Equilibrium molecular energies used to obtain molecular dissociation energies and heats of formation within the bond-order correlation approach

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Ab initio calculations including electron correlation are still extremely costly except for the smallest atoms and molecules. Therefore, our purpose in the present study is to employ a bond-order correlation approach to obtain, via equilibrium molecular energies, molecular dissociation energies and heats of formation for some 20 molecules containing C, H, and O atoms, with a maximum number of electrons around 40. Finally, basis set choice is shown to be important in the proposed procedure to include electron correlation effects in determining thermodynamic properties. With the optimum choice of basis set, the average percentage error for some 20 molecules is approximately 20% for heats of formation. For molecular dissociation energies the average error is much smaller: $\sim 0.4\%$.

Keywords: Molecular equilibrium energies; Molecular dissociation energies; Molecular heats of formation.
1 Introduction

In the last few years, much effort has been devoted to the development of theoretical techniques for the calculation of fundamental thermodynamical quantities related to molecular formation. These quantities include the molecular heat of formation, $\Delta H$, the variation of entropy, $\Delta S$, and the variation of free energy, $\Delta G$, as well as other physical quantities related to them, such as the molecular dissociation energy $D_0$, and the equilibrium constants of the chemical reactions.

The available theoretical techniques to extract such quantities are especially helpful whenever the experimental results, albeit accurate, are affected by uncertainties, due to the difficulty of obtaining pure samples of a given compound. Therefore, efficient and accurate theoretical methods are required to compute thermodynamical quantities.

In particular, the G2 methods ($x = 1, 2, 3$) have been recently developed to this purpose \[1\]. These techniques are based on the combination of several \textit{ab initio} molecular energy calculations, using various basis sets, and including correlation effects within the framework of Møller-Plesset (MP) theory \[2\], at MP2 and MP4 levels of approximation. However, one of the main drawbacks of the G2 methods is their computational complexity. Indeed, even for the energy calculation of relatively small size, both computation time and memory occupancy are quite expensive \[3\]. As a consequence, the application of this class of methods is effectively limited by the system size. Therefore, it is of considerable interest to investigate alternative theoretical techniques to calculate useful thermodynamical quantities for the formation of molecules, which require less computational resources, while maintaining a good level of accuracy.

In this context, Cremer \textit{et al.} \[5,6\] have demonstrated that it is possible to extract the Schrödinger energy of a molecule, $E_S$, \textit{i.e.} the energy corresponding to the exact solution of the Schrödinger equation for a given molecule, from the experimental values of some observable quantities, such as the molecular heat of formation and the molecular vibrational frequencies. Inversely, any theoretical model able to closely reproduce the molecular Schrödinger energies, is also expected to yield molecular heats of formation $\Delta H$ close to the experimental ones.

By definition, the difference between the molecular Schrödinger energy $E_S$ and the molecular energy obtained from a calculation at Hartree-Fock (HF) level is the ‘experimental’ correlation energy, $E_c^{\text{exp}}$. For this reason, in Ref. \[6\] we developed a semi-empirical method to calculate a theoretical estimate $E_c^{\text{theo}}$ (the bond-order correlation energy, or BOCE) to the correlation energy $E_c^{\text{exp}}$ based on the molecular bond-order matrix. Within the framework of the Lewis model \[8\], which describes the bond between atoms in a molecule as the sum of localized electron pairs, this ‘theoretical’ correlation energy $E_c^{\text{theo}}$ is calculated as the sum of the correlation energies of each atom, and the contribution due to the binding energy of each bond. The latter is in turn evaluated in terms of the product between the molecular bond-order matrix and some empirical parameters (see also Ref. \[2\] for more details). Since the BOCE method relies on a relatively simple transformation of the matrix of the molecular orbital coefficients, it turns out that it is a rather fast and accurate technique, as compared to the G2 methods.

The BOCE technique has been applied to calculate molecular properties, such as the molecular energy $E_c^{\text{theo}}$, the ionization potentials, and the electron affinities of closed and open shell molecules containing C, H, and O atoms \[7\], and recently it has been extended to closed and open shell molecules containing Si, H, F, and Cl \[9\]. In view of the previous satisfactory results for these molecular classes, in this paper we apply the BOCE method to the calculation of other molecular properties such as the molecular heat of formation and the molecular dissociation energies of several molecules containing C, H, and O. Since the bond-order matrix depends on the basis set used in the HF calculation, we compare the results within the G2 model with our BOCE results obtained using different basis sets.

2 Method

The starting point of the BOCE method is the experimental correlation energy, $E_c^{\text{exp}}$. This is defined as the difference between the Schrödinger molecular energy $E_S$ and the Hartree-Fock energy, $E_{\text{HF}}$,

$$E_c^{\text{exp}} = E_S - E_{\text{HF}}.$$  \hspace{1cm} (1)

In Eq. \[1\], $E_{\text{HF}}$ is the energy from an ideal Hartree-Fock calculation, requiring an infinite basis set. It should be emphasized that, in any practical calculation, $E_{\text{HF}}$ includes errors due to the particular
choice of basis set in the HF calculation. These errors can be made arbitrarily low, by choosing a sufficiently large basis set.

In analogy to Eq. (1), one can define a ‘theoretical’ correlation energy $E^\text{theo}_c$, as the difference between the molecular energy $E^\text{theo}$ obtained within a theoretical model at higher level than HF (below, the superscript ‘theo’ will alternatively refer to Gx or BOCE), and the HF molecular energy:

$$E^\text{theo}_c = E^\text{theo} - E^\text{HF}.$$  

(2)

Following the molecular dissociation scheme, reported in Ref. [9],

$$AB \rightarrow A + B + \text{binding energy},$$

(3)

both experimental and theoretical correlation energies can be partitioned into sums of atomic and bond contributions,

$$E^\text{exp}_c = \sum_A E^\text{exp}_c (A) + \sum_{AB} E^\text{exp}_c (AB),$$

(4a)

$$E^\text{theo}_c = \sum_A E^\text{theo}_c (A) + \sum_{AB} E^\text{theo}_c (AB),$$

(4b)

where the sums run over all atoms and pairs of atoms in the molecule, respectively, and both experimental and theoretical atomic correlation energies are defined as in Eqs. (1) and (2), respectively.

As assumed in Refs. [7, 9], within the BOCE method (theo = BOCE) we identify the theoretical energy of a single atom with its Schrödinger energy,

$$E^\text{BOCE}_S (A) = E^\text{BOCE}_c (A).$$

(5)

Therefore, the atomic theoretical correlation energies will be equal to the experimental ones:

$$E^\text{BOCE}_c (A) = E^\text{exp}_c (A).$$

(6)

On the other hand, the bond contribution within the BOCE method is described as an analytical function of the bond order $P_{AB}$ between atoms $A$ and $B$, as obtained within the HF calculation. Therefore, to lowest order in $P_{AB}$, one has [7, 9]

$$E^\text{BOCE}_c (AB) = a_{AB} P_{AB},$$

(7)

where $a_{AB}$ is a parameter which depends on the $A-B$ bond. Summarizing, the theoretical molecular correlation energy within the BOCE method can be expressed as

$$E^\text{BOCE}_c = \sum_A E^\text{exp}_c (A) + \sum_{AB} a_{AB} P_{AB}.$$  

(8)

The bonding parameters $a_{AB}$ in the second term of Eq. (5) can be obtained from the experimental correlation energies of model molecules. In particular, having $M$ different pairs of atoms in a molecule, each of them contained $n_i$ times, we can rewrite the second term of Eq. (5) as

$$\sum_{AB} a_{AB} P_{AB} = n_1 a_{AB} P_{AB} + n_2 a_{AC} P_{AC} + \ldots + n_M a_{WZ} P_{WZ},$$

(9)
where it has been assumed that the bond-order of each pair is approximately the same for each pair of the same kind in the molecule. In this sense, the parameter $a_{AB}$ is the binding correlation energy per bond $A - B$.

The procedure starts with the calculation of the parameter $a_{HH}$ obtained from the experimental correlation energy of a $H_2$ molecule,

$$a_{HH} = \frac{E_{c\exp}^{c}(H_2) - 2E_{c\exp}^{c}(H)}{P_{HH}}$$

In a similar way, the parameter $a_{CH}$ is obtained from the experimental correlation energy of the $CH_4$ molecule, and making use of the value for $a_{HH}$,

$$a_{CH} = \frac{E_{c\exp}^{c}(CH_4) - [4E_{c\exp}^{c}(H) + E_{c\exp}^{c}(C) + 6a_{HH}P_{HH}]}{4P_{CH}}$$

$$a_{CH} = \frac{E_{c\exp}^{c}(CH_4) - 6a_{HH}P_{HH}}{4P_{CH}}.$$  

Following an analogous procedure, the parameters $a_{CC}$, $a_{CO}$, $a_{OO}$, and $a_{OH}$ have been obtained starting from the experimental correlation energies of $C_2H_6$, $(CH_3)_2O$, $H_2O_2$, and $H_2O$, respectively (see Table 1).

In concluding this section, let us briefly recall the definition of the thermodynamical quantities which will be calculated in the next section, viz. the molecular dissociation energy and the molecular heat of formation.

### 2.1 Definition of some relevant thermodynamic quantities

The experimental molecular dissociation energy is defined as

$$D_0^{\exp} = \sum_A E_S(A) - E_S + E_{ZPE},$$

where $E_S(A)$ is the Schrödinger energy of atom $A$ in the molecule, $E_S$ is the total Schrödinger energy of the molecule, and $E_{ZPE}$ is the vibrational Zero Point Energy, which is calculated from the values of the molecular vibrational frequencies. In view of Eq. 5, within the BOCE approximation one has for the molecular dissociation energy:

$$D_0^{BOCE} = \sum_A E_S(A) - E_{BOCE} + E_{ZPE}.$$  

Therefore, the difference between the experimental and calculated dissociation energies can be expressed as

$$D_0^{\exp} - D_0^{BOCE} = E_{BOCE} - E_S$$

$$= \sum_{all AB} [E_{cBOCE}(AB) - E_{c\exp}^{c}(AB)].$$

In other words, only the difference between bonding BOCE and experimental energies contributes to $D_0^{\exp} - D_0^{BOCE}$. 
Finally, following Cremer et al. [5, 6], the experimental molecular heat of formation is related to $E_S$ by

$$\Delta H^{\text{exp}} = (H_{298 \text{ K}} - H_{0 \text{ K}}) - \left( \sum_A E_S(A) - E_S + E_{ZPE} \right)$$

and therefore the BOCE molecular heat of formation is related to $E_{BOCE}$ by

$$\Delta H^{BOCE} = (H_{298 \text{ K}} - H_{0 \text{ K}}) - \left( \sum_A E_S(A) - E_{BOCE} + E_{ZPE} \right)$$

In the above equations, $H_{298 \text{ K}} - H_{0 \text{ K}}$ is the variation of molecular enthalpy from 298 K to 0 K, and can be evaluated according to standard thermodynamical formulas [10]. Therefore, subtracting Eqs. (15) and (16), one obtains

$$\Delta H^{\text{exp}} - \Delta H^{BOCE} = D_0^{BOCE} - D_0^{\text{exp}}.$$  

We recall that the above derivation holds in the BOCE approximation, where $E_S = E_{BOCE}$, for atoms. In general, for other methods, such as the G2 method, one has $E_S \neq E^{G2}$, and Eqs. (15) and (16) become:

$$D_0^{G2} = \sum_A E^{G2}(A) - E^{G2} + E_{ZPE},$$

and

$$D_0^{\text{exp}} - D_0^{G2} = \sum_A [E_S(A) - E^{G2}(A)] + (E_S - E^{G2}),$$

respectively, whereas Eq. (17) holds also for the G2 method, i.e.

$$\Delta H^{\text{exp}} - \Delta H^{G2} = D_0^{G2} - D_0^{\text{exp}}.$$  

## 3 Results and discussion

The procedures involved in all G$x$ calculations ($x = 1, 2, 3$) are quite similar, and have been described in the original works by Curtiss et al. [1]. With respect to the calculation of the molecular heats of formation, the results of the G$x$ methods show that, in some classes of compounds, the G3 method is more accurate, while for other classes of compounds the G2 or the G1 methods seem to be more accurate than the G3. We have chosen to compare the molecular heats of formation calculated within the BOCE approximation with those obtained with the G2 method.

In all calculations involving the BOCE method, we have used the basis sets 3-21G, 6-311G, 6-31G**, 6-311G**, and 6-311G++**, and in the calculation of the bond-order matrix we have employed Löwdin’s definition [11] for all the latter basis sets. Our results for the bond parameters $a_{AB}$ for the different chosen basis sets are reported in Tab. 1, while our results for the bonding correlation energies, $E_{BOCE}^{AB}$, are reported in Tab. 2 for all pairs $AB$ between H, C, and O. It may be seen that the variations in the bond parameters from one basis set to another are closely correlated
with those in the bonding correlation energies for the same bond and between the same basis sets. This is in agreement with the procedure outlined in the previous section [see e.g. Eq. (11)], in view of the minor dependence of $a_{AB}$ on the bond-order matrix element $P_{AB}$ than on the experimental molecular correlation energy $E_{c}^{\text{exp}}$.

### 3.1 Molecular energies

Tab. 3 lists the set of 23 molecules, containing C, O, and H, considered in this work. For these molecules, Tab. 4 reports the experimental values of the Schrödinger energies, the total molecular energy (including correlation) within the G2 model, $E_{G2}^{\text{G2}}$, and the total molecular energy (again, including correlation) within the BOCE approximation, $E_{BOCE}^{\text{BOCE}} = E_{BOCE}^{\text{BOCE}} + E_{HF}$. The latter depends on the particular basis set chosen for the HF calculation, as described above.

It may be seen that the difference $|E_{G2}^{\text{G2}} - E_{S}|$ ranges between $\approx 140$ and $535$ mhartree, whereas $|E_{BOCE}^{\text{BOCE}} - E_{S}|$ is always below $\approx 25$ mhartree, for all the basis sets considered. Our first conclusion is therefore that, with respect to the Schrödinger result, the BOCE approximation is more accurate than the G2 method for the 23 molecules in our data set. While it is tempting to assume that this conclusion will remain true for the entire G2 data set, this is not decisive based solely on our present study. In particular, from Tab. 2 the best BOCE results correspond to the 6-311G basis set. This is due to a competition of various effects. First of all, the HF contribution to the total energy $E_{BOCE}^{\text{BOCE}} = E_{BOCE}^{\text{BOCE}} + E_{HF}$ clearly decreases on increasing the size of the basis set, owing to the variational nature of the HF calculation. Therefore, one invariably finds that $E_{HF}$ decreases along the series 3-21G $\rightarrow$ 6-311G++,+.+*.*. On the other hand, following Eq. (4b), and decomposing the correlation energy $E_{c}^{\text{BOCE}}$ into atomic and binding contributions, one finds that the atomic (respectively, binding) contributions for the various basis sets are minimum (respectively, maximum) for the 6-311G basis set. This is probably due to the nature of the 6-311G basis set (and of the 6-3xx basis set family, in general), usually employed to optimize the energies of the single atoms.

As a result of the compensation of these various contributions, the use of the 6-311G basis set within the BOCE method yields the best agreement with the Schrödinger energy. This is especially important, in view of the dependence of the dissociation energies $D_0$ on $E_S$.

In concluding this subsection on the molecular energies, let us discuss the dependence of the bond order for a given bond on the basis set employed. The average values of the bond order $P_{AB}$ for the bonds C–H, C–C, O–H, C–O appearing in the molecules listed in Tab. 3 have been reported in Tab. 4 for the various basis sets. (The bond O–O has not been included, since there is only one molecule in Tab. 3 involving such bond.) One can see that, in bonds involving H and C atoms, the bond order variation along the series of basis sets considered here is below 4%, whereas in bonds involving the oxygen atom, the bond order variation ranges from $\approx 18\%$ (C–O) to $\approx 27\%$ (O–H). This is in agreement with the study of Sannigrahi [12], where a more pronounced dependence of the bond-order and of the valency on the basis set employed. The average values of the bond order for a given bond on the basis set are clearly decreases on increasing the size of the basis set, owing to the variational nature of the HF calculation. However, for the total molecular energy (again, including correlation) within the G2 model, $E_{G2}^{\text{G2}}$, we find $\approx 8\%$ (corresponding to $\approx 5\%$ (corresponding to $\approx 1\%$ kcal).

### 3.2 Dissociation energy and molecular heat of formation

In Tab. 6 we report the experimental and theoretical molecular dissociation energies $D_0$ for the set of molecules listed in Tab. 3. In particular, Tab. 6 compares the theoretical values obtained within the G2 method (second column) and the BOCE approximation, for the five basis sets considered above. Analogously, Tab. 7 reports the experimental and theoretical molecular heats of formation $\Delta H$ for the same molecules, models, and basis sets.

In the case of the theoretical dissociation energy calculated within the G2 method, $D_0^{\text{G2}}$, we find an average percentage difference with respect to the experimental value of $\approx 0.2\%$ (corresponding to $\approx 1.5$ kcal). For the same quantity calculated within the BOCE approximation, we find an average percentage difference with respect to the experimental value of $\approx 0.4\%$ (corresponding to $\approx 2.4\%$ (corresponding to $\approx 5.9$ kcal), depending on the basis set employed (Tab. 5). Analogously, for the molecular heats of formation (Tab. 6), on the average we find $|\Delta H_0^{\text{G2}} - \Delta H_0^{\text{exp}}| \approx 8.2\%$ (corresponding to $\approx 1.5$ kcal), and $|\Delta H_0^{\text{BOCE}} - \Delta H_0^{\text{exp}}| \approx 21.4\%$ (corresponding to $\approx 2.4\%$ (corresponding to $\approx 5.9$ kcal)). Such larger values of the average percentage errors are justified by the smaller values of the experimental
molecular heats of formation, than the experimental molecular dissociation energies.) In both cases, the best agreement within the BOCE approximation is obtained for the 6-311G basis set, as it was the case for the molecular energies.

Therefore, we may conclude that, while the G2 method yields in general more accurate estimates of the molecular dissociation energies and the heats of formation, the BOCE approximation affords theoretical estimates of the above quantities of comparable accuracy, but now requiring much less computational effort. Within the BOCE approximation, moreover, the best agreement with the experimental results is obtained for the 6-311G basis set. As observed for the molecular energies, this is a result of the competition of the various atomic and binding contributions to the correlation energies (and therefore to the other thermodynamical quantities considered in this work). In particular, within the BOCE approximation, the binding contribution to the total correlation energy is relatively larger than the atomic contribution, and it can be therefore directly related to the bond-order value.

While it is agreed that the use of modest basis sets reduce the computing time required to obtain chemical accuracy relative to the Gx methods, it is appropriate, at this point, to expand on our reasoning as to why the 6-311G basis set gives better results than the somewhat larger basis sets we have also worked with. For such, still quite restricted, basis sets, there is rather non-uniform ‘convergence’. We offer, as an explanation of such non-uniformity, that the better results obtained with the 6-311G basis set rest on a somewhat delicate interplay between diffuse s-like (+) and polarization d-like (⋆) functions on the one hand, and functions corresponding to valence electrons on the other. As a consequence, in the larger basis sets considered here, the total bond-order of each atom is overestimated with respect to the 6-311G basis set. The latter point about bond-order can be illustrated with reference to Table 5. If we neglect the 3-21G basis set recorded there, then with just one exception (the C–C bond with the 6-311G* basis set and the C–H bond with the 6-311G+** basis set), the bond orders are smallest for the 6-311G set. Specifically then, the advantage among these small basis sets lies with the 6-311G basis set in that its diffuse and polarization functions increase, in the final bond-order matrix, the total number of electrons in each atom contributing to the bond.

A finer analysis of the various terms contributing to the molecular dissociation energies and heats of formation reveals that the very good agreement of the G2 method with the experimental results is due to a partial compensation of the two competing contributions for $E_{\text{exp}}^{\text{G2}} - D_{\text{exp}}^{\text{G2}}$ and $\Delta H_{\text{exp}} - \Delta H_{\text{G2}}$ in the right hand sides of Eqs. (19) and (20), respectively. Indeed, one finds $E_{\text{G2}} - E_S \approx 74.356 - 229.413$ kcal, while $\sum_A \left[ E_{G2}^{G2}(A) - E_S(A) \right] \approx 74.169 - 222.507$ kcal, for the various molecules of Tab. 3, with differences between the two quantities ranging between $-3.0$ kcal and $6.9$ kcal (Fig. 1). Therefore, in some way, within the G2 method the errors on the molecular part are compensated by the atomic part, i.e. the binding energy is very close to the Schrödinger value.

On the contrary, within the BOCE method [cf. Eqs. (14) and (17)], the difference between experimental and calculated molecular dissociation energies and heats of formation depends only on the difference between the Schrödinger and the BOCE molecular energy, given the assumption that the BOCE atomic energies are equal to the Schrödinger counterparts, Eq. 6. Therefore, even though the BOCE molecular energy is very close to the Schrödinger value, such a small difference (in kcal) cannot be compensated by the atomic contribution.

### 4 Conclusions and directions for future work

We have compared and contrasted the Gx method (especially with $x = 2$) and the BOCE approximation for estimating (a) molecular energies, (b) molecular dissociation energies, and (c) molecular heats of formation for some 20 molecules containing C, H, and O atoms. Although the G2 method usually yields better agreement with the experimental results, we find that the accuracy of the theoretical estimates of the above observable quantities within the BOCE approximation is comparable to that of the G2 calculations, but now with a remarkable saving in terms of computational complexity. With respect to previous studies [14], all BOCE parameters have been calculated on single model molecules, rather than averaging over several molecules. Therefore, each BOCE parameter $a_{AB}$ reflects the nature of the particular bond $A - B$, irrespective of its chemical surroundings. In other words, we find that the BOCE method is rather robust with respect to the inclusion of further than binary correlation terms. Moreover, we have extensively analyzed the dependence of the BOCE results on the basis set chosen for the underlying HF calculation.

Owing to the much reduced computational effort required in a BOCE calculation, we plan to apply the latter method to the evaluation of molecular properties of larger molecules, where Gx
methods are expected to require presently prohibitive resources. It is also intended, in the light of the excellent results for molecular dissociation energies, to study for such a set of larger molecules the relation between the findings of the BOCE approximation and Teller’s theorem [13], which states that molecules do not bind in a fully local density approximation (LDA), i.e. including kinetic energy density in LDA. Mucci and March [14] proposed to make a merit out of Teller’s theorem, by relating dissociation energy to molecular electron density gradients [15, 16]. However, electron correlation in the separated atoms seems important also in respect to heats of formation [see Eqs. (19) and (20) above], and this will also require further exploration.

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Table 1. Bond-order parameters $a_{AB}$ in Eq. (7) (in mhartree) for all possible bonds $A - B$ between C, O, and H. Their values depend on the HF reference energy, which depends in turn on the particular choice of basis set.

| $A - B$ | Model molecule | 3-21G | 6-311G | 6-31G** | 6-311G** | 6-311G+++ |
|---------|----------------|-------|--------|----------|-----------|-----------|
| H–H     | $\text{H}_2$   | 43.86 | 46.00  | 39.55    | 41.55     | 41.55     |
| C–H     | $\text{CH}_4$  | 39.79 | 41.51  | 35.12    | 34.85     | 35.59     |
| C–C     | $\text{C}_2\text{H}_6$ | 39.77 | 39.60  | 31.70    | 30.68     | 30.06     |
| O–H     | $\text{H}_2\text{O}$ | 88.43 | 84.63  | 60.54    | 51.20     | 51.71     |
| C–O     | $(\text{CH}_3)_2\text{O}$ | 67.85 | 68.14  | 49.11    | 43.91     | 41.11     |
| O–O     | $\text{H}_2\text{O}_2$ | 83.33 | 89.52  | 72.04    | 69.92     | 66.62     |
Table 2. Bond correlation energies, $E_c(AB)$, in hartree, for all possible bonds $A - B$ between C, O, and H. Their values depend on the HF reference energy, which depends in turn on the particular choice of basis set.

| $A - B$ | Model molecule | 3-21G | 6-311G | 6-311G$^{**}$ | 6-311G$^{**}$ | 6-311G$^{++}$ |
|---------|----------------|-------|--------|---------------|---------------|---------------|
| H–H     | H$_2$          | −1.1742 | −1.1742 | −1.1742       | −1.1742       | −0.1742       |
| C–H     | CH$_4$         | −40.51353 | −40.51353 | −40.51353 | −40.51353 | −39.51353 |
| C–C     | C$_2$H$_6$     | −79.82261 | −79.82261 | −79.82261 | −79.82261 | −78.82261 |
| O–H     | H$_2$O         | −76.43076 | −76.43076 | −76.43076 | −76.43076 | −75.43076 |
| C–O     | (CH$_3$)$_2$O  | −151.54948 | −151.54948 | −151.54948 | −151.54948 | −150.54948 |
| O–O     | H$_2$O$_2$     | −155.02013 | −155.02013 | −155.02013 | −155.02013 | −154.02013 |
### Table 3. List of the 23 molecules, containing C, O, H, considered in this work.

| No. | Molecule          | Formula  |
|-----|-------------------|----------|
| 1   | benzene           | C_6H_6   |
| 2   | ethylene          | C_2H_4   |
| 3   | acetylene         | C_2H_2   |
| 4   | formaldehyde      | HCHO     |
| 5   | methyl alcohol    | CH_3OH   |
| 6   | ketene            | CH_2CO   |
| 7   | carbon dioxide    | CO_2     |
| 8   | acetaldehyde      | CH_3CHO  |
| 9   | ethenol           | CH_2CHOH |
| 10  | formic acid       | HCOOH    |
| 11  | carbon monoxide   | CO       |
| 12  | cyclopropane      | (CH_2)_3 |
| 13  | 1,2 propadiene    | CH_2CCH_2|
| 14  | furan             | C_4H_4O  |
| 15  | cyclohexane       | (CH_2)_6 |
| 16  | glyoxal           | HCOCOH   |
| 17  | 1,3 butadiene     | CH_2CHCHCH_2|
| 18  | acetone           | CH_3COCH_3|
| 19  | acetic acid       | CH_3COOH |
| 20  | propene           | CH_3CHCH_2|
| 21  | 2-butene (E)      | t-CH_3CHCHCH_3|
| 22  | 2-butene (Z)      | c-CH_3CHCHCH_3|
| 23  | 2-methyl 1-propene| C(CH_3)_2CH_2|
Table 4. Total molecular energies (in hartree), $E^{BOCE} = E^{BOCE} + E_{HF}$, including correlation, for the 23 molecules listed in Tab. \textsuperscript{2}. The various columns refer to the different basis sets being considered in the HF calculation. The second and third columns are the total molecular Schrödinger energy, $E_S$, and $E^{G2}$, respectively.

|   | $E_S$     | $E^{G2}$ | $E^{BOCE}$ |
|---|-----------|----------|------------|
|   |           | 3-21G    | 6-31G      | 6-31G**    | 6-311G**  | 6-311G++  |
| 1 | -232.24219| -232.23115| -232.24129 | -232.22161 | -232.22495| -232.21644|
| 2 | -78.58567 | -78.58344 | -78.58651  | -78.58084  | -78.58302  | -78.58157  |
| 3 | -77.33430 | -77.33024 | -77.33251  | -77.31958  | -77.32522  | -77.32114  |
| 4 | -114.50344| -114.49660| -114.50112 | -114.50278 | -114.50176 | -114.49490 |
| 5 | -115.72137| -115.72411| -115.72416 | -115.72340 | -115.72350 | -115.72202 |
| 6 | -152.6    | -152.60331| -152.59168 | -152.59566 | -152.59897 | -152.58538 |
| 7 | -188.58504| -188.58684| -188.57255 | -188.60229 | -188.60371 | -188.58161 |
| 8 | -153.82924| -153.82178| -153.82718 | -153.82682 | -153.82746 | -153.82040 |
| 9 | -153.81314| -153.81266| -153.81354 | -153.80838 | -153.81022 | -153.80530 |
|10 | -189.76370| -189.77233| -189.76925 | -189.77838 | -189.77720 | -189.76468 |
|11 | -113.31751| -113.31573| -113.31644 | -113.32008 | -113.32148 | -113.31558 |
|12 | -117.89065| -117.87292| -117.88093 | -117.88280 | -117.88375 | -117.88177 |
|13 | -116.65212| -116.64590| -116.64947 | -116.63963 | -116.64355 | -116.63889 |
|14 | -230.01980| -230.01332| -230.01476 | -230.00899 | -230.00925 | -229.99859 |
|15 | -235.87496| -235.85806| -235.86391 | -235.86104 | -235.86280 | -235.86424 |
|16 | -227.81908| -227.81254| -227.82108 | -227.82216 | -227.82183 | -227.80646 |
|17 | -155.98889| -155.97929| -155.98644 | -155.97466 | -155.97879 | -155.97500 |
|18 | -193.15209| -193.14508| -193.15078 | -193.14894 | -193.14943 | -193.14242 |
|19 | -229.08873| -229.09387| -229.09385 | -229.09930 | -229.09921 | -229.08868 |
|20 | -117.90274| -117.89730| -117.90190 | -117.89541 | -117.89816 | -117.89658 |
|21 | -157.21942| -157.20633| -157.21660 | -157.21007 | -157.21245 | -157.18493 |
|22 | -157.21848| -157.20874| -157.21412 | -157.20760 | -157.21001 | -157.20536 |
|23 | -157.22188| -156.87670| -157.21716 | -157.21044 | -157.21311 | -157.18634 |
Table 5. Dependence of the bond-order $P_{AB}$ for a given bond $A-B$ on the basis set employed. Reported are the average bond-orders $P_{AB}$ for the bonds more frequently appearing in the molecules listed in Tab. 3.

|       | 3-21G | 6-311G | 6-311G* | 6-311G** | 6-311G++* |
|-------|-------|--------|---------|----------|-----------|
| C–H   | 0.94044 | 0.93456 | 0.94714 | 0.95081  | 0.91798   |
| C–C   | 1.05140 | 1.06971 | 1.07062 | 1.05695  | 1.09041   |
| O–H   | 0.92589 | 0.91894 | 1.00533 | 1.16700  | 1.12736   |
| C–O   | 1.32735 | 1.15963 | 1.24610 | 1.32735  | 1.37367   |

Table 6. Experimental and calculated dissociation energies $D_0$ (in kcal) for the 23 molecules listed in Tab. 3. Boldface values refer to the method yielding the best agreement with the experimental result, for each molecule. The two last lines refer to the average absolute difference and the average percentage difference, respectively, between the experimental and calculated $D_0$.

|       | $D_0^{exp}$ | $D_0^{G2}$ | $D_0^{BOCE}$ |
|-------|-------------|-------------|--------------|
|       | 3-21G | 6-311G | 6-311G* | 6-311G** | 6-311G++* |
| 1     | 1305.5 | 1301.8 | 1298.6 | 1305.0 | 1292.6 | 1289.4 |
| 2     | 531.9  | 531.7  | 530.5  | 532.4  | 528.8  | 530.2  | 529.3  |
| 3     | 388.8  | 387.2  | 386.2  | 387.6  | 379.5  | 383.1  | 380.5  |
| 4     | 359.0  | 359.3  | 354.7  | 357.6  | 358.6  | 358.0  | 353.7  |
| 5     | 480.9  | 482.3  | 482.6  | 482.6  | 482.1  | 482.2  | 481.3  |
| 6     | 512.8  | 513.6  | 516.6  | 509.3  | 511.8  | 513.8  | 505.3  |
| 7     | 381.9  | 384.6  | 383.1  | 374.1  | 392.8  | 393.7  | 379.8  |
| 8     | 643.7  | 643.9  | 639.0  | 642.4  | 642.2  | 642.6  | 638.2  |
| 9     | 633.6  | 631.9  | 633.3  | 633.9  | 630.6  | 631.8  | 628.7  |
| 10    | 480.0  | 482.0  | 485.4  | 483.4  | 489.2  | 488.4  | 480.6  |
| 11    | 256.2  | 258.0  | 255.1  | 255.5  | 257.8  | 258.7  | 255.0  |
| 12    | 802.9  | 802.1  | 791.7  | 796.8  | 797.9  | 798.5  | 797.3  |
| 13    | 669.1  | 668.2  | 665.1  | 667.4  | 661.2  | 663.7  | 660.7  |
| 14    | 950.5  | 949.6  | 946.4  | 947.3  | 943.7  | 943.9  | 937.2  |
| 15    | 1659.4 | 1652.5 | 1648.8 | 1652.5 | 1650.7 | 1651.8 | 1652.7 |
| 16    | 610.4  | 613.4  | 606.3  | 611.7  | 612.4  | 612.2  | 602.5  |
| 17    | 960.1  | 958.2  | 954.1  | 958.6  | 951.2  | 953.8  | 951.4  |
| 18    | 927.0  | 927.9  | 922.6  | 926.2  | 925.0  | 925.3  | 920.9  |
| 19    | 764.7  | 766.3  | 767.9  | 767.9  | 771.3  | 771.3  | 763.5  |
| 20    | 811.2  | 810.8  | 807.8  | 810.6  | 806.6  | 808.3  | 807.3  |
| 21    | 1090.5 | 1090.3 | 1082.3 | 1088.7 | 1084.9 | 1086.2 | 1084.9 |
| 22    | 1089.8 | 1089.0 | 1084.4 | 1087.0 | 1083.2 | 1084.7 | 1083.2 |
| 23    | 1092.2 | 1091.5 | 1086.5 | 1089.2 | 1085.1 | 1086.7 | 1085.9 |
| Avg. $|\Delta D_0|$ | 1.5   | 4.5   | 2.4   | 5.5   | 4.6   | 5.9   |
| Avg. $|\Delta D_0|$ (%) | 0.2   | 0.6   | 0.4   | 0.8   | 0.7   | 0.8   |
Table 7. Experimental and calculated molecular heats of formation at 298 K, $\Delta H$ (in kcal), for the 23 molecules listed in Tab. Boldface values refer to the method yielding the best agreement with the experimental result, for each molecule. The two last lines refer to the average absolute difference and the average percentage difference, respectively, between the experimental and calculated $\Delta H$.

|       | $\Delta H^\text{exp}$ | $\Delta H^0_{\text{G2}}$ | $\Delta H^\text{BOCE}$ |
|-------|------------------------|---------------------------|------------------------|
|       |                        | 3-21G | 6-311G | 6-31G** | 6-311G** | 6-31G++  |
| 1     | 19.8                   | 23.6  | 26.8   | 20.4    | 32.7     | 30.6     | 36.0     |
| 2     | 12.5                   | 14.3  | 13.9   | 12.0    | 16.6     | 14.2     | 15.1     |
| 3     | 54.2                   | 55.8  | 56.7   | 55.3    | 63.4     | 62.0     | 59.9     | 62.5     |
| 4     | -27.7                  | -28.0 | -23.4  | -26.2   | -27.3    | -26.7    | -20.9    | -22.3    |
| 5     | -48.0                  | -49.4 | -49.8  | -49.8   | -49.3    | -49.4    | -48.4    |
| 6     | -11.5                  | -12.2 | -15.2  | -7.9    | -10.4    | -12.5    | -4.0     |
| 7     | -94.1                  | -95.4 | -95.2  | -86.2   | -104.9   | -105.8   | -91.9    |
| 8     | -40.8                  | -41.0 | -36.1  | -39.5   | -39.3    | -39.7    | -35.3    |
| 9     | -30.6                  | -29.0 | -30.3  | -30.8   | -27.6    | -28.8    | -25.7    |
| 10    | -90.5                  | -92.6 | -95.9  | -94.0   | -99.7    | -99.0    | -91.1    |
| 11    | -26.4                  | -28.2 | -25.3  | -25.7   | -28.0    | -28.9    | -25.2    |
| 12    | 12.7                   | 13.5  | 23.9   | 18.8    | 17.7     | 17.1     | 18.3     |
| 13    | 45.5                   | 46.4  | 49.4   | 47.2    | 53.4     | 50.9     | 53.8     |
| 14    | -8.3                   | -7.4  | -4.2   | -5.1    | -1.5     | -1.7     | 5.0      |
| 15    | -29.4                  | -22.5 | -18.8  | -22.5   | -20.7    | -21.8    | -22.7    |
| 16    | -20.7                  | -53.6 | -46.6  | -51.9   | -52.6    | -52.4    | -42.7    |
| 17    | 26.0                   | 28.0  | 32.0   | 27.5    | 34.9     | 32.3     | 34.7     |
| 18    | -52.2                  | -53.0 | -47.8  | -51.4   | -50.2    | -50.6    | -46.2    |
| 19    | -103.44                | -105.1| -106.7 | -106.7  | -110.1   | -110.0   | -102.3   |
| 20    | 4.9                    | 5.3   | 8.3    | 5.4     | 9.5      | 7.8      | 8.7      |
| 21    | -2.6                   | -2.4  | 1.8    | -0.8    | 3.0      | 1.7      | 3.0      |
| 22    | -1.8                   | -1.0  | 3.6    | 0.9     | 4.8      | 3.4      | 4.7      |
| 23    | -4.3                   | -5.0  | 1.4    | -1.2    | 2.9      | 1.2      | 2.1      |

Avg. $|\Delta H^\text{theo} - \Delta H^\text{exp}|$ | 1.5  | 4.3  | 2.4  | 5.5  | 4.6  | 5.9  |
Avg. $|\Delta H^\text{theo} - \Delta H^\text{exp}|$ (%) | 8.2  | 44.3 | 21.4 | 52.9 | 41.8 | 58.5 |
Molecular dissociation energies and heats of formation within the BOCE approach

Figure 1. Atomic vs molecular contributions to the difference between experimental and theoretical dissociation energy, Eq. (19), within the G2 method, for the 23 molecules listed in Tab. 3. The dashed line is a guide to the eye.