The Post Hartree Fock methods for the electronic Schrödinger equation

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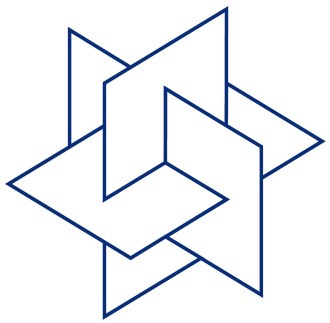

DFG Research Center MATHEON
Mathematics for key technologies

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Overview:

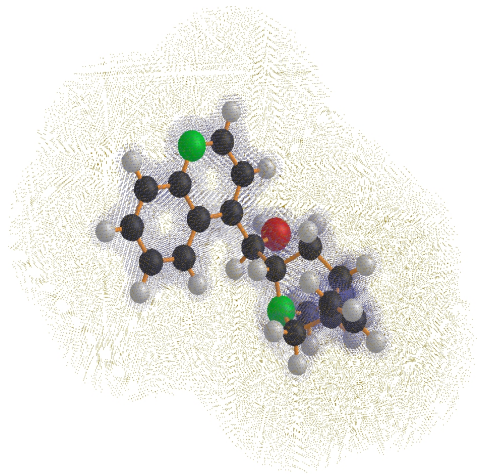
I. Introduction - the electronic Schrödinger equation

II. The full CI method method and second qunatization

IIII. The restricted CI and Coupled Cluster method

I.

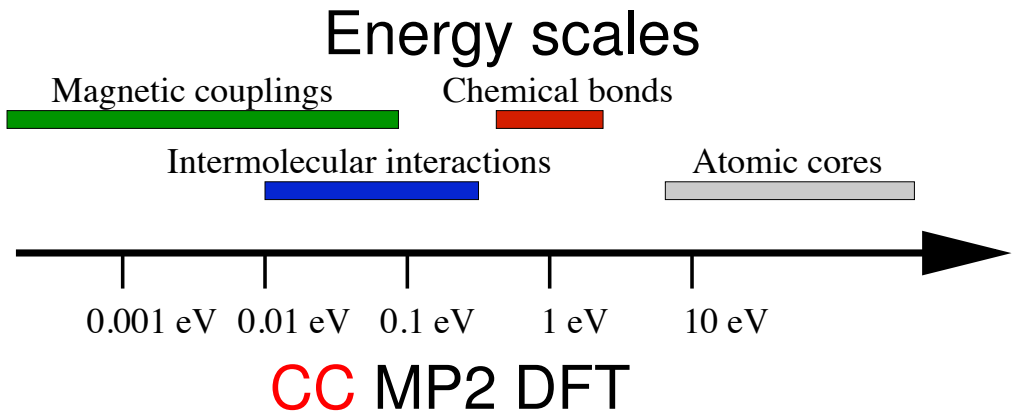
Introduction



The stationary electronic Schrödinger equation (variational formulation)

Find antisymmetric wave function $\Psi \in \mathbb{H}^1$ and eigenvalue $E \in \mathbb{R}$ such that

$$\langle \Phi, \widehat{H}\Psi \rangle = E \ \langle \Phi, \Psi \rangle \quad \text{for all} \ \ \Phi \in \mathbb{H}^1.$$



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- the wave function Ψ is antisymmetric (Pauli principle),

$$\begin{aligned} & \Psi((x_1, s_1), \ldots, (x_i, s_i), \ldots, (x_j, s_j), \ldots, (x_N, s_N)) \\ = \quad & -\Psi((x_1, s_1), \ldots, (x_j, s_j), \ldots, (x_i, s_i), \ldots, (x_N, s_N)). \end{aligned}$$

- N-fermion space:

$$\Psi \ \in \ \mathbb{L}_2 \ := \ \bigwedge_{i=1}^{N} L_2\big(\mathbb{R}^3 \times \{\pm\frac{1}{2}\}\big)$$

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▷

$$\hat{H}: \ \ H^1(\mathbb{R}^{3N} \times \{\pm\frac{1}{2}\}^N) \ \rightarrow \ H^{-1}(\mathbb{R}^{3N} \times \{\pm\frac{1}{2}\}^N)$$

is the weak Hamiltonian, defined via

$$\hat{H} \ = \ -\frac{1}{2}\sum_{i=1}^{N}\hat{\Delta}_i \ + \ \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{1}{|x_i - x_j|} \ - \ \sum_{i=1}^{N}\sum_{k=1}^{M}\frac{Z_k}{|x_i - R_k|}.$$

▷ $\mathbb{H}^1 := H^1(\mathbb{R}^{3N} \times \{\pm\frac{1}{2}\}^N) \cap \mathbb{L}_2$

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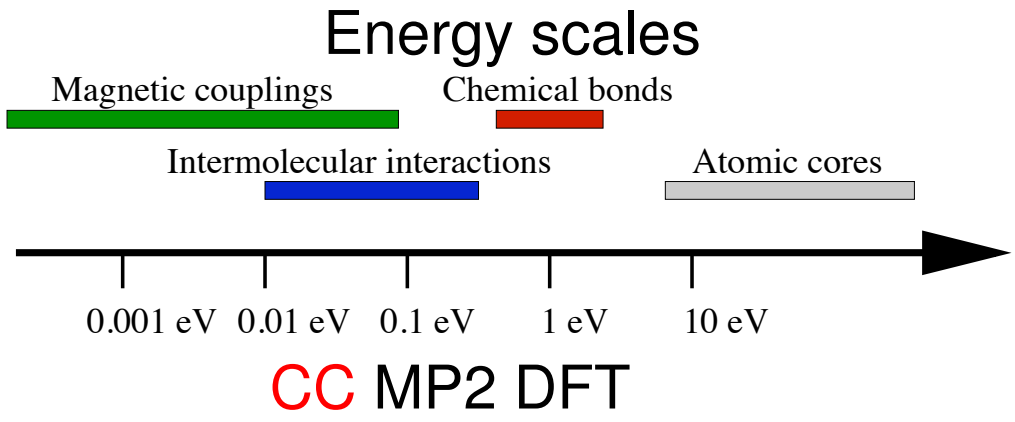
The stationary electronic Schrödinger equation (variational formulation), ground state problem

Find antisymmetric wave function $\Psi \in \mathbb{H}^1$ and eigenvalue $E^* \in \mathbb{R}$ such that

$$\langle \Phi, \widehat{H}\Psi \rangle = E^* \langle \Phi, \Psi \rangle \quad \text{for all} \quad \Phi \in \mathbb{H}^1.$$

and such that E^* is the lowest eigenvalue of $\widehat{H}$.



The "full CI" scheme

Starting point: One-particle (ortho-normal) basis

$$B = \{\psi_1, \ldots, \psi_d\},$$

$\rightsquigarrow$ antisymmetric tensor basis (Slater determinants)

$$\mathbb{B}_d \;=\; \{\Psi_\mu \;=\; \Psi[p_1, .., p_N],\; 1 \leq p_i < p_{i+1} \leq d\},$$

$$\Psi[p_1, .., p_N] \;:=\; \bigwedge_{i=1}^{N} \psi_{p_i} = \frac{1}{\sqrt{N!}} \det\big(\psi_{p_i}(x_j, s_j)\big)_{i,j=1}^{N}.$$

Galerkin (full CI) solution Ψ_d, solving

$$\langle \Psi_\mu, H\Psi_d \rangle \;=\; E\,\langle \Psi_\mu, \Psi_d \rangle \quad \text{for all } \Psi_\mu \in \mathbb{B}_d.$$

(an extremely high-dimensional problem, mostly unsolvable in practice)

Slater-Condon Rules

See e.g. Szabo &Ostlund (83)
Single particle operators:

1) $\Psi^1 = \Psi^2$	$\Psi^1 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	
	$\Psi^2 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	$\langle\Psi, h\Psi\rangle = \sum_{l=1}^{N}\langle l\|h\|l\rangle$
2) $\Psi^2 = T_j^a\Psi^1$	$\Psi^1 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	
	$\Psi^2 = \Psi[\ldots,\nu_i,\nu_a,\ldots]$	$\langle\Psi^2, h\Psi^1\rangle = \langle a\|h\|j\rangle$
3) $\Psi^1 = T_{i,j}^{a,b}\Psi^2$	$\Psi^1 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	
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Proof: Leibniz formula +

$$\langle \Psi^2, h_l \Psi^1 \rangle = \int \varphi_a(\mathbf{x}_l)(h_l \varphi_i)(\mathbf{x}_l) \cdot \int \varphi_b(\mathbf{x}_k)\varphi_j(\mathbf{x}_k) \int \varphi_m(\mathbf{x}_1)\varphi_m(\mathbf{x}_1) \ldots = \langle a|h|l \rangle \delta_{b,j}$$

Slater-Condon Rules

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	$\Psi^2 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	$\langle\Psi^1, G\Psi^1\rangle = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle ij\|\|ij\rangle$
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$$\langle\Psi^2, G_{l,k}\Psi^1\rangle = \int\int \varphi_a(\mathbf{x}_l)\varphi_b(\mathbf{x}_k)G_{l,k}[\varphi_i(\mathbf{x}_l)\varphi_j(\mathbf{x}_k) - \varphi_i(\mathbf{x}_k)\varphi_j(\mathbf{x}_l)]\cdot\int \varphi_m(\mathbf{x}_1)\varphi_m(\mathbf{x}_1)\cdot\ldots$$

$$\langle a,b|i,j\rangle := \sum_{s,s'=\pm\frac{1}{2}}\int\int \frac{\varphi_a^*(\mathbf{x},s)\varphi_b^*(\mathbf{x}',s')\varphi_i(\mathbf{x},s)\varphi_j(\mathbf{x}',s')}{|\mathbf{x}-\mathbf{x}'|}d\mathbf{x}d\mathbf{x}'$$

$$\langle a,b||i,j\rangle := \langle a,b|i,j\rangle - \langle a,b|j,i\rangle.$$

Ansatz space and reference determinant

Hartree-Fock (or DFT) calculation

gives

(a) a (quite good) rank-1 approximation of eigenfunction Ψ,

$$\Psi_0 = \Psi[1,..,N] := \bigwedge_{i=1}^{N} \psi_i(x_i, s_i) = \frac{1}{\sqrt{N!}} \det\left(\psi_{p_i}(x_j, s_j)\right)_{i,j=1}^{N}$$

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(b) one-particle basis B of $L^2_d(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$,

$$B = \{ \underbrace{\psi_1, \ldots, \psi_N}_{\text{occupied orbitals}} , \underbrace{\psi_{N+1}, \ldots, \psi_d}_{\text{virtual orbitals}} \}$$

occ $\perp$ virt in $\mathbb{L}^2$ and w.r.t. inner product $F \sim H^1$

$\rightsquigarrow$ tensor basis $\mathbb{B}_d = \{\Psi[p_1,..,p_N],\ 1 \le p_i < p_{i+1} \le d\}$ of $\mathbb{L}^2_d$

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$\Downarrow$

Post-Hartree-Fock calculation

$\swarrow$ $\qquad$ $\searrow$

CI (Galerkin) calculation $\qquad$ Coupled Cluster calculation

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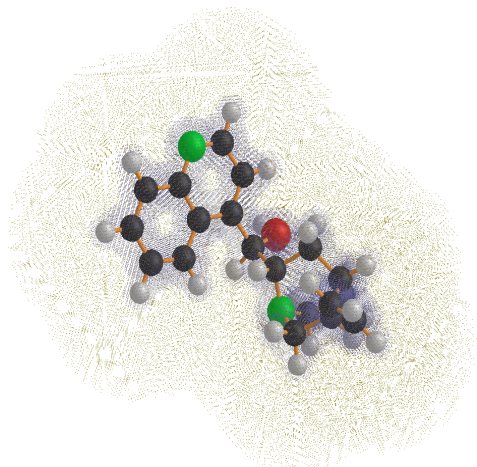
~~CI (Galerkin) calculation~~ $\qquad$ Coupled Cluster calculation

Accuracy, size consistency,...

I.

Full CI method and second quantization



Finite Dimensional Configuration Space

Consider a finite orthonormal basis $\{\varphi_i : i = 1, \ldots, d\}$

$$\mathcal{X}_d := \text{span}\,\{\varphi_i : i = 1, \ldots, d\} \subset \mathcal{X} = H^1(\mathbb{R}^3, \pm\frac{1}{2})$$

ONB of antisymmetric functions by *Slater determinants*

$$\Psi_{SL}[k_1, \ldots, k_N](\mathbf{x}_1, s_1; \ldots; \mathbf{x}_N, s_N) \quad := \quad \frac{1}{\sqrt{N!}} \det(\varphi_{k_i}(\mathbf{x}_j, s_j))_{i,j=1}^N$$

$$\mathcal{V}_{FCI}^N = \bigwedge_{i=1}^{N} \mathcal{X}_d = \text{span}\{\Psi_{SL} = \Psi[k_1, \ldots, k_N] : k_1 < \ldots < k_N \leq d\} \subset \mathcal{V}$$

Curse of dimensionality $\dim \mathcal{V}_{FCI}^N = \begin{pmatrix} d \\ N \end{pmatrix}$!

For a finite dimensional operator $H : \mathcal{V}_{FCI}^N =: \mathcal{V} \to \mathcal{V}'$

$$H\Psi = \sum_{\nu',\nu} \langle \Psi_{\nu'}, H\Psi_\nu \rangle c_\nu \Psi_{\nu'} = \sum_{\nu'} (\mathbf{Hc})_{\nu'} \Psi_{\nu'}.$$

(Finite dimensional) Fock space

Let $\Psi_\mu := \Psi_{SL}[\varphi_{k_1}, \ldots, \varphi_{k_N}] = \Psi[k_1, \ldots, k_N]$ basis Slater det.
Labeling of indices $\mu \in \mathcal{I}$ by an binary string of length d

$$\text{e.g.: } \mu \quad = \quad (0,0,1,1,0,\ldots) =: \sum_{i=0}^{d-1} \mu_i 2^i \ , \ \mu_i = 0,1 \ ,$$

- $\mu_i = 1$ means φ_i is (occupied) in $\Psi[\ldots]$.
- $\mu_i = 0$ means φ_i is absend (not occupied) in $\Psi[\ldots]$.

(discrete) Fock space $\mathcal{F}_d$ is of $\dim \mathcal{F}_d = 2^d$, $(\mathbb{K} := \mathbb{C}, \mathbb{R})$

$$\mathcal{F}_d := \bigoplus_{N=0}^{d} \mathcal{V}_{FCI}^N = \{\Psi : \Psi = \sum_\mu c_\mu \Psi_\mu\}$$

$$\mathcal{F}_d \simeq \{\mathbf{c} : \mu \mapsto \mathbf{c}(\mu_0, \ldots, \mu_{d-1}) = c_\mu \in \mathbb{K} \ , \ \mu_i = 0,1 \ \} = \bigotimes_{i=1}^{d} \mathbb{K}^2$$

This is a basis depent formalism $\Rightarrow$: Second Quantization

Discrete annihilation and creation operators

$$A := \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \; A^T = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

In order to obtain the correct phase factor, we define

$$S := \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

and the discrete annihilation operator

$$\boxed{a_p \simeq \mathbf{a}_p := S \otimes \ldots \otimes S \otimes A_{(p)} \otimes I \otimes \ldots \otimes I}$$

where $A_{(p)}$ means that A appears on the p-th position in the product.
The creation operator

$$\boxed{a_p^\dagger \simeq \mathbf{a}_p^T := S \otimes \ldots \otimes S \otimes A_{(p)}^T \otimes I \otimes \ldots \otimes I}$$

Schrödinger Operator in (discrete-finite) Fock Spaces

One and two electron integrals

$$h_q^p := \langle \varphi_q, (\frac{-1}{2}\Delta - V_{core})\varphi_p \rangle \ , \quad p, q, r, s = 1, \ldots, d \ ,$$

$$g_{r,s}^{p,q} := \frac{1}{2}\langle \varphi_r(\mathbf{x}, s_1)\varphi_s(\mathbf{y}, s_2), \frac{\varphi_p(\mathbf{x}, s_1)\varphi_q(\mathbf{y}, s_2)}{|\mathbf{x} - \mathbf{y}|} \rangle$$

Theorem (Slater -Condon, (HRS (2010)))

The Galerkin matrix $\mathbf{H}$ *of electronic Schrödinger Hamiltonian is sparse and can be represented by*

$$\mathbf{H} = \sum_{p,q=1}^{d} h_p^q \mathbf{a}_p^T \mathbf{a}_q + \sum_{p,q,r,s=1}^{d} g_{r,s}^{p,q} \mathbf{a}_r^T \mathbf{a}_s^T \mathbf{a}_p \mathbf{a}_q \ .$$

Modification, treating spin explicitely, (spin symmetries and other symmetries could be enfored (Legeza et al.))

$$\mathcal{F}_d = \bigotimes_{i=1}^{d} \mathbb{K}^4 \ , \quad (\mathbb{K} = \mathbb{C}, \mathbb{R})$$

Particle number operator and Schrödinger eqn.

$$P := \sum_{p=1}^{d} a_p^\dagger a_p \ , \quad \simeq \quad \mathbf{P} := \sum_{p=1}^{d} \mathbf{a}_p^T \mathbf{a}_p \ .$$

The space of N-particle states is given by

$$\mathcal{V}^N := \{\mathbf{c} \in \bigotimes_{i=1}^{d} \mathbb{K}^2 : \mathbf{Pc} = N\mathbf{c}\} \ .$$

Variational formulation of the Schrödinger equation

$$\boxed{\mathbf{c} = (c(\mu)) = \operatorname{argmin}\{\langle \mathbf{Hc}, \mathbf{c}\rangle : \langle \mathbf{c}, \mathbf{c}\rangle = 1 \ , \ \mathbf{Pc} - N\mathbf{c} = 0\} \ .}$$

Remark: Further approximation of $\mathbf{c}(\mu_1, \ldots, \mu_d) \in \otimes_{i=1}^{d} \mathbb{C}^2$ by tensor product approximation, e.g. Matrix product states (TT tensor trains) or tree ensor network states (hierarchical tensors) by DMRG (density matrix renormalization group) algorithm.

Optimizing the Configuration Space - MCSFC

Find a finite orthonormal basis $\{\varphi_i : i = 1, \ldots, d\}$ for $d < K$

$\mathcal{X}_d := \text{span}\,\{\varphi_i : i = 1, \ldots, d\} \subset \mathcal{X}_K := \text{span}\,\{\varphi_i : i = 1, \ldots, K\}$.

Iteratively: Given FCI solution $\mathbf{c}$

$$(\varphi_i)_{i=1,\ldots,K} := \text{argmin}\,\langle \mathbf{H}(\mathbf{U})\mathbf{c}, \mathbf{c}\rangle : U_{i,j} : i \leq d, k \leq K\}$$

where

$$\mathbf{H}(\mathbf{U}) = \sum_{p,q=1}^{d} h_p^q(\mathbf{U})\mathbf{a}_p^T\mathbf{a}_q + \sum_{p,q,r,s=1}^{d} g_{r,s}^{p,q}(\mathbf{U})\mathbf{a}_r^T\mathbf{a}_s^T\mathbf{a}_p\mathbf{a}_q \ .$$

$$h_p^q(\mathbf{U}) = \sum_{k_1,k_2} h_{k_1}^{k_2} U_{p,k_1} U_{q,k_2} \ , \ g_{r,s}^{p,q}(\mathbf{U}) = \sum_{k_1,k_2} h_{j_1,j_2}^{k_1,k_2} U_{p,j_1} U_{q,j_2} U_{p,k_1} U_{q,k_2}$$

$$\Rightarrow \ \varphi_i^{new} := \sum_{k=1}^{K} U_{i,k}\varphi_k \ , \ i = 1, \ldots, K$$

$\Rightarrow$ compute new FCI solution.

Multi-configurational self-consistent field (MCSCF)

Existence (for $K \to \infty$): G. Friesecke, M. Lewin

Second Quantization - in Function Spaces

Second quantization: annihilation operators:

$$a_j \Psi[j, 1, \ldots, N] := \Psi[1, \ldots, N]$$

and $:= 0$ if j not apparent in $\Psi[\ldots]$.
The adjoint of a_b is a creation operator v

$$a_b^\dagger \Psi[1, \ldots, N] = \Psi[b, 1, \ldots, N] = (-1)^N \Psi[1, \ldots, N, b]$$

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Theorem (Slater-Condon Rules)

$H : \mathcal{V} \to \mathcal{V}$ resp. $H : \mathcal{V}_{FCI} \to \mathcal{V}_{FCI}$ reads as

$$\boxed{\mathcal{H} = \mathcal{F} + \mathcal{U} = \sum_{p,q} f_r^p a_p^\dagger a_r + \sum_{p,q,r,s} u_{rs}^{pq} a_q^\dagger a_p^\dagger a_r a_s}$$

Excitation operators

Single excitation operator , Let $\Psi_0 = \Psi[1, \ldots, N]$ be a reference determinant then e.g.

$$\boxed{X_1^k \Psi_0 := a_k^\dagger a_1 \Psi_0}$$

$$(-1)^{-p} \Psi_1^k = \Psi[k, 2, \ldots, N] = X_1^k \Psi_0 = X_j^k \Psi[1, \ldots, \ldots, N] = a_k^\dagger a_1 \Psi_0$$

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higher excitation operators

$$X_\mu := X_{l_1,\ldots,l_k}^{b_1,\ldots,b_k} = \prod_{i=1}^{k} X_{l_i}^{b_i} \quad , \quad 1 \leq l_i < l_{i+1} \leq N \, , \; N < b_i < b_{i+1} \, .$$

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Single excitation operator , Let $\Psi_0 = \Psi[1, \ldots, N]$ be a reference determinant then e.g.

$$\boxed{X_1^k \Psi_0 := a_k^\dagger a_1 \Psi_0}$$

$$(-1)^{-p}\Psi_1^k = \Psi[k, 2, \ldots, N] = X_1^k \Psi_0 = X_j^k \Psi[1, \ldots, \ldots, N] = a_k^\dagger a_1 \Psi_0$$

higher excitation operators

$$X_\mu := X_{l_1,\ldots,l_k}^{b_1,\ldots,b_k} = \prod_{i=1}^{k} X_{l_i}^{b_i} \quad , \quad 1 \leq l_i < l_{i+1} \leq N \, , \; N < b_i < b_{i+1} \, .$$

A CI solution $\Psi = c_0\Psi_0 + \sum_{\mu\in\mathcal{J}} c_\mu \Psi_\mu$ can be written by

$$\Psi = \left(c_0 + \sum_{\mu\in\mathcal{J}} c_\mu X_\mu \right) \Psi_0 \, , \; c_0, c_\mu \in \mathbb{R} \, .$$

Intermediate normalization: $c_0 := 1$ i.e. $\langle \Psi . \Psi_0 \rangle = 1$

Single + double excitations

Discrete one-particle basis $B = \{\chi_1, \ldots, \chi_N, \chi_{N+1}, \ldots, \chi_{D+1}\}$.

Write (full Galerkin, "full CI") solution Ψ_{FCI} as

$$\begin{aligned}\Psi_{\text{FCI}} &= (I + T_{\text{full CI}})\Psi_0 \\ &= \Psi_0 + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} \Psi_0 + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2} \Psi_0 \\ &\quad + \ldots + \sum_{i_1,..,i_N,a_1,..,a_N} s_{i_1,..,i_N}^{a_1,..,a_N} X_{i_1,..,i_N}^{a_1,..,a_N} \Psi_0.\end{aligned}$$

Truncation according to excitation level, e.g.:

Is exact FCI for $N = 2$, e.g H_2 molecule or He atom

- CISD (single/double):

$$\begin{aligned}\Phi_{\text{CISD}} &= (I + T_{\text{SD}})\Psi_0 \\ &= (I + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2})\Psi_0\end{aligned}$$

Single + double excitations

Discrete one-particle basis $B = \{\chi_1, \ldots, \chi_N, \chi_{N+1}, \ldots, \chi_{D+1}\}$.

Write (full Galerkin, "full CI") solution Ψ_{FCI} as

$$\begin{aligned}
\Psi_{\text{FCI}} &= (I + T_{\text{full CI}})\Psi_0 \\
&= \Psi_0 + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} \Psi_0 + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2} \Psi_0 \\
&\quad + \ldots + \sum_{i_1,..,i_N,a_1,..,a_N} s_{i_1,..,i_N}^{a_1,..,a_N} X_{i_1,..,i_N}^{a_1,..,a_N} \Psi_0 .
\end{aligned}$$

Truncation according to excitation level, e.g.:

- CCSD (single/double):

$$\begin{aligned}
\Phi_{\text{CCSD}} &= e^{T_{\text{SD}}} \Psi_0 \\
&= \exp(I + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2}) \Psi_0
\end{aligned}$$

Single + double excitations

Discrete one-particle basis $B = \{\chi_1, \ldots, \chi_N, \chi_{N+1}, \ldots, \chi_{D+1}\}$.

Write (full Galerkin, "full CI") solution Ψ_{FCI} as

$$\begin{aligned}
\Psi_{\text{FCI}} &= (I + T_{\text{full CI}})\Psi_0 \\
&= \Psi_0 + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} \Psi_0 + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2} \Psi_0 \\
&\quad + \ldots + \sum_{i_1,..,i_N,a_1,..,a_N} s_{i_1,..,i_N}^{a_1,..,a_N} X_{i_1,..,i_N}^{a_1,..,a_N} \Psi_0 .
\end{aligned}$$

Truncation according to excitation level, e.g.:

- CCSD (single/double):

$$\begin{aligned}
\Phi_{\text{CCSD}} &= e^{T_{\text{SD}}} \Psi_0 \\
&= \exp(I + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2}) \Psi_0
\end{aligned}$$

Single + double excitations

Discrete one-particle basis $B = \{\chi_1, \ldots, \chi_N, \chi_{N+1}, \ldots, \chi_{D+1}\}$.

Write (full Galerkin, "full CI") solution Ψ_{FCI} as

$$\begin{aligned}\Psi_{\text{FCI}} &= (I + T_{\text{full CI}})\Psi_0 \\ &= \Psi_0 + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} \Psi_0 + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2} \Psi_0 \\ &\quad + \ldots + \sum_{i_1,..,i_N,a_1,..,a_N} s_{i_1,..,i_N}^{a_1,..,a_N} X_{i_1,..,i_N}^{a_1,..,a_N} \Psi_0.\end{aligned}$$

Truncation according to excitation level, e.g.:

- CCSD (single/double):

$$\begin{aligned}\Phi_{\text{CCSD}} &= e^{T_{\text{SD}}} \Psi_0 \\ &= \exp(I + \sum_{i_1,a_1} s_{i_1}^{a_1} X_{i_1}^{a_1} + \sum_{i_1,i_2,a_1,a_2} s_{i_1,i_2}^{a_1,a_2} X_{i_1,i_2}^{a_1,a_2}) \Psi_0\end{aligned}$$

Coupled Cluster Method - Exponential-ansatz

Theorem (S. 06)

Let Ψ_0 be a reference Slater determinant, e.g. $\Psi_0 = \Psi_{HF}$ and $\Psi \in \mathcal{V}_{FCI}$, $\mathcal{V}$, satisfying

$$\langle \Psi, \Psi_0 \rangle = 1 \quad \textit{intermediate normalization} \ .$$

Then there exists an excitation operator
(T_1 - single-, T_2 - double- , . . . excitation operators)

$$T = \sum_{i=1}^{N} T_i = \sum_{\mu \in \mathcal{J}} t_\mu X_\mu \quad \textit{such that}$$

$$\boxed{\Psi = e^T \Psi_0} = \Pi_\mu (I + t_\mu X_\mu) \Psi_0 \ .$$

Key observations: for analytic functions :

$$f(T) = \sum_{k=0}^{N} a_k T^k \text{ since } \ [X_\mu, X_\nu] = 0 \ , \ X_\mu^2 = 0 \ , \ T^N = 0 \ .$$

Ground State Energy in Intermediate normalization

$H = F + U$, F Fock operator (single particle operator $F\Psi_0 = \sum_{i=1}^{N} \epsilon_i \Psi_0$), $U = H - F$ fluctuation potential,
Let $\Psi_h = \Psi_0 + \Phi_h \approx \Psi$, $\Phi_h = Q_h \phi_h \perp \Psi_0$ an approximated ground state normalized by

$$\langle \Psi_h, \Psi_h \rangle = 1 \;\Rightarrow\; E_h = \langle \Psi_h, H\Psi_0 \rangle \approx E_{HF} + E_{cor}$$

Iterative solution: $\Psi_h^0 := \Psi_0$, residuum: $r_0 = (H - E_{HF})\Psi_0$
MP II : $\Phi_h = \Phi_D \perp \Psi_0$, a 1st iteration step with

$$\Psi_D := \Psi_h^1 = \Psi_0 + \Phi_h = \Psi_0 + Q_h (F - \sum \epsilon_i)^{-1} Q_h U \Psi_0 = \Psi_{MPII}$$

1st iteration step of Jacobi Davidson - close to: CEPA (0) - linearized CC:

$$\Phi_h = (Q_h(H_{CID} - E_{HF})Q_h)^{-1} r_0 = (Q_h(H - E_{HF})Q_h)^{-1} U\Phi_D \perp \Psi_0$$

ground state with RPA (random phase approximation) is equivalent to a simplified CCD (Sorensen & Scuceria & al.)