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Kepp, Kasper Planeta

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Comment on "Density functional theory is straying from the path toward the exact functional" (*Science*, 355, Issue 6320, 2017, pp. 49-52).

Kasper P. Kepp

Technical University of Denmark, DTU Chemistry, Building 206, 2800 Kgs. Lyngby, DK – Denmark. Phone: +045 45 25 24 09. E-mail: kpj@kemi.dtu.dk

Abstract

Medvedev et al. (Reports, 6 January 2017, p. 49) argue that recent density functionals stray from the path towards exactness. This conclusion rests on very compact $1s^2$ and $1s^2 2s^2$ systems favored by the Hartree-Fock picture. Comparison to actual energies for the same systems indicates the "straying" is not chemically relevant and at best specific to the studied dense systems.

Medvedev et al. (1) point out that electron densities ρ and energies $E[\rho]$ computed with density functional theory (DFT) not always increase in accuracy together. Cruz et al.(2) stated the problem in 1998 as "functionals which yield highly accurate energies often produce potentials which differ markedly from the exact ones." Medvedev et al. put errors in ρ on a time scale and show a trend of improvement impaired by nine specific recent functionals with reported high accuracy of $E[\rho]$ for diverse systems. The inverse relationship in Figure 1B may suggest an overfitting problem on the path towards universality, where both ρ and $E[\rho]$ should become increasingly accurate; off this track, accurate energies with inaccurate densities would seem successful only until applied outside the parameterization range. Some comments seem warranted:

1) Of the nine specific functionals that deviate from the "path", almost all are from 2011-2012 and all from one specific research group; other recent functionals perform well in the trend, and the only two functionals from 2014/2015 are on-path. With two functionals from 2015, none from 2014, and three from 2013, the recent history seems under-sampled; various post-2011 functionals by other groups have been not included(3)(4)(5)(6)(7). Thus, whereas some recent functionals from one research group have apparently sacrificed some accuracy in $1s^2$ and $1s^2 2s^2$ systems for accuracy in diverse molecular energies, arguing that DFT deviates from the path seems an over-generalization.

2) Another concern is whether the functionals are actually on a "path" as no direct comparison of $E[\rho]$ and ρ was done; the errors in E were from general benchmarks of diverse molecules(8). There is only a path if the errors of both $E[\rho]$ and ρ decrease together for the *same* systems; and the studied systems are very distinct. Also, the authors used maximum errors after normalization of both ρ , its gradient and Laplacian for ranking, which gives specific weights to terms that perhaps do not reflect their importance, as would be measured by their relative impact on E .

3) The Hartree-Fock (HF) method has a root-mean-squared deviation (RMSD) for ρ of only 0.049 for the $1s^2$ systems (B^{3+} , C^{4+} , N^{5+} , O^{6+} , F^{7+} , and Ne^{8+}) (Data S3 of Medvedev et al.). Six of the 14 systems studied (43%) are of this type. The high accuracy of HF is specific to systems with $2N^2$ valence electrons (the octet rule), where N is

the period number (e.g. Figure 2 where Ne requires much more HF exchange, as do the $1s^2$ systems). If one leaves out the six 2-electron systems, HF exhibits worse performance than many functionals (average RMSD of $\rho = 1.81$ without 2-electron systems, 0.92 with). Thus, the choice of benchmark systems favors the HF picture and is not a reasonable choice of norm. Accordingly, the top performers are all hybrid functionals and deviations from "exactness" are at best specific to these systems.

4) Similarly, Figure 2 in Medvedev et al. reports the maximum error of ρ , its gradient, and Laplacian (the inclusion of the latter affects the ranking, e.g. of M06-2X); inclusion of the six $1s^2$ systems would reveal the high HF demands of the $1s^2$ configurations, and for other portions of Periodic Table, *smaller* HF percentages are required(9)(10), yet in the $1s^2 2s^2$ systems the gap between virtual and occupied orbitals justifies 25%. Thus, a version of Figure 2 with all systems included would indicate that the significance of the 25% is diminished substantially.

5) Thirteen of the systems have $1s^2$ or $1s^2 2s^2$ configuration and 10 of the 14 studied ions have a charge ranging from +3 and to +8, representing extremely compact ρ with large dynamic (but no static) correlation, viz. the large improvement by MP4 over MP2 (Medvedev's Data S1). Such compact densities are not found in ordinary reaction chemistry as they require tens of eV to generate; it is thus questionable if this very compact ρ regime is chemically relevant.

To address points 1–5, because energy is a state function, the quality of $E[\rho]$ can be probed by comparing to ionization potentials (IP) from the NIST data base, e.g. $E[\rho]$ of B^{3+} and B^+ can be probed by the 2nd and 3rd experimental IP of boron (di-cation energies cancel out);

$$E(B^{3+}) - E(B^+) = IP3(B) + IP2(B) = 37.931 \text{ eV} + 25.155 \text{ eV} = 63.085 \text{ eV} \quad (1)$$

This experimental energy corresponds to removal of both 2s electrons from the $1s^2 2s^2$ configurations, with a trend of increasing charge. Comparing to $E[\rho]$ directly reveals whether errors in ρ have chemical relevance and whether there is a relationship between errors $E[\rho]$ and ρ implying a "path" towards universality, and accordingly, a deviation from such path, as claimed.

Computations were carried out with Turbomole 7.0(11) for $E(B^{3+}) - E(B^+) = IP3(B) + IP2(B) = 63.085 \text{ eV}$; $E(C^{4+}) - E(C^{2+}) = IP4(C) + IP3(C) = 112.381 \text{ eV}$; $E(N^{5+}) - E(N^{3+}) = IP5(N) + IP4(N) = 175.364 \text{ eV}$; $E(O^{6+}) - E(O^{4+}) = IP6(O) + IP5(O) = 252.018 \text{ eV}$; $E(F^{7+}) - E(F^{5+}) = IP7(F) + IP6(F) = 342.350 \text{ eV}$; and $E(Ne^{8+}) - E(Ne^{6+}) = IP8(Ne) + IP7(Ne) = 446.368 \text{ eV}$. This sampling covers 12 of the 14 systems using the same aug-cc-pwCV5Z basis set, tight densities, energies, and grids. For illustration, PBE0, TPSSh, and TPSS, B3LYP, BHLYP, BP86, M06 and SVWN, M06-2X, HF, MP2, and CCSD were studied. They spread across the ranking by Medvedev et al. CCSD(T) was also included because CCSD, though a full-CI method and thus exact non-relativistically for $1s^2$ systems, may miss some core-valence correlation of the 4- and 10-electron systems.

Figure 1A (non-relativistic) and 1B (corrected for relativistic effects) show that relativistic effects grow with charge, as 1s-electrons are accelerated. Relativistic stabilization and contraction of the s-shells favor the $1s^2 2s^2$ systems over $1s^2$ systems. Due to zero spin and angular momentum, scalar relativistic corrections recover this effect (Figure 1B) and are >0.6 eV for the neon systems (the neon-systems have the largest errors in Medvedev et al., probably because ρ is relativistic contracted). Relativistic corrected CCSD(T) and CCSD energies are within 0.03 eV (~3 kJ/mol) of experiment. Accordingly, the exact density functional methodology would provide

exact energies to within 3 kJ/mol if applied with this basis set and relativistic correction. Thus, we can compare the density functionals now also in the energy regime, $E[\rho]$.

Figure 1. Paths of Accuracy: A) Non-relativistic and B) relativistic errors in computed ionic energy differences vs. experimental values, in eV (eq. 1) (see Data S1 for computed energies in atomic units and conversion to errors in eV in rows with red color). C) Errors in densities of larger ions vs. errors in computed energies (see Data S2 for numerical data).

HF errors in energy exceed 3 eV for neon systems (Figure 1B). Local functionals M06 and SVWN produce errors almost as large as HF. Most other functionals perform similarly although B3LYP and M06-2X perform distinctly better. Only the first bar represents chemical relevance, as net atomic charges in molecules rarely exceed 2 under ambient conditions even for highly charged molecules. For chemically relevant boron, all DFT methods perform better than MP2, which only becomes more accurate in the very compact, highly charged ions. The error of B3LYP is 0.03 eV, and the worst performing functionals (PBE0, BP86) show 0.27–0.28 eV. Thus, the extremely compact regime mostly studied by Medvedev et al. is probably not chemically relevant yet clearly affects the ranking.

To produce consistent paths towards exactness, one has to study E and ρ for the *same systems*. To this end, the RMSD of ρ of the largest $1s^2 2s^2$ ions from Medvedev et al. (Data S4) was compared to errors in the energy of removing the two $2s^2$ electrons. Figure 1C reveals almost perfectly linear relationships. Since all the energies are for iso-electronic conversions, this relation reflects a sensitivity to charge, which accelerates the electrons and increases the kinetic energy and correlation in the very compact systems. Most DFT methods and MP2 follow a "path" of accuracy with errors in energy growing with errors in ρ (coefficients of -0.77 to -0.86). M06-2X errors in $E[\rho]$ increase slowly with ρ , whereas the local SVWN and HF energies deteriorate much more rapidly as ρ becomes compact. Notably, M06-2X is very "exact" when put on actual E, ρ paths and much more exact than MP2, PBE0, or TPSSh. In Medvedev et al.' (Table 2) M06-2X was ranked very low mainly because of the Laplacian of ρ and thus claimed to be off path, despite $E[\rho]$ and ρ being excellently on path (Fig. 1C).

In conclusion, the poor performance of some recent functionals for very compact densities of highly charged closed-shell systems does not imply that they are less exact: Since hybrid functionals are favored by system choice, they perform best in the test. More interestingly, functionals show distinct error relationships between ρ and $E[\rho]$ (Fig. 1C), with exactness being represented by CCSD(T) in the lower right corner. These relationships are on actual paths and are likely to be focus points in targeting exact functionals, but they would have to pertain to densities that are more chemically relevant and diverse.

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