Separation of Density-Driven and Functional Error of Density Functional Calculations via Kohn-Sham Inversion

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Despite the success of Kohn-Sham density functional theory (DFT)[1], the approximate nature of exchange-correlation energies and potential functionals in DFT provides only approximations to physical and chemical properties. Therefore, the role of approximate exchange-correlation potentials that generate the corresponding electron density is critical. However, the approximate exchange-correlation potential behaves untraceable during self-consistent procedures. As a result, some *abnormal* calculations can result in errors in the self-consistent electron density, causing severe energy errors. One example is the dissociation of hetero-diatomic molecules.[2] To improve functional approximation and ultimately achieve the universal functional, individual analysis of energy errors from the density error and the functional approximation is important. However, it is usually not easy to quantitatively separate the energy errors due to inaccurate electron density (density-driven error) and incorrect energy functional (function error). Here we quantify density-driven and functional errors using fairly accurate electron densities from high-level *ab-initio* calculations. The technical problem of this procedure is the calculation of Kohn-Sham kinetic energy, and we employ the Kohn-Sham inversion technique using the methods proposed by Zhao, Morrison, and Parr[3] and by Wu and Yang[4]. For local functionals such as LDA and GGA, we found that there is a delocalization error in both density and functional (i.e., energy), but the error ratio varies depending on the system. For global hybrids, although a particular system-specific portion of the exact-exchange appears to make the total error zero, which arises through cancellation between the density-driven and functional errors rather by zero density-driven error and zero functional error. We show that such error cancellation is not uncommon and demonstrate the importance of systematic analysis using error decomposition.

References
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