



**Figure 2.** GGA-PBE (left) and hybrid-PBE0 (right) deviations in the total energy, atomization energy, and electrostatic dipole moment for the set of 211 molecules with respect to highly accurate values obtained using MRCHEM. MAD, RMSD, and maxAD stand for the mean absolute deviation, root-mean-square deviation, and maximum absolute deviation, respectively. Results are included for two different DFT codes (NWCCHEM and FHI-AIMS) and four bases each: “light”, “tight”, “tier2”, and “tier4” for FHI-AIMS and aug-cc-pVXZ (X = D, T, Q, 5) for NWCCHEM.

the basis sets. For GTOs, we observe that the total energy error grows with the atomic number,  $Z$ . In contrast, the accuracy of NAOs is less affected by the nuclear charge, with errors generally below 0.1 mHa for the  $Z$  range examined here, irrespective of the choice of functional. For APW+lo, only the LDA-SVWN5 values are included in Figure 1; the corresponding GGA-PBE and hybrid-PBE0 errors achieved in this work are above the threshold of  $1 \times 10^3$  Ha (dashed line) and were not considered further because it is unclear how much they might be affected by implementation-specific aspects other than the basis set.

The total energies, atomization energies, and dipole moments of the 211 molecules considered have been computed within the GGA-PBE and hybrid-PBE0 functionals using MRCHEM with the highest affordable precision (below  $1 \mu\text{Ha}$  throughout). Figure 2 reports the MAD, RMSD, and maxAD obtained for the total energy (top panel), atomization energy (medium panel), and dipole moment (bottom panel) with NAO and Dunning GTO basis sets with respect to MRCHEM for the GGA-PBE and hybrid-PBE0 functionals, respectively. (Due to technical reasons in convergence,  $\text{CH}_3\text{CH}_2\text{O}$  was excluded from the PBE0 results, while CCH was excluded in both PBE and PBE0.) For all of the molecules, the correct ground-state spin multiplicity was specified.

Total energies are a measure of the accuracy achieved by each method/basis pair, whereas the atomization energies deserve special attention for their role in the development of density functionals, generally benchmarked against such thermodynamic values. However, as recently pointed out by Medvedev et al.,<sup>33</sup> the variational energy is not the optimal measure for the quality of the calculated electronic density, which influences numerous other observables. For this reason, we have included the dipole moment as a nonvariational quantity in our benchmarks (dipole errors are linear in the density error, whereas energies are quadratic). Dipole moments also serve as verification that the different methods converge to the same electronic state and not to a nearby metastable configuration. Although the existence of multiple metastable SCF solutions in KS DFT is well-known, it is often not detected by users of electronic structure codes. The solution strategy, also employed in the present paper, is to probe different spin initializations of each molecule to identify the global minimum. In the present work, the correct identification has been validated by ensuring consistency of the dipole moment as well as the KS eigenvalue spectra produced by the three distinct electronic structure methods.

Several important conclusions can be drawn from the results obtained: