$$

First Order Interacting Space: preliminary considerations

A key question in this approach is:
"Is it possible to restrict *a priori* the sum over $|K\rangle$ to a set of functions spanning a subspace of $\mathcal{R}$ and still taking into account the relevant effects of the full $\mathcal{R}$ space?"

To answer this question, one can use arguments of the perturbation theory. Indeed,

$$\Psi_m^{(1)} = - \sum_{K \in \mathcal{R}} \frac{\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| K \right\rangle}{E_K^{(0)} - E_m^{(0)}} |K\rangle$$

and only the K for which $\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| K \right\rangle \neq 0$ have a non vanishing coefficient in $\Psi_m^{(1)}$.

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First Order Interacting Space

A reasonable approximation is therefore to consider only the functions $|K\rangle$ directly interacting with $\Psi_m^{(0)}$. The space spanned by these functions is called "First Order Interacting Space" (FOIS). The concept of first order interacting space (FOIS) has been introduced in the seventies (McLean and Liu, Iberle and Davidson, Meyer) and it is a central aspect in all MR approaches.

Following McLean and Liu (1973) "FOIS spans the space of those and only those functions which can make correction to the zeroth-order wave function in first order PT".

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First Order Interacting Space

The definition of the FOIS looks obvious if one thinks in term of determinants, the "canonical" basis of the FCI space:

the FOIS is spanned by all determinants which are single and double excitations out from the determinants defining $\Psi_m^{(0)}$.

A first ambiguity: one can reduce the dimension of the FOIS by considering the CSFs with the spin multiplicity of $\Psi_m^{(0)}$.

Moreover, in 1982 Iberle and Davidson stated that only one combination of all determinants (or CSFs) in $\mathcal{R}$ sharing the same orbital occupation belongs to the FOIS.

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To further complicate the situation, Meyer (1977) pointed out that the use of CSFs in the FOIS does not comply with the request that it should not be possible to find a linear combination of CSFs that has a vanishing interaction with $\Psi_m^{(0)}$ (this combination should be projected out).

Indeed one can find combinations of single and double excited CSFs in $\mathcal{R}$ that have a vanishing interaction with $\Psi_m^{(0)}$. A new definition of the FOIS has been proposed, based on the "contracted" functions $E_{ri}E_{sj}\Psi_m^{(0)}$ ($E_{ri} = a_{r\alpha}^\dagger a_{i\alpha} + a_{r\beta}^\dagger a_{i\beta}$).

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First Order Interacting Space

In 2001 we have proposed a version of NEVPT2, the "strongly contracted" variant (SC-NEVPT2), in which the FOIS is much smaller than the "internally contracted" FOIS (used in PC-NEVPT2 and CASPT2).

PC-NEVPT2 and SC-NEVPT2 give normally very similar results $\rightarrow$ the reduction of the FOIS is very effective!!

First Order Interacting Space

Summarizing, starting from the determinant-based FOIS (all determinants which are single and double excitations out from the reference space), one can find in literature "standard" reductions (contractions) of the interacting space:

- only the CSFs with the spin multiplicity of $\Psi_m^{(0)}$ are considered;

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First Order Interacting Space

and more "exotic" reductions:

- integral dependent spin couplings with only one CSF for each orbital occupation pattern (Iberle and Davidson, 1982);

- use of "strongly contracted" functions in SC-NEVPT2.

The actual dimension of FOIS

A key question arises from these considerations: Is the definition of the FOIS unique? Or in other words: Is it possible to identify the smallest, or the "true" FOIS?

Note: these are not academic questions. The functions in the FOIS are those that have to be used in any CI or PT approach!

The actual dimension of FOIS

To answer these questions, let us consider the function $\tilde{\Psi}$

$$\tilde{\Psi} = \hat{\mathcal{P}}_{\mathcal{R}} \hat{\mathcal{H}} \Psi_m^{(0)}$$

where $\hat{\mathcal{P}}_{\mathcal{R}}$ is the projector on the space complementary to the space spanned by $\Psi_m^{(0)}$ ($\left\langle \tilde{\Psi} \,\middle|\, \Psi_m^{(0)} \right\rangle = 0$).

If one considers a generic wave function $\Psi^{\perp}$ orthogonal to both $\Psi_m^{(0)}$ and $\tilde{\Psi}$ (thus $\Psi^{\perp} \in \mathcal{R}$), it is easy to show that it does not interact with $\Psi_m^{(0)}$. Indeed,

$$\left\langle \Psi^{\perp} \,\middle|\, \hat{\mathcal{H}} \,\middle|\, \Psi_m^{(0)} \right\rangle = \left\langle \Psi^{\perp} \,\middle|\, \hat{\mathcal{P}}_{\mathcal{R}} \hat{\mathcal{H}} \,\middle|\, \Psi_m^{(0)} \right\rangle = \left\langle \Psi^{\perp} \,\middle|\, \tilde{\Psi} \right\rangle = 0$$

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Therefore in this case the FOIS is spanned by the $\tilde{\Psi}$ only and its dimension is equal to 1. Obviously, this is an "academic" case and a method (CI or PT) based on this FOIS is of low quality (moment expansion).

On the other hand, let us consider a PT in which

$$\hat{\mathcal{H}}_0 = |\Psi_m^{(0)}\rangle \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle \langle \Psi_m^{(0)}| + \hat{\mathcal{P}}_\mathcal{R} \hat{\mathcal{H}} \hat{\mathcal{P}}_\mathcal{R}$$

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The actual dimension of FOIS

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In order to obtain the zero order wave functions one has to diagonalize $\hat{\mathcal{H}}$ in $\mathcal{R}$. One cannot exclude that all zero order wave functions can contain single and double excited determinants with respect to $\Psi_m^{(0)}$

$$\Downarrow$$

in principle all zero order wave functions interact with $\Psi_m^{(0)}$.

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In this case the FOIS is spanned by all zero order wave functions in $\mathcal{R}$ and its dimension is equal to dim(FCI)-1.

This is again an "academic" case: this PT has a computational cost larger than the FCI!!

Nevertheless, these two examples are well defined "licit" methods and clearly indicate that there is a great freedom in the definition of the FOIS.

We can therefore state this important result:

the dimension of the FOIS has the only restriction
$1 \leq dim(\text{FOIS}) \leq dim(\text{FCI}) - 1!!$.

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The importance of the FOIS in PT methods

As said, perturbation methods are normally defined following two strategies.

The first is based on the direct definition of $\hat{\mathcal{H}}_0$:

- explicitly, as in MP2

$$\hat{\mathcal{H}}_0 = \sum_i^{\text{occ}} \varepsilon_i a_i^\dagger a_i + \sum_r^{\text{virt}} \varepsilon_r a_r^\dagger a_r$$

- by its spectral decomposition, as in EN2

$$\hat{\mathcal{H}}_0 = \sum_K |K\rangle \left\langle K \left| \hat{\mathcal{H}} \right| K \right\rangle \langle K|$$

In this case the FOIS is univocally fixed by $\hat{\mathcal{H}}_0$.

The importance of the FOIS in PT methods

In the second strategy, the PT method is defined first by identifying the FOIS (F) and then using a model Hamiltonian, $\hat{\mathcal{H}}'$, acting in the FOIS

$$\hat{\mathcal{H}}_0 = |\Psi_m^{(0)}\rangle \left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}}' \right| \Psi_m^{(0)} \right\rangle \langle \Psi_m^{(0)}| + \hat{\mathcal{P}}_F \hat{\mathcal{H}}' \hat{\mathcal{P}}_F$$

This is the way NEVPT2 and CASPT2 are defined.

In CASPT2 $\hat{\mathcal{H}}'$ is a one-electron operator (a generalization of the Fock operator) and a single FOIS is considered (internally contracted FOIS).

In NEVPT2 $\hat{\mathcal{H}}'$ is the Dyall Hamiltonian (fully bielectronic within the active space, monoelectronic in the inactive+virtual spaces) and two different FOIS are exploited.

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FOIS from a partition of $\hat{\mathcal{H}}$

Let us consider a partition of $\hat{\mathcal{H}}$ into n operators

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 + \cdots + \hat{\mathcal{H}}_n$$

The space spanned by the n functions $\tilde{\Psi}_i$

$$\tilde{\Psi}_i = \hat{\mathcal{P}}_R \hat{\mathcal{H}}_i \Psi_m^{(0)}$$

satisfies the definition of a FOIS ($\tilde{\Psi}_i = 0$ is possible).
The m $\tilde{\Psi}_i \neq 0$ can be non-orthogonal (they can show linear dependencies) and therefore the dimension of the FOIS is $\leq m$.

This can be seen as a partition of $\tilde{\Psi}$ (the smallest FOIS)

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FOIS from a partition of $\hat{\mathcal{H}}$

This approach has been used for the definition of the FOIS in different MR approaches.

For instance, the partition of $\hat{\mathcal{H}}$

$$\hat{\mathcal{H}} = \sum_{ij} h_{ij} E_{ij} + \frac{1}{2} \sum_{ijkl} \langle ij \, | \, kl \rangle \left[E_{ik} E_{jl} - \delta_{jk} E_{il} \right]$$

in terms like $E_{ik}E_{jl}$ is used to define the FOIS in:

- the contracted-CI (Werner and Knowles) method;

- the CASPT2 (Roos *et al*) method;

- the PC-NEVPT2 (Angeli, Cimiraglia, Malrieu) method.

FOIS in PC-NEVPT2, CASPT2, and contracted CI

The FOIS is different in PC-NEVPT and SC-NEVPT (it is greater in PC-NEVPT).

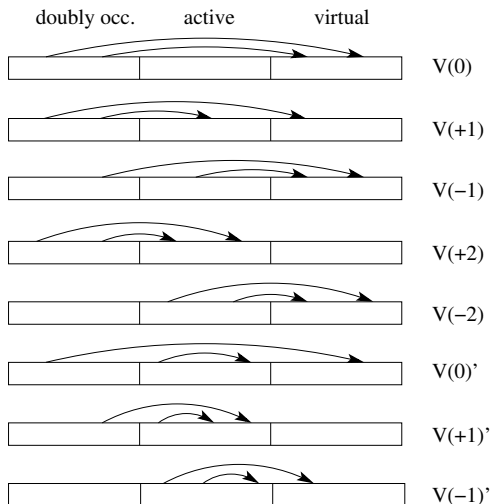The FOIS in PC-NEVPT is spanned by the contracted functions

$$\Phi_{ij}^{rs} = E_{ri}E_{sj}\Psi_m^{(0)} = \sum_{I \in \text{CASCI}} c_{m,I}^{(0)} E_{ri}E_{sj}|I\rangle$$

with $E_{ri} = a_{r\alpha}^\dagger a_{i\alpha} + a_{r\beta}^\dagger a_{i\beta}$ $\Psi_m^{(0)} = \sum_{I \in \text{CASCI}} c_{m,I}^{(0)}|I\rangle$

We indicate with i, j doubly occupied orbitals, with a, b, c active orbitals and with r, s virtual orbitals.

The contracted functions defining the FOIS can be divided in 8 classes.

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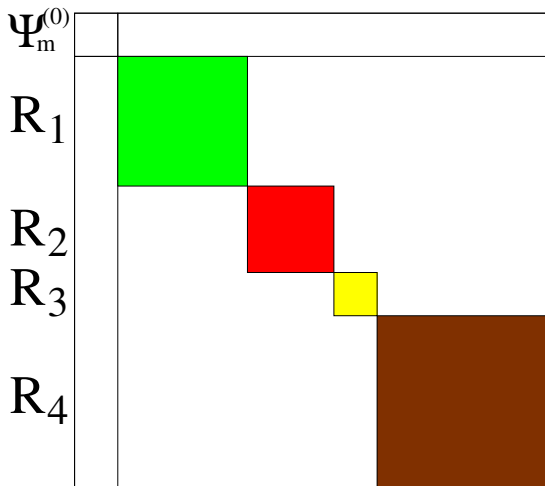
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FOIS from a partition of $\mathcal{R}$

Definition of a FOIS from a partition of the $\mathcal{R}$ space.

Let us consider a partition of $\mathcal{R}$ into n subspaces
$(n \leq dim(\text{FCI}) - 1)$

$$\mathcal{R} = \mathcal{R}_1 \cup \mathcal{R}_2 \cup \cdots \cup \mathcal{R}_n \ \text{ with } \ \mathcal{R}_i \cap \mathcal{R}_j = 0 \text{ if } i \neq j$$

FOIS from a partition of $\mathcal{R}$

FOIS from a partition of $\mathcal{R}$

The space spanned by the n functions $\tilde{\Psi}_i$

$$\tilde{\Psi}_i = \hat{\mathcal{P}}_{\mathcal{R}_i} \hat{\mathcal{H}} \Psi_m^{(0)}$$

satisfies the definition of a FOIS. Given that

$$\hat{\mathcal{P}}_{\mathcal{R}} = \hat{\mathcal{P}}_{\mathcal{R}_1} + \hat{\mathcal{P}}_{\mathcal{R}_2} + \cdots + \hat{\mathcal{P}}_{\mathcal{R}_n}$$
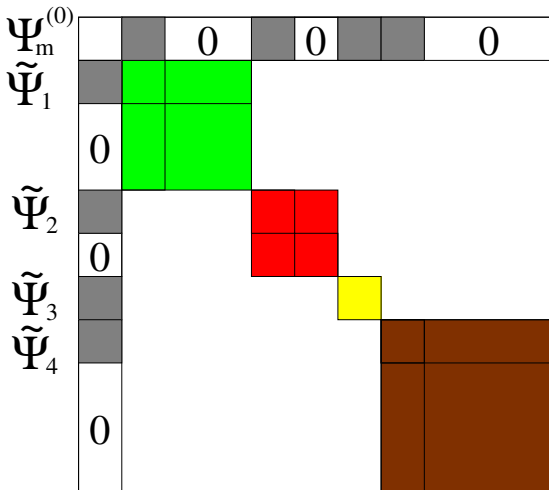
one has

$$\tilde{\Psi} = \tilde{\Psi}_1 + \tilde{\Psi}_2 + \cdots + \tilde{\Psi}_n$$

that is, we have split $\tilde{\Psi}$, the wf defining the smallest FOIS, in "bits".

Note that for some i, one can have $\tilde{\Psi}_i = 0$. The m $\tilde{\Psi}_i \neq 0$ are orthogonal and therefore the dimension of the FOIS is m.

FOIS from a partition of $\mathcal{R}$

FOIS from a partition of $\mathcal{R}$

It is worth noticing that if one considers an orthonormal basis $\{\Phi_1, \Phi_2, \cdots, \Phi_{k_i}\}$ spanning the subspace $\mathcal{R}_i$ of the outer space, then

$$\tilde{\Psi}_i = \sum_{j=1}^{k_i} c_{ji} \Phi_j$$

where

$$c_{ji} = \left\langle \Phi_j \,|\, \tilde{\Psi}_i \right\rangle = \left\langle \Phi_j \,|\, \hat{\mathcal{P}}_{\mathcal{R}_i} \hat{\mathcal{H}} \Psi_m^{(0)} \right\rangle = \left\langle \Phi_j \,\left|\, \hat{\mathcal{H}} \right|\, \Psi_m^{(0)} \right\rangle$$

FOIS from a partition of $\mathcal{R}$

This is a relevant result and can be enunciated as:

Given a set of orthonormal functions in the outer space, their linear combination (contraction) in which the coefficients are the interaction of the functions with $\Psi_m^{(0)}$, brings all the interaction of the full set with $\Psi_m^{(0)}$.

This approach is used in the following for the definition of the SC-NEVPT method.

FOIS from a partition of $\mathcal{R}$

A practical example: if $\mathcal{R}_i$ is spanned by all CSFs (or dets) (indicated with $\{\Phi_1, \Phi_2, \cdots, \Phi_{k_i}\}$) sharing the same orbital occupation, all functions in $\mathcal{R}_i$ and orthogonal to the combination

$$\tilde{\Psi}_i = \sum_{j=1}^{k_i} \left\langle \Phi_j \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle |\Phi_j\rangle$$

have a vanishing interaction with $\Psi_m^{(0)}$. For instance, if one considers a case with 12 unpaired electrons, there are 924 dets with $S_z = 0$, 134 singlet CSFs, but one can concentrate the interaction with $\Psi_m^{(0)}$ in a single CSF.

This is the "integral dependent spin coupling" method for CI calculation proposed by Iberle and Davidson in 1982 (8 citations!!).

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FOIS in SC-NEVPT2

The FOIS in SC-NEVPT2 can be seen as obtained from a partition of $\mathcal{R}$ or from a partition of $\hat{\mathcal{H}}$.

For instance, consider the case of the 2h-1p class

doubly occ.   active   virtual
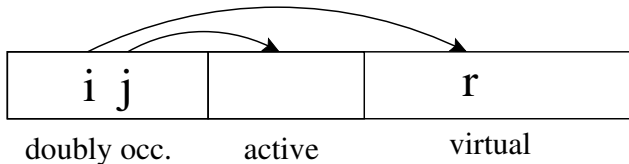
We suppose that one of the $\mathcal{R}_i$ spaces collects all determinants (or CSFs) of $\mathcal{R}$ with two inactive holes in the i and j orbitals, one particle in the r virtual orbital, and one more active electron. This space is indicated with S_{ijr}.

FOIS in SC-NEVPT2

For each space S_{ijr} we identify one function as

$$\Phi_i^{rs} = \hat{\mathcal{P}}_{S_{ijr}}\hat{\mathcal{H}}\Psi_m^{(0)} = \sum_{|I\rangle \in S_{ijr}} \left\langle I \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle |I\rangle$$

Alternatively, one has

$$\Phi_i^{rs} = \left[\sum_a \langle rs \,|\, ai \rangle \, E_{ra}E_{si} + \langle rs \,|\, ia \rangle \, E_{ri}E_{sa} \right] \Psi_m^{(0)}$$

It is a contraction of larger FOIS (F_{det} and $F_{\text{PC−NEVPT2}}$).

The definition of the NEVPT2 and CASPT2 MRPT

Definition of the MRPT

With the "ingredients" we have introduced, now the various MRPT2 can be defined as

$$\hat{\mathcal{H}}_0(\text{CASPT2}) = \hat{\mathcal{P}}_{\Psi_{\text{CAS}}}\hat{\mathcal{F}}\hat{\mathcal{P}}_{\Psi_{\text{CAS}}} + \hat{\mathcal{P}}_{F(\text{CASPT2})}\hat{\mathcal{F}}\hat{\mathcal{P}}_{F(\text{CASPT2})}$$

$$\hat{\mathcal{H}}_0(\text{PC-NEVPT2}) = \hat{\mathcal{P}}_{\Psi_{\text{CAS}}}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{\Psi_{\text{CAS}}} + \hat{\mathcal{P}}_{F(\text{PC-NEVPT2})}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{F(\text{PC-NEVPT2})}$$

$$\hat{\mathcal{H}}_0(\text{SC-NEVPT2}) = \hat{\mathcal{P}}_{\Psi_{\text{CAS}}}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{\Psi_{\text{CAS}}} + \hat{\mathcal{P}}_{F(\text{SC-NEVPT2})}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{F(\text{SC-NEVPT2})}$$

Definition of the MRPT

Note: the FOIS in PC-NEVPT is equal to the FOIS of CASPT2
(and very close to the FOIS of contracted-CI)!!
The perturber functions and their energies are obtained
diagonalizing a model Hamiltonian in the FOIS.

In CASPT2 this model Hamiltonian is a one-electron Fock-like
operator.

In PC-NEVPT the model Hamiltonian has two-electron
components (all interactions among active electrons): its has been
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Definition of the MRPT

Dyall's Hamiltonian, $\hat{\mathcal{H}}^D$

$$
\begin{aligned}
\hat{\mathcal{H}}^D &= \hat{\mathcal{H}}_i + \hat{\mathcal{H}}_v + C \\
\hat{\mathcal{H}}_i &= \sum_{ij}^{inac} f_{ij} E_{ij} + \sum_{rs}^{virt} f_{rs} E_{rs} \\
\hat{\mathcal{H}}_v &= \sum_{ab}^{act} h_{ab}^{eff} E_{ab} + \frac{1}{2} \sum_{abcd}^{act} \langle ab \,|\, cd \rangle \left(E_{ac} E_{bd} - \delta_{bc} E_{ad} \right)
\end{aligned}
$$

f_{ij} and f_{rs}: generalized Fock matrices
$(- \left\langle a_i \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| a_j \Psi_m^{(0)} \right\rangle + \delta_{ij} E_m^{(0)})$

Canonical orbitals $\mapsto f_{ij} = \epsilon_i \delta_{ij}, \ldots$

Definition of the MRPT

What remains at this point is just algebra!!

$$\langle\Psi_m^{(0)}|V_i^{(1)+}[H_v,V_i^{(1)}]|\Psi_m^{(0)}\rangle = \sum_{\substack{a'b'c'\\abc}}^{\text{act}} \langle b'a'|ic'\rangle\langle ba|ic\rangle\widetilde{A}_{a'b'c',abc} + \sum_{a'b'c'a}^{\text{act}} \langle b'a'|ic'\rangle\widetilde{B}_{a'b'c',a}h_{ai}^{\text{eff}}$$

$$+ \sum_{a'abc}^{\text{act}} \langle ba|ic\rangle\widetilde{C}_{a',abc}h_{a'i}^{\text{eff}} + \sum_{a'a}^{\text{act}} \widetilde{D}_{a'a}h_{a'i}^{\text{eff}}h_{ai}^{\text{eff}},$$

Definition of the MRPT

with

$$\bar{A}_{a'b'c',abc} = \langle \Psi_m^{(0)}|E_{c'a'}E_{ib'}[H_v, E_{bi}E_{ac}]|\Psi_m^{(0)}\rangle$$

$$= \sum_d^{\text{act}} (\bar{h}_{da}^{\text{eff}}\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'b}E_{dc}|\Psi_m^{(0)}\rangle - \bar{h}_{cd}^{\text{eff}}\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'b}E_{ad}|\Psi_m^{(0)}\rangle + \bar{h}_{db}^{\text{eff}}\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'd}E_{ac}|\Psi_m^{(0)}\rangle)$$

$$+ \sum_{def}^{\text{act}} (\langle de|fa\rangle\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'b}E_{df}E_{ec}|\Psi_m^{(0)}\rangle - \langle dc|fe\rangle\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'b}E_{df}E_{ae}|\Psi_m^{(0)}\rangle$$

$$+ \langle de|fb\rangle\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'e}E_{df}E_{ac}|\Psi_m^{(0)}\rangle) + \sum_{de}^{\text{act}} (\langle cd|ea\rangle\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'b}E_{de}|\Psi_m^{(0)}\rangle - \tfrac{1}{2}\langle de|ea\rangle$$

$$\times \langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'b}E_{dc}|\Psi_m^{(0)}\rangle - \tfrac{1}{2}\langle dc|ed\rangle\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'b}E_{ae}|\Psi_m^{(0)}\rangle + \tfrac{1}{2}\langle ed|db\rangle\langle \Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'e}E_{ac}|\Psi_m^{(0)}\rangle),$$

$$(A22)$$

Definition of the MRPT

$$\tilde{B}_{a'b'c',a} = \langle\Psi_m^{(0)}|E_{c'a'}E_{ib'}[H_v,E_{ai}]|\Psi_m^{(0)}\rangle$$
$$= \sum_c^{act} h_{ca}^{eff}\langle\Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'c}|\Psi_m^{(0)}\rangle + \sum_{cef}^{act} \langle ac|ef\rangle\langle\Psi_m^{(0)}|E_{c'a'}\tilde{E}_{b'e}E_{cf}|\Psi_m^{(0)}\rangle, \tag{A23}$$

$$\tilde{C}_{a',abc} = \langle\Psi_m^{(0)}|E_{ia'}[H_v,E_{bi}E_{ac}]|\Psi_m^{(0)}\rangle$$
$$= \sum_d^{act} (\bar{h}_{da}^{eff}\langle\Psi_m^{(0)}|\tilde{E}_{a'b}E_{dc}|\Psi_m^{(0)}\rangle - \bar{h}_{cd}^{eff}\langle\Psi_m^{(0)}|\tilde{E}_{a'b}E_{ad}|\Psi_m^{(0)}\rangle + \bar{h}_{bd}^{eff}\langle\Psi_m^{(0)}|\tilde{E}_{a'd}E_{ac}|\Psi_m^{(0)}\rangle) + \sum_{def}^{act} (\langle de|fa\rangle$$
$$\times \langle\Psi_m^{(0)}|\tilde{E}_{a'b}E_{df}E_{ec}|\Psi_m^{(0)}\rangle - \langle dc|fe\rangle\langle\Psi_m^{(0)}|\tilde{E}_{a'b}E_{df}E_{ae}|\Psi_m^{(0)}\rangle + \langle db|fe\rangle\langle\Psi_m^{(0)}|\tilde{E}_{a'e}E_{df}E_{ac}|\Psi_m^{(0)}\rangle)$$
$$+ \sum_{de}^{act} (\langle cd|ea\rangle\langle\Psi_m^{(0)}|\tilde{E}_{a'b}E_{de}|\Psi_m^{(0)}\rangle - \tfrac{1}{2}\langle de|ea\rangle\langle\Psi_m^{(0)}|\tilde{E}_{a'b}E_{dc}|\Psi_m^{(0)}\rangle - \tfrac{1}{2}\langle cd|de\rangle\langle\Psi_m^{(0)}|\tilde{E}_{a'b}E_{ae}|\Psi_m^{(0)}\rangle$$
$$+ \tfrac{1}{2}\langle bd|de\rangle\langle\Psi_m^{(0)}|\tilde{E}_{a'e}E_{ac}|\Psi_m^{(0)}\rangle), \tag{A24}$$

Actually a lot of "physics" is hidden in these equations. For NEVPT2, this "physics" can be made clear, looking at its definition from a different viewpoint.

The n-electron Valence State

Perturbation Theory:

a different viewpoint

Some general consideration concerning $\hat{\mathcal{H}}_0$

In MRPT one looks for a definition of $\hat{\mathcal{H}}_0$ which extends to the MR case the good properties of MP2 in the SR case.
As said, the key point in MP2 is related to the interpretation of the ε as energies associated to physical processes.
How can this be extended to the MR case?

For the doubly occupied and empty orbitals one can easily define the "orbitals energies" by a trivial extension of the SR case.

For active orbitals the problem is more complex: the active orbitals have fractional occupation and various processes are possible (ionization, electron attachment, excitation).

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The extended Koopmans' theorem

For the active orbitals, the question can be formulated as: is it possible to extend Koopmans' theorem to the MR case?
To answer this question, let us first recall the SR case.

Koopmans' theorem can be seen as a constrained variational solution for the ion.

Consider the set of determinants $\left\{ a_1 \Phi_{\mathrm{HF}}, a_2 \Phi_{\mathrm{HF}}, \cdots, a_n \Phi_{\mathrm{HF}} \right\}$,
and the linear combination, Ψ^{ion}, of them which diagonalize $\hat{\mathcal{H}}$

$$\hat{\mathcal{H}} \Psi^{\mathrm{ion}} = E^{\mathrm{ion}} \Psi^{\mathrm{ion}}$$

$$\Psi^{\mathrm{ion}} = \sum_{i=1}^{n} c_i \ a_i \Phi_{\mathrm{HF}}$$

The extended Koopmans' theorem

One can show (Slater's rules) that

$$E^{\text{ion}} = E_{\text{HF}} - \varepsilon_n$$

$$\phi = \sum_{i=1}^{n} c_i \phi_i$$

where ε_n is the highest eigenvalue of the occupied block of the Fock matrix (the smallest in absolute value) and ϕ is the corresponding canonical HF orbital (a linear combination of the ϕ_i HF orbitals, not necessarily canonical).

C. Angeli, "Physical interpretation of Koopmans' theorem: a criticism to the current didactic presentation" J. Chem. Educ., **75(11)**, 1494-1497, (1998).

The extended Koopmans' theorem

Now the extension to the MR case is simple.

Let us suppose that the neutral system is described at the CASSCF level.

For the ion we consider the set of functions $\left\{ a_1 \Psi_{\mathrm{CAS}}, a_2 \Psi_{\mathrm{CAS}}, \cdots, a_{nact} \Psi_{\mathrm{CAS}} \right\}$ where $nact$ is the number of active orbitals and the annihilation operators concern the active orbitals.

These functions have a MR nature and they are not orthogonal

$$\left\langle a_a \Psi_{\mathrm{CAS}} \,|\, a_b \Psi_{\mathrm{CAS}} \right\rangle = \left\langle \Psi_{\mathrm{CAS}} \left| a_a^\dagger a_b \right| \Psi_{\mathrm{CAS}} \right\rangle = \rho_{ba}$$

$\Rightarrow$ the density matrix, ρ, is the metric of this space.

The extended Koopmans' theorem

The diagonalization of $\hat{\mathcal{H}}$ on this space (generalized eigenvalue problem) gives an approximation for the ionized system

$$\hat{\mathcal{H}} \, \Psi^{\mathrm{ion}} = E^{\mathrm{ion}} \, \Psi^{\mathrm{ion}}$$

$$\Psi^{\mathrm{ion}} \; = \; \sum_{i=1}^{nact} c_i \, a_i \, \Psi_{\mathrm{CAS}}$$

which in matrix form is

$$\mathbf{H} \, \mathbf{c} = E^{\mathrm{ion}} \, \rho \, \mathbf{c}$$

with

$$\mathbf{H}_{ij} = \left\langle a_i \, \Psi_{\mathrm{CAS}} \left| \hat{\mathcal{H}} \right| a_j \Psi_{\mathrm{CAS}} \right\rangle = \left\langle \Psi_{\mathrm{CAS}} \left| a_i^{\dagger} \hat{\mathcal{H}} a_j \right| \Psi_{\mathrm{CAS}} \right\rangle$$

The extended Koopmans' theorem

By noting that

$$a_a^\dagger \hat{\mathcal{H}} a_b = a_a^\dagger \left[\hat{\mathcal{H}}, a_b \right] + a_a^\dagger a_b \hat{\mathcal{H}}$$

and that

$$
\begin{aligned}
\left\langle \Psi_{\text{CAS}} \left| a_a^\dagger a_b \hat{\mathcal{H}} \right| \Psi_{\text{CAS}} \right\rangle &= E_{\text{CAS}} \left\langle \Psi_{\text{CAS}} \left| a_a^\dagger a_b \right| \Psi_{\text{CAS}} \right\rangle \\
&= E_{\text{CAS}} \; \rho_{ba}
\end{aligned}
$$

one can write

$$\mathbf{H}_{ab} = \mathbf{K}_{ab} + E_{\text{CAS}} \; \rho_{ba}$$

with

$$\mathbf{K}_{ab} = \left\langle \Psi_{\text{CAS}} \left| a_a^\dagger \left[\hat{\mathcal{H}}, a_b \right] \right| \Psi_{\text{CAS}} \right\rangle$$

As in SR, the $\mathbf{H}$ matrix is equal to another matrix $(\mathbf{K})$, plus a "diagonal" shift equal to the CASSCF energy.

The extended Koopmans' theorem

K is called Koopmans matrix, it is the MR generalization of the Fock matrix and it is computed as a property of the CASSCF wave function. Its diagonalization gives approximations to the IPs for a MR wave function.

This is called extended Koopmans' theorem , published independently by two groups in 1975 (J. Chem. Phys. 62, 549, 1975; J. Chem. Phys. 62, 113, 1975).

One can develop a similar strategy for electron affinities and excitation energies.

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One can develop a similar strategy for electron affinities and excitation energies.

N-electron valence state perturbation theory

Zero order energies in PC-NEVPT.

For the 2h-2p class (2 inactive electrons promoted into the virtual orbitals) the zero order energies are:

$$E_m^{(0)} + \varepsilon_r + \varepsilon_s - \varepsilon_i - \varepsilon_j$$

These energies are equal to the zero order energies in the single reference MP2 method. The interactions with $\Psi_m^{(0)}$ are also equal to those of single reference MP2.

PC-NEVPT2 is fully equivalent to MP2 for a closed shell (no active orbitals) wave function.

N-electron valence state perturbation theory

For the 1h-2p class (one inactive and one active electron promoted into the virtual orbitals):

$$E_m^{(0)} + \varepsilon_r + \varepsilon_s - \varepsilon_i - \varepsilon_\mu$$

where ϵ_μ is computed solving the equation

$$\mathbf{K}\mathbf{c}_\mu = \varepsilon_\mu \rho \mathbf{c}_\mu$$

As said, this is the generalization of Koopmans' theorem for MR functions.

- $K_{ab} = \left\langle \Psi_m^{(0)} \left| a_b^\dagger \left[\hat{\mathcal{H}}, a_a \right] \right| \Psi_m^{(0)} \right\rangle$ is the Koopmans matrix;
- ρ is the one particle density matrix;
- $-\epsilon_\mu$ is an IP. Note: there are $nact$ IPs!

N-electron valence state perturbation theory

For the 2h-1p class (two inactive electrons promoted one into a virtual orbital and the other into an active orbital):

$$E_m^{(0)} + \varepsilon_r + \varepsilon_\mu - \varepsilon_i - \varepsilon_j$$

where ϵ_μ is a generalization of Koopmans' EA for MR functions. Again, there are $nact$ EAs!

Example: consider for instance the π and π^* orbitals in the GS of ethene. In MP2 one has two energies, ε_π (IP) and ε_{π^*} (EA).

In NEVPT2 (based on a CAS 2/2) one has two IPs and two EAs.

N-electron valence state perturbation theory

For the 2p class (two active electrons promoted into virtual orbitals):

$$E_m^{(0)} + \varepsilon_r + \varepsilon_s - \varepsilon_\mu$$

Here ε_μ is an effective energy for ionization of two electrons from the active space.

For the 2h class (two inactive electrons promoted into active orbitals):

$$E_m^{(0)} + \varepsilon_\mu - \varepsilon_i - \varepsilon_j$$

with ε_μ representing an effective energy for adding two electrons to the active space.

N-electron valence state perturbation theory

For the other classes the effective energy describes:

- 1h class (one inactive electron promoted into the active space) $\rightarrow$ adding one electron to the active space and performing a single excitation within the active space.

- 1p class (one active electron promoted into the virtual orbitals) $\rightarrow$ removing one electron from the active space and performing a single excitation within the active space.

- 1h-1p class (one inactive electron promoted into the virtual orbitals) $\rightarrow$ a single excitation in the active space.

The Strongly-Contracted NEVPT approach: definition of the FOIS

Each function defining the FOIS in SC-NEVPT2 is obtained as a linear combination (contraction) of the contracted functions of PC-NEVPT2 sharing the same inactive+virtual occupation pattern.

Following the prescriptions for the definition of the FOIS, one can easily identify the appropriate combinations of the functions defining the PC-NEVPT2 FOIS.

The Strongly-Contracted NEVPT approach: definition of the FOIS

For instance a function of the 2h-1p class has the form

$$\Phi_{ij}^r = \left[\sum_a \langle ra \,|\, ji \rangle E_{rj}E_{ai} + \langle ra \,|\, ij \rangle E_{ri}E_{aj} \right] \Psi_m^{(0)}$$

or, alternatively,

$$\Phi_{ij}^r = \hat{\mathcal{P}}_{S_{ijr}} \hat{\mathcal{H}} \Psi_m^{(0)} = \sum_{|I\rangle \in S_{ijr}} \left\langle I \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle |I\rangle$$

where S_{ijr} collects all determinants (or CSFs) of the outer space with two inactive holes in the i and j orbitals, one particle in the r virtual orbital, and one more active electron.

The Strongly-Contracted NEVPT approach: definition of the FOIS

The FOIS is much smaller in SC-NEVPT2 than in PC-NEVPT2 (and CASPT2). SC-NEVPT2 is a contracted version of PC-NEVPT2.

Note: the functions defining the SC-NEVPT2 FOIS are orthogonal → strong simplification and less numerical problems.

The model Hamiltonian is the same as in PC-NEVPT2 (Dyall's Hamiltonian): the zero order energies can be seen as a "weighted average" of the PC-NEVPT2 zero order energies of the functions involved in the contraction.

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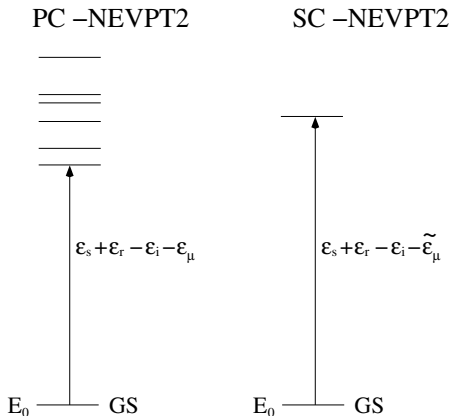# The Strongly-Contracted NEVPT approach: definition of the FOIS

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The Strongly-Contracted NEVPT approach

Zero order energies in SC-NEVPT2

PC –NEVPT2   SC –NEVPT2

$\varepsilon_s + \varepsilon_r - \varepsilon_i - \varepsilon_\mu$ $\varepsilon_s + \varepsilon_r - \varepsilon_i - \widetilde{\varepsilon}_\mu$

E_0 —— GS E_0 —— GS

Properties of NEVPT2

Properties of PC-NEVPT2 and SC-NEVPT2

- Invariance under transformations of orbitals inside a class (inactive, active, virtual): always for the active orbitals, for core and virtual orbitals one has to use canonical orbitals or a less efficient algorithm.

- Size consistence.

- Absence of (artificial) intruder states.

- PC-NEVPT2 and SC-NEVPT2 give very similar results (the difference for the excitation energies are normally less than 0.1 eV): this is a clear indication of the effectiveness of the PC→SC contraction.

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