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The Symmetry Behaviour of the First-Order Density Matrix and its Natural Orbitals for Linear Molecules

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The general results regarding the symmetry of density matrices constructed from wave functions of a given symmetry species and the consequences for the transformation properties of the natural p-states reviewed in a previous communication [1] are illustrated for the special case $p=1$ for linear molecules with $C_{\infty v}$- or $D_{\infty h}$-symmetry. It is shown that even if the wave function belongs to a degenerate species, the natural orbitals (NO's) can always choosen to be adapted to the effective symmetry group C_{∞}. The role played by the symmetry-adapted natural orbitals (SANO's) and of the "natural expansion" for 2-electron wave functions in this case is discussed.

Die in einer früheren Arbeit [1] zusammengestellten Ergebnisse über das Symmetrieverhalten reduzierter Dichtematrizen, die aus Wellenfunktionen bestimmter Symmetrie konstruiert sind, sowie die Transformationseigenschaften der „natürlichen p-Zustände" werden am Beispiel von linearen Molekülen mit $C_{\infty v}$- oder $D_{\infty h}$-Symmetrie für den Fall $p=1$ illustriert. Es wird gezeigt, daß auch dann, wenn die Wellenfunktion zu einer entarteten Symmetriespecies gehört, die natürlichen Orbitale (NO's) der effectiven Symmetriegruppe C_{∞} adaptiert sind.Die Rolle, die in diesem Fall die symmetrieadaptierten natürlichen Orbitale (SANO's) und die „natürliche Entwicklung" von 2-Elektronenwellenfunktionen spielen, werden diskutiert.

Les résultats généraux recensés dans une communication précédente [1] concernant la symétrie des matrices densités construites à partir de fonctions d'onde de symétrie donnée et ses conséquences sur les propriétés de transformation des états -p naturels, sont illustrés sur le cas spécial où $p=1$ dans les molécules linéaires à symétrie $C_{\infty v}$ ou $D_{\infty h}$. On montre que même si la fonction d'onde appartient à une catégorie dégénérée, les orbitales naturelles (NO's) peuvent toujours être choisies pour être adaptées au groupe de symétrie effectif C_{∞}. On discute le rôle joué par les orbitales naturelles adaptées à la symétrie (SANO's) et "l'expansion naturelle" des fonctions d'onde à deux électrons.

1. Introduction

Starting with two sets of – exact or approximate – wave functions $\Psi_{\alpha i}$ ($i=1,2\ldots d_\alpha$) and $\Phi_{\beta j}$ ($j=1,2\ldots d_\beta$) which respectively span the irreducible representations $\Gamma^{(\alpha)}$ and $\Gamma^{(\beta)}$ of the symmetry group of the system under consideration, the pth order transition density matrix in the normalization of Coleman [2] is defined by

$$D^{(p)}_{\alpha i,\beta j}(x,x') = \int \Psi_{\alpha i}(x,y)\,\Phi^*_{\beta j}(x',y)\,dy \tag{1}$$

where x and x' stand for two different sets of values of the spatial and spin variables of the first p particles and y for the remaining $(N-p)$ ones. If we put $x'=x$ we get the corresponding p-densities.

As was shown by Coleman [2] and others, the quantity $D^{(p)}_{\alpha i,\alpha i}(x,x')$ for fixed p, α, and i can be considered as the kernel of a density operator $\hat{D}$. Its eigenfunctions, defined by

$$\hat{D}\chi_i(x) = \int D(x,x')\,\chi_i(x')\,dx' = \mu_i \chi_i(x) \tag{2}$$

are called "natural p-states" with corresponding eigenvalues μ_i [1]. Since $\hat{D}^{(p)}$ is a completely continuous operator – by virtue of the normalization of the wave function – its spectrum is purely discrete and its eigenfunctions χ_i – including those with eigenvalue $\mu=0$ – span the whole function space.

One of the problems in connection with these density matrices is their behaviour under the symmetry operations of the system and the consequences this has for its eigenfunctions; assuming that the wave functions used in constructing the density matrix are themselves symmetry-adapted (cf. Eq. (1) and preceeding text). This subject, both for density matrices and p-densities, was reviewed in a recent article by the present author and W. Kutzelnigg [1]. However, it seemed desirable to exemplify the general results collected in that paper for a specific symmetry group. This is done in the present paper for the groups $C_{\infty v}$ and $D_{\infty h}$, which include the whole class of diatomic and linear polyatomic molecules.

2. General Results for the Symmetry Properties of Density Matrices and Natural p-States

In this section we will quote from [1] without proof those general results needed for the applications in the following sections.

1. If a symmetry operation R of $\mathfrak{G}$ is applied simultaneously to *both* sets of arguments x and x', the $d_\alpha d_\beta$ transition densities of Eq. (1) are transformed among themselves and span the direct product representation $\Gamma^{(\alpha)} \times \Gamma^{(\beta)*}$. If this representation is reducible, it can be reduced to give the decomposition

$$\Gamma^{(\alpha)} \times \Gamma^{(\beta)*} = \sum_{\gamma} n_\gamma \Gamma^{(\gamma)} \tag{3}$$

into irreducible parts. The transition density matrices can be likewise decomposed

$$D^{(p)}_{\alpha i,\beta j}(x,x') = \sum_{\gamma,k} \sum_{r=1}^{n_\gamma} D^{(p)}_{\gamma k,r}(x,x')\, C(\alpha i \beta j|\gamma k r) \tag{4}$$

into their irreducible components of species γ and subspecies k. The vector-coupling coefficients C are uniquely defined only if the n_γ are all either 0 or 1. Otherwise the index r is needed to count the different irreducible components of the same species. Since the C-coefficients are unitary, Eq. (4) can be inverted to give the composition of the irreducible components

$$D^{(p)}_{\gamma k,r}(x,x') = \sum_{i,j} D^{(p)}_{\alpha i,\beta j}(x,x')\, C^*(\alpha i \beta j|\gamma k r)\,. \tag{5}$$

2. In general the group $\mathfrak{G}$ will contain both spatial and spin symmetry operations. It is possible to treat these two symmetries separately. The way in which this can be done has been investigated in detail for the first- and second-

[1] They have been considered so far for density matrices only (i.e. if $\Psi_{\alpha i} \equiv \Phi_{\alpha i}$) and not for transition density matrices.

order density matrices ($p=1$ and 2 in Eq. (1)). Here we need only the result, that for wave functions which are pure spin states (i.e. for which S and M_S are good quantum numbers), the spin dependence of $D^{(1)}(x, x')$ can be separated off, leaving two spinfree quantities the spinfree first-order density matrix $P(r, r')$ and the spin-density matrix $Q_S(r, r')$.

$$P(r, r') = N \int D^{(1)}(rs, r's)ds \tag{6}$$

$$Q_S(r, r') = N \int [S_z D^{(1)}(rs, r's')]_{s'=s} ds . \tag{7}$$

Both quantities depend only on the *spatial* coordinates of particle 1. The whole argument of the previous section can be repeated, leading to the conclusion that both P and Q_S can be decomposed into irreducible components of the *spatial* symmetry group $\mathfrak{G}$ according to Eqs. (3) to (5)[2]. Furthermore, the decomposition (3) is the *same* for P and Q_S.

3. The eigenvalue Eq. (2) can likewise be separated into a spatial and a spin part. For $p=1$ the natural 1-states were first introduced by Löwdin [3], who called them natural spin-orbitals (NSO's). Under the assumptions of Sect. 2 each NSO is the product of a spatial part times an α- *or* β-spinfunction. Furthermore for states[3] with $M_S=0$ the spatial part of every NSO is identical with a natural orbital (NO). These NO's φ_i are the eigenfunctions of the spinfree density matrix P, i.e. we have (cf. Eq. (2))

$$\hat{P}\varphi_i(r) = \int P(r, r')\, \varphi_i(r')dr' = \lambda_i \varphi_i(r) . \tag{8}$$

Thus every NO φ_i gives rise to two NSO's $\varphi_i\alpha$ and $\varphi_i\beta$ both of which have the same eigenvalue (which is also called the "occupation number") $\mu_i = \lambda_i/N$. The spin density matrix Q_S vanishes identically for this case.

4. It remains only to discuss under what conditions the NO's (and the spatial parts of the NSO's) can be classified according to irreducible representations of the spatial symmetry group $\mathfrak{G}$.

If the wave function of the system belongs to a *1-dimensional representation* Γ of $\mathfrak{G}$ (which need not be the totally-symmetric one), $D^{(1)}(x, x')$ transforms like the totally-symmetric representation $\Gamma^{(0)}$ of $\mathfrak{G}$ (since for this case $\Gamma \times \Gamma^* = \Gamma^{(0)}$, cf. Sect. 2.1). The density operator $\hat{D}^{(1)}$ therefore has the full symmetry of the spatial group $\mathfrak{G}$ and the spatial parts of the NSO's transform like one of the irred. repr. of $\mathfrak{G}$. If that representation is multidimensional, those NSO's that are partners for this representation have the same occupation number. The same statements hold for the NO's.

If the wave function belongs to a *degenerate representation* $\Gamma^{(\alpha)}$, the d_α^2 quantities $D^{(1)}_{\alpha i, \alpha j}$ transform according to $\Gamma^{(\alpha)} \times \Gamma^{(\alpha)*}$. This reducible representation (cf. Eq. (3)) contains the totally-symmetric one $\Gamma^{(0)}$ exactly once ($n_0 = 1$). The decomposition (4) can in this case be shown to have the form[4]

$$D^{(1)}_{\alpha i, \alpha i}(x, x') = D^{(1)}_{00}(x, x') + \cdots , \tag{9a}$$

$$D^{(1)}_{\alpha i, \alpha j}(x, x') = \quad 0 \quad + \cdots \qquad (i \neq j) . \tag{9b}$$

[2] Instead of (x, x') the argument is now the pair of spatial coordinates (r, r').

[3] For systems with an even number of particles we can always choose the state to have $M_S = 0$, whatever the value of S may be.

[4] To simplify the discussion we now assume that the group $\mathfrak{G}$ is simply reducible, i.e. that all n_γ in Eq. (3) are either 0 or 1. Then the index r in Eqs. (4) and (5) can be omitted.

In other words, while the totally-symmetric component $D^{(1)}_{00}$ occurs in the diagonal elements $i=j$ only, the nontotally-symmetric contributions $D^{(1)}_{\gamma k}$, indicated by dots in Eqs. (9a, b) contribute to both the diagonal and nondiagonal transition density matrices. None of them is therefore purely totally-symmetric and we cannot expect to get NSO's which are symmetry-adapted, i.e. which belong solely to an irred. repr. of $\mathfrak{G}$. The same situation obtains for the spinfree quantities $P_{\alpha i, \alpha j}(r, r')$ and the NO's $\varphi_i(r)$.

5. There are two ways out of this dilemma. Either one chooses the highest possible subgroup $\mathfrak{G}'$ of $\mathfrak{G}$ with respect to which all wave functions $\Psi_{\alpha i}$ (α fixed, $i=1, 2 \dots d_\alpha$) belong to one-dimensional representations. The spatial parts of the NSO's and the NO's are then symmetry-adapted to irred. repr. of this "effective" symmetry group $\mathfrak{G}'$.

On the other hand one can use the totally-symmetric part $D^{(1)}_{00}$ of $D^{(1)}$ or P for the construction of natural orbitals. These SANO's, as they are called, are then symmetry-adapted to the full symmetry group $\mathfrak{G}$. The connection between the SANO's and the NO's is however not a simple one in the general case (see Sect. 4.2).

3. The First-Order-Density Matrix for Linear Molecules

To simplify the discussion we will make the assumption, that the wave functions used describe a pure spin state with $M_S=0$. We then need only consider the spinfree density matrix P and its eigenfunctions, the NO's.

The spatial symmetry group is either $C_{\infty v}$ or $D_{\infty h}$. Now $D_{\infty h}=C_{\infty v}\times C_i$ since the inversion operation i commutes with all elements of $C_{\infty v}$. It is therefore sufficient to consider the group $C_{\infty v}$ only; the results obtained can be trivially extended to linear molecules having a center of inversion.

The irred. repr. of $C_{\infty v}$ are collected in the following table of characters.

If the wave function Ψ transforms like Σ^+ or Σ^-, then according to sect. 2.4 $P(r, r')$ transforms according to the totally-symmetric representation Σ^+.

As an illustration for one of the twofold-degenerate representations of the Table let us consider a Π-state. There are now two wave functions, say Ψ_+ and Ψ_-, for the same energy, which are transformed into each other on application of the reflection $\sigma_v^{x,z}$ in the x, z-plane

$$\sigma_v^{xz}\Psi_+=\Psi_-, \qquad \sigma_v^{xz}\Psi_-=\Psi_+ . \tag{10}$$

Table. *Character table of the group $C_{\infty v}$*

Irr. repr.	E	$C_\varphi, C_{-\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	−1
Π	2	$2\cos\varphi$	0
⋮	⋮	⋮	⋮
Λ	2	$2\cos\Lambda\varphi$	0
⋮	⋮	⋮	⋮

If we introduce cylindrical coordinates $\varphi_i, \varrho_i, z_i$ for all electrons, then

$$\Psi_+(r_1 \dots r_N) = e^{i\varphi_1} F(\varrho_1 z_1, \varphi_2 - \varphi_1 \varrho_2 z_2, \dots \varphi_N - \varphi_1 \varrho_N z_N) \tag{11a}$$

and from (7)

$$\Psi_-(r_1 \dots r_N) = e^{-i\varphi_1} F(\varrho_1 z_1, \varphi_1 - \varphi_2 \varrho_2 z_2, \dots \varphi_1 - \varphi_N \varrho_N z_N). \tag{11b}$$

Since $d_\alpha = 2$, there are now $2^2 = 4$ density matrices. For P_{++} Eqs. (1), (6) and (11a) give[5]

$$P_{++} = e^{i(\varphi_1 - \varphi'_1)} N \int F(\varrho_1 z_1, \psi_2 \varrho_2 z_2, \dots) F^*(\varrho'_1 z'_1, \psi_2 + (\varphi_1 - \varphi'_1) \varrho_2 z_2 \dots) \mathrm{d}r_2 \dots \mathrm{d}r_N$$

where the relative angles $\psi_i = \varphi_i - \varphi_1$ have been introduced. P_{++} is therefore of the general form

$$P_{++}(r_1, r'_1) = e^{i(\varphi_1 - \varphi'_1)} f(\varphi_1 - \varphi'_1; \varrho_1 z_1 \varrho'_1 z'_1). \tag{12a}$$

In the same way one obtains

$$P_{--}(r_1, r'_1) = e^{-i(\varphi_1 - \varphi'_1)} f(-(\varphi_1 - \varphi'_1); \varrho_1 z_1 \varrho'_1 z'_1) \tag{12b}$$

and for the two transition density matrices

$$P_{+-}(r_1, r'_1) = e^{i(\varphi_1 + \varphi'_1)} g(\varphi_1 - \varphi'_1; \varrho_1 z_1 \varrho'_1 z'_1), \tag{12c}$$

$$P_{-+}(r_1, r'_1) = e^{-i(\varphi_1 + \varphi'_1)} g(-(\varphi_1 - \varphi'_1); \varrho_1 z_1 \varrho'_1 z'_1) \tag{12d}$$

with a different function g.

These four P's transform as $\Pi \times \Pi^*$ and Eq. (3) gives

$$\Pi \times \Pi^* = \Sigma^+ + \Sigma^- + \Delta. \tag{13}$$

It can easily seen from Eqs. (12) that P_{+-} and P_{-+} together span the Δ-component of (13). P_{++} and P_{--} are invariant against a rotation C_φ as applied to *both* φ_1 and φ'_1 but transform into each other for the reflection σ_v^{xz}. They do not yet belong to one of the irreducible representations of $C_{\infty v}$ as given in the Table. Each linear combination

$$P_{\Sigma^+} = \tfrac{1}{2}(P_{++} + P_{--}), \qquad P_{\Sigma^-} = \tfrac{1}{2}(P_{++} - P_{--})$$

is however transformed into itself and gives the remaining irreducible components of (13). Alltogether we have

$$P_{++} = (P_{\Sigma^+} + P_{\Sigma^-}), \qquad P_{--} = (P_{\Sigma^+} - P_{\Sigma^-}), \qquad P_{+-} = P_\Delta, \qquad P_{-+} = P_{\bar{\Delta}} \tag{14}$$

which illustrates the general decomposition of Eqs. (9a, b). These results can be modified if the wave function belongs to one of the other degenerate irr. reprs. "Λ" of the Table. The transition densities P_{+-} and P_{-+} now span the irr. repr. "2Λ" and a factor Λ occurs in all exponentials of Eqs. (11) and (12). The extension to D_∞-symmetry is trivial. The wave function belongs either to Γ_g or Γ_u with

[5] The $+$ and $-$ signs now take the place of the indices i, j, k in our previous equations which number the different subspecies.

respect to the inversion group C_i. Because of

$$\Gamma_g \times \Gamma_g = \Gamma_u \times \Gamma_u = \Gamma_g$$

the density matrix always belongs to Γ_g. All irreducible components in Eqs. (13) and (14) are therefore of g-species.

4. Symmetry Properties of the NO's of Linear Molecules

1. The wave function belongs to a 1-dimensional representation.

For linear molecules this is the case for a wave function of Σ^+- or Σ^--species. According to Sect. 2.4 the spinfree density matrix then belongs to the totally-symmetry representation Σ^+. The NO's are therefore symmetry-adapted to the full group $C_{\infty v}$, and can be classified as being of σ-, π-, δ-type[6]. σ-NO's are non-degenerate and real, whereas π-, δ-NO's are 2-fold degenerate, i.e. there are two NO's φ_i and φ_i^* with the same occupation number λ_i.

Now *any* first-order density matrix can be expanded in terms of its eigenfunctions

$$P(\boldsymbol{r}, \boldsymbol{r}') = \sum \lambda_i \varphi_i(\boldsymbol{r}) \, \varphi_i(\boldsymbol{r}')^* . \tag{15}$$

For the special case now considered this expansion can be split into sums over NO's of the same symmetry species

$$P(\boldsymbol{r}, \boldsymbol{r}') = \sum \alpha_i \sigma_i(\boldsymbol{r}) \, \sigma_i(\boldsymbol{r}')^* + \sum \beta_j (\pi_j(\boldsymbol{r}) \, \pi_j(\boldsymbol{r}')^* + \pi_j(\boldsymbol{r})^* \, \pi_j(\boldsymbol{r}')) + \cdots . \tag{16}$$

2. The wave function belongs to a degenerate representation.

Let us again consider as an example the case of a wave function for a Π-state. One would normally calculate the NO's from either one of the diagonal density matrices P_{++} or P_{--}. However, as we have seen, neither of them is by itself totally symmetric. The two procedures described in Sect. 2.5 lead to the following result.

If we reduce the symmetry from $C_{\infty v}$ to the effective symmetry group C_∞ (which has no mirror planes) the degenerate representation Π of $C_{\infty v}$ splits to give two different onedimensional repr. Π^+ and Π^- of C_∞; and the wave functions Ψ_+ and Ψ_- belong to Π^+ and Π^- respectively. The two irr. repr. Σ^+ and Σ^- of $C_{\infty v}$ coincide to give the totally-symmetric repr. Σ of C_∞. Instead of Eq. (13) we now have

$$\Pi^+ \times (\Pi^+)^* = \Pi^- \times (\Pi^-)^* = \Sigma .$$

We can therefore use either P_{++} or P_{--} to get NO's which can be classified as being of σ-, π^+-, π^- etc. type.

The other procedure is to use the totally-symmetric part P_{Σ^+} to obtain the symmetry-adapted natural orbitals (SANO's) mentioned before.

There is an interesting relation between the NO's and their occupation numbers obtained in these two different ways (see however the end of the Sect. 2), which can be derived as follows. Let φ_i^+ be an NO of D_{++} with occupation

[6] Here σ stands for σ^+; there can be no 1-particle functions of Σ^--species.

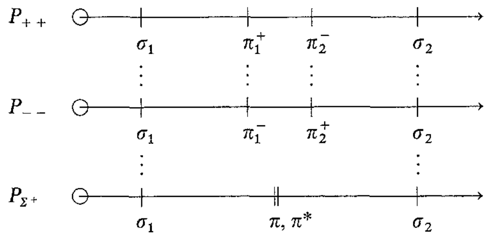

Fig. 1. Occupation number spectrum of P_{++}, P_{--} and P_{Σ^+} for a linear molecule in a Π-state

number λ_i^+

$$\hat{P}_{++}\varphi_i^+ = \lambda_i^+ \varphi_i^+ . \tag{17}$$

Then (σ_v stands for the special mirror plane σ_v^{xz} of Eq. (10))

$$\sigma_v(\hat{P}_{++}\varphi_i^+) = (\sigma_v \hat{P}_{++}\sigma_v^{-1})(\sigma_v\varphi_i^+) = \lambda_i^+(\sigma_v\varphi_i^+) .$$

Now comparison of Eqs. (12a) and (12b) shows that $(\sigma_v\hat{P}_{++}\sigma_v^{-1}) = (\hat{P}_{--})$. Therefore

$$\hat{P}_{--}(\sigma_v\varphi_i^+) = \lambda_i^+(\sigma_v\varphi_i^+) . \tag{18}$$

We therefore have following relationship:

If $\varphi_i(\varphi, \varrho, z)$ is an NO of P_{++} with occupation number λ_i^+, then $\sigma_v\varphi_i = \varphi_i(-\varphi, \varrho, z)$ is an NO of P_{--} with the same occupation number and vice versa.

This means that the σ-NO's (for which $\sigma_v\varphi = \varphi$) of P_{++}, P_{--} and also the σ-SANO's of P_{Σ^+} are identical with the same occupation number. For every π^+-NO π_j of P_{++}, $\sigma_v\pi_j = \pi_j^*$ is a π^--NO of P_{--} with the same occupation number and for every π^--NO, $\pi_k'^*$ of P_{++} there exists an NO $\sigma_v\pi_k'^* = \pi_k'$ of P_{--} of π^+-type, which has the same occupation number. These relations are illustrated in the occupation number spectrum of Fig. 1.

There does not seem to be any such simple connection between the SANO's of π-, ... type and the π^+-, π^-- ... NO's of P_{++} (or P_{--}) for the following rather subtle reason. For $P_{++}(\boldsymbol{r}, \boldsymbol{r}')$ the expansion (15) takes the form

$$P_{++}(\boldsymbol{r}, \boldsymbol{r}') = \sum \alpha_i \sigma_i(\boldsymbol{r})\, \sigma_i(\boldsymbol{r}')^* + \sum \beta_j \pi_j(\boldsymbol{r})\, \pi_j(\boldsymbol{r}')^* + \sum \gamma_k \pi_k'(\boldsymbol{r})^*\, \pi_k'(\boldsymbol{r}') + \cdots \tag{19}$$

in which the sum (15) over NO's has been split into sums over NO's of the same symmetry species of C_∞. Now different NO's are orthogonal, since P_{++} is a hermitian operator. In particular we have

$$(\pi_m, \pi_n) = (\pi_m', \pi_n') = \delta_{m,n} , \tag{20a}$$

$$(\pi_j, \pi_k'^*) = 0, \quad \text{all } j, k , \tag{20b}$$

but in general

$$(\pi_j, \pi_k') \neq 0 . \tag{20c}$$

Using the relation between the NO's of P_{++} and P_{--} we can get the NO-expansion of P_{--} directly from Eq. (19)

$$\begin{aligned} P_{--}(\boldsymbol{r}, \boldsymbol{r}') = \sum \alpha_i \sigma_i(\boldsymbol{r})\, \sigma_i(\boldsymbol{r}')^* + \sum \beta_j \pi_j(\boldsymbol{r})^*\, \pi_j(\boldsymbol{r}') \\ + \sum \gamma_k \pi_k'(\boldsymbol{r})\, \pi_k'(\boldsymbol{r}')^* + \cdots \end{aligned} \tag{21}$$

and from (14), (19), and (21)

$$P_{\Sigma^+}(\boldsymbol{r},\boldsymbol{r}') = \sum \alpha_i \sigma_i(\boldsymbol{r})\, \sigma_i(\boldsymbol{r}')^* + \sum_j \beta_j/2\, [\pi_j(\boldsymbol{r})\, \pi_j(\boldsymbol{r}')^* + \pi_j(\boldsymbol{r})^*\, \pi_j(\boldsymbol{r}')] + \sum_k \gamma_k/2\, [\pi'_k(\boldsymbol{r})\, \pi'_k(\boldsymbol{r}')^* + \pi'_k(\boldsymbol{r})^*\, \pi'_k(\boldsymbol{r}')] + \cdots. \tag{22}$$

If this expansion would be of the form (15) with *orthogonal* φ_i, we could then simply read off the eigenfunctions of P_{Σ^+} (i.e. the SANO's) and their occupation numbers. Now each σ_i is orthogonal to all other orbitals in (22) and is therefore a SANO as well as an NO of both P_{++} and P_{--}. The π-orbitals in the second sum are orthogonal among themselves as are the π'-orbitals of the third sum (cf. Eq. (20a)) but a π_j need not be orthogonal to any of the π'_k-orbitals (cf. Eq. (20c)). In order to get the + component of a π-SANO from (22), we first have to solve a certain secular equation resulting in a mixture

$$\pi = \sum a_j \pi_j + \sum b_k \pi'_k. \tag{23a}$$

The – component is then given by the conjugate complex expression

$$\pi^* = \sum a_j^* \pi_j^* + \sum b_k^* \pi_k'^*. \tag{23b}$$

Both π and π^* have the same eigenvalue, which can be determined from the secular equation together with the coefficients a_j and b_k.

We have seen, that for molecules of $D_{\infty h}$-symmetry the density matrix is always of the species Γ_g. It therefore has the full symmetry of the group C_i and the NO's are symmetry-adapted, i.e. they are *either g* or *u*.

5. The NO's and the Natural Expansion of the Wave Function for 2-Electron Molecules

For 2-electron systems the spatial part of the wave function must be either symmetric (for $S=0$) or antisymmetric (for $S=1$) against interchange of the two electrons. This can lead to degeneracies of the occupation numbers in addition to those resulting from the symmetry species of the NO's (cf. Eqs. (16, 19, 21 and 22)).

1. The wave function belongs to a 1-dimensional representation.

For a general $2N$-electron wave function the density matrix is then given by Eq. (16). For a 2-electron wave function we get different results for the subcases ${}^1\Sigma_g^+, {}^3\Sigma_g^+, {}^1\Sigma_u^+ \ldots$. To see how this comes about, we consider the "natural expansion", i.e. the expansion of the wave function into configurations built from its own NO's.

${}^1\Sigma_g^+$-species: Here the natural expansion is of the form

$$\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_i c_i \varphi_i(\boldsymbol{r}_1)\, \varphi_i(\boldsymbol{r}_2)^* \tag{24a}$$

$$= \sum a_i \sigma_i(\boldsymbol{r}_1)\, \sigma_i(\boldsymbol{r}_2)^* + \sum b_j(\pi_j(\boldsymbol{r}_1)\, \pi_j(\boldsymbol{r}_2)^* + \pi_j(\boldsymbol{r}_1)^*\, \pi_j(\boldsymbol{r}_2)) + \cdots \tag{24b}$$

which, with the use of Eqs. (1) and (6) leads to the general expansions (15) (with $\lambda_i = 2c_i^2$) and (16) (with $\alpha_i = 2a_i^2$, $\beta_j = 2b_j^2, \ldots$) of the density matrix P. In this case there are no additional degeneracies.

${}^3\Sigma_g^+$-species: Here the natural expansion must reflect the required antisymmetric behaviour against interchange of particle numbers. As was shown by

Löwdin and Shull [4], instead of (24) we now have

$$\Psi(\boldsymbol{r}_1\boldsymbol{r}_2)=\sum c_i(u_i(\boldsymbol{r}_1)\,v_i(\boldsymbol{r}_2)^*-v_i(\boldsymbol{r}_1)^*\,u_i(\boldsymbol{r}_2)) \tag{25a}$$

where all orbitals u_i, v_j are mutually orthogonal. Furthermore u_i and v_i belong to the *same* symmetry subspecies [7] of $D_{\infty h}$. Written in detail, Eq. (25a) takes the form

$$\Psi=\sum a_i(\sigma_i\sigma_i'-\sigma_i'\sigma_i)+\sum b_j(\pi_j\pi_j'^*-\pi_j'^*\pi_j+\pi_j^*\pi_j'-\pi_j'\pi_j^*)+\cdots \tag{25b}$$

where from now on we omit the arguments $\boldsymbol{r}_1, \boldsymbol{r}_2$ which always occur in the order $\boldsymbol{r}_1, \boldsymbol{r}_2$ reading from left to right. The density matrix for this wave function is (the order of the arguments being $\boldsymbol{r}, \boldsymbol{r}'$)

$$P=\sum \alpha_i(\sigma_i\sigma_i^*+\sigma_i'\sigma_i'^*)+\sum \beta_j(\pi_j\pi_j^*+\pi_j^*\pi_j+\pi_j'\pi_j'^*+\pi_j'^*\pi_j')+\cdots \tag{26}$$

with 2-fold degenerate occupation numbers $\alpha_i=2a_i^2$ for the σ-NO's and 4-fold degenerate ones $\beta_j=2b_j^2$ for the π- and other NO's. Comparison with Eq. (16) shows an overall *doubling* of the degeneracy.

${}^1\Sigma_u^+$-species: The same doubling occurs also for this case, although for a different reason. The natural expansion must reflect the required antisymmetric behaviour against inversion; at the same time it must be invariant against interchange of the two particles. These requirements lead to a natural expansion of the form

$$\Psi=\sum c_i(u_iv_i^*+v_i^*u_i) \tag{27a}$$

with mutually orthogonal NO's u_i and v_j. Now the pair u_i, v_i belongs to the same symmetry subspecies of $C_{\infty v}$, but they are of opposite parity. Written in detail, Eq. (27a) reads

$$\Psi=\sum a_i(\sigma_{ig}\sigma_{iu}+\sigma_{iu}\sigma_{ig})+\sum b_j(\pi_{jg}\pi_{ju}^*+\pi_{ju}^*\pi_{jg}+\pi_{jg}^*\pi_{ju}+\pi_{ju}\pi_{jg}^*)+\cdots. \tag{27b}$$

The density matrix is then given by Eq. (26) if we substitute

$$\sigma_i\to\sigma_{ig},\quad \sigma_i'\to\sigma_{iu},\quad \pi_i\to\pi_{ig},\quad \pi_i'\to\pi_{iu}\,. \tag{28}$$

${}^3\Sigma_u^+$-species: This case is just like ${}^3\Sigma_g^+$ except that u_i and its partner v_i are of opposite parity. The expansions of the wave function and the density matrix are obtained from (25b) and (26) by making the substitution (28).

${}^1\Sigma_g^-$-species: The doubling of the degeneracy occurs again, because the wave function must be antisymmetric against reflection in a plane containing the internuclear axis and at the same time be invariant against exchange of the two particles. These requirements lead to the natural expansion (27a) with u_i and v_i belonging to the same subspecies of $D_{\infty h}$.

Written out in detail we have

$$\Psi=\sum b_j\{\pi_j\pi_j'^*+\pi_j'^*\pi_j-\pi_j^*\pi_j'-\pi_j'\pi_j^*\}+\cdots. \tag{29}$$

There are no σ-NO's (see below). The density matrix expansion is given by Eq. (26) with $\beta_j=2b_j^2$ and $\alpha_j=0$.

[7] This is the reason for using the particular form of (25a), which differs somewhat from Ref. [4].

$^1\Sigma_u^-$-species: The same as $^1\Sigma_g^-$ but u_i and v_i of opposite parity. The wave function and the density matrix are obtained from (29) and (26) by omitting all σ-NO's and making the substitution (28).

$^3\Sigma_g^-$-species: This is the only case other than $^1\Sigma_g^+$, where no additional degeneracies arise, because the simple expansion (24a) is compatible with both requirements, that Ψ be antisymmetric against reflection and symmetric against particle interchange. Written in detail, the natural expansion takes the form

$$\Psi = \sum b_j \{\pi_j \pi_j^* - \pi_j^* \pi_j\} + \cdots \tag{30}$$

and the density matrix is given by Eq. (16) with $\alpha_i = 0$, $\beta_j = 2b_j^2$.

$^3\Sigma_u^-$-species: The symmetry requirements are the same as for $^3\Sigma_g^-$-states, except that the wave function must be antisymmetric against inversion. This additional requirement cannot be met by the natural expansion (30), and we must use Eq. (25a). The detailed form of the natural expansion for this case turns out to be

$$\Psi = \sum b_j \{\pi_j \pi_j'^* - \pi_j'^* \pi_j - \pi_j^* \pi_j' + \pi_j' \pi_j^*\} + \cdots \tag{31}$$

with the density matrix expansion given by Eq. (26) with $\alpha_j = 0$, $\beta_j = 2b_j^2$.

To summarize our results: All states other than those of $^1\Sigma_g^+$- and $^3\Sigma_g^-$-species of a 2-electron linear molecule have the degeneracies of the occupation numbers of their NO's doubled as compared to the general case of a $2N$-electron linear molecule. Furthermore Σ^--states of either multiplicity or parity have no σ-NO's. These results could have been anticipated from the fact, that only these two states can be obtained from configurations $(\pi)^2, (\delta)^2 \ldots$ of two *equivalent* electrons, and that no Σ^--states result from 2-electron configuration with either equivalent (σ^2) or nonequivalent $(\sigma\sigma')$ σ-electrons.

2. The wave function belongs to a degenerate representation.

It will be sufficient to consider the example of a Π-state, since states with $\Lambda = 2, 3 \ldots$ behave in exactly the same way. Using the conclusions at the end of the preceeding subsection as a guide, we expect a doubling of the degeneracy of the NO's of P_{++} or P_{--} for both singlet- or triplet-wave functions of either parity. The reason is, that a Π-state can be obtained only from configurations with 2 *inequivalent* electrons like $\sigma\pi, \pi\delta \ldots$ The natural expansion therefore must be of the general form (25a) for triplets or (27a) for singlets. Written out in detail we get for the $M_L = -1$ component

$$\Psi_- = \sum a_i (\sigma_i \pi_i^* \pm \pi_i^* \sigma_i) + \sum b_j (\pi_j' \delta_j^* \pm \delta_j^* \pi_j') + \cdots \tag{32a}$$

where the upper (lower) sign is for singlet-(triplet-) states. For a $\Pi_g(\Pi_u)$ state both functions of a pair u_i, v_i are of the same (of opposite) parity. The other component Ψ_+ can be obtained from (32) according to Eq (10)

$$\Psi_+ = \sum a_i (\sigma_i \pi_i \pm \pi_i \sigma_i) + \sum b_j (\pi_j'^* \delta_j \pm \delta_j \pi_j'^*) + \cdots. \tag{32b}$$

The density matrix for the wave function (32) is given by [8]

$$P_{--} = \sum 2|a_i|^2 (\sigma_i \sigma_i^* + \pi_i^* \pi_i) + \sum 2|b_j|^2 (\pi_j' \pi_j'^* + \delta_j^* \delta_j) + \cdots. \tag{33}$$

[8] Note that there are no cross terms between $\sigma_i \pi_i^*$ and $\delta_j \pi_j'$ of (32) because π_i and $\pi_j'^*$ are orthogonal by reason of symmetry (cf. Eq. (20b)).

A comparison with the general form of P_{--} given in Eq. (21) shows the following: In agreement with the general results obtained in Sect. 4.2, the NO's of P_{--} are symmetry-adapted to the effective group C_∞; i.e. they are of the species σ, π^+; π^-, δ^+; ... However we have a degeneracy not present in Eq. (21), since each σ-NO is paired with a π^--NO; each π^+-NO with a δ^--NO etc.

Taking the conjugate complex of Eq. (33) gives the expansion for P_{++} (cf. Eq. (20))

$$P_{++} = \sum 2|a_i|^2(\sigma_i\sigma_i^* + \pi_i\pi_i^*) + \sum 2|b_j|^2(\pi_j'^*\pi_j' + \delta_j\delta_j^*) + \cdots \tag{34}$$

and half of the sum of Eqs. (33) and (34) gives the totally symmetric component of the transition density matrices for a Π-state

$$\begin{aligned} P_{\Sigma^+} = &\sum |a_i|^2(2\sigma_i\sigma_i^* + \pi_i^*\pi_i + \pi_i\pi_i^*) \\ &+ \sum 2|b_j|^2(\pi_j'\pi_j'^* + \pi_j'^*\pi_j' + \delta_j^*\delta_j + \delta_j\delta_j^*) + \cdots . \end{aligned} \tag{35}$$

We first note that the difficulty mentioned in Sect. 4.2 arising from the non-orthogonality of the π_i- and π_j'-orbitals (cf. Eq. (20c)) is also present here. A comparison of Eqs. (22) and (34) leads to the following differences: In the general case σ-SANO's are nondegenerate. π-, δ- ... SANO's, formed as a mixture of the π_j- and π_k'-orbitals according to Eqs. (23), have their symmetry-determined 2-fold degeneracy. For a 2-electron molecule however, after determining the correct linear combinations (cf. Eqs. (23)), each σ-SANO is paired with a 2-fold degenerate π-SANO to give a group of *three* orbitals with equal occupation number, each of the remaining π-SANO's is paired with a δ-type SANO giving a *four*fold degenerate group etc.

6. Comparison with NO-Calculations for Linear Molecules

There are quite a number of determinations of NO's of linear molecules available in the literature [6–11]. In almost all cases, however, the calculations are performed for the $^1\Sigma^+$-ground state only. An exception is the work of Rothenberg and Davidson [5], who determined the NO's of CI-wave functions of the H_2-molecule for a number of excited states of various symmetry species. It should be noted, that for states with Π- or Δ-species, these authors use the density matrix P_{++}. A comparison of the "natural configurations" in their tables *IIA – G* with the results of Sect. 5 of this paper shows that the degeneracies of the numerically determined NO's in [5] agree with those obtained from the symmetry considerations of this paper. In particular, attention is drawn to the fact that for the lowest $^1\Pi_u$-state Rothenberg and Davidson find the first three terms of the natural expansion of Ψ_+ to be (cf. our Eq. (32b))

$$(1\sigma_g 1\pi_u + 1\pi_u 1\sigma_g),$$
$$(1\sigma_u 1\pi_g + 1\pi_g 1\sigma_u),$$
$$(1\pi_u'^* 1\delta_g + 1\delta_g 1\pi_u'^*),$$

where the orbital $1\pi_u'$ is *not* orthogonal to $1\pi_u$ (compare Figs. 8 and 10 of [5]). This result, which has been obtained purely numerically, illustrates the point mentioned in Sect. 4 and 5.2 regarding these orbitals.

In conclusion the author would like to express his wish, that NO- and SANO-calculations for linear molecules with more than two electrons in nontotally-symmetric states of which he might not be aware of, could be brought to his attention.

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