Nature Reviews Chemistry | Published online 1 Feb 2017; doi:10.1038/s41570-017-0019

QUANTUM CHEMISTRY

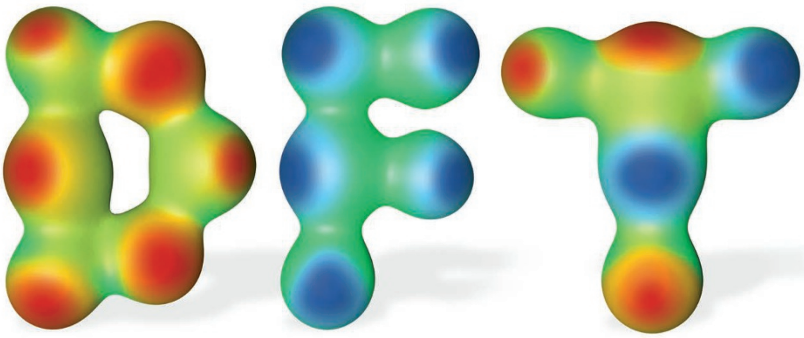
DFT's midlife crisis

> “functionals that produce ‘right’ energies from ‘wrong’ densities fail twice”

Density functional theory (DFT) — one of the most used quantum chemical approaches for the study of the electronic structure of atoms, molecules and materials — is about to reach its 52nd birthday. A new evaluation of its performance is now reported by Michael Medvedev *et al.* in *Science*. They show that the continued improvement in the prediction of energies has not been matched by improvements in the prediction of the corresponding electron densities. This is especially true for many of the newly developed density functionals, which have been developed using a reduced number of physical constraints with the goal of achieving greater versatility.

The core idea of DFT is that all of the properties of a molecular system in its ground state can be accessed if the electron density distribution is known. This assumption is the key to the success of DFT in chemistry, physics and materials science. It drastically reduces the number of electronic variables needed for the calculation of the wavefunction that describes a system — from three times the total number of electrons in a given system to only three — and therefore reduces the computational cost of DFT calculations compared with other methods. In addition, there is a direct correspondence between the electron density distribution of a system in the ground state and its minimum energy. Thus, by minimization of the system energy, it is in principle possible to access the exact electron density distribution. The exact formalism for the energy calculation (functional) is available through the Levy constrained search method; however, this approach is computationally prohibitive and approximations are needed.

Since the early days of DFT research, one of the computational community's main tasks has been to produce approximations of the exact energy functional such that estimates of system energies are as close as possible to reality. In general, the performance of new functionals is tested by comparing the energy predicted by DFT with that predicted by highly accurate (and therefore highly expensive) approaches, such as quantum Monte Carlo or coupled-cluster methods. How these functionals perform with respect to the electron density has, however, been largely neglected. “Electron density is a very important property of a system to be considered in DFT because the system energy is directly obtained from it,” notes Medvedev. “Therefore, functionals that produce ‘right’ energies from ‘wrong’ densities fail twice. There is a vanishingly small probability of error compensation over the whole enormous chemical space.”



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Medvedev and colleagues calculated the electron densities and energies of a selection of atoms and atomic cations using 128 functionals, including many of those commonly used. The predictions of functionals with different levels of approximation and complexity — local density approximation (LDA), generalized-gradient approximation (GGA), meta-GGA and hybrid-GGA — were compared against the predictions of all-electron CCSD (coupled-cluster method with single and double excitations) calculations, which produce very close estimates of the exact electron densities for the systems investigated in this work. Studying atomic systems clearly highlights any failure of the functionals that could propagate in molecular systems.

“Densities and energies go hand-in-hand for most of the analysed functionals, although few of them were built with the explicit target of producing better electron densities,” explains Ivan Bushmarinov, co-author of the paper. “This relationship is unfortunately broken for a few recently developed functionals that do produce good energies and are consequently relatively popular.” He concludes, “the electron density error as identified in our study can be considered as a measurement of the ‘theoretical rigor’ of a functional. There was no simple way to evaluate this before. However, thanks to recent developments, any chemist can check whether something strange is happening ‘under the hood’ of a chosen density functional.”

Gabriella Graziano

ORIGINAL ARTICLE Medvedev, M. G. *et al.* Density functional theory is straying from the path toward the exact functional. *Science* **355**, 49–52 (2017)