A posteriori errror estimators for Density Functional Theory and Hartree Fock

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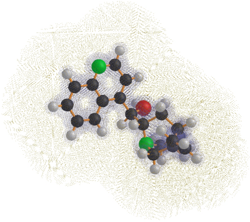
Mathematics for key technologies

Basic model - electronic Schrödinger equation

Electronic Schrödinger equation N' nonrelativistic electrons +

Born Oppenheimer approximation



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

The Hamilton operator

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

acts on *anti-symmetric* wave functions $\Psi \in H^1\left((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^{N'}\right)$,

$$\Psi(x_1, s_1, \ldots, x_{N'}, s_{N'}) \ , \ \mathbf{x}_i = (x_i, s_i) \in \mathbb{R}^3 \times \{\pm\frac{1}{2}\} \ .$$

Ground state energy $E_0 = \min\{\langle \mathcal{H}\psi, \psi\rangle : \langle \psi, \psi\rangle = 1\}$ and $n(x)$

Effective single particle models - DFT and

- *Closed Shell Restr. HF (RHF)* or *Density Functional theory*

  $N := \frac{N'}{2}$ number of electron pairs (spinfree formulations)
- minimization of the energy functional $\mathcal{J}_{KS}(\Phi)$

$$J_{KS}(\Phi) = \left\{ \int \frac{1}{2} \sum_{i=1}^{N} |\nabla \phi_i|^2 + \int n V_{core} + \frac{1}{2} \int \int \frac{n(x)n(y)}{|x-y|} dx\, dy - \alpha E_{xc}(n) + \beta EX_{HF}(D) \right\}$$

$\alpha = 0 \to$ Hartree Fock equations, $\beta = 0 \to$ Kohn-Sham equations.

- w.r.t. orthogonality constraints

  $\Phi = (\phi_i)_{i=1}^N \in H^1(\mathbb{R}^3)^N$ and $\langle \phi_i, \phi_j \rangle = \delta_{i,j}$
- $\phi_i \in H^1(\mathbb{R}^3)$, electron density $n(x) := \sum_{i=1}^N |\phi_i(x)|^2$

  Density matrix function $D(x,y) = \sum_{i=1}^N \phi_i(x)\overline{\phi_i(y)}$

Notations-Optimization with orthogonality constraints

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

Simplified Problem *(e.g appear in SC iteration)*: *minimize*

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

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

$$\boxed{A_\Phi \varphi_i = \frac{-1}{2}\Delta\varphi_i + \mathcal{V}_{core}\varphi_i + \mathcal{V}_H\varphi_i + \alpha\mathcal{V}_{XC}\varphi_i - \beta\frac{1}{2}\mathcal{W}\varphi_i}$$

density matrix op. projects onto $\text{span}\Phi := \text{span}\{\phi_i : i \leq N\}$

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

it satisfies $D^2 = D$, $tr\, D = N$, $D^T = D$

Geometry of admissible set

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

Definition

Stiefel manifold (orthogonality constraints)

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

Grassmann manifold is a quotient manifold

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

There is a one-to-one correspondence between

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

$V_\Phi = span\{\phi_1, \ldots, \phi_N\}$

$\mathcal{G}$ is also fundamental in tensor product approximation

Tangent space

Lemma

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

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

Edelman et al. (98); Blauert et al. (08), Maday, Turinici (02), Cances, et al. (10)

error measure on $\mathcal{G}$:

$\|[\Phi] - [\Psi]\| := \inf\{U \in \mathcal{U}(N) : \|\Phi - \Psi U\|_{V^N}\} \sim \|(I - \mathcal{D}_\Psi)\Phi\|$ loc.

1st order optimality conditions

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

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

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

For $[\Phi] \in \mathcal{G}$ there hold $\mathcal{J}'(\Phi) = 2\mathcal{A}_{[\Phi]}\Phi \in (V')^N$ where e.g.

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

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

At stationary points (Ψ, λ) there holds $\boxed{\Lambda = \langle A_{[\Psi]}\psi_i, \psi_j\rangle}$.

Goal oriented error estimation - revisited

Constr. optimization problem: $u = \text{argmin}\{J(v) : G(v) = 0\}$

Lagrangian: $L(x) := L(u, \Lambda) = J(u) - \Lambda G(u)$ $(x = (u, \Lambda) \in X)$

Theorem (- dual weighted residual method - Rannacher)

Let $X_h \subset X$ closed, consider the weak solutions (Galerkin)

$$L'(x)y = 0 \ \forall y \in X \ , \ L'(x_h)y_h = 0 \ \forall y_h \in X_h \ , \quad \textit{then}$$

$$L(x) - L(x_h) = \frac{1}{2} L'(x_h)(x - y_h) + \mathcal{O}(\|x - x_h\|_X^3) \ \forall y_h \in X_h$$

$$J(u) - J(u_h) = \frac{1}{2}\Big[J'(u_h)(u - u_h) - \Lambda_h G'(u_h)(u - u_h) - (\Lambda - \Lambda_h)G(u_h)\Big] \ .$$

Remainder $\mathcal{R}_3 = \frac{1}{2}\int_0^1 L^{(3)}(u_h + se)(e, e, e)s(s-1)ds = \mathcal{O}(e^3)$.

Orbital based functional

First attempt Maday & Turinici (2002) for HF

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

Theorem

If $\Psi \in V$ and $\Psi_h \in V_h$ are the corresponding stationary points

$$\begin{aligned} 0 \geq \mathcal{J}(\Psi) - \mathcal{J}(\Psi_h) &= \langle\langle(\Psi - \tilde{\Phi}_h), (\mathcal{A}_{[\Psi_h]}\Psi_h - \Psi_h\Lambda_h)\rangle\rangle + \mathcal{R}_3 \\ &= \langle\langle(\Psi - \tilde{\Phi}_h), (\mathcal{A}_{[\Psi_h]} - \Pi_h\mathcal{A}_{[\Psi_h]})\Psi_h\rangle\rangle + \mathcal{R}_3 \\ &= \eta(\Psi_h) + \mathcal{R}_3 \ \ \forall\tilde{\Phi}_h \in \mathcal{V}_h \end{aligned}$$

where $\Pi_h : V \to V_h$ is the L_2-orthogonal projection.

Truncation error at $|\mathbf{x}| \to \infty$ must be estimated seperately.

(Schwinger 2011)

Orbital based functional - Remainders

Theorem (Schwinger 2011)

The remainder term for linear eigenspace problem+$\mathcal{J}^{ES}$ is given by

$$\mathcal{R}_3^{ES} = \frac{1}{2}\langle\langle(\Psi - \Psi_h)(\Lambda - \Lambda_h), \Psi - \Psi_h\rangle\rangle \leq 0 \ .$$

and

$$|\mathcal{R}_3^{ES}| = \frac{1}{2}\|\Lambda - \Lambda_h\|_2\|(\Psi - \Psi_h)\|_{L_2}^2 \ .$$

If $\mathcal{A} + \mu \geq 1 - \Delta$ for some $\mu > 0$, then

$$\begin{aligned} |\mathcal{R}_3^{ES}| &= \frac{1}{2}\|\Lambda - \Lambda_h\|_2\|(\Psi - \Psi_h)\|_{L_2}^2 \\ &\lesssim \|(\Psi - \Psi_h)\|_{L_2}^2\|(\Psi - \Psi_h)\|_V \end{aligned}$$

Lemma (Remainders)

$$\mathcal{R}_3^{HF} = \mathcal{R}_3^{ES} + \mathcal{R}_3^{H} - \mathcal{R}_3^{W} \ , \ \mathcal{R}_3^{KS} = \mathcal{R}_3^{ES} + \mathcal{R}_3^{H} + \mathcal{R}_3^{EX}$$

where

$$\mathcal{R}_3^{H} = \sum_{k,l} \int \int 2 \frac{(\psi_{h,k} + \psi_k)(\psi_{h,k} - \psi_k)(\mathbf{x})(\psi_{h,l} - \psi_l)(\psi_{h,l} - \psi_l)(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}$$

$$\mathcal{R}_3^{W} = \sum_{k,l} 2 \int \int \frac{(\psi_{h,k} + \psi_k)(\psi_{h,l} - \psi_l)(\mathbf{x})(\psi_{h,k} - \psi_k)(\psi_{h,l} - \psi_l)(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}$$

$$|\mathcal{R}_3^{HF}| \lesssim \|(\Psi - \Psi_h)\|_V^3 \sup_h \|\Psi_h\|_{L_\infty} \leq \|(\Psi - \Psi_h)\|_V^3 \sup_h \|\Psi_h\|_{H^2}$$

But $\mathcal{R}_3^{EX} = \mathcal{O}(\|\Psi - \Psi_h\|_{L_2})$ *due to non-differentiability of Dirac Slater exchange at* $n(\mathbf{x}) \to 0$. *Otherwise* $\mathcal{R}_3^{EX} = \mathcal{O}(\|\Psi - \Psi_h\|_V^3)$

Ambiguity - unitary invariance ($N > 1$)

Error measure on $\mathcal{G}$:

$\|[\Phi] - [\Psi]\| := \inf\{\mathbf{U} \in \mathcal{U}(N) : \|\Phi - \Psi\mathbf{U}\|_{V^N}\}$ is invariant w.r.t. to $\mathbf{U} \in \mathcal{U}(N)$, as well as $\mathcal{J}(\Psi) - \mathcal{J}(\Psi_h) = \mathcal{J}([\Psi]) - \mathcal{J}([\Psi_h])$. But in fact $\eta(\Psi_h) = \eta(\Psi_h, \mathbf{U}, \mathbf{V})$ and $\mathcal{R}_3 = \mathcal{R}_3(\Psi_h, \mathbf{U}, \mathbf{V})$ for $\mathbf{U}, \mathbf{V} \in \mathcal{U}(N)$

Lemma (Schwinger)

$$\eta(\Psi_h, \mathbf{U}, \mathbf{V}) = \eta(, \Psi_h, \mathbf{U}) \ , \ \mathcal{R}_3(\Psi_h, \mathbf{U}, \mathbf{V}) = \mathcal{R}_3(, \Psi_h, \mathbf{U})$$

for $\mathcal{R}_3^{ES}, \mathcal{R}_3^{HF}, \mathcal{R}_3^{KS}$.

But $\mathbf{U} = \operatorname{argmin}_{\mathbf{U} \in \mathcal{U}(N)} |\mathcal{R}_3(\Psi_h, \mathbf{U})|$, $\mathcal{R}_3 = \mathcal{O}(\|\Psi_h - \Psi\mathbf{U}\|^3_{V^N})$ is unknown.

A posteriori error estimates - ambiguities

- For $\mathcal{J}^{ES}$, since $\mathcal{R}_3 \leq 0$, we obtain

$$\max_{\mathbf{U}\in\mathcal{U}(N)} \eta(\Psi_h, \mathbf{U}) = \min_{\mathbf{U}} \mathcal{R}_3^{ES}(\Psi_h, \mathbf{U})$$

  And therefore, we get efficiency! and reliability

$$C_1 |\mathcal{J}(\Psi) - \mathcal{J}(\Psi_h)| \leq \max_{\mathbf{U}} \eta(\Psi_h, \mathbf{U}) \leq |\mathcal{J}(\Psi) - \mathcal{J}(\Psi_h)|$$

- In the general case we have either this result, or only

$$|\mathcal{J}(\Psi) - \mathcal{J}(\Psi_h)| \leq \max_{\mathbf{U}} \eta(\Psi_h, \mathbf{U}) \ .$$

- $\widehat{\mathbf{U}} = \arg\max_{\mathbf{U}} \frac{|\eta(\mathbf{U})|}{|\mathcal{J}(\Psi) - \mathcal{J}(\Psi_h)|}$ could be computed ((S. Schwinger) - expensive!).

Interpolation estimates and H^2 regularity

For local basis functions like Finite Elements or wavelets

η could be computed $\approx$ by post- processing $\Psi \approx \widetilde{\Psi_h}$ or by

interpolation estimates: Let K be an element $K \subset \Omega_k := \mathrm{supp}\Psi_k \subset \widetilde{\Omega}_k$,

$V_h := \mathrm{span}\{\Phi_k\}$, $h_k \sim \mathrm{diam}K \sim \mathrm{diam}\Omega_k \sim \mathrm{diam}\widetilde{\Omega}_k$, then there ex. an operator

$i_h : V \to V_h$ reproducing polynomials s.t.

$$\|u - i_h u\|_{L_2(K)} \leq \tilde{C}_I h_k^2 \|u\|_{H^2(\widetilde{\Omega}_k)}$$

Lemma (H^2 regularity)

The minimizer $\Psi = (\psi_i)$ of $\mathcal{J}^{HF}, \mathcal{J}^{ES}, \mathcal{J}^{KS}$ is in $(H^2(\mathbb{R}^3))^N$,

there exists a shift $\mu \geq 0$ s.t.

$$\|\Phi\|_{H^2} \leq C_{H^2} \|(\mathcal{A}_{[\Psi]} + \mu)\Phi\|_{L_2}, \forall \Phi \in V$$

A posteriori error estimates

Theorem

If $[\Psi] \in \mathcal{G}$, $\Psi \in V^N$, $\Psi_h \in V_h^N$, *be the minimizers of* $\mathcal{J} = \mathcal{J}^{HF}, \mathcal{J}^{KS}, \mathcal{J}^{ES}$, $\mathbf{U} \in U(N)$ *, assume* H^2 *regularity*

$$\|\Phi\|_{H^2} \leq C_{H^2} \|(\mathcal{A}_{[\Psi]} + \mu)\Phi\|_{L_2} \; \forall \Phi \in V \; ,$$

and $\mathcal{R}_3 < \epsilon$ *suff. small, then* $\mathcal{J}(\Psi_h) - \mathcal{J}(\Psi) = \eta(\Psi_h, \mathbf{U}) + \mathcal{R}_3$

where

$$\begin{aligned}
\eta(\Psi_h, \mathbf{U}) &\leq C_I \sum_{i,k} \|(\Pi_h \mathcal{A}_{[\Psi_h]} - \mathcal{A}_{[\Psi_h]})\Psi_h\|^2_{L_2(K)} h_K^4 \|\mathbf{U}\Phi\|_{(H^2)^N} \\
&\leq C_I C_{H^2} \sqrt{tr(\Lambda^* \Lambda)} \sum_{i,k} \|(\Pi_h \mathcal{A}_{[\Psi_h]} - \mathcal{A}_{[\Psi_h]})\Psi_h\|^2_{L_2(K)} h_K^4 \\
&=: \eta(\Psi_h) \quad \textit{indep. of } \mathbf{U} \; .
\end{aligned}$$

A posteriori error estimates

- The error estimator η depends on the representation $\Psi_h \in \mathcal{V}$ of $[\Psi_h] \in \mathcal{G}$.
- $\sqrt{tr(\Lambda^*\Lambda)} \sim tr|\Lambda|$, and $\sqrt{tr(\Lambda^*\Lambda)} \approx \sqrt{tr(\Lambda_h^*\Lambda_h)}$
- if $\Psi_h \notin H^2$ - e.g. Finite Elements

$$\eta \leq C_I C_{H^2} C tr|\Lambda_h| \sum_K (\|\Pi \mathcal{A}_{[\Psi_h]} - \mathcal{A}_{[\Psi_h]}\Psi_h\|^2_{L_2(K)} h_K^4 + \|[\partial_n \Psi_h]\|^2_{L_2(e_K)} h_K^3$$

$[\partial_n \psi_{h,i}]|_{e_K}$ - jump of the normal derivatives across ∂K

- resembles eigenvalue error estimator of Larsen ($N = 1$)
- H^2 regularity is provided for HF etc. it simplifies proofs
- it allows an individual discretization of $\psi_{h,i}$, $i = 1, \ldots, N$.

Further assumptions

1. For DFT (LDA - Dirac-Slater term) $n(x) > 0 \; \forall x$ for regularity
2. $\Phi_h \in U_\delta(\Phi)$, $\mathcal{J}'(\Phi) = 0$ and

$$\langle\langle(\mathcal{J}''(\Phi)\Psi - \Psi\Lambda), \Psi\rangle\rangle \geq \gamma \, |||\Psi|||^2_{V^N} \quad \text{for all} \quad \Psi \in \mathcal{T}_{[\Phi]}\mathcal{G} \; ,$$

for a priori analysis (A. Zhou et al, Cances & Maday et al. , Ortner et al.)

Theorem

Under assumption (2), we obtain locally $\forall \Phi_h \in V_h^N$,

$$\|[\Psi]-[\Psi_h]\|^2 \lesssim \|(I-\mathcal{D}_\Psi)\Psi_h\|_V^2 \lesssim \langle\langle \mathcal{A}_{[\Psi_h]}\Psi_h - \Psi_h\Lambda_h, \Psi - \Phi_h\rangle\rangle = \eta(\Psi_h) \, .$$

Alternatively - Density operator based functional

Hartee-Fock energy: $\mathcal{E}(D) := tr(-\Delta + 2V_{core})D + tr(\mathcal{G}(D)D)$

$G(D)\phi := (n * \frac{1}{|.|})\phi - \frac{1}{2}\int \frac{\rho(.,y)}{|.-y|}\phi(y)dy$

Fock operator $\mathcal{F}(D) = A_\Psi = -\frac{1}{2}\Delta + V_{core} + \mathcal{G}(D)$.

Problem

minimize $\{\mathcal{E}(D) : D \in \mathcal{P}\}$ *w.r.t.* $\mathcal{P} = \{D = D^*, D^2 = D, trD = N\}$

ext. Lag. $\mathcal{L}(\lambda, D, \widehat{D}, \widehat{N}) = \lambda\mathcal{E}(D) - \langle \widehat{D}, D^2 - D\rangle - \widehat{N}(trD - N)$

Theorem (Schwinger)

If D *is a minimizer of* $\mathcal{E}$*, then there exists* $D \in \mathcal{P}$ *such that with* $\lambda = 1, \widehat{N} = 0, \widehat{D} := -D\mathcal{F}(D)D + (1-D)\mathcal{F}(D)(I-D)$ *(Lag. mult. is a diff.-operator!)* $(\lambda, D, \widehat{D}, \widehat{N})$ *is a stationary point of* $\mathcal{L}$*.*

Error representation

Theorem

Let D, D_h be corresp. minimizers, then

$$
\begin{aligned}
&\mathcal{E} - \mathcal{E}_h + \mathcal{R}_3^D \\
= \;& \langle\langle \mathcal{F}(D_h), D \rangle\rangle + \frac{1}{2} \langle\langle \widehat{D}_h D_h + D_h \widehat{D}_h - \widehat{D}_h, D - \tilde{D}^h \rangle\rangle \\
= \;& \langle\langle \mathcal{F}(D_h) - \mathcal{F}_h(D_h), D - \tilde{D}^h \rangle\rangle \; \forall \tilde{D}^h \in \mathcal{P}_h \\
= \;& \langle\langle \big(\mathcal{F}(D_h) - \mathcal{F}_h(D_h)\big)\Psi, \Psi \rangle\rangle \;\; \textit{choosen } \tilde{D}^h := 0
\end{aligned}
$$

Error representation

Corollary

Provided that $|\mathcal{R}_3$ *suff. small there holds*

$$|\mathcal{E} - \mathcal{E}_h| \approx \langle\langle \mathcal{F}(D_h) - \mathcal{F}_h(D_h), D - D^h \rangle\rangle \; \forall D^h \in V_h^D \; .$$

Approximate version

$$|\mathcal{E} - \mathcal{E}_h| \approx \langle\langle \mathcal{F}_h(D_h) - \mathcal{F}_h(D_h), D_H - D^h \rangle\rangle \; \forall D^h \in \mathcal{P}_h$$

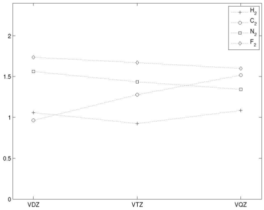
Remainder becomes (independent of ES, HF or KS)

$$\mathcal{R}_3^D = -\frac{1}{12} \langle\langle \widehat{D} - \widehat{D}_h, D - D_h D - D D_h + D_h \rangle\rangle \; .$$

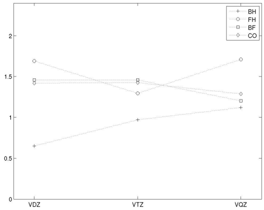
(PhD thesis of S. Schwinger submitted (2011))

Numerical tests by S. Schwinger — VXZ bases.

Plot of efficiency indices $\frac{\eta(\Psi_h)}{\mathcal{J}_h - \mathcal{J}}$

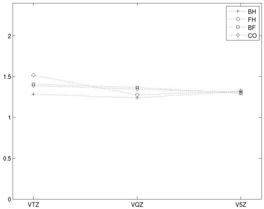


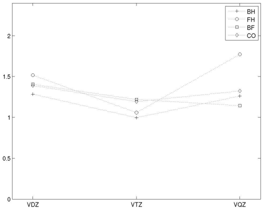
Hartree Fock



Hartree Fock

Numerical results





Kohn Sham with Dirac Slater exchange

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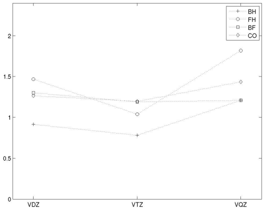
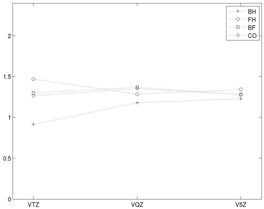
Numerical results



Kohn Sham with Perdew-Wang



Kohn Sham with Perdew-Wang