Proposal of a size-extensive uncontracted MR-PT2

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Single reference systems

Weakly correlated systems

- **Qualitatively** :
  - $|\Psi\rangle \approx |\mathbf{HF}\rangle$
  - Closed-shell grd. states
  - Large HOMO-LUMO gap
- **Dynamical correlation**
  - Short-range ($\approx$ cusp)
  - Long-range ($\approx$ VdW)
- e-e **correlation is weak** :
  - Perturbation
  - Coupled Cluster
- **Size extensivity**
  - Closed-shell systems
  - Large system

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Single-reference (SR) methods

- **Perturbative expansion** :
  - Rayleigh-Schroedinger
  - $|\Psi^{(0)}\rangle = |\mathbf{HF}\rangle$ (MPn)
  - Useful guide ! !
- **Important applications** :
  - Linked-Cluster Thm.
  - Size-extensivity
  - Coupled-Cluster
  - **CCSD(T)**
- **Nowadays developments** :
  - Bigger system (locality of e-e corr.)
  - Basis-set error (f_{12}, DFT-WFT)

Qualitative description of MR systems

- **Relatively few strongly correlated electrons**
  - Bond breakings
  - Magnetic systems
- **But rapidly large expansion for $|\Psi^{(0)}\rangle$!**

$$|\Psi^{(0)}\rangle = \sum_{\mathrm{I}=1}^{10^3-10^6} c_{\mathrm{I}} \, |\mathrm{I}\rangle$$

- **The ratios $\frac{c_{\mathrm{I}}}{c_{\mathrm{J}}}$ drive most of the physical properties**
- **Between the $|\mathrm{I}\rangle$ and $|\mathrm{J}\rangle$**
  - Large interactions
  - Energetic degeneracies
  - $\frac{\langle \mathrm{J}|H|\mathrm{I}\rangle}{\Delta E_{\mathrm{IJ}}} \gg 1$
- **Non perturbative**

Quantitative description : the physics beyond $|\Psi^{(0)}\rangle$

$$|\Psi\rangle = |\Psi^{(0)}\rangle \; + \; \sum_{\mu} \; c_{\mu} \; |\mu\rangle$$

- **In general** $|c_{\mu}| \ll 1 \Leftrightarrow$ **Perturbative**
- **Standard dynamical correlation** ($r_{12} \ll 1$, dispersion forces)
  - Week differential correlation effects

- **Differential correlation effects**
  - The $|\mathrm{I}\rangle$ are different
  - Correlation effects depend on $|\mathrm{I}\rangle$

- **Change** $|\Psi^{(0)}\rangle$
  - Affects the $\langle \mathrm{J}|H|\mathrm{I}\rangle$ and ΔE_{IJ}
  - Renormalization of H

- **Size consistency**
  - Able to break bonds
  - Correct scaling of the energy with N

The questions that must be answered for our MR methods

$$|\Psi\rangle = |\Psi^{(0)}\rangle + \sum_{\mu} c_{\mu} \, |\mu\rangle$$

- How do we **compute the energy** ?
- What **choice for** $|\Psi^{(0)}\rangle$?
- What **choice for the** $|\mu\rangle$?
- How do we **determine the** c_{μ} ?

Requirements for a good MR method

- **"Truly MR"**
  - Same status for all $|\mathrm{I}\rangle$ in $|\Psi^{(0)}\rangle$
- **Correct treatment of dynamic correlation**
  - No divergences
  - Accurate
- **Treat the coupling static / dynamical correlation**
  - Building an effective Hamiltonian $\tilde{H}$ within $\{|\mathrm{I}\rangle\}$
    $\tilde{H} = \sum_{\mathrm{I,J}} \left(H_{\mathrm{IJ}} + \tilde{O}_{\mathrm{IJ}}\right) |\mathrm{I}\rangle\langle \mathrm{J}|$
  - Diagonalize $\tilde{H}$ can change $|\Psi^{(0)}\rangle$
- **Size-consistent**
  - $E(A \cdots B) = E(A) + E(B)$
  - Correct even for open-shell sub-systems A and B
- **Lowest computational cost ..**

How to compute the energy …?

- **Variational calculations**
- **Projection technique**

To be variational or not, that is the question ...

Variational calculations : **CI calculations**

- **Average value** of H on $|\Psi\rangle$:

$$E_{\Psi}^{\text{Var}} = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\sum_{\text{IJ}} c_{\text{J}}\langle\text{J}|H|\text{I}\rangle c_{\text{I}}}{\langle\Psi|\Psi\rangle}$$

- **Upper bound to the FCI energy : ☺**
  - no divergences : can treat strong correlation
  - $E = \min_{\Psi} E_{\Psi}^{\text{Var}}$
  - easy to solve (Lanczos, Davidson)
- **Space is not closed : ☹**
  - always exist some $|\mu\rangle$ such that $\langle\mu|H|\Psi\rangle \neq 0$
  - linear parametrization are required
  - size consistency issues

To be variational or not, that is the question ...

Non-Variational calculations : **CC, PT, FCI-QMC**

- Suppose that $H|\Psi\rangle = E|\Psi\rangle$ **is valid** with :

$$|\Psi\rangle = |\Psi^{(0)}\rangle + \sum_{\mu \in \text{ FOIS}} c_\mu |\mu\rangle + |\mathcal{R}\rangle$$

  with FOIS $\Leftrightarrow \langle \Psi^{(0)}|H|\mu\rangle \neq 0$ and $\langle \Psi^{(0)}|H|\mathcal{R}\rangle = 0$

- Non variational $\Leftrightarrow$ **projection** on the **reference WF** $\langle \Psi^{(0)}|$:

$$\begin{aligned} E_\Psi^{\text{Proj}} &= \langle \Psi^{(0)}|H|\Psi\rangle \\ &= \underbrace{\langle \Psi^{(0)}|H|\Psi^{(0)}\rangle}_{E^{\text{Var}}_{\Psi^{(0)}}} + \sum_{\mu \in \text{ FOIS}} c_\mu \langle \Psi^{(0)}|H|\mu\rangle \end{aligned}$$

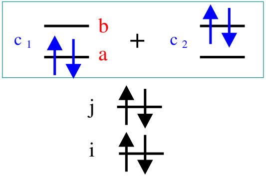
- **not necessary an upper bound** ☹
- **Variational for** $|\Psi^{(0)}\rangle$

  $\Rightarrow$ good for the strongly correlated electrons !
- Only needs the **coefficient of the FOIS** ☺
  - Much easier to close the space ☺
  - Size consistency ☺

The space in which we are going to work

- **The zeroth-order wave function : CAS-CI**
  - All determinants within n e and m orbitals

$$|\Psi^{(0)}\rangle = \sum_{\mathrm{I}} c_{\mathrm{I}} |\mathrm{I}\rangle$$



- **Size extensive ☺**
  - If active space is correctly chosen

$$E^{(0)}(A \cdots B) = E_A^{(0)} + E_B^{(0)}$$

  - Also works for open-shell systems A and B

How do we determine c_μ ?

Rayleigh-Schroedinger Perturbation Theory

- Assume a **partitioning of H**

$$H = H^{(0)} + V$$

- and **$H^{(0)}$ being diagonal on the $|\mu\rangle$ and $|\Psi^{(0)}\rangle$**

$$H^{(0)}|\Psi^{(0)}\rangle = E^{(0)}|\Psi^{(0)}\rangle$$
$$H^{(0)}|\mu\rangle = E^{(0)}_\mu|\mu\rangle$$

- Then the **coefficient c_μ at first order is simply** :

$$c^{(1)}_\mu = \frac{\langle\Psi^{(0)}|H|\mu\rangle}{E^{(0)} - E^{(0)}_\mu}$$

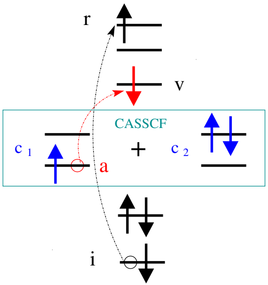
Choice of the $|\mu\rangle$

- **The $|\mu\rangle$: connected to $|\Psi^{(0)}\rangle$**

$$|\mu\rangle \text{ such that } \langle\mu|H|\Psi^{(0)}\rangle \neq 0$$

- **Singles and doubles exc. on top of $|\Psi^{(0)}\rangle$**

$$|\Psi\rangle = |\Psi^{(0)}\rangle + \underbrace{\sum_{\mu} c_\mu \, |\mu\rangle}_{\text{singles and doubles exc.}}$$



- **In SR methods $|\mu\rangle$ are Slater determinants**

$$|\mu\rangle = a_a^\dagger a_b^\dagger a_i a_j |\mathbf{HF}\rangle$$

- **In MR methods it is more complicated ..**

Choice of the $|\mu\rangle$ in MR method

- **Linear combinations** (Internally-contracted)

$$|\mu\rangle = a_a^\dagger a_b^\dagger a_i a_j \; |\Psi^{(0)}\rangle = \sum_{\mathrm{I}} \; c_{\mathrm{I}} \; a_a^\dagger a_b^\dagger a_i a_j \; |\mathrm{I}\rangle$$

- **Single determinants** (Externally-uncontracted)

$$|\mu\rangle = a_a^\dagger a_b^\dagger a_k a_j \; |\mathrm{I}\rangle \quad \forall \; |\mathrm{I}\rangle$$

- **Key questions** :
  - Size-extensivity
  - Changing $|\Psi^{(0)}\rangle \Leftrightarrow$ building $\tilde{H}$
  - Computational cost

Computational cost

The number of perturbers $|\mu\rangle$

- Using Linear combinations : number of excitations

$$(N_e * n_v)^2$$

  - Independent of the size of N_{I} ☺

- Using Single Slater determinants : much more !

$$N_{\mathrm{I}} * (N_e * n_v)^2$$

Be aware that N_{I} scales exponentially with the size of the CAS !

Better to work with Linear contractions regarding the computational cost

...

The size-extensivity

MRPT2 using Linear combinations

- **CASPT2**
  - Quite accurate (but empirical ..)
  - **Empirical parameters** (IP-EA shifts, imaginary shifts ...) ☹
  - $H^{(0)}$ is a generalized Fock operator
  - **One body operator** $\Leftrightarrow$ **Not size consistent** ☹
- **NEVPT2**
  - Quite accurate
  - **No empirical parameters** ☺
  - $H^{(0)}$ is hybrid : the Dyall Hamiltonian

$$\hat{H}_D = \hat{F}_{\text{core}} + \hat{F}_{\text{virtuals}} + \frac{1}{2} \sum_{a,b,c,d} (ab|cd) a_b^{\dagger} a_d^{\dagger} a_c a_a$$

  - **Two body operator in the active space + Linear combination $\Rightarrow$ size consistent ! !** ☺

The size-extensivity

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  - **Two body operator in the active space + Linear combination $\Rightarrow$ size consistent ! !** ☺

But really hard to build $\tilde{H}$ ... ☹

Building of $\tilde{H}$

MRPT2 using Slater determinants

- The **first order coefficient** of $|\mu\rangle$:

$$c_\mu^{(1)} = \frac{\langle \mu | H | \Psi^{(0)} \rangle}{E^{(0)} - E_\mu^{(0)}} = \sum_{\mathrm{I}} \; c_{\mathrm{I}} \; \frac{\langle \mu | H | \mathrm{I} \rangle}{E^{(0)} - E_\mu^{(0)}}$$

- The contribution of $|\mu\rangle$ to the **energy at second order** :

$$e_i^{(2)} = c_\mu^{(1)} \langle \Psi^{(0)} | H | \mu \rangle = \frac{\langle \Psi^{(0)} | H | \mu \rangle^2}{E^{(0)} - E_\mu^{(0)}}$$

- The **total contribution** $E^{(2)}$ is of course the sum over $e_\mu^{(2)}$:

$$E^{(2)} = \sum_\mu e_\mu^{(2)}$$

Building of $\tilde{H}$

MRPT2 using Slater determinants : the Shifted-B_k

- $E^{(2)}$ can be reinterpreted as an **expectation value** of a new operator :

$$E^{(2)} = \sum_{\mathrm{IJ}} c_{\mathrm{J}} \left(\sum_{\mu} \frac{\langle \mathrm{J}|H|\mu\rangle\langle\mu|H|\mathrm{I}\rangle}{E^{(0)} - E^{(0)}_{\mu}} \right) c_{\mathrm{I}}$$

$$= \langle \Psi^{(0)}|\tilde{O}|\Psi^{(0)}\rangle$$

$$\langle \mathrm{J}|\tilde{O}|\mathrm{I}\rangle = \sum_{\mu} \frac{\langle \mathrm{J}|H|\mu\rangle\langle\mu|H|\mathrm{I}\rangle}{E^{(0)} - E^{(0)}_{\mu}}$$

- And so the total dressed $\tilde{H}$ is simply :
(Shavitt, 1968 ; Davidson, 1983, Nakano, 1993)

$$\langle \mathrm{J}|\tilde{H}|\mathrm{I}\rangle = \langle \mathrm{J}|H|\mathrm{I}\rangle + \sum_{\mu} \frac{\langle \mathrm{J}|H|\mu\rangle\langle\mu|H|\mathrm{I}\rangle}{E^{(0)} - E^{(0)}_{\mu}}$$

A few remarks on $\tilde{H}$ ...

- **Differential correlation effects in Shifted-B_k**
  - Example : the diagonal terms of the dressed matrix

$$\tilde{O}_{\mathrm{II}} = \sum_{\mu} \frac{\left(H_{\mathrm{I}\mu}\right)^2}{E_0^{(0)} - E_\mu^{(0)}} < 0$$

  - Always stabilize the configurations $|\mathrm{I}\rangle$
  - $|\mathrm{I}\rangle$ = neutral $\dot{A} - \dot{A}$ / $|\mathrm{J}\rangle$ = ionic $A^+ - A^-$
  - particles are closer in A^- $\Leftrightarrow$ correlation effects are much larger
  - $\left|\tilde{O}_{\mathrm{II}}\right|$ larger for ionic forms
  - changes the energy differences within the $|\mathrm{I}\rangle$ and $|\mathrm{J}\rangle$
  - Diagonalization of $\tilde{H}$ will change $|\Psi^{(0)}\rangle$!
  - **Shifted-B_k got it !** ☺

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  - **Shifted-B_k got it !** ☺
- But ... **Size consistency errors ...**

Why a size consistency issue ....

The problem of Slater determinants ...

- The problem comes from **the energy denominators**

$$\Delta E_\mu^{(0)} = E^{(0)} - E_\mu^{(0)}$$

- Let's assume a Epstein-Nesbet H_0

$$E^{(0)} = \langle \Psi^{(0)} | H | \Psi^{(0)} \rangle$$
$$E_\mu^{(0)} = \langle \mu | H | \mu \rangle$$

- **This comparaison is unfair ! !**
  - $E^{(0)}$ contains correlation effects ☺
  - $E_\mu^{(0)}$ does not ! ☹
  - **Unlinked terms in** $E^{(0)} - E_\mu^{(0)}$
- Leads to **non separable correlated energies ...**

$$E(A \cdots B) \neq E(A) + E(B)$$

Some mumerical test of separability

TABLE – Total energies (a. u.) for the numerical separability check on $F_2 \ldots$ FH.

	CASSCF	Shifted-B_k
F_2	-198.746157368569	-199.122170300
FH	-100.031754985880	-100.289784498
F_2 + FH	-298.777912354448	-299.411954798
F_2 ... FH	-298.777912354443	-299.396752116
Absolute error (a.u.)	5.0×10^{-12}	1.5×10^{-2}
Relative error	1.7×10^{-14}	5.1×10^{-5}

Alternatives

- Proposal by **Lindgren** (QD-PT, 1974)

$$\Delta E_{\mu}^{(0)} = E_{\mathrm{I}}^{(0)} - E_{\mu}^{(0)} = \langle \mathrm{I}|H|\mathrm{I}\rangle - \langle \mu|H|\mu\rangle$$

  Intruder state problem $\Leftrightarrow$ $\Delta E_{\mu}^{(0)}$ too small ...
  $\Rightarrow$ **systematically diverges ! !** ☹

- Proposal by **Heully *et al.*** ($\mathrm{H_{int}}$, 1996)

$$\Delta E_{\mathrm{I}\mu}^{(0)} = \langle \mathrm{I}|H|\mathrm{I}\rangle - \langle \mu|H|\mu\rangle + \delta_{\mathrm{I}\mu}$$

  $\Rightarrow$ **Numerically instable** ☹

- Related proposal by **Mukherjee *et al.*** (Mk-MRPT2, 1999)
  $\Rightarrow$ **Numerically instable** ☹

- **Pathak*et al.*** (2017) : diagonalize **entirely** the Dyall $H^{(0)}$
  $\Rightarrow$ **Numerically stable and accurate** ☺
  $\Rightarrow$ **Computationally expensive** ☹

Proposal of a solution (Giner *et al.*, 2017) : key concept

- Each $|\mu\rangle$ might have many **parents** $|\mathrm{I}\rangle$

$$\langle\mu|H|\mathrm{I}\rangle \neq 0 \quad \Leftrightarrow \quad |\mathrm{I}\rangle \text{ is a parent of } |\mu\rangle$$

- As in Mk-MRPT or HMZ-MRPT, why not a $\mathbf{H^{(0)}}(\mathrm{I})$?

$$c_\mu = \sum_{\mathrm{I}} \frac{\langle \mathrm{I}|H|\mu\rangle}{\Delta E^{(0)}_{\mathrm{I}\mu}}$$

- $\langle\mu|H|\mathrm{I}\rangle \neq 0 \Leftrightarrow$ there is an excitation process $\hat{T}_{\mathrm{I}\mu}$ **linking** $|\mathrm{I}\rangle$ and

$$\langle\mu|H|\mathrm{I}\rangle \neq 0 \quad \Leftrightarrow \quad \exists \quad \hat{T}_{\mathrm{I}\mu}|\mathrm{I}\rangle = |\mu\rangle, \qquad \hat{T}_{\mathrm{I}mu} = a^\dagger_p a^\dagger_q a_n a_m \equiv \hat{T}^{pq}_{mn}$$

- We choose $\Delta E^{(0)}_{\mathrm{I}\mu} = f(m,n,p,q) = \Delta E^{pq}_{mn}$
- Same $\Delta E^{(0)}_{\mathrm{I}\mu}$ for many couples $(|\mathrm{I}\rangle, |\mu\rangle)$
- Definition of a **size extensive excitation energy** ΔE^{pq}_{mn} ?

Proposal of a solution : key concept

- $|\Psi^{(1)}\rangle$ can be built directly in 2 different ways :
  - By browsing the individual determinants $|\mu\rangle$

$$|\Psi^{(1)}\rangle = \sum_{\mu}\sum_{\mathrm{I}} c_{\mathrm{I}} \frac{\langle \mathrm{I}|H|\mu\rangle}{\Delta E^{(0)}_{\mathrm{I}\mu}} |\mu\rangle$$

  - By browsing the individual **excitations** $\hat{T}$

$$|\Psi^{(1)}\rangle = \sum_{T} \frac{1}{\Delta E^{(0)}_{\hat{T}}} \sum_{\mathrm{I}} c_{\mathrm{I}} \langle \mathrm{I}|H\hat{T}|\mathrm{I}\rangle \quad \hat{T}|\mathrm{I}\rangle$$
$$= \sum_{T} \frac{1}{\Delta E^{(0)}_{\hat{T}}} |\Psi(\hat{T})\rangle$$

- A possible definition for $\Delta E^{(0)}(\hat{T})$ could be :

$$\Delta E^{(0)}(\hat{T}) = \langle \Psi^{(0)}|H|\Psi^{(0)}\rangle - \frac{\langle \Psi(\hat{T})|\, H \,|\Psi(\hat{T})\rangle}{\langle \Psi(\hat{T})||\Psi(\hat{T})\rangle}$$

Proposal of a solution : actual equations

- $\Delta E^{(0)}(\hat{T})$ is free of unlinked terms :
  - $\langle \Psi^{(0)} | H | \Psi^{(0)} \rangle$ contains correlation effects
  - $\frac{\langle \Psi(\hat{T}) | \, H \, | \Psi(\hat{T}) \rangle}{\langle \Psi(\hat{T}) || \Psi(\hat{T}) \rangle}$ also !
- Nevertheless ... expensive quantities !
- Solution use the Dyall Hamiltonian ! $H \rightarrow H^D$

$$H^D = F_{core} + F_{virt} + \underbrace{\frac{1}{2} \sum_{abcd} V_{ab}^{cd} a_c^\dagger a_d^\dagger a_b a_a}_{\text{active space}}$$

- Still **size extensive** !
  correlation effects $\leftrightarrow$ CAS and H^D is two-body within the CAS

Proposal of a solution : actual equations

- Decomposition of the $\Delta E^{(0)}(\hat{T})$

$$\hat{T} = \hat{T}_{act} + \hat{T}_{core/virt}$$

$$\Delta E^{(0)}(\hat{T}) = \Delta E^{(0)}(\hat{T}_{core/virt}) + \Delta E^{(0)}(\hat{T}_{act})$$

- $\Delta E^{(0)}(\hat{T}_{core/virt})$ is determined by a generalized Fock operator

$$\Delta E^{(0)}(\hat{T}_{core/virt}) = \sum_{h \in \{\text{holes}\}} \epsilon_h - \sum_{p \in \{\text{particles}\}} \epsilon_p$$

- $\Delta E^{(0)}(\hat{T}_{core/virt})$ is determined by a generalized Fock operator
- $\Delta E^{(0)}(\hat{T}_{act})$ is an approx. to the energetical cost of the change of N_e in the active space

$$\Delta E^{(0)}(\hat{T}_{act}) = \langle \Psi^{(0)} | H^D | \Psi^{(0)} \rangle - \frac{\langle \Psi(\hat{T}_{act}) | \, H^D \, | \Psi(\hat{T}_{act}) \rangle}{\langle \Psi(\hat{T}_{act}) || \Psi(\hat{T}_{act}) \rangle}$$

Some examples : the 1h2p excitation class

- Double excitations $\hat{T}_{ia}^{rv}$

$$\hat{T}_{ia}^{rv} = a_r^\dagger a_v^\dagger a_a a_i$$

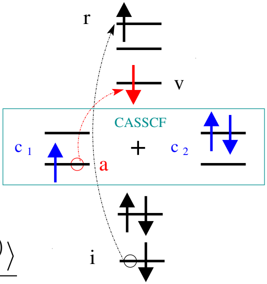
- Excitation energy ΔE_{ia}^{rv}

$$\Delta E_{ia}^{rv} = \Delta E^{(0)}(a_r^\dagger a_v^\dagger a_i) + \Delta E^{(0)}(a_a)$$

$$\Delta E^{(0)}(a_r^\dagger a_v^\dagger a_i) = \epsilon_i - \epsilon_r - \epsilon_v$$

$$\Delta E^{(0)}(a_a) = \langle \Psi^{(0)} | H^D | \Psi^{(0)} \rangle - \frac{\langle \Psi^{(0)} | a_a^\dagger \, H^D \, a_a | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | a_a^\dagger a_a | \Psi^{(0)} \rangle}$$

- $\Delta E^{(0)}(a_a)$ is the IP of the active orbital a



Some other examples

- Electronic affinities

$$\Delta E^{(0)}(a_a^\dagger) = \langle \Psi^{(0)} | H^D | \Psi^{(0)} \rangle - \frac{\langle \Psi^{(0)} | a_a \, H^D \, a_a^\dagger | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | a_a a_a^\dagger | \Psi^{(0)} \rangle}$$

- Double electronic affinities

$$\Delta E^{(0)}(a_b^\dagger a_a^\dagger) = \langle \Psi^{(0)} | H^D | \Psi^{(0)} \rangle - \frac{\langle \Psi^{(0)} | a_b a_a \, H^D \, a_b^\dagger a_a^\dagger | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | a_b a_a a_b^\dagger a_a^\dagger | \Psi^{(0)} \rangle}$$

- And so on ...

Important points

- Size extensive provided that active orbitals are localized
- Good definition of the excitation process $\Leftrightarrow$ no intruder state problem
  - Exemple in CASPT2 for a singly occupied MO

$$\epsilon_a = -\frac{1}{2}(IP_a + EA_a)$$

  - IP_a and EA_a have opposite signs in general ...
  - ϵ_a can be close to 0 ...
- No empirical parameters

At the end of the day ...

- The dressing hamiltonian is :

$$\langle \mathrm{J}|\tilde{O}|\mathrm{I}\rangle = \sum_{\mu} \frac{\langle \mathrm{J}|H|\mu\rangle\langle\mu|H|\mathrm{I}\rangle}{\Delta E^{(0)}(\hat{T}_{\mathrm{I}i})} \ , \qquad \hat{T}_{\mathrm{I}\mu}\ |\mathrm{I}\rangle = |\mu\rangle$$

- The second order correction to the energy is :

$$E^{(2)} = \langle \Psi^{(0)}|\tilde{O}|\Psi^{(0)}\rangle$$

- The dressed Hamiltonian $\tilde{H}$ is :

$$\langle \mathrm{J}|\tilde{H}|\mathrm{I}\rangle = \langle \mathrm{J}|H|\mathrm{I}\rangle + \langle \mathrm{J}|\tilde{O}|\mathrm{I}\rangle$$

- The corresponding dressed energy and wave function are obtained by :

$$\tilde{H}\ |\tilde{\Psi}\rangle \ = \ \tilde{\mathcal{E}}\ |\tilde{\Psi}\rangle$$

Some mumerical proof of separability

TABLE – Total energies (a. u.) for the numerical separability check on $F_2 \ldots FH$.

	CASSCF	$E^{(2)}$
F_2	-198.746157368569	-0.337009510134933
FH	-100.031754985880	-0.230422886638017
F_2 + FH	-298.777912354448	-0.5674323967729
F_2 ... FH	-298.777912354443	-0.5674323967730
Absolute error (a.u.)	5.0×10^{-12}	8.6×10^{-14}
Relative error	1.7×10^{-14}	1.5×10^{-13}

Some mumerical proof of separability

TABLE – Total energies (a. u.) for the numerical separability check on $F_2 \ldots FH$.

	CASSCF	$\tilde{\mathcal{E}}$
F_2	-198.746157368569	-199.085305155169
FH	-100.031754985880	-100.262424667296
F_2 + FH	-298.777912354448	-299.347729822466
F_2 ... FH	-298.777912354443	-299.347729822462
Absolute error (a.u.)	5.0×10^{-12}	4.4×10^{-12}
Relative error	1.7×10^{-14}	1.4×10^{-14}

Some examples of calculations

TABLE – Non parallelism error with respect to FCI (cc-pVDZ)

	H_2O	C_2H_4	N_2
CASSCF	40.9	26.2	18.2
SC-NEVPT2	2.4	2.4	2.3
PC-NEVPT2	2.5	3.2	1.3
CASPT2 (IPEA=0.)	5.5	6.0	9.6
CASPT2 (IPEA=0.25)	3.0	4.5	4.4
Shifted Bk	30.8	7.6	5.9
$E^{(2)}$	3.0	3.7	3.4
$\tilde{\mathcal{E}}$	4.8	4.0	4.5

Comparable accuracy with respect to NEVPT2, often better than CASPT2, no empirical parameter

Working on the computational cost ..

Main source of computational cost

- Keep in mind that we are interested in systems where
  - $10^3 < N_\mathrm{I} < 10^8$
  - $30 < n_e < 500$
  - $100 < n_{orb} < 1500$
- CPU time : the browsing of $|\mu\rangle$
  - The number scales as $N_\mathrm{I} \times (n_e \times n_{orb})^2$
  - For each $|\mu\rangle$ needs to compute $\langle \Psi^{(0)} | H | \mu \rangle \Rightarrow$ scales as N_I

$$\approx (N_\mathrm{I})^2 \times (n_e \times n_{orb})^2$$

- Memory : storing of the $\tilde{O}$

$$\approx (N_\mathrm{I})^2$$

Working on the computational cost ..

- But the $\Delta E^{(0)}_{\mathrm{I}\mu} = f(m,n,p,q)$ do not depend on $|\mathrm{I}\rangle$

$$E^{(2)} = \sum_{\mu} \sum_{\mathrm{I},\,\mathrm{J}} c_{\mathrm{I}}\, c_{\mathrm{J}} \frac{\langle \mathrm{J}|H|\mu\rangle\langle\mu|H|\mathrm{I}\rangle}{\Delta E^{(0)}_{\mathrm{I}\mu}} \;, \qquad |\mu\rangle = \hat{T}_{\mathrm{I}\mu}|\mathrm{I}\rangle = a^{\dagger}_{n} a^{\dagger}_{m} a_{p} a_{q} |\mathrm{I}\rangle$$

$$= \sum_{\mathrm{I},\,\mathrm{J}} c_{\mathrm{I}}\, c_{\mathrm{J}} \sum_{e,f,g,h,i,j,k,l,m,n,p,q} \frac{V^{lk}_{ij}\; V^{ef}_{gh}}{\Delta E^{(0)}(a^{\dagger}_{n} a^{\dagger}_{m} a_{p} a_{q})} \langle \mathrm{J}| a^{\dagger}_{e} a^{\dagger}_{f} a_{g} a_{h}\; a^{\dagger}_{l} a^{\dagger}_{k} a_{j} a_{i}\; a^{\dagger}_{n} a^{\dagger}_{m} a_{p} a_{q} |\mathrm{I}\rangle$$

- Defines **effective second quantized operator** !

Some examples : the 1h2p excitation class

- Double excitations $\hat{T}_{ia}^{rv}$

$$\hat{T}_{ia}^{rv} = a_r^\dagger a_v^\dagger a_a a_i$$

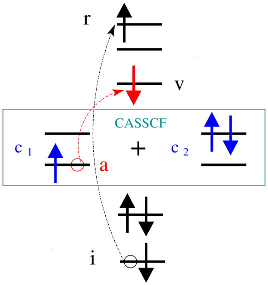
- 1h2p excitations can be mapped into an effective Fock operator in the active space :

$$\tilde{F}_{ab} \approx \sum_{i,t,v} \frac{V_{ia}^{tv} V_{ib}^{tv}}{\epsilon_i - \epsilon_v - \epsilon_t + \Delta E(a_a)}$$

$$E_{1h2p}^{(2)} = \sum_{ab} F_{ba} \langle \Psi^{(0)} | a_b^\dagger a_a | \Psi^{(0)} \rangle$$

- 2p excitations can be mapped into an effective coulomb operator in the active space :

$$\tilde{W}_{ab}^{cd} \approx \sum_{t,v} \frac{V_{cd}^{tv} V_{ab}^{tv}}{-\epsilon_v - \epsilon_t + \Delta E(a_a a_b)}$$



Working on the computational cost

The effective operator formalism

- "Simple" contraction of integrals and energy denominators

- Avoids any browsing of the $|\mu\rangle$
- No prefactor in N_{I}
  $\Rightarrow$ Large saving in CPU time ! ☺

- Reduce to effective many-body operators within the active space
  $\Rightarrow$ Large saving in Memory ! ☺

Current developments and summary

What we briefly saw ...

- Advantages of both worlds
  - Internal contractions : size extensivity + CPU time
  - Slater determinants : dressing of H
    $\Rightarrow$ bonus : weak storage !
- Requires flexible formalisms (and codes ! !)

Futur : Deal with very large CAS

- Use CIPSI to converge large CAS (typically 30 e in 30 orbitals)
  - Treat explicitely a part of dynamical correlation
- Reduce CPU time to its minimum to treat large CAS
  - Express all contributions as **effective operators**
  - Express all expectation values ($\Delta E(a_a)$, $\Delta E(a_b^\dagger a_a)$, ...) as functions of RDMs
- Coupling with range-separated DFT
  - Faster convergence with respect to single particle basis