

APPLICATION OF TRANSITION DENSITY MATRIX
FOR ANALYSIS OF EXCITED STATES

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Recent years in the field of molecular theory have seen the development of an effective method for calculating excited states on the basis of the transition density matrix [1, 2]. An excited state Φ_* is here construed as a superposition of singly excited configurations $\Phi_{i \rightarrow p}$

$$\Phi_* = \sum_{i=1}^N \sum_{p=N+1}^M d_{pi} \Phi_{i \rightarrow p}, \quad (1)$$

where d_{pi} are the configurational coefficients. The configurations $\Phi_{i \rightarrow p}$ are constructed from the single-determinant wave function of the ground state Φ by replacing in this determinant the filled spin orbitals $|i\rangle$ by vacant spin orbitals $|p\rangle$. In the formalism of the density matrix, the coefficients d_{pi} are replaced by the matrix equivalent, i.e., the Hermitian component D of the single-particle transition density matrix

$$D = \sum_{i,p} (d_{pi} |p\rangle \langle i| + d_{pi}^* |i\rangle \langle p|). \quad (2)$$

For the transition matrix D , a matrix equation was obtained in [2] in the form of a problem in eigenvalues for a certain supermatrix, and a method of numerical solution was indicated and was realized successfully in specific calculations [3-5]. Its application does not require any explicit assignment of molecular orbitals $|i\rangle$, but is based on a previously calculated one-electron density matrix of the ground state $\rho = \sum_{i=1}^N |i\rangle \langle i|$ or on the equivalent $Y = 2\rho - I$; direct means for finding this quantity (atomic basis) are available.

Calculation of the matrix D is also carried out successfully with a basis of atomic orbitals without the construction of a configuration interaction or solution of the complete eigenvalue problem. In the course of such calculations, however, the explicit form of the coefficients d_{pi} is not determined. Meanwhile, for the analysis of the structure of excited states, use is generally made of configuration coefficients in molecular orbitals, which are used to judge the degree of configuration interaction (number of ground configurations), localization of the electronic excitation on fragments of the molecule, etc., (see, for example, [6-9]).

Here we will show that in the solution of such problems, the transition matrix D is a more effective means, both in the formal and in the applied aspects, than the traditional approach we have just described. Let us examine first the formal problem of the maximum possible number of configurations $\Phi_{i \rightarrow p}$ in the wave function (1). Since there are a total of N filled spin orbitals $|i\rangle$ and the number of vacant spin orbitals is equal to $M-N$ (where M is the dimension of the basis one-particle functions, for example, the number of atomic spin orbitals), then the maximum possible number of terms in (1) is given by the product $N(M-N)$. We will show that there is always possible a representation Φ_* in which the maximum number of singly excited configurations is substantially smaller, no greater than $\min(N; M-N)$, i.e., no greater than the smaller of the pair of numbers N and $M-N$.

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To do this, let us carry out the transformation of the filled spin orbitals by a unitary matrix U of dimension N , and the vacant spin orbitals correspondingly by a unitary matrix V of dimension $M-N$. Having made use of the conventional rules for operations with determinants, we find that the configuration $\Phi_{i \rightarrow p}$ thereupon becomes the superposition

$$\Phi_{i \rightarrow p} = (\det U) \sum_{j,q} V_{pq} U_{ij}^* \Phi'_{i \rightarrow q}, \quad (3)$$

where $\Phi'_{j \rightarrow q}$ is a singly excited configuration made up of the transformed spin orbitals

$$|i'\rangle = \sum_j U_{ij}^* |j\rangle, \quad |p'\rangle = \sum_q V_{pq}^* |q\rangle. \quad (4)$$

The determinant of the unitary matrix forms a phase factor of the wave function and is not taken into account here. Then it follows from (3) that the superposition (1) with the unitary transformation (4) of the filled and (separately) vacant spin orbitals remains invariant, i.e.,

$$\Phi_s = \sum_{i,p} d'_{pi} \Phi'_{i \rightarrow p}, \quad (5)$$

where the matrix of the new configuration coefficients $d' = \|d'_{pi}\|$ is a special form of the transformed matrix $d = \|d_{pi}\|$ of the former coefficients

$$d' = VdU^+. \quad (6)$$

It is known from matrix theory [10] that an arbitrary rectangular matrix, by a transformation of the type of (6), can be reduced to diagonal form

$$d = \begin{pmatrix} d_1 & 0 & \dots & \dots & 0 \\ 0 & d_2 & \dots & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & d_r & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \dots & \dots & 0 \end{pmatrix}, \quad (7)$$

if we select as U a unitary matrix diagonalizing d^+d , and as V a matrix diagonalizing dd^+ . The number of nonzero diagonal elements coinciding with the rank r of the matrix d does not exceed the smallest of the dimensions of the matrix d , i.e., $\min(N; M-N)$. If we consider that the transition matrix D in the basis MO's has the form

$$D = \begin{pmatrix} 0 & d^+ \\ d & 0 \end{pmatrix}, \quad (7')$$

then the transformation of the matrix D by the unitary matrix

$$W = \begin{pmatrix} U & 0 \\ 0 & V \end{pmatrix},$$

diagonalizing, evidently, the matrix D^2 , is completely equivalent to transformation of the block d .

It is easy to determine that, by the matrix W , transformation is effected to a basis of natural spin orbitals of the excited state (1). Indeed, the one-particle density matrix of the excited state, according to [3, 11], has the form

$$\rho_s = \rho - D^2 Y. \quad (8)$$

In view of (2), the matrix D anticommutes with Y :

$$DY + YD = 0. \quad (9)$$

Therefore the matrix D^2 commutes with Y and this means that it also commutes with the density matrix of the ground state ρ . Consequently, the eigenfunctions of D^2 diagonalize the single-particle density matrix

ρ_* (8); i.e., they are by definition natural spin orbitals of the excited state.† In the end we arrive at an important statement: in the basis of natural spin orbitals, the number of configurations in the superposition of singly excited configurations is minimal and is equal to the rank of the matrix of the configuration coefficients:

$$\Phi_* = \sum_{\alpha=1}^r d_{\alpha} \Phi_{\alpha \rightarrow N+\alpha}, \quad (10)$$

where $r \leq \min(N; M-N)$.

Let us clarify the requirement upon which the superposition (1) is reduced to a single determinant. The known necessary and sufficient condition for this reduction is idempotentiality of the one-particle density matrix, in the given case $\rho_*^2 = \rho_*$. From (8), taking into account (9) and the condition of involution $Y^2 = 1$, we obtain

$$\rho_* = \rho - 2D^2Y\rho + D^4.$$

As a consequence of the identity $Y\rho = \rho = 1/2(1 + Y)$, we have $\rho_*^2 = \rho_* - D^2 + D^4$; and hence the requirement of idempotentiality ρ_* reduces to fulfillment of the equality

$$D^2 = D^4. \quad (11)$$

More convenient for calculations than the matrix relation (11) is its "integral" characteristic, i.e., its trace. As a consequence of normalization of the configuration coefficients $\text{Sp } d^+d = \text{Sp } dd^+ = 1$. And in the light of (7), for any matrix D

$$\text{Sp}D^2 = 2. \quad (12)$$

Hence, in the single-configuration case (11), the requirement that $\text{Sp}D^4 = 2$ is fulfilled.

This integral condition is also sufficient. For this we will show that the value 2 is the maximum possible value for the quantity $\text{Sp}D^4$, and that this value is reached only for a value of the rank $r = 1$. Let us designate eigennumbers D^2 in terms of $\mu_{\alpha} = |d_{\alpha}|^2 \geq 0$, for which, from normalization of (12) and double degeneracy of the spectrum of the matrix D^2 (nonzero eigennumbers d^+d and dd^+ are always equal), we have

$$\sum_{\alpha=1}^r \mu_{\alpha} = 1. \quad (13)$$

It is evident that the analysis of $\text{Sp}D^4$ reduces to a study of the sum $2 \sum_{\alpha} \mu_{\alpha}^2$ with the additional condition (13). Squaring the equality (13) and neglecting the quantity $\sum_{\alpha \neq \beta} \mu_{\alpha} \mu_{\beta} \geq 0$, we obtain $\sum_{\alpha=1}^r \mu_{\alpha}^2 \leq 1$, where the equality is possible only with $r = 1$. From the known inequality for the square of the arithmetic mean [12], it is easy to obtain the lower boundary, having thereby the two-sided inequality

$$1/r \leq \sum_{\alpha=1}^r \mu_{\alpha}^2 \leq 1,$$

which for $\text{Sp}D^4$ is written directly in the form

$$2/r \leq \text{Sp}D^4 \leq 2. \quad (14)$$

The left-hand equality is accomplished for the transition matrix D with $\mu = 1/r$, hence satisfying the equation

$$D^2 = rD^4, \quad (15)$$

i.e., the lower limit, in accordance with (10), is reached at the greatest collective (in our terminology) of the excited state in which all r configurations of the form $\Phi_{\alpha \rightarrow N+\alpha}$ participate with identical weight $1/\sqrt{r}$.

†It can be considered that the natural spin orbitals of the single-determinant ground state Φ and the excited state Φ_* (1) coincide, since the one-particle density matrix of the ground state is the operator of projection on the linear shell of occupied orbitals; and hence these orbitals, which for Φ are simultaneously the natural orbitals, are determined with an accuracy within a unitary transformation. The function of such a unitary transformation may be served by a transformation by the matrix U diagonalizing d^+d .

Thus, closeness of SpD^4 to the right-hand limit in (14) corresponds to a very nearly single-configuration description, and closeness to the left-hand limit signifies maximum development of configurational mixing, which is possible only for superposition of singly excited configurations.

When the inequality (14) is taken into account, the quantity SpD^4 can be used to evaluate the degree of collectivity of the excitation (1). In addition to the technical simplicity in using this matrix criterion, there are also advantages in principle; for example, it is possible to identify false collectivity of a transition that may be suggested by a superficial examination the configuration coefficients. As an example that is unfavorable to traditional analysis of (1) on the basis of coefficients d_{pi} , we can use the excited state

$$\Phi_s = \frac{1}{\sqrt{N(M-N)}} \sum_{i,p} \Phi_{i \rightarrow p}, \quad (16)$$

in which all $N(M-N)$ single excited configurations are represented with equal weight (such an example was used in [13] in illustrating the idea of collective excitation). Meanwhile, calculation of SpD^4 for the wave function (16) gives the value 2, i.e., a "multifunctional" wave function (16), by transformation to natural orbitals, is reduced to a single determinant. This also follows from the corresponding matrix of the configuration coefficients

$$d = \frac{1}{\sqrt{N(M-N)}} \begin{vmatrix} 1 & 1 & \dots & 1 \\ 1 & 1 & \dots & 1 \\ \dots & \dots & \dots & \dots \\ 1 & 1 & \dots & 1 \end{vmatrix},$$

the rank of which is obviously equal to 1. In the general case, utilization of the criterion of collectivity with respect to the quantity SpD^4 does not require knowledge of d_{pi} ; it is sufficient to use the method described in [2] to find the matrix D in the basis of atomic orbitals and to calculate the corresponding trace.

Another characteristic of the excited state that is usually found from calculational data on configuration interaction is the localization of electronic excitation on individual fragments of molecules. Experience in spectroscopic research on organic molecules gives obvious evidence for such statements [14-16]. Attempts have been made to obtain such information theoretically, operating with representations of charge transfer (see for example [8]); however, no clear-cut quantitative criterion has yet been introduced. Further, the magnitude of charge transfer, calculated as the algebraic sum of the changes in charge Δq_ν on the atoms of the fragments, does not give an adequate reflection of the nature of electron redistribution upon excitation. The weakness of this criterion is detected for even alternant hydrocarbons, where in the Pariser-Parr-Pople approximation $\Delta q_\nu = 0$ on all carbon atoms [3], and hence analysis of the localization of excitation on the fragments proves to be impossible.

A criterion free of such defects is naturally obtained on the basis of the transition density matrix. Here let us consider the change in the density matrix $\Delta\rho = \rho_* - \rho$ upon excitation. According to (8), $\Delta\rho = -D^2 Y$, and hence the absolute value $|\Delta\rho|$, which is understood in the matrix sense as the matrix $|\Delta\rho| = \sqrt{(\Delta\rho)^2}$, in view of (9) and the involutivity $Y = 1$, coincides with the matrix D^2 :

$$|\Delta\rho| = D^2. \quad (17)$$

It is proposed to use the elements of the matrix D^2 in the atomic basis for evaluating the degree of excitation on the atoms. If the matrix element $\langle \nu | D^2 | \nu \rangle$ differs substantially from zero, the electronic excitation will affect the given atom ν to a significant degree. The measure of localization L_A of the excitation on a certain molecular fragment A consisting of atoms $\nu \in A$ is introduced as the sum of such matrix elements

$$L_A = \frac{1}{2} \sum_{\nu \in A} \langle \nu | D^2 | \nu \rangle. \quad (18)$$

As a consequence of the nonnegative determinacy and the normalization of D^2 (12), we have the inequality

$$0 \leq L_A \leq 1. \quad (19)$$

The values of L_A are normalized in the sense that

$$\sum_A L_A = 1. \quad (20)$$

The upper limit in (19) corresponds to complete localization of the excitation on the fragment A, and the lower limit corresponds to the absence of localization.

Let us establish the physical sense of the criterion that has been introduced. On the basis of eigenfunctions D^2 , which, as indicated above, are the natural spin orbitals of the excited state, the following series is valid:

$$D^2 = \sum_{\alpha=1}^r \mu_{\alpha} (|\alpha\rangle\langle\alpha| + |N+\alpha\rangle\langle N+\alpha|). \quad (21)$$

The origin of Eq. (21) becomes evident if we consider that the wave function of the excited state in the basis of natural orbitals (10) corresponds to a transition density matrix (2) of the form

$$D = \sum_{\alpha=1}^r (d_{\alpha} |N+\alpha\rangle\langle\alpha| + d_{\alpha}^* |\alpha\rangle\langle N+\alpha|),$$

with $\mu_{\alpha} = |d_{\alpha}|^2$. Together with (18), this gives the following representation of the quantity L_A :

$$L_A = \frac{1}{2} \sum_{\alpha=1}^r \sum_{\nu \in A} \mu_{\alpha} (|C_{\alpha}^{\nu}|^2 + |C_{N+\alpha}^{\nu}|^2),$$

signifying that, if the transition is localized on the fragment A, then the natural orbitals that describe such excitation in accordance with (10) are also localized on this fragment, i.e.,

$$\sum_{\nu \in A} |C_{\alpha}^{\nu}|^2 \approx \sum_{\nu \in A} |C_{N+\alpha}^{\nu}|^2 \approx 1,$$

where $C_{\alpha}^{\nu} = \langle\nu|\alpha\rangle$ are the coefficients in the expansion of the natural orbitals $|\alpha\rangle$ with respect to the atomic spin orbitals $|\nu\rangle$.

Thus, localization of excitation on a certain fragment of the molecule means that the transition to the excited state takes place between natural orbitals that are localized on this fragment. This statement is based on the utilization of the matrix module $|\Delta\rho|$ for evaluating the localization of the transition, this matrix module having been introduced above on the basis of formal considerations.

This discussion applies to the orbital-spin matrices D , D^2 , etc., i.e., the matrices acting in the space of the spin orbitals. In practical calculations, the operations are usually with nonspin matrices, the transition to which in our case can be performed by a procedure that is described, for example, in [11]. For singlet excited states (the ground state is also considered singlet) and correspondingly for triplet states with zero projection of spin $s_z = 0$, we have

$$D_S = D_0 \sigma_0, \quad D_{T_0} = D_0 \sigma_z, \quad \text{Sp} D_0^2 = 1, \quad (22)$$

where D_0 represents the nonspin transition density matrices in the singlet and triplet states (in each case their own), which, according to [2], are direct elements of the numerical calculation of the excited states; σ_0 and σ_z are the single two-row matrix and the Pauli matrix for the spin operator \hat{s}_z .

In the case of a triplet state with a projection $s_z = \pm 1$, normalized to 2, the solutions of the secular equation for the orbital spin transition operator have the form

$$D_{T_{\pm}} = \frac{1}{\sqrt{2}} (D_0 \sigma_x \pm i D_0 Y_0 \sigma_y), \quad (23)$$

where as the orbital (i.e., nonspin) transition matrix we have that same matrix D_0 as for D_{T_0} in (21). For triplets with the transition matrix (23), by taking into account the simple properties of Pauli matrices of the type $\sigma_{\alpha}^2 = \sigma_0$, $\sigma_x \sigma_y = i \sigma_z$, etc., we can reduce the requirement of monodeterminant (11) to the analogous condition for the orbital matrix D_0 :

$$D_0^2 = 2D_0^4. \quad (24)$$

Since the matrices D_0 for D_{T_0} and $D_{T_{\pm}}$ coincide, the condition (24) for the orbital-spin transition operator has the same form

$$D_{T_{\pm}}^2 = 2D_{T_{\pm}}^4. \quad (25)$$

whence it follows that the integral value is given by $\text{Sp}D\tau_0^4 = 1$, and it never assumes larger values, in particular the maximum possible value of 2 that is achieved for the component of a triplet with $s_z = \pm 1$. In accordance with (15), this means that the corresponding wave function of the excited state is formed by at least two determinants, which, as is well known, are necessary for the construction of spin-free singly excited configurations.†

For the same reasons, in the case of a singlet state, the maximum value of $\text{Sp}D_S^4$ is equal not to 2 but 1; this can be shown independently by carrying out for the orbital matrix those same arguments that were used above in obtaining the inequality (14). Here it may be considered without loss of generality that, in the basis of molecular orbitals, D_0 has a block structure of the type of (7')

$$D_0 = \frac{1}{\sqrt{2}} \begin{vmatrix} 0 & d_0^+ \\ d_0 & 0 \end{vmatrix}, \quad \text{Sp}d_0^+d_0 = \text{Sp}d_0d_0^+ = 1. \quad (26)$$

Let us now adopt the following natural terminological definitions. We will define a configuration not as the determinant of the spin orbitals, but a regular-spin combination of determinants obtained by replacing the corresponding spin functions of occupied nonspin orbitals by vacant orbitals. Here, in the interest of uniformity, a degenerate set D for a triplet is conveniently represented by only a single component $D\tau_0$. Then $\max \text{Sp}D^4 = 1$, and the inequality (14), which is valid in the general case, is detailed as follows for singlet and triplet states:

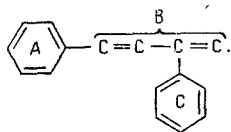
$$\frac{1}{2r_0} \leq \text{Sp}D^4 \leq 1. \quad (27)$$

Here r_0 is the rank of the matrix of the configuration coefficients d_0 for the configurations defined above, with $r_0 \leq \min(n, m-n)$, where n is the number of filled nonspin orbitals; m is the number of basis nonspin functions, for example, the number of atomic orbitals utilized $|\chi\nu\rangle$. As a result, it is evident that the right-hand limit in (27) corresponds to the single-configuration case in the sense indicated above, both for singlets and for triplets; deviation from this limit indicate a substantially multiconfigurational character of the excited state.

For the localization number L_A (18), it is easy to perform the integration with respect to spin (atomic spin orbital $|\nu\rangle = |\chi\nu\rangle \times |\eta\rangle$, where η is the spin function of the electron); as a result, there remain the purely atomic matrix elements of the orbital transition matrix D_0

$$L_A = \sum_{\nu \in A} \langle \chi_\nu | D_0^2 | \chi_\nu \rangle. \quad (28)$$

The inequality (19) evidently remains valid here. In accordance with [11], the matrix D_0^2 for the triplet is the spin density matrix normalized to 1. Hence, L_A (24) for triplet states simultaneously characterizes the measure of spin-density localization on the fragment. As an example illustrating our approach, let us consider singlet and triplet π -excitation of the alternant system 1, 3-diphenylbutadiene, for which it is natural to distinguish the fragments A, B, and C:



The values of $\text{Sp}D^4$ and L_A for the lower transitions are listed in Table 1, where the superscript "+" or "-" for the symbols of electronic states indicate respectively the allowed or forbidden character of the transitions with respect to alternacy. From these data it follows that the singlet transitions under consideration are strongly localized on the respective parts of the molecules: $L_{A+B}(S_1^+) = 0.959$; $L_{A+B}(S_2^-) = 0.999$; $L_{B+C}(S_3^-) = 0.997$; $L_{B+C}(S_4^+) = 0.892$. For the lowest singlet excitation, the $S_0 \rightarrow S_1^+$ transition proves to be very nearly one-electron. For the transitions $S_0 \rightarrow S_2^-$ and $S_0 \rightarrow S_3^-$, in accordance with (15), Φ_* is constructed mainly of two singly excited configurations formed from natural orbitals. If we judge by the configuration coefficients d_{pi} , the main contribution is made, in approximately the same weight, by four configurations formed by molecular orbitals (eigenvectors of the Fock matrix). Here not all of the orbitals

†For $S_z = \pm 1$, such configurations are represented by a single determinant that is constructed from the primary determinant by replacement of an occupied spin orbital by a vacant orbital with opposite spin.

TABLE 1. Collectivity and Localization of Electronic Transitions in 1,3-Diphenylbutadiene

Transition	spD ^a	L _A	L _B	L _C
S ₀ →S ₁ ⁺	0,984	0,309	0,650	0,041
S ₀ →S ₂ ⁻	0,499	0,869	0,130	0,001
S ₀ →S ₃ ⁻	0,499	0,003	0,127	0,870
S ₀ →S ₄ ⁺	0,676	0,108	0,379	0,513
S ₀ →T ₁ ⁺	0,979	0,124	0,761	0,115
S ₀ →T ₂ ⁺	0,567	0,412	0,168	0,420

participating in the configurational interaction prove to be localized on the corresponding fragments, and the fact of localization of excitation could be rather puzzling if we overlook the circumstance pointed out above, that only a transition to natural orbitals makes it explicit. Let us emphasize that, in order to detect the localization itself, there is no need to find local orbitals, it being sufficient to carry out calculations through Eq. (24).

Localization of excitation on fragments signifies that the corresponding spectroscopic characteristics of the molecules should also have very similar analogs for the isolated fragment. A comparison of the energy λ_i for the transitions S₀ → S_i with the excitation energies of the pure fragments, 1-phenylbutadiene (A + B) and 2-phenylbutadiene (B + C), which were calculated independently in the same semiempirical scheme, leads to internally self-consistent results (λ , eV):

$$\begin{aligned} \lambda_1^+ &= 4,316 & \lambda_2^- &= 4,560 & \lambda_3^- &= 4,670 \\ \lambda_1^+(A+B) &= 4,357 & \lambda_2^-(A+B) &= 4,540 & \lambda_1^-(B+C) &= 4,567 \\ & & \lambda_4^+ &= 5,060 & & \\ & & \lambda_2^+(B+C) &= 4,628. & & \end{aligned}$$

The agreement was rather poor only for the transition S₀ → S₄, the degree of localization of which is also less satisfactory than for the preceding excited states. On the whole, it can be concluded that the first two excited states in this particular system correspond to excitation of only the 1-phenylbutadiene fragment. Subsequent excitations S₀ → S₃⁻ and S₀ → S₄⁻ affect mainly the fragment corresponding to 2-phenylbutadiene and overlapping with the 1-phenylbutadiene fragment.

For triplet excitations, localization on these same fragments is less pronounced: $L_{A+B}(T_1^+) = 0,885$, $L_{A+B}(T_2^+) = 0,580$. Here, for the first singlet-triplet transition, 0,75 of the spin density is concentrated on the butadiene fragment.

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