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Valency Structures for N_2O_4

By

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Two alternative sets of valency structures are suggested for N_2O_4. They arise because its wave function can be expanded as a linear combination of either orthogonal or non-orthogonal basis functions. These bases imply varying amounts of delocalization of oxygen lone-pair electrons into an antibonding orbital between the nitrogen atoms. The non-orthogonal expansion implies fewer significant structures, the most important of which is covalent and *apparently* violates the octet rule for first row elements. This structure, however, better describes the NO bonds than do three covalent structures which have considerable weight arising from the orthogonal expansion.

Zwei Sätze von Valenzstrukturen werden für N_2O_4 angenommen. Sie entstehen dadurch, daß seine Wellenfunktion als Linearkombination von entweder zueinder orthogonalen oder nicht orthogonalen Basisfunktionen dargestellt werden kann. Diese Darstellungen bedingen unterschiedlich starke Delokalisierung von Elektronen aus einsamen Elektronenpaaren am Sauerstoff in ein antibindendes Orbital zwischen den Stickstoffatomen. Die nicht orthogonale Darstellung enthält weniger Strukturen von Gewicht, von denen die wichtigste eine kovalente ist und *scheinbar* die Oktettregel für die Elemente der ersten Periode verletzt. Diese Struktur beschreibt jedoch die NO-Bindung besser als drei kovalente Strukturen, die aus der orthogonalen Darstellung mit wesentlichem Gewicht resultieren.

Nous représentons le N_2O_4 par deux jeux alternatifs de structures en composant sa fonction d'onde linéairement de fonctions de base orthogonales au premier cas, non-orthogonales à l'autre. Ces bases impliquent de délocalisations différentes d'électrons de paires libres d'oxygène en dedans d'une orbitale antiliante entre les nitrogènes. Le développement non-orthogonale implique moins de structures importantes; celle à poids maximal est covalente et semble manquer à la règle d'octet pour la première période. Mais elle décrit mieux les liaisons NO que le font trois structures à poids considérable dans le développement orthogonal.

Introduction

The classical valency structural representation for N_2O_4 is a hybrid of structure I* and three other structures involving π-electron resonance [*5*]. It appears to be unsatisfactory for the following reasons:

1. It is well known [*2, 3, 5, 7, 8, 16*] that the NN bond of N_2O_4 is considerably longer and weaker than that of N_2H_4, yet I represents the NN bond as a single bond. Repulsion between adjacent positive charges cannot be responsible for the

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* An expression such as "structures of type I" used subsequently throughout the paper means that there are (in this treatment) other equivalent hybrid structures in addition to the one shown. With N_2O_4, the π-electron distribution is probably better represented by that of the non-paired structure Ia rather than by that of the hybrid of structures of type I. However for the present purpose it is satisfactory to use I, and so avoid confusion between π-electrons and any unpaired σ-electrons in the NO bond regions. A similar reason obtains for not using non-paired π-electron distributions for the other N_2O_4, NO_2^+, NO_2 and NO_2^- structures considered. The "three-electron bond" structures for NO and NO_2 are shown as represented by Green and Linnett [*7*] without spin designations.

long bond, because such charges must be present in $N_2H_6^{++}$, and for this species, the NN bond is shorter [*3*, *10*] than that of N_2H_4.

2. A hybrid of "three-electron bond" structures VIIIa and VIIIb has been suggested [*7*, *11*, *15*, *16*] to reasonably represent the NO_2 electron distribution. In the same way as X has been considered [*7*] to be a physically more realistic description of NO than is XI, VIII for NO_2 better describes its NO bonds and ONO angles than does IX, immediately implying that their properties are intermediate between those for NO_2^+ (XII) and NO_2^- (XIII) [*16*]. The NO bonds and ONO angles of N_2O_4 are very similar to those of NO_2 [*3*, *16*], but I does not suggest this.

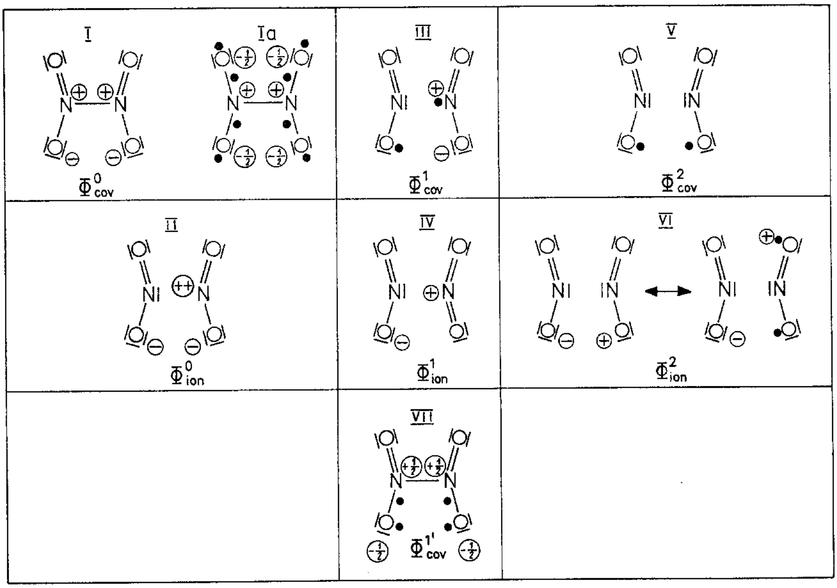
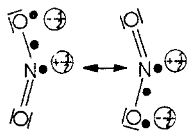
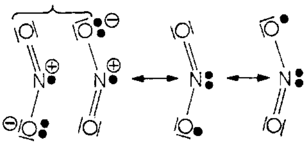


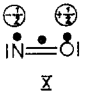
Fig. 1. Valency structures for N_2O_4. The Φ are the wave functions representing the structures. The superscripts 0, 1, or 2, of the Φ indicate the number of oxygen electrons that have effectively delocalized into the antibonding NN σ-orbital. The subscripts "cov" or "ion" imply either NO_2 NO_2, or NO_2^- NO_2^+ and NO_2^+ NO_2^- type electron distributions



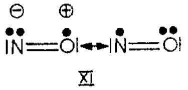
VIII a VIII b



IX a IX b IX c

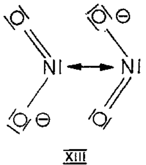


X



XI

XII



XIII

Therefore there must be other types of N_2O_4 valency structures apart from I, and the purpose of this paper is to find them by considering a recently suggested explanation for the above N_2O_4 properties [3], and then to calculate their weights.

Types of N_2O_4 Valency Structures

In a molecular orbital study of N_2O_4 [2, 3], the long NN bond was attributed to considerable delocalization of some of the oxygen lone-pair electrons into an antibonding σ-orbital between the nitrogen atoms. Therefore, in addition to I, covalent structures III and V (which involve delocalization of one and two oxygen lone-pair electrons) may also be significant ground-state structures. However, as for the NO_2 structures of IX, these structures give little insight into the nature of the NO bonds. A more satisfactory covalent structure may be obtained from the following considerations.

The N_2O_4 structures I, III, and V may be constructed by juxtapositioning two NO_2 structures with the various electron distributions of IX. If we do the same for two NO_2 structures of type VIII, we shall obtain the N_2O_4 structure VII, which (as does VIII) implies NO bond and ONO angle properties intermediate between those of NO_2^+ and NO_2^-. VII also suggests that the NN bond should be long and weak. This is because the two unpaired electrons of the NO bonds* of VII may be considered to be represented as "half delocalized" into the antibonding σ-orbital between the nitrogen atoms (the corresponding bonding σ-orbital being doubly filled, forming the $N-N$ bond of this structure). With respect to the NN bond, two electrons half delocalized should be similar in effect to one electron completely delocalized, as in III.

Structures of type VII have nine electrons "around" each of the nitrogen atoms. This does not constitute a true violation of the octet rule for first row elements, because the wave function for these structures may be shown to be a linear combination of the wave functions for structures of types I, III and V. For these, no such violation obtains.

To calculate the weights of these various N_2O_4 valency structures, it is necessary to express the N_2O_4 ground-state wave function (Ψ) as a linear combination of the wave functions for these various structures in such a manner that Ψ reproduces the experimental NN σ-bond order of about 0.4**. It will be shown below that Ψ may be expressed as a linear combination of either orthogonal or non-orthogonal basis functions. Each of these expansions implies covalent structures of types I, V and either III or VII, together with ionic structures of types II, IV and VI. The non-orthogonal expansion of Ψ suggests that VII is the most important type of structure.

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* The effect on the NN bond of the four π-electrons of the NO bonds of structures I – VII is different. Between the nitrogen atoms of these structures are two vacant bonding and antibonding π-electron orbitals. Two of the four electrons must therefore be NN bonding and the other two are NN antibonding. Their resultant effect on the NN bond is therefore non-bonding.

** Such an estimate may be obtained from a NN bond order – bond length curve. NN single, double and triple bond lengths [17] of 1.48 Å, 1.24 Å and 1.10 Å lie on the curve $R_{NN} = 1.48 - 0.80 \log_{10} P_{23}$. P_{23} is the total NN bond order. $R_{NN} = 1.75$ Å for N_2O_4 [19] corresponds to $P_{23} = 0.46$ which is a σ-bond order, because for this curve, the NN π-bond order becomes zero at 1.48 Å. However, the N_2O_4 σ-bond order should be a little less than 0.46 since a small amount of NN π-bonding obtains [9]. A value around 0.4 seems reasonable.

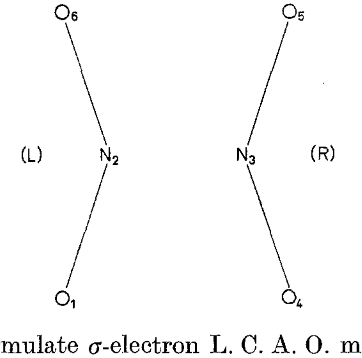
The wave functions for the various N_2O_4 structures are the products (antisymmetrized if necessary) of the wave functions for two non-interacting NO_2 (or NO_2^+ and NO_2^-) moieties obtaining to each structure. To construct Ψ, a V. E. S. C. F. molecular orbital procedure (see appendix 2) with configuration interaction is used. As with H_2 [6], configuration interaction reduces the importance of ionic structures in the representation at all distances, i. e. makes some allowance for electron correlation.

For the subsequent sections, the methods used to transform and expand determinantal wave functions are described in appendix 1.

σ-Electron Atomic Orbitals and Valency Structure Wave Functions

The previously reported [2, 3] V. E. S. C. F. molecular orbital treatment of N_2O_4 involved consideration of ten mobile σ-electrons (hereafter referred to as σ-electrons; these are the two $2p\bar{\pi}$-electrons from each oxygen atom of I and the two hybrid electrons which are assigned to the NN bond of the same structure) and eight mobile $2p\pi$-electrons*. The remaining electrons were assumed to be localized as in I. Structures such as those of VIII and IX for NO_2 imply four $2p\pi$-electrons, since it is known that the odd-electron of NO_2 occupies a σ- rather than a π-type molecular orbital [1, 8, 9, 13, 16]. Therefore, the π-electron distributions implied by I, VIII and IX (and all other structures of Fig. 1) are identical (and for the present purpose, they may be assumed to be so in the real NO_2 and N_2O_4 systems). It is then only the σ-electron distributions of these structures which differ, and therefore consideration will be given to the wave functions describing them.

The σ-electron atomic orbitals are the oxygen $2p\bar{\pi}$-orbitals, $\bar{\pi}_1$, $\bar{\pi}_4$, $\bar{\pi}_5$ and $\bar{\pi}_6$, and the nitrogen hybrid orbitals, h_2 and h_3. These are shown in reference [2]. It is convenient here to formulate σ-electron L. C. A. O. molecular orbitals for two NO_2 moieties, labelled L and R. These orbitals are



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* WILLIAMS [20, 21] has recently discussed double bonding and anti-bonding effects in various saturated compounds, and has suggested that in order to prevent violation of the octet rule, it is necessary to invoke Hückel's assumption that the filling of antibonding orbitals of first row elements involves the use of higher orbitals. This assumption is not made here, and has not been made in some other studies, e. g. [18] vinyl chloride, in which the chlorine π-electrons are partially delocalized into an antibonding π-orbital between the carbon atoms. The present work shows that by using only atomic orbitals with principal quantum number $n = 2$, covalent structures which apparently violate the octet rule may be constructed and are sometimes useful.

$$a_L = \frac{n_L + \varkappa h_2}{\sqrt{1+\varkappa^2}}\,;\; n_L^* = 2^{-\frac{1}{2}}(\overline{\pi}_1 - \overline{\pi}_6);\; a_L^* = \frac{\varkappa n_L - h_2}{\sqrt{1+\varkappa^2}}\,; \tag{1}$$

$$a_R = \frac{n_R + \varkappa h_3}{\sqrt{1+\varkappa^2}}\,;\; n_R^* = 2^{-\frac{1}{2}}(\overline{\pi}_4 - \overline{\pi}_5);\; a_R^* = \frac{\varkappa n_R - h_3}{\sqrt{1+\varkappa^2}}\,; \tag{2}$$

with $\varkappa = 1$ for VIII (see appendix 3), and

$$n_L = 2^{-\frac{1}{2}}(\overline{\pi}_1 + \overline{\pi}_6);\; n_R = 2^{-\frac{1}{2}}(\overline{\pi}_4 + \overline{\pi}_5)\,; \tag{3}$$

The antisymmetrized product wave functions for the σ-electrons of the various N_2O_4 structures of types I – VII are the following (a normalized determinant such as $|\,a_L^2\, n_L^{*2}\, a_L^{*\alpha}\,|$ for NO_2 being an abbreviation for* $|\,a_L(1)^\alpha\, a_L(2)^\beta\, n_L^*(3)^\alpha\, n_L^*(4)^\beta\, a_L^*(5)^\alpha\,|$):

$$\Phi^0_{\text{cov}} = \frac{1}{\sqrt{2}}\left(\,|\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_2^\alpha\,h_3^\beta\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,| + |\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,h_3^\alpha\,h_2^\beta\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,|\,\right) \tag{4}$$

$$\Phi^0_{\text{ion}} = \frac{1}{\sqrt{2}}\left(\,|\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_2^2\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,| + |\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_3^2\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,|\,\right) \tag{5}$$

$$\Phi^2_{\text{cov}} = \frac{1}{\sqrt{2}}\left(\,|\,n_L^{*\alpha}\,\overline{\pi}_1^\beta\,\overline{\pi}_6^\beta\,h_2^2\,h_3^2\,\overline{\pi}_4^\alpha\,\overline{\pi}_5^\alpha\,n_R^{*\beta}\,| + |\,n_R^{*\alpha}\,\overline{\pi}_4^\beta\,\overline{\pi}_5^\beta\,h_3^2\,h_2^2\,\overline{\pi}_1^\alpha\,\overline{\pi}_6^\alpha\,n_L^{*\beta}\,|\,\right) \tag{6}$$

$$\Phi^2_{\text{ion}} = \frac{1}{\sqrt{2}}\left(\,|\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_2^2\,h_3^2\,n_R^{*2}\,| + |\,n_L^{*2}\,h_2^2\,h_3^2\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,|\,\right) \tag{7}$$

$$\begin{aligned}\Phi^1_{\text{cov}} = \frac{1}{2}\big(\,&|\,n_L^{*\alpha}\,\overline{\pi}_1^\beta\,\overline{\pi}_6^\beta\,h_2^2\,h_3^\alpha\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,| + |\,n_L^{*\beta}\,\overline{\pi}_1^\alpha\,\overline{\pi}_6^\alpha\,h_2^2\,h_3^\beta\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,| \\ &- |\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_2^\alpha\,h_3^2\,\overline{\pi}_4^\beta\,\overline{\pi}_5^\beta\,n_R^{*\alpha}\,| - |\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_2^\beta\,h_3^2\,\overline{\pi}_4^\alpha\,\overline{\pi}_5^\alpha\,n_R^{*\beta}\,|\,\big)\end{aligned} \tag{8}$$

$$\begin{aligned}\Phi^1_{\text{ion}} = \frac{1}{2}\big(\,&|\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_2^2\,h_3^\alpha\,\overline{\pi}_4^\beta\,\overline{\pi}_5^\beta\,n_R^{*\alpha}\,| + |\,\overline{\pi}_1^2\,\overline{\pi}_6^2\,h_2^2\,h_3^\beta\,\overline{\pi}_4^\alpha\,\overline{\pi}_5^\alpha\,n_R^{*\beta}\,| \\ &- |\,n_L^{*\alpha}\,\overline{\pi}_1^\beta\,\overline{\pi}_6^\beta\,h_2^\alpha\,h_3^2\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,| - |\,n_L^{*\beta}\,\overline{\pi}_1^\alpha\,\overline{\pi}_6^\alpha\,h_2^\beta\,h_3^2\,\overline{\pi}_4^2\,\overline{\pi}_5^2\,|\,\big)\end{aligned} \tag{9}$$

$$\Phi^{1'}_{\text{cov}} = \frac{1}{\sqrt{2}}\left(\,|\,a_L^2\,n_L^{*2}\,a_L^{*\alpha}\,a_R^{*\beta}\,n_R^{*2}\,a_R^2\,| + |\,a_R^2\,n_R^{*2}\,a_R^{*\alpha}\,a_L^{*\beta}\,n_L^{*2}\,a_L^2\,|\,\right) \tag{10}$$

$\Phi^{1'}_{\text{cov}}$ is the wave function for the hybrid of structures of type VII because the NO_2 functions such as

$$\psi_L = |\,a_L^2\,n_L^{*2}\,a_L^{*\alpha}\,| \qquad \text{or} \qquad \psi_R = |\,a_R^2\,n_R^{*2}\,a_R^{*\alpha}\,| \tag{11}$$

may be shown (see appendix 3) to be wave functions describing the σ-electrons of the hybrid of the NO_2 structures of VIII.

In this work, differential overlap is neglected (see appendix 2). Therefore the functions (4) – (9) are orthogonal. However, the function $\Phi^{1'}_{\text{cov}}$ of (10) may be expressed as

$$\Phi^{1'}_{\text{cov}} = \frac{1}{2}\Phi^0_{\text{cov}} + \frac{1}{\sqrt{2}}\Phi^1_{\text{cov}} + \frac{1}{2}\Phi^2_{\text{cov}} \tag{12}$$

and is therefore not orthogonal to the other covalent functions.

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* The LONGUET-HIGGINS and POPLE [*12*] formulation of such functions for odd-electron systems is used here. α and β are spin functions.

N_2O_4 σ-Electron Ground State Wave Function Ψ

Ψ will be approximated to by a linear combination of A. S. M. O. configuration wave functions (Φ_i), i. e.

$$\Psi = C_1\Phi_1 + C_2\Phi_2 + \cdots . \tag{13}$$

The Φ_i are singlets and of A_g symmetry. They are constructed from the following D_{2h} symmetry group molecular orbitals:

$$\sigma_1(a_g) = \frac{s_3 + \lambda s_1}{\sqrt{1+\lambda^2}} ; \; \sigma_2(b_{1u}) = \frac{s_4 + \mu s_2}{\sqrt{1+\mu^2}} ; \; \sigma_3(b_{2u}) = s_5 ;$$

$$\sigma_4(b_{3g}) = s_6 ; \; \sigma_5(a_g) = \frac{\lambda s_3 - s_1}{\sqrt{1+\lambda^2}} ; \; \sigma_6(b_{1u}) = \frac{\mu s_4 - s_2}{\sqrt{1+\mu^2}} ; \tag{14}$$

$s_1, s_2 \cdots s_6$ are the symmetry orbitals shown in diagram 1 of reference [*3*] and defined as

$$s_1 = 2^{-\frac{1}{2}}(h_2 + h_3) ; \; s_2 = 2^{-\frac{1}{2}}(h_2 - h_3) ; \; s_3 = 2^{-\frac{1}{2}}(n_L + n_R) ;$$

$$s_4 = 2^{-\frac{1}{2}}(n_L - n_R) ; \; s_5 = 2^{-\frac{1}{2}}(n_L^* + n_R^*) ; \; s_6 = 2^{-\frac{1}{2}}(n_L^* - n_R^*) . \tag{15}$$

The n_L, n_R, n_L^* and n_R^* are defined in (1), (2) and (3).

μ and λ are parameters ≥ 0, and for all configurations, are assumed here to have the values obtaining to the lowest energy configuration Φ_1. For this configuration, μ is a measure of the extent of delocalization of the oxygen s_4 electrons into the antibonding s_2 orbital between the nitrogen atoms. μ and λ can be related to the Hückel nitrogen electronegativity parameter, h_N^σ, and the NN bond resonance integral parameter, k_{NN}^σ, by means of the expressions

$$\mu = \frac{1}{2\sqrt{2}}\left[\sqrt{(h_N^\sigma - k_{NN}^\sigma)^2 + 8} + h_N^\sigma - k_{NN}^\sigma\right] , \tag{16}$$

$$\lambda = \frac{1}{2\sqrt{2}}\left[\sqrt{(h_N^\sigma + k_{NN}^\sigma)^2 + 8} + h_N^\sigma + k_{NN}^\sigma\right] . \tag{17}$$

h_N^σ and k_{NN}^σ are defined in terms of V. E. S. C. F. matrix elements in reference [*3*].

When two NO_2 molecules are infinitely separated, $k_{NN}^\sigma = 0$ and therefore $\mu = \lambda$, which in turn is equal to $\varkappa$ for the NO_2 molecular orbitals given by (1) and (2).

Since $\sigma_6(b_{1u})$ is the most antibonding molecular orbital (being both NN and NO antibonding [*3*]), the lowest energy configuration is

$$\Phi_1 = \left| \sigma_1(a_g)^2 \, \sigma_2(b_{1u})^2 \, \sigma_3(b_{2u})^2 \, \sigma_4(b_{3g})^2 \, \sigma_5(a_g)^2 \right| .$$

Using (A 4) of appendix 1 together with (14), Φ_1 may then be expressed as

$$\Phi_1 = \left| s_1^2 s_3^2 s_5^2 s_6^2 \left(\frac{s_4 + \mu s_2}{\sqrt{1+\mu^2}}\right)^2 \right| . \tag{18}$$

The ${}^1A_g$ configuration closest in energy to Φ_1 is that obtained when two electrons are raised from the $\sigma_5(a_g)$ to the $\sigma_6(b_{1u})$ molecular orbital. This configuration is

$$\Phi_2 = \left| \sigma_1(a_g)^2 \, \sigma_2(b_{1u})^2 \, \sigma_3(b_{2u})^2 \, \sigma_4(b_{3g})^2 \, \sigma_6(b_{1u})^2 \right|$$
$$= \left| s_2^2 s_4^2 s_5^2 s_6^2 \left(\frac{s_3 + \lambda s_1}{\sqrt{1+\lambda^2}}\right)^2 \right| . \tag{19}$$

The remaining ${}^1A_g$ configurations are too high in energy to be of much significance in the expansion of Ψ. For the present purpose, they may be neglected*. Ψ may then be approximated to as

$$\Psi = C_1 \Phi_1 + C_2 \Phi_2 \tag{20}$$

and may be expanded as a linear combination of the structure functions given by (4), (5), (6), (7) and (9), together with either (8) or (10). These two types of expansions of Ψ will be referred to in the following sections as orthogonal and non-orthogonal expansions respectively.

For (20), the NN σ-bond order, P_{23}^{σ}, is calculated from

$$P_{23}^{\sigma} = C_1^2 \left(\frac{1}{1+\mu^2}\right) - C_2^2 \left(\frac{1}{1+\lambda^2}\right) . \tag{21}$$

To obtain C_1 and C_2, the following configuration interaction matrix elements are required [*14*]:

$$\begin{aligned} \Delta E &= \langle \Phi_2 | \mathscr{H} | \Phi_2 \rangle - \langle \Phi_1 | \mathscr{H} | \Phi_1 \rangle \\ &= 2\,\mathscr{E}_6 - 2\,\mathscr{E}_5 - 4\,J_{56} + J_{55} + J_{66} + 2\,K_{56} , \end{aligned} \tag{22}$$

$$\langle \Phi_1 | \mathscr{H} | \Phi_2 \rangle = K_{56} . \tag{23}$$

$\mathscr{E}_5$ and $\mathscr{E}_6$ are the $\sigma_5(a_g)$ and $\sigma_6(b_{1u})$ molecular orbital energies for the Φ_1 configuration. The J_{ij} and K_{ij} are molecular coulomb and exchange integrals based on the same orbitals.

Non-orthogonal expansion of Ψ

Using (A 3) of appendix 1 together with (18) and (19), Φ_1 and Φ_2 may be expanded as linear combinations of non-orthogonal basis functions:

$$\Phi_1 = \frac{1}{1+\mu^2} [(1-\mu)\,\Phi_1^{\mu=0} + 2\,\mu\,\Phi_1^{\mu=1} + (\mu^2-\mu)\,\Phi_1^{\mu=\infty}] \tag{24}$$

$$\Phi_2 = \frac{1}{1+\lambda^2} [(1-\lambda)\,\Phi_2^{\lambda=0} + 2\,\lambda\,\Phi_2^{\lambda=1} + (\lambda^2-\lambda)\,\Phi_2^{\lambda=\infty}] . \tag{25}$$

The six basis functions of (24) and (25) are defined in appendix 4. By using methods similar to that described for $\Phi_1^{\mu=1}$ in the same appendix, they may be expressed in terms of the functions (4) – (7), (9) and (10) as

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* Four higher energy ${}^1A_g$ configurations may be constructed by raising two electrons to the σ_6 (b_{1u}) orbital from the $\sigma_4(b_{3g})$, $\sigma_3(b_{2u})$, $\sigma_2(b_{1u})$ and $\sigma_1(a_g)$ orbitals. A configuration constructed by raising one electron from the $\sigma_2(b_{1u})$ to the $\sigma_6(b_{1u})$ orbital will not interact with Φ_1 if the orbitals are self-consistent. For $\mu = 1$ (which seems to be approximately the value for N_2O_4) and the classical valence π-electron distribution, these configurations are calculated to lie 15.5, 15.1, 21.9, 35.4 and 12.8 ev above Φ_1. The energy of Φ_2 is only 6.8 ev. For NO_2, the configurations of (11) are of ${}^2A_1$ symmetry, and will not combine with the ${}^2A_1$ configurations arising from $a_L \rightarrow a_L^*$ or $a_R \rightarrow a_R^*$ excitations [*12*].

It is not necessary to consider other ${}^1A_g$ (or ${}^2A_1$ for NO_2) configurations which arise from any low energy $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$ electron orbital excitations, since these will involve basis functions which imply different π-electron distributions to those assumed in the present study. In any case, for N_2O_4, the first two types of configurations will combine to only a small extent with Φ_1 since the interconfigurational matrix elements are the molecular exchange integrals $K_{\sigma\pi}$, and these are of small magnitude. No change in the σ-electron wave function will result from combination of Φ_1 with the configurations resulting from only $\pi \rightarrow \pi^*$ excitations.

$$\Phi_1^{\mu=0} = \frac{1}{\sqrt{2}}(\Phi^0_{\text{ion}} + \Phi^0_{\text{cov}}) \; ; \quad \Phi_2^{\lambda=0} = \frac{1}{\sqrt{2}}(\Phi^0_{\text{ion}} - \Phi^0_{\text{cov}}) \; ; \tag{26}$$

$$\Phi_1^{\mu=\infty} = \frac{1}{\sqrt{2}}(\Phi^2_{\text{ion}} + \Phi^2_{\text{cov}}) \; ; \quad \Phi_2^{\lambda=\infty} = \frac{1}{\sqrt{2}}(\Phi^2_{\text{ion}} - \Phi^2_{\text{cov}}) \; ; \tag{27}$$

$$\Phi_1^{\mu=1} = \frac{1}{\sqrt{2}}(\Phi^{1'}_{\text{ion}} + \Phi^{1'}_{\text{cov}}) \; ; \quad \Phi_2^{\lambda=1} = \frac{1}{\sqrt{2}}(\Phi^{1'}_{\text{ion}} - \Phi^{1'}_{\text{cov}}) \; ; \tag{28}$$

and Ψ ultimately expanded in terms of these.

The basis function of (28)

$$\Phi^{1'}_{\text{ion}} = \frac{1}{\sqrt{2}}(\,|\,a_L^2\, n_L^{*2}\, a_L^{*2}\, a_R^2\, n_R^{*2}\,| + |\,a_L^2\, n_L^{*2}\, a_R^2\, n_R^{*2}\, a_R^{*2}\,|\,) \tag{29}$$

has not been previously described. It cannot be represented by a single type of valency structure. However, it may be expressed as

$$\Phi^{1'}_{\text{ion}} = \frac{1}{2}\Phi^0_{\text{ion}} + \frac{1}{\sqrt{2}}\Phi^1_{\text{ion}} + \frac{1}{2}\Phi^2_{\text{ion}} \; . \tag{30}$$

For (16) and (17), it has been shown that $\mu = \lambda$ when the NN internuclear distance (R_{NN}) equals ∞. This means that for this distance in (22), $\mathscr{E}_5 = \mathscr{E}_6$, $J_{55} = J_{56} = J_{66} = K_{56}$ and therefore $\Delta E = 0$. Since K_{56} is positive definite, solution of the secular equations for (20) leads to $C_1 = -C_2 = \frac{1}{\sqrt{2}}$. It follows that

$$\Psi = \frac{1}{1+\mu^2}[(1-\mu)\Phi^0_{\text{cov}} + 2\mu\Phi^{1'}_{\text{cov}} + (\mu^2-\mu)\Phi^2_{\text{cov}}] \; . \tag{31}$$

For $\mu = 1$, $\Psi \equiv \Phi^{1'}_{\text{cov}}$, which is the wave function for two NO_2 molecules infinitely separated (if electron exchange between the two NO_2 moieties is neglected) as well as for N_2O_4 structures of type II.

Ψ therefore correctly predicts the products of dissociation of N_2O_4. (The lowest energy configuration Φ_1 implies both covalent and ionic dissociation products for N_2O_4.)

As two NO_2 molecules approach each other, the resonance integral parameter k^{σ}_{NN} of (16) and (17) becomes non-zero. Therefore $\mu \neq \lambda$ and $\Delta E \neq 0$. It follows then that $C_1 \neq -C_2$. This means that as R_{NN} decreases, the ionic functions become increasingly important in the expansion of Ψ.

By assuming $\mu = 1$ when $R_{NN} = 1.75$ Å (the equilibrium value [*19*]), the results of calculations (described later in this paper) show that a value of the NN σ-bond order is obtained which is in satisfactory agreement with the experimental estimate of about 0.4. Further, for this value of μ (and others near it), by far the most significant function in the non-orthogonal expansion of Ψ is $\Phi^{1'}_{\text{cov}}$, which represents N_2O_4 structures of type VII.

Orthogonal Expansion of Ψ

If one prefers to represent NO_2 as IX, then a similar representation for N_2O_4 may be obtained by using orthogonal expansions for Φ_1 and Φ_2 in (20). Using (A 2) of appendix 1 together with (18) and (19), one obtains

$$\Phi_1 = \frac{1}{1+\mu^2}(\Phi_1^{\mu=0} + \sqrt{2}\mu\Phi_1^{\mu} + \mu^2\Phi_1^{\mu=\infty}) \tag{32}$$

$$\Phi_2 = \frac{1}{1+\lambda^2}(\Phi_2^{\lambda=0} + \sqrt{2}\lambda\Phi_2^{\lambda} + \lambda^2\Phi_2^{\lambda=\infty}) \; . \tag{33}$$

Expressions for four of the basis functions of (32) and (33) are given by (26) and (27). Φ_1^μ and Φ_2^λ are defined in appendix 4 and may be expressed as

$$\Phi_1^\mu = \frac{1}{\sqrt{2}}\left(\Phi^1_{\text{ion}} + \Phi^1_{\text{cov}}\right) \quad \text{and} \quad \Phi_2^\lambda = \frac{1}{\sqrt{2}}\left(\Phi^1_{\text{ion}} - \Phi^1_{\text{cov}}\right) . \tag{34}$$

Ψ of (20) may therefore be expanded as a linear combination of the orthogonal functions (4) – (9). (The same result may be obtained by substituting (12) for $\Phi^{1'}_{\text{cov}}$ in the non-orthogonal expansion of Ψ.)

Some Calculations of σ-Electron Wave Functions

For $R_{NN} = 1.75$ Å and using the V. E. S. C. F. molecular orbital procedure [*2*, *3*, *9*], four different σ-electron wave functions have been calculated for each of the orthogonal and non-orthogonal expansions of Ψ. These calculations assume

i. The classical valence π-electron distribution and an NN σ-bond order, P^σ_{23}, equal to 0.5 for the configuration Φ_1, i. e. $\mu = 1$.

ii. $P^\sigma_{23} = 0.5$ for Φ_1, $\mu = 1$ and the V. E. S. C. F. π-electron distribution which is self-consistent with respect to these (and therefore the σ-electron core charges are different from those of i).

iii. $P^\sigma_{23} = 0.4$ for Φ_1, $\mu = 1.22$ and the resulting self-consistent π-electron distribution.

iv. The V. E. S. C. F. σ- and π-electron distributions for Φ_1 calculated as described in reference [*2*]. These give values of 0.67 and 0.70 for the P^σ_{23} of Φ_1 and μ.

Since the above values of P^σ_{23} for Φ_1 are fixed in calculations i, ii and iii, it is necessary to choose a parameter in the σ-electron V. E. S. C. F. equations for Φ_1 such that the molecular orbitals obtained from their solution are self-consistent and able to reproduce these bond orders. In calculation iv, the V. E. S. C. F. value of P^σ_{23} (0.67) is too large (and can be little altered by configuration interaction – see Tab. 1). This seems to be [*9*] mainly due to an overestimate in the magnitude of the σ-electron core resonance integral, β^σ_{23}. Therefore β^σ_{23} has been chosen as the adjustable parameter in calculations i, ii and iii.

In Tab. 1, the main quantities necessary to calculate the σ-electron wave functions are listed. Tab. 4 of appendix 2 gives the values of the quantities necessary to solve the V. E. S. C. F. equations for calculation i. For calculations ii, iii and iv, their magnitudes are slightly different, and will be reported elsewhere.

Table 1

	I.	II.	III.	IV.
β^σ_{23} (ev)	−4.620	−2.790	+0.220	−8.060
P^π_1	1.500	1.432	1.455	1.393
P^π_2	1.000	1.137	1.090	1.213
ΔE (ev)	6.8295	4.9159	−0.1734	13.6518
K_{56} (ev)	1.7294	1.7732	1.9053	1.2873
C_1	0.9727	0.9516	0.6908	0.9957
C_2	−0.2323	−0.3073	−0.7230	−0.0930

The resulting NN σ-bond orders (P^{σ}_{23}) calculated from (21) and the σ-electron wave functions are as follows. (Ψ_O and Ψ_N correspond to the orthogonal and non-orthogonal expansions of Ψ.)

$$\text{i. } P^{\sigma}_{23} = 0.47 \qquad \mu = 1.00 \;\; \lambda = 2.41$$

$$\Psi_O = 0.37\,\Phi^0_{\text{cov}} + 0.32\,\Phi^0_{\text{ion}} + 0.57\,\Phi^1_{\text{cov}} + 0.40\,\Phi^1_{\text{ion}} + 0.48\,\Phi^2_{\text{cov}} + 0.20\,\Phi^2_{\text{ion}}$$

$$\Psi_N = -0.03\,\Phi^0_{\text{cov}} + 0.32\,\Phi^0_{\text{ion}} + 0.80\,\Phi^{1'}_{\text{cov}} + 0.40\,\Phi^1_{\text{ion}} + 0.08\,\Phi^2_{\text{cov}} + 0.20\,\Phi^2_{\text{ion}}$$

$$\text{ii. } P^{\sigma}_{23} = 0.43 \qquad \mu = 1.00 \;\; \lambda = 1.90$$

$$\Psi_O = 0.38\,\Phi^0_{\text{cov}} + 0.29\,\Phi^0_{\text{ion}} + 0.60\,\Phi^1_{\text{cov}} + 0.35\,\Phi^1_{\text{ion}} + 0.51\,\Phi^2_{\text{cov}} + 0.17\,\Phi^2_{\text{ion}}$$

$$\Psi_N = -0.04\,\Phi^0_{\text{cov}} + 0.29\,\Phi^0_{\text{ion}} + 0.85\,\Phi^{1'}_{\text{cov}} + 0.35\,\Phi^1_{\text{ion}} + 0.08\,\Phi^2_{\text{cov}} + 0.17\,\Phi^2_{\text{ion}}$$

$$\text{iii. } P^{\sigma}_{23} = 0.01 \qquad \mu = 1.22 \;\; \lambda = 1.40$$

$$\Psi_O = 0.37\,\Phi^0_{\text{cov}} + 0.02\,\Phi^0_{\text{ion}} + 0.68\,\Phi^1_{\text{cov}} - 0.00\,\Phi^1_{\text{ion}} + 0.63\,\Phi^2_{\text{cov}} - 0.05\,\Phi^2_{\text{ion}}$$

$$\Psi_N = -0.11\,\Phi^0_{\text{cov}} + 0.02\,\Phi^0_{\text{ion}} + 0.96\,\Phi^{1'}_{\text{cov}} - 0.00\,\Phi^1_{\text{ion}} + 0.15\,\Phi^2_{\text{cov}} - 0.05\,\Phi^2_{\text{ion}}$$

$$\text{iv. } P^{\sigma}_{23} = 0.66 \qquad \mu = 0.70 \;\; \lambda = 2.93$$

$$\Psi_O = 0.48\,\Phi^0_{\text{cov}} + 0.47\,\Phi^0_{\text{ion}} + 0.50\,\Phi^1_{\text{cov}} + 0.44\,\Phi^1_{\text{ion}} + 0.29\,\Phi^2_{\text{cov}} + 0.17\,\Phi^2_{\text{ion}}$$

$$\Psi_N = 0.13\,\Phi^0_{\text{cov}} + 0.47\,\Phi^0_{\text{ion}} + 0.70\,\Phi^{1'}_{\text{cov}} + 0.44\,\Phi^1_{\text{ion}} - 0.06\,\Phi^2_{\text{cov}} + 0.17\,\Phi^2_{\text{ion}}$$

The weights of the various types of N_2O_4 valency structures are calculated by squaring these Ψ_O and Ψ_N. In the resulting expressions for $(\Psi_N)^2$, it is necessary to make the substitutions $1/2\,(\Phi^0_{\text{cov}})^2$ and $1/2\,(\Phi^2_{\text{cov}})^2$ for the products $\Phi^0_{\text{cov}}\,\Phi^{1'}_{\text{cov}}$ and $\Phi^2_{\text{cov}}\,\Phi^{1'}_{\text{cov}}$ in order to obtain the total weights of structures of types I and V. The resulting weights for all structures are given in Tab. 2.

Table 2. *Weights of* N_2O_4 *valency structures I – VII obtained from* $(\Psi_O)^2$ *and* $(\Psi_N)^2$

	I	II	III	IV	V	VI	VII
i. $P^{\sigma}_{23} = 0.47$							
$(\Psi_O)^2$	0.14	0.10	0.32	0.16	0.23	0.04	
$(\Psi_N)^2$	-0.03	0.10		0.16	0.07	0.04	0.65
ii. $P^{\sigma}_{23} = 0.43$							
$(\Psi_O)^2$	0.15	0.08	0.36	0.12	0.26	0.03	
$(\Psi_N)^2$	-0.03	0.08		0.12	0.08	0.03	0.73
iii. $P^{\sigma}_{23} = 0.01$							
$(\Psi_O)^2$	0.14	0.00	0.46	0.00	0.40	0.00	
$(\Psi_N)^2$	-0.10	0.00		0.00	0.17	0.00	0.93
iv. $P^{\sigma}_{23} = 0.66$							
$(\Psi_O)^2$	0.23	0.22	0.25	0.19	0.08	0.03	
$(\Psi_N)^2$	0.11	0.22		0.19	-0.04	0.03	0.49

The experimental NN σ-bond order of about 0.4 corresponds approximately to that obtaining to the functions i and ii[*]. However iii shows that choosing

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[*] For ii, the V. E. S. C. F. π-electron charges are a little different from those of i, which obtain for the classical structures (see Tab. 1). Therefore in our structural representation for ii, one should really include a small contribution from valency structures with different π-electron distributions, but this would not affect our conclusions concerning the σ-electron distributions. For i, we could improve the calculated NN σ-electron bond order by increasing the value of μ slightly, i. e. decreasing the magnitude of β^{σ}_{23}.

Φ_1 alone to reproduce the experimental NN σ-bond order is not satisfactory, because configuration interaction greatly reduces its value.

The $(\Psi_N)^2$ for i and ii imply only one important type of covalent structure, i. e. VII, whereas for the $(\Psi_O)^2$, three types of covalent structures, I, III and V, have considerable weight. For iii and iv, there are also fewer important covalent structures arising from $(\Psi_N)^2$ than from $(\Psi_O)^2$. In all cases, VII is the most important single type of structure — this is chiefly because the μ values are all near unity. The weights of the three types of ionic structures are much smaller than those of VII. We may conclude that for N_2O_4, the Ψ_N implies fewer important valency structures than does the Ψ_O, and that of these, VII is by far the most significant. VII also gives better insight into the nature of the NO bonds than does a hybrid of I, III and V. As for VIII of NO_2, it stresses that their properties should be intermediate between those for NO_2^+ and NO_2^- because of an intermediate value for the NO bond order.

Although VII involves nine electrons in bonding to each nitrogen atom, it does not represent a true violation of the octet rule due to expansion of the nitrogen valence shell (or due to a breakdown of the Pauli principle, which is impossible). This is because $\Phi_{\text{cov}}^{1'}$ is, by virtue of (12), a linear combination of orthogonal basis functions representing structures for which no such violation obtains.

For i and ii, IV is the most important type of ionic structure. As does VII, it implies that the NO bond and ONO angle properties of N_2O_4 should be intermediate between those for NO_2^+ and NO_2^-.

Application to Other Systems

YAAY, YHAAHY or Y_2AAY_2 type systems lend themselves to similar considerations to that described above for N_2O_4 if the possibility exists of some delocalization of Y-atom lone-pair electrons into an antibonding AA symmetry orbital, the corresponding AA bonding orbital being doubly filled prior to any delocalization. (Analysis of ABY systems such as vinyl chloride is complicated because the AB bonding and AB antibonding orbitals are not symmetry orbitals. Therefore, molecular orbitals arising from delocalization of Y-atom lone-pair electrons will usually involve combinations of both AB bonding and AB antibonding orbitals simultaneously.) The wave function for any such system may be expanded as a linear combination of six basis functions which form either orthogonal an or a non-orthogonal set. These functions correspond to the Φ_{cov}^0, Φ_{ion}^0, Φ_{cov}^2, Φ_{ion}^2,

Table 3. *Weights of covalent structures obtained from* $(\Phi_1)^2$

Orthogonal expansion		Non-orthogonal expansion	
Structure	Weight	Structure	Weight
I	$\frac{1}{2(1+\mu^2)^2}$	I	$\frac{1-\mu^2}{2(1+\mu^2)^2}$
III	$\frac{\mu^2}{(1+\mu^2)^2}$	VII	$\frac{2\mu^2}{(1+\mu^2)^2}$
V	$\frac{\mu^4}{2(1+\mu^2)^2}$	V	$\frac{\mu^4-\mu^2}{2(1+\mu^2)^2}$

Φ^1_{ion} and either the Φ^1_{cov} or the $\Phi^{1'}_{\text{cov}}$ of such expansions* for N_2O_4. When seeking the most significant types of covalent valency structures, the non-orthogonal expansion of Ψ will imply a smaller number if the value of μ is near unity, for then only $\Phi^{1'}_{\text{cov}}$ should be of great importance in the expansion. μ will be near unity if the energy of the antibonding orbital and the corresponding lone-pair electrons which can delocalize are approximately equal, i. e. if their electronegativities are similar.

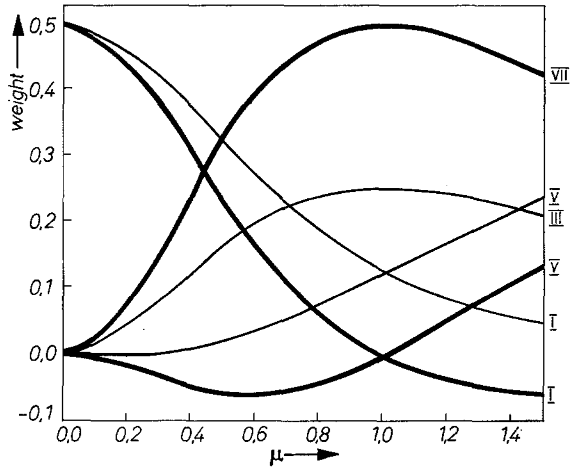

Fig. 2. Weights of covalent structures for $(\Phi_1)^2$. The heavy lines are those obtained from the non-orthogonal expansion (see Tab. 3)

When μ is not near unity, the orthogonal expansion of Ψ will imply fewer significant covalent structures, and therefore may be preferred.

If interaction between Φ_1 and Φ_2 type configurations is not expected to be extensive (and spectra could sometimes provide a guide to this), the above conclusions may be approximately illustrated by consideration of the orthogonal and non-orthogonal expansions of the lower energy configuration, Φ_1. From $(\Phi_1)^2$ we obtain the weights for the four types of covalent structures shown in Tab. 3.

The variation of these weights with μ is shown in Fig. 2.

If configuration interaction is not extensive, then an approximate estimate of μ may be obtained from the experimental AA bond-order.

Appendix

1. Properties of Determinantal Wave Functions

The following properties of determinantal wave functions have been used:

i. If

$$\varphi_i = \frac{1}{\sqrt{1+\mu_i^2}}(\chi_a + \mu_i\,\chi_b)$$

and

$$\varphi_j = \frac{1}{\sqrt{1+\mu_j^2}}(\chi_a + \mu_j\,\chi_b)$$

are two orthonormal combinations of two orthonormal basis functions χ_a and χ_b, then

$$\begin{aligned}\Phi &= |\cdots \varphi_i^\alpha\,\varphi_j^\beta| \\ &= \frac{1}{\sqrt{(1+\mu_i^2)(1+\mu_j^2)}}\left(|\cdots \chi_a^\alpha\,\chi_a^\beta| + \mu_i\,\mu_j\,|\cdots \chi_b^\alpha\,\chi_b^\beta| + \right. \\ &\quad \left. + \mu_j\,|\cdots \chi_a^\alpha\,\chi_b^\beta| + \mu_i\,|\cdots \chi_b^\alpha\,\chi_a^\beta|\right)\,. \qquad \text{(A1)}\end{aligned}$$

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* It is of course immaterial whether we refer to the functions (4) – (10) or those of (26) – (28) and (34) as the basis functions.

If

$$\mu_i = \mu_j = \mu \ ,$$

then

$$\Phi = \frac{1}{1+\mu^2}(\Phi^{\mu=0} + \sqrt{2}\,\mu\,\Phi^{\mu} + \mu^2\Phi^{\mu=\infty}) \tag{A2}$$

in which

$$\Phi^{\mu=0} = |\cdots \chi_a^\alpha \chi_a^\beta| \, , \quad \Phi^{\mu} = \frac{1}{\sqrt{2}}(|\cdots \chi_a^\alpha \chi_b^\beta| + |\cdots \chi_b^\alpha \chi_a^\beta|)$$

and

$$\Phi^{\mu=\infty} = |\cdots \chi_b^\alpha \chi_b^\beta| \ .$$

Alternatively, Φ may be expressed as

$$\Phi = \frac{1}{1+\mu^2}[(1-\mu)\Phi^{\mu=0} + 2\,\mu\,\Phi^{\mu=1} + (\mu^2-\mu)\Phi^{\mu=\infty}] \tag{A3}$$

in which

$$\Phi^{\mu=1} = \frac{1}{2}(|\cdots \chi_a^\alpha \chi_a^\beta| + |\cdots \chi_b^\alpha \chi_b^\beta| + |\cdots \chi_a^\alpha \chi_b^\beta| + |\cdots \chi_b^\alpha \chi_a^\beta|) \ .$$

The (normalized) basis functions $\Phi^{\mu=0}$, $\Phi^{\mu=\infty}$ and Φ^{μ} are orthogonal to each other but not to $\Phi^{\mu=1}$. (A2) and (A3) therefore correspond to expansions of Ψ in terms of orthogonal and non-orthogonal basis functions respectively.

ii. If two electrons with the same spin (e. g. α) are in the orthonormal orbitals

$$\varphi = \frac{1}{\sqrt{1+\mu^2}}(\chi_a + \mu\,\chi_b) \quad \text{and} \quad \varphi^* = \frac{1}{\sqrt{1+\mu^2}}(\chi_b - \mu\,\chi_a)$$

then

$$|\cdots \varphi^\alpha \varphi^{*\alpha}| \equiv |\cdots \chi_a^\alpha \chi_b^\alpha| = -|\cdots \chi_b^\alpha \chi_a^\alpha| \ . \tag{A4}$$

2. V.E.S.C.F. Procedure

The V. E. S. C. F. procedure [*2*, *3*, *4*] has been used to calculate the L. C. A. O. molecular orbitals for the lowest energy σ-electron configuration Φ_1 given by (18). The expressions for the V. E. S. C. F. matrix elements $F^\sigma_{\mu\mu}$ and $F^\sigma_{\mu\nu}$ are given by equations (5) and (6) of reference 3. The procedure for calculating the atomic valence state ionization potentials I^σ_μ, the repulsion integrals γ^σ_μ and $\gamma^\sigma_{\mu\nu}$, and the resonance integrals $\beta^\sigma_{\mu\nu}$ (except when chosen to reproduce a bond order) is that used in references 2 and 3. P^σ_μ, $P^\sigma_{\mu\nu}$ and X^σ_μ are σ-electron atom charges, bond orders and core charges. The self-consistent values of these quantities for calculation i are given in Tab. 4.

Table 4

P_1^σ	1.75	P_2^π	1.0	γ_1^σ	14.6995 ev	F_{22}^σ	−16.0398ev
P_2^σ	1.5	X_1^σ	1.5	γ_2^σ	14.7457 ev	F_{12}^σ	−4.9629 ev
P_{12}^σ	$(2\sqrt{2})^{-1}$	X_2^σ	2.0	γ_{12}^σ	6.1257 ev	F_{13}^σ	0.8551 ev
P_{13}^σ	$-(2\sqrt{2})^{-1}$	Z_1	4.4625	γ_{13}^σ	4.8369 ev	F_{14}^σ	−0.5224 ev
P_{14}^σ	0.25	Z_2	4.075	γ_{14}^σ	4.1788 ev	F_{15}^σ	−0.4099 ev
P_{15}^σ	0.25	I_1^σ	21.2419 ev	γ_{15}^σ	3.2794 ev	F_{16}^σ	0.5813 ev
P_{16}^σ	−0.25	I_2^σ	28.3791 ev	γ_{16}^σ	4.6507 ev	F_{23}^σ	−6.7207 ev
P_{23}^σ	0.5	β_{12}^σ	−3.8800 ev	γ_{23}^σ	8.4026 ev		
P_1^π	1.5	β_{23}^σ	−4.6200 ev	F_{11}^σ	−10.8339 ev		

The neglect of differential overlap for σ-electrons in this work should be a reasonable assumption because the magnitudes of the two types of nearest-neighbour σ-electron overlap integrals, $\langle \overline{\pi}_1 \mid h_2 \rangle$ and $\langle h_2 \mid h_3 \rangle$ are 0.16 and 0.30 – 0.31. These are not very different from those encountered in some π-electron calculations. In any case, the qualitative conclusions of this work will not depend on the type of molecular orbital procedure used, because for calculations i and ii, a parameter (β_{23}^{σ}) has been chosen so that the NN σ-bond order is approximately reproduced.

3. Wave functions for NO$_2$

For $\varkappa = 1$, the ψ_L and ψ_R of (11) generate nitrogen and oxygen σ-electron charges* of 1.5 e and 1.75 e, which are those for the hybrid of the NO$_2$ structures VIIIa and VIIIb.

The weights of the structures in the alternative representation IX may be obtained by expansion of the ψ_L or ψ_R for $\varkappa = 1$. For example, ψ_L may be expressed as

$$\psi_L = \left| a_L^{\alpha}\, a_L^{\beta}\, n_L^{*\alpha}\, n_L^{*\beta}\, a_L^{*\alpha} \right| = -\frac{1}{\sqrt{2}} \left| \overline{\pi}_1^2\, \overline{\pi}_6^2\, h_2^{\alpha} \right| + \frac{1}{2} \left| \overline{\pi}_1^2\, h_2^2\, \overline{\pi}_6^{\alpha} \right| + \frac{1}{2} \left| \overline{\pi}_6^2\, h_2^2\, \overline{\pi}_1^{\alpha} \right| . \quad \text{(A5)}$$

The weights of the structures IXa, IXb and IXc are equal to the squares of the coefficients of the three determinantal functions of (A5), i. e. 1/2, 1/4 and 1/4 respectively.

Structural representations VIII and IX may be shown to be equivalent by redistributing the weights of IX as follows:

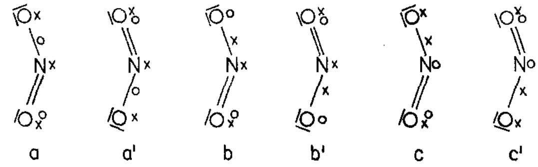
$$\begin{aligned} \text{IX} &= \frac{1}{2}\,\text{IXa} + \frac{1}{4}\,\text{IXb} + \frac{1}{4}\,\text{IXc} = \frac{1}{4}\,(\text{IXa} + \text{IXb}) + \frac{1}{4}\,(\text{IXa} + \text{IXc}) \\ &= \frac{1}{2}\,\text{VIIIa} + \frac{1}{2}\,\text{VIIIb} = \text{VIII} . \end{aligned}$$

ψ_L of (A5) is an eigenfunction of $\mathscr{S}^2$. It may be expressed as

$$\psi_L = x\,(\psi_a + \psi_{a'}) + y\,(\psi_b + \psi_{b'}) + z\,(\psi_c + \psi_{c'})$$

with (for $\varkappa = 1$), $y = x - 1/2$ and $z = x - \frac{1}{\sqrt{2}}$.

The $\psi_a\ \psi_{a'} \cdots \varphi_{c'}$ are (non orthogonal) determinantal wave functions for the space and spin distributions of the five σ-electrons of the structures a, a', b, b', c



and c'. In these, a × or o represents an electron with spin wave function α or β respectively.

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[*] E. S. R. estimates of the nitrogen odd-electron density of NO$_2$ are 0.56 – 0.57 [1]. These are not very different from the value of 0.5 obtained from the a_L^* or a_R^* orbitals with $\varkappa = 1$, and therefore the experimental σ-electron charges should be similar to those of VIII. In this paper, we are only concerned with ascertaining the most significant valency structures, and these will not depend critically on the exact magnitudes of the experimental odd electron density or NN bond order. Small differences in the observed geometries of NO$_2$ and N$_2$O$_4$ have been ignored.

4. Expressions for Basis Functions

From (18) and (19), the basis functions of (26), (27), (28) and (34) are

$$\Phi_1^{\mu=0} = | s_1^2\, s_3^2\, s_4^2\, s_5^2\, s_6^2 | \qquad \Phi_2^{\lambda=0} = | s_2^2\, s_3^2\, s_4^2\, s_5^2\, s_6^2 |$$

$$\Phi_1^{\mu=\infty} = | s_1^2\, s_2^2\, s_3^2\, s_5^2\, s_6^2 | \qquad \Phi_2^{\lambda=\infty} = | s_1^2\, s_2^2\, s_4^2\, s_5^2\, s_6^2 |$$

$$\Phi_1^{\mu=1} = \left| s_1^2\, s_3^2\, s_5^2\, s_6^2 \left(\frac{s_2+s_4}{\sqrt{2}}\right)^2 \right| \quad \Phi_2^{\lambda=1} = \left| s_2^2\, s_4^2\, s_5^2\, s_6^2 \left(\frac{s_1+s_3}{\sqrt{2}}\right)^2 \right|$$

$$\Phi_1^{\mu} = \frac{1}{\sqrt{2}} \left(| s_1^2\, s_3^2\, s_5^2\, s_6^2\, s_2^{\alpha}\, s_4^{\beta} | + | s_1^2\, s_3^2\, s_5^2\, s_6^2\, s_4^{\alpha}\, s_2^{\beta} | \right)$$

$$\Phi_2^{\lambda} = \frac{1}{\sqrt{2}} \left(| s_2^2\, s_4^2\, s_5^2\, s_6^2\, s_1^{\alpha}\, s_3^{\beta} | + | s_2^2\, s_4^2\, s_5^2\, s_6^2\, s_3^{\alpha}\, s_1^{\beta} | \right) .$$

These in turn may be expressed in the forms (26), (27), (28) and (34). The procedure will be illustrated for $\Phi_1^{\mu=1}$. By use of (A4) of appendix 1, $\Phi_1^{\mu=1}$ may be expressed as

$$\begin{aligned}
\Phi_1^{\mu=1} &= \left| \left(\frac{s_1+s_3}{\sqrt{2}}\right)^2 \left(\frac{s_3-s_1}{\sqrt{2}}\right)^2 s_5^2\, s_6^2 \left(\frac{s_2+s_4}{2}\right)^2 \right| \\
&= \left| \left(\frac{a_L+a_R}{\sqrt{2}}\right)^2 \left(\frac{a_L^*+a_R^*}{\sqrt{2}}\right)^2 \left(\frac{n_L^*+n_R^*}{\sqrt{2}}\right)^2 \left(\frac{n_L^*-n_R^*}{\sqrt{2}}\right)^2 \left(\frac{a_L-a_R}{\sqrt{2}}\right)^2 \right|
\end{aligned}$$

with $\varkappa = 1$ for the a_L, a_R, a_L^* and a_R^* molecular orbitals of (1) and (2). Using (A4) and then (A1), it follows that

$$\begin{aligned}
\Phi_1^{\mu=1} &= \left| a_L^2 \left(\frac{a_L^*+a_R^*}{\sqrt{2}}\right)^2 n_L^{*2}\, n_R^{*2}\, a_R^2 \right| \\
&= \frac{1}{2} \left(| a_L^2\, a_L^{*2}\, n_L^{*2}\, n_R^{*2}\, a_R^2 | + | a_L^2\, a_R^{*2}\, n_L^{*2}\, n_R^{*2}\, a_R^2 | \right. \\
&\quad \left. + | a_L^2\, a_L^{*\alpha}\, a_R^{*\beta}\, n_L^{*2}\, n_R^{*2}\, a_R^2 | + | a_L^2\, a_R^{*\alpha}\, a_L^{*\beta}\, n_L^{*2}\, n_R^{*2}\, a_R^2 | \right) \\
&= \frac{1}{2} \left(| a_L^2\, n_L^{*2}\, a_L^{*2}\, a_R^2\, n_R^{*2} | + | a_L^2\, n_L^{*2}\, a_R^2\, n_R^{*2}\, a_R^{*2} | \right. \\
&\quad \left. + | a_L^2\, n_L^{*2}\, a_L^{*\alpha}\, a_R^{*\beta}\, n_R^{*2}\, a_R^2 | + | a_R^2\, n_R^{*2}\, a_R^{*\alpha}\, a_L^{*\beta}\, n_L^{*2}\, a_L^2 | \right) \\
&= \frac{1}{\sqrt{2}} \left(\Phi_{\text{ion}}^{1'} + \Phi_{\text{cov}}^{1'} \right) .
\end{aligned}$$

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