# Quantum-Mechanical Energy Calculations in Chemistry

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Dedicated to Professor *Edgar Heilbronner*, a brilliant theoretical chemist and a great man, on the occasion of his 80th birthday

Truncation of the one-electron basis set is, in general, the main source of error in nonempirical quantum-chemical energy calculations. Total-energy estimates for infinite basis sets are needed. We use an efficient extrapolation to zero in linear dependences between total energies of atoms (H, He, Ne, Ar) and molecules ($H_2^+$, $H_2$, HF, HCl, $H_2O$, CO, $(Ne)_2$, $(Ar)_2$, $(HF)_2$, $(H_2O)_2$) and a reciprocal total number of basis-set functions; this is equivalent to the extrapolation to the infinite basis set. The procedure works satisfactorily when the coupled-cluster method [CCSD(T)] is employed with correlation-consistent polarized-valence (cc-PVXZ) basis sets. Energy changes rather than absolute energies play a role in molecular sciences. When calculating $\Delta E$, attention has to be paid to associations of the chemical and *van der Waals* type, where basis set superposition error should be considered, even with an extensive basis set. The original function counterpoise method by *Boys* and *Bernardi* is applied. In chemistry and in the whole area of biodisciplines, it is *Gibbs* energy rather than energy which plays a key role. When statistical mechanics for obtaining *Gibbs* energy changes and related characteristics are used, it is always desirable to investigate the propagation of error and to establish the critical, *i.e.*, the error-determining quantity.

**Introduction.** – In the middle of the 19th century, *i.e.*, 150 years ago, an early stage in the advent of energy considerations in chemistry was initiated. At the same time, the first chemical-kinetics measurements were carried out, and the second half of that century was devoted largely to thermodynamic studies. About 75 years ago, a most sophisticated and powerful tool for energy calculations – quantum mechanics – was developed. Extensive exploitation of quantum-mechanical energy calculations started about 50 years ago; for the past 25 years, these calculations have been routinely carried out at the *ab initio* level [1][2]. The 'besetting sin' of quantum chemistry, namely, the neglect of a proper consideration of electron correlation [3][4], has been overcome to a significant extent during the last 20 years [5].

It is fair to pose the following question: Is it still relevant to deal with the subject given in the title of this paper? Notwithstanding, we feel that it is meaningful and topical, and our reasons are as follows. The impressive efforts exerted by quantum chemists during the second half of the 20th century were traditionally accompanied by some rather unfortunate consequences. Specifically, because of the rapid development of computational methods, computer software, and hardware serving for energy calculation, the most recent methods were believed to be the right kind, and earlier procedures were regarded as more or less insufficient. This widespread meaning has never been proven true. Not only that: it has, in fact, produced losses for years. The point is that the very large spectrum of properties and structural types still needs a rather broad spectrum of computational tools. Even the simplest version of the molecular-orbital method is still functional and, in a proper context, still valuable. Not only that, it is obviously unending.

In connection with the nonempirical (*ab initio*) MO method, it is sometimes assumed that any basis-set extension manifests itself by an improvement of energy calculation. In principle, this is true, but an improper basis-set extension leads rather to a significant increase in computer time than to a significant improvement of the calculated-energy quality. Even a sophisticated basis-set extension is not sufficient for obtaining reliable $\Delta E$ values of association reactions when the basis set superposition error is not taken into account. Moreover, serious shortcomings occur frequently when using an improper basis set (*e.g.*, a poor nature set, or a good-quality basis set of small size, or a good basis set lacking in special instances diffuse functions) with correlation energy calculations.

For years it was a dream of computational chemists to reach, when calculating heats of formation, an accuracy of ± 1 kcal/mol with respect to the experimental value. This has been already achieved for a majority of small molecules due to three circumstances, namely, essential progress in calculating electron correlation, significant improvement of the basis-set quality, and an extraordinary expansion in computer efficiency, accompanied by a drop in computer prices. More specifically, although MB-RSPT (many body *Rayleigh-Schrödinger* perturbation treatment), labeled later MP (*Møller-Plesset*) [6], has made quantum-chemistry calculations semiquantitative or even quantitative, a real breakthrough has been achieved with the coupled-cluster (CC) methods [5]. The CCSD(T) (coupled cluster with all single and double substitutions and a perturbative treatment of connected triple substitutions) level of this method [7], *cf.* [8], when used with sophisticated basis sets and combined with some additional procedures, leads to a new horizon at which heats of formation can be obtained with an accuracy of ± 0.2 kcal/mol. To attain such an accuracy, correlation-consistent (cc) basis sets have to be used [9–13]. Nowadays, basis parameters are available for atoms ranging from H through Ar. Two types of sets are available, namely, cc-pVXZ (correlation-consistent polarized valence X-zeta) and aug-cc-pVXZ (aug stands for augmented). Label X assumes values 2, 3, 4, 5, 6 (*i.e.*, double, triple, quadruple, quintuple, and sextuple-zeta). The main source of error in nonempirical calculations is the truncation of the one-electron basis set. To obtain complete basis-set characteristics, it is necessary to carry out one of the proposed extrapolations to the infinite basis set [14–32]. Very simple (like exponential [9][20][25][30][31] or $1/n^3$ [27][29]) or slightly more involved [22][24][27][29] extrapolation formulas have been used for obtaining complete basis-set characteristics. Extrapolation schemes were used in connection with calculations of thermochemical characteristics [28][33], interaction energies [34], kinetic data [12], electron affinities [32], hyperpolarisability [32], and electronically excited states [30][31]. Abbreviated results of the present work were announced recently [35]. Our colleagues have used the procedure described here for accurate calculations of electron affinity and hyperpolarisability of oxygen [32]. (For valuable analyses of various extrapolation schemes, see [22][27][29]).

The purpose of this paper is to describe an efficient approach to the estimate of the *Hartree-Fock* (H.F.) energy limit and accurate nonrelativistic total energy of atoms and molecules. Moreover, proper attention will also be paid to the role of the basis set superposition error when calculating energy changes ($\Delta E$) of addition reactions. This will be tested by means of *van der Waals*' interactions, which are among the most demanding from the standpoint of $\Delta E$ calculations. In the final part of the study, the passing from energy changes to *Gibbs*-energy changes will be briefly outlined. Attention will be paid to finding the error-determining (*i.e.*, critical) quantity in $\Delta G$ calculations. To obtain the *Hartree-Fock-Roothaan* (H.F.) energy limit, it is necessary to carry out a set of energy calculations for basis sets possessing an increasing number of basis-set functions ($n$): extrapolation for $n \rightarrow \infty$ leads to the required energy value. Unfortunately, such an attempt requires quite a number of calculations for increasing $n$, and even then, it is not always easy to carry out the extrapolation for $n \rightarrow \infty$. We found it expedient to pass to an approximately linear dependence $E = \mathrm{f}(1/n)$ and to carry out the extrapolation to $1/n \rightarrow 0$, which is much easier. This possibility was exploited in this study for energies of atoms and molecules, and for calculations of energy changes.

The points of view adopted in this work arise from our interest in interactions (both chemical and *van der Waals*') between relatively large organic molecules. With such systems, there is little chance to calculate in the near future electron correlation at the same level currently available for atoms and small molecules. Moreover, it is not energy but rather enthalpy or *Gibbs* energy that represents our ultimate interest. Dealing with large systems requires a permanent search for a compromise between price and accuracy. This work is preparatory to these attempts.

**Calculations.** – All calculations in this paper were performed by means of the Gaussian98 program package, which makes it possible to exploit various *ab initio* and semiempirical quantum-chemical methods [36]. To find the electron correlations in the case of the $(HF)_2$, $(H_2O)_2$, $(Ar)_2$, and $(Ne)_2$ complexes, the *Møller-Plesset* second-order-perturbation theory (MP2) [37] was used. For atoms, $H_2^+$, and molecules, we applied the coupled-cluster theory including the single, double, and perturbatively triple substitutions CCSD(T) [7][38–40]. The H.F., MP2, and MP4 energy values were obtained as intermediate results in the CCSD(T) calculations. Several correlation-consistent Gaussian basis sets of atomic orbitals were used here. They ranged from valence double-zeta (cc-pVDZ) to valence quadruple-zeta (cc-pVQZ) for complexes $(HF)_2$, $(H_2O)_2$, $(Ar)_2$, and $(Ne)_2$, to valence quintuple-zeta for atoms and molecules, and to valence sextuple-zeta for H, $H_2^+$, and $H_2$. Because of the importance of diffuse functions, we used also the augmented basis sets, namely aug-cc-pVXZ, X = 2, ..., 6, where one diffuse function to each angular-momentum type is added.

The list of species under study includes atoms **1**–**4**, molecules **5**–**10**, and the '*van der Waals* molecules' **11**–**14**.

**Results and Discussion.** – In *Table 1*, total energies of the model species are summarized. For all the systems, total energies were plotted against the reciprocal values of the total number of atomic functions in the basis set. For a given set of bases, points are obtained that permit linear fits. The least-squares method was used for extrapolation, *i.e.*, for obtaining estimates for complete basis sets. In the case of SCF (*Hartree-Fock-Roothaan*) calculations, extrapolation of the $E$ *vs.* $1/n$ plots to zero

| $H$ | $He$ | $Ne$ | $Ar$ | $H_2^+$ | $H_2$ |
|---|---|---|---|---|---|
| **1** | **2** | **3** | **4** | **5** | **6** |

| $HF$ | $HCl$ | $H_2O$ | $CO$ |
|---|---|---|---|
| **7** | **8** | **9** | **10** |

| $(Ne)_2$ | $(Ar)_2$ | $(HF)_2$ | $(H_2O)_2$ |
|---|---|---|---|
| **11** | **12** | **13** | **14** |

represents a good approximation to the H.F. limit. Similar extrapolations for data based on a method picking up a high percentage of electron correlation, CCSD(T) in this paper, leads to a good estimate of the total non-relativistic energy. From the plots of *E vs.* 1/*n* it is seen that in all instances, data for the basis sets and augmented basis sets converge approximately to the same limit. *Fig. 1* presents, for illustration, the plots for hydrogen fluoride (**7**) and water (**9**). These dependences show, in accordance with previous experience, that the cc-pVDZ basis sets are not always good enough to be included in extrapolations. Generally, points for triple- through quintuple-zeta calculations fit linear dependences very well. However, comparison of extrapolated total energies with observed ones suggest curvature of the dependences in the region

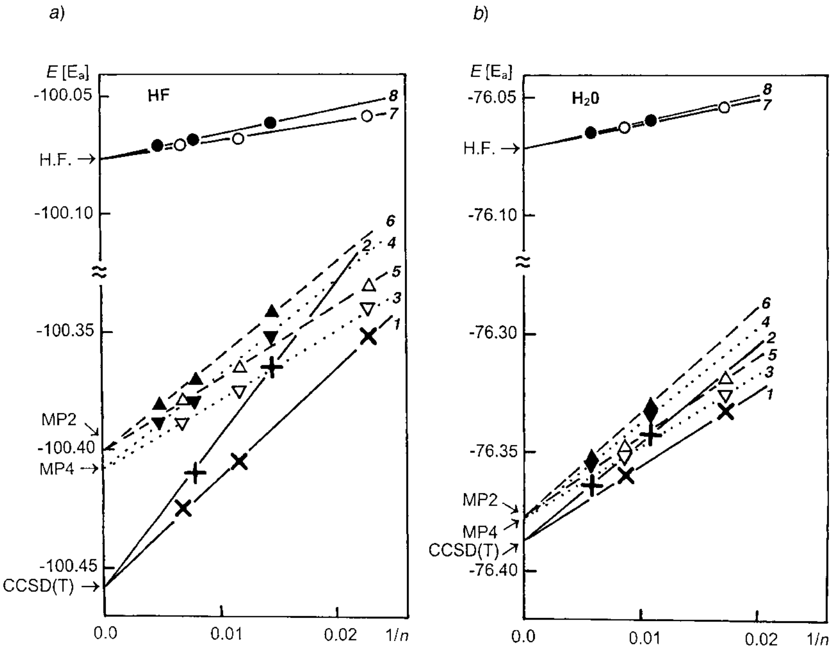

Fig. 1. *Total energies* E [$E_a$] *of* a) *hydrogen fluoride* (**7**) *and* b) *water* (**9**), *calculated at H.F., MP2, MP4, and CCSD(T) levels plotted against reciprocal values 1/*n *of number of functions in the respective basis set. 1,* CCSD(T)/cc-pVXZ; *2,* CCSD(T)/aug-cc-pVXZ; *3,* MP4/cc-pVXZ; *4,* MP4/aug-cc-pVXZ; *5,* MP2/cc-pVXZ; *6,* MP2/aug-cc-pVXZ; *7,* H.F./cc-pVXZ; *8,* H.F./aug-cc-pVXZ.

Table 1. *Total Energies* E [$E_a$] *for Species* **1**–**14**, *Total Number* n *of Atomic Functions in the Basis Set, and Extrapolated Energies for 1*/n → *0*

| Method and basis set | *n* | 1/*n* | *E* [$E_a$] | Limit for 1/*n* → 0 |
|---|---|---|---|---|
| H (**1**): | | | | |
| H.F./cc-pVTZ | 14 | 0.07143 | – 0.49981 | – 0.50005 |
| H.F./cc-pVQZ | 30 | 0.03333 | – 0.49995 | |
| H.F./cc-pV5Z | 55 | 0.01818 | – 0.49999 | |
| H.F./cc-pV6Z | 91 | 0.01099 | – 0.50000 | |
| H.F./aug-cc-pVTZ | 23 | 0.04348 | – 0.49982 | – 0.50005 |
| H.F./aug-cc-pVQZ | 46 | 0.02174 | – 0.49995 | |
| H.F./aug-cc-pV5Z | 80 | 0.01250 | – 0.49999 | |
| H.F./aug-cc-pV6Z | 127 | 0.00787 | – 0.50000 | |
| He (**2**): | | | | |
| H.F./cc-pVTZ | 14 | 0.07143 | – 2.86115 | – 2.86170 |
| H.F./cc-pVQZ | 30 | 0.03333 | – 2.86151 | |
| H.F./cc-pV5Z | 55 | 0.01818 | – 2.86152 | |
| MP2/cc-pVTZ | 14 | 0.07143 | – 2.89429 | – 2.89932 |
| MP2/cc-pVQZ | 30 | 0.03333 | – 2.89699 | |
| MP2/cc-pV5Z | 55 | 0.01818 | – 2.89803 | |
| MP4/cc-pVTZ | 14 | 0.07143 | – 2.90006 | – 2.90401 |
| MP4/cc-pVQZ | 30 | 0.03333 | – 2.90223 | |
| MP4/cc-pV5Z | 55 | 0.01818 | – 2.90297 | |
| Ne (**3**): | | | | |
| H.F./cc-pVTZ | 30 | 0.03333 | – 128.53186 | – 128.55492 |
| H.F./cc-pVQZ | 55 | 0.01818 | – 128.54347 | |
| H.F./cc-pV5Z | 91 | 0.01099 | – 128.54677 | |
| MP2/cc-pVTZ | 30 | 0.03333 | – 128.79618 | – 128.88214 |
| MP2/cc-pVQZ | 55 | 0.01818 | – 128.83704 | |
| MP2/cc-pV5Z | 91 | 0.01099 | – 128.85294 | |
| MP4/cc-pVTZ | 30 | 0.03333 | – 128.79853 | – 128.88108 |
| MP4/cc-pVQZ | 55 | 0.01818 | – 128.83853 | |
| MP4/cc-pV5Z | 91 | 0.01099 | – 128.85266 | |
| CCSD(T)/cc-pVTZ | 30 | 0.03333 | – 128.80245 | – 128.88767 |
| CCSD(T)/cc-pVQZ | 55 | 0.01818 | – 128.84369 | |
| CCSD(T)/cc-pV5Z | 91 | 0.01099 | – 128.85836 | |
| Ar (**4**): | | | | |
| H.F./cc-pVTZ | 34 | 0.02941 | – 526.81313 | – 526.82174 |
| H.F./cc-pVQZ | 59 | 0.01695 | – 526.81678 | |
| MP2/cc-pVTZ | 34 | 0.02941 | – 527.01904 | – 527.23479 |
| MP2/cc-pVQZ | 59 | 0.01695 | – 527.11045 | |
| MP4/cc-pVTZ | 34 | 0.02941 | – 527.03699 | – 527.24660 |
| MP4/cc-pVQZ | 59 | 0.01695 | – 527.12579 | |
| CCSD(T)/cc-pVTZ | 34 | 0.02941 | – 527.04307 | – 527.25983 |
| CCSD(T)/cc-pVQZ | 59 | 0.01695 | – 527.13490 | |
| H.F./aug-cc-pVTZ | 50 | 0.02000 | – 526.81335 | – 526.82188 |
| H.F./aug-cc-pVQZ | 84 | 0.01190 | – 526.81680 | |
| MP2/aug-cc-pVTZ | 50 | 0.02000 | – 527.05737 | – 527.19570 |
| MP2/aug-cc-pVQZ | 84 | 0.01190 | – 527.11339 | |
| MP4/aug-cc-pVTZ | 50 | 0.02000 | – 527.08026 | – 527.22220 |
| MP4/aug-cc-pVQZ | 84 | 0.01190 | – 527.13775 | |
| CCSD(T)/aug-cc-pVTZ | 50 | 0.02000 | – 527.08028 | – 527.22189 |
| CCSD(T)/aug-cc-pVQZ | 84 | 0.01190 | – 527.13763 | |

Table 1. *(cont.)*

| Method and basis set | *n* | 1/*n* | *E* [$E_a$] | Limit for 1/*n* → 0 |
|---|---|---|---|---|
| $H_2^+$ (**5**): | | | | |
| H.F./cc-pVTZ | 28 | 0.03571 | – 0.60224 | – 0.60273 |
| H.F./cc-pVQZ | 60 | 0.01667 | – 0.60252 | |
| H.F./cc-pV5Z | 110 | 0.00909 | – 0.60262 | |
| H.F./cc-pV6Z | 182 | 0.00549 | – 0.60263 | |
| H.F./aug-cc-pVTZ | 46 | 0.02174 | – 0.60230 | – 0.60273 |
| H.F./aug-cc-pVQZ | 92 | 0.01089 | – 0.60254 | |
| H.F./aug-cc-pV5Z | 160 | 0.00625 | – 0.60262 | |
| H.F./aug-cc-pV6Z | 254 | 0.00394 | – 0.60263 | |
| $H_2$ (**6**): | | | | |
| H.F./cc-pVTZ | 28 | 0.03571 | – 1.13294 | – 1.13379 |
| H.F./cc-pVQZ | 60 | 0.01667 | – 1.13345 | |
| H.F./cc-pV5Z | 110 | 0.00909 | – 1.13360 | |
| H.F./cc-pV6Z | 182 | 0.00549 | – 1.13362 | |
| MP2/cc-pVTZ | 28 | 0.03571 | – 1.16464 | – 1.16812 |
| MP2/cc-pVQZ | 60 | 0.01667 | – 1.16658 | |
| MP2/cc-pV5Z | 110 | 0.00909 | – 1.16727 | |
| MP2/cc-pV6Z | 182 | 0.00549 | – 1.16752 | |
| MP4/cc-pVTZ | 28 | 0.03571 | – 1.17173 | – 1.17418 |
| MP4/cc-pVQZ | 60 | 0.01667 | – 1.17318 | |
| MP4/cc-pV5Z | 110 | 0.00909 | – 1.17360 | |
| MP4/cc-pV6Z | 182 | 0.00549 | – 1.17372 | |
| CCSD(T)/cc-pVTZ | 28 | 0.03571 | – 1.17234 | – 1.17482 |
| CCSD(T)/cc-pVQZ | 60 | 0.01667 | – 1.17380 | |
| CCSD(T)/cc-pV5Z | 110 | 0.00909 | – 1.17422 | |
| CCSD(T)/cc-pV6Z | 182 | 0.00549 | – 1.17435 | |
| H.F./aug-cc-pVTZ | 46 | 0.02174 | – 1.13300 | – 1.13381 |
| H.F./aug-cc-pVQZ | 92 | 0.01087 | – 1.13346 | |
| H.F./aug-cc-pV5Z | 160 | 0.00625 | – 1.13360 | |
| H.F./aug-cc-pV6Z | 254 | 0.00393 | – 1.13362 | |
| MP2/aug-cc-pVTZ | 46 | 0.02174 | – 1.16501 | – 1.16824 |
| MP2/aug-cc-pVQZ | 92 | 0.01087 | – 1.16672 | |
| MP2/aug-cc-pV5Z | 160 | 0.00625 | – 1.16736 | |
| MP2/aug-cc-pV6Z | 254 | 0.00393 | – 1.16758 | |
| MP4/aug-cc-pVTZ | 46 | 0.02174 | – 1.17202 | – 1.17422 |
| MP4/aug-cc-pVQZ | 92 | 0.01087 | – 1.17325 | |
| MP4/aug-cc-pV5Z | 160 | 0.00625 | – 1.17387 | |
| MP4/aug-cc-pV6Z | 254 | 0.00393 | – 1.17374 | |
| CCSD(T)/aug-cc-pVTZ | 46 | 0.02174 | – 1.17264 | – 1.17484 |
| CCSD(T)/aug-cc-pVQZ | 92 | 0.01087 | – 1.17387 | |
| CCSD(T)/aug-cc-pV5Z | 160 | 0.00625 | – 1.17425 | |
| CCSD(T)/aug-cc-pV6Z | 254 | 0.00393 | – 1.17436 | |
| HF (**7**): | | | | |
| H.F./cc-pVTZ | 44 | 0.02273 | – 100.05805 | – 100.07648 |
| H.F./cc-pVQZ | 85 | 0.01176 | – 100.06777 | |
| H.F./cc-pV5Z | 146 | 0.00685 | – 100.07050 | |
| MP2/cc-pVTZ | 44 | 0.02273 | – 100.32979 | – 100.40072 |
| MP2/cc-pVQZ | 85 | 0.01176 | – 100.36520 | |
| MP2/cc-pV5Z | 146 | 0.00685 | – 100.37874 | |

Table 1. *(cont.)*

| Method and basis set | $n$ | $1/n$ | $E$ [$E_a$] | Limit for $1/n \to 0$ |
|---|---|---|---|---|
| MP4/cc-pVTZ | 44 | 0.02273 | – 100.33948 | – 100.40884 |
| MP4/cc-pVQZ | 85 | 0.01176 | – 100.37477 | |
| MP4/cc-pV5Z | 146 | 0.00685 | – 100.38701 | |
| CCSD(T)/cc-pVTZ | 44 | 0.02273 | – 100.35135 | – 100.45781 |
| CCSD(T)/cc-pVQZ | 85 | 0.01176 | – 100.40524 | |
| CCSD(T)/cc-pV5Z | 146 | 0.00685 | – 100.42443 | |
| HCl (**8**): | | | | |
| H.F./cc-pVTZ | 48 | 0.02083 | – 460.10679 | – 460.11635 |
| H.F./cc-pVQZ | 89 | 0.01124 | – 460.11119 | |
| MP2/cc-pVTZ | 48 | 0.02083 | – 460.30944 | – 460.36216 |
| MP2/cc-pVQZ | 89 | 0.01124 | – 460.33371 | |
| MP4/cc-pVTZ | 48 | 0.02083 | – 460.33684 | – 460.39119 |
| MP4/cc-pVQZ | 89 | 0.01124 | – 460.36187 | |
| CCSD(T)/cc-pVTZ | 48 | 0.02083 | – 460.33722 | – 460.39134 |
| CCSD(T)/cc-pVQZ | 89 | 0.01124 | – 460.36213 | |
| $H_2O$ (**9**): | | | | |
| H.F./cc-pVTZ | 58 | 0.01724 | – 76.05694 | – 76.07270 |
| H.F./cc-pVQZ | 115 | 0.00870 | – 76.06475 | |
| MP2/cc-pVTZ | 58 | 0.01724 | – 76.31866 | – 76.37714 |
| MP2/cc-pVQZ | 115 | 0.00870 | – 76.34764 | |
| MP4/cc-pVTZ | 58 | 0.01724 | – 76.32484 | – 76.37796 |
| MP4/cc-pVQZ | 115 | 0.00870 | – 76.35117 | |
| CCSD(T)/cc-pVTZ | 58 | 0.01724 | – 76.33222 | – 76.38787 |
| CCSD(T)/cc-pVQZ | 115 | 0.00870 | – 76.35980 | |
| CO (**10**): | | | | |
| H.F./cc-pVTZ | 60 | 0.01667 | – 112.77933 | – 112.79657 |
| H.F./cc-pVQZ | 110 | 0.00909 | – 112.78842 | |
| H.F./cc-pV5Z | 182 | 0.00550 | – 112.79028 | |
| MP2/cc-pVTZ | 60 | 0.01667 | – 113.13564 | – 113.20670 |
| MP2/cc-pVQZ | 110 | 0.00909 | – 113.16988 | |
| MP2/cc-pV5Z | 182 | 0.00550 | – 113.18233 | |
| MP4/cc-pVTZ | 60 | 0.01667 | – 113.14117 | – 113.20315 |
| MP4/cc-pVQZ | 110 | 0.00909 | – 113.17189 | |
| MP4/cc-pV5Z | 182 | 0.00550 | – 113.18148 | |
| CCSD(T)/cc-pVTZ | 60 | 0.01667 | – 113.15558 | – 113.22102 |
| CCSD(T)/cc-pVQZ | 110 | 0.00909 | – 113.18791 | |
| CCSD(T)/cc-pV5Z | 182 | 0.00550 | – 113.19819 | |
| $(Ne)_2$ (**11**): | | | | |
| MP2/cc-pVDZ | 28 | 0.03571 | – 257.34877 | – 257.78079 |
| MP2/cc-pVTZ | 60 | 0.01667 | – 257.59254 | |
| MP2/cc-pVQZ | 110 | 0.00909 | – 357.67420 | |
| MP2/cc-pV5Z | 182 | 0.00549 | – 257.70593 | |
| MP2/aug-cc-pVDZ | 46 | 0.02174 | – 257.40658 | – 257.78747 |
| MP2/aug-cc-pVTZ | 92 | 0.01087 | – 257.61172 | |
| MP2/aug-cc-pVQZ | 160 | 0.00625 | – 257.68211 | |
| MP2/aug-cc-pV5Z | 254 | 0.00394 | – 257.70961 | |

Table 1. *(cont.)*

| Method and basis set | $n$ | $1/n$ | $E$ [$E_a$] | Limit for $1/n \rightarrow 0$ |
|---|---|---|---|---|
| $(Ar)_2$ (**12**): | | | | |
| MP2/cc-pVDZ | 36 | 0.02778 | – 1053.88039 | – 1054.18028 |
| MP2/cc-pVTZ | 68 | 0.01471 | – 1054.03832 | |
| MP2/cc-pVQZ | 118 | 0.00847 | – 1054.09351 | |
| MP2/cc-pV5Z | 190 | 0.00526 | – 1054.11436 | |
| MP2/aug-cc-pVDZ | 54 | 0.01852 | – 1053.91100 | – 1054.18103 |
| MP2/aug-cc-pVTZ | 100 | 0.01000 | – 1054.04907 | |
| MP2/aug-cc-pVQZ | 168 | 0.00595 | – 1054.09842 | |
| MP2/aug-cc-pV5Z | 262 | 0.00382 | – 1054.11777 | |
| $(HF)_2$ (**13**): | | | | |
| MP2/cc-pVDZ | 38 | 0.02632 | – 200.45342 | – 200.82360 |
| MP2/cc-pVTZ | 88 | 0.01136 | – 200.66834 | |
| MP2/cc-pVQZ | 170 | 0.00588 | – 200.73818 | |
| MP2/aug-cc-pVDZ | 64 | 0.01562 | – 200.51907 | – 200.82809 |
| MP2/aug-cc-pVTZ | 138 | 0.00725 | – 200.68928 | |
| MP2/aug-cc-pVQZ | 252 | 0.00397 | – 200.74691 | |
| $(H_2O)_2$ (**14**): | | | | |
| MP2/cc-pVDZ | 48 | 0.02083 | – 152.46923 | – 152.76806 |
| MP2/cc-pVTZ | 116 | 0.00862 | – 152.64701 | |
| MP2/cc-pVQZ | 230 | 0.00435 | – 152.70403 | |
| MP2/aug-cc-pVDZ | 82 | 0.01220 | – 152.53021 | – 152.77084 |
| MP2/aug-cc-pVTZ | 184 | 0.00543 | – 152.66624 | |
| MP2/aug-cc-pVQZ | 344 | 0.00291 | – 152.71196 | |

between quintuple- and infinite-zeta. Linear extrapolations of the $E$ *vs.* $1/n$ plots do not take these slight curvatures into consideration and, therefore, the extrapolated absolute-energy values are always slightly larger than the correct values. Calculations with sextuple-zeta basis sets suggest that that curvature is real not only in the case of the hydrogen atom (**1**) and hydrogen molecule (**6**; s. *Fig. 2*), but also with a set [29] of first-row atoms.

The second- and fourth-order-perturbation calculations of electron correlation (MP2 and MP4) have played an essential role in passing from qualitative or semiquantitative to quantitative quantum chemistry. However, on the basis of results obtained, it is evident that a close enough approach to accurate total energy requires CCSD(T) theory combined with cc-pVXZ basis sets. An unfortunate aspect of extrapolated MPn calculations is that one never knows what percentage of electron correlation has been covered. This question deserves more attention. It would be extremely valuable in connection with calculations for larger systems, particularly polyatomic organic molecules, to be able to make a reliable extrapolation of the MP2 and MP4 calculations to the limit of accurate total energies.

In *Table 2*, extrapolated CCSD(T) atomization energies are compared with experimental ones and with the best calculated atomization energies [33]. The calculated atomization energies of molecules were obtained as a difference given by *Eqn. 1*, where the summation runs over all A atoms in the molecule M [28]. *Eqn. 2* permits the incorporation of zero-point energy, *ZPE*. The difference between our and the best calculated atomization energies amounts to *ca.* 1.5 kcal/mol (mean).

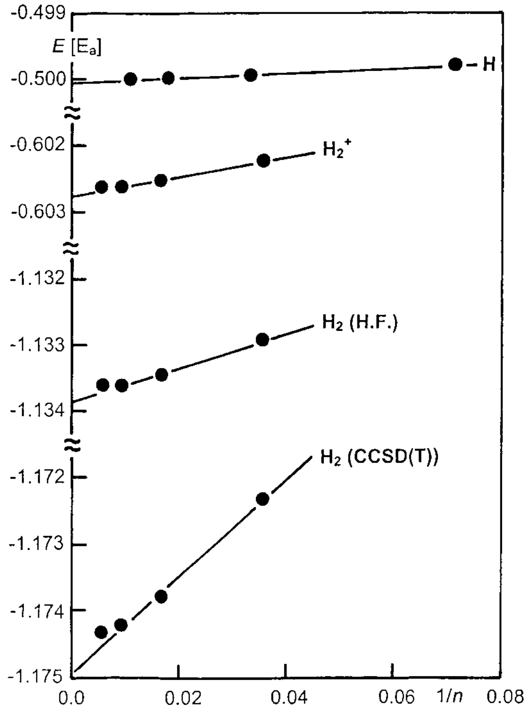

Fig. 2. *Total energies* E [E$_a$] *of H, $H_2^+$* (the H.F. level), *and $H_2$* (the H.F. and CCSD(T) level) *for triply through sextuply zeta cc-pVXZ basis sets*

$$D_e = \sum_A E(A) - E(M) \tag{1}$$

$$D_o = D_e - ZPE \tag{2}$$

*Table 3* shows the results of calculations of interaction energies related to the hydrogen-bonded dimers (*Eqns. 3* and *4*) and to the weak *van der Waals*' complexes (*Eqns. 5* and *6*). For all these dimerizations, the $\Delta E$ values were plotted against the 1/*n* values; for the $(H_2O)_2$ and $(HF)_2$ formation, the plot is presented in *Fig. 3*.

$$2\,H_2O \rightleftharpoons (H_2O)_2 \tag{3}$$

Table 2. *Calculated and Experimental Atomization Energies* (extrapolated for 1/*n* → 0) *and Zero-Point Energies* (*ZPE*). In kcal/mol.

| | CCSD(T) | Best calc. atomiz. energy[a]) | Exper. atomiz. energy[a]) | *ZPE* | *ZPE*[b]) |
|---|---|---|---|---|---|
| $H_2$ (**6**) | 109.69 | 109.53 | 109.48 | 6.27 | 6.21 |
| HF (**7**) | 143.13 | 141.15 | 141.18 | 5.96 | 5.85 |
| HCl (**8**) | 109.09 | 106.57 | 106.48 | 4.28 | 4.24 |
| $H_2O$ (**9**) | 234.55 | 232.62 | 232.60 | 13.80 | 13.25[c]) |
| CO (**10**) | 260.25 | 259.21 | 259.27 | 3.08 | 3.11 |

[a]) [33]. [b]) *ZPE* for diatomics were derived from spectroscopic constants presented in [41]. [c]) From [42].

Table 3. *Thermodynamic Characteristics of Dimerization* (*Eqns. 3–6*) *Based on MP2 Calculations.* In kcal/mol; $T = 298.1$ K, $p = 1$ atm. All symbols are specified in the text.

| Basis set | $1/n$ | $\Delta E$ | $ZPE$ | $\Delta H_0^0$ | $T\Delta S$ | $\Delta G_T^0$ | $\Delta E^{\mathrm{BSSE}}$ |
|---|---|---|---|---|---|---|---|
| $(H_2O)_2$ (**14**): | | | | | | | |
| cc-pVDZ | 0.0208 | –7.47 | 2.24 | –1.43 | –5.96 | 6.29 | –3.67 |
| cc-pVTZ | 0.0086 | –6.08 | 2.10 | –2.30 | –5.93 | 5.30 | –4.40 |
| cc-pVQZ | 0.0043 | –5.49 | – | – | – | – | –4.72 |
| cc-pVQZ | 0.0043 | – | – | – | – | – | –4.67[a]) |
| aug-cc-pVDZ | 0.0122 | –5.26 | 2.11 | –2.35 | –6.03 | 5.35 | –4.46 |
| aug-cc-pVTZ | 0.0054 | –5.18 | 2.04 | –2.71 | –6.05 | 4.92 | –4.75 |
| aug-cc-pVQZ | 0.0029 | –5.09 | – | – | – | – | –4.90 |
| aug-cc-pVQZ | 0.0029 | – | – | – | – | – | –4.79[a]) |
| $(HF)_2$ (**13**): | | | | | | | |
| cc-pVDZ | 0.0263 | –7.106 | 1.94 | –1.80 | –6.04 | 5.37 | –3.737 |
| cc-pVTZ | 0.0114 | –5.504 | 1.86 | –2.26 | –6.09 | 4.88 | –4.121 |
| cc-pVQZ | 0.0059 | –4.884 | – | – | – | – | –4.341 |
| aug-cc-pVDZ | 0.0156 | –4.684 | 1.74 | –2.30 | –6.05 | 4.72 | –4.039 |
| aug-cc-pVTZ | 0.0073 | –4.708 | 1.80 | –2.46 | –6.08 | 4.63 | –4.255 |
| aug-cc-pVQZ | 0.0040 | –4.634 | – | – | – | – | –4.407 |
| $(Ar)_2$ (**12**): | | | | | | | |
| cc-pVTZ | 0.0147 | –0.149 | 0.03 | –0.12 | –3.40 | 2.98 | –0.095 |
| cc-pVQZ | 0.0085 | –0.201 | 0.04 | –0.17 | –3.54 | 3.07 | –0.176 |
| cc-pV5Z | 0.0053 | –0.342 | – | – | – | – | –0.302 |
| aug-cc-pVTZ | 0.0100 | –0.317 | 0.05 | –0.27 | –3.70 | 3.13 | –0.238 |
| aug-cc-pVQZ | 0.0059 | –0.323 | 0.04 | –0.28 | –3.70 | 3.12 | –0.279 |
| aug-cc-pV5Z | 0.0038 | –0.342 | – | – | – | – | –0.302 |
| $(Ne)_2$ (**11**): | | | | | | | |
| cc-pVTZ | 0.01667 | –0.107 | 0.07 | 0.13 | –3.98 | 3.82 | 0.058 |
| cc-pVQZ | 0.00909 | –0.073 | 0.04 | 0.03 | –3.64 | 3.61 | –0.010 |
| cc-pV5Z | 0.00549 | –0.039 | – | – | – | – | –0.029 |
| aug-cc-pVTZ | 0.01087 | –0.082 | 0.04 | 0.01 | –3.64 | 3.35 | –0.032 |
| aug-cc-pVQZ | 0.00625 | –0.072 | 0.04 | –0.01 | –3.55 | 3.25 | –0.043 |
| aug-cc-pV5Z | 0.00394 | –0.062 | – | – | – | – | –0.049 |

[a]) [43].

$$2\,\mathrm{HF} \rightleftharpoons (\mathrm{HF})_2 \tag{4}$$

$$2\,\mathrm{Ne} \rightleftharpoons (\mathrm{Ne})_2 \tag{5}$$

$$2\,\mathrm{Ar} \rightleftharpoons (\mathrm{Ar})_2 \tag{6}$$

The most important feature of these calculations is that, speaking approximately, the extrapolations of uncorrected and (for the superposition error) corrected data converge to the same limit for $1/n \rightarrow 0$. The same is true for data connected with both the basis sets and augmented basis sets. All the calculations were performed at the MP2 level. The MP2/cc-pVQZ generated geometries of the dimer agree very well with available experimental features; the same holds true for the best calculated data [22] [34] [44]. The extrapolated MP2 interaction energies for the reactions of *Eqns. 3–6* are presented in *Table 4*, together with results of our previous calculations [45] [46] and

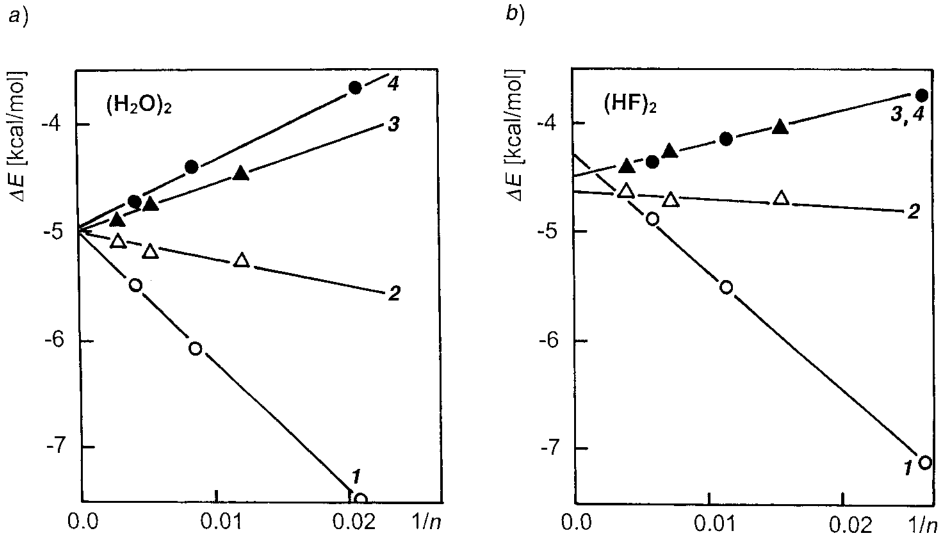

Fig. 3. *Calculated energy change* $\Delta$E [kcal/mol] *accompanying* a) *water and* b) *hydrogen fluoride dimerization plotted against reciprocal values* 1/n *of number of functions in the respective basis set, MP2 method: uncorrected* (*1* and *2*) *and for basis-set superposition error – by function counterpoise method – corrected* (*3* and *4*) *plots. 1,* MP2/cc-pVXZ; *2*, MP2/aug-cc-pVXZ; *3*, MP2, BSSE/aug-cc-pVXZ; *4*, MP2, BSSE/cc-pVXZ.

with the best theoretical values available in very recent literature [47][48]. For comparison, also experimental interaction energies are included [20][49][50]. Overall agreement is satisfactory. It is encouraging that the type of MP2 calculations used can be nowadays used also for significantly larger systems, which fits our need.

Table 4. *Interaction Energies of Dimerizations According to* Eqns. 3–6

| Process | $\Delta E$ [kcal/mol] | | | |
|---|---|---|---|---|
| | this paper a) | our previous calculations | the best available calculations | experiment |
| *Eqn. 3* | –4.92 | –6.74 b)<br>–5.96 c) | –5.027 h)<br>–5.1 i) | –5.4 ± 0.7 n) |
| *Eqn. 4* | –4.508 | –5.54 d)<br>–5.24 e | –4.15 j)<br>–4.18 k) | – |
| *Eqn. 5* | –0.058 | –0.050 f)<br>–0.074 g) | –0.055 l)<br>–0.083 m) | –0.082 o)<br>–0.084 |
| *Eqn. 6* | –0.341 | –0.303 f)<br>–0.259 g) | –0.323 l)<br>–0.277 m) | –0.280 p) |

a) MP2/aug-cc-pVXZ, $\lim_{1/n\to 0} \Delta E$, including BSSE.

b) MP2//MWB/DZ + P [45].

c) CCSD(T)//MWB/DZ [45].

d) MP2//AREP/DZ [45].

e) CCSD(T)//AREP/DZ [45].

f) MP2/aug-cc-pV5Z [44].

g) CCSD(T)/aug-cc-pV5Z [44].

h) CCSD(T)/cc-pVTZ//MP2/cc-pVTZ (CP corrected PES) [47].

i) Estimate for complete basis set, full CI [20].

j) MP2/6-311 + + G(3df,2p) [46].

k) CCSD(T)/6-311 + + G(3df,2p) [46].

l) MP2/aug-cc-pVXZ, CBS (complete basis set limit) [48].

m) CCSD(T)/aug-cc-pVXZ, CBS [48].

n) [20].

o) [49].

p) [50].

In chemistry, the ultimate goal, in some cases, is the calculation of equilibrium and rate constants in terms of statistical mechanics. If the respective *Gibbs* energy (equilibria) or *Eyring*'s activation *Gibbs* energy (rates) is relatively large (*i.e.*, large with respect to the other contributing terms), then the accuracy of the equilibrium (rate) constant critically depends on the quality of energy calculation. If the energy (activation energy) change is relatively small, it is appropriate to make at least an estimate of error propagation in the situation under study because the energy change need not be the critical quantity.

If the characteristics investigated, $Y$ is a function of the variables $x_1, x_2, \ldots, x_n$ (*Eqn. 7*), and $E_1, E_2, \ldots$, and $E_n$ are estimates of $x_1$ through $x_n$ (*Eqn. 8*), then the mean quadratic error of the quantity under study $Y$ is given by *Eqn. 9*. *Eqn. 9* serves not only for calculating the error of the quantity $Y$ but also for determining the largest, *i.e.*, the critical, term in *Eqn. 9*. To increase the accuracy of the calculated $Y$, it is necessary to improve the quality of the critical term.

$$Y = \mathrm{F}(x_1, x_2, \ldots, x_n) \tag{7}$$

$$Y = \mathrm{f}(E_1, E_2, \ldots, E_n) \tag{8}$$

$$\delta Y = \pm \sqrt{\sum_{i=1}^{n} (\partial Y / \partial E_i)^2 \delta^2 E_i} \tag{9}$$

For qualitative information and illustration, let us briefly outline the dimerization of M (*Eqn. 10*), which is a process of great importance for the field of the *van der Waals* interactions. Statistical-mechanical treatment [51] leads to *Eqns. 11–14*, where D is a dimer of M, $Q_X^0$ is a total partition function of X (= M or D), $K$ and $\Delta G^0$ stand for the equilibrium constant and the standard *Gibbs* energy change of the dimerization, and $R$ and $T$ are the gas constant and absolute temperature, respectively.

$$2\,\mathrm{M} \rightleftharpoons \mathrm{D} \tag{10}$$

$$K = [\mathrm{D}]/[\mathrm{M}]^2 = Q_\mathrm{D}^0/(Q_\mathrm{M}^0)^2 \exp(\Delta H_0^0/RT) \tag{11}$$

$$\ln K = -\Delta G^0/RT \tag{12}$$

$$\ln K = \ln Q_\mathrm{D}^0 - 2 \ln Q_\mathrm{M}^0 - (\Delta H_0^0/RT) \tag{13}$$

$$\Delta G^0 = -RT \ln Q_\mathrm{D}^0 + 2\,RT \ln Q_\mathrm{M}^0 + \Delta H_0^0 \tag{14}$$

For the enthalpy change $\Delta H_0^0$, *Eqn. 15* is valid, where $\Delta E_0$ is the best energy change obtained by solving the *Schrödinger* equation, $\Delta E_\mathrm{z}$ is zero-point energy, and $\Delta E_\mathrm{s}$ is a correction for the basis set superposition error. *Eqn. 16* is valid for $\Delta G^0$, and the expected error of $\Delta G^0$ is given by *Eqn. 17*. The largest term in *Eqn. 17* is due to the critical quantity. It is just this quantity, the quality of which has to be improved to get an equilibrium constant of better quality. In case of *van der Waals*' associates, the vibrational partition function can be the critical one. Therefore, in general, vibrational anharmonicity should be properly considered. The same is true for vibrational-rotational interaction. These aspects will be treated more extensively in another work.

$$\Delta H_0^0 = \Delta E_0 + \Delta E_z + \Delta E_s \tag{15}$$

$$\Delta G^0 = \mathrm{f}(\Delta E_0, \Delta E_z, \Delta E_s, Q_M^0, Q_D^0) \tag{16}$$

$$\delta \Delta G^0 = \pm \sqrt{\left[\left(\frac{\partial \Delta G^0}{\partial \Delta E_0}\right)\left(\frac{\partial \Delta E_0}{\partial n}\right)\right]^2 \delta^2 n + \ldots + \left[\left(\frac{\partial \Delta G^0}{\partial Q_D^0}\right)\left(\frac{\partial Q_D^0}{\partial v}\right)\right]^2 \delta^2 v} \tag{17}$$

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