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A Simple Extension of the External Magnasco–Perico Localization Procedure to the Virtual MO-Space

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The external localization procedure of Magnasco and Perico is extended to the unoccupied molecular orbitals of the Fock-operator. The formal correspondence between bonding orbitals and localized antibonding MOs is demonstrated. Localized occupied and virtual one-electron functions are calculated within a semiempirical INDO-Hamiltonian and are analyzed; the externally localized occupied MOs are compared with energy localized orbitals computed by the Edmiston and Ruedenberg procedure. Various applications of the fully localized (occupied and virtual) MO set are discussed.

Key words: External localization procedure – Extension of the Magnasco–Perico algorithm to the virtual MO-space.

1. Introduction

Qualitative intuitive arguments about the chemical bond in molecules are based on concepts that make use of localized molecular properties, e.g. two- and three-center bonds, lone-pairs or atomic core states. On the other hand this localized description is not part of conventional quantum chemical theoretical approaches within the Hartree–Fock approximation; the calculated canonical molecular orbitals (CMO's) are delocalized over the whole molecule. The theoretical link between the descriptive localized orbitals and computational results within the Hartree–Fock model is given by localization procedures establishing an orthogonal matrix $\boldsymbol{M}$ that transforms the delocalized MOs ϕ_{CMO} into a set of localized one-electron functions (LMOs) ϕ_{LMO} [1]

$$\phi_{\text{LMO}} = \boldsymbol{M}\phi_{\text{CMO}}. \tag{1}$$

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One reason to study quantitatively localized orbitals by well defined computational methods is the hope to find molecular entities that are transferable from one molecule to the other [2].

The theoretical methods for the formulation of the orthogonal transformation-matrix $\boldsymbol{M}$ connecting CMO's and LMO's can be divided into two classes, internal procedures and external localization routes [3]. For the first approach the localized MO basis ϕ_{LMO} is an intrinsic function of the selected HF SCF MO-basis while in the latter case additional external conditions are necessary for the determination of $\boldsymbol{M}$. Various intrinsic localization procedures were developed by Edmiston and Ruedenberg [4], Foster and Boys [5] and by von Niessen [6]. External methods have been developed by Peters [7] and by Magnasco and Perico [8]. In all these methods only the occupied subspace of the SCF space, F_o, has been the main subject of the various localization routes while there was no real attempt to localize the unoccupied SCF subspace F_v. This limitation in the first line holds for the external localization routes with their degrees of freedom. Thus it seems, that there is no explicit localization procedure for virtual orbitals of the Fock-operator while approximate methods for their direct evaluation avoiding the path via CMO's are existing [9].

In the present paper a simple extension of the external Magnasco–Perico (MP) procedure is presented which allows the evaluation of localized virtual orbitals (σ^*, π^*), starting from the unoccupied MO set F_v of an ordinary Hartree–Fock calculation.

2. Outline of the External Localization Procedure

According to Magnasco and Perico [8] the occupied canonical orbitals are transformed via $\boldsymbol{M}$ to ϕ_{LMO} in a way, that the first i LMOs represent the localized bonds of a molecule, the next j orbitals define the inner shells and k one-electron functions establish the set of lone-pairs. In the case of a closed shell system with α- and β-spin orbitals $(i+j+k)$ is $N/2$ while N is the number of electrons. The different MO-types are localized by maximization of the localization function P in preselected regions of space between two atoms (bonds) or of an atomic side (inner shells and lone-pairs).

$$2P=\sum_{o=1}^{N/2} 2P_o \tag{2}$$

$$2P_o=2\sum_{\mu}\sum_{\nu} c^M_{\mu o}c^M_{\nu o}S_{\mu\nu}. \tag{3}$$

P_o symbolizes the local orbital population in the oth transformed (M) molecular orbital. μ and ν are atomic orbitals participating in the oth localized function and $S_{\mu\nu}$ is the overlap integral between the AOs μ and ν. ϕ_{CMO} is transformed via $\boldsymbol{M}$ by means of consecutive (2×2) rotations where the rotational-angle θ

between the MOs o and q is defined in (4):

$$\cot 2\theta = \frac{\sum_{\mu}\sum_{\nu} (c_{\mu o}c_{\nu o} - c_{\mu q}c_{\nu q})S_{\mu\nu} + \sum_{\mu}\sum_{\nu} (c_{\mu q}c_{\nu q} - c_{\mu o}c_{\nu o})S_{\mu\nu}}{\sum_{\mu}\sum_{\nu} (c_{\mu o}c_{\nu q} + c_{\mu q}c_{\nu o})S_{\mu\nu} + \sum_{\mu}\sum_{\nu} (c_{\mu o}c_{\nu q} + c_{\mu q}c_{\nu o})S_{\mu\nu}} \tag{4}$$

(4) clearly is the solution of the stationary condition (5)

$$\frac{dP}{d\theta} = 0. \tag{5}$$

Localization functions for bonds, inner shells and lone-pairs of the occupied HF subspace are defined in (6)–(8). The various formulas correspond to an orthonormal AO basis used in this study, corresponding expressions in a full overlap basis can be found in Ref. 8

bond between atom A and B

$$2P_o = 4 \sum_{\mu \in A} \sum_{\nu \in B} c^M_{\mu o} c^M_{\nu o} S_{\mu\nu} \qquad o = \epsilon\{i\} \tag{6}$$

inner shell at atom A

$$2P_o = 2 \sum_{\mu \in A} (c^M_{\mu o})^2 \qquad o = \epsilon\{i\} \tag{7}$$

lone pair at atom A

$$2P_o = 2 \sum_{\mu \in A} (c^M_{\mu o})^2 \qquad o = \epsilon\{k\}. \tag{8}$$

The definition of localization functions of bonds and inner shells obviously can be transferred from the F_o subspace to the unoccupied HF orbitals F_v. The virtual counterpart of the occupied bonds is given by the set of antibonding MOs of σ^* or π^* type with index l

localized anti-bonding orbital between atom A and B

$$2P_o = 4 \sum_{\mu \in A} \sum_{\nu \in B} |c^M_{\mu o} c^M_{\nu o}| S_{\mu\nu}, \qquad o = \epsilon\{l\}. \tag{9}$$

The full virtual subspace is defined by means of the localization function (2) where o runs through the complete set l. In the case of F_o o is given by $(i+j+k)$. In contrast to (6), for the LCAO-coefficients of Eq. (9) and in the stationary equation (4) the absolute value of the cross terms $c^M_{\mu o}c^M_{\nu o}$, $|c^M_{\mu o}c^M_{\nu o}|$, has to be used in the orthogonal transformation.

It is even possible within a minimal basis set to define an analogue of an occupied lone-pair, virtual lone-pairs localizing at a single atomic side. These functions e.g. can be used as electron MO within an electron-hole-pair defining a Frenkel state [10] virtual lone-pair at Atom A

$$2P_o = \sum_{\mu \in A} (c^M_{\mu o})^2, \qquad o = \epsilon\{n\}. \tag{10}$$

It must be pointed out that the computational results are subject to the chosen MO basis (semiempirical or *ab initio* minimal basis, extended basis with polarization functions). The applicability of the general method, however, is not restricted to any specific choice and is easily implemented into current MO programs.

3. Computational Aspects

In the following section our results of the externally localized MOs for both subspaces of the Fock-operator are presented. The external localization procedure was implemented into a recently developed semiempirical all-valence ZDO-Hamiltonian of the INDO-type [11]. Therefore we have selected localization functions between the centers A and B for both F_o and F_v which are an adequate expression for the ZDO basis. Various other choices for the definition of P_o in Eq. (6) and (9) can be found in the publications of Magnasco and Perico [8] (occupied subspace). The extension from (9) of F_v to other possible two-center (A and B) fragmentation schemes is straightforward.

In detail we have studied the localized occupied and unoccupied MOs of acetylene (I), ethylene (II), diacetylene (III), trans-butadiene (IV), benzene (V) and the pentadienyl anion (VI). For the systems I to V geometrical parameters were taken from experimental work [12]. For the anionic pentadienyl molecule VI the *cis-trans* conformation has been used and a CC separation of 1.40 Å and a CH distance of 1.10 Å was assumed [13].

4. Computational Results

In Table 1 the localized orbitals (CC-σ, CH-σ, CC-σ^* and CH-σ^*) of acetylene I as derived by the already described localization routine are collected. For comparison also the two occupied LMOs are listed obtained according to the energy localization criterion of Edmiston and Ruedenberg [4] where the orbital self-interaction terms (11) are maximized:

$$\sum_{i=1}^{N/2} \left[i(1)i(1) \frac{1}{r_{12}} i(2)i(2) \right] = \text{Maximum} \tag{11}$$

$i(1)$ symbolizes the ith orbital within the F_o basis. In agreement with an earlier *ab initio* investigation [6], the localized MOs according to both routes are close to each other. Occupied and unoccupied MOs are strongly localized between two atoms, impurities from other centers are less than 1%. The diagonal elements of the Lagrange multiplicators ε_{ij} in the LMO basis (14) are separated by about 6 eV with respect to CC-σ and CH-σ while only a gap of 0.8 eV is observed

Table 1. Localized occupied and unoccupied orbitals of acetylene according to the intrinsic localization criterion; the occupied energy localized orbitals according to Edmiston and Ruedenberg (ER) are added for comparison

		CC-σ	CH-σ	CC-σ^*	CH-σ^*	CC-σ^{ER}	CH-σ^{ER}
ε_i (eV)		−27.24	−21.32	4.24	5.03	−25.45	−22.21
C_1	2s	−0.5403	−0.5470	0.4859	−0.4076	−0.4885	−0.5979
	2$p\sigma$	−0.4553	0.5402	0.5047	0.4924	−0.5099	0.4924
C_2	2s	−0.5403	0.0748	−0.4859	−0.0319	−0.4885	0.0239
	2$p\sigma$	0.4553	−0.0588	0.5047	0.0164	0.5099	−0.0110
H_1	1s	−0.0272	−0.6322	−0.0959	0.7682	0.0368	−0.6318
H_2	1s	−0.0272	−0.0145	0.0959	−0.0064	0.0368	−0.0140

within the virtual MO-set

$$F = F_0 + F_v \tag{12}$$

CMO basis $$F\phi_{\mathrm{CMO}} = \sum_i \varepsilon_{ii}\phi_{\mathrm{CMO}} \tag{13}$$

LMO basis $$F\phi_{\mathrm{LMO}} = \sum_i \varepsilon_{ii}\phi_{\mathrm{LMO}} \tag{14}$$

For CC-σ a $2s/2p\sigma$ ratio of 1.19 is calculated but only a value of 0.96 for the unoccupied CC-σ^* MO indicating stronger s-participation in the occupied CC-σ function. The comparison between CH-σ and CH-σ^* displays a more

Table 2. Fock-matrix of acetylene in the localized MO-basis; occupied and unoccupied orbitals, all values in eV

occupied

	C_1C_2-σ	C_1H_1-σ	C_2H_2-σ'	C_1C_2-π	C_1C_2-π'
C_1C_2-σ	−27.24	−4.74	−4.74		
C_1H_1-σ		−21.32	0.27		
C_2H_2-σ'			−21.32		
C_1C_2-π				−12.86	
C_1C_2-π'					−12.86

unoccupied

	C_1C_2-π^*	C_1C_2-π'^*	C_1H_1-σ^*	C_2H_2-σ'^*	C_1C_2-σ^*
C_1C_2-π^*	1.05				
C_1C_2-π'^*		1.05			
C_1H_1-σ^*			5.03	0.69	2.59
C_2H_2-σ'^*				5.03	2.59
C_1C_2-σ^*					4.24

pronounced H 1s contribution in the latter MO (59%) while in CH-σ this value is reduced to 40%.

In Table 2 diagonal and off-diagonal elements of the Fock-matrix are collected. It is seen that the interaction element between CC-σ and CH-σ differs by a

Table 3. Localized occupied and unoccupied orbitals of ethylene according to the intrinsic localization criterion; the occupied energy localized orbitals according to Edmiston and Ruedenberg (ER) are added for comparison

		CC-σ	CH-σ	CC-σ^*	CH-σ^*	CC-σ^{ER}	CH-σ^{ER}
ε_i (eV)		−25.66	−19.91	4.93	5.43	−22.54	−20.69
C_1	2s	0.4356	−0.4273	0.4478	−0.3465	0.3632	−0.4604
	2p_x	0.5534	0.3380	0.5400	0.2884	0.6066	0.2899
	2p_y		−0.5137		−0.4848		−0.5137
C_2	2s	0.4356	0.0253	−0.4478	−0.0394	0.3632	−0.0079
	2p_x	−0.5534	−0.0303	0.5400	0.0525	−0.6066	0.0178
	2p_y		−0.0220		0.0233		−0.0220
H_1	1s	0.0450	−0.6603	−0.0626	0.7457	−0.0083	−0.6618
H_2	1s	0.0450	0.0253	−0.0626	0.0192	−0.0083	0.0238
H_3	1s	0.0450	0.0156	0.0626	0.0108	−0.0083	0.0140
H_4	1s	0.0450	−0.0173	0.0626	−0.0211	−0.0083	−0.0189

Table 4. Fock-matrix of ethylene in the localized MO-basis; occupied and unoccupied orbitals; all values in eV

occupied

	CC-σ	C_1H_1-σ	C_1H_2-σ	C_2H_3-σ	C_2H_4-σ	CC-π
CC-σ	−25.66	4.69	4.69	4.69	−4.69	
C_1H_1-σ		−19.91	−3.69	−1.51	−1.46	
C_1H_2-σ			−19.91	1.46	1.51	
C_2H_3-σ				−19.91	−3.69	
C_2H_4-σ					−19.91	
CC-π						−11.66

unoccupied

	CC-π^*	C_1H_1-σ^*	C_1H_2-σ^*	C_2H_3-σ^*	C_2H_4-σ^*	CC-σ^*
CC-π^*	0.16					
C_1H_1-σ^*		5.43	−0.28	0.10	0.48	1.48
C_1H_2-σ^*			5.43	−0.48	0.10	1.48
C_2H_3-σ^*				5.43	−0.27	1.48
C_2H_4-σ^*					5.43	−1.48
CC-σ^*						4.93

Table 5. Localized occupied and unoccupied orbitals of diacetylene according to the intrinsic localization criterion; the occupied energy localized orbitals according to Edmiston and Ruedenberg (ER) are added for comparison

	C≡C-σ	CC-σ	CH-σ	CC-π	C≡C-σ*	CC-σ*	CH-σ*	CC-π*	C≡C-σ^{ER}	CC-σ^{ER}	CH-σ^{ER}	CC-π^{ER}
ε_i (eV)	−27.45	−25.49	−21.19	−13.31	4.10	4.69	4.82	0.78	−29.39	−25.39	−22.70	−13.31
C_1 2*s*	−0.5596	0.0223	−0.5325		−0.4863	−0.0148	0.4071		−0.4714	0.0138	−0.6123	
2*p*σ	−0.4334	0.0019	0.5564		−0.5166	0.0191	−0.4849		−0.5135	0.0125	0.4832	
2*p*π				0.7143				−0.6917				0.7143
C_2 2*s*	−0.5199	−0.4950	0.1045		0.5007	−0.4705	0.0303		−0.5320	−0.4925	0.0322	
2*p*σ	0.4742	−0.5044	0.0789		−0.4847	−0.5268	−0.0209		0.4786	−0.5070	0.0034	
2*p*π				0.6917				0.7143				0.6917
C_3 2*s*	0.0152	−0.4950	−0.0191		−0.0043	0.4705	0.0077		0.0156	−0.4925	−0.0100	
2*p*σ	0.0019	0.5044	0.0286		0.0248	−0.5268	0.0027		0.0037	0.5070	0.0187	
2*p*π				0.0767				−0.0743				0.0767
C_4 2*s*	−0.0770	0.0223	−0.0013		0.0141	0.0148	0.0041		−0.0051	0.0138		
2*s*σ	0.0137	−0.0018	−0.0007		−0.0066	0.0191	−0.0056		0.0154	0.0125		
2*s*π				−0.0743				−0.0767				−0.0743
H_1 1*s*	−0.0561	0.0017	−0.6233		0.1009	−0.0212	−0.7731		0.0400	−0.0092	−0.6245	
H_2 1*s*	−0.0077	0.0017	0.0022		0.0039	0.0212	−0.0010		−0.0056	−0.0092	0.0012	

factor 2 comparing the occupied (−4.74 eV) and virtual (2.59 eV) MO space. On the other hand the coupling between both CH fragments is larger in the case of CH-σ^* as hybridization (e.g. $s/p\sigma$ mixing) in CH-σ^* enhances the LCAO-amplitude in the direction of the neighbouring CH-fragment.

The same effects are observed in the LMOs of the ethylene molecule II; in Table 3 the localized orbitals (CC-σ, CH-σ, CC-σ^* and CH-σ^*) are listed. Additionally the Edmiston-Ruedenberg (ER) orbitals are also shown. In Table 4 the elements of F are collected. The C and H contribution to the four different MOs follows the lines observed in I. Once again a stronger CC-σ/CH-σ coupling within the occupied subspace F_0 is found.

In Table 5 and 6 our INDO results observed in the diacetylene III, case are shown. A graphical representation of the one-electron functions in the CMO and LMO basis is displayed in Fig. 1.

In the LMO basis, ϕ_{LMO}, the sequence $\sigma(\mathrm{C{\equiv}C}) \to \sigma(\mathrm{C{-}C}) \to \sigma(\mathrm{C{-}H})$ is found for the occupied MOs of σ-type and $\sigma^*(\mathrm{C{\equiv}C}) \to \sigma^*(\mathrm{C{-}C}) \to \sigma^*(\mathrm{C{-}H})$ within the virtual set. The energy width within the occupied σ-set is calculated to be

Table 6. Fock-matrix of diacetylene in the localized MO-basis; occupied and unoccupied orbitals; all values in eV

occupied

	C≡C-σ 1	C≡C-σ 2	CC-σ	CH-σ 1	CH-σ 2	CC-π_x 1	CC-π_y 1	CC-π_x 2	CC-π_y 2
C≡C-σ 1	−27.45	−0.01	−4.72	−4.16	−0.37				
C≡C-σ 2		−27.45	−4.72	0.37	4.16				
CC-σ			−25.49	0.93	−0.93				
CH-σ 1				−21.29	<|0.01|				
CH-σ 2					−21.29				
CC-π_x 1						−13.31		−1.39	
CC-π_y 1							−13.31		−1.39
CC-π_x 2								−13.31	
CC-π_y 2									−13.31

unoccupied

	CC-π_x^* 1	CC-π_y^* 1	CC-π_x^* 2	CC-π_y^* 2	CH-σ^* 1	CH-σ^* 2	CC-σ^*	C≡C-σ^* 1	C≡C-σ^* 2
CC-π_1^* 1	0.78		−0.89						
CC-π_y^* 1		0.78		0.89					
CC-π_x^* 2			0.78						
CC-π_y^* 2				0.78					
CH-σ^* 1					4.82	0.05	0.63	2.63	0.17
CH-σ^* 2						4.82	−0.63	0.17	2.63
CC-σ^*							4.69	3.59	−3.59
C≡C-σ^* 1								4.10	−0.26
C≡C-σ^* 2									4.10

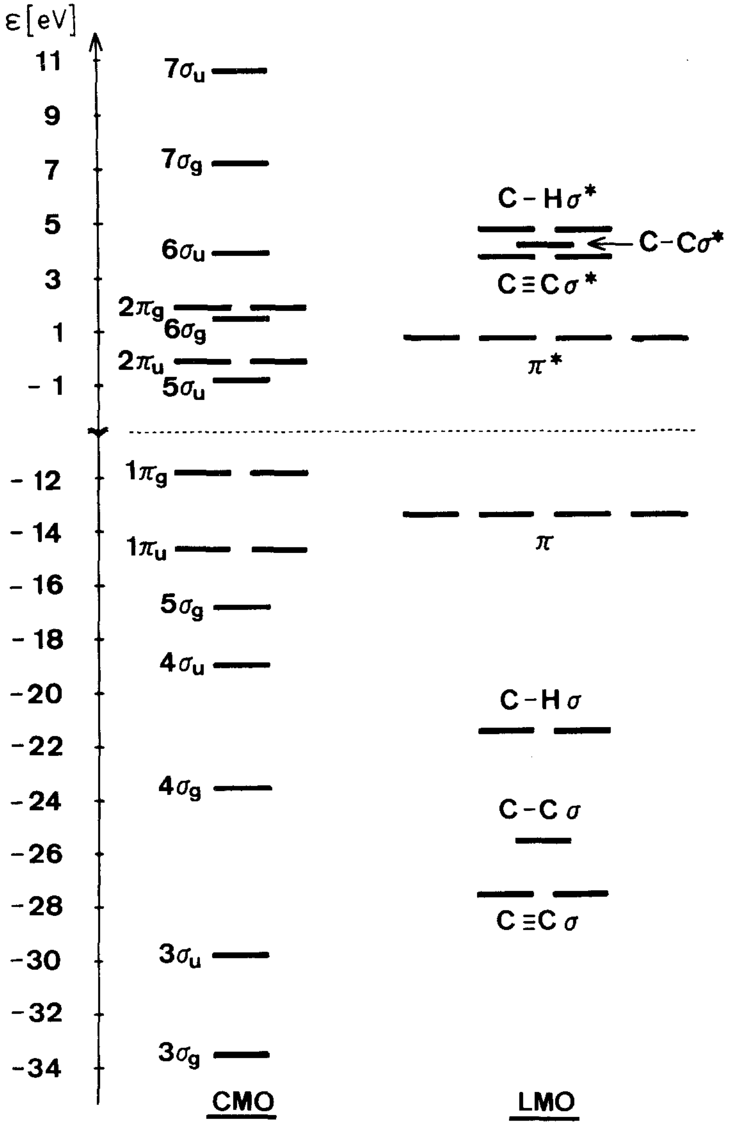

Fig. 1. Canonical molecular orbitals (CMO) and localized molecular orbitals (LMO) of diacetylene III according to an INDO-calculation followed by external localization

about 6.20 eV, the corresponding gap within the σ^* set is less than 1 eV. In the CMO basis both types of orbitals span an interval of about 17 eV and 11 eV respectively. It is seen in Table 5 that there are significant differences in the various one-electron functions if the contributions from the various AOs are analyzed in detail.

Inspection of Table 6 shows a stronger π/π coupling in F_o where on off-diagonal element of 1.39 eV is calculated; the corresponding F_v term is 0.89 eV. If the σ-type MOs are considered, it is seen that the coupling between neighbouring bonds is stronger for the occupied functions while long-range effects are of larger importance in the unoccupied one-electron MO set.

In the following examples, IV, V and VI, only the MOs of π-type have been transformed into localized orbitals. In Table 7 and 8 the localized orbitals (π and π^*) of transbutadiene IV as well as the matrix elements of the Fock-operator are collected. The corresponding values for benzene are shown in Table 9 and 10.

It is clearly seen that π and π^* MOs of the diene molecule are strongly localized between the formal double bonds (98.9%). The π and π^* functions of benzene, however, are only weekly localized between two carbon centers (82.9%). The

Table 7. Localized occupied and unoccupied π-orbitals of *trans*-butadiene

		CC-π	CC-π^*
ε_i (eV)		−11.80	0.14
C_1	$p\pi$	0.7155	−0.6905
C_2	$p\pi$	0.6905	0.7155
C_3	$p\pi$	0.0766	0.0739
C_4	$p\pi$	−0.0739	0.0766

3019

3020

Table 8. Fock-matrix of *trans*-butadiene in the localized basis; occupied and unoccupied orbitals; all values in eV

	occupied	
	C_1C_2-π	C_2C_3-π
C_1C_2-π	−11.80	1.21
C_2C_3-π		−11.80
	unoccupied	
	C_1C_2-π^*	C_2C_3-π^*
C_1C_2-π^*	0.14	−0.60
C_2C_3-π^*		0.14

3038

3039

Table 9. Localized occupied and unoccupied π-orbitals of benzene

		C_1C_2-π	C_1C_2-π^*
ε_i (eV)		−11.61	0.05
C_1	$p\pi$	0.6440	0.6440
C_2	$p\pi$	0.6440	−0.6440
C_3	$p\pi$	0.2357	0.2357
C_4	$p\pi$	−0.1725	0.1725
C_5	$p\pi$	−0.1725	−0.1725
C_6	$p\pi$	0.2357	−0.2357

Table 10. Fock-matrix of benzene in the localized basis; occupied and unoccupied orbitals; all values in eV

	occupied		
	C_1C_2-π	C_3C_4-π	C_5C_6-π
C_1C_2-π	−11.61	1.36	1.36
C_3C_4-π		−11.61	1.36
C_5C_6-π			−11.61
	unoccupied		
	C_1C_2-π^*	C_3C_4-π^*	C_5C_6-π^*
C_1C_2-π^*	0.05	0.67	0.67
C_3C_4-π^*		0.05	0.67
C_5C_6-π^*			0.05

same behaviour in the benzene case has been detected by Ruedenberg and coworkers [14]. The interaction constants for butadiene IV and benzene V in Table 8 and 10 show significant differences for the LMO coupling in the 0- and v-subspace. For the occupied π MOs in the localized basis interaction elements of 1.21 eV and 1.36 eV respectively for IV and V are calculated. Once again a remarkable reduction is found in the case of the π^* LMOs. The cross-term of the diene is 0.60 eV and the corresponding value of the benzene ring is 0.67 eV.

Table 11. Localized occupied and unoccupied π-orbitals of the pentadienyl anion; charge localized at the terminal C-atom C_5

		C_1C_2-π	C_3C_4-π	C_5-π_θ	C_1C_2-π^*	C_3C_4-π^*
ε_i (eV)		−5.67	−5.20	−4.27	5.46	6.11
C_1	$p\pi$	0.8022	0.2596	−0.1256	−0.5216	0.0364
C_2	$p\pi$	0.5877	−0.2286	0.1096	0.7531	−0.1524
C_3	$p\pi$	0.1033	−0.8129	0.2363	−0.2716	0.4460
C_4	$p\pi$	−0.0213	−0.4655	−0.4388	−0.2103	−0.7390
C_5	$p\pi$	−0.0031	−0.0535	−0.8507	0.2071	0.4801

Table 12. Localized occupied and unoccupied π-orbitals of the pentadienyl anion; charge localized at the central C-atom C_3

		C_1C_2-π	C_4C_5-π	C_3-π_θ	C_1C_2-π^*	C_4C_5-π^*
ε_i (eV)		−5.29	−5.29	−4.56	5.78	5.78
C_1	$p\pi$	0.8305	0.0328	−0.1894	0.5154	−0.0878
C_2	$p\pi$	0.5539	0.0493	0.3170	−0.7677	0.0298
C_3	$p\pi$	0.0043	−0.0043	0.8528	0.3692	0.3692
C_4	$p\pi$	−0.0494	−0.5539	0.3170	0.0298	−0.7677
C_5	$p\pi$	0.0328	−0.8305	−0.1894	−0.0878	0.5154

In Table 11–14 the localized orbitals of the pentadienyl anion VI together with the elements of the Fock-matrix in the LMO basis are displayed. Two different localization types defined by means of external localization conditions were applied. The pentadienyl anion was treated as diene with the negative charge at the terminal C-atom C_5 (*A*) and as π-system where two double bonds are separated by a localized hole-state C_3 (*B*). Both formulations of course correspond to different *VB* structures.

A B

The two localized π and π^* orbitals are defined by means of the localization functions (6) and (9), the localized hole-state at C_5 and C_3 is defined via the condition (8). In the case of the C_5H_7 cation the fragmentation scheme would lead to two occupied π orbitals, two π^* functions and to a virtual lone-pair alternatively localized at C_5 or C_3. With any intrinsic localization procedure it is not possible to control the route of the transformation into one of the possible choices (*A* or *B*).

A graphical representation of the canonical MOs and the two different LMOs (*A* and *B*) is given in Fig. 2.

The localized π-orbitals within the *A* representation (Table 11) indicate that C_1C_2-π is centered at both carbon atoms with a probability of 98.9% while the C_3C_4-π localization is reduced to 87.7%. The corresponding values for the two localized π^* functions are 83.9% and 74.5%. Thus they are less concentrated

Table 13. Fock-matrix of the pentadienyl anion in the localized basis; occupied and unoccupied orbitals; charge localized at the terminal C-atom C_5; all values in eV

occupied

	C_1C_2-π	C_3C_4-π	C_5-$\pi_\ominus$
C_1C_2-π	−5.67	1.56	−0.19
C_3C_4-π		−5.20	−1.74
C_5-$\pi_\ominus$			−4.27

unoccupied

	C_1C_2-π^*	C_3C_4-π^*
C_1C_2-π^*	5.46	−0.62
C_3C_4-π^*		6.11

Table 14. Fock-matrix of the pentadienyl anion in the localized basis; occupied and unoccupied orbitals; charge localized at the central C-atom C_3; all values in eV

occupied

	C_1C_2-π	C_4C_5-π	C_3-$\pi_\ominus$
C_1C_2-π	−5.29	0.06	1.71
C_4C_5-π		−5.29	1.71
C_3-$\pi_\ominus$			−4.56

unoccupied

	C_1C_2-π^*	C_4C_5-π^*
C_1C_2-π^*	5.78	0.70
C_4C_5-π^*		5.78

between two centers. C_5-$\pi_\ominus$ has 72.4% C_5-character. In the *B* representation both π MOs are strongly localized at two adjacent carbon centers (99.7%), the $\pi_\ominus$ localization at C_3 corresponds to *A*. Once again the π^* functions show stronger extension (85.5% localization between the CC-bond).

These differences of the localization properties of π, π^* and $\pi_\ominus$ lead to differences in the interaction elements of the Fock-matrix (Table 13 and 14). The π/π coupling term between the double bonds in *A* is 1.56 eV, the interaction constant with $\pi_\ominus$ is 1.74 and 0.19 eV. Within the π^* set an interaction constant of 0.62 eV is found. The direct interaction between the hole-state at C_3 and the terminal double bonds in *B* is calculated to be 1.71 eV, the coupling between both localized π-orbitals leads to an off-diagonal element of 0.06 eV. Once again this value is raised in the F_v subspace where the separated C_1C_2-π^* and C_4C_5-π^* orbitals show an interaction element of 0.70 eV, a value that exceeds the neighbour coupling in *A* (0.62 eV).

5. Future applications

We have presented an extension of the external Magnasco–Perico localization procedure to the virtual subspace F_v of the Fock-operator. Thus not only bonds, inner shells and lone-pairs within F_o can be transformed into localized orbitals, but also localized antibonding MOs and unoccupied lone-pairs can be derived from the virtual set of the CMOs. For F_o $\binom{N/2}{2}$ two-dimensional (2 × 2) rotations are necessary, for F_v $\binom{(M-N)/2}{2}$ transformation steps have to be performed up to convergence.

The combined localization of F_o and F_v allows various applications in the field of quantum chemistry.

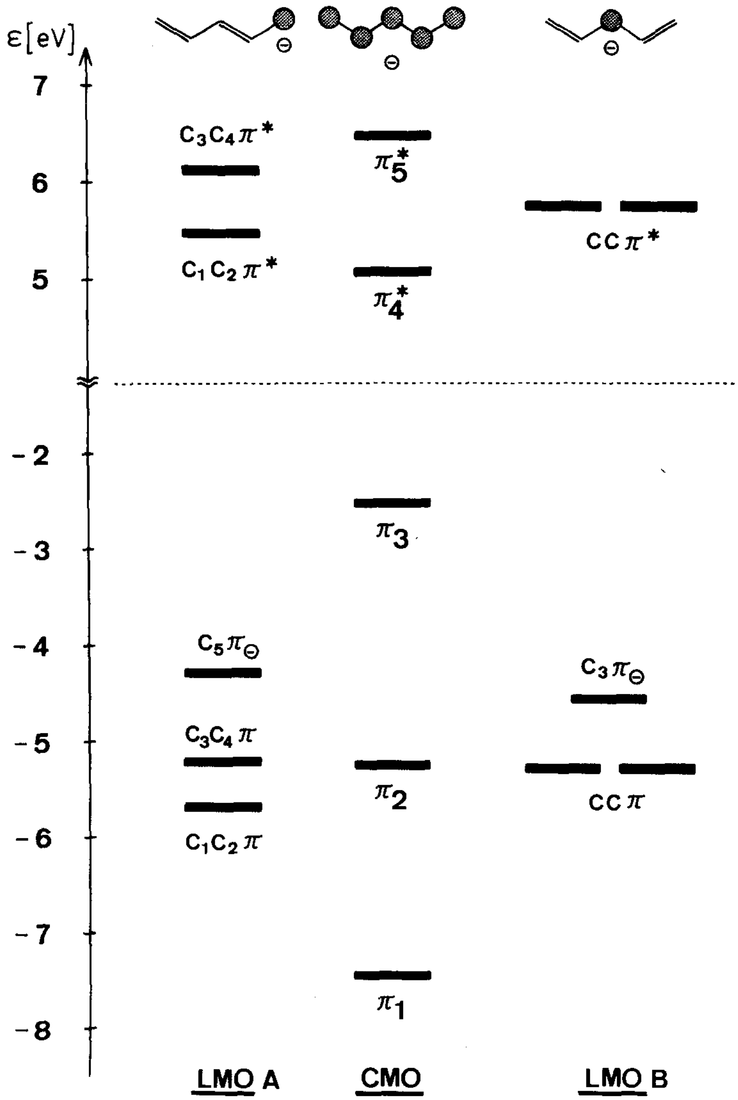

Fig. 2. Canonical molecular π orbitals (CMO) and two different types of localized molecular orbitals (LMO) *A* and *B* for the pentadienyl anion VI according to an INDO-calculation followed by external localization

(a) Within the *ab initio* framework F_v in the LMO basis ϕ_{LMO} can be used for the evaluation of transferable increments for MO procedures like SAMO (simulated *ab initio* molecular orbital method) [2].

(b) If semiempirical LCAO-versions are considered, the extension of a localization route to F_v can be useful for the design of an effective Hamilton operator beyond the occupied MO-space. Various theoretical approaches to this problem were performed by Iwata and Freed [15], Westhaus and coworkers [16] and very recently by Brandow [17].

(c) Moving from discrete molecular species to infinite polymers, F_o and F_v allow a linearcombination of localized orbitals to Bloch functions in the k-space. For the valence bands (F_o) this procedure was developed some time ago [9]. The extension to the conduction bands of an infinite system (F_v) allows the construction of the complete set of crystal orbitals at low computational expense for even complicated polymer structures. The dependence of F_o and F_v on the wave number k is given in (15) and (16) by the conventional trigonometric series. $(2L+1)$ is the total number of interacting cells and a symbolizes the cell parameter

$$F_o(k) = \sum_{j=-L}^{+L} F_0 \exp(ijka) \tag{15}$$

$$F_v(k) = \sum_{j=-L}^{+L} F_v \exp(ijka). \tag{16}$$

(d) Going beyond the one-determinantal HF-ansatz by means of configuration interaction (CI), the use of localized orbitals allows a CI expansion whose convergence properties are superiour to the ordinary CMO expansion [19]. This has been shown in various PCILO studies [20].

(e) Through-space and through-bond interaction has been studied quantitatively for the molecular ground-state by various localization, delocalization and decoupling procedures of molecular fragments [21]. With the already described method also an extension to the two interaction types in the excited state is possible. In the foregoing section the significant differences of the coupling strengths for the F_o and F_v subspace have been demonstrated. Obviously it must be expected that through-bond and through-space interaction in the excited state remarkably differs from the corresponding ground state coupling.

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