Regularized second order Møller-Plesset theory: A more accurate alternative to conventional MP2 for noncovalent interactions and transition metal thermochemistry for the same compute cost

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Abstract

Second order Møller-Plesset theory provides a remarkably simple form for the electron correlation energy with many desirable properties, e.g. it is size-consistent, free of self-interaction error, and scales with the fifth power of system size. However, MP2 exhibits well-known shortcomings including an incomplete description of dispersion

interactions and sizable failures for transition metal chemistry. Herein, we first explore multiple physically justified forms of single-parameter regularization and then demonstrate that with appropriate parameter choice, regularized MP2 with Hartree-Fock reference orbitals yields high and transferable accuracy across a wide variety of noncovalent interactions (S22, S66, XB40, A24, and L7 test sets) and (mostly closed-shell) transition metal thermochemistry (metal-carbonyl dissociations and a subset of MOR41). We find that, especially for systems with interacting π systems relevant to dispersion interactions and dative bonding, regularization serves to damp overestimated pair-wise additive contributions to the first-order amplitudes that affect correlation energy and charge-density. The optimal parameter values for the noncovalent and transition metal sets are 1.1 and 0.4 for two regularizers, κ and σ^2, respectively. These two regularizers slightly degrade the accuracy of conventional MP2 for some small-molecule test sets which are well-known to be sensitive to charge-density distribution (radical stabilization energies, barrier heights, dipole moments, and polarizabilities), most of which have relatively large gaps. Due to the relatively straightforward implementations of nuclear gradient and other properties, we recommend κ-MP2 with $\kappa = 1.1$ as a more accurate alternative to conventional MP2 and other related variants. Our results suggest that appropriately regularized MP2 models represent promising forms for the nonlocal correlation part of double hybrid density functionals, at no additional cost over conventional MP2.

1 Introduction

Reliably and efficiently evaluating the electron correlation energy of the electronic ground state of molecules at the lowest possible computational cost is a long-standing central challenge of quantum chemistry. In wavefunction-based quantum chemistry, given the Hartree-Fock (HF) mean field reference determinant, $|\Phi_0\rangle$, and its energy, E_0, the energetic effect

of other determinants is typically approximated by low-order Møller-Plesset (MP) pertur-
bation theory,[1] or by infinite order coupled cluster (CC) theory,[2,3] truncated at a relatively
low level of excitation from $|\Phi_0\rangle$. As the lowest order PT correction to HF, MP2 is widely
used, both for relative energies and properties, and also as a component of double hybrid
density functional theory (DFT).[4–6]

For stable closed shell organic and main group inorganic molecules, on the whole, MP2
provides a considerable improvement over HF in the quality of relative energies for ther-
mochemistry (e.g. isogryic reaction enthalpies[7]) and non-bonded interactions.[8] Of course
these improvements do not compete with the accuracy of the best hybrid density func-
tionals, except for some special cases such as hydrogen-bonding.[9,10] There are also notable
improvements in the quality of optimized molecular structures and properties of closed shell
molecules such as dipole moments[7,11] and electrical polarizabilities.[12]

In contrast with conventional DFT, MP2 offers the formal advantage of being free of
self-interaction or delocalization errors.[13,14] Yet MP2 is typically less accurate than the best
coupled cluster theory that can be routinely applied, such as taking CC with singles and
doubles (CCSD) and correcting for perturbative triples via CCSD(T).[15] However CCSD(T)
has vastly higher compute cost, as it scales $\mathcal{O}(A^7)$ with number of atoms (A) with $\mathcal{O}(A^4)$
memory/storage versus MP2's $\mathcal{O}(A^5)$ compute cost and $\mathcal{O}(A^3)$ memory/storage.

MP2 theory also exhibits some notable failures. One intractable class of failures is for
strongly correlated molecules, where the HF reference is very poor because multiple elec-
tron configurations are of comparable importance.[16] Such problems are challenging also for
common CC approaches such as CCSD or CCSD(T), and for many widely-used density func-
tionals. The presence of strong correlation is signified by spin-symmetry breaking in DFT
orbitals, as well as small energy gaps between occupied and virtual orbitals, and other indi-
cators.[17–19] Fortunately, strongly correlated problems[20] are not very common in main group
chemistry, or even in transition metal chemistry.[19] However, when strong correlation oc-

curs in the ground state, it typically requires substantially more sophisticated multireference approaches.[21–25]

A second well-known class of failures for MP2 theory are problems where the HF orbitals exhibit artificial symmetry-breaking even though there are no obvious strong correlations.[26] Symmetry-restoration is not accomplished by perturbation theory,[27] and thus MP2 cannot recover from symmetry-broken references. There are many examples of this type, most commonly with spin-unrestricted HF orbitals (UHF) leading to spin-contamination. It is therefore desirable to employ spin-restricted HF (RHF) for closed shell molecules, and spin-restricted open shell HF (ROHF) for radicals as references for MP2 calculations. The resulting RMP2 methods[28–33] typically perform significantly better provided there is no spatial symmetry-breaking, and orbital gaps remain large (i.e. there are no strong correlations). Alternatively, at additional cost of performing iterative $\mathcal{O}(A^5)$ steps, optimizing the orbitals in the presence of MP2 correlation via orbital optimized MP2 (OOMP2) can also resolve such issues.[34,35] Use of DFT orbitals can achieve similar improvements.[36]

Addressing a third class of MP2 failures will be the focus of this paper. These are problems that do not exhibit obvious strong correlations, but we think are instead characterized by the presence of significant non-additive weak correlation effects. As is clear in the canonical basis, MP2 theory treats electron correlation as a pairwise additive set of contributions from each double substitution of two occupied orbitals by two virtual orbitals. When non-additivity is important, one typically needs to attenuate electron correlation effects. A simple but important illustration may be helpful. MP2 is known to significantly overestimate the strength of π-stacking dispersion interactions, such as the slipped benzene dimer[37–40] and stacked DNA base pairs.[41] This effect becomes larger as the conjugated monomers become bigger, as exemplified by the coronene dimer, leading to the recent observation that MP2 produces "relative errors of over 100% for several benchmark compounds."[42]

These dispersion interactions are collective properties of the π electrons, and evidently

non-additive effects are important. For this reason, it has been argued that infinite order methods are necessary to resolve such problems. By contrast, MP2 is known to yield relatively accurate results for hydrogen-bonding, for example in water clusters[43] or even between the same DNA base pairs for which stacking interactions are overestimated.[44] The key distinction is arguably that the hydrogen bond has a strong electrostatic component, and to the extent that correlation is involved, it is to correct the HF charge distribution of the monomers[45] or the relatively weak charge-transfer from an oxygen lone pair to an $H-O$ σ^* orbital.

There are other examples that appear to fall into the same category. One example that is particularly important is the fact that MP2 performs relatively poorly for ligand-dissociation energies of transition metal (TM) complexes with dative bonds in which π electrons are involved.[19,34,46] The presence of multiple electron pairs in the same region of space is a characteristic feature of many organometallic complexes such as metal carbonyl species, whose bonding involve forward and back donation with their ligand set. MP2 theory typically overestimates the strength of such binding, which again suggests that important non-additive electron correlation effects are at play.[19] As for collective dispersion interactions, this information has been used to argue for the necessity of using infinite order methods.

In simpler terms, by non-additive effects, we mean higher-order contributions to the wavefunction amplitudes beyond the first-order perturbation theory. The failure of MP2 (or any modification of second-order perturbation theory) can be inferred by inspecting the magnitude of first-order wavefunction amplitudes. Namely, large first-order amplitudes are the direct indication of the failure of the second-order energies. When first-order amplitudes are unphysically large, the subsequent correlation energy contribution is too negative, leading to the overestimation of dispersion interactions[42,47] and dative bond energies.[19] Large amplitudes can arise either from large numerators (matrix elements) and/or small energy denominators.

There have been modifications to MP2 theory which have achieved notable success for problems where non-additive correlation effects are present. The first major development was the spin-component scaled MP2 (SCS-MP2), which was shown to significantly improve MP2 for TM complexes as well as main group chemistry by a heuristic scaling of same-spin and opposite-spin correlation contributions.[34,48,49] SCS-MP2 was also successful for dispersion interactions on smaller conjugated hydrocarbons although different scaling parameters were required.[50] The scaled opposite spin MP2 approach (SOS-MP2) also improved thermochemical results relative to MP2, and reduced the compute cost from $\mathcal{O}(A^5)$ to $\mathcal{O}(A^4)$.[51,52] For dispersion interactions, a similar approach was recently applied to MP2-F12;[53] alternatively, attenuating the long-range part of the MP2 correlation energy was also quite successful.[8,54–56]

However, none of these approaches reviewed above address the phenomenon of non-additive correlation effects directly. Yet it is well-known that perturbation theory is more accurate when correlation effects are smaller, and therefore the largest non-additivity errors in the MP2 correlation treatment will be for pair correlations with the smallest orbital energy gaps. This suggests that renormalizing the pair correlation amplitudes with the smallest energy gaps while leaving the perturbation expression for large-gap correlations unchanged could be a productive way to address the problem of non-additive correlation effects. Other researchers have indeed emphasized the potential for a renormalized low-order perturbation theory.[57–59]

The approach taken in this paper is to revisit an energy-gap dependent renormalization of the pair correlation amplitudes employed in OOMP2[60] for MP2 methods with HF orbitals. In principle renormalization is what is rigorously accomplished in infinite order methods such as CCD or CCSD, but to avoid their compute cost, it will be accomplished semi-empirically here. We employ an energy-dependent regularization form that was introduced previously to stabilize OOMP2 against the potentially divergent correlation contributions associated with closing the orbital gap.[60] Encouragingly, such a regularization strategy was found to be

effective in correcting the overestimation of noncovalent interactions in MP2,[47] although no attempt was made to optimize the associated parameter. After a brief review of MP2 itself, we assess the performance and transferability of candidate forms on a wide range of test sets representative of noncovalent interactions (NCIs), closed-shell TM thermochemistry, main-group thermochemistry and barrier heights, and properties including dipole moments and polarizabilities.

2 Theory

MP2 can be derived from time-independent PT with respect to the electron-electron interaction, or from second-order analysis of the coupled cluster equations:[61]

$$E_{\mathrm{MP2}} = \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t^{(1)}_{ij,ab} = -\frac{1}{4}\sum_{ijab}\frac{|\langle ij||ab\rangle|^2}{\Delta^{ab}_{ij}} \tag{1}$$

where i and j denote occupied orbital indices, a and b are virtual orbital indices, the energy denominator $\Delta^{ab}_{ij} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$, and $\{t^{(1)}_{ij,ab}\}$ are the first-order wavefunction amplitudes. The correlation energy from CCD can also be written as a contraction of doubles amplitudes with two-electron integrals (i.e., $t^{(1)}_{ij,ab}$ is replaced by CCD amplitudes), which suggests that a semi-empirical renormalization of the first-order amplitudes could potentially yield results of comparable quality to those from CCD.

Our group's initial effort at regularization involved a simple level shift,[62–64] called the δ regularizer which corresponds to $\Delta \to \Delta + \delta$, where $\delta > 0$. However, this form is energy-gap independent, which, as argued above, is not suited for correcting the non-additivity of the correlation energy. More sophisticated, energy-gap dependent forms of regularization are presented and detailed in Ref. 60, which we summarize here briefly. A Laplace transform of

Eq. $(1)^{65}$ yields

$$E_{\mathrm{MP2}} = -\frac{1}{4}\sum_{ijab}\int_0^\infty d\tau e^{-\tau\Delta_{ij}^{ab}}|\langle ij||ab\rangle|^2 \tag{2}$$

where it is apparent that when $\Delta_{ij}^{ab} \to 0$ the integral diverges. Setting the upper integration limit to $\sigma(\Delta_{ij}^{ab})^{p-1}$ gives

$$E_{\sigma^p\text{-MP2}}(\sigma) = -\frac{1}{4}\sum_{ijab}\frac{|\langle ij||ab\rangle|^2}{\Delta_{ij}^{ab}}(1-e^{-\sigma(\Delta_{ij}^{ab})^p}) \tag{3}$$

This equation with $p = 2$ can also be derived from a 2nd order PT analysis of the flow equations.[58,59] However for quantum chemical purposes the σ variable can be determined empirically. We will refer to $p = 1$ and 2 expressions as σ and σ^2, respectively. In the limit of $\Delta \to 0$, the corresponding contribution to $E_{\sigma\text{-MP2}}$ goes to a finite value, whereas the contribution to $E_{\sigma^2\text{-MP2}}$ vanishes. This energy expression corresponds to regularizing the first-order amplitudes of conventional MP2 theory:

$$\tilde{t}_{ij,ab}^{(1)} = -\frac{\langle ij||ab\rangle}{\Delta_{ij}^{ab}}(1-e^{-\sigma(\Delta_{ij}^{ab})^p}) \tag{4}$$

such that the otherwise large amplitudes corresponding to small gaps are attenuated.

Alternatively, the two-electron integrals can be modified such that the integrand is zero when $\Delta_{ij}^{ab} \to 0$, e.g.:

$$\langle ij||ab\rangle \to \langle ij||ab\rangle(1-e^{-\kappa(\Delta_{ij}^{ab})}) \tag{5}$$

This is known as κ regularization,[60] and the correlation energy reads:

$$E_{\kappa\text{-MP2}}(\kappa) = -\frac{1}{4}\sum_{ijab}\frac{|\langle ij||ab\rangle|^2}{\Delta_{ij}^{ab}}(1-e^{-\kappa(\Delta_{ij}^{ab})})^2 \tag{6}$$

κ regularization can be viewed as regularizing both the first-order amplitudes and the integrals, rather than the amplitudes alone.

8

These energy-gap dependent regularizers have been so far mainly used in the context of OOMP2.[26,47,60,66–68] Only recently, it was found that the κ regularizer (employing the value originally recommended for κ-OOMP2) can significantly improve noncovalent interactions at the MP2 level when used with HF orbitals for the systems not contaminated by any spurious symmetry breaking.[47] This encouraging result raises more general questions. What is the *optimal* value of κ for use with MP2 itself? Is the κ regularizer particularly suitable, or are other forms such as σ^2 or σ presented above comparable or better? Is the improvement specific to non-bonded interactions, or how general might it be? Our objective in this work is to address these interesting questions with the objective of attempting to define a regularized MP2 method for general use.

3   Data Sets

For NCIs we use the S22[41] and S66 sets,[69] which consist of hydrogen-bonded and disperson-bound complexes, the non-iodide-containing subset of XB40 for halogen-containing hydrocarbon interactions,[70] A24 for small molecule NCIs,[71] and the L7 set for very large dispersion-bound dimers and trimers.[72] L7 has been the focus of very recent debate: conventional MP2 has been convincingly argued to be unsuitable,[42] and supposedly reference-quality values from localized CCSD(T) and Diffusion Monte Carlo are not consistent.[73–75]

To assess the applicability of regularized MP2 variants to TM systems, we use a 39 molecules subset of MOR41[46] along with nine 3d metal-carbonyl dissociation reactions. Reference values are, respectively, from carefully performed DLPNO-CCSD(T) calculations and experimental results recently validated by an accurate quantum Monte Carlo method.[76]

We then turn to main-group sets such as W4-11[77] which consists of 140 atomization energies of small molecules and radicals. MP2 performs very well already for RSE43,[78,79] which consists of 43 radical stabilization energy reactions with reference data from D/T extrap-

olated CCSD(T). We also investigate dipole moments[11] and polarizabilities[12] with a non-spin-polarized set of small main-group systems, with reference values taken from CCSD(T) extrapolated with either aTZ/aQZ or aQZ/a5Z basis sets.

4   Computational Methods

In this work, the reference orbitals are from restricted Hartree-Fock (HF) calculations. ROHF was used for open-shell species together with the RMP2 correction,[32] since unrestricted orbitals with appreciable spin-contamination are well-known to degrade MP2 results. Main-group thermochemistry, radical stabilization energies, and barrier heights were extrapolated to the complete basis set (CBS) limit with the aug-cc-pVTZ and aug-cc-pVQZ basis sets; dipoles and polarizabilities were extrapolated with the aug-cc-pCVTZ and aug-cc-pCVQZ basis sets. We used the x^{-3} form for the correlation energy (x=3,4 for TZ and QZ), and QZ HF energies.[80]

As shown in the Supporting Information for the W4-11 and dipole moment data sets (Tables S2-S5), for a given value of regularization parameter the differences in the RMSDs that result from augmented triple-ζ and CBS-extrapolated regularized MP2 calculations are negligible, when comparing with CCSD(T)/CBS reference values. We also confirmed (Table S1) that for a representative NCI set, S22, the RMSDs and optimal regularization parameter are very similar in the aTZ and aQZ basis sets when the counterpoise correction is used, again comparing with CCSD(T)/CBS reference values. We therefore used the aug-cc-pVTZ basis with counterpoise correction for all NCI sets, with the exception of the L7 set for which the slightly more compact def2-TZVPD basis set was used.

The def2-TZVPP basis set, with the def2-ECP for 4d and 5d TM complexes, is used for the MOR39 set, as we compare to reference values in the same basis provided by A. Hansen. For the MCO9 set the def2-QZVPP basis is used for single-point energies, with

optimized geometries and thermal corrections obtained from the UB3LYP/cc-pVTZ-DKH level of theory (as obtained in Ref. 76). For all MP2 calculations, the RI approximation of the two-electron integrals is used.[81] Due to computational limitations, the I functions in the auxiliary RI basis sets were removed in TM calculations.

For dipole moments we follow Ref. 11 and show root mean squared regularized error (RMSRD):

$$\frac{\mu - \mu_{ref}}{max(\mu_{ref}, 1D)} * 100 \tag{7}$$

All MP2 and regularized MP2 calculations were performed in Q-Chem.[82]

5   Results

5.1   Comparison of regularizer functional forms

The κ, σ, and σ^2 regularizers for the S22, MOR39, and W4-11 sets are shown in Fig.s 1a, 1b, and 1c. For all three sets, the various regularization strategies yield RMSD minima which differ by sub-kcal/mol quantities: either all are very effective (S22 and MOR39) or none are (W411). The trends in the results for the S22 and MOR39 sets look qualitatively similar, further suggesting that there is no single form of regularization which stands out as obviously preferable in these cases. For W4-11 the σ^2 regularizer does not improve upon conventional MP2, in contrast to the $p = 1$ regularizers, however we note that the differences are rather minor given the energy scales.
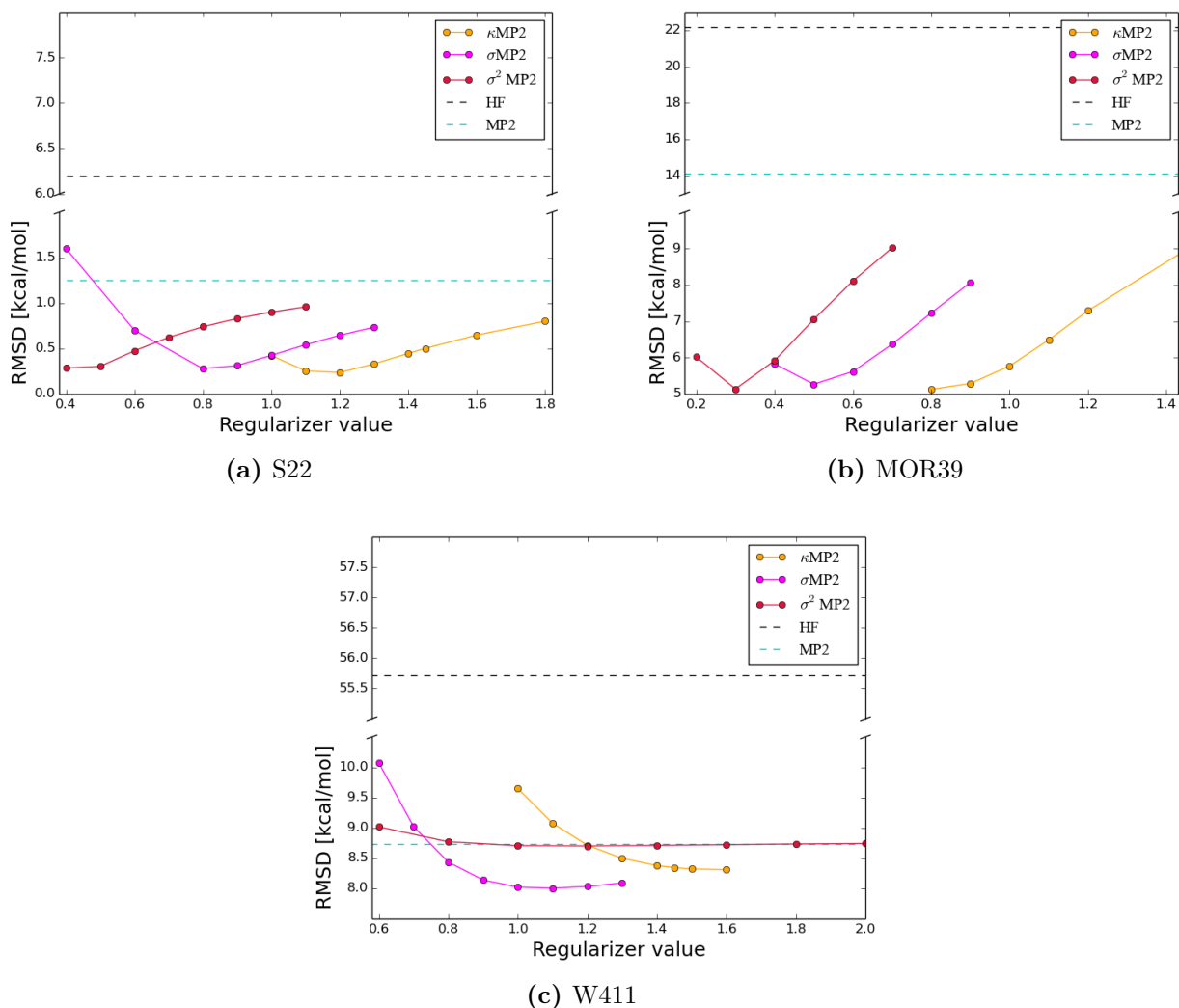
Figure 1: Comparing κ, σ, and σ^2 regularizers for representative data sets of (a) NCI, (b) (mostly) closed-shell TM thermochemistry, and (c) main-group atomization energies.

5.2 Assessing transferability across various test sets

For a number of NCI and TM thermochemistry test sets we have computed the root mean squared deviation [RMSD] from reference values as a function of regularization parameter, with both κ and σ^2 approaches. The results are shown in Tables 1 and 2, respectively.

Table 1: RMSDs [kcal/mol] for the NCI sets – S22, S66, XB40, A24, L7 – and TM sets – MCO9, MOR39 – from κMP2 over a range of κ values.

κMP2	S22	S66	XB40	A24	L7	MCO9	MOR39
0 (HF)	6.20	4.70	3.40	1.64	27.75	29.23	22.15
0.8	1.00	0.96	0.72	0.43	4.98	5.93	5.13
0.9	0.68	0.73	0.56	0.36	3.27	5.48	5.29
1.0	0.42	0.55	0.44	0.30	2.08	5.65	5.77
1.1	0.25	0.41	0.35	0.25	1.73	6.18	6.49
1.2	0.24	0.31	0.30	0.22	2.22	6.91	7.29
1.45	0.50	0.28	0.30	0.16	4.06	8.67	8.96
∞(MP2)	1.25	0.67	0.58	0.17	9.24	14.42	14.13

Table 2: RMSDs [kcal/mol] for the NCI sets – S22, S66, XB40, A24, L7 – and TM sets – MCO9, MOR39 – from σ^2MP2 over a range of σ values.

σ^2MP2	S22	S66	XB40	A24	L7	MCO9	MOR39
0 (HF)	6.20	4.70	3.40	1.64	27.75	29.23	22.15
0.2	1.38	1.21	0.92	0.52	7.39	7.22	6.02
0.3	0.66	0.68	0.55	0.36	3.37	5.20	5.14
0.4	0.29	0.37	0.36	0.26	1.48	5.46	5.92
0.5	0.30	0.24	0.28	0.20	2.25	6.49	7.05
0.6	0.48	0.25	0.29	0.16	3.46	7.57	8.11
0.7	0.62	0.32	0.33	0.14	4.44	8.52	9.02
0.8	0.74	0.38	0.37	0.13	5.22	9.33	9.78
∞(MP2)	1.25	0.67	0.58	0.17	9.24	14.42	14.13

In all cases, conventional MP2 provides a substantial improvement to HF, and both κ and σ^2 regularization further improve upon the accuracy of MP2. The improvement in accuracy due to regularization is, in most cases, quite remarkable, e.g. factors of 3-6x for S22, S66, and L7 along with nearly 3x for the two TM sets.

More important than the remarkably improved minimum RMSDs obtainable with the optimum regularizer *specifically for that dataset* is the fact that both choices of regularizer show a quite encouraging degree of *transferability* between data sets. Furthermore, comparing S22 (as a proxy for the NCI sets) with MCO9 and MOR39 results, the optimal κ

values are 1.2, 0.9, and 0.8 for κMP2 whereas the optimal σ values are 0.4, 0.3, and 0.3 for σ^2MP2. Indeed, visual inspection of Tables 1 and 2 shows that the color patterns associated with performance are remarkably similar. Therefore we cannot confidently suggest that one regularizer is better than the other: rather the key point is that *both* regularizers appear to yield substantial overall improvements versus conventional MP2 and HF.

5.2.1   Non-covalent interactions

The L7 test set consists of adenine and guanine-cytosine adsorbed on circumcoronene (C3A, C3GC), guinine-cytosine tetramer (GCGC), coronene dimer (C2C2), guanine trimer (GGG), octadecane dimer (CBH), and the phenylalanine trimer (PHE). Fig. 2 shows the results of HF, κMP2 with $\kappa = 0.9, 1.1, 1.2, 1.45$, and conventional MP2 (all raw values for HF, MP2, κMP2 and σ^2MP2 are given in the Supporting Information). HF drastically underbinds, as expected since mean-field theories do not account for dispersion interactions. MP2 overbinds most prominently in the largest π-stacked systems: the two circumcoronene systems (C3A and C3GC) along with the coronene dimer (C2C2). In contrast, conventional MP2 is nearly perfect for CBH, wherein each octadecane monomer is completely saturated (with σ-bonds only). This finding is consistent with a previous study showing that MP2 overestimates interlayer stacking of graphene but not graphane layers.[83] Importantly, Fig. 2 reveals that the overestimated π-driven dispersion interaction from conventional MP2 can be largely corrected with appropriate regularization, with stronger regularization moving the NCI energies closer to the HF values.
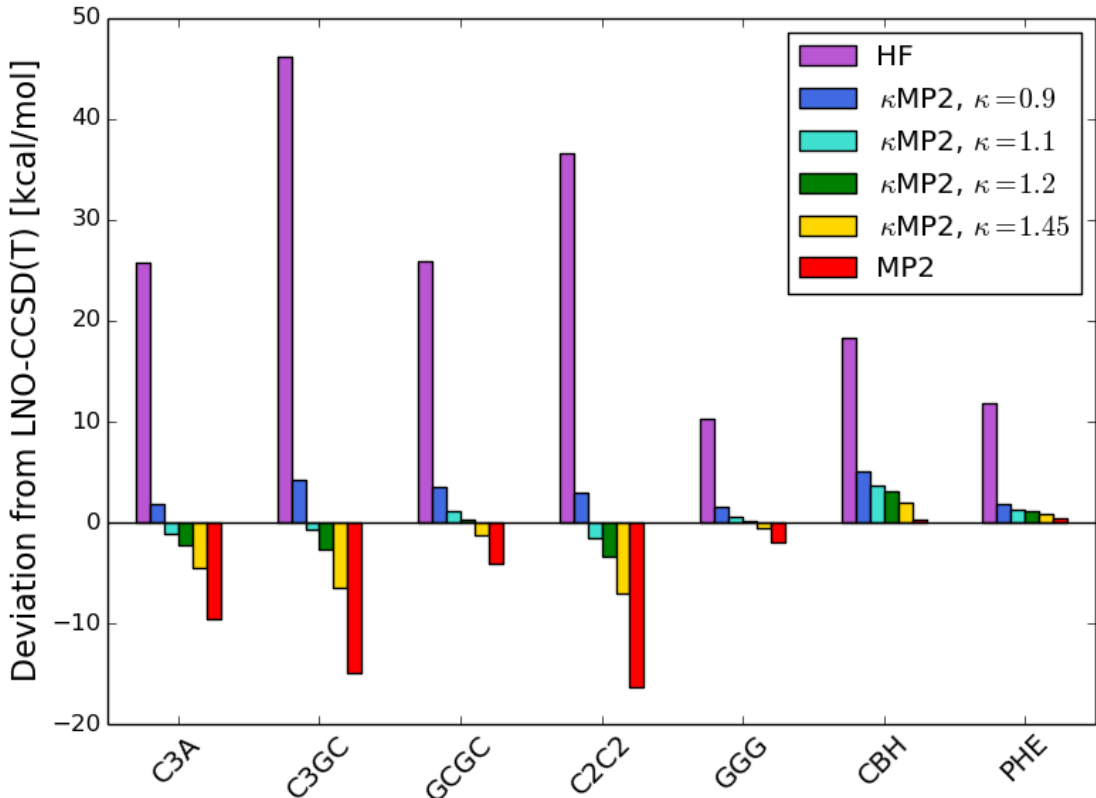
Figure 2: HF, κMP2, and MP2 results for the L7 test set. The deviation from reference LNO-CCSD(T) values [kcal/mol] is shown. A negative value means over-binding.

It is remarkable that a single choice of regularization parameter is simultaneously optimal for both S22 and L7, i.e. $\sim$1.1 and 0.4 for κ and σ^2 MP2, respectively. Results for the 22 systems in S22 are plotted in the Supporting Information (Figure S1), from which it is clear again (though with smaller energy scales) that the overestimated stacking interactions from conventional MP2 can be balanced out via regularization.

The overbinding of π-stacked dispersion-bound systems can be rationalized as follows.[84–86] The frontier energy gap of planar, conjugated monomers (denoted A or B) is well-known to decrease as the area of the molecule increases. We now consider the sum-over-states expression for the mean, imaginary-frequency-dependent polarizability of a spherical (for

simplicity) monomer:[87]

$$\bar{\alpha}(i\omega) = \frac{1}{3}[\alpha_{xx}(i\omega) + \alpha_{yy}(i\omega) + \alpha_{zz}(i\omega)] = \frac{2}{3}\sum_{n\neq 0}\frac{\omega_{n0}|\langle n|\hat{\mu}|0\rangle|^2}{\omega_{n0}^2 + \omega^2} \tag{8}$$

where the excitation frequencies, $\omega_{n0} = E_n - E_0$, can be approximated by differences between eigenvalues of the Fock operator. The attenuation of MP2 first-order amplitudes, as accomplished by κ and σ^2 regularization, effectively reflects an energetic separation of occupied and virtual molecular orbitals involved in each pairwise excitation (moving the virtuals higher in energy), with the energy-gap-dependent form serving to separate orbitals that are close in energy more than those with large gaps. Strong regularization, then, will reduce molecular polarizabilities. Since a large part of the total interaction potential, U, depends explicitly on monomer polarizabilities via the C_6 coefficient,[87,88] i.e.

$$U(R_{AB}) \sim \frac{-C_{6,AB}}{R_{AB}^6} \tag{9}$$

where

$$C_{6,AB} = \frac{3}{\pi}\int d\omega \bar{\alpha}_A(i\omega)\bar{\alpha}_B(i\omega), \tag{10}$$

it becomes clear that regularizing MP2 amplitudes for the π-stacked complexes in L7 and S22 makes the interaction potential less negative / smaller in magnitude. Hence, the predicted NCIs that are overestimated by conventional MP2 are attenuated via successful regularization, which nicely reflects the physical expectation that higher-order terms in the interaction are repulsive.

Table 3 implies that even for large systems such as the coronene dimer, the MP2 denominators (the minimum value is equal to twice the HOMO-LUMO gap) are far from zero. Nonetheless, the first-order amplitudes can still be unphysically overestimated, leading to overbinding of dispersion-bound complexes. In most cases the orbital gap can be taken to

be a good proxy for the first-order amplitudes (indeed, this is implied by the improved accuracy for the present NCI sets due to energy-gap-dependent regularization). Fig. 3 plots the average HOMO-LUMO gap of the dimeric species in each test set vs the RMSD reduction over conventional MP2. The R^2 value improves slightly going from κ to σ^2MP2, though in both cases regularization is more beneficial as the average gap decreases. The A24 set, with the largest average HOMO-LUMO gap of 12.9 eV, is interesting in that regularization actually worsens the accuracy of conventional MP2. As we will see (and as will be further discussed), even larger gaps are, in fact, characteristic of stable small molecules, implying that not all cases call for regularization. We note that the non-infinite slopes of the best-fit lines suggest that κ and σ^2 regularizers are by no means perfect, i.e. that alternate forms of energy-gap-dependent regularization might be more transferable.

Table 3: Average HOMO-LUMO gap [eV] from HF theory for dimer systems in the 5 NCI sets investigated presently.

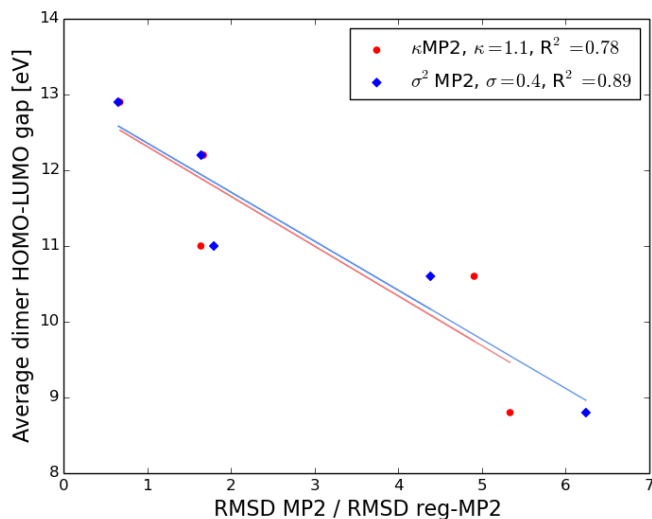| NCI set	avg. HOMO-LUMO gap
L7	8.8
S22	10.6
S66	11.0
XB40	12.2
A24	12.9

Figure 3: Correlation between average HOMO-LUMO gap of dimer systems with the factor of improvement of κ or σ^2 regularized MP2 (with κ=1.1, σ=0.4) over conventional MP2.

5.2.2   Transition metal thermochemistry

The TM systems investigated in this work do not display static correlation, as supported by the absence of spin-symmetry breaking at the UHF level.[19] All molecules in the MOR39 set are closed-shell singlets, and the systems in the MCO9 set have relatively large gaps (compared to other metal complexes) because the carbonyl ligands are strong-field. Indeed, the MOR39 molecules have an average HOMO-LUMO gap of 10.6 kcal/mol.

The largest errors from conventional MP2 occur for metal-carbonyl dissociations. The effect of regularization is shown in Fig. 4, in comparison to HF and conventional MP2 results.
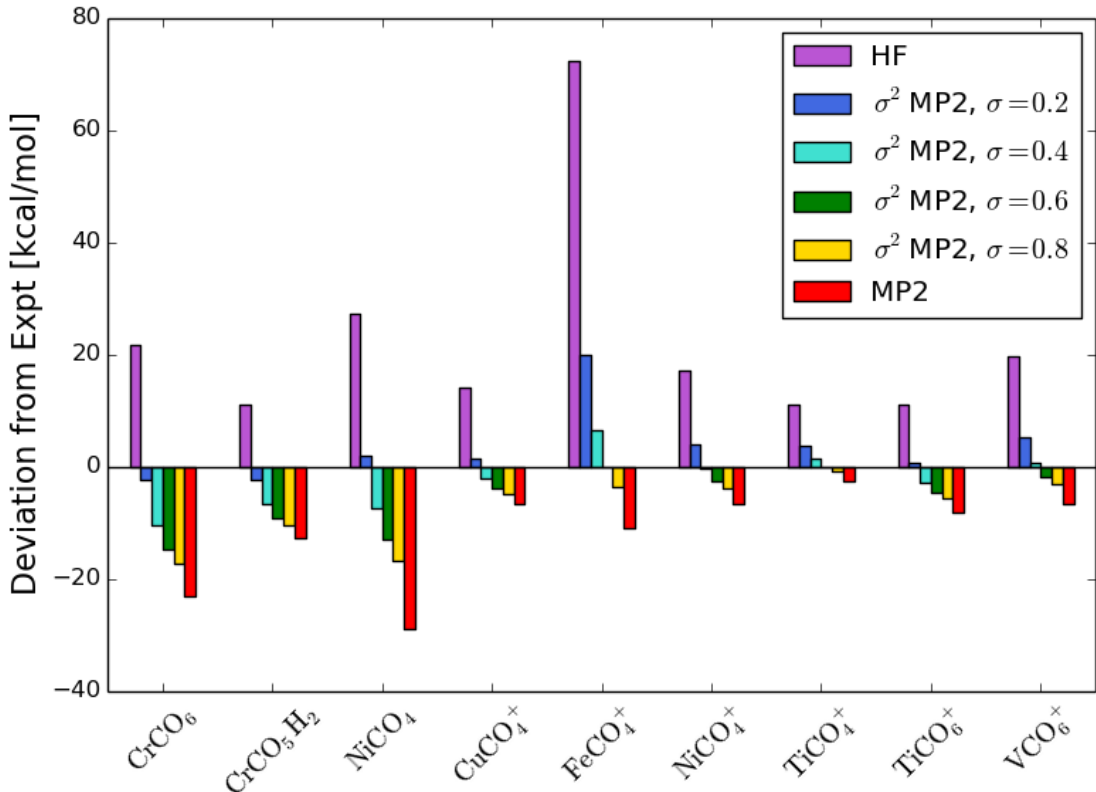
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Figure 4: HF, σ^2MP2, and MP2 results for the bond dissociations in the MCO9 test set. The deviation from experimental values [kcal/mol] is shown. A negative value means over-binding. In every case CO dissociates from the compounds shown in the x-axis, except for $CrCO_6H_2$ where H_2 dissociates.

As was the case for the NCI sets in the previous section, MP2 strongly overestimates the strength of the dissociating bond in every case. Interestingly, even the metal-dihydrogen bond is over-bound with conventional MP2 (see the $CrCO_5H_2$ reaction). On the other hand, HF consistently underbinds, and increasing regularization strength interpolates between the MP2 ($\sigma \to \infty$) and HF ($\sigma \to 0$) limits.

To gain further insight, let us consider just the isolated carbonyl ligand – a neutral diatomic with a triple bond between carbon and oxygen atoms. Despite the vastly more electronegative oxygen atom (relative to the carbon atom), the dipole moment is very small (0.127 Debye with CCSD(T)/aTZ,[11] 0.122 Debye experimentally[89]). Furthermore, the dipole is oriented such that the positive end points toward the oxygen. This has been rationalized

by the recognition of substantial dative (also known as coordinate-covalent) character of the bond. As can be seen in Table 4, the dipole predicted by HF ($\kappa \to 0$) points in the wrong direction due to an underestimation of the charge donation. Although the dipole predicted by MP2 ($\kappa \to \infty$) is oriented in the correct direction, it is vastly overestimated, especially in percentage terms.

Table 4: Dipole moment in Debye as a function of κ regularization parameter for the isolated CO molecule, in the aug-cc-pVTZ basis. Negative values indicate that the positive end of the dipole points toward the carbon atom. $\kappa = 0$ corresponds to HF theory, and $\kappa \to \infty$ corresponds to conventional MP2 theory.

Method	Dipole Moment
κMP2 ($\kappa = 0$)	-0.27
κMP2 ($\kappa = 0.7$)	-0.06
κMP2 ($\kappa = 0.8$)	-0.01
κMP2 ($\kappa = 0.9$)	0.02
κMP2 ($\kappa = 1.0$)	0.06
κMP2 ($\kappa = 1.1$)	0.09
κMP2 ($\kappa = 1.2$)	0.11
κMP2 ($\kappa = 1.3$)	0.14
κMP2 ($\kappa = \infty$)	0.28
CCSD	0.068
CCSD(T)	0.127
Expt.	0.122

The key to understanding these trends lies in the molecular orbital (MO) diagram (Fig. 5) and the relative composition of the MOs (Table 5).
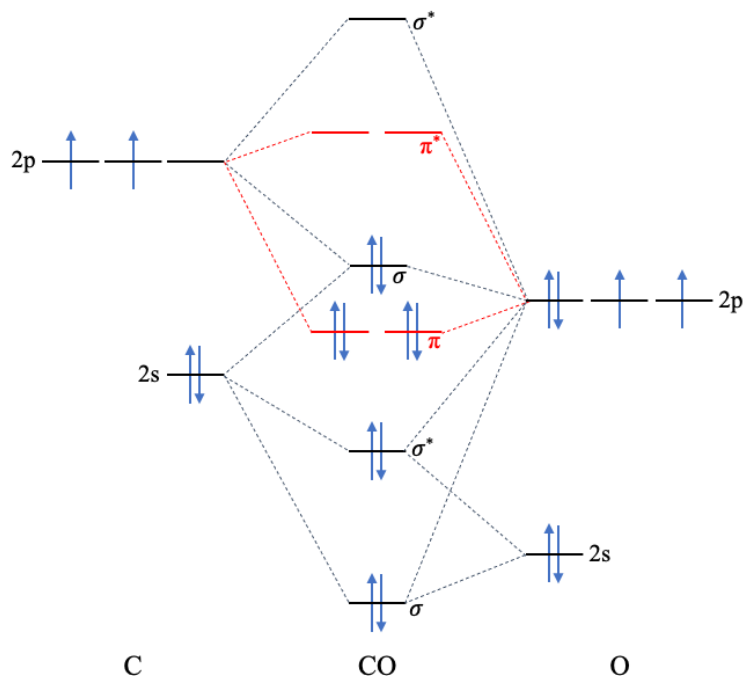
Figure 5: Molecular orbital diagram of the CO molecule, excluding 1s atomic orbital contributions (see the Supporting Information for quantitative orbital energies). Two-electron excitations from π to π^* orbitals corresponds to partial charge-transfer from O to C, and the effective raising in energy of the latter due to energy-gap-dependent regularization reduces the extent of charge transfer in the dative bond, thereby counteracting the overestimated dipole moment of conventional MP2.

Table 5: Molecular orbital number (bonding type), occupation number, energy eigenvalue [eV], and sum of Löwdin reduced orbital populations on C and O atoms [%], respectively (from left to right). Values from a HF/def2-QZVPP calculation, as performed in ORCA.[90]

MO index	Occ.	Energy	% C	%O
9 (σ^*)	0	5.0	**88.7**	11.3
8 (π^*)	0	3.1	**83.7**	16.1
7 (π^*)	0	3.1	**83.6**	15.9
6 (σ)	2	-15.1	**85.3**	14.6
5 (π)	2	-17.3	34.2	**65.6**
4 (π)	2	-17.3	34.2	**65.5**
3 (σ^*)	2	-21.9	19.3	**80.7**
2 (σ)	2	-41.3	43.7	**56.1**

With the exception of the highest occupied MO (index 6, σ), all occupied MOs are predominately derived from the atomic orbitals of the oxygen, while all virtual MOs are mostly

derived from those of the carbon. If only the configuration shown in the MO diagram is used to derive the charge density, as is done in HF theory, it is no surprise that the negative end of the dipole moment will incorrectly reside on the oxygen. In contrast, the conventional MP2 density will have sizable contributions from doubly-substituted configurations wherein electrons are excited from the occupied to virtual HF MOs. Due to the composition of these orbitals, this dynamical correlation provides some description of dative bonding from the O to the C, with the amplitudes controlling the extent of charge-transfer.

We can understand on physical grounds why a theory which dynamically correlates only two electrons at a time in a pair-wise additive way overestimates such amplitudes as follows. A pair excitation creates two holes and two particles, all of which polarize the surrounding electrons; however, MP2 cannot describe these higher-order polarization effects. Furthermore, simultaneous pair excitations can be non-negligible in these systems (e.g. a quadruple excitation involving π and π^* orbitals, both of which are doubly degenerate), but in a pair-wise additive description of each pair excitation will not adequately "feel" the instantaneous presence of the other electron pairs in the vicinity of the carbon. These effects must be relatively strong given that multiple σ and π electron pairs are confined to a relatively localized bonding region.

Hence, we find again that higher-order correlation effects will tend to reduce first-order amplitudes, and in the specific case of CO their inclusion will moderate the extent of electron donation from O to C. Indeed, the dipole moments predicted from infinite-order theories, CCSD and CCSD(T), are attenuated vs that of conventional MP2 (Table 4). This implies an effective picture in which the virtual MOs populated in the 1st-order wavefunction are too low in energy due to the exclusion of higher-order dynamical correlations. In this context regularization of MP2 first-order amplitudes acts to raise the virtual MOs higher in energy, in accordance with the physics of Pauli repulsion.

Table 4 shows that the optimal κ value for the dipole moment of carbon monoxide is

between 1.2 and 1.3 (depending on whether CCSD(T) or experiment is taken as the point of comparison). This optimal range for the dipole moment is close but not equal to the optimal κ value of 0.9 determined above for metal-carbonyl thermochemistry (Table 1). This suggests that only part of MP2's overestimation of M-CO bond strengths can be attributed to the exaggerated attractive electrostatic contribution to the metal-carbon bond that arises from the overestimated dipole moment of isolated CO. The M-CO bond, like the CO bond, is also a dative bond involving ligand-to-metal σ donation and metal-to-ligand π-backbonding. While an MO analysis is more complicated for the full metal complex (and we omit it here), the same physical effects discussed above are operative. We will just note that regularization pushes up the overstabilized antibonding π^* orbitals, which weakens π-backbonding and serves to destabilize the M-CO bond. MP2's overestimation of the metal-dihydrogen bond is likely due to the overestimated charge-density on the metal which is available to strengthen the metal-dihydrogen bond via π back-donation.

The fact that the HOMO-LUMO gap of isolated CO is 18.5 eV (i.e. very large relative to the average values for the metal complexes and NCI dimers above) should serve to reiterate that regularization does more than tame divergent small gap contributions to the correlation energy or 1st-order wavefunction. We find that it provides an appropriate description of dative bonding both within isolated ligands like CO and between metal and π-donating or -accepting ligands. More generally, appropriate regularization attempts to semi-empirically correct deficiencies due to the pair-wise additive form of the MP2 correlation energy, which can lead to overestimated interactions in both collective, π-driven NCIs and TM bonding in many organometallic systems. Both involve strong, dynamical interactions between multiple electron pairs, and therefore require (at least approximate) incorporation of beyond-2nd-order diagrams. (It is no surprise that the direct random phase approximation, which contains bubble diagrams to infinite order in many-body PT, performs much better than MP2 for NCI sets such as L7[42] and TM chemistry[91,92]). In summary, regularization

enables higher-order correlation effects to be incorporated effectively, and at MP2 cost, into a second-order theory, by damping first-order amplitudes that are artificially overestimated at the level of MP2 theory.

5.2.3   Main group thermochemistry, barrier heights, dipoles and polarizabilities

In this section we investigate the effect of regularization on main-group thermochemistry (W411) and selected properties that are known to be sensitive to a theory's rendering of the charge-distribution, namely radical stabilization energies (RSE43), barrier heights (HTBH38, NHTBH38), dipole moments and polarizabilities. We preface this section by noting that only small molecules are considered, due to the use of full CCSD(T) values extrapolated to the CBS limit, and thus conclusions can only be drawn for this restricted class of systems. For the electric properties we include only the non-spin-polarized subsets, for which R to U instabilities are not present. The resulting RMSDs and RMSRDs as a function of regularization parameter are shown for κ- and σ^2-MP2 in Tables 6 and 7, respectively.

Table 6: RMSDs [kcal/mol] (and RMSRD [%] for electric properties) for main group thermochemistry – W4-11 and RSE43 – and sets which are particularly sensitive to the electron density distribution – HTBH38 and NHTBH38 (barrier heights), dipole moments, and polarizabilities – from κMP2 over a range of κ values.

κMP2	W4-11	RSE43	HTBH38	NHTBH38	Dipoles	Polarizabilities
0 (HF)	55.72	4.92	19.07	16.14	12.07	6.93
1	9.65	1.43	6.94	6.45	7.51	5.91
1.1	9.08	1.33	6.47	5.81	6.82	5.53
1.2	8.71	1.24	6.09	5.27	6.24	5.19
1.3	8.50	1.16	5.79	4.81	5.75	4.89
1.4	8.38	1.10	5.55	4.41	5.34	4.61
1.45	8.34	1.07	5.44	4.24	5.17	4.49
1.5	8.32	1.04	5.35	4.08	5.01	4.37
1.6	8.31	0.99	5.20	3.81	4.73	4.16
∞(MP2)	8.73	0.77	4.64	2.55	3.60	2.17

Table 7: RMSDs [kcal/mol] (and RMSRD [%] for electric properties) for main group thermochemistry – W4-11 and RSE43 – and sets which are particularly sensitive to the electron density distribution – HTBH38 and NHTBH38 (barrier heights), dipole moments, and polarizabilities – from σ^2MP2 over a range of σ values.

σ^2MP2	W4-11	RSE43	HTBH38	NHTBH38	Dipoles	Polarizabilities
0 (HF)	55.72	4.92	19.07	16.14	12.07	6.93
0.4	9.90	1.49	6.71	6.39	7.85	6.41
0.6	9.02	1.22	5.62	4.70	6.17	5.37
0.8	8.77	1.06	5.12	3.76	5.27	4.69
1.0	8.71	0.95	4.87	3.24	4.75	4.24
1.2	8.70	0.88	4.75	2.94	4.42	3.92
1.4	8.71	0.84	4.68	2.78	4.21	3.69
∞(MP2)	8.73	0.77	4.64	2.55	3.60	2.17

W4-11 is the only test set for which any choice of regularization improves upon conventional MP2, yet with $\kappa = 1.1$ and $\sigma = 0.4$ (the optimal values for the NCI and TM sets) the RMSDs are slightly worse at 9.08 and 9.90 kcal/mol (vs 8.73 kcal/mol for conventional MP2). This choice of κ worsens the MP2 accuracy by factors of 1.7, 1.4, 2.3, 1.9, and 2.5 for RSE43, HTBH38, NHTBH38, dipoles, and polarizabilities, respectively. That said, the absolute deviations from conventional MP2 are only 0.56, 1.83, and 3.27 kcal/mol; and 3.22 and 3.37 percentage points for the respective test sets. For $\sigma = 0.4$, these factors are equal or slightly larger, at 1.9, 1.4, 2.5, 2.2, and 3.0.

No significant correlation was found between the average HOMO-LUMO gap (of all species) and the ratio of the RMS(R)Ds from regularized vs conventional MP2, yet we point out that the HOMO-LUMO gaps, respectively, are 13.4, 11.8, 14.3, 12.5, 12.4, and 13.1 eV for W411, RSE43, HTBH38, NHTBH38, dipoles, and polarizabilities. Compared to the NCI sets for which regularization yielded very large improvements, such as S22 and L7, these gaps are relatively large, with the possible exception of RSE43 (whose gap lies between those of S66 and XB40).

It is clear that regularizing MP2 first-order amplitudes can affect the accuracy of the predicted charge-density distribution, for better or worse. The case of CO (Table 4) provides

an example of a substantial improvement. We now focus on the hydrogen fluoride molecule (FH), to investigate a representative case from the dipole moment set for which regularization worsens MP2's prediction (albeit only slightly and quite slowly with increasing regularization strength).

Table 8: Dipole moment in Debye as a function of κ regularization parameter for the FH molecule, in the aug-cc-pVTZ basis. $\kappa = 0$ corresponds to HF theory, and $\kappa \to \infty$ corresponds to conventional MP2 theory.

Method	Dipole Moment	% dev. CCSD
κMP2 ($\kappa = 0$)	1.93	6.3
κMP2 ($\kappa = 0.7$)	1.88	4.0
κMP2 ($\kappa = 0.8$)	1.87	3.3
κMP2 ($\kappa = 0.9$)	1.86	2.7
κMP2 ($\kappa = 1.0$)	1.85	2.2
κMP2 ($\kappa = 1.1$)	1.84	1.8
κMP2 ($\kappa = 1.2$)	1.84	1.4
κMP2 ($\kappa = 1.3$)	1.83	1.1
κMP2 ($\kappa = \infty$)	1.80	0.4
CCSD	1.81	
CCSD(T)	1.79	

In light of our previous analysis, showing that MP2 overcorrelates π interactions both in the context of stacked NCIs and dative bonding involving multiple electron pairs, we immediately notice that the bonding in FH is purely covalent, and that there are no π-interactions. Furthermore, FH contains only one bonding orbital in its valence shell, involving correlations between two electrons. MP2 is tailor-made for this type of σ-bonding, and the shift from the MP2 prediction toward that from HF (which, in effect, is what is accomplished via intermediate regularization strengths) is relatively small vs the shift that occurs for the dipole of CO, and certainly counterproductive in terms of accuracy. We also note that although FH has the same HOMO-LUMO gap as CO (18.5 eV), the LUMO of FH is a Rydberg orbital (while the HOMO is of π symmetry) which implies that the first-order amplitude corresponding to the HOMO to LUMO transition is small on the grounds of a small numerator. Therefore the relevant frontier gap is likely to be larger than that of CO,

hence the accuracy of conventional MP2.

6   Conclusions

κ and σ^2 MP2 regularization have been shown to be viable models for a wide variety of non-covalent interactions, (typically closed shell) transition metal reactions, and main-group thermochemistry as represented by the W4-11 set. The energy-gap dependent forms are physically justifiable, in contrast to the spin-component-scaled or attenuated MP2 models. Overestimated MP2 first-order amplitudes (vs infinite-order theories) are more prominent for smaller orbital energy gaps, and in situations where the neglect of inter-electron-pair correlations is especially consequential. We find, quite generally, that interacting π systems fit this bill, both in the context of dispersion interactions between stacked, polarizable monomers and dative bonding that involves the dynamical correlation of more than one pair of electrons in a small region of space in that leading first-order amplitudes are overestimated. Energy-gap dependent regularizers attenuate those overestimated first-order amplitudes and significantly improve the description of dispersion-bound complexes and dative bonds.

Comparing κ and σ^2 regularizers, similar improvements in statistical accuracy over conventional MP2 can be obtained. Considering the range of data presented here, we recommend $\kappa = 1.1$ and $\sigma = 0.4$. From the standpoint of ease of implementing nuclear gradients and other properties, we think there is some advantage to κ-based regularization,[60] although the σ^2-MP2 gradient has also been successfully implemented.[59] More broadly, the exploration of other computationally tractable energy-gap-dependent regularization forms would be worthwhile in the future: could even better results be obtained? Likewise, a regularizer whose strength depends on the magnitude of the amplitudes directly is an interesting option to explore though the implementation of molecular properties could be challenging.

The presently-investigated approaches to regularizing MP2 can also be understood as

an interpolation between zero- and infinite-valued limits of the regularization parameter, representing HF and conventional MP2, respectively. Regularization is, then, most effective when HF underestimates and conventional MP2 overestimates – conditions which are satisfied with relatively small HOMO-LUMO gaps and/or collective π-electron effects (as beautifully exemplified in S22, L7, and the TM sets). The good correlation (Fig. 3) between the average HOMO-LUMO gap and the change in accuracy relative to conventional MP2 implies that we can expect systems with gaps larger than some threshold to be worsened by κ or σ^2 regularization. This was predicted from the trend in the NCI sets shown in Fig. 3. Another thing to note is that RSE43 and the other sets which are degraded by regularization incidentally are known to be very sensitive to the charge-density distribution, namely electric dipole moments and polarizabilities, radical stabilization energies, and barrier heights.

In a previous work on regularized orbital optimized MP2,[60] $\kappa = 1.45$ was recommended based on training by only the W4-11 set, in addition to requiring Coulson-Fischer points to occur at shorter bond distances going from C_2H_6 to C_2H_4 to C_2H_2. Our present work reveals that while this value is roughly optimal for the W4-11 set, a significantly smaller value of 1.1, corresponding to stronger regularization, is recommended for most NCI and TM sets while no regularization may be preferable for systems with very large HF energy gaps (e.g. > 12.4 eV). It will be interesting and useful to carefully revisit the optimal choice of κ for κ-OOMP2 in light of the results presented here, as well as in light of the use of that method for distinguishing artificial and essential symmetry-breaking.[26] We hope to report a study that addresses this question in due course.

Our group has previously shown that orbital choice is important in both perturbative and coupled-cluster approaches.[36,68,93,94] In this context, it is rather remarkable that for the cases investigated presently the use of HF orbitals leads to excellent results in the context of regularized MP2.

Finally, another significant step forward that we would like to emphasize is our use of

TM systems along with standard main-group test sets on the same footing. The majority of (mono-metal) TM complexes do not exhibit static correlation, and in our view there is no reason such systems should not be included in training sets for the development of quantum chemical methods such as regularized MP2. A second point is that our findings challenge the commonly accepted assumption that second-order PT is generally unsuitable for transition metals, as regularization largely eliminates the drastic errors previously found for systems such as metal-carbonyl complexes (and those with metal-ethene bonds which also represented large errors in the MOR39 set). Furthermore, 2-3 fold reductions in statistical errors in the MOR39 and MCO9 sets with κMP2 (or σ^2MP2) can be obtained with the same regularization parameter that is simultaneously nearly optimal for NCI sets such as S22 and L7. That said, we realize that closed-shell systems are not representative of the whole of TM chemistry, and are investigating the κ and σ^2 regularization for species with higher and/or changing spin multiplicities.

We are optimistic that this study could pave the way for future development of double-hybrid density functionals based on nonlocal correlation expressions that are more appropriate than conventional MP2 for large dispersion-bound systems and organometallic bonding, yet still free of self-correlation errors. κMP2 and σ^2MP2 are promising candidates in this regard. It is also interesting to examine orbital optimized MP2 for open and closed shell TM systems with the stronger regularization parameter that this work shows is necessary. We hope to report on this in due course.

7 Acknowledgements

References

(1) Cremer, D. Moller-Plesset perturbation theory: from small molecule methods to methods for thousands of atoms. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2011**, *1*, 509–530.

(2) Bartlett, R. J.; Musial, M. Coupled-cluster theory in quantum chemistry. *Rev. Mod. Phys.* **2007**, *79*, 291–352.

(3) Bartlett, R. J. Coupled-cluster theory and its equation-of-motion extensions. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 126–138.

(4) Goerigk, L.; Grimme, S. Double-hybrid density functionals. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2014**, *4*, 576–600.

(5) Mardirossian, N.; Head-Gordon, M. Survival of the most transferable at the top of Jacob's ladder: Defining and testing the ωB97M(2) double hybrid density functional. *J. Chem. Phys.* **2018**, *148*, 241736.

(6) Martin, J. M. L.; Santra, G. Empirical double-hybrid density functional theory: A 'third way' in between WFT and DFT. *Isr. J. Chem.* **2020**, *60*, 787–804.

(7) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; John Wiley & Sons, 2000.

(8) Goldey, M.; Dutoi, A.; Head-Gordon, M. Attenuated second order Moller-Plesset theory: Assessment and performance in the aug-cc-pVTZ basis. *Phys. Chem. Chem. Phys.* **2013**, *15*, 15869.

(9) Fanourgakis, G. S.; Apra, E.; Xantheas, S. S. High-level ab initio calculations for the four low-lying families of minima of (H 2 O) 20. I. Estimates of MP2/CBS binding energies and comparison with empirical potentials. *J. Chem. Phys.* **2004**, *121*, 2655–2663.

(10) Yoo, S.; Apra, E.; Zeng, X. C.; Xantheas, S. S. High-level ab initio electronic structure calculations of water clusters (H2O) 16 and (H2O) 17: A new global minimum for (H2O) 16. *J. Phys. Chem. Lett.* **2010**, *1*, 3122–3127.

(11) Hait, D.; Head-Gordon, M. How accurate is density functional theory at predicting dipole moments? An assessment using a new database of 200 benchmark values. *J. Chem. Theory Comput.* **2018**, *14*, 1969–1981.

(12) Hait, D.; Head-Gordon, M. How accurate are static polarizability predictions from density functional theory? An assessment over 132 species at equilibrium geometry. *Phys. Chem. Chem. Phys.* **2018**, *20*, 19800–19810.

(13) Zhang, Y.; Yang, W. A challenge for density functionals: Self-interaction error increases for systems with a noninteger number of electrons. *J. Chem. Phys.* **1998**, *109*, 2604–2608.

(14) Mori-Sánchez, P.; Cohen, A. J.; Yang, W. Many-electron self-interaction error in approximate density functionals. *J. Chem. Phys.* **2006**, *125*, 201102.

(15) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A fifth-order perturbation comparison of electron correlation theories. *Chem. Phys. Lett.* **1989**, *157*, 479.

(16) Small, D. W.; Head-Gordon, M. Post-modern valence bond theory for strongly correlated electron spins. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19285–19297.

(17) Head-Gordon, M. Characterizing unpaired electrons from the one-particle density matrix. *Chem. Phys. Lett.* **2003**, *372*, 508.

(18) Grimme, S.; Hansen, A. A Practicable Real-Space Measure and Visualization of Static Electron-Correlation Effects. *Angew. Chem. Int. Ed.* **2015**, *54*, 12308–12313.

(19) Shee, J.; Loipersberger, M.; Hait, D.; Lee, J.; Head-Gordon, M. Revealing the nature of electron correlation in transition metal complexes with symmetry breaking and chemical intuition. *J. Chem. Phys.* **2021**, *154*, 194109.

(20) Park, J. W.; Al-Saadon, R.; MacLeod, M. K.; Shiozaki, T.; Vlaisavljevich, B. Multireference electron correlation methods: Journeys along potential energy surfaces. *Chem. Rev.* **2020**, *120*, 5878–5909.

(21) Booth, G. H.; Thom, A. J.; Alavi, A. Fermion Monte Carlo without fixed nodes: A game of life, death, and annihilation in Slater determinant space. *J. Chem. Phys.* **2009**, *131*, 054106.

(22) Chan, G. K.-L.; Sharma, S. The density matrix renormalization group in quantum chemistry. *Annu. Rev. Phys. Chem.* **2011**, *62*, 465–481.

(23) Tubman, N. M.; Lee, J.; Takeshita, T. Y.; Head-Gordon, M.; Whaley, K. B. A deterministic alternative to the full configuration interaction quantum Monte Carlo method. *J. Chem. Phys.* **2016**, *145*, 044112.

(24) Sharma, S.; Holmes, A. A.; Jeanmairet, G.; Alavi, A.; Umrigar, C. J. Semistochastic heat-bath configuration interaction method: Selected configuration interaction with semistochastic perturbation theory. *J. Chem. Theory Comput.* **2017**, *13*, 1595–1604.

(25) Shee, J.; Rudshteyn, B.; Arthur, E. J.; Zhang, S.; Reichman, D. R.; Friesner, R. A. On Achieving High Accuracy in Quantum Chemical Calculations of 3 d Transition Metal-Containing Systems: A Comparison of Auxiliary-Field Quantum Monte Carlo with Coupled Cluster, Density Functional Theory, and Experiment for Diatomic Molecules. *J. Chem. Theory Comput.* **2019**, *15*, 2346–2358.

(26) Lee, J.; Head-Gordon, M. Distinguishing artificial and essential symmetry breaking in a single determinant: Approach and application to the C_{60}, C_{36}, and C_{20} fullerenes. *Phys. Chem. Chem. Phys.* **2019**, *21*, 4763–4768.

(27) Handy, N.; Knowles, P.; Somasundram, K. On the convergence of the Møller-Plesset perturbation series. *Theor. Chem. Acc.* **1985**, *68*, 87–100.

(28) Hubač, I.; Čársky, P. Correlation energy of open-shell systems. Application of the many-body Rayleigh-Schrödinger perturbation theory in the restricted Roothaan-Hartree-Fock formalism. *Phys. Rev. A* **1980**, *22*, 2392–2399.

(29) Murray, C.; Davidson, E. R. Perturbation theory for open shell systems. *Chem. Phys. Lett.* **1991**, *187*, 451 – 454.

(30) Lauderdale, W. J.; Stanton, J. F.; Gauss, J.; Watts, J. D.; Bartlett, R. J. Many-body perturbation theory with a restricted open-shell Hartree-Fock reference. *Chem. Phys. Lett.* **1991**, *187*, 21 – 28.

(31) Amos, R. D.; Andrews, J. S.; Handy, N. C.; Knowles, P. J. Open-shell Møller–Plesset perturbation theory. *Chem. Phys. Lett.* **1991**, *185*, 256 – 264.

(32) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. Restricted Møller–Plesset theory for open-shell molecules. *Chem. Phys. Lett.* **1991**, *186*, 130 – 136.

(33) Lee, T. J.; Jayatilaka, D. An open-shell restricted Hartree-Fock perturbation theory based on symmetric spin orbitals. *Chem. Phys. Lett.* **1993**, *201*, 1 – 10.

(34) Neese, F.; Schwabe, T.; Kossmann, S.; Schirmer, B.; Grimme, S. Assessment of orbital-optimized, spin-component scaled second-order many-body perturbation theory for thermochemistry and kinetics. *J. Chem. Theory Comput.* **2009**, *5*, 3060–3073.

(35) Lochan, R. C.; Head-Gordon, M. Orbital-optimized opposite-spin scaled second-order correlation: An economical method to improve the description of open-shell molecules. *J. Chem. Phys.* **2007**, *126*, 164101.

(36) Rettig, A.; Hait, D.; Bertels, L. W.; Head-Gordon, M. Third-order Møller–Plesset theory made more useful? The role of density functional theory orbitals. *J. Chem. Theory Comput.* **2020**, *16*, 7473–7489.

(37) Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. Estimates of the ab initio limit for π- π interactions: The benzene dimer. *J. Am. Chem. Soc.* **2002**, *124*, 10887–10893.

(38) Jaffe, R. L.; Smith, G. D. A quantum chemistry study of benzene dimer. *J. Chem. Phys.* **1996**, *105*, 2780–2788.

(39) Hobza, P.; Selzle, H. L.; Schlag, E. W. Potential energy surface for the benzene dimer. Results of ab initio CCSD (T) calculations show two nearly isoenergetic structures: T-shaped and parallel-displaced. *J. Phys. Chem.* **1996**, *100*, 18790–18794.

(40) Tsuzuki, S.; Uchimaru, T.; Matsumura, K.; Mikami, M.; Tanabe, K. Effects of the higher electron correlation correction on the calculated intermolecular interaction en-

ergies of benzene and naphthalene dimers: comparison between MP2 and CCSD (T) calculations. *Chem. Phys. Lett.* **2000**, *319*, 547–554.

(41) Jurečka, P.; Šponer, J.; Černỳ, J.; Hobza, P. Benchmark database of accurate (MP2 and CCSD (T) complete basis set limit) interaction energies of small model complexes, DNA base pairs, and amino acid pairs. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.

(42) Nguyen, B. D.; Chen, G. P.; Agee, M. M.; Burow, A. M.; Tang, M. P.; Furche, F. Divergence of many-body perturbation theory for noncovalent interactions of large molecules. *J. Chem. Theory Comput.* **2020**, *16*, 2258–2273.

(43) Temelso, B.; Archer, K. A.; Shields, G. C. Benchmark structures and binding energies of small water clusters with anharmonicity corrections. *J. Phys. Chem. A* **2011**, *115*, 12034–12046.

(44) Šponer, J.; Hobza, P. MP2 and CCSD (T) study on hydrogen bonding, aromatic stacking and nonaromatic stacking. *Chem. Phys. Lett.* **1997**, *267*, 263–270.

(45) Thirman, J.; Head-Gordon, M. Electrostatic domination of the effect of electron correlation in intermolecular interactions. *J. Phys. Chem. Lett.* **2014**, *5*, 1380–1385.

(46) Dohm, S.; Hansen, A.; Steinmetz, M.; Grimme, S.; Checinskii, M. P. Comprehensive thermochemical benchmark set of realistic closed-shell metal organic reactions. *J. Chem. Theory Comput.* **2018**, *14*, 2596–2608.

(47) Loipersberger, M.; Cabral, D. G. A.; Chu, D. B. K.; Head-Gordon, M. Mechanistic insights into Co and Fe quaterpyridine-based CO_2 reduction catalysts: Metal–ligand orbital interaction as the key driving force for distinct pathways. *J. Am. Chem. Soc.* **2021**, *143*, 744–763.

(48) Grimme, S. Improved second-order Møller–Plesset perturbation theory by separate scaling of parallel-and antiparallel-spin pair correlation energies. *J. Chem. Phys.* **2003**, *118*, 9095–9102.

(49) Grimme, S. Accurate Calculation of the Heats of Formation for Large Main Group Compounds with Spin-Component Scaled MP2 Methods. *J. Phys. Chem. A* **2005**, *109*, 3067.

(50) DiStasio, Jr., R. A.; Head-Gordon, M. Optimized spin-component scaled second-order Møller-Plesset perturbation theory for intermolecular interaction energies. *Mol. Phys.* **2007**, *105*, 1073.

(51) Jung, Y.; Lochan, R. C.; Dutoi, A. D.; Head-Gordon, M. Scaled opposite-spin second order Møller–Plesset correlation energy: an economical electronic structure method. *J. Chem. Phys.* **2004**, *121*, 9793.

(52) Lochan, R. C.; Shao, Y.; Head-Gordon, M. Quartic-scaling analytical energy gradient of scaled opposite-spin second-order Møller–Plesset perturbation theory. *J. Chem. Theory Comput.* **2007**, *3*, 988–1003.

(53) Urban, L.; Thompson, T.; Ochsenfeld, C. A scaled explicitly correlated F12 correction to second-order Møller–Plesset perturbation theory. *J. Chem. Phys* **2021**, *154*, 044101.

(54) Goldey, M.; Head-Gordon, M. Attenuating away the errors in inter- and intramolecular interactions from second-order Møller–Plesset calculations in the small aug-cc-pVDZ basis set. *J. Phys. Chem. Lett.* **2012**, *3*, 3592–3598.

(55) Goldey, M.; Head-Gordon, M. Separate electronic attenuation allowing a spin-component-scaled second-order Møller–Plesset theory to be effective for both thermochemistry and noncovalent interactions. *J. Phys. Chem. B* **2014**, *118*, 6519–6525.

(56) Goldey, M. B.; Belzunces, B.; Head-Gordon, M. Attenuated MP2 with a long-range dispersion correction for treating nonbonded interactions. *J. Chem. Theory Comput.* **2015**, *11*, 4159–4168.

(57) Ren, X.; Rinke, P.; Scuseria, G. E.; Scheffler, M. Renormalized second-order perturbation theory for the electron correlation energy: Concept, implementation, and benchmarks. *Phys. Rev. B* **2013**, *88*, 035120.

(58) Evangelista, F. A. A driven similarity renormalization group approach to quantum many-body problems. *J. Chem. Phys.* **2014**, *141*, 054109.

(59) Wang, S.; Li, C.; Evangelista, F. A. Analytic gradients for the single-reference driven similarity renormalization group second-order perturbation theory. *J. Chem. Phys.* **2019**, *151*, 044118.

(60) Lee, J.; Head-Gordon, M. Regularized orbital-optimized second-order Møller–Plesset perturbation theory: A reliable fifth-order-scaling electron correlation model with orbital energy dependent regularizers. *J. Chem. Theory Comput.* **2018**, *14*, 5203–5219.

(61) Raghavachari, K.; Pople, J. A.; Replogle, E. S.; Head-Gordon, M. Fifth order Moeller-Plesset perturbation theory: comparison of existing correlation methods and implementation of new methods correct to fifth order. *Journal of Physical Chemistry* **1990**, *94*, 5579–5586.

(62) Stück, D.; Head-Gordon, M. Regularized orbital-optimized second-order perturbation theory. *J. Chem. Phys.* **2013**, *139*, 244109.

(63) Sharada, S. M.; Stück, D.; Sundstrom, E. J.; Bell, A. T.; Head-Gordon, M. Wavefunction stability analysis without analytical electronic hessians: Application to orbital-optimized post-Hartree-Fock methods and VV10-containing density functionals. *Mol. Phys.* **2015**, *113*, 1802.

(64) Razban, R. M.; Stück, D.; Head-Gordon, M. Addressing first derivative discontinuities in orbital-optimised opposite-spin scaled second-order perturbation theory with regularisation. *Mol. Phys.* **2017**, *115*, 21029.

(65) Almlöf, J. Elimination of energy denominators in Møller—Plesset perturbation theory by a Laplace transform approach. *Chem. Phys. Lett.* **1991**, *181*, 319–320.

(66) Lee, J.; Head-Gordon, M. Two single-reference approaches to singlet biradicaloid problems: Complex, restricted orbitals and approximate spin-projection combined with regularized orbital-optimized Møller-Plesset perturbation theory. *J. Chem. Phys.* **2019**, *150*, 244106.

(67) Bertels, L. W.; Lee, J.; Head-Gordon, M. Third-order Møller–Plesset perturbation theory made useful? Choice of orbitals and scaling greatly improves accuracy for thermochemistry, kinetics, and intermolecular interactions. *J. Phys. Chem. Lett.* **2019**, *10*, 4170–4176.

(68) Bertels, L. W.; Lee, J.; Head-Gordon, M. Polishing the Gold Standard: The Role of Orbital Choice in CCSD (T) Vibrational Frequency Prediction. *J. Chem. Theory Comput.* **2020**,

(69) Rezác, J.; Riley, K. E.; Hobza, P. S66: A well-balanced database of benchmark interaction energies relevant to biomolecular structures. *J. Chem. Theory Comput.* **2011**, *7*, 2427–2438.

(70) Rezac, J.; Riley, K. E.; Hobza, P. Benchmark calculations of noncovalent interactions of halogenated molecules. *J. Chem. Theory Comput.* **2012**, *8*, 4285–4292.

(71) Rezac, J.; Hobza, P. Describing noncovalent interactions beyond the common approximations: How accurate is the "gold standard," CCSD (T) at the complete basis set limit? *J. Chem. Theory Comput.* **2013**, *9*, 2151–2155.

(72) Sedlak, R.; Janowski, T.; Pitonak, M.; Rezac, J.; Pulay, P.; Hobza, P. Accuracy of quantum chemical methods for large noncovalent complexes. *J. Chem. Theory Comput.* **2013**, *9*, 3364–3374.

(73) Al-Hamdani, Y. S.; Nagy, P. R.; Zen, A.; Barton, D.; Kállay, M.; Brandenburg, J. G.; Tkatchenko, A. Interactions between large molecules pose a puzzle for reference quantum mechanical methods. *Nat. Commun.* **2021**, *12*, 1–12.

(74) Benali, A.; Shin, H.; Heinonen, O. Quantum Monte Carlo benchmarking of large noncovalent complexes in the L7 benchmark set. *J. Chem. Phys.* **2020**, *153*, 194113.

(75) Carter-Fenk, K.; Lao, K. U.; Liu, K.-Y.; Herbert, J. M. Accurate and efficient ab initio calculations for supramolecular complexes: Symmetry-adapted perturbation theory with many-body dispersion. *J. Phys. Chem. Lett.* **2019**, *10*, 2706–2714.

(76) Rudshteyn, B.; Coskun, D.; Weber, J. L.; Arthur, E. J.; Zhang, S.; Reichman, D. R.; Friesner, R. A.; Shee, J. Predicting ligand-dissociation energies of 3d coordination complexes with auxiliary-field quantum Monte Carlo. *J. Chem. Theory Comput.* **2020**, *16*, 3041–3054.

(77) Karton, A.; Daon, S.; Martin, J. M. W4-11: A high-confidence benchmark dataset for computational thermochemistry derived from first-principles W4 data. *Chem. Phys. Lett.* **2011**, *510*, 165–178.

(78) Goerigk, L.; Hansen, A.; Bauer, C.; Ehrlich, S.; Najibi, A.; Grimme, S. A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions. *Phys. Chem. Chem. Phys.* **2017**, *19*, 32184–32215.

(79) Zipse, H. Radical stability—a theoretical perspective. *Radicals in Synthesis I* **2006**, 163–189.

(80) Helgaker, T.; Gauss, J.; Jorgensen, P.; Olsen, J. Basis-set convergence of correlated calculations on water. *J. Chem. Phys.* **1997**, *106*, 6430.

(81) Feyereisen, M.; Fitzgerald, G.; Komornicki, A. Use of approximate integrals in ab initio theory. An application in MP2 energy calculations. *Chem. Phys. Lett.* **1993**, *208*, 359–363.

(82) Epifanovsky, E.; Gilbert, A. T.; Feng, X.; Lee, J.; Mao, Y.; Mardirossian, N.; Pokhilko, P.; White, A. F.; Coons, M. P.; Dempwolff, A. L., et al. Software for the frontiers of quantum chemistry: An overview of developments in the Q-Chem 5 package. *J. Chem. Phys.* **2021**, *155*, 084801.

(83) Janowski, T.; Pulay, P. A Benchmark Comparison of σ/σ and π/π Dispersion: the Dimers of Naphthalene and Decalin, and Coronene and Perhydrocoronene. *J. Am. Chem. Soc.* **2012**, *134*, 17520–17525.

(84) Szabo, A.; Ostlund, N. S. The correlation energy in the random phase approximation: Intermolecular forces between closed-shell systems. *J. Chem. Phys.* **1977**, *67*, 4351–4360.

(85) Chałasiński, G.; Szcześniak, M. On the connection between the supermolecular Møller-Plesset treatment of the interaction energy and the perturbation theory of intermolecular forces. *Mol. Phys.* **1988**, *63*, 205–224.

(86) Tkatchenko, A.; DiStasio Jr, R. A.; Head-Gordon, M.; Scheffler, M. Dispersion-corrected Møller–Plesset second-order perturbation theory. *J. Chem. Phys.* **2009**, *131*, 094106.

(87) Stone, A. *The theory of intermolecular forces*; Oxford University Press, 2013.

(88) Casimir, H. B.; Polder, D. The influence of retardation on the London-van der Waals forces. *Phys. Rev.* **1948**, *73*, 360.

(89) Scuseria, G. E.; Miller, M. D.; Jensen, F.; Geertsen, J. The dipole moment of carbon monoxide. *J. Chem. Phys.* **1991**, *94*, 6660–6663.

(90) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA quantum chemistry program package. *J. Chem. Phys.* **2020**, *152*, 224108.

(91) Bates, J.; Mezei, P.; Csonka, G.; Sun, J.; Ruzsinszky, A. Reference determinant dependence of the random phase approximation in 3 d transition metal chemistry. *J. Chem. Theory Comput.* **2017**, *13*, 100–109.

(92) Waitt, C.; Ferrara, N. M.; Eshuis, H. Thermochemistry and geometries for transition-metal chemistry from the random phase approximation. *J. Chem. Theory Comput.* **2016**, *12*, 5350–5360.

(93) Beran, G. J.; Gwaltney, S. R.; Head-Gordon, M. Approaching closed-shell accuracy for radicals using coupled cluster theory with perturbative triple substitutions. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2488–2493.

(94) Bertels, L. W.; Lee, J.; Head-Gordon, M. Third-Order Møller–Plesset Perturbation Theory Made Useful? Choice of Orbitals and Scaling Greatly Improves Accuracy for Thermochemistry, Kinetics, and Intermolecular Interactions. *J. Phys. Chem. Lett.* **2019**, *10*, 4170–4176.