

Internal and external eigenvalue problems of Hermitian operators and their use in electronic structure theory

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Received: 22 October 2007 / Accepted: 23 November 2007 / Published online: 20 February 2008
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Abstract Within the fragment resolution of molecular systems the conceptual and interpretative advantages of using the separate eigenvalue problems for the *internal* and *external* part of the Hermitian matrix representing a physical quantity in quantum mechanics are examined. By definition, these two parts accordingly combine only the *diagonal* and *off-diagonal* subsystem-resolved blocks of matrix elements. These two partial eigenvalue problems bring about the matrix internal or external decouplings, respectively, which have recently been used in several interpretations of the molecular electronic structure. A character and structure of the external eigensolutions is examined in some detail and their recent applications in the Charge Sensitivity Analysis—to extract the most important electron-transfer effects between constituent atoms of model chemisorption systems, and in the Molecular-Orbital theory—to precisely identify the inter-orbital flows of electrons, are summarized and commented upon. The grouping relation, for combining the external/internal eigensolutions into those for the whole matrix, is derived in the context of the complementary “rotations” of the basis set vectors.

Keywords Charge sensitivity analysis · Collective charge displacements · Complementary transformations · Eigenvalue problems · Hardness decoupling schemes · Internal/external partition of operators · Eigenvectors for chemical valence · Intra- and inter-system channels · Normal modes · Partial eigenvalue problems · Partitioning technique

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1 Introduction

In what follows the symbol \mathbf{P} denotes a square or rectangular matrix, \mathbf{P} stands for a row vector, and P represents a scalar quantity.

Consider the finite, N -dimensional matrix representation $\mathbf{H} = \langle \chi | \hat{H} | \chi \rangle$ of the physical quantity H corresponding to the quantum-mechanical (Hermitian) operator \hat{H} , defined by the orthonormal basis vectors $|\chi\rangle = \{|1\rangle, \dots, |N\rangle\}$ in the molecular Hilbert space. In several computational and/or interpretative applications of the quantum theory one partitions this set into, two or several complementary subsets, say, $|\chi\rangle = |\chi^A, \chi^B\rangle = \{|\chi^X\rangle\}$, of dimensions A and B , respectively, $N = A + B$. For example, these subspaces may represent the atomic orbitals (AO) originating from atoms $X=(A, B)$ of a diatomic molecule $M = A - B$, or they constitute some arbitrary basis functions of the complementary fragments of a larger molecular system. This division of the representation basis set uniquely identifies the associated blocks of $\mathbf{H} = \{\mathbf{H}^{X,Y} = \langle \chi^X | \hat{H} | \chi^Y \rangle\}$. Such a partition, be it in a different *Configuration Interaction* (CI) scenario, is also invoked in the context of Löwdin's *partitioning technique* [1] for solving the eigenvalue equation of the system Hamiltonian, originating from the variation of the Rayleigh-Ritz functional for the expectation value of the system energy expressed in terms of the CI coefficients, when the two subsets of electronic configurations determine the complementary components of the system wave-function.

Another subject, in which one encounters such a partition, involves alternative decoupling schemes of the atomically resolved hardness tensor [2,3] of an N -atomic reactive system consisting of reactants A and B , $\eta = \{\eta^{X,Y} = \{\eta_{x,y}, x \in X, y \in Y\}\}$, $(X, Y) = (A, B)$, used in a search for the most compact representation of the *Charge-Transfer* (CT) phenomena in the externally open or closed molecular systems [2–6]. The diagonalization of η , determining its principal-axes representation, amounts to the matrix total decoupling and leads to the independent (collective) channels for electron displacements called the *Populational Normal Modes* (PNM) [2–6]. The molecular fragment resolution naturally divides the atomic modes into groups corresponding to constituent atoms of each subsystem. Therefore, the molecular hardness matrix can be partitioned into its *internal* (i) and *external* (e) parts, which respectively combine the intra-fragment (diagonal) and inter-fragment (off-diagonal) blocks of the hardness matrix elements between the system *Atoms-in-Molecules* (AIM):

$$\eta = \eta^i + \eta^e, \quad \eta^i = \{\eta^{X,X} \delta_{X,Y}\}, \quad \eta^e = \{\eta^{X,Y} (1 - \delta_{X,Y})\}. \quad (1)$$

The inter-fragment decoupled, internal part η^i of η can be viewed as representing the “unperturbed” (zeroth-order) “*promolecular*” system $M^0 = (A|B)$, consisting of the separate molecular fragments (subsets of bonded atoms), before formation of the inter-fragment chemical bonds in M , $\eta^i \equiv \eta^0$. It can be considered as the reference for the displacement aspect of the hardness matrix of the “perturbed” *molecular* system: $\eta = \eta^i + \eta^e \equiv \eta^0 + \Delta\eta$.

The so called *Internal Normal Modes* (INM) [2,3], the eigensolutions of η^i , then constitute the decoupled channels for the charge redistribution in the separate fragments of the *promolecule*. The *Inter-Subsystem Modes* (ISM), in the chemical reactivity

applications [2,3] also called the *Inter-Reactant Modes* (IRM), represent the eigensolutions of η^e . These externally decoupled channels have been found to generate an attractive framework for the compact description of the charge flows accompanying the formation of chemical bond(s) between A and B [2,3].

These two partial eigenvalue problems thus focus on the complementary aspects of the charge displacement in a transition from the promolecule to molecule: the internal (promolecular) modes characterize the independent channels of the charge polarization inside each of the mutually uncoupled (separate, non-bonded) fragments of the promolecule, while the external problem describes the CT-processes relative to this initial reference state. In other words, the external (interaction) channels focus solely on the inter-fragment bonding, i.e., the *displacement* aspect of the molecular electronic structure, while the internal channels deal with the intra-fragment bonds, already present in the promolecule, and as such they only characterize the *initial*-stage of the bond-formation process.

One should also mention at this point the partial transformations giving rise to the internal and external decouplings of the whole hardness tensor [2–5], rather than of its internal and external parts, which together amount to its total decoupling:

$$\mathbf{C}^\dagger \boldsymbol{\eta} \mathbf{C} = \mathbf{c}(\text{diagonal}) = \{\mathbf{c}^X \delta_{X,Y}\}, \quad \mathbf{C}^\dagger \mathbf{C} = \mathbf{I}. \quad (2)$$

Clearly, the internal decoupling transformation of $\boldsymbol{\eta}$, which leads to the diagonalization of only the *intra*-fragment blocks of $\boldsymbol{\eta}$, must be identical with that diagonalizing $\boldsymbol{\eta}^i$. By definition, the external decoupling of the whole hardness tensor leads to the vanishing off diagonal (coupling) blocks in the transformed tensor. However, since this requirement does not specify the transformation uniquely, the additional *Maximum Overlap Criterion* (MOC) has been used to generate the *localized* externally decoupled modes in this scheme [2,3].

Yet another example of the complementary internal/external perspectives on the charge reorganization in molecules involves the recently proposed Natural Orbitals for Chemical Valence (NOCV) [7,8], which have been successfully applied to interpret the metal–ligand bonds of coordination chemistry. They represent the eigenfunctions of the chemical-valence operator [9], $\hat{\mathbf{V}} = \hat{\mathbf{P}} - \hat{\mathbf{P}}^0$, defined by the difference between the molecular ($\hat{\mathbf{P}}$) and promolecular ($\hat{\mathbf{P}}^0$) projections on the respective occupied orbitals, with the occupied AO/MO of the separate fragments now determining the relevant “promolecular” reference. These projection operators respectively identify the occupied subspaces of the Molecular (Spin) Orbitals (MO) of the system as a whole, and of the AO/MO of the separate fragments of the promolecule. Their AO-representations in the LCAO MO theory thus define the associated *Charge-and-Bond-Order* (CBO) matrices $\mathbf{P} = n\langle \chi | \hat{\mathbf{P}} | \chi \rangle$ and $\mathbf{P}^0 = n\langle \chi | \hat{\mathbf{P}}^0 | \chi \rangle$, respectively, where n stands for the overall number of electrons in the isoelectronic molecular and promolecular systems. Hence the overall displacement of \mathbf{P} due to formation of the inter-fragment bonds: $\Delta \mathbf{P} = \mathbf{P} - \mathbf{P}^0 = n\langle \chi | \hat{\mathbf{V}} | \chi \rangle$. The subsets of basis functions originating from the separate fragments A and B, $|\chi\rangle = |\chi^A, \chi^B\rangle$, then partition these matrices into the corresponding subsystem-resolved blocks: $\mathbf{P} = \{\mathbf{P}^{X,Y}\}$, $\mathbf{P}^0 = \{\mathbf{P}^{X,X} \delta_{X,Y}\} \equiv \mathbf{P}^i$, and $\Delta \mathbf{P} = \{\Delta \mathbf{P}^{X,Y}\} = \{\Delta \mathbf{P}^{X,Y} (1 - \delta_{X,Y}) = \mathbf{P}^{X,Y} (1 - \delta_{X,Y})\} \equiv \mathbf{P}^e$.

Therefore, the AO-representation of the chemical-valence operator is proportional to the external part of the CBO matrix, so that its eigensolutions (NOCV) represent the bond-order ISM. They have been shown to generate an attractive framework for describing the inter-orbital flows of electrons, which accompany the formation of chemical bonds between A and B, capable of the precise separation of the *forward*- and *back*-donations in the coordination bonds [7, 8].

It is the main purpose of the present paper to clarify the relations between solutions of the alternative internal and external eigenvalue problems, which can be formulated in the context of partitioning the representation basis set, and to elucidate their relative merits in practical applications to interpreting the chemical bonds and related classical issues in the theory of molecular electronic-structure and reactivity.

2 Eigenvalue problems

Consider the N -dimensional representation of the quantum-mechanical (Hermitian) operator \hat{H} attributed to the physical quantity H , $\mathbf{H} = \langle \chi | \hat{H} | \chi \rangle = \{H_{i,j} = \langle i | \hat{H} | j \rangle\}$, e.g., the Hamiltonian operator $\hat{H}(n)$ of an n -electron system corresponding to the energy E . To simplify the following analysis we assume the ortho-normal metric of the basis set $|\chi\rangle = \{|i\rangle\}$, $\langle i | j \rangle = \delta_{i,j}$, e.g., that characterizing the orthogonalized AO, the MO configurations in the CI expansion of the system wave-function, or the underlying atomic modes of the *Charge Sensitivity Analysis* (CSA) [2–6], in terms of which various hardness decoupling schemes are formulated.

The overall diagonalization problem $\mathbf{C}^\dagger \mathbf{H} \mathbf{C} = \mathbf{E}(\text{diagonal}) = \{E_\alpha \delta_{\alpha,\beta}\}$, $\mathbf{C}^\dagger \mathbf{C} = \mathbf{I}$, where the columns of

$$\mathbf{C} = \left\{ \mathbf{C}_\alpha^\text{T} = \langle \chi | \alpha \rangle = \begin{bmatrix} \langle \chi^A | \alpha \rangle = \mathbf{C}_\alpha^{A,\text{T}} \\ \langle \chi^B | \alpha \rangle = \mathbf{C}_\alpha^{B,\text{T}} \end{bmatrix} \right\} \quad (3)$$

group the basis set projections for α th eigensolution corresponding to E_α , gives the following eigenvalue equation for this specific solution, written in the block-matrix form:

$$\begin{bmatrix} \mathbf{H}^{A,A} & \mathbf{H}^{A,B} \\ \mathbf{H}^{B,A} & \mathbf{H}^{B,B} \end{bmatrix} \begin{bmatrix} \mathbf{C}_\alpha^{A,\text{T}} \\ \mathbf{C}_\alpha^{B,\text{T}} \end{bmatrix} = E_\alpha \begin{bmatrix} \mathbf{C}_\alpha^{A,\text{T}} \\ \mathbf{C}_\alpha^{B,\text{T}} \end{bmatrix} \quad \text{or} \\ \mathbf{H}^{A,A} \mathbf{C}_\alpha^{A,\text{T}} + \mathbf{H}^{A,B} \mathbf{C}_\alpha^{B,\text{T}} = E_\alpha \mathbf{C}_\alpha^{A,\text{T}}, \quad \mathbf{H}^{B,A} \mathbf{C}_\alpha^{A,\text{T}} + \mathbf{H}^{B,B} \mathbf{C}_\alpha^{B,\text{T}} = E_\alpha \mathbf{C}_\alpha^{B,\text{T}}. \quad (4)$$

It forms the basis of the Löwdin partitioning technique [1]. More specifically, by using one of these equations to express one component of the eigenvector in terms of the other, e.g.,

$$\mathbf{C}_\alpha^{B,\text{T}} = (E_\alpha \mathbf{I}^B - \mathbf{H}^{B,B})^{-1} \mathbf{H}^{B,A} \mathbf{C}_\alpha^{A,\text{T}}, \quad (5)$$

and substituting the result into the other Eq. 4 then gives the effective eigenvalue problem for the independent component:

$$[\mathbf{H}^{A,A} + \mathbf{H}^{A,B}(E_\alpha \mathbf{I}^B - \mathbf{H}^{B,B})^{-1} \mathbf{H}^{B,A}] \mathbf{C}_\alpha^{A,T} = E_\alpha \mathbf{C}_\alpha^{A,T}. \quad (6)$$

This technique has been designed to determine the eigensolutions of Eq. 4 and as such it is widely applied in contemporary quantum chemistry [10]. For the analytical purposes, however, the reverse procedure can be also applied, e.g., of using the known solutions of Eq. 4 to infer the properties of matrices [11].

This partitioning also provides a framework for discussing the solutions of the partial internal and external eigenvalue problems in the subsystem resolution [2, 3]:

$$\begin{aligned} \mathbf{O}^\dagger \mathbf{H}^i \mathbf{O} = \mathbf{h} &= \{h_m \delta_{m,n}\} = \{\mathbf{h}_X \delta_{X,Y}\}, \quad \mathbf{H}^i = \{\mathbf{H}^{X,X} \delta_{X,Y}\}, \\ \mathbf{O} &= \{\mathbf{O}^X \delta_{X,Y}\}, \quad \mathbf{O}^X = \left\{ \mathbf{O}_m^{X,T} = \langle \chi^X | m \rangle \right\}, \quad \mathbf{O}^\dagger \mathbf{O} = \mathbf{I}; \end{aligned} \quad (7)$$

$$\mathbf{U}^\dagger \mathbf{H}^e \mathbf{U} = \boldsymbol{\varepsilon} = \{\varepsilon_k \delta_{k,l}\}, \quad \mathbf{H}^e = \{\mathbf{H}^{X,Y} (1 - \delta_{X,Y})\}, \quad \mathbf{U} = \{\mathbf{U}_k^T\}, \quad \mathbf{U}^\dagger \mathbf{U} = \mathbf{I}. \quad (8)$$

The former determines the decoupled eigensolutions of the two diagonal blocks of \mathbf{H} ,

$$\mathbf{H}^{A,A} \mathbf{O}_m^{A,T} = h_m^A \mathbf{O}_m^{A,T}, \quad \mathbf{H}^{B,B} \mathbf{O}_n^{B,T} = h_n^B \mathbf{O}_n^{B,T}, \quad (9)$$

while the solutions of the latter satisfy the coupled equations:

$$\begin{aligned} \begin{bmatrix} \mathbf{0}^{A,A} & \mathbf{H}^{A,B} \\ \mathbf{H}^{B,A} & \mathbf{0}^{B,B} \end{bmatrix} \begin{bmatrix} \mathbf{U}_k^{A,T} \\ \mathbf{U}_k^{B,T} \end{bmatrix} &= \varepsilon_k \begin{bmatrix} \mathbf{U}_k^{A,T} \\ \mathbf{U}_k^{B,T} \end{bmatrix} \quad \text{or} \\ \mathbf{H}^{A,B} \mathbf{U}_k^{B,T} &= \varepsilon_k \mathbf{U}_k^{A,T}, \quad \mathbf{H}^{B,A} \mathbf{U}_k^{A,T} = \varepsilon_k \mathbf{U}_k^{B,T}. \end{aligned} \quad (10)$$

A straightforward elimination of one component in the two preceding equations,

$$\mathbf{U}_k^{A,T} = \varepsilon_k^{-1} \mathbf{H}^{A,B} \mathbf{U}_k^{B,T}, \quad \mathbf{U}_k^{B,T} = \varepsilon_k^{-1} \mathbf{H}^{B,A} \mathbf{U}_k^{A,T}, \quad (11)$$

then gives the following effective external eigenvalue problems for each subsystem:

$$\begin{aligned} \mathbf{H}^{A,B} \mathbf{H}^{B,A} \mathbf{U}_k^{A,T} &\equiv \mathbf{F}_A^{eff} \mathbf{U}_k^{A,T} = \varepsilon_k^2 \mathbf{U}_k^{A,T}, \\ \mathbf{H}^{B,A} \mathbf{H}^{A,B} \mathbf{U}_k^{B,T} &\equiv \mathbf{F}_B^{eff} \mathbf{U}_k^{B,T} = \varepsilon_k^2 \mathbf{U}_k^{B,T}. \end{aligned} \quad (12)$$

They determine the two components of k th eigenvector in

$$\mathbf{U} = \left\{ \mathbf{U}_k^T = \langle \chi | k \rangle = \begin{bmatrix} \langle \chi^A | k \rangle = \mathbf{U}_\alpha^{A,T} \\ \langle \chi^B | k \rangle = \mathbf{U}_k^{B,T} \end{bmatrix} \right\}, \quad (13)$$

with the symmetrical effective external operators of molecular fragments defined by the respective diagonal blocks of the squared external part of \mathbf{H} , $(\mathbf{H}^e)^2 : (\mathbf{F}_X^{eff})^T =$

$\mathbf{F}_X^{eff} = (\mathbf{H}^e)_{X,X}^2$, $X = A, B$. Multiplying from the left Eq. 10 by $\mathbf{H}^{B,A}$ and $\mathbf{H}^{A,B}$, respectively, also gives

$$\mathbf{F}_B^{eff} \mathbf{U}_k^{B,T} = \varepsilon_k \mathbf{H}^{B,A} \mathbf{U}_k^{A,T}, \quad \mathbf{F}_A^{eff} \mathbf{U}_k^{A,T} = \varepsilon_k \mathbf{H}^{A,B} \mathbf{U}_k^{B,T}, \quad (14)$$

and hence the alternative expressions for one component in terms of the other:

$$\mathbf{U}_k^{A,T} = \varepsilon_k (\mathbf{F}_A^{eff})^{-1} \mathbf{H}^{A,B} \mathbf{U}_k^{B,T}, \quad \mathbf{U}_k^{B,T} = \varepsilon_k (\mathbf{F}_B^{eff})^{-1} \mathbf{H}^{B,A} \mathbf{U}_k^{A,T}. \quad (15)$$

It follows from Eq. 12 that the two subsystem components ($\mathbf{U}_k^A, \mathbf{U}_k^B$) of the external mode \mathbf{U}_k are the eigenvectors of the effective fragment-operators \mathbf{F}_A^{eff} ($A \times A$) and \mathbf{F}_B^{eff} ($B \times B$), where for definiteness we assume $A \leq B$, which exhibit the same eigenvalue ε_k^2 . Together these operators define the block-diagonal (externally decoupled) effective operator for the system as a whole, $\mathbf{F}^{eff} = \{\mathbf{F}_{eff}^X \delta_{X,Y}\} = (\mathbf{H}^e)^2$, the eigenvalue equation of which reads:

$$\mathbf{F}^{eff} \mathbf{U}_k^T = (\mathbf{H}^e)^2 \mathbf{U}_k^T = \varepsilon_k^2 \mathbf{U}_k^T \quad \text{or} \quad \mathbf{U}^\dagger (\mathbf{H}^e)^2 \mathbf{U} = \varepsilon^2 = \{\varepsilon_k^2 \delta_{k,l}\}. \quad (16)$$

Therefore, the external modes \mathbf{U} can be determined via the diagonalization of the inter-subsystem decoupled operator $(\mathbf{H}^e)^2$, which amounts to the separate subsystem diagonalization (eigenvalue) problems of Eq. 12. In the delocalized modes [2,3], for which $\varepsilon_k^2 > 0$, the A eigenvectors $\{\mathbf{U}_k^A\}$ of \mathbf{F}_A^{eff} will combine with their B conjugates $\{\mathbf{U}_k^B\}$ among the eigenvectors of \mathbf{F}_B^{eff} , which exhibit the same eigenvalue ε_k^2 , whereas the remaining $B - A \geq 0$ eigenvectors of \mathbf{F}_B^{eff} will combine with the zero component in A, thus giving rise to the B-localized (l) channels $\mathbf{U}_l = (\mathbf{0}_l^A, \mathbf{U}_l^B)$, which are inactive in the displacement process behind the $\mathbf{H}^e = \Delta \mathbf{H} \equiv \mathbf{H} - \mathbf{H}^i$ displacement. It can be verified using Eq. 8 that the eigenvalues of such localized external modes identically vanish: $\varepsilon_l = \mathbf{U}_l^* \mathbf{H}^e \mathbf{U}_l^T = 0$. In the hardness-decoupling scenario of the reactive system A–B [2,3] the B-localized solutions can only internally polarize B, playing no part in the CT between the two reactants. Similarly, in the NOCV eigenvalue problem [7,8] for $\Delta \mathbf{P}$ such natural orbitals do not participate in the inter-fragment redistribution of electrons, which accompanies the bond-formation process. This general structure of \mathbf{U} is summarized in Fig. 1.

The pairs of the mutually orthogonal, \mathbf{F}^e -degenerate modes $(\mathbf{U}_k, \mathbf{U}_{-k})$, $k = 1, 2, \dots, A$, for the complementary eigenvalues $(\varepsilon_k > 0, -\varepsilon_k < 0)$ of \mathbf{H}^e , respectively,

$$\mathbf{H}^e \mathbf{U}_k^T = \varepsilon_k \mathbf{U}_k^T \quad \text{and} \quad \mathbf{H}^e \mathbf{U}_{-k}^T = -\varepsilon_k \mathbf{U}_{-k}^T \equiv \varepsilon_{-k} \mathbf{U}_{-k}^T, \quad (17)$$

are represented by the symmetric (“bonding”) and anti-symmetric (“anti-bonding”) combinations of the subsystem components \mathbf{U}_k^A and \mathbf{U}_k^B , which constitute the independent, mutually orthogonal eigensolutions of $\mathbf{F}^{eff} = (\mathbf{H}^e)^2$ corresponding to the same eigenvalue ε_k^2 :

Fig. 1 The block structure of the eigenvector matrix $\mathbf{U} = \langle \chi | \xi \rangle$ determining the external modes $|\xi\rangle = |\chi\rangle \mathbf{U} = (| -k \rangle, |k\rangle, |I\rangle)$, including the delocalized vectors $| -k \rangle$ and $|k\rangle$, determined by the complementary columns of expansion coefficients $(\mathbf{U}_{-k}^T, \mathbf{U}_k^T)$, $k = 1, 2, \dots, A$ for the negative and positive eigenvalues, respectively, which are active in the $M^0 \rightarrow M$ displacement, and the B-localized vectors $|I\rangle$, which remain inactive in this chemical change

	$ -k \rangle$	$ k\rangle$	$ I\rangle$	$N = A + B$
$\langle \chi^A $	$\mathbf{U}_{-k}^{A,T}$	$\mathbf{U}_k^{A,T}$	$\mathbf{U}_I^A = \{\mathbf{0}_I^{A,T}\} = \mathbf{0}^{A,B-A}$	
$\langle \chi^B $	$\mathbf{U}_{-k}^{B,T}$	$\mathbf{U}_k^{B,T}$	$\mathbf{U}_I^B = \{\mathbf{U}_I^{B,T}\}$	
	$\varepsilon_{-k} < 0$ $M^0 \rightarrow M$ Active	$\varepsilon_k > 0$ $M^0 \rightarrow M$ Active	$\varepsilon_I = 0$ $M^0 \rightarrow M$ Inactive	

$$\mathbf{U}_k = (\mathbf{U}_k^A, \mathbf{U}_k^B), \quad \mathbf{U}_{-k} = (\mathbf{U}_k^A, -\mathbf{U}_k^B) \equiv (\mathbf{U}_{-k}^A, \mathbf{U}_{-k}^B). \quad (18)$$

The ($M^0 \rightarrow M$)-active external modes (eigenvectors of \mathbf{H}^e) exhibit intermediate degrees of inter-fragment delocalization between the *localized* internal modes of both fragments [eigenvectors of \mathbf{H}^i (Eqs. 7 and 9)] and the *delocalized* molecular modes [eigenvectors of $\mathbf{H} = \mathbf{H}^i + \mathbf{H}^e$ (Eq. 4)]. For example, the IRM in illustrative chemisorption complexes have been found to be more localized, compared to PNM of the whole reactive system [2, 3]. Similarly, the NOCV exhibit a relative localized character compared to less polarized canonical MO [7, 8].

The interpretative advantage of the external modes of the Hermitian operators, however, lies in their applications to the interaction/coupling between a small subsystem and its much larger molecular environment B, when $B \gg A$. Then, only a small number of $2A$ external modes (see Fig. 1) is active in the promolecule \rightarrow molecule transition, with a large number of the remaining $N - 2A$ inactive (B-localized) modes describing the response of the environment to this chemical displacement. Therefore, the external eigenvectors give a much more compact description of this bond-formation process, compared to the eigenvectors of the whole matrix.

3 Ensemble average quantities and their partitioning

As already argued above, the external modes represent eigensolutions of the *displacement* operator $\mathbf{H}^e = \Delta \mathbf{H} = \mathbf{H} - \mathbf{H}^i$ (Eqs. 8 and 16), which describes a transition from the promolecular collection of non-bonded molecular fragments of \mathbf{H}^i to the molecular system of the mutually interacting (bonded, coupled) subsystems of \mathbf{H} . Let us now briefly examine the ensemble average value $\langle H \rangle = \text{Tr}(\mathbf{H}\mathbf{D})$ of H in the statistical mixture of states defined by the density operator expressed in terms of the eigenstates

$|\gamma\rangle = \{|\gamma\rangle\}$ of another operator $\hat{\Gamma}$, $\hat{\Gamma}|\gamma\rangle = \Gamma_\gamma|\gamma\rangle$,

$$\hat{D} = \sum_\gamma |\gamma\rangle p_\gamma \langle\gamma| \equiv |\gamma\rangle \mathbf{p}^\gamma \langle\gamma|, \quad \sum_\gamma p_\gamma = 1,$$

$$\mathbf{p}^\gamma = \langle\gamma|\hat{D}|\gamma\rangle = \{p_\gamma\delta_{\gamma,\mu}\} \equiv \mathbf{D}^\gamma, \quad \mathbf{D} = \langle\chi|\hat{D}|\chi\rangle. \tag{19}$$

Here the diagonal matrix \mathbf{p}^γ groups the ensemble state-probabilities, which define the $|\gamma\rangle$ -representation \mathbf{D}^γ of the density operator itself, and matrix \mathbf{D} stands for the $|\chi\rangle$ -representation of \hat{D} . Therefore, for $|\chi\rangle = |\gamma\rangle$ this ensemble average gives rise to the probability-weighted mean of the expectation values $\{H_\gamma = \langle\gamma|\hat{H}|\gamma\rangle\}$:

$$\langle H \rangle = \sum_\gamma p_\gamma H_\gamma. \tag{20}$$

For example, in the LCAO MO theory $|\chi\rangle$ denotes the AO basis set and $|\gamma\rangle$ stands for the canonical MO, $|\gamma\rangle = |\psi\rangle$, eigenvectors of the effective (one-electron) Fock operator \hat{F} represented by the Fock matrix $\mathbf{F} = \langle\chi|\hat{F}|\chi\rangle$, $\hat{F}|\psi_\gamma\rangle = e_\gamma|\psi_\gamma\rangle$, and the density operator is represented by the density matrix $\mathbf{D} = \langle\chi|\hat{D}|\chi\rangle = \langle\chi|\psi\rangle\mathbf{p}^\psi\langle\psi|\chi\rangle = \mathbf{P}/n$, where \mathbf{P} denotes the CBO matrix. Hence the ensemble-average orbital energy reads:

$$\langle e \rangle = \text{Tr}(\mathbf{FD}) = n^{-1}\text{Tr}(\mathbf{FP}) = \sum_\gamma e_\gamma p_\gamma \quad \text{or} \quad \langle F \rangle = \text{Tr}(\mathbf{FP}) = n\langle e \rangle,$$

$$p_\gamma = n_\gamma/n, \tag{21}$$

where $n = \sum_\gamma n_\gamma$ is the overall number of electrons, n_γ denotes the MO occupation number, and $\mathbf{p}^\psi = \{p_\gamma\delta_{\gamma,\mu}\}$.

The difference between this average quantity $\langle H \rangle = \text{Tr}(\mathbf{HD})$ in M, and the corresponding reference value in M^0 , $\langle H^0 \rangle = \text{Tr}(\mathbf{HD}^0)$, characterized by the density operator involving projections on the same states $|\gamma\rangle$ with promolecular probabilities $\mathbf{p}^{\gamma,0} = \{p_\gamma^0\delta_{\gamma,\mu}\}$,

$$\hat{D}^0 = \sum_\gamma |\gamma\rangle p_\gamma^0 \langle\gamma| \equiv |\gamma\rangle \mathbf{p}^{\gamma,0} \langle\gamma|, \quad \sum_\gamma p_\gamma^0 = 1, \quad \mathbf{p}^{\gamma,0} = \langle\gamma|\hat{D}^0|\gamma\rangle = \{p_\gamma^0\delta_{\gamma,\mu}\},$$

$$\mathbf{D}^0 = \langle\chi|\hat{D}^0|\chi\rangle, \tag{22}$$

then reads:

$$\Delta\langle H \rangle = \langle H \rangle - \langle H^0 \rangle = \text{Tr}(\mathbf{H}\Delta\mathbf{D}), \quad \Delta\mathbf{D} = \mathbf{D} - \mathbf{D}^0. \tag{23}$$

For example, in the illustrative case of the LCAO MO theory, when the density operator is represented by the promolecular density matrix $\mathbf{D}^0 = \langle\chi|\hat{D}^0|\chi\rangle = \langle\chi|\psi\rangle\mathbf{p}^{\psi,0}\langle\psi|\chi\rangle \equiv \mathbf{P}^0/n$, the average orbital energy in such a promolecular ensemble reads:

$$\langle e^0 \rangle = \text{Tr}(\mathbf{FD}^0) = n^{-1} \text{Tr}(\mathbf{FP}^0) = \sum_{\gamma} e_{\gamma} p_{\gamma}^0 \quad \text{or} \quad \langle F^0 \rangle = \text{Tr}(\mathbf{FP}^0),$$

$$p_{\gamma}^0 = n_{\gamma}^0/n, \quad (24)$$

where n_{γ}^0 is the MO occupation number in the promolecule. The molecular displacement in this average orbital energy, relative to such a reference state gives:

$$\begin{aligned} \Delta \langle e \rangle &= \langle e \rangle - \langle e^0 \rangle = \text{Tr}(\mathbf{F}\Delta\mathbf{D}) = n^{-1} \text{Tr}(\mathbf{F}\Delta\mathbf{P}) \\ &= \sum_{\gamma} e_{\gamma} \Delta p_{\gamma}^0, \quad \Delta p_{\gamma} = p_{\gamma} - p_{\gamma}^0, \quad \text{or} \\ \Delta \langle F \rangle &= \langle F \rangle - \langle F^0 \rangle = \text{Tr}(\mathbf{F}\Delta\mathbf{P}). \end{aligned} \quad (25)$$

When the many-electron states are mixed in the density operators of Eqs. 19 and 22, e.g., the electron configurations of the CI theory, the ensemble-average many-electron quantities are determined. For example, as we have already indicated in Eqs. 21, 24 and 25, by multiplying the average one-electron quantities $\langle e \rangle$, $\langle e^0 \rangle$ and $\langle \Delta e \rangle$ by the number of electrons n one determines the corresponding averages of the corresponding total orbital energies $\langle F \rangle$, $\langle F^0 \rangle$ and $\langle \Delta F \rangle$ of the whole many-electron system.

It should be stressed at this point, that the *promolecular ensemble* defined by the density operator of Eq. 22 assumes the mixture of the same states as those used in the *molecular ensemble*, e.g., the canonical MO's in the LCAO MO theory. Alternatively, the promolecular canonical MO, $|\gamma^0\rangle = |\psi^0\rangle$, different from their molecular counterparts $|\psi\rangle$ and exhibiting different occupations, can be used to define the promolecular ensemble of $\tilde{\mathbf{M}}^0 = (\mathbf{A}^0|\mathbf{B}^0)$:

$$\begin{aligned} \hat{\mathbf{D}}^0 &= \sum_{\gamma} |\gamma^0\rangle \lambda_{\gamma}^0 \langle \gamma^0| \equiv |\gamma^0\rangle \lambda^{\gamma,0} \langle \gamma^0|, \quad \sum_{\gamma} \lambda_{\gamma}^0 = 1, \\ \lambda^{\gamma,0} &= \langle \gamma^0 | \hat{\mathbf{D}}^0 | \gamma^0 \rangle = \{\lambda_{\gamma}^0 \delta_{\gamma,\mu}\}, \quad \tilde{\mathbf{D}}^0 = \langle \chi | \hat{\mathbf{D}}^0 | \chi \rangle. \end{aligned} \quad (26)$$

It should be also observed that in the LCAO MO theory the corresponding CBO matrix will not be diagonal in the molecular MO representation:

$$\begin{aligned} \tilde{\mathbf{D}}^{0,\psi} &= \langle \psi | \hat{\mathbf{D}}^0 | \psi \rangle = \langle \psi | \psi^0 \rangle \lambda^{\psi,0} \langle \psi^0 | \psi \rangle \equiv \tilde{\mathbf{P}}^{0,\psi} / n \\ &\neq \tilde{\mathbf{D}}^{0,\psi^0} \equiv \langle \psi^0 | \psi^0 \rangle \lambda^{\psi^0,0} \langle \psi^0 | \psi^0 \rangle = \tilde{\mathbf{P}}^{0,\psi^0} / n = \{\lambda_{\gamma}^0 \delta_{\gamma,\mu}\}. \end{aligned} \quad (27)$$

The corresponding displacement in the average orbital energy for this definition of the promolecule then reads:

$$\tilde{\Delta} \langle F \rangle = \langle F \rangle - \langle \tilde{F}^0 \rangle = n^{-1} \text{Tr}(\mathbf{FP} - \mathbf{F}^0 \tilde{\mathbf{P}}^0) \approx n^{-1} \text{Tr}(\mathbf{F}\Delta\mathbf{P}), \quad (28)$$

where the promolecular Fock operator matrix $\mathbf{F}^0 = \langle \chi | \hat{F}^0 | \chi \rangle$, with $\hat{F}^0 | \psi_\gamma^0 \rangle = e_\gamma^0 | \psi_\gamma^0 \rangle$. The two reference states $\mathbf{M}^0 = (A|B)$ and $\tilde{\mathbf{M}}^0 = (A^0|B^0)$ differ by the intra-fragment molecular promotion, already present in \mathbf{M}^0 and missing in $\tilde{\mathbf{M}}^0$, where each fragment is in its separate ground-state configuration. However, since $\mathbf{F} \cong \mathbf{F}^0$ and $\langle \chi | \hat{D}^0 | \chi \rangle = n^{-1} \tilde{\mathbf{P}}^0 = \{n^{-1} \tilde{\mathbf{P}}^{0;X,X} \delta_{X,Y} = n^{-1} \tilde{\mathbf{P}}^{0,i} \cong n^{-1} \mathbf{P}^i$ one arrives at the approximate equality of Eq. 28, in which $\Delta \mathbf{P} = \mathbf{P}^e = \mathbf{P} - \mathbf{P}^i$.

The eigenvalue problem of $\Delta \mathbf{P} = \mathbf{P}^e \equiv n \langle \chi | \hat{V} | \chi \rangle$

$$\mathbf{u}^\dagger \Delta \mathbf{P} \mathbf{u} = \mathbf{v} = \{v_k \delta_{k,l}\}, \quad \Delta \mathbf{P} = \mathbf{P}^e = \{\mathbf{P}^{X,Y} (1 - \delta_{X,Y})\}, \quad \mathbf{u}^\dagger \mathbf{u} = \mathbf{I}, \quad (29)$$

which defines the NOCV [7,8], has been shown to determine only a small subset of pairs of complementary (CT-active) external channels $\varphi = \chi \mathbf{u}$, which correspond to the non-vanishing eigenvalues, $v_k > 0$,

$$\hat{V} \varphi_{-k} = -v_k \varphi_{-k} \quad \text{and} \quad \hat{V} \varphi_k = v_k \varphi_k. \quad (30)$$

They have been shown to provide a conceptually attractive framework for a precise division [7,8]

$$\Delta \rho(\mathbf{r}) = \text{Tr}[\rho(\mathbf{r}) \Delta \mathbf{P}] = \sum_k v_k [\varphi_k^2(\mathbf{r}) - \varphi_{-k}^2(\mathbf{r})] = \sum_k \Delta \rho_k(\mathbf{r}), \quad (31)$$

of the density-difference function, between molecular and promolecular electron densities,

$$\Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho^0(\mathbf{r}), \quad (32)$$

in terms of the inter-orbital flows $\{\Delta \rho_k(\mathbf{r})\}$, from the “anti-bonding” $\{\varphi_{-k}\}$ into the “bonding” $\{\varphi_k\}$ CT-active NOCV. In Eq. 31 the matrix $\rho(\mathbf{r}) = \langle \chi | \hat{\rho}(\mathbf{r}) | \chi \rangle$ represents the quantum mechanical operator $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^n \delta(\mathbf{r}_i - \mathbf{r})$ for the system electron density, $\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle$, where Ψ denotes the system wave-function.

Finally, by integrating Eq. 31 over the whole space of electron positions gives the closure relation expressed in terms of the $\varphi_{-k} \rightarrow \varphi_k$ electron flows v_k of the complementary pairs of the CT-active NOCV:

$$0 = \sum_k \int \Delta \rho_k(\mathbf{r}) d\mathbf{r} = \sum_k v_k. \quad (33)$$

It also follows from Eq. 25 that NOCV provide a natural framework for the division of the average value of the system total orbital energy, which can be expressed in terms of the φ -representation matrices $\Delta \mathbf{P}^\varphi = \mathbf{v}$ and $\mathbf{F}^\varphi = \mathbf{u}^\dagger \mathbf{F} \mathbf{u}$:

$$\begin{aligned} \Delta \langle F \rangle &= \text{Tr}(\mathbf{F} \Delta \mathbf{P}) = \text{Tr}(\mathbf{F}^\varphi \mathbf{v}) = \sum_k v_k [\langle \varphi_k | \hat{F} | \varphi_k \rangle - \langle \varphi_{-k} | \hat{F} | \varphi_{-k} \rangle] \\ &\equiv \sum_k v_k (e_k - e_{-k}) \equiv \sum_k \Delta \langle F \rangle_k. \end{aligned} \quad (34)$$

It is expressed in terms of the NOCV contributions $\{\Delta\langle F \rangle_k\}$, each given by the product of the corresponding displacement in the orbital energy, $\Delta e_k = e_k - e_{-k}$, and the associated flow of v_k electrons marking the $\varphi_{-k} \rightarrow \varphi_k$ CT.

This one-electron (orbital) development can be straightforwardly generalized to cover the *many*-electron density operators defining the mixture of the n -electron wavefunctions $\Psi = \{\Psi_r\}$, $|\chi\rangle = |\Psi\rangle$, expanded in terms of the given basis set of n -electron functions $\Phi = \{\Phi_s\}$, $|\chi\rangle = |\Phi\rangle$, e.g., the electron configurations in the CI theory. A given division of the basis set into configuration subsets $X=(A, B)$, $\Phi = \{\Phi^A, \Phi^B\}$, then determines the associated block structure of the CI-Hamiltonian $\hat{H}(n)$, $\mathbf{H} = \langle \Phi | \hat{H} | \Phi \rangle$ and of the density operator $\mathbf{D} = \langle \Phi | \hat{D} | \Phi \rangle = \mathbf{D}^i + \mathbf{D}^e$. Again, the external, displacement part $\mathbf{D}^e = \Delta \mathbf{D} = \{\mathbf{D}^{X,Y}(1 - \delta_{X,Y})\} \equiv \langle \Phi | \Delta \hat{D} | \Phi \rangle$ represents the shift in the density matrix relative to the “promolecular” reference of the uncoupled subsets of configurations, defined by the block-diagonal internal part of the density operator $\mathbf{D}^i = \{\mathbf{D}^{X,X} \delta_{X,Y}\} \equiv \langle \Phi | \hat{D}^0 | \Phi \rangle$. Here, the internal density operator $\hat{D}^0 = \hat{D}^i$ is implicitly defined by the internal eigenvalue problem of \mathbf{D}^i ,

$$\mathbf{Q}^\dagger \mathbf{D}^i \mathbf{Q} = \mathbf{q} = \{q_{u,w}\} = \{\mathbf{q}^X \delta_{X,Y}\}, \quad \mathbf{Q} = \{\mathbf{Q}^X \delta_{X,Y}\}, \quad \mathbf{Q}^\dagger \mathbf{Q} = \mathbf{I}, \quad (35)$$

which generates the internal modes of the promolecular density matrix $\Theta = \Phi \mathbf{Q} = \{\Theta^A = \Phi^A \mathbf{Q}^A, \Theta^B = \Phi^B \mathbf{Q}^B\}$,

$$\hat{D}^0 = \left| \Phi^A \right\rangle \mathbf{q}^A \left\langle \Phi^A \right| + \left| \Phi^B \right\rangle \mathbf{q}^B \left\langle \Phi^B \right|. \quad (36)$$

The related external eigenvalue problem of \mathbf{D}^e ,

$$\mathbf{T}^\dagger \Delta \mathbf{D} \mathbf{T} = \mathbf{d} = \{d_s \delta_{s,t}\}, \quad \mathbf{T}^\dagger \mathbf{T} = \mathbf{I}, \quad (37)$$

now provides the convenient framework of the n -electron external eigenfunctions, $\Omega = \Phi \mathbf{T}$, for partitioning the average (inter-subset) interaction energy:

$$\begin{aligned} \Delta \langle E \rangle &= \text{Tr}(\mathbf{H} \Delta \mathbf{D}) = \sum_s d_s [\langle \Omega_s | \hat{H} | \Omega_s \rangle - \langle \Omega_{-s} | \hat{H} | \Omega_{-s} \rangle] \\ &\equiv \sum_s d_s (E_s - E_{-s}) \equiv \sum_s \Delta \langle E \rangle_s. \end{aligned} \quad (38)$$

This division again involves the shifts in the expectation values of the energy for the complementary CT-active eigenfunctions of the displacement operator $\Delta \hat{D} = \hat{D}^e = \hat{D} - \hat{D}^0$, for the non-vanishing eigenvalues $d_s > 0$,

$$\Delta \hat{D} \Omega_{-s} = -d_s \Omega_{-s} \quad \text{and} \quad \Delta \hat{D} \Omega_s = d_s \Omega_s. \quad (39)$$

4 Complementary decoupling schemes of molecular hardness tensor

Yet another issue in CSA, which deals with the internal and external decoupling of the symmetric hardness tensor $\eta = \eta^i + \eta^e$ or its internal (η^i) or external (η^e) contributions, involves the complementary *partial* transformations of the representation

basis vectors [2,3], the product of which brings about the complete diagonalization (decoupling) of the whole hardness matrix (Eq. 2). For example, the initial (internal) decoupling transformation $\mathbf{R} = \{\mathbf{R}^X \delta_{X,Y}\}$ of η^i (Eq. 7),

$$\mathbf{R}^\dagger \eta^i \mathbf{R} = \mathbf{a}(\text{diagonal}), \quad \mathbf{R}^\dagger \mathbf{R} = \mathbf{I}, \quad (40)$$

defines the associated complementary “rotation” \mathbf{C}_R , such that $\mathbf{R}\mathbf{C}_R = \mathbf{C} : \mathbf{C}_R = \mathbf{R}^\dagger \mathbf{C}$. Similarly, the initial external transformation \mathbf{W} , which decouples η^e (Eq. 8),

$$\mathbf{W}^\dagger \eta^e \mathbf{W} = \mathbf{b}(\text{diagonal}), \quad \mathbf{W}^\dagger \mathbf{W} = \mathbf{I}, \quad (41)$$

generates the complementary transformation \mathbf{C}_W in $\mathbf{C} = \mathbf{U}\mathbf{C}_W : \mathbf{C}_W = \mathbf{W}^\dagger \mathbf{C}$. All these unitary matrices represent the associated “rotations” of the underlying (atomic) basis set vectors [2–5], giving rise to the collective (delocalized) charge displacement modes of molecular fragments $X=(A, B)$ or AIM in the whole molecular system M .

The initial internal decoupling \mathbf{R} brings about the diagonalization of only the *intra*-fragment blocks of η . This transformation generates the non-diagonal intermediate hardness tensor:

$$\eta_{int} = \mathbf{R}^\dagger \eta \mathbf{R} = \mathbf{R}^\dagger (\eta^i + \eta^e) \mathbf{R} = \mathbf{a} + \mathbf{R}^\dagger \eta^e \mathbf{R}, \quad (42)$$

the eigenvalue problem of which defines the complementary rotation \mathbf{C}_R (see Eq. 2):

$$\mathbf{C}_R^\dagger \eta_{int} \mathbf{C}_R = \mathbf{C}_R^\dagger \mathbf{a} \mathbf{C}_R + \mathbf{C}_R^\dagger \eta^e \mathbf{C} = \mathbf{C}_R^\dagger \eta \mathbf{C} = \mathbf{c}(\text{diagonal}) \equiv \{\mathbf{c}^X \delta_{X,Y}\}. \quad (43)$$

In the same way the initial external decoupling transformation \mathbf{W} generates the associated intermediate hardness tensor

$$\eta_{ext} = \mathbf{W}^\dagger \eta \mathbf{W} = \mathbf{W}^\dagger (\eta^i + \eta^e) \mathbf{W} = \mathbf{W}^\dagger \eta^i \mathbf{W} + \mathbf{b}, \quad (44)$$

the eigenvalue problem of which determines its complementary rotation \mathbf{C}_W :

$$\mathbf{C}_W^\dagger \eta_{ext} \mathbf{C}_W = \mathbf{C}_W^\dagger \mathbf{b} \mathbf{C}_W + \mathbf{C}_W^\dagger \eta^i \mathbf{C} = \mathbf{C}_W^\dagger \eta \mathbf{C} = \mathbf{c}. \quad (45)$$

Furthermore, expressing the overall eigenvalue problem of Eq. 2 in terms of these partial internal and external decoupling transformations and their respective complementary rotations gives:

$$\begin{aligned} \mathbf{C}^\dagger \eta \mathbf{C} &= \mathbf{C}^\dagger (\eta^i + \eta^e) \mathbf{C} = \mathbf{C}_R^\dagger (\mathbf{R}^\dagger \eta^i \mathbf{R}) \mathbf{C}_R + \mathbf{C}_W^\dagger (\mathbf{W}^\dagger \eta^e \mathbf{W}) \mathbf{C}_W \\ &= \mathbf{C}_R^\dagger \mathbf{a} \mathbf{C}_R + \mathbf{C}_W^\dagger \mathbf{b} \mathbf{C}_W = \mathbf{c}. \end{aligned} \quad (46)$$

This equation, which also follows from adding Eqs. 43 and 45, partitions the overall diagonalization of the hardness matrix into contributions involving the complementary rotations of the tensor internal and external eigenvalues \mathbf{a} and \mathbf{b} : the former are transformed using the external complement \mathbf{C}_R of the primary internal decoupling transformation, while the latter require the internal complement \mathbf{C}_W of the primary external

transformation. This grouping relation, for combining the results of the external and internal eigenvalue problems into eigensolutions of the whole matrix, complements Eq. 6 of Löwdin's partitioning technique.

We finally observe, that the external decoupling can be also formulated with reference to the total hardness tensor [2, 3], by requiring the vanishing off-diagonal coupling blocks in the transformed hardness matrix. This requirement does not specify the transformation uniquely, so that additional maximum overlap criterion has been used to specify such a scheme uniquely. Another example of such a transformation is provided by the product transformation $\tilde{\mathbf{U}} = \mathbf{C}\mathbf{R}$ [3], which "removes" the off-diagonal charge couplings in the resulting hardness tensor:

$$\mathbf{R}^\dagger(\mathbf{C}^\dagger\boldsymbol{\eta}\mathbf{C})\mathbf{R} = \mathbf{R}^\dagger\mathbf{c}\mathbf{R} = \{\mathbf{R}^{X\dagger}\mathbf{c}^X\mathbf{R}^X\delta_{X,Y}\}. \quad (47)$$

5 Conclusion

As we have already remarked in Sect. 3, within the standard SCF LCAO MO theory the non-diagonal Fock and density matrices of the AO representation, \mathbf{F} and \mathbf{D} , respectively, become diagonal in the canonical MO representation, $\mathbf{F}^\psi = \{e_\gamma\delta_{\gamma,\mu}\} = \mathbf{e}^\psi$ and $\mathbf{D}^\psi = \{p_\gamma^\psi\delta_{\gamma,\mu}\} = \mathbf{p}^\psi$, so that the underlying operators $\hat{\mathbf{F}} = |\psi\rangle\mathbf{e}^\psi\langle\psi|$ and $\hat{\mathbf{D}} = |\psi\rangle\mathbf{p}^\psi\langle\psi|$ commute: $[\hat{\mathbf{F}}, \hat{\mathbf{D}}] = 0$. Indeed, by construction the canonical MO constitute the simultaneous eigenvectors of both these operators. Partitioning next the two matrices \mathbf{F} and \mathbf{D} into their internal and external parts corresponding to a given division of the AO basis set $\boldsymbol{\chi} = \{\chi^X\}$, $X = A, B$,

$$\mathbf{F} = \mathbf{F}^i + \mathbf{F}^e = \mathbf{F}^0 + \Delta\mathbf{F} \quad \text{and} \quad \mathbf{D} = \mathbf{D}^i + \mathbf{D}^e = \mathbf{D}^0 + \Delta\mathbf{D}, \quad (48)$$

then gives rise to the associated sets of the internal and external eigenvalue problems for the corresponding components of the Fock and density operators, respectively:

$$\mathbf{o}^\dagger\mathbf{F}^i\mathbf{o} = \mathbf{d} = \{d_m\delta_{m,n}\} \equiv \mathbf{F}^{i,\xi} \quad \text{and} \quad \mathbf{o}^\dagger\mathbf{D}^i\mathbf{o} = \mathbf{p}^\xi = \{p_m^\xi\delta_{m,n}\} \equiv \mathbf{D}^{i,\xi}, \quad (49)$$

$$\xi = \{\xi_m\} = \boldsymbol{\chi}\mathbf{o}, \quad \sum_m p_m^\xi = 1, \quad \mathbf{o}^\dagger\mathbf{o} = \mathbf{I},$$

$$\mathbf{u}^\dagger\mathbf{F}^e\mathbf{u} = \mathbf{g} = \{g_k\delta_{k,l}\} \equiv \mathbf{F}^{e,\varphi} \quad \text{and} \quad \mathbf{u}^\dagger\mathbf{D}^e\mathbf{u} = \mathbf{p}^\varphi = \{p_k^\varphi\delta_{k,l}\} \equiv \mathbf{D}^{e,\varphi}, \quad (50)$$

$$\varphi = \{\varphi_k\} = \boldsymbol{\chi}\mathbf{u}, \quad \sum_k p_k^\varphi = 1, \quad \mathbf{u}^\dagger\mathbf{u} = \mathbf{I}.$$

Again, these simultaneous eigenvalue problems of the underlying pairs of operators,

$$\{\hat{\mathbf{F}}^i = |\xi\rangle\mathbf{d}\langle\xi|, \quad \hat{\mathbf{D}}^i = |\xi\rangle\mathbf{p}^\xi\langle\xi|\} \quad \text{and} \quad \{\hat{\mathbf{F}}^e = |\varphi\rangle\mathbf{g}\langle\varphi|, \quad \hat{\mathbf{D}}^e = |\varphi\rangle\mathbf{p}^\varphi\langle\varphi|\}, \quad (51)$$

respectively, imply that these operators commute, $[\hat{\mathbf{F}}^i, \hat{\mathbf{D}}^i] = [\hat{\mathbf{F}}^e, \hat{\mathbf{D}}^e] = 0$, thus having in each pair a common set of eigenvectors.

Hence, taking into account that $\text{Tr}(\mathbf{FD}) = \text{Tr}(\mathbf{F}^i \mathbf{D}^i + \mathbf{F}^e \mathbf{D}^e)$, though $\mathbf{FD} \neq \mathbf{F}^i \mathbf{D}^i + \mathbf{F}^e \mathbf{D}^e$, and the invariance of the trace with respect to similarity transformations of operators, one obtains the following alternative expression for the average orbital energy of Eq. 21:

$$\begin{aligned} \langle e \rangle &= \text{Tr}(\mathbf{FD}) = \sum_{\gamma} e_{\gamma} p_{\gamma} \\ &= \text{Tr}(\mathbf{F}^i \mathbf{D}^i + \mathbf{F}^e \mathbf{D}^e) = \text{Tr}(\mathbf{F}^{i,\xi} \mathbf{D}^{i,\xi} + \mathbf{F}^{e,\varphi} \mathbf{D}^{e,\varphi}) \\ &= \sum_m d_m p_m^{\xi} + \sum_k g_k p_k^{\varphi} \equiv \langle d^i \rangle + \langle g^e \rangle. \end{aligned} \quad (52)$$

This combination formula for the average orbital energy, the mean value of the eigenvalues of the Fock matrix, thus indicates that this quantity can be alternatively generated by the sum of the mean values $\langle d^i \rangle$ and $\langle g^e \rangle$ of the corresponding eigenvalues of the internal and external operators, respectively, calculated for the density operators defined by the relevant eigensolutions of these partial problems.

References

1. P.-O. Löwdin, J. Chem. Phys. **19**, 1396 (1951); P.-O. Löwdin, J. Math. Phys. **3**, 969 (1962); P.-O. Löwdin, J. Mol. Spectr. **10**, 12 (1963)
2. R.F. Nalewajski, J. Korchowiec, *Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity* (World-Scientific, Singapore, 1997) and refs. therein.
3. R.F. Nalewajski, J. Korchowiec, A. Michalak, Top. Curr. Chem. **183**, 25 (1996); R.F. Nalewajski, J. Korchowiec, A. Michalak, Proc. Indian. Acad. Sci. (Chemical Sci.) **106**, 353 (1994)
4. R.F. Nalewajski, Struct. Bonding **80**, 115 (1993); R.F. Nalewajski, J. Korchowiec, J. Mol. Catal. **54**, 324 (1989)
5. R.F. Nalewajski, J. Korchowiec, Z. Zhou, Int. J. Quantum Chem. Symp. **22**, 349 (1988); R.F. Nalewajski, Int. J. Quantum Chem. **40**, 265 (1991); **43**, 443 (1992) (Erratum)
6. R.F. Nalewajski, Adv. Quant. Chem. **51**, 235 (2006)
7. M. Mitoraj, A. Michalak, J. Mol. Model. **11**, 341 (2005); M. Mitoraj, Ph.D. Thesis, Jagiellonian University, 2007; M. Mitoraj, A. Michalak, J. Mol. Model. **13**, 347 (2007)
8. M. Mitoraj, H. Zhu, A. Michalak, T. Ziegler, J. Org. Chem. **71**, 9208 (2006); M. Mitoraj, H. Zhu, A. Michalak, T. Ziegler, Organometallics **26**, 1627 (2007)
9. R.F. Nalewajski, J. Mrozek, A. Michalak, Int. J. Quantum Chem. **61**, 589 (1997)
10. R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic Press, San Diego, 1989)
11. A.D. Bochevarov, C.D. Sherrill, J. Math. Chem. **42**, 59 (2007)