

Configuration-Interaction Calculations for the Ground State of OF_2 , NO_2^- , CN^- : Canonical Orbitals and Exclusive Orbitals

ROSANNA BONACCORSI, CARLO PETRONGOLO, EOLO SCROCCO, and JACOPO TOMASI
Istituto di Chimica Fisica, Università di Pisa, Italia*

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The C.I. method is applied to already published double- ζ SCF wave functions for OF_2 , NO_2^- and CN^- . All doubly excited configurations are considered. The second order approximation values presented for those cases are compared with the exact energy values in some minor cases. An attempt has been made to improve the rate of convergency of the process by transforming the canonical SCF occupied orbitals into localized ones and the virtual canonical orbitals into a particular type of localized orbitals. These latter show also an intuitively acceptable spatial conformation.

Die CI Methode wird auf bereits bekannte Doppel-Zeta-SCF-Wellenfuntionen für die Systeme OF_2 , NO_2^- und CN^- angewandt. Dabei werden alle doppelt angeregten Konfigurationen berücksichtigt. Um die Konvergenz zu verbessern, werden versuchsweise die kanonischen und besetzten SCF-Orbitale in lokalisierte Orbitale und die virtuellen kanonischen Orbitale in einen besonderen Typ von lokalisierten Orbitalen transformiert. Die letzteren zeigen eine besonders geeignete räumliche Anpassung.

Pour un calcul de interaction de configurations, comprenant toutes le configurations à double excitation, on a employé des fonctions d'onde SCF sur une base doublée. Pour le calcul complet on a essayé des formules d'approximation, qu'on a pu vérifier avec le calcul exact sur des cas réduits.

Pour améliorer la velocità de convergence du procés on a transformé les orbitales canoniques SCF en orbitales localisées et après on a construit, selon un procedé particulier, des orbitales virtuelles localisées qui montrent une conformation dans l'espace qui est intuitivement satisfaisante.

1. Introduction

In this paper the results of some configuration interactions (C.I.) calculations are reported for two angular three-center closed shell molecules (OF_2 and NO_2^-) and for a diatomic ion (CN^-). SCF wave functions have been already calculated for the formers with double- ζ exponents [1] and for the latter with a slightly more extended basis set [2].

Only doubly excited configurations have been considered, employing the same basis set as in Refs. [1], [2] and taking into account all possible configurations. Since the dimensions of the secular matrices were far beyond our diagonalization possibilities, second order approximations have been consistently applied throughout the whole paper and only for some partial calculations the exact diagonalization was performed.

In the second part of the paper an attempt has been made to search for some linear combinations of molecular orbitals (filled or virtual) more effective in

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improving the rate of convergency of the C.I. process. In this case also, only doubly excited configurations were considered, and of them all those have been discarded which in a geminal representation may be interpreted as contributions to the intergeminal correlation energy.

2. Terminology and Approximation Formulas

In the first part of this paper the canonical SCF orbitals are directly employed. The configurations are classified according to the number of unpaired electrons and their relations with the fundamental configuration. Thus: DC configurations (Double excitation, Closed shell), DO 1 configurations (Double excitation, Open shell in the excited orbitals), DO 2 (Double excitation, open shell in the fundamental orbitals) and DD (Double excitation, Doubly open shell). In the last case, for each combination of four unpaired electrons, two singlet configurations are possible. The adapted combinations of the spin functions are following: (1) = $\alpha\beta\alpha\beta$, (2) = $\beta\alpha\alpha\beta$, (3) = $\beta\beta\alpha\alpha$, (4) = $\alpha\beta\beta\alpha$, (5) = $\alpha\alpha\beta\beta$, (6) = $\beta\alpha\beta\alpha$:

$$\text{DD 1} = \frac{1}{2} [(2) + (3) + (4) + (5)]$$

$$\text{DD 2} = \frac{1}{\sqrt{3}} \left\{ (1) + \frac{1}{2} [(2) - (3) + (4) - (5)] + (6) \right\}.$$

By solving the secular equation with a perturbative technique, the total hamiltonian H is partitioned as follows

$$H = H_0 + V$$

H_0 being the "unperturbed" hamiltonian and V the "perturbation". The eigenvectors and eigenvalues of H_0 are assumed known and the eigenvectors form a complete, orthonormal set, i.e.

$$H_0|i\rangle = W_i|i\rangle$$

$$\langle i|j\rangle = \delta_{ij}$$

$$\sum_i |i\rangle\langle i| = 1.$$

If the "unperturbed" hamiltonian is the Hartree-Fock hamiltonian H_{HF} , the Rayleigh-Schrödinger expansion leads to the following expression for the second order correction to the energy of the ground state ($M_{ij} = \langle i|M|j\rangle$)

$$E - H_{00} = \sum_{i \neq 0} (H_{00}^{\text{HF}} - H_{ii}^{\text{HF}})^{-1} H_{0i}^2 \quad (1)$$

while the Brillouin-Wigner expansion leads to

$$E - H_{00} = \sum_{i \neq 0} (E - H_{ii}^{\text{HF}})^{-1} H_{0i}^2. \quad (2)$$

If the total hamiltonian is partitioned as follows (see, for example, Diner, Malrieu and Claverie [6])

$$H_0 = H_{\text{HF}} + \sum_{i \neq 0} \langle i | V | i \rangle | i \rangle \langle i |$$

$$V' = V - \sum_{i \neq 0} \langle i | V | i \rangle | i \rangle \langle i |$$

the RS expansion leads to

$$E - H_{00} = \sum_{i \neq 0} (H_{00} - H_{ii})^{-1} H_{0i}^2 \quad (3)$$

while the BW expansion leads to

$$E - H_{00} = \sum_{i \neq 0} (E - H_{ii})^{-1} H_{0i}^2. \quad (4)$$

In a paper on the correlation energy in the N_2 molecule, Grimaldi [10] analyzed extensively the performances of both Rayleigh-Schrödinger and Brillouin-Wigner expansions adopting for the RS formulation, Eq. (1), and, for the BW formulation Eq. (4). Results relative to Eq. (3) were also reported. For the case of the interaction of 101 configurations he also calculated the exact energy: all approximations are optimistic, approximation (1), (4), (3), in the order, being 6.5 %, 23.5 %, 44 % in error. Some related calculations will be shown below as a comparison.

3. C.I. Calculations with Canonical Orbitals

The electronic configuration of the SCF ground state of OF_2 is $(1b_1)^2 (1a_1)^2 (2a_1)^2 (3a_1)^2 (2b_1)^2 (4a_1)^2 (1b_2)^2 (3b_1)^2 (5a_1)^2 (1a_2)^2 (4b_1)^2 (6a_1)^2 (2b_2)^2$ (1A_1 symmetry). The computed SCF energy is -273.526 a. u. (Ref. [1]), while the experimental energy is about -274.930 a. u.¹ If one assumes for the relativistic energy -0.2152 a. u., i.e. the sum of the relativistic energies of the atoms (Hartmann and Clementi [11]), 1.1887 a. u. represent the energy gap between our SCF result and the final value.

The NO_2^- ion has also 1A_1 symmetry: the electronic configuration of the ground state, as resulting from the SCF calculations of Ref. [1], is: $(1b_1)^2 (1a_1)^2 (2a_1)^2 (3a_1)^2 (2b_1)^2 (4a_1)^2 (5a_1)^2 (1b_2)^2 (3b_1)^2 (4b_1)^2 (1a_2)^2 (6a_1)^2$. The calculated SCF energy, the experimental energy and the relativistic correction are respectively: -203.9859 , -205.3392^2 and -0.1263 a. u. The resulting energy gap is 1.2170 a. u.

The electronic configuration of the $^1\Sigma^+$ ground state of CN^- is given by $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2$. Our SCF energy (Ref. [2]) is -92.3233 a. u.; the experimental value is still controversial: the value -92.8773 a. u. is taken from the work of Napper and Page [13]. The energy gap, calculated with the usual approximation of the relativistic energy, is of 0.5128 a. u.

¹ The data are taken from the JANAF tables [12], supplemented by the atomic energies revised by Cade and Huo [4]. If one takes for the total atomization energy the value proposed by Dibeler *et al.* [5] the energy gap reduces to 1.1227 a. u.

² This value has been obtained from the JANAF data for NO_2 supplemented by the E. A. of NO_2 given by Farragher *et al.* [7]. This last value may be slightly in error (see Fehsenfeld and Ferguson [8]).

Table 1. Second order energy improvement to H₀₀, as calculated according to various approximations^a

Molecule	Conf. type contributions	Config. number	Approx. (1)	Approx. (2)	Approx. (3)	Approx. (4)
OF ₂	DC	221	-0.07473	-0.06742	-0.10045	-0.08174
	DO1	572	-0.01765	-0.01664	-0.02022	-0.01852
	DO2	374	-0.02454	-0.02154	-0.03400	-0.02686
	DD1	2900	-0.16601	-0.15301	-0.19815	-0.17442
	DD2	2900	-0.15756	-0.14525	-0.19003	-0.16819
	Total	6967	-0.44050	-0.40386	-0.54285	-0.46974
NO ₂ ⁻	DC	216	-0.07710	-0.06835	-0.10608	-0.08341
	DO1	552	-0.01903	-0.01790	-0.02167	-0.01981
	DO2	378	-0.01350	-0.01233	-0.01707	-0.01469
	DD1	2801	-0.14307	-0.13175	-0.17518	-0.15331
	DD2	2801	-0.15635	-0.14118	-0.19842	-0.16837
	Total	6748	-0.40906	-0.37151	-0.51842	-0.43995
CN ⁻	DC	133	-0.05305	-0.04937	-0.07222	-0.06145
	DO1	392	-0.03434	-0.03224	-0.04356	-0.03862
	DO2	190	-0.00690	-0.00653	-0.00832	-0.00760
	DD1	675	-0.07304	-0.06730	-0.10048	-0.08596
	DD2	675	-0.09805	-0.09007	-0.12979	-0.11197
	Total	2065	-0.26538	-0.24551	-0.35438	-0.30560

^a The approximations are labeled with the numbers of the corresponding equations in the text. The energies are expressed in atomic units.

Table 2. Comparison of the energy improvements to H₀₀ for the C.I. process involving only DC configurations. They have been calculated exactly and by means of some approximation formulas

Molecule	Exact diag.	Approx. (1)	Approx. (2)	Approx. (3)	Approx. (4)
OF ₂	-0.07714	-0.07473	-0.07321	-0.10045	-0.09546
NO ₂ ⁻	-0.08306	-0.07710	-0.07503	-0.10609	-0.09919
CN ⁻	-0.06795	-0.05305	-0.05219	-0.07222	-0.06921

A selection of the overall results is reported in Table 1³. The energies reported under the headings Appr. (1), Appr. (2), Appr. (3), Appr. (4) refer to the various increments to the SCF energy as calculated by means of Eqs. (1), (2), (3) and (4) respectively.

Table 2 refers to the DC configurations only: the first column contains the energy increment obtained by exact diagonalization, the other headings are as in Table 1. The numerical values of columns (3) and (1) coincide with those of Table 1 since they are independent of the basis length.

³ For CN⁻ the eigenfunctions of the hamiltonian H are also eigenfunctions of M_z operator. Accordingly, for this molecule we class as configurations with closed shell in the fundamental orbitals also those involving 1π orbitals if the two promoted electrons have both the same m_z value (+1 or -1).

Table 3. *Some important configurations for OF₂ with the corresponding energy contributions calculated according to Appr. (4). Canonical orbitals have been used*

Type of config.	holes	particles	Energy contr.	Type of config.	holes	particles	Energy contr.
DD1	$3b_1 6a_1$	$7a_1 5b_1$	-0.01185	DD1	$5a_1 4b_1$	$10a_1 8b_1$	-0.00253
DC	$(3b_1)^2$	$(5b_1)^2$	-0.00991	DC	$(4a_1)^2$	$(7a_1)^2$	-0.00251
DC	$(1a_1)^2$	$(13a_1)^2$	-0.00900	DD2	$5a_1 2b_2$	$7a_1 3b_2$	-0.00245
DD1	$1b_1 1a_1$	$10b_1 14a_1$	-0.00833	DC	$(4a_1)^2$	$(5b_1)^2$	-0.00240
DD2	$3b_1 5a_1$	$7a_1 5b_1$	-0.00715	DD1	$1b_2 2b_2$	$3b_2 4b_2$	-0.00228
DD2	$3b_1 2b_2$	$5b_1 3b_2$	-0.00504	DC	$(1a_1)^2$	$(10b_1)^2$	-0.00218
DD1	$4b_1 6a_1$	$7a_1 5b_1$	-0.00492	DC	$(1b_1)^2$	$(10b_1)^2$	-0.00218
DC	$(6a_1)^2$	$(5b_1)^2$	-0.00490	DD1	$3b_1 2b_2$	$5b_1 3b_2$	-0.00214
DC	$(6a_1)^2$	$(7a_1)^2$	-0.00427	DC	$(1b_1)^2$	$(14a_1)^2$	-0.00213
DC	$(4b_1)^2$	$(7a_1)^2$	-0.00423	DC	$(1a_1)^2$	$(14a_1)^2$	-0.00213
DO2	$5a_1 6a_1$	$(7a_1)^2$	-0.00420	DC	$(1a_2)^2$	$(2a_2)^2$	-0.00206
DD1	$3b_1 5a_1$	$7a_1 5b_1$	-0.00363	DO1	$(4b_1)^2$	$7a_1 10a_1$	-0.00204
DO2	$3b_1 4b_1$	$(7a_1)^2$	-0.00322	DD2	$1a_2 4b_1$	$10a_1 4b_2$	-0.00202
DC	$(2b_2)^2$	$(3b_2)^2$	-0.00321	DC	$(3b_1)^2$	$(7a_1)^2$	-0.00201
DC	$(5a_1)^2$	$(7a_1)^2$	-0.00312	DC	$(4b_1)^2$	$(10a_1)^2$	-0.00198
DD1	$1b_2 1a_2$	$2a_2 4b_2$	-0.00289	DD2	$4a_1 3b_1$	$5b_1 8a_1$	-0.00193
DD2	$6a_1 2b_2$	$7a_1 3b_2$	-0.00280	DD1	$4a_1 2b_2$	$8a_1 3b_2$	-0.00177
DD1	$1a_2 2b_2$	$2a_2 4b_2$	-0.00276	DD2	$4a_1 6a_1$	$7a_1 8a_1$	-0.00171
DD2	$4b_1 6a_1$	$5b_1 10a_1$	-0.00271	DO2	$1b_2 2b_2$	$(3b_2)^2$	-0.00167
DO2	$3b_1 4b_1$	$(5b_1)^2$	-0.00269	DD2	$4a_1 3b_1$	$7a_1 5b_1$	-0.00164

Table 4. *Energy improvements to H₀₀ of OF₂ for the some selected configurations (partial exact diagonalization and approx. (3))*

Config. type	Config. number	Exact diagon.	Approx. (3)
DC	100	-0.076296	-0.09864
DD1	100	-0.112465	-0.11826
DC + DD1	100 + 100	-0.193475	-0.21690

Table 3 presents the more important configurations for the OF₂ molecule with their energy contributions calculated according to Eq. (4). They are principally of the DC and DD type; after the first few terms, the energy contributions decrease slowly: the 100th contribution is -0.000825 a. u., the 200th -0.000482 a. u. etc. The sum of the first 100 and 200 contribution is, respectively, about 44 and 57 per cent of the total.

As a further check for the reliability of the approximation formulas, Table 4 contains the values of the energy improvements obtained by exact diagonalization of either *i*) a secular matrix of order 201 (corresponding to the best 100 DC and DD1 configurations for the OF₂ molecule), or *ii*) two smaller matrices the first containing the 100 best DC configurations and the second the best 100 DD1 configurations.

Comparison with the results of Appr. (3) reported in Table 4 seem to confirm the similarities between exact and perturbative results, as already found in Table 2.

Finally we have completely repeated the OF_2 molecule calculations by means of a different numerical code written by another research group of our Laboratory⁴. The results of both calculations are perfectly coincident.

The situation is similar for the other two molecular systems.

4. C.I. Calculations with the Localized Orbitals

The lack of a sufficient number of leading terms worsens the rate of convergency of the C.I. process: it is practically impossible to pick up, with an "a priori" method, a reasonable number of configurations without significantly losing the gained energy.

In a geminal formulation this difficulty partially disappears, at least for that portion of the correlation energy which is accounted for by intrageminal terms.

In order to extract from our wavefunctions something resembling the ideal geminals, the canonical occupied orbitals have first been transformed by means of orthogonal transformations, into localized orbitals. Suitable combinations of the virtual orbitals have therefore been constructed in order to build up proper expansion functions.

The localized orbitals are of the Foster and Boys [9] type (exclusive orbitals): the orthogonal transformation maximizes the sum of the square of the distances between the centers of charge of each pair of orbitals. The exclusive orbitals have clear meaning from a chemical point of view: in fact, OF_2 presents the three 1s inner shells, a σ bond between O and each of the two F atoms, two lone pairs on oxygen and three lone pairs for each F; NO_2^- is characterized by three inner shells, a σ lone pair for N, two banana bonds between N and each O and two σ lone pairs for each O. Finally, CN^- exhibits three banana bonds, a lone pair for the C and one for the N atom, both collinear with the molecular axis.

Several kind of orthogonal transformations of the virtual orbitals have been investigated: one in particular brings to more effective improvements of the C.I. process.

Let us introduce, for each localized orbital λ_α , a matrix, \mathbf{K}^α (having as K_{rs}^α element the integral $\langle \lambda_\alpha \lambda_\alpha | \phi_r \phi_s \rangle$, ϕ_t being a virtual orbital) and the corresponding diagonalizing transformation. The latter is the wanted transformation matrix. Among the newly defined virtual orbitals we pick up a few, corresponding to the larger eigenvalues of \mathbf{K}^α . The process is repeated for each \mathbf{K}^α .

This sort of separation has the gratifying feature of bringing to zero the second order contribution of the DO 1 configurations. This fact may be readily understood by noting that each K_{rs}^α element corresponds to a H_{0i} integral (first row of the secular matrix) where in the considered ψ_i configuration two electrons have jumped from the λ_α orbital to the ϕ_r and ϕ_s orbitals. The diagonal elements K_{rr}^α correspond to the DC configurations (exchange integrals): the largest eigenvalues thus correspond to virtual configurations which are more effective in the C.I. process.

⁴ The two programs are completely different. The second one was written by C. Guidotti and O. Salvetti, whose collaboration is here acknowledged.

Table 5. Energy improvement to H_{00} with DC C.I. process performed on a localized basis

Molecule	config. n°	Exact energy	Approx. (3)	Approx. (4)
OF ₂	39	-0.13777	-0.14416	-0.14061
NO ₂ ⁻	36	-0.11970	-0.12424	-0.12172
CN ⁻	21	-0.09160	-0.09545	-0.09352

Table 6. Localized orbitals DC energy contributions calculated according to *Appr. (3)* for CN⁻

1s _C	1s _N	l _C	l _N	b _{CN} ^a
-0.01185	-0.01181	-0.00601	-0.00442	-0.01066
-0.00058	-0.00081	-0.00511	-0.00461	-0.00160
-0.00049	-0.00053	-0.00511	-0.00461	-0.00092
-0.00049	-0.00053	-0.00156	-0.00215	-0.00029
-0.00001	-0.00001	-0.00023	-0.00004	-0.00028
-0.00000	-0.00000	-0.00023	-0.00019	-0.00023
-0.00000	-0.00000	-0.00002	-0.00019	-0.00018
-0.00000	-0.00000	-0.00003	-0.00003	-0.00008
-0.00000	-0.00000	-0.00004	-0.00003	-0.00003
-0.00000	-0.00000	-0.00004	-0.00003	-0.00001
-0.01343 ^b	-0.01370 ^b	-0.01839 ^b	-0.01630 ^b	-0.01436 ^b

^a The other two b_{CN} bonds have energy contributions equal to those here displayed.

^b Total energy contribution for all the possible 19 configurations.

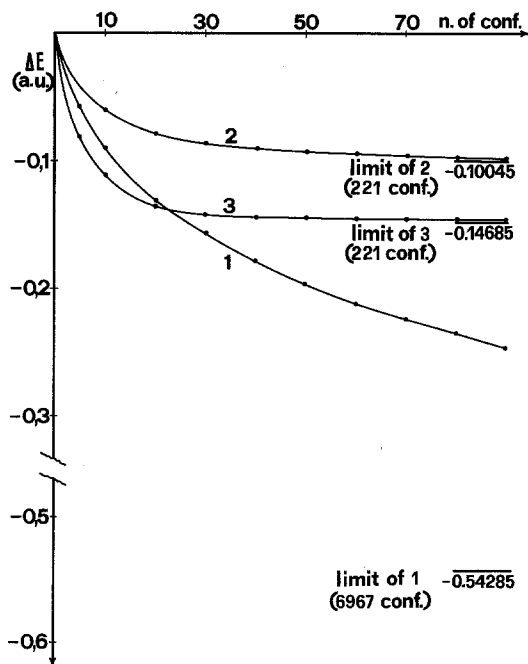


Fig. 1. Convergency behaviour of some C.I. processes for OF₂ with *Approx. (3)*. Curve 1 refers to the full calculation with canonical orbitals, curve 2 to the DC calculation with canonical orbitals and curve 3 to the DC calculation with localized orbitals

Only the energy contributions which may be interpreted as intrageminal contributions have, at present, been calculated. In other words, the only doubly excited configurations considered were those in which the two electrons jump from the same orbital λ_α (the index α running over all the exclusive orbitals) to two virtual orbitals ϕ_r^z and ϕ_s^z both pertaining to the same subset of virtual orbitals related to the same \mathbf{K}^α matrix⁵.

The results are collected in Table 5: the contribution of the DC configurations is noticeably greater than that obtained by the previous section calculations (see Table 2), although their number has been reduced.

The rejected configurations seem to be rather unrelevant: with all possible DC configurations the following energies are obtained: OF₂ -0.14009 a. u. (221), NO₂⁻ -0.12210 a. u. (216), CN⁻ -0.09911 a. u. (133). These energies were obtained by exact diagonalization; in parentheses the total number of possible DC configurations is reported.

Fig. 1 shows, for the OF₂ case, the various rates of convergency for the approximation 3. Curve 1 refers to the full canonical calculation, curve 2 to the DC canonical calculation, and curve 3 to the localized orbitals calculation. For each curve the configurations are ordered according to the magnitude of their energy contribution.

The plotting is relative to 90 configurations only; the curve limits are also reported.

Table 6 shows, for the CN⁻ localized orbitals, the actual contributions of the first ten excited configurations to the second order energy. They are ordered according to the corresponding eigenvalues of the \mathbf{K}^α 's, the first three terms being those retained in the calculations of Table 5: the terms not reported in the table are even smaller.

We must recall that these calculations refer only to the configurations extracted from the SCF basis set and therefore only a small part of the total correlation energy has been accounted for. Hence Table 5 results do not represent the complete sum of the intrageminal correlation energy. On the other hand, the first virtual localized orbitals seem well in agreement with the intuitive picture of the first terms of the geminals. It may be interesting to recall here Boys' suggestion [3] for the construction of a satisfactory set of expansion functions (oscillator orbitals).

For a given localized orbital λ_α , a system of primary functions is introduced:

$$\bar{\lambda}_{\alpha pqr} = X_c^p Y_c^q Z_c^r \lambda_\alpha$$

with coordinates X_c, Y_c, Z_c measured from the charge center of the orbital density $\lambda_\alpha^* \lambda_\alpha$, the axes being parallel to the principal axes of the orbital distribution tensor. These functions, suitably orthonormalized, are the proposed oscillator orbitals.

⁵ The virtual localized orbitals belonging to different λ_α 's are not orthogonal to each other. This is not inconvenient for they all are orthogonal to the fundamental ones and in our case all the configurations selected are orthogonal to each other. In order to extend the present work and to take into account the intergeminal correlation, a symmetric orthogonalization among the virtual localized orbitals was attempted, but this process leads, at the same time, to noticeable delocalization.

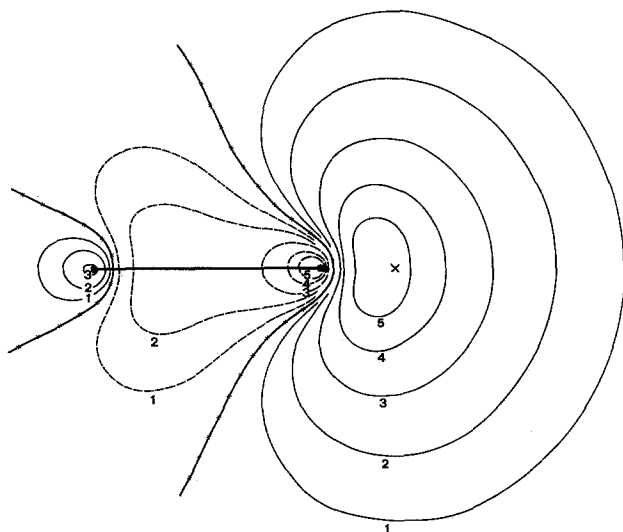


Fig. 2a

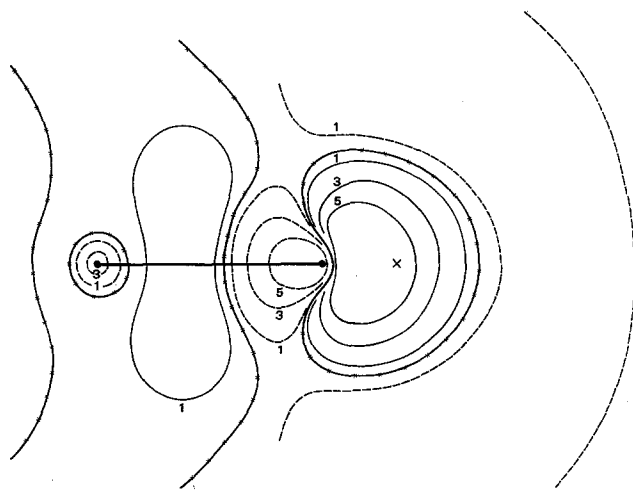


Fig. 2b

Fig. 2. Maps of: a) the N lone pair orbital of CN^- , b) its first virtual orbital, c) its second virtual orbital. The contour values are as follows: 1 = 0.045, 2 = 0.10, 3 = 0.20, 4 = 0.33, 5 = 0.45. The nodal surfaces are represented by a full line with crosses. The full lines refer to the positive portions of the orbital, the broken ones to the negative portion. The C atom (at left) and the N atom are marked by a dot

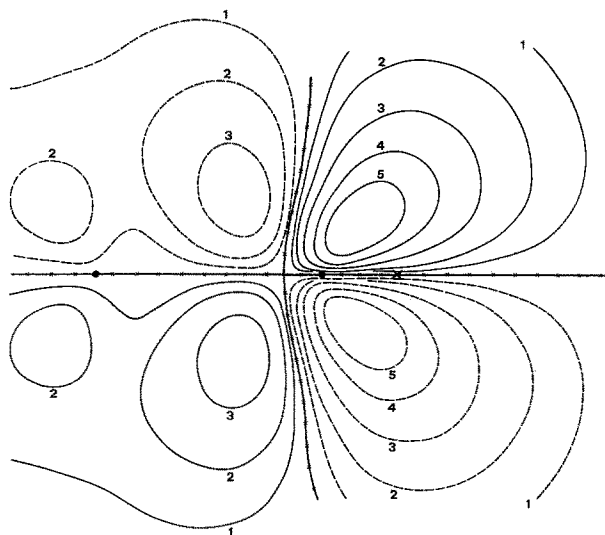


Fig. 2c

Our virtual localized orbitals selected for the C.I. calculation resemble the first Boys' primary functions $z_c\lambda_\alpha$, $x_c\lambda_\alpha$, $y_c\lambda_\alpha$, since the first (according to the corresponding \mathbf{K}^α eigenvalue) is polarized along the principal axis of the tensor and the other two are also polarized in the right order.

Fig. 2a, 2b, 2c, show, as an example, the contours of the nitrogen lone pair of CN^- , and its first and second virtual orbitals. The center of charge of the exclusive orbital lies on the molecular axis at 0.7250 a. u. (measured from the N nucleus). The first virtual orbital shows an additional nodal surface, which intercepts the molecular axis at 1.53 a.u. The second and the third orbitals (this last differing from the previous only by a $\pi/2$ rotation) have each a nodal plane containing the molecular axis.

Fig. 3a, 3b and 3c refer to one of the three equivalent bond orbitals in CN^- and to its first virtual orbitals. The charge center, in this case, is at $z = 1.2838$, $x = -0.2491$, $y = 0.5252$ (the coordinates are centered on N, z being the molecular axis). The maps are drawn for a plane containing the molecular axis and the charge center. The principal axis of the orbital distribution also lies on this plane. The first virtual orbital, as one may see in Fig. 3b, has a nodal surface, noticeably polarized, at a distance of 0.14 a. u. from the charge center. The nodal surface of the second virtual orbital is perpendicular to the figure plane and passes at 0.60 a. u. from the charge center.

For all the exclusive orbitals examined, their first excited orbitals show similar behaviour. On the other hand, the higher virtual orbitals spread all over the molecule. This is a serious drawback to the extension of the method.

For a more accurate description of the correlation energy, other expansion functions, not necessarily related to the virtual Hartree-Fock orbitals, are probably needed.

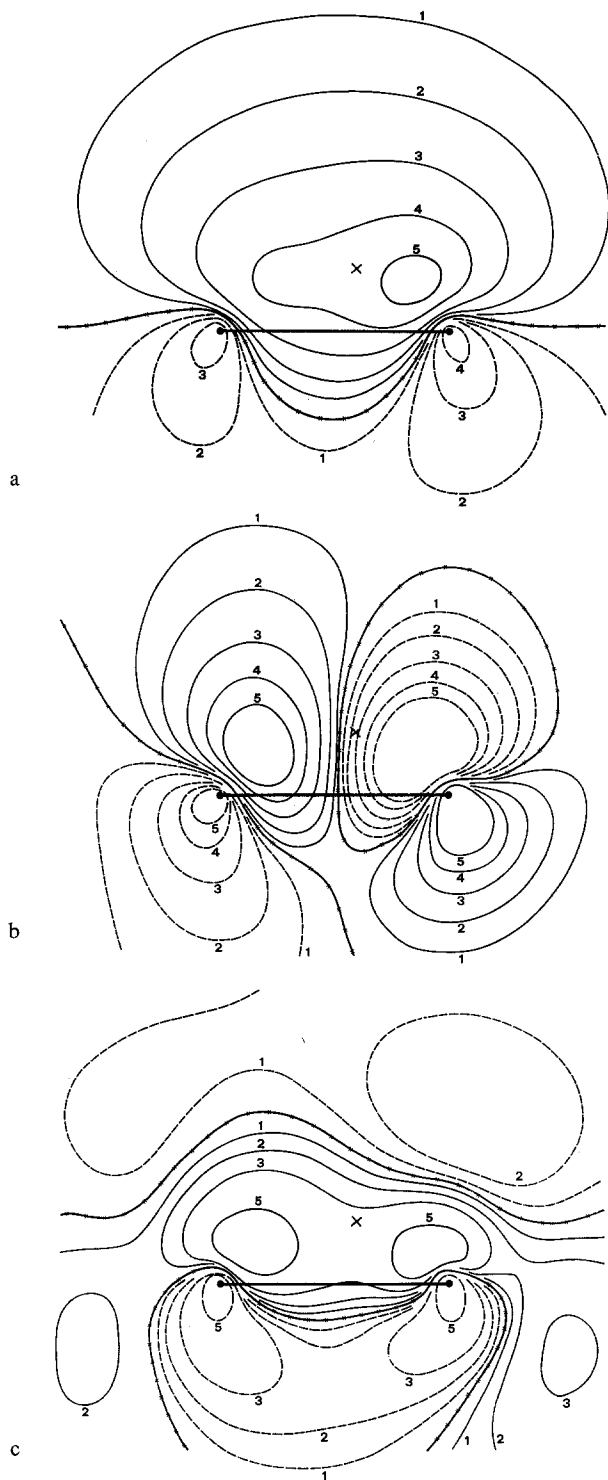


Fig. 3. Maps of: a) a CN^- bond orbital, b) its first virtual orbital, c) its second virtual orbital. The planes of the maps contain the molecular axis and the charge center of the exclusive orbital (marked by X). For other explanations see Fig. 2

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Dr. Eolo Scrocco
Laboratorio di Chimica Quantistica
ed Energetica Molecolare del C.N.R.
Via Risorgimento, 35
56100 Pisa, Italia