The Coupled Cluster method for the electronic Schrödinger equation

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Overview:

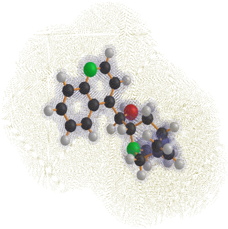
I. Introduction - the electronic Schrödinger equation

II. The (projected) Coupled Cluster method

IIII. The continuous Coupled Cluster method

I.

Introduction

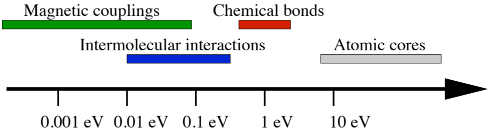


The stationary electronic Schrödinger equation (variational formulation)

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

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

Energy scales ($1E_h \approx 27,2114eV$ Hartree)



CC MP2 DFT

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

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

- N-fermion space:

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

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

  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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▷

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

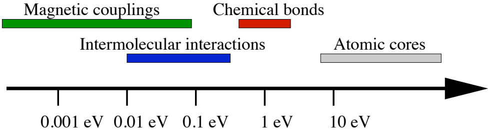
The stationary electronic Schrödinger equation (variational formulation), ground state problem

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

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

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

Energy scales ($1 E_h \approx 27,2114 eV$ Hartree)



CC MP2 DFT

II.

The (projected) Coupled Cluster method

$$|\Psi_d\rangle \quad = \quad e^{T_d}|\Psi_0\rangle$$

Projected CC = approximation to fixed Galerkin/"full CI" scheme

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

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

$\leadsto$ antisymmetric tensor basis (Slater determinants)

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

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

CC is approximation of 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)

Ansatz space and reference determinant

Hartree-Fock (or DFT) calculation

gives

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

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

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

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

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 $\mathbb{L}_d^2$

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$\Downarrow$

Post-Hartree-Fock calculation

$\swarrow$ $\searrow$

CI (Galerkin) calculation — Coupled Cluster calculation

Ansatz space and reference determinant

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~~CI (Galerkin) calculation~~ Coupled Cluster calculation

Accuracy, size consistency,...

Reformulation of the Galerkin ansatz

- One-particle basis $B = \{\underbrace{\psi_1, ..., \psi_N}_{\text{occupied}}, \underbrace{\psi_{N+1}, ..., \psi_d}_{\text{virtual}}\}$,

  tensor basis $\mathbb{B}_d = \{\Psi[p_1, .., p_N],\ 1 \leq p_1 < ... < p_N \leq d\}$.

- Replacement of occupied by virtual orbitals in reference Ψ_0,

  $\Psi[1, \ldots, i_1, .., i_k, .., N] \overset{\text{“excitation”}}{\longrightarrow} \Psi_\mu = \Psi[1, ., \not{i_1}, .., \not{i_k}, .., a_1, .., a_k]$,

  gives $$\mathbb{B}_d = \{\Psi_0\} \cup \{\Psi_\mu \mid \mu \in \mathcal{I}\}.$$

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- Reformulation: Excitation operator $X^{a_1,..,a_k}_{i_1,..,i_k} : \mathbb{L}^2_d \to \mathbb{L}^2_d$

$$X^{a_1,..,a_k}_{i_1,..,i_k} \Psi[p_1, .., p_N] = \begin{cases} \Psi[\not{i_1}, .., \not{i_k}, a_1, .., a_k .., p_i, ..] \\ \quad \text{if} \quad i_1, .., i_k \in \operatorname{ind}(\Psi) \\ \quad \text{and} \quad a_1, .., a_k \notin \operatorname{ind}(\Psi) \\ 0 \ \ \text{elsewise} \end{cases}$$

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With this, $\Psi[i_1, .., , i_{N-k}, a_1, .., a_k] = X^{a_1,...,a_k}_{i_1,...,i_k} \Psi_0$.

Reformulation of the Galerkin ansatz

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With this, $\mathbb{B}_d = \{\Psi_0\} \cup \{X_\mu \Psi_0 \mid \mu \in \mathcal{I}_d\}$.

Cluster operator/Coupled-Cluster ansatz

Choosing $\mathcal{I}_d \subset \mathcal{I}$:

- Galerkin solution Ψ_d is expressed by excitations,

$$\Psi_d = \Psi_0 \oplus_{\mathbb{L}^2,F} \Psi_d^* = \Psi_0 + \sum_{\mu \in \mathcal{I}_d} s_\mu \Psi_\mu$$

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- Reformulated Galerkin ansatz:

Linear Parametrisation for $\Psi_d = \Psi_0 + \Psi_d^*$:

Find cluster operator $S = S(s_d) = \sum_{\mu \in \mathcal{I}_d} s_\mu X_\mu$ such that

$$\Psi_d = (I + S(s_d))\Psi_0,$$

$$\boxed{\langle \Phi_d, \widehat{H}(I + S(s_d))\Psi_0 \rangle \;=\; E^* \langle \Phi_d, (I + S(s_d))\Psi_0 \rangle \quad \forall \;\; \Phi_d \in \mathbb{B}_d.}$$

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- ▷ Coupled-Cluster-Ansatz:

Nonlinear Parametrisation for $\Psi_d = \Psi_0 + \Psi_d^*$:

Find cluster operator $T = T(t_d) = \sum_{\mu \in \mathcal{I}_d} t_\mu X_\mu$ such that

$$\Psi_d = e^{T(t_d)}\Psi_0,$$

$$\boxed{\langle \Phi_d, \widehat{H} e^{T(t_d)} \Psi_0 \rangle \;=\; E^* \langle \Phi_d, e^{T(t_d)} \Psi_0 \rangle \quad \forall \;\; \Phi_d \in \mathbb{B}_d.}$$

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- <u>Coupled-Cluster-Ansatz:</u>

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$$\boxed{\langle \Phi_d, e^{-T(t_d)}\widehat{H}e^{T(t_d)}\Psi_0\rangle \;=\; E^*\langle \Phi_d, \Psi_0\rangle = 0 \quad \forall \;\; \Phi_d \in \mathbb{B}_d \backslash \{\Psi_0\}.}$$

$$E^* = \langle \Psi_0, e^{-T(t_d)}\widehat{H}e^{T(t_d)}\Psi_0\rangle$$

Coupled Cluster - Exponential-ansatz - Full CC

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 :

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

CC Energy and Projected Coupled Cluster Method

Let $\Psi \in \mathcal{V}_{FCI}$ satisfying $\mathcal{H}\Psi := \mathcal{H}_h\Psi = E_0\Psi$, then, due to the Slater Condon rules and $\langle \Psi, \Psi_0 \rangle = 1$

$$E^* = \langle \Psi_0, H\Psi \rangle = \langle \Psi_0, H(I + T_1 + T_2 + \frac{1}{2}T_1^2)\Psi_0 \rangle$$

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Variants: (probably better but not computable)

- unitary CC:

$$\Psi = e^{\frac{1}{2}(T - T^*)}\Psi_0 \ ,$$

- variational CC

$$\Psi = argmin\{\langle e^T\psi_0, He^T\Psi_0 \rangle\}$$

- general CC (Noijens conjecture)

$$\Psi = e^{\left(\sum_{i,j,p,q,r,s} t_i^j a_i^\dagger a_j + t_{r,s}^{p,q} a_r^\dagger a_p^\dagger a_q a_s\right)}\Psi_0 \ .$$

Projected Coupled Cluster Method

Let $T = \sum_{k=1}^{l} T_k = \sum_{\mu \in \mathcal{J}_h} t_\mu X_\mu$, $0 \neq \mu \in \mathcal{J}_h \subset \mathcal{J}$ using

$$0 = \langle \Psi_0, (H - E)\Psi \rangle = \langle \Psi_0, (H - E(\mathbf{t}_h) e^{T(\mathbf{t}_h)} \Psi_0 \rangle$$

The unlinked projected Coupled Cluster formulation

$$0 = \langle \Psi_\mu, (H - E(\mathbf{t}_h)) e^{T(\mathbf{t}_h)} \Psi_0 \rangle =: g_\mu(\mathbf{t}) \ , \ \ \mathbf{t} = (t_\nu)_{\nu \in \mathcal{J}_h} \ , \ \mu, \nu \in \mathcal{J}_h$$

The linked projected Coupled Cluster formulation consists in

$$0 = \langle \Psi_\mu, e^{-T} H e^{T} \Psi_0 \rangle =: f_\mu(\mathbf{t}) \ , \ \ \mathbf{t} = (t_\nu)_{\nu \in \mathcal{J}_h} \ , \ \mu, \nu \in \mathcal{J}_h$$

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These are $L = \sharp \mathcal{J}_h << \mathcal{N}$ nonlinear equations for L unknown excitation amplitudes t_μ.

Theorem

The CC Method is size consistent!:

$$H_{AB} = H_A + H_B \ \Rightarrow \ E_{AB}^{CC} = E_A^{CC} + E_B^{CC} \ .$$

$$e^{-(T_A + T_B)} (H_A + H_B) e^{T_a + T_B} = e^{-T_A} H_A e^{T_A} + e^{-T_B} H_B e^{T_B}$$

Single + double excitations

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

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.:

- CISD (single/double):

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

Truncation according to excitation level, e.g.:

- CCSD (single/double):

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

Single + double excitations

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

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

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

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Truncated CC is not equivalent to corresponding CI truncation
(but superior due to favourable properties).

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Evaluation of the CC function: BCH-formula, operator algebra, Second quantization, Wick's theorem, anti-commutation laws.

The (linked) CCSD equations

$$
\begin{aligned}
E(t) &= \langle \Psi_0, H\Psi_0 \rangle + \sum_{IA} f_{IA} t_I^A + \frac{1}{4}\sum_{IJAB} \langle IJ \| AB \rangle t_{IJ}^{AB} + \frac{1}{2}\sum_{IJAB} \langle IJ \| AB \rangle t_I^A t_J^B , \\
f(t)_I^A &= f_{IA} + \sum_C f_{AC} t_I^C - \sum_K f_{KI} t_K^A + \sum_{KC} \langle KA \| CI \rangle t_C^K + \sum_{KC} f_{KC} t_{IK}^{AC} + \frac{1}{2}\sum_{KCD} \langle KA \| CD \rangle t_{KI}^{CD} \\
&- \frac{1}{2}\sum_{KLC} \langle KL \| CI \rangle t_{KL}^{CA} - \sum_{KC} f_{KC} t_I^C t_K^A - \sum_{KLC} \langle KL \| CI \rangle t_K^C t_L^A + \sum_{KCD} \langle KA \| CD \rangle t_K^C t_I^D \\
&- \sum_{KLCD} \langle KL \| CD \rangle t_K^C t_I^D t_L^A + \sum_{KLCD} \langle KL \| CD \rangle t_C^K t_{LI}^{DA} - \frac{1}{2}\sum_{KLCD} \langle KL \| CD \rangle t_{KI}^{CD} t_L^A - \frac{1}{2}\sum_{KLCD} \langle KL \| CD \rangle t_{KL}^{CA} t_I^D \\
f(t)_{IJ}^{AB} &= \langle IJ \| AB \rangle + \sum_C \left(f_{BC} t_{IJ}^{AC} - f_{AC} t_{IJ}^{BC} \right) - \sum_K \left(f_{KJ} t_{IK}^{AB} - f_{KI} t_{JK}^{AB} \right) + \frac{1}{2}\sum_{KL} \langle KL \| IJ \rangle t_{KL}^{AB} \\
&+ \frac{1}{2}\sum_{CD} \langle AB \| CD \rangle t_{IJ}^{CD} + P(IJ)P(AB)\sum_{KC} \langle KB \| CJ \rangle t_{IK}^{AC} + P(IJ)\sum_C \langle AB \| CJ \rangle t_I^C - P(AB)\sum_K \langle KB \| IJ \rangle t_A^K \\
&+ \frac{1}{2}P(IJ)P(AB)\sum_{KLCD} \langle KL \| CD \rangle t_{IK}^{AC} t_{LJ}^{DB} + \frac{1}{4}\sum_{KLCD} \langle KL \| CD \rangle t_{IJ}^{CD} t_{KL}^{AB} + \frac{1}{2}P(AB)\sum_{KLCD} \langle KL \| CD \rangle t_{IJ}^{AC} t_{KL}^{BD} \\
&- \frac{1}{2}P(IJ)\sum_{KLCD} \langle KL \| CD \rangle t_{IK}^{AB} t_{JL}^{CD} + \frac{1}{2}P(AB)\sum_{KL} \langle KL \| IJ \rangle t_K^A t_L^B + \frac{1}{2}P(IJ)\sum_{CD} \langle AB \| CD \rangle t_I^C t_J^D \\
&- P(IJ)P(AB)\sum_{KC} \langle KB \| IC \rangle t_K^A t_J^C + P(AB)\sum_{KC} f_{KC} t_K^A t_{IJ}^{BC} + P(IJ)\sum_{KC} f_{KC} t_I^C t_{JK}^{AB} - P(IJ)\sum_{KLC} \langle KL \| CI \rangle t_K^C t_{LJ}^{AB} \\
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\end{aligned}
$$

Baker-Campell-Hausdorff expansion

Solving $\mathbf{f}(\mathbf{t}_h) = \mathbf{0}$ we recall the Baker-Campell-Hausdorff formula

$$e^{-T}Ae^{T} = A + [A, T] + \frac{1}{2!}[[A, T], T] + \frac{1}{3!}[[[A, T], T], T] + \ldots =$$

$$A + \sum_{k=1}^{\infty} \frac{1}{k!}[A, T]_k.$$

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For $\Psi \in \mathcal{V}_h$ the above series terminates, exercise**

$$e^{-T}He^{T} = H + [H,T] + \frac{1}{2!}[[H,T],T] + \frac{1}{3!}[[[H,T],T],T] + \frac{1}{4!}[H,T]_4$$

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e.g. for a single particle operator e.g. $\mathcal{F}$ there holds

$$e^{-T}\mathcal{F}e^{T} = \mathcal{F} + [\mathcal{F},T] + [[\mathcal{F},T],T]$$

Iteration method to solve CC amplitude equations

We decompose the (discretized) Hamiltonian

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Lemma

There holds for MOs (discrete eigenfunctions of F)

$$[\mathcal{F}, X_\mu] = [\mathcal{F}, X^{a_1,\ldots,a_k}_{l_1,\ldots,l_k}] = (\sum_{j=1}^{k} (\lambda_{a_j} - \lambda_{l_j}))X_\mu =: \epsilon_\mu X_\mu \ .$$

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and $[[\mathcal{F}, X_\mu], X_\mu] = 0$ *together with*

$$\epsilon_\mu \geq \lambda_{N+1} - \lambda_N > 0$$

(due to Bach-Lieb-Solojev)

Iteration method to solve CC amplitude equations

The amplitude function $\mathbf{t} \mapsto \mathbf{f}(\mathbf{t}) = (f_\mu(\mathbf{t}))_{\mu \in \mathcal{J}_h} = \mathbf{0}$

$$f_\mu(\mathbf{t}) = \langle \Psi_\mu, e^{-T} H e^{T} \Psi_0 \rangle = \langle \Psi_\mu, e^{-\sum_{\nu \in \mathcal{J}_h} t_\nu X_\nu} H e^{\sum_{\nu \in \mathcal{J}_h} t_\nu X_\nu} \Psi_0 \rangle = \mathbf{0}.$$

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The nonlinear amplitude equation $\mathbf{f}(\mathbf{t}) = \mathbf{0}$ is solved by

Algorithm (quasi Newton-scheme)

1. *Choose* $\mathbf{t}^0$, *e.g.* $\mathbf{t}^0 = \mathbf{0}$.
2. *Compute*
$$\mathbf{t}^{n+1} = \mathbf{t}^n - \mathbf{A}^{-1} \mathbf{f}(\mathbf{t}^n),$$
where $\mathbf{A} = \textit{diag}\, (\epsilon_\mu)_{\mu \in \mathcal{J}} > 0$.

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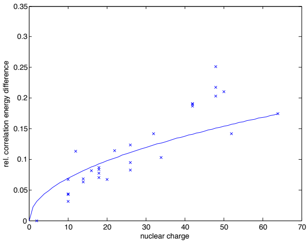
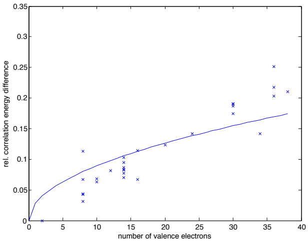
Numerical Examples – CCSD versus CISD

The relative difference in the correlation energy between CI and CC for several molecules in bonding configuration is plotted over the total number of electrons N and the number of valence electrons.

The lack of size consistency suggests a behavior $\sqrt{N}$.





Adaptive Coupled Cluster scheme

Rohwedder & Flad §. 2010, implemented by T. Rohwedder - in collaboration with A. Auer (CCSD-NWCHEM)
Since

$$0 = \mathbf{f}_\mu(\mathbf{t}) = \langle \Psi_\mu, e^{-T} H e^{T} \Psi_0 \rangle = \langle \Psi_\mu, [\mathcal{F}, T] \Psi_0 \rangle + \langle \Psi_\mu, e^{-T} U e^{T} \Psi_0 \rangle$$

suppose the normalization $\|\mathbf{t}\| \sim \| T \Psi_0 \|_{H^1}$:

$$\widetilde{\mathbf{f}}(\mathbf{t}) = \mathbf{F}\mathbf{t} - \Phi(\mathbf{t}) = \mathbf{0}$$

Augmented Newton type scheme

$$\boxed{\mathbf{t}^{n+1} := \mathbf{F}^{-1} \Phi(\mathbf{t}^n)}$$

We need the procedures $APPLY(\mathbf{u}, \eta) \approx \mathbf{F}^{-1}\Phi(\mathbf{u})$ up to accuracy η

- $\mathbf{t}^0 = \mathbf{0}$
- For $n = 0, 1, \ldots$
  - $\widehat{\mathbf{t}}^0 := \mathbf{t}^n$
  - While $\|\widehat{\mathbf{t}^{k+1}} - \widehat{\mathbf{t}}^k\| \geq 2^{-n}\theta\epsilon_0$ do $\widehat{\mathbf{t}^{k+1}} := APPLY(\mathbf{t}^k, 2^{-n}\epsilon_0)$
  - $\mathbf{t}^{n+1} := COARSE(\widehat{t}^k, \alpha 2^{-n}\epsilon_0)$

Universal algorithm detects sparsity. Practically, too expensive, not a good idea. But the Monte Carlo variant (A. Alavi, Alavi & Thom) works extremely well.

Coupled Cluster...

....in practice:

- CC ansatzes introduced $\sim$ 1960 (Coester, Kümmel)
- CC is nowadays standardly used in commercial quantum chemistry codes
- CCSD(T): often yields chemical accuracy, (*golden standard in quantum chemistry*, comparable to practical experiments

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- ▷ CC is nowadays standardly used in commercial quantum chemistry codes
- ▷ CCSD(T): often yields chemical accuracy, (*golden standard in quantum chemistry*, comparable to practical experiments

- ▷ allow only a single reference determinant
- ▷ not suitable for systems, where RHF (and MP2) do not provide already good results *Strong Correlation*

III.

Analysis of the Coupled Cluster method

S: & Th. Rohwedder (Dissertation 2010)

$$|\Psi\rangle \quad = \quad e^T|\Psi_0\rangle$$

Globalization to continuous Coupled Cluster method

i.e analogeous reformulation of the continuous equation

$$\widehat{H}\Psi = E\Psi$$

to continuous Coupled Cluster equation

$$\langle \Psi_\mu, e^{-T(t^*)}\hat{H}e^{T(t^*)}\Psi_0 \rangle \quad = \quad E \langle \Psi_\mu, \Psi_0 \rangle \quad \forall \mu \in \mathcal{M}$$

for $\Psi = e^{T(t^*)}\Psi_0$.

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for $\Psi = e^{T(t^*)}\Psi_0$. Now formulated in continuous basis sets,

$$B = \underbrace{\{\psi_1, ..., \psi_N\}}_{\text{occupied}} \cup \underbrace{\{\psi_a | a \in \text{virt}\}}_{\text{virtual}}, \qquad \mathbb{B} = \{\Psi_\mu | \mu \in \mathcal{I}\}.$$

with analogous definition of cluster operator

$$T(t) : \mathbb{L}^2 \to \mathbb{L}^2, \quad T(t) = \sum_{\mu \in \mathcal{I}} t_\mu X_\mu$$

and suitable reference determinant

$$\Psi_0 = \Psi[1, .., N] := \bigwedge_{i=1}^{N} \psi_i(x_i, s_i).$$

Main problem, assumption on the basis

Main problem:

H^1-continuity of cluster operator T and L^2-adjoint $T^\dagger$ have to be established!

(to make $\langle \Psi_\mu, e^{-T(t^*)} \hat{H} e^{T(t^*)} \Psi_0 \rangle$ well-defined)

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Assumption:

There holds

$$\langle F\chi_I, \chi_A \rangle = \langle \chi_I, \chi_A \rangle = 0 \quad \text{for all } I \in \text{occ}, \ A \in \text{virt}.$$

for a symmetric operator

$$F : H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\}) \to H^{-1}(\mathbb{R}^3 \times \{\pm\frac{1}{2}\}),$$

spectrally equivalent to the $H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$-norm.
(e.g. Fock operator, if HF ground state exists.)

Continuity of the cluster operator

Theorem (S., 2009; R., 2010)

For any $\Psi^* = \sum_{\alpha \in \mathcal{M}^*} t_\alpha \Psi_\alpha \in H^1$, $T = T(t)$ *and* $T^\dagger$ *its* L^2*-adjoint,*

$$\|T\|_{H^1 \to H^1} \sim \|\Psi^*\|_{H^1}, \quad \|T^\dagger\|_{H^1 \to H^1} \leq \|\Psi^*\|_{H^1}.$$

Sketch of proof:

- Reduction to L_2-orthogonal basis set,
- projection on F_i-orthonormal basis sets, $F \sim H_1$.
- Estimation with $\ell_1 \lesssim \ell_2$-estimate (Schneider 2009).

The continuous Coupled Cluster equations

Theorems (S., 2009; R., 2010)

The eigenvalue equation

$$\langle \Psi_\mu, (\hat{H} - E^*)\Psi \rangle = 0, \quad \forall \mu \in \mathcal{I},$$

holds for $\Psi = \Psi_0 + \Psi^* \in H^1$, $E^* \in \mathbb{R}$ *iff the Coupled Cluster equations*

$$\begin{aligned} \langle \Psi_\mu, e^{-T(t^*)}\hat{H}e^{T(t^*)}\Psi_0 \rangle &= 0, \quad \forall \mu \in \mathcal{I}^*, \\ \langle \Psi_0, e^{-T(t^*)}\hat{H}e^{T(t^*)}\Psi_0 \rangle &= E^*, \end{aligned}$$

hold for $\Psi = e^{T(t^*)}\Psi_0, \quad T(t^*) = \sum_{\mu \in \mathcal{I}^*} t^*_\mu X_\mu, \quad \|t^*_\mu\|_{\mathbb{V}} < \infty.$

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Coefficient vector $t^* \in \mathbb{V}$ *is solution of CC root equation,*

$$\boxed{f(t^*) = 0 \in \mathbb{V}'}$$

for CC function

$$f : \mathbb{V} \to \mathbb{V}', \quad f(t) := \left(\langle \Psi_\mu, e^{-T(t)} \hat{H} e^{T(t)} \Psi_0 \rangle \right)_{\mu \in \mathcal{I}^*}.$$

Local strong monotonicity of the CC function

Theorem (S., 2009; R., 2010)

If $E^* < \sigma_{ess}(h)$ is simple and Ψ_0 close enough to Ψ, then f is locally strongly monotone at the solution t^*, i.e. there are $\gamma, \delta > 0$ such that

$$\langle f(s) - f(t), s - t \rangle \;\geq\; \gamma \cdot \|s - t\|_{\mathbb{V}}^2$$

holds for $s, t \in \mathbb{V}$ with $\|s - t^*\|_{\mathbb{V}}, \|t - t^*\|_{\mathbb{V}} < \delta$.

Sketch of proof:

- Local Lipschitz continuity from continuity of T
- $\langle \Phi, (\widehat{H} - E^*)\Phi \rangle \geq \gamma' ||\Phi||_1^2$ on $\{\Psi_0\}^\perp$
  from Gårding estimate for h, perturbation argument
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(Abstract) Galerkin Scheme

H - Hilbert space, V is a (reflexive) Banach space, V' its dual

$$V \subset H \subset V' \,,$$

e.g. $H := L_2, V = H^1 = \{u : \|u\|_{H^1}^2 := \langle u, (I - \Delta)u \rangle < \infty\}$,

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Definition (Galerkin scheme)

An approximate solution $\mathbf{u}_h \in V_h$ is obtained by the Galerkin scheme solving

$$\boxed{\langle \mathbf{v}_h, \mathbf{f}(\mathbf{u}_h) \rangle = 0 \ \forall \mathbf{v}_h \in V_h}$$

i.e. the residual $\mathbf{f}(\mathbf{u}_h) \perp V_h$ is perpendicular to V_h.

Abstract Convergence Analysis

Definition

A function **f** is called *(locally) strongly monotone* at **u** if

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Example

Let $\mathbf{A} := f'(\mathbf{u}) : V \to V'$ (linear) with

$$\langle \mathbf{v}, \mathbf{A}\mathbf{u} \rangle \leq L \|\mathbf{u}\|_V \|\mathbf{v}\|_V \text{ and}$$

$$\langle \mathbf{u}, \mathbf{A}\mathbf{u} \rangle \geq \gamma \|\mathbf{u}\|_V^2 \text{ i.e. } Re\mathbf{A} > 0,$$

then **f** is Lipschitz continuous and strongly monoton.

Quasi-Optimal Convergence

Theorem (standard result)

Let f be Lipschitz continuous and strongly monotone, the Galerkin scheme admits a (unique) solution $\mathbf{u}_h \in V_h$, $C > 0$ satisfying $\forall h < h_0$ the estimates

$$\|\mathbf{u} - \mathbf{u}_h\|_V \leq \frac{L}{\gamma}\|\mathbf{f}(\mathbf{u}_h)\|_{V'} \; , \; \|\mathbf{u}_h\|_V \leq C\|\mathbf{u}\|_{V'}$$

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together with the quasi-optimal error estimate

$$\boxed{\|\mathbf{u} - \mathbf{u}_h\|_V \leq \frac{L}{\gamma} \inf_{\mathbf{v}_h \in V_h} \|\mathbf{u}_h - \mathbf{v}_h\|_V}$$

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Example (CI-method)

If $\|\Psi - \Psi_0\|_{\mathcal{V}} < \delta$ sufficiently small and $E_0 = \langle \Psi_0, H\Psi_0 \rangle$, then $(\tilde{\mathbf{t}}) \mapsto h_\nu(\tilde{\mathbf{t}}) := \langle \Psi_\nu, (H - E_0)(I + T(\tilde{\mathbf{t}}))\Psi_0 \rangle$ is strongly monotone.

Local existence and quasi-optimal convergence

Let $T(\mathbf{t}) := \sum_\mu t_\mu X_\mu$
we consider $\mathbf{g} : V \to V$, $g(\mathbf{t})_\nu := \langle \Psi_\nu, (H - E(\mathbf{t})e^{T(\mathbf{t})})\Psi_0 \rangle$.

Theorem (S. 2008)

Let E be a simple EV. If $\|\Psi - \Psi_0\|_{\mathcal{V}} < \delta$ sufficiently small, and $\mathcal{J}_h$ excitation complete, then

1. *for $E = E(\mathbf{t}_h) := \langle \Psi_0, He^{T(\mathbf{t}_h)}\Psi_0 \rangle$, there holds*
$$\langle \mathbf{g}(\mathbf{t}_h), \mathbf{v} \rangle = 0 \ , \ \forall \mathbf{v} \in V_h \quad \Longleftrightarrow \quad \langle \mathbf{f}(\mathbf{t}_h), \mathbf{v} \rangle = 0 \ , \ \forall \mathbf{v} \in V_h$$
2. *g is strongly monontone at $\mathbf{t}$ $\forall \|\mathbf{t}\| \leq \delta'$*
3. *there ex. $\mathbf{t}_h \in V_h$ with $\langle \mathbf{g}(\mathbf{t}_h), \mathbf{v} \rangle = \langle \mathbf{f}(\mathbf{t}_h), \mathbf{v} \rangle = 0$, $\forall \mathbf{v} \in V_h$,*
$$\|\mathbf{t} - \mathbf{t}_h\|_V \lesssim \inf_{\mathbf{v} \in V_h} \|\mathbf{t} - \mathbf{v}_h\|_V .$$

Existence and uniqueness; quasi-optimality

Theorem (S., 2009; R., 2010)

(i) *Under assumptions as above, the solution t^* is unique in the neighbourhood $B_\delta(t^*)$.*

(ii) *For closed subspaces $\mathbb{V}_d$ for which $d(t^*, \mathbb{V}_d) := \min_{v \in \mathbb{V}_d} \|t^* - v\|_{\mathbb{V}}$ is sufficiently small,*

$$\langle f(t_d), v_d \rangle \ = \ 0 \quad \textit{for all} \quad v_d \in \mathbb{V}_d$$

admits a solution t_d in $B_{\delta,d} := \mathbb{V}_d \cap B_\delta(t^*)$ which is unique on $B_{\delta,d}$ and fulfils the quasi-optimality estimate

$$\|t_d - t^*\|_{\mathbb{V}} \ \leq \ \frac{L}{\gamma}\, d(t^*, \mathbb{V}_d).$$

Sketch of proof:

- Uniqueness from strong monotonicity
- Ex. of discrete solutions uses lemma based on Browder's fixed point theorem

Error estimators (following Rannacher et al.)

Lagrangian approach:

Minimize CC energy

$$E(t) = \langle \Psi_0, e^{-T(t)} \hat{H} e^{T(t)} \Psi_0 \rangle,$$

under side condition $f(t) = 0$:

$$\mathcal{L}(t, z) = E(t) + \langle f(t), z \rangle$$

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Lemma (S., 2009; R., 2010)

Monotonicity $\Rightarrow$ First order condition

$$\mathcal{L}'(t^*, z^*) = \left\{ \begin{array}{c} \langle E'(t^*), s \rangle - \langle Df(t^*)s, z^* \rangle \\ \langle f(t^*), s \rangle \end{array} \right\} = 0 \quad \textit{for all} \ \ s \in \mathbb{V}.$$

has unique dual solution (Lagrangian multiplier) $z^* \in \mathbb{V}$.

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Lemma (S., 2009; R., 2010)

Monotonicity $\Rightarrow$ *Discrete first order condition*

$$\mathcal{L}'(t_d, z_d) = \left\{ \begin{array}{c} \langle E'(t_d), s_d \rangle - \langle Df(t_d) s_d, z_d \rangle \\ \langle f(t_d), s_d \rangle \end{array} \right\} = 0 \quad \textit{for all } \ s_d \in \mathbb{V}_d$$

has unique dual solution (Lagrangian multiplier) $z_d \in \mathbb{V}$*, and*

$$\| z_d - z^* \|_{\mathbb{V}} \ \lesssim \ \max\{ d(\mathbb{V}_d, t^*), \ d(\mathbb{V}_d, z^*) \}.$$

Dual weighted residual approach

Theorem (Becker/Rannacher, 2001)

Let $(t^*, z^*) \in \mathbb{V}^2$ *and* $(t_d, z_d) \in \mathbb{V}_d^2$ *be the solutions of the Lagrange equations for a thrice differentiable functional* $\mathcal{L}$*, and denote*

$$\rho(t_d) := \langle f(t_d), \cdot \rangle_{\mathbb{V}} \qquad \rho^*(t_d, z_d) := \langle E'(t_d), \cdot \rangle_{\mathbb{V}} - \langle Df(t_d)\cdot, z_d \rangle_{\mathbb{V}}.$$

Then there holds

$$E(t^*) - E(t_d) = \frac{1}{2}\rho(t_d)(z^* - v_d) + \frac{1}{2}\rho^*(t_d, z_d)(t^* - w_d) + \mathcal{R}_d^3$$

for all v_d, w_d *in* $\mathbb{V}_d$*, where*

$$\mathcal{R}_d^3 = \mathcal{O}(\max\{\|t^* - t_d\|, \|z^* - z_d\|\}^3).$$

Error estimators for the CC equation

Theorem (S., 2009; R., 2010)

(i) *For* $\max\{d(\mathbb{V}_d, t^*),\ d(\mathbb{V}_d, z^*)\}$ *sufficiently good, under the above assumptions, there holds*

$$|E(t^*) - E(t_d)| \;\leq\; \|t_d - t^*\|_{\mathbb{V}} \Big(c_1 \,\|t_d - t^*\|_{\mathbb{V}} \;+\; c_2 \,\|z_d - z^*\|_{\mathbb{V}} \Big),$$

$$|E(t^*) - E(t_d)| \;\lesssim\; \big(\, d(\mathbb{V}_d, t^*) \;+\; d(\mathbb{V}_d, z^*) \,\big)^2$$

for the solutions (t^*, z^*), (t_d, z_d) *of the continuous/discrete Coupled Cluster equations and corr. dual solutions.*

Error estimators for the CC equation

Theorem (S., 2009; R., 2010)

(i) *For* $\max\{d(\mathbb{V}_d, t^*),\ d(\mathbb{V}_d, z^*)\}$ *sufficiently good, under the above assumptions, there holds*

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for the solutions (t^*, z^*)*,* (t_d, z_d) *of the continuous/discrete Coupled Cluster equations and corr. dual solutions.*

(ii) *For* $\Psi = \Psi_0 + \Psi^* = e^{T(t^*)}\Psi_0,\ \Psi^{z^*} := \Psi_0 + \Psi^{z^*} := e^{T(z^*)}\Psi_0,$ *there holds*

$$|E(t^*) - E(t_d)| \;\lesssim\; \Big(\inf_{\Phi\in H^1_{d,\perp}} \|\Phi - \Psi^*\|_{H^1} \;+\; \inf_{\Phi\in H^1_{d,\perp}} \|\Phi - \Psi^{z^*}\|_{H^1}\Big)^2.$$

Extended: bi-variational appr. of Arponen by S. Kvaal (2013)

Comparison with Jastrow factor ansatz

Example (– Quantum Monte Carlo Methods)

Let us consider the Jastrow factor ansatz:

$$\boxed{\Psi(\mathbf{x}) \approx F(\mathbf{x})\Psi_0(\mathbf{x})}$$

$\Psi_0(\mathbf{x})$ - reference (determinant), F - multiplication operator

1. Linear ansatz:
   $F(\mathbf{x}) = \sum_i^N f_1(\mathbf{x}_i) + \sum_{i>j}^N f_2(\mathbf{x}_i, \mathbf{x}_j) + f_3 \ldots$
2. exponential ansatz : (*Krotzschek, ...*)
   $F(\mathbf{x}) = e^{\left[\sum_i^N f_1(\mathbf{x}_i) + \sum_{i>j}^N f_2(\mathbf{x}_i, \mathbf{x}_j) + f_3 \ldots\right]}$. ANOVA approx. is size cons. only for the exponential ansatz 2)
3. In Coupled Cluster and Perturbation Theory

$$\boxed{\Psi(\mathbf{x}) = F\Psi_0(\mathbf{x})}\ , \ CC: \ F = e^T$$

is an operator. (In principle this is an exact ansatz - no fixed node error.)

Quantum Monte Carlo Methods (QMC)

$$\Psi(\mathbf{x}) \approx F(\mathbf{x})\Phi(\mathbf{x}) = F(\mathbf{x})\Psi_0(\mathbf{x})e^{\frac{1}{2}\sum_{i>j}^{N}\|\mathbf{x}_i-\mathbf{x}_j\|\chi}$$

- $\Phi(\mathbf{x}) = \Psi_0(\mathbf{x})e^{\frac{1}{2}\sum_{i>j}^{N}\|\mathbf{x}_i-\mathbf{x}_j\|\chi}$ -reference, $\Psi_0 = \Psi_{SL}[1,\ldots,N]$
- $f_{1/2} := e^{\frac{1}{2}\sum_{i>j}^{N}\|\mathbf{x}_i-\mathbf{x}_j\|}$ (e-e cusp) ($f_{1/2}$ - e.g. *Klopper* in CC)
- F - unknown Jastrow factor (*Ceperly, Umrigar, ...*)

Schrödinger eqn. $\Rightarrow$ EVP for F $\Rightarrow$ Fokker Planck eqn. $t \to \infty$

$$\frac{\partial}{\partial t}F = \frac{1}{2}\big(\Delta F + \nabla \log|\Phi|^2 \cdot \nabla F\big) - \big(\frac{\Delta\Phi}{\Phi} - V_{core} + E_0\big)F \to 0\ .$$

Dirichlet boundary conditions $F|_{\partial\Omega} = 0$, $\partial\Omega := \{\mathbf{x} : \Psi_0(\mathbf{x}) = 0\}$.

$\overset{\text{(Itó Calculus)}}{\Longleftrightarrow}$ Stochastic differential equation (SDE) $\Rightarrow$ MC

(Small) systematic error: fixed node approximation (*Cances & Jourdan & Lelievre*) - but accuracy comparable with CCSD!

Notes

- Projected CC is a compromise making the exponential ansatz computable
- it is more a perturbational approach for improving a reference solution Ψ_0.
- Analysis lays base for goal-oriented error estimators for CC, for example in combination with extrapolation schemes

- Analysis is only local, but it shows
  - importance of quality of reference determinant Ψ_0
  - importance of gap $\inf \sigma(h) \setminus \{E^*\} \quad - \quad E^*$

  These do not only enter in convergence estimates for algorithms (and reflect in practical experience), but also enter in quasi-optimality estimates.

Summary

- Schrödinger equation = high dimensional eigenvalue problem with additional antisymmetry constraint
- Reformulation of linear Galerkin ansatz by nonlinear (projected) Coupled Cluster ansatz gives practical method
- Formulation in infinite dimensional spaces gives continuous CC ansatz, equivalent to electronic Schrödinger equation
- Local existence/uniqueness statements for CC ansatz
- Error estimators for energy
-

Thank you
for your attention.

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