Constructing the exchange-correlation hole of density functional theory

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Abstract

The exchange-correlation (XC) hole is a fundamental concept of density functional theory, it is crucial for your understanding of the theory and for the analysis and construction of approximations to the XC energy. The approximations to the XC hole $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$ that we pursue in our research are based on the correlation factor (CF) approach [1-4] where the XC hole is, for instance, represented as, $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u}) = f(\mathbf{r},\mathbf{r}+\mathbf{u})\ \rho_{X}(\mathbf{r},\mathbf{r}+\mathbf{u})$. The correlation factor $f(\mathbf{r},\mathbf{r}+\mathbf{u})$ turns an X hole model $\rho_{X}(\mathbf{r},\mathbf{r}+\mathbf{u})$, yielding the exact exchange energy, into the XC hole. More generally, the CFs that we develop can be combined with various X or exchange-plus-static-correlation hole models to yield new XC holes and functionals. We discuss specific examples and show that the CF approach can be implemented in a self-consistent fashion. The XC hole $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$ at a given reference point $\mathbf{r}$ represents a function of the electron-electron separation $\mathbf{u}$. Interpreting the XC hole as a parameter-dependent function of $\mathbf{u}$, we propose a $\mathbf{r}$-dependent, one-particle Schrödinger equation with operators acting on the variable $\mathbf{u}$. This equation describes quasi particles whose density distribution yields $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$. This means that, instead of approximating $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$, we approximate a potential $v_{\mathbf{r}}(\mathbf{u})$ in a quasi-particle Schrödinger equation such that the resulting one-particle density distribution $\rho_{\mathbf{r}}(\mathbf{u})$ equals $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$.

[1] Wang, Zhou, Ernzerhof, JCP 150, 084107 (2019); JCP 151, 194102 (2019).
[2] Roy, Cuierrier, Ernzerhof, JCP, 152, 211101 (2020).
[3] Cuierrier, Roy, Ernzerhof, JCP, 155, 174121 (2021).
[4] Cuierrier, Roy, Wang, Ernzerhof, JCP 156, 184110 (2022); JCP, 157, 171103 (2022).