Scaling all correlation energy in perturbation theory calculations of bond energies and barrier heights

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Scaling All Correlation Energy in Perturbation Theory Calculations of Bond Energies and Barrier Heights

Mark S. Gordon*[†] and Donald G. Truhlar

Contribution from the Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455. Received February 28, 1986

Abstract: We present and test a new method for scaling all correlation energy as estimated by Møller–Plesset many-body perturbation theory with popular basis sets. Scale factors that may be useful for future applications are estimated from known bond dissociation energies. We also use scale factors to estimate the barrier heights for two hydrogen-transfer reactions, $CH_3 + H_2 \rightleftharpoons CH_4 + H$ and $OH + CH_4 \rightleftharpoons H_2O + CH_3$.

I. Introduction

Ab initio electronic structure calculations are improving steadily in accuracy and usefulness.[1] Nevertheless, in many cases, implicit and explicit extrapolation and correction schemes are needed and are used to obtain useful accuracy with lower levels of theory than would be required with unextrapolated results. An example of an implicit extrapolation scheme is the widely used assumption that errors are constant across a potential energy surface. This is equivalent to assuming that the extrapolated value E_e of the accurate (exact) total energy is given in terms of the calculated value E_c by

$$E_e = E_c + C \qquad (1)$$

where C is a constant for a given reaction, i.e., C is independent of geometry and/or bond rearrangement. This assumption has proved particularly accurate when applied only to reactants and products of isodesmic or isogyric reactions,[2] but it is often applied, for lack of a better assumption, to more general reactions and to transition states. Notice of course that C need never be specified if only energy differences are considered. Another form of extrapolation, applicable only for perturbation theory, is the use of Padé extrapolants[3] to estimate the infinite-order correlation limit for a given one-electron basis set. The closest analogue for configuration-interaction-based methods is the use of threshold selection and increasingly large reference spaces to estimate the complete configuration interaction limit for a given one-electron basis.[4] Unfortunately the effects of incompleteness of the one-electron basis set are often larger than the neglect of higher order correlation effects. The method of scaled external correlation (SEC)[5] attempts to extrapolate to the full-CI limit and the complete one-electron-basis-set limit in a single step. The SEC method

is based on combining the results of two ab initio calculations: a multi-configuration self-consistent-field (MCSCF)[6] calculation that accounts for specific geometry-dependent correlation effects and a multi-reference configuration interaction (MR–CI)[7] calculation that accounts for an appreciable fraction of the external (or dynamical) correlation. Then the accurate energy is approximated by[5]

$$E_{SEC} = E_{MCSCF} + \frac{E_{MRCI} - E_{MCSCF}}{\mathcal{F}} \qquad (2)$$

where $\mathcal{F}$ is assumed constant, i.e., independent of geometry and/or bond rearrangement for a given system. When the one-electron basis set is very extensive, the MCSCF calculation is a full-valence

[†] Visiting Fellow, Minnesota Supercomputer Institute, 1985–1986. Permanent address: Department of Chemistry, North Dakota State University, Fargo, ND 58105-5516.

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complete-active-space one,[8] and the MR–CI calculation includes all interacting[9] single and double excitations out of the occupied or partially occupied orbitals of the MCSCF reference space, the SEC method has been found to yield useful improvements over the original MR–CI calculations even for processes involving bond breaking and for transition states.[5]

An important element in the physical basis for the SEC method is that the MCSCF calculation must be large enough to include all or most of the near-degeneracy and other "nondynamical"[10] effects that are sensitive to the optimization of the reference space. The effects included in the MCSCF wave function are called internal correlation, and the additional correlation included in the MR–CI calculation is called external. Provided that the external correlation does not include any nondynamical effects and provided that the one-electron basis set is large enough for the calculation to include an appreciable fraction (say 50% or more) of the external valence correlation, it is quite reasonable that this fraction depends more on the size of the system than on its specific geometry or bond arrangement. But the very features of the SEC method that promotes its success, namely a large one-electron basis set (in order that $F > 0.5$ and preferably as large as possible) and a large reference space out of which all single and double excitations are considered (in order to separately estimate internal and external correlation), mitigate against its widespread applicability by making the MR–CI step computationally expensive. Thus we seek a simpler (although probably less reliable) extrapolation method for the case where full SEC calculations are prohibitive. The refinement we propose and test here is scaling all correlation, estimated by many-body perturbation theory[11] with respect to the best single-determinant wave function and as calculated with various popular basis sets. Thus, using nth order Møller–Plesset (MPn)[12] perturbation theory based on a restricted or unrestricted Hartree–Fock (RHF or UHF)[13] single-configuration reference state, as appropriate (for the cases considered in this paper, this means RHF for singlets and UHF for doublets), we write

$$E_{\text{MP-SAC}n} = E_{\text{UHF}} + \frac{E_{\text{MP}n} - E_{\text{UHF}}}{\mathcal{F}_n} \quad (3)$$

The new abbreviation (MP-SACn) denotes scaling all the correlation energy as estimated by Møller–Plesset theory of order n. The orders specifically considered here are $n = 2$ and 4, yielding extrapolation methods to be called MP-SAC2 and MP-SAC4. In both SEC and MP-SAC calculations we correlate only the valence electrons. Core correlation is assumed to cancel for chemical processes in the sense of eq 1.

The use of MPn ingredients in the MP-SACn methods is motivated in part by the wide availability of efficiently coded programs, e.g., GAUSSIAN82,[14] for the evaluation of both energies and energy gradients by these methods. Efficient gradient programs are particularly well suited to finding transition states[15]

Table I. Experimental Energies (kcal/mol) for Reactions $AH_n \rightarrow AH_{n-1} + H$

A	n	$\Delta H_0°$	$D_e(\text{expt})$
H	1	103.2	109.2
C	4	103.8	112.7
N	3	107.1	116.3
O	2	118.0	125.7
F	1	135.2	140.7

and calculating reaction-path potentials.[16] Two other advantages of using many-body perturbation theory are that it scales properly with molecular size and, since we always use a single determinant reference state, there is no question about how to choose the reference state when new systems are considered. The unfortunate trade-off is that, as compared to an MCSCF reference state, use of the UHF reference state is often quantitatively deficient, and it forces us to scale internal as well as external correlation effects. The present article examines the resulting question: it is nevertheless sometimes useful to scale all the correlation energy?

Although this introduction cannot review all previous extrapolation methods, we also mention the work of Meyer, Davidson, and Melius and their co-workers.[17-19]

Section IIa presents a table of accurate classical bond dissociation energies calculated from data in the literature to serve as a basis for estimating scale factors, and section IIB presents estimates of classical barrier heights for two reactions to serve as tests of the theory for reaction barriers. Section III presents the methods used for the electronic structure calculations, and sections IV and V present the results. Section VI presents our conclusions about the constancy of $\mathcal{F}_n$ for various classes of bond energies and suggests "standard" values for various classes of processes and basis sets. It also discusses illustrative applications of the MP-SAC2 and MP-SAC4 methods for the problem of calculating barrier heights for atom-transfer reactions. Section VII summarizes the main findings.

II. Reference data

A. Bond-Dissociation Energies. The approach used to allow direct comparisons between experiment and theory is similar to that described by Pople, Luke, Frisch, and Binkley,[20] except that we prefer to compare theory and experiment by converting experimental heats of reaction and heats of formation to electronic energy differences (including nuclear repulsions), rather than converting theoretical electronic energy differences to enthalpy changes. Given an experimental heat of formation of AH_n at 298 K ($\Delta H_f°_{298}$), the corresponding value at 0 K ($\Delta H_f°_0$) may be obtained from

$$\Delta H_f°_0(AH_n) =$$
$$\Delta H_f°_{298}(AH_n) - [H°_{298}(AH_n) - H°_0(AH_n)] + (1/m) \times$$
$$[H°_{298}(A_m) - H°_0(A_m)] + (n/2)[H°_{298}(H_2) - H°_0(H_2)] \quad (4)$$

where A_m refers to the standard state of the element A (in this work, A = H, C, N, O, or F). The $\Delta H_f°_{298}$ values were taken from the CODATA recommended values for the elements and

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from the JANAF Thermochemical Tables, as tabulated in ref 20, for compounds, and the bracketed finite-temperature corrections for A_m, AH_n, and H_2 are obtained from ab initio frequencies[20] and thermochemical data[21] described in ref 20.

To obtain the values of $\mathcal{F}_2$ and $\mathcal{F}_4$, we will be particularly interested in the reactions

$$AH_n(g) \rightarrow AH_{n-1}(g) + H(g) \qquad (5)$$

where AH_n is a closed-shell gaseous saturated hydride. Thus, the next step is to convert $\Delta H_f{}^\circ{}_0$ values obtained from (4) to $\Delta H^\circ{}_0$ values for reaction 5. Finally (again following Pople and co-workers[20] but in the opposite direction) these enthalpy changes are converted to electronic energy differences ΔE by using the zero-point vibrational energies from SCF/6-31G(d)[22] calculations, scaled by a factor of 0.89. The resulting $\Delta H^\circ{}_0$ and ΔE values for reaction 5 are summarized in Table I. The latter values will hereafter be referred to as the experimental equilibrium dissociation energies, $D_e(\text{exptl})$. (For consistency we use this procedure even for H_2, for which it yields $\Delta E = 109.2$ kcal mol, even though in the case of H_2 a more accurate value, 109.5 kcal mol, is available from other sources.[23])

B. Classical Barrier Heights. We also wish to test our method for the prediction of chemical reaction barrier heights. We denote the electronic energy differences (including nuclear repulsion) between the saddle point and the reactants as the classical barrier height, V^*. Experimental values of V^* are estimated for two reactions of current interest

$$CH_3 + H_2 \underset{6r}{\overset{6f}{\rightleftharpoons}} CH_4 + H \qquad (6)$$

$$OH + CH_4 \underset{7r}{\overset{7f}{\rightleftharpoons}} H_2O + CH_3 \qquad (7)$$

as follows. For reaction 6 a semiempirical potential energy surface was adjusted by Steckler and one of the authors[24] so that the transition-state zero-point energy is within 0.1 kcal/mol of the ab initio polarization configuration interaction (PolCI) value of Schatz et al.,[25] scaled by 0.98, so that rate constants calculated from it by variational transition-state theory with semiclassical transmission coefficients[26] agree with the experimental rate constants recommended by Shaw[27] at 667 K, and so that reactant and product vibrational frequencies and equilibrium constants calculated from it agree with experimental values and thermochemical tabulations.[28] This yields a forward classical barrier height $V^*{}_{6f} \cong 8$ kcal mol, a backward one of $V^*{}_{6r} \cong 11$ kcal mol, and a reaction energy, ΔE, of about 3.5 kcal/mol.

For reaction 7 we do not have reliable dynamical calculations for a global potential energy surface to aid in estimating V^* so we use cruder estimates. We will consider two different estimates, one of which probably overestimates V^* and one of which probably underestimates it.

The phenomenological activation energy, E_a, for reaction 7f is 6 kcal/mol lower than that for reaction 6r.[26] If we assume V^* exceeds E_a by the same amount for these two similar radical–molecule reactions, then $V^*{}_{7f} \cong V^*{}_{6r} - 6$ kcal/mol = 5 kcal/mol. Table I then yields $V^*{}_{7r} = V^*{}_{7f} + 13$ kcal/mol $\cong 18$ kcal/mol. This procedure probably overestimates V^* because tunneling is

Figure 1. Transition-state geometries with bond lengths in Å and bond angles in deg. The level used to optimize each transition-state geometry is indicated below the structure. The CH_5 structures have C_{3v} symmetry, and the CH_4OH structures have C_s symmetry.

more important for higher barrier reactions and hence $V^* - E_a$ is probably greater for reaction 6r than for reaction 7f.

Another way to estimate the barrier height for reaction 7f is to completely ignore tunneling and entropic effects, as well as the dislocation of the dynamical bottleneck from the saddle point. Under these assumptions we may equate the observed activation energy to the zero-point-corected saddle-point height. Then, estimating the zero-point energies of the reactants and transition state from the SCF/6-31G(d) frequencies adjusted by a factor of 0.89, we obtain an estimate of the classical barrier height as E_a minus the zero-point difference of the transition state from reactants. Recent experiments[29,30] yield $E_{a,7f} = 3.3 - 4$ kcal mol^{-1} at $T \leqslant 300$ K, and this implies $V^*{}_{7f} \cong 2$ kcal mol^{-1}, and hence $V^*{}_{7b} \cong 15$ kcal mol^{-1}. This is probably an underestimate because of the neglect of tunneling effects, which tend to lower E_a for a given V^*.

Combining the two estimates we obtain $V^*{}_{7f} \cong 3.5 \pm 2$ kcal mol^{-1} and $V^*{}_{7r} \cong 16.5 \pm 2$ kcal mol^{-1}.

III. Computational Methods

Several popular basis sets were used in this study. For the evaluation of thermodynamic energy differences, the 6-31G(d)[22] structures for the AH_n and AH_{n-1} compounds [obtained at the SCF level using RHF or UHF wave functions as appropriate] were taken from ref 20. MP2 and MP4 energies at these geometries were calculated or obtained from the literature for several basis sets. For the 6-311G(d,p),[31] 6-311+G(d,p),[32] and 6-311G(2d,p)[32] basis sets, the MP4 energies were taken from ref 20. The SCF and MP2 energies for these basis sets and all energies for the 6-31G(d),[22] 6-31G(d,p),[22] 6-31+G(d,p),[32] and 6-31G(2d,p)[32] basis sets were computed in this laboratory.

For the barrier height calculations, we used the same six basis sets and again used SCF/6-31G(d) geometries. The transition-state geometries are shown in Figure 1. In addition, since the determination of transition-state geometries and the evaluation of the associated reaction paths

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Table II. Total Energies (hartrees)[a] for AH_n Compounds

	H_2	CH_4	NH_3	H_2O	HF
6-31(d)					
SCF	-1.126 83	-40.195 17	-56.184 36	-76.010 75	-100.002 91
MP2	-1.144 10	-40.332 44	-56.353 71	-76.195 96	-100.181 58
MP4	-1.150 82	-40.354 55	-56.370 50	-76.206 32	-100.187 80
6-31G(d,p)					
SCF	-1.131 33	-40.201 70	-56.195 53	-76.023 57	-100.011 55
MP2	-1.157 65	-40.364 62	-56.382 95	-79.219 36	-100.194 51
MP4	-1.164 54	-40.388 61	-56.401 03	-76.230 81	-100.201 31
6-31+G(d,p)					
SCF	-1.131 33	-40.202 13	-56.200 74	-76.031 13	-100.024 21
MP2	-1.157 65	-40.365 94	-56.391 73	-76.232 60	-100.215 53
MP4	-1.164 54	-40.390 03	-56.409 70	-76.244 10	-100.222 71
6-31G(2d,p)					
SCF	-1.131 33	-40.203 34	-56.198 73	-76.028 28	-100.014 71
MP2	-1.157 65	-40.374 31	-56.399 64	-76.247 89	-100.231 76
MP4	-1.164 54	-40.399 27	-56.418 72	-76.260 79	-100.240 22
6-311G(d,p)					
SCF	-1.132 47	-40.208 95	-56.210 39	-76.046 92	-100.046 62
MP2	-1.160 22	-40.379 23	-56.408 46	-76.263 58	-100.267 21
MP4[b]	-1.167 63	-40.404 81	-56.427 54	-76.275 90	-100.274 21
6-311+G(d,p)					
SCF	-1.132 47	-40.209 09	-56.214 59	-76.053 22	-100.053 03
MP2	-1.160 22	-40.379 41	-56.415 00	-76.274 37	-100.278 76
MP4[b]	-1.167 63	-40.405 11	-56.433 89	-76.286 62	-100.286 08
6-311G(2d,p)					
SCF	-1.132 47	-40.210 24	-56.211 55	-76.048 13	-100.047 48
MP2	-1.160 22	-40.387 65	-56.420 19	-76.279 19	-100.288 07
MP4[b]	-1.167 63	-40.413 88	-56.439 70	-76.291 92	-100.295 68

[a] 1 hartree = 627.51 kcal/mol.   [b] Energies taken from ref 20 of text.

and energetics is rather more time consuming than is the calculation of thermodynamic energy differences, it is of interest to determine whether SAC extrapolations using smaller basis sets might yield consistently reliable results. For this purpose, the smaller 3-21G[33] basis was also considered. For the 3-21G calculations, the geometries used were those obtained with the SCF/3-21G wave functions. Again the saddle-point geometries are shown in Figure 1.

The CH_5 structure was also optimized at the MP2/6-311G(d,p) level, and this geometry is also shown in Figure 1. The CH_5 transition states were optimized in C_{3v} symmetry, and the CH_4OH ones were optimized in C_1 symmetry. In all cases, however, the Hessian matrix was calculated and diagonalized and yielded only one negative eigenvalue, indicating a true saddle point was found.

For reaction 6 we also performed calculations with one very large basis set. In particular, MP2 and MP4 calculations were carried out at the SCF/6-31G(d) geometries with the 6-311++G(3df,2pd)[32] basis set.

Finally, because the use of the basis sets discussed so far can be rather expensive for larger compounds, parallel calculations have been carried out with the more economical 3-21G basis set. (We do not recommend using even smaller basis sets, e.g., STO-3G[34] or STO-2G,[34] with the MP-SACn method; such basis sets are too small to yield even a qualitatively correct estimate of correlation energy trends. Even the 3-21G basis set does not always predict qualitatively correct correlation trends, and in fact the use of any basis set that does not include polarization functions for estimates of the correlation energy cannot be recommended as a general procedure.)

Since the SAC method is designed to scale the correlation energy in cases where the UHF wave function provides at least a reasonable first-order description, it would not be expected to be successful at removing spin contamination due to the fact that UHF wave functions are not spin eigenfunctions. We therefore monitored the expectation of S^2 in all UHF and MP2 wave functions. For doublets, it was always in the range 0.75–0.78, where 0.75 is the correct value. Thus spin contamination is not severe.

IV. Results for Bond Energies

The total energies for the 6-31G(d) and larger basis sets are summarized in Tables II and III for the AH_n and AH_{n-1} species, respectively. (The MP4 values for the three largest basis sets are reproduced from ref 20 for comparison.) The resulting ab initio bond energies corresponding to reaction 5 are listed in Table IV.

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These bond energies are used to calculate an $\mathcal{I}_n$ for each bond type and each basis set. This is accomplished with the expression

$$\mathcal{I}_n = \frac{D_e(MP n) - D_e(SCF)}{D_e(expt) - D_e(SCF)} \tag{8}$$

where the bond energy D_e refers to the energy difference for reaction 5 as obtained from experiment (expt), SCF wave functions, or the appropriate level of perturbation theory (UMPn). The values obtained in this way are presented in Table V.

Since one will frequently be interested in reactions in which different kinds of A–H bonds are being broken or formed, e.g., reaction 6 or 7, it may be of interest to have a single "standard" value of $\mathcal{I}_n$ for each basis set. This may be done separately for each row of the periodic table or globally for all atoms A. The most straightforward approach for obtaining such standard $\mathcal{I}_n$ values is to take a simple average of the $\mathcal{I}_n$ for the atoms of interest. These standard values so obtained, with and without the inclusion of H–H bonds, are also listed in Table V. The two kinds of average are denoted A1 and A2, respectively.

For the 6-311++G(3df,2pd) basis set, the $\mathcal{I}_2$ values for H–H and C–H are 0.78 and 0.92, respectively, while the corresponding $\mathcal{I}_4$ values are 0.95 and 0.96. The $\mathcal{I}_2$ and $\mathcal{I}_4$ values for the 3-21G basis set are given in Table VI.

V. Results for Barrier Heights

To test the ability of the SAC method to predict reaction energetics, the method was applied to reactions 6 and 7. The 6-31G(d) transition-state structures for these reactions are displayed in Figure 1, and the energetics are summarized in Tables VII, VIII, and IX.

VI. Discussion

A. Constancy of $\mathcal{I}_n$ Values. As expected, the addition of correlation corrections, here in the form of perturbation theory, results in a dramatic improvement in the predicted bond-dissociation energies, as seen by comparing the unextrapolated calculated results in Table IV to the experimental values in Table I. The variation in improving the order from MP2 to MP4 is generally much smaller than that for improving from SCF to MP2.

The first and most crucial question to be answered by the present research is the following: do perturbation theory calculations based on a single-configuration SCF reference state recover an approximately constant (independent of bond type for a given

Table III. Total Energies (hartrees) for AH_{n-1} Compounds

	H	CH$_3$	NH$_2$	OH	F
6-31G(d)					
SCF	-0.498 23	-39.558 99	-55.557 70	-75.382 28	-99.364 96
MP2	-0.498 23	-39.668 67	-55.690 47	-75.520 63	-99.487 27
MP4	-0.498 23	-39.689 18	-55.709 43	-75.535 61	-99.498 65
6-31G(d,p)					
SCF	-0.498 23	-39.564 46	-55.564 82	-75.388 32	-99.364 96
MP2	-0.498 23	-39.692 70	-55.709 71	-75.531 91	-99.487 27
MP4	-0.498 23	-39.714 72	-55.729 50	-75.547 34	-99.498 65
6-31+G(d,p)					
SCF	-0.498 23	-39.566 70	-55.568 22	-75.393 26	-99.371 65
MP2	-0.498 23	-39.696 32	-55.715 62	-75.540 83	-99.498 82
MP4	-0.498 23	-39.718 42	-55.735 59	-75.556 66	-99.510 87
6-31G(2d,p)					
SCF	-0.498 23	-39.566 16	-55.568 63	-75.392 02	-99.366 17
MP2	-0.498 23	-39.701 16	-55.724 58	-75.556 57	-99.518 97
MP4	-0.498 23	-39.724 38	-55.745 38	-75.573 38	-99.532 31
6-311G(d,p)					
SCF	-0.499 81	-39.572 91	-55.578 93	-75.410 69	-99.396 87
MP2	-0.499 81	-39.707 15	-55.732 32	-75.572 84	-99.554 17
MP4^a	-0.499 81	-39.730 60	-55.752 62	-75.588 22	-99.565 34
6-311+G(d,p)					
SCF	-0.499 81	-39.573 64	-55.581 99	-75.414 66	-99.399 89
MP2	-0.499 81	-39.708 43	-55.737 19	-75.579 62	-99.559 59
MP4^a	-0.499 81	-39.731 87	-55.757 51	-75.595 23	-99.571 12
6-311G(2d,p)					
SCF	-0.499 81	-39.574 16	-55.580 90	-75.411 96	-99.397 54
MP2	-0.499 81	-39.714 56	-55.743 75	-75.587 76	-99.573 14
MP4^a	-0.499 81	-39.738 56	-55.764 77	-75.604 23	-99.585 80

^{a} Energies taken from ref. 20 of text.

Table IV. Theoretical Equilibrium Dissociation Energies (kcal/mol) for the Reaction $AH_n \rightarrow AH_{n-1} + H$

	A =				
	H	C	N	O	F
6-31G(d)					
SCF	81.8	86.6	80.6	81.7	87.7
MP2	92.6	103.9	103.5	111.1	123.0
MP4	96.9	104.9	102.2	108.2	119.8
6-31G(d,p)					
SCF	84.6	87.2	83.1	86.0	93.1
MP2	101.1	109.0	109.8	118.7	131.2
MP4	105.5	110.2	108.7	116.2	128.3
6-31+G(d,p)					
SCF	84.6	86.1	84.3	87.6	96.8
MP2	101.1	107.6	111.6	121.4	137.1
MP4	105.5	108.8	110.4	118.7	134.0
6-31G(2d,p)					
SCF	84.6	87.2	82.8	86.6	94.3
MP2	101.1	109.8	111.0	121.2	134.6
MP4	105.5	110.9	109.9	118.7	131.6
6-311G(d,p)					
SCF	83.4	85.5	82.6	85.6	94.1
MP2	100.8	108.1	110.6	119.8	133.8
MP4	105.4	109.4	109.9	117.9	131.2
6-311+G(d,p)					
SCF	83.4	85.1	83.3	87.1	96.2
MP2	100.8	107.4	111.7	122.3	137.6
MP4	105.4	108.8	110.8	120.2	135.0
6-311G(2d,p)					
SCF	83.4	85.5	82.1	85.6	94.2
MP2	100.8	108.7	110.8	120.2	135.0
MP4	105.4	110.1	109.9	117.9	131.8

order of perturbation theory and basis) fraction of the valence correlation energy change in a bond-breaking process? This translates into an equivalent question, namely, are the $\mathscr{F}_n$ values in a given row of Table V approximately constant? The answer is yes for $n = 2$ if we exclude H_2 as a special case, and yes for $n = 4$ even including H_2. This is immediately encouraging, and it provides a motivation for further explorations of the validity of the theory.

We note for discussion purposes that unextrapolated MPn calculations may now be considered as special cases of MP-SACn with $\mathscr{F}_n = 1$. Then the question "Is MP-SACn more accurate than MPn for the bond-breaking process?" is equivalent to "Is

my best available estimated $\mathscr{F}_n$ value closer to the true $\mathscr{F}_n$ value for this process than the true $\mathscr{F}_n$ value is to unity?" In general we want to apply the MPn and MP-SACn methods to more complicated molecules than those involved in Tables II and III. Nevertheless, these simple molecules are probably adequate for a reliable general answer to the question for processes in which the only bonds being broken or made involve H bonded to itself or a nonmetal from the second row of the periodic table. In particular, 32 of the 35 $\mathscr{F}_2$ values in Table V are closer to the A1 average values for their row than the A1 average is to unity, and 33 of the 35 $\mathscr{F}_4$ values are closer to $\mathscr{F}_4$(A1) than the latter is to unity. This means that the MP-SACn method with the A1

Table V. $\mathcal{F}_n$ Values[a]

	H	C	N	O	F	A1	A2
6-31G(d)							
$\mathcal{F}_2$	0.39	0.66	0.64	0.67	0.67	0.61	0.66
$\mathcal{F}_4$	0.55	0.70	0.61	0.60	0.61	0.61	0.63
6-31G(d,p)							
$\mathcal{F}_2$	0.67	0.85	0.80	0.83	0.80	0.79	0.82
$\mathcal{F}_4$	0.85	0.90	0.77	0.76	0.74	0.80	0.79
6-31+G(d,p)							
$\mathcal{F}_2$	0.67	0.81	0.85	0.88	0.92	0.83	0.86
$\mathcal{F}_4$	0.85	0.85	0.82	0.82	0.85	0.84	0.83
6-31G(2d,p)							
$\mathcal{F}_2$	0.67	0.89	0.84	0.88	0.87	0.83	0.87
$\mathcal{F}_4$	0.85	0.93	0.81	0.82	0.80	0.84	0.84
6-311G(d,p)							
$\mathcal{F}_2$	0.67	0.83	0.83	0.85	0.85	0.81	0.84
$\mathcal{F}_4$	0.85	0.88	0.81	0.81	0.80	0.83	0.82
6-311+G(d,p)							
$\mathcal{F}_2$	0.67	0.81	0.86	0.91	0.93	0.84	0.88
$\mathcal{F}_4$	0.85	0.86	0.83	0.86	0.87	0.85	0.86
6-311G(2d,p)							
$\mathcal{F}_2$	0.67	0.85	0.84	0.86	0.89	0.82	0.86
$\mathcal{F}_4$	0.85	0.90	0.81	0.81	0.81	0.84	0.83

[a] A1 and A2 refer to average $\mathcal{F}$ values with and without the inclusion of hydrogen, respectively.

Table VI. $\mathcal{F}_n$ Values for the 3-21G Basis Set

	H	C	N	O	F	A1
$\mathcal{F}_2$	0.39	0.54	0.49	0.44	0.41	0.45
$\mathcal{F}_4$	0.53	0.60	0.49	0.43	0.40	0.49

average $\mathcal{F}_n$ values would yield more accurate D_e values than unextrapolated MPn calculations in over 90% of the cases. This is especially striking when we note that the MP–SACn extrapolation step involves negligible additional work, i.e., only the three floating point operations of eq 3 are required.

Note that the $\mathcal{F}_n$ values for the 3-21G basis set are much smaller than those for the larger basis sets, reflecting the fact that the improvement obtained from adding correlation corrections here is much smaller. The spread of $\mathcal{F}_n$ values for the atoms considered is greater than that for the larger basis sets considered above, particularly at the MP4 level. In this respect the use of an average $\mathcal{F}$ may be more tenuous here; however, there is also more to gain, and the typical $\mathcal{F}_n$ value is still much closer to the average than the average is to unity. In fact the relative constancy of the $\mathcal{F}_n$ values as compared to the deviation of the average $\mathcal{F}_n$ from unity is even better satisfied for the 3-21G basis sets than for the larger ones.

Clearly the MP–SACn method becomes more accurate if one has better estimates of $\mathcal{F}_n$. The "standard" values of Table V may be useful for processes in which the only bonds being made or broken involve H when no additional information is available or for treating whole sets of such processes at a consistent level. If, however, one is interested, for example, in a process in which only C–H bonds are made and broken, it may be desirable to use the $\mathcal{F}_n$ values from the C–H column of Table V or Table VI or even to perform additional calibration calculations based on known thermochemical data for a series of C–H bond-rearranging reactions. Alternatively, for the reaction such as (6) one might use an average of the C–H and H–H $\mathcal{F}_n$ values, or for (7) one might use an average of the C–H and O–H values. At an even finer level of tuning or to consider reactions in which a wider variety of bond types are made or broken, one might specially adjust a basis set so that $\mathcal{F}_n$ comes out the same for all the bond types involved in a given rearrangement. Then the electronic endoergicity would be correct by construction, and one might hope that the accuracy of additional features of the potential energy surface, such as saddle point location and/or height, would also be improved. We recommend such procedures for calculations of specific potential energy surfaces and barrier heights in the future, but, except for one calculation with the 6-311++G-(3pd,2df) basis for which $\mathcal{F}_n$ has not been calculated for all the cases in Table V, we restrict our attention in the rest of this article to the use of the A1 standard values of $\mathcal{F}_n$ to see what improvements, if any, we can obtain without any additional, more specific calibrations.

B. Barrier Heights for Basis Sets Including Polarization Functions on All Centers. We first discuss the barrier height calculations for the six basis sets of Tables II–V that include

Table VII. Calculated Reaction Energies and Barrier Heights (kcal/mol) for the Reaction $CH_3 + H_2 \rightarrow H + CH_4$[a]

basis	SCF	MP2	MP4	MP-SAC2/A1	MP-SAC4/A1	expt
forward barrier						8
6-31G(d)	20.5	14.4	14.9	10.5	11.3	
6-31G(d,p)	21.2	14.3	14.7	12.5	13.1	
6-31+G(d,p)	22.2	15.5	15.8	14.2	14.6	
6-31G(2d,p)	21.3	13.7	14.2	12.3	12.8	
6-311G(d,p)	21.5	13.3 (13.3)	13.3 (13.4)	11.4	11.6	
6-311+G(d,p)	21.9	13.8	13.8	12.3	12.4	
6-311G(2d,p)	21.7	13.1	13.0	11.2	11.3	
6-311++G(3df,2pd)	22.0	13.0	12.6	11.4	12.2	
reverse barrier						11
6-31G(d)	25.2	25.6	23.0	25.8	21.6	
6-31G(d,p)	23.8	22.2	19.4	21.8	18.3	
6-31+G(d,p)	23.7	21.9	19.1	21.6	18.2	
6-31G(2d,p)	23.8	22.4	19.6	22.1	18.8	
6-311G(d,p)	23.7	20.7 (20.9)	17.3 (17.2)	20.0	16.0	
6-311+G(d,p)	23.6	20.5	17.2	19.9	16.1	
6-311G(2d,p)	23.8	21.0	17.7	20.4	16.5	
6-311++G(3df,2pd)	23.6	19.8	16.3	19.1	16.0	

[a] Values in parentheses calculated with MP2/6-311G(d,p) geometries; other values calculated with SCF/6-31G(d) geometries.

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Table VIII. Calculated Barrier Heights (kcal/mol) for the Reaction OH + CH$_4$ → H$_2$O + CH$_3$

basis	SCF	MP2	MP4	MP-SAC2/A1	MP-SAC4/A1	expt
forward reaction						2–5
6-31G(d)	31.2	12.6	14.3	0.7	3.5	
6-31G(d,p)	29.2	10.4	12.0	5.1	7.7	
6-31+G(d,p)	28.1	7.5	9.1	3.3	5.2	
6-31G(2d,p)	28.7	8.8	10.3	4.7	6.5	
6-311G(d,p)	28.3	8.6	9.3	4.0	5.4	
6-311+G(d,p)	27.8	6.5	7.2	2.4	3.6	
6-311G(2d,p)	28.5	7.8	8.9	3.3	5.2	
6-311+G(2d,p)[a]	28.0	5.7	6.8	1.1	2.5	
reverse reaction						15–18
6-31G(d)	26.4	19.9	17.7	15.7	12.1	
6-31G(d,p)	28.0	20.1	18.0	18.0	15.5	
6-31+G(d,p)	29.7	21.4	19.0	19.7	16.8	
6-31G(2d,p)	28.1	20.2	18.1	18.6	16.1	
6-311G(d,p)	28.5	20.3	17.7	18.4	15.5	
6-311+G(d,p)	29.7	21.4	18.6	19.8	16.6	
6-311G(2d,p)	28.6	19.3	16.7	17.3	15.1	
6-311+G(2d,p)[a]	29.8	20.4	17.6	18.6	15.3	

[a] Extrapolated values—see text.

Table IX. Barrier Heights (kcal/mol) Calculated with the 3-21G Basis Set

	CH$_3$ + H$_2$ → CH$_4$ + H		OH + CH$_4$ → H$_2$O + CH$_3$	
	forward	reverse	forward	reverse
SCF	19.1	24.3	29.3	17.6
MP2	15.0	23.8	15.7	12.3
MP4	15.5	21.4	15.8	10.6
MP–SAC2	10.1	23.2	−0.7	10.6
MP–SAC4	11.7	18.4	1.7	3.3

polarization functions on all centers, i.e., the 6-31G(d,p) and better bases. For reaction 6, Table VII shows that both the forward and reverse barrier heights are severely overestimated at the SCF level, as expected. The addition of MP2 corrections decreases the forward barrier for all basis sets by about 30–40%; however, this level of perturbation theory has only a small effect on the reverse barrier. This is not unexpected since the treatment of H$_2$ at this level of theory is less accurate than that for the other species. This is apparent, for example, from the $\mathscr{T}_2$ values for H$_2$ relative to the others in Table V, and a similar difficulty of treating the H–H bond relative to the H$_3$C–H bond in a configuration interaction context has been noted previously by Walch.[35] On the other hand, fourth-order perturbation theory has only a small effect relative to MP2 for the forward barrier, but it has a larger effect on the reverse barrier. For the 6-311G(d,p), 6-311+G(d,p), and 6-311G(2d,p) basis sets, at the SAC4 level of theory, both barriers are overestimated by 3–5 kcal/mol, relative to the estimated experimental values of 8 and 11 kcal/mol, respectively. For the forward barrier, the much less expensive MP–SAC2 method does as well as SAC4, but for the reasons discussed above, the MP–SAC4 reverse barriers are 3–4 kcal/mol more accurate than those for MP–SAC2.

In an effort to improve the agreement between theory and experiment for reaction 6, two additional sets of calculations were performed. First, the structures of reactants and transition states were re-evaluated at the MP2/6-311G(d,p) level. As indicated in Table VII, the predicted MP2 and MP4 barriers are hardly changed by optimizing the geometries at this higher level. Second, MP2 and MP4 calculations were carried out at the SCF/6-31G(d) geometries with use of the 6-311++G(3df,2pd)[32] basis set. As shown in Table VII, the corresponding MP–SAC2 and MP–SAC4 barriers (obtained by using the average of the H–H and C–H $\mathscr{T}_n$ values) are not much different from those for the smaller 6-311G(2d,p) basis. Thus although MP–SACn barrier heights for reaction 6 appear to be about 1–2 kcal/mol more accurate than

(35) Walch, S. P. *J. Chem. Phys.* **1980**, *72*, 4932.

the MPn values, the forward barriers are still systematically too high by 3–6 kcal/mol at either the MP-SAC2 or MP-SAC4 level, and the reverse barrier heights are too high by about 8–11 kcal/mol at the MP-SAC2 level and 5–8 kcal/mol at the MP-SAC4 level.

We should note that reaction 6 is a very difficult case for the MP-SAC method, especially with $n = 2$, because of the difficulty of treating H$_2$ consistently with bonds to atoms heavier than H. Many reactions of interest do not involve H in the form of H$_2$, and the MP-SAC method is expected to work better for these. Note also that at least partly as a consequence of this special difficulty, the overall energy difference, ΔE, for reaction 6, which is the difference of the forward and reverse barrier heights, is not predicted particularly accurately by the MP-SAC2 method. (The most accurate ΔE values are predicted by MP4 and MP–SAC4 calculations with the basis sets that include diffuse functions, 6-31+G(d,p), 6-311+G(d,p), and 6-311++G(3df,2pd).) Nevertheless, as discussed above, the SAC method does improve the predicted barrier heights. Since this occurs for many basis sets we judge the improvements to be a systematic feature of the method, rather than fortuitous.

The results in Table VII may be compared with the best previously available calculation, which is the PolCI calculation of Walch,[35] using an [11s6p2d/5s1p]/[4s3p2d/3s1p] basis set, which yielded barriers of 10.7 and 15.9 kcal/mol for the forward and reverse reactions, respectively. The present MP–SAC4 barrier heights for the four basis sets with the largest s,p (6-311... or 6-311+...) subspaces and the PolCI barrier heights are in mutual agreement within 1.7 kcal/mol for the forward reaction and 0.6 kcal/mol for the reverse. The average reaction energy, ΔE, predicted by these four MP-SAC4 calculations is 4.3 kcal/mol, and it is closer to the accurate value of 3.5 kcal/mol (see Table I and section IIB) than is the PolCI value of 5.2 kcal/mol; this is consistent with our expectations since the SAC method has been calibrated here against bond energies, and ΔE is the difference of two bond energies.

Reaction 7 is more typical of what might be expected for many organic hydrogen atom transfer and hydrogen shift reactions since the bonds being made and broken both involve a second period atom and not H$_2$. Table VIII shows that the improvements in barrier heights for reaction 7 are more significant than those for (6), and the MP-SAC2 method provides a more consistent improvement for the forward and reverse reactions in this case. Indeed, the MP–SAC2 results are in better agreement with the experimental barriers than are the uncorrected (and much more expensive) MP4 values. The effects of adding both diffuse functions and a second set of d orbitals can be estimated by assuming the two effects to be additive. These extrapolated results are also listed in Table VIII, where one can see that the MP–SAC4 barriers so obtained are both within the estimated uncertainty of the experimental values.

Overall, for the six most complete basis sets studied for reaction 7, from the 6-31G(d,p) basis set to the 6-311G(2d,p) basis set in Table VIII, the MP-SAC2 forward barriers, in kcal/mol, of 3 ± 2 and the SAC4 forward barriers of 5 ± 3 are both in better agreement with the experimental estimate of 2–5 than are the unextrapolated MP2 values of 8 ± 2 or the unextrapolated MP4 values of 9 ± 3. Similarly, for all seven basis sets for the reverse reaction the MP-SAC2 barriers of 18.5 ± 1.5 are in better agreement with the experimental estimates, 15–18, than are the MP2 barriers of 20 ± 1, but the relative accuracy of the SAC4 method vs. the MP4 method may lie within the experimental uncertainty.

C. Barrier Heights Calculated with Partially Polarized or Unpolarized Basis Sets. Next we consider what happens if the MP-SACn barrier heights are computed with the more economical 6-31G(d) and 3-21G basis sets. The former includes polarization functions only on the second-row atoms, and the latter is unpolarized.

Tables VII and VIII show that the MP-SACn results for the 6-31G(d) basis set are slightly less reliable than those for the larger basis sets, but on the whole they are not greatly different.

The use of the 3-21G basis though shows how eventually the results become somewhat erratic if we cut back too far on the basis set. For reaction 6 the difficulty with treating H_2 is again apparent from the much better agreement in Table IX for the forward than the reverse barrier at the MP2 and MP-SAC2 levels. This is improved somewhat at the MP4 and MP-SAC4 levels of theory. For the latter, the forward barrier is roughly the same as that predicted by the much larger basis sets (Table VII), while the reverse barrier is about 2 kcal/mol higher than the more accurate results. Nonetheless, it is important to recognize that the MP-SAC4/3-21G results for this reaction are better than those predicted by any of the much more expensive unextrapolated MP2 or MP4 values in Table VII. As an example of the difference in computing time, the Cray-1 CPU time required for the MP4/3-21G calculations at the transition state is 14 s, which is much less than that for MP4 calculations with the 6-31G(2p,d) basis, 323 s.

For reaction 7 the MP2 corrections for the forward and reverse barriers are rather large. As a result, SAC2 underestimates the forward barrier (the predicted interaction energy is actually negative at the SCF/3-21G saddle-point geometry) and may be fortuitously accurate for the backward one. At the MP-SAC4/3-21G level, the forward barrier is within the range of experimental estimates, while the reverse barrier is much too small. Nonetheless, whereas both MP2/3-21G and MP4/3-21G calculations predict the energy difference for the overall reaction to have the wrong sign, the MP-SAC2/3-21G and MP-SAC4/3-21G calculations both, remarkably, remove this error. Nevertheless, it appears to be asking too much of the extrapolation procedure to predict an accurate berrier height for a case where the unextrapolated ΔE has such a large error.

VII. Concluding Remarks

The concept of scaling all the correlation energy, as estimated by nth-order Møller–Plesset perturbation theory (MP-SACn), has been advanced and tested for the class of processes in which bonds to H are made and broken. Even using standard basis sets, the method is very promising and should allow for improved estimates of bond dissociation energies and reaction barrier heights. Use of specially balanced basis sets may lead to even greater accuracy and allow the method to be extended to wider classes of processes.

The MP-SAC method is an economical way to improve the accuracy of ab initio electronic structure calculations, thereby turning them into advanced semiempirical methods. For example, the semiempirical MP-SAC2 method with medium-size basis sets, which involves the same computational labor as the ab initio MP2 method, is often more accurate than the more computationally demanding ab initio MP4 method with much larger basis sets. We conclude that the SAC method should be of widespread usefulness for improving the accuracy of electronic energies in cases where multi-configuration reference states are not essential.

Registry No. CH$_3$·, 2229-07-4; CH$_4$, 74-82-8.