In the main part of our results, we have considered four different basis sets each within NWCHEM and FHI-AIMS (APW +lo results with ELK could be obtained only for a small subset), ranging from *small ones* intended for prerelaxations and energy differences between bonded structures ("light", aug-cc-pVDZ), *production* basis sets considered in most publications ("tight", "tier2" for FHI-AIMS and aug-cc-pVTZ, aug-cc-pVQZ for Gaussian codes), as well the *largest available* basis sets ("tier4" for FHI-AIMS and aug-cc-pV5Z for NWCHEM). For Li, Be, Na, and Mg, the largest basis set is aug-cc-pVQZ and has therefore been employed. For the other elements, the corresponding 6Z basis is also available, but attempts to employ such a basis led to overcompleteness problems, often resulting in energies higher than the 5Z results.

The construction and philosophy behind GTO basis sets is well documented in the quantum chemical literature, for example, in the recent review by Jensen.[81] In particular, for the aug-cc-pVXZ bases, the reader is referred to the original works from Dunning and co-workers.[82−85]

The construction of the NAO basis sets used here is documented in detail in ref 64, and precise basis set definitions can be found in the SI.[79] The "tier" radial functions form a fixed basis set library, established for elements 1−102, and the choice of the exact radial functions for each element was carried out by an automated, computer-guided strategy as described in ref 64. The sequence of successive "tier" basis sets is strictly hierarchical, beginning from a minimal basis of radial functions for the occupied core and valence states of free atoms. Additional "tiers" or groups of radial functions (constructed for free ions or hydrogen-like potentials) can then be added to increase the basis set size toward numerical convergence for DFT. An accurate, global resolution-of-identity approach ("RI-V" in ref 65) is employed to evaluate the four-center Coulomb operator in hybrid-PBE0 in FHI-AIMS. It is important to note that the NAO basis sets include a "minimal basis" of atomic radial functions determined for the same XC functional as used later in the three-dimensional SCF calculations. This is standard practice in FHI-AIMS for semilocal density functionals. For hybrid-PBE0, these radial functions are provided by linking FHI-AIMS to the "atom_sphere" atomic solver code for spherically symmetric free atoms developed in the Goedecker group for several years.[14]

The ground-state energy of atoms from hydrogen ($Z = 1$) to argon ($Z = 18$) has been computed with the three chosen functionals. Our results are summarized in Figure 1. For all computational methods employed, the results of this section refer to the largest bases and tighter parameters: μHa for MRCHEM, "tier4" for FHI-AIMS, and aug-cc-pV5Z for NWCHEM (see the previous section and the SI[79] for details). The top panel reports the LDA-SVWN5 values as absolute errors with respect to the reference values of the NIST[20] database for nonrelativistic, spin-polarized, spherically symmetric atoms. As expected, MWs yield differences that are consistently below the requested accuracy of 1 μHa. The NAO and APW+lo approaches achieve average errors of ~0.01−0.1 and ~0.1−1 mHa, respectively. GTOs are limited to around mHa accuracy. The GTO outliers (Li, Be, Na, and Mg) have been computed with the aug-cc-pVQZ basis because the aug-cc-pV5Z basis set is not available for these elements. Had 5Z-quality functions been available for all elements, a more uniform error for GTO would have resulted along the series, but the overall picture would only improve slightly.
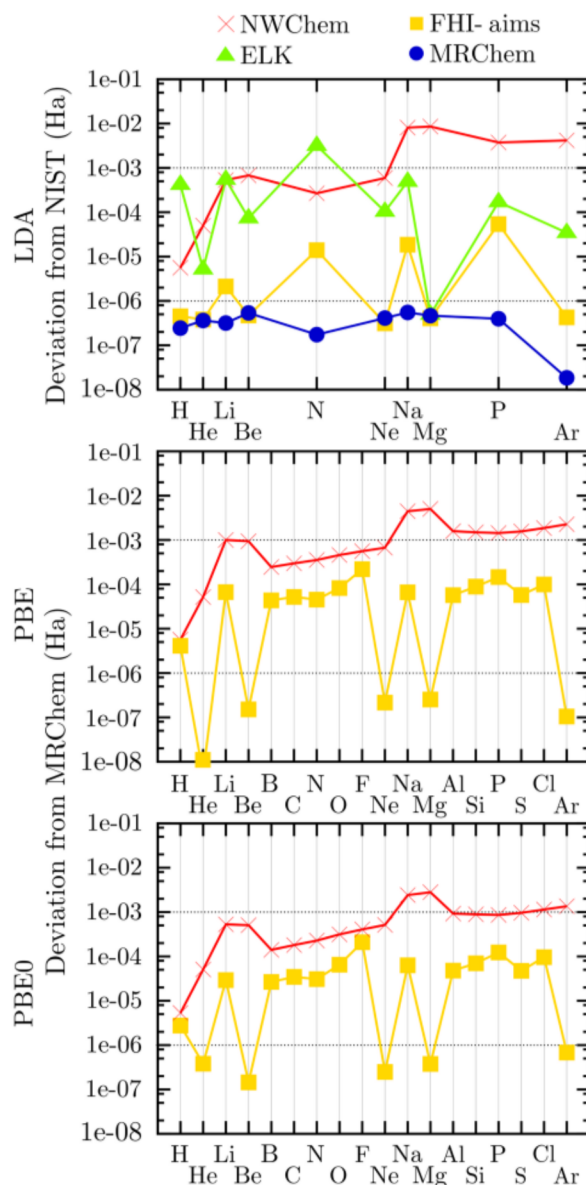

Figure 1. Absolute deviations in total energy found for different functionals for selected atoms. For LDA-SVWN5, energy differences are with respect to NIST all-electron values.[20] For GGA-PBE and hybrid-PBE0, the energy differences are with respect to MRCHEM. In all codes, the largest basis set and tighter parameters were used. In all plots, the reference values (NIST for LDA and MRCHEM for PBE/ PBE0) are given with 6 decimal precision; a displayed error below 1 × 10^6 Ha means that no discrepancy is detectable.

In the GGA-PBE (middle) and hybrid-PBE0 (bottom) panels, all 18 atoms (both spherical and not) are included. The nonrelativistic, spin-polarized electronic density and the total energy of the ground state computed using MRCHEM (converged within μHa) serves as the reference to which the other approaches are compared. For both functionals, NWCHEM performs at the limit of chemical accuracy (~1 mHa). The NAOs in FHI-AIMS achieve 0.1 mHa or better, except for fluorine (0.3 mHa). For closed-shell atoms, FHI-AIMS is essentially exact because the exact radial functions of spherically symmetric, spin-unpolarized atoms are included in