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A Method for Molecular Correlation Energy Calculations. Application to the Determination of Dissociation Energies of Diatomic and Polyatomic Molecules

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A simple and economical method for molecular correlation energy calculations is developed. In this method, the internal part of the correlation energy is calculated by means of a CI in a minimal basis set and the non-internal part (semi-internal and all-external) is evaluated using an original "atoms-in-molecule" method. It is successfully applied to the determination of dissociation energies of some diatomic (H_2, NH, C_2, CN, N_2, CO, NO, O_2, F_2) and polyatomic (H_2O, N_2O, CO_2, N_3H, CH_2N_2, CH_2CO, C_2N_2) molecules. The results are compared to those obtained using very elaborate variational methods.

Key words: Correlation energy – dissociation energy.

1. Introduction

It is well known that the SCF model fails to describe most of the chemical properties of the molecules. Even very elaborate basis sets approaching the Hartree–Fock limit often lead to chemically meaningless results. One of the properties that cannot be predicted by a SCF wave-function is the bond dissociation energy (see for example H.F. results for diatomic molecules in Table 5). Very important efforts have been made these last two decades to provide new methods able to calculate the difference between the SCF energy and the exact nonrelativistic solution, the so-called "correlation energy".

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The most popular method is undoubtedly the "configuration interaction" method (CI), which is also the most generally applicable. In a CI calculation, the exact solution is approached by a linear expansion of Slater determinants of which the coefficients are variationally optimized. Although a very simple concept is at the heart of this method (Ritz variation principle), it involves considerable computational difficulties. It is not only the size of the expansion that increases rapidly with the size of the system under study (enormous matrices requiring always more computer time and memory space) but also that nearly each problem has to be treated specifically with respect to the choice of the basis set, the molecular orbital sub-set to be considered, and the configurations to be selected. This made Shavitt say [1]: "Thus, even though the limits on the size of practical calculations are continuously being extended by improvements in techniques and in computer capabilities, adequate CI calculations on large molecules are not in sight". A particularly efficient method is the MCSCF procedure where the orbitals of the configurations as well as the expansion coefficients are optimized to lower the energy. However, on the one hand, the necessary knowledge of the starting configurations needed to describe the chemical process under study and on the other hand, the increasing computer difficulties for larger systems make this method quickly unpracticable.

Nevertheless, quite good results can be obtained for small systems as is pointed out in Table 1 where some elaborate calculations of dissociation energies are shown.

Other methods, such as the iterative natural orbital method [8], the higher-order perturbation theory [9], the "pair theory" [10–12], have been used successfully. Among them, the fragmentation of the correlation energy proposed by Oksüz and Sinanoglu [13] is at the heart of the method we propose here. The method to be described is devoted to calculate economically the molecular correlation energy of systems for which an accurate variational treatment would be unpracticable. It combines the use of CI calculations with minimal basis sets together with a modified version of an "atoms-in-molecule" method first developed by Liu and Verhaegen [14]. Although not variational, it has been successfully

Table 1. Elaborate calculations of dissociation energies (eV) of some small systems

Mol	Method of calculation[a]	(Ref.)	*De*(calc)	*De*(exp)[b]
C_2	MCSCF($n=4$)/CI($n=142$)	[3]	5.55	6.33
N_2	Multi-réf. *db.exc*($n=150234$)	[4]	9.33	9.91
O_2	MCSCF($n=6$)/CI($n=248$)	[5]	4.99	5.21
F_2	MCSCF($n=6$)	[6]	1.68	1.65
H_2O[c]	FO/CI(INO)($n(C_{2v})=4120$; $n(C_s)=7996$)	[7]	9.245	10.1

[a] All calculations made with very large basis sets; n = number of configurations included in CI or MCSCF

[b] All values from Ref. [2].

[c] $H_2O(^1A_1) \rightarrow 2H(^2S) + O(^3P)$.

applied to the calculation of the dissociation energy of the molecules H_2, NH, C_2, N_2, CO, CN, NO, F_2, H_2O, N_2O, N_3H, CH_2N_2, CH_2CO, CO_2, C_2N_2.

2. Methods of Calculation

2.1. Separate Correlation Effects

An advantageous alternative to purely variational techniques is given by the theory developed by Oksüz and Sinanoglu [13] where the correlation effects in atomic systems are separated into three types: internal, semi-internal and all-external correlation effects. A physical and mathematical support of this partition is proposed by the authors in a context of pair correlation theory. In this decoupled approach, the total energy can be approximated by:

$$E \simeq E_{\mathrm{HF}} + E^{\mathrm{I}}_{\mathrm{CORR}} + E^{\mathrm{SI}}_{\mathrm{CORR}} + E^{\mathrm{E}}_{\mathrm{CORR}} \tag{1}$$

where E_{HF} is the Hartree–Fock energy and $E^{\mathrm{I}}_{\mathrm{CORR}}$, $E^{\mathrm{SI}}_{\mathrm{CORR}}$ and $E^{\mathrm{E}}_{\mathrm{CORR}}$ refer to internal, semi-internal and all-external correlation energies respectively.

These three contributions to the correlation energy are characterized by different types of electron pair excitations with respect to a particular subspace defined in the complete orbital space. This subspace, called the "Hartree–Fock sea" is composed of the shells partially or completely occupied in the Hartree–Fock Slater determinant, i.e. the $1s$, $2s$ and $2p$ orbitals for first-row atoms. The three possible types of pair excitations are the following:

(1) excitations from filled to vacant orbitals within the H.F. sea giving rise to *internal correlation*
(2) excitations where one electron shifts within the H.F. sea and the other outside, giving rise to *semi-internal correlation.*
(3) biexcitations from the inside to the outside of the H.F. sea, giving rise to *all-external correlation.*

It has been postulated that these three correlation energy contributions can be calculated by separate CI calculations [13]. The internal part is concerned with biexcitations within a finite set of orbitals (H.F. sea) and can therefore be represented by a finite CI expansion. Oppositely the two other parts involving excitations to the infinite orbital space out of the H.F. sea give rise to infinite CI expansions. These expansions are slowly convergent with an increasing number of configurations, and therefore only very large CI calculations can approach the corresponding energy limits. In the following, the two parts of the correlation energy will be calculated separately over the SCF wavefunction. This approach is in keeping with the original theory of Oksüz and Sinanoglu which is based on a perturbation analysis of correlation effects. In this work, the internal part will be calculated variationally as detailed in Sect. 2.2. The semi-internal and all-external parts will be calculated by an "atoms-in-molecule" method described in Sect. 3.3. These two latter parts will be called hereafter the *non-internal correlation energy.*

Relation (1) thus becomes:

$$E \simeq E_{HF} + E_{CORR}^{I} + E_{CORR}^{NI} \quad (2)$$

2.2. *Internal Correlation Energy*

The internal correlation effect is generally known in the atomic case as the important "near-degeneracy" effect. It has, in the molecular case, an analogous physical meaning and represents the most important part of the correlation energy contribution to chemical processes as will be seen further (Table 5). It seemed therefore important to calculate it variationally.

In order to set up the finite CI expansion corresponding to the internal correlation effect in a molecular case, we will define the molecular H.F. sea as the set of molecular valence orbitals developed in terms of the atomic shells describing the H.F. seas of the constituent atoms, i.e. the molecular H.F. sea of a diatomic molecule AB composed of two first row atoms A and B is formed by the 1σ to 6σ, 1π and 2π molecular orbitals; indeed these orbitals span the atomic bases $1s_A$, $2s_A$, $2p_A$ and $1s_B$, $2s_B$, $2p_B$. This set is also referred to in the literature as the full valence space of the molecule because its orbitals correlate asymptotically with the valence orbitals of the constituent atoms [15].

In a minimal basis set, all the molecular orbitals occupied as well as virtual, thus belong to the molecular H.F. sea. Therefore in this type of basis, all biexcitations from occupied to virtual orbitals should correspond to internal correlation. The CI expansion can be of course simplified by excluding the core ($1s$ components) from the atomic H.F. seas: in fact, since we are concerned with processes which do not affect the electronic structure of inner shells, this approximation will not influence significantly correlation energy differences describing these processes.

However, because of uncontrollable basis polarisation effects it could well be that a CI in a minimal basis set provides more than the actual internal correlation energy. For this reason this approach will be tested by comparison with MCSCF-CI calculations carried out with extended basis sets.

2.3. *Non-Internal Correlation Energy*

We develop here an "atoms-in-molecule" method for the calculation of the non-internal correlation energy based on Mulliken population analyses [16]. The basic idea of this method has been described in a previous paper [14]. The method proposed here is revised and the formalism is modified in terms of probabilistic theory.

We first postulate that it is possible to evaluate the molecular non-internal correlation energy by a sum of contributions from the constituent atoms of the molecule. Let P_{iq} represent the Mulliken gross population of each basis orbital χ_q in MO ϕ_i: $P_{iq} = \sum_{p=1}^{n} C_{ip}C_{iq}S_{pq}$; a similar definition holds for $\bar{P}_{iq}$ of opposite spin. $P_{iq}(\bar{P}_{iq})$ is interpreted by Mulliken [16] as the electronic population breakdown of the molecular spinorbital $\phi_i(\bar{\phi}_i)$ on the atomic spinorbital $\chi_q(\bar{\chi}_q)$. From a probabilistic point of view, we can say that it represents the occupation probability of $\chi_q(\bar{\chi}_q)$ in $\phi_i(\bar{\phi}_i)$.

The summation over all the molecular spinorbitals defines an occupation probability of $\chi_q(\bar{\chi}_q)$ in the molecule:

$$P_q = \sum_{i=1}^{k} P_{iq}; \qquad \bar{P}_q = \sum_{i=1}^{k} \bar{P}_{iq}.$$

The definition of an inoccupation probability $(1-P_q)$ for each χ_q, guarantees the normalization of the probabilities. It is easy to show that the quantity $P_q(\bar{P}_q)$ is invariant with respect to any unitary transformation of the occupied spinorbitals.

The substitution of the notion of occupation probability to the initial notion of population breakdown allows us to define a simultaneous occupation probability of several atomic spinorbitals by simple product of the individual probabilities. For a given molecule we can thus associate to each atomic configuration of the constituent atoms an occupation probability.

For each atom X_i of the given molecule, we have then $K(X_i)$ atomic configurations $\tilde{S}_k(\tilde{S}_k(X_i);\ k=1, K(X_i))$ with the associated occupation probability $\tilde{P}_k(X_i)$ given by:

$$\tilde{P}_k(X_i) = \prod_{p \in X_i} (P_p)^{n_p}(1-P_p)^{1-n_p}$$

where the product over p refers to the atomic spinorbitals of atom X_i and n_p equals 1 or 0 depending on whether χ_p is occupied or not in the atomic configuration $\tilde{S}_k(X_i)$. Since the Mulliken gross populations $(P_{iq}, \bar{P}_{iq})$ are normalized, it follows that:

$$\sum_{k=1}^{K(X_i)} \tilde{P}_k(X_i) = 1.$$

Let $n(\tilde{S}_k(X_i))$ be the number of electrons of a fully occupied $\tilde{S}_k(X_i)$ configuration. From the above normalization condition, it can be shown that the products $\tilde{P}_k(X_i).\ n(\tilde{S}_k(X_i))$ are population breakdowns of the total gross populations of each atom X_i and hence, the total number of electrons considered for the calculation of the non-internal correlation energy is equal to the number of electrons in the molecule.

The Mulliken populations do not allow to distinguish between the different states of a given atomic configuration. Nevertheless, the non-internal correlation energy of an atomic configuration $\tilde{S}_k(X_i)$ may be evaluated as the weighted average of the non-internal correlation energies of its constituent electronic states [17–18]. Thus, the non-internal correlation energy of the molecule $(X_1X_2 \cdots X_N)$ will be simply the sum of the average atomic non-internal correlation energies multiplied by their occupation probability:

$$E^{\mathrm{NI}}_{\mathrm{CORR}}(X_1 \cdots X_N) = \sum_{i=1}^{N} \sum_{k=1}^{K(X_i)} \tilde{P}_k(X_i) E^{\mathrm{AT}}_{\mathrm{CORR}}(\tilde{S}_k(X_i)) \tag{3}$$

where $E^{\mathrm{AT}}_{\mathrm{CORR}}(\tilde{S}_k(X_i))$ represents the *non-internal configurational* correlation energy of atom (ion) X_i in $\tilde{S}_k$ configuration.

This formalism can be used either with a RHF or an UHF wavefunction.

A necessary condition associated with such a decomposition of the molecular structure into atomic components in a LCAO context is that the molecular orbitals have to be expressed unambiguously in terms of purely atomic basis orbitals; this is achieved only in a minimal basis set calculation [19–20].

To illustrate the above theory, an application of the formalism to the $X^3\Sigma_g^-$ state of the O_2 molecule is presented in Appendix I. The $E_{\mathrm{CORR}}^{\mathrm{AT}}$ values corresponding to all atomic configurations relative to the atoms C, N, O, F and H are listed in Appendix II.

3. Results and Discussion

3.1. Programs

The SCF energies for closed-shell systems were obtained with the program GAUSSIAN 76 [21] that ensures the solution of Roothaan's equations. Open-shell structures were calculated by the method of Davidson (OCBSE) [22] coded by Morokuma and Iwata [23]. The CI calculations were run with the programs written by Whitten and his collaborators [24] and adapted to GAUSSIAN 76 by one of us (J.L.). The MCSCF calculations were run on the ALIS program of Ruedenberg et al. [25]. Finally the non-internal correlation energy was calculated with a very simple program coded by us (J. L. and J. B.).

All calculations were performed on the CDC 6500-6600 and CYBER 170/750 computers of the Free Universities of Brussels Computing Center.

3.2. Basis Sets and Geometry Optimization

As it has been suggested in the preceding chapter, the different fragments of Eq. (2) have to be calculated with different basis sets.

On the one hand, the best possible basis set should be used in order to apprach as closely as possible the Hartree–Fock limit; on the other hand both $E_{\mathrm{CORR}}^{\mathrm{I}}$ and $E_{\mathrm{CORR}}^{\mathrm{NI}}$, for reasons explained above, must be calculated with a minimal basis set.

We have used here a selection of different basis sets in-built to GAUSSIAN 76. The "polarized" basis set 6-31G** [26], consisting of a "double-zeta quality" basis set 6-31G [27] completed with one d-function for second-row elements and one p function for hydrogens will be used here to approach the H.F. limit and the minimal STO-3G [28] basis set will serve for both $E_{\mathrm{CORR}}^{\mathrm{I}}$ and $E_{\mathrm{CORR}}^{\mathrm{NI}}$ calculations. Of course, it is often too expensive to determine a complete potential surface for large systems with the method described in Sect. 2, essentially because of the computer time spent by the 6-31G** calculations. Therefore it is not trivial to choose adequately the points at which the dissociation energy will be calculated since different basis sets are used for the different fragments of the total energy. If the dissociation products are atoms, the dissociation limit is not ambiguous; oppositely the minimum equilibrium geometry of the molecular systems may vary considerably if one uses one basis set or another. In order to simplify the geometry optimization we made a few tests on the molecule N_2.

The results are given in Table 2 where R_{eq} refers to the interatomic equilibrium distance (in a parabolic approximation) of the potential curve calculated with different basis sets and with basis set 6-31G* to which successive fragments of correlation energy have been added.

Table 2. Equilibrium internuclear distance (R_{eq}) and force constant (k) of $N_2(^1\Sigma_g^+)$

Type of calculation	R_{eq} (Å)	k (10^6 dyn/cm)
STO-3G	1.14	3.73
6-31G	1.10	2.79
6-31G*	1.09	2.79
6-31G* + $E^{\mathrm{I}}_{\mathrm{CORR}}$	1.13	2.70
6-31G* + $E^{\mathrm{I}}_{\mathrm{CORR}}$ + $E^{\mathrm{NI}}_{\mathrm{CORR}}$	1.12	2.67
Expt$^{(2)}$	1.094	2.29

One observes immediately that the bond length is overestimated using basis set STO-3G and relatively well reproduced with 6-31G and 6-31G* basis sets. The 6-31G result offers undoubtedly the best "quality to price" ratio for this property. This conclusion was previously established on larger systems than N_2, such as NH_3 [29]. Thus, we propose to run the calculations of the different energy contributions at the optimized 6-31G geometry. The energy difference with respect to the total curve is negligible in N_2. In larger systems, with many more geometrical parameters to optimize, this energy difference may be significantly larger. However, in this case, one may reasonably expect some compensation with the dissociation fragments which involve many of the same parameters.

An interesting feature is that the force constant obtained with our method approaches the actual value within 15% and, as can be seen in Table 2, the introduction of $E^{\mathrm{I}}_{\mathrm{CORR}}$ and $E^{\mathrm{NI}}_{\mathrm{CORR}}$ tends to improve the SCF results.

We can conclude that the calculation of the dissociation energy at the 6-31G equilibrium geometry gives rise to a slight displacement on a curve of a relatively correct shape but doesn't affect greatly the final energetic result. Similar tests carried out on the O_2 molecule give rise to the same conclusions. Since the 6-31G geometries are close to the experimental ones, an advantageous alternative to the present choice would be to carry out the calculations at the experimental geometries, if they are available.

3.3. Correlation Energy Calculations

3.3.1. Internal Correlation

Since it is not evident that a CI calculation carried out with a minimal basis set gives a correct estimate of the internal correlation energy of a system, it seemed necessary to test this hypothesis on a series of molecules. The molecules H_2, F_2, NH, C_2, CO, O_2 and H_2O were selected for this purpose. For these systems, the CI minimal basis set (STO-3G) results were compared to parallel results obtained with the polarized 6-31G** set.

With an extended basis set, the orbitals of the molecular H.F. sea form a sub-space of the full orbital space and must therefore be optimized variationally. For the simple systems selected here, this can be done conveniently by means of MCSCF calculations. Two types of procedures were adopted:

(1) For H_2, F_2 and NH, the full configurational space, such as defined in 2.2 – respectively two, nine and four configurations – was introduced in the MCSCF calculation.

(2) For the other molecules, the full configurational space is too large, and so, only the "dissociation" configurations[1] were first introduced in the MCSCF calculation. Since these configurations include all the valence orbitals participating to the H.F. sea, it may be hoped that already the first MCSCF calculation provides a good preliminary optimization. The CI over this valence space was then carried out and other major configurations arising from this calculation added to the MCSCF space and so on, until convergence of this iterative procedure was reached. In fact, for the simple systems considered here, the convergence limit was obtained directly with the "dissociation" configurations only.

With both procedures one should obtain the internal correlation energy.

In Table 3 we compare the large and small basis set internal correlation energy results. As could be expected, on account of basis polarization effects, the $E^{\mathrm{I}}_{\mathrm{CORR}}$

Table 3. Comparison between minimal and extended basis-set calculations of the internal correlation energy

	$E^{\mathrm{I}}_{\mathrm{CORR}}$ (eV)		$E^{\mathrm{NI}}_{\mathrm{CORR}}$ (eV)
	STO-3G[a]	6-31G*[b]	
H_2	−0.561	−0.490[c]	−0.544
NH	−0.544	−0.550[c]	−5.96
C_2	−5.58	−5.47	−8.60
CO	−3.46	−3.46	−11.7
O_2	−2.86	−2.86	−14.6
F_2	−2.26	−2.18[c]	−17.9
H_2O	−1.31	−1.33	−8.44

[a] Minimal basis set.
[b] Extended basis set.
[c] All biexcitations in MCSCF calculation.

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[1] The dissociation configurations are those which have to be added to the ground equilibrium configuration in order to obtain proper Wigner–Witmer products at dissociation geometries.

values calculated with the minimal set are most often slightly overestimated, but nevertheless give quantitatively correct results.

The above tests tend to show that one can still hope to obtain quantitatively meaningful results for larger molecules, such as those discussed below (c.f. Table 7), as well as for yet larger systems for which the above MCSCF procedures have become unpracticable, but for which the minimal basis-set CI calculations are still operative.

3.3.2. Non-Internal Correlation

In all cases the non-internal correlation energy was calculated according to Eq. 3. As an example of the order of magnitude of this energy contribution, values are given in the third column of Table 3.

3.3.3. Total Correlation Energy

In Table 4, we compare calculated and estimated [30] values of correlation energies for some of the molecules considered here. The overall agreement may be considered as satisfactory since in all cases the error is <7% and <1 eV. It is interesting to note that the error does not seem to be size-dependent; this is certainly comforting in view of applying this formalism to larger systems. Further, in these cases, one may expect some cancellation between the error in E_{CORR} calculated for the molecule, and those of the dissociation products.

Table 4. Comparison between calculated and estimated values of total correlation energy for various molecules (eV)

Mol.	$E_{\mathrm{CORR}}^{\mathrm{est}}$ [a]	$E_{\mathrm{CORR}}^{\mathrm{calc.}}$
H_2	−1.12	−1.12
H_2O	−9.90	−9.77
N_2	−14.7	−15.6
CO	−14.1	−15.2
BH_3CO	−20.2	−20.9

[a] Ref. [30].

3.4. Dissociation Energies of Some Small Molecules

It is possible today, as shown in Table 1, to obtain very good results for the calculation of a property like the dissociation energy of small systems with variational methods (MCSCF/CI). Therefore it seemed interesting to test our method on a variety of small systems and compare the results to those obtained with very elaborate calculations.

3.4.1. Diatomic Molecules

All the calculations performed here concern the dissociation process of homo- and hetero-diatomic molecules in their ground state to the ground states of the atomic products. Both closed- and open-shell structures are present in the systems considered.

Table 5. Dissociation energies (eV) calculated for some-diatomic molecules

Molecule \ Method	STO-3G	6-31G	6-31G*(*)	H.F.[a]	6-31G*(*) + $E^{\mathrm{I}}_{\mathrm{CORR}}$	6-31G*(*) + $E^{\mathrm{I}}_{\mathrm{CORR}} + E^{\mathrm{NI}}_{\mathrm{CORR}}$	H.F. + $E^{\mathrm{TOT}}_{\mathrm{CORR}}$	Expt.[b]
H_2	4.99	3.55	3.67	3.65 [30]	4.23	4.78	4.76	4.75
NH	1.95	1.58	2.05	2.10 [31]	2.59	3.14	3.19	≤3.67
C_2	0.62	−0.13	0.66	0.73 [32]	5.14	5.96	6.03	6.33
CN	2.17	2.18	3.55	(3.64) [33]	6.99	8.11	8.20	7.89
N_2	1.59	2.82	4.85	5.28 [34]	8.78	9.57	10.00	9.91
CO	6.05	5.77	7.67	7.93 [35]	10.57	11.33	11.59	11.22
NO	0.07	0.06	2.17	(2.31) [36]	5.55	6.20	6.34	6.62
O_2	0.64	−0.76	1.06	1.45 [37]	3.92	4.41	4.80	5.21
F_2	−0.21	−2.02	−1.29	−1.37 [38]	0.97	1.23	1.15	1.65

[a] Near H.F. values except for CN and NO which are the best R.H.F. values available.

[b] All values from Ref. [2].

Calculated dissociation energies are listed in Table 5 where two levels of approximation have been taken into account: the first part of the table collects the SCF results obtained with basis sets of increasing complexity, the second part shows the progressive incorporation of correlation energy. The final results are compared to the corresponding experimental values.

At the SCF level the basis effect on the dissociation energy results appears strongly. The 6-31G basis set, although reproducing well the geometrical parameters, gives very poor results for the binding energy, particularly with respect to the qualitatively good predictions of the simple STO-3G basis set. The polarization effect included in the 6-31G* basis is decisive to approach near Hartree–Fock values.

Concerning the correlation energy, it is striking to note that although the internal correlation energy represents only a relatively small fraction (10–30%) of the total molecular energy, it is the dominant (~80%) contribution to the extramolecular correlation energy, i.e. the correlation energy directly associated to the dissociation energy.

Except for the particular case of F_2, the incorporation of the non-internal part gives final results which can be compared to the corresponding experimental values and for which the agreement is about 5%. These results are close to those obtained with accurate calculations (Table 1).

Finally, we note that, as pointed out in Sect. 3.3, the comparison of the results of Tables 4 and 5 show that the major part of the discrepancy found in the *absolute* values of the correlation energy have disappeared in the dissociation energy results.

3.4.2. H_2O Molecule

In Table 6 we present calculated values of dissociation energies for two dissociation processes of H_2O. Our results are compared with those obtained by very elaborate calculations and with experimental data. It is obvious that in this case our method is certainly competitive – in fact our results are closer to the experimental values than the CI calculations in both cases and they certainly needed far less computational time.

It is also interesting to note that our results for H_2O, N_2 and CO, respectively 9.7, 10.0 and 11.6 eV, are at least as good as those obtained by the non-variational but nevertheless powerful UMP4(SDQ) [41] method which gives 9.24, 8.64 and 10.51 eV respectively.

Table 6. Calculated dissociation energies of two dissociation channels of H_2O (eV)

Process	6-31G** $+E_{\mathrm{CORR}}^{\mathrm{TOT}}$ [a]	H.F. $+E_{\mathrm{CORR}}^{\mathrm{TOT}}$ [a]	Elaborate CI calc.	Exp.
$H_2O(^1A_1) \rightarrow 2H(^2S) + O(^3P)$	9.41	9.69	9.245 [7]	10.08 [40]
$H_2O(^1A_1) \rightarrow H_2(^1\Sigma_g^+) + O(^3P)$	4.63	4.93	4.77 [39]	5.03 [41]

[a] Our method.

3.4.3. Application to Polyatomic Molecules

Since we want to apply this method to systems larger than diatomic molecules, we have performed test calculations on the fundamental dissociation process of several polyatomic molecules. The results are presented in Table 7 and compared to the corresponding experimental values. Although some of the experimental values are still quite doubtful, such as those for CH_2N_2 and N_3H, comparison with well-established values for other molecules shows the same type agreement as that obtained for simpler systems.

These results are very gratifying particularly with respect to the minimal computational efforts involved.

Table 7. Dissociation energies (eV) of polyatomic molecules

Mol.	Process	$D_e(6\text{-}31G^{*(*)} + E^{\mathrm{I}}_{\mathrm{CORR}} + E^{\mathrm{NI}}_{\mathrm{CORR}})^{\mathrm{a}}$	D_e (exp)
N_3H	$N_3H(^1A') \rightarrow NH(^3\Sigma^-) + N_2(^1\Sigma_g^+)$	0.5	1.0 [43], 0.6 [44]
N_2O	$N_2O(^1\Sigma^+) \rightarrow N_2(^1\Sigma_g^+) + O(^3P)$	1.1 (1.2)	1.8 [45]
CH_2CO	$CH_2CO(^1A_1) \rightarrow CH_2(^3B_1) + CO(^1\Sigma^+)$	3.4	3.6 [46–47]
CO_2	$CO_2(^1\Sigma_g^+) \rightarrow CO(^1\Sigma^+) + O(^3P)$	5.7 (7.0)	5.6 [45]
CH_2N_2	$CH_2N_2(^1A_1) \rightarrow CH_2(^3B_1) + N_2(^1\Sigma_g^+)$	0.9	<2.0 [48], <2.1 [49]
C_2N_2	$C_2N_2(^1\Sigma_g^+) \rightarrow 2CN(^2\Sigma^+)$	5.7	5.9 [45]

[a] Values in brackets refer to D_e (H.F. + $E^{\mathrm{TOT}}_{\mathrm{CORR}}$). H.F. energies come from Ref. [50] for atoms and Ref. [35] for molecules.

4. Conclusion

In the present work, we have developed a computationally inexpensive method for calculating the molecular correlation energy. It consists in treating separately internal and non-internal correlation contributions in the following manner: internal correlation is variationally calculated by a CI in a minimal basis set, and non-internal correlation is calculated by the "atoms-in-molecule" method proposed here.

This method has been applied successfully, in conjunction with the use of Pople's basis sets (STO-3G, 6-31G, 6-31G*(*) included in the GAUSSIAN 76 program) to the calculation of the dissociation energy of some diatomic and polyatomic molecules.

Although our method was tested on only one chemical property (dissociation energy), we think it could be applied to the calculation of other energies of chemical interest. Owing to its simplicity and its economical application, this method becomes particularly interesting for non-trivial systems.

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Appendix I

The calculation of $E^{\mathrm{NI}}_{\mathrm{CORR}}$ of $\mathrm{O}_2(X\,^3\Sigma_g^-)$ is illustrated here in extenso. In Table 8, one finds the Mulliken gross atomic populations. These data allow us to determine the occupation probabilities of all the possible atomic structures of each oxygen atom. These structures, the corresponding states and probabilities are collected in Table 9. The use of the probabilities and the individual $E^{\mathrm{AT}}_{\mathrm{CORR}}$ contributions (see data in Appendix II) in expression (6) gives the result: $E^{\mathrm{NI}}_{\mathrm{CORR}} = -0.538$ a.u.

Table 8. Mulliken gross atomic populations of one oxygen atom in the $\mathrm{O}_2(X\,^3\Sigma_g^-)$ molecule ($R = 1.2$ Å; basis set STO-3G)

χ_q	P_q	P_q^0	$\bar{P}_q$	$\bar{P}_q^0$
$1s$	1	0	1	0
$2s$	0.944	0.056	0.944	0.056
$2p_x$	0.5	0.5	1	0
$2p_y$	0.5	0.5	1	0
$2p_z$	0.557	0.443	0.557	0.443

Table 9. Atomic configurations $\tilde{S}_k$ of one oxygen atom in $\mathrm{O}_2(X\,^3\Sigma_g^-)$ with probability $\tilde{P}_k \geq 0.001$

k	Configuration $\tilde{S}_k$	States (degeneracy)	Probability $\tilde{P}_k$
1	$1s^2 2s^2 2p^6$	^1S	0.069
2	$1s^2 2s^2 2p^5$	^2P	0.248
3	$1s^2 2s^2 2p^4$	$^3P(9) + {}^1D(5) + {}^1S(1)$	0.333
4	$1s^2 2s^2 2p^3$	$^4S(4) + {}^2D(10) + {}^2P(6)$	0.197
5	$1s^2 2s^2 2p^2$	$^3P(9) + {}^1D(5) + {}^1S(1)$	0.044
6	$1s^2 2s 2p^6$	^2S	0.008
7	$1s^2 2s 2p^5$	$^3P(9) + {}^1P(3)$	0.029
8	$1s^2 2s 2p^4$	$^4P(12) + {}^2P(6) + {}^2D(10) + {}^2S(2)$	0.039
9	$1s^2 2s 2p^3$	$^5S(5) + {}^3S(3) + {}^3D(15) + {}^1D(5) + {}^3P(9) + {}^1P(3)$	0.023
10	$1s^2 2s 2p^2$	$^4P(12) + {}^2P(6) + {}^2D(10) + {}^2S(2)$	0.005
11	$1s^2 2p^5$	^2P	0.001
12	$1s^2 2p^4$	$^3P(9) + {}^1D(5) + {}^1S(1)$	0.001
13	$1s^2 2p^3$	$^4S(4) + {}^2D(10) + {}^2P(6)$	0.001

Appendix II.

Atomic non-internal correlation data[a] (a.u.)

	Configurational correlation energy $-E^{\mathrm{AT}}_{\mathrm{CORR}}$ (b)			
Configuration	C	N	O	F
$1s^22s^22p^6$	0.413[c]	0.409[c]	0.406[c]	0.398[c]
$1s^22s^22p^5$	0.318[c]	0.319[c]	0.321[c]	0.324
$1s^22s^22p^4$	0.257[c]	0.259[c]	0.260	0.262
$1s^22s^22p^3$	0.195[c]	0.199	0.203	0.206
$1s^22s^22p^2$	0.143	0.148	0.152	0.156
$1s^22s^22p$	0.098	0.102	0.105	0.108
$1s^22s^2$	0.054	0.056	0.057	0.058
$1s^22s2p^6$	0.449[c]	0.446[c]	0.441[c]	0.439
$1s^22s2p^5$	0.315[c]	0.315[c]	0.317	0.322
$1s^22s2p^4$	0.244[c]	0.244[c]	0.243	0.241
$1s^22s2p^3$	0.170	0.169	0.172	0.186
$1s^22s2p^2$	0.113	0.117	0.120	0.122
$1s^22s2p$	0.073	0.076	0.078	0.079
$1s^22s$	0.050	0.051	0.051	0.051
$1s^22p^6$	0.463[c]	0.466[c]	0.468[d]	0.470[c]
$1s^22p^5$	0.330[c]	0.332[c]	0.335	0.336
$1s^22p^4$	0.227[c]	0.228[c]	0.230	0.231[c]
$1s^22p^3$	0.146	0.146	0.148[c]	0.150
$1s^22p^2$	0.085	0.086	0.089	0.092
$1s^22p$	0.052	0.054	0.055	0.056
$1s^2$[f]	0.045[e]	0.045[e]	0.046[e]	0.046[c]

[a] From data in Ref. [17, 18].

[b] Weighted average non-internal correlation energy: See for example Table 9.

[c] Extrapolated or interpolated value.

[d] Ref. [51].

[e] Ref. [52].

[f] For H atom: $-E^{\mathrm{AT}}_{\mathrm{CORR}}(1s^2) = -0.039$ a.u. [53].

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