Multireference Perturbation Theory

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Prerequisites

In the following these concepts are supposed to be known:

- the Born-Oppenheimer approximation;
- the electronic Hamiltonian;
- the concept of molecular orbitals and spinorbitals;
- second quantization and integral representation;
- the Slater determinants and the Configuration State Functions;
- Hartree-Fock and CASSCF approaches.

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.

Limiting factor: one must solve the second equation $\Rightarrow$ $\hat{\mathcal{H}}_0$ cannot be too complicate.

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Working equations:

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

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

General considerations on perturbation theory

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

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

$$\begin{aligned} E_m^{(0)} + E_m^{(1)} &= \left\langle \Psi_m^{(0)} \middle| \hat{\mathcal{H}}_0 \middle| \Psi_m^{(0)} \right\rangle + \left\langle \Psi_m^{(0)} \middle| \hat{\mathcal{V}} \middle| \Psi_m^{(0)} \right\rangle \\ &= \left\langle \Psi_m^{(0)} \middle| \hat{\mathcal{H}} \middle| \Psi_m^{(0)} \right\rangle \end{aligned}$$

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Given that $\Psi_m^{(1)}$ and $E_m^{(2)}$ (but also $E_m^{(3)}$) depend on $\left\langle \Psi_m^{(0)} \middle| \hat{\mathcal{H}}_0 \middle| \Psi_i^{(0)} \right\rangle$, 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 PT 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 $\left\langle \Psi_m^{(0)} \middle| \hat{\mathcal{H}} \middle| \Psi_i^{(0)} \right\rangle$ is complex in MRPT methods, given that both $\Psi_m^{(0)}$ and $\Psi_i^{(0)}$ are in general MR wfs.

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

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- Quasi degenerate states must be treated carefully (Quasi Degenerate Perturbation Theory).
- The intruder state problem.

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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 electrons with the same spin (“Fermi hole”, Fermi correlation). *J. Chem. Phys., 145, 124114, 2016*

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: static and dynamic contributions

Electron correlation is an important concept and it is explained in terms of

- dynamic correlation → "true" correlation of the electron movement, in general "short range" (often not true!) → it introduces the so called Coulomb hole;
- static (non dynamic) correlation → "long range" effect, actually not a "true" correlation → due to the quasi-degeneracy of the HF det with other determinants (inadequacy of the HF wave function);
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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}

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

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

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

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

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

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

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

This approach gives very stable results (no divergences in the PT expansion at second order). It brings an important 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.

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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

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

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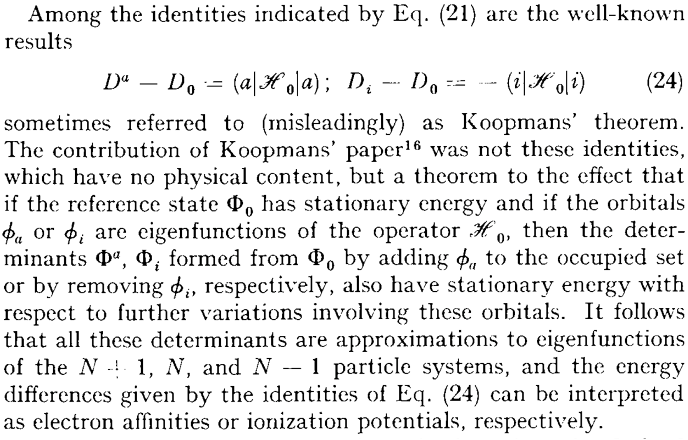

Among the identities indicated by Eq. (21) are the well-known results

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

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 ($\mathrm{N}-1$ electrons) on the various $a_i \Phi_{\mathrm{HF}}$

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

The c_i are found by diagonalization of the Hamiltonian matrix

$$\begin{aligned} H_{ij} &= \left\langle a_i \Phi_{\mathrm{HF}} \left| \hat{\mathcal{H}} \right| a_j \Phi_{\mathrm{HF}} \right\rangle = \left\langle \Phi_{\mathrm{HF}} \left| a_i^{\dagger} \hat{\mathcal{H}} a_j \right| \Phi_{\mathrm{HF}} \right\rangle \\ &= \left\langle \Phi_{\mathrm{HF}} \left| a_i^{\dagger} a_j \hat{\mathcal{H}} \right| \Phi_{\mathrm{HF}} \right\rangle + \left\langle \Phi_{\mathrm{HF}} \left| a_i^{\dagger} \left[\hat{\mathcal{H}}, a_j \right] \right| \Phi_{\mathrm{HF}} \right\rangle \\ &= \delta_{ij} E_{\mathrm{HF}} - \mathrm{F}_{ij} \end{aligned}$$

$\Rightarrow$ the $\mathbf{H}$ matrix is, apart from a diagonal shift and a sign change, equal to the $\mathbf{F}$ matrix.

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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). *J. Chem. Ed., 75, 1494, 1998*

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×IP $\rightarrow$ the energy of this process is largely underestimated (6×21.6 eV versus 503 eV)!
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This error leads to the “strange” behavior of MPn: very good results for low n (2-10) and possible divergences for large n.

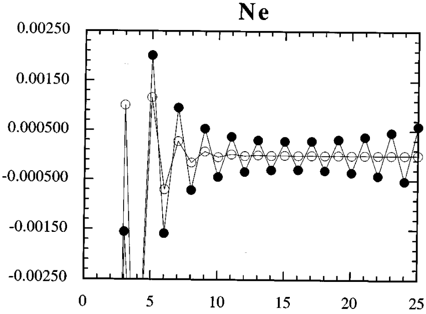


FIG. 1. Correlation contributions for Ne in the cc-pVTZ-(f/d) (○) and aug-cc-pVDZ (●) basis sets.

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

The Møller-Plesset approach

Similar results have been found for F^- (already at third order!), HF, and H_20.

This problem can be solved using the Epstein-Nesbet partition

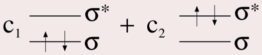
$$\hat{\mathcal{H}}_0 = \sum_K |K\rangle \left\langle K \left| \hat{\mathcal{H}} \right| K \right\rangle \langle K|$$

In this case one has a very good behavior for large n, but the results are quite poor at second order!

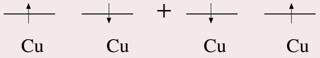
Multireference Chemical Systems

Why multi reference approaches are required?

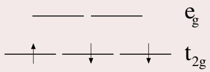
Different chemical systems require a multireference description



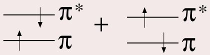
Bond breaking



Magnetic systems



Transition metal complexes



Excited states

Many “interesting” chemical processes need a multireference description!!

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 these aspects are shortly described (PT in particular).

Internal and external contraction/decontraction

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

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

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.

Internal and external contraction/decontraction

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 correlation
- the outer space introduces the dynamic correlation

Internal and external contraction/decontraction

Low Level	High Level
$\Psi = \sum_{I \in S} c_I \lvert I \rangle$	$\Psi = \sum_{I \in S} \tilde{c}_I \lvert I \rangle + \sum_{K \in P} \tilde{c}_K \lvert K \rangle$

One can call a method:

- "internally contracted" if $\tilde{c}_I = c_I$
- "externally contracted" if there is a fix relation between some of the $\tilde{c}_K$ (they are not "optimized" individually).

Internal and external contraction/decontraction

The MR methods can be classified following the level of contraction in the reference space and in the outer space:

- CAS+SD, DDCI, selected CI → MR-CI approaches internally and externally decontracted;
- CIPSI and younger brothers → MR-PT approaches internally contracted and externally decontracted;
- NEVPT2, CASPT2 (and third order versions) → MR-PT approaches internally and externally contracted;
- QD-NEVPT2, MS-CASPT2 → MR-PT approaches internally partially decontracted and externally contracted.

Internally contracted MR methods

The internal contraction can be a drastic approximation in the following situations:

- when the state under study is quasi-degenerate with other states (*e.g.* avoided crossing or conical intersection, valence/Rydberg mixing);
- when the reference space contains interacting determinants (or VB structures) with very different dynamical electronic correlation energies (e.g. magnetic systems, excited states with ionic components, neutral/ionic crossing).

Quasi-degenerate perturbation theory

In the case of quasi-degeneracy in MR-PT, one can resort to the Quasi Degenerate Perturbation Theory (QDPT), where the quasi-degenerate states are considered together (model space) in the frame of the effective Hamiltonian theory.

The second order corrected effective Hamiltonian is

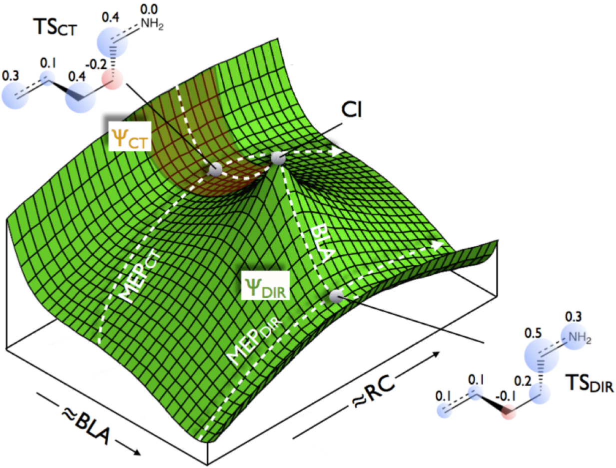
$$\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}}_{\text{eff}}^{0+2} \right| \Psi_n^{(0)} \right\rangle = E_m^{(0)} \delta_{mn} - \sum_{K \in P} \frac{\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{V}} \right| \Psi_k^{(0)} \right\rangle \left\langle \Psi_k^{(0)} \left| \hat{\mathcal{V}} \right| \Psi_n^{(0)} \right\rangle}{E_k^{(0)} - E_n^{(0)}}$$

Quasi-degenerate perturbation theory

This approach is in general very effective but:

- it can be hard to define a model space valid for a wide range of internuclear coordinates;
- a correct revision of the wf can depend on unphysical states very high in energy (as in magnetic systems) and difficult to identify;
- the revision of the wave function is limited to a rotation among the states defining the model space;
- if many states are included in the model space, the intruder state problem becomes more probable.

Quasi-degenerate perturbation theory



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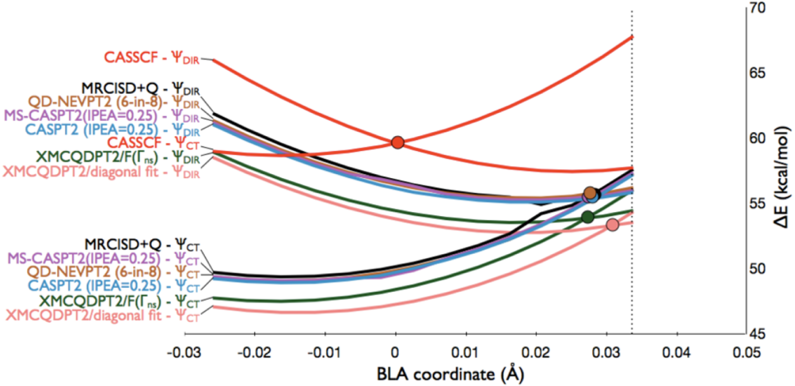

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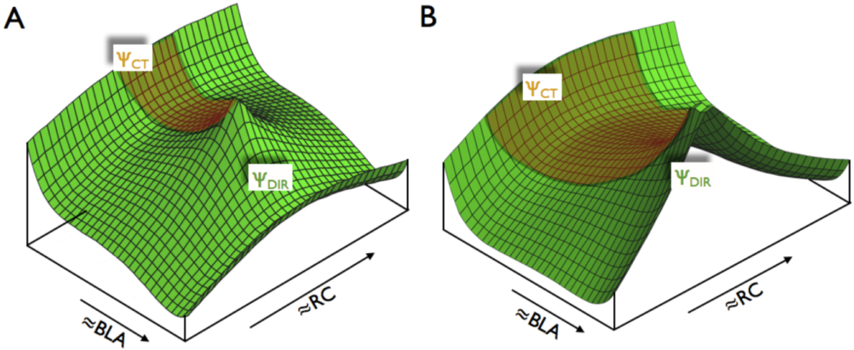

S. Gozem, *et al*, *J. Chem. Theor. Comp.*, **8**, *4069*, 2012.

Intruder state problem in MR-PT

An intruder state is a state included in perturbation expansion of the first order correction to the wave function with a zero-order energy close to that of the state under study.

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

Intruder state problem in MR-PT

One must differentiate two extreme cases:

- the system presents an actual quasi degeneracy → one has to use a QDPT approach;
- the system does not present an actual quasi degeneracy → it is an artifact of the zero order Hamiltonian which is not able to qualitatively reproduce the spectrum of the full Hamiltonian. Removing the quasi degeneracy with level shift techniques (as in CASPT2) avoids the numerical instabilities but does not improve the unrealistic zero order description!

In the last case, one has to improve the quality of $\hat{\mathcal{H}}_0$!

Cr_2: an example of the intruder state problem in CASPT2

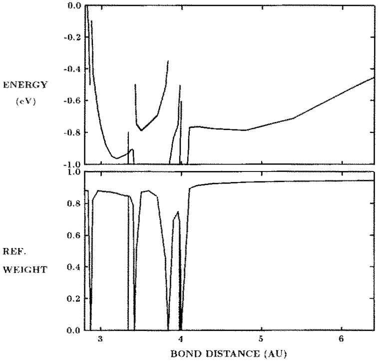

Fig. 2. The potential curve of Cr_2 obtained with CASPT2 above and the weight of the CASSCF wavefunction in the first-order wavefunction below. The basis set is of ANO type of size 6s5p4d3f and the active space is formed by 3d, 4s and $4\pi_u$ orbitals. Neither 3s, 3p correlation nor relativistic effects are included.

K. Andresson *et al Chem. Phys. Lett.*, **230**, *391*, 1994.

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 dets 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 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

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

Pay attention: it is not equivalent to

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

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

These are not $\hat{\mathcal{H}}_0$ of CASPT2 (but you can find them in literature!!).

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

Moreover, the SD space generically indicated with “the interacting space”, is not unique (see hereafter).

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.

$$\hat{\mathcal{H}}_0(\mathrm{CASPT2}) = \hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}}\hat{\mathcal{F}}\hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}} + \hat{\mathcal{P}}_{F_{\mathrm{CASPT2}}}\hat{\mathcal{F}}\hat{\mathcal{P}}_{F_{\mathrm{CASPT2}}}$$
$$\hat{\mathcal{H}}_0(\mathrm{PC-NEVPT2}) = \hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}} + \hat{\mathcal{P}}_{F_{\mathrm{PC-NEVPT2}}}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{F_{\mathrm{PC-NEVPT2}}}$$
$$\hat{\mathcal{H}}_0(\mathrm{SC-NEVPT2}) = \hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{\Psi_{\mathrm{CAS}}} + \hat{\mathcal{P}}_{F_{\mathrm{SC-NEVPT2}}}\hat{\mathcal{H}}^D\hat{\mathcal{P}}_{F_{\mathrm{SC-NEVPT2}}}$$

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 $\Psi_m^{(0)}$

$$\left\{ \Psi_m^{(0)} \right\} \cup \mathcal{R} = \mathrm{FCI}$$

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,

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

and only the K for which $\left\langle \Psi_m^{(0)} \middle| \hat{\mathcal{H}} \middle| K \right\rangle \neq 0$ 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 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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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.

In 1985 Duch showed that the FOIS contains at most only twice as many CSFs as those defining $\Psi_m^{(0)}$.

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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 $E_{ri}E_{sj}\Psi_m^{(0)}$.

This definition of FOIS is the basis of internally-contracted CI (Werner and Knowles), of CASPT2 (Roos *et al*), and of PC-NEVPT2 (Angeli, Cimiraglia, Malrieu).

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The “internally contracted” FOIS has been (and still is!) considered the “true” FOIS, the good (smallest??) FOIS.

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 → the reduction of the FOIS is very effective!!

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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!

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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 $\Psi_m^{(0)}$ $(\left\langle \tilde{\Psi} \,\middle|\, \Psi_m^{(0)} \right\rangle = 0)$.

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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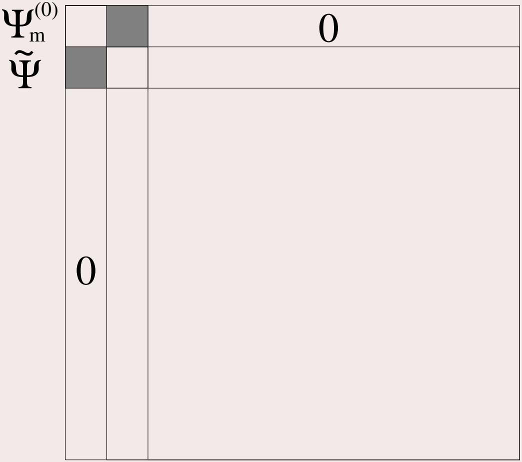

The actual dimension of FOIS

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

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

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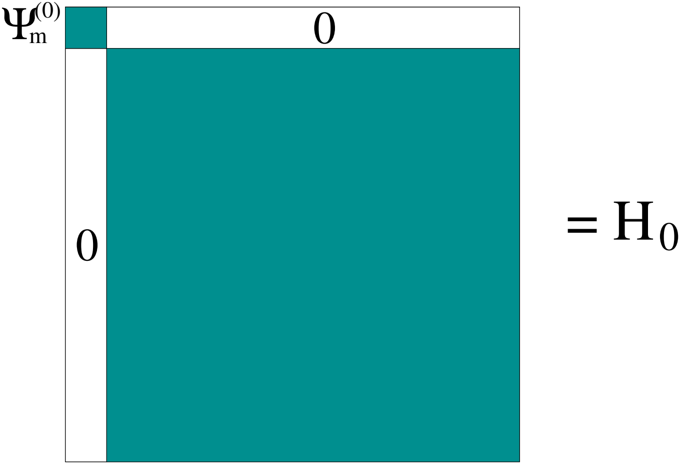


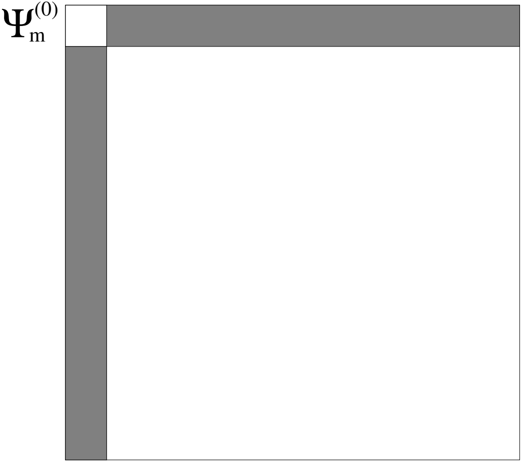
The actual dimension of FOIS

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 $\Psi_m^{(0)}$.

The actual dimension of FOIS



The actual dimension of FOIS

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

The actual dimension of FOIS

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

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We can therefore state this important result:

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$1 \leq dim(\mathrm{FOIS}) \leq dim(\mathrm{FCI}) - 1!!$.

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

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

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

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

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 $\leq m$.

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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 in PC-NEVPT and CASPT2 is spanned by the contracted functions

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

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

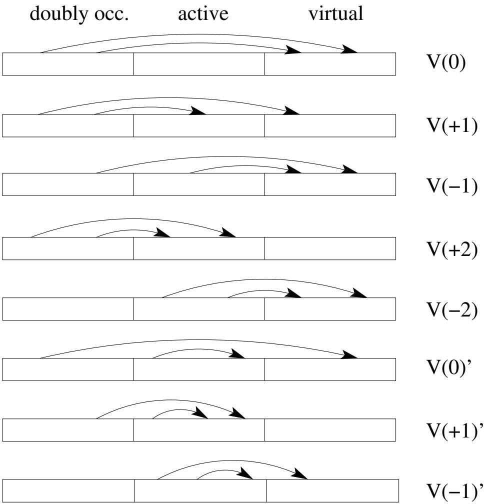
We indicate with i, j doubly occupied orbitals, with a, b, c active orbitals and with r, s virtual orbitals.

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

FOIS in PC-NEVPT2, CASPT2, and contracted CI

- $V(0)$, BJAI: $E_{ri}E_{sj}$, $E_{si}E_{rj}$ $\Rightarrow$ 2h-2p
- $V(+1)$, VJAI: $E_{ri}E_{bj}$, $E_{rj}E_{bi}$ $\Rightarrow$ 2h-1p
- $V(-1)$, BJAT: $E_{ri}E_{sb}$, $E_{si}E_{rb}$ $\Rightarrow$ 1h-2p
- $V(+2)$, VJTI: $E_{bi}E_{cj}$ $\Rightarrow$ 2h
- $V(-2)$, BVAT: $E_{rb}E_{sc}$ $\Rightarrow$ 2p
- $V(+1)'$, VJTU: $E_{ai}E_{bc}$, E_{ai} $\Rightarrow$ 1h
- $V(-1)'$, ATVX: $E_{ra}E_{bc}$, E_{ra} $\Rightarrow$ 1p
- $V(0)'$, AIVX: $E_{ai}E_{rb}$, $E_{ri}E_{ab}$, E_{ri} $\Rightarrow$ 1h-1p

FOIS in PC-NEVPT2, CASPT2, and contracted CI



FOIS in PC-NEVPT2, CASPT2, and contracted CI

NEVPT2

```
          Norm  SC       Energy SC      Norm  PC       Energy PC
(0)      0.1740739383  -0.6037530375   0.1740739383  -0.6037530375
(+1)     0.0120177519  -0.0391910736   0.0122694540  -0.0394394314
(-1)     0.0363900616  -0.1204208326   0.0366209972  -0.1206458306
(+2)     0.0048855197  -0.0157612326   0.0053096624  -0.0161681757
(-2)     0.0053657167  -0.0160087260   0.0054570044  -0.0160852959
(+1)'    0.0000000000   0.0000000000   0.0000000000   0.0000000000
(-1)'    0.0019810617  -0.0044037040   0.0022226299  -0.0045584290
(0)'     0.1223559471  -0.2547265143   0.1289800021  -0.2588719291
-----------------------------------------------------------------
Total    0.3570699970  -1.0542651207   0.3649336884  -1.0595221292
```

CASPT2

```
------------------------------------------------------------------------------------------------
  IT.   VJTU     VJTI     ATVX     AIVX     VJAI     BVAT     BJAT     BJAI     TOTAL    RNORM
------------------------------------------------------------------------------------------------
   1  0.000000-0.010770-0.007729-0.216124-0.040476-0.020591-0.152897-0.612799-1.061386 0.013598
   2  0.000000-0.010982-0.007814-0.218184-0.040701-0.020632-0.152767-0.612891-1.063972 0.002216
   3  0.000000-0.010985-0.007817-0.218358-0.040701-0.020632-0.152815-0.612893-1.064201 0.000390
   4  0.000000-0.010985-0.007816-0.218335-0.040696-0.020633-0.152813-0.612892-1.064169 0.000099
   5  0.000000-0.010985-0.007816-0.218328-0.040695-0.020633-0.152812-0.612891-1.064159 0.000030
   6  0.000000-0.010985-0.007816-0.218329-0.040695-0.020633-0.152812-0.612892-1.064160 0.000012
   7  0.000000-0.010985-0.007816-0.218329-0.040695-0.020633-0.152812-0.612892-1.064162 0.000004
   8  0.000000-0.010985-0.007816-0.218329-0.040695-0.020633-0.152812-0.612892-1.064161 0.000001
------------------------------------------------------------------------------------------------
```

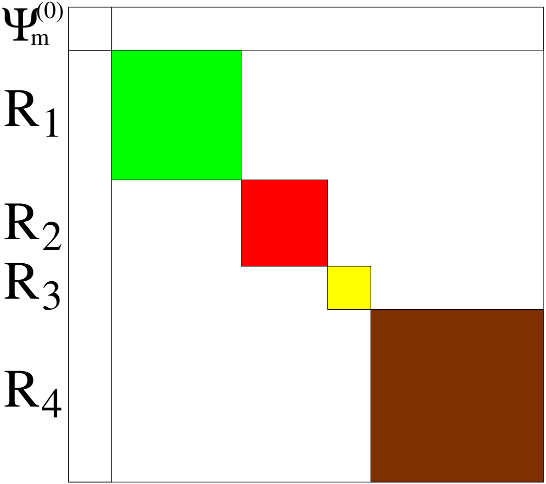
FOIS from a partition of $\mathcal{R}$

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

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

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

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

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

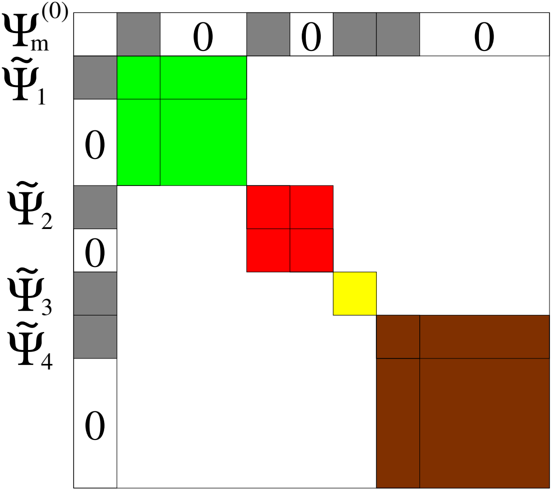
one has

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

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

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

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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Reduction of the dimension of FOIS

The strategy described above allows one to identify a way to reduce the dimension of a given FOIS. Let us consider a FOIS with dimension n and spanned by the basis $\{\Phi_1, \Phi_2, \cdots, \Phi_n\}$. Consider now the function

$$\tilde{\Phi} = \left\langle \Phi_{n-1} \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle |\Phi_{n-1}\rangle + \left\langle \Phi_n \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle |\Phi_n\rangle$$

then the basis $\left\{\Phi_1, \Phi_2, \cdots, \Phi_{n-2}, \tilde{\Phi}\right\}$ spans a FOIS with dimension $n-1$. This FOIS is a subspace of the starting FOIS. With this strategy one can systematically reduce the dimension of the FOIS!

Increase of the dimension of FOIS

A similar strategy can be followed to increase the dimension of a given FOIS.
Let us consider a FOIS with dimension n and spanned by the basis $\{\Phi_1, \Phi_2, \cdots, \Phi_n\}$ and a function $\Phi' \in \mathcal{R}$ outside the FOIS.
Consider now the functions

$$\Phi_a = \lambda|\Phi_n\rangle + \mu|\Phi'\rangle$$

$$\Phi_b = \mu|\Phi_n\rangle - \lambda|\Phi'\rangle$$

then the basis $\{\Phi_1, \Phi_2, \cdots, \Phi_a, \Phi_b\}$ spans a FOIS with dimension $n + 1$. The original FOIS is a subspace of this FOIS.

With this strategy one can systematically increase the dimension of the FOIS!

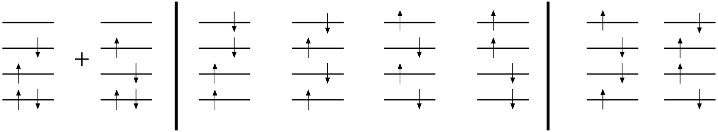
A note concerning FOIS of different dimension

One can guess that if two FOIS have different dimension (say n and m, $m < n$), the smaller must be a subspace of the other. This is false!

Indeed, consider the FOIS defined in dets (F_{det}) and that defined in CSFs (F_{CSF}). One has dim(F_{CSF}) $\leq$ dim(F_{det}), but $F_{\mathrm{CSF}} \not\subset F_{\mathrm{det}}$.

A note concerning FOIS of different dimension

Example: a single core→virt excitation on a singlet open-shell function. $dim\,(F_{\mathrm{det}}) = 4$, $dim\,(F_{\mathrm{CSF}}) = 2$ (# of singlets for a system with six unpaired electrons).



CASSCF Singles Doubles

Note: in the Integral Dependent Spin Coupling method, only one CSF.

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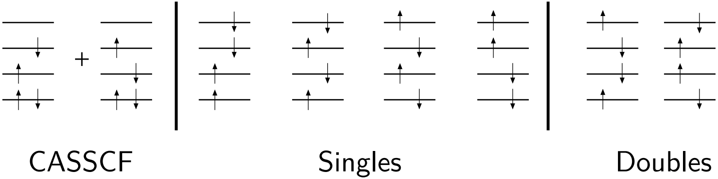

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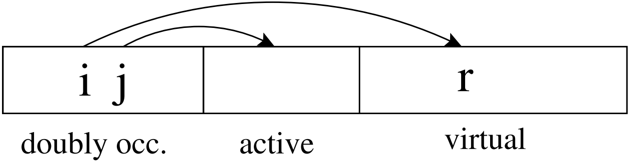
FOIS in SC-NEVPT2

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



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

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

Alternatively, one has

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

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

The FOIS in CI methods

Variational (CI) methods are univocally defined by their FOIS.

One has the trivial relation

$$E_{CI}\left(F_{\mathrm{a}}\right) \leq E_{CI}\left(F_{\mathrm{b}}\right) \quad \text{if} \quad F_{\mathrm{b}} \subset F_{\mathrm{a}}$$

$$E_{CI}\left(F_{\mathrm{PC-NEVPT}}\right) \leq E_{CI}\left(F_{\mathrm{SC-NEVPT}}\right)$$

$$E_{CI}\left(F_{\mathrm{det}}\right) \leq E_{CI}\left(F_{\mathrm{ICCI}}\right)$$

but one cannot assure that

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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

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

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

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

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 defined by Dyall in 1995 and it is equivalent to the full Hamiltonian in the CAS-CI space.

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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
$(- \left\langle a_i \Psi_m^{(0)} \middle| \hat{\mathcal{H}} \middle| a_j \Psi_m^{(0)} \right\rangle + \delta_{ij} E_m^{(0)})$

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

$$
\begin{aligned}
\widetilde{A}_{a'b'c',abc} &= \langle \Psi_m^{(0)} | E_{c'a'} E_{ib'} [H_v, E_{bi} E_{ac}] | \Psi_m^{(0)} \rangle \\
&= \sum_{d}^{\text{act}} \left(\bar{h}_{da}^{\text{eff}} \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'b} E_{dc} | \Psi_m^{(0)} \rangle - \bar{h}_{cd}^{\text{eff}} \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'b} E_{ad} | \Psi_m^{(0)} \rangle + \bar{h}_{db}^{\text{eff}} \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'd} E_{ac} | \Psi_m^{(0)} \rangle \right) \\
&\quad + \sum_{def}^{\text{act}} \left(\langle de | fa \rangle \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'b} E_{df} E_{ec} | \Psi_m^{(0)} \rangle - \langle dc | fe \rangle \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'b} E_{df} E_{ae} | \Psi_m^{(0)} \rangle \right. \\
&\quad \left. + \langle de | fb \rangle \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'e} E_{df} E_{ac} | \Psi_m^{(0)} \rangle \right) + \sum_{de}^{\text{act}} \left(\langle cd | ea \rangle \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'b} E_{de} | \Psi_m^{(0)} \rangle - \tfrac{1}{2} \langle de | ea \rangle \right. \\
&\quad \left. \times \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'b} E_{dc} | \Psi_m^{(0)} \rangle - \tfrac{1}{2} \langle dc | ed \rangle \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'b} E_{ae} | \Psi_m^{(0)} \rangle + \tfrac{1}{2} \langle ed | db \rangle \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'e} E_{ac} | \Psi_m^{(0)} \rangle \right),
\end{aligned}
\tag{A22}
$$

Definition of the MRPT

$$\begin{aligned}\widetilde{B}_{a'b'c',a} &= \langle \Psi_m^{(0)} | E_{c'a'} E_{ib'} [H_v, E_{ai}] | \Psi_m^{(0)} \rangle \\ &= \sum_{c}^{\text{act}} h_{ca}^{\text{eff}} \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'c} | \Psi_m^{(0)} \rangle + \sum_{cef}^{\text{act}} \langle ac|ef \rangle \langle \Psi_m^{(0)} | E_{c'a'} \widetilde{E}_{b'e} E_{cf} | \Psi_m^{(0)} \rangle, \qquad \text{(A23)}\end{aligned}$$

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

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

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

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

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

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

⇒ 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

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

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

which in matrix form is

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

with

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

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

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

one can write

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

with

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

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

$\mathbf{K}$ 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;
- -ϵ_μ 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.

N-electron valence state perturbation theory

Table: Vertical ionization potentials (eV) for the N_2 molecule.

Method	Ionized states		
	$^2\Sigma_g^+$	$^2\Pi_u$	$^2\Sigma_u^+$
ANO basis, CAS 10/8			
Exp.	15.60	16.98	18.78
HF orb. energies	17.26	16.59	21.32
$V(-1)\varepsilon_\mu$	17.70	17.55	21.29
$V(-1)'\varepsilon_\mu$	16.28	17.17	19.00
ΔCASSCF	14.34	15.85	17.53
ΔNEVPT2	15.07	16.54	18.32

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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.

One can easily devise a SC-CASPT2 method, a “Strongly-Contracted” version of CASPT2 (or, in our nomenclature, of PC-CASPT2).

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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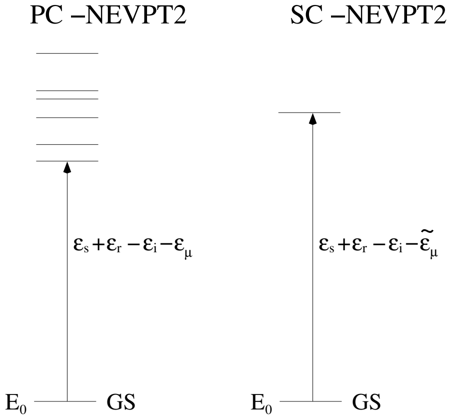
The Strongly-Contracted NEVPT approach

Zero order energies in SC-NEVPT2



Properties of NEVPT2

Properties of PC-NEVPT2 and SC-NEVPT2

- 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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The importance of the FOIS in PT methods

One can demonstrate this theorem: if two PT approaches (A and B) are based on the same $\hat{\mathcal{H}}'$ and F_B is obtained from F_A by an "integral dependent" contraction (as, for example, PC-NEVPT2 and SC-NEVPT2), then

$$E^{(2)}(A) \leq E^{(2)}(B)$$

This inequality is valid for each space involved in the contraction.

In the case of contraction of degenerate (under $\hat{\mathcal{H}}'$) functions the equality holds (MP2 in dets or MP2 with IDSC).

The importance of the FOIS in PT methods

One has for instance

$$E^{(2)}\left(\mathrm{PC}-\mathrm{NEVPT}\right) \leq E^{(2)}\left(\mathrm{SC}-\mathrm{NEVPT}\right)$$

$$E^{(2)}\left(\mathrm{EN}-\mathrm{det}\right) \leq E^{(2)}\left(\mathrm{EN}-\mathrm{IDSC}\right)$$

$$E^{(2)}\left(\mathrm{EN}-\mathrm{CSF}\right) \leq E^{(2)}\left(\mathrm{EN}-\mathrm{IDSC}\right)$$

A few example of applications of MRPT

An example of the intruder state problem

The ground state of the Cr atom is ^{7}S, corresponding to the [Ar]3d^{5}4s^1 electronic structure (six unpaired electrons).

In order to have a correct dissociation to the ground state of the atoms one has to consider for the dimer a CAS 12 electrons / 12 orbitals wave function.

The ground state of the molecule is $^1\Sigma_g^+$: the molecule is stable with one of the shortest M-M distance ($R_e = 1.679$ Å, formally a sextuple bond), but the dissociation energy is small ($D_e \simeq 1.5$ eV).

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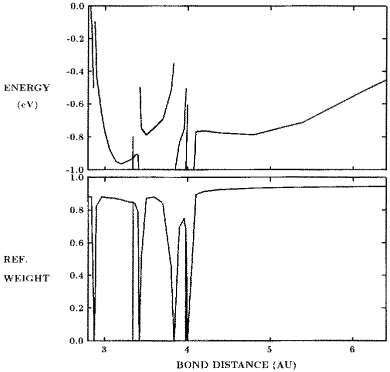


Fig. 2. The potential curve of Cr_2 obtained with CASPT2 above and the weight of the CASSCF wavefunction in the first-order wavefunction below. The basis set is of ANO type of size 6s5p4d3f and the active space is formed by 3d, 4s and $4\pi_u$ orbitals. Neither 3s, 3p correlation nor relativistic effects are included.

K. Andresson *et al Chem. Phys. Lett.*, **230**, *391*, 1994.

An example of the intruder state problem

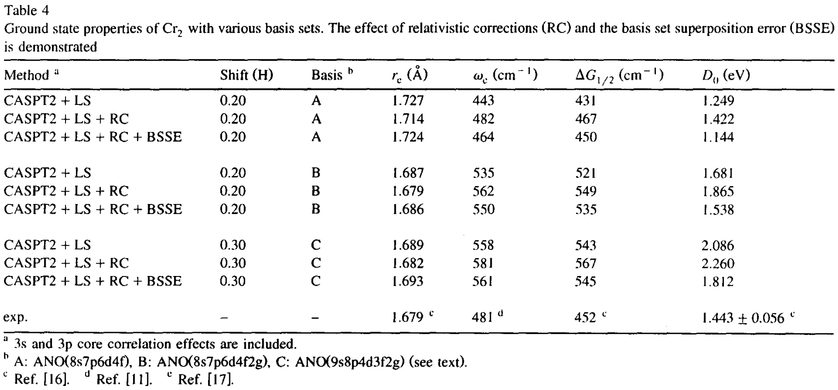


Table 4
Ground state properties of Cr_2 with various basis sets. The effect of relativistic corrections (RC) and the basis set superposition error (BSSE) is demonstrated

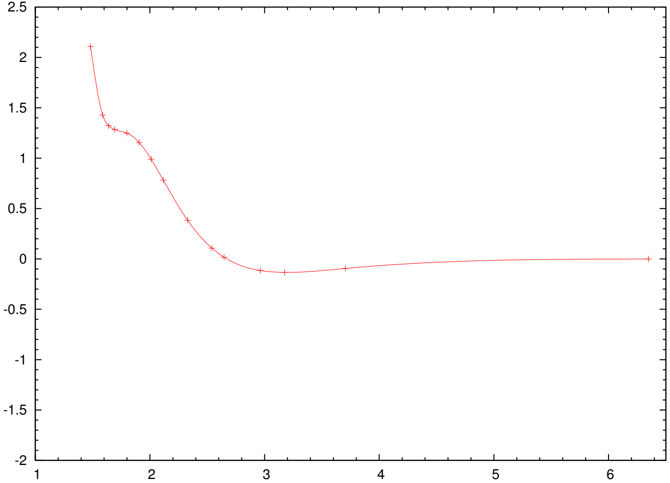
Method [a]	Shift (H)	Basis [b]	r_e (Å)	ω_e (cm^{-1})	$\Delta G_{1/2}$ (cm^{-1})	D_0 (eV)
CASPT2 + LS	0.20	A	1.727	443	431	1.249
CASPT2 + LS + RC	0.20	A	1.714	482	467	1.422
CASPT2 + LS + RC + BSSE	0.20	A	1.724	464	450	1.144
CASPT2 + LS	0.20	B	1.687	535	521	1.681
CASPT2 + LS + RC	0.20	B	1.679	562	549	1.865
CASPT2 + LS + RC + BSSE	0.20	B	1.686	550	535	1.538
CASPT2 + LS	0.30	C	1.689	558	543	2.086
CASPT2 + LS + RC	0.30	C	1.682	581	567	2.260
CASPT2 + LS + RC + BSSE	0.30	C	1.693	561	545	1.812
exp.	–	–	1.679 [c]	481 [d]	452 [c]	1.443 ± 0.056 [e]

[a] 3s and 3p core correlation effects are included.
[b] A: ANO(8s7p6d4f), B: ANO(8s7p6d4f2g), C: ANO(9s8p4d3f2g) (see text).
[c] Ref. [16]. [d] Ref. [11]. [e] Ref. [17].

B. O. Roos and K. Andresson, *Chem. Phys. Lett.*, **245**, *215*, 1995.

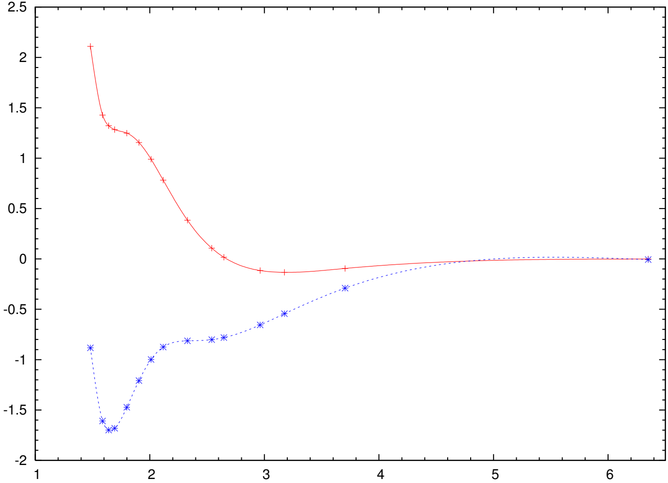
An example of the intruder state problem

The CASSCF potential energy curve



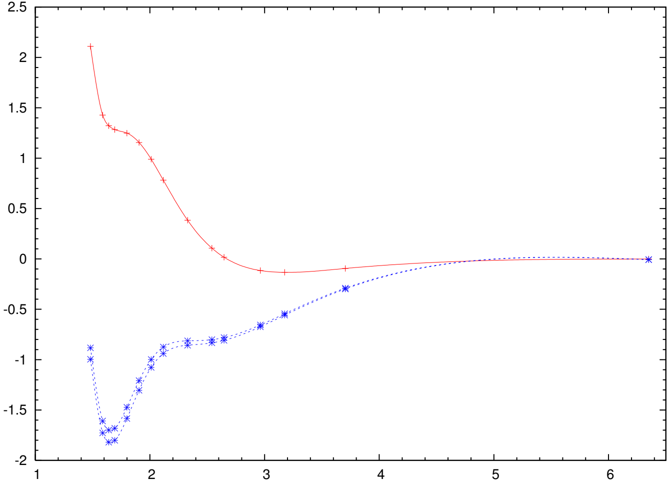
An example of the intruder state problem

The SC-NEVPT2 potential energy curve



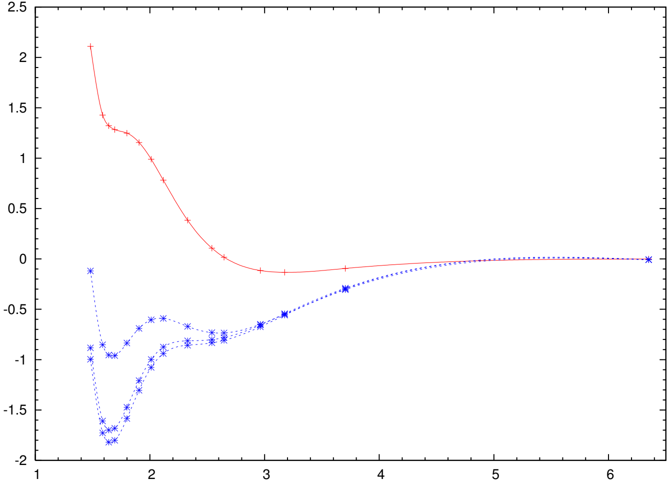
An example of the intruder state problem

The PC-NEVPT2 potential energy curve



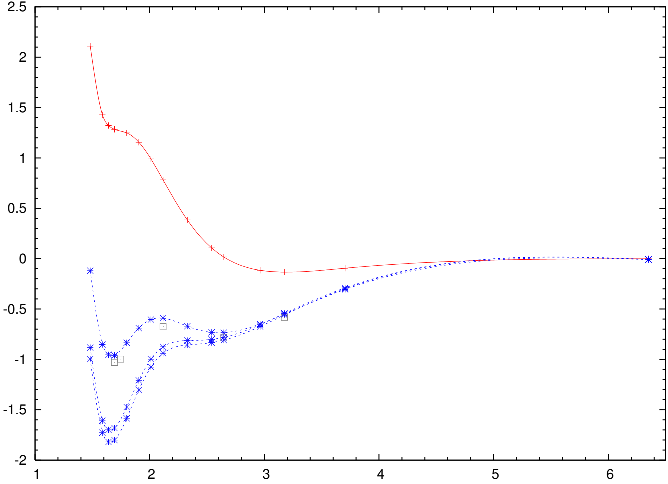
An example of the intruder state problem

The SC-NEVPT3 potential energy curve



An example of the intruder state problem

The PC-NEVPT3 potential energy curve



Spectroscopic constants for Cr_2

Characteristics of the calculated Cr_2 potential energy curve

Method	r_{in}(Å)	r_{out}(Å)	D_e (eV)	$\Delta G_{\frac{1}{2}}$(cm^{-1})
SC-NEVPT2	1.6551	-	1.702	579.7
PC-NEVPT2	1.6551	-	1.822	587.5
SC-NEVPT3	1.6711	2.6053	0.966	490.8
Exp.	1.679	-	$\begin{cases} 1.45 \\ 1.56 \end{cases}$	452

The V state of ethylene

The first singlet state of ethene is well described by the single $\pi \rightarrow \pi^*$ excitation.

From the experimental point of view: broad band with a maximum at 7.66 eV (partially overlapped with various Rydberg series).

Many theoretical studies have been published: in general, the computed vertical excitation energy is higher (> 8 eV) $\Rightarrow$ this transition is supposed to show a non-vertical behavior.

The best theoretical estimate

In 1999 Müller, Dallos and Lischka have obtained a value of 7.7 eV for the vertical excitation energy (with a great computational effort) and they argued that:

> “it is not necessary to refer to nonadiabatic effects in order to achieve agreement with the experimental data”

and that

> “this transition conforms to the Franck-Condon principle”.

The spatial extent of V state

Some information on the nature of this state can be obtained by its diffuseness ($\langle x^2 \rangle$).
The accepted value is in the range 17.0-18.0 a_0^2 ($\simeq$ 11 a_0^2 for the triplet and the ground states).
The key results for $\langle x^2 \rangle$ are:

- at the ROHF and CASSCF level $\langle x^2 \rangle$ is too large (larger than 40 a_0^2);
- introducing the dynamic correlation leads to a decrease of the computed values, but a marked dependence on the adopted strategy has been observed (the basis set, the strategy to build the CI space, the starting orbitals);
- very slow convergence of the computed values.

The accepted interpretative scheme

The common interpretative scheme is based on the following points:

- it is known that there is a Rydberg state higher in energy than the V state ($\simeq$ 1.2 eV);
- the dynamic correlation energy is larger for the valence V state than for the Rydberg state;
- if the dynamic correlation energy is not considered, the V and the Rydberg states are close in energy and a valence/Rydberg mixing can appear.

This scheme explains various characteristics of this state.

Open problems

However, there are open questions:

- in this scheme, a QDPT approach with two states should give good results, but QD-NEVPT2 and MS-CASPT2 give poor values for the vertical excitation energy and for $\langle x^2 \rangle$;
- using a basis set without diffuse functions (no Rydberg states) should give good results, but the CASSCF value for $\langle x^2 \rangle$ is 22.7 a_0^2 (CAS 2,2) and the NEVPT2 and NEVPT3 vertical excitation energy are higher than 8.1 eV (even for the CASSCF 12/12);
- what is the reason of the slow convergence observed in the MRCI approaches?

The ionic nature of the V state

The V state is qualitatively well described by:

$$^1\Psi_{B_{1u}} = \frac{\|\mathrm{core}\,\pi\bar{\pi}^*\| + \|\mathrm{core}\,\pi^*\bar{\pi}\|}{\sqrt{2}} \ ,$$

and introducing two “Orthogonal Atomic Orbitals” (OAOs):

$$p_a = \frac{\pi + \pi^*}{\sqrt{2}} \qquad p_b = \frac{\pi - \pi^*}{\sqrt{2}} \ ,$$

one has

$$^1\Psi_{B_{1u}} = \frac{\|\mathrm{core}\,p_a\bar{p}_a\| - \|\mathrm{core}\,p_b\bar{p}_b\|}{\sqrt{2}} \ .$$

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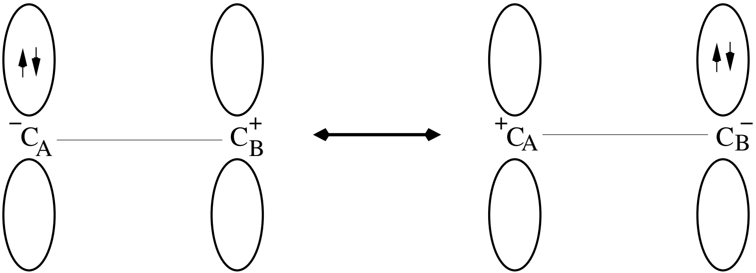
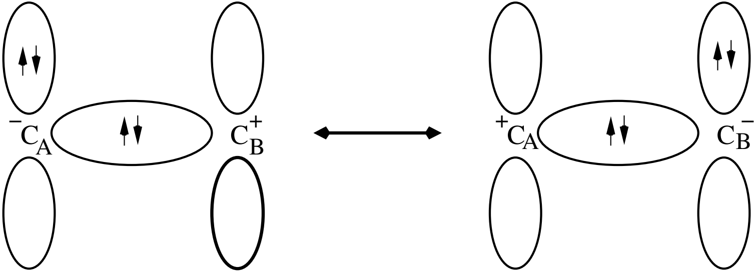


The V state is purely "ionic", the $\pi \rightarrow \pi^*$ triplet is neutral, while the ground state has a neutral (larger) and a ionic (smaller) component. This explains the origin of the different spatial extent of the V state with respect to the triplet and ground states.

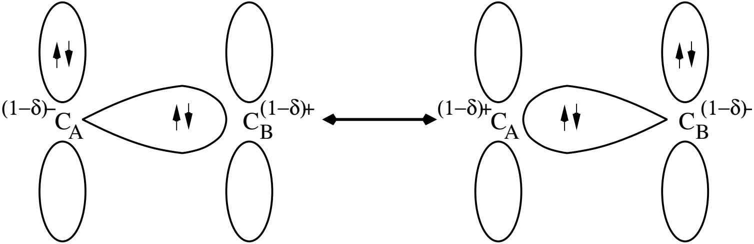
The dynamic σ polarization

One notes that the σ network is “statically” symmetric because the V state does not show charge separation.



The dynamic σ polarization

The σ skeleton is however “dynamically ” polarized on the two individual OVB structures. This effect is called dynamic σ polarization.



The dynamic σ polarization

By introducing two "σ" OAOs

$$\sigma_a = \frac{\sigma + \sigma^*}{\sqrt{2}} \qquad \sigma_b = \frac{\sigma - \sigma^*}{\sqrt{2}}\ ,$$

the V state

$$^1\Psi_{B_{1u}} = \frac{\|\mathrm{core}\,\sigma\bar{\sigma}\pi\bar{\pi}^*\| + \|\mathrm{core}\,\sigma\bar{\sigma}\pi^*\bar{\pi}\|}{\sqrt{2}}\ ,$$

is decomposed as

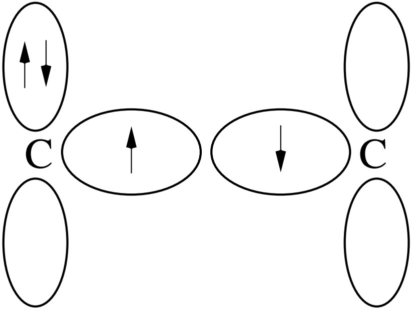
$$\begin{aligned} ^1\Psi_{B_{1u}} \quad = \quad & \frac{1}{2\sqrt{2}}\left(\|\sigma_a\bar{\sigma}_b p_a\bar{p}_a\| + \|\sigma_b\bar{\sigma}_a p_a\bar{p}_a\| + \right. \\ & -\|\sigma_a\bar{\sigma}_b p_b\bar{p}_b\| - \|\sigma_b\bar{\sigma}_a p_b\bar{p}_b\| + \|\sigma_a\bar{\sigma}_a p_a\bar{p}_a\| + \\ & \left. -\|\sigma_b\bar{\sigma}_b p_b\bar{p}_b\| + \|\sigma_b\bar{\sigma}_b p_a\bar{p}_a\| - \|\sigma_a\bar{\sigma}_a p_b\bar{p}_b\|\right) \end{aligned}$$

The dynamic σ polarization

The structures:

$$\|\sigma_a\bar{\sigma}_b p_a\bar{p}_a\|,\ \|\sigma_b\bar{\sigma}_a p_a\bar{p}_a\|,\ \|\sigma_a\bar{\sigma}_b p_b\bar{p}_b\|,\ \|\sigma_b\bar{\sigma}_a p_b\bar{p}_b\|$$

are ionic in the π manifold and neutral in the σ one.

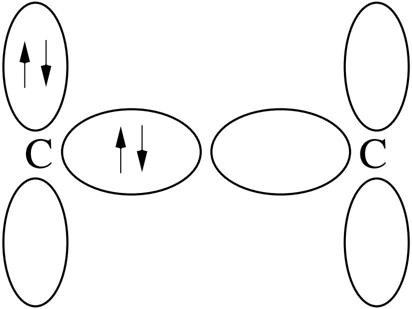


The dynamic σ polarization

The structures:

$$\|\sigma_a\bar{\sigma}_a p_a\bar{p}_a\|, \ \|\sigma_b\bar{\sigma}_b p_b\bar{p}_b\|$$

are ionic in both manifolds, (C^{-2}-C^{+2} and C^{+2}-C^{-2}).

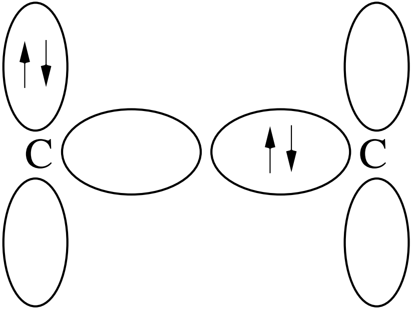


The dynamic σ polarization

The structures:

$$\|\sigma_b\bar{\sigma}_b p_a \bar{p}_a\|, \ \|\sigma_a\bar{\sigma}_a p_b \bar{p}_b\|$$

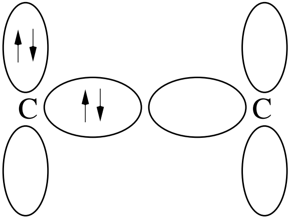
are ionic in both manifolds, but globally neutral.



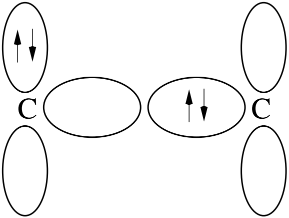
The dynamic σ polarization: the OVB description

All OVB structures have the same weight in the CASSCF 2/2 wf, but $\|\sigma_a\bar{\sigma}_a p_a\bar{p}_a\|$ and $\|\sigma_b\bar{\sigma}_b p_b\bar{p}_b\|$ are much higher in energy. To improve the wf

DECREASE



INCREASE



→ dynamic $\boldsymbol{\sigma}$ **polarization**.

The dynamic σ polarization: the MO description

By an OVB analysis of the double excitations, one can show that the dynamic σ polarization is described by the mixing of the $\|\sigma\bar{\sigma}\pi\bar{\pi}^*\|$ and $\|\sigma\bar{\sigma}\pi^*\bar{\pi}\|$, CASSCF 2/2 determinants with the
$\|\sigma\bar{\sigma}^*\pi\bar{\pi}\|$ and $\|\sigma^*\bar{\sigma}\pi\bar{\pi}\|$,
$\|\sigma\bar{\sigma}^*\pi^*\bar{\pi}^*\|$ and $\|\sigma^*\bar{\sigma}\pi^*\bar{\pi}^*\|$,
determinants.

Results with the ANO basis set

Following the previous points, the V state should be correctly described by:

- using a basis set without diffuse function (ANO C/H 5s4p2d1f /3s2p1d) ⇒ the Rydberg states are not (or very poorly) described ⇒ no valence/Rydberg mixing;
- MRPT2 (NEVPT2) calculation with a CAS (2,2) zero-order wave function ⇒ the dynamic σ polarization is described at the second order for the energy.

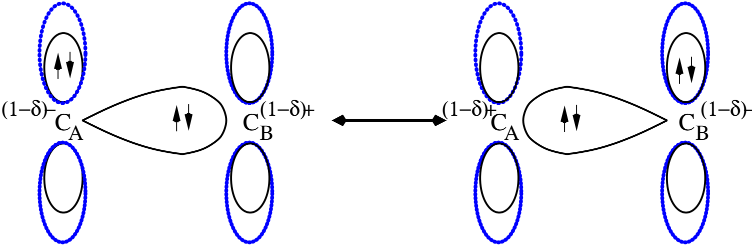
Results with the ANO basis set

CASSCF (2,2):	ΔE=8.46 eV, $\langle x^2\rangle$=22.7 a_0^2;
CASSCF (2,2) + NEVPT2:	ΔE=8.57 eV;
CASSCF (2,2) + NEVPT3:	ΔE=8.49 eV;
CASSCF (6,6):	ΔE=8.64 eV, $\langle x^2\rangle$=20.5 a_0^2;
CASSCF (6,6) + NEVPT2:	ΔE=8.20 eV;
CASSCF (12,12):	ΔE=8.69 eV, $\langle x^2\rangle$=18.5 a_0^2;
CASSCF (12,12) + NEVPT2:	ΔE=8.19 eV;
CASSCF (12,12) + NEVPT3:	ΔE=8.22 eV.

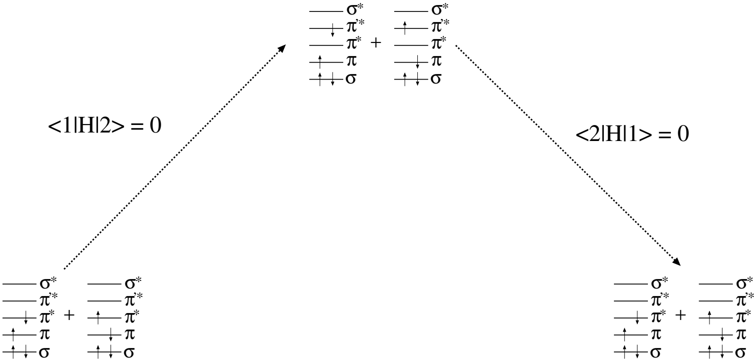
Very poor results: at CASSCF (12,12) + NEVPT3 level ΔE is 0.4 eV higher than the best theoretical estimate (7.7 eV).

The contraction of the p OAOs

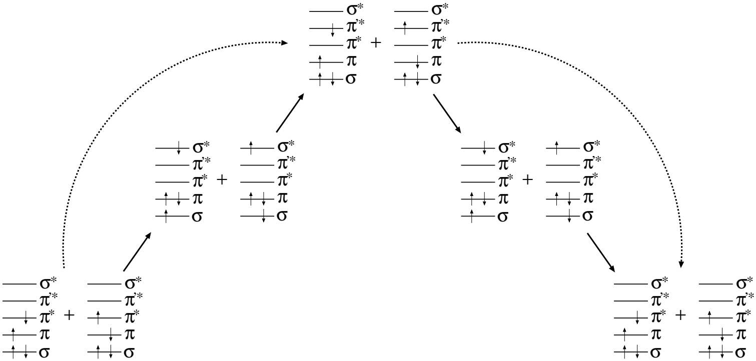
Actually, besides the dynamic σ polarization, another effect is important, that is the contraction of the p orbitals due to the reduction of ionicity originated by the dynamic σ polarization:



The contraction of the p OAOs



The contraction of the p OAOs



The contraction of the p OAOs

An approach to define contracted p OAOs (π and π^*).

Optimize the orbitals in a self-consistent field manner using an MR wave function describing the dynamic σ polarization.
RASSCF calculation with

- RAS 1 space: the C–C bond orbital (a_g) and the four SALCs of the C–H bond orbitals (a_g, b_{2u}, b_{1u} and b_{3g}) with 1 hole at maximum;
- RAS 2 space: π (b_{3u}) and π^* (b_{2g}) orbitals;
- RAS 3 space: b_{1u} C–C antibonding orbital and the four SALCs of the C–H antibonding orbitals (a_g, b_{2u}, b_{1u} and b_{3g}) with 1 particle at maximum.

Results with large basis sets

	$\langle x^2 \rangle$			Vertical excitation energy					
ANO+8Ry basis									
				SC-NEVPT2			PC-NEVPT2		
1	17.8			7.76			7.70		
2	18.6	97.7		7.76	9.00		7.70	8.98	
3	18.7	101.2	311.4	7.76	8.98	9.47	7.70	8.97	9.48
TZ-C basis									
				SC-NEVPT2			PC-NEVPT2		
1	17.6			7.73			7.67		
2	18.7	102.9		7.75	9.03		7.69	9.01	
3	18.7	102.9	197.4	7.70	8.95	9.49	7.65	8.89	9.48
aug-QZ basis									
				SC-NEVPT2			PC-NEVPT2		
1	17.7			7.74			7.67		
2	18.5	98.8		7.74	9.02		7.68	9.01	
3	18.4	102.4	225.6	7.74	9.00	9.52	7.68	8.99	9.52

Results with large basis sets

CASPT2 vertical excitation energies (eV):

Basis set	standard	G1	G2	G3
	CAS-CI (2,2)			
ANO+8Ry	8.05	7.58	7.57	7.58
TZ-C	7.73	7.55	7.55	7.55
aug-QZ	7.57	7.56	7.55	7.56
	CAS-CI (6,6)			
ANO+8Ry	6.38	7.64	7.70	7.71
TZ-C	7.50	7.75	7.80	7.80
aug-QZ	7.48	7.75	7.80	7.80

The V state can be correctly described, if the interference of the Rydberg states is removed, by an MRPT2 treatment based on a CAS-CI (2,2) wf, provided that the p orbitals are allowed to contract under the effect of the dynamic σ polarization.

Orbital relaxation induced by the dynamic correlation of the electrons

The contraction of the p OAOs triggered by the σ polarization is a particular case of an orbital relaxation induced by the dynamic correlation of the electrons.

In the Coupled Cluster language it is also called "Brueckner effect": the interference between the double excitations describing the dynamic σ polarization and the single excitations in the π manifold leads to large one body amplitudes.

A similar effect has been recently found also in the calculation of the magnetic coupling in binuclear systems where a correlation-induced delocalization of the magnetic orbitals on the ligands is found.

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