

High-accuracy extrapolated *ab initio* thermochemistry. IV. A modified recipe for computational efficiency.

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## Abstract

A number of economical modifications to the high-accuracy extrapolated *ab initio* thermochemistry (HEAT) model chemistry are evaluated. The two resulting schemes, designated as mHEAT and mHEAT+, are designed for efficient and pragmatic evaluation of molecular energies in systems somewhat larger than can be practically studied by the unapproximated HEAT scheme. It is found that mHEAT+ produces heats of formation with nearly sub-chemical ( $\pm 1$  kJ/mol) accuracy, at a substantially reduced cost relative to the full scheme. Total atomization energies calculated using the new thermochemical recipes are compared to the results of the HEAT-345(Q) model chemistry, and enthalpies of formation for the three protocols are also compared to ATcT. Last, a small selection of transition states are studied using mHEAT and mHEAT+, which illuminates some interesting features of reaction barriers and serves as an initial benchmark of the performance of these model chemistries for chemical kinetics applications.

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## I. INTRODUCTION

In the last decade, quantum chemical calculations of molecular energies have achieved levels of accuracy that would have astounded early pioneers of the field. Such calculations provide a powerful tool by which bond energies, enthalpies of formation, and other thermochemical properties of molecules can be studied. Theorists have long surpassed Pople's stated goal of "chemical accuracy" [1] ( $\pm 1$  kcal/mol), with a number of 21<sup>st</sup> century protocols now capable of evaluating bond energies to within 1 kJ/mol. This level, sometimes called "subchemical accuracy", is equivalent to roughly  $80\text{ cm}^{-1}$ , a unit of energy not commonly employed in thermochemistry. However, its use here provides some perspective as to how accurate these calculations have become.

This progress would not have been possible without the inception of the Active Thermochemical Tables (ATcT) of Ruscic et al. [2–4], which are now widely regarded as the most accurate source of thermochemical data available. The advent of ATcT provided precise quantities needed to benchmark highly accurate computational methods such as HEAT [5–7], the  $W_n$  methods of Martin and co-workers [8–11], the focal-point approach of Allen and co-workers [12, 13], the somewhat loosely defined Feller-Peterson-Dixon (FPD) method [14], and the new ANL- $n$  of Klippenstein, Harding, and Ruscic [15]. Since all these methods are designed to approach the exact answer, it is not altogether surprising that all are similar in concept. Each family includes a geometry optimization of varying levels of theory, and a basis set extrapolation of the electronic energy evaluated using the CCSD and/or CCSD(T) methods [16, 17]. The latter is invariably corrected for higher level electronic correlation and harmonic zero-point vibrational energy. The pursuit of sub-chemical accuracy further necessitates a treatment of scalar relativistic effects, as well as the diagonal Born-Oppenheimer correction, and last, but not least, anharmonic contributions to the zero-point energy. The degree of overlap between these thermochemical recipes is encouraging; it indicates that theorists have largely agreed on the best approach to this computational goal.

All of the model chemistries mentioned above are sophisticated, and their cost of calculation nontrivial. Indeed, many of the aforementioned methods would struggle (on modern computers) to handle molecules with more than a few heavy atoms and low symmetry. This is particularly true for the HEAT family of methods as they generally eschew separation of valence and core corrections, and use larger basis sets (aug-cc-pCV5Z) in the extrapolation sequence. Additionally, the HEAT methods employ expensive frozen-core CCSDT/cc-pVQZ single-point energy and all-electron CCSD(T)/cc-pVQZ anharmonic calculations. These three contributions are the bottlenecks of HEAT total energy calculations, and limit the degree to which these methods can be applied to chemically interesting systems and reactions. As such, it is worthwhile to investigate alternative procedures to extend the potential range of study.

This paper is our first attempt to address this issue, and here we present two modifications to the HEAT-345(Q) protocol: mHEAT and mHEAT+, and benchmark the accuracy of these new methods against the HEAT-345(Q) protocol and Active Thermochemical Tables [18].

## II. METHODOLOGY

### A. Overview

The formula for the total energy of a molecule in the formalism studied here (provisionally designated as mHEAT) is very much similar to that of HEAT-345(Q) [6],

$$E_{mHEAT} = E_{HF}^{\infty} + \Delta E_{CCSD(T)}^{\infty} + \Delta E_{CCSDT} + \Delta E_{CCSDT(Q)} + \Delta E_{core} + \Delta E_{rel} + \Delta E_{DBOC} + \Delta E_{SO} + \Delta E_{ZPE} \quad (1)$$

with  $\Delta E_{core}$  representing a new contribution that results from the separation of core/valence correlation in this work. **The  $\infty$  symbol designates properties obtained via complete basis-set extrapolation.** Each component will be discussed in turn, with a focus given to how they differ from their equivalents in HEAT. A useful comparison between the various procedures is provided in Table I.

### B. Geometry

The first step in any thermochemical recipe must be a geometry optimization. Here, the rather expensive all-electron CCSD(T)/cc-pVQZ [19] optimizations of HEAT are replaced with the more efficient frozen-core CCSD(T)/ANO1 [20, 21]. In conjunction with CCSD(T), these triple- $\zeta$  quality basis sets have been shown to accurately describe potential energy surfaces of molecules, especially with regard to their vibrational frequencies [22]. As the total energy at (true) stationary points is relatively insensitive to geometry [5], the effect of excluding core-correlation in the geometry optimization is expected to be to have a minimal impact on final energies. Moreover, the use of the (valence) cc-pVQZ basis set in an all-electron treatment is certainly not optimal; the present scheme could even be viewed as superior.

The Hartree-Fock energy of mHEAT is calculated using a complete basis set extrapolation of Dunning's cc-pVXZ basis sets ( $X=T,Q,5$ ) [19] and the equation of Feller [23]:

$$E_{HF}^X = E_{HF}^\infty + a \exp(-bX) \quad (2)$$

In this paper, the electronic energies of all open-shell species have been calculated with UHF reference wave functions. It is often interesting to compare the results of ROHF and UHF references, and ROHF certainly comes with many benefits, but, following the precedent of previous literature, energy calculations here will be performed with only RHF and UHF wavefunctions.

It should be remembered that high accuracy thermochemistry protocols like HEAT endeavor to reach the exact (full-CI) correlation energy. To the degree that these methods succeed in doing so, the choice of ROHF v. UHF is irrelevant. Of course, the extrapolated SCF limit *will* be different, but the inclusion of correlated terms largely resolves any disagreement. It is important only to be consistent: the first four terms of eq. 1 must be acquired with exclusively ROHF or UHF references.

For reasons that will become apparent later, a method designated as mHEAT+ slightly modifies mHEAT's SCF treatment by using the aug-cc-pVXZ basis sets for hydrogen atoms, restricted to include diffuse functions for only s and p orbitals [19]. Non-hydrogen atoms use cc-pVXZ, the same as in mHEAT. Both differ from the original HEAT, which employed Dunning's augmented, core-correlated basis sets (aug-cc-pCVXZ) [24] in the HF extrapolation. As is later demonstrated, this contracted augmentation improves the performance of mHEAT+ vs that of mHEAT with very little increase to the total calculation time.

#### D. $\Delta E_{CCSD(T)}^\infty$

The largest portion of mHEAT's electron correction is recovered, unsurprisingly, via a two point CCSD(T) [16, 17] extrapolation using cc-pVXZ ( $X=Q, 5$ ) basis sets within the frozen-core approximation. The complete basis set limit is found by the extrapolation approach advocated by Helgaker *et al.* [25], which is based on the partial-wave expansion of the correlation energy, *viz.*

$$\Delta E_{CCSD(T)}^X = E_{CCSD(T)}^\infty + aX^{-3} \quad (3)$$

It is important to note that the use of the frozen-core treatment here marks one of the largest deviations from previous HEAT protocols. The accuracy of HEAT is due in no small part to a rigorous treatment of the complete basis set (CBS) extrapolation of the correlation energy that treats core and valence correlation together. In that recipe, CCSD(T) contributions to the total energy are determined using augmented, core correlated Dunning basis sets: aug-cc-pCVXZ ( $X=Q,5$ ).

The explicit inclusion of both core and valence correction is certainly preferable to any sort of core-valence separation scheme. However, these calculations require very large basis sets with core-correlating functions and are consequently very expensive. Moreover, experience has shown that such calculations carried out with the larger basis sets (Q and 5) often encounter linear dependence issues that plague evaluations of both the SCF and correlation energy. It is for these reasons that mHEAT settles for an extrapolation that involves only basis sets designed for the treatment of valence correlation and frozen-core evaluation of the correlation energies. Additionally, the diffuse functions are also abandoned, in part due to their contribution to the linear dependence issues, but mostly for the significant added expense they lend to calculations. However, the mHEAT+ recipe again adds augmented s and p functions on hydrogen atoms.

#### E. $\Delta E_{CCSDT}$

While the iterative treatment of coupled cluster single and double excitations with perturbative treatment of triples via CCSD(T) is an unquestionably successful approach, it has also been amply demonstrated that one must go beyond this level of theory to achieve “sub-chemical” (better than 1 kJ/mol) accuracy. This is especially true for molecules that exhibit significant non-dynamic electron correlation, such as those with multiple bonds as well as many transition states. Connected triple excitations in the form of CCSDT [26–28] are a step towards addressing these issues. As such, HEAT features a two point CCSDT - CCSD(T) extrapolation with cc-pVXZ ( $X=T,Q$ ) basis sets, using the frozen-core approximation. Unfortunately, this marks the second of three bottlenecks for HEAT-345(Q), as the full CCSDT calculations in the cc-pVQZ basis set are often impossible with typically available computational resources. In the approaches here – and one of the largest approximations made to the original HEAT strategy – this extrapolation is abandoned and is replaced with the following energy difference:

$$\Delta E_{CCSDT} = E_{CCSDT}^{cc-pVTZ}(fc) - E_{CCSD(T)}^{cc-pVTZ}(fc) \quad (4)$$

One could justify this approximation to a certain degree by noting that contributions beyond CCSDT in the older HEAT methods came in the form of similar differences calculated with CCSDT(Q), CCSDTQ, or CCSDTQP using a valence, double- $\zeta$  basis set (cc-pVDZ). One might then assume that the T-(T) correction above could be handled with a similar strategy. However, the results shown later in this paper reveal that this is not the case, and the simplification here systematically differs from the more theoretically (and computationally) rigorous extrapolation found in HEAT.

#### F. $\Delta E_{CCSDT(Q)}$

As discussed in the original HEAT papers, the full triples treatment does not recover all of the electron correlation required to achieve sub-chemical accuracy. Some consideration of quadruple excitations must be made, and mHEAT follows the strategy taken by HEAT-345(Q) where this correction is obtained with a simple energy difference between frozen-core CCSDT(Q) [29, 30] and CCSDT with the Dunning double- $\zeta$  basis set, cc-pVDZ:

$$\Delta E_{CCSDT(Q)} = E_{CCSDT(Q)}^{cc-pVDZ}(fc) - E_{CCSDT}^{cc-pVDZ}(fc) \quad (5)$$

Due to the use of small basis sets, and the advent of efficient algorithms for the evaluation of CCSDT(Q) (or CCSDTQ) energies [31], this contribution is not unduly expensive to calculate.

#### G. $\Delta E_{core}$

The contributions above may be considered as the frozen-core electronic energy of mHEAT, where core-correlation has been completely neglected. For relative energies, one might be tempted to ignore these latter contributions. However, to achieve the desired levels of accuracy, some treatment of core-correlation effects is necessary. This contribution to the total energy (which is significant) and to the relative energies (which is smaller, but vital), is taken to be the difference between all-electron and frozen-core CCSD(T)/cc-pCVQZ energies:

$$\Delta E_{core} = E_{CCSD(T)}^{cc-pCVQZ}(ae) - E_{CCSD(T)}^{cc-pCVQZ}(fc) \quad (6)$$

Where it is implicitly assumed that: 1) the core correlation energy is converged with the cc-pCVQZ basis set; 2) the frozen-core correlation energy is well represented by a valence calculation in the cc-pCVQZ basis; and 3) effects of

core correlation beyond CCSD(T) are negligible.

#### H. $\Delta E_{\text{rel}}$

Scalar relativistic effects are incorporated into mHEAT by adding the one-electron mass-velocity and one-electron Darwin energies to the two-electron Darwin energy [32, 33] evaluated using MP2 and the aug-cc-pCVTZ basis set, with all electrons included. This differs from HEAT, which uses CCSD(T) instead. The effect of this change is relatively small, as shown later.

#### I. $\Delta E_{\text{DBOC}}$

An oft-neglected, but nonetheless important adjustment to the total energy comes from the deficiencies of the clamped-nucleus Born-Oppenheimer approximation [34]. Various iterations of the HEAT have employed the adiabatic correction, otherwise known as the diagonal Born-Oppenheimer correction [35] to account for the finite mass of the nucleus at either the SCF/aug-cc-pVTZ [36, 37] or CCSD/aug-cc-pVTZ [38] with **frozen core**. The difference between the two methods is sometimes surprisingly large (a few tenths of a kJ/mol), but the CCSD treatment is rather expensive. Hence, mHEAT uses the more efficient SCF/aug-cc-pVTZ, with RHF and UHF reference wave functions for closed and open-shell molecules respectively. It should be noted that the use of UHF references differs from previous HEAT procedures, where ROHF was preferred. This change is motivated by complications arising from the DBOC for some transition states, and will be discussed in the following sections.

#### J. $\Delta E_{\text{SO}}$

The second in the set of relativistic considerations, the spin-orbit correction, accounts for the coupling between spin and orbital angular momentum. To first order, this term vanishes for any atom or molecules in a non-degenerate ground state. This contribution is based on experimental data when available, which is the case for all of the atoms and molecules in the HEAT test suite used for benchmarking here [39].

The treatment of the zero-point vibrational energy (ZPE) is the last of the three largest departures from the original HEAT scheme. At the time of the original work, the benefits of the atomic natural orbital basis sets [20, 21], particularly their aptitude for providing accurate vibrational level energies [22], was not sufficiently appreciated by the authors. As such, HEAT used the expensive combination of all-electron CCSD(T) with cc-pVQZ basis sets to obtain both harmonic and anharmonic VPT2 [40] contributions to the ZPE. Efficient algorithms for obtaining these properties in parallel have been implemented in the quantum chemistry software CFOUR [41]. Even so, these anharmonic corrections are extraordinarily expensive when calculated with an all-electron method and a quadruple- $\zeta$  basis set. In mHEAT and mHEAT+, the Dunning basis sets have been abandoned in favor of a hybrid approach where the harmonic zero-point energy is evaluated using the combination of frozen-core CCSD(T) with the triple- $\zeta$  atomic natural orbital (ANO1) basis set, and the VPT2 corrections are computed using double- $\zeta$  ANO0:

$$\Delta E_{ZPE} = G_{CCSD(T)}^{ANO0} + \frac{1}{2} \sum_i \omega_i^{ANO1} + \frac{1}{4} \sum_{i \geq j} X_{ij}^{ANO0} \quad (7)$$

Spin contamination in UHF wave functions must be monitored, and several molecules in our test suite require ROHF reference wave functions in order to obtain accurate anharmonic corrections [42, 43]. In such cases, the vibrational calculation is performed with ROHF-based CCSD(T) at the appropriate (ROHF) optimized geometry.

## L. Thermochemical References

Here, the method by which thermochemical data is obtained should be discussed. The heat of formation of a molecule is defined as the enthalpy difference between said molecule and its constituent elements in their most stable forms. Naturally, determining this value directly from computation is impractical for atoms such as carbon, where the most stable form at standard pressure is solid graphite. Instead, these quantities are calculated from the difference between ATcT enthalpies of formation of the individual atoms and the total atomization energy determined from the model chemistry of choice, as illustrated in Figure 1. It should be noted that, by convention, the reference states of elements correspond to the most stable form at a given temperature, with the exception of room-temperature gaseous elements, which are referenced to gas-phase at all temperatures[44]. In their recent paper, Klippenstein, Harding, and Ruscic [15] propose an alternate method employing algebraic combinations of H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, and



$\text{NH}_3$  to obtain the enthalpies of formation for species consisting of H, C, N, and O atoms. They remark that this method dramatically reduces computational thermochemical errors as compared to the ATcT data, with roughly a factor of two improvement in the RMSE over the more commonly used atomic reference scheme employed here as well as in most other commonly employed model chemistries. In this paper, where the emphasis is on differences between the present (simplified) and existing (more expensive) HEAT protocols, we have elected to stick with atomic references in order to simplify the comparison. However, it is noted that methods presented here are well suited for this ANL-n treatment as there are no empirical factors to optimize to the choice of reference.

### III. RESULTS

The contributions to the total atomization energies (TAE) for each molecule in the test-suite are tabulated in Table II. The differences between these individual values obtained via the mHEAT/mHEAT+ and HEAT-345(Q) methods are displayed in Table III. Individual contributions to the total energy are included in the supplementary material.

#### A. mHEAT

The mHEAT total atomization energies differ from those of HEAT-345(Q) by an average of 0.45 kJ/mol, with a standard deviation of 0.89 kJ/mol and maximum observed error of 2.54 kJ/mol. Given the simplifications made from the original HEAT protocol, it may be surprising that mHEAT performs as well as it does. This accuracy largely results from a subtle cancellation of errors, which will be addressed later.

The equilibrium geometries for the species in this work are included in the supplementary material. The change from all-electron CCSD(T)/cc-pVQZ to frozen-core CCSD(T)/ANO1 based geometries systemically increases the bond lengths of the test suite molecules by an average of 0.006 Å, and a maximum of 0.011 Å. Since the energy of stationary points only depends on the geometry to second order, the overall geometry effect is small, but the SCF and correlation contributions are not individually stationary and thus exhibit larger, but compensating, responses to the change in geometries. ~~The expansion of the bond lengths can be attributed to the smaller ANO1 basis.~~ To clarify the analysis of the energy contributions, calculations have also been performed using the original cc-pVQZ geometries. These results can be found in the supplementary material.

The HF CBS, of course, contributes a significant portion of the total atomization energy for molecules. Compared to HEAT-345(Q), mHEAT's SCF TAE is shifted by an average of -1.73 kJ/mol and a max of -4.77 kJ/mol for F<sub>2</sub>.

This is almost entirely due to the change in geometry, as the equivalent calculations using the standard HEAT geometries produce an average difference and maximum of 0.04 and 0.81 kJ/mol, respectively (see supplementary material). As would be expected, the HF energy extrapolations appear to have largely converged to the basis set limit even without the addition of augmented basis functions in the Dunning basis sets, which add one extra 'diffuse' gaussian at each angular momentum. On inspection, one may notice that molecules containing hydrogen atoms tend to exhibit the largest differences between the recipes, an observation that will be expounded upon later.

The CCSD(T) correlation energy is a major source of disagreement between mHEAT and HEAT-345(Q). This is perhaps unsurprising, as the former neglects both the diffuse basis functions and the core correlation energy. mHEAT attempts to recover the missing, *extrapolated* core correlation of HEAT via an *additive* correction using CCSD(T)/cc-pCVQZ. The sum of mHEAT's frozen-core CCSD(T) CBS and frozen-core correction can be compared to the HEAT all-electron CCSD(T) CBS (which explicitly extrapolates core and valence correlation together). The corresponding contributions to the total atomization energies differ between mHEAT and HEAT by an average of +1.48 kJ/mol, with standard deviation of 1.32 kJ/mol and a maximum difference (for H<sub>2</sub>O<sub>2</sub>) of 4.38 kJ/mol. This analysis is displayed in Table III. The SCF and CCSD(T) correlation+core errors mostly cancel, as might be expected as the geometry differences occur in a range where the sum of these two is approximately stationary while neither contribution is so by itself. However, the scatter (with respect to HEAT) in the correlation energy extrapolation is quite large, which can in part be attributed to the fact that correlation energies are more sensitive to basis set expansion and diffuse functions than are SCF energies. Note also that the differences between mHEAT and HEAT are most significant for molecules containing hydrogen atoms.

Unlike CCSD(T), the change from HEAT's extrapolated CCSDT correlation correction to the simple differences of mHEAT leads to a systematic and positive shift of 0.50 kJ/mol (mean) in the atomization energies, with a maximum difference of 1.18 kJ/mol and a standard deviation of 0.33 kJ/mol. The sign of this correction will be discussed in a later section. It should be noted that the change in CCSDT is smaller in magnitude than the CCSD(T) differences discussed in the previous paragraph. The last contributor to the electronic energy, CCSDT(Q), is obtained by the same procedure for both mHEAT and HEAT-345(Q), though at different geometries. The differences for this contribution between the schemes are small, with values that differ from those at the cc-pVQZ geometry by an average and standard deviation of 0.06 kJ/mol, and a maximum error of 0.17 kJ/mol (for O<sub>2</sub>).

The scalar relativistic correction is a relatively minor, but nonetheless essential component of the enthalpy of formation ( $\Delta_f H$ ). In mHEAT, the CCSD(T) evaluation of the Darwin and mass-velocity energies is exchanged for the more affordable MP2. As one might expect, the change in total atomization energies is essentially negligible: 0.01 kJ/mol on average, with a standard deviation of 0.06 kJ/mol, and a max difference of 0.11 kJ/mol.

For minima on the potential energy surface, changing from correlated to SCF DBOCs has generally little effect, with an entirely negligible average difference of 0.04 kJ/mol (st. dev. 0.18). There is one molecule for which the SCF calculation produces a value moderately ( $> 0.2$  kJ/mol) different from CCSD: NO. Changing to ROHF reduces this discrepancy from -0.79 to 0.03 kJ/mol. Other than this pathological molecule, the UHF references seem to work well.

The spin-orbit correction, which is now obtained from experimental data where available, varies negligibly between HEAT and mHEAT, and thus does not warrant discussion here.

The expedited calculation of the zero-point energy using the hybrid ANO1 harmonic and ANO0 VPT2 corrections, one of the major sources of computational savings in the mHEAT protocol, performs quite well. The average difference between mHEAT and HEAT ZPE contributions to the TAEs is 0.15 kJ/mol, with a maximum difference of -1.19 kJ/mol and a standard deviation of 0.30 kJ/mol. The largest difference is seen for the ethynyl radical, HCC, a problematic species which will be discussed later. Given the demonstrated performance of the ANO basis sets in determining vibrational frequencies and anharmonic force fields, it may even be true that this treatment is superior to that of the original HEAT, which employs the more expensive all-electron calculations with a larger, but suboptimal, valence basis set.

Table IV compares the calculated enthalpies of formation to those of ATcT [18]. Briefly, mHEAT differs from ATcT with a 95% confidence interval of  $\pm 1.824$  kJ/mol [45]. There are a few molecules for which the error relative to ATcT is larger than 2 kJ/mol:  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ , which is concerning. As the reader may have noticed, all of these molecules contain hydrogen atoms. The treatment of these molecules will be improved with the mHEAT+ strategy, as will now be discussed.

## B. mHEAT+

Though it requires a little more computational effort, mHEAT+ provides a marked improvement over basic mHEAT, with an average difference from HEAT total atomization energies of 0.06 kJ/mol, a standard deviation of 0.49 kJ/mol, and a maximum observed difference of -1.51 kJ/mol (HCC, a troublesome species discussed later).

Enthalpies of formation compared to ATcT are excellent ( $-0.24$  kJ/mol on average), with a 95% confidence interval and rms observed error of  $\pm 1.039$ , and  $1.395$  kJ/mol, respectively. The comparison of mHEAT+ with HEAT-345(Q) is included in Table II, and comparison with ATcT in Table III. While mHEAT+ does not quite achieve sub-chemical accuracy, it is rather close, and the aforementioned approximations allow for calculations on molecules that would require considerable effort with the HEAT protocol, or simply be out of reach. The basis for this performance will be discussed below. It should be noted that if mHEAT+ employed the same molecular reference scheme as suggested in Klippenstein *et al.*, and further assuming that this model chemistry benefits from this change in reference in the same manner as theirs, these values would be well within sub-kJ/mol levels of accuracy.

Additionally, mHEAT+ addresses the issues encountered in mHEAT, where molecules containing hydrogen atoms produce disproportionately less satisfactory enthalpies of formation. If only hydrogen-containing molecules are considered, mHEAT's average error for enthalpies of formation vs ATcT is  $-0.87 \pm 2.00$  kJ/mol, whereas this value is  $-0.18 \pm 0.92$  kJ/mol for molecules without hydrogen. For mHEAT+, the average  $\Delta_f H$  error vs ATcT of hydrogen containing molecules is only  $-0.27 \pm 1.11$  kJ/mol, indicating that these species are treated with essentially the same level of accuracy as those without hydrogen atoms (where, of course, the two schemes are equivalent).

### C. Activation Energies

High-quality activation energies are required for accurately modeling chemical reactions. The HEAT protocol has been used in the past for many such studies [46–49], and it is natural to wonder how mHEAT and mHEAT+ will perform in comparison to HEAT-345(Q) for transition states. To this end, mHEAT and mHEAT+ are employed in the evaluation of a small, but representative, set of barrier heights displayed in Table V. The raw data can be found in the supplementary material. While it is somewhat meaningless to discuss the statistics for a dataset of only seven reactions, some qualitative comments on the performance of these model chemistries can be made. First, mHEAT+ is not more than  $0.83$  kJ/mol off of the HEAT-345(Q) results for any barrier height, while mHEAT performs less well (error:  $-1.4$  kJ/mol) for the reaction of  $O(^3P)+H_2 \rightarrow H+OH$ , and comparable to mHEAT+ for the others. Thus, mHEAT+ would seem to be appropriate as a relatively inexpensive model chemistry for transition states too large to be studied with the canonical HEAT recipes, provided, of course, that the transition state at hand is expected to work well with HEAT (free of pathological multireference effects). Second, each electronic component of the mHEAT+ barrier heights compare well to their counterparts in HEAT-345(Q), indicating that the error of these individual contributions (SCF, CCSD(T), etc.) cancel between minima and transition states on surfaces. Last, the

in nuclear terms' of these protocols (the ZPE and DBOC) differ more significantly between the mHEAT and HEAT treatments. These observations will be discussed in greater detail in the following section.

## IV. DISCUSSION

### A. Error Cancellation in mHEAT and mHEAT+

The excellent performance of mHEAT and mHEAT+ can in part be attributed to a rather delicate (and fortuitous) cancellation of errors between individual components of each model. The source and sign of these cancellations will be discussed first for mHEAT, and once understood in that framework, will make apparent both the motivation for and the superior performance of mHEAT+. It will be helpful to focus on differences between contributions to the total atomization energies of mHEAT and HEAT-345(Q). Table III contains the relevant values, and Figure 2 demonstrates the key ideas elaborated below.

The evaluation of the basis-set limit SCF energies in mHEAT differs from HEAT in two ways: the diffuse basis functions are neglected, and the geometries (which are optimized at the frozen-core CCSD(T)/ANO1 level instead of all-electron CCSD(T)/cc-pVQZ) used have systematically longer bond lengths. The result of these two changes, particularly the longer bond lengths, is that the SCF molecular binding energies of mHEAT are generally lower than those of HEAT-345(Q). Consequentially, the SCF contributions to the total atomization energy of mHEAT are, on average, 1.73 kJ/mol smaller than those of HEAT. For molecules that contain hydrogen, this TAE shift is -1.06 kJ/mol on average, while for molecules that do not, it is -2.99 kJ/mol.

The lack of diffuse basis functions and the new geometries also affect the CCSD(T) correlation energy. However, it is more important that the mHEAT CCSD(T) treatment replaces the explicit all-electron CCSD(T) correlation extrapolation of HEAT with a frozen-core extrapolation, which is then augmented with a core-correlation correction. The resulting (frozen-core CCSD(T) + core correction) contributions to the total atomization energy are 1.48 kJ/mol larger on average than the all-electron CCSD(T) extrapolation in HEAT. As with the SCF results, these values (mHEAT vs HEAT) are markedly different between hydrogen- and non-hydrogen-containing molecules: +1.17 kJ/mol and +2.06 kJ/mol respectively. Note that the relative magnitudes and signs are consistent with the SCF differences, in the sense that the sums involved for the most part cancel, since the total energy is nearly stationary. In passing, we note that the individual signs of the changes are what is expected - as bonds become longer, correlation effects are more pronounced.

CCSD(T) overestimates the role of the triple excitations in molecular binding energies, with associated contributions to the TAEs that are too positive. HEAT employs a CCSDT correction to, in part, account for this. In mHEAT, this correction is no longer based on extrapolated values, which results in CCSDT contributions that are smaller in magnitude than their HEAT counterparts by an average of 0.50 kJ/mol. The sign of this correction is generally negative, as it tends to correct the “overshoot” of the CCSD(T) TAE. The total atomization energies are further refined via a CCSDT(Q) correction that is equivalent in mHEAT and HEAT, albeit at different geometries. The combined CCSDT and CCSDT(Q) corrections constitute the so-called “higher level correction” (HLC), which is, on average, 0.57 kJ/mol larger than the equivalent HEAT value, largely due to the differences in protocols for the CCSDT-CCSD(T) correction term.

The folded cumulative distribution function displayed in Figure 2 reveals mHEAT’s difficulties with hydrogen-containing molecules. For molecules that do *not* contain hydrogen, the changes made to the SCF and CCSD(T) procedures serve to make these contributions to the TAE somewhat smaller than HEAT. This is balanced by the new CCSDT and CCSDT(Q) TAE contributions, which are larger than those of HEAT. Thus, the overall performance of mHEAT for these molecules is quite good; the errors (relative to HEAT) are similar in magnitude and opposite in sign. However, for hydrogen-containing species, this is no longer the case: the sum of the effects of the new SCF and CCSD(T) procedures causes mostly *positive* differences with respect to HEAT-345(Q) for these TAE contributions, which exacerbates the already positive shifts in the TAE caused by mHEAT’s CCSDT and CCSDT(Q) corrections. This results in total atomization energies that are too large, and thermochemical calculations that are systematically less satisfactory than those performed on non-hydrogen-containing species.

In the course of this research, various alternative procedures have been investigated in order to address these issues. One such scheme, which may even be considered a third model chemistry (aug-mHEAT), employs the fully augmented Dunning basis sets (aug-cc-pVXZ, in the frozen-core approximation) for the SCF and CCSD(T) basis set extrapolations. The data for this protocol is presented in the supplementary material. It was found that aug-mHEAT performs well compared to mHEAT, and it resolves the latter’s difficulties with hydrogen containing molecules, although at *significantly* increased computational expense. The mHEAT+ protocol was developed in an attempt to include diffuse function effects at minimal cost: only the s,p functions of hydrogen atoms are augmented with diffuse basis functions. Remarkably, for the species studied here the inclusion of this small number of additional functions seems sufficient to largely achieve the accuracy of the fully augmented basis sets, where every atom receives an additional diffuse function per orbital angular momentum, i.e. a diffuse s,p,d,f, and g set of functions (25 total)

for each carbon atom with a quadruple- $\zeta$  basis.

Consequently, the computational savings of mHEAT+, relative to aug-mHEAT, are significant. As an example, for H<sub>2</sub>O<sub>2</sub>, the largest calculation needed for mHEAT is frozen-core CCSD(T)/cc-pV5Z, which involves 292 basis functions. Going to mHEAT+ requires just eight additional functions, and the improvement in accuracy is well worth the rather minimal incremental expense of the calculation. In aug-mHEAT, which includes the full complement of diffuse functions on all atoms, 414 basis functions are needed for H<sub>2</sub>O<sub>2</sub>. For reference, the equivalent calculation in HEAT (all-electron CCSD(T)/aug-pCV5Z) requires 522 basis functions, and is far from a trivial undertaking.

Though the time and memory performance of these various methods will necessarily depend on the hardware, software, and molecule in question, for the above quintuple- $\zeta$  CCSD(T) calculation on H<sub>2</sub>O<sub>2</sub>, mHEAT+ is only 1.2x slower than mHEAT, while aug-mHEAT and HEAT-345(Q) require 4.2x and 11.9x more time, respectively. Additionally, given that mHEAT and mHEAT+ use roughly half as many basis functions (on heavy atoms) as HEAT-345(Q), these new methods should be applicable to systems somewhere less than twice the size of what was reasonable with the parent HEAT method, subject, of course, to symmetry considerations.

## B. Troublesome Species

In general, the total atomization energies and enthalpies of formation resulting from mHEAT+ are in excellent agreement with both HEAT-345(Q) and ATcT. However, there are a few troublesome species for which a bit of elaborated discussion is appropriate.

### CCH

One conspicuous outlier in the mHEAT/mHEAT+ results is the ethynyl radical, and the energy decomposition detailed in Table III reveals the source of differences from HEAT-345(Q) to be localized almost entirely in the zero-point energy contribution. Ultimately, this can be traced, at least in part, to the well-known presence of the low-lying <sup>2</sup>Π electronically excited state in CCH, which gives rise to profound vibronic coupling effects on the degenerate  $\pi$  vibration. As a result, the treatment of this mode (harmonic frequency and anharmonic force constants involving motion along this degenerate normal coordinate) is problematic. In HEAT-345(Q), the all-electron cc-pVQZ VPT2 calculation gives fundamental frequencies of 380, 1845 and 3319 cm<sup>-1</sup>, all of which agree reasonably well with the experimental values of 372, 1846, and 3293 cm<sup>-1</sup>, and it can be assumed that the zero-point energy obtained here is

a plausible estimate of the true value. Of note, the anharmonic contribution to this value ( $-68\text{ cm}^{-1}$ ) is in line with that obtained with the ANO0 and ANO1 basis sets used in the mHEAT protocols with UHF reference functions (and ANO1 for ROHF), but the ROHF-based ANO0/CCSD(T) result (ANO0 being the basis specified by mHEAT) is  $+93\text{ cm}^{-1}$ , which largely accounts for the difference noted in Table III. The manner in which this (pseudo-Jahn-Teller) effect is treated by quantum chemical calculations is complicated [50], but it appears that it is vastly overestimated by ROHF-based CCSD(T)/ANO0 in this case. Significantly, the EOM-CCSD  ${}^2\Sigma \rightarrow {}^2\Pi$  vertical gaps (which affect the response of the CCSD(T) wavefunction [50]) are  $7314$  and  $7897\text{ cm}^{-1}$  (UHF) and  $5193$  and  $5845\text{ cm}^{-1}$  (ROHF) with the ANO0 and ANO1 basis sets. The ROHF-based ANO0 value is lowest here, and this is consistent with the perhaps simplistic attribution of the poor zero-point estimate to this vibronic interaction. This is an area where the protocol-based methodology of HEAT (and most other computational thermochemistry approaches) is potentially problematic, as it is tacitly assumed that the molecules studied belong to relatively well isolated electronic states where simple adiabatic treatments of the vibrational ZPE are appropriate.

### Polar Hydrides

The most dramatic differences between mHEAT and mHEAT+ are observed for molecules with highly-polar X-H bonds, with X being oxygen or fluorine:  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$ ,  $\text{OH}$  and, to a lesser extent, ammonia and  $\text{NH}_2$ . In these cases, the electron distribution in the region of the proton is highly distorted from the atomic spherical arrangement, and the importance of added basis functions (both polarization and diffuse functions) is heightened. Not surprising is that this effect is largely seen in the correlation energy contribution (second column of numbers in Table III), since correlation effects are more sensitive to basis set than are SCF energies. It is interesting that the effect of adding diffuse functions to the hydrogen atoms is clearly more important than to the second row elements in this case. In earlier work, in which HEAT was applied to the benzene molecule, a similar strategy was adopted [51]. In that work, another benefit of adding diffuse functions to only the hydrogen atoms (there viewed alternately as *removing* diffuse functions only from non-hydrogen atoms) was noted; the problems sometimes encountered with linear dependence – and associated convergence difficulties of the SCF and CC equations – in large basis set (aug-cc-pCVQZ and aug-cc-pCV5Z) calculations necessitated by the standard HEAT protocol were effectively eliminated when the diffuse functions were retained on the hydrogens but omitted from the carbon atoms. The present results suggest that this choice may also be beneficial from the standpoint of accuracy, as well.



This work is certainly not the first attempt to create a model chemistry that can achieve sub-chemical accuracy at a reduced cost. The closest relative, so to speak, of the HEAT protocols are the  $W_n$  methods of Martin *et al.* [8–10], which similarly avoid extensive empirical parameterization. The W3.2 protocol [10] is particularly similar to mHEAT and mHEAT+. In W3.2, the SCF and frozen-core CCSD energies are obtained via a two point extrapolation using cc-pVXZ ( $X=Q,5$ ) basis sets for hydrogen atoms, and aug-cc-pVXZ ( $X=Q,5$ ) basis sets for all second row elements. The frozen-core CCSD(T) energies come from similar extrapolations, except with  $X=T,Q$ . Additionally, the CCSDT correction is obtained via a two point extrapolation with unaugmented cc-pVXZ, where  $X=D,T$ . Most of the other contributions to the TAE are essentially equivalent between W3.2 and mHEAT/mHEAT+, except the ZPE, which W3.2 acquires from the best possible available data.

It is interesting that mHEAT+ and the W3.2 methods employ opposite strategies for the inclusion of the diffuse functions in the basis set extrapolations. W3.2 fully augments all non-hydrogen atoms, with no diffuse functions on the protons, whereas mHEAT/mHEAT+ do not augment second row elements at all, and only place a limited number of diffuse functions on hydrogen.

In practice, it appears that W3.2 consistently outperforms mHEAT, while mHEAT+ and W4lite (which improves upon W3.2 with extrapolated core corrections) achieve effectively the same level of accuracy and precision relative to ATcT. Though mHEAT+ is less expensive due to the smaller basis sets employed, it relies heavily on cancellation of errors between unextrapolated components, and thus may be less theoretically justified. Both thermochemical recipes are the same in spirit however, as they attempt to capture all potentially significant contributions to the total energy of molecules. They differ only in how simplification of the more elaborate “parent methods” is approached, and the computational effort and accuracy thereof.

#### D. Activation Energies

The mHEAT and mHEAT+ protocols were designed, in part, with applications to chemical kinetics in mind, as this has been a significant area of effort in our group during recent years. To this end, a small selection of barrier heights partially evaluated using HEAT-345(Q) have been recalculated with the model chemistries proposed in this paper. These results can be found in Table V. A few observations can be made, though the dataset is too small for any significant statistical analysis and a more detailed study is warranted.

As previously mentioned, the mHEAT+ protocol produces barrier heights that, for this set of reactions, are not more than 0.83 kJ/mol off of the HEAT-345(Q) results. Given that mHEAT+ reproduces the HEAT-345(Q) total atomization energies for minima within 1 kJ/mol (excepting CCH and H<sub>2</sub>O<sub>2</sub>), this statement may not be overly surprising. The mHEAT protocol also performs rather well, but underestimates the barrier height for the reaction of O(<sup>3</sup>P)+H<sub>2</sub> → H+OH by -1.43 kJ/mol relative to HEAT-345(Q). As it requires such a modest increase in cost, and generally performs better for the studied reactions, mHEAT+ should be the preferred method between the two proposed in this work. This small test set suggests that both mHEAT and mHEAT+ achieve chemical accuracy (within ± 1 kcal/mol) with apparent ease, and mHEAT+ appears to provide activation energies that differ only negligibly from those calculated by the considerably more expensive HEAT-345(Q) approach.

Encouraging is that it appears that errors within the electronic components of mHEAT+ (but not mHEAT) largely cancel between transition states and minima: the individual contributions (SCF, CCSD(T), etc.) to the activation energy obtained by mHEAT closely match their counterparts in HEAT-345(Q) for reactions in this test set. Hence, activation energies – central to any kinetic study – are somewhat insensitive to the computational simplifications of the ‘electronic’ terms made here. The largest observed differences between mHEAT+ and HEAT-345(Q) come from the ‘nuclear’ terms: the DBOC and ZPE. It is difficult to discuss the ZPE, for it is not clear which scheme, the hybrid frozen-core ANO1//ANO0 of mHEAT/mHEAT+ or the all-electron cc-pVQZ of HEAT-345(Q), provides the more accurate results. Interestingly, the DBOC, which is related to the sensitivity of the wavefunction with respect to variation of the nuclear coordinates (it is the expectation value of the nuclear kinetic energy operator over the clamped nucleus Born-Oppenheimer wavefunction), contributes significantly to the barrier heights. For four of the seven reactions studied here, the magnitude of its effect on the activation energy is comparable to that of the CCSDT and CCSDT(Q) corrections. It is worrying that the mHEAT/mHEAT+ DBOC, which is calculated using SCF/aug-cc-pVTZ, is consistently greater, sometimes by nearly a kJ/mol, than frozen-core CCSD/aug-cc-pVTZ, to which it is compared. Furthermore, the SCF-level DBOC for the CH<sub>2</sub>O → H<sub>2</sub>+CO and O(<sup>3</sup>P)+H<sub>2</sub> → H+OH reactions are sensitive to the choice of reference wavefunction: the ROHF-DBOC results are far too large. Similar problems for UHF-DBOCs can be observed near the equilibrium geometry of the NO radical. That the SCF-level DBOC is not as safe as it may seem is at least partially related to orbital (near-)instability issues, a discussion of which will be reported in a separate publication.

While these DBOC corrections would ideally be obtained via the CCSD procedure, the cost of such a treatment may not be practical for many reactions of interest. Additionally, the fact that the DBOC is generally a small term

(in terms of the scale of the total activation energy) mitigates its importance to some degree. For now, mHEAT+ with the SCF-based DBOC treatment – will be recommended for kinetics studies involving molecules outside the scope of what is reasonable for HEAT proper to handle, subject to the qualifications expressed in this section.

### Summary

The HEAT protocol has been successfully applied to many small molecules, but rapidly becomes intractable for molecules that lack symmetry and that contain more than a few heavy atoms. In this work, two new model chemistries are proposed, mHEAT and mHEAT+, that are modifications of the original HEAT-345(Q) and attempt to significantly reduce computational time with an acceptably small reduction in accuracy. These new models are largely identical, but mHEAT+ (which includes one shell of diffuse s,p orbitals for hydrogen atoms in the evaluation of the SCF and CCSD(T) correlation energies) provides nearly sub-chemical enthalpies of formation compared to ATcT, and is thus our recommendation. Additionally, the performance of mHEAT and mHEAT+ are compared to HEAT-345(Q) for a small selection of activation energies. These preliminary results indicate that mHEAT+ matches HEAT-345(Q) barrier heights within 1 kJ/mol, and thus is appropriate for chemical kinetics studies that require high levels of accuracy.

### Supplementary Material

See supplementary material for the molecular geometries used in this work, and the complete data for mHEAT, mHEAT+, and aug-mHEAT calculations on the molecules studied.

### Acknowledgments

The authors are members of the Active Thermochemical Tables Task Force One. The work at Argonne National Laboratory (BR and DHB) was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, under Contract No. DE-AC02-06CH11357, through the Gas-Phase Chemical Physics Program (BR) and the Computational Chemical Sciences Program (DHB). The work by JHT, CAL, TLM, and JFS was supported by the National Science Foundation under Award CHE-

- [1] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
- [2] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. J. Bittner, S. G. Nijssure, K. A. Amin, M. Minkoff, and A. F. Wagner, The Journal of Physical Chemistry A **108**, 9979 (2004).
- [3] B. Ruscic, R. E. Pinzon, G. von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoy, and A. F. Wagner, Journal of Physics: Conference Series **16**, 561 (2005).
- [4] B. Ruscic, R. E. Pinzon, M. L. Morton, N. K. Srinivasan, M. C. Su, J. W. Sutherland, and J. V. Michael, The Journal of Physical Chemistry A **110**, 6592 (2006).
- [5] A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, The Journal of Chemical Physics **121**, 11599 (2004).
- [6] Y. J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P. G. Szalay, A. G. Császár, J. Gauss, and J. F. Stanton, The Journal of Chemical Physics **125**, 064108 (2006).
- [7] M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, The Journal of Chemical Physics **128**, 114111 (2008).
- [8] J. M. L. Martin and G. de Oliveira, The Journal of Chemical Physics **111**, 1843 (1999).
- [9] A. D. Boese, M. Oren, O. Atasoylu, J. M. L. Martin, M. Kállay, and J. Gauss, The Journal of Chemical Physics **120**, 4129 (2004).
- [10] A. Karton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, The Journal of Chemical Physics **125**, 144108 (2006).
- [11] A. Karton, Wiley Interdisciplinary Reviews: Computational Molecular Science **6**, 292 (2016).
- [12] M. S. Schuurman, S. R. Muir, W. D. Allen, and H. F. Schaefer, The Journal of Chemical Physics **120**, 11586 (2004).
- [13] H. M. Jaeger, H. F. Schaefer, J. Demaison, A. G. Császár, and W. D. Allen, Journal of Chemical Theory and Computation **6**, 3066 (2010).
- [14] K. A. Peterson, D. Feller, and D. A. Dixon, Theoretical Chemistry Accounts **131**, 1079 (2012).
- [15] S. J. Klippenstein, L. B. Harding, and B. Ruscic, The Journal of Physical Chemistry A **121**, 6580 (2017).
- [16] G. D. Purvis and R. J. Bartlett, The Journal of Chemical Physics **76**, 1910 (1982).
- [17] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chemical Physics Letters **157**, 479 (1989), ISSN 0009-2614.
- [18] B. Ruscic and D. H. Bross, ATcT Enthalpies of Formation based on Version 1.22d of the Thermochemical Network, available at ATcT.anl.gov, 2018.
- [19] T. H. Dunning, The Journal of Chemical Physics **90**, 1007 (1989).

- [20] J. Almlöf and P. R. Taylor, *The Journal of Chemical Physics* **86**, 4070 (1987).
- [21] J. Almlöf and P. R. Taylor (Academic Press, 1991), vol. 22 of *Advances in Quantum Chemistry*, pp. 301 – 373.
- [22] L. McCaslin and J. F. Stanton, *Molecular Physics* **111**, 1492 (2013).
- [23] D. Feller, *The Journal of Chemical Physics* **96**, 6104 (1992).
- [24] D. E. Woon and T. H. Dunning, *The Journal of Chemical Physics* **103**, 4572 (1995).
- [25] T. Helgaker, W. Klopper, H. Koch, and J. Noga, *The Journal of Chemical Physics* **106**, 9639 (1997).
- [26] J. Noga and R. J. Bartlett, *The Journal of Chemical Physics* **86**, 7041 (1987).
- [27] G. E. Scuseria and H. F. Schaefer, *Chemical Physics Letters* **152**, 382 (1988), ISSN 0009-2614.
- [28] J. D. Watts, J. Gauss, and R. J. Bartlett, *The Journal of Chemical Physics* **98**, 8718 (1993).
- [29] Y. J. Bomble, J. F. Stanton, M. Kállay, and J. Gauss, *The Journal of Chemical Physics* **123**, 054101 (2005).
- [30] M. Kállay and J. Gauss, *The Journal of Chemical Physics* **123**, 214105 (2005).
- [31] D. A. Matthews and J. F. Stanton, *The Journal of Chemical Physics* **142**, 064108 (2015).
- [32] R. D. Cowan and D. C. Griffin, *Journal of the Optical Society of America* **66**, 1010 (1976).
- [33] R. Martin, *The Journal of Physical Chemistry* **87** (1983).
- [34] M. Born and R. Oppenheimer, *Annalen der Physik* **389**, 457 (1927).
- [35] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956).
- [36] H. Sellers and P. Pulay, *Chemical Physics Letters* **103**, 463 (1984), ISSN 0009-2614.
- [37] N. C. Handy, Y. Yamaguchi, and H. F. Schaefer, *The Journal of Chemical Physics* **84**, 4481 (1986).
- [38] J. Gauss, A. Tajti, M. Kállay, J. F. Stanton, and P. G. Szalay, *The Journal of Chemical Physics* **125**, 144111 (2006).
- [39] *NIST-JANAF Thermochemical Tables.*, edited by M. Chase, Jr. (NIST, Washington, DC, 1998).
- [40] I. M. Mills, in *Molecular Spectroscopy: Modern Research*, edited by K. N. Rao and C. W. Matthews (Academic, New York, 1972), pp. 115–140.
- [41] J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, and P. G. Szalay, *CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package*, With contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, O. Christiansen, F. Engel, R. Faber, M. Heckert, O. Heun, M. Hilgenberg, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, T. Kirsch, K. Klein, W.J. Lauderdale, F. Lipparini, T. Metzroth, L.A. Müick, D.P. O’Neill, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkiewicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.
- [42] The ZPE of the following molecules was calculated using ROHF wavefunctions: NO, CF, CN, OF. Note that the ZPE of CCH, which was calculated with ROHF in previous HEAT publications, was obtained with UHF, here.

- [43] T. G. Szalay, J. Vázquez, C. Simmons, and J. F. Stanton, *The Journal of Chemical Physics* **121**, 7624 (2004).
- [44] B. Ruscic, and D. H. Bross, “Thermochemistry”, Chapter 1 in: *Mathematical Modeling of Complex Reaction Systems: Pyrolysis and Combustion*, Elsevier, New York, 2019 (in press)”.
- [45] The 95% confidence interval is equivalent to twice the RMSD.
- [46] T. L. Nguyen, J. F. Stanton, and J. R. Barker, *The Journal of Physical Chemistry A* **115**, 5118 (2011).
- [47] T. L. Nguyen, B. C. Xue, R. E. Weston, J. R. Barker, and J. F. Stanton, *The Journal of Physical Chemistry Letters* **3**, 1549 (2012).
- [48] T. L. Nguyen, J. H. Thorpe, D. H. Bross, B. Ruscic, and J. F. Stanton, *The Journal of Physical Chemistry Letters* **9**, 2532 (2018).
- [49] T. L. Nguyen and J. F. Stanton, *The Journal of Physical Chemistry A* **122**, 7757 (2018).
- [50] J. F. Stanton, *The Journal of Chemical Physics* **115**, 10382 (2001).
- [51] M. E. Harding, J. Vázquez, J. Gauss, J. F. Stanton, and M. Kállay, *The Journal of Chemical Physics* **135**, 044513 (2011).

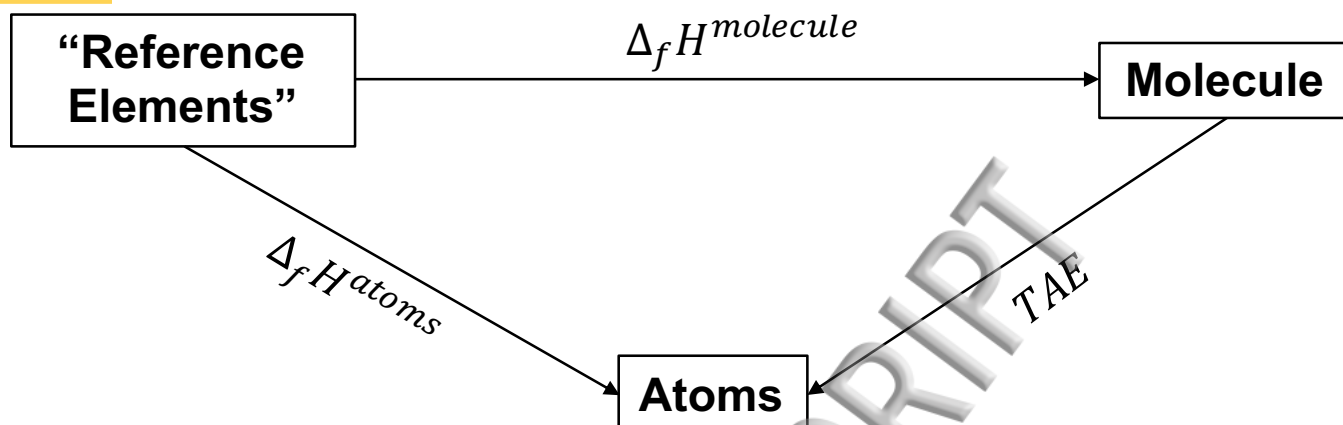


FIG. 1: Diagrammatic representation of how enthalpies of formation are calculated. Enthalpies of formation for the individual atoms are obtained from ATcT, and the total atomization energies are calculated using an *ab initio* model chemistry.

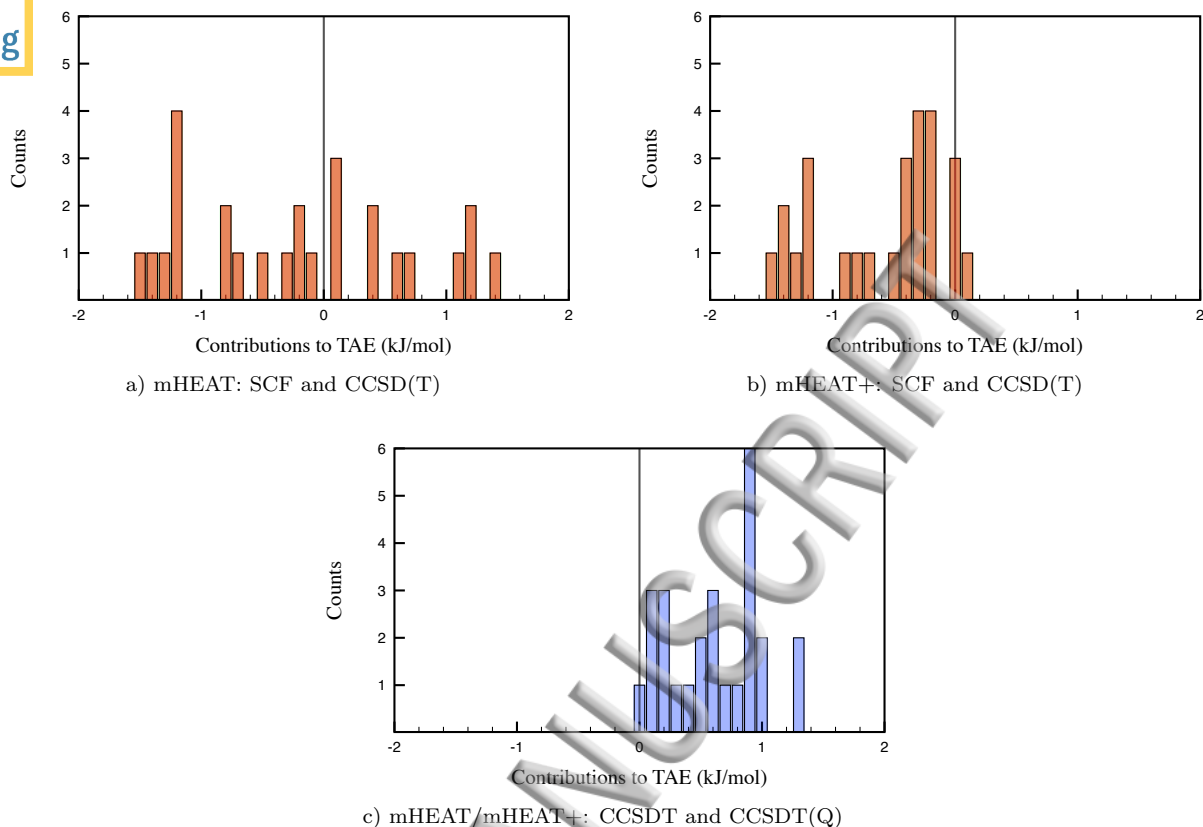


FIG. 2: Histograms of mHEAT and mHEAT+ contributions to the TAE minus their equivalents in HEAT-345(Q). From here on, ‘contributions’ may be understood to mean ‘contributions to the total atomization energies’. The data points are grouped into two sets. The red points represent the  $E_{SCF}^{\infty} + \Delta E_{fc-CCSD(T)}^{\infty} + \Delta E_{core}$  contributions of mHEAT (a) and mHEAT+ (b) compared to the  $E_{SCF}^{\infty} + \Delta E_{cc-CCSD(T)}^{\infty}$  contributions of HEAT. The blue points similarly compare the  $\Delta E_{CCSDT} + \Delta E_{CCSDT(Q)}$  contributions of mHEAT/mHEAT+ (c) to the  $\Delta E_{CCSDT}^{\infty} + \Delta E_{CCSDT(Q)}$  of HEAT. These histograms elucidate the performance of mHEAT and mHEAT+. Molecules for which the red and blue data points lie on opposite sides of zero match the HEAT total atomization energies due to cancelation of errors. However, in mHEAT, hydrogen containing species frequently produce  $E_{SCF}^{\infty} + \Delta E_{fc-CCSD(T)}^{\infty} + \Delta E_{core}$  contributions that are more positive than their equivalent in HEAT-345(Q). These positive ‘shifts’ compound with the effects of the new CCSDT and CCSDT(Q) procedures to cause mHEAT to overestimate the TAE for these important molecules.



TABLE I: A schematic comparison of HEAT-345(Q), mHEAT, and mHEAT+ model chemistries

	HEAT-345(Q)	mHEAT	mHEAT+ <sup>a</sup>
Geometry	ae-CCSD(T)/cc-pVQZ	fc-CCSD(T)/ANO1	
$E_{SCF}^{\infty}$	SCF/aug-cc-pCVXZ (X=T,Q,5)	SCF/cc-pVXZ (X=T,Q,5)	SCF/cc-pVXZ(+sp) <sup>b</sup> (X=T,Q,5)
$\Delta E_{CCSD(T)}^{\infty}$	ae-CCSD(T)/ aug-cc-pCVXZ (X=Q,5)	fc-CCSD(T)/cc-pVXZ (X=Q,5)	fc-CCSD(T)/cc-pVXZ(+sp) <sup>b</sup> (X=Q,5)
$\Delta E_{core}$	-	ae-fc CCSD(T)/cc-pCVQZ	
$\Delta E_{CCSDT}$	fc-CCSDT-(T)/cc-pVXZ <sup>c</sup> (X=T,Q)	fc-CCSDT-(T)/cc-pVTZ	
$\Delta E_{CCSDT(Q)}$	fc-CCSDT(Q)-T/cc-pVDZ	fc-CCSDT(Q)-T/cc-pVDZ	
$\Delta E_{rel}$	ae-CCSD(T)/aug-cc-pCVTZ	ae-MP2/aug-cc-pCVTZ	
$\Delta E_{DBOC}$	ae-CCSD/aug-cc-pCVQZ or SCF/aug-cc-pVTZ <sup>d</sup>	SCF/aug-cc-pVTZ <sup>d</sup>	
$\Delta E_{SO}$	<i>experiment</i>	<i>experiment</i>	
$\Delta E_{ZPE}$	$G_0, \omega_i, X_{ij}$ : ae-CCSD(T)/cc-pVQZ	$\omega_i$ : fc-CCSD(T)/ANO1 $G_0, X_{ij}$ : fc-CCSD(T)/ANO0	

<sup>a</sup>Unless otherwise noted, mHEAT+ components are identical to mHEAT.

<sup>b</sup>Hydrogen atoms use aug-cc-pVXZ contracted to include diffuse functions for only s, p orbitals. Non-hydrogen atoms use the standard cc-pVXZ sets.

<sup>c</sup>This is the difference between the extrapolated CCSDT correlation energy and the extrapolated CCSD(T) correlation energy.

<sup>d</sup>In HEAT, this correction has historically been treated with ROHF, while UHF is recommended in mHEAT/mHEAT+. Whichever produces the more reasonable results for the system in question should be preferred.

TABLE II: Total atomization energies of mHEAT and mHEAT+<sup>a</sup>  
(kJ/mol)

Species	Recipe	$E_{SCF}^{\infty}$	$\Delta E_{CCSD(T)}^{\infty}$	$\Delta E_{CCSDT}$	$\Delta E_{CCSDT(Q)}$	$\Delta E_{core}$	$\Delta E_{rel}$	$\Delta E_{dboc}$	$\Delta E_{SO}$	$\Delta E_{ZPE}$	TAE
N <sub>2</sub>	mHEAT	479.01	470.77	-2.47	4.39	3.98	-0.44	0.08	0.00	-13.94	941.38
	mHEAT+										
H <sub>2</sub>	mHEAT	350.78	107.45	0.00	0.00	0.00	0.00	0.22	0.00	-26.08	432.37
	mHEAT+	350.79	107.44								432.37
F <sub>2</sub>	mHEAT	-159.75	320.18	-0.97	3.98	0.04	-0.08	0.02	-3.22	-5.33	154.87
	mHEAT+										
O <sub>2</sub>	mHEAT	136.40	364.24	-1.65	4.82	1.42	-0.68	0.05	-1.86	-9.43	493.31
	mHEAT+										
CO	mHEAT	726.77	354.49	-1.63	2.69	4.48	-0.61	0.07	-1.29	-12.80	1071.89
	mHEAT+										
C <sub>2</sub> H <sub>2</sub>	mHEAT	1227.30	458.71	-2.32	2.62	9.94	-1.22	0.50	-0.71	-68.82	1626.00
	mHEAT+	1227.26	458.57								1625.83
CCH	mHEAT	777.01	323.61	1.50	2.51	8.52	-1.25	0.13	-0.71	-37.66	1073.66
	mHEAT+	777.00	323.54								1073.58
CH <sub>2</sub>	mHEAT	648.95	145.87	0.07	0.13	3.23	-0.69	0.13	-0.35	-44.71	752.63
	mHEAT+	648.94	145.76								752.51
CH	mHEAT	238.06	113.11	0.47	0.11	0.72	-0.18	-0.34	-0.19	-16.85	334.90
	mHEAT+	238.05	113.02								334.80
CH <sub>3</sub>	mHEAT	1017.12	266.74	0.02	0.24	4.32	-0.78	0.20	-0.35	-77.55	1209.96
	mHEAT+	1017.10	266.54								1209.72
CO <sub>2</sub>	mHEAT	1029.14	594.36	-3.31	5.14	7.72	-1.96	0.20	-2.22	-30.24	1598.82
	mHEAT+										
H <sub>2</sub> O <sub>2</sub>	mHEAT	559.72	564.92	-1.63	3.45	2.23	-1.51	0.52	-1.86	-68.25	1057.58
	mHEAT+	559.45	563.67								1056.06
H <sub>2</sub> O	mHEAT	652.12	322.73	-0.56	1.10	1.90	-1.10	0.53	-0.93	-55.56	920.23
	mHEAT+	651.45	321.64								918.47
HCO	mHEAT	762.12	400.50	-1.01	2.75	5.02	-1.13	-0.14	-1.29	-33.65	1133.18
	mHEAT+	762.10	400.36								1133.02
HF	mHEAT	405.70	187.55	-0.39	0.80	0.94	-0.81	0.34	-1.61	-24.71	567.81
	mHEAT+	405.24	186.61								566.41
HO <sub>2</sub>	mHEAT	299.17	432.06	0.01	3.04	1.65	-1.13	0.02	-1.86	-36.68	696.28
	mHEAT+	299.13	431.67								695.84
NO	mHEAT	222.78	411.04	-0.68	3.70	2.43	-0.85	-0.77	-0.22	-11.27	626.17
	mHEAT+										
OH	mHEAT	286.17	162.23	0.02	0.48	0.81	-0.52	0.05	-0.10	-22.15	426.98
	mHEAT+	285.87	161.58								426.03
HNO	mHEAT	328.31	529.29	-1.73	4.23	2.51	-1.06	-0.22	-0.93	-35.81	824.57
	mHEAT+	328.23	528.98								824.19
CN	mHEAT	377.84	367.11	4.23	5.24	4.84	-0.70	-0.07	-0.35	-12.20	745.92
	mHEAT+										

		mHEAT+									
HCN	mHEAT	830.52	472.33	-2.50	3.73	7.05	-0.92	0.31	-0.35	-41.53	1268.63
	mHEAT+	830.53	472.26								1268.57
CF	mHEAT	337.27	215.88	-0.13	1.27	1.58	-0.66	0.03	-1.50	-7.75	545.98
	mHEAT+										
NH <sub>2</sub>	mHEAT	492.51	270.10	0.24	0.49	1.65	-0.66	-0.04	0.00	-49.34	714.94
	mHEAT+	492.24	269.54								714.12
NH <sub>3</sub>	mHEAT	840.95	404.49	-0.28	0.80	3.02	-1.06	-0.56	0.00	-88.97	1159.50
	mHEAT+	840.23	403.66								1157.95
NH	mHEAT	214.67	132.27	0.33	0.20	0.65	-0.31	-0.20	0.00	-19.35	328.26
	mHEAT+	214.58	131.96								327.86
OF	mHEAT	-65.76	283.61	1.50	2.77	0.28	-0.42	-0.04	-1.37	-6.25	214.31
	mHEAT+										

<sup>a</sup>Unless otherwise indicated, mHEAT and mHEAT+ contributions to the TAE are equivalent.

TABLE III: mHEAT and mHEAT+<sup>a</sup> total atomization energy contributions compared to HEAT-345(Q) (kJ/mol)<sup>b</sup>

Species	Recipe	$E_{SCF}^{\infty}$	$\Delta E_{CCSD(T)}^{\infty} + \Delta E_{core}$	$\Delta E_{CCSDT}$	$\Delta E_{CCSDT(Q)}$	$\Delta E_{rel}$	$\Delta E_{dboc}$	$\Delta E_{SO}$	$\Delta E_{ZPE}$	TAE
N <sub>2</sub>	mHEAT	-3.93	2.49	0.67	0.14	0.04	0.05	0.00	0.18	-0.36
	mHEAT+									
H <sub>2</sub>	mHEAT	-0.03	0.04	0.00	0.00	0.00	0.16	0.00	-0.01	0.16
	mHEAT+	-0.02	0.03							0.16
F <sub>2</sub>	mHEAT	-4.77	4.22	0.34	0.11	0.09	0.01	-0.21	0.17	-0.04
	mHEAT+									
O <sub>2</sub>	mHEAT	-3.96	3.1	0.42	0.17	0.11	0.04	-0.22	0.13	-0.21
	mHEAT+									
CO	mHEAT	-3.09	1.77	0.74	0.06	0.04	0.05	-0.09	0.19	-0.32
	mHEAT+									
C <sub>2</sub> H <sub>2</sub>	mHEAT	-1.68	0.45	0.71	0.06	-0.06	0.17	0.05	0.26	-0.04
	mHEAT+	-1.72	0.32							-0.21
CCH	mHEAT	-0.34	-0.88	0.94	0.05	-0.09	0.03	0.05	-1.19	-1.43
	mHEAT+	-0.35	-0.95							-1.51
CH <sub>2</sub>	mHEAT	-0.16	-0.03	0.09	0.00	-0.04	0.07	0.03	0.24	0.20
	mHEAT+	-0.17	-0.14							0.08
CH	mHEAT	-0.22	0.26	0.04	0.00	0.00	0.10	0.19	0.15	0.52
	mHEAT+	-0.23	0.17							0.42
CH <sub>3</sub>	mHEAT	-0.18	-0.05	0.17	0.00	-0.04	0.14	0.03	0.41	0.48
	mHEAT+	-0.20	-0.26							0.24
CO <sub>2</sub>	mHEAT	-3.94	2.43	1.18	0.11	0.06	0.05	-0.20	0.23	-0.09
	mHEAT+									
H <sub>2</sub> O <sub>2</sub>	mHEAT	-3.25	4.38	0.74	0.10	0.09	0.16	-0.22	0.55	2.54
	mHEAT+	-3.52	3.13							1.02
H <sub>2</sub> O	mHEAT	-0.28	1.61	0.41	0.01	0.03	0.12	-0.11	0.23	2.02
	mHEAT+	-0.95	0.52							0.26
HCO	mHEAT	-2.43	1.61	0.77	0.06	0.03	0.07	-0.09	0.11	0.13
	mHEAT+	-2.45	1.47							-0.03
HF	mHEAT	0.01	1.14	0.28	0.01	0.02	0.06	-0.10	-0.01	1.41
	mHEAT+	-0.45	0.21							0.01
HO <sub>2</sub>	mHEAT	-1.76	2.14	0.61	0.07	0.04	0.06	-0.22	0.24	1.18
	mHEAT+	-1.80	1.75							0.74
NO	mHEAT	-2.74	1.97	0.86	0.11	-0.06	-0.79	-0.12	0.19	-0.57
	mHEAT+									
OH	mHEAT	-0.24	0.92	0.15	0.01	0.01	0.06	-0.06	0.10	0.94
	mHEAT+	-0.54	0.28							-0.01
HNO	mHEAT	-3.38	3.45	0.72	0.13	0.09	0.18	-0.11	0.19	1.25
	mHEAT+	-3.46	3.14							0.87
CN	mHEAT	-1.54	0.31	1.09	0.16	-0.09	-0.13	0.03	0.20	0.01
	mHEAT+									

		$E_{SCF}^{\infty}$	$\Delta E_{CCSD(T)}^{\infty} + \Delta E_{core}$	$\Delta E_{CCSDT}$	$\Delta E_{CCSDT(Q)}$	$\Delta E_{rel}$	$\Delta E_{dboc}$	$\Delta E_{SO}$	$\Delta E_{ZPE}$	TAE
mHEAT+										
HCN	mHEAT	-2.98	1.77	0.71	0.11	0.00	0.11	0.03	0.15	-0.12
	mHEAT+	-2.97	1.69							-0.18
CF	mHEAT	-1.19	0.84	0.47	0.04	0.05	0.02	-0.08	0.14	0.27
	mHEAT+									
NH <sub>2</sub>	mHEAT	-0.42	0.99	0.18	0.01	-0.01	0.1	0.00	0.27	1.11
	mHEAT+	-0.69	0.43							0.29
NH <sub>3</sub>	mHEAT	-0.43	1.48	0.35	0.01	0.01	0.14	0.00	0.47	2.02
	mHEAT+	-1.15	0.65							0.47
NH	mHEAT	-0.21	0.52	0.04	0.00	-0.01	0.04	0.00	0.14	0.52
	mHEAT+	-0.3	0.21							0.12
OF	mHEAT	-1.72	1.45	0.45	0.08	-0.04	-0.04	-0.13	0.12	0.16
	mHEAT+									
		$E_{SCF}^{\infty}$	$\Delta E_{CCSD(T)}^{\infty} + \Delta E_{core}$	$\Delta E_{CCSDT}$	$\Delta E_{CCSDT(Q)}$	$\Delta E_{rel}$	$\Delta E_{dboc}$	$\Delta E_{SO}$	$\Delta E_{ZPE}$	TAE
mHEAT	average	-1.73	1.48	0.50	0.06	0.01	0.04	-0.06	0.15	0.45
	st. dev.	1.54	1.32	0.33	0.06	0.06	0.18	0.11	0.30	0.89
	max	-4.77	4.38	1.18	0.17	0.11	0.79	-0.22	-1.19	2.54
	avg. hyd. <sup>c</sup>	-1.06	1.17	0.41	0.04	0.00	0.10	-0.03	0.13	0.76
	avg. nonhyd. <sup>d</sup>	-2.99	2.06	0.69	0.11	0.02	-0.08	-0.11	0.17	-0.13
mHEAT+	average	-1.84	1.20	0.50	0.06	0.01	0.04	-0.06	0.15	0.06
	st. dev.	1.47	1.29	0.33	0.06	0.06	0.18	0.11	0.30	0.49
	max	-4.77	4.22	1.18	0.17	0.11	0.79	-0.22	-1.19	-1.51
	avg. hyd. <sup>c</sup>	-1.23	0.74	0.41	0.04	0.00	0.10	-0.03	0.13	0.16
	avg. nonhyd. <sup>d</sup>	-2.99	2.06	0.69	0.11	0.02	-0.08	-0.11	0.17	-0.13

<sup>a</sup>Unless otherwise indicated, mHEAT and mHEAT+ contributions to the TAE are equivalent.

<sup>b</sup>Values are mHEAT or mHEAT+ contributions - equivalent in value in HEAT-345(Q).

<sup>c</sup>Molecules containing hydrogen.

<sup>d</sup>Molecules not containing hydrogen.

TABLE IV: mHEAT, mHEAT+, and HEAT-345(Q) enthalpies of formation vs ATcT (version 1.122d)

Species	Recipe	$\Delta_f H$ (kJ/mol)	ATcT (kJ/mol)	Difference
N <sub>2</sub>	mHEAT	-0.22	0.00	-0.22
	mHEAT+	-0.22	0.00	-0.22
	HEAT-345(Q)	-0.58	0.00	-0.58
H <sub>2</sub>	mHEAT	-0.30	0.00	-0.30
	mHEAT+	-0.30	0.00	-0.30
	HEAT-345(Q)	-0.15	0.00	-0.15
F <sub>2</sub>	mHEAT	-0.36	0.00	-0.36
	mHEAT+	-0.36	0.00	-0.36
	HEAT-345(Q)	-0.43	0.00	-0.43
O <sub>2</sub>	mHEAT	0.37	0.00	0.37
	mHEAT+	0.37	0.00	0.37
	HEAT-345(Q)	0.17	0.00	0.17
CO	mHEAT	-113.64	-113.80	0.16
	mHEAT+	-113.64	-113.80	0.16
	HEAT-345(Q)	-113.97	-113.80	-0.17
C <sub>2</sub> H <sub>2</sub>	mHEAT	228.88	228.83	0.05
	mHEAT+	229.06	228.83	0.23
	HEAT-345(Q)	228.84	228.83	0.01
HCC	mHEAT	565.19	563.87	1.32
	mHEAT+	565.26	563.87	1.39
	HEAT-345(Q)	563.75	563.87	-0.12
CH <sub>2</sub>	mHEAT	390.84	391.03	-0.19
	mHEAT+	390.96	391.03	-0.07
	HEAT-345(Q)	391.05	391.03	0.01
HC	mHEAT	592.54	592.81	-0.27
	mHEAT+	592.64	592.81	-0.17
	HEAT-345(Q)	593.05	592.81	0.24
CH <sub>3</sub>	mHEAT	149.55	149.83	-0.28
	mHEAT+	149.78	149.83	-0.04
	HEAT-345(Q)	150.03	149.83	0.20
CO <sub>2</sub>	mHEAT	-393.73	-393.11	-0.62
	mHEAT+	-393.73	-393.11	-0.62
	HEAT-345(Q)	-393.82	-393.11	-0.71
H <sub>2</sub> O <sub>2</sub>	mHEAT	-131.82	-129.49	-2.33
	mHEAT+	-130.31	-129.49	-0.82
	HEAT-345(Q)	-129.28	-129.49	0.21
H <sub>2</sub> O	mHEAT	-241.31	-238.94	-2.38
	mHEAT+	-239.56	-238.94	-0.62
	HEAT-345(Q)	-239.30	-238.94	-0.36
HCO	mHEAT	41.10	41.43	-0.33
	mHEAT+	41.26	41.43	-0.17
	HEAT-345(Q)	41.24	41.43	-0.19
HF	mHEAT	-274.52	-272.68	-1.85
	mHEAT+	-273.13	-272.68	-0.45
	HEAT-345(Q)	-273.10	-272.68	-0.42

HO <sub>2</sub>	mHEAT	13.44	15.12	-1.68
	mHEAT+	13.88	15.12	-1.24
	HEAT-345(Q)	14.62	15.12	-0.50
NO	mHEAT	91.26	90.62	0.64
	mHEAT+	91.26	90.62	0.64
	HEAT-345(Q)	90.68	90.62	0.07
OH	mHEAT	35.90	37.24	-1.34
	mHEAT+	36.85	37.24	-0.40
	HEAT-345(Q)	36.83	37.24	-0.41
HNO	mHEAT	108.88	109.93	-1.05
	mHEAT+	109.27	109.93	-0.66
	HEAT-345(Q)	110.14	109.93	0.21
CN	mHEAT	436.06	436.71	-0.65
	mHEAT+	436.06	436.71	-0.65
	HEAT-345(Q)	436.09	436.71	-0.62
HCN	mHEAT	129.39	129.67	-0.28
	mHEAT+	129.45	129.67	-0.21
	HEAT-345(Q)	129.27	129.67	-0.40
CF	mHEAT	242.68	243.14	-0.46
	mHEAT+	242.68	243.14	-0.46
	HEAT-345(Q)	242.94	243.14	-0.20
NH <sub>2</sub>	mHEAT	187.70	188.91	-1.21
	mHEAT+	188.53	188.91	-0.38
	HEAT-345(Q)	188.82	188.91	-0.09
NH <sub>3</sub>	mHEAT	-40.81	-38.57	-2.25
	mHEAT+	-39.27	-38.57	-0.71
	HEAT-345(Q)	-38.80	-38.57	-0.23
NH	mHEAT	358.35	358.74	-0.39
	mHEAT+	358.76	358.74	0.02
	HEAT-345(Q)	358.87	358.74	0.13
OF	mHEAT	109.78	110.27	-0.49
	mHEAT+	109.78	110.27	-0.49
	HEAT-345(Q)	109.94	110.27	-0.33
mHEAT	average			-0.63
	st. dev.			0.91
	max error			-2.38
mHEAT+	average			-0.24
	st. dev.			0.52
	max error			1.39
HEAT-345(Q)	average			-0.18
	st. dev.			0.28
	max error			-0.76

TABLE V: mHEAT, mHEAT+<sup>a</sup>, and HEAT-345(Q)<sup>b</sup> contributions to barrier heights (kJ/mol)<sup>c</sup>

Reaction Barrier	Recipe	$E_{SCF}^{\infty}$	$\Delta E_{CCSD(T)}^{\infty} + \Delta E_{core}$	$\Delta E_{CCSDT}$	$\Delta E_{CCSDT(Q)}$	$\Delta E_{rel}$	$\Delta E_{dboc}^b$	$\Delta E_{ZPE}$	Total	Difference
O( <sup>3</sup> P)+H <sub>2</sub> → H+OH	HEAT-345(Q)	134.44	-78.53	-0.73	-0.42	0.17	0.72	-9.56	46.09	
	mHEAT	136.15	-81.46	-0.63	-0.44	0.23	1.40	-10.59	44.66	-1.43
	mHEAT+	136.37	-80.65						45.69	-0.40
H+NH <sub>3</sub> → H <sub>2</sub> +NH <sub>2</sub>	HEAT-345(Q)	97.13	-31.53	-1.07	-0.03	-0.34	0.71	-6.85	58.03	
	mHEAT	99.14	-33.39	-0.93	-0.05	-0.31	1.00	-7.27	58.19	0.16
	mHEAT+	98.66	-33.50						57.61	-0.42
CH <sub>2</sub> O → H <sub>2</sub> +CO	HEAT-345(Q)	170.59	-43.99	0.41	-1.73	-0.41	0.85	-20.88	104.84	
	mHEAT	170.76	-43.74	0.10	-1.81	-0.43	1.70	-20.87	105.72	0.87
	mHEAT+	170.80	-43.82						105.67	0.83
H+H <sub>2</sub> → H <sub>2</sub> +H	HEAT-345(Q)	73.67	-33.15	-0.32	0.00	0.00	0.65	-5.19	35.66	
	mHEAT	73.62	-33.21	-0.31	0.00	0.00	1.00	-4.86	36.24	0.58
	mHEAT+	73.64	-33.15						36.32	0.66
CH <sub>3</sub> NC → CH <sub>3</sub> CN	HEAT-345(Q)	183.25	-14.90	0.31	-0.85	-0.54	0.07	-7.53	159.81	
	mHEAT	183.14	-15.55	0.32	-0.88	-0.54	0.07	-7.35	159.21	-0.61
	mHEAT+	183.13	-15.40						159.34	-0.47
HOCO → H+CO <sub>2</sub>	HEAT-345(Q)	423.01	-59.39	-0.60	-1.11	-0.26	0.05	-22.04	339.66	
	mHEAT	196.73	-60.56	-0.77	-1.13	-0.28	0.09	-21.85	340.12	0.46
	mHEAT+	424.42	-60.64						339.83	0.17
HCN → HNC	HEAT-345(Q)	197.26	4.18	-0.67	0.41	-0.29	0.05	-14.15	186.78	
	mHEAT	196.73	4.28	-0.67	0.43	-0.27	0.11	-14.27	186.34	-0.45
	mHEAT+	196.75	4.38						186.45	-0.33
mHEAT	average									-0.06
	st. dev.									0.85
mHEAT+	average									0.01
	st. dev.									0.55

<sup>a</sup>Unless otherwise noted, mHEAT+ components are identical to mHEAT.

<sup>b</sup>The HEAT DBOC values here are obtained using fc-CCSD/aug-cc-pVTZ for expediency.

<sup>c</sup>Note that contributions of the spin-orbit coupling term have been assumed to cancel.