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# How accurate are static polarizability predictions from density functional theory? An assessment over 132 species at equilibrium geometry.[†]

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Static polarizabilities are the first response of the electron density to electric fields, and are therefore important for predicting intermolecular and molecule-field interactions. They also offer a global measure of the accuracy of the treatment of excited states by density functionals in a formally exact manner. We have developed a database of benchmark static polarizabilities for 132 small species at equilibrium geometry, using coupled cluster theory through triple excitations (extrapolated to the complete basis set limit), for the purpose of developing and assessing density functionals. The performance of 60 popular and recent functionals are also assessed, which indicates that double hybrid functionals perform the best, having RMS relative errors in the range of 2.5-3.8% . Many hybrid functionals also give quite reasonable estimates with 4-5% RMS relative error. A few meta-GGAs like mBEEF and MVS yield performance comparable to hybrids, indicating potential for improved excited state predictions relative to typical local functionals. Some recent functionals however are found to be prone to catastrophic failure (possibly as a consequence of overparameterization), indicating a need for caution in applying these.

## 1 Introduction

The vast majority of present day electronic structure calculations employ some flavor of Kohn-Sham (KS) density functional theory (DFT)[1–4]. The exact functional mapping ground state electron density to ground state energy however remains computationally inaccessible, despite proof of its existence[5]. This has led to development of hundreds of density functional approximations (DFAs) of varying complexities through strategies ranging from a sole focus on satisfaction of exact physical constraints[6–8] to exclusively fitting to benchmark data[9,10]. Empirically fitted functionals are expected to be extremely accurate within the datasets employed for fitting, but they can be overparametrized to a point where performance outside of that comfort zone becomes rather suspect[11–14]. Conversely, functionals with none or few fitted parameters may not be as accurate for specific datasets but are believed to be much more transferable to systems not employed in the development process. Many modern functionals have consequently been developed through approaches that draw from both extremes[15,16], in the hope of having an acceptable balance between fit accuracy and transferability.

In general, a DFA should be transferable to any system of interacting electrons subjected to some external one particle potential $v(r)$. Isolated molecules often employed in fitting functionals satisfy the above condition (with $v(r)$ being the electrostatic potential of the nuclei) but they represent only a small fraction of systems where DFT is applicable. Molecular systems studied with DFT in fact often interact with external fields in chemically relevant scenarios—such as light-matter interactions or in condensed phase. The behavior of density functionals outside the traditional zero external field conditions thus has direct relevance to simulations of spectroscopy, dielectric solvation models[17] and QM/MM, amongst other things.

The simplest possible external field is a constant electric field $\vec{\mathscr{E}}$, and the corresponding responses of the energy $E(\vec{\mathscr{E}})$ are well known molecular properties[18]. The first response of the zero-field energy $E(0)$ to $\mathscr{E}$ is the dipole moment $\vec{\mu} = -\left(\dfrac{\partial E}{\partial \vec{\mathscr{E}}}\right)_{\vec{\mathscr{E}}=0}$, which is a simple global measure of the accuracy of electron density in a polar molecule. We studied the accuracy of DFT in predicting $\vec{\mu}$ in an earlier work for the purpose of gauging the quality of DFT densities[13], and will not consider it further here.

The dipole however contains no information about the response of the ground state wave function to the electric field as it can be computed from the zero-field density alone. The first property to contain information about the wave function response is the static polarizability tensor $\boldsymbol{\alpha}$ which is the second response of the zero field energy to the external field. The components $\alpha_{ij}$ are given by $-\left(\dfrac{\partial^2 E}{\partial \mathscr{E}_i \partial \mathscr{E}_j}\right)_{\vec{\mathscr{E}}=0}$, which allows us to express it in terms of excited electronic states at zero external field using perturbation theory. Specifically, given a ground state $|\Psi_0\rangle$ with energy $E_0$ and excited states $\{|\Psi_n\rangle\}$ with energies $\{E_n\}$ at $\vec{\mathscr{E}} = 0$, we have:

$$\alpha_{ij} = 2 \sum_{n=1} \frac{\langle \Psi_n | \hat{\mu}_i | \Psi_0 \rangle \langle \Psi_0 | \hat{\mu}_j | \Psi_n \rangle}{E_n - E_0} \quad (1)$$

where $\hat{\vec{\mu}}$ is the dipole operator. The ability of a functional to predict static polarizabilities therefore not only reveals how the electron density responds to an external field, but also gives indirect information about the treatment of dipole allowed excited states by the functional. This is a coarser measure than linear response TDDFT[19] in that the information about a single excited state cannot be disentangled, but it is formally exact as it does not involve use of the adiabatic local density approximation (ALDA)[20]. Polarizability predictions therefore indirectly measure both the transferability of a functional and the quality of excited state predictions (within the limits of the Hohenberg-Kohn[5] theorem), making it useful for assessing functional quality. Fitting functionals to polarizabilities should also assist in ensuring correct response of the energy to external electric fields.

There however does not appear to be a large database of benchmark static polarizabilities which could be used for either fit-

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ting density functionals to, or for assessing their performance. Past assessments [21,22] have often utilized experimental values, which may contain nuclear quantum effects that no *accurate* electronic structure method should reproduce within the Born-Oppenheimer approximation. Some studies [23,24] also appear to suggest that many experimental polarizabilities may contain substantial errors, making a comparison to benchmark wave function theories necessary for a truly fair assessment of the accuracy of polarizability predictions from DFAs. There have been several such studies [25–28], but they appear to either consider only a narrow range of molecules or use an apparently inadequate level of theory for reference values. The closest approximation to a benchmark database of polarizabilities appears to be CCSD(T)/aug-cc-pVTZ values for 145 organic molecules compiled by Wu, Kalugina and Thakkar for assessing the performance of 34 DFAs [29]. We however feel that these values may not be of benchmark quality on account of basis set incompleteness errors, which can be substantial for dipole moments [13] and polarizabilities (as will be shown later). The absence of split core orbitals also leads to an incomplete description of core electrons, and such effects could be significant (as they are already known to matter for dipole moments [30]). Ref [29] also only considered closed shell molecules and did not assess the performance of double hybrid functionals, which are known to be excellent for predicting energetics [31] and densities [13,32].

We have consequently developed a database of the diagonal components of static polarizabilities of 132 species (composed of main group elements lighter than Ar) at equilibrium geometry, using coupled cluster singles and doubles with perturbative triples (CCSD(T)) [33], extrapolated to the complete basis set limit (CBS). 75 of the species have a stable spin-unpolarized Hartree-Fock (HF) solution while the remaining 57 have a stable spin polarized HF solution either due to open-shell character or spin-symmetry breaking. The not spin-polarized (NSP) subset is expected to be relatively well described by conventional electronic structure methods, but the spin-polarized (SP) subset has the potential to be more challenging. This database is used to assess the performance of 60 popular and recent density functionals, along with HF, second order Møller-Plesset perturbation theory (MP2) and coupled cluster singles and doubles (CCSD). This dataset should also be useful for future functional development and assessment. In particular, it permits evaluation of the accuracy with which various DFAs predict individual diagonal elements of the static polarizability tensor, instead of just their average (where some cancellation of errors may occur) as is the case in Ref [29]. The high computational cost of large basis set coupled cluster calculations however constrained us to only consider species smaller than most studied in Ref [29], though we feel general features from this dataset ought to be transferable to larger systems where KS-DFT can be applied. It is however quite likely that somewhat different behavior is observed for systems with substantial multi-reference character, like long chains where the accuracy of KS-DFT polarizability calculations have long been suspect [34,35].

## 2  Computational Methods

All the calculations were done using a development version of Q-Chem 5 [36]. Most of the equilibrium geometries employed in the study were either obtained from experimental values in the NIST Computational Chemistry Database [37] or were optimized with MP2/cc-pVTZ if experimental geometries were unavailable. The exceptions to this general principle are $BH_2F$ and $BH_2Cl$, whose experimental geometries were taken from Refs [38] and [39] respectively, as well as the non-covalent complexes FH-OH and $H_2O$-Li, whose geometries were obtained from the TA13 [40] database. All the geometries employed in the present study are provided in the Supporting Information, along with the source.

Polarizabilities were obtained from finite differences using a central three point formula $\alpha_{ii} = \frac{E(\mathscr{E}\hat{i}) + E(-\mathscr{E}\hat{i}) - 2E(0)}{\mathscr{E}^2}$, which should be correct to $O(\mathscr{E}^2)$. The field strength $\mathscr{E}$ was set to 0.01 a.u. for most species, but a few s block atom containing species with large polarizabilities appeared to have large higher-order responses (made evident by a $> 0.5\%$ shift in HF polarizability estimates on changing $\mathscr{E}$ from $0.01 \rightarrow 0.005$ a.u.) that necessitated use of $\mathscr{E} = 0.001$ a.u. for that subset. This smaller field however was not universally employed due to larger risk of contamination from numerical error, especially in species without a highly polarizable s block atom where the HF polarizability estimate was shifting very little on halving the field strength to 0.005 a.u. anyways ($< 0.2\%$ for the vast majority). A full list of field strengths used for each molecule is given in the Supporting Information.

HF polarizabilities were obtained from spin unrestricted calculations with the aug-cc-pCV5Z [41–44] basis, which appeared to be close to the CBS limit (0.2% RMS deviation versus the equivalent aug-cc-pCVQZ numbers). Stability analysis was performed at the aug-cc-pCVQZ level to ensure all solutions were at a minima. Spin unrestricted DFT calculations were done with the aug-pc-4 [45–49] basis for functionals spanning Rungs 1-4 in Jacob's Ladder and it was assumed that such $5\zeta$ basis results ought to be essentially at CBS as well (though behavior for dipole moments suggest that this may not strictly be true for all functionals [13]). Local xc integrals were calculated over a radial grid with 99 points and an angular Lebedev grid with 590 points for all atoms, while non-local VV10 [50] correlation was calculated over an SG-1 [51] grid (which consists of a subset of points employed in a grid with 50 radial and 194 angular points). Stability analysis was done at the aug-pc-2 level to determine which SCF solutions were potentially unstable, and the problematic aug-pc-4 cases were reoptimized to ensure that the energy was at a minimum.

No orbitals were held frozen for any correlated wave function theory (WFT) calculation. All coupled cluster calculations (CCSD/CCSD(T)) were done employing unrestricted orbitals, but known N-representability violations [13,52] in unrestricted MP2 led us to calculate both unrestricted (henceforth referred to as MP2) and restricted (RMP2) values for comparison. The CBS limit was obtained by extrapolating the correlation component of $\alpha_{ii}$ from aug-cc-pCV5Z and aug-cc-pCVQZ results for the smaller species; and from the aug-cc-pCVQZ and aug-cc-pCVTZ results for the re-

mainder of the dataset. The extrapolation was done via:

$$(\alpha_{ii})_n^{\text{corr}} = (\alpha_{ii})_\infty^{\text{corr}} + A/n^3 \qquad (2)$$

which is known to be accurate for dipole moments[13,53]. Eqn 2 was found to be accurate to $\approx 0.1\%$ in predicting aug-cc-pCV5Z polarizabilities of some of the smaller species from aug-cc-pCVQZ and aug-cc-pCVTZ results, indicating that it was reasonably accurate for polarizabilities as well.

The superior performance of RMP2 over unrestricted MP2 led us to only perform calculations with restricted orbitals for double hybrid functionals, with no orbitals held frozen here as well. The xc integrals for double hybrid functionals were calculated using the same grids as all other functionals. The non-MP2 component of $\alpha_{ii}$ for double hybrid functionals was assumed to be essentially at the CBS limit when the aug-cc-pCV5Z basis was employed ($0.2 - 0.3\%$ RMS deviation versus the equivalent aug-cc-pCVQZ numbers). The MP2 correlation component was extrapolated to CBS from aug-cc-pCVQZ and aug-cc-pCVTZ results, using Eqn 2. Calculations employing the XYGJ-OS[54] functional were accelerated using the RI approximation[55] with the riMP2-cc-pVTZ auxiliary basis[56,57] for aug-cc-pCVTZ calculations and riMP2-cc-pVQZ auxiliary basis[57] for aug-cc-pCVQZ calculations.

The error in $\alpha_{ii}$ against the reference value $\alpha_{ii,\text{ref}}$ was defined to be $\dfrac{\alpha_{ii} - \alpha_{ii,\text{ref}}}{\alpha_{ii,\text{ref}}} \times 100\%$, which is a purely relative error. This was used to calculate root-mean squared, mean and maximum absolute errors for each of three diagonal components of the $\boldsymbol{\alpha}$ tensor, which are listed in the Supporting Information. The components themselves however have very similar relative error values, and so we only report the root mean square relative error (RMSRE), mean relative error (MRE) and maximum magnitude relative error (MAX) *over all the species and over the three diagonal components*, in the manuscript. In other words, if $\varepsilon_{i,n}$ is the error in $\alpha_{ii}$ for species $n$, we have:

$$\text{RMSRE} = \sqrt{\frac{1}{3N} \sum_{i=x,y,z} \sum_{n=1}^{N} \varepsilon_{i,n}^2} \qquad (3)$$

$$\text{MRE} = \frac{\sum_{i=x,y,z} \sum_{n=1}^{N} \varepsilon_{i,n}}{3N} \qquad (4)$$

$$\text{MAX} = \max\left(|\varepsilon_{i,n}| \forall i \in \{x,y,z\} \text{ and } 1 \le n \le N\right) \qquad (5)$$

where $N$ is the total number of species. The difference between the RMS relative errors for the $\alpha_{ii}$'s with the largest and smallest RMS errors (DIFF) is also reported, in order to determine if performance varies considerably along different axes.

# 3 Results

The error metrics defined in the preceding section were used to evaluate the performance of HF, MP2, CCSD and 60 DFAs against the CCSD(T) benchmark. The errors for all the electronic structure methods are given in Table 1, while Table 2 contains the benchmark average static polarizabilities ($\alpha = \dfrac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$) for

all 132 species, along with the values predicted by the functional with the lowest cumulative RMSRE in each rung of Jacob's ladder. The full list of all errors for all methods is provided in the Supporting Information, along with all computed $\alpha_{ii}$ polarizability components.

## 3.1 Performance of Wave function Theory

CCSD proves to be the most effective method for predicting dataset polarizabilities overall, producing an RMSRE of 1.62% and giving very similar performance over the NSP and SP subsets. This is partly on account of a conscious choice to only include species with maximum deviation less than 7% between CCSD and CCSD(T) $\alpha_{ii}$ in the dataset, in the hope that this would restrict the dataset to species where higher order excitations like exact triples or quadruples would not be necessary to obtain benchmark quality numbers. A large portion of the CCSD error appears to stem from systematic underestimation (MRE is $-1.2\%$) due to the absence of correlation energy from connected triples. It is therefore possible that CCSD (and potentially even CCSD(T)) may not be adequately accurate in predicting benchmark quality polarizabilities outside of our carefully curated dataset, necessitating incorporation of higher order excitations into the coupled cluster scheme. The closeness between CCSD and CCSD(T) values for our dataset, however, indicate that this is not likely to be a concern in the present case.

MP2 performs very well over the NSP species, yielding a small RMSRE of 2.17% that compares very favorably to the equivalent CCSD RMSRE of 1.55%. This behavior is consistent with the excellent performance of MP2 in predicting polarizabilities of closed shell organic molecules noted in Ref [29]. N-representability violations[52] in unrestricted MP2 however leads to catastrophically poor performance (including a few negative $\alpha_{ii}$'s!) over the SP dataset, resulting in a rather high RMSRE of 11.12% over the entire dataset. Switching over the restricted MP2 (RMP2) only partially ameliorates the problem by bringing the RMSRE down to 8.14%, which is still quite large relative to many density functionals. The large SP subset RMSRE likely stems from RMP2 operating on a restricted HF reference that is higher in energy than the spin-polarized solution, which leads to extremely large errors for some species like $O_2$ (predicted $\alpha_{zz} = 6.732$ Å$^3$ vs benchmark value of $2.263$ Å$^3$)–despite lack of N-representability violations. MP2 therefore is likely to be a poor choice in general for predicting polarizabilities of spin-polarized species, although it remains an excellent choice for spin unpolarized species.

HF gives quite poor performance, yielding an RMSRE of 8.45%. Lack of correlation energy in HF theory typically leads to larger excitation energies (as can be seen in CIS[20]), which leads to larger denominators in Eqn 1 and consequently smaller $\alpha_{ii}$. This systematic underestimation however is likely only part of the problem, as the MRE is a relatively small -3.04% vs the RMSRE, and the extra error likely stems from the poor quality of the method itself. Interestingly enough, restricted HF (RHF) has a slightly smaller RMSRE of 7.6% while the MRE remains essentially unchanged, suggesting that the constraint of spin restriction eliminated some minor sources of non-systematic error. It is also

| Method | Class | RMSRE All | RMSRE NSP | RMSRE SP | MRE | MAX | DIFF |
|---|---|---|---|---|---|---|---|
| CCSD | WFT | 1.62 | 1.55 | 1.71 | -1.20 | 6.26 | 0.34 |
| MP2 | WFT | 11.12 | 2.17 | 16.68 | -0.28 | 134.01 | 16.14 |
| HF | WFT | 8.45 | 6.84 | 10.15 | -3.04 | 58.99 | 3.21 |
| RMP2 | WFT | 8.14 | 2.17 | 11.94 | 0.71 | 197.48 | 15.07 |
| RHF | WFT | 7.60 | 6.84 | 8.48 | -2.81 | 30.37 | 1.56 |
| SPW92[6,64] | LSDA | 11.93 | 10.61 | 13.31 | 8.57 | 119.87 | 4.22 |
| Slater[6] | LSDA | 19.15 | 19.39 | 18.83 | 16.74 | 102.68 | 1.99 |
| N12[66] | GGA | 8.92 | 7.93 | 9.98 | 5.72 | 48.35 | 1.60 |
| MPW91[101] | GGA | 9.20 | 8.70 | 9.81 | 7.22 | 62.06 | 1.37 |
| B97-D[68] | GGA | 9.48 | 8.57 | 10.56 | 7.40 | 53.07 | 0.46 |
| PBE[7] | GGA | 10.11 | 9.64 | 10.69 | 7.91 | 68.07 | 1.73 |
| BLYP[65,71] | GGA | 12.14 | 10.73 | 13.78 | 8.94 | 75.44 | 1.06 |
| SOGGA11[73] | GGA | 77.54 | 24.91 | 113.80 | 14.79 | 1036.85 | 45.91 |
| mBEEF[76] | mGGA | 4.36 | 3.75 | 5.05 | 2.02 | 18.04 | 0.50 |
| MVS[75] | mGGA | 4.59 | 3.64 | 5.54 | 0.57 | 22.19 | 0.46 |
| SCAN[16] | mGGA | 5.31 | 4.79 | 5.91 | 3.25 | 17.93 | 0.37 |
| M06-L[78] | mGGA | 6.06 | 3.98 | 7.99 | 2.10 | 45.06 | 1.88 |
| MS2[72] | mGGA | 6.26 | 5.27 | 7.30 | 4.11 | 35.89 | 0.75 |
| revM06-L[81] | mGGA | 6.31 | 5.32 | 7.33 | 0.88 | 41.83 | 1.12 |
| TPSS[8] | mGGA | 7.39 | 6.99 | 7.89 | 5.76 | 34.52 | 0.55 |
| B97M-V[83] | mGGA | 7.65 | 6.73 | 8.68 | 5.13 | 31.55 | 0.06 |
| MN15-L[85] | mGGA | 7.95 | 7.18 | 8.84 | 6.12 | 43.16 | 0.12 |
| t-HCTH[87] | mGGA | 8.27 | 7.39 | 9.31 | 6.05 | 40.83 | 1.03 |
| MN12-L[88] | mGGA | 15.14 | 7.05 | 21.52 | 3.98 | 200.38 | 11.27 |
| M11-L[89] | mGGA | 15.41 | 11.86 | 19.01 | 7.65 | 126.79 | 3.12 |
| MPW1K[102] | hGGA | 3.27 | 2.94 | 3.67 | -0.38 | 17.36 | 0.85 |
| PBE50[108] | hGGA | 3.71 | 3.45 | 4.03 | -1.10 | 18.25 | 1.00 |
| MPW1PW91[101] | hGGA | 3.84 | 3.51 | 4.23 | 2.35 | 14.99 | 0.21 |
| BHHLYP[65,71] | hGGA | 3.95 | 2.92 | 4.99 | -0.17 | 22.08 | 0.18 |
| LRC-ωPBEh[93] | hGGA | 4.28 | 3.93 | 4.68 | 2.51 | 18.28 | 0.63 |
| PBE0[95] | hGGA | 4.29 | 3.98 | 4.67 | 2.84 | 16.19 | 0.28 |
| HSEHJS[97] | hGGA | 4.31 | 4.00 | 4.69 | 2.86 | 16.99 | 0.26 |
| ωB97X-V[98] | hGGA | 4.58 | 4.02 | 5.23 | 2.38 | 20.12 | 0.39 |
| SOGGA11-X[100] | hGGA | 4.65 | 3.39 | 5.88 | 1.50 | 27.71 | 0.42 |
| rcamB3LYP[58] | hGGA | 4.67 | 4.10 | 5.31 | 1.37 | 24.07 | 0.73 |
| B97-2[59] | hGGA | 4.96 | 3.88 | 6.08 | 3.05 | 25.13 | 0.08 |
| camB3LYP[60] | hGGA | 4.97 | 4.18 | 5.85 | 2.67 | 20.21 | 0.11 |
| LRC-ωPBE[61] | hGGA | 5.07 | 4.84 | 5.35 | 3.05 | 21.63 | 0.69 |
| ωB97X-D[62] | hGGA | 5.18 | 4.13 | 6.29 | 3.37 | 21.44 | 0.50 |
| B3LYP[63] | hGGA | 6.24 | 5.37 | 7.20 | 4.18 | 29.50 | 0.39 |
| B97[9] | hGGA | 6.40 | 4.91 | 7.88 | 4.19 | 49.07 | 1.28 |
| HFLYP[65] | hGGA | 8.61 | 8.61 | 8.60 | -6.21 | 34.30 | 1.36 |
| SCAN0[67] | hmGGA | 3.98 | 2.60 | 5.23 | 0.39 | 18.73 | 0.76 |
| ωM05-D[69] | hmGGA | 4.33 | 3.73 | 5.00 | 2.31 | 19.89 | 0.09 |
| PW6B95[70] | hmGGA | 4.53 | 3.75 | 5.48 | 2.42 | 19.31 | 0.11 |
| MS2h[72] | hmGGA | 4.98 | 3.91 | 6.06 | 2.72 | 29.23 | 0.59 |
| MN15[74] | hmGGA | 5.00 | 3.50 | 6.47 | 2.13 | 20.54 | 0.34 |
| MVSh[75] | hmGGA | 5.08 | 4.17 | 5.96 | -1.83 | 21.91 | 0.12 |
| M06-2X[10] | hmGGA | 5.22 | 3.38 | 6.93 | 0.34 | 35.47 | 0.35 |
| M06[10] | hmGGA | 5.24 | 4.71 | 5.85 | 2.99 | 29.79 | 0.76 |
| TPSSh[77] | hmGGA | 5.44 | 5.06 | 5.88 | 3.97 | 23.04 | 0.24 |
| M11[79] | hmGGA | 6.13 | 4.64 | 7.58 | 1.71 | 66.69 | 3.99 |
| M05[80] | hmGGA | 6.46 | 6.12 | 6.89 | 3.35 | 33.30 | 1.95 |
| ωB97M-V[15] | hmGGA | 6.83 | 5.55 | 8.19 | 3.91 | 26.32 | 0.96 |
| BMK[82] | hmGGA | 9.49 | 3.00 | 13.75 | 1.53 | 90.11 | 6.72 |
| MN12-SX[84] | hmGGA | 10.39 | 5.35 | 14.56 | 3.12 | 90.29 | 4.92 |
| M06-HF[86] | hmGGA | 10.69 | 9.65 | 11.84 | 0.04 | 58.68 | 1.76 |
| XYGJ-OS[54] | dhGGA | 2.44 | 1.33 | 3.37 | 0.70 | 15.46 | 0.45 |
| XYG3[90] | dhGGA | 2.68 | 1.53 | 3.68 | 0.20 | 14.98 | 0.44 |
| DSD-PBEPBE-D3[91] | dhGGA | 2.73 | 1.76 | 3.63 | 1.12 | 14.30 | 0.25 |
| B2GPPLYP[92] | dhGGA | 3.40 | 2.16 | 4.55 | 1.31 | 20.23 | 0.24 |
| ωB97X-2[94] | dhGGA | 3.60 | 2.89 | 4.37 | 1.79 | 16.89 | 0.46 |
| B2PLYP[96] | dhGGA | 4.36 | 3.10 | 5.60 | 2.49 | 27.45 | 0.36 |
| PTPSS-D3[99] | dhmGGA | 3.59 | 2.89 | 4.23 | 2.05 | 25.63 | 0.28 |
| PWPB95-D3[99] | dhmGGA | 3.72 | 2.54 | 4.85 | 1.81 | 24.37 | 0.39 |

**Table 1** RMS relative errors (RMSRE), mean relative errors (MRE) and maximum magnitude relative errors (MAX) for electronic structure methods over the dataset, expressed as percentages. The RMSRE of the spin-polarized (SP) and non-spin polarized (NSP) subsets of the dataset are also reported separately. Additionally, the difference between the RMS relative errors of the components $\alpha_{ii}$ with the largest and smallest RMS relative errors is reported under DIFF. WFT stands for wave function theory, LSDA for local spin density approximation, GGA for generalized gradient approximation, mGGA for meta-GGA, hGGA for hybrid GGA, hmGGA for hybrid meta-GGA, dhGGA for double hybrid GGA and dhmGGA for double hybrid meta-GGA.

interesting to note that the RHF RMSRE is slightly lower than the RMP2 RMSRE, indicating that the expensive perturbation theory correction did little to help for SP species.

## 3.2 Performance of DFT

Table 1 reveals a number of general features that are likely to be transferable beyond our specific dataset. It is firstly striking that all but five functionals have a positive MRE. This systematic overestimation of polarizabilities for most functionals can be rationalized in terms of self-interaction error resulting in softer, more polarizable densities. The positive MRE can also interpreted in terms of Eqn 1: most DFAs tend to underestimate excitation energies (with both TDDFT[20] and to a lesser extent, ΔSCF[103] type approaches[104]), leading to a smaller denominator in Eqn 1 and consequently larger polarizabilities. The values in Table 1 are consistent with this interpretation, with four of the five functionals producing negative MRE containing 40% or more exact exchange. MVSh[75] is the exception as it contains only 25% exact exchange, but this is likely on the account of the base MVS[75]

functional already having a very low MRE of 0.57% despite being a local functional.

It is also important to note that the best DFA in each Rung of Jacob's ladder has a lower RMSRE than the best DFAs in the Rungs below, which is likely a consequence of the additional physical content at each Rung. However, not all functionals employ that extra physical content optimally, as can be seen from the best Rung 3 functionals like mBEEF[76] and MVS outperforming widely used hybrid functionals like B3LYP[63] and M06[10]. There is in fact substantial overlap in accuracy between Rungs 3 and 4, indicating that exact exchange is not always necessary to improve polarizability predictions.

The best functionals for polarizability predictions are however the double hybrids XYGJ-OS[54] and XYG3[90] (RMSRE of 2.44% and 2.68% respectively), with DSD-PBEPBE-D3[91] not far behind (2.73% RMSRE). All three of these functionals were found to be excellent for predicting dipole moments as well[13], indicating that they might be good options for predicting electric field responses in general. They also have a much lower NSP RMSRE (< 2%)

| NSP Species | CCSD(T) | Rung 1 | Rung 2 | Rung 3 | Rung 4 | Rung 5 | SP Species | CCSD(T) | Rung 1 | Rung 2 | Rung 3 | Rung 4 | Rung 5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $AlF$ | 5.691 | 5.966 | 6.114 | 6.005 | 5.870 | 5.787 | $Be$ | 5.622 | 6.551 | 6.351 | 6.327 | 6.434 | 6.107 |
| $Ar$ | 1.634 | 1.779 | 1.690 | 1.656 | 1.641 | 1.642 | $BeH$ | 4.872 | 5.423 | 5.394 | 5.129 | 5.012 | 4.921 |
| $BeH_2$ | 2.933 | 3.282 | 3.150 | 3.043 | 2.968 | 2.944 | $BH_2$ | 2.922 | 3.353 | 3.477 | 3.049 | 2.974 | 2.919 |
| $BF$ | 2.862 | 3.207 | 3.129 | 3.022 | 2.937 | 2.936 | $BN$ | 3.479 | 3.824 | 3.906 | 3.603 | 3.392 | 3.688 |
| $BH_2Cl$ | 4.360 | 4.701 | 4.516 | 4.412 | 4.338 | 4.380 | $BO$ | 2.430 | 2.666 | 2.582 | 2.516 | 2.397 | 2.534 |
| $BH_2F$ | 2.450 | 2.699 | 2.585 | 2.543 | 2.437 | 2.464 | $BS$ | 4.987 | 5.321 | 5.355 | 5.022 | 5.010 | 5.082 |
| $BH_3$ | 2.520 | 2.768 | 2.672 | 2.602 | 2.545 | 2.528 | $C_2H$ | 3.304 | 3.922 | 4.078 | 3.599 | 3.390 | 3.479 |
| $BHF_2$ | 2.385 | 2.645 | 2.510 | 2.478 | 2.340 | 2.396 | $C_2H_3$ | 3.855 | 4.194 | 4.155 | 3.975 | 3.897 | 3.887 |
| $C_2H_2$ | 3.339 | 3.565 | 3.547 | 3.435 | 3.421 | 3.350 | $CH_2F$ | 2.368 | 2.683 | 2.627 | 2.447 | 2.333 | 2.362 |
| $C_2H_4$ | 4.007 | 4.281 | 4.232 | 4.151 | 4.106 | 4.059 | $CH_2NH$ | 3.255 | 3.557 | 3.494 | 3.405 | 3.323 | 3.344 |
| $CH_2BH$ | 4.496 | 4.797 | 4.781 | 4.615 | 4.554 | 4.547 | $CH_2PH$ | 6.060 | 6.338 | 6.191 | 6.107 | 6.120 | 6.067 |
| $CH_3BH_2$ | 4.272 | 4.683 | 4.522 | 4.411 | 4.279 | 4.278 | $^3CH_2$ | 2.143 | 2.462 | 2.465 | 2.227 | 2.160 | 2.110 |
| $CH_3Cl$ | 4.417 | 4.727 | 4.569 | 4.475 | 4.414 | 4.429 | $CH_3$ | 2.341 | 2.629 | 2.632 | 2.372 | 2.334 | 2.340 |
| $CH_3F$ | 2.435 | 2.656 | 2.558 | 2.513 | 2.423 | 2.442 | $CH_3O$ | 3.450 | 4.043 | 3.764 | 3.656 | 3.406 | 3.438 |
| $CH_3NH_2$ | 3.743 | 4.086 | 3.976 | 3.839 | 3.708 | 3.758 | $CN$ | 2.864 | 3.004 | 3.121 | 3.080 | 2.993 | 2.845 |
| $CH_3OH$ | 3.104 | 3.382 | 3.277 | 3.192 | 3.074 | 3.120 | $F_2$ | 1.244 | 1.319 | 1.273 | 1.284 | 1.250 | 1.255 |
| $CH_3SH$ | 5.417 | 5.821 | 5.627 | 5.480 | 5.416 | 5.438 | $FCO$ | 2.584 | 2.789 | 2.729 | 2.632 | 2.513 | 2.604 |
| $CH_4$ | 2.426 | 2.636 | 2.547 | 2.484 | 2.434 | 2.441 | $FH\text{-}OH$ | 1.923 | 2.991 | 2.177 | 2.079 | 1.882 | 1.869 |
| $Cl_2$ | 4.502 | 4.747 | 4.549 | 4.530 | 4.481 | 4.521 | $H_2CN$ | 2.897 | 3.142 | 3.071 | 2.958 | 2.881 | 2.910 |
| $ClCN$ | 4.471 | 4.749 | 4.614 | 4.544 | 4.464 | 4.495 | $H_2O\text{-}Li$ | 38.594 | 34.568 | 30.348 | 33.183 | 36.137 | 38.614 |
| $ClF$ | 2.683 | 2.859 | 2.735 | 2.712 | 2.663 | 2.696 | $HCHS$ | 5.045 | 5.313 | 5.181 | 5.098 | 5.072 | 5.022 |
| $CO$ | 1.930 | 2.034 | 1.975 | 1.930 | 1.888 | 1.939 | $HCO$ | 2.485 | 2.691 | 2.685 | 2.565 | 2.466 | 2.511 |
| $CO_2$ | 2.579 | 2.640 | 2.560 | 2.528 | 2.467 | 2.599 | $HCP$ | 5.258 | 5.474 | 5.363 | 5.276 | 5.318 | 5.242 |
| $CS$ | 4.207 | 4.373 | 4.242 | 4.149 | 4.165 | 4.210 | $HNO$ | 2.217 | 2.435 | 2.362 | 2.316 | 2.209 | 2.235 |
| $CSO$ | 5.113 | 5.183 | 5.018 | 4.966 | 4.968 | 5.130 | $HNS$ | 4.327 | 4.608 | 4.507 | 4.473 | 4.411 | 4.346 |
| $FCN$ | 2.682 | 2.850 | 2.779 | 2.736 | 2.666 | 2.694 | $HO_2$ | 1.972 | 2.101 | 2.041 | 1.983 | 1.913 | 1.978 |
| $FNO$ | 2.552 | 2.644 | 2.547 | 2.525 | 2.441 | 2.585 | $HOF$ | 1.737 | 1.761 | 1.750 | 1.761 | 1.690 | 1.727 |
| $H$ | 0.667 | 0.902 | 0.825 | 0.761 | 0.736 | 0.692 | $Li$ | 24.304 | 23.016 | 19.851 | 22.030 | 23.456 | 23.160 |
| $H_2$ | 0.768 | 0.878 | 0.829 | 0.805 | 0.794 | 0.786 | $Li_2$ | 30.932 | 30.119 | 29.315 | 29.351 | 29.445 | 29.807 |
| $H_2O$ | 1.409 | 1.575 | 1.509 | 1.452 | 1.369 | 1.431 | $N$ | 1.077 | 1.216 | 1.226 | 1.137 | 1.108 | 1.041 |
| $HBO$ | 2.457 | 2.596 | 2.549 | 2.482 | 2.401 | 2.498 | $N_2H_2$ | 2.813 | 3.055 | 2.987 | 2.903 | 2.796 | 2.824 |
| $HBS$ | 5.033 | 5.240 | 5.129 | 4.984 | 5.023 | 5.047 | $Na$ | 24.320 | 20.884 | 30.942 | 23.619 | 25.705 | 23.693 |
| $HCCCl$ | 5.372 | 5.773 | 5.645 | 5.517 | 5.451 | 5.386 | $Na_2$ | 38.661 | 34.350 | 37.229 | 36.256 | 38.301 | 36.884 |
| $HCCF$ | 3.423 | 3.692 | 3.628 | 3.541 | 3.475 | 3.436 | $NaLi$ | 35.124 | 32.398 | 33.333 | 32.730 | 33.718 | 33.435 |
| $HCHO$ | 2.611 | 2.829 | 2.756 | 2.682 | 2.585 | 2.638 | $NCO$ | 3.131 | 3.214 | 3.144 | 3.113 | 3.058 | 3.155 |
| $HCl$ | 2.542 | 2.758 | 2.633 | 2.565 | 2.544 | 2.558 | $NH$ | 1.452 | 1.617 | 1.587 | 1.501 | 1.441 | 1.433 |
| $HCN$ | 2.472 | 2.611 | 2.574 | 2.519 | 2.488 | 2.478 | $NH_2$ | 1.784 | 1.982 | 1.927 | 1.821 | 1.749 | 1.788 |
| $HCONH_2$ | 4.081 | 4.433 | 4.306 | 4.124 | 3.923 | 4.099 | $NO$ | 1.723 | 1.910 | 1.873 | 1.791 | 1.710 | 1.740 |
| $HCOOH$ | 3.309 | 3.594 | 3.473 | 3.373 | 3.204 | 3.331 | $NOCl$ | 5.045 | 5.176 | 4.984 | 4.928 | 4.918 | 5.130 |
| $He$ | 0.205 | 0.245 | 0.223 | 0.220 | 0.211 | 0.209 | $NP$ | 4.152 | 4.311 | 4.202 | 4.156 | 4.130 | 4.209 |
| $HF$ | 0.819 | 0.924 | 0.875 | 0.857 | 0.800 | 0.825 | $O_2$ | 1.561 | 1.623 | 1.603 | 1.575 | 1.564 | 1.601 |
| $HNC$ | 2.700 | 2.847 | 2.784 | 2.695 | 2.642 | 2.701 | $O_3$ | 2.819 | 2.893 | 2.822 | 2.756 | 2.618 | 2.729 |
| $HOCl$ | 3.312 | 3.524 | 3.392 | 3.353 | 3.282 | 3.331 | $OCl$ | 3.004 | 3.254 | 3.129 | 3.074 | 3.031 | 3.094 |
| $HOOH$ | 2.216 | 2.365 | 2.297 | 2.264 | 2.177 | 2.239 | $OF$ | 1.407 | 1.568 | 1.484 | 1.464 | 1.382 | 1.439 |
| $LiBH_4$ | 4.420 | 4.985 | 4.800 | 4.571 | 4.433 | 4.418 | $OF_2$ | 2.129 | 2.260 | 2.179 | 2.187 | 2.096 | 2.148 |
| $LiCl$ | 3.842 | 4.408 | 4.281 | 3.968 | 3.803 | 3.915 | $OH$ | 1.159 | 1.330 | 1.266 | 1.061 | 1.132 | 1.160 |
| $LiCN$ | 3.581 | 3.931 | 3.906 | 3.653 | 3.468 | 3.595 | $P$ | 3.705 | 4.161 | 4.168 | 3.809 | 3.835 | 3.680 |
| $LiH$ | 4.186 | 5.073 | 5.256 | 4.403 | 3.968 | 4.228 | $P_2$ | 7.334 | 7.573 | 7.337 | 7.266 | 7.373 | 7.279 |
| $Mg$ | 10.591 | 10.580 | 11.378 | 11.028 | 11.195 | 10.699 | $PH$ | 4.059 | 4.455 | 4.373 | 4.125 | 4.108 | 4.072 |
| $Mg_2$ | 23.068 | 23.616 | 25.576 | 24.589 | 24.681 | 23.442 | $PH_2$ | 4.329 | 4.693 | 4.553 | 4.360 | 4.345 | 4.361 |
| $N_2$ | 1.732 | 1.820 | 1.776 | 1.744 | 1.725 | 1.729 | $PS$ | 6.532 | 6.973 | 6.590 | 6.447 | 6.479 | 6.889 |
| $N_2H_4$ | 3.333 | 3.649 | 3.560 | 3.417 | 3.267 | 3.347 | $S_2$ | 6.000 | 6.172 | 6.055 | 5.960 | 5.996 | 6.078 |
| $NaCl$ | 4.402 | 5.487 | 5.430 | 4.826 | 4.421 | 4.537 | $SCl$ | 5.325 | 5.725 | 5.482 | 5.358 | 5.276 | 5.347 |
| $NaCN$ | 4.007 | 4.633 | 4.670 | 4.225 | 3.903 | 4.028 | $SF$ | 3.328 | 3.695 | 3.503 | 3.429 | 3.315 | 3.351 |
| $NaH$ | 6.596 | 7.448 | 7.321 | 6.814 | 5.726 | 6.920 | $SH$ | 3.442 | 3.795 | 3.616 | 3.503 | 3.460 | 3.465 |
| $Ne$ | 0.393 | 0.452 | 0.420 | 0.419 | 0.392 | 0.392 | $SiH_3$ | 5.002 | 5.507 | 5.407 | 5.061 | 5.005 | 4.998 |
| $NH_2Cl$ | 3.954 | 4.215 | 4.074 | 4.002 | 3.919 | 3.972 | $^3SO$ | 3.412 | 3.601 | 3.549 | 3.444 | 3.390 | 3.446 |
| $NH_2F$ | 2.189 | 2.364 | 2.285 | 2.230 | 2.143 | 2.196 | | | | | | | |
| $NH_2OH$ | 2.789 | 3.015 | 2.930 | 2.842 | 2.724 | 2.806 | | | | | | | |
| $NH_3$ | 2.081 | 2.313 | 2.240 | 2.123 | 2.035 | 2.110 | | | | | | | |
| $NH_3O$ | 3.010 | 3.547 | 3.469 | 3.229 | 2.929 | 3.080 | | | | | | | |
| $OCl_2$ | 5.523 | 5.999 | 5.770 | 5.675 | 5.502 | 5.516 | | | | | | | |
| $P_2H_4$ | 8.499 | 9.033 | 8.691 | 8.513 | 8.481 | 8.532 | | | | | | | |
| $PH_2OH$ | 4.892 | 5.288 | 5.089 | 4.972 | 4.862 | 4.925 | | | | | | | |
| $PH_3$ | 4.475 | 4.829 | 4.624 | 4.515 | 4.494 | 4.505 | | | | | | | |
| $PH_3O$ | 4.367 | 4.727 | 4.555 | 4.434 | 4.275 | 4.424 | | | | | | | |
| $S_2H_2$ | 6.523 | 6.930 | 6.662 | 6.513 | 6.486 | 6.552 | | | | | | | |
| $SCl_2$ | 7.563 | 8.021 | 7.701 | 7.575 | 7.483 | 7.584 | | | | | | | |
| $SF_2$ | 3.478 | 3.765 | 3.591 | 3.567 | 3.428 | 3.500 | | | | | | | |
| $SH_2$ | 3.587 | 3.894 | 3.726 | 3.610 | 3.597 | 3.619 | | | | | | | |
| $SiH_3Cl$ | 6.160 | 6.691 | 6.379 | 6.234 | 6.144 | 6.163 | | | | | | | |
| $SiH_3F$ | 4.114 | 4.539 | 4.308 | 4.237 | 4.103 | 4.120 | | | | | | | |
| $SiH_4$ | 4.589 | 5.061 | 4.802 | 4.685 | 4.603 | 4.588 | | | | | | | |
| $SiO$ | 4.372 | 4.546 | 4.506 | 4.432 | 4.276 | 4.522 | | | | | | | |
| $SO_2$ | 3.764 | 3.894 | 3.776 | 3.738 | 3.631 | 3.808 | | | | | | | |

**Table 2** Benchmark CCSD(T)/CBS average static polarizabilities (in $\text{Å}^3$) for all 132 species at equilibrium geometry, along with the values predicted by the functional with lowest cumulative RMSRE at each Rung of Jacob's ladder. These functionals are SPW92 (Rung 1), N12 (Rung 2), mBEEF (Rung 3), MPW1K (Rung 4) and XYGJ-OS (Rung 5) respectively. We counted the H atom as a NSP species despite the odd electron count as the alpha and beta orbitals are formally the same.

than SP RMSRE ($> 3\%$), indicating that use of restricted orbitals likely prevented them from realizing their full potential. This, in conjunction with other failures of conventional double hybrid functionals for spin polarized systems[13,105] seems to suggest that it is desirable to develop double hybrid functionals based on orbital optimized MP2 type approaches[106,107] in order to take full advantage of their complexity. It is nonetheless interesting to note that the SP RMSRE for most double hybrids (3-5%) is comparable to, or lower than the SP RMSRE for most hybrid functionals (despite the latter using unrestricted orbitals) and mark a substantial improvement over RMP2. It is therefore likely quite safe to use double hybrid functionals with restricted orbitals for spin-polarized systems at equilibrium geometry, unlike RMP2 (which gives quite poor performance for some species like $O_2$).

MPW1K[102] proves to be the best Rung 4 functional by far with 3.27% RMSRE–partially as a consequence of the functional employing a large fraction of HF exchange (42.8%), which eliminates the systematic overestimation of polarizabilities present in the related hybrid MPW1PW91[101] (25% HF exchange) and local functional MPW91[101] and indeed, results in a small bias towards underestimating polarizabilities (MRE of -0.38%). A similar trend is also seen in the case of the second best performing hybrid functional PBE50[108] (50% HF exchange), relative to the related hybrid PBE0[95] (25% HF exchange) and local functional PBE[7]. The higher exact exchange fractions present in these functionals however could worsen predictions of other properties (as can be seen from the mediocre performance of PBE50 in predicting dipoles relative to the excellent PBE0 functional[13]). The excellent overall performance of MPW1K in predicting polarizabilities could partially stem from the improved accuracy of the base MPW91 GGA relative to PBE and BLYP, resulting in superior predictions by MPW1K relative to other large HF exchange containing functionals like PBE50 and BHHLYP, and could also explain why MPW1PW91 outperforms the classic PBE0 functional. Other hybrid functionals like $\omega$B97X-V[98], $\omega$M05-D[69], PW6B95[70] and PBE0 also yield quite good performance with around 4.5% or so RMSRE, and are also excellent for dipole moments[13], making them safe choices for estimating electric field responses in general. There are also several others that have errors in the 5-7% range. Hybrid functionals overall also have somewhat larger RMSRE over the SP subset than the NSP one, showing that the former are more challenging. The performance gap however is often quite small (<1%), indicating that this is not a major issue for many functionals. BMK[82] however proves to be a major exception, with the SP species increasing the total RMSRE to 9.49% relative to the excellent NSP subset RMSRE of 3%. BHHLYP, SCAN0, B97-2[59], SOGGA11-X[100] and MN15[74] are also impacted by the NSP/SP performance difference, though to a much lesser extent. It is also interesting that hybrid meta-GGAs (hmGGAs) do not appear to outperform hybrid GGAs (hGGAs), despite meta-GGAs (mGGAs) being much more accurate than GGAs. This suggests that the vastness of the hmGGA functional space has not been optimally utilized for improving polarizability predictions, which is similar to behavior observed for dipole moments[13].

It is therefore noteworthy that many mGGAs (mBEEF, MVS and SCAN in particular) are essentially as good as hybrid functionals at predicting polarizabilities, which is quite unlike the behavior observed for dipole moments[13]. These three functionals also do not have particularly large systematic biases relative to hybrid functionals (as reflected by their MRE), indicating that this particular manifestation of self-interaction error might be rather minimized. It would therefore be interesting to examine whether these functionals are comparable to hybrids for excitation energy predictions. The case of MVS is rather interesting in particular as its hybrid variant MVSh predicts worse polarizabilities (unlike other similar local/hybrid pairs like SCAN/SCAN0 or TPSS[8]/TPSSh[77]) due to MVS already having a very low systematic bias. MVS was also mediocre in predicting dipole moments, whereas mBEEF and SCAN were the best local functionals tested for dipole predictions[13].

Overall, there is no great chasm in performance between local functionals and hybrids (unlike in dipole moments[13]), with several less accurate mGGAs like MS2[72] and M06-L[78] giving performance comparable to many hybrid functionals, and some others like TPSS and B97M-V[83] being not much worse. The only potentially problematic aspect is the larger gap between NSP and SP RMSREs relative to hybrid functionals, but the actual errors remain fairly low. There is however a rather wide gulf separating mGGAs from GGAs, with the latter being rather poor at predicting polarizabilities relative to mGGAs. Aside from the special case of SOGGA11[73] however, GGAs represent an improvement over LSDA but nonetheless ought not be employed to estimate polarizabilities as mGGAs make significantly better predictions for the same computational complexity.

Coming to the matter of poor performers, we find that the worst double hybrid functional B2PLYP[96] actually does not have particularly bad RMSRE (4.36%) relative to Rungs 3 and 4. However, its performance is quite poor relative to its Rung 5 brethren (as was also observed to be the case dipole moment predictions[13]), and it has a higher RMSRE than the related BHHLYP hybrid functional, indicating that the excess functional complexity did not lead to any evident advantages. Interestingly enough, the PWPB95-D3 functional appears to be one of the worse performing double hybrids, despite being the most accurate of the Rung 5 functionals tested for dipole moment predictions[13]. The worst hybrid functionals give much less satisfactory performance with RMSRE $\approx$ 10% but are still better than LSDA. The worst GGA (SOGGA11) and mGGA (M11-L[89]) however are worse than Rung 1 LSDA, suggesting overparametrization has led to a subsequent decrease in accuracy. SOGGA11's performance in particular is exceptionally poor for even simple species like $H_2$ and HCl, to say nothing of more challenging cases like $Li_2$. This functional also has a rather poor basis set convergence for dipole moments[13], suggesting that the aug-pc-4 numbers may not be adequately close to the CBS limit. SOGGA11 therefore should not be used for molecular property predictions. Paradoxically however, the related SOGGA11-X hybrid functional performs quite well, suggesting that there may exist some scope for improving SOGGA type functionals.

It is also interesting to note that the best performing functionals have small DIFF values ($\approx$ 1% or lower). MRE for individual $\alpha_{ii}$ are also quite similar in value, suggesting that these functionals are about equally as effective in estimating $\alpha_{xx,yy,zz}$. This is encouraging, as it suggests that good functionals would predict accurate static polarizabilities on account of getting individual components correct, instead of relying on cancellation of errors between them. Several of the poor performing functionals however have quite large DIFF values, largely as a consequence of catastrophic failure in predicting $\alpha_{zz}$ (polarizability along the bond axis) for certain s-block diatomics like $Li_2$ or NaLi, while getting more reasonable estimates for the components perpendicular to the bond axis.

| Species | Subset |
|---------|--------|
| Be | SP |
| H | NSP |
| CN | SP |
| $C_2H$ | SP |
| $H_2O$-Li | SP |
| Na | SP |
| $Li_2$ | SP |
| NaLi | SP |

**Table 3** The 8 most difficult species in the dataset. These were selected on the basis of the first quartile of relative RMS DFA errors for each species (the RMS being taken over the three components). The selected species giving $\geq 5\%$ first quartile error, which corresponded to a break in the distribution. Coincidentally, this number is also comparable to typical Rung 4 RMSREs.

## 3.3 Challenging Species

The eight most challenging species for DFT polarizibility predictions are listed in Table 3, roughly in descending order of difficulty. Most are NSP species, which is entirely unsurprising on account of the best performing functionals being double hybrids that are constrained to act on restricted references alone. The two most challenging species in the dataset by far are the H and Be atoms, which is somewhat surprising on account of their simplicity. The polarizabilities for both are systematically overestimated by $\approx 10\%$ or more, although the errors for H decrease on increasing the fraction of exact exchange over families of similar functionals (expectedly, as HF is exact for the H atom), suggesting that self-interaction error is to blame in this case. On the other hand, Be is likely challenging due to multi-reference character (HF breaks spin-symmetry despite Be formally being a closed-shell singlet atom) and not self-interaction, as the errors remain similar over related functionals with different exchange fractions. The behavior for both atoms is quite troubling as it indicates that thirty years of functional development involving many comparisons and fits to such simple atoms nonetheless fails to predict response under a constant electric field. We recommend that the zero external field atomic energies typically used for fitting functionals be augmented with energies and densities for atoms subjected to diverse field strengths, in order to generate a more complete description of such so called 'perfect norms'[11].

Other challenging species are the triple bonded $C_2H$ and CN radicals, and highly polarizable alkali atom containing species like NaLi. Their presence on the list is unsurprising, especially since the latter poses a major challenge to functionals with regards to density predictions[13]. MN12-L[88] and MN12-SX[84] in particular fail catastrophically in predicting properties for such alkali atom containing species, indicating a need for caution in applying these Minnesota functionals to s block elements. In general however, the species in Table 3 are challenging for the vast majority of functionals and no class of DFAs appear to have an evident advantage for any of them. The list of best and worst performing functionals for each species in Table 3 contain a mix of both local functionals and hybrids, irrespective of the extent of single/multi-reference character.

It is also interesting to note that the most challenging species

in Table 3 are not amongst the largest species in the dataset. KS-DFT is known to have significant difficulties in predicting $\alpha$ for long chains[34,35,109], although none of the molecules studied were anywhere close to the problematic length scales. The possibility of different behavior on very large length scales therefore cannot be ruled out, especially if the systems have substantial multi-reference character like long polyene or acene chains. For the 132 systems studied in this work however, atoms as a rule prove to be the most challenging for most methods, followed by linear molecules and then non-linear species. The precise ranking of functionals shifts only slightly depending on whether atoms, linear molecules or non-linear systems are being studied. A few functionals like BMK and M06-2X exhibit somewhat larger variation in performance on account of catastrophic failure for a few systems (diatomics for the former and atoms for the latter). The overall relative performance of functionals (especially within a given rung) however appear to be independent of the size/geometry of systems. The best functionals consistently yield excellent results for both atoms and molecules, while the worst performers continue to generate poor results.

| Method | RMSRE | | MRE | | MAX | |
|--------|-------|------|-------|-------|------|------|
| | CVQZ | CVTZ | CVQZ | CVTZ | CVQZ | CVTZ |
| CCSD(T) | 0.46 | 1.33 | 0.16 | -0.12 | 2.54 | 9.14 |
| CCSD | 0.44 | 1.19 | 0.21 | -0.02 | 2.08 | 8.05 |
| RMP2 | 0.43 | 1.42 | 0.05 | -0.37 | 2.76 | 9.55 |
| HF | 0.19 | 1.04 | -0.03 | -0.60 | 1.43 | 6.86 |

**Table 4** Percentage differences between the CBS estimate and aug-cc-pCV(Q/T)Z $\alpha_{ii}$ for WFT methods. RHF has essentially same basis set convergence as HF, while MP2 basis-set convergence rate is unreasonably slow due to N-representability violations. A full table with all deviations is supplied in the Supporting Information.

## 3.4 Basis Set Convergence

HF polarizabilities converge somewhat slowly (relative to behavior seen for dipole moments) on increasing basis set size. The RMS deviation between aug-cc-pCV5Z and aug-cc-pCVQZ numbers is 0.2%, while the equivalent deviation between aug-cc-pCV5Z and aug-cc-pCVTZ is 1 %. This indicates that the aug-cc-pCV5Z are likely essentially at the CBS limit, but the aug-cc-pCVTZ numbers are not an optimal replacement. No detailed investigation of basis set convergence of DFT polarizabilities were carried out, but it is not unreasonable to expect behavior similar to HF for all but a few ill behaved functionals that are notorious for slow basis set convergence[13,14]. This would indicate that quadruple zeta basis numbers might be sufficiently close to CBS for practical purposes, but triple zeta basis numbers are likely insufficiently converged.

Correlated WFT estimates for polarizability converge more slowly with increasing basis set size, but does so in a relatively well described manner given by Eqn 2. A comparison between the CBS estimate and aug-cc-pCVTZ/aug-cc-pCVQZ numbers (as given in Table 4) reveal that neither finite basis is an acceptable estimate, and extrapolation almost essential to have benchmark quality numbers. This further indicates that the triple zeta CCSD(T) estimates in Ref [29] would benefit from some refine-

ment (which ought to also incorporate a more complete description of excitations out of the core).

## 4 Conclusion

In summary, we find that it is possible to get quite accurate static polarizability estimates for small and medium sized species from several DFAs, although most seem to systematically overestimate the values on account of self-interaction error. The best performing functionals are double hybrids, with RMSRE in the range of 2.5-3.8%–placing them within striking distance of CCSD (which has 1.61% RMSRE). A few (XYGJ-OS and XYG3 in particular) are essentially as good as CCSD for non spin-polarized (NSP) species, but their overall performance is worsened on account of being constrained to a restricted reference for even spin-polarized (SP) systems, in order avoid N-representability breakdowns. Double hybrid functionals employing an orbital optimized MP2 like formalism[110] therefore could lead to significant further improvement in prediction of polarizability (and other molecular properties), as such N-representability violations would not be a concern.

Hybrid functionals also give quite decent performance, with several yielding RMSREs between 4-5%. Truly exceptional performance however is obtained from the mBEEF and MVS mGGAs, which give hybrid functional level performance at a much lower computational cost. This suggests that these functionals are able to minimize some aspect of self-interaction error, and indicate they may yield better excited state predictions than what might typically be expected of local functionals. Other mGGAs like SCAN and M06-L also give satisfactory performance, indicating that there is no large difference in performance between Rungs 3 and 4 of Jacob's ladder. It would be interesting to see if similar features transfer over to long carbon chains where large fractions of exact exchange have long been held to be essential for decent polarizability predictions[34,109] but that is beyond the scope of our present study due to difficulty in getting CBS quality benchmark reference data. There is however a fairly large gap between Rungs 2 and 3, on account of GGAs performing considerably worse than mGGAs. We therefore recommend that only functionals from Rung 3 or higher be used for calculations where polarizabilities matter.

Several of the best performing functionals within each rung (N12[66], mBEEF, SCAN0, XYGJ-OS etc.) are quite recent, indicating that some measure of progress has been made in improving polarizability predictions over time (which also indirectly suggests an improvement in functional transferability and treatment of excited states). Several of the worst performers like SOGGA11, MN11-L and MN12-SX however are also recent, indicating an inconsistent improvement over time. This is in no small part due to catastrophic failures for a few species, which indicates a lack of transferability of the functional, perhaps as a consequence of overfitting.

It is also quite interesting that the large performance gap between GGAs and mGGAs does not carry over to hGGAs and hmGGAs, which give essentially similar performance. It is possible that exact-exchange and kinetic energy density correct similar aspects in polarizability predictions, and their combination can do little

better. However the hmGGA functional space[83] is vast, and the emphasis till date has been to improve zero-field energetics alone. This has led to functionals like $\omega$B97M-V[15], that are highly accurate for zero-field energetics[4], but somewhat lacking with regards to prediction of properties like dipole moments[13] and polarizabilities. It may therefore be possible to employ information about molecular properties to assist exploration of a larger section of functional space in order to develop hmGGAs that are simultaneously accurate for zero-field energies and properties.

We hope therefore hope that our dataset of CCSD(T)/CBS benchmark static polarizabilities will assist in development and/or testing of future functionals that predict better energy and density responses to external electric fields, and also provide a better description of dipole allowed excited states. This would ideally assist in developing more transferable functionals that would be better approximations to the exact one. Such functionals would also likely prove useful for studies that go beyond isolated systems in gas phase–such as in simulations of spectroscopy or condensed phase processes. A comparison between the supplied DFT polarizibilities and ones calculated from TDDFT could also prove useful in examining the validity of the adiabatic approximation employed in the latter, which ought to prove useful in improving DFT excited state predictions in general.

## Conflicts of Interest

There are no conflicts of interest to declare.

## Supporting Information

Geometries, benchmark polarizabilities and table of errors.

## Acknowledgement

## References

1  W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133.

2  A. D. Becke, *J. Chem. Phys.*, 2014, **140**, 18A301.

3  R. O. Jones, *Rev. Mod. Phys.*, 2015, **87**, 897.

4  N. Mardirossian and M. Head-Gordon, *Mol. Phys.*, 2017, **115**, 2315–2372.

5  P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.

6  P. A. Dirac, Proc. R. Soc. A, 1931, pp. 60–72.

7  J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

8  J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.

9  A. D. Becke, *J. Chem. Phys.*, 1997, **107**, 8554–8560.

10  Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

11  M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew and K. A. Lyssenko, *Science*, 2017, **355**, 49–52.

12  K. R. Brorsen, Y. Yang, M. V. Pak and S. Hammes-Schiffer, *J. Phys. Chem. Lett.*, 2017, **8**, 2076–2081.

13 D. Hait and M. Head-Gordon, *J. Chem. Theory Comput.*, 2018, **14**, 1969–1981.

14 N. Mardirossian and M. Head-Gordon, *J. Chem. Theory Comput.*, 2013, **9**, 4453–4461.

15 N. Mardirossian and M. Head-Gordon, *J. Chem. Phys.*, 2016, **144**, 214110.

16 J. Sun, A. Ruzsinszky and J. P. Perdew, *Phys. Rev. Lett.*, 2015, **115**, 036402.

17 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.

18 F. Jensen, *Introduction to computational chemistry*, John wiley & sons, 2017.

19 E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997.

20 A. Dreuw and M. Head-Gordon, *Chem. Rev.*, 2005, **105**, 4009–4037.

21 A. L. Hickey and C. N. Rowley, *J. Phys. Chem. A*, 2014, **118**, 3678–3687.

22 S. Maekawa and K. Moorthi, *J. Chem. Eng. Data*, 2014, **59**, 3160–3166.

23 U. Hohm, *J. Mol. Struct.*, 2013, **1054**, 282–292.

24 A. J. Thakkar and T. Wu, *J. Chem. Phys.*, 2015, **143**, 144302.

25 P. Sałek, T. Helgaker, O. Vahtras, H. Ågren, D. Jonsson and J. Gauss, *Mol. Phys.*, 2005, **103**, 439–450.

26 J. R. Hammond, N. Govind, K. Kowalski, J. Autschbach and S. S. Xantheas, *J. Chem. Phys.*, 2009, **131**, 214103.

27 A. S. Karne, N. Vaval, S. Pal, J. M. Vásquez-Pérez, A. M. Köster and P. Calaminici, *Chem. Phys. Lett.*, 2015, **635**, 168–173.

28 H.-S. Hu, Y.-F. Zhao, J. R. Hammond, E. J. Bylaska, E. Aprà, H. J. van Dam, J. Li, N. Govind and K. Kowalski, *Chem. Phys. Lett.*, 2016, **644**, 235–242.

29 T. Wu, Y. N. Kalugina and A. J. Thakkar, *Chem. Phys. Lett.*, 2015, **635**, 257–261.

30 C. Puzzarini, *Theor. Chem. Acc.*, 2008, **121**, 1–10.

31 L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi and S. Grimme, *Phys. Chem. Chem. Phys.*, 2017, **19**, 32184–32215.

32 N. Q. Su, Z. Zhu and X. Xu, *Proc. Natl. Acad. Sci. U.S.A.*, 2018, 201713047.

33 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479–483.

34 B. Champagne, E. A. Perpète, S. J. van Gisbergen, E.-J. Baerends, J. G. Snijders, C. Soubra-Ghaoui, K. A. Robins and B. Kirtman, *J. Chem. Phys.*, 1998, **109**, 10489–10498.

35 B. Kirtman, V. Lacivita, R. Dovesi and H. Reis, *J. Chem. Phys.*, 2011, **135**, 154101.

36 Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kús, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock III, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio Jr., H. Dop, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, P. A. Pieniazek, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, N. Sergueev, S. M. Sharada, S. Sharmaa, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, V. Vanovschi, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhou, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard III, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer III, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xua, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Mol. Phys.*, 2015, **113**, 184–215.

37 R. D. Johnson III, *http://cccbdb.nist.gov/*, 2015.

38 H. Takeo, M. Sugie and C. Matsumura, *J. Mol. Spectrosc.*, 1993, **158**, 201–207.

39 Y. Kawashima, H. Takeo, M. Sugie, C. Matsumura and E. Hirota, *J. Chem. Phys.*, 1993, **99**, 820–826.

40 P. R. Tentscher and J. S. Arey, *J. Chem. Theory Comput.*, 2013, **9**, 1568–1579.

41 T. H. Dunning Jr, *J. Chem. Phys.*, 1989, **90**, 1007–1023.

42 D. E. Woon and T. H. Dunning Jr, *J. Chem. Phys.*, 1995, **103**, 4572–4585.

43 K. A. Peterson and T. H. Dunning Jr, *J. Chem. Phys.*, 2002, **117**, 10548–10560.

44 B. P. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning and A. K. Wilson, *Theor. Chem. Acc.*, 2011, **128**, 69–82.

45 F. Jensen, *J. Chem. Phys.*, 2001, **115**, 9113–9125.

46 F. Jensen, *J. Chem. Phys.*, 2002, **116**, 7372–7379.

47 F. Jensen, *J. Chem. Phys.*, 2002, **117**, 9234–9240.

48 F. Jensen and T. Helgaker, *J. Chem. Phys.*, 2004, **121**, 3463–3470.

49 F. Jensen, *J. Phys. Chem. A*, 2007, **111**, 11198–11204.

50 O. A. Vydrov and T. Van Voorhis, *J. Chem. Phys.*, 2010, **133**, 244103.

51 P. M. Gill, B. G. Johnson and J. A. Pople, *Chem. Phys. Lett.*, 1993, **209**, 506–512.

52 W. Kurlancheek and M. Head-Gordon, *Mol. Phys.*, 2009, **107**, 1223–1232.

53 A. Halkier, W. Klopper, T. Helgaker and P. Jørgensen, *J. Chem. Phys.*, 1999, **111**, 4424–4430.

54 I. Y. Zhang, X. Xu, Y. Jung and W. A. Goddard, *Proc. Natl. Acad. Sci. U.S.A.*, 2011, **108**, 19896–19900.

55 M. Feyereisen, G. Fitzgerald and A. Komornicki, *Chem. Phys. Lett.*, 1993, **208**, 359–363.

56 F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143–152.

57 F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 2002, **116**, 3175–3183.

58 A. J. Cohen, P. Mori-Sánchez and W. Yang, *J. Chem. Phys.*, 2007, **126**, 191109.

59 P. J. Wilson, T. J. Bradley and D. J. Tozer, *J. Chem. Phys.*, 2001, **115**, 9233–9242.

60 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51–57.

61 M. A. Rohrdanz and J. M. Herbert, *J. Chem. Phys.*, 2008, **129**, 034107.

62 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.

63 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

64 J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.

65 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

66 R. Peverati and D. G. Truhlar, *J. Chem. Theory Comput.*, 2012, **8**, 2310–2319.

67 K. Hui and J.-D. Chai, *J. Chem. Phys.*, 2016, **144**, 044114.

68 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.

69 Y.-S. Lin, C.-W. Tsai, G.-D. Li and J.-D. Chai, *J. Chem. Phys.*, 2012, **136**, 154109.

70 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 5656–5667.

71 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.

72 J. Sun, R. Haunschild, B. Xiao, I. W. Bulik, G. E. Scuseria and J. P. Perdew, *J. Chem. Phys.*, 2013, **138**, 044113.

73 R. Peverati, Y. Zhao and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2011, **2**, 1991–1997.

74 S. Y. Haoyu, X. He, S. L. Li and D. G. Truhlar, *Chem. Sci.*, 2016, **7**, 5032–5051.

75 J. Sun, J. P. Perdew and A. Ruzsinszky, *Proc. Natl. Acad. Sci. U.S.A.*, 2015, **112**, 685–689.

76 J. Wellendorff, K. T. Lundgaard, K. W. Jacobsen and T. Bligaard, *J. Chem. Phys.*, 2014, **140**, 144107.

77 V. N. Staroverov, G. E. Scuseria, J. Tao and J. P. Perdew, *J. Chem. Phys.*, 2003, **119**, 12129–12137.

78 Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101.

79 R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2011, **2**, 2810–2817.

80 Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Phys.*, 2005, **123**, 161103.

81 Y. Wang, X. Jin, S. Y. Haoyu, D. G. Truhlar and X. He, *Proc. Natl. Acad. Sci. U.S.A.*, 2017, **114**, 8487–8492.

82 A. D. Boese and J. M. Martin, *J. Chem. Phys.*, 2004, **121**, 3405–3416.

83 N. Mardirossian and M. Head-Gordon, *J. Chem. Phys.*, 2015, **142**, 074111.

84 R. Peverati and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16187–16191.

85 H. S. Yu, X. He and D. G. Truhlar, *J. Chem. Theory Comput.*, 2016, **12**, 1280–1293.

86 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2006, **110**, 13126–13130.

87 A. D. Boese and N. C. Handy, *J. Chem. Phys.*, 2002, **116**, 9559–9569.

88 R. Peverati and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2012, **14**, 13171–13174.

89 R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2011, **3**, 117–124.

90 Y. Zhang, X. Xu and W. A. Goddard, *Proc. Natl. Acad. Sci. U.S.A.*, 2009, **106**, 4963–4968.

91 S. Kozuch and J. M. Martin, *J. Comput. Chem.*, 2013, **34**, 2327–2344.

92 A. Karton, A. Tarnopolsky, J.-F. Lamére, G. C. Schatz and J. M. Martin, *J. Phys. Chem. A*, 2008, **112**, 12868–12886.

93 M. A. Rohrdanz, K. M. Martins and J. M. Herbert, *J. Chem. Phys.*, 2009, **130**, 054112.

94 J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2009, **131**, 174105.

95 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

96 S. Grimme, *J. Chem. Phys.*, 2006, **124**, 034108.

97 A. V. Krukau, O. A. Vydrov, A. F. Izmaylov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106.

98 N. Mardirossian and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9904–9924.

99 L. Goerigk and S. Grimme, *J. Chem. Theory Comput.*, 2010, **7**, 291–309.

100 R. Peverati and D. G. Truhlar, *J. Chem. Phys.*, 2011, **135**, 191102.

101 C. Adamo and V. Barone, *The Journal of chemical physics*, 1998, **108**, 664–675.

102 B. J. Lynch, P. L. Fast, M. Harris and D. G. Truhlar, *The Journal of Physical Chemistry A*, 2000, **104**, 4811–4815.

103 T. Ziegler, A. Rauk and E. J. Baerends, *Theor. Chem. Acc.*, 1977, **43**, 261–271.

104 D. Hait, T. Zhu, D. P. McMahon and T. Van Voorhis, *J. Chem. Theory Comput.*, 2016, **12**, 3353–3359.

105 D. Hait and M. Head-Gordon, *J. Chem. Phys.*, 2018, **148**, 171102.

106 R. C. Lochan and M. Head-Gordon, *J. Chem. Phys.*, 2007, **126**, 164101.

107 F. Neese, T. Schwabe, S. Kossmann, B. Schirmer and S. Grimme, *J. Chem. Theory Comput.*, 2009, **5**, 3060–3073.

108 Y. A. Bernard, Y. Shao and A. I. Krylov, *J. Chem. Phys.*, 2012, **136**, 204103.

109 M. B. Oviedo, N. V. Ilawe and B. M. Wong, *J. Chem. Theory*

*Comput.*, 2016, **12**, 3593–3602.

110 R. Peverati and M. Head-Gordon, *J. Chem. Phys.*, 2013, **139**, 024110.