How to Improve Functionals in Density Functional Theory? —Formalism and Benchmark Calculation—

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Abstract. We proposed in Ref. [J. Phys. B 39, 13120 (2019)] a way to improve energy density functionals in the density functional theory based on the combination of the inverse Kohn-Sham method and the density functional perturbation theory. In this proceeding, we mainly focus on the results for the Ar and Kr atoms.

1. Introduction
The density functional theory (DFT) is one of the most successful approaches to the calculation of the ground-state properties of the quantum many-body problems including nuclear systems [1, 2, 3, 4]. In principle, the DFT gives the exact ground-state density $\rho_{\text{gs}}$ and energy $E_{\text{gs}}$: 

$$
E_{\text{gs}} = T_0[\rho_{\text{gs}}] + \int V_{\text{ext}}(r) \rho_{\text{gs}}(r) \, dr + E_{\text{H}}[\rho_{\text{gs}}] + E_{\text{xc}}[\rho_{\text{gs}}],
$$

where $T_0$ is the Kohn-Sham (KS) kinetic energy, $V_{\text{ext}}$ is the external field, and $E_{\text{H}}[\rho]$ and $E_{\text{xc}}[\rho]$ are the Hartree and exchange-correlation energy density functionals (EDFs), respectively [1, 2]. However, in practice, the accuracy of the DFT calculation depends on that of the approximations for $E_{\text{xc}}[\rho]$, as it is unknown. Hence, the derivation or construction of accurate EDFs is one of the primary goals in DFT for both electron and nuclear systems. In Ref. [5], we proposed a novel way to improve EDFs based on the combination of the inverse Kohn-Sham (IKS) method [6, 7] and the density functional perturbation theory (DFPT) [8, 9, 10, 11], the so-called IKS-DFPT method. In this method, the first-order DFPT, also called the Hellmann-Feynman theorem [12], is used, and the known functional is improved by using the IKS-DFPT. As benchmark calculations, we verify this method by reproducing the exchange functional in the local density approximation (LDA) [13]. In this proceeding, we mainly focus on the results for the Ar and Kr atoms.

2. Theoretical Framework
In the DFT, $\rho_{\text{gs}}(r)$ and $E_{\text{gs}}$ of an $N$-particle system are obtained by solving the KS equations,

$$
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{KS}}(r)\right] \psi_i(r) = \varepsilon_i \psi_i(r), \quad V_{\text{KS}}(r) = V_{\text{ext}}(r) + \frac{\delta E_{\text{Hxc}}[\rho_{\text{gs}}]}{\delta \rho(r)},
$$

where $\psi_i(r)$ is the KS wave function of the $i$th electron.
where \( m \) is the mass of particles, \( \psi_i (r) \) and \( \varepsilon_i \) are the single-particle orbitals and energies, respectively. \( V_{KS} (r) \) is the KS effective potential, and \( \rho_{gs}(r) = \sum_{i=1}^{N} |\psi_i (r)|^2 \).

The IKS provides \( V_{KS} \) for each system from the ground-state density \( \rho_{gs} \), which can be determined from experiments or high-accuracy calculations, such as the coupled cluster and the configuration interaction methods for atoms and light molecules and several \textit{ab initio} methods for light nuclei. As mentioned in Ref. [14], the KS potential \( V_{KS} (r) \) is unique concerning the system. Furthermore, improvement of the EDFs by using the IKS is promising since the EDF is, in principle, unique for all the electron systems. In our novel method IKS-DFPT [5], the conventional Hartree-exchange-correlation-functional \( E_{\text{Hxc}} \) will be improved by using the IKS.

Here, \( E_{\text{Hxc}} [\rho] \) is assumed to be close enough to the exact one \( E_{\text{Hxc}}^{\text{exact}} [\rho] \), since \( E_{\text{Hxc}} [\rho] \) is known to work well. Hence, the difference between \( E_{\text{Hxc}}^{\text{exact}} \) and \( E_{\text{Hxc}} \) is treated as a perturbation. If the difference is not small enough to be treated as the perturbation, the final results would be unreasonable.

The first-order perturbation theory is used for the treatment of the difference between \( E_{\text{Hxc}}^{\text{exact}} \) and \( E_{\text{Hxc}} \) as

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

with a small parameter \( \lambda \). Then, the exact single-particle orbitals \( \psi_{i}^{\text{exact}} (r) \), ground-state density \( \rho_{gs}^{\text{exact}} (r) \), and energy \( E_{gs}^{\text{exact}} \) are also expanded perturbatively:

\[
\psi_{i}^{\text{exact}} (r) = \tilde{\psi}_{i} (r) + \lambda \psi_{i}^{(1)} (r) + O (\lambda^2),
\]

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

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

where quantities shown with the tilde are given by \( \tilde{E}_{\text{Hxc}} \). The first-order perturbation term \( \psi_{i}^{(1)} (r) \) is assumed to be orthogonal to \( \tilde{\psi}_{i} (r) \). The perturbation is assumed not to affect the external field, i.e., \( V_{ext}^{\text{exact}} (r) = \tilde{V}_{ext} (r) \). Moreover, \( \rho_{gs}^{\text{exact}} (r) \) is assumed to be given, and thus \( \psi_{i}^{\text{exact}} (r) \) is calculated from the IKS.

Under these assumptions, we calculate \( E_{gs}^{\text{exact}} \) in two different ways. One way is based on the first-order DFPT, and the other way is based on the IKS and KS equations. In the former way, substitution of Eqs. (3), (4a), and (4b) into Eq. (1) gives

\[
E_{gs}^{\text{exact}} = T_{0} [\rho_{gs}^{\text{exact}}] + \int V_{ext} (r) \tilde{\rho}_{gs} (r) \, dr + \tilde{E}_{\text{Hxc}} [\tilde{\rho}_{gs}] + \lambda E_{\text{Hxc}}^{(1)} [\tilde{\rho}_{gs}]
\]

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

In the latter way, Eq. (3) and integration of the KS equation (2) give

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

\[
= \sum_{i=1}^{N} \varepsilon_{i}^{\text{exact}} + \tilde{E}_{\text{Hxc}} [\rho_{gs}^{\text{exact}}] + \lambda E_{\text{Hxc}}^{(1)} [\rho_{gs}^{\text{exact}}]
\]

\[
- \int \frac{\delta \tilde{E}_{\text{Hxc}} [\rho_{gs}^{\text{exact}}]}{\delta \rho (r)} \rho_{gs}^{\text{exact}} (r) \, dr - \lambda \int \frac{\delta E_{\text{Hxc}}^{(1)} [\rho_{gs}^{\text{exact}}]}{\delta \rho (r)} \rho_{gs}^{\text{exact}} (r) \, dr + O (\lambda^2),
\]
where $\varepsilon_i^{\text{exact}}$ are obtained from $\rho_{\text{gs}}^{\text{exact}}$ by using the IKS. By comparing these two expressions of the ground-state energy and neglecting the $O(\lambda^2)$ term, the equation for $E_{\text{Hxc}}^{(1)}[\rho]$ is obtained:

$$
\lambda E_{\text{Hxc}}^{(1)}[\tilde{\rho}_{\text{gs}}] - \lambda E_{\text{Hxc}}^{(1)}[\rho_{\text{gs}}^{\text{exact}}] + \lambda \int \frac{\delta E_{\text{Hxc}}^{(1)}[\rho_{\text{gs}}^{\text{exact}}]}{\delta \rho(r)} \rho_{\text{gs}}^{\text{exact}}(r) \, dr
$$

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

(7)

The right-hand side of this equation can be calculated from the known quantities and its value depends only on the exact ground-state density $\rho_{\text{gs}}^{\text{exact}}$ and the known functional $E_{\text{Hxc}}$. Thus, hereafter the right-hand side of the equation is shown as $C[\rho]$.

Finally, solving Eq. (7), the Hartree-exchange-correlation functional in the IKS-DFPT in the first-order, i.e., the IKS-DFPT1, is derived as

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

(8)

Because Eq. (8) is a functional equation, it is difficult to be solved directly. In this work, we assume

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

(9)

with the values of $A$ and $\alpha$ to be determined, and then we get

$$
\lambda A \int \{ [\tilde{\rho}_{\text{gs}}(r)]^\alpha + (\alpha - 1) [\rho_{\text{gs}}^{\text{exact}}(r)]^\alpha \} \, dr = C [\rho_{\text{gs}}^{\text{exact}}].
$$

(10)

To determine $A$ and $\alpha$, two systems, Systems 1 and 2, are required. Here, $\rho_1$ and $\rho_2$ are the exact ground-state densities, and $\tilde{\rho}_1$ and $\tilde{\rho}_2$ are the ground-state densities of Systems 1 and 2 calculated from $\tilde{E}_{\text{Hxc}}[\rho]$, respectively. Substituting $\rho_1$ and $\tilde{\rho}_1$ $(i = 1, 2)$ for Eq. (7), it leads to the two equations for $\lambda A$ and $\alpha$. In such a way, $\lambda A$ and $\alpha$ can be determined. Note that in principle the Hartree-exchange-correlation EDF is system independent, and thus any system can be used as Systems 1 and 2.

3. Benchmark Calculations and Discussions

As benchmark calculations, to avoid ambiguity coming from the experimental data, we use $\rho_{\text{gs}}^{\text{target}}(r)$ calculated from the theoretical $E_{\text{Hxc}}^{\text{target}}[\rho]$ as $\rho_{\text{gs}}^{\text{exact}}(r)$, and we test whether $E_{\text{Hxc}}^{\text{target}}[\rho]$ can be reproduced from $\tilde{E}_{\text{Hxc}}[\rho]$ in this scheme. The Hartree and the Hartree plus LDA exchange functional (Hartree-Fock-Slater approximation) [13] are used for $\tilde{E}_{\text{Hxc}}[\rho]$ and $E_{\text{Hxc}}^{\text{target}}[\rho]$, respectively, as a benchmark:

$$
\tilde{E}_{\text{Hxc}}[\rho] = \frac{1}{2} \int \int \rho(r) \rho(r') \frac{dr \, dr'}{|r - r'|}, \quad E_{\text{Hxc}}^{\text{target}}[\rho] = \tilde{E}_{\text{Hxc}}[\rho] - \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int |\rho(r)|^{4/3} \, dr
$$

(11)

in the Hartree atomic unit. All the pairs of the isolated noble-gas atoms (He, Ne, Ar, Kr, Xe, and Rn) are used as Systems 1 and 2. The external field $V_{\text{ext}}^{\text{target}}(r) = V_{\text{ext}}(r)$ is the Coulomb interaction between the nucleus and electron.

In Table 1, the coefficients $\alpha$ and $\lambda A$ and the ground-state energies $E_{\text{gs}}$ calculated in the IKS-DFPT are shown for the pair of atoms Ar-Kr. It is found that $\alpha$ and $\lambda A$ are obtained within 0.3% and 3.7% errors from their target values, respectively. In Table 2, the coefficients calculated in all the pairs and their errors with respect to the target valued are shown. Among
much improved after the IKS-DFPT is performed. The polynomial form of the functional in Eq. (9) is more sensitive to the high-density region. Reproduction in the high-density region leads to better reproduction of the coefficients, since the generally better than the pair of He-Ne. As comparing He-Ne, Ar-Kr, and Xe-Rn cases, better atomic unit.

\[ \varepsilon_x (r) \] and the ground-state energies \( E_{gs} \) calculated in the IKS-DFPT for the pair of atoms Ar and Kr. The Hartree functional is used for \( E_{Hxc} [\rho] \) and the Hartree plus LDA exchange functional is used for \( E_{Hxc}^{\text{target}} [\rho] \) given in Eq. (11). All units are in the Hartree atomic unit.

| Pairs         | Exchange α | Error for α (%) | Exchange λA | Error for λA (%) |
|---------------|------------|-----------------|-------------|------------------|
| Target        | 1.3333333  | —               | −0.7385588  | —                |
| He-Ne         | 1.3199872  | 1.000960       | −0.7920448  | 7.241947         |
| He-Ar         | 1.3209765  | 0.926762       | −0.7926638  | 7.325759         |
| Ne-Ar         | 1.3235352  | 0.734860       | −0.7841588  | 6.174192         |
| He-Kr         | 1.3227758  | 0.791815       | −0.7937863  | 7.477744         |
| Ne-Kr         | 1.3263436  | 0.524230       | −0.7779323  | 5.331131         |
| Ar-Kr         | 1.3290958  | 0.317815       | −0.7658732  | 5.093843         |
| He-Xe         | 1.3235844  | 0.731170       | −0.7942892  | 7.548536         |
| Ne-Xe         | 1.3270817  | 0.468872       | −0.7762984  | 5.109903         |
| Ar-Xe         | 1.3292187  | 0.308597       | −0.7654719  | 3.644007         |
| Kr-Xe         | 1.3294148  | 0.293890       | −0.764846   | 3.510328         |
| He-Rn         | 1.3244450  | 0.666625       | −0.7948236  | 7.618193         |
| Ne-Rn         | 1.3279028  | 0.407290       | −0.7744818  | 4.863937         |
| Ar-Rn         | 1.3297748  | 0.266890       | −0.7636589  | 3.398529         |
| Kr-Rn         | 1.3303022  | 0.227335       | −0.7606336  | 2.988907         |
| Xe-Rn         | 1.3311445  | 0.164162       | −0.7558229  | 2.337544         |
| Average       | 1.3263722  | 0.522085       | −0.7770949  | 5.217753         |

all the pairs, \( \alpha \) is obtained within more or less 1.0\% errors. In contrast, \( \lambda \) is obtained within around 5\% errors. Both coefficients calculated from the heavier atoms are more accurate. This comes from the fact that the density of heavier atom ranges wider than that of lighter atom.

The calculated exchange energy density \( \varepsilon_x (r) \) and the ratios to the target one \( \varepsilon_x (r_s) / \varepsilon_x^{\text{target}} (r_s) \) are shown as a function of \( r_s \) in Fig. 1 for the pairs of He-Ne, Ar-Kr, and Xe-Rn with the dashed, dot-dashed, and dotted lines, respectively, while the target one is shown with the solid line. Here, the energy density \( \varepsilon_x (\rho) \) and the Wigner-Seitz radius \( r_s \) are defined as \( E_x [\rho] = \int \varepsilon_x (\rho) \rho (r) \, dr \) and \( r_s = [3/(4\pi \rho)]^{1/3} \), respectively. The pair of Xe-Rn reproduces the target functional within a few percents in the range of 0.01 a.u. \( \leq r_s \leq 100 \) a.u., which is generally better than the pair of He-Ne. As comparing He-Ne, Ar-Kr, and Xe-Rn cases, better reproduction in the high-density region leads to better reproduction of the coefficients, since the polynomial form of the functional in Eq. (9) is more sensitive to the high-density region.

The Wigner-Seitz radii \( r_s \) calculated in the functional before and after the IKS-DFPT and the target one \( r_s^{\text{target}} \) for Kr are shown as a functions of \( r \) in Fig. 2 with the dot-dashed, dashed, and solid lines, respectively. The ratios of calculated Wigner-Seitz radius to the target one, \( r_s / r_s^{\text{target}} \), are also shown in the insert of Fig. 2. It is found that the ground-state density is also much improved after the IKS-DFPT is performed.
Figure 1. Energy density $\varepsilon_x$ for the LDA exchange functional as a function of $r_s$. Ratios of $\varepsilon_x/\varepsilon_x^{\text{target}}$ are shown in the insert. All units are in the Hartree atomic unit.

Figure 2. Wigner-Seitz radii $r_s$ as a function of $r$ for Kr. Ratios of $r_s/r_s^{\text{target}}$ are shown in the insert. All units are in the Hartree atomic unit.

4. Conclusion and Perspectives

In summary, the way to improve conventional EDFs based on the combination of the IKS and the DFPT was proposed in Ref. [5]. As benchmark calculations, we test whether the LDA exchange functional can be reproduced in this novel scheme IKS-DFPT. By improving the exchange functional, the accuracy of the ground-state energies is improved by two to three orders of magnitude, and the accuracy of the ground-state densities is also improved one to two orders of magnitude. Therefore, the IKS-DFPT is promising to improve the conventional functionals. Application of this IKS-DFPT to the nuclear DFT is promising.

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