Canonical and DLPNO-based composite wavefunction methods parametrized against large and chemically diverse training sets. 2. Correlation consistent basis sets, core-valence correlation, and F12 alternatives

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Abstract

A hierarchy of wavefunction composite methods (cWFT), based on G4– type cWFT methods available for elements H through Rn, was recently reported by Semidalas and Martin [J. Chem. Theor. Comput. 2020, 16, 4238]. We extend this hierarchy by considering the inner-shell correlation energy in the second-order Møller-Plesset correction and replacing the Weigend-Ahlrichs def2-mZVPP(D) basis sets used in the aforementioned paper with complete basis set extrapolation from augmented correlation consistent core-valence triple-zeta, aug-cc-pwCVTZ(-PP), and quadruple-zeta, aug-cc-pwCVQZ(-PP), basis sets, thus creating cc-G4– type methods. For the large and chemically diverse GMTKN55 benchmark suite, they represent a substantial further improvement and bring WTMAD2 (weighted mean absolute deviation) down below 1 kcal/mol. Intriguingly, the lion’s share of the improvement comes from better capture of valence correlation; the inclusion of core-valence correlation is almost an order of magnitude less important. These robust correlation consistent cWFT methods approach the
CCSD(T) complete basis limit with just one or a few fitted parameters. Particularly the DLPNO variants such as cc-G4-T-DLPNO are applicable to fairly large molecules at modest computational cost, as is (for a reduced range of elements) a different variant using MP2-F12/cc-pVTZ-F12 for the MP2 component.
Introduction

Composite wavefunction theoretical (cWFT) methods continue to be a mainstay for reaching kcal/mol level “chemical accuracy” for reaction energies. Some of the well-established approaches include the Gaussian-n (Gn)\textsuperscript{1–7}, CBS-QB3\textsuperscript{5,9}, multi-coefficient correlation methods (MCCM)\textsuperscript{10–12}, and, in sub-kcal/mol accuracy regimes, the correlation consistent composite approach (ccCA),\textsuperscript{13–15} the Weizmann-n variants,\textsuperscript{16–23} the HEAT-n methods,\textsuperscript{24–26} and the Feller-Peterson-Dixon (FPD)\textsuperscript{27–29} approach. All of these share a canonical coupled-cluster CCSD(T)\textsuperscript{30,31} component. One step towards the pursuit of accurate low-cost cWFTs was a recent DLPNO-CCSD(T) based method (DLPNO-ccCA)\textsuperscript{32} suitable for the elements of the first and second rows of the PTE; it was parametrized to the small G2/97 training set\textsuperscript{33,34} of 148 small closed-shell species, the largest organic molecule in it being benzene.

Double-hybrid density functional theory methods\textsuperscript{35} (see refs.\textsuperscript{36–39} for reviews), which both are fairly low-cost and naturally allow for analytical derivatives, have recently begun to approach the accuracy of cWFT methods, with WTMAD2 (weighted mean absolute deviations) over the large and chemically diverse GMTKN55 test suite (general main-group thermochemistry, kinetics, and noncovalent interactions, with 55 problem sets\textsuperscript{40}) bottoming out just above 2 kcal/mol.\textsuperscript{39,41}

Some issues with the widely used cWFT methods (G4, G4(MP2), or CBS-QB3) are that they were trained/parametrized on comparatively small datasets (all rooted in small-molecule thermochemistry), and entail empirical “high-level corrections” for basis set incompleteness with many parameters. (A separate issue consists of their restricted applicability to the first 2-3 rows of the Periodic Table owing to basis set limitations. One attempt to remedy the latter issue has been the G4(MP2)-XK method\textsuperscript{42} by Chan, Karton, and Raghavachari (CKR), which covers the spd blocks of H–Rn by means of Weigend-Ahlrichs/Karlsruhe/def2 type basis sets.\textsuperscript{43})

As always with empirical parameters, their transferability to chemical systems other than those in the original training set is an open question. Like in our research on empirical double hybrids, we strive for “minimal empiricism”, i.e., we seek to retain as few adjustable parameters as possible without unduly compromising performance, and obtain those from large and chemically diverse training sets.
When we applied G4(MP2)-XK to the larger and more chemically diverse GMTKN55 benchmark suite (with almost 2,500 unique calculations on systems as large as 81 atoms), we were astonished to find\textsuperscript{44} WTMAD2 values inferior to the best available double-hybrid DFT functionals. Hence we set out on a systematic search for a hierarchy of minimally empirical G4– type cWFT methods using def2 basis sets. Among the best performers lowest statistical errors for the GMTKN55 database were the newly developed\textsuperscript{44} G4-T and G4-T-DLPNO methods, with just three empirical parameters each, and for which WTMAD2 values are just 1.51 and 1.66 kcal/mol, respectively. Particularly G4-T-DLPNO is an economical option.

In these papers, inner-shell correlation was generally excluded, as the def2 basis sets are not designed for core-core and core-valence correlation.\textsuperscript{[Basis set convergence for core-core (CC) and core-valence (CV) correlation contributions to atomization energies was recently studied in great detail in ref. 45]} The importance of inner-shell correlation will not be homogenous across the GMTKN55 test suite; while it is well known (see, e.g., ref. \textsuperscript{46}) that small-molecule atomization energies have contributions of several kcal/mol from inner-shell correlation, their contribution to noncovalent interactions between 1\textsuperscript{st} and 2\textsuperscript{nd}-row compounds will generally be very small\textsuperscript{47} owing to the long-distance nature of dispersion and the fairly short-range nature of CV correlation. (Correlation from the (n-1)d subvalence shells of Br and I is rather more important in halogen bonding.\textsuperscript{48}) For conformer equilibria and large-molecule isomerization reactions, one can expect a large degree of CC and CV cancelation between reactants and products. However, at least in principle, the inclusion of CV correlation should improve overall GMTKN55 performance.

Now doing so would require switching to a different family of basis sets that have the required radial and angular flexibility in the core-valence (high-exponent) region, such as the cc-pwCVnZ (correlation consistent, core-valence weighted, n-tuple zeta basis sets) of Peterson and Dunning.\textsuperscript{49} But such basis sets would likely have a different convergence behavior for the valence contribution as well, and hence require reparametrization. (In fact, there is evidence\textsuperscript{21} that additional radial flexibility such as offered by core-valence basis sets benefits valence properties as well.)

In this paper, we will present a hierarchy of cc-G4 and cc-G4-DLPNO type approaches. Core-valence correlation will only be considered at the MP2 level. We will show that we can actually reduce WTMAD2 below the 1 kcal/mol threshold. Somewhat surprisingly, we find that this improvement in accuracy is due much less to core-valence correlation itself than to basis set expansion. The correlation consistent methods deliver an attractive compromise
between accuracy and computational cost for systems dominated by dynamic correlation. (For systems with severe static correlation,\textsuperscript{50} CCSD(T) is inadequate anyhow and one needs to resort to approaches such as W4,\textsuperscript{51,52} W4-F12,\textsuperscript{21} HEAT-III,\textsuperscript{26,53} or FPD.\textsuperscript{27-29}
Computational Details

Valence-only CCSD(T) calculations\textsuperscript{30,31} were performed utilizing Gaussian 16, revision C.01;\textsuperscript{54} MP3 and RI-MP2\textsuperscript{55,56} calculations were performed utilizing Q-CHEM 5.2\textsuperscript{57}; the DLPNO-MP2\textsuperscript{58}, DLPNO-CCSD(T)\textsuperscript{59}, and DLPNO-CCSD(T)\textsuperscript{60} energies were obtained from ORCA 4.2.1.\textsuperscript{61} Most RI-MP2-F12 calculations likewise relied on ORCA, but for technical reasons we employed MOLPRO\textsuperscript{62} version 2019.2 for the heavy p-block systems.

All calculations were performed on the ChemFarm HPC cluster of the Faculty of Chemistry at the Weizmann Institute. The 4TB SSD (solid-state disk) arrays on its “heavyio” nodes benefited the canonical MP3 and CCSD(T) calculations, even though they were insufficient for a few of the largest MP3/def2-TZVPP jobs; for those, we turned to a 40TB shared-over-InfiniBand storage server custom-developed for us by Access Technologies of Ness Ziona, Israel.

The following basis sets were employed in the all-electron MP2 calculations. For the light atoms H and He, those were the correlation consistent aug-cc-pV\textit{m}Z\textsuperscript{63,64} along with the corresponding RI auxiliary basis sets.\textsuperscript{65} For the second-row (Li–Ne) and third-row (Na–Ar) atoms, we utilized the weighted core-valence basis sets aug-cc-pwCV\textit{m}Z\textsuperscript{49,63,64} along with the corresponding auxiliary RI ones.\textsuperscript{66,67} The atoms K and Ca were also treated with aug-cc-pwCV\textit{m}Z, but for molecules containing K or Ca, the RI approximation was not considered for want of corresponding auxiliary basis sets. For the heavier elements, Ga-Kr, In-Xe, and Tl-Rn, we resorted to the aug-cc-pwCV\textit{m}Z-PP\textsuperscript{68} associated with small-core multiconfiguration-Dirac-Hartree-Fock (MCDHF) relativistic pseudopotentials\textsuperscript{69,70} (PP stands for the pseudopotential approximation). As auxiliary basis sets for the heavy p-block elements, we employed cc-pV\textit{m}Z-PP-F12/MP2FIT.\textsuperscript{71} The cardinal number \textit{m} refers to T or Q, and in this text, we shall denote the core valence basis sets used as aug-cc-pwCV\textit{m}Z(-PP).

For the valence-only CCSD(T), we applied the frozen-core approximation as in the G4-type methods along with the def2-SVSP (standard def2-SVP without the polarization functions on hydrogen), and def2-TZVP basis sets of the Weigend-Ahlrichs/Karlsruhe def2 family.\textsuperscript{43} Hence, we were able to repurpose the CCSD(T) total energies from our previous study.\textsuperscript{44} Similarly, we repurposed MP3/def2-TZVPP along with the def2 small-core energy-consistent relativistic pseudopotentials\textsuperscript{72} for elements heavier than Kr. The augmented def2- basis sets are available for the elements H–La and Hf–Rn; the non-augmented ones are additionally available for Ce–Lu. We retrieved the core-valence basis sets and their auxiliary variants from the Basis Set Exchange\textsuperscript{73} and the ccRepo basis set repository.\textsuperscript{74} We have provided all basis sets files used in this work in the Supporting Information.
The open-shell cases were treated with unrestricted HF orbitals (UHF), analogously to the reported G4–type approaches, CBS-QB3, and G4 methods. A few G4(MP2) variants make use of ROHF determinants, which could be appropriate for radicals prone to severe spin contamination. The dispersion model considered was that of Grimme et al. denoted as ‘D3(BJ)’. In our previous work on double-hybrid functional parametrization, we arrived at \( \{a_1 = s_8 = 0, a_2 = 5.5\} \) as reasonable compromise values for the damping function’s shape parameters; we retained these parameters in the present work, leaving the R\(^{-6}\) overall scaling parameter \( s_6 \) as the single fitted parameter.

For the DLPNO-CCSD(T) and DLPNO-CCSD(T\(_1\)) calculations, the details are the same as in our previous work. The “TightPNO” option was applied throughout and “chemical cores” were kept frozen as in ref., while, as with all “def2” basis sets, the deepest core electrons of elements heavier than Kr were modeled utilizing Stuttgart-Cologne relativistic energy-consistent pseudopotentials. The “VeryTight” keyword was selected for SCF convergence criteria; the RIJCOSX (chain-of-spheres-exchange) approximation for constructing the Fock matrices was applied, both with the default integration grid GRIDXS2 and with the most stringent option GRIDX9. We employed the def2-SVPD, def2-TZVPP, and def2-QZVPP basis sets along with the auxiliary versions of def2/J, see ref., and def2-SVP/C, def2-TZVPP/C, and def2-QZVPP/C, see ref., as stored in ORCA’s internal basis set library. For the subsets AHB21, G21EA, IL16, RG18, and WATER27, we similarly applied the diffuse-function augmented def2-TZVPPD and def2-QZVPPD, inspired by ref. For the avoidance of doubt, in the DLPNO-CCSD(T)-based or DLPNO-CCSD(T\(_1\))-based cWFTs discussed here, the \( E_{\text{CCSD-MP2}} \) term is calculated by subtracting the DLPNO-MP2 energy from separate single-point calculations in the same basis set, and not from the “semi-local (SL) MP2” energy reported at the post-SCF stage of a DLPNO-CCSD(T) or DLPNO-CCSD(T\(_1\)) run.

For the explicitly correlated RI-MP2-F12 calculations, the computational details largely follow those in Ref. . We consider here the cc-pVTZ-F12 and cc-pVQZ-F12 basis sets along with the corresponding auxiliary basis sets aug-cc-pV\(_n\)Z/JK, cc-pV\(_n\)Z-F12-MP2-FIT, and cc-pV\(_n\)Z-F12-OPTRI (\( n = T \) or Q for cc-pVTZ-F12 or cc-pVQZ-F12, respectively), as implemented in ORCA. For molecules involving heavy p-block elements (e.g. halogen-bonded species involving bromine and iodine), the subvalence \((n-1)d\) shell has been correlated, analogous to Ref. For these elements, we employed the cc-pVQZ-PP-F12 basis set along with the various auxiliary basis sets set from the same reference, as stored in the internal basis set library of MOLPRO 2019.2. The fixed amplitude ansatz is considered throughout and the geminal exponent \((\beta)\) was set equal to 1.0 as recommended in Ref. for the RI-MP2-F12 calculations.
The primary standard for training the presented cWFT methods was the GMTKN55 benchmark; as in Ref. for the minimally empirical double hybrids, and in our previous paper on G4-T type methods, the reference data, geometries, and charge/multiplicity information were extracted from the ACCDB database of Morgante and Peverati and reused verbatim (without geometry optimization). See Ref. for details of all the reference data, which were either CCSD(T)/CBS (i.e., extrapolation to the complete basis set limit) or higher level, many taken from previous benchmark studies in our group. These reference data are in the hypothetical motionless state without ZPE and thermal corrections. The most computationally demanding subsets C60ISO (isomerization energies of fullerene C60 molecules) and UPU23 (relative energies of uracil dinucleotides) were currently not within reach for MP3/def2-TZVPP and canonical CCSD(T)/def2-TZVP. As these subsets have comparatively small weights in the WTMAD2 formula, their omission does not have a significant effect on WTMAD2, as has been explained at some length in ref. 

The calculation of the reaction energies from total energies and a reference data file, as well as the evaluation of WTMAD2 and associated statistics, was performed using a Fortran program developed in-house, which is available upon request.

For the optimization of parameters, we employed the BOBYQA (Bound Optimization BY Quadratic Approximation) gradient-free deterministic optimizer to optimize the energy coefficients. Numerous initial guesses were evaluated, and re-optimizations ensured that a global minimum was indeed reached.

The performance of the presented cWFT methods for the GMTKN55 database was quantified utilizing the Weighted Mean Absolute Deviation, type 2 (abbreviated WTMAD2), as defined in Eq.2 of the GMTKN55 paper. The WTMAD2 is a function of the sizes and energy ranges of each subset,

\[ WTMAD2 = \frac{\sum_{i}^{55} \frac{56.84 \text{ kcal/mol} \cdot N_i \cdot \text{MAD}_i}{|\Delta E_i|}}{\sum_{i}^{55} N_i} \]  

(1)

Where \( N_i \) is the number of systems of subset i, MAD\(_i\) is its mean absolute deviation from the reference values, and the average absolute reference reaction energy \(|\Delta E_i|\) ensures that errors are weighted proportionally to their importance on the varying energy scales of the different subsets.

As typically implemented, WTMAD2 is based on MAD, a more ‘robust’ accuracy measure relative to the root-mean-square deviation (RMSD) measure, and more suitable for the GMTKN55 database. Besides, WTMAD2 was the key metric in developing the double-hybrid DFT and G4– type cWFT methods.
Description and nomenclature of correlation consistent cc-G4– type methods

The standard G4– type methods share similar energy expressions with the correlation consistent cc-G4– type ones: post-MP2 terms, particularly valence CCSD(T), are evaluated with the same def2 basis sets (in part to permit recycling the most CPU-intensive parts of the calculation from the previous work). This leaves the extrapolated Hartree–Fock reference and \( E_2 \) correlation energies as the key differences; both of them are calculated using the aug-cc-pwCV\{T,Q\}Z(-PP) basis sets.

The two-tier methods are based on the extrapolated Hartree–Fock energy, the post-HF second-order MP correction, and a CCSD(T)–MP2 component in a smaller basis set. For instance, the highly accurate G4-T method from Ref.\(^4\)\(^4\) has the following energy expression:

\[
E = E_{\text{HF/def2}} - \left[ (c_1 + 1)E_{\text{corr,MP2/def2-QZVPPD}} - c_1E_{\text{corr,MP2/def2-TZVPPD}} \right] + c_2(E_{\text{CCSD/def2-TZVP}} - E_{\text{corr,MP2/def2-TZVP}}) + c_3E_{\text{C,(T)/def2-TZVP}}
\]  

(2)

where \( E_{\text{corr,MP2}} \) is the total second-order MP energy, \( E_{\text{CCSD}} \) is the coupled-cluster singles and doubles valence correlation energy, and \( E_{\text{C,(T)}} \) is the quasiperturbative coupled-cluster triples excitation term. The extrapolated HF energy to the basis limit in the standard G4– type methods is given by:

\[
E_{\text{HF/CBS}} \equiv E_{\text{HF/def2}} = \frac{E_{\text{HF/def2-QZVPPD}} - E_{\text{HF/def2-TZVPPD}} \exp(-1.63)}{1-\exp(-1.63)}
\]  

(3)

The correlation consistent two-tier methods share amended versions of the energy expressions of their two-tier G4 cognates. For the top performer, cc-G4-T, both the HF/CBS and the \( E_2 \) correlation energy utilizing the Schwenke-type\(^9\)\(^6\),\(^9\)\(^7\) extrapolation, are obtained with the correlation consistent basis sets (aug-cc-pwCV\(m\)Z(-PP)):

\[
E = E_{\text{HF/aug-cc-pwCV}} + \left[ (c_1 + 1)E_{\text{corr,MP2/aug-cc-pwCQZ(-PP)}} - c_1E_{\text{corr,MP2/aug-cc-pwCVTZ(-PP)}} \right] + c_2(E_{\text{CCSD/def2-TZVP}} - E_{\text{corr,MP2/def2-TZVP}}) + c_3E_{\text{C,(T)/def2-TZVP}}
\]  

(4)

The extrapolated HF/aug-cc-pwCV\{T,Q\}Z(-PP) energy expression for all correlation consistent cc-G4– type methods has the form:

\[
E_{\text{HF/CBS}} \equiv E_{\text{HF/aug-cc-pwCV(T,Q)Z(-PP)}} = \frac{E_{\text{HF/aug-cc-pwCQZ(-PP)}} - E_{\text{HF/aug-cc-pwCVTZ(-PP)}} \exp(-1.63)}{1-\exp(-1.63)}
\]  

(5)

We also considered the inexpensive cc-G4(MP2)-XK– type methods, which have energy expressions similar to those of CKR; howbeit, with an HF extrapolation given by eq. 5, and the scaled \( E_2 \) components of same-spin, \( E_{\text{corr,MP2,SS}} \), and opposite-spin, \( E_{\text{corr,MP2,OS}} \), obtained
using the aug-cc-pwCV\textit{m}Z(-PP) basis sets. For instance, the energy expression of \textit{cc-G4(MP2)-XK-D} becomes:

\begin{equation}
E = E_{\text{HF/\text{aug-cc-pwCV}\{}T,Q\}\text{Z}(-\text{PP})} + [c_3E_{\text{corr,MP2,OS/\text{aug-cc-pwCVQZ}}(-\text{PP})} + c_4E_{\text{corr,MP2,SS/\text{aug-cc-pwCVQZ}}(-\text{PP})} + \\
(\text{c5}E_{\text{CCSD/def2-SVSP}} - c_1E_{\text{corr,MP2,OS/def2-SVSP}} - c_2E_{\text{corr,MP2,SS/def2-SVSP}}) + c_6E_{\text{C,(T)/def2-SVSP}}]
\end{equation}

(6)

We note that the coefficients of the \(E_{\text{corr,MP2,OS}}\) and \(E_{\text{corr,MP2,SS}}\) terms are adjustable parameters obtained together with the other parameters through minimization of WTMAD2 for the GMTKN55 database, and should not be misconstrued as identical to the original SCS-MP2.\cite{98,99}

For the three-tier basis set methods, we similarly follow the pattern of their G4(MP3)—type cognates from ref. \cite{44}, but substitute \(\text{HF/\text{aug-cc-pwCV}\{}T,Q\}\text{Z}(-\text{PP})\) and \(E_2/\text{aug-cc-pwCVQZ}(-\text{PP})\). Both valence-only MP3 and CCSD(T) energies are retained with the same basis sets as in ref. \cite{44}. Consequently, for G4(MP3)-D:

\begin{equation}
E = E_{\text{HF/\text{aug-cc-pwCV}\{}T,Q\}\text{Z}(-\text{PP})} + [c_3E_{\text{corr,MP2,OS/\text{aug-cc-pwCVQZ}}(-\text{PP})} + c_4E_{\text{corr,MP2,SS/\text{aug-cc-pwCVQZ}}(-\text{PP})} + \\
c_5E_{\text{[MP3-MP2]/def2-TZVPP}} + c_4E_{\text{[CCSD-MP3]/def2-SVSP}} + c_5E_{\text{C,(T)/def2-SVSP}} + c_6E_{\text{[D3(BJ)]}}]
\end{equation}

(7)

The five-parameter “high-level correction” (HLC), as defined in eq. 7 of ref. \cite{44} following CKR, was originally introduced in Ref.\cite{100} as a correction for residual basis set incompleteness. (In its original, simplest, two-parameter form introduced in ref. \cite{6} as part of G1 theory, the two parameter values were fixed from the exact total energies of the hydrogen atom and hydrogen molecule.\cite{6}) In the present work (see below), like in our previous study,\cite{44} we found that the addition of HLC did not significantly enhance statistics, especially not at any level that would justify the introduction of five additional parameters. (It indeed introduces discontinuities on bond-breaking surfaces, and might otherwise jeopardize transferability to other chemical systems.) Hence, none of our final recommended levels include an HLC term.

The naming of the correlation consistent cWFTs is analogous to the original one for the standard G4—type methods.\cite{44} The extrapolation of the total \(E_2\) or of the individual \(E_{2,\text{OS}}\) and \(E_{2,\text{SS}}\), all using aug-cc-pwCV\{T,Q\}Z(-PP), determines the method’s name. In the first case, combining the total \(E_2/\text{CBS}\) with CCSD(T) yields cc-G4-n (otherwise, cc-G4-DLPNO-n if DLPNO-CCSD(T) is included). Adding an MP3 step leads to the cc-G4(MP2.X)-n variant. If we similarly scale the same and opposite spin \(E_2\) terms, we will denote this cc-G4-scs-n or cc-G4(scsMP2.X)-n (if an MP3 step is added for the latter). \(n=D, T,\) or \(Q\) refer to the basis set used in the CCSD(T) step, i.e., def2-SVPD, def2-TZVPP, and def2-QZVPP, respectively.
Figure 1. Naming scheme of the correlation consistent G4– type methods.

Results and Discussion

The error statistics and the WTMAD2 component breakdown for selected methods (in kcal/mol) appear in Table 1. The respective abbreviations ‘Thermo’, ‘Barrier’, ‘Large’, ‘Confor’, and ‘Intermol’ refer to the five basic subdivisions of GMTKN55: basic thermochemistry, barrier heights, reactions of large molecules, conformer equilibria, and intermolecular interactions. The table is grouped into four blocks: presently obtained “correlation consistent” cWFT methods; cWFT from the literature; simple WFT; and the better-performing and most commonly used DFT methods.

| Methods | WTMAD2 | Thermo | Barrier | Large | Confor | Intermol |
|---------|--------|--------|--------|-------|--------|----------|
| cc-G4-T-v2 | 0.87 | 0.20 | 0.09 | 0.17 | 0.11 | 0.29 |
| Ditto frozen core | 0.94 | 0.21 | 0.10 | 0.19 | 0.12 | 0.32 |
| cc-G4-T | 0.90 | 0.19 | 0.11 | 0.17 | 0.12 | 0.30 |
| Ditto frozen core | 0.99 | 0.21 | 0.12 | 0.20 | 0.13 | 0.33 |
| cc-G4-Q-DLPNO | 1.00 | 0.17 | 0.08 | 0.17 | 0.31 | 0.27 |
| cc-G4-F12-T | 1.03 | 0.20 | 0.14 | 0.24 | 0.17 | 0.28 |
| cc-G4(MP2)-XK-T | 1.18 | 0.29 | 0.11 | 0.21 | 0.11 | 0.47 |
| cc-G4-T-DLPNO | 1.19 | 0.22 | 0.09 | 0.21 | 0.36 | 0.31 |
| cc-G4(MP2)-XK-D | 1.19 | 0.25 | 0.12 | 0.22 | 0.36 | 0.41 |
| cc-G4(D)-DLPNO | 1.21 | 0.27 | 0.14 | 0.24 | 0.17 | 0.28 |
| cc-G4(MP3)-D | 1.37 | 0.27 | 0.14 | 0.25 | 0.30 | 0.41 |
| cc-G4-D-DLPNO | 1.38 | 0.25 | 0.12 | 0.35 | 0.48 | 0.64 |
| cc-G4(MP2)-XK-D | 2.21 | 0.43 | 0.28 | 0.31 | 0.58 | 0.61 |
| cc-MP2X-Q | 2.89 | 0.57 | 0.70 | 0.62 | 0.60 | 0.40 |
| cc-MP2X-T | 3.09 | 0.60 | 0.64 | 0.63 | 0.61 | 0.61 |
| G4(MP2)-XK-T44 (e) | 1.42 | 0.39 | 0.16 | 0.18 | 0.13 | 0.56 |
| G4-T-v144 (e) | 1.46 | 0.31 | 0.16 | 0.22 | 0.16 | 0.61 |
| G4-T-v244(e) | 1.49 | 0.32 | 0.15 | 0.23 | 0.17 | 0.63 |
 Obtained from ref. 44.

All cWFT results without inner shell correlation.

WATER27) were obtained from refs. 39, 41, while the WFT (MP2, SCS-MP2, and HF) data in the same basis

D3(BJ) is abbreviated as D3 in this table; M06-2X was evaluated with a D3(0) correction, for want of D3BJ

parameters and the WTMAD2 value of M06-2X without D3(0) is identical. Tabulated data for the DFT

methods employing the def2-QZVPP basis set (def2-QZVPPD for subsets AHB21, G21EA, IL16, RG18, and

WATER27) were obtained from refs. 39, 41, while the WFT (MP2, SCS-MP2, and HF) data in the same basis

sets were obtained from ref. 44 as were all cWFT results without inner shell correlation.

(a) The results from the conventional G4, G4(MP2), CBS-QB3, and G4(MP2)-XK methods were obtained from ref. 44.

| Method                   | ωB97M(2) | ωB97M(2) | ωB97M(2) | ωB97M(2) | ωB97M(2) | ωB97M(2) |
|--------------------------|----------|----------|----------|----------|----------|----------|
| G4-Q-DLPNO              | 1.52     | 0.25     | 0.12     | 0.20     | 0.46     | 0.49     |
| G4-T-DLPNO              | 1.66     | 0.26     | 0.12     | 0.24     | 0.52     | 0.52     |
| G4(MP3)-D               | 1.65     | 0.37     | 0.17     | 0.28     | 0.30     | 0.55     |
| G4(MP3(KS))-D           | 1.96     | 0.41     | 0.28     | 0.26     | 0.45     | 0.56     |
| G4(MP2)-XK              | 2.56     | 0.46     | 0.29     | 0.34     | 0.68     | 0.79     |
| G4                     | 2.52     | 0.38     | 0.23     | 0.75     | 0.38     | 0.78     |
| G4(MP2)                 | 2.96     | 0.53     | 0.34     | 0.91     | 0.33     | 0.85     |
| CBS-QB3                 | 3.10     | 0.40     | 0.35     | 0.60     | 0.20     | 1.55     |
| MP2.X-Q                 | 3.29     | 0.71     | 0.78     | 0.88     | 0.42     | 0.50     |
| rev-G4MP2X              | 3.53     | 0.50     | 0.29     | 0.61     | 1.16     | 0.96     |
| G4(MP2)-XK              | 3.71     | 0.45     | 0.31     | 0.67     | 1.25     | 1.02     |
| MP2.X-T                 | 3.78     | 0.76     | 0.81     | 0.89     | 0.51     | 0.81     |
| SCS-MP2-D               | 5.22     | 1.23     | 0.95     | 1.39     | 0.91     | 0.75     |
| SCS-MP2                 | 5.35     | 0.94     | 1.01     | 1.15     | 1.02     | 1.23     |
| MP2-D                   | 5.83     | 1.21     | 1.21     | 1.66     | 0.87     | 0.87     |
| MP2-D                   | 5.54     | 1.20     | 1.18     | 1.52     | 0.80     | 0.84     |
| MP2                     | 6.91     | 1.21     | 1.23     | 1.78     | 1.47     | 1.21     |
| HF-D3                   | 13.08    | 5.05     | 2.65     | 2.06     | 1.85     | 1.48     |
| HF                      | 29.46    | 5.87     | 3.74     | 3.66     | 7.27     | 8.92     |

D3(BJ) is abbreviated as D3 in this table; M06-2X was evaluated with a D3(0) correction, for want of D3BJ
(b) D3(BJ) parameters obtained from Table S1 of ref. 107.
(c) \( \alpha_1 = 0, \alpha_2 = 5.5, s_6 = -0.345, s_8 = 0 \) from ref. 44.
(d) From ref. 44; D3(BJ) parameters from Table 2 of the original D3(BJ) paper. 77
(e) The WTMAD2 component breakdown is for 1320 reactions (+63 more than in our previous work). 44
Table 2. WTMAD2 (kcal/mol) and optimized parameters of selected standard and correlation consistent cWFT methods.

| MP2 | MP3 | CCSD(T) | N_{param} | Method                        | WTMAD2 | Energy components coefficients |
|-----|-----|---------|-----------|-------------------------------|--------|-------------------------------|
|     |     |         |           |                               | c_{(E2,os)} | c_{(E2,os)} | c_{E2,os} | c_{(E2,gs)} | c_{E2,gs} | c_{(E1,CSSD)} | C_{T}   | C_{Disp} | HLC |
| T   |     |         |           |                               | 3.71   | 1.131 | 0.512 | 1.041 | 0.704 | 1.048 | 0.526 | 0.526 | 0.526 | 0.526 | 0.526 |
| T   |     |         |           |                               | 3.53   | 1.307 | 0.385 | 1.170 | 0.614 | 0.984 | 0.736 | 0.736 | 0.736 | 0.736 | 0.736 |
| Q   |     |         |           |                               | 2.56   | 1.309 | 0.674 | 1.124 | 0.890 | 1.113 | 0.699 | -0.383 | -0.383 | -0.383 | -0.383 |
| Q   |     |         |           |                               | 2.73   | 1.482 | 0.271 | 1.320 | 0.457 | 1.052 | 0.778 | [0]   | [0]   | [0]   | [0]   |
| Q*  |     |         |           |                               | 2.21   | 1.379 | 0.414 | 1.187 | 0.617 | 1.094 | 0.854 | -0.358 | -0.358 | -0.358 | -0.358 |
| Q*  |     |         |           |                               | 2.25   | 1.307 | 0.510 | 1.118 | 0.751 | 1.103 | 0.726 | -0.418 | -0.418 | -0.418 | -0.418 |
| Q*  |     |         |           |                               | 2.46   | 1.392 | 0.220 | 1.239 | 0.384 | 1.061 | 0.713 | [0]   | [0]   | [0]   | [0]   |
| Q*  |     |         |           |                               | 2.52   | 1.441 | 0.147 | 1.284 | 0.327 | 1.050 | 0.756 | [0]   | [0]   | [0]   | [0]   |
| Q   | T   |         |           |                               | 1.42   | 1.624 | 0.811 | 1.526 | 0.833 | 1.070 | 0.959 | [0]   | [0]   | [0]   | [0]   |
| Q*  | T   |         |           |                               | 1.19   | 1.317 | 0.586 | 1.234 | 0.597 | 1.059 | 0.976 | [0]   | [0]   | [0]   | [0]   |
| Q*  | T   |         |           | Ditto (with MP2(FC))          | 1.24   | 1.442 | 0.438 | 1.345 | 0.453 | 1.059 | 0.995 | [0]   | [0]   | [0]   | [0]   |
|     |     |         |           |                               |        |       |       |       |       |       |       |       |       |       |       |       |
| Q   |     |         |           |                               | 2.68   | 1.226 | 0.977 | 1.111 | 0.776 | -0.456 | -      | -      | -      | -      | -      | -      |
| Q   |     |         |           |                               | 3.01   | 1.045 | 0.968 | 1.033 | 0.796 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| Q*  |     |         |           |                               | 2.35   | 1.123 | 0.979 | 1.078 | 0.951 | -0.487 | -      | -      | -      | -      | -      | -      |
| Q*  |     |         |           |                               | 2.77   | 0.954 | 0.968 | 0.998 | 0.947 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
|     |     |         |           |                               |        |       |       |       |       |       |       |       |       |       |       |       |
| (T,Q) |     |         |           |                               | 1.46   | 0.577 | 0.577 | 1.064 | 1.177 | -0.072 | -      | -      | -      | -      | -      | -      |
| (T,Q) |     |         |           |                               | 1.49   | 0.593 | 0.593 | 1.061 | 1.103 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 0.87   | 0.668 | 0.668 | 1.053 | 1.128 | -0.006 | -      | -      | -      | -      | -      | -      |
| (T,Q) |     |         |           |                               | 0.93   | 0.822 | 0.822 | 1.053 | 1.115 | 0.040  | -      | -      | -      | -      | -      | -      |
| (T,Q) |     |         |           |                               | 0.87   | 0.671 | 0.671 | 1.054 | 1.126 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 0.94   | 0.787 | 0.787 | 1.051 | 1.139 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 0.90   | 0.626 | 0.626 | 1.029 | 1.029 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 0.99   | 0.707 | 0.707 | 1.017 | 1.017 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 0.92   | 0.642 | 0.642 | 1.000 | 1.000 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 0.99   | 0.727 | 0.727 | 1.000 | 1.000 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 1.66   | 0.601 | 0.601 | 1.019 | 1.204 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 1.52   | 0.513 | 0.513 | 1.003 | 1.185 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 1.19   | 0.604 | 0.604 | 0.999 | 1.181 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           | (ditto with GRIDX9 in SCF)    | 1.14   | 0.617 | 0.617 | 1.001 | 1.175 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 1.21   | 0.708 | 0.708 | 0.999 | 1.193 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 1.00   | 0.554 | 0.554 | 0.998 | 1.156 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| (T,Q) |     |         |           |                               | 1.00   | 0.679 | 0.679 | 0.997 | 1.173 | [0]   | [0]   | [0]   | [0]   | [0]   | [0]   |
| a | b | c | d | e |
|---|---|---|---|---|
| Q | T | D | 6 | G4(MP3)-D-v1<sup>b</sup> | 1.65 | 1.284 | 1.018 | 1.089 | 1.119 | 0.411 | -0.185 | — |
| Q<sup>a</sup> | T | D | 6 | cc-G4(MP3)-D-v1 | 1.37 | 1.196 | 1.010 | 1.021 | 1.121 | 0.572 | -0.235 | — |
| Q | T | — | 4 | MP2-X-Q<sup>4</sup> | 3.28 | 1.117 | 1.036 | 0.824 | [0] | [0] | -0.062 | — |
| Q<sup>a</sup> | T | — | 4 | cc-MP2.X-Q | 2.89 | 0.879 | 1.133 | 0.689 | [0] | [0] | -0.052 | — |
| (T,Q) | T | D | 3 | G4(scsMP2.X)-D-v8<sup>b</sup> | 1.84 | 0.633 | 0.906 | 0.965 | 1.026 | 1.026 | [0] | — |
| (T,Q)<sup>a</sup> | T | D | 3 | cc-G4(scsMP2.X)-D-v8 | 1.44 | 1.617 | 0.412 | 0.926 | 1.003 | 1.003 | [0] | — |
| MP2-F12 | MP3 | CCSD(T) | | | | | | | | | | | |
| T | — | T | — | cc-G4-F12-T-v1 | 1.04 | 1.000 | 1.000 | 1.000 | [0] | — |
| Q | — | T | — | cc-G4-F12-T-v2 | 1.03 | 1.000 | 1.000 | 1.000 | [0] | — |
| T | — | T(DLPNO) | 1 | cc-G4-F12-T-DLPNO | 1.19 | 1.000 | 1.000 | 1.204 | [0] | — |

| G4<sup>a</sup>,<sup>b</sup> | 2.52 |
| G4MP2<sup>a</sup>,<sup>b</sup> | 2.96 |
| CBS-QB3<sup>a</sup>,<sup>b</sup> | 3.10 |

<sup>a</sup> aug-cc-pwCVmZ(-PP) for both HF/CBS and $E_2$ correlation energy.
<sup>b</sup> The results from the conventional G4,<sup>3</sup> G4(MP2)<sup>4</sup>, CBS-QB3<sup>8,9</sup>, G4(MP2)-XK<sup>42</sup>, and standard eWFT methods were obtained from ref. 44.
<sup>c</sup> The WTMAD2 component breakdown is for 1320 reactions (+63 more than in our previous work<sup>44</sup>).
Effects of basis set expansion and of CV correlation energy inclusion

The best approximations in Table 2 are cc-G4-T-v1 and cc-G4-T-v2, both with WTMAD2 of just 0.87 kcal/mol. cc-G4-T-v1 has four adjustable parameters, of which the fourth is the coefficient of the dispersion correction, being just –0.006. If we set it to zero instead (i.e. eliminate the dispersion correction), we obtain cc-G4-T-v2 with just three adjustable parameters (see Table S2 for the WTMAD2 contributions per subset).

This represents a substantial improvement over the WTMAD2 statistics of 1.46 and 1.49 kcal/mol, respectively, for G4-T-v1 and G4-T-v2 from ref. 44. Breakdown by the five top-level subdivisions of GMTKN55 (Table 1) reveals that all five of them benefit, least so the large-molecule reactions and most so the intermolecular interactions (for which the WTMAD2 component is cut in half, from 0.63 to 0.32 kcal/mol).

Particularly for intermolecular interactions, which are a long-range phenomenon where one would intuitively expect the impact of core-valence correlation to be negligible, rationalizing this improvement entirely in terms of core-valence correlation seems implausible. But in truth, we are making two major changes at once: basis sets and core-valence correlation. Disentangling these two requires carrying out an additional set of calculations in which the same frozen-core approximation as in G4-T-v2 is applied to cc-G4-T-v2. Somewhat surprisingly, perhaps, such a cc-G4-T-v2(FC) [“frozen core”] recovers the lion’s share of the improvement, at WTMAD2 = 0.94 kcal/mol.

A more detailed inspection of the individual subsets reveals that RG18 and HAL59 are the two largest contributors to the difference, with MADs reduced by two-thirds. Next are BSR36 (MAD reduced by three-quarters), HEAVY28 (MAD reduced by four-tenths), following by a string of subsets like BH76, W4-11, G21EA, MB16-43, and the conformation subsets BUT14DIOL and AMINO20X4, for which improvements of 40-60% are seen. Because of the way subsets are weighted in WTMAD2, the small reaction energies in HAL59 and HEAVY128, and especially RG18, have an outsize contribution: the same is true to a lesser extent of BSR36 and BH76. But while the improvement in W4-11 atomization energies does not weigh greatly in WTMAD2, the RMSD for this subset is cut in half: for small-molecule thermochemistry, an improvement from RMSD = 2.9 to 1.6 kcal/mol is significant, as is an RMSD improvement for electron affinities from 0.08 to 0.05 eV. Nevertheless, for the AMINO20X4 and BUT14DIOL conformation sets, the larger and more flexible basis sets prove very useful, although arguably, we already have quite small errors to begin with.
The difference between WTMAD2 = 0.94 kcal/mol with frozen cores, and WTMAD2 = 0.87 kcal/mol without frozen cores, implies that MP2 inner-shell correlation accounts for just 0.07 kcal/mol on WTMAD2. Half of that fairly meager improvement comes from just RSE43, where the error is cut in half. But incremental improvements for many other sets are outweighed by a deterioration in BSR36, where the valence calculation fortuitously leads to outstanding results.

Still, for W4-11, RMSD drops from 1.57 to 1.27 kcal/mol, which small-molecule thermochemists would definitely regard as a nontrivial improvement.

It was found previously in the context of the W4-F12 paper that the additional radial flexibility in core-valence basis sets is beneficial even when only valence electrons are correlated.

We considered a similar breakdown for several additional cases and consistently found that the improvement in WTMAD2 from the larger basis sets is about an order of magnitude more important than the effect of including those additional core electrons. So is their inclusion computationally wasteful?

For the largest calculations in our sample, CPU time for the largest basis set RI-MP2 calculation is, in any case, still dominated by the SCF step. The including of the additional core electrons in that step will only insignificantly add to total computational overhead; hence we have decided to include them throughout in what follows below.

The three fitted parameters of cc-G4-T-v2 (Table 2) are $c_{MP2/CBS} = 0.671$, $c_{CCSD-MP2} = 1.054$, and $c_T = 1.126$; for its frozen-core (FC) version, $c_{MP2/CBS} = 0.787$, $c_{CCSD-MP2} = 1.051$, and $c_T = 1.139$. The pronounced change in the $c_{MP2/CBS}$ parameter (+0.116) reflects the absence of core-valence correlation energy. For the standard G4-T-v2 and 1320 systems in GMTKN55, we obtain $c_{MP2/CBS} = 0.593$, $c_{CCSD-MP2} = 1.061$, and $c_T = 1.103$; that with these less complete basis sets we find a smaller $c_{MP2/CBS}$ coefficient (by 0.194) might compensate for the larger basis set superposition error and its effect on noncovalent interaction sets. (Note that, if the extrapolation to the CBS limit were exact, BSSE should of course vanish. For extensive discussion of BSSE with and without counterpoise corrections, in noncovalent test sets similar to those in GMTKN55, see refs.108–110)

Next, setting $c_{CCSD-MP2} = c_T$ slightly raises WTMAD2 by 0.03 kcal/mol, but leaves us with just two parameters (cc-G4-T-v6) where $c_{MP2/CBS} = 0.626$, $c_{CCSD-MP2} = c_T = 1.029$. The standard G4-T-v6 had WTMAD2 = 1.52 kcal/mol and $c_{MP2/CBS} = 0.557$, $c_{CCSD-MP2} = c_T = 1.044$. 
Therefore, since the statistics are not substantially affected, it is beneficial to treat all post-MP2 corrections as a single correction in cc-G4-T-v6. Figure 2 depicts the contribution to the WTMAD2 (kcal/mol) of each subset for the best two-tier methods.

We might indeed go one step further and set $c_{\text{CCSD-MP2}} = c_T = 1.0$, leaving just a single adjustable parameter. The resulting method is arguably akin to the ccCA approach without relativistic corrections. With $c_{\text{MP2/CBS}} = 0.642$, this “inspired by ccCA” composite approach with inner-shell correlation, cc-G4-T-v7 has WTMAD2 = 0.922 kcal/mol. Its counterpart cc-G4(FC)-T-v7 without core-valence correlation has WTMAD2 = 0.993 kcal/mol for $c_{\text{MP2/CBS}} = 0.727$. We could however take this one final step, and replace the one-parameter two-point extrapolation with the parameter-free three-point extrapolation combo in ccCA-PS3\textsuperscript{14}. For such a “quasi-ccCA” we obtain WTMAD2 = 1.01 kcal/mol without inner-shell correlation, and for quasi-ccCA(noFC) without frozen cores, WTMAD2 = 0.92 kcal/mol. It is quite intriguing from a scientific point of view that in the guise of cc-G4-T-v2, we obtained something not dissimilar from ccCA from a completely different angle, and the comparatively small improvement in WTMAD2 obtainable by introducing the adjustable parameters represents a “feather in the cap” of the original designers of ccCA.

Figure 2. The contribution of each subset of the GMTKN55 database to the WTMAD2 (kcal/mol) for the most accurate two-tier standard (G4-T-v1) and correlation consistent (cc-G4-T-v1 and cc-G4-T-v6) cWFT methods.

Do the energy expressions of the G4-T variants (less empirical than G4(MP2)-XK–type variants) hold any material advantages over the G4(MP2)-XK-T ones when including the
inner-shell energy? The WTMAD2 of standard G4(MP2)-XK-T (six parameters) is 0.07 kcal/mol lower than that of G4-T (three parameters). The additional parameters of G4(MP2)-XK-T are due to the separate scaling of $E_{2,OS}$ and $E_{2,SS}$ terms with large and small basis sets. In the correlation consistent methods, cc-G4-T-v2 comes with WTMAD2 = 0.87 kcal/mol and three parameters and it surpasses cc-G4(MP2)-XK-T-v2 by 0.32 kcal/mol. The $E_2/\{T,Q\}$ extrapolation and the incorporation of the triples term in cc-G4-T variants, is clearly adequate to recover a significant part of electron correlation instead of separately scaling the $E_{2,OS}$ and $E_{2,SS}$ components.

When reducing the CCSD(T) basis set to the smaller def2-SVSP in the two-tier methods, cc-G4(MP2)-XK-D-v1 yields the best result with WTMAD2 = 2.21 kcal/mol and seven parameters. Eliminating the dispersion term raises WTMAD2 by 0.25 kcal/mol. Switching from def2 to cc basis sets, and including the CV correlation energy, together improve the WTMAD2 by 0.35 kcal/mol (cc-G4(MP2)-XK-D-v1 vs G4(MP2)-XK-D-v1) and 0.27 kcal/mol (cc-G4(MP2)-XK-D-v2 vs G4(MP2)-XK-D-v2), with and without dispersion, respectively. The subsets that present the greatest improvement from G4(MP2)-XK-D-v1 to cc-G4(MP2)-XK-D-v1 are AMINO20X4, BHPERI, HAL59, MB16-43, PCONF21, S66, and TAUT15 (see Table S3 in the Supporting Information).

By scaling the $E_{2,SS}$, $E_{2,OS}$, and ECCSD-MP2 terms, we can eliminate two semi-redundant parameters at the expense of $\Delta$WTMAD2 = 0.14 kcal/mol, attaining 2.35 kcal/mol for cc-G4(MP2)-D-v1. The switch from def2 to cc basis sets, and the incorporation of the CV correlation energy, together lower WTMAD2 by 0.33 kcal/mol for cc-G4(MP2)-D-v1 relative to G4(MP2)-D-v1 (see Table S4 in Supporting Information), the same subsets as above being most affected.

**Including the CV correlation energy in the three-tier methods**

Reducing the basis set of CCSD(T) from def2-TZVPP to split-valence greatly reduces overall computational cost, and when a scaled MP3/def2-TZVPP correction is added as a middle tier, G4(MP3)-D was obtained, with WTMAD2 = 1.65 kcal/mol and six parameters.44 Said three-tier method employed the post-HF components from MP2/def2-QZVPPD, a scaled MP3–MP2 difference with the def2-TZVPP basis set, and the $E_{\text{CCSD(T)-CCSD}}$ and $E_{\text{CCSD-MP3}}$ differences from CCSD(T) using the smallest basis set def2-SVSP (i.e., def2-SVP without p polarization functions on hydrogen atoms). The present three-tier methods substitute HF and MP2 utilizing the aug-cc-pwCVQZ(-PP) basis sets and retain the other components, with
energy expressions of the correlation consistent methods following the previously reported three-tier approaches (aside from the inner-shell correlation energy being included in the MP2 part.

This leads to cc-G4(MP3)-D-v1 with WTMAD2 = 1.37 kcal/mol and six parameters. The overall WTMAD2 improvement relative to the standard G4(MP3)-D-v1 is 0.28 kcal/mol, when using larger basis sets and including the CV energy in cc-G4(MP3)-D-v1; it is an accumulative amelioration rising from most subsets as they slightly benefit from the larger basis sets and the CV inclusion (Table S5 in Supporting Information). Eliminating the dispersion term raises WTMAD2 by 0.17 kcal/mol (cc-G4(MP3)-D-v2). Setting $c_T = c_{CCSD-MP3}$ yields WTMAD2 = 1.65 kcal/mol (cc-G4(MP3)-D-v8). In addition, when $c_T = c_{CCSD-MP3} = c_E$ we obtain WTMAD2 = 1.69 kcal/mol, but with just three parameters.

**Correlation consistent DLPNO-CCSD(T)-based cWFT methods.**

One way to improve computational efficiency would be to substitute DLPNO-CCSD(T) for CCSD(T), leading to two-tier cWFTs that combine RI-MP2 for the larger basis sets with a smaller basis set CCSD(T)-MP2 correction computed at the DLPNO-CCSD(T) level. While the latter asymptotically scales linearly with system size, RI-MP2 still has $O(n^5)$ scaling — however, as discussed in Section 5 of Weigend et al., and demonstrated in Table 5 there, the prefactor of the $O(n^5)$ term is small enough that it does not dominate until molecules the size of 44-alkane are reached.

These correlation consistent cWFT approaches follow the previously reported energy expressions (Table 2 of ref. 44), but substituting RI-MP2/aug-cc-pwCV{T,Q}Z(-PP) extrapolations without frozen cores. For example, cc-G4-Q-DLPNO-v1 then entails the following corrections: the difference [DLPNO-CCSD – DLPNO-MP2]/def2-QZVPP, the extrapolated RI-MP2/aug-cc-pwCV{T,Q}Z(-PP), the triples excitation DLPNO-(T)/def2-QZVPP, and the dispersion. The only common terms between cc-G4-Q-DLPNO-v1 and the standard G4-Q-DLPNO-v1 are the post-MP2 ones provided by DLPNO-CCSD(T) and DLPNO-MP2 using def2-QZVPP with the frozen core approximation.

We obtain the lowest WTMAD2, 1.001 kcal/mol, for cc-G4-Q-DLPNO-v1; in view of the very small $c_{\text{disp}} = 0.04$, omitting the dispersion correction unsurprisingly leads to an essentially identical WTMAD2 = 1.005 kcal/mol for cc-G4-Q-DLPNO-v2, compared to 1.52 kcal/mol for G4-Q-DLPNO-v2. According to Table S6 in the Supporting Information, the half-
dozen subsets that present the largest reduction in WTMAD2 are RG18, PCONF21, HAL59, AMINO20X4, HEAVY28, and BH76, the main difference from our observations for cc-G4-T-v2 above being the presence of PCONF21, which are computationally feasible for DLPNO-CCSD(T)/def2-QZVPP but proved too demanding for canonical CCSD(T) even with the smaller def2-TZVPP basis set. Once again, the improvement for W4-11 only contributes -0.022 kcal/mol to the change in WTMAD2, but an improvement of RMSD from 2.9 to 0.9 kcal/mol is most definitely significant for small-molecule thermochemistry.

The WTMAD2 component breakdown reveals that all five top-level subsets are ameliorated (cc-G4-Q-DLPNO-v2 vs G4-Q-DLPNO-v2), with conformers (0.152 kcal/mol) and intermolecular interactions (0.214 kcal/mol) accounting together for 2/3 of the total improvement in ΔWTMAD2 of 0.52 kcal/mol. The three fitted parameters of cc-G4-Q-DLPNO-v2 are $c_{\text{MP2/CBS}} = 0.554$, $c_{\text{CCSD–MP2}} = 0.998$, and $c_T = 1.156$; for the standard G4-Q-DLPNO-v2, we obtained $c_{\text{MP2/CBS}} = 0.513$, $c_{\text{CCSD–MP2}} = 1.003$, and $c_T = 1.185$. The slight change for $c_{\text{MP2/CBS}}$ may be attributed to the larger basis sets and the inclusion of the inner-shell correlation in the $E_2$ energy. The cc-G4-T-DLPNO-v2 and cc-G4-D-DLPNO-v2 follow with WTMAD2 = 1.18 and 1.83 kcal/mol, respectively; when eliminating dispersion, the statistics similarly change negligibly. We note that $c_{\text{CCSD–MP2}}$ is essentially unity, while $c_T$ takes on larger values; this compensates for the known fact\textsuperscript{60,111} that (T) in DLPNO-CCSD(T) is known to not fully recover the triples because of the neglect of off-diagonal Fock matrix elements.

This latter effect can be gauged by substituting the more elaborate (and resource-hungry) DLPNO-CCSD(T$_1$) for DLPNO-CCSD(T). We considered the cc-G4-D-DLPNO-T$_1$ and cc-G4-T-DLPNO-T$_1$ variants based on DLPNO-CCSD(T$_1$)/def2-SVP and DLPNO-CCSD(T$_1$)/def2-TZVPP, respectively. The best overall result was WTMAD2 = 1.11 kcal/mol for cc-G4-T-DLPNO-T$_1$-v1, which marginally increases by 0.03 kcal/mol when discarding the dispersion correction (cc-G4-T-DLPNO-T$_1$-v2). DLPNO-CCSD(T$_1$) is much more demanding in resources, particularly I/O bandwidth, than DLPNO-CCSD(T), and as in our previous study, we find (somewhat surprisingly) that it offers no significant advantage in accuracy in the present context: For the same number of systems, cc-G4-T-DLPNO-T$_1$-v2 yields WTMAD2 = 1.14 kcal/mol, compared to 1.13 kcal/mol for cc-G4-T-DLPNO-v2. The individual contributions to the WTMAD2 per subset are summarized in Table S7.

In the DLPNO-CCSD(T) based variants, the exploitation of the RIJCOSX procedure in SCF is limited to the default numerical precision, i.e., the GridXS2: how does a larger RIJCOSX grid affect statistics? To elucidate this point, we repeated the DLPNO-
CCSD(T)/def2-TZVPPD and DLPNO-MP2/def2-TZVPPD calculations using GRIDX9 (the most stringent built-in option) for the RIJCOSX step. By way of illustration, for phenol and for melatonin this added just 7.0% and 3.8%, respectively, to the wall clock time for DLPNO-CCSD(T)/def2-TZVPP. The new terms \( (E_{\text{C,DLPNO-CCSD}} - E_{\text{C,DLPNO-MP2}}) \) and \( E_{\text{C,DLPNO-(T)}} \) were then substituted in cc-G4-T-DLPNO-v2; the resulting WTMAD2 = 1.140 kcal/mol is 0.053 kcal/mol lower than for the default GRIDXS2, narrowing the gap with the canonical CCSD(T)-based cc-G4-T to 0.17 kcal/mol. The difference is concentrated in the conformer subsets ACONF, AMINO20X4, and PCONF21 (together -0.037 kcal/mol), as well as HEAVY28; the rest of the subsets are not noticeably affected. The optimized parameters for cc-G4-T-DLPNO-v2 with GRIDX9 marginally change to \( c_{\text{MP2/CBS}} = 0.61717, c_{\text{CCSD-MP2}} = 1.00053, c_T = 1.1754 \), while for cc-G4-T-DLPNO-v2 with default grid those are \( c_{\text{MP2/CBS}} = 0.61192, c_{\text{CCSD-MP2}} = 0.99895, c_T = 1.18091 \). A detailed comparison of the WTMAD2 breakdown per subset for cc-G4-T-DLPNO with GRIDX9 vs default GRIDXS2 is reported in the SI (see Table S8). Clearly, one can set \( c_{\text{CCSD-MP2}} = 1.0 \) with impunity, reducing the number of empirical parameters to just two.

Regarding the explicitly correlated RI-MP2-F12 based approximations, we begin by considering additivity approximations of the following form:

\[
E = E_{\text{HF(CABS)/cc-pVQZ-F12}} + cE_2E_{\text{RI-MP2-F12/cc-pVQZ-F12}} + c_{\text{CCSD-MP2}}E_{\text{CCSD-MP2/def2-TZVP}} + c_TE_{\text{C,(T)/def2-TZVP}}
\]

(8)

The cc-G4-F12-T-v2 with \( c_{E2} = c_{\text{CCSD-MP2}} = c_T = 1.0 \) reaches WTMAD2 = 1.030 kcal/mol and a comparison with cc-G4(FC)-T-v2 (\( E_2/aug-cc-pwCV{T,Q}(-PP) \) extrapolation of Schwenke-style) shows that thermochemistry and intermolecular reactions are not affected, though there is some deterioration for barrier heights and reactions involving large molecules (see Table 2). There is a detailed comparison of each subset’s contribution in Table S9 of the SI.

Reducing the RI-MP2-F12 basis set to TZ only marginally increases WTMAD2 by 0.014 kcal/mol [cc-G4-F12-T-v1]. This is a testament to the ability of explicitly correlated methods\(^{112-115} \) to drastically speed up basis set convergence, typically by two or three angular momentum steps over their orbital counterparts.\(^{116} \) We attempted RI-MP2-F12/cc-pV\{T,Q\}Z-F12 extrapolation using the Schwenke coefficient \( c_{E2/CBS} = 0.446336 \) from Table VI of Hill et al.\(^ {90} \) \( \{E_2/CBS = E_2(L+1) + c_{E2/CBS}[E_2(L+1) - E_2(L)]\} \), but found that WTMAD2 actually slightly increases to 1.048 kcal/mol. Likely, seeing an advantage to larger basis sets in the F12
step would require tightening the post-MP2 steps as well. Thus, TZ quality basis sets in RI-MP2-F12 and the post-MP2 terms represent a ‘sweet spot’ for cc-G4-F12-T-v1.

Next, we address the question whether DLPNO-CCSD(T) can replace the canonical CCSD(T) terms in the cc-G4-F12 variants. Substituting $E_{\text{DLPNO-CCSD} - \text{DLPNO-MP2}}/\text{def2-TZVPP}$ and $E_{\text{DLPNO-CCSD(T)}},T/\text{def2-TZVPP}$ in eq. (8) and setting $c_{E_2} = c_{\text{DLPNO-CCSD} - \text{DLPNO-MP2}} = c_{T,\text{DLPNO-CCSD(T)}} = 1$, WTMAD2 increases to 1.44 kcal/mol. However, if we optimize all three parameters, WTMAD2 drops to 1.189 kcal/mol for $c_{E_2} = 0.994; c_{\text{DLPNO-CCSD} - \text{DLPNO-MP2}} = 0.993; c_{T,\text{DLPNO-CCSD(T)}} = 1.237$. That is, while the first two parameters can be set to unity, (T) clearly needs to be scaled up as we saw above. Doing so leads to the single-parameter methods cc-G4-F12-T-DLPNO-v2 with WTMAD2 = 1.194 kcal/mol for $c_{T,\text{DLPNO-CCSD(T)}} = 1.204$ and $c_{E_2} = c_{\text{DLPNO-CCSD} - \text{DLPNO-MP2}} = 1.0$. This is analogous to cc-G4-T-DLPNO-v2 (WTMAD2 = 1.193 kcal/mol) with its triples coefficient being equal to 1.181; in both cases, this reflects that (T) in DLPNO-CCSD(T) — which should actually have been called DLPNO-CCSD(T0) and is referred to as such in Ref. 111 — does not recoup the full thermochemical contribution of triples owing to the T0 (neglect of off-diagonal Fock matrix elements) approximation.

**Final selected methods**

The hierarchy of the cc-G4– type cWFT closely parallels that of the standard G4– type cWFT methods, especially for the two-tier approaches. When a CCSD(T)/def2-TZVP or DLPNO-CCSD(T)/def2-TZVPP component is present in these cc-cWFTs, WTMAD2 values below 1 kcal/mol can be reached for GMTKN55.

The top performers are correlation consistent two-tier methods. These include [cc-G4-T-v6] cc-G4-T with WTMAD2 = 0.90 kcal/mol and only two parameters, followed by the low-cost DLPNO-CCSD(T)-based [cc-G4-Q-DLPNO-v2] cc-G4-Q-DLPNO with WTMAD2 equal to 1.00 kcal/mol, and finally, [cc-G4-F12-T-v1] cc-G4-F12-T WTMAD2 = 1.04 kcal/mol. To put this in perspective, the top performers of the standard G4– type methods likewise belong to the two-tier family, though G4(MP2)-XK-T was found to have 0.09 and 0.08 kcal/mol lower WTMAD2 than G4-Q-DLPNO and G4-T, respectively. These energy differences are marginal, below 0.1 kcal/mol, and in our previous work we considered 1257 reactions for the CCSD(T)/def2-TZVP based methods. Even when extending to 1320 reactions (i.e., completing CCSD(T)/def2-TZVP for some large species that we were unable to finish in the previous study), these differences do not vary (Table 2).
Combining the $E_2$/aug-cc-pwCVQZ(-PP) with an MP3/def2-TZVPP component and a low-cost CCSD(T)/def2-SVPD step yields [cc-G4(MP3)-D-v1] cc-G4(MP3)-D with WTMAD2 = 1.37 kcal/mol and six parameters. This result is competitive with the CCSD(T)/def2-TZVP and MP2/def2-QZVPP based two-tier G4– type methods. An efficient RI-MP3 algorithm would dramatically reduce the computational cost of G4(MP3)-D due to the I/O overhead of the MP3/def2-TZVPP step ($O(N_0^6)$ scaling over system size).

By reducing the basis set of CCSD(T) to def2-SVSP, we arrive at the lowest-cost two-tier methods, cc-G4-D-DLPNO (cc-G4-D-DLPNO-v2) with WTMAD2 = 1.84 kcal/mol and cc-G4(MP2)-XK-D (cc-G4(MP2)-XK-D-v1) with WTMAD2 = 2.21 kcal/mol. When omitting the CCSD(T) step entirely, we obtain as best overall approximations cc-MP2.X-Q (without dispersion) with WTMAD2 = 2.89 kcal/mol and cc-MP2.X-T (with dispersion) with WTMAD2 = 3.09 kcal/mol. We summarize the suggested correlation consistent cWFT methods in Table 3, and in Figure 3 we depict the overall performance of selected G4– type and cc-G4– type cWFTs, standard cWFTs, and double hybrid DFTs.

| Methods                  | WTMAD2 (kcal/mol) | parameters |
|--------------------------|-------------------|------------|
| cc-G4-T                  | 0.90              | 2          |
| cc-G4-Q-DLPNO            | 1.00              | 3;2\textsuperscript{a} |
| cc-G4-F12-T              | 1.04              | –          |
| cc-G4(MP2)-XK-T          | 1.18\textsuperscript{s} | 6          |
| cc-G4-T-DLPNO            | 1.19\textsuperscript{3} | 3;2\textsuperscript{a} |
| cc-G4-F12-T-DLPNO        | 1.19\textsuperscript{4} | 1          |
| cc-G4(MP3)-D             | 1.37              | 6          |
| cc-G4-D-DLPNO            | 1.84              | 3          |
| cc-G4(MP2)-XK-D          | 2.21              | 7          |

(a) If one fixes $\epsilon_{\text{CCSD-MP2}}=1$; effect on WTMAD2 invisible to the precision given.
Figure 3. Overall performance of selected composite methods and double-hybrid DFT over the GMTKN55 database based on the weighted mean absolute deviation (WTMAD2 in kcal/mol).

The cc-G4– type methods provide a low-cost and quite accurate approximation to the CCSD(T) electronic energy at the complete basis set limit. As such, an inherent limitation are the shortcomings of the CCSD(T) method itself for species with strong static correlation; post-CCSD(T) approaches are currently out of reach for the larger species in GMTKN55. This may limit the applicability of these cWFT methods to transition metals, although they may still be valuable for applications like coinage metal-based catalysts (see, e.g., refs. 117,118 for reviews). This issue will be investigated in future work. Suffice to say for now that for main-group systems such as those in the GMTKN55 dataset, correlation consistent cWFT approaches, both ccCA and the parametrized approaches offered here, represent felicitous combinations of moderate cost and fairly high accuracy, with WTMAD2 values less than half what can be achieved by the best empirical double hybrids.39,41,101

Conclusions

We have extended the hierarchy of the composite wavefunction methods by (a) considering inner-shell correlation in the second-order Møller-Plesset step; (b) replacing the Karlsruhe basis sets by augmented correlation-consistent core-valence basis sets of triple and quadruple zeta quality. The resulting cc-G4-type methods reach WTMAD2 statistics below 1 kcal/mol for the large and diverse GMTKN55 benchmark suite.
Somewhat to our surprise, the lion’s share of the improvement did not come from core-core and core-valence contributions, but from enhancements in the basis sets. Nevertheless, the extra cost of including the additional electrons in the RI-MP2 step is such a small component of the overall CPU time that there is no downside to including them.

A thorough investigation of each subset’s contribution showed that the statistical improvement for the two-tier methods lies in the larger molecules, e.g., improved energies of amino acids conformers, barrier heights of pericyclic reactions, binding energies in halogenated dimers, relative energies in the tri- and tetrapeptide conformers, binding energies of noncovalently bound dimers, and relative energies in tautomers. In contrast, amelioration in the three-tier methods is seen across the board and is not concentrated in specific subsets.

The minimally empirical cc-G4-T breaches the 1 kcal/mol threshold, with WTMAD2 = 0.90 kcal/mol and only two fitted parameters for the chemically diverse GMTKN55 database. (A nonempirical variant is very similar to the nonrelativistic part of a ccCA calculation, except for including MP2 core-valence correlation throughout.) The corresponding efficient DLPNO-CCSD(T)-based cWFTs are also very attractive owing to the replacement of the costly CCSD(T) by the linear-scaling DLPNO-CCSD(T) component. The lower-cost cc-G4-T-DLPNO reaches a WTMAD2 of 1.20 kcal/mol at moderate computational cost: by way of illustration, a melatonin conformer takes 24.2 h of wall clock time on two 8-core Intel Haswell processors (Xeon CPU E5-2630v3 clocked at 2.40 GHz).

The three-tier method cc-G4(MP3)-D method is in the same accuracy range as cc-G4-T-DLPNO. Said method has an MP2/aug-cc-pwCVQZ(-PP) term, an MP3/def2-TZVPP component, and the lower-cost CCSD(T)/def2-SVPD; this combination yields a WTMAD2 of 1.37 kcal/mol. An efficient RI-MP3 algorithm will render cc-G4(MP3)-D more efficient and dramatically reduce its cost and I/O overhead.

The two-tier cc-G4-T-v7 (inspired by ccCA) reaches WTMAD2 of 0.92 kcal/mol; it is available for the spd block of H-Rn in the PTE, and cMP2/CBS is the single parameter since \( c_{CCSD-MP2} = c_T = 1.0 \). As post-HF corrections, the extrapolated \( E_2/aug-cc-pwcv{T,Q}Z(-PP) \) and the CCSD(T)/def2-TZVP components are used.

Finally, cc-G4-F12-T-DLPNO, which combines explicitly correlated MP2-F12/cc-pVTZ-F12 with DLPNO-CCSD(T)/def2-TZVPP and has just one empirical parameter, is an accurate and fairly inexpensive alternative for compounds where cc-pVTZ-F12 or cc-pVTZ-PP-F12 basis sets are available for all elements.
All in all, the cc-G4 type approaches offer a material improvement in terms of accuracy over G4-T and similar cWFT approaches, at a comparable computational cost.

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Supporting Information

Sample input files and postprocessing scripts are included in the Supporting Information for top performers: cc-G4-T, cc-G4-T-v7, cc-G4-Q-DLPNO, cc-G4-F12-T-DLPNO, cc-G4(MP2)-XK-T, cc-G4-T-DLPNO, cc-G4(MP3)-D, cc-G4-D-DLPNO, cc-G4(MP2)-XK-D.
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GMTKN55 Database

- cc-G4(MP2)XK-D
- cc-G4-T-DLPNO
- cc-G4-T

kcal/mol

WTMAD2
Thermochemistry
Barrier heights
Large species
Conformers
Intermolecular