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Addressing first derivative discontinuities in orbital-optimized opposite-spin scaled second-order perturbation theory with regularization

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Orbital-optimized opposite-spin scaled second-order perturbation theory (O2) generates a single reference wave function composed of approximate Brueckner orbitals with fourth order computational scaling. While O2 provides significantly improved treatment of radicals by reducing spin contamination, it has been shown to suffer from first derivative discontinuities for bond stretching near the unrestricted point. That qualitative failure is resolved in this work by the implementation of regularized O2, which includes a regularization parameter in the denominator of its second order term. The value of the regularization parameter is semi-empirically chosen to qualitatively describe bond stretching energetics of hydrogen, ethane, and ethene, while also considering the effect of the regularization parameter on thermochemical errors for the well-known Gaussian-2 (G2) test set. The generality of the empirical scaling and semi-empirical regularization parameter is studied by application to the 3dMLBE20, DBH24, RSE43 and W4-11 test sets. We demonstrate that accuracy of O2 is roughly maintained and sometimes even improved by regularization, with root mean squares of regularized O2 between factors of 1.6 and 0.8 from corresponding root mean squares of O2.

I. INTRODUCTION

Rayleigh-Schrödinger perturbation theory¹, henceforth referred to as PT, is a powerful tool in electronic structure theory to account for correlation energy. Second order Möller-Plesset perturbation theory (MP2) is second order PT performed on converged Hartree-Fock (HF) orbitals². Its accuracy is dependent on the accuracy of the ground state wave function, gauged by whether it is an eigenvalue of the spin squared operator³. MP2 performs poorly for radicals and radical complexes⁴⁻⁷ because unrestricted Hartree-Fock orbitals are notorious for spin contamination.

An alternative method involves applying PT on approximate Brueckner orbitals (BOs), which are well-known to generate ground state

wave functions that are much closer to spin pure^{8,9}. BOs are defined as a set of orbitals whose ground state wave function maximally overlaps with the full configuration interaction wave function or equivalently, whose single excitations in the full configuration interaction wave function is zero¹⁰. For approximate BO methods which include up to a limited order of excitations, the two aforementioned definitions lead to two different methods, projective and variational, respectively¹¹.

Orbital-optimized (OO) opposite-spin scaled second-order perturbation theory (O2) is an approximate variational BO (VBO) method which includes up to double excitations, with the ground state energy at each iteration being the sum of the mean-field reference energy and opposite-spin scaled second-order PT energy terms. Within each iteration, the O2 energy is minimized with respect to orbital rotations whilst enforcing the condition that single excitations are zero¹². The reason for discarding the same-spin energy term and scaling the

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opposite-spin second-order PT energy term to compensate is that with careful implementation, O2 scales only as $O(N^4)$ ¹²⁻¹⁴. Indeed O2 was shown to yield ground state wave functions for open shell systems with far less spin contamination than UMP2, resulting in improved molecular properties^{12,15}. Opposite spin methods have been successfully extended to yield $O(N^4)$ scaling methods for excited states as well¹⁶⁻¹⁸. Additionally there has been considerable effort to develop OOMP2 itself¹⁹⁻²², and OO methods based on higher order perturbation theory²³⁻²⁶. There is also interest in the use of orbital optimization in conjunction with the second order perturbation theory contribution to rung 5 density functionals^{27,28}.

Another reason to prefer use of VBOs over Hartree-Fock orbitals is that MP2 theory does not transition smoothly from spin-restricted orbitals to spin unrestricted orbitals²⁹. As a chemical bond is stretched through the Coulson-Fischer point³⁰, the HF orbitals undergo a spin polarization transition from RHF to UHF. While the RMP2 and UMP2 energies are continuous, the first derivative is different on either side of the Coulson-Fischer point, resulting in a kink in the MP2 potential energy surface³¹, and a discontinuity in the first derivative (the nuclear force). This qualitative failure also presents itself in another way, which is that the MP2 relaxed one-particle density matrix is not N-representable in the vicinity of the Coulson-Fischer point²⁹. By contrast, the HF energy is continuous through first derivatives as a result of the Hellman-Feynman theorem for variationally optimized wavefunctions, and of course there is no N-representability issue. In principle, by restoring a Hellman-Feynman theorem, the use of VBOs with MP2 either as O2 or orbital-optimized MP2 (OOMP2) should restore first derivative continuity on the potential energy surface, and N-representability, as was demonstrated for the H₂ potential energy curve²⁹.

Efficient analytical derivatives with respect to nuclear coordinates are available for O2 (4th order scaling^{14,15}), as well as OOMP2 (5th order scaling^{32,33}). In practice, surprisingly, O2

and OOMP2 often do not give potential energy surfaces that are continuous through first derivatives. The reason is that the Coulson-Fischer point that is anticipated along a bond-stretch coordinate often does not in fact appear. Sharada et al.³⁴, with the development of a novel stability analysis procedure, demonstrated that for OOMP2, the restricted solution remains stable with respect to unrestricted solutions at all values of the bond length. This means that the transition from the restricted solution (ROOMP2) being lower in energy to the unrestricted solution (UOOMP2) occurs with a discontinuous jump in the orbitals, from one stable solution to the other as the energy ordering changes. Therefore restricted and unrestricted orbitals do not coalesce at the energy cross-over point and as a direct consequence, first derivative discontinuities are present³⁴. Similar observations were made in the context of active space orbital optimized methods^{35,36}, though the underlying explanation was different.

To make the restricted solution unstable with respect to the unrestricted solution at a Coulson-Fischer point, Sharada et al regularized the OOMP2 method, by introducing a level shift parameter into the orbital energy difference that makes the denominator of the second order energy³⁴. Regularized OOMP2 was originally implemented to make OOMP2 robust to divergences due to highest occupied and lowest unoccupied molecular orbitals becoming degenerate³⁷. In the context of bond stretching, the semi-empirical regularization parameter rebalances restricted and unrestricted solutions to transform the topology of the orbital Hilbert space to be qualitatively correct. The regularization parameter is semi-empirical because one can think of it as a crude way to correct OO-MP2 so as to be closer to its parent theory, OOCCD (sometimes shortened to OD)¹¹. A regularization parameter of 0.4 E_h for regularized OOMP2 correctly describes the energetics of the hydrogen molecule dissociating into two hydrogen atoms in the cc-pVDZ basis set³⁴, in the sense that ROOMP2 becomes unstable with respect to UOOMP2 at a Coulson-

Fischer point.

The purpose of this work is to regularize the O2 model so that first order properties have continuous first derivatives. A simple level shift is an effective choice because the desirable fourth order computational scaling of O2 will be maintained. After briefly reviewing the formulation of the O2 method, the roadmap for developing regularized O2 is as follows:

- A Semi-empirically choose the regularization parameter (δ) by considering the energetics of hydrogen, ethane, ethene and ethyne bond stretching.
- B Empirically fit the scaling parameter (c_{OS}) alongside the chosen δ to the G2 test set to generate the empirical scaling and semi-empirical regularization parameter combination (c_{OS}, δ).
- C Apply regularized O2 (δ -O2) to thermochemistry test sets and compare results to fit O2.

II. THEORY

Two-electron integrals, $(pq|rs)$, are written in so-called chemist's notation, where the first two indexes are functions of electron 1, and the last two are functions of electron 2. Indices $i, j, \dots$ refer to occupied molecular orbitals; $a, b, \dots$ refer to virtual molecular orbitals; $p, q, \dots$ refer to occupied and virtual molecular orbitals; $K, L, \dots$ refer to auxiliary basis functions. ϵ_i refers to the energy of molecular orbital i . And w_τ refers to the weight corresponding to a Laplace quadrature point τ .

1. O2 energy

The O2 energy is a post-HF quantity defined as follows:

$$E_{O2} = E_{\text{ref}} + c_{OS}E_{OS} \quad (1)$$

E_{ref} is the mean-field reference energy. c_{OS} is the scaling parameter and from a previous fitting procedure determined to be 1.2¹². E_{OS} approximates the exact opposite-spin second order PT term, E_{OS-PT2} .

$$E_{OS-PT2} = - \sum_{ia}^{\alpha} \sum_{jb}^{\beta} \frac{(ia|jb)^2}{(\epsilon_a - \epsilon_i) + (\epsilon_b - \epsilon_j)} \quad (2)$$

Having α as the limit of the sum corresponds to a sum over all α -spin electrons, likewise for β . Conventional evaluation of Eq. 2 by integral transformation scales as $O(N^5)$, just like MP2 theory.

By employing auxiliary basis functions to evaluate 2-electron integrals³⁸ and eliminating the energy denominator with a Laplace transform³⁹, E_{OS} ¹³ approximates E_{OS-PT2} .

$$E_{OS} = - \sum_{\tau}^{N_{\tau}} w_{\tau} \sum_{KL}^{\tau} X_{KL}^{\alpha} X_{KL}^{\beta} \quad (3)$$

where

$${}^{\tau}X_{KL}^{\alpha} = \sum_{ia}^{\alpha} B_{ia}^K B_{ia}^L ({}^{\tau}\xi_i^a)^2 \quad (4)$$

$$B_{ia}^K = \sum_M (ia|M)(M|K)^{-1/2} \quad (5)$$

$${}^{\tau}\xi_i^a = \exp[(\epsilon_i - \epsilon_a)t_{\tau}/2] \quad (6)$$

As is evident from Eqs. 4 and 5, no step in the O2 implementation scales worse than $O(N^4)$, one power smaller than MP2 or OOMP2. For further details, the reader is referred to References¹² and¹⁴.

2. Regularized O2 energy

By simply adding a level shift or regularization parameter to the denominator (rather akin to energy-shifted perturbation theory⁴⁰), the opposite-spin second order PT term is

$$E_{\delta-OS-PT2} = - \sum_{ia}^{\alpha} \sum_{jb}^{\beta} \frac{(ia|jb)^2}{(\epsilon_a - \epsilon_i) + (\epsilon_b - \epsilon_j) + \delta} \quad (7)$$

For efficient $O(N^4)$ evaluation of $E_{\delta\text{-OS-PT2}}$, the corresponding equations for E_{OS} hold except that Equation 6 is altered by the level shift:

$$\tau \xi_i^a = \exp[(\epsilon_i - \epsilon_a - \delta/2)t_\tau/2] \quad (8)$$

By adding a parameter to the exponent of the exponential, ξ is the only term that directly changes from the implementation of O2 for the implementation of δ -O2. Desirable formal properties of the O2 method, including size-consistency (i.e. additive energies for non-interacting systems) and orbital invariance to occupied-occupied and virtual-virtual rotations, are readily shown to be unaffected by regularization.

III. COMPUTATIONAL METHODS

Regularized O2 is implemented within a development version of Q-Chem 4.2⁴¹. Single point energy and stability analysis calculations are performed with an integral threshold of 10^{-14} and convergence of 10^{-7} and 10^{-5} , respectively. For all O2 and δ -O2 calculations, converged and stable Hartree-Fock orbitals are used as initial orbitals and geometric direct minimization⁴², as the optimization procedure. Bond stretching energetics of hydrogen, ethane, ethene and ethyne are studied in the aug-cc-pVTZ basis set. As summarized in Table I, the molecules that comprise the test sets are main group elements, with energetics calculated in the cc-pVQZ basis set. The lone exception is the 3dMLBE20 test set⁴³, which is composed of first row, diatomic organometallics with energetics calculated in the cc-pVTZ basis. Table I highlights the reaction types and respective number of reactions. All test sets involve molecules deemed not to be of multi-reference character.

Henceforth, the W4-11_ label preceding each test set in the W4-11 collection of test sets shall be omitted for simplicity. In all tables and graphs for which it appears, the G2 test set is in bold to highlight that it is the fitting test set.

TABLE I. Test sets to which O2 and δ -O2 are applied with reaction types and in brackets, total number of reactions involving only non-multi-reference molecules. In bold is the fitting test set.

Test set	Reaction type [total reactions]
G2	atomization energy [146] ⁴⁴
3dMLBE20	metal-ligand binding [13] ⁴³
DBH24	diverse barrier height [24] ⁴⁵
RSE43	radical stabilization [43] ¹⁹
W4-11_BDE99	bond dissociation [83] ⁴⁶
W4-11_HAT707	hydrogen-atom transfer [505] ⁴⁶
W4-11_ISOM20	isomerization [18] ⁴⁶
W4-11_SN13	nucleophilic substitution [13] ⁴⁶
W4-11_TAE140	atomization energy [124] ⁴⁶

IV. RESULTS AND ANALYSIS

A. Choosing δ by studying hydrogen, ethane, ethene and ethyne bond stretching energetics

For restricted and unrestricted orbitals to coalesce at the unrestriction point, restricted solutions must be saddle points with respect to unrestricted solutions or equivalently, its Hessian must have a negative eigenvalue in the subspace of unrestricted solutions. Then, energies as a function of bond distance have a continuous first derivative. Bond stretching energetics are studied to find a regularization parameter for which a two-fragment molecule smoothly dissociates into separate single fragments. The scaling parameter is roughly increased as the regularization parameter is increased to ensure differences in correlation energies between unrestricted and restricted solutions are captured by stability analysis. For this subsection, its exact value is unimportant as it only quantitatively affects results.

The bond stretching energetics near the unrestriction point of hydrogen, ethane, ethene and ethyne for O2 and δ -O2, where δ equals the minimum regularization parameter to the $0.1 E_h$ which demonstrates qualitative accuracy, are illustrated in Figure 1. Beyond the unrestriction point, the smallest eigenvalue of the electronic

FIG. 1. Bond stretching energetics near the unrestriction point of molecules under study for O₂, top row and corresponding δ -O₂ with minimal δ that exhibits qualitatively correct behavior, bottom row, in the aug-cc-pVTZ basis. Full lines refer to absolute energy, exact values not shown; points refer to lowest eigenvalues of the electronic Hessian for internal stability analysis of unrestricted solutions (U-U) and external stability analysis (R-U). In addition to the δ -UO₂ energy as a function of distance appearing to the naked eye as smooth, δ -RO₂ exhibits lowest eigenvalues from external stability analysis less than zero beyond the unrestriction point and monotonically decreasing. Note that the x-axis scales and the top and bottom row y-axis scales among the graphs differ.

Hessian for regularized restricted O2 (δ -RO2) in δ -UO2 space becomes negative and internal stability analysis for δ -UO2 yields continuous eigenvalues, two features not present in O2. Notice that the unrestriction point for δ -O2 occurs at a smaller bond distance than that of O2. δ -O2 uncovers unrestricted solutions which are not accessible by O2. Generally speaking, the regularization parameter rebalances restricted and unrestricted solutions such that their orbitals smoothly transition between each other at the unrestriction point.

Minimum regularization parameters which exhibit smooth bond stretching energetics for hydrogen, ethane, ethene and ethyne are 0.8, 1.0, 1.1 and 2.1 E_h , respectively. Thus a regularization parameter of 2.1 E_h qualitatively describes bond stretching for the four molecules studied while 0.8 E_h only qualitatively describes hydrogen. Although the parameter of 2.1 E_h generates smooth orbitals for a larger subspace of molecules, we proceed to fit the scaling parameter of δ -O2 for δ equal to 1.1 E_h . The reason for this choice is that for regularization parameters as large as 2.1 E_h dramatically worsen O2 accuracy on reaction energies (see below). The regularization parameter acts on each electron pair; the scaling parameter, the sum of all electron pairs. The ability of the scaling parameter to quantitatively correct for the regularization parameter is thus limited. A regularization parameter of 1.1 E_h ensures a correct physical description for many molecules with multi-reference character and as will be seen, maintains quantitative accuracy of O2 by sacrificing qualitative accuracy for molecules with very strong multi-reference character, such as ethyne bond stretching, which warrants the use of a multi-reference method.

B. Fitting c_{OS} to the G2 test set

By fitting c_{OS} to atomization energies, the goal is to generate a scaling parameter for regularized O2 that quantitatively describes radical complexes, the main reason for using O2, a BO based method, rather than MP2, a Hartree-

Fock orbital based method. O2 was previously fit to the G2 test set and the fitted scaling parameter was shown to be extensible to chemical properties besides energetics, such as bond lengths and vibrational harmonic frequencies of small organic radicals¹². Although fitting to the same test set, the fitting procedure in this study differs. Reference values are from theory⁴⁴ rather than experiment⁴⁷ and the scaling parameter is fit by iteratively applying a linear least squares procedure. From Equation 1, the linear least squares equation is derived as

$$\Delta c_{OS} = \frac{\mathbf{E}_{OS}^{RE\top}(\mathbf{E}_{Ref}^{RE} - \mathbf{E}_{O2}^{RE})}{(\mathbf{E}_{OS}^{RE\top}\mathbf{E}_{OS}^{RE})} \quad (9)$$

RE refers to reaction energies and Δc_{OS} is the difference between the fit scaling parameter and the present scaling parameter. In bold are vectors whose elements correspond to specific reactions in the test set. O2 is also fit by Equation 9 to fairly compare O2 and δ -O2 within the same fitting procedure.

TABLE II. Self-consistently applying linear least squares to fit the scaling parameter to the G2 test set in the cc-pVQZ basis set. Initial scaling/regularization (c_{OS} , δ) parameters for O2 and δ -O2 are from the previous fitting and the ethene dissociation curve, respectively. Δc_{OS} is the change from its present value to become fit and Δ RMS is the predicted root mean squares (RMS) reduction from employing Δc_{OS} . Convergence is reached when Δ RMS $< 10^{-2}$. RMS is in kcal/mol.

G2	(c_{OS}, δ)	RMS	Δc_{OS}	ΔRMS
Iteration 0	(1.2, 0)	8.791	0.054	4.306
	(1.6, 1.1 E_h)	6.309	0.004	0.016
Iteration 1	(1.254, 0)	4.488	0.0003	0.0003
	(1.604, 1.1 E_h)	6.293	0.0002	0.00003

After one iteration, the scaling parameter converges to 1.604 for a fixed regularization parameter of 1.1 E_h , as demonstrated in Table II. Although generating a root mean square deviation from reference values (RMS) smaller than that of the previous fit, fit δ -O2 generates an RMS about three-halves larger than the

O2 fit using the same protocol. This result is consistent with the claim made in Section A when choosing the regularization parameter: the regularization parameter constrains the reaction energy space, making it more difficult for the scaling parameter to undo the quantitative harm done by the regularization parameter on reactions which do not require it. In other words, while regularization stabilizes the second order correction against the presence of small gaps, it degrades the performance of the modified O2 method for predicting thermochemistry. To further illustrate the tradeoff, note that if we were to choose $\delta = 2.1E_h$, the resulting RMS error in the best fit to the G2 set yields an RMS error of 8.0 kcal/mol, up from 6.3 kcal/mol for $\delta = 1.1E_h$.

C. Applying fit O2 and δ -O2 to 3dMLBE20, DBH24, RSE43 and W4-11 test sets

O2 and δ -O2 as parameterized in the previous section are applied to thermochemistry test sets and results are summarized in Table III. Being fit to G2, the scaling parameter transfers well to the other thermochemistry test sets. Upon application of the fitting procedure to scaling/regularization parameters of (1.254, 0) and (1.604, 1.1 E_h) within each test set, only reductions in RMS less than one kcal/mol are predicted except for 3dMLBE20, O2: 2.35 kcal/mol, which has the largest RMS values among test sets studied. We can make statements about RMS differences between O2 and δ -O2, knowing that a different qualitative conclusion would not be reached if a more thorough and accurate fitting procedure is employed for the scaling parameter.

The 3dMLBE20 and DBH24 test sets have RMS values for O2 that are larger than that of δ -O2, which is predicted to remain larger if the methods are fit within the respective test set for only DBH24. For the other six test sets, the regularization parameter is unnecessary and its detrimental effects in describing reaction energies cannot be undone by the scaling parameter to achieve O2 RMSs. Regularized O2 RMSs are

TABLE III. Statistics of test sets for fit O2 (1.254, 0) and δ -O2 (1.604, 1.1 E_h) in the cc-pVQZ basis set, except for 3dMLBE20: cc-pVTZ. ME stands for mean error; MAE, mean absolute error; RMS, root mean square. For ME, positive values equate to absolute reaction energies greater than that of the reference. Δc_{OS} is the change from its present value to become optimal for the specific test set and method. Δ RMS is the predicted RMS reduction from employing Δc_{OS} . Values are in kcal/mol except Δc_{OS} , which is unit-less.

		ME	MAE	RMS	Δc_{OS}	Δ RMS
G2	O2	-0.17	3.24	4.49	0.00	0.00
	δ -O2	-1.08	4.58	6.29	0.00	0.00
3dMLBE20	O2	3.03	9.66	12.03	-0.11	2.35
	δ -O2	-0.44	8.52	10.27	0.01	0.01
DBH24	O2	-0.91	5.24	7.09	-0.03	0.01
	δ -O2	2.16	5.80	6.89	0.47	0.81
RSE43	O2	-0.40	0.75	1.36	0.15	0.08
	δ -O2	-0.80	1.12	1.57	0.47	0.23
BDE99	O2	0.69	2.19	2.85	-0.04	0.53
	δ -O2	0.10	2.61	3.48	0.01	0.01
HAT707	O2	0.83	3.88	4.85	-0.09	0.61
	δ -O2	2.44	5.23	6.63	0.05	0.07
ISOM20	O2	0.82	1.43	1.72	-0.13	0.36
	δ -O2	1.70	1.99	2.72	0.26	0.27
SN13	O2	-0.55	0.56	0.66	0.04	0.25
	δ -O2	0.79	0.82	0.93	-0.07	0.40
TAE140	O2	1.50	3.17	4.59	-0.02	0.46
	δ -O2	-0.44	4.37	6.56	0.00	0.00

within a factor of 1.6 from O2 RMSs as shown in Figure 2. It is noteworthy that the addition of 1.1 Hartrees to the exponent of E_{OS} to correct for first derivative discontinuities worsens RMSs relative to O2 by a factor less than 1.6.

O2 RMSs for 3dMLBE20 (12.03 kcal/mol) and DBH24 (6.89 kcal/mol) are the largest among the test sets and benefit from the regularization parameter the most. Molecules in 3dMLBE20 are large and the sheer number of electrons highlights imbalances between restricted and unrestricted solutions, as evidenced in Section A with ethane requiring a larger minimum regularization parameter to generate a smooth bond dissociation curve compared to that of the hydrogen molecule. However, this imbalance can be quantitatively better addressed by altering the scaling parameter with

FIG. 2. Relative root mean square (RMS) between fit O2 (1.254, 0) and δ -O2 (1.604, 1.1 E_h) for test sets. RMS(δ -O2) is less than RMS(O2) for the 3dMLBE20 and DBH24 test sets.

no regularization parameter, as shown in the rightmost column in Table III. The DBH24 test set has a lower RMS for δ -O2 because it is composed of molecules with stretched bonds, the class of molecules for which δ -O2 is developed to provide an improved physical description. As a result, the regularization parameter is quantitatively beneficial. When the scaling parameter is fit within the test set, the RMS advantage of δ -O2 over that of O2 increases from 0.20 to 1.00 kcal/mol.

V. CONCLUSION

The purpose of δ -O2 is to qualitatively describe bond stretching while maintaining O2 accuracy. O2 is susceptible to first derivative discontinuities, shown by employing a newly developed stability analysis procedure³⁴. The qualitative inaccuracy is resolved by implementing regularized O2: O2 with a regularization parameter added to the denominator of its second order term. Its simplicity retains the fourth order scaling that makes O2 such an attractive electronic structure method. A more comprehensive method has been proposed for OOMP2 which weights individual second order energy terms according to orbital energy differences⁴⁸, however if implemented for O2 its fourth order scaling would be lost.

The semi-empirical regularization parameter for δ -O2 is determined from qualitatively de-

scribing hydrogen, ethane and ethene bond stretching energetics and the empirical scaling parameter from fitting alongside the chosen regularization parameter to the G2 test set. Upon application to thermochemistry test sets: 3dMLBE20, DBH24, RSE43 and W4-11, regularized O2 is shown to be robust. Not only are first derivative discontinuities resolved, but regularized O2 maintains accurate O2 RMSs for RSE43 and W4-11 test sets to within a factor of 1.6 and improves upon O2 RMSs for 3dMLBE20 and DBH24.

We saw that a tradeoff emerged between larger regularization parameters (which provide improved stability against small gaps, and proper Coulson-Fischer points for larger classes of problems) versus smaller parameters which on the whole promote higher accuracy for the δ -O2 method across most test sets. Our recommended choice, ($c_{os} = 1.604$, $\delta = 1.1E_h$), is a balance that yields a δ -O2 method that can be applied to wider classes of problems than the parent O2 method itself, while yielding nearly comparable accuracy for chemical energy differences. This work should also have interesting implications for the future development of orbital optimized double hybrid density functionals²⁷.

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