How to Improve Functionals in Density Functional Theory?

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Density Functional Theory

### Many-body Hamiltonian

\[ H = \sum_j t_j + \sum_j V_{\text{ext}}(r_j) + \sum_{j<k} V_{\text{int}}(r_j, r_k) \]

- \( t_j \): single-particle kinetic operator
- \( r_j \): coordinate of particle \( j \)
- \( V_{\text{ext}} \): external potential
- \( V_{\text{int}} \): interaction

### Ground-state Energy in Kohn-Sham Scheme

\[ E_{\text{gs}} = T_0 + \int V_{\text{ext}}(r) \rho_{\text{gs}}(r) \, dr + E_d[\rho_{\text{gs}}] + E_x[\rho_{\text{gs}}] + E_c[\rho_{\text{gs}}] \]

- \( T_0 \): kinetic energy of non-interacting system
- \( E_d \): Hartree functional
- \( E_x \): exchange functional
- \( E_c \): correlation functional


If \( E_{xc} = E_x + E_c \) is known, the exact \( E_{\text{gs}} \) and \( \rho_{\text{gs}} \) can be derived.
Density Functional Theory

Kohn-Sham Effective Potential

\[ V_{\text{KS}}(r) = V_{\text{ext}}(r) + \int V_{\text{int}}(r, r') \rho_{\text{gs}}(r') \, dr' + \left. \frac{\delta E_{\text{xc}}[\rho(r)]}{\delta \rho(r)} \right|_{\rho=\rho_{\text{gs}}} \]

\[ [t + V_{\text{KS}}(r)] \varphi_j = \varepsilon_j \varphi_j, \quad \rho(r) = \sum_j |\varphi_j(r)|^2 \]

Problems of Density Functional Theory

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

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

According to Hohenberg-Kohn theorem, \( V_{\text{KS}} \) is unique for each system
→ “Inverse Kohn-Sham Method” may be applicable to “derive” \( E_{\text{xc}} \) !
The exact $V_{KS}$ is unique for the system.
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“Inverse Kohn-Sham Method”

$V_{KS}$ can be derived from $\rho_{gs}$ exactly


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

Summary of Our Work “IKS-DFPT”

• The way to improve known functional $\tilde{E}_{Hxc}$ is proposed

• Difference between known $\tilde{E}_{Hxc}$ & exact $E_{Hxc}^{exact}$ is treated as a perturbation

$\rightarrow$ Density Functional Perturbation Theory (DFPT) can be used

Benchmark Calculations

• Known functionals are used for “exact” $E_{Hxc}^{exact}$ as well, and we will see whether the functional is reproduced

• Exact $\rho_{gs}$ is generated by “exact” $E_{Hxc}^{exact}$ (pseudo data)

• Two cases of Coulomb systems are tested

1. Known $\tilde{E}_{Hxc}$ Hartree
   Exact $E_{Hxc}^{exact}$ Hartree & LDA Exchange

2. Known $\tilde{E}_{Hxc}$ Hartree & LDA Exchange
   Exact $E_{Hxc}^{exact}$ Hartree & LDA Exchange-Correlation
Theoretical Framework

Assumption: First-order Perturbation Theory

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

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

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

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

Flow of Our Method “IKS-DFPT”

1. Exact ground-state energy is expressed by two methods
2. Compare two equations → 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 \( \rho_{\text{gs}} \) of several systems
Ground-state Energy: Based on DFPT

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

Ground-state Energy: Based on KS & IKS

\[
E_{gs}^{\text{exact}} = \sum_i \varepsilon_i^{\text{exact}} + \tilde{E}_{\text{Hxc}} \left[ \rho_{gs}^{\text{exact}} \right] - \int \frac{\delta \tilde{E}_{\text{Hxc}} \left[ \rho_{gs}^{\text{exact}} \right]}{\delta \rho(r)} \rho_{gs}^{\text{exact}}(r) \, dr \\
+ \lambda E_{\text{Hxc}}^{(1)} \left[ \rho_{gs}^{\text{exact}} \right] - \lambda \int \frac{\delta E_{\text{Hxc}}^{(1)} \left[ \rho_{gs}^{\text{exact}} \right]}{\delta \rho(r)} \rho_{gs}^{\text{exact}}(r) \, dr + O(\lambda^2)
\]
IKS-DFPT Equation

With comparing two equations

\[
\lambda E_{\text{Hxc}}^{(1)} [\tilde{\rho}_{\text{gs}}] - \lambda E_{\text{Hxc}}^{(1)} [\rho_{\text{gs}}^{\text{exact}}] + \lambda \int \frac{\delta E_{\text{Hxc}}^{(1)} [\rho_{\text{gs}}^{\text{exact}}]}{\delta \rho (r)} \rho_{\text{gs}}^{\text{exact}} (r) \, dr \\
= \sum_{i=1}^{N} \varepsilon_i^{\text{exact}} + \tilde{E}_{\text{Hxc}} [\rho_{\text{gs}}^{\text{exact}}] - \int \frac{\delta \tilde{E}_{\text{Hxc}} [\rho_{\text{gs}}^{\text{exact}}]}{\delta \rho (r)} \rho_{\text{gs}}^{\text{exact}} (r) \, dr - \tilde{E}_{\text{gs}} =: C [\rho_{\text{gs}}^{\text{exact}}].
\]

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

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

IKS-DFPT1 equation with the ansatz for two systems provides two algebraic equations \( \rightarrow \) unknown parameters \( \lambda A \) & \( \alpha \) are determined
Noble gas atoms are used for the systems to determine $\lambda A$ and $\alpha$ since spherical symmetry is hold in noble gas atoms.

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

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\alpha_n$</th>
<th>$\lambda A_n$</th>
<th>$E_{gs}^{nth}$ of Xe</th>
<th>$E_{gs}^{nth}$ of Rn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.3311445</td>
<td>$-0.7558229$</td>
<td>$-7054.6485$</td>
<td>$-21479.344$</td>
</tr>
<tr>
<td>1</td>
<td>1.3333333</td>
<td>$-0.7385588$</td>
<td>$-7223.1853$</td>
<td>$-21848.954$</td>
</tr>
<tr>
<td>2</td>
<td>1.0436323</td>
<td>0.0306234</td>
<td>$-7223.0601$</td>
<td>$-21848.894$</td>
</tr>
<tr>
<td>Target</td>
<td>1.3333333</td>
<td>$-0.7385588$</td>
<td>$-7223.1853$</td>
<td>$-21848.954$</td>
</tr>
</tbody>
</table>

### Hartree Atomic Unit

$m_e = 1, \quad \hbar = 1, \quad e^2 = 1, \quad 4\pi\varepsilon_0 = 1, \quad c = \frac{1}{\alpha}$
Benchmark Results of IKS-DFPT

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

$$r_s = \left( \frac{3}{4\pi \rho} \right)^{1/3}$$
Benchmark Results of IKS-DFPT

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

$$r_s = \left( \frac{3}{4\pi \rho} \right)^{1/3}, \quad E_x[\rho] = \int \varepsilon_x^1 (r_s(r)) \rho(r) \, dr$$
Conclusion

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

  **Energy Density $\varepsilon$** Reproduced the exact one, if ansatz is good enough
  **G.S. Energy $E_{gs}$** Reproduced the exact one less than 1% error
  **Density $\rho_{gs}$** Reproduced the exact one

Perspectives

- Other ansatz
- Application for nuclear systems
- Application for actual problem (improve actual functional)
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Thank you for attention!!