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A Simplified Method for Molecular Correlation Energy Calculations by Separation into Internal and Non-internal Parts. Application to Multiconfigurational Zeroth-order Wavefunctions

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A simplified method of determining the molecular correlation energy by two separate calculations, one for the internal and one for the non-internal correlation energies, is extended to multiconfigurational zeroth-order wavefunctions. This extension offers the possibility of deriving correlated potential energy curves or surfaces for processes involving configurational changes. The internal correlation energy is shown to be correctly determined by an MC/CI procedure combining the use of minimal and extended basis sets. An original semi-empirical "atoms-in-molecules" method based on the L.C.A.O. expansion of the molecular wavefunction is proposed for the non-internal correlation energy calculations. This method is shown to be able to overcome some of the shortcomings of a previous populations analysis approach. Test calculations concern potential curve parameters (D_e, T_e, R_e, ω_e) of the ground and some excited states of the NH, C_2, HCN and CN molecules. The results are found to be in good agreement with corresponding experimental and large CI results.

Key word: Correlation energy.

1. Introduction

We have recently proposed an economical but non-variational method for molecular correlation energy calculations [1]. In this method we had calculated

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separately the internal and non-internal correlation energies, a partition inspired by the work of Sinanoglu and coworkers [2]. The internal correlation energy had been evaluated by us by means of a CI calculation including all configurations resulting from biexcitations with respect to the SCF function within the valence orbital space in a minimal basis set. The validity of this approximation had been tested by MCSCF/CI calculations using an extended basis set. The non-internal correlation energy had been evaluated by an original "atoms-in-molecule" method, in which the semi-empirical non internal correlation energies of the atoms in the molecule are weighted by their Mulliken population [3]. Dissociation energies had been calculated by this method for several di- and polyatomic molecules and successfully compared to the experimental values in so far as they were available [4]. However, the two parts of the correlation energy had been then calculated on the basis of monoconfigurational SCF functions of the bond molecule on the one hand and of the dissociation products on the other hand. Since we are interested in potential energy hypersurfaces we need to extend our method for correct zeroth-order wavefunctions, i.e., for example, wavefunctions that describe properly a dissociation process. This will imply the development of a new formalism to calculate the non-internal correlation energy. The molecules chosen here for our purpose are: $\mathrm{NH}(X\ {}^3\Sigma^-, a\ {}^1\Delta, b\ {}^1\Sigma^+)$, $\mathrm{HCN}(X\ {}^1\Sigma^+)$, $\mathrm{C_2}(X\ {}^1\Sigma_g^+, a\ {}^3\Pi_u)$, $\mathrm{CN}(X\ {}^2\Sigma^+)$.

2. Description of the Method

2.1. *Zeroth-Order Wavefunctions*

As it is well-known, a single Slater determinant is nearly always insufficient to describe properly the dissociation behaviour of a molecule. Indeed, the orbitals of a monoderminantal wavefunction most often correlate asymptotically with orbitals of ionized states of the dissociation products instead of the proper Wigner–Witmer partners. Let us take for example the following dissociation process of the HCN molecule in its ground ${}^1\Sigma^+$ state:

$$\mathrm{HCN}({}^1\Sigma^+) \rightarrow \mathrm{H}({}^2S) + \mathrm{CN}({}^2\Sigma^+).$$

It can be shown that the SCF configuration for this state:

$$\Psi_a = |1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi_+^2 1\pi_-^2 5\sigma^2|$$

correlates at infinite separation to

$$|(1-4)\sigma^2 1\pi_+^2 1\pi_-^2 5\sigma^2|$$

of CN^-, leading to the ionic dissociation products $\mathrm{CN}^-({}^1\Sigma^+) + \mathrm{H}^+({}^1S)$. Thus if the function Ψ_a can be chosen as a "zeroth-order wavefunction" in the vicinity of the equilibrium geometry, this is no longer the case at large distances. Oppositely, the function $\Psi_b = |(1-4)\sigma^2 1\pi_+^2 1\pi_-^2 5\sigma 6\sigma|$ is a good zeroth-order wavefunction for the dissociation products because it correlates to $|((1-4)\sigma^2 1\pi^4 5\sigma)_{\mathrm{CN}} 1s_{\mathrm{H}}|$ corresponding to the proper Wigner–Witmer products. Therefore it will be convenient to use the biconfigurational wavefunction $\Psi =$

$a\Psi_a + b\Psi_b$ as zeroth-order function in order to describe the portion of the potential energy hypersurface relative to that particular dissociation process. It is even more convenient to include a third configuration: $\Psi_c = |(1-4)\sigma^2 1\pi^4 6\sigma^2|$ in the zeroth-order wavefunction in order to ensure a smooth change from Ψ_a to Ψ_b along the dissociation coordinate. In this particular case, however, $\Psi_a + \Psi_c$ could be sufficient in the MCSCF framework. Similar zeroth-order wavefunctions constructed from dissociative configurations for all the cases studied in this work are collected in the Appendix 1. As may be seen these functions are not always limited to two configurations; their structure depends on the particular degeneracy breakdown which occurs when the product point groups are combined to form the resulting molecular point group and to the spin projections requirements.

It should be noted that the interest of such dissociative functions is not limited to the study of dissociation paths but also to the determination of equilibrium geometries and other spectroscopic constants through an improvement of anharmonic terms in the potential expression.

The best zeroth-order wavefunction constructed in such a way will be obtained in the framework of the MC-SCF method where LCAO coefficients and configuration expansion coefficients are simultaneously optimized. Further, the use of a "double-zeta plus polarization" basis set will be imperative in order to obtain meaningful energy results.

2.2. *Partition of the Correlation Energy*

If we consider the valence orbital space (also eventually referred to below as the "molecular Hartree–Fock sea"[1]) i.e. the orbitals that asymptotically correlate with the valence orbitals of the constituent atoms, one can distinguish three types of orbitals depending on their occupancy in the zeroth-order wavefunction. There are respectively the fully, the partially and the unoccupied orbitals. In the case of HCN, for example, with the zeroth-order wavefunction given above, we have, in addition to the frozen 1σ and 2σ orbitals:

(i) fully occupied orbitals: 3σ, 4σ, 1π
(ii) partially occupied orbitals: 5σ, 6σ
(iii) unoccupied valence orbitals: 7σ, 2π

In the case of a minimal basis set, the valence orbital space coincides with the complete orbital space. In a non-minimal basis set, however, there are also the unoccupied non-valence orbitals, arising from the SCF procedures. On the basis of this partitioning of the orbital space, we extend the open-shell treatment of Silverstone and Sinanoglu (2.a) of the correlation energy. In their work, they divided the orbital space into an internal space, constituted of all the orbitals fully or partially occupied in the zeroth order wavefunction (and also called

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[1] The "valence orbital space" is identical to the "Hartree–Fock sea" except that it does not include the core electrons of the atoms constituting the molecule. Since these are always frozen in our MC or CI (not SCF) calculations, the two notions are equivalent in the present context.

"Hartree–Fock sea") and an external space spanned by the unoccupied orbitals. They defined three physically distinct contributions to the correlation energy:

(1) the internal correlation energy, represented by the complete CI (mono, bi, tri . . . substitutions) within the "Hartree–Fock sea"
(2) the semi-internal correlation energy represented by a CI of n-substitutions where at least one electron leaves the "Hartree–Fock sea" and at least one remains in it.
(3) the all-external correlation energy, represented by the CI of n-substitutions outside the "Hartree–Fock sea".

In our calculations we have extended for the molecular case the concept of internal space to the valence orbital space, which correlates asymptotically with the internal spaces of the constituting atoms, but we have limited the CI expansion to the first order of perturbation, i.e. the biexcitations. The monosubstitutions play the special role of spin and symmetry polarization. However in the case of a fully optimized MC function, the mono-substitutions by unoccupied orbitals vanish to the first order, as shown in the generalized Brillouin–Levy–Berthier theorem [5].

In this paper, as in the preceding ones we calculate separately the internal correlation energy and the non-internal (i.e. semi-internal plus all-external) correlation energy:

$$E_{\mathrm{CORR}} \simeq E^{I}_{\mathrm{CORR}} + E^{\mathrm{NI}}_{\mathrm{CORR}}.$$

2.3. *Internal Correlation Energy*

It is clear that the zeroth-order MCSCF energy contains an important part of the internal correlation energy. However, since it is not possible to perform the complete MCSCF calculation spanning all the biexcitations contributing to the internal correlation energy as defined in 2.2., we have tested the possibility of evaluating the remaining fraction of the internal correlation energy by means of a CI in a minimal basis set, just as we had proposed in the case of a monodeterminantal wavefunction [1].

In the present case however, the double substitutions are of course generated with respect to the zeroth-order MC function. This means that, in order to obtain the same level in the self consistency conditions using the minimal basis set as those using the extended basis set, we perform an equivalent MCSCF calculation in the minimal basis set before doing the CI calculation. The validity of the use of a minimal basis set will be tested below in the same manner as before i.e. by comparison with equivalent calculations using as extended basis sets as possible.

2.4. *Non-Internal Correlation Energy*

2.4.1. *Shortcomings of the Population Analysis Approach*

This part of the correlation energy is evaluated by an "atoms-in-molecule" method, i.e. a method in which the known semi-empirical non-internal correlation energies (6, 7) of all possible states of a given atom in the molecule under study are summed according to their "weights" in the molecule. This method is based on the fact that all-external energy consists of transferable electron pair energies (2.b). In a previous paper, the weights had been evaluated by means of a Mulliken gross population analysis. Thus, for each atom X_i of a given molecule the $K(X_i)$ possible atomic configurations $\tilde{S}_k$ are weighted by an occupation probability:

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

the sum being taken over all the atomic spinorbitals; P_p is the gross Mulliken population of an atomic spinorbital χ_p in the molecule, and n_p^k equals 1 or 0 depending on whether the spinorbital is occupied or not in configuration $\tilde{S}_k$. This method while having the advantage of being very simple implies a partial loss of the L.S. coupling information of the atomic components as a consequence of the use of the density function in place of the wave function itself. In this context of population analysis, it is in fact possible to calculate the weight of an atomic configuration but not the weight of a particular state arising from that configuration. That is why we had previously used averaged non-internal correlation energies. This shortcoming will have the two following consequences on the results. First, term energies between states of different multiplicities tend to be improperly predicted. Secondly, improper correlations can appear with a multiconfigurational zeroth-order wavefunction.

To explain the first point, let us take as an example the dissociation of the $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states of the NH molecule. The three states dissociate into the ^2S state of H and respectively to the ^4S, ^2D and ^2P states of N arising from the same $1s^22s^22p^3$ configuration. It follows that, at their dissociation limit, the three states will have the same non-internal correlation energy, equal to the averaged value of the $1s^22s^22p^3$ configuration. At equilibrium geometry a more complex mixture of atomic configurations takes place but one can expect that the same type of average will affect the validity of term energies. It is interesting to point out that the errors resulting from these average values will to a large extent cancel in dissociation energy calculations [1, 4].

The second point can be illustrated by considering the simple case of the dissociation of the H_2 ground state where the zeroth-order biconfigurational wavefunction $1/\sqrt{2}(|1\sigma_g^2|-|1\sigma_u^2|)$ must describe at large distance the correct dissociation products, i.e. two independent H atoms in ^2S states. A population analysis carried out on this multiconfigurational function will not reproduce this result but will give the erroneous superposition $\frac{1}{2}H^- + H$. This result induces, therefore, an error of $\frac{1}{2}E_{\text{CORR}}^{\text{NI}}(H^-)$ in the calculation of the dissociation energy of H_2. The loss of information in this case is clearly due to the square of the expansion coefficients that occur in the density function.

In order to keep the symmetry information contained in the wavefunction we propose to work directly on the wavefunction itself in the following way.

2.4.2. Monodeterminantal Approach

In the L.C.A.O. context a Slater determinant

$$\Psi = |\Phi_1(1)\alpha(1) \cdots \Phi_{n_\alpha}(n_\alpha)\alpha(n_\alpha)\Phi_{n_\alpha+1}(n_\alpha+1)\beta(n_\alpha+1)$$
$$\cdots \Phi_{n_\alpha+n_\beta}(n_\alpha+n_\beta)\beta(n_\alpha+n_\beta)|$$

can be expanded over a linear combination of N Slater determinants in which each molecular orbital $\Phi_i(i)$ is replaced by the atomic orbitals $\{\chi_p;\ p=1, m\}$ of its L.C.A.O. expansion:

$$\Phi_i = \sum_p^m c_{ip}\chi_p.$$

The number of terms (N) of the determinantal expansion is simply the number of simultaneous possible combinations of the n_α electrons over the m components of the atomic basis set with those of the n_β electrons over the same basis set, i.e.:

$$N = C^m_{n_\alpha} \cdot C^m_{n_\beta} = \frac{m!}{(m-n_\alpha)!n_\alpha!} \cdot \frac{m!}{(m-n_\beta)!n_\beta!}.$$

Obviously this number includes many combinations that are in fact forbidden for reasons of symmetry.

The expansion can thus be written:

$$\Psi = \sum_p^{C^m_{n_\alpha}} \sum_q^{C^m_{n_\alpha}} d_{pq}\Psi_{pq}$$

with

$$\Psi_{pq} = |\chi_{p_1} \cdots \chi_{pn_\alpha}\bar{\chi}_{q_1} \cdots \bar{\chi}_{qn_\beta}|$$

and

$$d_{pq} = \det(\mathscr{A}_p)\det(\mathscr{B}_q)$$

where $\mathscr{A}_p$ is a $(n_\alpha \times n_\alpha)$ matrix constructed by restricting the L.C.A.O. matrix to the n_α molecular spinorbitals and to the n_α atomic orbitals which define combination p. $\mathscr{B}_q$ of dimension $(n_\beta \times n_\beta)$ is the equivalent L.C.A.O. matrix for the β spinorbitals corresponding to combination q. Ψ_{pq} is of course a polyatomic determinant since the $\chi_{p_k}(\bar{\chi}_{p_k})$ belong to the different constituent atoms.

For the simplicity of the development, let us restrict ourselves to the case of a diatomic molecule A–B. Since we have no data concerning non-internal correlation energies relative to diatomic (or polyatomic) molecules, we will neglect the interatomic interactions and rewrite Ψ_{pq} as a simple product of two atomic determinants:

$$\Psi_{pq} = (-1)^{n_p}|\chi_{p_1} \cdots \chi_{p_{k\alpha}}\bar{\chi}_{q_1} \cdots \bar{\chi}_{q_{l\alpha}}| \times |\chi_{p_{k_\alpha+1}} \cdots \chi_{p_{n_\alpha}}\bar{\chi}_{q_{l_\alpha+1}} \cdots \bar{\chi}_{q_{n_\beta}}|$$
$$= \Psi_{pq}(A)\Psi_{pq}(B)$$

where n_p is the number of permutations necessary to rearrange the electrons on atom A and B. Each determinant $\Psi_{pq}(A)$ can be expanded over a linear combination of eigenfunctions of L^2 and S^2 arising from the atomic configuration to which this Slater determinant belongs:

$$\Psi_{pq}(A)=\sum_{\tau=1}^{\mathrm{ND}} a_\tau^{pq}\Gamma_\tau^{pq}(A)$$

where ND is the degeneracy of the configuration. Thus we can rewrite the diatomic determinant:

$$\Psi_{pq}=\sum_\tau\sum_\lambda a_\tau^{pq}a_\lambda^{pq}\Gamma_\tau^{pq}(A)\Gamma_\lambda^{pq}(B).$$

A polyatomic function can be written in the same way:

$$\Psi=\sum_p\sum_q d_{pq}\sum_\tau\cdots\sum_\rho a_\tau^{pq}\cdots a_\rho^{pq}\Gamma_\tau^{pq}(A)\cdots\Gamma_\rho^{pq}(X)$$

or in shorter notation:

$$\Psi=\sum_i b_i(\Gamma^i(A)\Gamma^i(B)\cdots\Gamma^i(X))$$

where the summation over i refers to all the possible products of eigenfunctions of the different atoms.

Finally:

$$E_{\mathrm{CORR}}^{\mathrm{NI}}(\Psi)=\frac{\sum_i b_i^2\sum_A E_{\mathrm{CORR}}^{\mathrm{NI}}(\Gamma^i(A))}{\sum_i b_i^2}.$$

Where $E_{\mathrm{CORR}}^{\mathrm{NI}}(\Gamma^i(A))$ is the known (6, 7) non-internal correlation energy of a given ionic or neutral state of the atom A. The renormalization factor, $\sum_i b_i^2$, is due to the neglect of overlap between the atomic Ψ_{pq}.

As in the case of the population approach, 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 in a minimal basis calculation.

We are now able to describe the non-internal molecular energy in terms of weighted atomic contributions where the L.S. coupling information has been kept.

2.4.2. Multiconfigurational L.C.A.O. Approach

Let us now consider a multiconfigurational expression

$$\Psi_{\mathrm{MC}}=\sum_k^M c_k\Psi_k.$$

Each Ψ_k can be treated in the manner described above. Let $\tilde{\Psi}_{pq}$ be the complete set of combinations arising from the M Ψ_k functions:

$$\Psi = \sum_p \sum_q \Big(\sum_k c_k d^k_{pq}\Big)\tilde{\Psi}_{pq}$$

where some of the d^k_{pq} will vanish since a given $\tilde{\Psi}_{pq}$ doesn't necessarily arise in each Ψ_k.

In this way the multiconfigurational information is taken into account.

The formalism is illustrated in Appendix 2 where the simple case of $|1\sigma^2 2\sigma|$ wavefunction of LiH^+ is developed in some detail. Another illustration is presented in Fig. 1 where we have plotted the evolution of the most important atomic weights in the dissociation process of $NH(^3\Sigma^-)$ using a MC function containing the dissociative configurations. It shows clearly that at large interatomic distances the function is entirely composed by $N(^4S)+H(^2S)$ as desired. In the same figure, the evolution of E^{NI}_{CORR} is also shown.

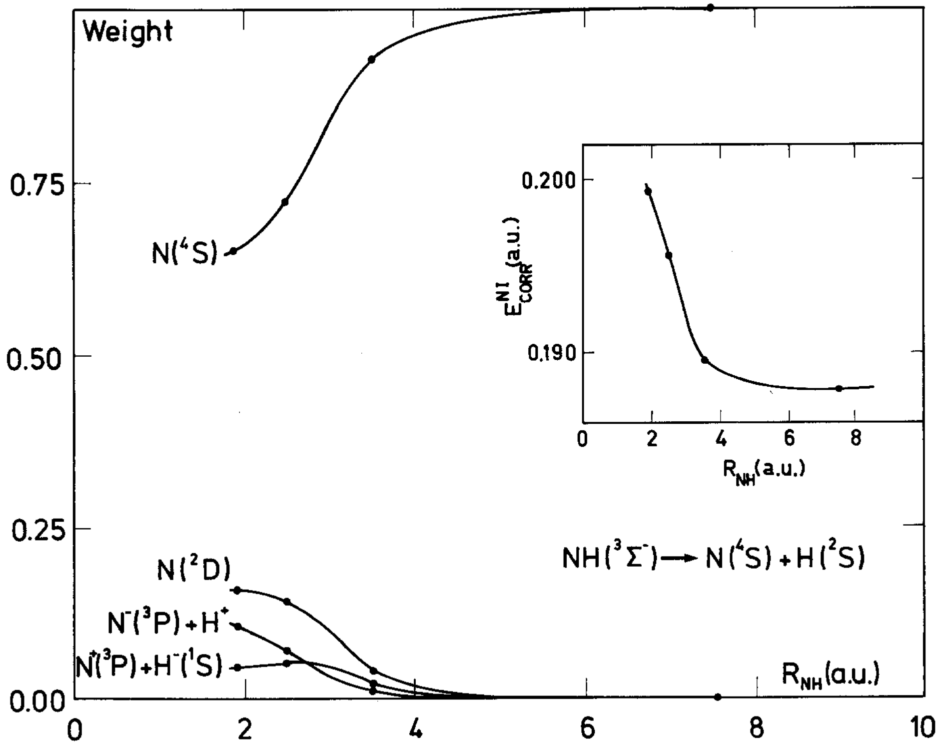

Fig. 1. Evolution of the most important atomic contributions to the non-internal correlation energy in the course of the dissociation of $NH(^3\Sigma^-) \rightarrow N(^4S)+H(^2S)$. Insert: parallel evolution of E^{NI}_{CORR}

3. Programs and Basis Sets.

Three computer programs have been used:

(1) MC-SCF program ALIS written by Ruedenberg et al. [8]
(2) CI programs written by Whitten et al. [9]
(3) $E^{\mathrm{NI}}_{\mathrm{CORR}}$ program written in our laboratory.

Two gaussian basis sets were commonly used:

(i) the "double-zeta plus polarization" quality basis set 6-31G** [10]
(ii) the minimal basis set STO-3G [11].

4. Results and Discussion

4.1. Internal Correlation Energy Results

We present in this section several tests on the validity of the use of a minimal basis set CI to calculate the part of the internal correlation energy which has not been introduced by the zeroth-order wavefunction. A comparison of the minimal basis set results will be made with the corresponding extended basis set results taken as a reference.

The best way to calculate the internal correlation energy in the sense defined above with an extended basis consists in performing a complete MCSCF calculation on the configurational space built up by generating all the double excitations with respect to the zeroth-order wavefunction within the valence orbital space. Let us denote this calculation as $\mathrm{MC_{tot}}$(ext), where "ext" refers to the use of an extended basis set. Such calculations are unfortunately limited to very small systems, like the NH molecule considered in this work.

That is why we will be interested by an alternative two-step MC/CI procedure that we will denote in a general way by the shorthand notation: MC_i(basis 1)/CI(basis 2). This notation means that in a first step, an MCSCF calculation is performed with basis set 1 in a configurational space described by the subscript i and, in a second step, an MCSCF/CI calculation with basis 2 is performed using the same MCSCF reference configurations as in the first step. If basis 2 is not the same as basis 1 the ΔCI increment of the second calculation is then added to the MCSCF energy of the first calculation.

The subscript i can take the following values: "0" referring to the zeroth-order wavefunction, "n" corresponding to a n-configurational space and "tot" corresponding to the total biexcitations space.

As in the case of an SCF zeroth-order wavefunction [1], we have developed an iterative procedure which can provide, in an economical way, a very good approximation of the $\mathrm{MC_{tot}}$(ext) results. It consists in the following steps:

(1) an $\mathrm{MC_0}$(ext)/CI(ext) calculation is performed

(2) the n_1 most important configurations appearing in the CI wavefunction in addition to the n_0 configurations of MC_0 are included in a new MCSCF configurational space of order $n = n_0 + n_1$ and a new MC_n(ext)/CI(ext) calculation is performed

(3) a set of n_2 new dominant configurations is extracted from the last CI wavefunction and an $MC_{n'}$(ext)/CI(ext) calculation is performed, with $n' = n + n_2$

(4) step 3 is iteratively repeated until a limit value is reached, called $MC_{\lim}$(ext)/CI(ext), corresponding to the convergence limit of the CI energy. In our opinion this limit defines a very good approximation of the MC_{tot}(ext) energy.

Fig. 2 compares the convergence of this iterative procedure together with the corresponding convergence of the MC_n(ext) method in the case of NH($^3\Sigma^-$). It appears that the MC/CI procedure converges more rapidly than the MC one, so that, hopefully, we can apply this procedure with success to cases for which the MC_{tot}(ext) limit is inaccessible. Such cases are illustrated in Fig. 3 for the $X\ ^1\Sigma_g^+$ and $a\ ^3\Pi_u$ states of C_2 and in Fig. 4*a* for the ground state of HCN. We also find in these cases a rapid convergence of the MC/CI procedure which can be interpreted by the fact that the valence molecular orbitals are almost fully optimized by the MCSCF step even if these orbitals are occupied in only one or two configurations of the MCSCF configurational space. In the case of HCN, for example, the valence orbitals 7σ, $2\pi_x$, $2\pi_y$ are not occupied in the zeroth-order function. It is necessary to extend the multi-configurational space to at least six

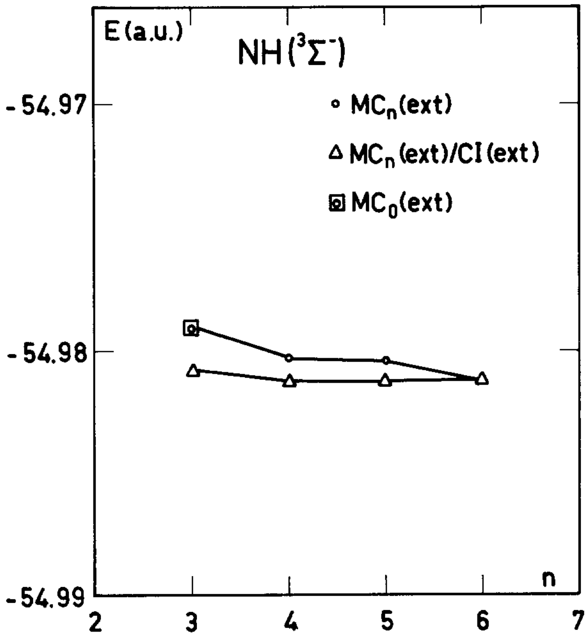

Fig. 2. Comparison of the MC and MC/CI convergences with an increase of the number *n* of configurations included in the MC calculation. NH($^3\Sigma^-$) at equilibrium geometry; "ext" denotes the 6-31G** basis set

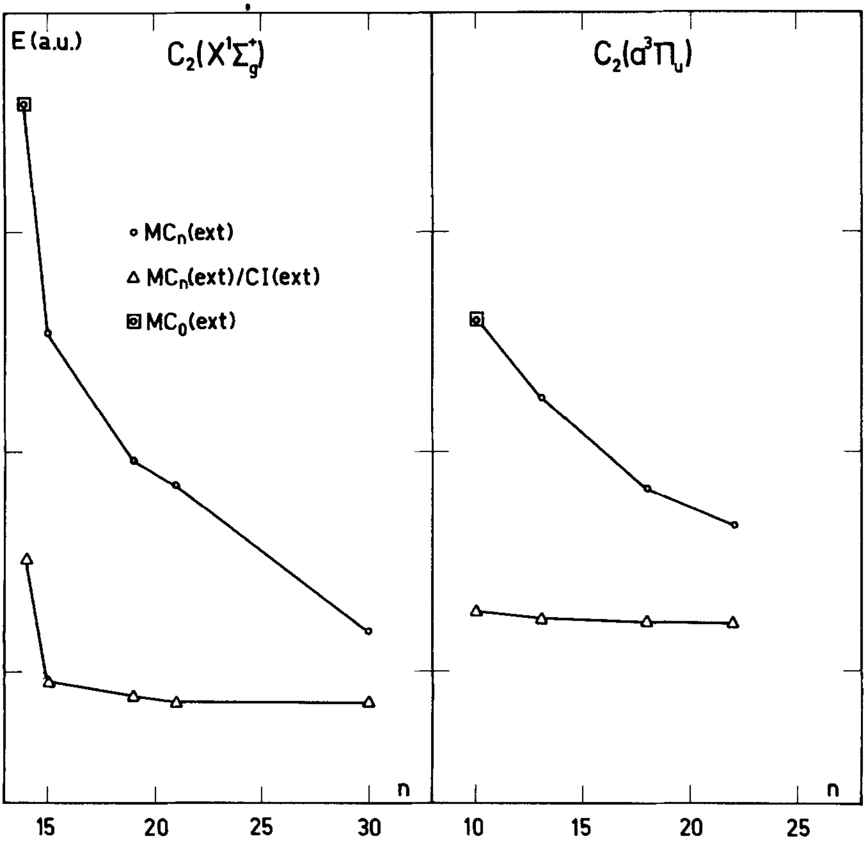

Fig. 3. Same comparison as in Fig. 2 for the $X\ ^1\Sigma_g^+$ and $a\ ^3\Pi_u$ states of C_2 at equilibrium geometries

configurations to ensure their occupancy. At this level, as can be seen from Fig. 4*a*, the MC_6(ext)/CI(ext) has nearly reached the value of MC_{lim}(ext)/CI(ext). However, in the case of $C_2(^1\Sigma_g^+)$ all the valence orbitals are occupied in the zeroth order wavefunction but, as it is obvious in Fig. 3, a very important optimization effect is induced by the fifteenth configuration which arises from the important $2\sigma_u^2 \rightarrow \pi_u^2$ replacement.

Fig 4 introduces the basis set effect in the case of the $^1\Sigma^+$ state of HCN by a comparison between the 6-31G** extended and the STO-3G minimal basis sets. The three parts of the figure show the convergence of the MC/CI procedure respectively for MC_n(ext)/CI(ext), MC_n (min)/CI(min) and MC_n(ext)/CI(min) calculations. It appears from Fig. 4b that the minimal basis set induces an immediate convergence already reached at the zeroth-order wavefunction level. This can be explained by the poor flexibility of the minimal basis set which, as a consequence reduces the importance of the MCSCF optimization of the unoccupied valence orbitals.

Since the MCSCF calculations with STO-3G and 6-31G** basis sets behave very similarly (Fig. 4a and b), it is not surprising that the MC_n(ext)/CI(min) (Fig. 4c)

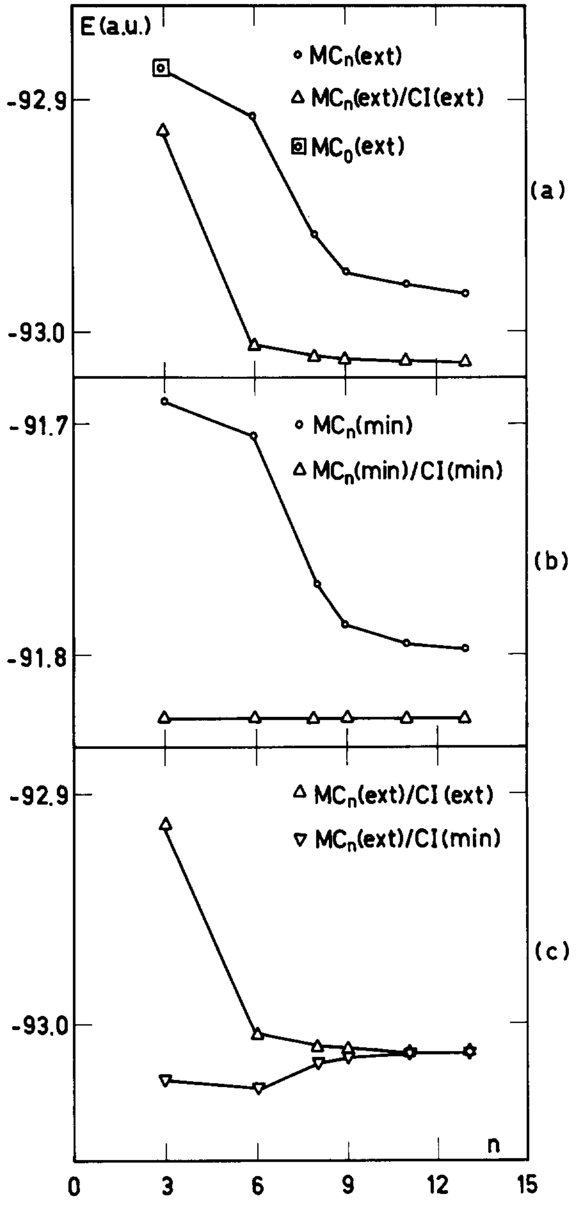

Fig. 4. Basis set comparison of the MC and MC/CI convergences on the HCN molecule (equilibrium geometry). "ext" refers to the 6-31G** basis set and "min" to the STO-3G one

result is nearly constant for any value of $n \geq n_0$. The resulting overestimate of $E^{\mathrm{I}}_{\mathrm{CORR}}$ observed for low n values can be attributed to a polarization effect of the minimal basis set CI that disappears with increasing n values since it is incorporated in the MCSCF calculation with the minimal basis set. Finally, the

Table 1. Electronic energies (in a.u.) calculated at different levels of approximation

Method	$NH(^3\Sigma^-)$	$C_2(^1\Sigma_g^+)$	$C_2(a\ ^3\Pi_u)$	$HCN(^1\Sigma^+)$	$CN(^2\Sigma^+)$
MC_{tot}(ext)	−54.98110	—	—	—	—
MC_{lim}(ext)/CI(ext)	−54.98110	−75.6069	−75.5885	−93.013	−92.319
MC_0(ext)/CI(min)	−54.98222	−75.6186	−75.6046	−93.023	−92.344

MC_n(ext)/CI(min) and MC_n(ext)/CI(ext) curves tend to the same limit. Fig. 4c illustrates the validity of this combined use of the two basis sets.

These results together with similar tests carried out for the other systems studied in this work show that the MC_n(ext)/CI(min) method gives a good approximation of the internal correlation energy already for the lowest values of the number of configurations n, and even at the zeroth-order level. This prompts us to compare in Table 1 the results obtained at the MC_{lim}(ext)/CI(ext) and MC_0(ext)/CI(min) levels of approximation for the set of systems studied in this work. In all cases, the second method gives slightly larger results than the first one owing to the polarization effect of the minimal basis set. However two comments can be made on this point:

(1) even if one considers absolute values, the approximation seems very good in view of the minimal effort it requires.

(2) for properties like dissociation energies, the observed overestimate of E^{I}_{CORR} will be more or less present along the whole hypersurface and one may expect a cancellation of this effect to a large extent.

4.2. Non-Internal Correlation Energy

Since the method we propose in Sect. 2.4. is a semi-empirical evaluation of the non-internal correlation energy and since this contribution cannot be calculated by means of a CI method which would have to be realised over an infinite expansion, we are not able to compare values for E^{NI}_{CORR} in the same way as we did in the preceding section for E^{I}_{CORR}. That is why we will test the validity of our method with the results obtained at the level of total energy calculations. Since we know quite well the quality of our E^{I}_{CORR} calculations (some of them being very accurate as in the case of NH), the comparison of our results with experimental data will give us an indication concerning the quality of our semi-empirical calculations for E^{NI}_{CORR}. This is the object of the next section.

4.3. Total Energy Results

4.3.1. The NH *Molecule*

As shown in Sect. 4.1, the NH molecule is a privileged system for which the internal correlation energy can be determined accurately by an MC_{tot}(ext) calculation. Indeed, the total configurational spaces to be considered for the $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states arising from the fundamental configuration, are only composed

Table 2. Results for the NH molecule

		calculated (this work)				calculated			
State	Property	SCF	$\mathrm{MC_{tot}(ext)}$	$\mathrm{MC_{tot}(ext)}$ $+E^{\mathrm{NI}}_{\mathrm{CORR}}$ $(A)^{(a)}$	$\mathrm{MC_{tot}(ext)}$ $+E^{\mathrm{NI}}_{\mathrm{CORR}}$ $(B)^{(a)}$	O.S.$^{(b)}$	H.D.$^{(c)}$	M.R.$^{(e)}$	Exp. (12)
$^3\Sigma^-$	R_e (Å)	1.023	1.053	1.040	—	1.041	1.061	1.039	1.036
	ω_e (cm^{-1})	3606	3023	3160	—	3300	3211	3269	3282
	D_e (eV)	2.06	2.75	3.06	3.26	3.06	3.08	3.38	$\leq$3.67
$^1\Delta$	R_e (Å)	1.021	1.047	1.038	—	1.037	1.057	—	1.034
	ω_e (cm^{-1})	3581	3199	3304	—	3362	3290	—	(3188)
	D_e (eV)	3.06	3.61	3.82	4.20	3.97	3.96	—	($\leq$4.5)$^{(d)}$
	T_e (eV)	1.86	2.00	1.61	1.92	2.00	1.83	—	1.57
$^1\Sigma^+$	R_e (Å)	1.020	1.046	1.034	—	1.035	1.066	—	1.036
	ω_e (cm^{-1})	3615	3233	3312	—	3396	3205	—	3352
	D_e (eV)	3.10	3.62	3.86	4.22	4.13	3.97	—	($\leq$4.6)$^{(d)}$
	T_e (eV)	3.68	2.89	2.78	2.75	2.79	2.88	—	2.63

[a] $E^{\mathrm{NI}}_{\mathrm{CORR}}$ (A) or $E^{\mathrm{NI}}_{\mathrm{CORR}}$ (B) refer to method A or B respectively (see text)

[b] Ref. [13]; INO-CI

[c] Ref. [14]; GVB (1+2) calculations for the $^3\Sigma^-$ and $^1\Delta$ states, POL-CI calculations for the $^1\Sigma^+$ state

[d] calculated from experimental data

[e] Ref. [18]; CEPA

of 6, 12 and 19 configurations respectively. The use of such accurate internal correlation energies will provide us with the possibility to test the validity of the method developed in section 2.4 to derive the non-internal correlation energies. The formalism has been applied to MC_0(STO-3G) wavefunctions to ensure a correct dissociation behaviour.

Equilibrium geometries, vibrational frequencies, dissociation energies and term energies, calculated at three levels of approximation, are listed in Table 2. These results are compared to the corresponding experimental data [12] and to the elaborate results[2] of O'Neil and Schaefer [13] (referred below as O.S.) and of Hay and Dunning [14] (referred as H.D.) and for the ground state to the accurate CEPA results of Meyer and Rosmus [18] (M.R.). The R_e and ω_e values have been determined by means of quartic polynomial fittings of the potential curves near the minima. The numerical accuracy of the values obtained in that way has been checked on the $^1\Delta$ state with polynomial fits of higher degree (five, six and seven) at the $MC_{tot}(ext)+E^{NI}(A)$ level. At the seventh degree, the values are stable and diverge from the values obtained at degree four by an amount of 0.0005 a.u. for R_e and 1 cm^{-1} for ω_e.

Let us first discuss the effect of the progressive inclusion of the correlation energy on the results:

(1) The discrepancies observed at the SCF level are not surprising and their nature are well known: too low values for R_e and D_e and too large ω_e values.
(2) The addition of internal correlation energy at the MC_{tot}(ext) level has for consequence an important improvement of the energy results, but also to overshoot the equilibrium distances and underestimate the frequencies. These predictable deformations which correspond to a flattening of the potential energy curves, can be attributed to the greater importance of the multiconfigurational treatment in the valence shell configuration space at large internuclear distances than at equilibrium ones. The same conclusions apply to the H.D. results, which incorporates principally internal correlation and polarization effects.
(3) Further inclusion of E^{NI}_{CORR} energies gives a new significant improvement of the energy results as well as of the geometrical parameters, which are now in good agreement with the experimental data and with the O.S. CI results. The shapes of the potential curves are particularly well reproduced, which means that the non-internal correlation energies have balanced correctly the correlation effects between the equilibrium and dissociation regions. Another point to be emphasized is the term energy value of the $^1\Delta$ state which is close to the experimental value. This agreement is particularly interesting since the CI calculations of O.S. and H.D. fail to describe correctly this quantity. The conclusion of this set of data is that the non-internal correlation energy calculations seem quite accurate.

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[2] O.S. results proceed from INO calculations performed on 277 to 418 configurations, depending on the state considered. H.D. calculations of GVB(1+2) type for the $^3\Sigma^-$ and $^1\Delta$ states, including respectively 2197 and 1054 configurations, and of POL-CI type for the $^1\Sigma^+$ state, with 259 configurations

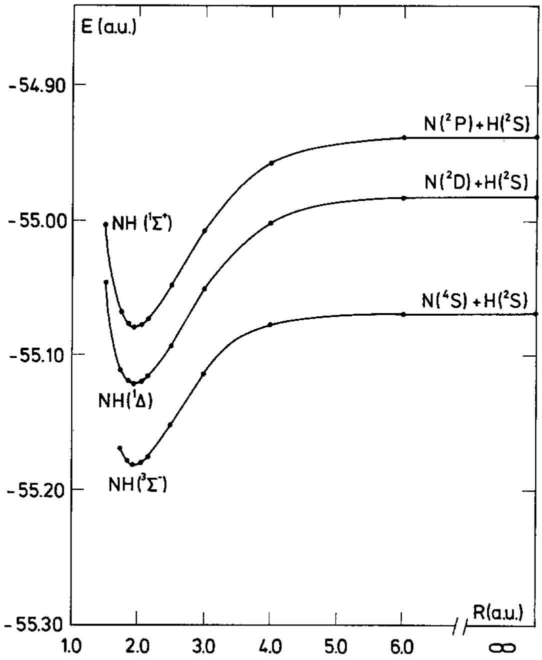

Fig. 5. Potential curves of the NH molecule calculated at the $MC_{tot}(ext)+E^{NI}_{CORR}$ level

Fig. 5 gives an illustration of the calculated potential curves of NH.

The dissociation and term energies calculated here are also compared in Table 2 to the corresponding results obtained by applying the method developed in the previous work [1] for E^{NI}_{CORR} calculations, based on a Mulliken population analysis. Let us call "method B" this last method and "method A" the one developed in this work. It can be seen that, as expected on the basis of the discussion made in Sect. 2.4., method A reproduces more correctly the term energies. Oppositely this method gives lower values for the dissociation energies. This is due to the fact that the absolute values of the E^{NI}_{CORR} are observed to be smaller at equilibrium distances in the case of method A, without any compensation at infinite separation. However, the difference which appears between the E^{NI}_{CORR} of the ${}^3\Sigma^-$ and ${}^1\Delta$ states improves the ${}^1\Delta$ term energy as predicted above. It should be emphasized however that the population approach (method B) is not to be completely discarded. Indeed, it has been shown to give quite good results for dissociation energies of non-trivial systems [1, 4] and this at much lesser effort than that of the present LCAO approach. So, we suggest the use of method B in conjunction with SCF wavefunctions in the case of large polyatomic systems for which only energy differences are needed, without having to describe the complete potential surfaces.

Table 3 illustrates the effect of the introduction of approximate internal correlation energies calculated at the $MC_0(ext)/CI(min)$ level, by comparison to the corresponding $MC_{tot}(ext)$ results. The accuracy of the approximate treatment is confirmed here also. However it can be pointed out that the use of a minimal

Table 3. Comparison between MC and MC/CI procedures in the case of the $^3\Sigma^-$ state of NH

Property	$\mathrm{MC_{tot}(ext)} + E^{\mathrm{NI}}_{\mathrm{CORR}}$	$\mathrm{MC_0(ext)/CI(min)} + E^{\mathrm{NI}}_{\mathrm{CORR}}$
R_e (Å)	1.040	1.038
ω_e (cm^{-1})	3160	3342
D_e (eV)	3.06	3.09

basis set CI produces larger ω_e values as a consequence of the basis polarization effect mentioned above. The related excess of internal correlation energy decreases rapidly going from the equilibrium distance to the dissociation limit, deforming the potential curve in the sense of an increase of ω_e.

Finally, we have tested on the $^3\Sigma^-$ state of NH the validity of the partition of the correlation energy by a comparison of the $E^{\mathrm{NI}}_{\mathrm{CORR}}$ values calculated on the basis of different size multiconfigurational wavefunctions. These values are found to be −0.1997 a.u. and −0.1995 a.u. for a 3 and 6 (total) configurations function respectively. This is at least an indication of the validity of the present partition.

4.3.2. *The C_2 Molecule*

To proceed further with our tests, we have investigated the $X\ ^1\Sigma^+$ and $a\ ^3\Pi_u$ states of the C_2 molecule which both dissociate to $C(^3P)+C(^3P)$. The interesting fact is that they lie very close in energy to each other (0.09 eV experimentally [12]) so that the calculation of term energy of the $a\ ^3\Pi_u$ state is a very demanding test. It often happens that elaborate CI or MCSCF calculations lead to the conclusion that the $a\ ^3\Pi_u$ should be regarded as the ground state. It is of course due to the fact that a difference of 0.09 eV is at the very limit of accuracy of the most sophisticated present theoretical models.

Although the internal correlation energy could be calculated by means of a total MCSCF calculation with an accurate program, this would certainly cost a lot. The reference for the internal correlation energy will then be determined by the limit reached by the iterative $\mathrm{MC_{lim}(ext)/CI(ext)}$ procedure. The configurations to be included in this $\mathrm{MC_{lim}}$ were selected at 2.4038 a.u. (which is the 6-31G equilibrium geometry of $^1\Sigma_g^+$) for both states. The energy threshold was 0.0003 a.u.

The values of R_e, ω_e, T_e and D_e calculated at different levels of approximation are listed in Table 4. The R_e and ω_e values have been extracted from a quartic polynomial analytical expression of the potential curve at the level of internal correlation energy calculation ($\mathrm{MC_{lim}(ext)/CI(ext)}$ and $\mathrm{MC_0(ext)/CI(min)}$) as well as at the total energy level ($\mathrm{MC_{lim}(ext)/CI(ext)} + E^{\mathrm{NI}}_{\mathrm{CORR}}$ and $\mathrm{MC_0(ext)/CI(min)} + E^{\mathrm{NI}}_{\mathrm{CORR}}$). As in section 4.3.1. we have checked the numerical accuracy of a polynomial fit of degree four, at the $\mathrm{MC_0(ext)}$ and $\mathrm{MC_{lim}(ext)}$ levels for both $^1\Sigma_g^+$ and $^3\Pi_u$ states. This accuracy is, at the worst, of 0.001 a.u. for R_e and 20 cm^{-1} for ω_e.

Table 4. Results for the C_2 molecule

State	Property	exp.[12]	K.L.[15]	MC_{lim}(ext)/ CI(ext)	MC_{lim}(ext)/ CI(ext) $+E_{CORR}^{NI}$	MC_0(ext)/ CI(min)	MC_0(ext)/ CI(min) $+E_{CORR}^{NI}$
$X\,^1\Sigma_g^+$	R_e (Å)	1.243	1.260	1.260	1.248	1.254	1.241
	ω_e (cm^{-1})	1855	1789	1703	1782	1568	1694
	D_e (eV)	6.33	5.55	5.92	6.53	6.15	6.77
$a\,^3\Pi_u$	R_e (Å)	1.312	1.34	1.334	1.326	1.329	1.324
	ω_e (cm^{-1})	1641	1554	1539	1825	1801	1995
	T_e (eV)	0.09	−0.03	0.37	0.51	0.26	0.43
	D_e (eV)	~6.27	5.58	5.55	6.02	5.90	6.34

The column K.L. refers to the results obtained by K. Kirby and B. Liu [15] with Slater type functions for 64 valence states of C_2. In their work, they used a "valence CI" carried out on all possible CSF that can be constructed within the valence orbital space, using the orbitals obtained after a MCSCF calculation with the dissociative configurations of the $a\ ^3\Pi_u$ state. This kind of CI should give an accurate value of internal correlation energy plus polarization energy. These results can then be compared to our $\mathrm{MC_{lim}(ext)/CI(ext)}$ calculations and can help us in the discussion of the quality of the $E^{\mathrm{NI}}_{\mathrm{CORR}}$ calculation.

Indeed the following observations can be made from the comparison of the results obtained for the two states by K.L. and by us at the $\mathrm{MC_{lim}(ext)/CI(ext)}$ level:

(1) the equilibrium geometries are nearly the same, i.e. they are larger than the experimental values
(2) the ω_e values are also quite similar though slightly better in K.L.'s work
(3) the dissociation energies are of course too small since only a part of the correlation energy has been included. These observations allow us to discuss the improvements due to the introduction of an evaluation of $E^{\mathrm{NI}}_{\mathrm{CORR}}$. The equilibrium geometries are now really close to the experimental data and our spectroscopic constants are slightly improved although they are not necessarily better than those of K.L. This could be interpreted by the fact that the introduction of $E^{\mathrm{NI}}_{\mathrm{CORR}}$ shifts the minimum of the curve to smaller internuclear separations but doesn't improve its shape in a decisive manner. The second main amelioration lies in the energy results. The dissociation energies are nicely reproduced. A slight excess is observed in the singlet and a defect in the triplet state. This leads to a term energy that is overestimated. However, the two states are calculated in the right order.

The same parameters were calculated with the $\mathrm{MC_0(ext)/CI(min)}+E^{\mathrm{NI}}_{\mathrm{CORR}}$ method. The same conclusion can be drawn as above. However, the excess of internal correlation energy due to the use of a minimal basis set deforms the shape of the curve and gives rise to overestimated dissociation energies which however remain within acceptable limits. This excess doesn't change drastically the term energy of the $a\ ^3\Pi_u$ state, since it is present in the two states.

The dissociation curves of the two states calculated at the level $\mathrm{MC_0(ext)/CI(min)}+E^{\mathrm{NI}}_{\mathrm{CORR}}$ are plotted in Fig. 6.

Finally, let us compare the dissociation energy values obtained for the $^1\Sigma_g^+$ state using several approximations:

(1) $\mathrm{SCF(ext)/CI(min)}+E^{\mathrm{NI}}_{\mathrm{CORR}}(B)=5.96$ eV [1]
(2) $\mathrm{MC_{lim}(ext)/CI(ext)}+E^{\mathrm{NI}}_{\mathrm{CORR}}(A)$: 6.53 eV
(3) $\mathrm{MC_0(ext)/CI(min)}+E^{\mathrm{NI}}_{\mathrm{CORR}}(A)$: 6.77 eV

These values are to be compared to the experimental value: 6.33 eV. The most accurate calculation 2) gives of course the best result. Nevertheless the easiest and cheapest method 1) gives a worthwhile result although, as has been written

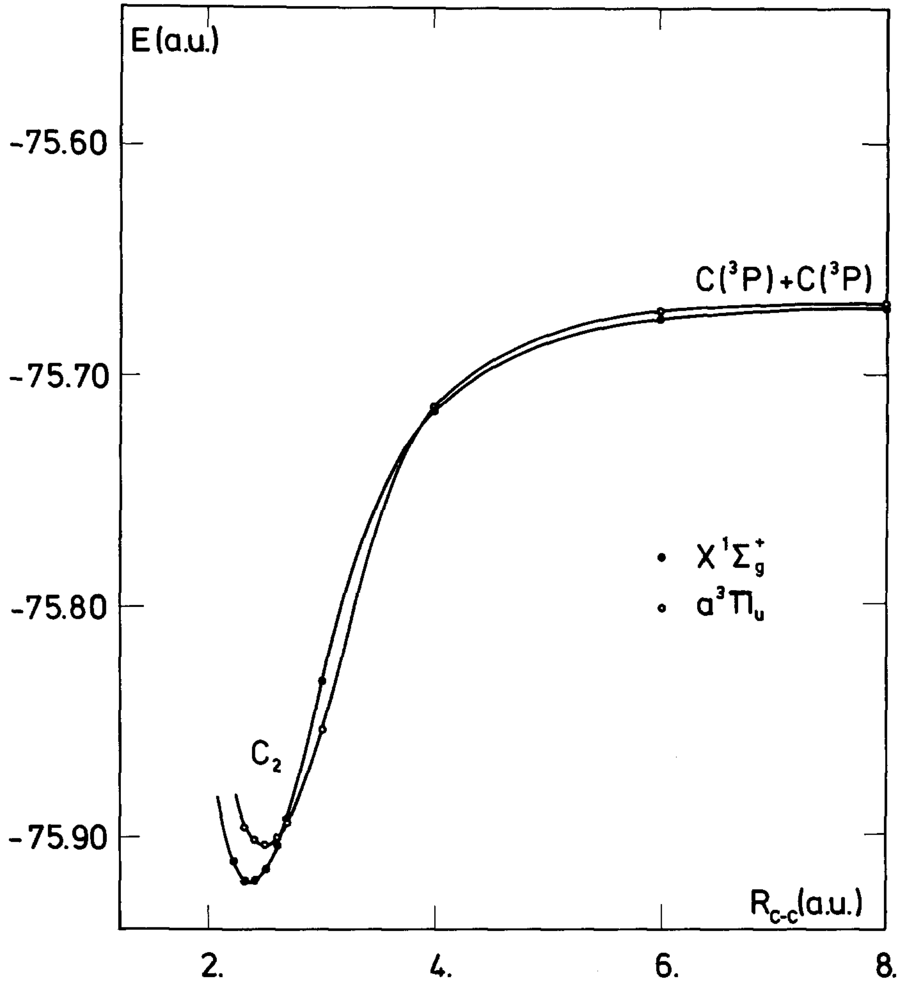

Fig. 6. Potential curves of the C_2 molecule calculated at the $MC_0(ext)/CI(min)+E_{CORR}^{NI}$ level

above, this method doesn't allow to calculate the whole potential curve. This is possible with the intermediate method 3) which provides us with a satisfying result also.

4.3.3. The HCN *and* CN *Molecules*

HCN is the largest system that has been considered here. For this molecule, as well as for CN, the approximate $MC_{lim}(ext)/CI(ext)$ calculation of the internal correlation energy can still be used although it becomes quite expensive. We have only derived here the dissociation energies of HCN and CN for the two following processes:

(a) $HCN(^1\Sigma^+) \rightarrow CN(^2\Sigma^+) + H(^2S)$
(b) $CN(^2\Sigma^+) \rightarrow C(^3P) + N(^4S)$

Table 5. Results for the HCN and CN molecules (eV)

Process	MC_{lim}(ext)/ CI(ext)	MC_{lim}(ext)/ CI(ext) $+E^{NI}_{CORR}$ (A)	MC_0(ext)/ CI(min)	MC_0(ext)/ CI(min) $+E^{NI}_{CORR}$ (A)	SCF(ext)/ CI(min)	SCF(ext)/ CI(min) $+E^{NI}_{CORR}$ (B)	Exp. [16, 17]
HCN → H + CN	5.55	6.00	5.03	5.48	5.22	6.01	5.60 (±0.25) 5.70 (±0.23)
CN → C + N	7.67	7.76	8.35	8.43	6.91	8.03	7.79 (±0.15) 7.89 (±0.17)
HCN → C + N + H	13.22	13.75	13.38	13.92	12.13	14.04	13.49 (±0.15)

These two reactions also allow us to derive the atomization energy of HCN: (c) $HCN(^1\Sigma^+) \rightarrow C(^3P) + N(^4S) + H(^2S)$. All these values calculated at the two levels of approximation $MC_{lim}(ext)/CI(ext) + E^{NI}_{CORR}(A)$ and $MC_0(ext)/CI(min) + E^{NI}_{CORR}$ (A) are compared to the values obtained with the method $SCF(ext)/CI(ext) + E^{NI}_{CORR}$ (B) and to the experimental data in Table 5. For the first two methods the total energies have been calculated at the 6-31G equilibrium geometries and at large internuclear separation. For the reasons explained above it is not possible to perform a calculation at large distance with the method SCF(ext)/CI(min) so that for this entry the energy at the dissociation limit is the sum of the total energies of the dissociation products at their 6-31G equilibrium geometries. The experimental dissociation energy of HCN has been derived from a thermochemical cycle where the heat of formation of CN has been introduced. Since the latter is still controversal in the literature we have selected two of the available values [16, 17]. This leads of course to two values for D_e(HCN) also.

The results are all in good agreement with the experimental values whatever method is used. The fact that the results are of the same accuracy for HCN and CN is rather interesting. Indeed, in the case of CN a C—N bond is broken. This process involves a greater electronic rearrangement than that of HCN where only a CH bond is broken. This means that the contribution of the internal correlation energy to the dissociation energy is evaluated to the same accuracy in simple or in complicated cases. This allows us to derive atomization energy values which are of course of the same quality as for the two preceding cases.

5. Conclusions

In this work, we have presented an extension of a method of calculation of the molecular correlation energy, developed in previous work. This method was based on a partition of the correlation energy into an internal and a non-internal part. The extension tends to generalize the method to be applied to a multiconfigurational zeroth-order wavefunction. This improvement offers the possibility to calculate whole potential energy curves or hyperfaces describing processes which involve configuration changes (dissociation processes, chemical reactions etc.).

Several tests have demonstrated the efficiency of MC/CI procedures and particularly that of the inexpensive $MC_0(ext)/CI(min)$ calculations which combine economically minimal and extended basis sets.

To overcome some shortcomings inherent to the population analysis approach of the non-internal correlation, we have developed an alternative method based on the LCAO expansion of the wavefunction. This new approach presents the advantage of preserving the L.S. coupling information concerning the atomic components deriving from the decomposition of the molecular structure and therefore is applicable to multiconfigurational functions.

The results obtained in this way for the ground state and some excited states of the NH, C_2, HCN and CN molecules have been shown to be in good agreement with the corresponding experimental and elaborate CI results. They concern energy properties (dissociation energies and term energies) as well as geometric properties (equilibrium internuclear separations and vibrational frequencies) which are related to the correct shapes of the potential curves.

We think therefore that the method proposed here can provide an economic method to calculate potential energy surfaces of good quality for non trivial systems, which may be larger than the test molecules treated in this work.

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Appendix 1

Zeroth-order wavefunctions for the molecules studied here (= "dissociative" configurations)

The number of cartesian SAAP'S (fundamental plus those ones which do not vanish at large interatomic separation) is given in the third column. This gives the size of our zeroth-order MCSCF wavefunctions

Molecule	Configurations	Number of cartesian SAAPS	Products
$NH(^3\Sigma^-)$	$1\sigma^2 2\sigma^2\{3\sigma^2 1\pi^2+4\sigma^2 1\pi^2+3\sigma 4\sigma 1\pi^2\}$	3	$N(^4S)+H(^2S)$
$NH(^1\Delta)$	$1\sigma^2 2\sigma^2\{3\sigma^2 1\pi^2+4\sigma^2 1\pi^2+3\sigma 4\sigma 1\pi^2\}$	6	$N(^2D)+H(^2S)$
$NH(^1\Sigma^+)$	$1\sigma^2 2\sigma^2\{3\sigma^2 1\pi^2+4\sigma^2 1\pi^2+3\sigma 4\sigma 1\pi^2\}$	6	$N(^2P)+H(^2S)$
$HCN(^1\Sigma^+)$	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4(5\sigma^2+6\sigma^2+5\sigma 6\sigma)$	3	$CN(^2\Sigma^+)+H(^2S)$
$CN(^2\Sigma^+)$	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2(1\pi^4 5\sigma+1\pi^2 2\pi^2 5\sigma)$	2	$C(^3P)+N(^4S)$
$C_2(^1\Sigma_g^+)$	$1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 2\sigma_u^2\{3\sigma_g^2\pi_u^2+3\sigma_g^2\pi_g^2+3\sigma_u^2\pi_u^2$ $+3\sigma_u^2\pi_g^2+\pi_u^4+\pi_g^4+\pi_u^2\pi_g^2\}$	14	$C(^3P)+C(^3P)$
$C_2(a\ ^3\Pi_u)$	$1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 2\sigma_u^2\{\pi_u^3 3\sigma_g+\pi_g^3 3\sigma_u+\pi_u^2\pi_g 3\sigma_u$ $+\pi_g^2\pi_u 3\sigma_g$	10	$C(^3P)+C(^3P)$

Appendix 2

We develop here, as an example of the formalism presented in Sect. 2.4.2, the LCAO expansion of the monodeterminantal $|1\sigma^2 2\sigma|$ wavefunction of LiH^+ over a three-component $\{1s_{Li}, 2s_{Li}, 1s_H\}$ basis set.

Let us suppose the following L.C.A.O. expression of the MOs:

$$1\sigma=a\ 1s_{Li}+b\ 2s_{Li}+c\ 1s_H$$

$$2\sigma=d\ 1s_{Li}+e\ 2s_{Li}+f\ 1s_H.$$

Table 6. LCAO expansion of the $|1\sigma^2 2\sigma|$ wavefunction LiH$^+$

Ψ_{pq}	$d_{pq} = \det(\mathscr{A}_p)\cdot\det(\mathscr{B}_q)$	$\Psi_{pq}(\mathrm{Li})\Psi_{pq}(\mathrm{H})$	$(-1)^{n_p}$	$\left(\sum_\tau a_\tau^{pq}\Gamma_\tau^{pq}(\mathrm{Li})\right)\cdot\Gamma_\tau^{pq}(\mathrm{H})$
$1s\ 2s\ \overline{1s}$	$(ae\text{-}bd)\cdot a$	$1s^2\ 2s$	-1	${}^2S(\mathrm{Li})\cdot{}^1S(\mathrm{H}^+)$
$1s\ 2s\ \overline{2s}$	$(ae\text{-}bd)\cdot b$	$1s\ 2s^2$	$+1$	${}^2S(\mathrm{Li})\cdot{}^1S(\mathrm{H}^+)$
$1s\ 2s\ \overline{1s}_\mathrm{H}$	$(ae\text{-}bd)\cdot c$	$1s\ 2s\cdot\overline{1s}_\mathrm{H}$	$+1$	${}^3S(\mathrm{Li}^+)\cdot{}^2S(\mathrm{H})$
$1s\ 1s_\mathrm{H}\ \overline{1s}$	$(af\text{-}cd)\cdot a$	$1s^2\cdot 1s_\mathrm{H}$	-1	${}^1S(\mathrm{Li}^+)\cdot{}^2S(\mathrm{H})$
$1s\ 1s_\mathrm{H}\ \overline{2s}$	$(af\text{-}cd)\cdot b$	$1s\ \overline{2s}\cdot 1s_\mathrm{H}$	-1	$1/\sqrt{2}\,({}^3S+{}^1S)(\mathrm{Li}^+)\cdot{}^2S(\mathrm{H})$
$1s\ 1s_\mathrm{H}\ \overline{1s}_\mathrm{H}$	$(af\text{-}cd)\cdot c$	$1s\cdot 1s_\mathrm{H}^2$	$+1$	${}^2S(\mathrm{Li}^{2+})\cdot{}^1S(\mathrm{H}^-)$
$2s\ 1s_\mathrm{H}\ \overline{1s}$	$(bf\text{-}ce)\cdot a$	$\overline{1s}\ 2s\cdot 1s_\mathrm{H}$	$+1$	$1/\sqrt{2}\,({}^3S-{}^1S)(\mathrm{Li}^+)\cdot{}^2S(\mathrm{H})$
$2s\ 1s_\mathrm{H}\ \overline{2s}$	$(bf\text{-}ce)\cdot b$	$2s^2\cdot 1s_\mathrm{H}$	-1	${}^1S(\mathrm{Li}^+)\cdot{}^2S(\mathrm{H})$
$2s\ 1s_\mathrm{H}\ \overline{1s}_\mathrm{H}$	$(bf\text{-}ce)\cdot c$	$2s\cdot 1s_\mathrm{H}^2$	$+1$	${}^2S(\mathrm{Li}^{2+})\cdot{}^1S(\mathrm{H}^-)$

There are 3 possible combinations of α spinorbitals (C_2^3) and 3 of β spinorbitals (C_1^3) leading to the nine diatomic determinants Ψ_{pq} listed in table 6 together with their respective weights d_{pq}, calculated as the product of two determinants. The third column of the table gives the $\Psi_{pq}s'$ reordered on separated Li and H atoms.

The consequent changes of sign resulting from orbital permutation are listed in the fourth column. Finally, the last column gives the linear combinations of atomic eigenfunctions that arise from each of the diatomic determinant.

The contributions to a given (M_L, M_S) state of each atom that arise from different Ψ_{pq} in a given superposition of atomic configurations must be regrouped before taking the square of the coefficients, since there is a linear transformation between the set of the possible determinants of an atomic configuration and the states arising from it. If this sum is not performed prior to taking the square of the coefficient the L-S coupling information is lost. The non-internal correlation energy of LiH^+ will therefore be the superposition of the non-internal atomic correlation energies corresponding to these eigenstates weighted by the squares of the coefficients.

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