W1 and W2 Theories, and Their Variants: Thermochemistry in the kJ/mol Accuracy Range

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Chapter 2

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1. INTRODUCTION AND BACKGROUND

The last fifteen years witnessed the development of a number of "black-box" computational thermochemistry methods. Among them, the G1/G2/G3 theories and their variants, and the CBS-Q family of methods by Petersson and coworkers are worth mentioning in particular. In addition to these wavefunction-based approaches, density functional methods – aside from their great popularity as a general tool for practical computational chemistry – have gained some currency for computational thermochemistry in the medium accuracy range, as have group equivalent-based models. For very large systems, semiempirical methods remain popular.

At the other extreme in terms of system size and accuracy stand brute-force approaches such as those based on wavefunctions with explicit interelectronic distances.

Methods such as G3 and CBS-QB3 do reach the goal of "chemical accuracy" (generally defined as ±1 kcal/mol) on average, but worst-case errors for problematic molecules may exceed this criterion by almost an order of magnitude. In addition, almost all of these approaches involve some level of parameterization and/or empirical correction against experimental data. While this is by and large possible (albeit not without pitfalls) in the kcal/mol accuracy range for first- and second-row compounds, experimental data of sub-kcal/mol accuracy are thin on the
ground, and the available data for transition metal compounds are simply too scarce for this to be a useful approach.

There would thus appear to be room for a more or less "black box" computational thermochemistry method that has the following properties:

1. it on average achieves "benchmark accuracy", which we shall arbitrarily define as one unit of the most common tabulation unit in thermochemical reference tables, i.e. 1 kJ/mol (0.24 kcal/mol);

2. the worst-case error should not exceed 1 kcal/mol ("chemical accuracy") except perhaps in intrinsically pathological cases;

3. it is still efficient enough for applications to systems with up to six heavy atoms on modern workstations;

4. it is entirely devoid of parameters derived from experiment (and hence from bias towards the systems used for parameterization).

These have been the design goals in our development of the W1 and W2 (Weizmann-1 and Weizmann-2) theories [1].

The usual design philosophy for this type of methods is bottom-up: one starts with an approximate model, compares results with experiments, analyzes the deviations, and uses them to determine empirical corrections and/or additional terms to be added to the model, after which the cycle is repeated if desired.

Our philosophy was instead "top-down". We decomposed the molecular TAE (total atomization energy: TAE\textsubscript{e} at the bottom of the well, TAE\textsubscript{0} at absolute zero) into all components that can reasonably affect it at the kJ/mol level. Then we carried out exhaustive benchmark calculations on each component separately for a representative "training set" of molecules. Finally, for each component separately, we progressively introduced approximations up to the point where reproduction of that particular component started deteriorating to an unacceptable extent. Thus, experimental data entered the picture only at the validation stage, not at the design stage.

Another philosophical issue centers on whether a method should be a "protocol" specified down to the last detail (i.e. be truly "black-box"), or whether it should merely outline a general approach with minor details to be decided on a case-by-case basis. Obviously a method where empirical parameterization is kept to the absolute minimum or is absent altogether will offer more 'degrees of freedom' in this regard than the one where a minor change in the protocol would, for consistency, require reparameterization against a large experimental data set. Yet
our general guideline was that, while such choices should be possible for an experienced computational chemist, they should not be an essential part of the process itself.

2. STEPS IN THE W1 AND W2 THEORIES, AND THEIR JUSTIFICATION

The more cost-effective W1 theory and the more rigorous W2 theory have a lot of points in common. Aside from issues relating to the reference geometry and the zero-point energy, the main difference concerns the basis sets used in the extrapolation steps for the SCF and the valence correlation contribution.

These basis sets belong to the "correlation consistent" family of Dunning and coworkers [2, 3]. The correlation consistent (cc) basis sets, besides being arguably the most compact ones in their accuracy range [4], have the important property that, by design, they treat radial and angular correlation in a balanced way. In addition to the regular cc-pVnZ (correlation consistent polarized valence n-tuple zeta, or VnZ for short) basis sets, several variants have been published. In particular we note the aug-cc-pVnZ or AVnZ basis sets [5] for anions (with the combination of regular cc-pVnZ on hydrogen and aug-cc-pVnZ on other elements generally being denoted aug'-cc-pVnZ [6], or AVnZ for short), the MT (Martin-Taylor [7, 8]) and cc-pCVnZ [9] basis sets for inner-shell correlation, and the cc-pVnZ+1 [10], cc-pVnZ+2d1f [11], and (most recently) cc-pV(n+d)Z [12] basis sets for second-row atoms exhibiting ‘inner polarization’ [11] (vide infra).

We consider here the following sequence of correlation consistent basis sets: A'VDZ+2d, A'VTZ+2d1f, A'VQZ+2d1f, and A'V5Z+2d1f, which we shall denote "small", "medium", "large", and "extra large" (for first-and second-row compounds, these basis sets are of spd, spdf, spdfg, and spdfgh quality, respectively). W1 theory, then, carries out all extrapolations using "small", "medium", and "large", while W2 theory employs "medium", "large", and "extra-large" basis sets.

The W1 and W2 protocols for obtaining the total atomization energy (TAE) of a given molecule involve the following steps:

1. Geometry optimization at the B3LYP/VTZ+1 level for W1, and at the CCSD(T)/VQZ+1 level for W2.

2. Extrapolation of the SCF component of TAE from the "small", "medium", and "large" basis sets (W1) or "medium", "large", and "extra-large" basis sets (W2), by means of either the geometric
extrapolation formula \( E(n) = E_\infty + A/B^n \) (old-style) or the two-point formula \( E(n) = E_\infty + A/n^5 \) (new-style).

3. Extrapolation of the CCSD valence correlation component of TAE from the "medium" and "large" basis sets (W1) or from the "large" and "extra-large" basis sets (W2) employing the two-point formula \( E(n) = E_\infty + A/B^n \), where \( \alpha = 3.22 \) (W1) or 3 exactly (W2).

4. Extrapolation of the contribution to TAE of the connected triple excitations, (T), from the valence orbitals using the same formulae as for CCSD, but employing instead the "small" and "medium" basis sets (W1) or the "medium" and "large" basis sets (W2).

5. The contribution of inner-shell correlation is taken as the difference between the CCSD(T)/MTsmall TAE with and without constraining the inner-shell orbitals to be doubly occupied.

6. The scalar relativistic contribution is computed as the first-order Darwin and mass-velocity corrections from the ACPF/MTsmall wave function, including inner-shell correlation.

7. The contribution to TAE of spin-orbit splitting in the constituent atoms is trivially obtained from a tabulation, while for molecules in degenerate ground states, CISD/MTsmall spin-orbit splittings are computed (allowing correlation from the 2s and 2p orbitals in second-row atoms).

8. The zero-point vibrational energy (\( E_{ZPV} \)) is obtained from harmonic B3LYP/VTZ+1 frequencies scaled by 0.985 in the case of W1 theory. For W2 theory, anharmonic values of \( E_{ZPV} \) from quartic force fields at the CCSD(T)/VQZ+1 (or comparable) level are preferred; where this is not feasible, the same procedure as for W1 theory is followed as a "fallback solution".

We shall now proceed to explain in detail these steps and the rationale behind them.

### 2.1. Reference Geometry

Near the equilibrium geometry, dependence of the energy on geometric displacements is approximately quadratic. As a result, small errors in the reference geometry will insignificantly affect computed energies, but more substantial errors (say, several hundredths of an Å in covalent bond lengths) will compromise the reliability of a thermochemical calculation.
For W1 theory, we chose B3LYP [13, 14] density functional theory with the VTZ+1 basis set as the level of theory for the reference geometry, where the +1 suffix denotes the addition to second-row atoms of the highest-exponent \( d \) function from the V5Z basis set [10]. For first-row molecules, B3LYP/VTZ bond lengths are generally within 0.003 Å from experiment [15]; for second-row molecules, significant errors can be seen [10, 16] unless a tight \( d \) function is added to the basis set to account for inner polarization (see below).

For W2 theory, we opted for CCSD(T)/VQZ+1 as the level of theory for reference geometries. For geometries, the VQZ basis set is known to be close to the one-particle basis set limit [17, 18], while the addition of the inner polarization functions again takes care of inner polarization effects.

\subsection*{2.2. The SCF Component of TAE}

For systems devoid of nondynamical correlation effects, this is the largest individual contribution to the molecular binding energy. Its basis set convergence is relatively rapid, yet our discussion will be disproportionately long because a number of the "dramatis personae" that reappear in the remainder of the story need to be introduced here.

For the SCF energy, we can – at least for small systems – obtain an exact answer by means of numerical SCF calculations. There is substantial empirical evidence that its convergence behavior is exponential. Jensen studied the SCF convergence behavior of the SCF energy in \( \text{H}_2 \) [19] and \( \text{H}_3^+ \) and \( \text{N}_2 \) [20] and found clear evidence of geometric convergence behavior in terms of both the maximum angular momentum in the basis set and the number of primitives within a given angular momentum.

Martin and Taylor [21] compared numerical SCF energies with extrapolations from calculated SCF/A’VQZ, SCF/A’V5Z, and SCF/A’V6Z energies using the formula

\[ E(L) = E_\infty + A/L^B \]

which is equivalent to \( E(L) = E_\infty + A \exp(-BL) \) originally proposed by Feller [22]) and, for a number of number of molecules, found discrepancies of 10 µEh or less between the numerical and extrapolated values.

Petersson et al. had earlier proposed [23] an alternative expression \( E(n) = E_\infty + \sum_{l=n+1}^{\infty} A/(l+1/2)^b \) in the context of the CBS methods developed in his group. The summation is carried out numerically in that paper, but in fact an elegant analytical approximation exists for
summations of this type:

\[
\sum_{m=L+1}^{\infty} \frac{A}{(m + 1/2)^n} = \frac{A\psi^{(n-1)}(L + 3/2)}{(n-1)!},
\]  

(2.2)

where \(\psi^{(n)}(x)\) represents the order \(n\) polygamma function [24] of \(x\). Its asymptotic expansion has the leading terms

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

\[
= (-1)^{n-1} \frac{(n-1)!}{(x-1/2)^n} + O(x^{-n-2}).
\]  

(2.3)

Hence

\[
\frac{A\psi^{(n-1)}(L + 3/2)}{(n-1)!} = \frac{(-1)^{n-2}A(n-2)!}{(n-1)!(L+1)^{n-1}} + O(L^{-(n+1)})
\]

\[
\approx \frac{A}{(n-1)(L+1)^{n-1}}.
\]  

(2.4)

This suggests the simple extrapolation formula \(E(n) = E_\infty + A/n^5\), i.e. \(E_\infty = E(n) + \frac{E(n)-E(n-1)}{(n/n-1)^{n-1}}\), where \(n\) is identified with the “\(n\)-tuple zetanness” of the Dunning correlation consistent VnZ basis sets. (For hydrogen and helium, \(n\) equals the maximum angular momentum plus one; for the main group elements it is equal to the maximum angular momentum). While an argumentation in favor of the Petersson-type formula can be built on the convergence behavior of triplet-coupled pairs, neither this formula nor the geometric one have a solid formal basis.

Fortunately, convergence on the SCF component of atomization energies is even more rapid than for the total energies; Martin and Taylor found for 14 first-row molecules [25] that differences between unextrapolated SCF/A’V5Z, geometrical extrapolations from SCF/A’V{T,Q,5}Z, and \(A + B/L^5\) extrapolations from SCF/A’V{Q,5}Z results are on the order of 0.01 kcal/mol. For the method that we designated W2, which uses this basis set sequence, the choice of SCF extrapolation method is largely a non-issue. For the method that we designated W1, however, the geometric formula entails the use of results from the comparatively small A’VDZ basis set, which compromises the reliability of extrapolated SCF limits in systems with slow basis set convergence. In some cases (see Table 1 in Ref. 26), these can lead to errors of several kcal/mol. In addition, the two-point \(A + B/L^5\) formula has the elegant property
that it becomes immaterial whether the extrapolation is carried out on a reaction energy or on the individual absolute energies.

In the original W1/W2 paper [1], we opted for the geometric formula in view of the observed geometric convergence behavior. In a subsequent validation study [26] on a much wider variety of systems, we however found the two-point formula to be much more reliable, and we have adopted it henceforth.

Finally, an issue that arises with second-row systems should be addressed. It was first noted by Bauschlicher and Partridge [27] that the atomization energy of SO$_2$ is exceedingly sensitive to the presence of high-exponent $d$ and $f$ functions in the basis set. This phenomenon was ascribed to hypervalence; Martin and Uzan [10], however, found that the same phenomenon exists in systems that cannot be considered hypervalent by the wildest stretch of the imagination, like AlF. In addition, it was found [11, 16] that properties other than the energy are affected as well, with (e.g. in SO$_2$ [11] and SO$_3$ [16]) errors of up to 50 cm$^{-1}$ in harmonic frequencies and hundredths of Å in bond lengths unless high-exponent $d$ and $f$ functions (termed "inner polarization functions") in Ref. 11 are added to the basis set.

We should note that inner polarization is strictly an SCF-level effect: while, for instance, switching from an A′VDZ to an A′VDZ+2d basis set affects the computed atomization energy of SO$_3$ by as much as 40 kcal/mol (!), almost all of this effect is seen in the SCF component of the TAE [28]. In fact, we have recently found [29] that the effect persists if the (1s, 2s, 2p) orbitals on the second-row atom are all replaced by a pseudopotential. What is really getting "polarized" here is the inner part of the valence orbitals, which requires polarizations functions that are much "tighter" (higher-exponent) than those required for the outer part of the valence orbital. The fact that these inner polarization functions are in the same exponent range as the $d$ and $f$ functions required for correlation out of the (2s, 2p) orbitals is merely coincidental; the "inner polarization" effect has nothing to do with correlation, let alone with inner-shell correlation.

After extensive numerical experimentation, we have decided [1] on the sequence of basis sets noted above: "small" A′VDZ+2d, "medium" A′VTZ+2d1f, "large" A′VQZ+2d1f, and "extra large" A′V5Z+2d1f.

As the present review was being finalized for publication, we received a preprint by Dunning et al. [12] where new cc-pV(n+d)Z basis sets are proposed for the second-row atoms. These basis sets do have just an added tight $d$ function (hence the acronym) and no tight $f$ functions, but the remaining $d$ functions in the underlying cc-pVnZ basis set are in
addition reoptimized. We are currently investigating their performance in W1 and W2-type schemes.

2.3. The CCSD Valence Correlation Component of TAE

The valence correlation component of TAE is the only one that can rival the SCF component in importance. As is well known by now (and is a logical consequence of the structure of the exact nonrelativistic Born-Oppenheimer Hamiltonian on one hand, and the use of a Hartree-Fock reference wavefunction on the other hand), molecular correlation energies tend to be dominated by double excitations and disconnected products thereof. Single excitation energies become important only in systems with appreciable nondynamical correlation. Nonetheless, since the number of single-excitation amplitudes is so small compared to the double-excitation amplitudes, there is no point in treating them separately.

For all intents and purposes then, we are concerned here with the CCSD (coupled cluster with all single and double substitutions \[30\]) correlation energy. Its convergence is excruciatingly slow: Schwartz \[31\] showed as early as 1963 that the increments of successive angular momenta \(l\) to the second-order correlation energy of helium-like atoms converge as

\[
\Delta E(l) = \frac{A}{l + 1/2}^4 + \frac{B}{l + 1/2}^6 + \ldots . \tag{2.5}
\]

His conclusions were generalized to other methods and general pair correlation energies by Hill \[32\] and by Kutzelnigg and Morgan \[33\].

This clearly spells a rather bleak picture of basis set convergence. Indeed, Martin \[17\] showed in 1994 that while convergence of \(\sigma\) bond energies appeared in sight at the CCSD(T)/\(spdfg\) level, this did not yet appear to be the case for \(\pi\) bond energies. This earlier study was extended in 1996 \[34\] to basis sets of \(spdfgh\) quality: somewhat depressingly, residual errors in the binding energies as high as 2 kcal/mol were still found for small systems.

However, rather than "knuckling under" to Eq.(2.5) at this stage, we might instead exploit it for an extrapolation formula. Martin \[34\] suggested a three-point extrapolation of the form \(A + B/(n + 1/2)^C\) (where \(n\) is identified with the cardinal number of the cc-pVnZ basis set), and obtained dramatically improved computed total atomization energies. A slight further improvement was achieved if the SCF and valence correlation energies – which have fundamentally different convergence behaviors – are extrapolated separately using the respective appropriate formulae \[25\].
The denominator shift of 1/2 was chosen as a compromise between the situation for hydrogen and helium (where \( n = l + 1 \) for the cc-pVnZ basis set) and main-group elements (where \( n = 1 \)). As is immediately obvious upon series expansion, there is considerable coupling between the denominator shift and the exponent. As a result, the three-point extrapolation generally leads to exponents well in excess of three [34].

Halkier et al. [35] found that the simple expression \( E(L) = E_\infty + A/L^3 \) [i.e. \( E_\infty = E(L) + \frac{E(L)-E(L-1)}{(L/L-1)-1} \)] works at least equally well. In view of its simplicity and the fact that no results with the questionable A'VDZ basis set are required, we have adopted this simple formula for extrapolation of the CCSD valence correlation energy in W1 and W2 theories.

For the smaller basis sets used in W1 theory, the regime where the leading \( E_\infty + A/L^3 \) term dominates convergence behavior has not yet been reached, and using the formula in its unmodified form leads to overestimated (in absolute value) CCSD limits. One unelegant solution would be the use of three-term extrapolations like \( E_\infty + A/L^3 + B/L^4 \), but in light of the poor quality of the VDZ basis set this is a most unsatisfactory alternative. Another alternative is the use of a two-point extrapolation \( E_\infty + A/L^\alpha \), in which \( \alpha \) is a fixed empirical parameter. By minimizing the deviation from the W2 CCSD limit for the so-called W2-1 set of 28 molecules (vide infra), we determined \( \alpha = 3.22 \), which is the value used in W1 theory and its variants.

2.4. Connected Triple Excitations: the (T) Valence Correlation Component of TAE

It has been well known for some time (e.g. [36]) that the next component in importance is that of connected triple excitations. By far the most cost-effective way of estimating them has been the quasiper-turbative approach known as CCSD(T) introduced by Raghavachari et al. [37], in which the fourth-order and fifth-order perturbation theory expressions for the most important terms are used with the converged CCSD amplitudes for the first-order wavefunction. This account for substantial fractions of the higher-order contributions; a very recent detailed analysis by Cremer and He [38] suggests that 87, 80, and 72 %, respectively, of the sixth-, seventh-, and eighth-order terms appearing in the much more expensive CCSDT-1a method are included implicitly in CCSD(T).

Nevertheless, the formidable \( n^3N^4 \) (with \( n \) the number of electrons and \( N \) the number of basis functions) cost scaling of the CCSD(T)
method creates a substantial barrier to applications of methods that require A’V5Z+2d1f basis sets. However, two things should be kept in mind. First of all, the (T) component of TAE is a small fraction of the CCSD component, and hence a larger relative error can be tolerated. Secondly, evidence exists [39] that basis set convergence of the (T) contribution is substantially more rapid than that of the CCSD energy.

As a result, one may justifiably extrapolate the (T) contribution from smaller basis sets than its CCSD counterpart: in W1 theory, we extrapolate from the "small" and "medium" basis sets, and in W2 theory from the "medium" and "large" basis sets. This means that the most extensive basis sets in the calculations, namely "large" in W1 theory and "extra large" in W2 theory only require CCSD calculations, which are both much less expensive than CCSD(T) and much more amenable to direct algorithms such as those described in Refs. 40-41.

2.5. The Inner-Shell Correlation Component of TAE

Inner-shell correlation is a substantial part of the absolute correlation energy even for late first-row systems; for second-row systems, it in fact rivals the absolute valence correlation energy in importance. However, its relative contribution to molecular TAEs is fairly small: in benzene, for instance, it amounts to less than 0.7 % of the TAE. Even so, at 7 kcal/mol, its contribution is important by any reasonable thermochemical standard. By the same token, a 1 % relative error in a 7 kcal/mol contribution is tolerable even by benchmark thermochemistry standards, while the same relative error in a 300 kcal/mol contribution would be unacceptable even by the "chemical accuracy" standards.

In addition, for thermochemical purposes we are primarily interested in the core-valence correlation, since we can reasonably expect the core-core contributions to largely cancel between the molecule and its constituent atoms. (The partitioning between core-core correlation – involving excitations only from inner-shell orbitals – and core-valence correlation – involving simultaneous excitations from valence and inner-shell orbitals – was first proposed by Bauschlicher, Langhoff, and Taylor [42]).

For these reasons, we feel justified in treating the inner-shell correlation contribution to TAE as a separate contribution, rather than together with the valence correlation. There are substantial cost advantages to this: rather than having to carry out very elaborate all-electrons-correlated CCSD(T) calculations in basis sets near saturation for both valence and inner-shell correlation, we can limit these costly calculations to a basis set that is primarily saturated for inner-shell correlation.
Inner-shell correlation contributions for the W2-1 set were studied in some detail in the original W1/W2 paper, while subsequently, Martin, Sundermann, Fast, and Truhlar (MSFT) [43] studied inner-shell correlation contributions to TAE for 125 molecules spanning the first two rows of the periodic table. The following conclusions can be drawn from these two studies: (a) the use of the CCSD(T) electron correlation method is absolutely required for reliable contributions: the use of MP2 or CCSD can lead to underestimates in the order of 50%; (b) the smallest basis set which gives acceptable agreement with near-basis set limit contributions is the MTsmall basis set, which is a completely decontracted cc-pVTZ basis set with (2d1f) additional high-exponent correlation functions; (c) the effect of including even higher excitations in the correlation treatment is insignificant.

A tentative explanation for the importance of connected triple excitations for the inner-shell contribution to TAE can be found in the need to account for simultaneously correlating a valence orbital and relaxing an inner-shell orbital, or conversely, requiring a double and a single excitation simultaneously.

In principle, one could contract at least the few innermost s primitives and reduce the basis set further. By leaving the basis set completely uncontracted, however, we can recycle the integrals and SCF wavefunction for the next step of the calculation.

Finally, it is generally advised not to correlate the very deep-lying (1s) orbitals on second-row elements, as the MTsmall basis set does not have angular correlation functions in the required exponent range, and in addition the orbitals concerned are in the same energy range as the (2s, 2p) orbitals in third-row main group elements, for which being able to take a [Ne] core out of the correlation problem does result in appreciable CPU time savings.

### 2.6. Scalar Relativistic Correction

The importance of scalar relativistic effects for compounds of transition metals and/or heavy main group elements is well established by now [44]. Somewhat surprisingly (at first sight), they may have non-trivial contributions to the TAE of first-row and second-row systems as well, in particular if several polar bonds to a group VI or VII element are involved. For instance, in BF$_3$, SO$_3$, and SiF$_4$, scalar relativistic effects reduce TAE by 0.7, 1.2, and 1.9 kcal/mol, respectively – quantities which clearly matter even if only ”chemical accuracy” is sought. Likewise, in a benchmark study on the electron affinities of the first-and second-row atoms [45] – where we were able to reproduce the experimental values to
within 0.001 eV on average – we saw that neglect of the scalar relativistic contributions increased mean deviation from experiment by more than an order of magnitude.

Perhaps the simplest and most cost-effective way of treating relativistic contributions in an all-electron framework is the first-order perturbation theory of the one-electron Darwin and mass-velocity operators [46, 47]. For variational wavefunctions, these contributions can be evaluated very efficiently as expectation values of one-electron operators.

It has been found repeatedly [1, 43, 45] that scalar relativistic contributions are overestimated by about 20–25% in absolute value at the SCF level. Hence inclusion of electron correlation is essential: we found the ACPF method (which is both variational and approximately size extensive) to be an excellent compromise between quality and cost. It is reasonable to suppose that for a property that becomes more important as one approaches the nucleus, one wants maximum flexibility of the wavefunction near the nucleus as well as correlation of all electrons; thus we finally opted for ACPF/MTsmall as our approach of choice. Typically the cost of the scalar relativistic step is a fairly small fraction of that of the core correlation step, since only $n^2N^4$ scaling is involved in the ACPF calculations.

Bauschlicher [48] compared a number of approximate approaches for scalar relativistic effects to Douglas-Kroll quasirelativistic CCSD(T) calculations. He found that the ACPF/MTsmall level of theory faithfully reproduces his more rigorous calculations, while the use of non-size extensive approaches like CISD leads to serious errors. For third-row main group systems, studies by the same author [49] indicate that more rigorous approaches may be in order.

### 2.7. Spin-Orbit Coupling

The other relativistic effect entirely neglected so far is the spin-orbit coupling. For systems in nondegenerate states, the only first-order contribution to TAE comes from the fine structures in the corresponding atoms. Their effects can trivially be obtained from the observed electronic spectra, and hence the computational cost of this correction is fundamentally zero.

For systems in degenerate states, first-order corrections may need to be computed. In our work [26] we found that this significantly reduced the mean absolute error for the G2-1 and G2-2 test sets for ionization potentials and electron affinities, in no small part due to the preponderance of atoms and linear molecules in these sets. We found that CISD/MTsmall generally yields quite satisfactory spin-orbit correc-
tions, but that it is advisable to correlate the \((2s, 2p)\)-like electrons in the second-row elements. For the halogen atoms, convergence of these contributions with the level of theory was studied in some detail by Nicklass et al. \[50\]. These authors came to fundamentally the same conclusions.

2.8. The Zero-Point Vibrational Energy

It has been noted repeatedly (e.g. \[51, 52, 53\]) that one-half the sum of the harmonic frequencies, \(\frac{1}{2} \sum \omega_i d_i\) (with \(d_i\) representing the degeneracy of mode \(i\)) generally leads to an overestimate of the \(E_{ZPV}\), and that one-half the sum of the fundamentals, \(\frac{1}{2} \sum \nu_i d_i\), generally leads to an underestimate. In fact, it is easily shown that the average of these two estimates is a fairly good approximation to the anharmonic \(E_{ZPV}\).

For the sake of convenience, we shall restrict ourselves to the case of symmetric tops, asymmetric tops being a special case thereof with no degenerate modes. Including only up to first-order anharmonicities \(X_{ij}\), and excluding the small constant \(E_0\), the vibrational energy is given as

\[
G(n, l) = \sum_i \omega_i (n_i + \frac{d_i}{2}) + \sum_{i \leq j} X_{ij} (n_i + \frac{d_i}{2})(n_j + \frac{d_j}{2}) + S(l),
\]

(2.6)

in which \(S\) is the splitting term involving the angular momenta \(l\) of the degenerate vibrations, and \(n_i\) represents the vibrational quantum number for mode \(i\). It trivially follows that the zero-point energy \(E_{ZPV}\) is given by

\[
E_{ZPV} = \sum_i \omega_i \frac{d_i}{2} + \sum_{i \leq j} X_{ij} \frac{d_i d_j}{4}.
\]

(2.7)

In addition we find that [introducing the shorthand \(G(n, l)^0 \equiv G(n, l) - G(0)\)]

\[
G(n, l)^0 = \sum_i \omega_i n_i + \sum_{i \leq j} X_{ij} [(n_i + \frac{d_i}{2})(n_j + \frac{d_j}{2}) - \frac{d_i d_j}{4}] + S(l)
\]

\[
= \sum_i \omega_i n_i + \sum_{i \leq j} X_{ij} [n_i n_j + \frac{d_i}{2} n_j + n_j \frac{d_j}{2}] + S(l)
\]

\[
= \sum_i \omega_i n_i + \sum_i X_{ii} n_i (n_i + d_i)
\]

\[
+ \frac{1}{2} \sum_{i \neq j} X_{ij} [n_i n_j + \frac{d_i}{2} n_j + n_j \frac{d_j}{2}] + S(l).\]

(2.8)

Now assume only \(n_k\) is nonzero, then
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\[
G(n_k, l_k)^0 = \omega_k n_k + X_{kk} n_k (n_k + d_k)
\]

\[
+ \frac{1}{2} \sum_{i \neq k} (X_{ik} + X_{ki}) \frac{n_k d_i}{2} + S(l_k)
\]

\[
= \omega_k n_k + X_{kk} n_k (n_k + d_k) + \sum_{i \neq k} X_{ik} n_k \frac{d_i}{2} + G_{kk} l_k^2.
\]

(2.9)

It then follows that

\[
\sum_k \nu_k \frac{d_k}{2} = \sum_k \omega_k \frac{d_k}{2} + \sum_k X_{kk} \frac{d_k(1 + d_k)}{2} + \sum_k \sum_{i \neq k} X_{ik} \frac{d_i d_k}{4}
\]

\[
+ \text{degen.} \sum_k \frac{d_k}{2} G_{kk} l_k^2
\]

\[
= \sum_k \omega_k \frac{d_k}{2} + \sum_k X_{kk} \frac{d_k^2}{2} + \sum_k X_{kk} \frac{d_k}{2} + \sum_{k \geq i} X_{ik} \frac{d_i d_k}{2}
\]

\[
+ \text{degen.} \sum_k \frac{d_k}{2} G_{kk} l_k^2
\]

\[
= \sum_k \omega_k \frac{d_k}{2} + \sum_{k \geq i} X_{ik} \frac{d_i d_k}{2} + \sum_k X_{kk} \frac{d_k}{2} + \sum_k \frac{d_k}{2} G_{kk} l_k^2.
\]

(2.10)

That is,

\[
\sum_k (\nu_k + \omega_k) \frac{d_k}{4} = \sum_k \omega_k \frac{d_k}{2} + \sum_{k \geq i} X_{ik} \frac{d_i d_k}{4} + \sum_k X_{kk} \frac{d_k}{4}
\]

\[
+ \text{degen.} \sum_k \frac{d_k}{4} G_{kk} l_k^2
\]

\[
= E_{ZPV} + \sum_k X_{kk} \frac{d_k}{4} + \text{degen.} \sum_k \frac{d_k}{4} G_{kk} l_k^2, \ (2.11)
\]

in which the $G_{kk}$ are the diagonal $l$-coupling constants. The last term is generally negligible. If so desired, the term involving the diagonal anhar-
monicity constants can be estimated from anharmonicities in diatomic molecules.

The common practice of scaling computed vibrational frequencies for comparison with experimental fundamentals attempts at approximately addressing two issues: (a) the imperfections of the theoretical model for the harmonic frequency (which for CCSD(T), or even B3LYP, in sufficiently large basis sets is basically unnecessary); and (b) the anharmonic contribution to the fundamental. The above analysis suggests that a scaling factor that is intermediate between those used for reproducing harmonics and fundamentals would be the most appropriate for anharmonicities. In the original W1 paper [1], we considered the essentially exact anharmonic values of $E_{ZPV}$ of the 28 W2-1 molecules (determined from experiment or large basis set CCSD(T) quartic force field calculations, e.g. [54] and the references therein) and found the appropriate scaling factor for B3LYP/VTZ+1 harmonic frequencies to be 0.985. The largest individual deviation between the scaled harmonic and exact anharmonic values of $E_{ZPV}$ was only 0.3 kcal/mol (for PH$_3$).

Some of the above remarks are probably best illustrated by an example. For benzene, a B3LYP/TZ2P quartic force field was computed by Handy and coworkers [55]. From the published anharmonicity constants (specifically, the set deperturbed for Fermi resonances closer than 100 cm$^{-1}$), we obtain an anharmonic $E_{ZPV}$ of 62.04 kcal/mol. For comparison, one-half the sum of the harmonics comes out 0.9 kcal/mol too high at 62.96 kcal/mol, and one-half the sum of the fundamentals comes out 1 kcal/mol too low at 60.98 kcal/mol. The average of both values, 61.97 kcal/mol, is in excellent agreement with the anharmonic value, while the W1 estimate accidentally agrees to within two decimal places with the B3LYP/TZ2P anharmonic value. From the best available computed harmonic frequencies [56] and the best available experimental fundamentals [55], we obtain $E_{ZPV} = 62.01$ kcal/mol or, after correction for the difference between this estimate and the true anharmonic $E_{ZPV}$ at the B3LYP/TZ2P level, 0.07 kcal/mol, we find $E_{ZPV} = 62.08$ kcal/mol as possibly the best estimate. (Note that HF/6-31G* harmonic frequencies scaled by 0.8929, as used in G2 and G3 theories, yields only 60.33 kcal/mol. In this accuracy range, one certainly cannot indulge in a 1.7 kcal/mol underestimate in the zero-point energy!)

In a recent benchmark study [57] on the CH$_2$=NH molecule, we explicitly computed a CCSD(T)/VTZ quartic force field at great expense (the low symmetry necessitated the computation of 2241 energy points in $C_s$ symmetry and 460 additional points in $C_1$ symmetry). The resulting anharmonic $E_{ZPV}$, 24.69 kcal/mol, is only 0.10 kcal/mol above the scaled B3LYP/VTZ estimate, 24.59 kcal/mol. At least for fairly rigid
molecules, it appears hard to justify the additional expense and effort for the anharmonic force field unless it were required anyway for other purposes.

If we use B3LYP/VTZ+1 harmonics scaled by 0.985 for the E\textsubscript{ZPV} rather than the actual anharmonic values, mean absolute error at the W1 level deteriorates from 0.37 to 0.40 kcal/mol, which most users would regard as insignificant. At the W2 level, however, we see a somewhat more noticeable degradation from 0.23 to 0.30 kcal/mol — if kJ/mol accuracy is required, literally "every little bit counts". If one is primarily concerned with keeping the maximum absolute error down, rather than getting sub-kJ/mol accuracy for individual molecules, the use of B3LYP/VTZ+1 harmonic values of E\textsubscript{ZPV} scaled by 0.985 is an acceptable "fallback solution". The same would appear to be true for thermochemical properties to which the E\textsubscript{ZPV} contribution is smaller than for the TAE (e.g., ionization potentials, electron affinities, proton affinities, and the like).

3. PERFORMANCE OF W1 AND W2 THEORIES

A reliable assessment of the performance of a method in the kJ/mol accuracy range is, by its very nature, only possible where experimental data are themselves known to this accuracy.

3.1. Atomization Energies (the W2-1 Set)

In the original W1/W2 paper [1], we selected a set of 28 first- and second-row molecules (which we shall call the W2-1 set) containing at most three nonhydrogen atoms for which (a) the experimental total atomization energies $\sum D_0$ are available to the highest possible accuracy (preferably 0.1 kcal/mol); (b) no strong nondynamical correlation effects exist that would hinder the applicability of single-reference electron correlation methods; (c) near-exact anharmonic values of E\textsubscript{ZPV} are available from either experimental anharmonicity constants or highly accurate ab initio anharmonic force fields.

Results using W1 and W2 theories are shown in Table 2.1. For W2 theory we find a mean absolute deviation (MAD) of 0.23 kcal/mol, which further drops to 0.18 kcal/mol when the NO, O\textsubscript{2}, and F\textsubscript{2} molecules are deleted (all of which have mild nondynamical correlation in common). Our largest deviation is 0.70 kcal/mol. We can hence state that W2 meets our design goals.
Table 2.1  Comparison of W2 and W1 theories, and their variants for the evaluation of TAE₀ (kcal/mol) for the W2-1 test set.

| Species | Experimentalᵃ | Deviation (experiment – theory) |
|---------|---------------|---------------------------------|
|         | TAE₀ ± (uncert.) | W²ᵇ  W²ᶜ  W²ʰᵈ  W¹  W¹ʰᵈ  W¹ᶜ |
| H₂      | 103.27 0.00  | -0.05 -0.04  | -0.07  | -0.07 |
| N₂      | 225.06 0.04  | 0.36 0.45   | 0.53   | 0.54  |
| O₂      | 117.97 0.04  | 0.64 0.68   | 0.41   | 0.18  |
| F₂      | 36.94 0.10   | 0.60 0.78   | 0.70   | 0.52  |
| HF      | 135.33 0.17  | 0.02 -0.07  | -0.47  | -0.41 |
| CH      | 79.90 0.23   | -0.08 -0.15 | -0.14  | -0.11 -0.37 |
| CO      | 256.16 0.12  | 0.12 0.12   | 0.14   | -0.08 -0.06 -0.41 |
| NO      | 149.82 0.03  | 0.47 0.54   | 0.56   | 0.33  |
| CS      | 169.41 0.23  | 0.30 0.31   | 0.32   | 0.77   0.95   0.46 |
| SO      | 123.58 0.04  | -0.02 -0.04 | 0.52   | 0.57  |
| HCl     | 102.24 0.02  | -0.04 -0.14 | -0.15  | -0.17 |
| CIF     | 60.36 0.01   | 0.09 0.08   | 0.15   | 0.03  |
| Cl₂     | 57.18 0.00   | -0.20 -0.24 | 0.60   | 0.50  |
| HNO     | 196.85 0.06  | 0.38 0.37   | 0.20   | -0.03 |
| CO₂     | 381.91 0.06  | 0.14 0.13   | 0.10   | -0.37 -0.34 -0.37 |
| H₂O     | 219.35 0.12  | -0.04 -0.14 | -0.55  | -0.58 |
| H₂S     | 173.15 0.12  | -0.37 -0.49 | -0.47  | -0.51 |
| HOCl    | 156.61 0.12  | -0.16 -0.24 | -0.18  | -0.40 |
| OCS     | 328.53 0.48  | -0.19 -0.21 | -0.21  | -0.01 0.11 0.10 |
| CICN    | 279.20 0.48  | 0.41 0.52   | 0.78   | 0.78   0.91   0.82 |
| SO₂     | 253.92 0.08  | -0.31 -0.33 | 0.63   | 0.81  |
| CH₃     | 289.00 0.10  | -0.21 -0.32 | -0.38  | -0.53 -0.51 -0.39 |
| NH₃     | 276.73 0.13  | 0.13 -0.03  | -0.28  | -0.17 |
| PH₃     | 227.13 0.41  | -0.01 0.28  | 0.23   | 0.05  |
| C₂H₂     | 388.90 0.24  | 0.42 0.64   | 0.53   | 0.26   0.51   0.29 |
| CH₂O    | 357.25 0.12  | -0.27 -0.40 | -0.35  | -0.59 -0.56 -0.76 |
| CH₄     | 392.51 0.14  | -0.11 -0.13 | -0.19  | -0.35 -0.47 -0.34 |
| C₂H₄     | 531.91 0.17  | -0.19 -0.31 | -0.32  | -0.63 -0.41 -0.72 |

Mean Absolute Deviation 0.23 0.29 0.30 0.40 0.41 0.39
Max. Absolute Deviation 0.64 0.78 0.78 0.78 0.95 0.82

ᵃ See [1] for experimental references.
ᵇ Values of E₂PV derived from anharmonic vibrational frequencies. See Ref. 1 for details.
ᶜ Values of E₂PV derived from B3LYP/VTZ+1 harmonic vibrational frequencies scaled by 0.985. Same remark applies to W²h, W¹, W¹h and W¹c data given.
ᵈ For systems where W²h and W¹h are equivalent to W² and W¹, respectively, entries have been left blank.
For W1 theory, MAD is increased to 0.37 kcal/mol (old SCF extrapolation) or 0.40 kcal/mol (new SCF extrapolation), with the maximum error being 0.78 kcal/mol. This should be compared with a MAD of 1.25 kcal/mol for G2 theory, 0.89 kcal/mol for G3 theory, 0.88 kcal/mol for CBS-Q, and 0.61 kcal/mol for CBS-QB3, and the much higher maximum errors of these methods of 4.90 kcal/mol (SO\textsubscript{2}), 3.80 kcal/mol (SO\textsubscript{2}), 3.10 kcal/mol (OCS), and 1.90 kcal/mol (OCS), respectively. While we would prefer to use W2 theory for no-nonsense benchmarking if at all possible, W1 theory still seems to offer great advantages over the other techniques.

### 3.2. Electron Affinities (the G2/97 Set)

Some representative results can be found in Table 2.2. For the G2-1 set of electron affinities, W1 theory has a mean absolute error of 0.016 eV [26]. Not unexpectedly – given the slow basis set convergence of electron affinities – the extra effort invested in W2 theory pays off with a further reduction of the mean absolute error to 0.012 eV. Accuracy appears to be limited principally by imperfections in the CCSD(T) method: for the atoms B–F and Al–Cl, using even larger basis sets we achieve 0.009 eV at the CCSD(T) level, which decreases to 0.001 eV if approximate full CI energies are used.

Normally W1 theory does not involve diffuse functions on H, Li, Na, Be, and Mg; not surprisingly, this leads to very poor electron affinities for Li and Na. Upon switching to W1aug (i.e. using augmented basis sets on all elements), perfect agreement with experiment is obtained. Within the G2-2 set, substantial discrepancies between W1 theory and experiment are found for O\textsubscript{3} and CH\textsubscript{2}NC, both of which are systems with pronounced multireference character. (The same remark applies to a lesser extent to FO.) Scalar relativistic effects almost invariably decrease the electron affinity. Neglect of spin-orbit splitting leads to significant deterioration in MAD.

### 3.3. Ionization Potentials (the G2/97 Set)

Some representative results can again be found in Table 2.2. At the W1 level, the G2-1 ionization potentials are reproduced with a MAD of only 0.013 eV [26]. No further improvement is seen at the W2 level for this property. Note that if the B3LYP/VTZ geometry for CH\textsubscript{4}\textsuperscript{+} is employed, a serious error is seen for IP(CH\textsubscript{4}) which disappears when a CCSD(T)/VTZ reference geometry is used instead. (Only BH & HLYP
Table 2.2 Comparison of W2 and W1 theories, and their variants for the evaluation of electron affinity and ionization potential (eV) for selected species from G2-1 test set.

| Species | Experimentala | Deviation (experiment - theory) |
|---------|---------------|---------------------------------|
|         | Value ± (uncert.) | W2 | W2h | W1 | W1h |
| Electron Affinities | | | | | |
| C       | 1.2629 0.0003 | 0.007 0.041 | 0.011 0.210 |
| Si      | 1.38946 0.0006 | 0.010 0.081 | 0.011 0.060 |
| CH      | 1.238 0.0078 | 0.029 0.060 | 0.032 0.248 |
| CH₂     | 0.652 0.006 | 0.002 0.042 | 0.011 0.236 |
| CH₃     | 0.08 0.03 | 0.034 0.088 | 0.051 0.284 |
| SiH     | 1.2771 0.0087 | 0.031 0.094 | 0.034 0.084 |
| SiH₂    | 1.123 0.022 | 0.039 0.088 | 0.043 0.087 |
| SiH₃    | 1.406 0.014 | 0.011 0.033 | 0.019 0.044 |
| CN      | 3.862 0.005 | -0.026 -0.036 | -0.031 -0.023 |
| Ionization Potentials | | | | | |
| B       | 8.29802 0.0002 | 0.007 0.009 | 0.019 0.020 |
| C       | 11.2603 0.0001 | 0.010 -0.002 | 0.012 0.012 |
| Al      | 5.986 0.001 | 0.023 0.022 | 0.024 0.025 |
| Si      | 8.15166 0.00003 | 0.018 -0.004 | 0.021 0.022 |
| CH₄ (b) | 12.61 0.01 | -0.033 -0.035 | -0.032 -0.035 |
| SiH₁    | 11 0.02 | 0.006 0.006 | -0.005 -0.005 |
| C₂H₂    | 11.403 0.0003 | -0.004 -0.004 | -0.001 0.005 |
| C₂H₄    | 10.5138 0.0006 | -0.001 0.001 | -0.005 0.000 |
| CO      | 14.0142 0.0003 | -0.014 -0.013 | -0.009 -0.008 |
| CS      | 11.33 0.01 | -0.017 -0.018 | -0.017 -0.016 |

a See Ref. 26 for experimental references.

b CCSD(T)/VTZ geometry. B3LYP/VTZ optimization erroneously yields D₂d structure for cation rather than correct C₂v symmetry. See Ref. 26 for details.

[58] and mPW1K [59] correctly predict a C₂v structure for CH₄⁺; other exchange-correlation functionals wrongly lead to a D₂ structure.

Inner-shell correlation contributions are found to be somewhat more important for ionization potentials than for electron affinities, which is understandable in terms of the creation of a valence ‘hole’ by ionization.
into which inner-shell electrons can be excited. Again, inclusion of spin-orbit splitting is worthwhile.

3.4. Heats of Formation (the G2/97 Set)

A detailed discussion and a table can be found in Ref. 26. First of all, we note that the mean uncertainty for the experimental values in the G2-1 set is itself 0.6 kcal/mol. MAD values for W1 and W2 theory stand at 0.6 and 0.5 kcal/mol, respectively, suggesting that these theoretical methods have a reliability comparable to the experimental data themselves.

For a subset of 27 G2-2 molecules with fairly small experimental uncertainties, W1 theory had MAD of 0.7 kcal/mol, compared to the average experimental uncertainty of 0.4 kcal/mol. Some systems exhibit deviations from experiment in excess of 1 kcal/mol: in the cases of BF$_3$ and CF$_4$, very slow basis set convergence is responsible, and W2 calculations in fact remove nearly all remaining disagreement with experiment for the latter system. (The best available value for BF$_3$ is itself a theoretical one, so a comparison would involve circular reasoning.) Other molecules (NO$_2$ and ClNO) suffer from severe multireference effects.

3.5. Proton Affinities

For proton affinities, W1 theory can basically be considered converged [26]. The W2 computed values are barely different from their W1 counterparts, and the latter’s MAD of 0.43 kcal/mol is well below the about 1 kcal/mol uncertainty in the experimental values. W1 theory would appear to be the tool of choice for the generation of benchmark proton affinity data for calibration of more approximate approaches.

4. VARIANTS AND SIMPLIFICATIONS

4.1. W1’ Theory

It was noted that the original W1 theory (old-style SCF extrapolation) performed considerably more poorly for second-row than for first-row species. This was ascribed to the lack of balance in the basis sets for second-row atoms used in the SCF and valence correlation steps of W1; in particular, the A/VTZ+2d1f basis set contains as many “tight” $d$ and $f$ functions as regular ones, which would appear to be a bit top-heavy.
It was proposed to replace the \( A^\prime \text{VTZ} + 2d \) basis set by \( A^\prime \text{VTZ} + 2d1f \), a conclusion borne out by calculations on the \( \text{SO}_3 \) molecule [28], which suffers from extreme inner polarization effects and as such provides a good "proving ground".

Compared to its prototype, the modification (the so-called \( W_1' \) theory) did appear to yield improved results for second-row molecules. However, in the \( W_1/W_2 \) validation study [26] we found this to be an artifact of the exaggerated sensitivity of the (old-style) 3-point geometric SCF extrapolation. Use of the new-style \( E_\infty + A/L^5 \) extrapolation largely eliminates both the problem and the difference between \( W_1 \) and \( W_1' \) theory.

### 4.2. \( W_1h \) and \( W_2h \) Theories

While the need for diffuse-function augmented basis sets for highly electronegative elements is well established (e.g. [34]), it could be argued that they are not really required on group III and IV elements. For organic-type molecules in particular, this would result in significant savings.

We define here \( W_1h \) and \( W_2h \) theories, respectively, as the modifications of \( W_1 \) theory for which \( AVnZ \) basis sets are only used on elements of groups V, VI, VII, and VIII, but regular \( VnZ \) basis sets on groups I, II, III, and IV. (The "h" stands for "heteroatom", as we originally investigated this for organic molecules.) For the purpose of the present paper, we have repeated the validation calculations described in the previous section for \( W_1h \) and \( W_2h \) theories. (For about half of the systems, \( W_1 \) and \( W_1h \) are trivially equivalent.) Some representative results can be found in Table 2.1 for atomization energies/heats of formation, and in Table 2.2 for ionization potentials and electron affinities.

For the heats of formation in the G2-1 set, the largest difference between \( W_1 \) and \( W_1h \) theory is 0.3 kcal/mol for \( \text{Si}_2 \); the average difference is less than 0.1 kcal/mol. For some of the systems in the G2-2 set, however, differences are more pronounced, e.g. 0.6 kcal/mol for \( \text{CF}_4 \) and 0.8 kcal/mol for benzene. (Note that the benzene calculation reported as an example application in the original \( W_1 \) paper [1] is in fact a \( W_1h \) calculation: the remaining small difference between that reference and the present work is due to the different SCF extrapolations used.) For the G2-1 heats of formation, \( W_2h \) and \( W_2 \) are essentially indistinguishable in quality, as could reasonably be expected.

For the G2-1 ionization potentials, the largest differences are 0.005 and 0.006 eV, respectively, for ethylene and acetylene. Differences in the G2-2 set are likewise small, although \( \text{Si}_2\text{H}_2 \) (0.009 eV) and \( \text{CH}_3\text{OF} \).
(0.024 eV) stand out. Clearly W1h is of a quality comparable to W1 for ionization potentials, and we recommend it as a moderately inexpensive high-accuracy method for this property. (As noted before, W2 does not represent an improvement over W1 for ionization potentials, and the same goes for W2h theory.)

For electron affinities, the differences between W1h and W1 are very pronounced, and become (as expected) particularly large (e.g. 0.284 eV in CH₃) for species where none of the atoms carry diffuse functions in W1h theory. The differences between W2 and W2h theory are still quite sizable, and in fact agreement with experiment for W2h is inferior to that for the less expensive W1 method. In summary, we do not recommend W1h or W2h for electron affinities.

4.3. A Bond-Equivalent Model for Inner-Shell Correlation

In a pilot W1h calculation on benzene [1], it was found that 85 % of the CPU time was spent on the inner-shell correlation step. Given that this contribution is about 0.5 % of the TAE of benzene, the CPU time proportion appears to be lopsided to say the least. On the other hand, a contribution of 7 kcal/mol clearly cannot be neglected by any reasonable standard. However, inner-shell correlation is by its very nature a much more local phenomenon than valence correlation, and a relative error of a few percent in such a small contribution is more tolerable than a corresponding error in the major contributions, Martin, Sundermann, Fast and Truhlar (MSFT) [43] investigated the applicability of a bond equivalent model.

We started by generating a data base of inner-shell correlation contributions for some 130 molecules that cover the first two rows of the periodic table. In order to reduce the number of parameters in the model to be fitted, we introduced a Mulliken-type approximation for the parameters $D_{AB} \approx (D_A+D_B)/2$. Furthermore we did retain different parameters for single and multiple bonds, but assumed $D_{A=B} \approx (3/2)D_{A=B}$.

The model (which requires essentially no CPU time) was found to work very satisfactorily; its performance for the W2-1 set can be seen in Table 2.3. Somewhat to our surprise, we found that the same model performs reasonably well when applied to the scalar relativistic contributions, albeit with larger individual deviations.

It was recently suggested by Nicklass and Peterson [60] that the use of core polarization potentials (CPPs) [61] could be an inexpensive and effective way to account for the effects of inner shell correlation. The great potential advantage of this indeed rather inexpensive method over the MSFT bond-equivalent model is that it does not depend on
Table 2.3  Comparison of core correlation contributions to TAE₀ (kcal/mol) for the W2-1 test set.

| Species | CCSD(T)/ very large\(^a\) | CCSD(T)/ MTsmall | MSFT model | CPP n = 1\(^b\) | CPP n = 2\(^b\) |
|---------|-----------------|-----------------|------------|----------------|----------------|
| H₂      | 0.00            | 0.00            | 0.00       |
| N₂      | 0.75            | 0.82            | 0.80       | 0.74           | 1.08           |
| O₂      | 0.24            | 0.24            | 0.50       | 0.28           | 0.43           |
| F₂      | -0.09           | -0.08           | 0.18       | 0.05           | 0.06           |
| HF      | 0.18            | 0.18            | 0.09       | 0.10           | 0.19           |
| CH      | 0.14            | 0.14            | 0.30       | 0.29           | 0.48           |
| CO      | 0.94            | 0.90            | 1.26       | 0.76           | 1.12           |
| NO      | 0.40            | 0.41            | 0.51       | 0.46           | 0.69           |
| CS      | 0.75            | 0.66            | 1.08       |
| SO      | 0.46            | 0.42            | 0.38       |
| HCl     | 0.20            | 0.15            | 0.15       |
| ClF     | 0.08            | 0.09            | 0.23       |
| Cl₂     | 0.19            | 0.18            | 0.29       |
| HNO     | 0.40            | 0.41            | 0.68       | 0.41           | 0.69           |
| CO₂     | 1.64            | 1.67            | 1.68       | 1.12           | 1.88           |
| H₂O     | 0.37            | 0.37            | 0.36       | 0.20           | 0.39           |
| H₂S     | 0.34            | 0.25            | 0.24       |
| HOCl    | 0.31            | 0.29            | 0.50       |
| OCS     | 1.68            | 1.58            | 1.49       |
| ClCN    | 1.76            | 1.71            | 1.73       |
| SO₂     | 0.67            | 0.78            | 0.68       |
| CH₃     | 1.04            | 1.04            | 0.89       | 0.37           | 0.84           |
| NH₃     | 0.62            | 0.64            | 0.49       | 0.29           | 0.62           |
| PH₃     | 0.30            | 0.22            | 0.35       |
| C₂H₂    | 2.44            | 2.34            | 2.38       | 1.17           | 2.17           |
| CH₂O    | 1.25            | 1.26            | 1.44       | 0.65           | 1.24           |
| CH₄     | 1.21            | 1.21            | 1.19       | 0.48           | 1.01           |
| C₂H₄    | 2.36            | 2.27            | 2.38       | 1.02           | 2.02           |

Mean Absolute Deviation: 0.04  0.12  0.39  0.19  0.19
Max. Absolute Deviation: 0.11  0.33  1.34  0.34  0.34

\(^a\) See Ref. 1 for details.
\(^b\) See Ref. 60 for details.
any explicit connectivity information. The different approximate treatments of inner-shell correlation are compared with large-scale CCSD(T) results for the W2-1 set in Table 2.3. As seen there, while the CPP approach is indeed quite promising (clearly superior to MP2 calculations, for instance), it clearly requires further refinement. The MSFT bond-equivalent model in fact outperforms all other approximate methods, with a computational cost that is essentially nil.

4.4. Reduced-Cost Approaches to the Scalar Relativistic Correction

The fact that the additivity model for the scalar relativistic correction worked at all is a pleasant surprise: yet alternatives clearly merit exploration. As noted above, the SCF-level scalar relativistic contributions of Kedziora et al. [62] are systematically overestimated. One possibility which suggests itself then would be applying a scaling factor to the SCF values: we have considered this approach for the set of 120 molecules for which ACPF/MTsmall data were generated by MSFT for the purposes of parameterizing their empirical model. However, rather than following the more elaborate approach of Kedziora et al., we simply evaluated the first-order Darwin and mass velocity corrections by perturbation theory. We considered variation of the basis set, and found not surprisingly that typical contracted VnZ basis sets are insufficiently flexible in the core region. We found VTZuc+1 (where VTZuc stands for an uncontracted cc-pVTZ basis set) to be the best compromise between cost and quality.

The best scale factor in the least-squares sense is 0.788; while the mean absolute error of 0.04 kcal/mol is more than acceptable, the maximum absolute error of 0.20 kcal/mol (for SO$_2$) is somewhat disappointing. Representative results (for the W2-1 set) can be found in Table 2.4.

This error can be considerably reduced, at very little cost, by employing B3LYP density functional theory instead of SCF. The scale factor, 0.896, is much closer to unity, and both mean and maximum absolute errors are cut in half compared to the scaled SCF level corrections. (The largest errors in the 120-molecule data set are 0.10 kcal/mol for P$_2$ and 0.09 kcal/mol for BeO.) It could in fact be argued that the remaining discrepancy between the scaled B3LYP/cc-pVTZuc+1 values is on the same order of magnitude as the uncertainty in the ACPF/MTsmall values themselves.
Table 2.4  Comparison of scalar relativistic effect contributions to TAE₀ (kcal/mol) for the W2-1 test set.

| Species | ACPF/MTsmall scaled 0.896 | MSFT model | B3LYP/VTZuc+1 scaled 0.788 | SCF/VTZuc+1 |
|---------|---------------------------|------------|-------------------------------|-------------|
| H₂      | 0.00                      | 0.00       | 0.00                          | 0.00        |
| N₂      | -0.11                     | -0.14      | -0.15                         | -0.16       |
| O₂      | -0.15                     | -0.30      | -0.18                         | -0.22       |
| F₂      | 0.03                      | -0.37      | -0.04                         | -0.09       |
| HF      | -0.20                     | -0.19      | -0.18                         | -0.20       |
| CH      | -0.03                     | -0.05      | -0.04                         | -0.04       |
| CO      | -0.14                     | -0.33      | -0.17                         | -0.19       |
| NO      | -0.16                     | -0.20      | -0.20                         | -0.22       |
| CS      | -0.15                     | -0.29      | -0.21                         | -0.25       |
| SO      | -0.31                     | -0.27      | -0.34                         | -0.40       |
| HCl     | -0.26                     | -0.17      | -0.25                         | -0.26       |
| ClF     | -0.12                     | -0.35      | -0.16                         | -0.23       |
| Cl₂     | -0.15                     | -0.34      | -0.19                         | -0.26       |
| HNO     | -0.24                     | -0.28      | -0.27                         | -0.29       |
| CO₂     | -0.45                     | -0.44      | -0.48                         | -0.50       |
| H₂O     | -0.26                     | -0.26      | -0.25                         | -0.26       |
| H₂S     | -0.41                     | -0.43      | -0.39                         | -0.40       |
| HOCl    | -0.28                     | -0.43      | -0.31                         | -0.37       |
| OCS     | -0.53                     | -0.41      | -0.57                         | -0.57       |
| ClCN    | -0.43                     | -0.40      | -0.47                         | -0.47       |
| SO₂     | -0.71                     | -0.61      | -0.79                         | -0.90       |
| CH₃     | -0.17                     | -0.14      | -0.17                         | -0.16       |
| NH₃     | -0.25                     | -0.24      | -0.25                         | -0.24       |
| PH₃     | -0.46                     | -0.60      | -0.45                         | -0.46       |
| C₂H₂    | -0.27                     | -0.31      | -0.28                         | -0.26       |
| CH₂O    | -0.32                     | -0.32      | -0.33                         | -0.34       |
| CH₄     | -0.19                     | -0.19      | -0.19                         | -0.18       |
| C₂H₄    | -0.33                     | -0.34      | -0.33                         | -0.31       |

Mean Absolute Deviation 0.08 0.03 0.05
Max. Absolute Deviation 0.40 0.08 0.20
4.5. W1c Theory

Here we propose a new reduced-cost variant of W1 theory which we shall denote W1c (for "cheap"), with W1ch theory being derived analogously from W1h theory. Specifically, the core correlation and scalar relativistic steps are replaced by the approximations outlined in the previous two sections, i.e. the MSFT bond additivity model for inner-shell correlation and scaled B3LYP/cc-pVTZuc+1 Darwin and mass-velocity corrections. Representative results (for the W2-1 set) can be seen in Table 2.1; complete data for the molecules in the G2-1 and G2-2 sets are available through the World Wide Web as supplementary material [63] to the present paper.

As seen in Table 2.1, W1c is an acceptable "fallback solution" for systems for which W1 calculations are not feasible because of the number of inner-shell orbitals; for heats of formation and certainly for ionization potentials, W1ch offers a significant further cost reduction over W1h at a negligible loss in accuracy.

4.6. Detecting Problems

While CCSD and especially CCSD(T) are known [36] to be less sensitive to nondynamical correlation effects than low-order perturbation theoretical methods, some sensitivity remains, and deterioration of W1 and W2 results is to be expected for systems that exhibit severe nondynamical correlation character. A number of indicators exist for this, such as the $T_1$ diagnostic of Lee and Taylor [64], the size of the largest amplitudes in the converged CCSD wavefunction, and natural orbital occupations of the frontier orbitals.

One pragmatic criterion which we have found to be very useful is the percentage of the TAE that gets recovered at the SCF level. For systems that are wholly dominated by dynamical correlation, like CH$_4$ and H$_2$, this proportion exceeds 80 %, while it drops to 50 % for the N$_2$ molecule, O$_2$ is only barely bound at the SCF level, and F$_2$ is even metastable. In the W1/W2 validation paper [26], we invariably found that large deviations from what appeared to be reliable experimental data tend to be associated with strong nondynamical correlation, and a small SCF component of TAE (e.g. 27 % for NO$_2$, 32 % for F$_2$O, and 15 % for ClO).

Would the use of full CCSDT [65] energies, instead of their quasi-perturbative-triples CCSD(T) counterparts, solve the problem? Our experience has taught us that this generally leads to a deterioration of the results; it has been shown (e.g. [66]) that the excellent performance
of CCSD(T) for binding energies is at least in part due to error compensation between partial neglect of higher-order $T_3$ effects and complete neglect of $T_4$ effects. Unfortunately, explicit treatment of $T_4$ (connected quadruple excitations) is at present not feasible for practical-sized systems.

For some very small systems (e.g. Be$_2$ [67] and OH/OH$^-$ [68]), we have considered what one might term W1CAS and W2CAS, in which the CCSD(T) calculations were replaced by full valence (or larger) CAS-ACPF calculations. The SCF extrapolation was then applied to the CASSCF (i.e. Hartree-Fock plus static correlation) energy, and the CCSD/CCSD(T) extrapolation to the dynamical correlation energy only. Aside from limited applicability due to the explosive increase in the number of reference configurations with the number of atoms, the formal objection of course applies that any separation between "internal" and "external" orbital spaces is to a large extent arbitrary.

Common sense also suggests that the larger the "gap" being bridged by the extrapolation from the actual computed number with the largest basis set to the hypothetical basis set limit, the larger the uncertainty in the latter will be. (See the example of benzene in section 5.3.)

Finally, the GIGO ("garbage in, garbage out") theorem applies here as well as in any other matter. For instance, if a B3LYP/cc-pVTZ+1 reference geometry is used for a system where the B3LYP geometry is known to be qualitatively wrong (such as CH$_4^+$), the computed W1 energetics will not be very reliable either.

5.  EXAMPLE APPLICATIONS

5.1.  Heats of Vaporization of Boron and Silicon

First-principle computation of gas-phase molecular heats of formation by definition requires the gas-phase heats of formation of the elements:

$$
\Delta H_f^0(X_k Y_l \cdots) = \Delta H_f^0(T) - k \Delta H_f^0(T) - \Delta H_f^0(Y) - \cdots
$$

Somewhat disappointingly, the values of $\Delta H_f^0[A(g)]$ of some first- and second-row elements A (notably boron and silicon) are not precisely known because of a variety of experimental difficulties. However, well-established precise heats of formation of BF$_3(g)$ [69] and SiF$_4$ [70] are
available that do not involve the heats of vaporization of boron and silicon in their determination. Thus, if accurate computed TAE$_0$ values of BF$_3$ and SiF$_4$ were available, then, in combination with the established value [71] of D$_0$(F$_2$), the quantities sought for could be derived from a thermochemical cycle. These were obtained by means of W2 theory for BF$_3$ [72] and for SiF$_4$ [73]. The final recommended values are $\Delta H_{f,0}^0[B(g)] = 135.1 \pm 0.75$ kcal/mol and $\Delta H_{f,0}^0[Si(g)] = 107.15 \pm 0.38$ kcal/mol. The boron value is about 2 kcal/mol higher than the CODATA recommended value and in between a recent evaluation by Hildenbrand [74] and a 1977 measurement by Storms and Mueller [75]. The silicon value is slightly higher than the CODATA recommended value, and with a much smaller uncertainty. We note in passing that one of the first arguments for revision of $\Delta H_{f,0}^0[B(g)]$ and $\Delta H_{f,0}^0[Si(g)]$ was given in [76] on computational (CBS-Q) grounds.

5.2. Validating DFT Methods for Transition States: the Walden Inversion

It is well known (e.g., [77, 78]) that the prediction of reaction barrier heights is one of the main "Achilles' heels" of density functional theory. For instance [79], for the prototype $S_N2$ reaction,

$$X^- + CH_3Y \rightarrow CH_3X + Y^-,$$

B3LYP predicts a negative overall barrier if X = Y = Cl (i.e. a barrier between the entry and exit ion-molecule complexes that lies below the entrance channel). Adamo and Barone [79] demonstrated that their new mPW1PW91 (modified Perdew-Wang) functional at least yields the correct sign for this problem.

In Ref. 80 we carried out a W1 and W2 investigation for all six cases with X, Y $\in \{F, Cl, Br\}$, in order to assess the performance of a number of DFT exchange-correlation functionals. W2 is in excellent agreement with experiment where reliable experimental data are available; in some other cases, the W1 calculations either suggest revisions or provide the only reliable data available (see Ref. 80 for details).

Of the different exchange-correlation functionals considered, the new mPW1K [59] functional of Truhlar and coworkers appears to yield the best performance among "hybrid" functionals (i.e. those including a fraction of exact exchange), followed by BH&HLYP (a half-and-half mixture [58] of Hartree-Fock and Becke 1988 exchange [81] with Lee-Yang-Parr correlation). Among "pure DFT" functionals, the best performance is delivered by HCTH-120 [82] (the 120-molecule reparameterization of the Hamprecht-Cohen-Tozer-Handy functional). (We note in
passing that this latter functional was parameterized entirely against ab initio data.) The G2 data of Pross et al. [83], despite some quantitative discrepancies, is qualitatively in perfect agreement with W1 theory.

We also note that in one case (F, Br) it was impossible to obtain all required stationary points at the B3LYP level, since the F· · ·CH$_3$Br minimum does not show up at all at this level. Only mPW1K and BH&HLYP find this stationary point, as does CCSD(T).

5.3. Benzene as a "Stress Test" of the Method

As an illustrative example of "stress-testing" W1 and W2 theory, we shall consider the benzene molecule[86]. The most accurate calculation we were able to carry out is at the W2h level: the rate-determining step was the direct CCSD/cc-pV5Z calculation (30 electrons correlated, 876 basis functions, carried out in the $D_2h$ subgroup of $D_6h$) which took nearly two weeks on an Alpha EV67/667 MHz CPU. Relevant results are collected in Table 2.5.

At first sight, the disagreement between the computed W2h value of $\Delta H^\circ_{f,0K} = 23.0$ kcal/mol and the experimental value of $24.0\pm0.2$ kcal/mol seems disheartening. (Note that it "errs" on the other side as the most recent previous benchmark calculation [53], $24.7\pm0.3$ kcal/mol, using similar-sized basis sets as W1 theory.) However, the comparison with experiment is not entirely "fair" since it neglects the experimental uncertainties in the atomic heats of formation required to convert an atomization energy into a heat of formation (or vice versa). Combining these with the experimental $\Delta H^\circ_{f,0K}$ leads to an experimentally derived TAE$_0 = 1305.7 \pm 0.7$ kcal/mol, where the uncertainty is dominated by six times that in the heat of vaporization of graphite. In other words, our calculated TAE$_0 = 1306.7$ kcal/mol is only 0.3 kcal/mol removed from the upper end of the experimental uncertainty interval. (After all, an error of 0.02 % seems to be a bit much to ask for.)

Secondly, let us consider the "gaps" bridged by the extrapolations. For the SCF component, that gap is a very reasonable 0.3 kcal/mol (0.03 %), but for the CCSD valence correlation component this rises to 5 kcal/mol (1.7 %) while for the connected triple excitations contribution it amounts to 1 kcal/mol (3.7 % — note however that a smaller basis set is being used than for CCSD). It is clear that the extrapolations are indispensable to obtain even a *useful* result, let alone an accurate one, even with such large basis sets.

Inner-shell correlation, at 7 kcal/mol, is of quite nontrivial importance, but even scalar relativistic effects (at 1 kcal/mol) cannot be ig-
Table 2.5 Individual components in W1h, W1, and W2h total atomization energy \( e \) cum heat of formation of benzene. All data in kcal/mol.

| Reference geometry | B3LYP/cc-pVTZ W1h | W1 | CCSD(T)/cc-pVQZ W2h |
|--------------------|-------------------|----|---------------------|
| SCF                | VDZ 1024.19       | A'VDZ 1024.59 | VTZ 1042.16         |
|                    | VTZ 1042.10       | A'VTZ 1042.62 | VQZ 1044.02         |
|                    | VQZ 1044.56       | A'VQZ 1044.84 | V5Z 1045.30         |
| old-style          | V\( \infty \)Z 1045.95 | V\( \infty \)Z 1045.15 | V\( \infty \)Z 1045.56 |
| new-style          | V\( \infty \)Z 1045.33 | V\( \infty \)Z 1045.53 | V\( \infty \)Z 1045.63 |
| CCSD               | VDZ 225.94        | A'VDZ 226.11  | VTZ 265.49          |
|                    | VTZ 265.55        | A'VTZ 268.44  | VQZ 280.91          |
|                    | VQZ 280.97        | A'VQZ 282.39  | V5Z 285.72          |
|                    | V\( \infty \)Z 291.08 | V\( \infty \)Z 291.53 | V\( \infty \)Z 290.77 |
| (T)                | VDZ 18.72         | A'VDZ 19.64   | VTZ 24.41           |
|                    | VTZ 24.42         | A'VTZ 24.78   | VQZ 25.74           |
|                    | V\( \infty \)Z 26.55 | V\( \infty \)Z 26.69 | V\( \infty \)Z 26.71 |
| Inner-shell correlation | -0.99          | -0.99        | -0.99               |
| Darwin and mass-velocity | -0.51          | -0.51        | -0.51               |
| Spin-orbit coupling | 1368.54          | 1369.33      | 1368.71             |
| TAE\( e \)         | 62.04            | 62.04        | 62.04               |
| TAE\( 0 \)         | 1306.49          | 1307.29      | 1306.67             |
| \( \Delta H^\circ_{0K}[C_6H_6(g)] \) | 23.18           | 22.39        | 23.01               |
| \( \Delta H^\circ_{298.15} - H_0 \) | -4.24           | -4.24        | -4.24               |
| \( \Delta H^\circ_{298.15K}[C_6H_6(g)] \) | 18.95           | 18.15        | 18.78               |

\( a \) Lower level TAE\( 0 \): 1301.9 (G2), 1305.2 (G3), 1303.7 (CBS-QB3), and 1304.3 (CBS-Q) \( \text{kcal/mol. Experiment: } \Delta H^\circ_{0K}[C_6H_6(g)] = 24.0 \pm 0.2 \text{ kcal/mol. } \) [J. B. Pedley, Thermodynamic Data and Structures of Organic Compounds (Thermodynamics Research Center College Station, TX, 1994); Vol. 1.] This standard enthalpy of formation produces TAE\( 0 \) = 1305.7 \pm 0.7 \text{ kcal/mol, where the uncertainty equals } \sqrt{0.2^2 + (6 \times 0.11)^2}; 0.11 \text{ kcal/mol being the uncertainty in the CODATA } \Delta H^\circ_{f,0}[C(g)] = 169.98 \pm 0.11 \text{ kcal/mol [69]. (The uncertainty in } \Delta H^\circ_{f,0}[H(g)] \text{ is negligible.)}

nored. And manifestly, even a 2% error in a 62 kcal/mol zero-point vibrational energy would be unacceptable.

Let us now consider the more approximate results. While W1h coincidentally agrees to better than 0.2 kcal/mol with the W2h result, W1 deviates from the latter by 0.6 kcal/mol. Note, however, that in W1h theory, the extrapolations bridge gaps of 0.8 (SCF), 10.1 (CCSD), and 2.1 (T) kcal/mol, the corresponding amounts for W1 theory being 0.7, 9.1, and 1.9 kcal/mol, respectively. Common sense suggests that if extrapolations account for 13.0 (W1h) and 11.7 (W1) kcal/mol, then a discrepancy of 1 kcal/mol should not come as a surprise — in fact, the relatively good agreement between the two sets of numbers and the more rigorous W2h result (total extrapolation: 6.3 kcal/mol) testifies, if anything, to the robustness of the method.
As for the difference of about 0.4 kcal/mol between the old-style and new-style SCF extrapolations in W1h and W1 theories, comparison with the W2h SCF limits clearly suggests the new-style extrapolation to be the more reliable one. (The two extrapolations yield basically the same result in W2h.) This should not be seen as an indication that the $E_{\infty} + A/L^5$ formula is somehow better founded theoretically, but rather as an example of why reliance on (aug-)cc-pVDZ data should be avoided if at all possible. Users who prefer the geometric extrapolation for the SCF component could consider carrying out a direct SCF calculation in the “extra large” (i.e. V5Z) basis set and applying the $E_{\infty} + A/L^4$ extrapolation to the ”medium”, ”large”, and ”extra large” SCF data.

6. CONCLUSIONS AND PROSPECTS

W1/W2 theory and their variants would appear to represent a valuable addition to the computational chemist’s toolbox, both for applications that require high-accuracy energetics for small molecules and as a potential source of parameterization data for more approximate methods. The extra cost of W2 theory (compared to W1 theory) does appear to translate into better results for heats of formation and electron affinities, but does not appear to be justified for ionization potentials and proton affinities, for which the W1 approach yields basically converged results. Explicit calculation of anharmonic zero-point energies (as opposed to scaling of harmonic ones) does lead to a further improvement in the quality of W2 heats of formation; at the W1 level, the improvement is not sufficiently noticeable to justify the extra expense and difficulty.

Of the various reduced-cost variants introduced in this paper, W2h performs basically as accurately as to W2 for heats of formation. Likewise, W1h is essentially as good as W1 theory for ionization potentials, and almost as good for heats of formation. Neither method is recommended for electron affinities.

In systems where a large number of inner-shell electrons makes the inner-shell correlation (and, to a lesser extent, scalar relativistic) steps in W1 and W2 theory unfeasible, the use of a bond equivalent model for the inner-shell correlation and scaled B3LYP/cc-pVTZuc+1 scalar relativistic corrections offers an alternative under the name of W1c and W1ch theories.

One plan for the future is the extension to heavier element systems; the first step in this direction has been made recently with the development of the SDB-cc-pVnZ valence basis sets [84] (for use with the
Stuttgart-Dresden-Bonn relativistic ECPs [85]) for third- and fourth-row main group elements.

Further improvement of accuracy, as well as applicability to systems exhibiting nondynamical correlation, will almost certainly require some level of treatment of connected quadruple excitations.

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