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ABSTRACT

Second-order Møller-Plesset perturbation theory (MP2) often breaks down catastrophically in small-gap systems, leaving much to be desired in its performance for myriad chemical applications such as noncovalent interactions, thermochemistry, and dative bonding in transition metal complexes. This divergence problem has reignited interest in Brillouin-Wigner perturbation theory (BWPT), which is regular at all orders but lacks size consistency and extensivity, severely limiting its application to chemistry. In this work, we propose an alternative partitioning of the Hamiltonian that leads to a regular BWPT perturbation series that, through the second order, is size-extensive, size-consistent (provided its Hartree-Fock reference is also), and orbital invariant. Our second-order size-consistent Brillouin-Wigner (BW-s2) approach can describe the exact dissociation limit of H₂ in a minimal basis set, regardless of the spin polarization of the reference orbitals. More broadly, we find that BW-s2 offers improvements relative to MP2 for covalent bond breaking, noncovalent interaction energies, and metal/organic reaction energies, although rivaling coupled-cluster with single and double substitutions for thermochemical properties.

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I. INTRODUCTION

The oldest and most tractable wave function approach that captures electron correlation from first principles is the second-order Møller-Plesset perturbation theory (MP2). Although the $\mathcal{O}(N^5)$ asymptotic scaling of MP2¹ does not compete with the $\mathcal{O}(N^3)$ scaling of density functional theory (DFT), MP2 is immune to many of the nonphysical problems that manifest in DFT such as self-interaction errors, which can obfuscate the underlying physics of chemical systems by artificially delocalizing charge density.²⁻⁴ The *ab initio*, and therefore self-interaction-free, correlation offered by MP2 has led to its incorporation into double-hybrid density functionals, which combine MP2 with DFT exchange-correlation.⁵⁻¹⁰ On its own, MP2 can promote fundamental insights into the physical properties of chemical systems that are untarnished by self-interaction errors, making it a valuable tool in the arsenal of quantum chemistry.

The Møller-Plesset many-body perturbation series is based on the Rayleigh-Schrödinger perturbation theory (RSPT),¹¹ which imbues MP2 with the size-consistency and extensivity that lead to its proper treatment of many-body systems. On the other hand, the Møller-Plesset series inherits a divergence problem from RSPT, such that in the limit of zero-gap systems, the Møller-Plesset correlation energy becomes singular. Although exact degeneracy is perhaps an extreme case that occurs relatively infrequently in nature, nonphysically large correlation energies brought on by near degeneracies are more commonly encountered. Large, but not necessarily divergent, correlation energies are often found in systems that exhibit significant nonadditive correlation effects,¹² such as dative bonds in metal complexes¹³ and dispersion-bound complexes dominated by π - π interactions.¹⁴⁻¹⁷ The nonadditive correlation energy can be defined as the difference between the true correlation energy and the pairwise correlations captured by MP2, $E_c^{\text{NA}} = E_c - E_c^{\text{PW}}$. In cases where MP2 yields poor estimates of the

correlation energy, the nonadditive component is generally large and positive, implying that the dominant nonadditive contribution comes from a screening of the pair correlations. Indeed, in large systems with extended π networks, the MP2 correlation energy becomes catastrophically large, and without nonadditive screening, interaction energies can be overestimated by more than 100%.^{18,19}

Many useful strategies that account for nonadditive electron correlation have been developed over the years. A simple one is to directly scale the same-spin and/or opposite-spin correlation energies,^{20–23} which can improve the performance of MP2 for thermochemistry and noncovalent interactions.²⁴ Another strategy is to use only the short-range part of the Coulomb operator when evaluating the MP2 energy, thereby attenuating the range of the correlation interaction and improving results for a wide range of chemical problems.^{25–28} However, although these approaches treat the symptoms of a completely pairwise correlation energy approximation, they do not directly address the underlying cause.

One approach that offers direct screening of pair correlations is regularized MP2. Broadly speaking, regularization modifies the MP2 energy expression with a function that damps any divergent or excessively large correlations, ideally while retaining the unvarnished MP2 energy for weaker correlations. Regularization has been used to avoid singular correlation energies that are encountered while optimizing molecular orbitals under a potential that contains the MP2 energy (orbital-optimized MP2),^{24,29–34} but even without orbital optimization regularized MP2 can outperform MP2 across myriad chemical problems.¹²

Regularized MP2 corrects the divergent nature of the Rayleigh-Schrödinger perturbation series in zero-gap systems. Singularities manifest in the second-order RSPT energy,

$$E_{\text{RS}}^{(2)} = \sum_{k=0} \frac{\langle \Phi_0 | \hat{V} | \Phi_k \rangle \langle \Phi_k | \hat{V} | \Phi_0 \rangle}{E_0 - E_k}, \quad (1)$$

in cases of degeneracy, i.e., when $E_k = E_0$. More appropriate formulations of perturbation theories have been developed throughout the years in efforts to sidestep this divergence problem. These include retaining the excitation degree (RE) methods,^{35–37} which define the unperturbed Hamiltonian as one that is block-diagonal in configuration space and the perturbation as the couplings between ancillary excitation blocks. The RE approaches offer substantial improvements over MP2, with orbital-optimized RE/MP2 approaches often attaining chemical accuracy for thermochemical properties.³⁸ There has also been substantial effort to improve many-body perturbation theory with Green's function-based methods.^{39–41}

A less modern approach that has regained considerable attention in recent years was pioneered in the 1930s by Lennard-Jones, Brillouin, and Wigner as an alternative to the Rayleigh-Schrödinger power series and came to be known as Brillouin-Wigner (or Lennard-Jones-Brillouin-Wigner) perturbation theory (BWPT).^{42–45} The first term where BWPT differs from RSPT is the second-order energy, which takes the form

$$E_{\text{BW}}^{(2)} = \sum_{k=0} \frac{\langle \Phi_0 | \hat{V} | \Phi_k \rangle \langle \Phi_k | \hat{V} | \Phi_0 \rangle}{E_0 - E_k + E_{\text{BW}}^{(2)}}. \quad (2)$$

There are a few distinct advantages to BWPT: it converges more rapidly than RSPT for a given problem,^{43,44} and it is regular at all orders due to $E_{\text{BW}}^{(n)}$ in the denominator. In fact, second-order BWPT is exact for a two-level system, whereas RSPT requires summation to infinite order to achieve the exact result.⁴⁵ On the other hand, $E_{\text{BW}}^{(2)}$ appears on both sides of the above expression and must, therefore, be determined self-consistently. Although this does increase the cost of the perturbation theory, it is not the fatal flaw that has limited the application of BWPT in quantum chemistry over the last half-century. Instead, BWPT fell into disuse after it was found that it is not size-extensive and, therefore, fails as a proper many-body theory.⁴⁶

Despite its failures for single-reference systems, the mathematical form of the Brillouin-Wigner series is convenient for multireference theories and is still actively used in this context.^{47–53} In particular, it is notable that the Brillouin-Wigner cluster expansion of the wave function is equivalent to the Rayleigh-Schrödinger one with the key exception that multireference Brillouin-Wigner coupled-cluster theory is immune to the intruder state problem.⁵⁴ The treatment of intruder states and the divergences encountered in single-reference perturbation theories are closely linked⁵⁵; hence, it is natural to wonder whether the problems in single-reference BWPT can be amended to obtain a regular correlation energy at MP2 cost.

If BWPT could be made size-consistent and size-extensive, it could supply correlation energies that naturally incorporate nonadditive screening effects at all orders. This has spurred interest in deriving size-extensivity corrections for BWPT from the Bloch equations⁵⁶ and through renormalization of the second-order energy.⁵⁷ Recently, an alternative *ansatz* to standard BWPT was proposed,⁵⁸ where the correlation energy per electron ($E_{\text{BW}}^{(2)}/N_e$) was inserted into the denominator of Eq. (2) in an effort to restore size-extensivity. Importantly, Ref. 58 pointed out that the derivation of Eq. (2) can be generalized to an arbitrary level shift in place of $E_0 + E_{\text{BW}}^{(2)}$, thus opening the door for a wide variety of level-shift energies to be conceived and applied.

In this work, we present a different approach to this problem, based on a partitioning of the Hamiltonian that incorporates a judiciously designed one-electron regularization operator into the zero-order Hamiltonian, whereas the remainder of the correlation energy is described as a perturbation. Furthermore, we cast the second-order energy expression into a tensor framework, ensuring that our approach retains invariance to unitary transformations among the occupied or virtual orbitals. Our chosen form of the regularization operator satisfies size-consistency and extensivity through the second order. We benchmark the performance of our proposed method across a wide variety of datasets where MP2 performs rather poorly, including covalent bond breaking, noncovalent interaction energies, reaction barrier heights, thermochemical properties, and metal/organic reaction energies.

II. THEORY

Throughout this work, $\{i, j, k, \dots\}$ refer to occupied orbitals, $\{a, b, c, \dots\}$ refer to unoccupied orbitals, $\{p, q, r, \dots\}$ are arbitrary orbitals, and $\{P, Q, R, \dots\}$ are auxiliary functions.

A. Orbital-energy dependent regularized MP2

The MP2 correlation energy in the canonical molecular orbital basis is

$$E_c = -\frac{1}{4} \sum_{ijab} \frac{|\mathbb{I}_{ijab}|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} = -\frac{1}{4} \sum_{ijab} \frac{|\mathbb{I}_{ijab}|^2}{\Delta_{ij}^{ab}}, \quad (3)$$

where

$$\mathbb{I}_{ijab} = (ij||ab), \quad (4)$$

are the antisymmetrized two-electron integrals and ε_p is the orbital energy of orbital p . This expression for the correlation energy is clearly divergent when the denominator approaches zero, but the energy may become much too large long before this limit is reached if nonadditive screening is particularly important.

A straightforward approach to tempering this bad behavior is to add a level shift to the denominator of the form $\Delta_{ij}^{ab} + \delta$ where $\delta > 0$,^{29,30,32} but this approach generally provides too weak of regularization and lacks input from the underlying physics of the system. More sophisticated regularizers that have orbital energy dependence can be derived by Laplace transform of Eq. (3) where the correlation energy can be exactly rewritten as⁵⁹

$$E_c = -\frac{1}{4} \sum_{ijab} \int_0^\infty d\tau e^{-\tau \Delta_{ij}^{ab}} |\mathbb{I}_{ijab}|^2. \quad (5)$$

From here, the upper integration bound can be truncated to a finite value, $\sigma(\Delta_{ij}^{ab})^{p-1}$ to give

$$E_c = -\frac{1}{4} \sum_{ijab} \frac{|\mathbb{I}_{ijab}|^2}{\Delta_{ij}^{ab}} \left(1 - e^{-\sigma(\Delta_{ij}^{ab})^p}\right), \quad (6)$$

where $p = 1$ gives what is known as σ -MP2. The case $p = 2$ gives σ^2 -MP2 and can be derived through second-order perturbative analysis of the flow equations.^{60,61}

In this work, we will focus on a flavor of empirical regularization known as κ -MP2,³³ where the integrals themselves are damped by a factor of $(1 - \exp[-\kappa \Delta_{ij}^{ab}])$ leading to

$$E_c = -\frac{1}{4} \sum_{ijab} \frac{|\mathbb{I}_{ijab}|^2}{\Delta_{ij}^{ab}} \left(1 - e^{-\kappa \Delta_{ij}^{ab}}\right)^2. \quad (7)$$

All of the above orbital-energy dependent (Δ -dependent) regularizers rely on a single empirical parameter (σ or κ) that is somewhat transferable but expresses different optimal values for different classes of chemical problem.¹² We will limit our investigations in this work to κ -MP2, but given that all of the aforementioned flavors of Δ -dependent regularization yield similar results,¹² we expect the conclusions drawn here for κ -MP2 to be general for this class of regularizer.

B. Brillouin-Wigner theory with modified energy

It was recently proposed that the second-order Brillouin-Wigner energy can be derived as a specific case of the more general correlation expression,⁵⁸

$$E^{(2)} = \sum_{k \neq 0} \frac{\langle \Phi_0 | \hat{V} | \Phi_k \rangle \langle \Phi_k | \hat{V} | \Phi_0 \rangle}{E_{LS} - E_k}, \quad (8)$$

where E_{LS} is an arbitrary level shift. Usually, E_{LS} is taken to be the exact ground-state energy, $E_{LS} = E$, but the consideration of a more general E_{LS} unlocks myriad possibilities for the precise form of the correlation energy. In effect, this reframes the BWPT problem in terms of $E_c[E_{LS}(\Psi_0)]$, where the correlation energy is expressed in terms of a level-shift energy that itself depends on the wave function. Inserting various *ansätze* into Eq. (8) leads to different correlation energies. For example, setting $E_{LS} = E_0$ yields second-order Møller-Plesset perturbation theory and $E_{LS} = E_0 + \delta$ gives δ -MP2. Other choices include the pair-correlation energy ($E_{LS} = E_0 + e_{ij}$), which leads to the independent electron pair approximation (IEPA) or the second-order Bethe-Goldstone equation (BGE2),^{11,62,63} the second-order correlation energy ($E_{LS} = E_0 + E^{(2)}$) gives second-order BWPT, and the correlation energy per electron ($E_{LS} = E_0 + E^{(2)}/N_e$) gives the size-extensive xBW2 method.⁵⁸ Each choice results in a different correlation energy with different mathematical properties that are summarized in Table I.

C. Repartitioned Brillouin-Wigner perturbation theory

Inspired by the generality of such a modification to BWPT, we consider a slightly more formalized approach by partitioning the Hamiltonian such that the zero-order Hamiltonian contains a

TABLE I. Various choices for E_{LS} in Eq. (8) and properties of the resultant correlation energy.

Method	E_{LS}	Size-consistent	Size-extensive	Invariant
MP2, κ -MP2, σ^p -MP2	E_0	✓	✓	✓
δ -MP2	$E_0 + \delta; \delta > 0$	✓	✓	✓
IEPA/BGE2	$E_0 + e_{ij}; e_{ij} = -\frac{1}{4} \sum_{ab} \frac{ \mathbb{I}_{ijab} ^2}{\Delta_{ij}^{ab} + e_{ij}}$	✓	✗	✗
BW2	$E_0 + E_c^{BW2}$	✗	✗	✓
xBW2	$E_0 + E_c^{BW2}/N_e$	✗	✓	✓
BW-s2 ^a	$\bar{E}_0 + E^{(2)} - E_{R,k}$	✓	✓	✓

^aSecond-order size-consistent Brillouin-Wigner perturbation theory with shifted \hat{H}_0 (BW-s2); this work.

regularizing operator that modulates the occupied orbital energies. Specifically, we propose the following partition:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}, \quad (9)$$

where

$$\begin{aligned} \hat{H}_0 &= \hat{H}_0 + \hat{R}, \\ \hat{V} &= \hat{V} - \hat{R}, \end{aligned} \quad (10)$$

where \hat{H}_0 is the Fock operator, \hat{V} contains all of the many-body correlations that are not contained within \hat{H}_0 and \hat{R} , and \hat{R} is a one-electron regularizer operator of the form

$$\hat{R} = \sum_{ij} r_{ij} a_i^\dagger a_j. \quad (11)$$

Of particular note is the fact that the infinite summation of the Brillouin-Wigner perturbation series is invariant to partitioning the Hamiltonian in this way.⁶⁴

Next, we write the perturbed Schrödinger equation as

$$(E - \hat{H}_0)|\Psi\rangle = \lambda \hat{V}|\Psi\rangle. \quad (12)$$

Defining $\hat{Q} = 1 - |\Phi_0\rangle\langle\Phi_0|$ and multiplying by this quantity on the left, we find

$$\hat{Q}|\Psi\rangle = \lambda \hat{Q}(E - \hat{H}_0)^{-1} \hat{V}|\Psi\rangle = \lambda \hat{\Gamma}_0 \hat{V}|\Psi\rangle, \quad (13)$$

where

$$\hat{\Gamma}_0 = \sum_{k \neq 0} \frac{|\Phi_k\rangle\langle\Phi_k|}{E - \bar{E}_k} \quad (14)$$

is the resolvent. In the above, we have assumed that Φ_k are also eigenfunctions of \hat{H}_0 , such that

$$\bar{E}_k = \langle\Phi_k|\hat{H}_0|\Phi_k\rangle = \sum_i^{\text{occ}} (F_{\bullet i}^i + R_{\bullet i}^i), \quad (15)$$

where $\bar{E}_k = E_k + E_{R,k}$ is the energy of state k as modulated by the regularizer operator.

Taking the usual assumption of intermediate normalization, i.e., $\langle\Phi_0|\Psi\rangle = 1$, allows us to expand the wave function and energy in a perturbation series,

$$\begin{aligned} \Psi^{(n)} &= \sum_{m=0}^n (\lambda \hat{\Gamma}_0 \hat{V})^m |\Phi_0\rangle, \\ E^{(n)} &= \lambda \langle\Phi_0|\hat{V}|\Psi^{(n-1)}\rangle. \end{aligned} \quad (16)$$

Therefore, to first order in E , we find

$$\begin{aligned} E^{(1)} &= \langle\Phi_0|\hat{V}|\Psi^{(0)}\rangle \\ &= \langle\Phi_0|\hat{H}|\Phi_0\rangle - \langle\Phi_0|\hat{H}_0|\Phi_0\rangle = E_{\text{HF}} - \bar{E}_0, \end{aligned} \quad (17)$$

which when combined with Eq. (15) (for $k = 0$) gives the usual result for the first-order energy, $E = \bar{E}_0 + E^{(1)} = E_{\text{HF}}$. Thus, there is no first-order correction to the Hartree-Fock energy, E_{HF} .

The second-order correction differs from BWPT and RSPT,

$$\begin{aligned} E^{(2)} &= \sum_{k \neq 0} \frac{\langle\Phi_0|\hat{V}|\Phi_k\rangle\langle\Phi_k|\hat{V}|\Phi_0\rangle}{E - \bar{E}_k} \\ &= \sum_{k \neq 0} \frac{\langle\Phi_0|\hat{V}|\Phi_k\rangle\langle\Phi_k|\hat{V}|\Phi_0\rangle}{(E_0 - E_k) + (E_{R,0} - E_{R,k}) + E^{(2)}}, \end{aligned} \quad (18)$$

where $E = \bar{E}_0 + E^{(2)}$ has been substituted in the denominator, as per the usual BWPT approach. The fully expanded denominator now consists of the zero-order energy gap $E_0 - E_k$, the correlation energy $E^{(2)}$, and a new contribution from the regularizer $E_{R,0} - E_{R,k}$ that changes the state energies. Interestingly, if we take $\bar{E}_0 + E^{(2)} - E_{R,k} = E_{\text{LS}}$ in accordance with the proposed approach in Ref. 58, we recover Eq. (8).

D. Tensor formulation of the second-order energy

A convenient tool that ensures orbital invariance of our final correlation energy expression is the tensor formulation of many-body perturbation theory.^{65–67} For MP2, the linear amplitude equation takes the form

$$\sum_{klcd} \Delta_{ijkl}^{abcd} \cdot t_{kl}^{cd} = -\mathbb{I}_{ijab}, \quad (19)$$

where t_{kl}^{cd} are the amplitudes and

$$\Delta_{ijkl}^{abcd} = (F_{ac}\delta_{bd} + \delta_{ac}F_{bd})\delta_{ik}\delta_{jl} - (F_{ik}\delta_{jl} + \delta_{ik}F_{jl})\delta_{ac}\delta_{bd} \quad (20)$$

is the usual 8-rank tensor composed of Fock matrix elements, F_{pq} . In the basis of canonical molecular orbitals, where the Fock matrix is diagonal and the orbitals form an orthonormal set, Eq. (20) is trivially diagonal such that solving Eq. (19) leads to the well-known form of the MP2 amplitudes,

$$t_{ij}^{ab} = -\frac{\mathbb{I}_{ijab}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \quad (21)$$

which gives way to the usual MP2 energy expression in Eq. (3).

Within this framework, the shifted zero-order Hamiltonian from Eq. (10) leads to

$$\sum_{klcd} (\Delta_{ijkl}^{abcd} + R_{ijkl}^{abcd}) \cdot t_{kl}^{cd} = -\mathbb{I}_{ijab}, \quad (22)$$

where \mathbf{R} is a regularizing tensor. In the hypothetical case of diagonal Δ and \mathbf{R} tensors, the amplitudes

$$t_{ij}^{ab} = -\frac{\mathbb{I}_{ijab}}{\Delta_{ij}^{ab} + R_{ij}^{ab}} \quad (23)$$

result in the same energy expression as that of Eq. (18) with \mathbf{R} playing the role of $E_{R,0} - E_{R,k}$. To retain size-consistency at the second order, it is crucial to choose a form of \mathbf{R} that cancels $E^{(2)}$ while still modulating the orbital energy gap to avoid divergences.

An important feature of Eq. (18) is that it enables a straightforward mechanism for canceling out the redundant correlation terms in the denominator that result in size-consistency errors in standard BWPT. Namely, if we can define \hat{R} such that

$\langle \Phi_{ij}^{ab} | (E - \hat{H}_0 - \hat{R}) | \Phi_{kl}^{cd} \rangle = \Delta_{ijkl}^{abcd} + R_{ijkl}^{abcd}$, then the contributions to the denominator of the resolvent that arise from the correlation energy of the entire system (i.e., $E^{(2)}$ at the second order) will vanish, thereby eliminating size-inconsistent terms. To this end, we choose a form of \mathbf{R} that ensures that the correlation between any two orbitals $\{i, j\}$ goes to zero when the orbitals are far apart:

$$R_{ijkl}^{abcd} = \frac{1}{2} (W_{ik} \delta_{jl} + \delta_{ik} W_{jl}) \delta_{ac} \delta_{bd}, \quad (24)$$

where

$$W_{ij} = \frac{1}{2} \sum_{kab} \left[t_{ik}^{ab} (jk \| ab) + t_{jk}^{ab} (ik \| ab) \right]. \quad (25)$$

An important property of \mathbf{W} is that $\text{tr}(\mathbf{W}) = E^{(2)}$, which results in the total cancellation of $E^{(2)}$ in the resolvent, leading to a size-consistent energy expression at the second order. Specifically, it can be shown that

$$\langle \Phi_{ij}^{ab} | \hat{R} | \Phi_{kl}^{cd} \rangle = \sum_n W_{nn} + \frac{1}{2} (W_{ik} \delta_{jl} + \delta_{ik} W_{jl}) \delta_{ac} \delta_{bd}, \quad (26)$$

thus straightforwardly canceling $E^{(2)}$ while modifying the matrix elements connecting pairs of occupied orbitals (and the occupied-orbital energies). However, we note that size-inconsistent terms enter at third and higher orders.

Matrix elements of Eq. (25) appear also in an orbital invariant CEPA(3) correction⁶⁸ and share similarities with one of the terms in the MP2 orbital energy gradient.³³ In particular, Eq. (25) is related to the correlation contribution to the ionization energy of orbital i ,

$$E_c^{\text{IP},i} = \frac{1}{2} \sum_{kab} t_{ik}^{ab} (ik \| ab), \quad (27)$$

where the orbitals are fixed at those of the n -electron system. One may notice that the elements of \mathbf{W} in Eq. (25) correspond to $2E_i^{\text{IP},\text{corr}}$. Not only does this factor of 2 naturally emerge from the necessity of canceling $E^{(2)}$ in the resolvent but also can also be understood as a means of modulating the energies of both occupied orbitals involved in any double substitution with $E_c^{\text{IP},i}$. We elaborate further on this point in Appendix A.

One complication that arises in the solution of Eq. (22) with our proposed form of \mathbf{R} is that in the canonical orbital basis, the left-hand side of Eq. (22) is not diagonal. Instead, it takes the form

$$\sum_{klcd} \left\{ [F_{ac} \delta_{bd} + \delta_{ac} F_{bd}] \delta_{ik} \delta_{jl} - \delta_{ac} \delta_{cd} [F_{ik} \delta_{jl} + \delta_{ik} F_{jl}] - \frac{\delta_{ac} \delta_{bd}}{2} (W_{ik} \delta_{jl} + \delta_{ik} W_{jl}) \right\} t_{kl}^{cd} = -\mathbb{I}_{ijab}, \quad (28)$$

which, after contracting the first two terms over all orbital indices $\{k, l, c, d\}$ and the final four terms over virtual-orbital indices $\{c, d\}$ gives

$$[\varepsilon_a + \varepsilon_b] t_{ij}^{ab} - \sum_{kl} \left[\left(F_{ik} + \frac{W_{ik}}{2} \right) \delta_{jl} + \delta_{ik} \left(F_{jl} + \frac{W_{jl}}{2} \right) \right] t_{kl}^{ab} = -\mathbb{I}_{ijab}, \quad (29)$$

where we have not carried out the contraction over indices k and l for the occupied-occupied block of $(\Delta + \mathbf{R}) \cdot \mathbf{t}$ as to emphasize both

that \mathbf{W} only changes the occupied-occupied block and that \mathbf{W} is not diagonal in the basis of canonical orbitals.

One way to solve Eq. (29) is to store the amplitudes in memory and solve for them using an iterative scheme, as is often done in local correlation methods.^{69–71} However, amplitude storage can be avoided if we find a suitable basis, wherein the left-hand side of Eq. (29) is diagonal. To accomplish this goal, we can leverage the orbital invariance of Eq. (29) by rotating the occupied molecular orbitals into a basis where the matrix $\mathbf{F}_{\text{oo}} + \frac{1}{2} \mathbf{W}$ is diagonal (where \mathbf{F}_{oo} is the occupied-occupied block of the Fock matrix). To find the appropriate rotation, we solve the Hermitian eigenvalue equation,

$$\left(\mathbf{F}_{\text{oo}} + \frac{1}{2} \mathbf{W} \right) \mathbf{U} = \tilde{\varepsilon} \mathbf{U}, \quad (30)$$

where $\tilde{\varepsilon}$ are a set of *dressed* occupied orbital eigenvalues. Rotating the occupied molecular orbital coefficients, \mathbf{C}_{occ} , into this new basis via the unitary matrix, \mathbf{U} ,

$$\tilde{\mathbf{C}}_{\text{occ}} = \mathbf{C}_{\text{occ}} \mathbf{U} \quad (31)$$

ensures that the tensor $\Delta + \mathbf{R}$ is diagonal. In this new basis, Eq. (29) takes the form

$$(\varepsilon_a + \varepsilon_b - \tilde{\varepsilon}_i - \tilde{\varepsilon}_j) \tilde{t}_{ij}^{ab} = -\tilde{\mathbb{I}}_{ijab}, \quad (32)$$

where the integrals in $\tilde{\mathbb{I}}_{ijab}$ have been rotated into the new basis. Solving the transformed equation gives the amplitudes

$$\tilde{t}_{ij}^{ab} = -\frac{\tilde{\mathbb{I}}_{ijab}}{(\varepsilon_a + \varepsilon_b - \tilde{\varepsilon}_i - \tilde{\varepsilon}_j)}, \quad (33)$$

and the energy

$$\tilde{E}_c = -\frac{1}{4} \sum_{ijab} \frac{|\tilde{\mathbb{I}}_{ijab}|^2}{(\varepsilon_a + \varepsilon_b - \tilde{\varepsilon}_i - \tilde{\varepsilon}_j)}. \quad (34)$$

Note the use of the dressed eigenvalues $\tilde{\varepsilon}_p$ in the above equations, which are a consequence of the change of basis. These dressed eigenvalues are modulated by the choice of \mathbf{R} , which in our case is related to the ionization potential of the orbital. Specifically, using Koopmans' theorem,⁷² we may rewrite the canonical orbital-energy differences as

$$\Delta_{ij}^{ab} = E_i^{\text{IP}} + E_j^{\text{IP}} - E_a^{\text{EA}} - E_b^{\text{EA}}, \quad (35)$$

where E_p^{IP} and E_p^{EA} are the ionization energy and electron affinity of orbital p , respectively. Considering the relationship in Eq. (27), the action of our regularizer is to replace E_p^{IP} with their correlated counterparts, $\tilde{E}_i^{\text{IP}} = E_i^{\text{IP}} + E_i^{\text{IP},\text{corr}}$, thus augmenting the gap by correlating the ionization energies. Notably, this concept of correcting the quasiparticle energies has strong similarities to Green's function-based perturbation theories,^{39,40} which are actively being explored in the context of regularized perturbation theories.⁴¹

Our adherence to the tensorial formalism and careful consideration of exact conditions ensures that this *ansatz* for the form of \hat{R} retains crucial properties such as size-consistency, size-extensivity, and orbital invariance in the second-order energy. Therefore, we

limit our studies in this work to those that probe the properties of Brillouin-Wigner perturbation theory with a size-consistent second-order correlation energy, herein denoted as BW-s2. The size-consistency of BW-s2 can indeed be proven, and we have done so in Appendix B.

Although we avoid amplitude storage, the BW-s2 energy expression remains self-consistent because the \mathbf{W} matrix depends on the amplitudes, which themselves depend on the modulation of the energy gap supplied by the \mathbf{W} matrix. The flowchart in Fig. 1 shows the iterative protocol that we use to solve for the amplitudes. We opt for an energy convergence threshold such that once the change in energy between iterations is sufficiently small, the algorithm converges. We note that this procedure is general and can be

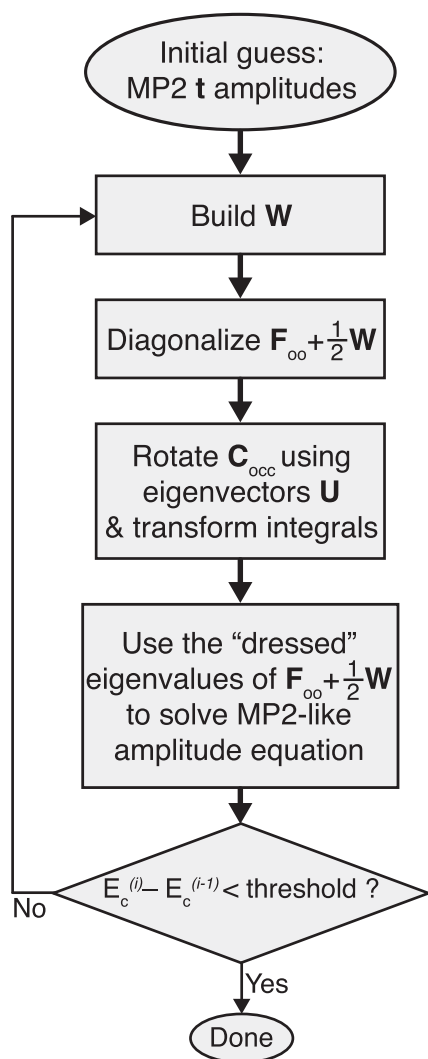


FIG. 1. Flowchart outlining the iterative procedure for solving for the amplitudes for any orbital-invariant second-order correlation method. $E_c^{(i)}$ indicates the correlation energy on the current iteration i , and $E_c^{(i-1)}$ is the correlation energy from the previous iteration.

used in conjunction with all of the orbital-invariant methods listed in Table I. As an example, for MP2, the \mathbf{R} tensor is simply the zero matrix; hence, the rotations supplied by \mathbf{U} are the identity matrix, \mathbf{I} , and the algorithm converges in one step. This corresponds to setting $E = E_0$ in Eq. (18) with the matrix representation of \hat{R} being the zero matrix. Similarly, for δ -MP2, \mathbf{R} is a diagonal matrix whose nonzero entries are the value of δ , leading again to a one-step solution. In the case of the BW2 and xBW2 methods, the \mathbf{W} matrix is diagonal with elements $E_c^{\text{BW2}} \delta_{ij}$ or $(E_c^{\text{xBW2}}/N_e) \delta_{ij}$, again leading to $\mathbf{U} = \mathbf{I}$, but with a self-consistent energy expression that will still require several cycles to converge.

In order to greatly speed up the evaluation of the two-electron integrals, we use the resolution-of-the-identity (RI) approximation,^{73,74} where

$$\langle ia|jb \rangle = \sum_{PQ} \langle ia|P \rangle (P|Q)^{-1} \langle Q|jb \rangle. \quad (36)$$

The RI fit coefficients, C_{pq}^P , for the $|pq\rangle$ charge distribution are

$$C_{pq}^P = \sum_{pqQ} (P|Q)^{-1} \langle Q|pq \rangle, \quad (37)$$

the 3-center, 2-particle density matrix is

$$\Gamma_{ai}^P = \sum_{jb} t_{ij}^{ab} C_{jb}^P, \quad (38)$$

and finally, we also define

$$V_{ia}^P = \langle ia|P \rangle. \quad (39)$$

This allows us to rewrite Eq. (25) as

$$W_{ij} = \frac{1}{2} \sum_{aP} V_{ia}^P \Gamma_{aj}^P + \Gamma_{ia}^P V_{aj}^P, \quad (40)$$

which is bottlenecked by the $\mathcal{O}(N^5)$ construction of Γ , therefore, adding only trivial overhead to the usual MP2 energy evaluation. Finally, we rewrite the MP2-like energy expression from Eq. (34) in the dressed-orbital basis as

$$\tilde{E}_c = -\frac{1}{2} \sum_{iaP} \tilde{V}_{ia}^P \tilde{\Gamma}_{ai}^P, \quad (41)$$

where $\tilde{\Gamma}$ and \tilde{V} are constructed using the transformed integrals and amplitudes according to Eqs. (31) and (32). With iterative $\mathcal{O}(N^5)$ cost, the RI approximation makes the BW-s2 approach comparable in cost with other common methods like CC2^{75,76} or EOM-MBPT2.⁷⁷

III. COMPUTATIONAL DETAILS

All calculations were performed in a development version of Q-Chem v6.0.2.⁷⁸ All SCF convergence thresholds were set to 10^{-8} root-mean-square error and the convergence threshold for the correlation energy was likewise set to 10^{-8} hartree for all calculations except for those of the L7 dataset, where it was reduced to 10^{-5} hartree for the sake of computational cost. This should not influence the accuracy of the calculations because an energy difference of

10^{-5} hartree is only 0.006 kcal/mol. We note that even in the case of a tight Brillouin-Wigner correlation energy threshold of 10^{-8} hartree, only six cycles were required on average (regardless of the dataset) to converge the correlation energy.

To avoid the well-known degradation of perturbation theory results in systems with appreciable spin-contamination,^{79–84} we use restricted open-shell orbitals, which are separately pseudocanonically in the α and β spaces before computing the correlation energy in all open-shell systems, akin to the RMP2 method.⁸³ We include the non-Brillouin singles (NBS) contributions via

$$E_{\text{NBS}} = -\sum_{ia} \frac{|F_{ia}|^2}{\epsilon_a - \epsilon_i}, \quad (42)$$

where F_{ia} are off-diagonal Fock matrix elements. Notably, E_{NBS} is invariant to the change of basis that is used to solve the BW-s2 equations. Although Kohn–Sham orbitals have been applied to Møller–Plesset perturbation theory with great effect,^{85–87} we emphasize that we use the Hartree–Fock reference determinant throughout this work, leaving the prospect of combining Kohn–Sham orbitals with BW-s2 for future exploration.

IV. RESULTS AND DISCUSSION

We first assess the fundamental properties of various second-order correlation methods with some simple numerical tests. We have proven the size-consistency, and by extension size-extensivity of BW-s2 in Appendix B, but from a practical perspective, it is important to recover these properties in numerical calculations; hence, these tests will serve to aid in the verification of our implementation. Although we make some conclusions about the size-extensivity, size-consistency, and unitary invariance of other methods in this section, we emphasize that these tests are insufficient to prove that a given method has these properties in general. However, it is necessary that any method that is size-consistent, size-extensive, and unitary invariant must recover the expected results in the following tests; hence, a failure on any one of these metrics is sufficient to discount a method from having the property that the metric was designed to test.

For the first test, we check for orbital invariance by using canonical and Edmiston–Freudenberg localized orbitals^{88,89} with the cc-pVDZ^{90,91} basis set on the H_2 dimer, placed in a parallel configuration at 5.4 Å separation. A method that yields the same correlation energy despite arbitrary orbital rotations in the occupied (or virtual) subspace is considered to be orbital invariant; therefore, we should expect no change in the correlation energy on the change from canonical to localized orbital representations. In the cases of the MP2, BW2, xBW2, and BW-s2 methods, the correlation energy remains exactly the same, regardless of the orbital representation, but the IEPA/BGE2 method is not invariant to orbital rotations, leading to an energy difference of 6.3 meV between canonical and localized representations. This is a well-known result^{11,62,63} and actually requires that we skip the orbital rotation step in the algorithm in Fig. 1 for the IEPA/BGE2 method, instead opting for a direct solution of the correlation energy expression with off-diagonal contributions from the pair-correlation energy in the denominator.

We next assess size-consistency by calculating the interaction energy between He and Xe at 40 Å separation using the Def2-SVP/Def2-ECP basis set and effective core potential.⁹² A method is considered to be size-consistent if the total energy for a supersystem comprised of noninteracting subsystems A and B is the same as the sum of the energies of the individual subsystems, $E(A+B) = E(A) + E(B)$. In our case, the He...Xe interaction energy at 40 Å separation should obviously be zero if a method is properly size-consistent, which is precisely the result obtained with the MP2, IEPA/BGE2, and BW-s2 methods. The BW2 method has a large residual correlation energy of 111 meV and xBW2 gives a smaller, but still significant 1 meV interaction energy for this system. This implies that the size-extensive xBW2 method is not size-consistent, which could have dramatic consequences in calculations on extended systems, for which it was proposed.⁵⁸

Finally, as a metric for size-extensivity, Fig. 2 examines the correlation energy per electron in a linear chain of He atoms. A method is considered to be size-extensive if, for any chain of identical subsystems, the total correlation energy grows linearly with the number of electrons in the system. Thus, the slope of each line in Fig. 2 should be zero for a size-extensive method. This is the case for MP2, xBW2, and BW-s2, but not for BW2 or IEPA/BGE2. The Brillouin–Wigner series is infamous for its failure as a many-body theory, and the monotonic decrease in correlation energy per electron of BW2 makes this abundantly clear. IEPA/BGE2 exhibits a strange behavior, approaching a slope of zero in the limit of an infinitely large He chain, but with an inverse-power dependence on the number of electrons. In this sense, for finite systems, IEPA/BGE2 is not size-extensive, and because finite systems encompass nearly all practical calculations, we consider this a notable failure of IEPA/BGE2. Finally, we note that for a single He atom, the BW2, IEPA/BGE2, and BW-s2 methods yield the same correlation energy, which is expected for two-electron systems. The summary of the findings of all of these tests can be seen in Table I.

So far, we have used the raw form of Eq. (24), but we should note that this form is somewhat arbitrary and may be amenable to a scaling parameter, α , that modulates the extent of regularization in the form $\alpha\mathbf{R}$. Such a parameter would maintain the size-consistent/extensive nature of the perturbation theory, as

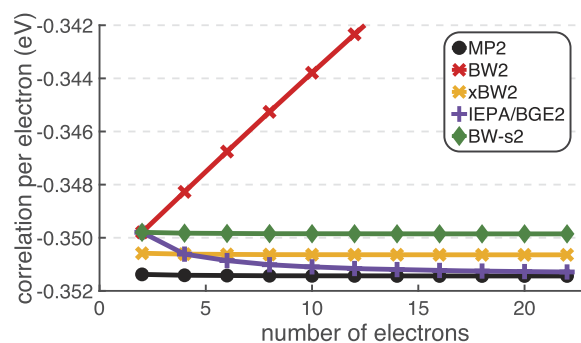


FIG. 2. Correlation energy per electron in He chains of increasing size using the cc-pVDZ basis set. The spacing between He atoms was set to 3 Å. All calculations were done in the full basis of all He atoms by including ghost functions for the atoms that are not included explicitly.

$E = \bar{E}_0 + \alpha E^{(2)}$ in Eq. (18) and $\text{tr}(\mathbf{W}) = \alpha E^{(2)}$ in this case. Fortunately, the agreement between BW-s2 and BW2 for two-electron systems offers an exact condition for which the parameter α can be set. For a two-state system, BWPT yields the exact energy at the second order⁴⁵; hence, we should expect BW2 and a properly parameterized BW-s2 to achieve the exact dissociation limit for the hydrogen molecule in a minimal (two-orbital) basis set. It can be shown that in such a minimal basis set, the regularizer tensor in Eq. (24) reduces to the BW2 correlation energy if and only if $\alpha = 1$ (i.e., the unmodified tensor), allowing us to set the value of α from first principles. Somewhat more laboriously, it can also be shown that at the dissociation limit in this minimal basis, the optimal BW2 and BW-s2 amplitude is exactly $t_{ii}^{aa} = 1$, as expected for a two-electron, two-orbital system where the orbitals i and a are exactly degenerate.

From here, we resort to numerical testing to illustrate the behavior of BW-s2($\alpha = 1$) for H_2 dissociation in minimal and non-minimal basis sets. Dissociation curves in both STO-3G⁹⁴ and aug-cc-pV5Z basis sets for the $\alpha = 1$ case are shown in Fig. 3(a). As one might expect, the STO-3G results with restricted Hartree-Fock (RHF) orbitals show a steep rise to energies that are too high, whereas the energies using unrestricted Hartree-Fock (UHF) orbitals quickly meet the full configuration interaction (FCI) result for the dissociation limit, leading to the appearance of a Coulson-Fischer point at 1.3 Å. What is most interesting is the

behavior at the asymptotic limit, where the highest occupied molecular orbital and lowest unoccupied molecular orbital are exactly degenerate and the RHF MP2 energy diverges. In this limit, we find that the appropriately parameterized BW-s2($\alpha = 1$)/STO-3G theory converges to the exact FCI result, regardless of whether the initial orbitals were spin-polarized. However, with BW-s2($\alpha = 1$, RHF)/aug-cc-pV5Z, the FCI limit is no longer attained at the second order, and we instead find an upper bound to the exact result. Encouragingly, the RHF/UHF difference remains quite small even in the large basis set at roughly 12 mhartree; hence, we shall retain the *ab initio* $\alpha = 1$ parameter throughout this work.

Repeating this exercise by fitting the value of κ such that the κ -MP2/STO-3G energy with RHF orbitals equates to the FCI energy at the asymptotic limit results in an optimal $\kappa = 495.2$ hartree⁻¹, amounting to what appears to be almost no regularization. However, with a gap of almost zero, the Δ -dependent regularizers naturally suppress most of the correlation energy as the extent of regularization is proportional to $(1 - \exp[-\kappa\Delta_{ij}^{ab}])$; hence, the optimal κ value must be large to retain any appreciable amount of correlation. Such a limit of near-degenerate orbitals, therefore, leads to a situation where the optimal value of κ becomes exponentially sensitive to the particular value of the (very small) energy gap, introducing acute basis set dependence. For instance, using the same value of κ from the STO-3G calculation leads to an RHF-like energy of -0.76 hartree in the aug-cc-pV5Z basis set. Unfortunately, this implies

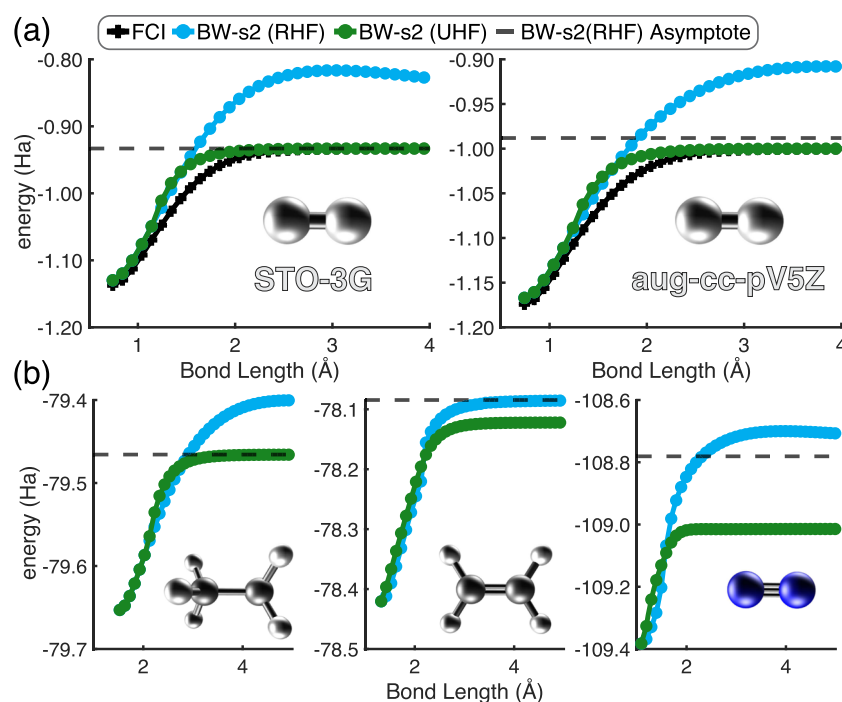


FIG. 3. Bond-stretching potential energy curves for (a) dissociation of the hydrogen molecule with BW-s2($\alpha = 1$) in (left) a minimal basis set of two orbitals and (right) a fairly complete basis set and (b) from left to right, C–C, C=C, and N≡N dissociation curves of ethane, ethene, and nitrogen, respectively. The gray-dashed lines mark the asymptotic limit of BW-s2 with RHF orbitals as numerically estimated by a calculation in which the bond length was set to 100 000 Å. The potential energy curves in (b) were calculated using the aug-cc-pVQZ basis set. All equilibrium geometries were optimized at the ω B97X-V/Def2-TZVPPD level,⁹³ and the equilibrium bond distance was incremented by 0.1 Å steps to generate the potential surfaces.

that such *ab initio* parameterization for Δ -dependent regularizers is not appropriate, but these results also showcase a crucial advantage of amplitude-dependent regularization in BW-s2; namely, BW-s2 will predict nonzero correlation energies between orbitals that are exactly degenerate, perhaps improving its performance for statically correlated systems.

Additional potential energy curves that feature single-bond breaking in ethane, double-bond breaking in ethene, and triple-bond breaking in nitrogen are shown in Fig. 3(b). Remarkably, BW-s2 succeeds in breaking the C–C sigma bond in ethane without error in the dissociation limit such that the RHF and UHF solutions are asymptotically equivalent. Although it might be expected that BW-s2 performs well in the case of a two-electron, two-orbital strong correlation, one might be less optimistic about how a double-substitution theory will hold up when multiple bonds are dissociated. Indeed, as the bond order increases, the asymptotic solution of BW-s2 with RHF orbitals deviates further and further from the spin-polarized result, leading to the errors of 47 and 233 mhartree for ethene and nitrogen, respectively. Despite this, the potential energy curves are smooth and do not yield any particularly surprising results. The performance of BW-s2 in the sigma-bond breaking of H₂ and ethane is highly encouraging for future single-bond breaking applications.

We now turn our attention to the statistical performance of the BW-s2 method across several noncovalent interaction (NCI) datasets. The NCI datasets span a wide range of molecular sizes and interaction types. Where A24,⁹⁵ S22,¹⁷ S66,⁹⁶ and the non-I containing a subset of X40 (herein called X31)⁹⁷ are datasets of small to medium-sized nonbonded molecular complexes with a variety of interaction motifs, the L7 dataset contains mostly nanoscale π -stacking interactions that are particularly difficult for MP2.⁹⁸ To compare with the benchmark complete basis set limit (CBS) coupled-cluster with single, double, and perturbative triple substitutions [CCSD(T)] data, all perturbation theory results are extrapolated to the CBS limit using the aug-cc-pVDZ/aug-cc-pVTZ^{90,99} extrapolation scheme from Ref. 100. We note for the L7 set that we compare with the updated domain-localized pair natural orbital CCSD(T₀)/CBS^{101–104} benchmarks of Lao and co-workers and that we use the heavy-aug-cc-pVDZ/heavy-aug-cc-pVTZ extrapolation method that was recommended therein.¹⁰⁵

The results for the NCI datasets in Fig. 4 compare BW-s2, MP2, and κ -MP2 using several κ parameters for each respective dataset. Regularized perturbation theories outperform MP2 for S22, S66, and X31 datasets and are only marginally different from MP2 for the A24 set where MP2 already performs quite well. The optimal value of κ changes a fair amount between the NCI datasets ($1.1 \leq \kappa \leq 1.45$ hartree⁻¹); hence, we report results from κ -MP2 with the optimal parameter along with the two previously suggested “universal” parameters $\kappa = 1.1$ ¹² and $\kappa = 1.45$.³³ The results obtained with $\kappa = 1.1$ and the optimized value of κ , $\kappa(\text{opt})$, offer consistently low errors across the NCI benchmarks, and $\kappa = 1.45$ performs well across all but the L7 dataset, where the error increases dramatically from 1.3 to 4.2 kcal/mol with $\kappa(\text{opt})$ and $\kappa = 1.45$, respectively. Across all NCI datasets, BW-s2 performs roughly the same as $\kappa = 1.45$ with slightly larger errors on average. Notably, on the A24 dataset, BW-s2 outperforms all methods, which contrasts with the fact that all κ -MP2 results give errors greater than or equal to MP2. This suggests that BW-s2 has some degree of flexibility in its

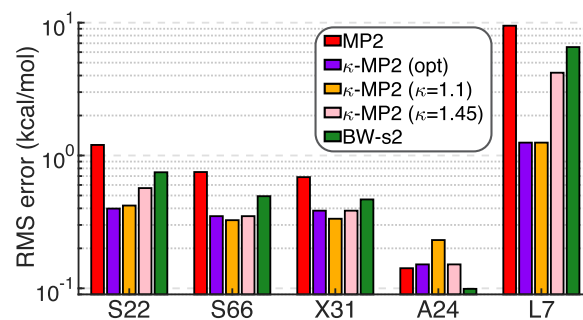


FIG. 4. Root-mean-squared errors (log scale) of various second-order perturbation theories against CCSD(T)/CBS reference energies for noncovalent interaction datasets. The optimal (opt) κ parameters for κ -MP2 were set to 1.2 hartree⁻¹ for S22; 1.45 hartree⁻¹ for S66, X31, and A24; and 1.1 hartree⁻¹ for L7 as per Ref. 12.

regularization that is not present in κ -MP2, perhaps hinting at some additional transferability offered by the BW-s2 framework. Overall, it is encouraging to see such a similar performance between BW-s2 and one of the suggested “universal” κ parameters, especially given that BW-s2 is parameter-free.

This notion of transferability can be further tested by examining H and heavy-atom transfer barrier heights of HTBH38 and NHTBH38,^{106,107} where MP2 performs better without regularization.¹² The data in Fig. 5 show that MP2 still performs better without regularization, but BW-s2 comes very close to this unregularized limit. As the κ parameter in κ -MP2 is adjusted away from the rather large (optimal) value of $\kappa = 1.6$ to either of the two “universal” values of $\kappa = 1.45$ or $\kappa = 1.1$, the errors climb dramatically. This is a clear reminder that κ -MP2 does not truly have a universal parameter that works well for all chemical problems, but the good performance of BW-s2 here seems to indicate that BWPT may be more versatile. The self-consistent nature of the BWPT equations leads to a modulation

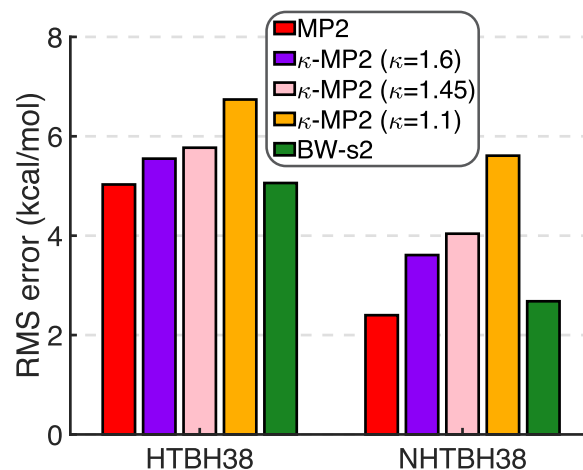


FIG. 5. Root-mean-squared errors of various second-order perturbation theories against theoretical best-estimate values for H-atom transfer (HTBH38) and non-H-atom transfer (NHTBH38) datasets. All data were extrapolated to the CBS limit using an aug-cc-pVTZ/aug-cc-pVQZ extrapolation scheme.

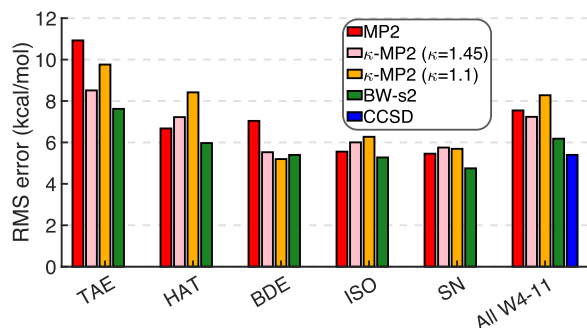


FIG. 6. Root-mean-squared errors for various second-order perturbation theories with respect to the subsets of thermochemical data within W4-11 that includes total atomization energies (TAE), heavy-atom transfer (HAT), bond-dissociation energies (BDE), isomerization (ISO), and nucleophilic substitution (SN) energies. The CBS limit results for all of W4-11 were obtained with an aug-cc-pVTZ/aug-cc-pVQZ extrapolation scheme and are compared with CCSD data from Ref. 108.

of the fundamental gap that is informed by the value of \mathbf{W} , which in turn is informed by the amplitudes, introducing a feedback loop that leads to improved transferability of BW-s2 over that of noniterative gap-dependent regularizers.

We now consider the nonmultireference subset of the W4-11 thermochemical database,¹⁰⁹ which includes 124 atomization energies, 505 heavy-atom transfer energies, 83 bond-dissociation energies, 20 isomerization energies, and 13 nucleophilic substitution energies of small molecules and radicals. The data in Fig. 6 show that κ -MP2 does not generally improve upon the MP2 results, occasionally making matters worse for heavy-atom transfers, isomerization, and nucleophilic substitution energies. Even the value of $\kappa = 1.45$, which was parameterized on the W4-11 dataset, performs only about as well as MP2 overall. On the other hand, BW-s2 far exceeds the performance of κ -MP2 with tangible reductions in errors across all subsets of W4-11 except for bond-dissociation energies that remain roughly the same. For the whole W4-11 set, the BW-s2 results are markedly better than MP2 and κ -MP2, even rivaling the overall performance of CCSD.

The largest improvements offered by BW-s2 are in the total atomization energies, improving upon the MP2 results by 3 kcal/mol. Overall, BW-s2 has a root-mean-squared error (RMSE) of 6.2 kcal/mol for W4-11, improving thermochemical properties relative to MP2 and κ -MP2 by roughly 1.5 kcal/mol. These data suggest that the BW-s2 method does not only track well with gap-dependent regularizers for NCIs, but for barrier heights and general thermochemical properties, it exceeds their performance, implying that BWPT approaches may be more transferable across chemical problems.

Another setting where regularized MP2 seems to thrive, whereas MP2 often fails is in transition metal systems.¹² To assess our approach, we report a finite-basis set comparison of MP2, κ -MP2, and BW-s2 against the def2-TZVPP data of the metal-organic reactions (MOR41) dataset in Fig. 7.¹³ For transition metal systems, MP2 performs poorly with an RMSE of 12.4 kcal/mol and κ -MP2 with a very low $\kappa = 0.8$ performs quite admirably with an RMSE of 5 kcal/mol. However, this value of κ represents very strong regularization, and values of $\kappa = 1.1$ or $\kappa = 1.45$ are more appropriate

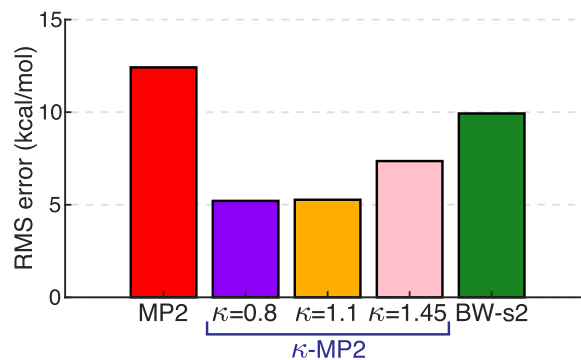


FIG. 7. Root-mean-squared error for the MOR41 dataset for MP2, κ -MP2, and BW-s2 using the def2-TZVPP basis along with the def2-ECP for 4d and 5d metal atoms. An optimal value of $\kappa = 0.8$ was determined in Ref. 12.

for general usage. The error does not increase when going to $\kappa = 1.1$, but it increases noticeably to 7.4 kcal/mol with $\kappa = 1.45$. Although BW-s2 does not perform as well as κ -MP2 on MOR41, the RMSE is still reduced by 2.4 kcal/mol relative to MP2.

Regarding the κ -MP2 results, the parameter $\kappa = 0.8$ is very small and performs poorly for NCIs, barrier heights, and thermochemical properties, suggesting that it is highly adapted to transition metal complexes. Although the results in Fig. 7 highlight some limitations in the flexibility of BW-s2, whose errors are most similar to κ -MP2 ($\kappa = 1.45$), it also shows that empirical parameterization can be tailor-made for a given class of chemical problem. Overall, BW-s2 provides a satisfactory improvement relative to MP2 for transition metal systems while remaining comparable with κ -MP2 within a more typical κ parameter range.

V. CONCLUSIONS

We have suggested a novel partitioning of the Hamiltonian into a zero-order part that includes the usual sum of Fock operators along with a regularizer operator that acts to screen the pair correlations in the resultant theory. We cast the second-order Brillouin Wigner energy from this theory into a tensor framework such that orbital invariance was straightforwardly preserved, and we chose a form of the regularizer operator that resulted in a size-consistent and size-extensive second-order energy. We also suggested a general algorithm to solve the self-consistent second-order equation at $\mathcal{O}(N^5)$ cost and without the need to store amplitudes.

Over a small set of single-, double-, and triple-bond dissociations, second-order size-consistent Brillouin-Wigner perturbation theory with a shifted zero-order Hamiltonian (BW-s2) performs encouragingly by dissociating the C-C bond in ethane to an asymptotic limit that is invariant to the spin-polarization of the reference orbitals, while also supplying smooth potential energy curves for multiple-bond dissociation in ethene and nitrogen. Our approach is exact for two-electron, two-orbital systems and dissociates minimum basis H_2 to the full configuration interaction limit, regardless of the choice of reference orbitals. The BW-s2 approach also performs about as well as the κ -MP2 approach across noncovalent interactions of small molecules, and although performing only

slightly worse than κ -MP2 ($\kappa = 1.45$) for metal/organic reaction barriers and noncovalent interaction energies of nanoscale π -stacked systems, BW-s2 still improves significantly upon the MP2 results. Importantly, for broad thermochemical properties, BW-s2 outperforms κ -MP2 by a wide margin, even nearing the performance of CCSD.

The L7 and MOR41 datasets require exceptionally strong regularization for κ -MP2 to be successful ($\kappa = 1.1$ and $\kappa = 0.8$, respectively). In these cases, BW-s2 does not match the accuracy of κ -MP2 as it generally supplies softer regularization that tends to be more comparable with a more conservative κ -MP2 ($\kappa = 1.45$). Hence, although BW-s2 is less flexible than empirically parameterized regularizers, it still gives results that are consistent with typical values of κ when the requisite κ -regularizer becomes extreme. All of this was accomplished with an *ab initio* partitioning of the Hamiltonian, which itself could be parameterized to augment the strength of the regularization.

SUPPLEMENTARY MATERIAL

Geometries for H₂, N₂, ethane, and ethene at each point along the potential energy surfaces shown in Fig. 3.

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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: Formal analysis (equal); Investigation (equal); Software (lead); Writing - original draft (lead); Writing - review & editing (equal). **Martin Head-Gordon:** Conceptualization (lead); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Supervision (lead); Writing - review & editing (equal).

DATA AVAILABILITY

Cartesian coordinates for each point along the bond-dissociation potential energy curves are available in the supplementary material. The data that support the findings of

this study are available from the corresponding authors upon reasonable request.

APPENDIX A: ADDITIONAL NOTES ON THE FORM OF W

Let us consider the simple case of a system with a single doubly occupied orbital and n_v virtual orbitals. In this case, Eq. (22) can be iteratively solved directly in the canonical molecular orbital basis, as **W** is trivially diagonal when only one occupied orbital is present (i.e., the orbitals are fixed in the canonical representation). The amplitudes take the form t_{ii}^{ab} , and the matrix elements W_{ii} work out to be

$$W_{ii} = \sum_{ab} t_{ii}^{ab} (ii||ab) = 2E_c^{\text{IP},i}. \quad (\text{A1})$$

When we consider constructing the full denominator with Δ_{ii}^{ab} and R_{ii}^{ab} [Eq. (24)], it becomes apparent that this factor of two is necessary,

$$R_{ii}^{ab} = \frac{1}{2} (W_{ii} + W_{ii}) = 2E_c^{\text{IP},i}, \quad (\text{A2})$$

leading to the full denominator,

$$\Delta_{ii}^{ab} + R_{ii}^{ab} = \varepsilon_a + \varepsilon_b - 2\varepsilon_i + 2E_c^{\text{IP},i} = 2E^{\text{IP},i} + 2E_c^{\text{IP},i} - E^{\text{EA},a} - E^{\text{EA},b}. \quad (\text{A3})$$

Therefore, the factor of 2× the ionization energy is required to augment both occupied orbital energies (ionization potentials) by the correlation contribution.

We note that analysis of the MP2 correlation energy in terms of Koopmans' theorem has been employed to understand why MP2 energy denominators are typically overestimated, even in manifestly nondegenerate cases; namely, that this can be understood in terms of missing particle-hole interactions, which would otherwise stabilize the zeroth-order double-excitations.¹¹⁰ The contribution of $E_i^{\text{IP},\text{corr}}$ is consistently positive, though for any given orbital pair, the corresponding elements W_{ij} are not necessarily negative. The overall effect of this is to increase the energy gaps, but **W** still incorporates off-diagonal contributions that destabilize the final orbital energies.

APPENDIX B: PROOF OF BW-s2 SIZE-CONSISTENCY

We consider two closed shell subsystems, *A* and *B*, that are infinitely far apart. As the subsystems are isolated from one another and the BW-s2 energy is orbital invariant by nature of the tensor formulation, we can cleanly ascribe occupied and virtual orbitals to each subsystem. We first examine the form of the **W** matrix, Eq. (25), in this localized orbital basis,

$$\mathbf{W} = \begin{bmatrix} \mathbf{W}_{AA} & \mathbf{W}_{AB} \\ \mathbf{W}_{BA} & \mathbf{W}_{BB} \end{bmatrix}, \quad (\text{B1})$$

where *A* and *B* denote the subsystem. In this form, we can readily rule out the cross terms by examining

$$W_{i_A j_B} = \frac{1}{2} \sum_{PQR} \sum_{k_p a_Q b_R} t_{i_A k_p}^{a_Q b_R} (j_B k_p || a_Q b_R) + t_{j_B k_p}^{a_Q b_R} (i_A k_p || a_Q b_R), \quad (\text{B2})$$

where P , Q , and R run over A and B subsystem indices. In the case $P = A$, the integrals $(j_B k_A \| ab) = 0$, which includes $t_{j_B k_A}^{ab}$, and in the case $P = B$, all integrals $(i_A k_B \| ab) = 0$, resulting in $W_{i_A j_B} = 0 \forall k_P$. The only terms that survive are those where i , j and k belong to the same subsystem. Of those, the integrals $(i_A k_A \| a_B b_A) = (i_A k_A \| a_B b_B) = 0$ as these are excitations from occupied orbitals in one subsystem to virtual orbitals in another. Thus, the only integrals that are nonzero are those that satisfy $\{i, j, k, a, b\} \in A$ or $\{i, j, k, a, b\} \in B$. The matrix \mathbf{W} , therefore, takes the form

$$\mathbf{W} = \begin{bmatrix} \mathbf{W}_{AA} & \mathbf{0} \\ \mathbf{0} & \mathbf{W}_{BB} \end{bmatrix}, \quad (\text{B3})$$

whenever i and j are disjoint. This result verifies that \mathbf{W} itself does not couple non-interacting subsystems, just like the Fock matrix, \mathbf{F} or the two-electron integral tensor. In addition, just like \mathbf{F}_{AA} , contributions to \mathbf{W}_{AA} are completely independent of the presence of B and vice versa.

Next, we turn to the correlation energy, which can be written in the dressed orbital basis as

$$E_c^{(2)} = -\frac{1}{4} \sum_{ijab} \frac{|(ij \| ab)|^2}{\Delta_{ij}^{ab} + \frac{1}{2}(W_{ii} + W_{jj})}. \quad (\text{B4})$$

Since we ruled out any cross terms from \mathbf{W} above, W_{ii} and W_{jj} simply shift the orbital energies i and j within their respective subsystems, independent of the presence of other subsystems. This establishes the BW-s2 energy of each subsystem is independent of the other, since we can tag each molecular orbital with a subsystem index and repeat the above exercise that was carried out for the elements of \mathbf{W} ,

$$E_c^{(2)} = -\frac{1}{4} \sum_{PQRS} \sum_{i_P j_Q a_R b_S} \frac{|(i_P j_Q \| a_R b_S)|^2}{\Delta_{i_P j_Q}^{a_R b_S} + \frac{1}{2}(W_{i_P i_P} + W_{j_Q j_Q})}. \quad (\text{B5})$$

Hence, we find that the only terms that survive are $\{i, j, a, b\} \in A$ and $\{i, j, a, b\} \in B$. Thus, BW-s2 is size-consistent and by trivial extension, size-extensive.

REFERENCES

- D. Cremer, "Møller–Plesset perturbation theory: From small molecule methods to methods for thousands of atoms," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **1**, 509–530 (2011).
- Y. Zhang and W. Yang, "A challenge for density functionals: Self-interaction error increases for systems with a noninteger number of electrons," *J. Chem. Phys.* **109**, 2604–2608 (1998).
- P. Mori-Sánchez, A. J. Cohen, and W. Yang, "Many-electron self-interaction error in approximate density functionals," *J. Chem. Phys.* **125**, 201102 (2006).
- P. Mori-Sánchez, A. J. Cohen, and W. Yang, "Localization and delocalization errors in density functional theory and implications for band-gap prediction," *Phys. Rev. Lett.* **100**, 146401 (2008).
- K. Sharkas, J. Toulouse, and A. Savin, "Double-hybrid density-functional theory made rigorous," *J. Chem. Phys.* **134**, 064113 (2011).
- J. C. Sancho-García and C. Adamo, "Double-hybrid density functionals: Merging wavefunction and density approaches to get the best of both worlds," *Phys. Chem. Chem. Phys.* **15**, 14581–14594 (2013).
- L. Goerigk and S. Grimme, "Double-hybrid density functionals," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **4**, 576–600 (2014).
- E. Brémond, I. Ciofini, J. C. Sancho-García, and C. Adamo, "Nonempirical double-hybrid functionals: An effective tool for chemists," *Acc. Chem. Res.* **49**, 1503–1513 (2016).
- C. Kalai and J. Toulouse, "A general range-separated double-hybrid density-functional theory," *J. Chem. Phys.* **148**, 164105 (2018).
- J. M. L. Martin and G. Santra, "Empirical double-hybrid density functional theory: A 'third way' in between WFT and DFT," *Isr. J. Chem.* **60**, 787–804 (2020).
- A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (Macmillan, New York, 1982).
- J. Shee, M. Loipersberger, A. Rettig, J. Lee, and M. Head-Gordon, "Regularized second-order Møller–Plesset theory: A more accurate alternative to conventional MP2 for noncovalent interactions and transition metal thermochemistry for the same computational cost," *J. Phys. Chem. Lett.* **12**, 12084–12097 (2021).
- S. Dohm, A. Hansen, M. Steinmetz, S. Grimme, and M. P. Checinski, "Comprehensive thermochemical benchmark set of realistic closed-shell metal organic reactions," *J. Chem. Theory Comput.* **14**, 2596–2608 (2018).
- M. O. Sinnokrot, E. F. Valeev, and C. D. Sherrill, "Estimates of the *ab initio* limit for π - π interactions: The benzene dimer," *J. Am. Chem. Soc.* **124**, 10887–10893 (2002).
- R. L. Jaffe and G. D. Smith, "A quantum chemistry study of benzene dimer," *J. Chem. Phys.* **105**, 2780–2788 (1996).
- S. Tsuzuki, T. Uchimaru, K. Matsumura, M. Mikami, and K. Tanabe, "Effects of the higher electron correlation correction on the calculated intermolecular interaction energies of benzene and naphthalene dimers: Comparison between MP2 and CCSD(T) calculations," *Chem. Phys. Lett.* **319**, 547–554 (2000).
- P. Jurečka, J. Šponer, J. Černý, and P. Hobza, "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.* **8**, 1985–1993 (2006).
- K. Carter-Fenk, K. U. Lao, K.-Y. Liu, and J. M. Herbert, "Accurate and efficient *ab initio* calculations for supramolecular complexes: Symmetry-adapted perturbation theory with many-body dispersion," *J. Phys. Chem. Lett.* **10**, 2706–2714 (2019).
- B. D. Nguyen, G. P. Chen, M. M. Agee, A. M. Burow, M. P. Tang, and F. Furche, "Divergence of many-body perturbation theory for noncovalent interactions of large molecules," *J. Chem. Theory Comput.* **16**, 2258–2273 (2020).
- S. Grimme, "Improved second-order Møller–Plesset perturbation theory by separate scaling of parallel- and antiparallel-spin pair correlation energies," *J. Chem. Phys.* **118**, 9095–9102 (2003).
- Y. Jung, R. C. Lochan, A. D. Dutoi, and M. Head-Gordon, "Scaled opposite-spin second order Møller–Plesset correlation energy: An economical electronic structure method," *J. Chem. Phys.* **121**, 9793–9802 (2004).
- R. C. Lochan, Y. Shao, and M. Head-Gordon, "Quartic-scaling analytical energy gradient of scaled opposite-spin second-order Møller–Plesset perturbation theory," *J. Chem. Theory Comput.* **3**, 988–1003 (2007).
- R. C. Lochan, Y. Jung, and M. Head-Gordon, "Scaled opposite spin second order Møller–Plesset theory with improved physical description of long-range dispersion interactions," *J. Phys. Chem. A* **109**, 7598–7605 (2005).
- F. Neese, T. Schwabe, S. Kossmann, B. Schirmer, and S. Grimme, "Assessment of orbital-optimized, spin-component scaled second-order many-body perturbation theory for thermochemistry and kinetics," *J. Chem. Theory Comput.* **5**, 3060–3073 (2009).
- M. Goldey, A. Dutoi, and M. Head-Gordon, "Attenuated second-order Møller–Plesset perturbation theory: Performance within the aug-cc-pVTZ basis," *Phys. Chem. Chem. Phys.* **15**, 15869–15875 (2013).
- M. Goldey and M. Head-Gordon, "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.* **3**, 3592–3598 (2012).
- M. Goldey and M. Head-Gordon, "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* **118**, 6519–6525 (2014).

- ²⁸M. B. Goldey, B. Belzunces, and M. Head-Gordon, "Attenuated MP2 with a long-range dispersion correction for treating nonbonded interactions," *J. Chem. Theory Comput.* **11**, 4159–4168 (2015).
- ²⁹D. Stück and M. Head-Gordon, "Regularized orbital-optimized second-order perturbation theory," *J. Chem. Phys.* **139**, 244109 (2013).
- ³⁰S. M. Sharada, D. Stück, E. J. Sundstrom, A. T. Bell, and M. Head-Gordon, "Wavefunction stability analysis without analytical electronic Hessians: Application to orbital-optimized second-order Møller–Plesset theory and VV10-containing density functionals," *Mol. Phys.* **113**, 1802–1808 (2015).
- ³¹E. Soydaş and U. Bozkaya, "Assessment of orbital-optimized MP2.5 for thermochemistry and kinetics: Dramatic failures of standard perturbation theory approaches for aromatic bond dissociation energies and barrier heights of radical reactions," *J. Chem. Theory Comput.* **11**, 1564–1573 (2015).
- ³²R. M. Razban, D. Stück, and M. Head-Gordon, "Addressing first derivative discontinuities in orbital-optimized opposite-spin scaled second-order perturbation theory with regularisation," *Mol. Phys.* **115**, 2102–2109 (2017).
- ³³J. Lee and M. Head-Gordon, "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.* **14**, 5203–5219 (2018).
- ³⁴U. Bozkaya, A. Ünal, and Y. Alagöz, "Energy and analytic gradients for the orbital-optimized coupled-cluster doubles method with the density-fitting approximation: An efficient implementation," *J. Chem. Phys.* **153**, 244115 (2020).
- ³⁵R. Fink and V. Staemmler, "A multi-configuration reference CEPA method based on pair natural orbitals," *Theor. Chim. Acta* **87**, 129–145 (1993).
- ³⁶R. F. Fink, "Two new unitary-invariant and size-consistent perturbation theoretical approaches to the electron correlation energy," *Chem. Phys. Lett.* **428**, 461–466 (2006).
- ³⁷R. F. Fink, "The multi-reference retaining the excitation degree perturbation theory: A size-consistent, unitary invariant, and rapidly convergent wavefunction based *ab initio* approach," *Chem. Phys.* **356**, 39–46 (2009).
- ³⁸S. Behnle and R. F. Fink, "UREMP, RO-REMP, and OO-REMP: Hybrid perturbation theories for open-shell electronic structure calculations," *J. Chem. Phys.* **156**, 124103 (2022).
- ³⁹T. N. Lan, A. A. Kananenka, and D. Zgid, "Rigorous *ab initio* quantum embedding for quantum chemistry using Green's function theory: Screened interaction, nonlocal self-energy relaxation, orbital basis, and chemical accuracy," *J. Chem. Theory Comput.* **12**, 4856–4870 (2016).
- ⁴⁰D. Neuhauser, R. Baer, and D. Zgid, "Stochastic self-consistent second-order Green's function method for correlation energies of large electronic systems," *J. Chem. Theory Comput.* **13**, 5396–5403 (2017).
- ⁴¹C. J. N. Coveney and D. P. Tew, [arXiv:2302.13296](https://arxiv.org/abs/2302.13296) (2023).
- ⁴²J. E. Lennard-Jones, "Perturbation problems in quantum mechanics," *Proc. R. Soc. A* **129**, 598–615 (1930).
- ⁴³L. Brillouin, "Les problèmes de perturbations et les champs self-consistents," *J. Phys. Radium* **3**, 373–389 (1932).
- ⁴⁴E. P. Wigner, *On a Modification of the Rayleigh–Schrödinger Perturbation Theory, Part I: Physical Chemistry. Part II: Solid State Physics, The Collected Works of Eugene Paul Wigner*, edited by A. S. Wightman (Springer, 1997).
- ⁴⁵I. Hubač and S. Wilson, *Brillouin-Wigner Methods for Many-Body Systems* (Springer, 2010).
- ⁴⁶N. H. March, W. H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Cambridge University Press, 1967); reprinted by Dover Publications, New York.
- ⁴⁷W. Wenzel, "Excitation energies in Brillouin-Wigner-based multireference perturbation theory," *Int. J. Quantum Chem.* **70**, 613–622 (1998).
- ⁴⁸J. Mášik, I. Hubač, and P. Mach, "Single-root multireference Brillouin-Wigner coupled-cluster theory: Applicability to the F₂ molecule," *J. Chem. Phys.* **108**, 6571–6579 (1998).
- ⁴⁹J. Pittner, P. Nachtigall, P. Čársky, and I. Hubač, "State-specific Brillouin-Wigner multireference coupled cluster study of the singlet-triplet separation in the tetramethylethane diradical," *J. Phys. Chem. A* **105**, 1354–1356 (2001).
- ⁵⁰U. Sinha Mahapatra, S. Chattopadhyay, and R. K. Chaudhuri, "Study of the ground state dissociation of diatomic molecular systems using state-specific multireference perturbation theory: A Brillouin-Wigner scheme," *J. Chem. Theory Comput.* **6**, 662–682 (2010).
- ⁵¹S. Manna, S. S. Ray, S. Chattopadhyay, and R. K. Chaudhuri, "A simplified account of the correlation effects to bond breaking processes: The Brillouin-Wigner perturbation theory using a multireference formulation," *J. Chem. Phys.* **151**, 064114 (2019).
- ⁵²S. Chattopadhyay, "Investigation of multiple-bond dissociation using Brillouin-Wigner perturbation with improved virtual orbitals," *J. Phys. Chem. A* **124**, 1444–1463 (2020).
- ⁵³S. Chattopadhyay, "Single-root multireference Brillouin-Wigner perturbative approach to excitation energies," *ACS Omega* **6**, 1668–1686 (2021).
- ⁵⁴I. Hubač and P. Neogrády, "Size-consistent Brillouin-Wigner perturbation theory with an exponentially parametrized wave function: Brillouin-Wigner coupled-cluster theory," *Phys. Rev. A* **50**, 4558–4564 (1994).
- ⁵⁵S. Battaglia, L. Fransén, I. F. Galván, and R. Lindh, "Regularized CASPT2: An intruder-state-free approach," *J. Chem. Theory Comput.* **18**, 4814–4825 (2022).
- ⁵⁶J. Pittner, "Continuous transition between Brillouin-Wigner and Rayleigh-Schrödinger perturbation theory, generalized Bloch equation, and Hilbert space multireference coupled cluster," *J. Chem. Phys.* **118**, 10876–10889 (2003).
- ⁵⁷H. Aksu, "Second-order Brillouin-Wigner perturbation theory: Size-extensivity correction," *Theor. Chem. Acc.* **131**, 1285 (2012).
- ⁵⁸E. Keller, T. Tsatsoulis, K. Reuter, and J. T. Margraf, "Regularized second-order correlation methods for extended systems," *J. Chem. Phys.* **156**, 024106 (2022).
- ⁵⁹J. Almlöf, "Elimination of energy denominators in Møller–Plesset perturbation theory by a Laplace transform approach," *Chem. Phys. Lett.* **181**, 319–320 (1991).
- ⁶⁰F. A. Evangelista, "A driven similarity renormalization group approach to quantum many-body problems," *J. Chem. Phys.* **141**, 054109 (2014).
- ⁶¹S. Wang, C. Li, and F. A. Evangelista, "Analytic gradients for the single-reference driven similarity renormalization group second-order perturbation theory," *J. Chem. Phys.* **151**, 044118 (2019).
- ⁶²I. Y. Zhang, P. Rinke, and M. Scheffler, "Wave-function inspired density functional applied to the H₂/H₂⁺ challenge," *New J. Phys.* **18**, 073026 (2016).
- ⁶³I. Y. Zhang, P. Rinke, J. P. Perdew, and M. Scheffler, "Towards efficient orbital-dependent density functionals for weak and strong correlation," *Phys. Rev. Lett.* **117**, 133002 (2016).
- ⁶⁴E. Feenberg, "Invariance property of the Brillouin-Wigner perturbation series," *Phys. Rev.* **103**, 1116–1119 (1956).
- ⁶⁵M. Head-Gordon, P. E. Maslen, and C. A. White, "A tensor formulation of many-electron theory in a nonorthogonal single-particle basis," *J. Chem. Phys.* **108**, 616–625 (1998).
- ⁶⁶M. S. Lee, P. E. Maslen, and M. Head-Gordon, "Closely approximating second-order Møller–Plesset perturbation theory with a local triatomics in molecules model," *J. Chem. Phys.* **112**, 3592–3601 (2000).
- ⁶⁷R. A. DiStasio, Y. Jung, and M. Head-Gordon, "A resolution-of-the-identity implementation of the local triatomics-in-molecules model for second-order Møller–Plesset perturbation theory with application to alanine tetrapeptide conformational energies," *J. Chem. Theory Comput.* **1**, 862–876 (2005).
- ⁶⁸M. Nooijen and R. J. Le Roy, "Orbital invariant single-reference coupled electron pair approximation with extensive renormalized triples correction," *J. Mol. Struct.: THEOCHEM* **768**, 25–43 (2006).
- ⁶⁹P. E. Maslen and M. Head-Gordon, "Noniterative local second-order Møller–Plesset perturbation theory: Convergence with local correlation space," *J. Chem. Phys.* **109**, 7093–7099 (1998).
- ⁷⁰P. Pulay, "Localizability of dynamic electron correlation," *Chem. Phys. Lett.* **100**, 151–154 (1983).
- ⁷¹S. Saebo and P. Pulay, "Local treatment of electron correlation," *Annu. Rev. Phys. Chem.* **44**, 213–236 (1993).
- ⁷²T. Koopmans, "Über die zuordnung von wellenfunktionen und eigenwerten zu den einzelnen elektronen eines atoms," *Physica* **1**, 104–113 (1934).
- ⁷³M. Feyereisen, G. Fitzgerald, and A. Komornicki, "Use of approximate integrals in *ab initio* theory. An application in MP2 energy calculations," *Chem. Phys. Lett.* **208**, 359–363 (1993).
- ⁷⁴D. E. Bernholdt and R. J. Harrison, "Large-scale correlated electronic structure calculations: The RI-MP2 method on parallel computers," *Chem. Phys. Lett.* **250**, 477–484 (1996).

- ⁷⁵O. Christiansen, H. Koch, and P. Jørgensen, "The second-order approximate coupled cluster singles and doubles model CC2," *Chem. Phys. Lett.* **243**, 409–418 (1995).
- ⁷⁶C. Hättig and F. Weigend, "CC2 excitation energy calculations on large molecules using the resolution of the identity approximation," *J. Chem. Phys.* **113**, 5154–5161 (2000).
- ⁷⁷Y. C. Park, A. Perera, and R. J. Bartlett, "Low scaling EOM-CCSD and EOM-MBPT(2) method with natural transition orbitals," *J. Chem. Phys.* **149**, 184103 (2018).
- ⁷⁸E. Epifanovsky *et al.*, "Software for the frontiers of quantum chemistry: An overview of developments in the Q-Chem 5 package," *J. Chem. Phys.* **155**, 084801 (2021).
- ⁷⁹I. Hubač and P. Čársky, "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* **22**, 2392–2399 (1980).
- ⁸⁰C. Murray and E. R. Davidson, "Perturbation theory for open shell systems," *Chem. Phys. Lett.* **187**, 451–454 (1991).
- ⁸¹W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, "Many-body perturbation theory with a restricted open-shell Hartree-Fock reference," *Chem. Phys. Lett.* **187**, 21–28 (1991).
- ⁸²R. D. Amos, J. S. Andrews, N. C. Handy, and P. J. Knowles, "Open-shell Møller-Plesset perturbation theory," *Chem. Phys. Lett.* **185**, 256–264 (1991).
- ⁸³P. J. Knowles, J. S. Andrews, R. D. Amos, N. C. Handy, and J. A. Pople, "Restricted Møller-Plesset theory for open-shell molecules," *Chem. Phys. Lett.* **186**, 130–136 (1991).
- ⁸⁴T. J. Lee and D. Jayatilaka, "An open-shell restricted Hartree-Fock perturbation theory based on symmetric spin orbitals," *Chem. Phys. Lett.* **201**, 1–10 (1993).
- ⁸⁵L. W. Bertels, J. Lee, and M. Head-Gordon, "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.* **10**, 4170–4176 (2019).
- ⁸⁶A. Rettig, D. Hait, L. W. Bertels, and M. Head-Gordon, "Third-order Møller-Plesset theory made more useful? The role of density functional theory orbitals," *J. Chem. Theory Comput.* **16**, 7473–7489 (2020).
- ⁸⁷M. Loipersberger, L. W. Bertels, J. Lee, and M. Head-Gordon, "Exploring the limits of second- and third-order Møller-Plesset perturbation theories for noncovalent interactions: Revisiting MP2.5 and assessing the importance of regularization and reference orbitals," *J. Chem. Theory Comput.* **17**, 5582–5599 (2021).
- ⁸⁸C. Edmiston and K. Ruedenberg, "Localized atomic and molecular orbitals," *Rev. Mod. Phys.* **35**, 457–464 (1963).
- ⁸⁹C. Edmiston and K. Ruedenberg, "Localized atomic and molecular orbitals. II," *J. Chem. Phys.* **43**, S97–S116 (1965).
- ⁹⁰T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," *J. Chem. Phys.* **90**, 1007–1023 (1989).
- ⁹¹D. E. Woon and T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties," *J. Chem. Phys.* **100**, 2975–2988 (1994).
- ⁹²F. Weigend and R. Ahlrichs, "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy," *Phys. Chem. Chem. Phys.* **7**, 3297–3305 (2005).
- ⁹³N. Mardirossian and M. Head-Gordon, " ω B97X-V: A 10-parameter, range-separated hybrid, generalized gradient approximation density functional with nonlocal correlation, designed by a survival-of-the-fittest strategy," *Phys. Chem. Chem. Phys.* **16**, 9904–9924 (2014).
- ⁹⁴W. J. Hehre, R. F. Stewart, and J. A. Pople, "Self-consistent molecular-orbital methods. I. Use of Gaussian expansions of Slater-type atomic orbitals," *J. Chem. Phys.* **51**, 2657–2664 (1969).
- ⁹⁵J. Řezáč and P. Hobza, "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.* **9**, 2151–2155 (2013).
- ⁹⁶J. Řezáč, K. E. Riley, and P. Hobza, "S66: A well-balanced database of benchmark interaction energies relevant to biomolecular structures," *J. Chem. Theory Comput.* **7**, 2427–2438 (2011); erratum **10**, 1359–1360 (2014).
- ⁹⁷J. Řezáč, K. E. Riley, and P. Hobza, "Benchmark calculations of noncovalent interactions of halogenated molecules," *J. Chem. Theory Comput.* **8**, 4285–4292 (2012).
- ⁹⁸R. Sedlak, T. Janowski, M. Pitoňák, J. Řezáč, P. Pulay, and P. Hobza, "Accuracy of quantum chemical methods for large noncovalent complexes," *J. Chem. Theory Comput.* **9**, 3364–3374 (2013).
- ⁹⁹D. E. Woon and T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon," *J. Chem. Phys.* **98**, 1358–1371 (1993).
- ¹⁰⁰F. Neese and E. F. Valeev, "Revisiting the atomic natural orbital approach for basis sets: Robust systematic basis sets for explicitly correlated and conventional correlated *ab initio* methods?," *J. Chem. Theory Comput.* **7**, 33–43 (2011).
- ¹⁰¹C. Riplinger and F. Neese, "An efficient and near linear scaling pair natural orbital based local coupled cluster method," *J. Chem. Phys.* **138**, 034106 (2013).
- ¹⁰²C. Riplinger, B. Sandhoefer, A. Hansen, and F. Neese, "Natural triple excitations in local coupled cluster calculations with pair natural orbitals," *J. Chem. Phys.* **139**, 134101 (2013).
- ¹⁰³C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, and F. Neese, "Sparse maps—A systematic infrastructure for reduced-scaling electronic structure methods. II. Linear scaling domain based pair natural orbital coupled cluster theory," *J. Chem. Phys.* **144**, 024109 (2016).
- ¹⁰⁴Y. Guo, U. Becker, and F. Neese, "Comparison and combination of 'direct' and fragment based local correlation methods: Cluster in molecules and domain based local pair natural orbital perturbation and coupled cluster theories," *J. Chem. Phys.* **148**, 124117 (2018).
- ¹⁰⁵C. Villot, F. Ballesteros, D. Wang, and K. U. Lao, "Coupled cluster benchmarking of large noncovalent complexes in L7 and S12L as well as the C₆₀ dimer, DNA-ellipticine, and HIV-indinavir," *J. Phys. Chem. A* **126**, 4326–4341 (2022).
- ¹⁰⁶Y. Zhao, N. González-García, and D. G. Truhlar, "Benchmark database of barrier heights for heavy atom transfer, nucleophilic substitution, association, and unimolecular reactions and its use to test theoretical methods," *J. Phys. Chem. A* **109**, 2012–2018 (2005); erratum **110**, 4942 (2006).
- ¹⁰⁷J. Zheng, Y. Zhao, and D. G. Truhlar, "Representative benchmark suites for barrier heights of diverse reaction types and assessment of electronic structure methods for thermochemical kinetics," *J. Chem. Theory Comput.* **3**, 569–582 (2007).
- ¹⁰⁸J. Lee, H. Q. Pham, and D. R. Reichman, "Twenty years of auxiliary-field quantum Monte Carlo in quantum chemistry: An overview and assessment on main group chemistry and bond-breaking," *J. Chem. Theory Comput.* **18**, 7024 (2022).
- ¹⁰⁹A. Karton, S. Daon, and J. M. L. Martin, "W4-11: A high-confidence benchmark dataset for computational thermochemistry derived from first-principles W4 data," *Chem. Phys. Lett.* **510**, 165–178 (2011).
- ¹¹⁰R. F. Fink, "Why does MP2 work?," *J. Chem. Phys.* **145**, 184101 (2016).