The Electronic Schrödinger equation, CI and QCDMRG method

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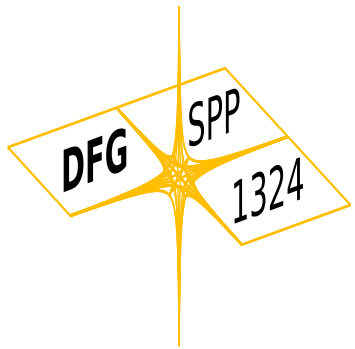
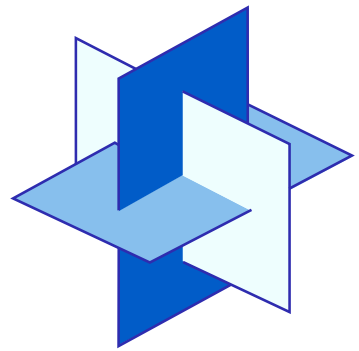
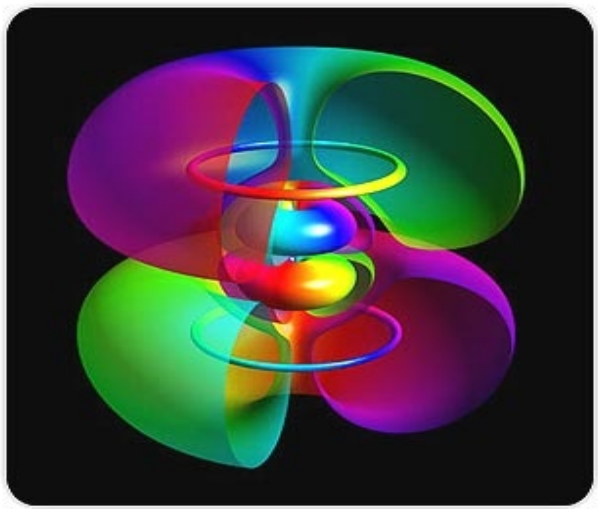
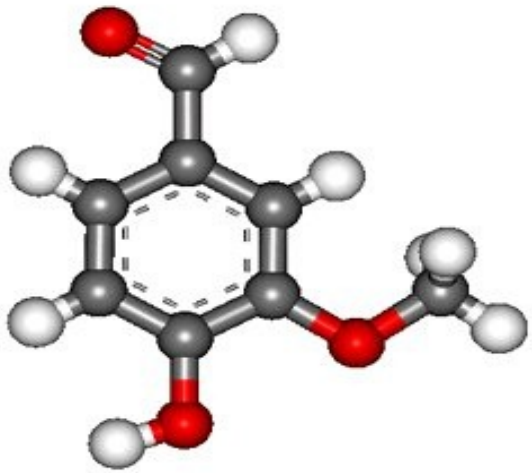




Introduction

Electronic Schrödinger Equation

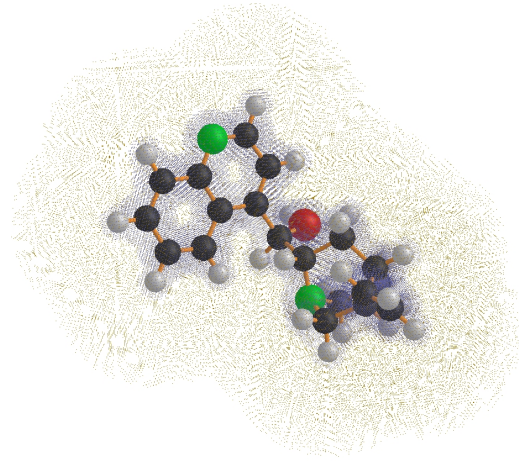




Electronic Schrödinger equation

N nonrelativistic electrons + Born Oppenheimer approximation

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



The Hamilton operator in atomic units

$$\boxed{H = -\frac{1}{2}\sum_i \Delta_i - \sum_{i}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|x_i - x_j|}}$$

acts on *anti-symmetric* wave functions (Pauli principle)

$$\Psi(x_1, s_1, \ldots, x_N, s_N) \in \mathbb{R}\ ,\ \mathbf{x}_i = (x_i, s_i) \in \mathbb{R}^3 \times \{\pm\frac{1}{2}\},$$

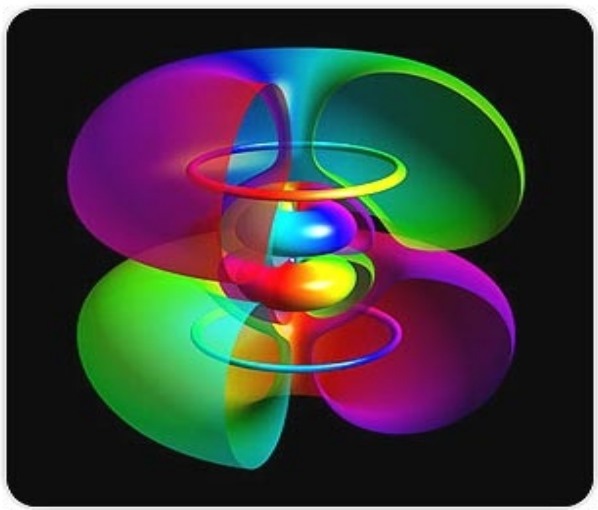
$$\Psi(\ldots; x_i, s_i; \ldots; x_j, s_j; \ldots) = -\Psi(\ldots; x_j, s_j; \ldots; x_i, s_i; \ldots)$$

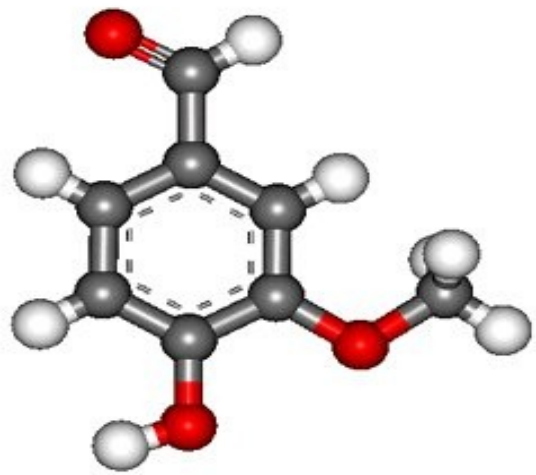
We are mainly interested in the ground state energy

$$\boxed{E_0 = \min\{\langle H\Psi, \Psi\rangle : \Psi \in \mathcal{V}\ ,\ \langle\Psi, \Psi\rangle = 1\}}$$

Slater determinants

and Full CI method





Anti-symmetric tensor products - Slater determinants

Approximation by sums of anti-symmetric tensor products:

$$\Psi = \sum_{k=1}^{\infty} c_k \Psi_k$$

$$\Psi_k(\mathbf{x}_1, s_1; \ldots; \mathbf{x}_{N'}, s_{N'}) = \varphi_{1,k} \wedge \ldots \wedge \varphi_{N',k} = \frac{1}{\sqrt{N'!}} \det(\varphi_{i,k}(\mathbf{x}_j, s_j))$$

with $\varphi_{i,k} \in \{\varphi_j : j = 1, \ldots\}$, w.l.o. generality

$$\langle \varphi_i, \varphi_j \rangle = \sum_{s=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \varphi_i(\mathbf{x}, s) \overline{\varphi_j(\mathbf{x}, s)} d\mathbf{x} = \delta_{i,j} \ .$$

A Slater determinant: Ψ_k is an (anti-symmetric) product of N' orthonormal functions φ_i, called spin orbital functions

$$\varphi_i : \mathbb{R}^3 \times \{\pm\frac{1}{2}\} \to \mathbb{R} \ , \ i = 1, \ldots, N,$$

For present applications it is sufficient to consider real valued functions Ψ, φ .

Slate Condon Rules revisited

Single and two particle operators

Abbreviations:

a) Single particle operators $A = h = \sum_{i=1}^{N'} h_i = \sum_{i=1}^{N'} (\frac{1}{2}\Delta_i + \sum_{j=1}^{M} \frac{-Z_j}{|\mathbf{x}_i - \mathbf{R}_j|}) = \sum_{i=1}^{N'} (\frac{1}{2}\Delta_i + V_{core}(\mathbf{x}_i))$, $h_i = h_j$,

$$\langle i|h|j\rangle := \langle \varphi_i, h_j \varphi_j \rangle$$

a) Two particle operators $G = \sum_i^{N'} \sum_{j>i}^{N'} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}$, $H = h + G$

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

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

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

Slater-Condon Rules

Single particle operators: $\Psi^1 = \Psi_{SL} = \Psi[\ldots, \nu_i, \nu_j, \ldots]$

1) $\Psi^1 = \Psi^2 =: \Psi$	$\Psi^1 = \Psi[\ldots, \nu_i, \nu_j, \ldots]$	
	$\Psi^2 = \Psi[\ldots, \nu_i, \nu_j, \ldots]$	$\langle \Psi, h\Psi \rangle = \sum_{l=1}^{N} \langle l\|h\|l \rangle$
2) $\Psi^2 = X_j^a \Psi^1$	$\Psi^1 = \Psi[\ldots, \nu_i, \nu_j, \ldots]$	
	$\Psi^2 = \Psi[\ldots, \nu_i, \nu_a, \ldots]$	$\langle \Psi^2, h\Psi^1 \rangle = \langle a\|h\|j \rangle$
3) $\Psi^1 = X_{i,j}^{a,b} \Psi^2$	$\Psi^1 = \Psi[\ldots, \nu_i, \nu_j, \ldots]$	
or higher excitations	$\Psi^2 = \Psi[\ldots, \nu_a, \nu_b, \ldots]$	$\langle \Psi^2, h\Psi^1 \rangle = 0$

Proof *exercise Hint: 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

Slater-Condon Rules for two particle operators:

1) $\Psi^1 = \Psi^2$	$\Psi^1 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	
	$\Psi^2 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	$\langle\Psi^1, G\Psi^1\rangle = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle ij\|\|ij\rangle$
2) $\Psi^2 = X_j^a\Psi^1$	$\Psi^1 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	
	$\Psi^2 = \Psi[\ldots,\nu_i,\nu_a,\ldots]$	$\langle\Psi^2, G\Psi^1\rangle = \sum_{i=1}^{N}\langle ji\|\|ai\rangle$
3) $\Psi^1 = X_{i,j}^{a,b}\Psi^2$	$\Psi^1 = \Psi[\ldots,\nu_i,\nu_j,\ldots]$	
	$\Psi^2 = \Psi[\ldots,\nu_a,\nu_b,\ldots]$	$\langle\Psi^2, G\Psi^1\rangle = \langle ij\|\|ab\rangle$
3) $\Psi^1 = X_{i,j,l}^{a,b,c}\Psi^2$	$\Psi^1 = \Psi[\ldots,\nu_i,\nu_j,\nu_l\ldots]$	
or higher excitations	$\Psi^2 = \Psi[\ldots,\nu_a,\nu_b,\nu_c\ldots]$	$\langle\Psi^2, G\Psi^1\rangle = 0$

with

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

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

Spin functions and spatial orbitals

Spin orbital function: $\varphi(\mathbf{x}, s) \in \mathbb{R}$, $(\mathbb{C})$, $\mathbf{x} \in \mathbb{R}^3$ $s = \pm\frac{1}{2}$,
spin functions χ and spatial orbital functions ϕ:

$$\boxed{\varphi(\mathbf{x}, s) = \phi_\alpha(\mathbf{x})\chi_\alpha(s) + \phi_\beta(\mathbf{x})\chi_\beta(s)}$$

with spin functions $\chi_\alpha(+\frac{1}{2}) = 1, \chi_\alpha(-\frac{1}{2}) = 0, \chi_\beta(s) = 1 - \chi_\alpha(s)$

$$\varphi^\alpha(\mathbf{x}, s) = \phi_\alpha(\mathbf{x})\chi_\alpha(s)$$

UHF (Unrestricted Hartree Fock, single spin state orbitals) :

$$\phi_{\alpha,i}, \phi_{\beta,j} \ , \ N' = N_\alpha + N_\beta \ .$$

Closed shell RHF (Restricted Hartree Fock) :

$$\phi_{\alpha,i} = \phi_{\beta,i} = \phi_i \ , \ i = 1, \ldots, N = \frac{N'}{2} \ .$$

Hartree-Fock approximation

Closed shell RHF Model Minimize w.r.t. $\langle \varphi_i, \varphi_j \rangle = \delta_{i,j}$,

$$\frac{1}{2}\mathcal{J}^{HF}(\Phi) = \sum_{i=1}^{N} \frac{1}{2}\langle \nabla\varphi_i, \nabla\varphi_i \rangle + \langle \mathcal{V}_{core}(\mathbf{x})\varphi_i, \varphi_i \rangle + \frac{1}{2}\langle \mathcal{V}_H(\mathbf{x})\varphi_i, \varphi_i \rangle - \frac{1}{4}\langle \mathcal{W}\varphi_i, \varphi_i \rangle$$

Density matrix function: $\rho(\mathbf{x}, \mathbf{y}) := \sum_{i=1}^{N} \overline{\varphi_i(\mathbf{x})}\varphi_i(\mathbf{y})$,
$n(\mathbf{x}) := \rho(\mathbf{x}, \mathbf{x})$ is called the electron density
With the Hartree potential $\mathcal{V}_H$ and the exchange energy term $\mathcal{W}$

$$-\Delta\mathcal{V}_H(\mathbf{x}) = 4\pi n(\mathbf{x}, \mathbf{x}) \quad , \quad \mathcal{W}u(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{\rho(\mathbf{x}, \mathbf{y})}{|\mathbf{x} - \mathbf{y}|} u(\mathbf{y}) d\mathbf{y}$$

General setting

- $\Phi := (\phi_1, \ldots, \phi_N) \in (H^1(\mathbb{R}^3))^N = V^N$
- *Gelfand triple* $V := H^1(\mathbb{R}^3) \subseteq L^2(\mathbb{R}^3) \subseteq H^{-1}(\mathbb{R}^3) = V'$
- $\left\langle \Phi^T \Psi \right\rangle := (\langle \phi_i, \psi_j \rangle)_{i,j} \in \mathbb{R}^{N \times N}$
- *scalar product* $\langle\langle \Phi, \Psi \rangle\rangle := tr \left\langle \Phi^T \Psi \right\rangle = \sum_{i=1}^{N} \langle \phi_i, \psi_i \rangle \in \mathbb{R}$
- $\mathcal{A}\Phi := (A\phi_1, \ldots, A\phi_N)$, $A : V \to V'$

Simplified Problem: minimize

$$\mathcal{J}_A^{SCF}(\Phi) := \sum_{i=1}^{N} \langle A\phi_i, \phi_i \rangle = tr \left\langle \Phi^T \mathcal{A}\Phi \right\rangle = \langle\langle \Phi, \mathcal{A}\Phi \rangle\rangle$$

w.r.t. to orthogonality constraints $\left\langle \Phi^T \Phi \right\rangle = I$.

Remarks

- $\mathcal{J} = \mathcal{J}^{HF}, \mathcal{J}^{KS}, \mathcal{J}^{SCF}$ are invariant under unitary transformations $\mathbf{U} \in \mathcal{U}$

$$\mathcal{J}(\Phi) = \mathcal{J}(\Phi\mathbf{U}),\ \Phi\mathbf{U} := (\sum_{i=1}^{N} \phi_i u_{ij})_{j=1,\ldots,N}$$

- gradient $\mathcal{J}'(\Phi) = \mathcal{A}_{[\Phi]}\Phi$, $A_{[\Phi]} : V \to V'$

The *density matrix operator*

$$\boxed{D_\Phi := \sum_{i=1}^{N} \langle \phi_i, \cdot \rangle_{L^2}\, \phi_i}$$

projects onto span $\Phi :=$ span$\{\phi_i : 1 \le i \le N\}$,
$D^2 = D$, $tr\, D = N$, $D^T = D$

Stiefel and Grassmann manifolds

Definition

Stiefel manifold

$\mathcal{S}_{V,N} := \mathcal{S} := \{\Phi = (\phi_i)_{i=1}^{N} | \phi_i \in V, \langle \Phi^T \Phi \rangle - I_{N\times N} = \mathbf{0} \in \mathbb{R}^{N\times N}\}$

Grassmann manifold is a quotient manifold

$$\mathcal{G}_{V,N} := \mathcal{G} := \mathcal{S}_{V,N}/\sim, \quad \Phi \sim \widetilde{\Phi} \Leftrightarrow \widetilde{\Phi} = \Phi \mathbf{U}\ ,\ \mathbf{U} \in \mathcal{U}(N)$$

(identify ONB spanning the same subspace span Φ)

see *[Edelman, Arias, Smith]* for $V = \mathbb{R}^n$.

There is a one-to-one correspondence between

$[\Phi] \in \mathcal{G} \ \leftrightsquigarrow\ D_\Phi$ *(density matrix operator)*

Tangent space

Proposition (Edelman, Arias, Smith (98); Blauert, Neelov, Rohwedder, S. (08))

- *tangent space* $\mathcal{T}_{[\Phi]}\mathcal{G} = \{\delta\Psi \in V^N | \left\langle (\delta\Psi)^T \Phi \right\rangle = 0 \in \mathbb{R}^{N\times N}\}$
- $(I - \mathcal{D}_\Phi) : V^N \to \mathcal{T}_{[\Phi]}\mathcal{G}$, *is an orthogonal projection onto the tangent space* $T_{[\Phi]}\mathcal{G}$
- *tangent space* $\mathcal{T}_\Phi\mathcal{S} = \mathcal{T}_{[\Phi]}\mathcal{G} + \{\Phi\mathbf{A} : \mathbf{A}^T = -\mathbf{A}\}$

$$= \{\Theta \in V^N : \left\langle \Theta^T \Phi \right\rangle = -\left\langle \Phi^T \Theta \right\rangle\}$$

Existence and uniqueness – known results

Problem

Minimize $\mathcal{J} : \mathcal{G} \to \mathbb{R}$, $\mathcal{J} = \mathcal{J}^{HF}, \mathcal{J}^{KS}, \mathcal{J}_A^{SCF}$

Theorem (Lieb-Simon (78), P.L. Lions (89))

There exists a minimizer $\Phi \in (H^1(\mathbb{R}^3))^N$ *for* $\mathcal{J}^{HF}$ *provided that* $N' < \sum Z_\nu$.

Uniqueness is not know yet?

- $\mathcal{J}_A^{SCF}$ has unique minimizer on Grassmann manifold $\mathcal{G}$ if there is a gap for the lowest eigenvalues of A: $\lambda_N < \lambda_{N+1}$
- no uniqueness on Stiefel manifold $\mathcal{S}$.

1st order optimality conditions

For $[\Phi] \in \mathcal{G}$ there hold $\mathcal{J}'(\Phi) = \mathcal{A}_{[\Phi]}\Phi \in (V')^N$ where $A^{SCF}_{[\Phi]} = A$ and $A^{HF}_{[\Phi]}, A^{KS}_{[\Phi]}$ are the Hamilton Fock operators

Definition

E.g. the Kohn-Sham Hamilton Fock operator is given by

$$A^{KS}_{[\Phi]} := -\frac{1}{2}\Delta + V_{core} + \left(n \star \frac{1}{|\cdot|}\right) + v_{xc}(n) = -\frac{1}{2}\Delta + V(n)$$

Nec. cond.: If $[\Psi] = \mathit{argmin}\,\{\mathcal{J}(\Phi) : [\Phi] \in \mathcal{G}\} \in V^N(V_h^N)$ *then*

$$\boxed{\langle\langle \mathcal{A}_{[\Psi]}\Psi, \delta\Phi\rangle\rangle = 0 \,\forall\, \delta\Phi \in \mathcal{T}_{[\Psi]}\mathcal{G} \subset V^N(V_h^N)}$$

$$\boxed{\langle\langle (I - \mathcal{D}_\Psi)\mathcal{A}_{[\Psi]}\Psi, \delta\Phi\rangle\rangle = 0 \,\forall\, \delta\Phi \in V^N(V_h^N)}$$

Canonical HF - KS equations

Lagrangian $\mathcal{L}(\Phi, \Lambda) := \mathcal{J}(\Phi) - tr\Lambda(\langle \Phi^T \Phi \rangle - I)$

At a (local) minimum $\Psi \in \mathcal{V}$, i.e. at stationary points (Ψ, λ) of $\mathcal{L}$ there holds $\boxed{\Lambda = \langle A_{[\Psi]} \hat{\psi}_i, \hat{\psi}_j \rangle}$.

There exists a representation $\Psi = \hat{\Psi}\mathbf{U}$ of $[\hat{\Psi}] \in \mathcal{G}$, s. t. $\lambda_{i,j} = \lambda_i \delta_{ij}$ and $\lambda_1 \leq \lambda_2 \leq \ldots$ s.t.

There hold the canonical (HF or KS) equations

$$\boxed{\mathcal{A}_{[\Psi]} \psi_i = \lambda_i \psi_i \ , \quad \lambda_1 \leq \lambda_2 \leq \ldots \leq \lambda_N < 0 \ .}$$

Self consistent iteration: $A_{[\Psi^{(n)}]} \psi_i^{(n+1)} = \lambda_i^{(n+1)} \psi_i^{(n+1)}$ (Cances-LeBris)

Self consistent iteration - SCF

We define A_{D^n} such that $A_{[\Psi]} = A_{D_\Psi}$ for an appropriate $D^n \in \mathcal{P} := \{D : D^* = D, trD = N, D^2 \leq D\}$.

Algorithm (Self consistent iteration)

1. $\widehat{\Psi^{n+1}} := argmin\,\{\mathcal{J}^{SCF}_{A_{D^n}}(\Phi) : \Phi \in \mathcal{G}\} = argmin\,\{\langle\langle A_{D^n}\Phi, \Phi\rangle\rangle : \Phi \in \mathcal{G}\}$
2. $D^{n+1} := \mu D_{\Psi^n} + (1-\mu) D_{\widehat{\Psi^{n+1}}} \in \mathcal{P}$ *for some* $\mu \in [0,1]$

Roothaan algorithm: $A_{[\Psi(n)]}\psi_i^{(n+1)} = \lambda_i^{(n+1)}\psi_i^{(n+1)}$ fails often
Optimal damping algorithm (Cances-LeBris 02) converges
$D^{n+1} := \mu D_{\Psi^n} + (1-\mu) D_{\widehat{\Psi^{n+1}}} \in \mathcal{P}$ with optimal choice of $\mu \in [0,1]$

Gradient flow

The minimizer Ψ is spanning an invariant subspace
$V_\Psi := \text{span}\{\psi_1, \ldots, \psi_N\}$ of $A_{[\Psi]}$ corresponding to the N lowest eigenvalues.
A local minimizer Ψ is a fix point of the gradient flow $[\Phi](t)$,
$\Psi = \lim_{t\to\infty} \Phi(t)$

$$\langle\langle \frac{d}{dt}\Phi - \mathcal{A}_{[\Phi]}\Phi(t), \theta\rangle\rangle = 0 \; \forall\theta \in \mathcal{T}_{[\Phi]}\mathcal{G} \subset V^N \; (V_h^N)$$

or

$$\langle\langle \frac{d}{dt}\Phi(t) - (I - \mathcal{D}_\Phi)\mathcal{A}_{[\Phi]}\Phi, \theta\rangle\rangle = 0 \; \forall\theta \in V^N \; (V_h^N)$$

Direct Minimization

Algorithm (direct minimization)

1. $\mathcal{A} := \mathcal{J}'(\Phi^{(n)}) = \mathcal{A}_{[\Phi^{(n)}]} : V^N \to V'^N$
2. $\Lambda^{(n)} := \left\langle \Phi^T \mathcal{A} \Phi \right\rangle = (\left\langle A\phi_i, \phi_j \right\rangle)_{i,j=1,\dots,N} \in \mathbb{R}^{N \times N}$
3. $\hat{\Phi}^{(n+1)} := \Phi^{(n)} - \alpha \mathcal{B}^{-1}(\mathcal{A}\Phi^{(n)} - \Phi^{(n)}\Lambda^{(n)})$, *preconditioner B*
4. $\hat{\Phi}^{(n+1)} \rightsquigarrow \Phi^{(n+1)}$, $\Phi^{(n+1)} := P\hat{\Phi}^{(n+1)}$ *by projection onto* $\mathcal{G}$, *e.g. orthogonalization*

$(\mathcal{A}\Phi^{(n)} - \Phi^{(n)}\Lambda^{(n)}) = [\mathcal{A}, \mathcal{D}_{\Phi^{(n)}}]\Phi^{(n)} = (I - \mathcal{D}_{\Phi^{(n)}})\mathcal{A}\Phi^{(n)}$
$B, \hat{B} : V \to V', \mathcal{B} : V^N \to V'^N, \hat{B} := (I - D)B(I - D) + DBD,$
$D = D_\Psi$

Projection onto the Stiefel manifold

$\widehat{\Phi} = \widehat{\Phi}^{(n+1)} = (\hat{\phi}_i)_{i=1}^N$, *and* $P\widehat{\Phi} =: \Phi \in \mathcal{V}$ *resp.* $\mathcal{G}$ *s.t.*
span $\{\hat{\phi}_i : i = 1, \ldots, N\}$ = *span* $\{\phi_i : i = 1, \ldots, N\}$
Projection $P : V^N \to \mathcal{S}$,*resp.* $\mathcal{G}$

- Gram Schmidt orthogonalization
- Löwdin transformation $\Phi = \mathbf{L}^{-1}\widehat{\Phi}$ where $\mathbf{L}\mathbf{L}^T = \langle \widehat{\Phi}^T \widehat{\Phi} \rangle$
- Diagonalization of $\Lambda^{(n+1)} = \langle \widehat{\Phi}^T \mathcal{A}_{[\Phi]} \widehat{\Phi} \rangle$, yields the first N eigenvalues $\lambda_1^{(n)} \leq \ldots \leq \lambda_N^{(n)}$ of $A_{[\Phi]}$.

Comment on direct minimization

improvement by subspace acceleration: e.g. line search and DIIS

$\Phi^{(n+1)} = \mathit{Function}(\hat{\Phi}^{(n+1)}, \Phi^{(n)}, \ldots, \Phi^{(0)})$

- gradient directed $\rightarrow$ convergence with Armijo line search
- $B : V \rightarrow V'$, $\|\phi\|_B^2 = \langle \phi, \phi \rangle_B := \langle B\phi, \phi \rangle \sim \|\phi\|_{H^1}^2$
  e.g.: $B \approx \frac{-1}{2}\Delta + C$, e.g. multigrid or convolution by FFT
- also valid if $V := V_h$ is a finite dimensional subspace
- for the simplified problem cf. e.g. Knyazev et al.

CI Configuration Interaction Method

Approximation space for (spin) orbitals $(\mathbf{x}_j, s_j) \to \varphi(\mathbf{x}_j, s_j)$

$$\mathcal{X}_h := \text{span}\,\{\varphi_i : i = 1, \ldots, \mathcal{N}\}\ ,\ \langle \varphi_i, \varphi_j \rangle = \delta_{i,j}$$

E.g. Canonical orbitals φ_i, $i = 1, \ldots, \mathcal{N}$ are eigenfunctions of the discretized single particle operator (e.g Fock operator)

$$\mathcal{F} := \mathcal{F}_h = \sum_{k=1}^{N} F_k : \mathcal{V}_{FCI} \to \mathcal{V}_{FCI}\ ,$$

$$\langle F\varphi_i - \lambda_i \varphi_i, \phi_h \rangle = 0\ \forall \phi_h \in \mathcal{X}_h$$

Full CI (for benchmark computations $\leq N = 18$) is a Galerkin method w.r.t. the subspace

$$\mathcal{V}_{FCI} = \bigwedge_{i=1}^{N} \mathcal{X}_h = \text{span}\{\Psi_{SL} = \Psi[\nu_1, ..\nu_N] = \frac{1}{N!}\det(\varphi_{\nu_i}(\mathbf{x}_j, s_j))_{i,j=1,}^{N}\}$$

CI Configuration Interaction Method

$\mathcal{N}$ (discrete) eigenfunction φ_i, $\langle F\varphi_i - \lambda_i\varphi_i, \phi_h\rangle = 0 \; \forall \phi_h \in \mathcal{X}_h$
The first N eigenfunctions φ_i are called occupied orbitals the others are called unoccupied orbitals (traditionally)

$$\varphi_1, \ldots, \varphi_N, \varphi_{N+1}, \ldots, \varphi_{\mathcal{N}}$$

Galerkin ansatz: $\Psi = c_0\Psi_0 + \sum_{\nu\in\mathcal{J}} c_\nu\Psi_\nu$

$$\boxed{\mathbf{H} = (\langle \Psi_{\nu'}, H\Psi_\nu\rangle) \;,\; \mathbf{Hc} = E\mathbf{c}} \quad , \quad \dim \mathcal{V}_h = \begin{pmatrix} \mathcal{N} \\ N \end{pmatrix}$$

The matrix coefficients of $\mathbf{H} = (\langle \Psi_{\nu'}, H\Psi_\nu\rangle)$ can be computed by Slater-Condon-rules. (sparse matrix)

Configuration Interaction Method

Assumption: For any $\varphi \in H^1$ there exist $\varphi_h \in \mathcal{X}_h$ such that $\|\varphi_h - \varphi\|_{H^1} \to 0$, if $h \to 0$ (roughly: $\lim_{h\to 0} \mathcal{X}_h = H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$)

Theorem

Let E_0 be a single eigenvalue and $H\Psi = E_0\Psi$ and $E_{0,h}$, $\Psi_h \in \mathcal{V}_h \subset \mathcal{V}_{FCI}$ be the Galerkin solution, then for $h < h_0$ hold

$$\begin{aligned} \|\Psi - \Psi_h\|_{\mathcal{V}} &\leq c \inf_{\phi_h \in \mathcal{V}_h} \|\Psi - \phi_h\|_{\mathcal{V}} \\ E_{0,h} - E_0 &\leq C \inf_{\phi_h \in \mathcal{V}_h} \|\Psi - \phi_h\|_{\mathcal{V}}^2. \end{aligned}$$

Since dim $\mathcal{V}_h = \mathcal{O}(\mathcal{N}^N)$, (curse of dimension), the full CI method is infeasible for large N or $\mathcal{N}$!!!!

Second quantization

Second quantization: annihilation operators:

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

and $= 0$ if j not apparent in $\Psi[\ldots]$.
sign-normalization: j appears in the first place in $\Psi[j, 1, \ldots, N]$.
The adjoint of a_b is a creation operator $a_b^\dagger$

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

Lemma

$$a_k a_l = -a_l a_k \ , \ a_k^\dagger a_l^\dagger = -a_l^\dagger a_k^\dagger \ , \ a_k^\dagger a_l + a_l a_k^\dagger = \delta_{k.l}$$

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

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)

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

$$H := H_h = \sum_{p,q=1}^{d} h_q^p a_q^\dagger a_p \sum_{p,q,r,s=1}^{d} g_{r,s}^{p,q} a_r^\dagger a_s^\dagger a_q a_p \ .$$

Reduced Density Matrices

Definition

For an N-electron wave funtion $\Psi \in \mathcal{V}$ resp. $\mathcal{V}_h$, we define the k-particle density matrices

$$\begin{aligned}
\gamma_1 : \gamma_q^p &= \langle \Psi, a_p^\dagger a_q \Psi \rangle \\
\gamma_2 : \gamma_{rs}^{pq} &= \langle \Psi, a_q^\dagger a_q^\dagger a_s a_r \Psi \rangle \\
\Gamma_1(\mathbf{x}, s; \mathbf{x}', s') &= \int \dots \int \overline{\Psi(\mathbf{x}, s; \mathbf{x}_2, s_2; \dots)} \Psi(\mathbf{x}', s'; \mathbf{x}_2, s_2; \dots) d\mathbf{x}_2 ds_2
\end{aligned}$$

Theorem

For $\Psi \in \mathcal{V}$ there holds

$$\begin{aligned}
E = \langle \Psi, H\Psi \rangle &= \sum_{p,q} h_p^q \gamma_q^p + \frac{1}{2} \sum_{p,q,r,s} g_{pq}^{rs} \gamma_{rs}^{pq} \\
&= \frac{1}{2} \sum_{p,q,r,s} \left[\frac{h_p^r \delta_q^s + \delta_p^r h_q^s}{N-1} + g_{pq}^{rs} \right] \gamma_{rs}^{pq}
\end{aligned}$$

Multi-Configuration theory (MCSCF) – Tucker format

Problem: How to optimize the basis set $\Phi = (\varphi_i)_{i=1,\dots,d}$?
Variational problem:

$$E_0 = \text{argmin}\widetilde{\mathcal{E}}\,(\Phi, \mathbf{c})\ ,\ \langle\varphi_i, \varphi_j\rangle = \delta_{i,j}$$

For simplicity of presentation we fix $\mathbf{c}$, and therefore the density matrices $\gamma^q_p, \gamma^{rs}_{pq}$, i.e.

$$E_0 = \text{argmin}\mathcal{E}(\Phi)\ ,\ \text{orthogonality constraints}\ \ \langle\varphi_i, \varphi_j\rangle = \delta_{i,j}$$

(and unitary invariance).
Define

$$\frac{\delta h^q_p}{\delta\varphi_p}(\mathbf{x}, s) = (\frac{-1}{2}\Delta - V_{core}(\mathbf{x}))\varphi_q(\mathbf{x}, s)\ ,$$

$$\frac{\delta g^{p,q}_{r,s}}{\delta\varphi_p}(\mathbf{x}, s) = 2\varphi_q(\mathbf{x}, s)\int \frac{\overline{\varphi_s(\mathbf{y}, s')}\varphi_r(\mathbf{y}, s')}{|\mathbf{x} - \mathbf{y}|}d\mathbf{y}ds'$$

Multi-Configuration theory (MCSCF) – Tucker format

First order conditions - Euler-Lagrange equations for basis optimization:
For $q = 1, \ldots, d$:

$$\sum_{p=1}^{d} \gamma_p^q \frac{\delta h_p^q}{\delta \varphi_p}(\mathbf{x}, s) + \frac{1}{2} \sum_{p,r,s=1}^{d} \gamma_{r,s}^{p,q} \frac{\delta g_{r,s}^{p,q}}{\delta \varphi_p}(\mathbf{x}, s) - \sum_{p=1}^{q} \lambda_p^q \varphi_q(\mathbf{x}, s) = 0$$

or

$$\sum_{p=1}^{d} \gamma_p^q \left(\frac{-1}{2}\Delta - V_{core}(\mathbf{x})\right)\varphi_q(\mathbf{x}, s) +$$

$$+ \sum_{p,r,s=1}^{d} \gamma_{r,s}^{p,q} \varphi_q(\mathbf{x}, s) \int \frac{\overline{\varphi_s(\mathbf{y}, s')}\varphi_r(\mathbf{y}, s')}{|\mathbf{x} - \mathbf{y}|} d\mathbf{y} ds' = \sum_{p=1}^{q} \lambda_p^q \varphi_q(\mathbf{x}, s)$$

Existence and uniqueness – known results

The variation w.r.t. to **c** yield the corresponding Ful CI equations

Problem

Minimize $\widetilde{\mathcal{E}} : \mathcal{G} \times \mathbb{R}^{dim V_{FCI}} \to \mathbb{R}$,

Theorem (Friesecke (03), M. Lewin (04?))

There exists a minimizer $(\Phi, \mathbf{c}) \in (H^1(\mathbb{R}^3))^d \times \mathbb{R}^{dim V_{FCI}}$ *for* $\widetilde{\mathcal{E}}((\Phi, \mathbf{c}))$ *with orthogonality constraints, provided that* $N' \leq \sum Z_\nu$.

Uniqueness is not know yet?

Remark: the Full CI solution can be replaced by MPS (TT) tensor format eqn. for basis optimization.