

How to Improve Functionals in Density Functional Theory?

内藤 智也 (Tomoya Naito)

Department of Physics, Graduate School of Science, the University of Tokyo, JAPAN
RIKEN Nishina Center, JAPAN

July 30, 2019

International Nuclear Physics Conference 2019
Scottish Event Campus, Glasgow, United Kingdom



In collaboration with Haozhao Liang and Daisuke Ohashi
Ohashi, Naito, and Liang. arXiv:1812.09285 [physics.chem-ph]

Density Functional Theory

Many-body Hamiltonian

$$H = \sum_j t_j + \sum_j V_{\text{ext}}(\mathbf{r}_j) + \sum_{j < k} V_{\text{int}}(\mathbf{r}_j, \mathbf{r}_k)$$

t_j : single-particle kinetic operator \mathbf{r}_j : coordinate of particle j ,

V_{ext} : external potential, V_{int} : interaction

Ground-state Energy in Kohn-Sham Scheme

$$E_{\text{gs}} = T_0 + \int V_{\text{ext}}(\mathbf{r}) \rho_{\text{gs}}(\mathbf{r}) d\mathbf{r} + E_{\text{d}}[\rho_{\text{gs}}] + E_{\text{x}}[\rho_{\text{gs}}] + E_{\text{c}}[\rho_{\text{gs}}]$$

T_0 : kinetic energy of non-interacting system,

E_{d} : Hartree functional, E_{x} : exchange functional, E_{c} : correlation functional

Kohn and Sham. *Phys. Rev.* **140**, A1133 (1965)

If $E_{\text{xc}} = E_{\text{x}} + E_{\text{c}}$ is known, the exact E_{gs} and ρ_{gs} can be derived

Density Functional Theory

Kohn-Sham Effective Potential

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int V_{\text{int}}(\mathbf{r}, \mathbf{r}') \rho_{\text{gs}}(\mathbf{r}') d\mathbf{r}' + \left. \frac{\delta E_{\text{xc}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right|_{\rho=\rho_{\text{gs}}}$$
$$[t + V_{\text{KS}}(\mathbf{r})] \varphi_j = \varepsilon_j \varphi_j, \quad \rho(\mathbf{r}) = \sum_j |\varphi_j(\mathbf{r})|^2$$

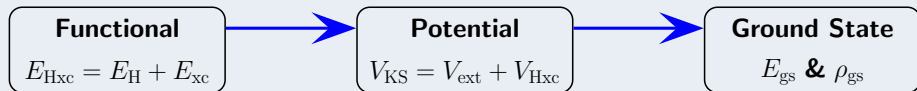
Problems of Density Functional Theory

Since DFT is low numerical cost,
it is a strong method for quantum many-body problem, but. . .

- Even if V_{int} is known, **the way to derive exact E_{xc} is unknown**
- Moreover, V_{int} is also still under discussion in nuclear physics
→ **Only phenomenological & empirical functionals are used**

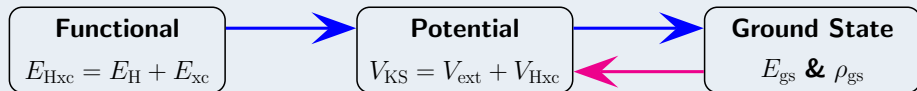
According to Hohenberg-Kohn theorem, V_{KS} is unique for each system
→ **“Inverse Kohn-Sham Method”** may be applicable to “derive” E_{xc} ?!

Original & Inverse Kohn-Sham Method



- The exact V_{KS} is unique for the system

Original & Inverse Kohn-Sham Method

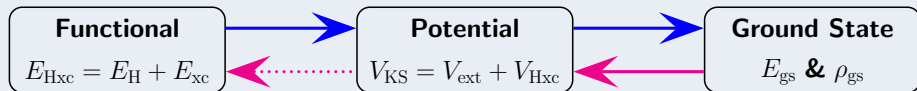


- The exact V_{KS} is unique for the system
- “Inverse Kohn-Sham Method”
 V_{KS} can be derived from ρ_{gs} exactly

Wang and Parr. *Phys. Rev. A* **47**, R1591 (1993)

Zhao and Parr. *J. Chem. Phys.* **98**, 543 (1993)

Original & Inverse Kohn-Sham Method



- The exact V_{KS} is unique for the system
- “Inverse Kohn-Sham Method”
 V_{KS} can be derived from ρ_{gs} exactly

Wang and Parr. *Phys. Rev. A* **47**, R1591 (1993)

Zhao and Parr. *J. Chem. Phys.* **98**, 543 (1993)

- However,
how to use V_{KS} given by IKS or how to derive E_{Hxc} from V_{KS}
is unknown

Summary of Our Work “IKS-DFPT”

- The way to improve known functional \tilde{E}_{Hxc} is proposed
- Difference between known \tilde{E}_{Hxc} & exact $E_{\text{Hxc}}^{\text{exact}}$ is treated as a perturbation
→ Density Functional Perturbation Theory (DFPT) can be used

Benchmark Calculations

- Known functionals are used for “exact” $E_{\text{Hxc}}^{\text{exact}}$ as well, and we will see whether the functional is reproduced
- Exact ρ_{gs} is generated by “exact” $E_{\text{Hxc}}^{\text{exact}}$ (pseudo data)
- Two cases of Coulomb systems are tested
 - ① Known \tilde{E}_{Hxc} Hartree
Exact $E_{\text{Hxc}}^{\text{exact}}$ Hartree & LDA Exchange
 - ② Known \tilde{E}_{Hxc} Hartree & LDA Exchange
Exact $E_{\text{Hxc}}^{\text{exact}}$ Hartree & LDA Exchange-Correlation

Assumption: First-order Perturbation Theory

$$E_{\text{Hxc}}^{\text{exact}}[\rho] = \tilde{E}_{\text{Hxc}}[\rho] + \lambda E_{\text{Hxc}}^{(1)}[\rho] + O(\lambda^2)$$

$$\psi_i^{\text{exact}}(\mathbf{r}) = \tilde{\psi}_i(\mathbf{r}) + \lambda \psi_i^{(1)}(\mathbf{r}) + O(\lambda^2)$$

$$\rho_{\text{gs}}^{\text{exact}}(\mathbf{r}) = \tilde{\rho}_{\text{gs}}(\mathbf{r}) + \lambda \rho_{\text{gs}}^{(1)}(\mathbf{r}) + O(\lambda^2)$$

$$E_{\text{gs}}^{\text{exact}} = \tilde{E}_{\text{gs}} + \lambda E_{\text{gs}}^{(1)} + O(\lambda^2)$$

Flow of Our Method “IKS-DFPT”

- 1 Exact ground-state energy is expressed by two methods
- 2 Compare two equations \rightarrow Functional equation for $E_{\text{Hxc}}^{(1)}$ is derived
- 3 Simple ansatz for $E_{\text{Hxc}}^{(1)}$ is introduced with unknown parameters
- 4 Then, equation for $E_{\text{Hxc}}^{(1)}$ is now algebraic equation
- 5 This equation is solved with substituting ρ_{gs} of several systems

Ground-state Energy: Based on DFPT

$$E_{\text{gs}}^{\text{exact}} = T_0[\rho_{\text{gs}}^{\text{exact}}] + \int V_{\text{ext}}(\mathbf{r}) \tilde{\rho}_{\text{gs}}(\mathbf{r}) d\mathbf{r} + \tilde{E}_{\text{Hxc}}[\tilde{\rho}_{\text{gs}}] + \int V_{\text{ext}}(\mathbf{r}) \rho_{\text{gs}}^{(1)}(\mathbf{r}) d\mathbf{r} \\ + \lambda \int \frac{\delta \tilde{E}_{\text{Hxc}}[\tilde{\rho}_{\text{gs}}]}{\delta \rho(\mathbf{r})} \rho_{\text{gs}}^{(1)}(\mathbf{r}) d\mathbf{r} + \lambda E_{\text{Hxc}}^{(1)}[\tilde{\rho}_{\text{gs}}] + O(\lambda^2)$$

Ground-state Energy: Based on KS & IKS

$$E_{\text{gs}}^{\text{exact}} = \sum_i \varepsilon_i^{\text{exact}} + \tilde{E}_{\text{Hxc}}[\rho_{\text{gs}}^{\text{exact}}] - \int \frac{\delta \tilde{E}_{\text{Hxc}}[\rho_{\text{gs}}^{\text{exact}}]}{\delta \rho(\mathbf{r})} \rho_{\text{gs}}^{\text{exact}}(\mathbf{r}) d\mathbf{r} \\ + \lambda E_{\text{Hxc}}^{(1)}[\rho_{\text{gs}}^{\text{exact}}] - \lambda \int \frac{\delta E_{\text{Hxc}}^{(1)}[\rho_{\text{gs}}^{\text{exact}}]}{\delta \rho(\mathbf{r})} \rho_{\text{gs}}^{\text{exact}}(\mathbf{r}) d\mathbf{r} + O(\lambda^2)$$

IKS-DFPT Equation

With comparing two equations

$$\begin{aligned} & \lambda E_{\text{Hxc}}^{(1)} [\tilde{\rho}_{\text{gs}}] - \lambda E_{\text{Hxc}}^{(1)} [\rho_{\text{gs}}^{\text{exact}}] + \lambda \int \frac{\delta E_{\text{Hxc}}^{(1)} [\rho_{\text{gs}}^{\text{exact}}]}{\delta \rho(\mathbf{r})} \rho_{\text{gs}}^{\text{exact}}(\mathbf{r}) d\mathbf{r} \\ &= \sum_{i=1}^N \varepsilon_i^{\text{exact}} + \tilde{E}_{\text{Hxc}} [\rho_{\text{gs}}^{\text{exact}}] - \int \frac{\delta \tilde{E}_{\text{Hxc}} [\rho_{\text{gs}}^{\text{exact}}]}{\delta \rho(\mathbf{r})} \rho_{\text{gs}}^{\text{exact}}(\mathbf{r}) d\mathbf{r} - \tilde{E}_{\text{gs}} =: C [\rho_{\text{gs}}^{\text{exact}}]. \end{aligned}$$

Ansatz for $E_{\text{Hxc}}^{(1)}$

$$E_{\text{Hxc}}^{(1)}[\rho] = A \int [\rho(\mathbf{r})]^\alpha d\mathbf{r},$$

IKS-DFPT1 equation with the ansatz for two systems provides two algebraic equations \rightarrow unknown parameters λA & α are determined

Benchmark Results of IKS-DFPT

Noble gas atoms are used for the systems to determine λA and α since spherical symmetry is hold in noble gas atoms

Energy: $E_{\text{Hxc}}^{\text{exact}}$ is Hartree & LDA Exchange (Hartree atomic unit)

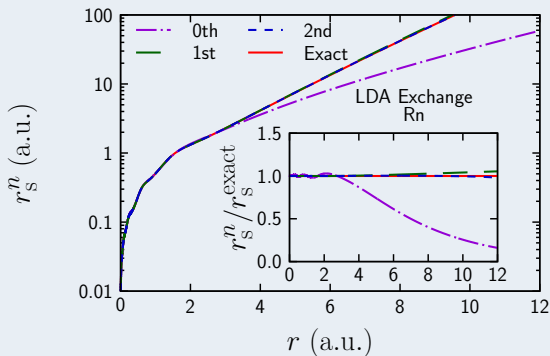
n	α_n	λA_n	$E_{\text{gs}}^{\text{nth}}$ of Xe	$E_{\text{gs}}^{\text{nth}}$ of Rn
0			-7054.6485	-21479.344
1	1.3311445	-0.7558229	-7224.9365	-21852.010
2	1.0436323	0.0306234	-7223.0601	-21848.894
Target	1.3333333	-0.7385588	-7223.1853	-21848.954

Hartree Atomic Unit

$$m_e = 1, \quad \hbar = 1, \quad e^2 = 1, \quad 4\pi\epsilon_0 = 1, \quad c = \frac{1}{\alpha}$$

Benchmark Results of IKS-DFPT

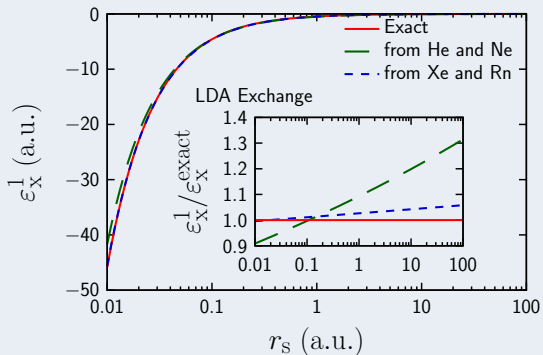
Density: $E_{\text{Hxc}}^{\text{exact}}$ is Hartree & LDA Exchange



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

Benchmark Results of IKS-DFPT

Functional: $E_{\text{Hxc}}^{\text{exact}}$ is Hartree & LDA Exchange



$$r_s = \left(\frac{3}{4\pi\rho} \right)^{1/3}, \quad E_X[\rho] = \int \epsilon_X^1(r_s(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r}$$

Conclusion and Perspectives

Conclusion

- The IKS-DFPT is tested in noble gas atoms
- The IKS-DFPT method improves E_{gs} , ρ_{gs} , and E_{Hxc} well from the known functional

Energy Density ε Reproduced the exact one, if ansatz is good enough

G.S. Energy E_{gs} Reproduced the exact one less than 1 % error

Density ρ_{gs} Reproduced the exact one

Perspectives

- Other ansatz
- Application for nuclear systems
- Application for actual problem (improve actual functional)

Conclusion

- The IKS-DFPT is tested in noble gas atoms
- The IKS-DFPT method improves E_{gs} , ρ_{gs} , and E_{Hxc} well from the known functional

Energy Density ε Reproduced the exact one, if ansatz is good enough

G.S. Energy E_{gs} Reproduced the exact one less than 1 % error

Density ρ_{gs} Reproduced the exact one

Perspectives

- Other ansatz
- Application for nuclear systems
- Application for actual problem (improve actual functional)

Thank you for attention!!