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# Optimizing the regularization in size-consistent second-order Brillouin-Wigner perturbation theory

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## ABSTRACT

Despite its simplicity and relatively low computational cost, second-order Møller-Plesset perturbation theory (MP2) is well-known to overbind noncovalent interactions between polarizable monomers and some organometallic bonds. In such situations, the pairwise-additive correlation energy expression in MP2 is inadequate. Although energy-gap dependent amplitude regularization can substantially improve the accuracy of conventional MP2 in these regimes, the same regularization parameter worsens the accuracy for small molecule thermochemistry and density-dependent properties. Recently, we proposed a repartitioning of Brillouin-Wigner perturbation theory that is size-consistent to second order (BW-s2), and a free parameter ( $\alpha$ ) was set to recover the exact dissociation limit of H<sub>2</sub> in a minimal basis set. Alternatively  $\alpha$  can be viewed as a regularization parameter, where each value of  $\alpha$  represents a valid variant of BW-s2, which we denote as BW-s2( $\alpha$ ). In this work, we semi-empirically optimize  $\alpha$  for noncovalent interactions, thermochemistry, alkane conformational energies, electronic response properties, and transition metal datasets, leading to improvements in accuracy relative to the *ab initio* parameterization of BW-s2 and MP2. We demonstrate that the optimal  $\alpha$  parameter ( $\alpha = 4$ ) is more transferable across chemical problems than energy-gap-dependent regularization parameters. This is attributable to the fact that the BW-s2( $\alpha$ ) regularization strength depends on all of the information encoded in the  $\mathbf{t}$  amplitudes rather than just orbital energy differences. While the computational scaling of BW-s2( $\alpha$ ) is iterative  $\mathcal{O}(N^5)$ , this effective and transferable approach to amplitude regularization is a promising route to incorporate higher-order correlation effects at second-order cost.

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## INTRODUCTION

Møller-Plesset perturbation theory (MP2) is a remarkable theoretical model chemistry with a simple pairwise additive form of the electron correlation energy and relatively low  $\mathcal{O}(N^5)$  compute cost scaling. It is the simplest *ab initio* theory that can approximately describe many forms of weak electron correlations, most notably dispersion but also short-ranged exchange effects. The correlation energy in the canonical molecular orbital basis can be written

$$E_c = -\frac{1}{4} \sum_{ijab} \frac{|\mathbb{I}_{ijab}|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} = -\frac{1}{4} \sum_{ijab} \frac{|\mathbb{I}_{ijab}|^2}{\Delta_{ij}^{ab}}, \quad (1)$$

where  $\mathbb{I}_{ijab} = (ij||ab)$  are antisymmetrized two-electron integrals and  $\epsilon_p$  is the  $p$ -th orbital eigenvalue. Throughout this text we apply the standard notation where  $\{i, j, k, \dots\}$  refer to occupied orbitals,  $\{a, b, c, \dots\}$  to unoccupied orbitals, and  $\{p, q, r, \dots\}$  to arbitrary (occupied or virtual) orbitals.

Formally, MP2 has many desirable properties. For example, it is free of delocalization errors, unlike the widely popular density

functional theory (DFT).<sup>1–3</sup> In contrast to both DFT and the direct random phase approximation (RPA),<sup>4</sup> there is no self-correlation error. Consistent with Pople's high standards for an approximate model chemistry<sup>5</sup> (at the heart of which are formal principles which are practically useful in chemical predictions), MP2 is size-consistent, size-extensive, and orbital invariant.<sup>6</sup> A model is size-consistent if the total energy of a supersystem comprised of noninteracting subsystems is the same as the sum of the energies of the isolated subsystems; this is an essential property when studying phenomena such as bond breaking. Second, a method is size-extensive if the total correlation energy in a linear chain of atoms grows linearly with number of electrons, which is essential for reaching the thermodynamic limit. Third, a method that yields the same correlation energy despite arbitrary orbital rotations in the occupied (or virtual) subspace is considered to be orbital invariant – a property that enables transformations to chemically-relevant bases such as the natural orbital or localized orbital representations.

MP2 routinely outperforms Hartree–Fock (HF) theory across myriad test sets with respect to experimental or near-exact numerical reference values.<sup>7</sup> The accuracy of MP2 can be very high in the case of closed-shell and small organic molecules, and can exceed the accuracy of popular DFT functionals for important chemical properties such as reaction barrier heights (which are sensitive to delocalization errors).<sup>8</sup> Indeed, MP2 is the most popular wavefunction component to be incorporated into double-hybrid density functionals, with promising results in many chemically-relevant situations.<sup>9–16</sup>

However, over the years many shortcomings of MP2 have been found. It is well-known that perturbation theory in general is not suitable for multi-reference states, in which higher order (connected) excitations are required for a qualitatively correct description of the wavefunction. In addition, MP2 (and even higher orders of perturbation theory) can fail in certain cases where the reference determinant is severely spin-contaminated.<sup>17–22</sup> In strongly correlated cases, this is a fatal issue; however, in weakly correlated systems, where the spin-symmetry breaking is artificial (i.e., due to deficiencies in the model chemistry's treatment of dynamic correlation), MP2 with a restricted open-shell (RO) reference determinant can at times remedy this situation.<sup>21</sup> Approximate Brueckner orbital approaches,<sup>23,24</sup> e.g., orbital optimized (MP2) methods,<sup>25–32</sup> can also clean up spin-symmetry breaking at the level of the Hartree–Fock orbitals.

Yet even after putting the above issues (stemming from multireference character and open-shell situations) aside, there are still serious difficulties that have historically limited the use and accuracy of MP2 approaches. For example, when bonds are stretched, the denominator of Eq. (1) can become zero, causing the correlation energy to diverge. This severely complicates the calculation of smooth potential energy surfaces. Interestingly, pair energies (corresponding to occupied orbitals  $i$  and  $j$ ) can be overestimated even at equilibrium geometries, most notably in the cases of dispersion-dominated noncovalent interaction energies (NC) among polarizable monomers (e.g., those with conjugated  $\pi$  systems)<sup>33–35</sup> and organometallic bonds involving, e.g., metal-carbonyl moieties.<sup>25,36,37</sup> Physically-motivated regularization schemes that aim to remove divergences due to the energy denominator in Eq. (1) offer a promising approach to ameliorating the above problems. One example,  $\kappa$ -MP2, takes the form,

$$E_c = -\frac{1}{4} \sum_{ijab} \frac{|\mathbb{I}_{ijab}|^2}{\Delta_{ij}^{ab}} \left(1 - e^{-\kappa \Delta_{ij}^{ab}}\right)^2, \quad (2)$$

and improves upon conventional MP2 for large-molecule NC and closed-shell transition-metal thermochemistry (TMTC) by factors of 5 and 2, respectively.<sup>7</sup>

Despite such notable improvements over conventional MP2, energy-gap dependent protocols for MP2 regularization lack the desired level of transferability required to be widely used in a black-box fashion. For example, with regularization parameters optimized for NC and transition metal systems, the accuracy for main-group thermochemistry (TC) and electronic response properties is notably deteriorated – at times these regularized MP2 approaches are worse than conventional MP2 by factors of 2 or 3.<sup>7</sup> Similarly,  $\kappa$ -MP2 demonstrated very promising improvements in accuracy relative to MP2 for nuclear magnetic resonance (NMR) chemical shifts only when element-specific  $\kappa$  values were employed.<sup>38</sup> The prospect of developing a more transferable approach to regularized second-order perturbation theory, which preserves high accuracy for NC and TM datasets, is the primary motivation for the present work.

Brillouin–Wigner perturbation theory (BWPT)<sup>39–42</sup> is an alternative to the Rayleigh–Schrödinger approach (the latter gives rise to MP2). We recently proposed a size-consistent variant of second-order BWPT, which naturally regularizes the  $\mathbf{t}$ -amplitudes by shifting the occupied orbital energies in the denominator to lower values, thus increasing the effective orbital energy gaps and damping artificially overestimated amplitudes.<sup>43</sup> The single free parameter in our BW-s2 approach was determined such that the dissociation limit of a system with two electrons in two orbitals (e.g., the  $\text{H}_2$  molecule in a minimal basis set) is exact. Importantly, this model, which we refer to as BW-s2, is size-consistent, size-extensive, and orbital invariant. While BW-s2 was found to be less accurate than (optimally parameterized)  $\kappa$ -MP2 in cases where exceptionally strong regularization was required, for a wide variety of main group TC its performance is superior to  $\kappa$ -MP2 and conventional MP2. In this work we aim to explore the landscape of the free parameter, which we will call  $\alpha$ , by investigating many different data sets representative of NC, large-gap TMTC, main-group TC, barrier heights, and molecular dipoles and polarizabilities.

## THEORY

Recently, we have shown that with the following repartitioning of the Hamiltonian (with  $\hat{R}$ , a one-electron regularizer operator):

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}, \quad (3)$$

where

$$\begin{aligned} \hat{H}_0 &= \hat{H}_0 + \hat{R} \\ \hat{V} &= \hat{V} - \hat{R} \end{aligned} \quad (4)$$

the second-order BWPT correction becomes

$$E^{(2)} = \sum_{k \neq 0} \frac{\langle \Phi_0 | \hat{V} | \Phi_k \rangle \langle \Phi_k | \hat{V} | \Phi_0 \rangle}{(\tilde{E}_0 - \tilde{E}_k) + E^{(2)}}, \quad (5)$$

where  $\tilde{E}_0$  and  $\tilde{E}_k$  are eigenvalues of the shifted zero-order Hamiltonian,  $\hat{H}_0$ . The energy gap  $\tilde{\Delta} = \tilde{E}_0 - \tilde{E}_k$  generally satisfies the relationship  $\tilde{\Delta} \geq \Delta$  where  $\Delta = E_0 - E_k$  is the gap derived from the usual eigenvalues of the unshifted  $\hat{H}_0$ . The use of these barred quantities is the only difference between our approach and typical BWPT.

The above expressions are general, and while there are infinitely many partitions of  $\hat{H}_0$ , there are finitely many that are size-consistent. We have chosen a particular form of  $\hat{R}$  that is size-consistent, and is represented in an arbitrary molecular orbital basis as,

$$R_{ijkl}^{abcd} = \frac{\alpha}{2} (W_{ik}\delta_{jl} + \delta_{ik}W_{jl})\delta_{ac}\delta_{bd}. \quad (6)$$

with,

$$W_{ij} = \frac{1}{2} \sum_{kab} \left[ t_{ik}^{ab}(jk||ab) + t_{jk}^{ab}(ik||ab) \right]. \quad (7)$$

The generalized tensor formulation of the second-order amplitude equation then reads,<sup>44–46</sup>

$$\sum_{klcd} \left( \Delta_{ijkl}^{abcd} + R_{ijkl}^{abcd} \right) \cdot t_{kl}^{cd} = -\mathbb{I}_{ijab}. \quad (8)$$

where

$$\Delta_{ijkl}^{abcd} = (F_{ac}\delta_{bd} + \delta_{ac}F_{bd})\delta_{ik}\delta_{jl} - (F_{ik}\delta_{jl} + \delta_{ik}F_{jl})\delta_{ac}\delta_{bd}. \quad (9)$$

Given the definition in Eqs. (6) and (8) (which is orbital invariant) can be solved by rotating the occupied subspace from the canonical basis into a basis where the matrix  $\mathbf{F}_{00} + \frac{\alpha}{2}\mathbf{W}$  is diagonal. To do this, we solve the following eigenvalue equation,

$$\left( \mathbf{F}_{00} + \frac{\alpha}{2}\mathbf{W} \right) \mathbf{U} = \tilde{\epsilon} \mathbf{U} \quad (10)$$

to obtain a set of dressed occupied orbital eigenvalues. In this dressed-orbital basis, Eq. (8) can be written as,

$$(\epsilon_a + \epsilon_b - \tilde{\epsilon}_i - \tilde{\epsilon}_j) \tilde{t}_{ij}^{ab} = -\tilde{\mathbb{I}}_{ijab} \quad (11)$$

leading to,

$$\tilde{t}_{ij}^{ab} = -\frac{\tilde{\mathbb{I}}_{ijab}}{(\epsilon_a + \epsilon_b - \tilde{\epsilon}_i - \tilde{\epsilon}_j)} \quad (12)$$

and,

$$\tilde{E}_c = -\frac{1}{4} \sum_{ijab} \frac{|\tilde{\mathbb{I}}_{ijab}|^2}{(\epsilon_a + \epsilon_b - \tilde{\epsilon}_i - \tilde{\epsilon}_j)} \quad (13)$$

Thus, the dressed eigenvalues  $\tilde{\epsilon}_p$  have the effect of augmenting the original denominator,  $\Delta_{ij}^{ab}$ , by adding a correlation contribution to the occupied orbital energies. The undetermined parameter  $\alpha$  was set to 1 based on making the theory exact for the two electron in two orbital problem. Similar ideas have recently been presented in Green's function based perturbation theories,<sup>48–50</sup> but unlike these methods, our BW-s2 approach retains the crucial property of orbital invariance. There are also notable similarities between BW-s2 and

the perturbation-adapted perturbation theory (PAPT) of Knowles, which seeks to optimize the partitioning of  $\hat{H}$ .<sup>51</sup> Whereas PAPT costs  $\mathcal{O}(N^6)$  already at second order, BW-s2 scales much more favorably at iterative  $\mathcal{O}(N^5)$ .

## RESULTS AND DISCUSSION

In our original set of benchmarks,<sup>43</sup> we found that BW-s2 consistently outperforms MP2 across myriad chemical problems, which is very encouraging. However, it was evident that specific, optimal choices of  $\kappa$  in  $\kappa$ -MP2 could significantly outperform BW-s2 in problems where strong regularization was required (such as transition metal thermochemistry). How much improvement is possible if we lift the restriction of  $\alpha = 1$ , and instead view  $\alpha$  as a parameter that controls regularization strength? That is the question that we will investigate here.

In this work, we benchmark the performance of various values of  $\alpha$  against a variety of data sets in an effort to tune the accuracy of BW-s2 [henceforth, the empirical variant will be referred to as BW-s2( $\alpha$ )]. Notably, the particular value of  $\alpha$  does not influence the size-consistency of the method, but it may be a determining factor in the overall quality of the results. We will assess the transferability of the  $\alpha$  parameter across various chemical problems, and attempt to make a recommendation for a broadly applicable  $\alpha$  value.

The results for all benchmark sets apart from electronic properties are shown in Table I and are plotted individually as a function of  $\alpha$  for each data set in Figs. S6–S9. These data include NC for sets of small dimers such as A24,<sup>54</sup> S22,<sup>55</sup> S66,<sup>56</sup> and the non-I-containing subset of X40 (hereafter referred to as X31),<sup>57</sup> along with the large  $\pi$ -stacked dimers of L7.<sup>58</sup> TC is assessed on H-atom transfer (HTBH38) and non-H-atom transfer (NHTBH38) sets,<sup>59,60</sup> along with the more comprehensive single-reference subset of W4-11.<sup>61</sup> As compared to our original work, we extend our coverage of TMTC with reaction energies from MOR39<sup>36</sup> (a subset of MOR41 with triple- $\zeta$  reference values),<sup>43</sup> MC09,<sup>62</sup> and a set of 13 Au, Pt, and Ir reaction energies that we call AuPtIr13.<sup>63</sup> Finally, we also include the ACONFL set of relative alkane conformational isomer energies.<sup>64</sup>

The MP2 results always improve on those obtained from HF, and gap-regularized  $\kappa$ -MP2 improves further on these results in all benchmark sets, apart from TC where the results degrade by up to 3.2 kcal/mol. A similar trend emerges for BW-s2( $\alpha$ ), with noticeable improvements over MP2 for NC, TMTC, and ACONFL data sets, but the results for barrier heights degrade by only about half as much as  $\kappa$ -MP2 (0.03–1.9 kcal/mol less accurate for modest parameters in the range  $1 \leq \alpha \leq 4$ ). Furthermore, BW-s2( $\alpha$ ) performs roughly 1 kcal/mol better than MP2 on the W4-11 benchmark set regardless of the particular value of  $\alpha$ , whereas  $\kappa$ -MP2 performs slightly (0.7 kcal/mol) worse. The improvements in NC, TMTC, and ACONFL sets with minimal degradation in the results for TC suggest that the BW-s2( $\alpha$ )  $\alpha$ -parameter is more transferable than the  $\kappa$  in  $\kappa$ -MP2.<sup>7,43</sup>

Regarding the transferability argument, it is instructive to consider electronic properties such as dipole moments and polarizabilities that are shown in Table II. Whereas  $\kappa$ -MP2 doubles the errors relative to MP2 for both dipoles and polarizabilities, BW-s2( $\alpha$ ) exhibits an exceptional flatness in the errors as a function of  $\alpha$ , peaking at 4% for the most severe  $\alpha = 8.0$  where the errors

TABLE I. Root-mean-square error in kcal/mol across chemical benchmark sets.

Type	Benchmark	HF	MP2	$\kappa$ -MP2 <sup>a</sup>	BW-s2( $\alpha$ ): $\alpha$ -parameter								
					1.0	2.0	3.0	3.5	4.0	4.5	5.0	6.0	8.0
NC <sup>c</sup>	L7 <sup>b</sup>	27.62	9.49	1.25	6.55	4.30	2.57	1.93	1.47	1.33	1.37	1.94	3.57
	A24	1.64	0.14	0.15	0.10	0.11	0.14	0.16	0.19	0.21	0.23	0.27	0.35
	X31	3.43	0.69	0.38	0.47	0.32	0.25	0.26	0.28	0.32	0.36	0.45	0.62
	S66	4.70	0.75	0.35	0.49	0.35	0.34	0.38	0.43	0.49	0.56	0.68	0.91
	S22 <sup>d</sup>	6.18	1.36	0.35	0.91	0.58	0.39	0.37	0.40	0.47	0.55	0.72	1.05
TC <sup>e</sup>	HTBH38	19.02	5.03	6.74	5.06	5.21	5.42	5.54	5.66	5.79	5.92	6.18	6.68
	NHTBH38	16.29	2.40	5.61	2.68	3.16	3.73	4.01	4.28	4.54	4.79	5.25	6.06
	W4-11	55.61	7.55	8.28	6.18	5.63	5.76	6.01	6.33	6.71	7.13	8.01	9.79
TMTC <sup>f</sup>	MOR39	22.15	14.13	6.49	9.93	8.11	6.77	6.23	5.78	5.40	5.09	4.66	4.43
	MC09	29.34	14.42	6.18	11.26	9.08	7.56	6.99	6.55	6.22	5.98	5.76	6.01
	AuIrPt13	6.40	4.30	2.60	3.64	3.13	2.74	2.58	2.45	2.33	2.23	2.08	1.93
ACONFL <sup>g</sup>	ACONF12	4.18	0.83	0.26	0.63	0.45	0.29	0.22	0.16	0.11	0.10	0.16	0.36
	ACONF16	4.11	0.85	0.20	0.63	0.44	0.27	0.19	0.13	0.09	0.09	0.19	0.40
	ACONF20	5.00	1.07	0.29	0.80	0.56	0.35	0.27	0.19	0.15	0.15	0.24	0.49

<sup>a</sup> $\kappa = 1.1$ .<sup>b</sup>heavy-aug-cc-pVDZ/heavy-aug-cc-pVTZ extrapolation to the complete basis set limit.<sup>c</sup>Noncovalent interaction energies, aug-cc-pVDZ/aug-cc-pVTZ extrapolation to the complete basis set limit, unless otherwise noted.<sup>d</sup>Using the reference data from Ref. 47.<sup>e</sup>Thermochemistry, aug-cc-pVTZ/aug-cc-pVQZ extrapolation to the complete basis set limit.<sup>f</sup>Transition metal thermochemistry, MOR39: Def2-TZVPP/Def2-ECP, MC09: Def2-QZVPP/Def2-ECP, AuIrPt13: cc-pVTZ/cc-pVTZ-PP.<sup>g</sup>Alkane conformational isomer energies, heavy-aug-cc-pVDZ/heavy-aug-cc-pVTZ extrapolation to the complete basis set limit.

TABLE II. Root-mean-square relative error in % for electronic properties.

Benchmark	HF <sup>a</sup>	MP2 <sup>b</sup>	$\kappa$ -MP2 <sup>b,c</sup>	BW-s2( $\alpha$ ) <sup>b</sup> : $\alpha$ -parameter								
				1.0	2.0	3.0	3.5	4.0	4.5	5.0	6.0	8.0
Dipoles <sup>d</sup>	12.69	3.60	6.81	3.30	3.48	3.88	4.11	4.34	4.58	4.81	5.25	6.03
Polarizabilities <sup>e</sup>	6.93	2.16	5.52	2.33	2.42	2.61	2.74	2.87	3.02	3.24	3.34	3.98

<sup>a</sup>aug-cc-pCVQZ basis set.<sup>b</sup>aug-cc-pCVTZ/aug-cc-pCVQZ extrapolation to complete basis set limit.<sup>c</sup> $\kappa = 1.1$ .<sup>d</sup>Dipole benchmark data from Ref. 52.<sup>e</sup>Polarizability benchmark data from Ref. 53.

nonetheless remain lower than  $\kappa$ -MP2. Reference 7 reports  $\kappa$ -MP2 errors ( $1.6 \geq \kappa \geq 1$ ) for dipoles that span the range 4.7%–7.5% while polarizability errors span 4.2%–5.9%. Not only are these close to the largest errors that we report for BW-s2( $\alpha$ ), but BW-s2( $\alpha = 1$ ) actually improves the results for dipole moments relative to MP2, whereas  $\kappa$ -MP2 errors monotonically increase as  $\kappa$  decreases. These results for electronic properties suggest that the  $\alpha$  parameter in BW-s2( $\alpha$ ) is indeed much more transferable between classes of chemical problem than gap-dependent regularizers.

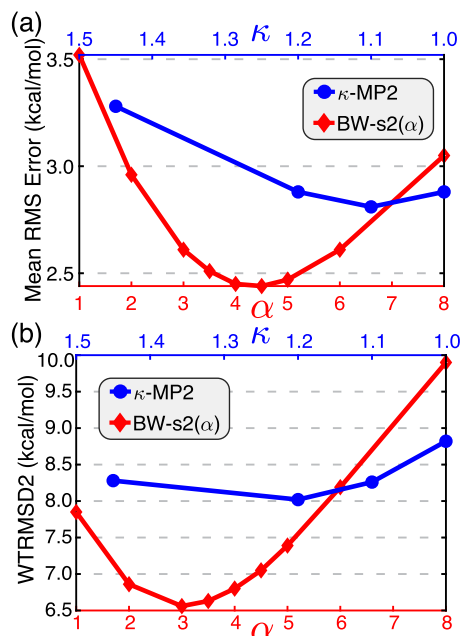
Comparison of mean root-mean square deviation (MRMSD) values in Fig. 1(a) emphasizes the enhanced transferability of BW-s2( $\alpha$ ) relative to  $\kappa$ -MP2. The MRMSD, evaluated as a simple average over RMSD values of each data set in Table I, reveals that BW-s2( $\alpha$ ) outperforms the previously suggested<sup>7</sup> optimal  $\kappa$ -MP2( $\kappa = 1.1$ ) over the wide range of  $3 \leq \alpha \leq 6$ . While this data weighs the error of each

data set on equal footing, we also report the weighted total RMSD (WTRMSD2) statistics in Fig. 1(b), which accounts for the different sizes and energy scales of each data set. Specifically, WTRMSD2 is analogous to the type-2 weighted total mean absolute deviation metric proposed in Ref. 65, and it is calculated as,

$$\text{WTRMSD2} = \frac{78.29}{\sum_i N_i} \sum_i N_i \frac{\text{RMSD}_i}{|\bar{E}_i|} \quad (14)$$

where  $N_i$  is the number of values in set  $i$ ,  $|\bar{E}_i|$  is the average absolute value of the benchmark energies in set  $i$ , and the constant 78.29 kcal/mol was determined as the average of all  $\bar{E}$  values for all sets. The WTRMSD2 data reinforce the idea that BW-s2( $\alpha$ ) is more flexible than  $\kappa$ -MP2, with an even wider range of  $1 \leq \alpha \leq 5$  that outperform  $\kappa$ -MP2( $\kappa = 1.1$ ). Notably, WTRMSD2 suggests





**FIG. 1.** A comparison of errors across all of the data sets in Table I using (a) the mean root-mean square deviation (MRMSD) and (b) the weighted total root-mean square deviation – type 2 (WTRMSD2) for the most successful range of  $\kappa$ -MP2  $\kappa$  values from Ref. 7 contrasted with BW-s2( $\alpha$ )  $\alpha$  values from this work. X-axes are oriented in the direction of increasing regularization strength.

that even the original BW-s2( $\alpha = 1$ ) outperforms the best  $\kappa$  value. WTRMSD2 is likely to skew the results towards nominal performance on TC properties due to the relative enormity of the W4-11 set (which contains 745 reactions), hence the preference for lower  $\alpha$  values in this case. While the optimal value of  $\alpha$  shifts depending on the particular averaging scheme used, a value of  $\alpha = 4$  is roughly optimal relative to both MRMSD and WTRMSD2 metrics, and is likely a sensible compromise value that performs well for most chemical problems.

Some particularly interesting highlights are that BW-s2( $\alpha$ ) can reduce errors relative to MP2 in the L7 data set from 9.5 to 1.3 kcal/mol. TMTC data can also be improved by a factor of 2–3 relative to the MP2 results, reducing errors from 14 kcal/mol to 4–6 kcal/mol for MOR39 and MCO9 sets if moderate to large  $\alpha$  parameters are applied. Finally, errors in alkane conformational energies can be reduced from  $\sim 1$  kcal/mol with MP2 to just 0.1 kcal/mol with BW-s2( $\alpha$ ), achieving something close to chemical accuracy. Of course, excellent performance for particular kinds of chemical problem does not suggest a “universal”  $\alpha$  value, and there is likely no  $\alpha$  parameter that is entirely satisfactory in all chemical contexts. However, we make the recommendation of  $\alpha = 4$  based on the analysis presented alongside Fig. 1. Taking a closer look, the BW-s2( $\alpha = 4$ ) error statistics suggest considerable improvements relative to MP2 for NC, main-group TC (W4-11), TMTC, and ACONFL sets, while minimal damage is done to the results for H-atom/non-H-atom transfer barrier heights and electronic properties.

While there is no universal parameter, BW-s2( $\alpha$ ) stands out from gap-dependent regularizers like  $\kappa$ -MP2 (and the similarly-performing  $\sigma$ -MP2 and  $\sigma^2$ -MP2 methods)<sup>7</sup> in the sense that it is clearly more transferable across different chemical problems. This may be due to the fact that BW-s2( $\alpha$ ) defines a valid second order BW correction for each  $\alpha$ . As a consequence it incorporates the full set of  $\mathbf{t}$  amplitudes in the regularizer, whereas gap-dependent schemes rely only on the orbital energy gaps. The self-consistent nature of BW-s2( $\alpha$ ) may also act to further refine the orbital energy gap, introducing a feedback loop that fine-tunes the resultant amplitudes.

As a final test for the robustness of our parameterization, we consider a secondary free parameter,  $\beta$ , that directly modulates the amount of BW-s2( $\alpha$ ) correlation energy such that,  $E = E_{\text{HF}} + \beta E_{\text{BW-s2}(\alpha)}$ . The results in Sec. S1 show that the optimal  $\beta$  parameter generally hovers in the range  $0.9 \leq \beta \leq 1.1$ . Furthermore, when  $\alpha$  nears its optimal value,  $\beta \rightarrow 1.0$  with the exception of non-H-atom barrier heights in NHTBH38 (Fig. S2) where  $\beta = 1.1$  when  $\alpha = 1$ . A  $\beta > 1$  implies systematic under-correlation, and points to an optimal  $\alpha$  for NHTBH38 that is less than 1. In stark contrast to this, the landscape of the parameter space for TMTC in Fig. S3 features an optimal  $\beta = 0.7$  at low  $\alpha = 1$ , which increases to  $\beta = 1$  only when  $\alpha \rightarrow 8$ . This implies a significant over-correlation for transition-metal systems that is tempered only by larger  $\alpha$  parameters.

The NC, W4-11, and ACONFL data sets in Figs. S1, S2, and S4, respectively, show a relatively flat slope defined by the line tracing  $\min_{\alpha, \beta} \text{Error}(\alpha, \beta)$ . For these sets, the optimal  $\beta$  is very close to 1 across  $\alpha$  parameters, suggesting that BW-s2( $\alpha$ ) offers a balanced description of correlation for NC, main-group TC, and conformational isomers. Overall, the relatively low slopes across the parameter space and the proximity of  $\beta$  to 1 across various  $\alpha$  both speak to the transferability of the BW-s2( $\alpha$ ) approach. Thus, moving forward we suggest the single parameter BW-s2( $\alpha = 4$ ) approach for general chemical applications.

## COMPUTATIONAL DETAILS

All calculations were performed in a development version of Q-Chem v6.0.2.<sup>66</sup> All calculations (aside from evaluations of electronic properties) feature SCF convergence thresholds that were set to  $10^{-8}$  root-mean-square error. The correlation energy was considered to be converged at a change of  $10^{-8}$  Ha between iterations for all calculations except for those of the L7 dataset, where this was relaxed to  $10^{-5}$  Ha. Relevant derivatives with respect to electric fields for properties such as dipoles and polarizabilities were evaluated via finite difference. Because finite difference results are especially sensitive to numerical errors, the SCF convergence and correlation energy thresholds were set to  $10^{-11}$ . To achieve complete basis set limit extrapolations for NC, TC, and ACONFL we follow the protocol in Ref. 67, which has been verified to perform well with the heavy-aug-cc-pVDZ/heavy-aug-cc-pVTZ basis sets used for L7.<sup>68</sup> For electronic response properties, we use the same extrapolation method reported in Ref. 7.

We use restricted open-shell orbitals which are separately pseudocanonicalized in the  $\alpha$  and  $\beta$  spaces before computing the correlation energy in all open-shell systems.<sup>17–22</sup> For such systems, non-Brillouin singles (NBS) contributions are included via,

$$E_{\text{NBS}} = -\sum_{ia} \frac{|F_{ia}|^2}{\epsilon_a - \epsilon_i} \quad (15)$$

where  $F_{ia}$  are off-diagonal Fock matrix elements.

Since  $\mathbf{W}$  depends on the  $\mathbf{t}$  amplitudes, which themselves depend on the modulation of the energy gap supplied by the  $\mathbf{W}$  matrix, the BW-s2 equations must be solved self-consistently. We begin each BW-s2 calculation with canonical Hartree–Fock orbitals and an MP2 guess for the initial  $\mathbf{t}$  amplitudes, though we note the possibility of obtaining a strictly non-divergent initial guess by means of Davidson’s repartitioning of the one-electron Fock operator.<sup>69</sup> To accelerate these calculations, our implementation uses the resolution-of-the-identity (RI) approximation for the two-electron integrals,<sup>70,71</sup> resulting in a formal scaling of  $m \times \mathcal{O}(N^5)$ , where  $m$  is the number of iterations (typically between 4 and 6) and  $N$  is the number of basis functions. Due to computational limitations, the  $I$  functions in the auxiliary RI basis sets were removed for transition-metal calculations in the MOR39, MCO9, and AuIrPt13 data sets.

## SUPPLEMENTARY MATERIAL

Additional figures pertaining to scans over  $\alpha$ , and the secondary  $\beta$  parameter in BW-s2( $\alpha$ ). Detailed data are provided for NC, main-group TC, TMTc, ACONFL, and electronic response properties.

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## AUTHOR DECLARATIONS

### Conflict of Interest

Martin Head-Gordon is a part-owner of Q-Chem, which is the software platform used to perform the developments and calculations described in this work.

## Author Contributions

**Kevin Carter-Fenk:** Data curation (lead); Investigation (lead); Methodology (equal); Software (lead); Writing – original draft (equal); Writing – review & editing (equal). **James Shee:** Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Martin Head-Gordon:** Conceptualization (lead); Funding acquisition (lead); Supervision (lead); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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