

Improvement of functionals in density functional theory using inverse Kohn-Sham method and density functional perturbation theory[†]

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The density functional theory (DFT) is one of the most successful approaches to calculate the ground-state properties. The ground-state density ρ_{gs} and energy E_{gs} are obtained by solving the Kohn-Sham (KS) equation.^{1,2)} The ground-state energy is given by $E_{\text{gs}} = T_0[\rho_{\text{gs}}] + \int v_{\text{ext}}(\mathbf{r}) \rho_{\text{gs}}(\mathbf{r}) d\mathbf{r} + E_{\text{Hxc}}[\rho_{\text{gs}}]$, where T_0 is the KS kinetic energy, v_{ext} is the external field, and $E_{\text{Hxc}}[\rho]$ is the Hartree-exchange-correlation energy density functional (EDF). However, the accuracy of DFT calculations depends on the determination of $E_{\text{Hxc}}[\rho]$ as it is unknown. The inverse Kohn-Sham (IKS) method was proposed toward the improvement of EDFs. Nevertheless, the actual method to improve EDFs has not been explicitly determined.

In this work, for the first time, a new way to improve EDFs by the combination of the IKS method and density functional perturbation theory (DFPT) is proposed. In this method, a conventional $\tilde{E}_{\text{Hxc}}[\rho]$ is assumed to be close enough to $E_{\text{Hxc}}[\rho]$ and the difference is considered in the first-order DFPT with small λ as $E_{\text{Hxc}}[\rho] = \tilde{E}_{\text{Hxc}}[\rho] + \lambda E_{\text{Hxc}}^{(1)}[\rho] + O(\lambda^2)$. In addition, $\rho_{\text{gs}}(\mathbf{r})$ and E_{gs} are expanded perturbatively. The perturbation is assumed to not affect the external field, and $\rho_{\text{gs}}(\mathbf{r})$ is assumed to be given.

Under the assumptions, we calculate E_{gs} based on the first-order DFPT and on the IKS method. By comparing them, the following equation for $E_{\text{Hxc}}^{(1)}[\rho]$ is obtained:

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

where ε_i is the single-particle energy obtained from ρ_{gs} using the IKS method. Because it is difficult to solve this equation, we assume $E_{\text{Hxc}}^{(1)}[\rho] = \sum_k A_k \int [\rho(\mathbf{r})]^{\alpha_k} d\mathbf{r}$ and iteratively determine its value. Finally, $\tilde{E}_{\text{Hxc}}[\rho]$ is improved to be $\tilde{E}_{\text{Hxc}}[\rho] + \lambda E_{\text{Hxc}}^{(1)}[\rho]$.

As benchmark calculations, $\rho_{\text{gs}}(\mathbf{r})$ is calculated from the known $E_{\text{Hxc}}^{\text{target}}[\rho]$ and we attempt to reproduce it from a less accurate \tilde{E}_{Hxc} . Here, we use the Hartree and LDA exchange functional as $E_{\text{Hxc}}^{\text{target}}$ and the Hartree one as \tilde{E}_{Hxc} . The pairs of noble-gas atoms He-Ne and Xe-Rn are used because two unknowns A_i and α_i should be determined at each iteration. Addi-

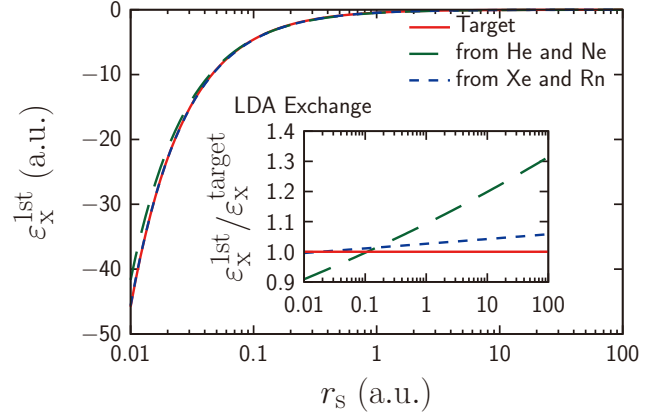


Fig. 1. Exchange energy density $\varepsilon_x^{\text{1st}}(r_s)$ calculated in the first iteration and ratios $\varepsilon_x^{\text{1st}}(r_s)/\varepsilon_x^{\text{target}}(r_s)$. The Hartree atomic unit is used here.

tionally, they are easy to handle owing to their spherical symmetry.

It is found that A_1 and α_1 are obtained within 7.2% and 1.0% errors in He-Ne, and within 2.3% and 0.2% errors in Xe-Rn, respectively, from the LDA results.

The calculated exchange energy density at the first iteration, $\varepsilon_x^{\text{1st}}(r_s)$, and its ratio to the LDA are shown in Fig. 1 for the pairs of He-Ne and Xe-Rn with dashed and dot lines, respectively, while the LDA exchange functional is represented with a solid line. The energy density $\varepsilon_x(\rho)$ and the Wigner-Seitz radius r_s are defined as $E_x[\rho] = \int \varepsilon_x(\rho) \rho(\mathbf{r}) d\mathbf{r}$ and $r_s = [3/(4\pi\rho)]^{1/3}$, respectively. The Xe-Rn pair reproduces the LDA functional within a few percents.

Moreover, it is found that the ground-state energy becomes closer to the LDA as the iteration proceeds. The ground-state energies of He, Ne, Xe, and Rn are finally reproduced within 0.4%, 0.003%, 0.002%, and 0.0003% errors, respectively, comparing with 28%, 8%, 2%, and 2% errors at the zeroth step. It is also found that the ground-state density is improved by the iterations.

To summarize, our method accurately reproduces the LDA functionals. The accuracy of ground-state energies and densities are improved by two to three orders and one to two orders of magnitude, respectively. This method can be effective for nuclear DFT as well.

References

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