Theoretical interpretation of Grimme's spin-component-scaled second order Møller-Plesset theory

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It is shown that spin-component-scaled second order Møller-Plesset theory proposed by Grimme [J. Chem. Phys. **118**, 9095 (2003)] can be interpreted as a two-parameter scaling of the zero order Hamiltonian, a generalization of the approach reported by Feenberg [Phys. Rev. **103**, 1116 (1956)]. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2404660]

I. INTRODUCTION

Second order perturbation theory (PT) in the Møller-Plesset (MP) partitioning[1] is among the most popular approaches to approximate total energies of atoms and also of molecules at around equilibrium geometry. Its cost per performance ratio has become relatively advantageous since computationally efficient formulations have been worked out in terms of localized orbitals[2–4] or in atomic orbitals using Laplace transformation[5–8] or by utilizing various approximate local treatments[9–11] complemented by auxiliary basis set fitting[12] and applying a dual basis set approach.[13,14] Though errors of the MP2 method are relatively small it has been a challenge since its introduction to improve it *within* the framework of second order PT. The partitioning proposed by Epstein and Nesbet[15,16] may had offered a way to calculate second order PT energies better than MP2; numerical experience, however, indicates that EN2 energies are often inferior to MP2,[17,18] sometimes overshooting the full configuration interaction (FCI) result.

A more successful approach, in terms of numerical results, to get a better performing second order PT formula was reported by Feenberg and Goldhammer[19] and Feenberg,[20] who applied one parameter to scale the zero order Hamiltonian and modify the perturbation operator accordingly. The scaling parameter was determined by requiring that the energy, written up to order of 3 is minimal. Feenberg scaling provides second order total energies remarkably better than MP2;[21] moreover convergence radius of the PT expansion was shown to get enlarged by Feenberg's approach.[22] Another criterion for the scaling parameter, different from Feenberg's proposition, was given by Goodson,[23–25] who used the scaling to improve convergence in a more direct manner. He suggested to calculate quadratic Padé approximants to judge the position of the singularity (branching) of function $E(z)$, lying closest to the origin on the complex plain, and use the scaling parameter to shift the singularity away from the origin. Numerical tests of this procedure indicate that improving the convergence has a considerable benefit at the second

order PT energy. Unfortunately, neither Feenberg's nor Goodson's method to set the scaling parameter preserves order by order size consistency of the PT series.[26] The simplest workaround for this problem is to fix one value for the parameter in a system-independent manner.

Apart from Feenberg scaling, level shifts are also extensively applied in PT corrections mainly for avoiding quasidegenerate situations.[27–29] Introducing separate shift parameters for each level and setting them in Feenberg's spirit leads to the so-called CEPA-0 or DMBPT-∞ or LCCD energy at second order if starting from the MP partitioning of the Hamiltonian.[30] As compared to the one-parameter Feenberg theory, the number of shift parameters needed to reach the CEPA-0 energy is given by the number of doubly excited determinants. A nondiagonal representation of the zero order Hamiltonian in the determinantal basis was also reported to lead to the CEPA-0 energy at second order PT.[31,32] An explicit expression for such a zero order Hamiltonian in the Fock space has been given recently by Fink.[33]

An alternative modification of the MP2 energy formula suggested by Grimme[34] operates with two scaling parameters, one multiplying the so-called parallel spin component of the expression and the other multiplying the antiparallel component. This scaling is fully empirical in nature and has been proved to give second order results superior to MP2. In the present work it is shown that Grimme's scaling qualitatively corresponds to a two-parameter extension of Feenberg's scaling. In Feenberg's spirit, a variational criterion can be used to set the values of the scaling parameters: the total energy, written up to order of 3 in perturbation theory, is set stationary. The characteristic feature of Grimme's scaling factors that antiparallel spin-component is overweighted and parallel spin-component is damped with respect to MP2 is recovered also from the Feenberg procedure. In this respect Grimme's scaling can be viewed as a two-parameter approximation to the many-parameter procedure leading to CEPA-0. Conversely, Grimme's argument for the value of the scaling parameters provides a qualitative interpretation of the improvement obtained when stepping from MP2 to CEPA-0.

II. THEORY

A. Feenberg's scaling

Starting from a

$$H = H^{(0)} + W$$

partitioning of the total Hamiltonian, Feenberg redefined the splitting,[20]

$$H = \underbrace{\frac{1}{1-\mu}H^{(0)}}_{H^{(0)\prime}} + \underbrace{W - \frac{\mu}{1-\mu}H^{(0)}}_{W^{\prime}},$$

and set the value of the scaling parameter μ from the condition that the energy up to the order of 3 in the primed partitioning is minimal. Spectral form of the primed zero order Hamiltonian is given by

$$H^{(0)\prime} = \sum_K \frac{E_K}{1-\mu}|K\rangle\langle K|,$$

where E_K and $|K\rangle$ are eigenvalues and eigenfunctions of $H^{(0)}$. For the present purpose it is useful to rewrite $H^{(0)\prime}$ as

$$H^{(0)\prime} = E_0 \frac{\mu}{1-\mu} + E_0|0\rangle\langle 0|$$
$$+ \sum_{K \neq 0}\left(E_K\frac{1}{1-\mu} - E_0\frac{\mu}{1-\mu}\right)|K\rangle\langle K|. \quad (1)$$

Omitting the constant term from Eq. (1), one gets

$$H^{(0)\prime\prime} = E_0|0\rangle\langle 0| + \sum_{K \neq 0} E_K^{\prime\prime}|K\rangle\langle K|, \quad (2)$$

with

$$E_K^{\prime\prime} = E_K\frac{1}{1-\mu} - E_0\frac{\mu}{1-\mu}. \quad (3)$$

From the point of view of PT, forms (1) and (2) of the zero order Hamiltonian are essentially equivalent, since a constant shift of the zero order spectrum affects only the zero and first order energies (their sum being invariant) and the corrections are identical from second order on. It is form (2) that is extended to two parameters in Sec. II C by considering scaling factors that depend on the nature of the excited levels $|K\rangle$.

The redefined zero order Hamiltonian and perturbation generate the new second order energy correction,

$$E^{(2)\prime} = (1-\mu)E^{(2)},$$

which by Feenberg's minimal condition takes the form

$$E_{\text{FE}}^{(2)} = \frac{(E^{(2)})^2}{E^{(2)} - E^{(3)}}. \quad (4)$$

Apparently, $E_{\text{FE}}^{(2)}$ is equivalent to a [2, 1] Padé approximant of the original PT series. The Feenberg-optimized scaling parameter behind Eq. (4) is given by

$$1 - \mu = \frac{E^{(2)}}{E^{(2)} - E^{(3)}}.$$

It is easy to see that the condition $d(E^{(2)}+E^{(3)})/d\mu=0$ is equivalent to the requirement that the third order energy in the modified perturbation series is zero, i.e., $E^{(3)\prime}=0$.

By simple substitution it can be shown that Eq. (4) scales correctly with the number of identical isolated subsystems, i.e., for the noninteracting dimer $A\ldots A$

$$E_{\text{FE}}^{(2)}(A\ldots A) = 2E_{\text{FE}}^{(2)}(A)$$

holds. On the other hand, for nonidentical noninteracting units, e.g., $A\ldots B$

$$E_{\text{FE}}^{(2)}(A\ldots B) \neq E_{\text{FE}}^{(2)}(A) + E_{\text{FE}}^{(2)}(B),$$

which gives rise to a size inconsistency of Eq. (4) in the general case.

B. Grimme's spin-component scaling

A zero order Hamiltonian written as

$$H^{(0)} = E_0|0\rangle\langle 0| + \sum_{K \neq 0} E_K|K\rangle\langle K|, \quad (5)$$

and the perturbation defined as $W=H-H^{(0)}$ leads to the well-known second order PT energy expression

$$E^{(2)} = -\sum_{K \neq 0}\frac{|\langle 0|H|K\rangle|^2}{\Delta_K},$$

with

$$\Delta_K = E_K - E_0. \quad (6)$$

Specifying Eq. (5) for the Møller-Plesset partitioning in canonical molecular orbitals $|0\rangle$ denotes the Hartree-Fock wave function $|\text{HF}\rangle$, $|K\rangle$ refers to excited determinants, and E_0 and E_K are sums of orbital energies occupied in the given determinant. Provided that the Hartree-Fock problem is solved, only doubly excited determinants contribute to the second order energy. Among double excitations one can distinguish parallel-spin excitations T_K, which are of the type

$$|T_K\rangle = b_\sigma^+ a_\sigma^+ i_\sigma^- j_\sigma^-|\text{HF}\rangle,$$

and antiparallel-spin excitations S_K, that can be of the form

$$|S_K\rangle = b_\sigma^+ a_{\bar{\sigma}}^+ i_{\bar{\sigma}}^- j_\sigma^-|\text{HF}\rangle$$

or

$$|S_K\rangle = b_\sigma^+ a_{\bar{\sigma}}^+ i_\sigma^- j_{\bar{\sigma}}^-|\text{HF}\rangle.$$

We apply the notation that $i,j,\ldots$ refer to occupied indices, $a,b,\ldots$ to virtual indices, and σ and $\bar{\sigma}$ denote orthogonal spin functions. In closed shell theory, excitation energy denominators corresponding to the above functions are all the same, independent of the spin labels

$$\Delta_K = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j,$$

where ϵ_i stand for molecular orbital energies. Using the above notation the MP2 formula breaks down for a parallel-spin and a anti-parallel-spin terms,

$$E_{\text{MP}}^{(2)} = -\sum_{T_K} \frac{|\langle \text{HF}|H|T_K\rangle|^2}{\Delta_K} - \sum_{S_K} \frac{|\langle \text{HF}|H|S_K\rangle|^2}{\Delta_K}$$

$$= -\sum_{ijab} \left(\frac{\langle ij|ab\rangle\langle ij\|ab\rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} + \frac{\langle ij|ab\rangle^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \right), \qquad (7)$$

with two-electron integrals written in $\langle 12|12\rangle$ convention and $\langle ij\|ab\rangle = \langle ij|ab\rangle - \langle ij|ba\rangle$. To alter the weight of parallel- and antiparallel-spin pair energies Grimme introduces two scaling factors p_S and p_T as

$$E_{\text{SCS-MP}}^{(2)} = -p_T \sum_{T_K} \frac{|\langle \text{HF}|H|T_K\rangle|^2}{\Delta_K} - p_S \sum_{S_K} \frac{|\langle \text{HF}|H|S_K\rangle|^2}{\Delta_K}.$$

$$(8)$$

Based on numerical experience, the value $p_S = 6/5$ was proposed to cure the usual underestimation of the MP2 energy for two electron systems, where only the antiparallel pair energy is nonzero. Least-squares fitting to a set of reaction energies computed by the QCISD(T) method in valence quadruple-ζ quality basis set provided $p_T = 1/3$ for the other parameter.[34]

Since its introduction, Grimme's scaling has been successively used for various systems.[35–37]

C. Spin-component scaling as a Feenberg scaling

The second order SCS-MP expression [Eq. (8)] can be looked upon as if there were two, spin-dependent excitation energy denominators for a given orbital quartet $\{a, b, i, j\}$ in the form

$$\Delta_K^T = \Delta_K / p_T \qquad (9)$$

and

$$\Delta_K^S = \Delta_K / p_S. \qquad (10)$$

These denominators involve a zero order Hamiltonian similar to Eq. (5),

$$H_{\text{SCS-MP}}^{(0)} = E_0|0\rangle\langle 0| + \sum_{T_K} E_K^T |T_K\rangle\langle T_K| + \sum_{S_K} E_K^S |S_K\rangle\langle S_K|$$

$$+ \sum_K^{\text{singly,triply,etc.,excited}} E_K |K\rangle\langle K|. \qquad (11)$$

Spin-component dependent zero order energies of doubly excited determinants are obtained by combining Eqs. (9) and (10) with Eq. (6) to get

$$E_K^T = \frac{\Delta_K}{p_T} + E_0 = E_K \frac{1}{p_T} + E_0 \frac{p_T - 1}{p_T}$$

and

$$E_K^S = \frac{\Delta_K}{p_S} + E_0 = E_K \frac{1}{p_S} + E_0 \frac{p_S - 1}{p_S}.$$

Substituting p_S or p_T for $1 - \mu$ it is readily seen that the above zero order energies have the same form as Feenberg-scaled excited energies shown in Eq. (3).

Following Feenberg, we require that the total energy, written up to order of 3 in perturbation theory, is stationary with respect to p_S and p_T. The main purpose of the present paper is to compare this choice with Grimme's empirical values. It has been shown that the above variational condition results a vanishing third order correction not only in the case of a one-parameter scaling but also if using levels shifts to repartition the Hamiltonian.[30] If working with level shift parameters, this condition leads to the CEPA-0 or LCCD energy at second order which outperforms the MP2 energy in most cases.[30,38]

As no scaling is applied to the ground state in Eq. (11), zero and first order energies are unaffected. Conditions for the two parameters are written as

$$\frac{\partial(E_{\text{SCS-MP}}^{(2)} + E_{\text{SCS-MP}}^{(3)})}{\partial p_S} = 0,$$

and similarly for p_T. The scaled second order energy is given in Eq. (8) and the scaled third order has the form

$$E_{\text{SCS-MP}}^{(3)} = p_T^2 \sum_{T_K T_L} \frac{\langle \text{HF}|H|T_K\rangle(\langle T_K|H|T_L\rangle - \delta_{T_K T_L}((\Delta_K/p_T) + E^{(0)} + E^{(1)}))\langle T_L|H|\text{HF}\rangle}{\Delta_K \Delta_L}$$

$$+ p_S^2 \sum_{S_K S_L} \frac{\langle \text{HF}|H|S_K\rangle(\langle S_K|H|S_L\rangle - \delta_{S_K S_L}((\Delta_K/p_S) + E^{(0)} + E^{(1)}))\langle S_L|H|\text{HF}\rangle}{\Delta_K \Delta_L}$$

$$+ 2p_T p_S \sum_{T_K S_L} \frac{\langle \text{HF}|H|T_K\rangle\langle T_K|H|S_L\rangle\langle S_L|H|\text{HF}\rangle}{\Delta_K \Delta_L}. \qquad (12)$$

Altogether, the sum of second and third order spin-scaled correction can be written as

$$E_{\text{SCS-MP}}^{(2)} + E_{\text{SCS-MP}}^{(3)} = p_T^2 A_{TT} - 2p_T B_T + p_S^2 A_{SS} - 2p_S B_S + 2p_T p_S A_{ST}, \qquad (13)$$

introducing the notation

$$B_T = \sum_{T_K} \frac{\langle \text{HF}|H|T_K\rangle\langle T_K|H|\text{HF}\rangle}{\Delta_K},$$

a similar definition for B_S,

$$A_{TT} = \sum_{T_K T_L} \frac{\langle \mathrm{HF}|H|T_K\rangle (\langle T_K|H|T_L\rangle - \delta_{T_K T_L}(E^{(0)} + E^{(1)}))\langle T_L|H|\mathrm{HF}\rangle}{\Delta_K \Delta_L},$$

an analogous expression for A_{SS} and finally,

$$A_{ST} = \sum_{T_K S_L} \frac{\langle \mathrm{HF}|H|T_K\rangle \langle T_K|H|S_L\rangle \langle S_L|H|\mathrm{HF}\rangle}{\Delta_K \Delta_L}.$$

Equating the derivative of Eq. (13) with respect to p_T and p_S zero results

$$\begin{pmatrix} A_{TT} & A_{ST} \\ A_{ST} & A_{SS} \end{pmatrix} \begin{pmatrix} p_T \\ p_S \end{pmatrix} = \begin{pmatrix} B_T \\ B_S \end{pmatrix},$$

giving the scaling parameters as

$$\begin{pmatrix} p_T \\ p_S \end{pmatrix} = \frac{1}{D} \begin{pmatrix} A_{SS} & -A_{ST} \\ -A_{ST} & A_{TT} \end{pmatrix} \begin{pmatrix} B_T \\ B_S \end{pmatrix}, \tag{14}$$

with $D = A_{TT}A_{SS} - A_{ST}^2$.

Substituting expression (14) for p_T and p_S into the formula for $E_{\mathrm{SCS-MP}}^{(3)}$ one gets

$$E_{\mathrm{SCS-MP}}^{(3)} = \frac{1}{D^2}(A_{SS}B_T^2 D + A_{TT}B_S^2 D - 2A_{ST}B_T B_S D)$$
$$- \frac{1}{D}(A_{SS}B_T^2 + A_{TT}B_S^2 - 2A_{ST}B_T B_S) = 0,$$

giving zero for the third order correction, similarly to previous experiences.[20,30] Quantities A and B are spin components of the second and third order MP corrections, respectively, and can be easily evaluated[39] to give

$$B_T = \sum_{ij} \sum_{ab} \frac{\langle ij|ab\rangle\langle ij||ab\rangle}{\Delta_{ij}^{ab}},$$

$$B_S = \sum_{ij} \sum_{ab} \frac{\langle ij|ab\rangle^2}{\Delta_{ij}^{ab}},$$

$$A_{SS} = 2\sum_{ijk}\sum_{abc} \frac{\langle ij|ba\rangle\langle jc||ak\rangle\langle bc|ik\rangle}{\Delta_{ij}^{ab}\Delta_{ik}^{bc}}$$
$$- 2\sum_{ijk}\sum_{abc} \frac{\langle ij|ab\rangle\langle jc|ka\rangle\langle bc|ki\rangle}{\Delta_{ij}^{ab}\Delta_{ik}^{bc}}$$
$$+ \sum_{ijkl}\sum_{ab} \frac{\langle ij|ab\rangle\langle ij|kl\rangle\langle ab|kl\rangle}{\Delta_{ij}^{ab}\Delta_{kl}^{ab}}$$
$$+ \sum_{ij}\sum_{abcd} \frac{\langle ij|ab\rangle\langle cd|ab\rangle\langle cd|ij\rangle}{\Delta_{ij}^{ab}\Delta_{ij}^{cd}} + \sum_{ij}\sum_{ab}\frac{\langle ij|ab\rangle^2}{\Delta_{ij}^{ab}},$$

$$A_{TT} = 2\sum_{ijk}\sum_{abc} \frac{\langle ij||ab\rangle\langle ci||ak\rangle\langle cb||jk\rangle}{\Delta_{ij}^{ab}\Delta_{jk}^{bc}}$$
$$+ \sum_{ijkl}\sum_{ab} \frac{\langle ij||ab\rangle\langle ij|kl\rangle\langle ab|kl\rangle}{\Delta_{ij}^{ab}\Delta_{kl}^{ab}}$$
$$+ \sum_{ij}\sum_{abcd} \frac{\langle ij||ab\rangle\langle cd|ab\rangle\langle cd|ij\rangle}{\Delta_{ij}^{ab}\Delta_{ij}^{cd}}$$
$$+ \sum_{ij}\sum_{ab} \frac{\langle ij|ab\rangle\langle ij||ab\rangle}{\Delta_{ij}^{ab}},$$

$$A_{ST} = 2\sum_{ijk}\sum_{abc} \frac{\langle ij||ab\rangle\langle ci|ka\rangle\langle cb|kj\rangle}{\Delta_{ij}^{ab}\Delta_{jk}^{bc}}.$$

Shorthand $\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$ is used in the denominators, and again the $i, j, \ldots$ occupied and $a, b, \ldots$ virtual convention are applied.

Stepping from second to third order MP there are no new excitation levels, hence no new repartitioning parameters can enter the energy formula. Further freedom at third order is therefore not present, the energy is given by Eq. (12) in the extended Feenberg-scaled framework. This is different from Grimme's third order approach where a further single scaling parameter is used to multiply the MP3 contribution,[40]

$$E_{\mathrm{Grimme}}^{(3)} = p_3 E_{\mathrm{MP}}^{(3)}. \tag{15}$$

This cannot be reasoned by the zero order Hamiltonian of Eq. (11). Still it is interesting to observe that while Feenberg's approach leads to explicitly zero third order contribution, Grimme's parameter at third order is also rather small, $p_3 = 0.25$ as obtained by least-squares fitting on more than 30 reaction energies.

III. RESULTS AND DISCUSSION

The aim of the few illustrative examples presented in this section is to compare spin-component-scaling with Grimme's parameters (SCS-GR) and Feenberg-optimized parameters (SCS-FE) in terms of correlation energies and parameter values.

Table I collects second order energy errors, the difference taken with either the FCI or the CCSD(T) value as reference. For two-electron systems, H_2 molecule and Be atom in the table, SCS-FE falls back to the one-parameter Feenberg scaling (FE) due to the missing parallel-spin pair energy term. Energy errors in Table I typically decrease as the number of scaling parameters increase in the order MP2 > FE2 > SCS-FE2 > LCCD. Spin-component scaling with Grimme's parameters (SCS-GR) fits worse than expected into this order. The SCS-GR2 values are though better than MP2, they are rather similar to FE2, instead of being of

TABLE I. Second order energy errors ($E-E_{\text{reference}}$) in mH. Reference value is either FCI[a] or CCSD(T)[b]. Geometries are $R=0.742$ Å for the H_2 molecule, $R=1.411$ Å for the F_2 molecule, $R=1.094$ Å for the N_2 molecule, $R=1.128$ Å for the CO molecule, $R=0.923$ Å for the HF molecule, $R=0.957$ Å and $\angle(\text{HOH})=104.5°$ for the water molecule, $R=1.259$ Å and $\angle(\text{OOO})=118.4°$ for the O_3 molecule, $R_{\text{NH}}=1.013$ Å and $R_{\text{HH}}=1.643$ Å for the NH_3 molecule, and $R_{\text{CH}}=1.090$ Å for the CH_4 molecule. Standard Pople basis sets, Dunning's valence triple-zeta (Ref. 41) with polarization functions (pVTZ) and correlation consistent polarized valence triple-zeta (cc-pVnZ) (Ref. 42) basis sets are applied. Polarization functions' exponents to VTZ are taken from HONDO 7 (Ref. 43) (H: 1.0, Be: 0.32, C: 0.72, N: 0.98, O: 1.28, and F: 1.62).

System/basis	MP2	FE2	SCS-GR2	SCS-FE2	LCCD
H_2 molecule					
STO-3G[a]	7.43	−0.27	4.79	−0.27	−0.27
cc-pVTZ[a]	7.69	0.89	1.33	0.89	−0.59
cc-pV5Z[a]	6.98	1.26	0.25	1.26	−0.62
Be atom					
pVTZ[b]	20.02	4.55	12.10	4.50	−4.48
HF molecule					
pVTZ[b]	6.39	7.38	11.29	6.27	3.35
cc-pVTZ[b]	8.59	8.60	13.93	7.62	4.04
H_2O molecule					
6-31G[a]	8.08	6.52	8.46	4.54	2.05
6-311G[b]	8.91	8.88	7.43	7.11	3.97
cc-pVTZ[b]	13.62	14.02	20.71	12.87	3.83
NH_3 molecule					
pVTZ[b]	19.35	7.48	16.54	6.23	2.10
cc-pVTZ[b]	20.42	8.53	17.68	7.56	2.63
CH_4 molecule					
pVTZ[b]	26.57	5.38	17.76	4.58	0.72
cc-pVTZ[b]	27.27	6.63	17.56	6.08	1.23
N_2 molecule					
pVTZ[b]	15.52	23.17	21.45	19.77	8.39
cc-pVTZ[b]	17.46	24.48	23.99	21.59	9.00
CO molecule					
pVTZ[b]	19.23	23.05	23.87	20.30	10.13
cc-pVTZ[b]	20.54	23.89	26.09	21.57	10.34
F_2 molecule					
pVTZ[b]	18.79	21.49	25.50	18.33	4.72
cc-pVTZ[b]	21.86	23.61	30.26	20.83	5.78
O_3 molecule					
pVTZ[b]	12.19	54.29	31.66	47.67	20.45
cc-pVTZ[b]	14.76	57.68	37.44	51.74	21.68

TABLE II. Feenberg-optimized scaling parameters in the one- and two-parameter pictures. Systems, geometries, and basis sets are the same as in Table I. For comparison, Grimme's empirical parameter values are $p_S=1.2$ and $p_T=1/3$.

System/basis	FE2 $1-\mu$	SCS-FE2 p_S	SCS-FE2 p_T
H_2 molecule			
STO-3G	1.583 85	1.583 85	⋯
cc-pVTZ	1.213 85	1.213 85	⋯
cc-pV5Z	1.170 03	1.170 03	⋯
Be atom			
pVTZ	1.379 41	1.383 32	0.956 28
HF molecule			
pVTZ	0.995 87	1.058 27	0.826 78
cc-pVTZ	0.999 97	1.042 71	0.886 51
H_2O molecule			
6-31G	1.012 04	1.116 56	0.735 91
6-311G	1.000 16	1.082 22	0.760 62
cc-pVTZ	1.014 65	1.062 17	0.882 99
NH_3 molecule			
pVTZ	1.055 12	1.109 26	0.885 25
cc-pVTZ	1.046 92	1.089 57	0.911 73
CH_4 molecule			
pVTZ	1.114 35	1.154 88	0.948 93
cc-pVTZ	1.094 29	1.124 57	0.970 02
N_2 molecule			
pVTZ	0.978 75	1.059 52	0.774 01
cc-pVTZ	0.982 73	1.050 18	0.808 21
CO molecule			
pVTZ	0.988 77	1.060 73	0.801 62
cc-pVTZ	0.991 31	1.051 41	0.832 79
F_2 molecule			
pVTZ	0.994 19	1.058 27	0.826 78
cc-pVTZ	0.996 85	1.049 91	0.856 21
O_3 molecule			
pVTZ	0.941 45	1.023 69	0.744 95
cc-pVTZ	0.947 89	1.018 12	0.778 09

the same quality as SCS-FE2. This behavior can be attributed to the fact that Grimme's parameters were determined with a polarized quadruple-ζ quality basis set, while bases indicated in Table I are just polarized triple ζ or poorer. The case of the H_2 molecule in polarized pentuple-ζ basis supports this reasoning: here SCS-GR2 outperforms SCS-FE2 and even LCCD.

For molecules HF, N_2, CO, and F_2 Feenberg scaling gives worse second order energy than MP2, in accordance with earlier observations on HF and F_2.[22] The fact that these molecules represent difficult cases is also demonstrated by

SCS-FE2 numbers: these are just slightly different from MP2, being either better or worse. Introduction of more than two parameters by LCCD helps to reduce the error of MP2 significantly.

The O_3 molecule is an exception to all the above statements. In this example both one- and two-parameter Feenberg scalings are much poorer than MP2. Values by LCCD, though somewhat better than Feenberg-scaled numbers, are also inferior to MP2. An insight to this problem is provided by inspecting the third order MP corrections, which are large positive numbers, pointing at the probably poor convergence of the MP series. The error of MP3 compared to CCSD(T) is also much larger than that of MP2: 56.91 mH for the pVTZ basis and 60.04 mH error in the cc-pVTZ basis. The fact that FE2, SCS-FE2, and LCCD, which are inherently third order numbers, compare favorably with MP3 but not with MP2

TABLE III. Reaction energies in kcal/mol units by second order PT methods. Geometries of all species were optimized by B3LYP with pVTZ basis set.

Reaction/basis	MP2	FE2	SCS-GR2	SCS-FE2	LCCD	CCSD(T)
$H_2+F_2\rightarrow 2HF$						
pVTZ	−138.86	−134.92	−133.50	−134.32	−128.83	−130.30
cc-pVTZ	−138.95	−135.77	−133.53	−135.26	−129.38	−131.18
$N_2+3H_2\rightarrow 2NH_3$						
pVTZ	−28.79	−35.32	−25.78	−34.76	−30.92	−28.97
cc-pVTZ	−36.38	−42.90	−31.94	−42.30	−37.79	−36.56
$O_3+CH_4\rightarrow 2H_2O+CO$						
pVTZ	−155.63	−170.74	−157.21	−169.53	−161.34	−158.41
cc-pVTZ	−149.21	−166.09	−151.06	−164.91	−155.91	−152.81
$4Be\rightarrow Be_4$						
pVTZ	−95.99	−71.32	−81.79	−72.65	−58.55	−73.58
$2P_2\rightarrow P_4$						
pVTZ	−42.35	−37.89	−37.36	−37.44	−32.73	−36.71

shows that higher order effects of the MP series are responsible for the poor performance of the scaled second order corrections.

Feenberg-optimized parameters shown in Table II agree with Grimme's parameters ($p_S=1.2$ and $p_T=1/3$) as to the deviation of the parameters from 1: $p_S>1$ and $p_T<1$ in all cases. Feenberg-optimized parameters show a considerable variation with basis and system size. Both parameters tend to 1 with increasing basis, hence p_S gets smaller and p_T gets larger. Feenberg-optimized p_S varies around Grimme's p_S parameter. The average value of the few examples presented is 1.12, in nice agreement with Grimme's $p_S=1.2$. There is more discrepancy in parameter p_T, which is 0.84 on average, instead of $p_T=1/3$ by Grimme. The agreement however, can be accepted as (i) Grimme's parameters were optimized on a much larger set of examples than presented here and (ii) Grimme fitted the parameters on energy differences while Feenberg optimization is based on total energies.

Inspecting the optimal $1-\mu$ parameter of Feenberg's original scaling it is notable that this parameter is either larger or smaller than 1, and shows a more complicated dependence on basis set than p_S and p_T. It would be worthwhile to investigate whether the two parameters of spin-components scaling are more transferable from one system to the other than the $1-\mu$ parameter of Feenberg. This would support that the repartitioning involved in Grimme's scaling is more than a mere mathematical operation and has also a physical basis as argued by Grimme.[34] However, in the present work we do not wish to enter into a thorough numerical study that would enable to draw a reliable statistical conclusion.

Reaction energies presented in Table III show less sensitivity on the nature of scaling than correlation energies. One- and two-parameter scalings give values within a rough 10 kcal/mol. Second order reaction energies scaled by Feenberg's parameters are particularly similar, they fall within a few kcal/mol. Taking CCSD(T) as the reference value, the accuracies show a diverse picture. The first three of the reactions in Table III were part of Grimme's benchmark set.

For these SCS-GR2 is the closest to CCSD(T) among FE2, SCS-GR2, SCS-FE2, and LCCD. Only the first reaction is an exception, where LCCD is slightly closer to CCSD(T), but it is hard to judge which is better eventually. The hydrogenation of N_2 to NH_3 is a notable case, where neither of the scaled second order energies improve upon the MP2 reaction energy.

For the last two reactions in Table III the picture is different. Interestingly LCCD is the worst among non-MP second order for these systems, but still better than MP2. In these two cases, which were not present in Grimme's benchmark set, SCS-FE2 is better for the Be tetramerization reaction and it is of the same quality as SCS-GR2 with just a 0.1 kcal/mol difference between the two.

IV. CONCLUSION

In this work we have presented an extension of the one-parameter scaling of the zero order Hamiltonian proposed by Feenberg to two parameters in a way that Grimme's spin-component-scaled Møller-Plesset second order formula is recovered. We have used Feenberg's minimal condition on the third order energy to set the value of the scaling parameters. Comparison of Grimme's empirical parameter values with Feenberg optimized values shows good numerical agreement for the p_S parameter while for the other parameter $p_T<1$ holds by both methods. It should be noted that an empirical choice for the scaling parameters has the advantage over Feenberg's approach that it preserves size consistency of the second order PT expression.

We have found considerable variation of the Feenberg-optimal scaling parameters with basis size which may point to a possible refinement of the empirically parametrized formula by introducing basis set dependent parameters.

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