Applications of the exact factorization in density-functional theory

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ABSTRACT

The exact factorization is an overarching strategy in quantum mechanics, which stems from probability theory and has been applied to several fields, including molecular dynamics (MD) calculations and density-functional theory (DFT).

In the former case, numerical algorithms based on this strategy have been developed to describe the nuclear dynamics beyond the Born-Oppenheimer approximation.

Within Kohn-Sham (KS) DFT, the exact factorization provides a means to break down the exchange-correlation potential, revealing the individual components responsible for features of the exact potential like “peaks” and “steps” [1]. These features are extremely challenging to reproduce with current approximations. As I will show, by leveraging the exact factorization, it becomes possible to develop functionals that can qualitatively capture these features while remaining orbital-independent.

Moreover, this strategy has been considered mostly for real-valued wavefunctions. However, in the case of complex current-carrying states, an effective vector potential associated to the paramagnetic electronic current density emerges [2], which has so far received little attention. I will present some examples of such electronic vector potential in simple paradigmatic cases.

References

[1] Giarrusso S., Neugarten R., Baerends E. J., & Giesbertz K.J.H.* (2022): Secondary kinetic peak in the Kohn-Sham potential and its connection to the response step. *Journal of Chemical Theory and Computation*, 18(8), 4762-4773.

[2] Giarrusso S., Gori-Giorgi P., & Agostini F. (2024) Electronic vector potential from the exact factorization of a complex wavefunction. Submitted to ChemPhysChem, arXiv preprint 10.26434/chemrxiv-2024-jcvkh