AB INITIO THERMOCHEMISTRY BEYOND CHEMICAL ACCURACY
FOR FIRST-AND SECOND-ROW COMPOUNDS

JAN M.L. MARTIN
Department of Organic Chemistry, Weizmann Institute of Science,
76100 Rehovot, Israel. Email: comartin@wicc.weizmann.ac.il

Abstract. By judicious use of extrapolations to the 1-particle basis set
limit and n-particle calibration techniques, total atomization energies of
molecules with up to four heavy atoms can be obtained with calibration
accuracy (1 kJ/mol or better, on average) without any empirical correc-
tion. For the SCF energy a 3-point geometric extrapolation is the method
of choice. For the MP2 correlation energy, a 2-point \( A + B / (l + 1/2) \)
extrap-
olation is recommended, while for CCSD and CCSD(T) correlation energies
we prefer the 3-point \( A + B / (l + 1/2)^C \) formula. Addition of high-exponent
‘inner polarization functions’ to second-row atoms is essential for reliable
results. For the highest accuracy, accounts are required of inner-shell corre-
lation, atomic spin-orbit splitting, anharmonicity in the zero-point energy,
and scalar relativistic effects.

1. Introduction and statement of the problem

From an experimental point of view, the most fundamental thermochemical
property of a compound is its heat of formation in the gas phase. From a
theoretical point of view, it is the total atomization energy (TAE, \( \Sigma D_0 \)),
that is, the energy required to dissociate a ground-state molecule into its
constituent ground-state atoms in the gas phase. The two definitions, of
course, differ merely by their choice of reference points for the constituent
elements.

The TAE of a molecule is one of the most difficult properties, from
an ab initio perspective, to compute accurately. The use of homodesmic
and isodesmic reactions (as shown in the contribution of Irikura [1] in the
present volume) may greatly accelerate convergence of the computed result
with the level of theory, but obviously presupposes that accurate data are
already available for the related compounds occurring in the thermodynamic cycle — a condition which is by no means always fulfilled.

The taxonomy of ab initio-based methods for theoretical thermochemistry (for molecular mechanics-based and semiempirical methods, see the recent reviews of Allinger [2] and Thiel [3], respectively) can roughly be presented as follows:

- empirical corrections
  - additive corrections
    * pair correction schemes such as G2 theory [4] and its variants
    * connectivity-based schemes such as Martin’s 3-parameter correction (3PC) [6, 7]
    * bond additivity corrections such as the BAC-MP4 scheme [8]
    * atom equivalent schemes (see e.g. [1])
  - multiplicative corrections
    * the PCI-X schemes of Siegbahn and coworkers [9]
    * the SAC (scaling all correlation) schemes [10]

- hybrid correction/extrapolation schemes: the CBS family of methods [11, 12]
- ‘pure’ extrapolation methods

Classifying by accuracy and applicability range, PCI-X, SAC, BAC-MP4, and similar schemes aim at near-chemical accuracy (2–5 kcal/mol) for large systems — a goal also attainable, in many cases, through modern density functional methods. [13,14] G2 theory, CBS-Q, and 3PC/spdf permit chemical accuracy (about 1 kcal/mol), on average, for medium-sized molecules. CBS-QCI/APNO and 3PC/spdfg permit mean absolute errors near 0.5 kcal/mol, while 3PC/spdfgh permits 0.24 kcal/mol (1 kJ/mol) accuracy.

The final alternative however — which relies on no other information than computed results for the molecule itself in a systematic sequence of basis sets — can reach the highest accuracies of all, 0.12 kcal/mol (0.5 kJ/mol) on average. With the present state of computer technology, this technique is limited to a system with about four heavy atoms, although larger systems can be treated at some trade-off in accuracy. It forms the subject of the present contribution.

Because this volume is primarily aimed at a readership of non-quantum chemists, we will briefly review some of the electronic structure methods used in this paper. Further details can be found in the review articles cited in the relevant sections.
2. Major Issues

2.1. TREATMENT OF DYNAMICAL CORRELATION

Our discussion of electron correlation methods will be restricted to single-reference methods, i.e. methods for which the zero-order wave function $\psi_0$ is a single Slater determinant. We will in addition assume that the Hartree-Fock orbitals have been expanded in a finite basis set of size $N$. The Hartree-Fock equations then also have $N$ solutions, of which the $n$ electrons in the system fill the occupied orbitals (for which by convention we will use indices $i, j, k, \ldots$). The remaining solutions constitute the space of virtual (unoccupied) orbitals, by convention denoted by indices $a, b, c, \ldots$.

The exact wave function $\psi$ can then be expanded as

$$\psi = \psi_0 + \sum_{i,a} C_{ia} \psi_{i\rightarrow a} + \sum_{i>j,a>b} C_{ijab} \psi_{ij\rightarrow ab} + \ldots$$

$$\equiv (1 + \hat{C}_1 + \hat{C}_2 + \ldots + \hat{C}_n) \psi_0$$

in which the $\psi_{i\rightarrow a}$, $\psi_{ij\rightarrow ab}$, $\psi_{ijk\rightarrow abc}$, $\ldots$ are singly, doubly, and triply excited configurations and the $C_{iabc\ldots}$ are termed configuration interaction (CI) coefficients. (CI and related methods were very recently reviewed by Shavitt [15], where references to older reviews can also be found.) Grouping the latter by excitation level (i.e. the number of electrons moved from occupied to virtual orbitals), we have also introduced the excitation operators $\hat{C}_i$ ($i=1, 2, 3, \ldots$).

A calculation in which the complete expansion, eq. (1), is used is termed an FCI (full configuration interaction) calculation, and represents the exact solution of the nonrelativistic clamped-nuclei Schrödinger equation within the given finite basis set. Unfortunately the computational cost thereof increases factorially with the size of the basis set and the number of electrons, and becomes impractical for all but the fewest-electron systems in modest basis sets. Where it can be done at all, even in a small basis set, it is an invaluable gauge for the quality of more approximate electron correlation methods.

An obvious approximation would be to truncate the FCI expansion at a given finite excitation level. This leads to limited CI methods, with truncation at $(1 + \hat{C}_1 + \hat{C}_2)$ being known as CISD (CI with all single and double excitations), $(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3)$ as CISDT (single, double, and triple excitations), and so forth. Unfortunately such methods are not size-extensive [16], i.e. the computed energy does not scale properly with the size of the system. This is a particularly severe disadvantage in thermochem-

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1 Size consistency [17], i.e. the property that $\lim_{r_{AB} \to \infty} E_{AB} = E_A + E_B$, in addition requires correct dissociation behavior of the reference wave function.
istry since the inextensivity error on a typical association energy of two medium-sized monomers $A$ and $B$ may well rival or exceed the interaction energy itself.

An alternative route is to use $\psi_0$ as the zero-order wave function in a perturbation theoretical treatment, with the sum of the Fock operators (of which $\psi_0$ is an eigenfunction) as the zero-order Hamiltonian and the difference with the true Hamiltonian as a small perturbation. Truncating this expansion at low order yields the MP$n$ ($n$-th order Møller-Plesset [18]) or MBPT-$n$ ($n$-th order many-body perturbation theory) methods. They can be rigorously proven [19] to be size extensive at all orders. The first-order correction is actually included in the Hartree-Fock energy (which is why it differs from the sum of the orbital energies, which is the zero-order energy). The second-order correction is very easily and rapidly computed

$$E^{(2)} = \sum_{i>j,a>b} \frac{|\langle ij||ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

which explains both its popularity and its use for the basis set additivity steps in G2 theory [5] and similar methods. Note that only double excitations enter at second order, as is the case at third order. Single, triple, and disconnected (see below) quadruple excitations enter the picture at fourth order, connected quadruple excitations only at fifth order, and the like [20]. Fifth- and even sixth-order methods have been implemented, but both algebraic complexity and mounting computational expense make higher than fourth orders progressively impractical (see e.g. [20–22]). The chief disadvantage of MP$n$ methods is that, since orbital energy differences appear in the denominators of the relevant energy expressions, convergence of the MP$n$ series is very slow in the presence of low-lying excited states.

The third, and most satisfactory, route to an approximate solution is to replace eq. (1) by the equivalent “cluster expansion”

$$\psi = \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots + \hat{T}_n)\psi_0$$

$$\hat{T}_1\psi_0 \equiv \sum_{i,a} t_{ia}\psi_{i\rightarrow a}$$

$$\hat{T}_2\psi_0 \equiv \sum_{i>j,a>b} t_{ijab}\psi_{ij\rightarrow ab}$$

$$\hat{T}_3\psi_0 \equiv \sum_{i>j>k,a>b>c} t_{ijkabc}\psi_{ijk\rightarrow abc}$$

$$\ldots$$

in which the $\hat{T}_m$ are known as cluster operators and the $t_{ij...ab...}$ as cluster amplitudes. This leads to a powerful method known as coupled cluster (CC) theory. [23–27]
Obviously, a full CC expansion would not offer any material advantage over an FCI expansion. Truncated CC expansions however offer two priceless advantages over their CI counterparts: not only does the truncated CC expansion converge vastly more rapidly than the truncated CI expansion, but it is also rigorously size-extensive. (See e.g. [23, 25] for proofs.)

The physical meaning of a CC expansion truncated at substitution order \( m \) is that the wave function contains not only excitations up to order \( m \) but also all higher excitations (up to and including \( n \)-fold), approximated by the (so-called “disconnected”) contribution from simultaneous but statistically independent lower-order excitations of at most order \( m \). For instance, CCSD (coupled cluster with all single and double substitutions, [28] i.e. \( \psi = \exp(\hat{T}_1 + \hat{T}_2)\psi_0 \) includes such “disconnected” quadruple excitations \( \langle \hat{T}_2^2/2, \hat{T}_1^2\hat{T}_2/2, \hat{T}_4^4/24 \rangle \) as arise from simultaneous and independent double excitations (starting at fourth order in MBPT) as well as those from simultaneous but independent single, single, and double excitations (starting at sixth order). In fact, CCSD contains such terms to infinite order in perturbation theory: what are missing are the “connected” quadruple excitations (which start at fifth order) as well as disconnected terms arising from simultaneous single and (connected) triple excitations (also starting at fifth order). The CPU time requirement of CCSD, like that of CISD, scales \( \propto n^2N^4 \), but it consistently recovers a high percentage of the exact correlation energy for most systems. The next step up would be CCSDT (coupled cluster with all single, double, and triple substitutions, [29] i.e. \( \psi = \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)\psi_0 \) which yields results exceedingly close to FCI but has a CPU time scaling \( \propto n^3N^5 \). By comparison with perturbation theory, we find that the most important improvements over CCSD reside in fourth- and fifth-order terms involving \( \hat{T}_3 \). By estimating these “quasiperturbatively” (i.e. using the corresponding perturbation theory expressions but substituting the converged \( T_1 \) and \( T_2 \) amplitudes for the corresponding terms in the second- and first-order MBPT wavefunctions) we obtain the very popular CCSD(T) method [30] which only has a \( \propto n^3N^4 \) operation count (for the final (T) step) but yields results almost identical to CCSDT for systems where \( \psi_0 \) is a good zero-order approximation [31].

The QCISD and QCISD(T) methods [32], which occur in G2 theory, were originally developed as a new correlation method (“quadratic configuration interaction”) but can be derived by omitting certain terms nonlinear in \( \hat{T}_1 \) from the CCSD and CCSD(T) methods, respectively (see pp.179–181 of [24] for discussion and further references).

Finally, it should be pointed out that CCSD(T) energies for open-shell systems slightly differ depending on whether an unrestricted [30] or a restricted open-shell [33, 34] reference was used, and in the latter case, on which definition for the open-shell (T) correction was used (that of Scuse-
ria [33] or that of the Bartlett group [34]). Differences between the two latter definitions are on the order of 0.1 kcal/mol or less [35], but when considering very small differences between computed data from different sources, care should be taken to ensure consistency.

2.2. STATIC CORRELATION AND QUALITY OF THE ZERO-ORDER REFERENCE

Aside from FCI which, as an exact solution, is unaffected by the quality of \( \psi_0 \), all of the methods discussed above presuppose that \( \psi_0 \) is a good zero-order approximation. Deviation from this regime (i.e. the presence of low-lying excited states, which leads to a situation in which one or more excited determinants have large coefficients in \( \psi \)) is known as static or nondynamical correlation.

The quality of all nonexact single-reference electron correlation treatments is to a greater or lesser extent affected by nondynamical correlation. Hence some form of measuring its importance is essential in practical calculations.

One quantitative measure for the importance of static correlation is the \( T_1 \) diagnostic of Lee and Taylor [36], defined in the closed-shell case as

\[
T_1 = \sqrt{\frac{\sum_{ia} t_{ia}^4}{N}} \tag{7}
\]

where \( N \) is the number of electrons being correlated. (In the open-shell case, some double-counting needs to be avoided: see Ref. [37] for details.) MP\( n \), as noted before, is the most sensitive to static correlation: experience has taught [26] that MP2 results are essentially unusable for \( T_1 \) values as low as 0.02. CCSD(T), by contrast, will produce acceptable results for \( T_1 \) values as high as 0.055, while QCISD(T) breaks down for somewhat lower values of \( T_1 \) due to the omission of the higher-order terms in \( \hat{T}_1 \). [38] CCSDT is amazingly robust, yielding reliable results for, e.g., the \( X^1\Sigma^+ \) state of BN [39], for which \( T_1 = 0.08 \) and the low-lying excited state \( (3\sigma)^2(4\sigma)^0(1\pi)^4(5\sigma)^2 \) contributes about 30% to the wave function. Systems with even stronger static correlation (e.g. the Cr\(_2\) molecule [40]) demand the use of multireference methods, which are beyond the scope of this discussion.

Occasionally a problem may ‘slip by’ a \( T_1 \) test. For instance, the lowest \( ^1\Sigma^+ \) state of linear BNB\(^+\) is almost perfectly biconfigurational, despite a deceptively low \( T_1 = 0.040 \). While the latter value does indicate strong static correlation, one might erroneously be led into believing CCSD(T) to be still applicable for this system. An alternative, but less quantitative, criterion is inspection of the most important excited configurations in the converged wavefunction: yet another possibility is obtaining natural orbitals...
from a small basis set CISD or CASSCF (complete active space SCF [41], a multireference method) calculation and inspecting the natural orbital occupations.

A related problem which should be mentioned here is symmetry breaking. This occurs when at geometries slightly distorted from a symmetric structure there exists a strong near-degeneracy interaction, but the two partners of the interaction correlate to (nearly degenerate) states of different symmetry at the high-symmetry geometry. Both $\mathcal{T}_1$ and the SCF energy then change drastically upon near-infinitesimal displacements from the symmetric structure, and the potential energy surface may exhibit a discontinuity. This effect may be real (in which case it is known as pseudo-Jahn-Teller effect [42]) or artifactual — in which latter case even very sophisticated electron correlation methods based on a single-determinant SCF reference often fail. Aside from multireference methods, the use of Brueckner orbitals [43] as the zero-order reference — leading to the BD [44], BD(T) [45], and BDT [46] methods — often resolves symmetry breaking (e.g. [47–49]). Brueckner orbitals are defined as those for which all $T_1$ amplitudes are identically zero, and can be alternatively viewed as constituting the single-determinant wave function which has the greatest overlap with the FCI wave function [50]. These orbitals and the BD or BDT amplitudes are determined simultaneously in an iterative process which will take substantially longer than a CCSD or CCSD(T) calculation, although it has the same CPU time scaling behavior. In the absence of symmetry breaking, BD(T) does not appear to offer significant advantages over CCSD(T) [51].

2.3. 1-PARTICLE CALIBRATION: QUALITY OF THE FINITE BASIS SET

Perhaps the most recent and comprehensive review of basis sets is that by Helgaker and Taylor [52]. We will only mention a few salient points for the present application here.

For an atomic calculation at the SCF level, a basis set can be of ‘minimal’ quality and still recover essentially the exact SCF energy, as long as the individual functions closely mimic true Hartree-Fock orbitals. In a molecular calculation, flexibility is required — which requires splitting up the valence functions — as well as the ability to accommodate polarization of the atomic charge cloud in the molecular environment, which is done by adding higher angular momentum ($d, f, \ldots$) basis functions (so-called polarization functions). Nevertheless, the basis set convergence of the SCF energy is fairly rapid compared to the correlation energy.

In a correlated calculation on an atom, the basis set must accommodate two important kinds of dynamical correlation effects. The first, radial correlation (or “in-out correlation”), involves the tendency of one electron to
be near the nucleus when the other is near the periphery, or conversely. It is accommodated by permitting basis functions with extra radial nodes to mix into the wave function, i.e. by uncontracting $s$ and $p$ functions.

The second, angular correlation (or left-right correlation), involves the tendency of one electron to be on a different side of the atom as the other. This is accommodated by permitting basis functions with extra angular nodes to mix into the wave function, i.e. by adding $d, f, g, \ldots$ functions. The convergence of this effect in particular is quite slow.

Note that except for the special cases of hydrogen and the alkali metals, the basis set extensions required for an adequate description of radial and angular valence correlation will generally cover all the requirements noted above for atomic SCF calculations, except for inner-shell polarization in second-row compounds (see next section). The guiding principle for basis set development for high-level correlated calculations has therefore traditionally been that a molecular basis set should, at the very least, accommodate all basis set effects occurring in the isolated atom.

Both main families of such basis sets in usage are based on general contractions [53], i.e. all primitive Gaussians can contribute to all contracted functions.

The older of the two families are the atomic atomic natural orbital (ANO) basis sets of Almlöf and Taylor [54]. The starting point here are natural orbitals obtained from an atomic CISD calculation in a very large primitive basis set. The natural orbitals with the highest occupation numbers are then selected as basis functions. It was found that these always occur in groups of almost equal occupation numbers: e.g., the first $f$, second $d$, and third $p$ function have similar natural orbital occupations. This systematically leads, for first-row elements, to contractions like $[4s^3p^2d^1f]$, $[5s^4p^3d^2f^1g]$, $[6s^5p^4d^3f^2g^1h]$, and so forth. (Corresponding contractions for second-row elements are $[5s^4p^2d^1f]$, $[6s^5p^3d^2f^1f]$, $[7s^6p^4d^3f^2g^1h]$, and the like.)

The second family, the correlation consistent (cc) basis sets of Dunning [55] and coworkers, is establishing itself as the de facto standard for calibration calculations. Dunning subjected relatively compact atomic basis sets to energy optimization, and considered the energy gain from adding different kinds of primitives. He then found that these energy contributions likewise occur in groups: thus, the energy gain from adding the first $f$, second $d$, or third $p$ function is similar. Again this suggests adding them in shells, which again leads to the same typical contraction patterns as for their ANO counterparts. Based on the number of different functions available for the valence orbitals, these basis sets are known as cc-pVnZ (correlation consistent valence $n$-tuple zeta), where $n=$D for double (a $[3s^2p^1d]$ contraction), T for triple (a $[4s^3p^2d^1f]$ contraction), Q for quadruple (a
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[5s4p3d2f1g] contraction), and 5 for quintuple zeta (a [6s5p4d3f2g1h] contraction). For compactness, the present author and coworkers generally use the notation \( V_nZ \).

Martin [56] carried out a detailed comparison of computed TAE values with equivalent ANO and \( cc \) basis sets. The results were found to be nearly identical, while the integral evaluation time for the \( cc \) basis sets was considerably shorter due to their more compact primitive size. Therefore \( cc \) basis sets are more commonly used, although for certain other applications (like weak molecular interactions or electrical properties) ANO basis sets and particularly the “averaged ANO” variant [57] may be preferable.

For the computation of electron affinities and calculations on anions in general, special low exponent \( s \) and \( p \) functions (so-called ‘soft’ or ‘diffuse’ functions) are required at the SCF level (e.g. [58]). At correlated levels, the regular \( s \) and \( p \) functions are adequate as radial correlation functions thereto, but angular correlation in the tail range requires the addition of ‘soft’ \( d \), \( f \), \ldots \) functions. Kendall et al. [59] proposed the aug-cc-pV\( n \)Z basis sets (AV\( n \)Z for short), in which the cc-pV\( n \)Z basis set is ‘augmented’ with one ‘soft’ (or low-exponent) basis set of each angular momentum. It was subsequently found (e.g. [60, 61]) that these functions are indispensable for calculating properties such as geometries and harmonic frequencies of highly polar neutral molecules as well. It is also noteworthy [60] that including just the soft \( s \) and \( p \) functions only recovers about half the effect.

Del Bene [62] noted that, except in such compounds as LiH in which hydrogen has a significant negative partial charge, omission of the diffuse functions on H generally does not affect results. This practice is denoted by the acronym aug'-'cc-pV\( n \)Z (or A'V\( n \)Z for short).

Some authors (e.g. [63]) have obtained excellent results for the first-row hydrides using basis sets of only spdf quality, combined with sp bond functions (i.e. basis functions centered around the bond midpoint). However, as the extension of bond function basis sets to multiple bonds will require \( d \) bond functions, which in turn will require [64] atom basis sets of up to spdf\( g \) quality to keep to keep down basis set superposition error (BSSE, Sec. 3.4) to an acceptable level, the usefulness of bond functions for our purpose appears to be somewhat limited. Bauschlicher and Partridge [65] very recently compared basis set convergence between very large atom-centered and bond function-augmented basis sets for eight covalently bound diatomics. If the underlying atom-centered basis set is large enough to effectively suppress BSSE, then bond function augmented basis sets are found not to offer a material improvement over purely atom-centered sets of similar size. For weakly bound systems (like rare gas dimers), however, Tao [66] found greatly improved results upon addition of bond functions, a finding corroborated by Partridge and Bauschlicher [67].
2.4. 1-PARTICLE CALIBRATION VERSUS N-PARTICLE TREATMENT

Situations may arise where the electron correlation method of choice simply cannot be used in the largest basis set that would be preferable for an extrapolation to the infinite-basis limit. In that case, one may need to select a less computationally demanding method and apply the additivity approximation

\[ E(\text{Method2}/\text{Basis2}) \approx E(\text{Method2}/\text{Basis1}) + E(\text{Method1}/\text{Basis2}) - E(\text{Method1}/\text{Basis1}) \] (8)

This presupposes, of course, that only weak coupling exists between improvement of the n-particle treatment from Method1 to Method2 and enlargement of the 1-particle basis set from Basis1 to Basis2. Needless to say, how well this assumption holds will depend to a large extent on how different the methods and basis sets involved are, as well as on the system under study. For instance, in a system with pronounced static correlation, using MP2 to estimate basis set extension effects in this manner may yield really poor results.

Several levels of such approximations can be nested, e.g.

\[ E(\text{Method3}/\text{Basis3}) \approx E(\text{Method3}/\text{Basis1}) + E(\text{Method2}/\text{Basis2}) - E(\text{Method2}/\text{Basis1}) + E(\text{Method1}/\text{Basis3}) - E(\text{Method1}/\text{Basis2}) \] (9)

For instance, in standard G2 theory one has Method1=MP2, Method2=MP4, Method3=QCISD(T), and Basis1=6-311G**, Basis2=6-311+G(2df,p), Basis3=6-311++G(3df,2pd). Below, for the atomic electron affinities, we will consider Method1=CCSD(T), Method2=CCSDT, Method3=FCI, and Basis1=AVDZ, Basis2=AVQZ, Basis3=AV6Z.

Also, if the difference between basis sets A and B comprises two or more sets of basis functions that do not overlap appreciably, and cover quite different effects and/or regions of the wave function (e.g. diffuse functions and core correlation functions), additivity approximations may be invoked. For instance, if B is the set union of B1 and B2, both of which are supersets of A, then

\[ E(M/B) \approx E(M/B_1) + E(M/B_2) - E(M/A) \] (10)

E.g. with \( A=VnZ, B_1=AVnZ, B_2=VnZ+\text{IPF} \) (inner polarization functions, Sec. 2.6), and \( B=AVnZ+\text{IPF} \), this approximation was found [68] to hold to 0.02 kcal/mol or better in CCSD(T) calculations on SO2.
2.5. INNER-SHELL CORRELATION

Conventional wisdom would have it that core correlation effects will not be important for first- and perhaps second-row compounds. The truth is a little more complex.

In a systematic study [69] of inner-shell correlation effects on atomization energies of first-row compounds, contributions as large as 2.44 kcal/mol for C₂H₂ and 1.78 kcal/mol for CO₂, were found. Clearly, one cannot afford to neglect such effects even when striving for mere chemical accuracy.

The smaller gap between the inner-shell (2s, 2p) and valence (3s, 3p) orbitals in second-row atoms would suggest that the effects of inner-shell correlation would be stronger, if anything, than in the case of first-row compounds. While this is certainly true in terms of the absolute correlation energy (where (2s, 2p) correlation may meet or exceed the valence contribution in importance), the differential contributions to the binding energy tend to be quite modest, reaching some 0.77 kcal/mol for SO₂ [68] and only 0.09 kcal/mol for H₂SiO [70]. In fact, as found previously [71], contributions to binding energies of silanes may actually be negative: e.g. -0.54 [71] or -0.56 [70] kcal/mol in the case of triplet silylene. These contributions are dwarfed by those from inner polarization (see below).

Explicit consideration of core correlation requires the use of special basis sets that accommodate inner-shell correlation effects by the addition of extra radial nodes in the s functions (in practice, uncontracting the innermost s function a little will do the job) as well as ‘tight’ or ‘hard’ (high-exponent) extra p and d functions. The two main alternatives for practical calculations are the Dunning group cc-pCVnZ basis sets [72, 73] (which are available for B through F) and the Martin-Taylor core correlation basis sets [60], which are available for Li through F and for Al through Cl. In the author’s experience for first-row compounds, the Martin-Taylor basis set is of about the same quality as the cc-pCVQZ basis set, while the cc-pCVTZ basis set generally only recovers about 75–80% of the inner-shell correlation effects.

Finally, it cannot be stressed enough that including core correlation in basis sets not designed to handle core correlation (such as the regular cc-pVnZ basis sets or the Pople basis sets [74], which are only minimal in the core) will generally yield erratic core correlation contributions, and therefore is simply a waste of CPU time. (All electronic structure programs presently allow for correlated calculations with frozen core electrons.)

2.6. INNER POLARIZATION IN SECOND-ROW COMPOUNDS

In the course of studies (e.g., [68, 75]) on the computed geometry and vibrational frequencies (harmonic as well as anharmonic) of some second-row compounds, it was found that basis set convergence was atypically slow.
Adding a single high-exponent \( d \) function to the standard Dunning \( cc\text{-}pVTZ \) basis set for \( S \) (which is of \([5s4p2d1f]\) quality) was found to affect the geometry in \( SO_2 \) by as much as 0.013 Å and 1 degree, and the harmonic frequencies by as much as 34 cm\(^{-1}\). (Similar effects are seen \([76]\) in \( SO_3 \).) The addition of such a function is denoted by the \( \text{“}+1\text{”} \) suffix, as in \( VTZ+1 \). Likewise, the computed total atomization energy at this level is affected by as much as 8 kcal/mol, an observation previously made by Bauschlicher and Partridge \([77]\) and, in passing, in the paper \([78]\) on the extension of \( G1 \) theory \([79]\) (a predecessor of \( G2 \) theory) to second-row compounds. Refs. \([77,78]\) both ascribed the phenomenon to hypervalence but, while this may play a role in the case of \( SO_2 \), it cannot account for the same phenomenon occurring in \( SO \) \([68]\), \( SiO \) \([75]\), and \( AlF \) \([75]\), none of which are hypervalent by any reasonable definition. The fact that a clear correlation exists \([75]\) between the polarity of the bonds and the magnitude of the effect supports an explanation in terms of core polarization \([80]\); the fact that the bulk of the effect is seen at the SCF level (as well as in density functional calculations for energetics \([77]\), geometries \([76]\) and harmonic frequencies \([76]\)) is consistent with both explanations. Comparison of the orbitals and orbital energies from SCF/VTZ and SCF/VTZ+1 calculations on \( SO_2 \) revealed that while the tight \( d \) function only contributes to the highest occupied valence orbitals, the only orbital energies seriously affected are those of the \( (2s, 2p) \) like orbitals on sulfur.

Inner-shell polarization is usually adequately accommodated by the addition of a single tight \( d \) function. The optimum values at the SCF level for molecules were found \([75]\) to be surprisingly close to those of the tightest \( d \) exponent in the Dunning \( cc\text{-}pV5Z \) basis set, which were therefore taken as the recommended values. In cases where the effect is strong, we recommend the use of even-tempered sequences \( \alpha\beta^n \) with \( \alpha \) the tightest exponent in the underlying basis set and \( \beta=2.5 \) or 3.0. Such basis sets we denote \( VTZ+1d, \ VQZ+2d1f, \) and the like.

It should be noted that since this effect is not at all present in the separated atoms, it forms an apparent exception to the “what is good for correlated atomic calculations will do for molecular ones” rule that generally guides basis set development. This holds true if only valence correlation is considered: basis sets augmented for \( (2s, 2p) \) inner-shell correlation (such as the Martin-Taylor basis set \([60]\)) however amply provide for inner-shell polarization, such that the above rule prevails in a wider sense.

Infinite-basis extrapolations from a \( VnZ \) or \( AVnZ \) series tend to give grossly exaggerated binding energies when inner polarization is involved, because the \( d \) and \( f \) functions progressively intrude into the ‘inner polarization’ region as \( n \) increases. The remedy obviously consists of adding inner polarization functions — this should be done in a ‘balanced’ way.
since for the lower terms of the $VnZ$ series, the inner polarization functions span the same region as the tightest $d$ and $f$ exponents in the higher terms of the $VnZ$ series. The present author favors the sequence VTZ+1d, VQZ+2d1f, V5Z+3d2f1g, while Bauschlicher and Ricca [81] suggest the sequence $VnZ+2d$.

3. Secondary Issues

3.1. QUALITY OF THE ZERO-POINT ENERGY

Aside from the issue of the accuracy of the vibrational frequencies used in the zero-point energy, one also has to contend with the effect of anharmonicity. We will illustrate our remarks for the case of asymmetric tops, but the conclusions are valid in general.

Correct to second order in rotation-vibration perturbation theory [82], the zero-point energy of an asymmetric top is given by

$$ZPE = E_0 + \frac{1}{2} \sum_i \omega_i + \frac{1}{4} \sum_{i \geq j} X_{ij}$$

(11)

in which the $\omega_i$ and $X_{ij}$ are the harmonic frequencies and first anharmonicity constants, respectively, and the $E_0$ term [83] is usually very small.

Two common approximations to eq.(11) are one-half the sum of the harmonic frequencies, and one-half the sum of the vibrational fundamentals. These approximation err on the top and bottom side, respectively: the errors (assuming no strong Fermi resonances are present) are

$$ZPE - \sum_i \omega_i / 2 = E_0 + \frac{1}{4} \sum_{i \geq j} X_{ij}$$

(12)

$$ZPE - \sum_i \nu_i / 2 = E_0 - \frac{1}{4} \sum_{i \geq j} X_{ij} - \frac{3}{4} \sum_i X_{ii}$$

(13)

The larger the molecule becomes, the larger these deviations will grow, especially with molecules containing X–H bonds (which have strongly anharmonic stretching frequencies). The usual practice (as used, e.g., in G2 theory) of estimating the zero-point energy by scaling relatively low-level computed harmonic frequencies by a factor intended to approximate observed fundamentals (e.g., 0.89 for HF/6-31G* frequencies [84]) is therefore not appropriate, as first suggested by Grev et al. [85]. (For a sample of 14 small molecules where the exact ZPE values are known, this procedure was found [7] to result in mean and maximum absolute errors of 0.26 and 0.72 kcal/mol, respectively.) Scott and Radom [86] (see also Ref. [87]) propose different scale factors for frequencies and zero-point energies for a variety of density functional and conventional ab initio methods.
For diatomics and some small polyatomic molecules, experimentally derived sets of anharmonicity constants may be available, and are the method of choice for determining zero-point energies. We follow this approach in our highest accuracy work whenever possible (e.g. [68,88–90]). For yet others, accurate anharmonic zero-point energies are available as by-products of ab initio anharmonic force field studies (e.g. [68,70,91–94] and references therein) — at the levels of theory used in such studies, zero-point energies generally are converged to 0.1 kcal/mol or better.

One additional alternative, if both computed $\omega_i$ and observed $\nu_i$ are available, would be to take the average of $\sum_i \omega_i/2$ and $\sum_i \nu_i/2$:

$$ZPE - \frac{1}{4} \sum_i \omega_i + \nu_i = E_0 - \frac{3}{8} \sum_i X_{ii} \approx 0$$

and either estimate the diagonal stretching anharmonicities among the $X_{ii}$ (which will be the largest) from data [95] for the corresponding diatomics or neglect that term altogether.

### 3.2. QUALITY OF THE REFERENCE GEOMETRY

As pointed out in, e.g., Ref. [7], the leading quadratic dependence of the total energy on displacements from the equilibrium geometry ensures that computed thermochemical properties are fairly insensitive to errors in the reference geometry on the order of 0.01 Å or less. Some commonly used levels of theory for reference geometries may however lead to much larger errors or even qualitatively incorrect geometries: at a result, an MP2/6-31G* reference geometry for N$_2$O will cause an error of 1.8 kcal/mol in the CCSD(T)/cc-pVTZ atomization energy. [7]

A particularly good compromise between accuracy and computational cost is offered by the B3LYP [13,96] density functional method, particularly with a cc-pVTZ or better basis set. (Average errors in bond distances at the B3LYP/cc-pVTZ level are on the order of 0.003 Å for first-row compounds. [97]) For second-row atoms, the use of the cc-pVTZ+1 basis set (see above) is desirable [76].

### 3.3. THERMAL CONTRIBUTIONS

Except for floppy molecules, thermal contributions at room temperature can be quite accurately evaluated using the familiar rigid rotor-harmonic oscillator (RRHO) approach. If data at high temperatures are required, this approach is no longer sufficient, and an anharmonic force field and analysis, combined with a procedure for obtaining the rotation-vibration partition function therefrom, are required. Two practical procedures have
been proposed. The first one, due to Martin and coworkers [98,99] is based on asymptotic expansions for the nonrigid rotor partition function inside an explicit loop over vibration. It yields excellent results in the medium temperature range but suffers from vibrational level series collapse above 2000 K or more. A representative application (to FNO and ClNO) is found in Ref. [61].

The second method, due to Topper and coworkers [100], is based on Feynman path integrals, and works best in the high temperature limit. Therefore the two methods are complementary.

3.4. BASIS SET SUPERPOSITION ERROR

When one carries out a calculation on the AB diatomic using a basis set for A and B that is incomplete (as all finite basis sets by definition are), the atomic energy of A in AB, and of B within AB, will be slightly overestimated (in absolute value) due to the fact that the basis functions on the other atom have become available. (It is easily verified that basis functions on B can be expanded as a series of higher angular momentum functions around A.)

This phenomenon is known as basis set superposition error (BSSE). The standard estimate is using the Boys-Bernardi [101] counterpoise method:

\[
BSSE \approx E[A(B)] + E[B(A)] - E[A] - E[B]
\]

where \(E[A(B)]\) represents the energy of A with the basis set of B present on a ‘ghost atom’, and conversely for \(E[B(A)]\).

While the counterpoise correction is commonly used as a correction term for interaction energies in weak molecular complexes, virtually no authors apply it to the calculation of total atomization energies, for the simple reason that it invariably produces worse results. In addition, the extension of the counterpoise correction to systems with more than two fragments is not uniquely defined [102–104].

The anomaly that neglecting BSSE would yield better results is only an apparent one: after all, BSSE is a measure of basis set incompleteness — which is precisely what we are trying to get rid of — but the correction has the opposite sign. For sufficiently large basis sets (say, of spd\(g\) quality), the NASA Ames group actually found that 150\% of the counterpoise BSSE is a fair estimate of the remaining basis set incompleteness [105]. However, given the complications for systems larger than diatomics, the present author prefers the use of extrapolation to the infinite-basis limit above such methods. (It goes without saying that the BSSE goes to zero at the infinite-basis set limit. Therefore, a sufficiently reliable extrapolation to the infinite-basis set limits effectively obviates the issue.)
Very recently, there has been some indication [81] that inner shell correlation contributions to TAE may exhibit (relatively speaking) quite substantial BSSEs unless very large basis sets are used.

3.5. RELATIVISTIC EFFECTS

A review of relativistic quantum chemistry is beyond the scope of this work: the reader is referred to review articles by, e.g., Dyall [106], Pyykkö [107], Sadlej [108]. We will restrict ourselves to introducing a popular approximation to relativistic effects.

Upon expanding the Dirac-Fock Hamiltonian in powers of $(v/c)^2$ (where $v$ is the fraction of the speed of light that the electron attains), adding the Breit retardation term, and discarding higher-order terms in $(v/c)^2$, one obtains [109] the Breit-Pauli Hamiltonian:

$$
\hat{H} = \hat{H}_{NR} - \sum_i \nabla_i^2 + \sum_{i,A} \frac{\pi Z_A \delta(\vec{r}_i - \vec{R}_A)}{2e^2} + \sum_i \hat{s}_i (\nabla V \hat{p}_i) + \ldots
$$

in which $V$ is the total one-electron potential, $\delta(\vec{x})$ is a Dirac delta function, $\hat{s}$ and $\hat{p}$ are spin and momentum operators, respectively, and two-electron components of the third and fourth terms (which are much smaller than the corresponding one-electron contributions) have been omitted.

The first term is the nonrelativistic Hamiltonian. The second term, known as the mass-velocity term, arises from the relativistic mass increase of the electron $m = m_e/(1 - (v/c)^2)$ — in which $m_e$ represents the electron rest mass. (For the $(1s)$ orbital of a hydrogen-like atom, $\langle v \rangle / c = Z/c$.) The third term, known as the Darwin term, arises because [109] in this approximation, the electron is most appropriately described as a diffuse charge distribution with dimensions on the order of $\alpha$ ($\alpha = 1/c = 137.037 a_0$) rather than a point charge — leading to reduced nuclear attraction and electron-electron Coulomb repulsion. (The sum of these latter two terms is often referred to as the ‘scalar relativistic’ contribution.) Finally, the fourth term represents spin-orbit coupling.

Cowan and Griffin [110] suggested an approximate Hamiltonian consisting of only $\hat{H}_{NR}$ and the mass-velocity and one-electron Darwin terms — with spin-orbit splitting to be treated separately by perturbation theory from the converged wave function. (This latter approximation is only justified if the spin-orbit splittings are much smaller in magnitude than the electronic state splittings — as is the case for lighter atoms.)

3.5.1. Scalar relativistic contributions

Martin [111] (no relation to the present author) went one step further and suggested the evaluation of the Darwin and mass-velocity terms by
first-order perturbation theory. Since this approach involves only the non-relativistic wave function and expectation values of one-electron operators therefrom, these relativistic corrections can readily be obtained from any converged nonrelativistic Hartree-Fock or correlated wave function for which such expectation values can be evaluated, such as CISD or the averaged coupled pair functional (ACPF) method [112].

Since the Darwin and mass-velocity (DMV) terms predominantly sample effects near the atomic nuclei, the basis set for these types of calculations should be flexible in the high-exponent region. Since it seems to be obvious that inner-shell correlation would be important, a core-correlation basis set, if necessary uncontracted in the $s$ and $p$ primitives, appears to be the basis set of choice.

Another technique that permits the incorporation of relativistic effects in an otherwise nonrelativistic computational framework is the use of relativistic effective core potentials. [113, 114] While this may be the only alternative for future accurate work on, say, first-row transition metal and heavy p-block compounds, this approach is generally not recommended for first- and second-row compounds.

The DMV corrections usually lead to a reduction in TAE, because on average electrons are closer to the nucleus in the separated atom than in the molecule. Inclusion of electron correlation usually appears to reduce the size of the DMV terms. Since the effect will be the largest for the innermost electrons, it is usually recommended to correlate all electrons in calculations of the DMV contributions.

How do perturbative DMV corrections compare with results from more rigorous relativistic methods? Collins and Grev [115] found the relativistic contribution to the binding energy of SiH$_4$ to be $-0.67$ kcal/mol using relativistic (Douglas-Kroll [116]) CCSD(T) in a very large basis set. At the ACPF level with the Martin-Taylor core correlation basis set [60], we obtain $-0.69$ kcal/mol using 1st order Darwin and mass-velocity terms by perturbation theory. Obviously, such excellent agreement cannot be automatically assumed for fourth-row, let alone fifth-row compounds.

### 3.5.2. Spin-orbit coupling

The ab initio evaluation of spin-orbit matrix elements was reviewed in detail by Richards et al. [117] and recently by Heß et al. [118]. The most important aspect for us, however — the atomic spin-orbit splitting and its effect on atomization energies — can be derived directly from experimental data.

In a nonrelativistic calculation, the spin-orbit component states of, for instance, B($^2P$), C($^3P$), O($^3P$), and F($^2P$) are all degenerate, which of course does not hold true in Nature. This means that any nonrelativistic calculation involving atoms with $L > 0$ ground states will intrinsically
overestimate binding energies. One possible workaround is to adjust the experimental binding energy to obtain “experimental nonrelativistic” (more correctly: spin-orbit averaged) contribution. More elegantly the spin-orbit correction can be added to the computed binding energy. For example, for every oxygen or sulfur atom present, the computed TAE should be decreased by \( E(3P_0) + 3E(3P_1) + 5E(3P_2)/9 - E(3P_0) \), and for every fluorine or chlorine atom, by \( 2E(3P_{1/2}) + 4E(3P_{3/2})/6 - E(2P_{1/2}) \) (The required energy levels can be found in the JANAF tables [119] for the corresponding atoms in the gas phase.) While these contributions are commonly neglected in more approximate methods like G2 theory and CBS-4, one cannot do so ‘unpunished’ in a rigorous extrapolation calculation — some typical contributions to TAE for chalcogenides and halogenides of the first and second row are 0.8 kcal/mol for \( F_2 \), 0.6 kcal/mol for \( CO_2 \), 1.0 kcal/mol for \( SO_2 \), and 1.2 kcal/mol for \( BF_3 \). These contributions are clearly on the order of the accuracy we are trying to achieve.

4. Extrapolation to the infinite-basis limit

4.1. EXTRAPOLATION OF THE SCF ENERGY

Dunning observed, in his original landmark paper on correlation consistent basis sets [55], that the energy gain from adding extra functions of a given angular momentum, as well as that from adding the first function of the next higher angular momentum, roughly follow a geometric series.

Feller [120] then noted that total energies for molecules calculated with successive cc-pV\( n \)Z basis set themselves roughly followed geometric series, and suggested the use of an expression of the form

\[
E(n) = E_\infty + A \exp(-Bn) \tag{17}
\]

which is itself a special case of a geometric extrapolation based on \( A + B.C^{-n} \).

Performance of the Feller exponential 3-point extrapolation for SCF total energies cannot be described as other than impressive. Table 1 compares extrapolated SCF total energies with values obtained from numerical Hartree-Fock calculations. The largest discrepancy, for the BF diatomic, amounts to 19 \( \mu E_h \), or 0.01 kcal/mol. A two-point \( A + B/(l + 1/2)^5 \) formula, following a suggestion in Ref. [124], works substantially less well.

Generally, the SCF component of atomization energies converges even faster than these total energies, and extrapolations beyond cc-pV5Z or aug-cc-pV5Z rarely contribute more than 0.01 kcal/mol or so.
TABLE 1. Comparison of performance for SCF basis set extrapolations.

|       | numerical HF | Feller(Q56) | Schwartz5(56) |
|-------|--------------|-------------|---------------|
| Ne    | -128.54709809 | -128.547089 | -128.547284   |
| N₂(R=2.068 a₀) | -108.9938257  | -108.993818  | -108.993988  |
| BH(R=2.336 a₀)  | -25.1315987   | -25.131601   | -25.131629   |
| H₂(R=1.4 a₀)    | -1.13362957   | -1.133625    | -1.133634    |
| H     | -0.5 exactly  | -0.500000    | -0.500003    |
| BF(R=2.386 a₀)  | -124.1687792  | -124.168760  | -124.168904  |
| CO(R=2.132 a₀)  | -112.790907   | -112.790890  | -112.791033  |

(a) Refs. [121, 122]. Bond distances R taken from these references.
(b) geometric extrapolation $A + B.C^{l}$ from SCF/cc-pVQZ, SCF/cc-pV5Z, and SCF/cc-pV6Z energies
(c) 2-point extrapolation $A + B/(l+1/2)^5$ from SCF/cc-pV5Z and SCF/cc-pV6Z energies
(d) aug-cc-pVnZ basis sets used [123]

4.2. EXTRAPOLATION OF THE VALENCE CORRELATION ENERGY

Feller originally proposed his formula as a general extrapolation for energies, and in fact, in much of the earlier work of the Dunning group, this formula was employed for extrapolation of the total CCSD(T) or MRCI energy. The fact that the formula is largely phenomenological and has no physical basis would, from a pragmatic point of view, not be of serious concern if it worked well. However, contrary to the SCF case, performance of the geometric extrapolation for correlation energies leaves something to be desired. Table 2 collects error statistics for the total atomization energies of 15 molecules for which they are very precisely (on the order of 0.1 kcal/mol) known experimentally (data compiled in Ref. [6], including recently revised values for HCN [125] and HNO [126]), after correction for inner-shell correlation.

Needless to say, the conclusion that even with aug-cc-pV5Z basis sets a mean absolute error of 0.7 kcal/mol is the best we can do seems rather depressing. Alternatives were therefore sought, and found.

In his pioneering contribution, Schwartz [127] showed that the second-order correlation energy of a helium-like atom in a singlet state has an asymptotic expansion of the form

$$\Delta E(l) = A/(l + 1/2)^4 + B/(l + 1/2)^5 + O(l^{-8})$$  \hspace{1cm} (18)

in which $\Delta E(l)$ represents the contribution of basis functions with angular momentum $l$. Hill [128] then generalized this result to a variational calculation:

$$\Delta E(l) = A/(l + 1/2)^4 + B/(l + 1/2)^5 + O(l^{-6})$$  \hspace{1cm} (19)
TABLE 2. Summary of Errors (kcal/mol) in Extrapolated CCSD(T) Values for TAE after Correction for Core Correlation

| cc-pVnZ          | aug'-cc-pVnZ       |
|------------------|--------------------|
|                  | absolute error     | absolute error     |
|                  | mean | maximum | mean | maximum |
| Feller(DTQ)      | 0.72 | 1.86    | 0.66 | 1.50    |
| Feller(TQ5)      | 0.70 | 1.87    | 0.73 | 1.89    |
| Schwartz4(TQ)    | 0.46 | 1.27    | 0.35 | 0.69    |
| Schwartz4(TQ5)   | 0.32 | 0.72    | 0.36 | 1.18    |
| with triple bond correction | 0.22 | 0.64    | 0.23 | 0.78    |
| Schwartz4(Q5)    | 0.37 | 0.90    | 0.31 | 0.90    |
| with triple bond correction | 0.26 | 0.83    | 0.22 | 0.69    |
| Schwartz46(TQ5)  | 0.35 | 0.81    | 0.33 | 0.94    |
| with triple bond correction | 0.24 | 0.67    | 0.22 | 0.68    |
| Separate extrapolation\(a\) | 0.12 | 0.49    |

(a) SCF contribution Feller(TQ5); CCSD(T) valence correlation Schwartz\(\alpha\)(TQ5) (see Table 5)

Kutzelnigg and Morgan [129] derived similar asymptotic expansions of the second- and third-order MBPT energy of a two-electron atom in singlet as well as triplet states. For the singlet, they found the expansion

\[
\Delta E(l) = A/(l + 1/2)^4 + B/(l + 1/2)^5 + C/(l + 1/2)^6 + O(l^{-7})
\]

(20)

where the \(l^{-5}\) term has no second-order contribution while for the triplet, the expansion starts two orders later, at \((l + 1/2)^{-6}\). As pointed out in Ref. [129], this result can be generalized to the second-and third-order energies of many-electron atoms having an asymptotic correlation energy expansion of the form eq. (20).

If so, the error for a calculation in a basis set truncated at angular momentum \(L\) is given by

\[
E_\infty - E(L) = \sum_{l=L+1}^{\infty} \left[ \frac{A}{(l + 1/2)^4} + \frac{B}{(l + 1/2)^5} + \cdots \right]
\]

(21)

\[
= \frac{A \psi^{(3)}(L + 3/2)}{6} + \frac{B \psi^{(4)}(L + 3/2)}{24} + \cdots
\]

(22)

where \(\psi^{(n)}(x)\) represents the polygamma function [130] of order \(n\). Its asymptotic expansion has the leading terms

\[
\psi^{(n)}(x) = (-1)^{n-1} \left[ \frac{(n-1)!}{x^n} + \frac{n!}{2x^{n+1}} + O(x^{-n-2}) \right]
\]

(23)
Hence

\[ E(L) = E_\infty - \frac{A(L+1)^{-3}}{3} + \frac{B(L+1)^{-4}}{4} + O(L^{-5}) \] (24)

Assuming that higher orders in perturbation theory would behave similarly, the idea of carrying out successive (say, CCSD(T)) calculations in completely saturated basis sets up to given angular momenta \( L_1, L_2, L_3, \) followed by an extrapolation, then naturally suggests itself. In practice complete saturation of a basis set up to a given angular momentum \( L \) is not necessarily the most computationally efficient alternative; the next best solution would be to use a sequence of basis sets which are balanced in their quality for radial and angular correlation, such as the ANO or correlation consistent basis sets.

If we identify \( L \) with the \( n \) in the cc-pVnZ basis sets, an ambiguity arises, in that the highest angular momentum present in the cc-pVnZ basis set is \( n \) for first- and second-row atoms, and \( n - 1 \) for hydrogen and helium. As a compromise, we proposed [131] an extrapolation in terms of inverse powers of \( L + 1/2 \).

Extending this approach to molecular calculations involves not so much a leap of faith as the suggestion that molecular correlation effects would be predominantly atomic in character. We will introduce the following notations for two-point extrapolations to cc-pV\( l \)Z and cc-pV\( m \)Z energies:

Schwartz\( 3 (kl) \) \[ A + B/(l + 1/2)^3 \]

Schwartz\( 4 (kl) \) \[ A + B/(l + 1/2)^4 \]

and for three-point extrapolations to cc-pV\( l \)Z, cc-pV\( m \)Z, and cc-pVnZ energies:

Schwartz\( 46 (klm) \) \[ A + B/(l + 1/2)^4 + C/(l + 1/2)^6 \]

Schwartz\( \alpha (klm) \) \[ A + B/(l + 1/2)^\alpha \]

and so forth. (Note that the parameters in Schwartz\( \alpha \) have to be determined iteratively, while the others can be found by solving a \( 2 \times 2 \) or \( 3 \times 3 \) linear system.)

Let us first consider the MP2 energy. Klopper [132] obtained what are considered essentially exact MP2 correlation energies for \( \text{N}_2, \text{H}_2\text{O}, \text{Ne}, \) and \( \text{HF} \) using an explicitly correlated method. As seen below in Table 3, a Schwartz\( 3 (56) \) extrapolation to MP2/AV5Z and MP2/AV6Z correlation energies yields values in excellent agreement with the MP2-R12 results: deviations are \(-0.27 \text{ m}E_h\) for Ne, \(-0.25 \text{ m}E_h\) for HF, \(+0.10 \text{ m}E_h\) for \( \text{N}_2, \) and \(-0.14 \text{ m}E_h\) for \( \text{H}_2\text{O}, \) leading to a mean absolute deviation of 0.19 m\( E_h. \) (Wilson and Dunning [133] found similar results with VnZ basis sets.) A Schwartz\( \alpha (Q56) \) extrapolation to MP2/AVQZ, MP2/AV5Z, and MP2/AV6Z actually results in less good agreement (mean absolute deviation of 0.6 m\( E_h\)). This clearly suggests that Schwartz\( 3 \) is the extrapolation of choice for large basis set MP2 calculations, as well as that convergence
TABLE 3. Comparison of extrapolated and essentially exact MP2 valence correlation energies ($E_h$)

|       | MP2-R12$^a$ | Schwartz$\alpha$(Q56) | $\alpha$ | Schwartz3(56) | Feller(456) |
|-------|-------------|------------------------|---------|---------------|-------------|
| H$_2$O$^b$ | -0.30053    | -0.29991               | 3.44    | -0.30069      | -0.298325   |
| Ne     | -0.3202     | -0.31985               | 3.21    | -0.32047      | -0.317078   |
| N$_2$  | -0.42037    | -0.41928               | 3.44    | -0.42027      | -0.417277   |
| HF     | -0.3198     | -0.31931               | 3.31    | -0.32003      | -0.317190   |

(a) MP2 in basis set with explicit interelectronic bond distances [132]
(b) AV$nZ$ basis set on O, V$nZ$ basis set on H

of the MP2 energy for aug-cc-pV5Z and larger basis sets is almost entirely dominated by the leading Schwartz expansion term. Varying the $\alpha$ exponent and adding MP2/AVQZ results does not result in an improvement: it appears that for basis sets this size, the $(l + 1/2)^{-3}$ term dominates basis set convergence. By contrast, Feller(456) undershoots the MP2-R12 results by as much as 3 millihartree.

TABLE 4. Comparison of extrapolated and essentially exact CCSD and CCSD(T) valence correlation energies ($E_h$)

|       | CCSD-R12$^a$ | Schwartz$\alpha$(Q56) | $\alpha$ | Schwartz3(56) | Feller(456) |
|-------|-------------|------------------------|---------|---------------|-------------|
| H$_2$O$^b$ | -0.29753    | -0.29755               | 3.96    | -0.29853      | -0.29668    |
| Ne$^b$  | -0.31542    | -0.31519               | 3.64    | -0.31650      | -0.31343    |
| F-$^b$  | -0.32262    | -0.32207               | 3.76    | -0.32326      | -0.32076    |
| HF     | -0.31391    | -0.31350               | 3.77    | -0.31472      | -0.31234    |

|       | CCSD(T)-R12$^a$ | Schwartz$\alpha$(Q56) | $\alpha$ | Schwartz3(56) | Feller(456) |
|-------|----------------|------------------------|---------|---------------|-------------|
| H$_2$O$^c$ | -0.30737    | -0.30734               | 3.97    | -0.30842      | -0.30648    |
| Ne$^c$  | -0.32167    | -0.32165               | 3.67    | -0.32305      | -0.31986    |
| HF     | -0.32245    | -0.32238               | 3.80    | -0.32360      | -0.32110    |
| F-$^c$  | -0.33427    | -0.33402               | 3.80    | -0.33532      | -0.33266    |

(a) from CCSD-R12 and CCSD(T)-R12 results in Ref. [134] derived as CCSD-R12(valence)/X + CCSD-R12(all)/Y - CCSD-R12(valence)/X (with X being their smaller and Y their bigger basis set).
(b) more recent results [135]: -0.297527 (H$_2$O) and -0.315523 (Ne) $mE_h$
(c) more recent results [135]: -0.307211 (H$_2$O) and -0.321882 (Ne) $mE_h$

Very recently, M"uller, Kutzelnigg, and Noga (MKN) [134] (see Table 4) published CCSD-R12 and CCSD(T)-R12 studies on a number of closed-shell ten-electron systems, including F$^-$, HF, Ne, and H$_2$O. Some further results of this type are available from the work of Halkier et al. [135]. MKN quote all-electron results with two basis sets which we will denote A and
B, but valence-only results only with the smaller of the two basis sets, A. Since the main improvement in basis B over basis A is in the valence region and, in Ref. [132], a basis set equivalent to A appeared to yield inner-shell pair energies essentially equivalent to exact solution for Ne, we would argue that the main deficiency in A will be for the valence region and not for the inner-shell region. Therefore, the exact valence only CCSD(T) energy is expected to lie close to valence(A)+all(B)-all(A).

Again, Feller(456) undershoots the CCSD-R12 and CCSD(T)-R12 results by several millihartree. Schwartz3(56) appears to overshoot the energies, while Schwartzα(456) appears to be in close agreement. It should be noted that the exponent α here systematically favors values significantly higher than 3, in fact centering around 4. (This tendency is what led, in our first paper [131] on these extrapolations, to the suggestion of Schwartz4 and Schwartz46 as extrapolation formulas.) While Helgaker and coworkers [135, 136] advocate the use of a fixed exponent of 3 for CCSD and CCSD(T) correlation energies as well, we would argue that the difference with the convergence behavior at the MP2 level reflects the importance of higher-order terms in eq.(20) in methods that include higher-order MBPT terms (such as CCSD and CCSD(T), both of which include the complete third-order energy, as well as important subclasses of excitations to infinite order). This is also consistent with the observation of the present author [137] who found that the basis set increment ratio

\[ \frac{TAE[MP2/AVnZ] - TAE[MP2/AV(n-1)Z]}{TAE[CCSD/AVnZ] - TAE[CCSD/AV(n-1)Z]} \]

becomes progressively larger as \( n \) increases, and exceeds unity for \( n=4 \) and upwards.

Following the adage “the proof of the pudding is in the eating”, we considered [90] separate extrapolation of the CCSD(T)/AVnZ (\( n=T, Q, 5 \)) valence correlation component of TAE using Schwartzα(TQ5), and of the SCF component to Schwartz5(Q5) (or Feller(TQ5) — the results differ negligibly), for our 15 reference molecules. Agreement with experiment (Table 5) speaks for itself, with mean and maximum absolute errors of 0.23 and 0.88 kcal/mol. If an additional small correction is introduced [90] for the especially slow basis set convergence in nitrogen compounds (0.126 kcal/mol per bond order involving N), mean and maximum errors can be further brought down to 0.12 and 0.49 kcal/mol, respectively — benchmark quality by any reasonable standard. The same methodology was also applied to the first-row hydrides and hydride radicals AH\(_n\) [138], and some variants were considered and extensively tested in Refs. [139, 140].

Finally, it is perhaps worth mentioning that the convergence of the sum of SCF and correlation energies for relatively small basis sets (particularly
TABLE 5. Computed (CCSD(T)), extrapolated, and observed total atomization energies and auxiliary quantities. All units are kcal/mol except \( \alpha \), which is dimensionless.

|     | Observed total | Extrapolated SCF val. corr. | \( \alpha \) | core corr |
|-----|----------------|-----------------------------|--------------|-----------|
| HNO | 205.64(6)      | 205.67 85.44 119.38         | 3.89         | 0.48      |
| CO 2| 389.68(6)      | 389.75 258.08 129.89        | 3.91         | 1.78      |
| CO  | 259.58(12)     | 259.56 259.56 216.42        | 3.69         | 0.96      |
| F   | 39.01(10)      | 38.29 38.29 -31.07          | 4.63         | -0.07     |
| N   | 228.42(3)      | 228.16 228.53 119.71        | 3.52         | 0.85      |
| N 2 | 270.60(10)     | 269.73 270.23 95.15         | 3.93         | 1.26      |
| C   | 405.53(24)     | 405.04 405.04 299.93        | 4.37         | 2.44      |
| CH  | 420.23(14)     | 420.18 420.18 331.60        | 4.55         | 1.25      |
| H 2 | 374.09(16)     | 374.33 374.33 264.86        | 4.13         | 1.32      |
| H 2 | 232.83(2)      | 232.83 232.83 160.03        | 4.66         | 0.38      |
| H  | 109.48(0)      | 109.48 109.48 83.86         | 4.31         | 0.00      |
| H  | 313.27(25)     | 312.96 313.33 204.42        | 3.94         | 1.67      |
| H  | 141.57(17)     | 141.54 141.54 100.04        | 4.32         | 0.18      |
| NH  | 298.06(10)     | 297.77 298.15 203.31        | 4.44         | 0.66      |
| C 2 | 563.68(29)     | 563.77 563.77 435.11        | 4.25         | 2.36      |
| mean abs. err. w/o F 2 | 0.23 | 0.12 |

(a) see Ref. [90] for detailed references
(b) using the additional correction \( \sum_i (\text{bond order})_i \times 0.126 \text{ kcal/mol} \), where \( i \) runs over all bonds with at least one N atom

if the total energy, rather than TAE, is considered) would be dominated to a substantial extent by the SCF convergence behavior, which would lead to the erroneous conclusion that overall convergence behavior is best described by an exponential series.

4.3. INDIVIDUAL OR GLOBAL EXTRAPOLATION?

For the two-point \( A + B/(l + 1/2)^n \) extrapolations (\( n \) fixed), it is easily seen that extrapolation on individual energies or any reaction energy yields identical results. With the other extrapolations, this equality does not hold. In most cases, the final result for total atomization energies will only differ by about 0.1 kcal/mol between the two approaches. Two observations are relevant here.

First of all, as seen for the example of the ten-electron hydrides in Table 6 below, the correlation component to atomization energies appears to converge faster than that of the constituent total energies. For instance, while the percentage of the valence correlation energy recovered by the
AV5Z basis set varies from 99.0 % for CH\(_4\) to 97.8% in HF, consistently 99.5% to 99.7% is recovered for the valence correlation component to the dissociation energy, which suggests a significant cancellation of correlation effects between atom and molecule.

| Extrapolated valence corr. energy (\(E_h\)) | \(\alpha\) | Percentage recovered at CCSD(T)/aug-\(\text{cc-pVnZ}\) level |
|---------------------------------------------|---------|-------------------------------------------------------------|
| \(n=\text{D}\) | \(n=\text{T}\) | \(n=\text{Q}\) | \(n=5\) |
| B -0.072849 | 4.250 | 88.1 | 96.4 | 98.8 | 99.5 |
| C -0.100642 | 3.841 | 81.2 | 94.3 | 97.8 | 99.0 |
| N -0.129075 | 3.634 | 75.1 | 92.3 | 96.9 | 98.5 |
| O -0.192694 | 3.421 | 69.9 | 89.4 | 95.5 | 97.7 |
| F -0.257675 | 3.277 | 67.7 | 87.6 | 94.6 | 97.2 |
| Ne -0.323458 | 3.194 | 65.8 | 86.4 | 93.9 | 96.8 |
| BH\(_3\) -0.145407 | 4.698 | 81.4 | 94.9 | 98.4 | 99.4 |
| CH\(_4\) -0.239761 | 4.262 | 80.9 | 94.4 | 98.1 | 99.2 |
| NH\(_3\) -0.278460 | 4.034 | 78.3 | 93.1 | 97.5 | 98.9 |
| H\(_2\)O -0.307884 | 3.743 | 74.9 | 91.3 | 96.6 | 98.4 |
| HF -0.323184 | 3.493 | 71.0 | 89.1 | 95.5 | 97.8 |
| Ne -0.323458 | 3.194 | 65.8 | 86.4 | 93.9 | 96.8 |
| BH\(_3\)\(\rightarrow\)B+3H -0.072570 | 4.94 | 74.5 | 93.4 | 98.1 | 99.3 |
| CH\(_4\)\(\rightarrow\)C+4H -0.138758 | 4.55 | 81.0 | 94.8 | 98.5 | 99.6 |
| NH\(_3\)\(\rightarrow\)N+3H -0.148944 | 4.44 | 81.3 | 94.1 | 98.3 | 99.5 |
| H\(_2\)O\(\rightarrow\)O+2H -0.115048 | 4.66 | 83.6 | 94.4 | 98.5 | 99.6 |
| HF\(\rightarrow\)F+H -0.065716 | 5.38 | 85.6 | 94.9 | 98.8 | 99.7 |

Secondly, it is easily seen from considering the difference of two asymptotic series (for \(E_{\text{corr}}(X)\) and \(E_{\text{corr}}(Y)\)) in \((l + 1/2)\)

\[
A_x - A_y + (B_x - B_y)/(l + 1/2)^3 + (C_x - C_y)/(l + 1/2)^4 + \ldots
\]

that situations may arise in which the coefficients of the difference do not decay as fast with increasing \(l\) as one might like, e.g. if \(X\) and \(Y\) are close in energy to begin with. Under such circumstances, a three-point extrapolation of the form \(A + B/(l + 1/2)^C\) may not behave well numerically, and extrapolation on the individual energies may be preferable. (We found this to be the case, for instance, with electron affinities.)

As a rule, the present author favors extrapolation on the energy difference when the latter is fairly large (e.g. total atomization energies), and
extrapolation on the constituent total energies when small energy differences have to be determined (e.g. electron affinities, conformational energy differences).

5. Case studies

5.1. ELECTRON AFFINITIES OF THE FIRST-ROW ATOMS

Electron affinities have in the past been notorious as a ‘tough nut to crack’ computationally. On the one hand, wave functions for anions extend fairly far in space (requiring accommodation thereof in the basis set by the addition of ‘diffuse functions’). On the other hand, electron affinities involve small differences in energy between systems with different numbers of electrons — a balanced description of which is a very taxing test for electron correlation methods.

As a result, the electron affinities of the first-row atoms have traditionally been used as a benchmark for computational methods (e.g. [59, 141–144]) not only because of the small size of the system but because the corresponding experimental quantities are accurately known. [145]

This problem is a good illustration of the issues that enter if one wants to carry out a calculation to the very highest accuracy.

Since even for atoms, full configuration interaction is not an option with sufficiently large basis sets, we will use CCSD(T) as our ‘baseline’ electron correlation method. Our computed results are given in Table 7.

For the SCF and valence correlation contributions, we have carried out CCSD(T)/AVQZ, CCSD(T)/AV5Z, and CCSD(T)/AV6Z calculations. (The SCF energies are of course obtained on the fly.) These involve basis sets of $[6s5p4d3f2g]$, $[7s6p5d4f3g2h]$, and $[8s7p6d5f4g3h2i]$ quality, respectively. For the SCF energy, we will use the $A + B.\exp^{-l}$ exponential extrapolation [120], for the valence correlation contribution the $A + B/(l + 1/2)^C$ formula [131].

The extrapolation contributes on average much less than 0.001 eV to the SCF component, which is basically completely converged with an AV6Z basis set. Contributions to the valence correlation energy are somewhat more significant, reaching -0.016 eV for O and -0.014 eV for F. In all cases, further basis set expansion is predicted to increase the EA, as expected.

The contribution of inner-shell correlation was obtained by carrying out CCSD(T)/ACV5Z calculations both with all electrons correlated, and with the $(1s)$ like orbitals constrained to be doubly occupied. While the core correlation energy may converge quite slowly in absolute terms, in relative terms (in this case, its contribution to EA) convergence is usually fairly rapid, with an ACVQZ basis set usually being large enough even for accurate work, and an ACV5Z basis set definitely so. As expected, its
TABLE 7. Computed (this work) and observed electron affinities (eV) of the first-row atoms

|     | SCF     | CCSD(T)  | core | Relativistics | FCI corr. | best | Expt. [145] |
|-----|---------|----------|------|--------------|-----------|------|-------------|
|     | val. corr. | corr. | spin-orbit | scalar | correction | calc. |              |
| H   | -0.3288 | 1.0821   | 0    | 0            | -4×10^{-5} | 0a   | 0.7533      | 0.75420(2) |
| B   | -0.2675 | 0.5245   | 0.0043 | -0.0005      | -0.0013   | 0.0191b | 0.2786      | 0.277(10)  |
| C   | 0.5483  | 0.7001   | 0.0072 | -0.0037      | -0.0028   | 0.0140c | 1.2631      | 1.2629(3)  |
| N   | -0.5390 | 1.9936   | 0.0017 | -0.0023      | -0.0059   | 0.0114d | 1.4595      | 1.46122(3) |
| O   | 1.3073  | 2.1175   | 0.0043 | -0.0167      | -0.0093   | -0.0004d| 3.4027      | 3.401190(4)|

SCF: exponential extrapolation from SCF/AVQZ, SCF/AV5Z, and SCF/AV6Z
valence correlation: $A + B/(l + 1/2)^{1/2}$ extrapolation on correlation energy from CCSD(T)/AVQZ, CCSD(T)/AV5Z, and CCSD(T)/AV6Z
spin-orbit coupling: from experimental fine structure [119]
scalar relativistics: Darwin and mass-velocity terms by perturbation from ACPF/ACVQZ(uncontracted)
core correlation: CCSD(T)/ACV5Z(all)-CCSD(T)/ACV5Z(valence)
FCI correction: difference between CCSD(T) and FCI. See following footnotes:
(a) CCSD(T) is exact for a two-electron system
(b) FCI/AVQZ − CCSD(T)/AVQZ
(c) FCI/AVTZ − CCSD(T)/AVQZ
(d) CCSDT/AVQZ − CCSD(T)/AVQZ + FCI/AVDZ − CCSDT/AVDZ

contribution increases EA in all cases (except of course for the trivial case of H/H^−).

The relativistic contribution can be decomposed into two terms: the scalar contribution and the effect of spin-orbit splitting. While an ab initio purist would obtain the latter from computed spin-orbit coupling elements, we have obtained them here from the observed fine structure of the atomic ground states. Especially for F/F^−, its contribution to EA is quite significant; in all cases, a lowering of EA is seen.

The scalar relativistic contribution was obtained by first-order perturbation theory applied to the Darwin and mass-velocity contributions. [110,111] Since they can be evaluated as a simple expectation value from the converged wave function using this method, we have computed them at the ACPF (augmented coupled pair functional) level. [112] Relativistic calculations generally require greatly improved flexibility of the wave function in the high-exponent region, particularly in the s functions: we opted for an uncontracted ACVQZ basis set. In all cases, the scalar relativistic contribution decreases EA; as expected, the size of this contribution goes up superlinearly with Z. (From a fit of $aZ^b$ to the computed contributions, we find $b \approx 3.4$ in this case.) While the importance of relativistic contributions to this type of quantity for heavy elements is well known (e.g., the existence
of the alkali aurides Rb\textsuperscript{+}Au\textsuperscript{-} and Cs\textsuperscript{+}Au\textsuperscript{-} is due to relativistic stabilization of the 6s shell \cite{109}, a contribution of -0.01 eV for an element as light as F may seem surprising at first. Since all electron affinities discussed here except EA(H) involve addition of an electron to a 2p orbital, Kendall et al. \cite{59} conclude that “relativistic effects should contribute insignificantly to the calculated electron affinities”. Of course, whether or not -0.01 eV is insignificant is a matter of the accuracy being pursued, as well as the relative magnitude of the other possible sources of error.

Last but not least, we need to make an allowance for imperfect ions in the CCSD(T) treatment. For B/B\textsuperscript{-}, we have done so by comparing an FCI/AVQZ calculation with the corresponding CCSD(T)/AVQZ results. This calculation took about five hours on an SGI Origin 2000 minisupercomputer, and could not be carried to completion even for C\textsuperscript{-}. Since however the FCI-CCSD(T) correction for EA(B) appears to converge very rapidly (with the AVDZ, AVTZ, and AVQZ basis sets we obtain values of 0.0186, 0.0197, and 0.0191 eV, respectively), we may fairly safely use the difference between FCI/AVTZ and CCSD(T)/AVTZ in the case of EA(C). For O/O\textsuperscript{-} and F/F\textsuperscript{-}, even FCI/AVTZ calculations are not feasible. Assuming that the error in the full CCSDT method with respect to FCI is fairly constant, we have therefore employed a two-stage additivity approximation in these cases:

\[
E[\text{FCI/AVQZ}] \approx E[\text{CCSD(T)/AVQZ}] + (E[\text{CCSDT/AVQZ}] - E[\text{CCSD(T)/AVQZ}]) + (E[\text{FCI/AVDZ}] - E[\text{CCSDT/AVDZ}])
\]  

(27)

As seen in Table 7, the final results agree with experiment to within about 0.001 eV on average. The largest discrepancies, 0.0015 eV, occur for EA(O) and EA(F), which are also the largest and for which some of the individual contributions (e.g. the relativistics) are also the largest.

5.2. ATOMIZATION ENERGY OF SiH\textsubscript{4} AND THE HEAT OF FORMATION OF Si(G)

The heat of formation of Si(g) is the subject of some controversy. In the JANAF tables it is given as 106.6±1.9 kcal/mol. Desai \cite{146} reviewed the available data and recommended the JANAF value, but with a reduced uncertainty of ±1.0 kcal/mol. Recently, Grev and Schaefer \cite{71} found that their ab initio calculation of the TAE of SiH\textsubscript{4}, despite basis set incompleteness, was actually larger than the value derived from the experimental heats of formation of Si(g), H(g), and SiH\textsubscript{4}(g). They suggested that the heat of vaporization of silicon be revised upwards to $\Delta H_{f,0}^{\circ}[\text{Si}(g)] = 108.07(50)$ kcal/mol, a suggestion supported by Ochterski et al. \cite{147}. Clearly, some
calibration calculation to resolve this controversy would be desirable: we will here report some preliminary results obtained as a by-product of an anharmonic force field study [148] on SiH$_4$. While Grev and Schaefer’s work was definitely state of the art in its time, the attainable accuracy for this type of compound may well have gone up an order of magnitude in the six years since it was published.

From a calibration calculation along the lines discussed above, our best calculation for the nonrelativistic valence CCSD(T) limit is 324.62 kcal/mol. For this molecule, we may assume fairly safely that CCSD(T) is close to full CI. Deducting the Si spin-orbit splitting correction (0.43 kcal/mol), adding a core correlation contribution of -0.34 kcal/mol (with the MT core correlation basis set) and deducting a fully anharmonic zero-point energy of 19.57 kcal/mol (from a CCSD(T)/VQZ+1 quartic force field) we obtain TAE$_0$=304.28 kcal/mol. Using the revised ∆H$_{f,0}$[SiH$_4$(g)]=108.07(50) kcal/mol of Grev and Schaefer [71] we obtain ∆H$_{f,0}$[SiH$_4$(g)]=10.34 kcal/mol, in excellent agreement with the JANAF value of 10.5(5) kcal/mol. At first sight this supports the new value.

Upon introducing the scalar relativistic correction of -0.67 kcal/mol, however, we obtain a value of 11.0 kcal/mol, which is only just compatible with the experimental measurement. Using the older JANAF/CODATA value ∆H$_{f,0}$[Si(g)]=106.6±1.0 kcal/mol, we would find 9.54 kcal/mol, seemingly incompatible with the experimental result for SiH$_4$. However, as pointed out by Grev and Schaefer [71], the JANAF value is in fact the Gunn and Green [149] value of 9.5 kcal/mol increased by a correction [150] of +1 kcal/mol for the phase transition Si(amorphous)→Si(cr). If one were to follow Gunn and Green in considering this correction to be an artifact of the method of preparation and in neglecting it, our calculations would in fact support the old JANAF/CODATA ∆H$_{f,0}$[Si(g)].

Regardless of who is ‘right’ here (CODATA or Grev and Schaefer), the above serves as an illustration that, where the accurate determination of fundamental thermochemical quantities is at stake, the greatest care is required, both in performing the calculations and in interpreting the experiments.

5.3. HEAT OF FORMATION OF B(G) VIA THE TOTAL ATOMIZATION ENERGY OF BF$_3$

Nonthermochemists are often surprised when they hear that the heats of formation in the gas phase of three first-and second-row atoms (namely, Be, B, and Si) are imprecisely known because of various experimental complications. The most uncertain value among them, B, carries an error bar of no less than 3 kcal/mol, ∆H$_{f,0}$(B(g))=132.7±3.0 kcal/mol [119]. This is obviously a very unsatisfactory state of affairs given the fact that just about
any ab initio or semiempirical scheme for calculating molecular heats of formation relies on the heats of formation of the constituent atoms through the identity

\[
\Delta H^\circ_{f,T}(A_k B_l C_m \ldots) = k \Delta H^\circ_{f,T}(A) - l \Delta H^\circ_{f,T}(B) - m \Delta H^\circ_{f,T}(C) - \ldots
\]

(28)

(where T is the temperature).

Storms and Mueller (SM) [151] had previously recommended a much higher and more precise value of 136.2±0.2 kcal/mol. Ruščić et al. [152], reviewing the experimental data, concluded that the JANAF value was in error and recommended the SM value. Recently, Ochterski et al. [147] combined calculated atomization energies using the CBS-APNO hybrid ab initio/empirical scheme [124] with an accurate CODATA [153] heat of formation for BF$_3$, 271.2±0.2 kcal/mol, and the established heat of formation for F($g$), 18.47±0.07 kcal/mol, to obtain 135.7 kcal/mol. On the basis thereof, they too recommended the SM value. Note that their calculation does not include a correction for the spin-orbit splitting in atomic fluorine and therefore is about 1.1 kcal/mol too high (see below). In another study, Schlegel and Harris [154] found that computed heats of formation using the Gaussian-2 (G2) method [4] for a number of boron compounds agreed much better with experiment if the reference value for gaseous boron was taken as the SM rather than the JANAF value.

Martin and Taylor [123] carried out a calibration calculation aimed at resolving this discrepancy for once and for all. All relevant energies are given in Tables 8 and 9.

The largest calculation we could carry out on BF$_3$ was CCSD(T)/AV5Z (508 basis functions), which required 60 GB of disk space and 720 MB of memory on the CRAY T90. Because the next step up in basis set, CCSD(T)/AV6Z (756 basis functions) was simply beyond the available computational hardware, we used the BF diatomic as a model system for the effect of further basis set extension.

The SCF component of the atomization energy of BF$_3$ differs only -0.02 kcal/mol between AVQZ and AV5Z basis sets, and is essentially converged. For BF, increasing the basis set another step to AV6Z only affects the result by 0.01 kcal/mol; upon exponential extrapolation, the Feller(Q56) total SCF energy, $-124.168760 \ E_h$, is found to be only 20 $\mu E_h$ above the numerical Hartree-Fock result [122].

Improving the basis set from AVQZ to AV5Z increases the valence correlation energy by some 1.39 kcal/mol, compared to 4.46 kcal/mol from AVTZ to AVQZ. The Schwartz $\alpha$(TQ5) extrapolation adds on another 0.84
### Table 8. Convergence of individual contributions to the TAE of BF$_3$ and to $D_e$(BF). All values are in kcal/mol

|                | BF$_3$ | BF  |
|----------------|--------|-----|
| **SCF component of TAE$_e$** |        |     |
| SCF/AVTZ       | 373.59 | 142.30 |
| SCF/AVQZ       | 374.61 | 143.03 |
| SCF/AV5Z       | 374.59 | 143.08 |
| SCF/AV6Z       | —      | 143.09 |
| Feller(TQ5)    | 374.59 | 143.08 |
| Feller(Q56)    | —      | 143.08 |
| Best SCF$^a$   | 374.59 | 143.09 |
| **Valence correlation component of TAE$_e$** |        |     |
| CCSD(T)/AVTZ   | 87.38  | 35.63 |
| CCSD(T)/AVQZ   | 91.83  | 37.63 |
| CCSD(T)/AV5Z   | 93.19  | 38.19 |
| CCSD(T)/AV6Z   | —      | 38.44 |
| Schwartz(TQ5)  | 94.03  | 38.35 |
| Schwartz(Q56)  | —      | 38.76 |
| Best valence corr.$^b$ | 95.13  | 38.76 |
| **Inner shell correlation component of TAE$_e$** |        |     |
| CCSD(T)/CVTZ   | 1.366  | 0.482 |
| CCSD(T)/CVQZ   | 1.724  | 0.629 |
| CCSD(T)/CV5Z   | —      | 0.670 |
| Schwartz(TQ5)  | —      | 0.696 |
| CCSD(T)/ACVTZ  | 1.563  | 0.557 |
| CCSD(T)/ACVQZ  | 1.772  | 0.648 |
| CCSD(T)/ACV5Z  | —      | 0.676 |
| aug-Schwartz(TQ5) | —      | 0.698 |
| Best core corr.$^c$ | 1.922  | 0.698 |

(a) Feller(TQ5)[BF$_3$] + 3 × (Feller(Q56)[BF] − Feller(TQ5)[BF])
(b) Schwartz(TQ5) [BF$_3$] + 3 × (Schwartz(Q56)[BF] − Schwartz(TQ5)[BF])
(c) CCSD(T)/ACVQZ[BF$_3$] + 3 × (aug-Schwartz(TQ5)[BF] − CCSD(T)/ACVQZ[BF])

kcal/mol; note that while the value of $\alpha$ for BF$_3$ is about 3.40, the $\alpha$ found for the MP2 correlation energy, 2.88, strongly suggests dominance of the leading $(l + 1/2)^{-3}$ term. The difference between the MP2 and CCSD(T) values of $\alpha$ suggests the importance of higher-order contributions, which add [129] higher powers in $(l+1/2)$. For the BF model system, the Schwartz(TQ5) extrapolated value is no less than 0.37 kcal/mol below the Schwartz(Q56) value: this unusually large difference is to some extent
due to the very polar character of the B–F bond. (In fact, Gillespie [155] argues that BF₃ is best regarded as a tricoordinate ionic compound of B³⁺.)

Since BF₃ actually contains three bonds that are quite similar to the one in BF, it seems reasonable that the difference between Schwartzα(TQ5) and Schwartzα(Q56) would be approximately three times that in BF. Hence we obtain an estimated basis set limit for the correlation part of TAE of 95.14 kcal/mol. In combination with the SCF contribution of 374.57 kcal/mol this yields a valence-only TAE, without spin-orbit correction, of 469.71 kcal/mol.

The contribution of inner-shell correlation to the TAE of BF₃ is found to be 1.37 kcal/mol at the CCSD(T)/CVTZ level and 1.72 kcal/mol at the CCSD(T)/CVQZ level. Given the polarity of the system, some mild coupling between the effects of core correlation and inclusion of diffuse functions cannot be ruled out a priori, and indeed extending the CVQZ to an ACVQZ basis set adds some 0.05 kcal/mol to the core correlation energy. Based on experience [69] we normally expect the core correlation contribution to be near convergence with such basis sets.

Again using the BF diatomic as a model system permits us to gauge the effects of further improvement of the core correlation basis set. At the CCSD(T)/ACVQZ level, the core correlation contribution to $\Delta E_e$ (BF) is 0.65 kcal/mol, or slightly more than one-third the value in BF₃. Enlarging the basis from CVQZ to CV5Z leads to an increase of 0.04 kcal/mol: the effect from ACVQZ to ACV5Z is somewhat smaller at 0.03 kcal/mol. (The CV5Z and ACV5Z values differ by only 0.01 kcal/mol.) Carrying out a Schwartzα(TQ5) extrapolation on the ACVTZ, ACVQZ, and ACV5Z numbers leads to an estimated infinite-basis limit core correlation contribution to the BF $\Delta E_e$ of 0.70 kcal/mol, or 0.05 kcal/mol more than the computed ACVQZ value.

If we again use three times this value as a correction for BF₃, we obtain a best estimate for the inner-shell correlation contribution to TAE(BF₃) of 1.92 kcal/mol. We hence obtain a TAE$_{e,NR}$ (i.e. without spin-orbit correction) of 471.65 kcal/mol; deducting the atomic spin-orbit corrections finally yields TAE$_e$=470.46 kcal/mol.

From the computed CCSD(T)/VTZ harmonic frequencies and anharmonicity constants given in Ref. [156], we obtain ZPE=7.89 kcal/mol. If we substitute experimental fundamentals (see Ref [156] for details) and employ the computed anharmonicity constants only for the small difference between the zero-point energy and one-half the sum of the fundamentals, ZPE decreases to 7.83 kcal/mol. We hence obtain the total atomization energy for BF₃ at 0 K, TAE$_0$ = 462.63 kcal/mol.

In combination with the JANAF [119] heat of formation for F(g) of 18.47±0.07 kcal/mol and the CODATA [153] heat of formation of BF₃(g),
TABLE 9. Computed thermochemical properties for BF₃, BF, and B in the gas phase. All values are in kcal/mol

|                  | BF₃          | BF          |
|------------------|--------------|-------------|
| Best TAEₑNR     | 471.65       | 182.54      |
| spin-orbit correction \(\text{a}\) | \(-1.184\) | \(-0.414\) |
| Best TAEₑ      | 470.46       | 182.13      |
| ZPVE            | 7.887\(^b\) | 1.996\(^c\) |
| Best TAE₀      | 462.63       | 180.13      |

Derivation of \(\Delta H₀^{f,0}[\text{B(g)}]\)

\(\Delta H₀^{f,0}[\text{BF₃(g)}]\), Ref. [153]\(^*\) \(-270.8±0.2\) kcal/mol

\(\Delta H₀^{f,0}[\text{F(g)}]\), Ref. [119] \(+18.47±0.07\) kcal/mol

calculated \(\Delta H₀^{f}[\text{B(g)}]\) \(136.4±0.4\) kcal/mol

Expt. JANAF [119] \(133±3\) kJ/mol

Expt. SM [151], 298 K \(137.4±0.2\) kcal/mol

\(\Delta H₀^{f,298}-\Delta H₀^{f,0}\), Ref. [119] \(1.219\) kcal/mol

Expt. SM [151], 0 K \(136.2±0.2\) kcal/mol

\(\Delta H₀^{f,298}[\text{BF₃(g)}]=271.5±0.2\) kcal/mol; \(\Delta H₀^{f,0}[\text{BF₃(g)}]-\Delta H₀^{f,298}[\text{BF₃(g)}] = -(H_{298} - H₀)[\text{BF₃(g)}]-B(g)-3/2 F₂(g)] = -(11.65 - 1.222 - (3/2) 8.825)/4.184 = +0.675\) kcal/mol.

(All data from Ref. [153].)

(a) computed from atomic sublevels for electronic ground states given in Ref. [119].

(b) from observed \(\nu_i\) and computed \(X_{ij}, G_{ij}\) given in Ref. [156]

(c) from computed CCSD(T)/VQZ \(\omega_e=1398.0\), \(\omega_e x_e=11.55\), and \(\omega_e y_e=0.054\) cm\(^{-1}\); experimental values [95] 1402.1, 11.8, and 0.056 cm\(^{-1}\), respectively.

\(-270.84±0.2\) kcal/mol, we then obtain \(\Delta H₀^{f,0}(\text{B(g)})=136.38±0.3\) kcal/mol, in which the uncertainty only reflects the uncertainties in the experimental quantities. The possible further error in the calculations is somewhat more difficult to quantify: past experience suggests a mean absolute error of 0.12 kcal/mol, but in the light of the fairly substantial correction terms applied, it would probably be appropriate to increase the error margin to about 0.3 kcal/mol. This would then bring our best estimate to 136.4±0.4 kcal/mol, the uncertainty of which encompasses that of the SM value of 136.2±0.2 kcal/mol.

In the published study [123], we did not consider two contributions: imperfections in the CCSD(T) method and scalar relativistic contributions. The former are rather hard to quantify since a full CI calculation for this system, even in a fairly small basis set, is not a realistic option at present. We can determine the latter by an ACPF/CVTZ(uncontracted) calculation of the Darwin and mass-velocity contributions, which we find to be \(-0.68\) kcal/mol. Adding another 0.1 kcal/mol to the error bar in order to accommodate uncertainty in this contribution, we then have a best estimate for
the heat of atomization at 0 K of B of 135.7±0.5 kcal/mol, which is still compatible with the SM value.

6. Conclusions

We have shown that by judicious use of extrapolations to the 1-particle basis set limit and n-particle calibration techniques, total atomization energies of molecules with up to four heavy atoms can be obtained with calibration accuracy (1 kJ/mol or better, on average) without any empirical correction. For the SCF energy a 3-point geometric extrapolation is the method of choice. For the MP2 correlation energy, a 2-point \( A + B/(l + 1/2)^3 \) extrapolation is recommended, while for CCSD and CCSD(T) correlation energies we prefer the 3-point \( A + B/(l + 1/2)^C \) formula. Addition of high-exponent ‘inner polarization functions’ to second-row atoms is essential for reliable results. For the highest accuracy, accounts are required of inner-shell correlation, atomic spin-orbit splitting, anharmonicity in the zero-point energy, and scalar relativistic effects.

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Previously unpublished calculations reported in this work were carried out using ACES II [157], Gaussian 94 [158], and a prerelease version of MOLPRO97.3 [159] made available courtesy of Prof. Peter J. Knowles (Birmingham University, UK). Some unpublished correlation consistent basis sets were taken from the EMSL library [160]; others (particularly the AV6Z sets used) are ‘unofficial’ ones generated by the author.

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160. Some basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information. World Wide Web address: \url{http://www.emsl.pnl.gov:2080/forms/basisform.html}