Kohn-Sham GGA Models and Their Approximations

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A joint work with Bin Yang and Siyu Zhao

Acknowledgements:
National Key R & D Program of China
National Natural Science Foundation of China

AI	Chip	Science
Model	Data	Calculation

$$
\begin{tikzcd}
\text{Chip} \arrow[r, "\text{AI}"] & \text{Science} \\
? \arrow[u, "\text{Model}"] \arrow[r, "\text{Calculation}"] & \text{Data} \arrow[u, "\text{AI}"']
\end{tikzcd}
$$

$$
\begin{tikzcd}
\text{Chip} \arrow[r, "\text{AI}"] & \text{Science} \\
\text{DFT} \arrow[u, "\text{Model}"] \arrow[r, "\text{Calculation}"] & \text{Data} \arrow[u, "\text{AI}"']
\end{tikzcd}
$$

DFT=Density Functional Theory

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\text{Chip} \arrow[r, "\text{AI}"] & \text{Science} \\
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\end{tikzcd}$$

DFT=Density Functional Theory

AI for Science

$\Uparrow$

Chip $\oplus$ Data

$\Uparrow$

DFT

Understand and make use of numerical DFT

AI for Science

$\Uparrow$

Chip $\oplus$ Data

$\Uparrow$

DFT

Understand and make use of numerical DFT

A basic mathematical model for (non-relativistic) interacting electrons and nuclei is the Schrödinger equation:

$$(T + V_{ne} + V_{ee})\psi = E\psi \quad \text{in} \quad \mathbb{R}^{3N},$$

where

$$T = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_{x_i}^2,$$

$$V_{ne} = -\sum_{i=1}^{N} \sum_{j=1}^{N_{atom}} \frac{Z_j e^2}{|x_i - r_j|}, \qquad V_{ee} = \frac{1}{2} \sum_{i,j=1, i\neq j}^{N} \frac{e^2}{|x_i - x_j|},$$

E is the electronic energy, ψ is the wavefunction, T is the kinetic energy operator, V_{ne} is the electron-nucleus/ions attraction energy operator, V_{ee} is the electron-electron repulsion energy operator.

Uncomputable/intractable...

A basic mathematical model for (non-relativistic) interacting electrons and nuclei is the Schrödinger equation:

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Uncomputable/intractable...

The general theory of quantum mechanics is now almost complete... The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to the explanation of the main features of complex atomic systems without too much computations.

P.A.M. Dirac (1929)

- Wavefunction approach
  - Hartree-Fock equations
  - Configuration interaction
  - Coupled cluster theory
- Density function theory
  - Orbital-free: Thomas-Fermi-von Weizsäcker type equations
  - Orbital-based: Kohn-Sham equations
- Quantum Monte-Carlo method
  - Variational Monte-Carlo
  - Diffusion Monte-Carlo
- Reduced density matrix method
- Density matrix functional theory
- ...

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Scientific importance

DFT has been extensively applied in science, engineering, and technology

Walter Kohn and John Pople won 1998 Nobel Prize in Chemistry

DFT literally underlies everything

Axel D. Becke

To understand numerical DFT mathematically

- Accuracy
- Efficiency

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The ground state energy E_* of a many-body system can be obtained by

$$E_0* = E(\rho_*) = \min\left\{E(\rho) \;:\; \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \rho = N\right\},$$

where ρ_* is the density of the ground state and Kohn-Sham energy

$$E(\rho_\Phi) \equiv E(\Phi) \;=\; \int_{\mathbb{R}^3}\left(\frac{1}{2}\sum_{i=1}^{N}|\nabla\phi_i|^2 + V_{ne}\rho_\Phi\right) + E_H(\rho_\Phi) + E_{xc}(\rho_\Phi)$$

for $\Phi = (\phi_1, \phi_2, \cdots, \phi_N) \in \left(H_0^1(\Omega)\right)^N$. Here and hereafter

$$\rho \equiv \rho_\Phi = \sum_{i=1}^{N}|\phi_i|^2$$

$$E_H(\rho) = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dxdy$$

$$E_{xc}(\rho) = \int_{\mathbb{R}^3}\mathcal{E}(\rho(x), |\nabla\rho(x)|)\rho(x)dx$$

Find $(\lambda_i, \phi_i)(i = 1, 2, \ldots, N)$ satisfying

$$\begin{cases} (-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(x))\phi_i &= \lambda_i\phi_i, \ \ i = 1, 2, \cdots, N \\ (\phi_i, \phi_j) &= \delta_{ij}, \ \ i, j = 1, 2, \cdots, N \end{cases}$$

where

$$\rho(x) = \sum_{i=1}^{N} |\phi_i|^2$$

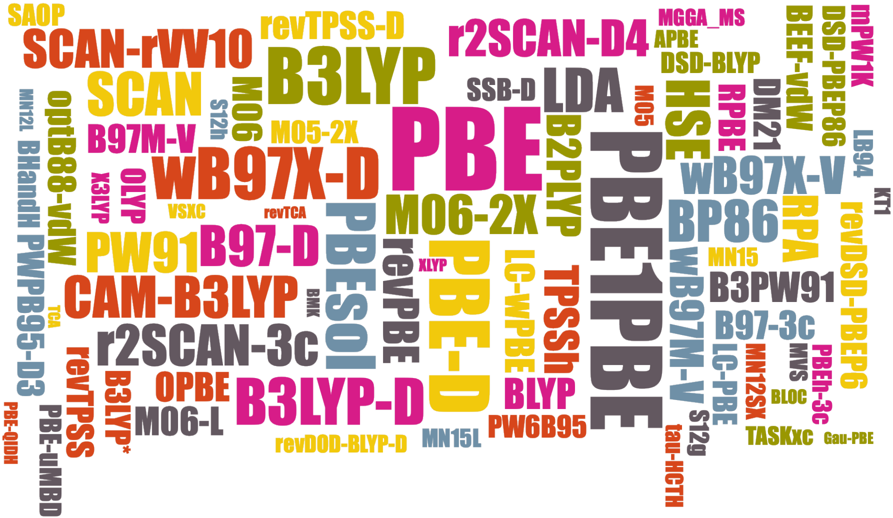
$$V_{eff}(\rho) = V_{ne} + V_H(\rho) + V_{xc}(\rho)$$

$$V_{ne}(x) = -\sum_{j=1}^{N_{atom}} \frac{Z_j e^2}{|x - r_j|}$$

$$V_H(\rho)(x) = e^2 \int \frac{\rho(r)}{|x - r|} \mathrm{d}r$$

and exchange-correction term V_{xc} contains all the many-body complexity

Exchange-correction functional approximations



https://www.marcelswart.eu/dft-poll/

LDA=Local density approximation

$$E_{xc}(\rho) = \int \varepsilon_{xc}(\rho)(\cdot)\rho(\cdot), \quad \varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$

$$\varepsilon_x = -\frac{3}{4}\left(\frac{3\rho}{\pi}\right)^{1/3}$$

$$\varepsilon_c = \begin{cases} -0.1423/(1 + 1.0529\sqrt{r_*} + 0.334 r_*), & \text{if } r_* \geq 1 \\ 0.0311 \ln r_* - 0.048 + 0.0020 r_* \ln r_* - 0.0116 r_*, & \text{if } r_* < 1 \end{cases}$$

where $r_* = \left(\frac{3}{4\pi\rho}\right)^{1/3}$

Problems in LDA DFT application:

- Correction energy is double higher than the exact one
- The relative error of exchange energy is about 10%
- The bond energy is higher
- ......

GGA and hybrid-GGA type density functional approximations are most utilized

Bound energy is accurate as MP(M∅ller-Plesset)2, the performance of PBE(Perdew Burke Ernzerhof) functional(1996) is good enough
GGA= Generalized Gradient Approximation

The annual popularity poll for density functionals:
edition 2017

DFT2017 poll

organized by:
marcel swart
f. matthias bickelhaupt
miquel duran

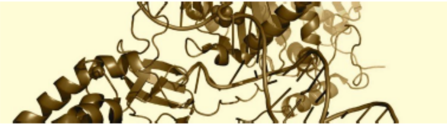
Results for the 2017 edition of the Annual DFT Popularity Poll: Primera D

	functional	like		neutral		hate	
1	PBE0	31	48.4 %	8	12.5 %	7	10.9 %
2	PBE	29	45.3 %	11	17.2 %	8	12.5 %
3	wB97X-D	26	40.6 %	10	15.6 %	3	4.7 %
4	B3LYP-D	22	34.4 %	12	18.8 %	5	7.8 %
5	CAM-B3LYP	19	29.7 %	15	23.4 %	5	7.8 %
6	B97-D	18	28.1 %	14	21.9 %	2	3.1 %
7	B3LYP	21	32.8 %	16	25.0 %	14	21.9 %
8	TPSSh	13	20.3 %	14	21.9 %	7	10.9 %
9	BP86	13	20.3 %	12	18.8 %	9	14.1 %
10	B2PLYP	12	18.8 %	13	20.3 %	8	12.5 %
11	PW91	7	10.9 %	20	31.2 %	6	9.4 %
12	HSE	8	12.5 %	16	25.0 %	6	9.4 %
13	LC-wPBE	8	12.5 %	15	23.4 %	6	9.4 %
14	M06-2X	12	18.8 %	14	21.9 %	20	31.2 %
15	revPBE	7	10.9 %	14	21.9 %	5	7.8 %
16	BLYP	5	7.8 %	20	31.2 %	10	15.6 %
17	RPA	6	9.4 %	12	18.8 %	5	7.8 %
18	OLYP	4	6.2 %	14	21.9 %	7	10.9 %
19	LDA	4	6.2 %	17	26.6 %	14	21.9 %
20	BHandH	2	3.1 %	16	25.0 %	10	15.6 %

Exchange-correction functional popularity

DFT2022 poll

organized by:
marcel swart
f. matthias bickelhaupt
miquel duran



The annual popularity poll for density functionals:
edition 2022

Results for the 2022 edition of the Annual DFT Popularity Poll: Primera Divisió

	functional	like		neutral		hate	
1	**PBE**	177	62.5 %	55	19.4 %	16	5.7 %
2	**PBE0**	120	42.4 %	85	30.0 %	17	6.0 %
3	**PBE-D**	101	35.7 %	96	33.9 %	16	5.7 %
4	**wB97X-d**	103	36.4 %	78	27.6 %	15	5.3 %
5	**PBEsol**	80	28.3 %	108	38.2 %	17	6.0 %
6	**SCAN**	82	29.0 %	98	34.6 %	24	8.5 %
7	**HSE**	84	29.7 %	97	34.3 %	31	11.0 %
8	**LDA**	94	33.2 %	83	29.3 %	52	18.4 %
9	**B3LYP**	79	27.9 %	118	41.7 %	60	21.2 %
10	**B3LYP-D**	61	21.6 %	127	44.9 %	40	14.1 %
11	**B97-D**	47	16.6 %	137	48.4 %	18	6.4 %
12	**PW91**	52	18.4 %	120	42.4 %	25	8.8 %
13	**CAM-B3LYP**	50	17.7 %	122	43.1 %	26	9.2 %
14	**RPA**	51	18.0 %	114	40.3 %	21	7.4 %
15	**SCAN-rVV10**	55	19.4 %	97	34.3 %	23	8.1 %
16	**BP86**	36	12.7 %	141	49.8 %	25	8.8 %
17	**M06-2X**	65	23.0 %	83	29.3 %	58	20.5 %
18	**revPBE**	40	14.1 %	115	40.6 %	21	7.4 %
19	**optB88-vdW**	37	13.1 %	112	39.6 %	17	6.0 %
20	**RPBE**	34	12.0 %	115	40.6 %	19	6.7 %

Exchange-correction functional popularity

DFT2023 poll

organized by:
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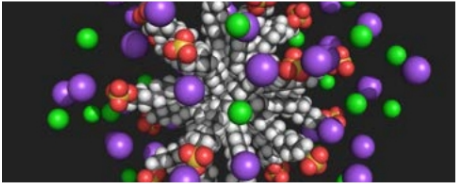

The annual popularity poll for density functionals: edition 2023

Results for the 2023 edition of the Annual DFT Popularity Po

	functional	like		neutral		hate	
1	PBE	105	63.3 %	37	22.3 %	9	5.4 %
2	wB97X-D	72	43.4 %	35	21.1 %	6	3.6 %
3	PBE-D	65	39.2 %	51	30.7 %	10	6.0 %
4	PBE0	61	36.7 %	39	23.5 %	9	5.4 %
5	B3LYP	54	32.5 %	54	32.5 %	41	24.7 %
6	PBEsol	41	24.7 %	56	33.7 %	14	8.4 %
7	HSE	39	23.5 %	57	34.3 %	11	6.6 %
8	B3LYP-D	40	24.1 %	63	38.0 %	26	15.7 %
9	wB97X-V	37	22.3 %	51	30.7 %	5	3.0 %
10	CAM-B3LYP	43	25.9 %	46	27.7 %	21	12.7 %
11	wB97M-V	33	19.9 %	54	32.5 %	6	3.6 %
12	SCAN	33	19.9 %	61	36.7 %	13	7.8 %
13	r2SCAN-D4	33	19.9 %	55	33.1 %	13	7.8 %
14	LDA	44	26.5 %	41	24.7 %	43	25.9 %
15	B97-D	25	15.1 %	68	41.0 %	15	9.0 %
16	SCAN-rVV10	22	13.3 %	58	34.9 %	10	6.0 %
17	PW91	19	11.4 %	74	44.6 %	17	10.2 %
18	B97M-V	20	12.0 %	62	37.3 %	10	6.0 %
19	RPA	20	12.0 %	58	34.9 %	18	10.8 %
20	B97-3c	16	9.6 %	64	38.6 %	15	9.0 %

Existence, uniqueness of solution

Approximativity of numerical solutions

- Discretization error: convergence, convergence rate
- Algebraic error: SCF convergence, convergence rate
- Machine error

Implementation/parallelization

Solution may not exist, may not be unique if it exists

- A. Anantharaman and E. Cances, Ann. Inst. Henri Poincare, 26(2009) LDA + GGA two-electron system
- H. Chen et al, Adv. Comput. Math., 2013 general LDA bounded domain
- C. Le Bris, PhD thesis, 1993 LDA
- S. Zhao, PhD thesis, 2024 general LDA, GGA

- E. Cancès, R. Chakir and Y. Maday (M2AN, 2012)

  Second-order optimality conditions, Kohn-Sham equation, convergence rate of planewave approximations

- P. Suryanarayana, V. Gavini, T. Blesgen, K. Bhattacharya, and M. Ortiz (JMPS, 2010)

  Energy minimization, convergence of finite element approximations

Chen, Dai, and Zhou, et al, Nonlinearity, ACOM, MMS, ... 2004–

- Local isomorphism of the associated Hamiltonian, finite dimensional approximations; adaptive finite element computations
- Convergence and a priori error analysis of eigenpair approximations
- A posteriori error estimates of eigenpair approximations, convergence and complexity of adaptive approximations

- A. Zhou (Nonlinearity, 2004; MMAS, 2007)
  Convex $\rightsquigarrow$ convergence of eigenpair, upper bounds, $+$TFW model
- V. Gavini, K. Bhattacharya, and M. Ortiz (JMPS, 2007)
  direct minimization,convergence of energy   Not eigenvalue problem
- E. Cancès, R. Chakir, and Y. Maday (JSC, 2010)
  Convex $\rightsquigarrow$ convergence rate of eigenpair, $+$TFW model
- H. Chen, X. Gong, and A. Zhou (MMAS, 2010)
  Noncovex $\rightsquigarrow$ convergence of eigenpair, Orbital-free model
- B. Langwallner, C. Ortner, and E. Süli (M^3AS, 2011)
  Second-order optimality condition $\rightsquigarrow$ convergence of eigenpair, TFW type model
- H. Chen, L. He, and A. Zhou (CMAME, 2011)
  Local isomorphism condition $\rightsquigarrow$ convergence rate, Orbital-free model
- E. Cancès, R. Chakir, and Y. Maday (M2AN, 2012)
  Second-order optimality condition $\rightsquigarrow$ convergence rate, Kohn-Sham model, planewave
- H. Chen, X. Gong, L. He, Z. Yang, and A. Zhou (ACOM, 2013)
  Local isomorphism condition$\rightsquigarrow$ convergence rate, Kohn-Sham model

H. Chen, X. Gong, L. He, and, A. Zhou (AAMM, 2011)

Second-order optimality condition + fine initial mesh $\rightsquigarrow$ convergence, Orbital-free DFT model

H. Chen, L. He, and A. Zhou (CMAME, 2011)

Local isomorphism condition + fine initial mesh $\rightsquigarrow$ convergence rate and complexity, Orbital-free DFT model

H. Chen, X. Dai, X. Gong, L. He, and A. Zhou (MMS, 2014)

Local isomorphism condition + fine initial mesh $\rightsquigarrow$ convergence rate and complexity, Kohn-Sham DFT model

B. Yang and A. Zhou (M2AN, 2021)

Local isomorphism condition $\rightsquigarrow$ convergence rate and complexity, Kohn-Sham DFT model

...

Energy functional

$$E(\Phi) = \int_\Omega \left(\sum_{i=1}^N \frac{1}{2} |\nabla \phi_i|^2 + V_{\text{loc}}(x)\rho_\Phi + \sum_{i=1}^N \phi_i V_{\text{nl}} \phi_i + \mathcal{E}\Big(\rho_\Phi, |\nabla \rho_\Phi|\Big)\rho_\Phi \right) + \frac{1}{2} D(\rho_\Phi, \rho_\Phi)$$

Hamitonian

$$H_\Phi = -\frac{1}{2}\mathrm{div}\left[\nabla \cdot +2\frac{\partial \mathcal{E}}{\partial \kappa}\Big(\rho_\Phi, |\nabla \rho_\Phi|\Big)\frac{\nabla \rho_\Phi}{|\nabla \rho_\Phi|}\cdot\right] + \frac{\partial \mathcal{E}}{\partial \kappa}\Big(\rho_\Phi, |\nabla \rho_\Phi|\Big)\frac{\nabla \rho_\Phi}{|\nabla \rho_\Phi|}\nabla\cdot$$
$$+ V_{\text{nl}} + \rho_\Phi * |r|^{-1} + \frac{\partial \mathcal{E}}{\partial \rho}\Big(\rho_\Phi, |\nabla \rho_\Phi|\Big)$$

where $\kappa = |\nabla \rho|$

Function class

$$\mathscr{P}_p = \{f : [0,\infty)^2 \to \mathbb{R} : \exists c \in [0,\infty) \text{ such that } \sup_{t_2 \in [0,\infty)} |f(t_1,t_2)| \leqslant c(t_1^p + 1) \quad \forall t_1 \in [0,\infty)\}$$

Introduce

$$\mathcal{S}^{N\times N} = \{M \in \mathbb{R}^{N\times N} : M^T = M\},$$

$$\mathcal{A}^{N\times N} = \{M \in \mathbb{R}^{N\times N} : M^T = -M\},$$

$$\mathbb{Q} = \{\Phi \in (H_0^1(\Omega))^N : \Phi^T\Phi = I^{N\times N}\}$$

For any $\Phi \in \mathbb{Q}$,

$$\mathcal{H} \equiv (H_0^1(\Omega))^N = \mathcal{S}_\Phi \oplus \mathcal{A}_\Phi \oplus \mathcal{T}_\Phi,$$

where

$$\mathcal{S}_\Phi = \Phi\mathcal{S}^{N\times N},$$

$$\mathcal{A}_\Phi = \Phi\mathcal{A}^{N\times N},$$

$$\mathcal{T}_\Phi = \left\{\Psi \in (H_0^1(\Omega))^N : \Psi^T\Phi = 0 \in \mathbb{R}^{N\times N}\right\}$$

The ground state Φ can be obtained by minimizing the associated energy in $\mathbb{Q}$. Namely,

$$\Phi \in \arg\min \{E(\Psi) : \Psi \in \mathbb{Q}\}$$

The set of ground states:

$$\mathcal{G} = \left\{\Phi \in \mathbb{Q} : \; E(\Phi) = \min_{\Psi \in \mathbb{Q}} E(\Psi)\right\}$$

$$\Theta = \left\{(\Lambda, \Phi) \in \mathbb{R}^N \times \mathcal{U} : (\Lambda, \Phi) \text{ is an exact eigenpair}\right\}$$

$$\Phi \in \mathcal{G} \iff \Phi U \in \mathcal{G} \quad \forall \; U \in \mathcal{O}^{N\times N}$$

where $\mathcal{O}^{N\times N}$ is the set of orthogonal matrices.

A weak form of Kohn-Sham equation: find $\Lambda \in \mathbb{R}^{N\times N}$, $\Phi \in \mathbb{Q}$ such that

$$(H_\Phi \phi_i, v) = \Big(\sum_{j=1}^{N} \lambda_{ij}\phi_j, v\Big) \quad \forall \; v \in (H_0^1(\Omega))^N \;, \quad i = 1, 2, \cdots, N$$

Let $X_n \subset H_0^1(\Omega)(n = 1, 2, \cdots)$ be finite dimensional subspaces satisfying

$$\lim_{n\to\infty} \inf_{v\in X_n} \|u - v\|_{1,\Omega} = 0 \quad \forall u \in H_0^1(\Omega)$$

Approximations in X_n:

$$\Phi_n \in \arg\min\{E(\Psi) : \Psi \in (X_n)^N \cap \mathbb{Q}\}$$

The set of ground states of finite dimensional problems:

$$\begin{aligned} \mathcal{G}_n &= \{\Phi_n \in (X_n)^N \cap \mathbb{Q} : \ E(\Phi_n) = \min_{\Psi\in(X_n)^N\cap\mathbb{Q}} E(\Psi)\} \\ \Theta_n &= \left\{(\Lambda_n, \Phi_n) \in \mathbb{R}^N \times \mathcal{U} : (\Lambda_n, \Phi_n) \text{ is a discrete eigenpair}\right\} \end{aligned}$$

$$\Phi_n \in \mathcal{G}_n \iff \Phi_n U \in \mathcal{G}_n \quad \forall\ U \in \mathcal{O}^{N\times N}$$

Finite dimensional discretization of Kohn-Sham equation: find $\Lambda_n \in \mathbb{R}^{N\times N}$, $\Phi_n \in (X_n)^N \cap \mathbb{Q}$ such that

$$(H_{\Phi_n}\phi_{i,n}, v) = \Big(\sum_{j=1}^{N} \lambda_{ij,n}\phi_{j,n}, v\Big) \quad \forall\ v \in (X_n)^N, \quad i = 1, 2, \cdots, N$$

Nonlinear operator

Nonconvex functional

Many and degenerate eigenvalues

Nonlinear operators

Nonlinear operator $\mathcal{F} : \mathbb{R}^{N\times N} \times \mathcal{H} \to \mathcal{H}^*$ by

$$\langle \mathcal{L}(\Lambda,\Phi),\Gamma\rangle = \sum_{i=1}^{N}\Big(H_\Phi \phi_i - \sum_{j=1}^{N}\lambda_{ij}\phi_j,\gamma_i\Big) \quad \forall\ \Gamma = (\gamma_i)_{i=1}^{N} \in \mathcal{H}$$

associated with Fréchet derivative $\mathcal{L}'_\Phi(\Lambda,\Phi) : \mathcal{H} \to \mathcal{H}^*$ as follows

$$\langle \mathcal{L}'_\Phi(\Lambda,\Phi)\Psi,\Gamma\rangle = \frac{1}{4}E''(\Phi)(\Psi,\Gamma) - \sum_{i,j=1}^{N}(\lambda_{ij}\psi_j,\gamma_i)$$

$$\begin{aligned}\langle \mathcal{L}'_\Phi(\Lambda,\Phi)\Psi,\Gamma\rangle = \sum_{i=1}^{N}\Bigg(&\frac{1}{2}(\nabla\psi_i,\nabla\gamma_j) + (V_{\mathrm{loc}}\psi_i,\gamma_j) + \sum_{j=1}^{M}(\zeta_j,\psi_i)(\zeta_j,\gamma_i)\\ &+\Big(\frac{\partial\mathcal{E}}{\partial\rho}(\rho_\Phi,\kappa)\psi_i,\gamma_i\Big) + D(\rho_\Phi,\psi_i\gamma_j) - \Big(\sum_{j=1}^{N}\lambda_{ij}\psi_j,\gamma_i\Big)\\ &+2\phi_i\frac{\partial^2\mathcal{E}}{\partial\rho^2}(\rho_\Phi,\kappa)\sum_{j=1}^{N}(\phi_j\psi_j,\gamma_i) + \sum_{j=1}^{N}2D(\phi_j\psi_j,\phi_i\gamma_i)\Bigg)\end{aligned}$$

Nonlinear operator $\mathcal{F} : \mathbb{R}^{N\times N} \times \mathcal{H} \to \mathcal{H}^*$ by

$$\langle \mathcal{L}(\Lambda, \Phi), \Gamma \rangle = \sum_{i=1}^{N} \Big(H_\Phi \phi_i - \sum_{j=1}^{N} \lambda_{ij}\phi_j, \gamma_i \Big) \quad \forall\ \Gamma = (\gamma_i)_{i=1}^{N} \in \mathcal{H}$$

associated with Fréchet derivative $\mathcal{L}'_\Phi(\Lambda, \Phi) : \mathcal{H} \to \mathcal{H}^*$ as follows

$$\langle \mathcal{L}'_\Phi(\Lambda, \Phi)\Psi, \Gamma \rangle = \frac{1}{4} E''(\Phi)(\Psi, \Gamma) - \sum_{i,j=1}^{N} (\lambda_{ij}\psi_j, \gamma_i)$$

$$\begin{aligned}
\langle \mathcal{L}'_\Phi(\Lambda, \Phi)\Psi, \Gamma \rangle = \sum_{i=1}^{N} \Bigg(& \frac{1}{2}(\nabla\psi_i, \nabla\gamma_i) + (V_{\mathrm{loc}}\psi_i, \gamma_i) + \sum_{j=1}^{M} (\zeta_j, \psi_i)(\zeta_j, \gamma_i) \\
& + \Big(\frac{\partial \mathcal{E}}{\partial \rho}(\rho_\Phi, \kappa)\psi_i, \gamma_i \Big) + D(\rho_\Phi, \psi_i\gamma_i) - \Big(\sum_{j=1}^{N} \lambda_{ij}\psi_j, \gamma_i \Big) \\
& + 2\phi_i \frac{\partial^2 \mathcal{E}}{\partial \rho^2}(\rho_\Phi, \kappa) \sum_{j=1}^{N} (\phi_j\psi_j, \gamma_i) + \sum_{j=1}^{N} 2D(\phi_j\psi_j, \phi_i\gamma_i) \Bigg)
\end{aligned}$$

Assumption for GGA model

A1 $\mathcal{E}(\rho, \kappa) \in \mathscr{P}_p$ and $p < 5/3$, or $\mathcal{E}(t_1, t_2) \in \mathscr{P}_3$ and $\inf\limits_{(t_1,t_2)\in[0,\infty)^2} \mathcal{E}(t_1, t_2) > -\infty$

A2 $\nabla\mathcal{E}(t_1, t_2) \in \mathscr{P}_2 \times \mathscr{P}_1$

A3 $t_1\nabla\dfrac{\partial\mathcal{E}(t_1, t_2)}{\partial t_1}, t_2\nabla\dfrac{\partial\mathcal{E}(t_1, t_2)}{\partial t))2} \in \mathscr{P}_2 \times \mathscr{P}_1.$

A0 (Λ_*, Φ_*) is a solution of Kohn-Sham equation and there exists a constant $\beta > 0$ depending on (Λ_*, Φ_*) such that

$$\inf_{\Gamma\in\mathcal{T}_\Phi} \sup_{\Psi\in\mathcal{T}_\Phi} \frac{\langle \mathcal{L}'_\Phi(\Lambda_*, \Phi_*)\Psi, \Gamma\rangle}{\|\Psi\|_{1,\Omega}\|\Gamma\|_{1,\Omega}} \geq \beta \qquad (1)$$

A stronger condition than (1)

$$\langle \mathcal{L}'_\Phi(\Lambda_*, \Phi_*)\Gamma, \Gamma\rangle \geq \gamma\|\Gamma\|^2_{1,\Omega} \quad \forall\ \Gamma \in \mathcal{T}_\Phi$$

is satisfied for a linear self-adjoint operator when there is a gap between the lowest Nth eigenvalue and $(N+1)$th eigenvalue

PBE functional satisfy Assumptions **A1-A3**

PBE functional

$$E_{xc}(\rho) = \int_{\mathbb{R}^3} \rho(y)\Big(\varepsilon_x(\rho)(y)F(s)(y)\mathrm{d}y + H(t,\rho)(y) + \varepsilon_c(\rho)(y)\Big)\mathrm{d}y$$

where
$$F(s) = 1 + \frac{\beta s^2}{1+\beta\nu^{-1}s^2}, H(t,\rho) = \vartheta \ln\left(1 + \frac{\upsilon}{\vartheta}t^2 \cdot \frac{1+Bt^2}{1+Bt^2+B^2t^4}\right)$$

$$\varepsilon_x(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}}, \varepsilon_c(\rho) = \begin{cases} -0.1423/(1+1.0529\sqrt{r_*}+0.3334r_*), & r_* \geqslant 1, \\ -0.0480 + 0.0311\ln r_* - 0.0116 r_s + 0.0020 r_* \ln r_*, & r_* \leqslant 1 \end{cases}$$

with $\beta = 0.21951$, $\nu = 0.804$, $\vartheta = \pi^{-2}(1-\ln 2)$, $\upsilon = 3\pi^{-2}\beta$ and

$$s = \frac{|\nabla\rho|}{2k_f\rho}, k_f = (3\pi^2\rho)^{\frac{1}{3}}, t = \left(\frac{\pi}{4}\right)^{\frac{1}{2}}k_f^{\frac{1}{2}}s, B = \frac{\upsilon}{\vartheta}\left[\exp\left(-\frac{\varepsilon_c(\rho)}{\vartheta}\right)-1\right]^{-1}, r_* = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$

Theorem

If $\mathcal{E}(t_1, t_2) \in \mathscr{P}_3$, then

$$\lim_{n\to\infty} E(\Phi_n) = \inf_{\Psi\in\mathcal{Q}} E(\Psi)$$

where $\Phi_n \in \mathcal{G}_n, \;\; n \geqslant 1.$

Theorem

If Assumptions A2 and A3 hold, then

$$|E - E_n| \lesssim d^2_{\mathcal{H}}(\mathcal{G}, \mathcal{H}_n)$$

Theorem

Let $(\Lambda_\star, \Phi_\star) \in \Theta$. If Assumptions A2, A3 and A0 hold, then there exists $\delta > 0$ such that for sufficiently large n, there exists a unique local solution $(\Lambda_n, \Phi_n) \in X_{\Phi_\star,n} \cap B_\delta(y_\star)$ satisfying

$$|\Lambda_n - \Lambda_\star| \lesssim \|\Phi_n - \Phi_\star\|_{1,\Omega}^2 + \|\Phi_n - \Phi_\star\|_{1,\Omega} + \|\Phi_n - \Phi_\star\|_{0,\Omega},$$

and

$$||\Phi_\star - \Phi_n||_{0,\Omega} \lesssim \rho_n||\Phi_\star - \Phi_n||_{1,\Omega},$$

with $\rho_n \to 0$ as $n \to \infty$.

Conclusion

Existence?

Convergence, error estimation

Uniqueness?

Conclusion

Existence?

Convergence, error estimation

Uniqueness?

Thank You !