Orbital-free density functional theory in phase space

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ABSTRACT

Density functional theory (DFT) is an extraordinarily widespread tool used in various scientific fields, ranging from quantum chemistry to astrophysics. However, in its conventional Kohn-Sham form, DFT exhibits an unfavorable computational scaling with the cube of the number of electrons. Orbital-free DFT, on the other hand, offers a more favorable linear scaling with the system size. Still, this computational advantage is counterbalanced by the fact that the quantum mechanical kinetic energy functional is unknown. Here, we demonstrate that shifting the focus from the electronic density $\rho(\mathbf{r})$ to the quasidensity $\omega(\mathbf{r},\mathbf{p})$ (defined in phase space) enables us to overcome many of the shortcomings of orbital-free DFT while maintaining its computational efficiency. This orbital-free quasidensity functional theory (quasi-DFT) circumvents the problems of finding the Pauli potential and approximating the kinetic energy functional. Similar to orbital-free DFT, the quasidensity satisfies an eigenequation:

$$h_{\text{eff}}(\mathbf{r},\mathbf{p}) \star \omega(\mathbf{r},\mathbf{p}) = \mu\, \omega(\mathbf{r},\mathbf{p}), \tag{1}$$

where $h_{\text{eff}}(\mathbf{r},\mathbf{p}) = \frac{1}{2}\mathbf{p}^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{eff}}(\mathbf{r},\mathbf{p})$. Here $v_{\text{ext}}(\mathbf{r})$ represents the external potential, $v_{\text{eff}}(\mathbf{r},\mathbf{p})$ is certain effective potential, and the symbol $\star$ is the so-called star product of phase-space quantum mechanics. To implement this novel quasi-DFT, an approximative form for the corresponding universal functionals $\mathcal{F}[\omega]$ is necessary. In this work, we introduce a set of strategies to derive quasi-DFT functionals from the functionals of the one-body reduced density matrix [1]. We leverage the analytical properties of these functionals and employ machine learning techniques, similar to those recently introduced in standard DFT [2].

References

[1] Benavides-Riveros, C L. Orbital-free quasidensity functional theory. *Physical Review Research* **2024**, *6*, 013060.

[2] Schmidt, J; Benavides-Riveros, C L; Marques, M A L. Machine learning the physical nonlocal exchange–correlation functional of density-functional theory. *Journal of Physical Chemistry Letters* **2019**, *10*, 6425.