A Journey from Generalized Valence Bond Theory to the Full CI Complete Basis Set Limit

George A. Petersson*

Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, Connecticut 06459-0180

Michael J. Frisch

Gaussian, Inc., 140 Washington Avenue, North Haven, Connecticut 06473

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A qualitative examination of generalized valence bond pair correlation energies leads us to a quantitative relationship (interference effect) between basis set truncation errors in MP2 energies and basis set truncation errors in CCSD(T) energies. Thus, a knowledge of the MP2 complete basis set limit can be combined (for example) with CCSD(T)/[5s4p3d2f/4s3p2d] calculations to estimate the CCSD(T) limit to within ±0.46 kcal/mol. Explicit MP2−R12 calculations are then compared to three extrapolation schemes employing cc-pVnZ correlation consistent basis sets in an attempt to find an inexpensive route to the required MP2 limit. The first employs the N^{-1} asymptotic convergence of pair natural orbital (PNO) expansions to extrapolate to the complete basis set (CBS2) limit. The second employs $(l + {}^1/_2)^{-3}$ extrapolations of more than one MP2/cc-pVnZ calculation to estimate this MP2 limit. The third method combines the PNO extrapolations with a linear and thus size-consistent $(l + {}^1/_2)^{-3}$ extrapolation. This linear $(l + {}^1/_2)^{-3}$ extrapolation of first CBS2/cc-pVDZ and CBS2/cc-pVTZ then CBS2/cc-pVDZ and CBS2/cc-pVQZ energies gives the absolute MP2−R12 limit to within ±0.86 and ±0.49 kcal/mol respectively for a test set of 12 small closed shell molecules, which represents a new level of accuracy for calculations fast enough to be routinely applied to molecules as large as naphthalene. Combining these MP2 limits with the interference corrected CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ energies respectively, gives the absolute CCSD(T) basis set limit to within ±1.74 and ±0.93 kcal/mol.

I. Introduction

The introduction of an innovative new conceptual framework can have a broad influence in the development of a scientific discipline. The generalized valence bond (GVB) theory[1] of Goddard is an example of such a conceptual framework. On a qualitative level, GVB theory has formed the basis for the interpretation of a wide range of chemistry.[2] It is especially useful for the description of diradicals generally and the homolytic dissociation of chemical bonds in particular. Our own interest was in the development of improved quantitative methods for computational quantum chemistry. We therefore turned our attention to the quantitative errors in the GVB energy, that is, the GVB correlation energy.

II. Pair Correlation Energies

Since the self-consistent field (SCF) energy is correct to first order,[3] the correlation energy begins with the second-order correction to the energy:[4]

$$E^{(2)} = \sum_{i,j}^{occ} e_{ij}^{(2)} = \sum_{i,j}^{occ} \left\{ \sum_{a,b}^{virt} \frac{\langle ij|r_{12}^{-1}|ab\rangle\langle ab|r_{12}^{-1}|ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \right\} \quad (1)$$

This second-order Møller−Plesset (MP2) perturbation energy can be partitioned into a sum of pair correlation energies, e_{ij}, one for each pair of occupied orbitals, ij, providing an intuitively appealing understanding of electron correlation in polyatomic molecules.[5,6] These pair energies are often further partitioned into intraorbital pair energies, ${}^{\alpha\beta}e_{ij}$, between α and β spin electrons in the same restricted Hartree−Fock (RHF) spatial orbital and interorbital pair energies, ${}^{\alpha\beta}e_{ij}$ and ${}^{\alpha\alpha}e_{ij}$, between electrons in different orbitals. The intraorbital pair energies are usually larger than the interorbital pair energies.

III. GVB Pair Energies

Generalized valence bond theory relaxes the RHF constraint of orbital double occupancy[3]

$$\psi_{RHF}(1,2) = \varphi_1(1)\varphi_1(2) \quad (2)$$

while a pure spin state is maintained[1]

$$\psi_{GVB}(1,2) = 2^{-1/2}(1 + S_{ab}^{\ 2})^{-1/2}[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)] \quad (3)$$

thus reducing the RHF intraorbital pair correlation energy, $e_{11}(\text{RHF}) \equiv (E_{exact} - E_{RHF})$, to the GVB pair correlation energy, $e_{ab}(\text{GVB}) \equiv (E_{exact} - E_{GVB})$. The GVB pair energy is comparable in magnitude to an interorbital pair energy, and thus, GVB theory provides an immediate improvement in predicted energy differences between open- and closed-shell states. To cite a famous example, HF theory predicts that the CH_2 $^1A_1$ state lies 25.0 kcal/mol above the $^3B_1$ ground state.[7] The GVB energy difference[8] of 10.5 kcal/mol is in much better agreement with the experimental value,[9] 9.0 ±0.1 kcal/mol.

In our first paper on this subject, we presented a simple interpretation for the magnitude of the GVB pair energies.[10] The approximation that the HF doubly occupied orbital, ϕ_1, is the geometric mean of the two GVB orbitals, ϕ_a and ϕ_b, led us to the overlap approximation for the relationship between RHF and GVB pair correlation energies:[10,11]

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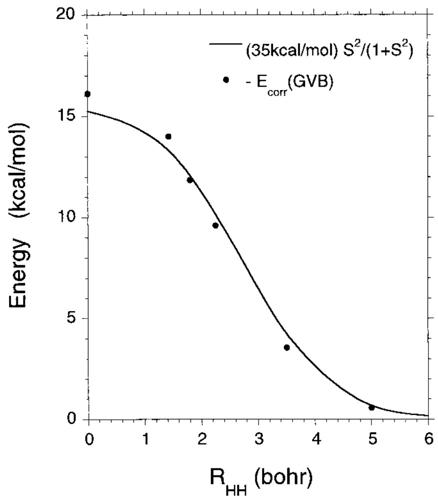

Figure 1. The overlap approximation in eq 4 describes the qualitative variation of the GVB correlation energy with the bond length for H_2.

$$E_{\text{corr}}(\text{GVB}) = e_{ab}(\text{GVB}) \approx \frac{2S_{ab}^{\ 2}}{1 + S_{ab}^{\ 2}} e_{11}(\text{RHF}) = \frac{2S_{ab}^{\ 2}}{1 + S_{ab}^{\ 2}} E_{\text{corr}}(\text{RHF}) \quad (4)$$

where S_{ab} is the overlap integral between the two GVB orbitals, E_{corr}(GVB) is the difference between the full CI energy vs the GVB energy, and E_{corr}(RHF) is the difference between the full CI energy vs the RHF energy. This semiempirical approximation for the variation of GVB pair correlation energies gives a simple intuitive understanding of the decrease in the GVB energy error as a covalent bond dissociates (Figure 1). The GVB pair energy varies with the extent to which the two electrons overlap each other.

IV. Generalization to GVBpp(1/*N*): Interference Effects

If we transform from the GVB orbital pair, ϕ_a and ϕ_b, to the natural orbital representation, ϕ_1 and ϕ_2:[12]

$$\psi_{\text{GVB}}(1,2) = C_1\varphi_1(1)\varphi_1(2) + C_2\varphi_2(1)\varphi_2(2) \quad (5)$$

then eq 4 transforms to[13]

$$E_{\text{corr}}(\text{GVB}) \approx [C_1 + C_2]^2 E_{\text{corr}}(\text{RF}) \quad (6)$$

If we take C_1 as positive, then C_2 is always negative. In H_2 for example, C_1 (i.e. $C_{1\sigma g^2}$) decreases from 0.99 to $1/\sqrt{2}$ and C_2 (i.e. $C_{1\sigma u^2}$) changes from -0.11 to $-1/\sqrt{2}$ as the H_2 molecule dissociates into two hydrogen atoms. This leads us to an alternative interpretation for the magnitude of GVB pair energies: the fact that C_1 and C_2 differ in sign leads to a partial cancellation or *interference effect* in eq 6. We can get a better appreciation of the origin of this interference if we consider the GVB analogue of eq 1, in which the matrix elements $[\langle 11|r_{12}^{-1}|ab\rangle]$ are replaced by $[C_1\langle 11|r_{12}^{-1}|ab\rangle + C_2\langle 22|r_{12}^{-1}|ab\rangle]$, but with the term having $a = b = 2$ omitted from the sum on the right side. If we make the approximation that $\langle 11|r_{12}^{-1}|ab\rangle \approx \langle 22|r_{12}^{-1}|ab\rangle$, then eq 6 follows (this approximation is exact in the limit as a and b approach infinity).[13] If we generalize eq 5 to the *N*-configuration perfect pairing generalized valence bond, or GVBpp(1/*N*), wave function

$$\psi_{\text{GVBpp}(1/N)}(1,2) = \sum_{\mu=1}^{N} C_\mu \varphi_\mu(1)\varphi_\mu(2) \quad (7)$$

then this reasoning provides the *N*-configuration generalization of eq 6

$$E_{\text{corr}}[\text{GVB}_{\text{pp}}(1/N)] \approx [\sum_{\mu=1}^{N} C_\mu]^2 \Delta E_{\text{corr}}^{\ (2)}(\text{RHF})]_{N+1}^{\infty} \quad (8)$$

where $\Delta E^{(2)}_{\text{corr}}(\text{RHF})]^{\infty}_{N+1}$ is the residual part of the RHF second-order correlation energy beyond the first N natural orbitals (i.e. omitting the contributions of NOs 2 through N to the second-order correlation energy). Substitution of eq 1 for $\Delta E^{(2)}_{\text{corr}}$(RHF) then gives

$$E_{\text{corr}}[\text{GVBpp(1/N)}] \approx [\sum_{\mu=1}^{N} C_\mu]^2 \left\{ \sum_{a,b=N+1}^{\text{virt}} \frac{\langle ii|r_{12}^{\ -1}|ab\rangle\langle ab|r_{12}^{\ -1}|ii\rangle}{\epsilon_i + \epsilon_i - \epsilon_a - \epsilon_b} \right\} \quad (9)$$

where the *interference factor*, $[\sum C_\mu]^2$, is just the square of the trace of the density matrix.[13,14] The left-hand side of eq 9 is the error, $\Delta e_{ii}^{(\text{CI})}(N)$, in an N natural orbital CI calculation, GVBpp-(1/*N*), describing an electron pair, *ii*. The right-hand side of eq 9 is the interference factor times the error, $\Delta e_{ii}^{(2)}(N)$, in an MP2 calculation, using the same basis set. Thus, the interference factor provides the relationship between CI vs second-order MP2 basis set truncation error. Generalization to the interorbital pair energies found in many−electron species follows the same arguments, giving:[13,14]

$$\lim_{N\to\infty} \Delta e_{ij}^{\ (\text{CI})}(N) = [\sum_{\mu=1}^{N} C_\mu]^2 \Delta e_{ij}^{\ (2)}(N) \quad (10)$$

where we have used the limit to indicate that eq 10 is asymptotically correct for large *N*.

Consideration of the qualitative nature of GVB pair correlation energies ultimately led us to this quantitative connection between MP2 basis set truncation errors and full CI basis set truncation errors.[13−15] In practice, we must know (or at least have an estimate for) the second-order MP2 basis set truncation error, $\Delta e_{ij}^{(2)}(N)$, to apply eq 10.

V. CCSD(T) Basis Set Truncation Errors

If we apply eq 10 to each of the electron pairs in a molecule, we obtain an estimate of the ratio of the total FCI basis set truncation error to the MP2 basis set truncation error:

$$\langle\text{Interference Factor}\rangle \equiv \frac{\sum_{ij} [\sum_{\mu} C_{\mu_{ij}}]^2 \Delta e_{ij}^{\ (2)}}{\sum_{ij} \Delta e_{ij}^{\ (2)}} \quad (11)$$

Klopper et al. have recently pointed out that our interference effect predicts the observed ratio of the coupled-cluster[16] singles and doubles with perturbative triples,[17] CCSD(T), to MP2 basis set errors to very high accuracy.[18] A comparison of the observed and predicted ratios for 12 small molecules and two atoms is presented in Figure 2. These calculations employed fairly robust quadruple-ζ [5s4p3d2f,4s3p2d] basis sets, since eq 10 is exact only in the limit of a complete basis set.

The results in Figure 2 suggest a method for improving the accuracy of CCSD(T) energies by nearly 2 orders of magnitude. *If we know the MP2 CBS limit*, then we can use eq 11 to estimate the CCSD(T) CBS limit given a CCSD(T) calculation with *only* a [5s4p3d2f,4s3p2d] basis set. We present a test of this

TABLE 1: Interference Effect from Eq 11, Combined with a Knowledge of the MP2 Limit, Can Be Used To Estimate the CCSD(T) Limit, E_{Int}, using Eq 12[a]

	CCSD(T)/QZ	E2/QZ	MP2-R12	⟨Int Fact.⟩	E_{Int}	CCSD(T)-R12
C_2H_2	−77.20339	−0.32233	−0.34650	0.58597	−77.21755	−77.21750
CH_4	−40.44772	−0.20598	−0.21930	0.58751	−40.45554	−40.45520
CO	−113.18016	−0.37292	−0.40530	0.65142	−113.20126	−113.20190
CO_2	−188.37023	−0.63146	−0.68870	0.67092	−188.40863	−188.41010
H_2	−1.17358	−0.03269	−0.03430	0.43535	−1.17428	−1.17420
H_2O	−76.35559	−0.27716	−0.30110	0.66501	−76.37150	−76.37180
HCN	−93.29468	−0.36028	−0.38800	0.61304	−93.31167	−93.31200
HF	−100.36730	−0.29052	−0.31970	0.71352	−100.38812	−100.38870
NH_3	−56.48974	−0.24684	−0.26500	0.61989	−56.50100	−56.50090
N_2	−109.39748	−0.39130	−0.42250	0.63051	−109.41715	−109.41810
H_2CO	−114.36069	−0.41448	−0.44950	0.64991	−114.38345	−114.38400
F_2	−199.34698	−0.55618	−0.61360	0.72026	−199.38834	−199.38980
rms error	0.02285	0.03305			0.00074	

[a] All energies are given in hartree atomic units.

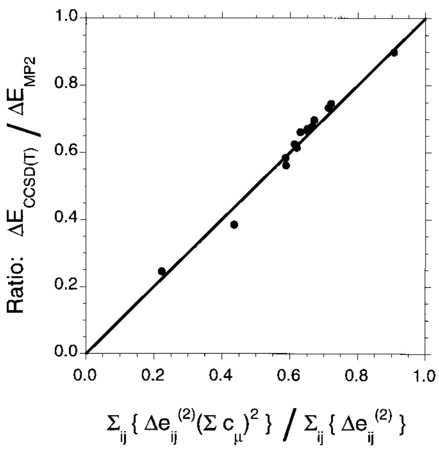

Figure 2. The interference effect in eq 11 gives a quantitative description of the relationship between the MP2 and CCSD(T) basis set truncation errors. These calculations employed [5s4p3d2f,4s3p2d] basis sets for the species: Be, H_2, C_2H_2, CH_4, HCN, NH_3, N_2, H_2CO, CO, H_2O, CO_2, HF, F_2, and O^+.[6]

hypothesis in Table 1. We have used the explicit r_{ij} results of Klopper et al. for both the MP2 limit and the CCSD(T) limit.[18] The column in Table 1 labeled E_{Int} is given by:

$$E_{Int} = E_{CCSD(T)/QZ} + \langle \text{Int Fact.} \rangle \times [E^{(2)}(\text{MP2}-\text{R12}) - E^{(2)}/\text{QZ}] \quad (12)$$

These results in Table 1 demonstrate that *if we know the exact MP2 limit, then modest CCSD(T) calculations are adequate to estimate the CCSD(T) limit to within better than 1 mE_h*! The very expensive CCSD(T)−R12 calculations can be avoided with little penalty in absolute accuracy. We next consider the question of how best to obtain the MP2 limit.

VI. The MP2 Limit

Several methods have been developed for establishing the MP2 limit. For the present, we shall restrict ourselves to a comparison of three of the most currently popular methods and a novel combination of two of these methods that achieves a new level of efficiency in obtaining chemically accurate absolute MP2 energy limits.

Early work on atoms[19,20] employed increasing sets of s, p, d, etc. basis functions, explicitly seeking convergence to the complete basis set limit. The power of such methods was greatly enhanced by the classic papers of Schwartz establishing the asymptotic convergence of such angular momentum expansions:[21,22]

$$\lim_{l_{max}\to\infty} {}^{\alpha\beta}e_{ij}^{(2)}(l \le l_{max}) = {}^{\alpha\beta}e_{ij}^{(2)}(\text{CBS}) + \left(\frac{15}{256}\right)^{\alpha\beta} f_{ij}(l_{max} + {}^1/_2)^{-3}$$

$$\lim_{l_{max}\to\infty} {}^{\alpha\alpha}e_{ij}^{(2)}(l \le l_{max}) = {}^{\alpha\alpha}e_{ij}^{(2)}(\text{CBS}) + \left(\frac{15}{256}\right)^{\alpha\alpha} f_{ij}(l_{max} + {}^1/_2)^{-5} \quad (13)$$

where the exponents −3 and −5 apply to opposite spin $\alpha\beta$ and equal spin $\alpha\alpha$ or $\beta\beta$ pairs, respectively. Extrapolations to the complete basis set limit using the asymptotic formulas of Schwartz were employed first by Bunge and later by Jankowski, Malinowski, and Polasik to establish a database of CBS−MP2 limits for closed-shell atoms.[23,24]

A. Pair Natural Orbital Extrapolations. Twenty years ago we extended this approach to polyatomic molecules by transformation of the Schwartz formulas to a symmetry independent form based on the total number, N, of pair natural orbitals (PNOs):[13]

$$\lim_{N\to\infty} {}^{\alpha\beta}e_{ij}^{(2)}(N) = {}^{\alpha\beta}e_{ij}^{(2)}(\text{CBS}) + \left(\frac{25}{512}\right)^{\alpha\beta} f_{ij}(N + \delta_{ij})^{-1}$$

$$\lim_{N\to\infty} {}^{\alpha\alpha}e_{ij}^{(2)}(N) = {}^{\alpha\beta}e_{ij}^{(2)}(\text{CBS}) + \left(\frac{25}{512}\right)^{\alpha\alpha} f_{ij}(N + \delta_{ij})^{-5/3} \quad (14)$$

where the exponents −1 and $-^5/_3$ now apply to opposite spin $\alpha\beta$ and equal spin $\alpha\alpha$ or $\beta\beta$ pairs, respectively. The exclusion parameter, δ_{ij}, can be determined as the solution of a quadratic equation.[25] The algorithm employed for these PNO extrapolations selects the value of N giving the largest (i.e. most negative) value for the CBS pair energy, with the constraint that $N > N_{min}$. Convergence to the exact CBS pair energy is ensured by systematically increasing N_{min} as the basis set is expanded. For example, we generally set N_{min} equal to 5 for spd basis sets and equal to 10 for spdf basis sets. These nonlinear extrapolations are size-consistent if the SCF orbitals are first localized before extrapolation of each of the individual pair energies to the CBS limit. We assume that N is large enough for the asymptotic form to be applicable and that the low−lying natural orbitals are accurately described with the basis set employed. These extrapolations served as polyatomic benchmarks for their time,[26] but improvements in both hardware and software now make more demanding standards possible.

B. Explicit r_{ij} Calculations. An ingenious method for explicitly including the interelectronic cusp:

$$\lim_{r_{ij}\to 0} \psi(r_{ij}) = \psi(r_{ij}=0)\left[1 + \frac{1}{2}r_{ij} + \ldots\right] \quad (15)$$

TABLE 2: Convergence of the cc-pVnZ Basis Set MP2 Correlation Energy (in hartree atomic units) to the MP2−R12 Limit

	E2(DZ)	E2(TZ)	E2(QZ)	E2(5Z)	E2(6Z)	MP2−R12
C_2H_2	−0.25590	−0.31017	−0.32948	−0.33695	−0.34041	−0.3465
CH_4	−0.16113	−0.19827	−0.21008	−0.21435	−0.21631	−0.2193
CO	−0.28730	−0.35560	−0.38146	−0.39216	−0.39700	−0.4053
CO_2	−0.48211	−0.60152	−0.64691	−0.66557	−0.67398	−0.6887
H_2	−0.02639	−0.03168	−0.03312	−0.03366	−0.03390	−0.0343
H_2O	−0.20171	−0.26155	−0.28288	−0.29159	−0.29528	−0.3011
HCN	−0.28489	−0.34582	−0.36806	−0.37697	−0.38103	−0.3880
HF	−0.20159	−0.27173	−0.29748	−0.30826	−0.31294	−0.3197
NH_3	−0.18639	−0.23519	−0.25162	−0.25802	−0. 26074	−0.2650
N_2	−0.30708	−0.37439	−0.39944	−0.40980	−0.41450	−0.4225
H_2CO	−0.31664	−0.39557	−0.42411	−0.43563	−0.44082	−0.4495
F_2	−0.39402	−0.52259	−0.56967	−0.58968	−0.59863	−0.6136
rms error	0.12519	0.05154	0.02449	0.01336	0.00837	

through the resolution of the identity has been developed by Kutzelnigg and Klopper.[27] The details are given in several recent reviews[28,29] and a recent comparison with one-electron basis set methods puts these calculations in perspective.[18] The interelectronic cusp is explicitly built into these wave functions, but large one-electron basis sets are still required both to accurately describe the remainder of the wave function and to converge the resolution of the identity. Thus, Klopper et al. employ [13s8p6d5f/7s5p4d] one-electron basis sets to determine both the MP2 limit and the CCSD(T) limit.[18]

These calculations are listed as MP2−R12 and CCSD(T)−R12 in our tables. We have selected the version called MP2−R12/A as a benchmark reference for our study of the convergence to the MP2 limit. This is the version that Klopper et al. found to agree best with our interference effect. The close agreement with extrapolations of one-electron basis set expansions justifies this choice.

C. Correlation Consistent Basis Sets. The third and most recent addition to this arena is the Dunning sequences of correlation consistent basis sets.[30,31] They provide a well-defined sequence of convergent approximations through the systematic construction of basis sets rather than the projection of pair−natural orbitals after completion of the MP2 calculation. We had previously shown that atomic pair natural orbitals (APNOs) form shells, each member of which makes a similar contribution to the correlation energy,[13] and that linear combinations these APNOs produced the corresponding molecular pair natural orbitals,[26] making the APNOs a sensible choice for calculations of molecular correlation energies. Adding each new shell of APNOs forms a new member of a consistent sequence of basis sets for electron correlation. Thus, Dunning has provided a systematic sequence of "correlation consistent" basis sets ranging from the simple [3s2p1d,2s1p] cc-pVDZ valence double-ζ plus polarization basis sets to the very large [7s6p5d4f3g2h1i,6s5p4d3f2g1h] cc-pV6Z basis sets.[30,31] Each successive member of the sequence is fully optimized for the neutral atom and includes one more function of each angular momentum type present in the previous member, plus one higher angular momentum function. The systematic structure was designed to allow for the possibility of using this well-defined sequence of calculations to extrapolate to the CBS limit, in much the same way that we had used pair natural orbital sequences. We shall employ these basis sets as a vehicle to compare the three approaches.

D. MP2 Results. The MP2 second-order energy components obtained with the Dunning cc-pVnZ (n = 2−6) basis sets for our test set of 12 closed-shell molecules (at the molecular geometries specified by Klopper et al.)[18] are given in Table 2, along with the root-mean-square (rms) deviations from the MP2−R12 limit determined by Klopper et al. This rms error is reduced by about a factor-of-two with each increment in the size of the basis set, but even with the largest cc-pV6Z basis sets the rms error is still an unacceptable 8.4 mE_h. This nicely demonstrates the slow convergence of the correlation energy with the size of the one−electron basis set, but ignores the reason Dunning developed these systematic sequences of basis sets, which was to permit well-defined extrapolations to the complete basis set limit.[30]

A variety of extrapolation algorithms have been applied to the sequences generated by the correlation consistent basis sets.[30,32−36] Dunning and his colleagues had initially suggested fitting their calculations to an exponentially decaying function:[30,32,33]

$$E^{(2)}(n) = E^{(2)}(n{=}\infty) + A\exp(-an) \qquad (16)$$

which consistently fits the cc-pVTZ through cc-pV6Z (i.e. n = 3, 4, 5, and 6) energies quite nicely, as illustrated by the neon atom results in Figure 3. However, as definitive values for $E^{(2)}$(CBS) became available from the MP2−R12 calculations of Klopper,[38] it became clear that eq 16 seriously underestimates the magnitude of the basis set truncation error (Figure 3). Exponential extrapolation of the n = 3, 4, 5, and 6 second-order energies in Table 2 merely reduces the rms error from 8.37 to 5.25 mE_h. Wilson and Dunning therefore examined[34] a wide variety of extrapolations (24 variations) based on generalizations of eq 13

$$E^{(2)}(l_{\max}) = E^{(2)}(l_{\max}{=}\infty) + \sum_j A_j(l_{\max} + a)^{-j} \qquad (17)$$

where $l_{\max} = n$ is the maximum angular momentum for each cc-pVnZ basis set. They obtained rms deviations from Klopper's results of less than 1 mE_h using several different combinations of values for a and sets of j values. The accuracy of these extrapolations can be understood by recalling the shell structure for APNOs noted above[13] and assumed in the construction of the cc-pVnZ basis sets.[30] This hydrogenic shell structure implies that eq 17 should describe the asymptotic contribution of all APNOs with the principal quantum number, n, equal to $l_{\max}$ + 1. This is precisely the form of the increment between successive members of the cc-pVnZ sequence of bass sets, and hence the angular momentum extrapolations of Wilson and Dunning can account for both radial and angular basis set truncation error. We obtain comparable results with just one term fixing $a = {}^1/_2$ and j = 3

$$E^{(2)}(l_{\max}) = E^{(2)}(l_{\max}{=}\infty) + A_3(l_{\max} + {}^1/_2)^{-3} \qquad (18)$$

as shown in Figure 3 and Table 3. Although our choice offers no numerical accuracy advantage over those of Wilson and

TABLE 3: Convergence of the $(l + {}^1/_2)^{-3}$ Extrapolated MP2/cc-pVnZ Correlation Consistent Basis Set MP2 Correlation Energy (in hartree atomic units) to the MP2−R12 Limit (see eq 19)

	E2(DZ,TZ)	E2(DZ,TZ,QZ)	E2(TZ,QZ)	E2(TZ,5Z)	E2(TZ,6Z)	MP2−R12
C_2H_2	−0.34128	−0.34670	−0.34664	−0.34625	−0.34600	−0.3465
CH_4	−0.21957	−0.22057	−0.22056	−0.21993	−0.21965	−0.2193
CO	−0.39475	−0.40454	−0.40445	−0.40485	−0.40466	−0.4053
CO_2	−0.66999	−0.68741	−0.68724	−0.68781	−0.68738	−0.6887
H_2	−0.03472	−0.03439	−0.03439	−0.03434	−0.03431	−0.0343
H_2O	−0.29586	−0.30189	−0.30184	−0.30202	−0.30153	−0.3011
HCN	−0.38076	−0.38789	−0.38782	−0.38778	−0.38754	−0.3880
HF	−0.31195	−0.32043	−0.32035	−0.32095	−0.32056	−0.3197
NH_3	−0.26316	−0.26626	−0.26623	−0.26594	−0.26547	−0.2650
N_2	−0.41299	−0.42178	−0.42170	−0.42209	−0.42193	−0.4225
H_2CO	−0.44083	−0.44954	−0.44946	−0.44953	−0.44919	−0.4495
F_2	−0.59631	−0.61165	−0.61150	−0.61297	−0.61269	−0.6136
rms error	0.00956	0.00096	0.00100	0.00067	0.00065	

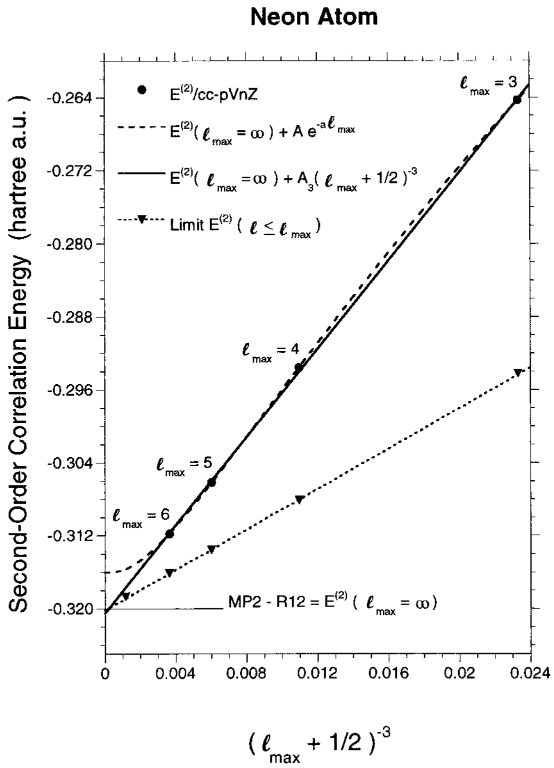

Figure 3. The MP2 correlation energy for the neon atom calculated with the Dunning sequence of cc-pVnZ correlation consistent basis sets (●) converges monotonically to the limit, $E^{(2)}(n=\infty)$, which is the intercept, $E^{(2)}(x=0)$, in this graph. The four calculations (n = 3, 4, 5, and 6) can be fit equally well with either an exponential function, $-0.3160 + A \exp(-an)$, or with a function, $-0.3204 + A_3(l_{max} + {}^1/_2)^{-3}$, where l_{max} = n is the maximum angular momentum for each basis set. However, only the extrapolation based on $(l_{max} + {}^1/_2)^{-3}$ gives a value for the intercept, $E^{(2)}(l_{max}=\infty) = -0.3204$, in agreement with both the MP2−R12 value of Klopper,[37] −0.3200, and the sequence of limit $E^{(2)}(l \leq l_{max}$ = 3, 4, 5, 6, and 9) calculations (▼) from Jankowski and Malinowski, converging to $E^{(2)}(l_{max}=\infty) = -0.3201$.[24]

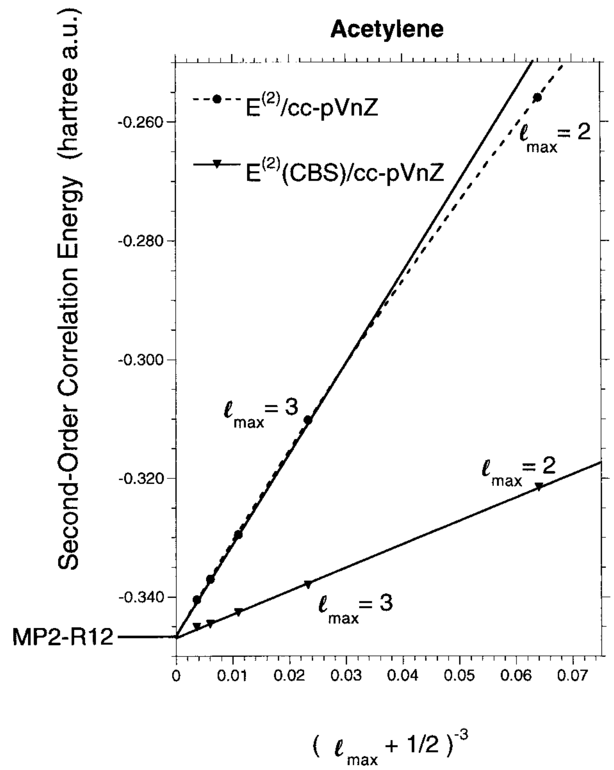

Figure 4. The MP2 correlation energy for acetylene calculated with the Dunning cc-pVnZ basis sets (●) converges smoothly with $(l_{max} + {}^1/_2)^{-3}$, where l_{max} is the maximum angular momentum for the basis set. The function becomes linear for $l_{max} \geq 3$. The CBS PNO extrapolated energies (▼) show a linear convergence with $(l_{max} + {}^1/_2)^{-3}$, beginning with $l_{max} = 2$, and thus permit such extrapolations from smaller basis sets. These sequences are both in good agreement with the explicit interelectronic cusp MP2−R12 results of Klopper et al.[18]

Dunning in the present context, we find it more satisfying to achieve success with the simplest extrapolation based on eq 13. We have used just two points, $E^{(2)}(l_{max2})$ and $E^{(2)}(l_{max1})$, so that our single term extrapolation is linear

$$E^{(2)}(l_{max}=\infty) = E^{(2)}(l_{max2}) + \{E^{(2)}(l_{max2}) - E^{(2)}(l_{max1}) \times \{(l_{max2} + {}^1/_2)^{-3}/[(l_{max1} + {}^1/_2)^{-3} - (l_{max2} + {}^1/_2)^{-3}]\} \quad (19)$$

and thus is rigorously size-consistent. *In addition, eq 19 provides a basis for easily obtaining analytical derivatives of the extrapolated MP2 basis set limit.*[37] A second term with a = $^1/_2$ and $j = 5$ is necessary to fit the cc-pVDZ energy (Figure 4 and Table 3). However, this three parameter fit of three cc-pVnZ energies (n = 2, 3, and 4) is of no obvious value, since we obtain equally good extrapolations if we simply start our two-parameter fit with the cc-pVTZ basis set (i.e. n = 3 and 4; see Figure 4 and Table 3).

We note that even though there is virtually no difference in the quality of the fit to the set of four cc-pVnZ energies (Figure 3), the extrapolation using eq 19 reduces the error by 1 order of magnitude relative to eq 16, demonstrating the importance of basing extrapolations on a fundamental mathematical analysis of the form for the asymptotic convergence,[21,22] rather than simple empiricism.[32] The extrapolated second-order MP energy components in Table 3 provide a dramatic improvement over the raw data in Table 2. The excellent agreement with both the

TABLE 4: Convergence of the Pair Natural Orbital Extrapolated Complete Basis Set Second-Order, CBS2/cc-pVnZ, Correlation Consistent Basis Set MP2 Correlation Energy (in hartree atomic units) to the MP2−R12 Limit

	E2(DZ)	E2(TZ)	E2(QZ)	E2(5Z)	E2(6Z)	MP2−R12
C_2H_2	−0.32147	−0.33801	−0.34239	−0.34415	−0.34466	−0.3465
CH_4	−0.20536	−0.21451	−0.21731	−0.21839	−0.21862	−0.2193
CO	−0.36565	−0.38988	−0.39754	−0.40132	−0.40257	−0.4053
CO_2	−0.61816	−0.66127	−0.67496	−0.68139	−0.68355	−0.6887
H_2	−0.03283	−0.03393	−0.03416	−0.03421	−0.03423	−0.0343
H_2O	−0.26293	−0.28767	−0.29483	−0.29815	−0.29926	−0.3011
HCN	−0.35593	−0.37687	−0.38252	−0.38515	−0.38590	−0.3880
HF	−0.27285	−0.30263	−0.31231	−0.31645	−0.31797	−0.3197
NH_3	−0.23939	−0.25595	−0.26100	−0.26319	−0.26374	−0.2650
N_2	−0.38353	−0.40846	−0.41524	−0.41879	−0.41995	−0.4225
H_2CO	−0.40538	−0.43325	−0.44156	−0.44534	−0.44668	−0.4495
F_2	−0.52774	−0.58030	−0.59847	−0.60561	−0.60850	−0.6136
rms error	0.04429	0.01667	0.00793	0.00409	0.00237	

TABLE 5: Convergence of the $(l + 1/2)^{-3}$ Extrapolated Complete Basis Set Second-Order CBS2/cc-pVnZ Correlation Consistent Basis Set MP2 Correlation Energy (in hartree atomic units) to the MP2−R12 Limit

	E2(DZ,TZ)	E2(DZ,QZ)	E2(DZ,5Z)	E2(DZ,6Z)	MP2−R12
C_2H_2	−0.34749	−0.34673	−0.34650	−0.34606	−0.3465
CH_4	−0.21976	−0.21978	−0.21974	−0.21942	−0.2193
CO	−0.40377	−0.40414	−0.40502	−0.40480	−0.4053
CO_2	−0.68599	−0.68671	−0.68794	−0.68750	−0.6887
H_2	−0.03457	−0.03443	−0.03435	−0.03431	−0.0343
H_2O	−0.30185	−0.30144	−0.30180	−0.30145	−0.3011
HCN	−0.38888	−0.38803	−0.38818	−0.38771	−0.3880
HF	−0.31970	−0.32047	−0.32097	−0.32070	−0.3197
NH_3	−0.26544	−0.26547	−0.26566	−0.26521	−0.2650
N_2	−0.42275	−0.42180	−0.42245	−0.42215	−0.4225
H_2CO	−0.44923	−0.44905	−0.44949	−0.44917	−0.4495
F_2	−0.61043	−0.61310	−0.61368	−0.61337	−0.6136
rms error	0.00137	0.00079	0.00053	0.00053	

explicit r_{12} calculations of Klopper et al.[18] and the $E^{(2)}(l \leq 9)$ calculations of Jankowski and Malinowski,[24] clearly demonstrates the virtues of extrapolation based on eq 13.[21,22]

To compare extrapolation schemes, we have also employed the Dunning correlation consistent basis sets for our pair natural orbital CBS extrapolation algorithm (eq 14).[13−15,25,26] We have considerable experience with spd basis sets for which we set $N_{\min}$, the minimum number of PNOs, equal to 5, and with spdf basis sets for which we set $N_{\min}$ equal to 10. After some experimentation, we have selected the $N_{\min}$ values 5, 10, 21, 35, 57 for the cc-pVDZ through cc-pV6Z basis sets. These values correspond to the sequence {1s2s2p, +3d, +3s3p4f, +4d5g, +4s4p5f6h}. The results in Table 4 give a substantial improvement over the raw second-order energies in Table 2 but are clearly inferior to the $(l_{\max} + 1/2)^{-3}$ extrapolations in Table 3. Our CBS-4, CBS-Q, and CBS-APNO models[25] employ basis sets that are roughly comparable to the cc-pVDZ, cc-pVTZ, and cc-pVQZ correlation consistent basis sets, respectively, and thus give absolute accuracies before empirical corrections that are also roughly comparable to the first three columns of Table 4. Of course, much of this absolute error cancels when we calculate chemical energy changes, and the remainder is reduced with the small empirical corrections that are included in the definitions of these models. Nevertheless, the magnitude of the absolute errors in Table 4 is sobering and obligates us to reconsider the design of these models.

E. If One Extrapolation Is Good ... The residual underestimate of the magnitude of the second-order energy component after pair natural orbital extrapolations can have two possible origins. Either the number of PNOs employed for the extrapolation was too small for the asymptotic formula in eq 14 to be applicable or the correlation consistent basis sets did not describe these PNOs to sufficient accuracy. The former is less likely since the relative performance of the PNO extrapolations does not improve with increasing $l_{\max}$. In either case, one might reasonably expect a correlation of this residual error with $(l_{\max} + 1/2)^{-3}$, as indicated in Figure 4. If one extrapolation is good, perhaps two could be better.

The results of this double extrapolation are presented in Table 5. The dramatic improvement over *both* Tables 3 *and* 4 is rather remarkable for the $(l_{\max} + 1/2)^{-3}$ extrapolation of the cc-pVDZ and cc-pVTZ PNO extrapolated results, which gives an *absolute* accuracy of *better than 1 kcal/mol* with the largest calculation using just a [4s3p2df/3s2pd] basis set. These calculations are quite routine for molecules as large as naphthalene! Application to several C_{20} species required 1−2 days each (depending on the specific example) on an SGI Origin 2000 with eight 193 MHz R10000 processors running Gaussian 98.[39]

To preserve size consistency for the CBS PNO extrapolations, we have restricted the $(l_{\max} + 1/2)^{-3}$ extrapolation to a linear form (eq 19). The new double extrapolation that we propose employs this linear extrapolation of pairs of CBS2/cc-pVnZ calculations and thus is rigorously size-consistent. Note that nonlinear N-parameter $(l_{\max} + a)^{-\alpha}$ extrapolations employing least-squares fits to more than N cc-pVnZ energies are *not* size−consistent.[34,35]

F. Extrapolation of the Higher Order Contributions. The higher order contributions to the correlation energy [i.e. CCSD(T)−MP2] are more than an order of magnitude smaller than the second-order contributions. However, the basis set convergence to the CCSD(T)−R12 limit (Table 6) does not follow the simple linear behavior found for the second-order correlation energy (Figure 5). This is a consequence of the interference effect described above in eqs 10 and 11. Since the full CI or CCSD(T) basis set truncation error is attenuated by the interference factor:

TABLE 6: Convergence of the cc-pVnZ Basis Set Higher Order [i.e. CCSD(T) − MP2] Correlation Energy (in hartree atomic units) to the CCSD(T)−R12 Limit

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	CCSD(T)−R12
C_2H_2	−0.0277	−0.0285	−0.0258	−0.0238	−0.0225	−0.0201
CH_4	−0.0270	−0.0265	−0.0246	−0.0232	−0.0225	−0.0213
CO	−0.0181	−0.0200	−0.0180	−0.0158	−0.0144	−0.0120
CO_2	−0.0148	−0.0189	−0.0165	−0.0132	−0.0109	−0.0069
H_2	−0.0083	−0.0077	−0.0072	−0.0069	−0.0068	−0.0068
H_2O	−0.0125	−0.0136	−0.0122	−0.0104	−0.0094	−0.0074
HCN	−0.0206	−0.0217	−0.0194	−0.0172	−0.0159	−0.0133
HF	−0.0065	−0.0081	−0.0075	−0.0060	−0.0049	−0.0034
NH_3	−0.0199	−0.0202	−0.0184	−0.0168	−0.0159	−0.0140
N_2	−0.0145	−0.0166	−0.0144	−0.0122	−0.0108	−0.0087
H_2CO	−0.0255	−0.0266	−0.0243	−0.0219	−0.0203	−0.0178
F_2	−0.0179	−0.0216	−0.0211	−0.0187	−0.0168	−0.0146
rms error	0.0059	0.0074	0.0057	0.0036	0.0022	

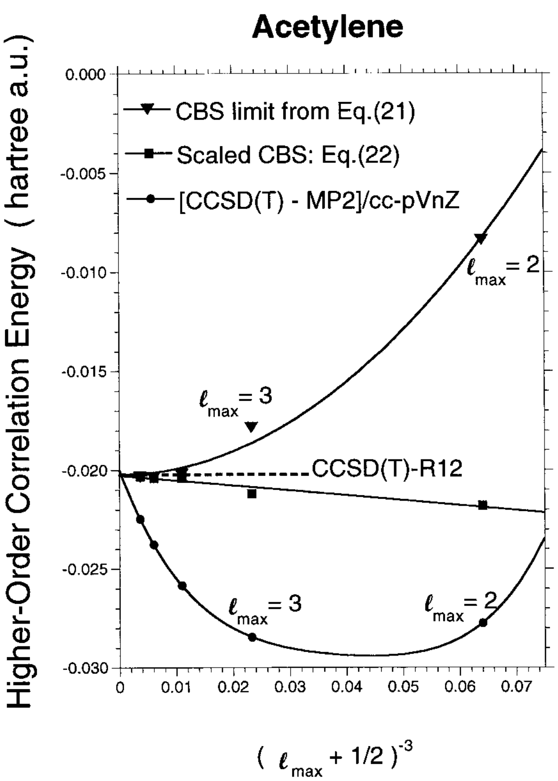

Figure 5. The higher order correlation energy for acetylene, CCSD(T) − MP2 (●), converges slowly and nonlinearly with the size (i.e. $n = l_{max}$) of the cc-pVnZ basis set. For basis sets larger than triple-ζ plus polarization (i.e. $l_{max} = 3$), the CBS interference correction (eq 20) (▼) dramatically accelerates convergence to the CCSD(T)−R12 limit determined by Klopper et al.[18] An empirical scale factor (eq 21) can extend the utility of this interference correction to the cc-pVTZ and cc-pVDZ basis sets (■).

$$\mathrm{CCSD(T)}/_{\mathrm{CBS}} = \mathrm{CCSD(T)/cc\text{-}pVnZ} + \langle \mathrm{Int\ Fact.}\rangle\{E^{(2)}/_{\mathrm{CBS}} - E^{(2)}/\mathrm{cc\text{-}pVnZ}\} \quad (20)$$

it follows by simply subtracting {MP2/CBS − MP2/cc-pVnZ} from both sides that the CBS limit for the higher order correlation energy is

$$\Delta E_{\mathrm{CCSD(T)}}/_{\mathrm{CBS}} = \Delta E_{\mathrm{CCSD(T)}}/\mathrm{cc\text{-}pVnZ} + \{\langle \mathrm{Int\ Fact.}\rangle - 1\}\{E^{(2)}/_{\mathrm{CBS}} - E^{(2)}/\mathrm{cc\text{-}pVnZ}\} \quad (21)$$

where ΔECCSD(T) ≡ CCSD(T) − MP2. This CBS extrapolation reduces the errors in the cc-pVQZ and cc-pV5Z higher order correlation energy by 1 order of magnitude (Table 7) but seriously overcorrects the cc-pVDZ and cc-pVTZ higher order energies (Figure 5). A simple scaling to reduce the CBS correction to the cc-pVDZ and cc-pVTZ energies

$$\Delta E_{\mathrm{CCSD(T)}}/_{\mathrm{CBS}} = \Delta E_{\mathrm{CCSD(T)}}/\mathrm{cc\text{-}pVnZ} + \{\mathrm{Scale}\}\{\langle \mathrm{Int\ Fact.}\rangle - 1\}\{E^{(2)}/_{\mathrm{CBS}} - E^{(2)}/\mathrm{cc\text{-}pVnZ}\} \quad (22)$$

reduces the rms errors below 1 kcal/mol for both (Table 7).

We can now combine the extrapolated second-order correlation energies from Table 5 with the extrapolated higher order contributions from Table 7. Keeping in mind the higher cost of the CCSD(T) calculations, we combine E2(DZ,TZ) from Table 5 with the scaled CCSD(T)/DZ from Table 7, E2(DZ,QZ) from Table 5 with the scaled CCSD(T)/TZ from Table 7, E2(DZ,5Z) from Table 5 with the unscaled CCSD(T)/QZ from Table 7, and E2(DZ,6Z) from Table 5 with the CCSD(T)/5Z from Table 7. The rms deviations from the CCSD(T)−R12 correlation energies[18] are 1.74, 0.93, 0.54, and 0.41 kcal/mol, respectively. The agreement between these basis set extrapolations and the explicit r_{12} results is certainly encouraging.

G. Invariance. The PNO extrapolations in Tables 4 and 5 require localization of the occupied SCF orbitals to ensure size consistency. The $(l_{max} + {}^1/_2)^{-3}$ extrapolations in Table 3 are rigorously invariant to unitary transformations of the occupied SCF orbitals. The lack of such invariance has been a weakness of the PNO extrapolations. For example, PNO extrapolation with the cc-pVTZ basis set for SO_2 gives −729.71 mE_h for the estimated valence shell MP2 limit if we use the population localized[40] occupied SCF orbitals, but −726.71 mE_h if we use the Boys localized[41] SCF orbitals. Further extrapolation using eq 19 increases the value to −757.87 mE_h for the population localized MP2 limit, which is in somewhat better agreement with the new value obtained with Boys localization, −756.88 mE_h. Localization is still required for rigorous size consistency, but the results are now less sensitive to the choice of localization scheme. The residual lack of MP2 invariance will be reduced further by the interference factor applied to the CCSD(T) limit.

The approach to invariance seems to be a natural consequence of the increased accuracy with the double extrapolation. We also note a significant reduction in the importance of diffuse basis functions. The population localized CBS2/aug-cc-pVTZ correlation energy for SO_2 is −738.05 mE_h, or 8.34 mE_h below the value without diffuse functions. The new double extrapolation converts this to −758.47, only 0.6 mE_h below the value without diffuse functions.

VII. Conclusions

The qualitative behavior of GVB pair energies leads us down a road to a better understanding of basis set truncation errors at both the MP2 level and at the CCSD(T) level. The shell structure

TABLE 7: Convergence of the PNO CBS Extrapolated (eq 21) cc-pVnZ Higher Order [i.e. CCSD(T) − MP2] Correlation Energy (in hartree atomic units) to the CCSD(T)−R12 Limit

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	CCSD(T)−R12
C_2H_2	−0.0084	−0.0178	−0.0202	−0.0204	−0.0203	−0.0201
CH_4	−0.0136	−0.0202	−0.0214	−0.0213	−0.0213	−0.0213
CO	0.0013	−0.0089	−0.0121	−0.0121	−0.0120	−0.0120
CO_2	0.0164	−0.0007	−0.0066	−0.0071	−0.0070	−0.0069
H_2	−0.0057	−0.0065	−0.0066	−0.0066	−0.0066	−0.0068
H_2O	0.0009	−0.0056	−0.0079	−0.0078	−0.0077	−0.0074
HCN	−0.0008	−0.0106	−0.0135	−0.0135	−0.0136	−0.0133
HF	0.0059	−0.0002	−0.0030	−0.0032	−0.0031	−0.0034
NH_3	−0.0060	−0.0130	−0.0145	−0.0145	−0.0145	−0.0140
N_2	0.0049	−0.0052	−0.0083	−0.0084	−0.0084	−0.0087
H_2CO	−0.0038	−0.0144	−0.0178	−0.0179	−0.0178	−0.0178
F_2	0.0047	−0.0073	−0.0126	−0.0135	−0.0133	−0.0146
rms error	0.0085	0.0036	0.0006	0.0004	0.0004	
scale[a]	0.31	0.68	0.96	0.99	0.95	
scale rms[a]	0.0015	0.0011	0.0006	0.0004	0.0004	

[a] Equation 22.

of atomic pair natural orbitals implies a linear $(n + {}^{1}/_{2})^{-3}$ asymptotic convergence of the second-order cc-pVnZ correlation energies, which in turn offers the possibility of analytical derivatives for the MP2 basis set limit. A more immediate if less ambitious result focuses on the single point MP2 limit. Without any extrapolation, the very large [7s6p5d4f3g2h1i,-6s5p4d3f2g1h] cc-pV6Z basis sets are still 5.3 kcal/mol from the MP2−R12 limit for a test set of 12 small molecules. In contrast, a linear size−consistent $(l + {}^{1}/_{2})^{-3}$ extrapolation of just the MP2/cc-pVTZ and MP2/cc-pVQZ energies is accurate to ±0.60 kcal/mol. If we try to further reduce the basis sets to cc-pVDZ and cc-pVTZ, the error in the extrapolation increases to ±6.0 kcal/mol. However, a new double extrapolation provides the complete basis set MP2 limit with an absolute accuracy of ±0.86 kcal/mol without recourse to basis sets larger than cc-pVTZ [4s3p2d1f,3s2p1d]. The interference effect can then provide an equally accurate (±0.93 kcal/mol) complete basis set CCSD(T) limit. Although we still are a long way from a complete new "model chemistry",[42] the absolute accuracy that we have now achieved makes it clear that a new generation of model chemistry methods will no longer require significant error cancellation and probably can dispense with "number of electron pairs" type empirical corrections.[25,43]

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References and Notes

(1) Bobrowicz, F. W.; Goddard, W. A., III In *Methods of Electronic Structure Theory*, edited by Schaefer, H. F., III; Plenum: New York, 1977; vol. 3, p 79.
(2) Goddard, W. A., III.; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J.; *Acc. Chem. Res.* **1973**, *6*, 368.
(3) Roothan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.
(4) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(5) Sinanoglu, O. *Adv. Chem. Phys*. **1964**, *VI*, 315.
(6) Nesbet, R. K. *Adv. Chem. Phys*. **1969**, *XIV*, 1.
(7) Bauschlicher, C. W.; Shavitt, I. *J. Am. Chem. Soc.* **1978**, *100*, 739.
(8) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *Chem. Phys. Lett.* **1972**, *13*, 30.
(9) Leopold, D. G.; Murry, K. K.; Stevens Miller, A. E.; Lineberger, W. C. *J. Chem. Phys*. **1985**, *83*, 4849.
(10) Petersson, G. A. *Proc. Nat. Acad. Sci.* **1974**, *71*, 2795.
(11) Petersson, G. A. *Int. J. Quan. Chem*. **1977**, *11*, 775.
(12) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1474.
(13) Nyden, M. R.; Petersson, G. A. *J. Chem. Phys.* **1981**, *75*, 1843.
(14) Petersson, G. A.; Nyden, M. R. *J. Chem. Phys*. **1981**, *75*, 3423.
(15) Petersson, G. A.; Licht, S. L. *J. Chem. Phys*. **1981**, *75*, 4556.
(16) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 516.
(17) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(18) Klopper, W.; Bak, K. L.; Jørgensen, P.; Olsen, J.; Helgaker, T. *J. Phys. B: At. Mol. Opt. Phys*. **1999**, *32*, R103.
(19) Byron, F. W., Jr.; Joachain, C. J. *Phys Rev.* **1966**, *146*, 1.
(20) Byron, F. W., Jr.; Joachain, C. J. *Phys Rev.* **1967**, *157*, 7.
(21) Schwartz, C. *Phys. Rev.* **1962**, *126*, 1015.
(22) Schwartz, C. In *Methods in Computational Physics*; Alder, B., Fernbach, S., Rotenberg, M., Eds.; Academic: New York, 1963; Vol. 2.
(23) Bunge, C. F. *Theor. Chim. Acta (Berlin)* **1970**, *16*, 126.
(24) Jankowski, K.; Malinowski, P. *Chem. Phys. Lett.* **1978**, *54*, 68. Jankowski, K.; Malinowski, P.; Polasik, M. *J. Phys. B: Atom. Mol. Phys.* **1979**, *12*, 3157. Jankowski, K.; Malinowski, P. *Phys. Rev. A* **1980**, *21*, 45. Jankowski, K.; Malinowski, P.; Polasik, M. *Phys. Rev. A* **1980**, *21*, 51.
(25) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys*. **1996**, *104*, 2598.
(26) Petersson, G. A.; Braunstein, M. *J. Chem. Phys.* **1985**, *83*, 5129.
(27) Kutzelnigg, W.; *Theor. Chim. Acta* **1985**, *68*, 445; Klopper, W.; Kutzelnigg, W. *Chem. Phys. Lett*. **1987**, *134*, 17; W. Klopper and W. Kutzelnigg, *Stud. Phys. Theor. Chem.* **1989**, *62*, 45.
(28) Noga, J.; Klopper, W.; Kutzelnigg, W. In *Recent Advances in Coupled Cluster Methods*; Bartlett, R. J., Ed.; World Scientific: Singapore, 1997; p 1.
(29) Klopper, W. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., *et al.*, Eds.; Wiley: Chichester, 1998; p 2351.
(30) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
(31) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys*. **1992**, *96*, 6796. Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358; **1994**, *100*, 2975; **1995**, *103*, 4572. Wilson, A. K.; Mourik, T. van; Dunning, T. H., Jr. *J. Mol. Struct. (THEOCHEM)* **1996**, *388*, 339. Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr., *J. Chem. Phys.* **1998**, *109*, 2233.
(32) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104; **1993**, *98*, 7059.
(33) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.
(34) Wilson A. K.; Dunning, T. H., Jr. *J. Chem. Phys*. **1997**, *106*, 8718.
(35) Martin, J. M. L. *Theor. Chem. Acc.* **1997**, *97*, 227.
(36) Dixon D. A.; Feller, D. *J. Phys. Chem.* **1998**, *102*, 8209.
(37) We expect this to provide a significant improvement for highly basis set sensitive properties such as IR and Raman intensities and polarizabilities, which will be the subject of a future paper.
(38) Klopper, W. *J. Chem. Phys.* **1995**, *102*, 6168.
(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Baboul, A. G.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.8; Gaussian, Inc., Pittsburgh, PA, 1998.
(40) Pipek, J.; Mezey, P. *J. Chem. Phys*. **1989**, *90*, 4916.
(41) Boys, S. *Rev. Mod. Phys*. **1960**, *32*, 296. Foster, J.; Boys, S. *Rev. Mod. Phys*. **1960**, *32*, 300.
(42) Pople, J. A. In *Energy, Structure and Reactivity*; Smith, D. W., McRae, W. B., Eds.; Wiley: New York, 1973, p 51.
(43) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys*. **1991**, *94*, 7221.