Improving DFT results by improving densities

Suhwan Song, Stefan Vuckovic, Eunji Sim, and Kieron Burke

DFT calculations are widespread in both chemistry and materials, because they usually provide useful accuracy at much lower computational cost than wavefunction-based methods. All practical DFT calculations require an approximation to the unknown exchange-correlation energy, which is then used self-consistently in the Kohn-Sham scheme to produce an approximate energy from an approximate density. Density-corrected DFT is simply the study of the relative contributions to the total energy error. In the vast majority of DFT calculations, the error due to the approximate density is negligible. But with certain classes of functionals applied to certain classes of problems, the density error is sufficiently large as to contribute to the energy noticeably, and its removal leads to much better results. These problems include reaction barriers, torsional barriers involving π-conjugation, halogen bonds, radicals and anions, most stretched bonds, etc. In all such cases, use of a more accurate density significantly improves performance, and often the simple expedient of using the Hartree-Fock density is enough. I will explain what DC-DFT is, where it is likely to improve results, and how DC-DFT can produce more accurate functionals. I will highlight recent successes.

Work supported by NSF CHE-2154371 in the US

- **Improving results by improving densities: Density-corrected density functional theory** E. Sim, S. Song, S. Vuckovic, and K. Burke, *J. Am. Chem. Soc.* **144**, *15*, 6625–6639 (2022). DOI: 10.1021/jacs.1c11506
- **Density-Corrected DFT Explained: Questions and Answers** S. Song, S. Vuckovic, E. Sim, and K. Burke, *J. Chem. Theory and Comput.* **18**, *2*, 817-827 (2022). DOI: 10.1021/acs.jctc.1c01045
- **Explaining and Fixing DFT Failures for Torsional Barriers** S. Nam, E. Cho, E. Sim, and K. Burke, *J. Phys. Chem. Lett.* **12**, *11*, 2796-2804 (2021). DOI: 10.1021/acs.jpclett.1c00426
- **Density Sensitivity of Empirical Functionals** S. Song, S. Vuckovic, E. Sim, and K. Burke, *J. Phys. Chem. Lett.* **12**, *2*, 800-807 (2021). DOI: 10.1021/acs.jpclett.0c03545
- **Quantifying and Understanding Errors in Molecular Geometries** S. Vuckovic and K. Burke, *J. Phys. Chem. Lett.* **11**, *22*, 9957-9964 (2020). DOI: 10.1021/acs.jpclett.0c03034
- **Measuring Density-Driven Errors Using Kohn–Sham Inversion** S. Nam, S. Song, E. Sim, and K. Burke, *J. Chem. Theory and Comput.* **16**, *8*, 5014-5023 (2020). DOI: 10.1021/acs.jctc.0c00391
- **Density Functional Analysis: The Theory of Density-Corrected DFT** S. Vuckovic, S. Song, J. Kozlowski, E. Sim, and K. Burke, *J. Chem. Theory and Comput.* **15**, *12*, 6636-6646 (2019). DOI: 10.1021/acs.jctc.9b00826