Valence Bond Studies of N₅⁺

Richard D. Harcourtᵃ and Thomas M. Klapötkeᵇ

ᵃ School of Chemistry, University of Melbourne, Victoria 3010, Australia
ᵇ Department of Chemistry, University of Munich.

Butenandtstraße 5-13 (Haus D) D-81377 Munich, Germany

Reprint requests to Dr. R. D. Harcourt. Fax: +61 3 9 347 5180.
E-mail: hrefc@rubens.its.unimelb.edu.au

Z. Naturforsch. 57 b, 983–992 (2002); received May 18, 2002

Valence-Bond Structures, Increased-Valence Structures

The results of STO-6G valence-bond studies are reported for the six π-electrons of C₂ᵥ symmetry N₅⁺, with π-electron core charges determined from the valence bond structures. Important types of canonical Lewis structures are calculated to carry either three atomic formal charges, arranged spatially as (+), (-) and (+), as in

\[ \overset{\circ}{:N=N} - N - \overset{\circ}{:N= :N} : \]

or a single (+) atomic formal charge, as in the “long-bond” structure

\[ \overset{\circ}{:N=N} - N - \overset{\circ}{:N= :N} : \]

When localized molecular orbitals are used to accommodate bonding electrons between pairs of adjacent atoms, each of these types of Lewis structures, and others, are components of the increased-valence structure

\[ \overset{\circ}{:N=N} - N - \overset{\circ}{:N= :N} : \]

whose bond properties are in qualitative accord with experimental estimates of the bond lengths for N₅⁺. Consideration is also given to other types of valence bond representations for N₅⁺, and the results of MP2 molecular orbital calculations for the hypothetical N₆²⁺ are reported. For the latter species, a stable energy minimum with C₂ᵥ symmetry is obtained. Its bond lengths are related to those implied by a Lewis-type valence-bond structure.

1. Introduction

Both prior to and after the initial report of the preparation of the cation N₅⁺ [1], consideration has been given to the nature of the electronic structure of this species [1 - 16], using either molecular orbital (MO) and/or valence bond (VB) procedures. Here, we focus attention on aspects of the qualitative VB formulation of its electronic structure, with particular attention given to the 5-centre bonding unit that arises for six π-electrons. Because qualitative VB representations of electronic structure use localized (2-centre) bonds in the VB structures, they are usually better able to indicate succinctly “primitive patterns of understanding” [17] of the primary nature of bond properties than can delocalized MO representations with multicenter MOs.

In the present paper, the results of STO-6G VB calculations for the six π-electrons of N₅⁺ will be used to help provide support for the hypotheses that (a) the primary canonical Lewis-type VB structures involve either a single (+) atomic formal charge, or three atomic formal charges arranged spatially as (+), (-) and (+), and (b) the primary VB structure is the “increased-valence” form XII below, which has been displayed previously as structure 6 in refs.
[14, 15], and structure 83 in ref. [16]. Use of the latter structure provides a compact procedure that can be used to summarize resonance between numerous canonical Lewis structures, and its bond properties are in qualitative accord with calculated and measured estimates of the bond lengths [14 - 16].

For a given σ-electron distribution, there are 50 singlet-spin (S = 0) canonical Lewis structures for the six π-electrons of N₅⁺. All of these structures can be incorporated easily into VB calculations when only the π-electrons are included explicitly in the canonical structure wave-functions. Of course six-electron VB calculations for N₅⁺ involve a drastic simplification. However with estimates of the π-electron atomic core charges which are obtained by removing the π-electrons from the important Lewis structure I below, the six-electron calculations can be used to provide plausible qualitative comparisons of different types of VB representations. The results of these types of calculations do reflect effects that have been obtained from all-electron calculations for 1,3-dipolar molecules [18] in particular, namely that important Lewis-type VB structures are those that have the maximum number of nearest-neighbor covalent bonds (the “standard” octet structures) and favorable sets of atomic formal charges. However if “long-bond” Lewis structures with fewer nearest-neighbor covalent bonds involve less formal charge separation than do the standard structures, then for 1,3-dipolar molecules, the importance of the “long-bond” Lewis structures increases relative to the standard Lewis structures [18]. An analogous type of result is obtained from the six-electron VB calculations for N₅⁺.

VB considerations suggest that the (hypothetical) reaction of N₅⁺ with N₃⁺ could generate planar N₈⁺, with either C₂ᵥ or C₃ᵥ symmetry, whose primary VB structure has bond properties which are similar to those of increased-valence structure XII for N₅⁺. To test this hypothesis, we have performed MP2 MO calculations. We report the results of these calculations here, which show that C₂ rather than C₂ᵥ or C₃ᵥ is the preferred symmetry.

2. Valence Bond Structures

Free N₅⁺ as N₄N₅N₆N₇N₈N₉ has C₂ᵥ symmetry [1], cf. Fig. 1 in which the π-electron atomic orbitals (AOs) and relevant in-plane AOs are displayed. Experimental and theoretical estimates of the N₅⁺ bond-lengths indicate that the N₆-N₇ and N₅-N₈ bond lengths of 1.10 - 1.12 Å [13] are longer than the triple bond of N₂ (~ 1.07 Å with the same σ-electron AO hybridization [19], whereas the lengths of the N₇-N₈ and N₅-N₆ bonds (1.30 - 1.33 Å [13]) are longer than the N-N double bond of H₂CN=NCH₃ (1.25 Å [20]) but shorter than the single bond of H₂N-NH₂ (1.45 Å [21]). Part of the VB representation provided in ref. [13] for N₅⁺ involves resonance between the Lewis-octet structures I, II and III, which differ in the locations of the 2pπ electrons. Structures II and III are two of the structures that arise when the N₅(cπ) electrons of structure I are delocalized. Structures IV and V are analogous to structures II and III, and arise from the delocalization of the N₅(cπ) of N₅⁺. Because of overlap \( \langle \psi | c \psi' \rangle = \sqrt{2} \langle \psi | c \psi' \rangle = \sqrt{2} \langle \psi | c \psi' \rangle \) for \( c = sp^3 \) and energetic considerations (\( E(sp^3) \)), the N₅(cπ) electrons should be delocalized more appreciably than the N₅(cπ) electrons. Resonance between structures I - V does provide a VB representation which is in qualitative accord with the observed bond lengths.

Each of the above VB structures can be stabilized via one-electron delocalizations of N₅ electrons into bonding N-N localized MOs. For example, delocalization of one N₅(cπ) electron of the Lewis structure I into the N₅N₆MO \( \psi_{cb} = c + k \), and the other N₅(cπ) electron into the N₅N₆MO \( \psi_{cd} = c + k \), as indicated in structure VI, generates structure VII.

With Heitler-London type formulations of the wave-functions for the electron-pair πₐb(NN) and
\( \pi_{de} \) (NN) bonds, (for example, \( \pi_{ab}(NN) = |a^\sigma b^\pi \rangle + |b^\sigma a^\pi \rangle \)) it is easy to demonstrate that VB structure VII is equivalent to resonance between the Lewis structure I and the “long-bond” or formal bond Lewis structures VIII - X (cf. refs. [22 - 26]). The latter three VB structures involve \( N_C-N_E \), \( N_A-N_C \) and \( N_A-N_E \) “long-bond” interactions. These types of interactions have been detected by Ponce et al. [9] in their MO studies.

VB structure VII is an example of an “increase-valence” structure for a molecular species that possesses a 6-electron 5-centre bonding unit [16, 22 - 26]. This VB structure can be stabilized further by means of one electron delocalizations of the \( N_C^{-} \) sp\(^{2} \) electrons into the \( N_C-N_B \) and \( N_C-N_D \) bonding MOs \( \psi_{CB} = c^\prime + k^b b \) and \( \psi_{CD} = c^\prime + k^d d \), as indicated in structures XI and XII. (In ref. [9], the non-zero eigenvalues for the Fermi holes indicate that \( N_C^{-} \) lone-pair \( \sigma \)-electrons of the Lewis structure I as well as \( N_C \) lone-pair \( \pi \)-electrons are delocalized.)

VB structure XII involves increased-valence representations for two 6-electron 5-centre bonding units. The corresponding VB structure for isoelectronic \( N_2CN_2 \), together with its derivation, is displayed in ref. [22]. With Heitler-London type wavefunctions for the (fractional) electron-pair \( \pi_{ab}(NN) \), \( \pi_{de}(NN) \), \( \pi_{ab}(NN) \) and \( \pi_{de}(NN) \) bonds, structure XII is equivalent to resonance between the Lewis structures I, VIII - X, and twelve other Lewis structures. Two of these structures are XIII and XIV, with “long” or formal \( a' - c' \) and \( c' - e' \) bonds, respectively.

Each of the “long-bond” Lewis structures VIII, IX, XIII and XIV involves a (+) formal charge on one atom, and zero formal charges on the remaining atoms. Appeal to the adjacent charge rule and the electroneutrality principle [27] suggests that (+), (+), (-) or (-), (+), (+) values for three formal charges in each of the standard Lewis structures II - V are less satisfactory than is the single (+) in the “long-bond” structures. Therefore the latter structures are expected to make non-negligible contributions to the ground-state resonance scheme. Use of increased-valence structure XII, which we have presented previously [14 - 16], ensures that each of the “long-bond” Lewis structures, as well as the Lewis structure I, participates in a Lewis structure resonance scheme. As discussed in refs. [14 - 16], the bond properties that are implied by structure XII are in qualitative accord with the bond lengths, and therefore structure XII alone provides a more compact VB formulation of the electronic structure than does either I \( \leftrightarrow \) II \( \leftrightarrow \) III or I \( \leftrightarrow \) II \( \leftrightarrow \) III \( \leftrightarrow \) IV \( \leftrightarrow \) V.

In this paper, we provide computational support for the hypothesis that structure VII provides a lower-energy VB representation for the \( \pi \) electrons than does the I \( \leftrightarrow \) II \( \leftrightarrow \) III resonance, via the results of STO-6G VB calculations for the \( \pi \)-electrons. We also give consideration to other types of VB representations for the electronic structure of \( N_5^+ \). In the Appendix, one aspect of the delocalized
MO theory for a 6-electron 5-centre bonding unit is described.

3. Method

A quantitative VB study of the 6-electron 5-centre $\sigma$-bonding for $H_5^-$ has been reported previously [23], and the present study provides a $\pi$-electron analogue of the $H_5^-$ study. The VB calculations were performed using Roso’s ab initio program [23, 28, 29], with Slater orbital exponents for the N$^-$, N and N$^+$ AOs (c, a and e, and b and d, cf. Fig. 1) of the primary Lewis structure I. Estimates of 1.12, 1.33, 1.33 and 1.12 Å for the $N_A-N_B$, $N_B-N_C$, $N_C-N_D$ and $N_D-N_E$ bond-lengths were used, together with idealized values of 180°, 120° and 180° for the $N_A-N_B-N_C$, $N_B-N_C-N_D$ and $N_C-N_D-N_E$ bond-angles, to give $c' \equiv sp^3 = sp^2$.

Because only the six $\pi$-electrons are considered explicitly, it is necessary to provide estimates of values for the atomic core charges for these electrons. Three sets of core charges were used in the calculations, which were assigned as follows.

When the six $\pi$ electrons are removed from any of the VB structures I - III, and VI - X, the $\pi$-electron core of structure XV is obtained.

Assuming that the remaining electron-pair bonds are homopolar, as they are in the above VB structures, the resulting atomic core charges for the six $\pi$-electrons which occupy the 2$\pi$ AOs a-e are then (+), (+2), (+), (+2) and (+).

Because the N$^-$ sp$^3$ electrons of structure I are also delocalized, as indicated in XI $\rightarrow$ XII, the core charges for the $\pi$-electrons of each atom will change. For illustrative purposes, we have assumed that 0.2 electrons are delocalized from the sp$^3$ AO into the four $\pi'$ AOs of Fig. 1. We have performed further $\pi$-electron calculations for the two extreme cases, namely when the delocalized charge occupies the $\pi_B$ and $\pi_D$ AOs, and when the delocalized charge occupies the $\pi_A$ and $\pi_E$ AOs. The resulting atomic core charges for the 2$\pi$ electrons are then (+1.0), (+1.9), (+1.2), (+1.9) and (+1.0), and (+0.9), (+2.0), (+1.2), (+2.0) and (+0.9), respectively. Calculations that use the above three sets of $\pi$-electron core charges are designated as (a), (b) and (c) in Tables 1 - 4.

The $\pi$-electron VB structures that we have included initially in the calculations correspond to those of structures I - III and I, VIII - X, six of
are reported in Tables 1-4. Weights for the VB structures have been calculated using the Chirgwin-Coulson formula [30].

MP2(FULL)/6-311G(2d) calculations for N₈²⁺ were performed using GAUSSIAN 98 [31].

4. Results

The following π-electron VB resonance schemes have been studied.

(i) I → II ↔ III and VII ≡ I ↔ VIII ↔ IX ↔ X with Heitler-London AO-type wavefunctions for the electron-pair bonds (Table 1). Regardless of the atomic core charges, VII is calculated to have a lower energy than has I ↔ II ↔ III. The lower energy for VII is associated with the occurrence of smaller formal charge separations in structures VIII and IX relative to those of structures II and III, and a better overlap of Ψ₁ with Ψ_{VII} and Ψ_{IX} relative to that of Ψ₁ with Ψ_{II} and Ψ_{III}.

(ii) I, I ↔ II ↔ III and VII but with (2-centre) Coulson-Fischer type MOs [32] (for example Ψ_{ab} =...
a + k′b and \( \psi_{n\alpha} = b + k′a \) for the N\(_A\)-N\(_B\) \( \pi \)-bond) rather than AOs used to accommodate the electrons that form nearest-neighbor electron-pair \( \pi \)-bonds (see Appendix for wave-functions). Structure I is then equivalent to resonance between the canonical Lewis structures 1 - 9 of Table 2. With (2-centre) Coulson-Fischer type MOs, the I \( \leftrightarrow \) II \( \leftrightarrow \) III resonance also includes structures 10 - 21 of Fig. 2, and structure VII is equivalent to resonance between structures 1 - 9 of Table 2, structures 22 - 27 of Fig. 3, and structure X. (It is noted that structures 1, 10, 11, 22 and 25 correspond to structures I - III, VIII and IX of Table 1, with Heitler-London type wave-functions for the electron-pair \( \pi \)-bonds in each case.) As is the case for the calculations of (i), structure VII generates an energy (Table 3) which is lower than I \( \leftrightarrow \) II \( \leftrightarrow \) III for each set of atomic core charges.

With either Heitler-London or Coulson-Fischer wave-functions for the N-N \( \pi \)-bonds, in each of Tables 1 and 2, the primary Lewis structure is structure I. This result is in accord with the findings of Ponec et al. [9] in their Fermi hole analysis of a MO wave-function. Structure I has the maximum number of nearest-neighbor \( \pi \)-bonds and a favorable distribution of atomic formal charges ((0), (+), (-), (+) and (0)).

(iii) As well as structures 1 - 28, there are 17 other canonical Lewis structures, when VB structures with an \( S = 0 \) spin-pairing which is similar to that of eq. (2) are excluded. Calculations have been performed with the 45 canonical structures included in the resonance scheme, and their energies are reported in Table 3. Many of the latter \( \pi \)-electron canonical structures contribute when increased-valence structures XVII and XIX are generated from the Lewis structures II and III, as indicated in XVI \( \rightarrow \) XVII and XVIII \( \rightarrow \) XIX, and Coulson-Fischer MOs are used to accommodate the electrons that form electron-pair \( \pi \)-bonds.

(iv) As discussed in (iii), the calculations for (iii) correspond to the VII \( \leftrightarrow \) XVII \( \leftrightarrow \) XIX resonance, with Coulson-Fischer type MOs to accommodate the bonding electrons. We have omitted those canonical structures which contribute only to the increased-valence structure VII to demonstrate that the latter structure generates a substantially lower energy than does the II \( \leftrightarrow \) III resonance. The latter pair of structures were used initially in ref. [1].

For each of (i) and (ii), the results of the calculations (Tables 1 and 3) indicate that increased-valence structure VII should have a lower energy than has I \( \leftrightarrow \) II \( \leftrightarrow \) III. The structural weights reported in Tables 1 and 3 indicate that the primary reason for this is associated with the larger contribution made by the “long-bond” structures VIII and IX (or 22 and 25 in Fig. 3) than is made by structures II and III.

Other Valence Bond Resonance Schemes

(i) To account for estimates of (+0.33) for the atomic formal charges on the terminal atoms, Christe et al. [13] have suggested that structures 4, 5 and 9 of Table 2, as well as structures I, II and III, contribute significantly to the ground-state resonance scheme. We have performed further calculations with structures 4, 5 and 9 included in resonance schemes with structures I, II and III, and with structures I and VIII - X. Heitler-London type wave-functions for the electron-pair \( \pi \)-bonds are used. The weights for structures 4 and 5 reported in both Tables 2 and 4 indicate that they are important.
lence structures XXIIIa and XXIIIb [33] when Coulson-Fischer MOs are used to accommodate the two electrons that form the (fractional) electron-pair bonds in the latter two structures. Therefore for the six \(\pi\)-electrons, the Ponec et al. representation of XXIVa \(\leftrightarrow\) XXIVb is equivalent to resonance between the increased-valence structures XXVa - XXVd.

This representation is a restricted form of the VII \(\leftrightarrow\) XVII \(\leftrightarrow\) XIX resonance for the \(\pi\)-electrons, i.e. XXVIa \(\leftrightarrow\) XXVIb \(\leftrightarrow\) XXVIc, with Coulson-Fischer type MOs to accommodate the bonding \(\pi\) electrons in these structures. Whereas XXVb and XXVd are identical with XXVIb and XXVIc, XXVa \(\leftrightarrow\) XXVc does not correspond to XXVIa. The XXVa \(\leftrightarrow\) XXVc resonance does not include the “long-bond” canonical Lewis structure X, i.e. structure XVII as a component Lewis structure. Therefore XXVIa \(\leftrightarrow\) XXVIb \(\leftrightarrow\) XXVIc must provide a more compact, lower-energy VB representation than does XXVa \(\leftrightarrow\) XXVb \(\leftrightarrow\) XXVc \(\leftrightarrow\) XXVd for the six \(\pi\)-electrons. The same type of conclusion is reached for the in-plane 6-electron 5-centre bonding unit.

The formation of \(N_2^+\) from \(N_3^+ + N_2\)

Standard Lewis-type VB structures for the \(3\Sigma_g^+\) ground-state of \(N_3^+\) are those of XXVIII and XXIX, together with their mirror-image structures. From these structures, increased-valence structures XXX and XXXI and their mirror-image structure can be generated via the one-electron delocalizations indicated in XXVIII and XXIX. Excitation of the lone-pair electrons on \(N^+\) of structure XXXI gives the \(S = 0\) spin VB structure of XXXII, which can coordinate to \(N_2\) and generate increased-valence structure XII via XXXIII. Thus there is an increase in the number of bonding electrons as one proceeds from \(N_3^+ + N_2\) to \(N_5^+\).
The new species \( \text{N}_5^2^+ \)

The above VB representation for the formation of \( \text{N}_5^+ \) from \( \text{N}_3^+ + \text{N}_2 \) suggests that \( \text{N}_5^2^+ \), for which increased-structures of the type XXXIV for \( \text{C}_2v \) and \( \text{C}_{2h} \) isomers can be constructed (cf. ref. [34] for isoelectronic \( \text{N}_2 \text{CN}_2 \text{CN}_2 \)), might also have stability. However, the results of MP2 MO calculations indicate that only a \( \text{C}_2 \) isomer (Fig. 4) has a stable energy minimum. The N-N bond-lengths for this isomer (Fig. 4), are in qualitative accord with those which are implied by the Lewis structure XXXV with triple, single, double, single, double, single, and triple N-N bonds. Perhaps the preference for the \( \text{C}_2 \) isomer is associated with the greater spatial separation of the (+) formal charges in VB structure XXXV compared with that which occurs in VB structure XXXIV.

5. Conclusions

Although the VB calculations treat explicitly only the six \( \pi \)-electrons, the results provide support for plausible hypotheses with regard to qualitative VB descriptions of the electronic structure of \( \text{N}_5^+ \). Important Lewis-type VB structures are calculated to involve either (a) a formal charge on one atom only (as (+)) or (b) (+), (-) and (+) formal charges on three atoms, and zero formal charges on the remaining atoms. The relevant Lewis structures are (a) the “long-bond” Lewis structures VIII and IX, which are calculated to be more important than the familiar standard Lewis structures II and III with (+), (+) and (-) arrangements of formal charges, and (b) the standard Lewis structure I, and the “non-octet” structures 4 and 5 of Table 2, which were included in a VB resonance scheme provided by Christe et al. [13].

With localized MOs used to accommodate the electrons that form (fractional) electron-pair bonds, many of the \( \pi \)-electron canonical Lewis structures can be included in a compact VB resonance scheme by invoking resonance between the increased-valence structures VII, XVI and XVII, for which the primary increased-valence structure is VII.

Stabilization of structure VII via the one-electron delocalizations indicated in XI, generates increased-valence structure XII of refs. [14 - 16], the bond-properties of which are in qualitative accord with experimental and calculated estimates of the bond-lengths [14 - 16]. Structure XII is the primary VB structure which is needed to provide a qualitative VB representation of the electronic structure of \( \text{N}_5^+ \).

6. Note

Since submitting this paper for publication, two further papers dealing with the bonding in \( \text{N}_5^+ \) have appeared. Whereas one publication by R. J. Bartlett et al. focuses on DFT calculations and almost totally ignores recent VB considerations [35], the other report by A. Mavridis et al. [36] describes the bonding of \( \text{N}_5^+ \) in terms of two dative bonds which link \( \text{N}_2 \) molecules to \( \text{N}^+ (1^1 \text{D}) \). This description corresponds to the Lewis structure (I) that we use to generate our increased-valence structure (XII) via the one-electron delocalizations that are indicated in VI and XI. Structure (XII) has been displayed previously as structure 6 in refs. [14, 15], and structure 83 in ref. [16], and use of it provides a compact procedure that can be used to summarize resonance between numerous “long bond” Lewis structures and the Lewis
structure (I). Therefore, as discussed in our paper, XII is more stable than I. Its bond properties are in qualitative accord with calculated and measured estimates of the bond lengths [14 - 16].

Acknowledgements

We are indebted to and thank Dr. W. Roso for his ab initio VB program, and Dr. F. L. Skrezenek for installing it.

Appendix: Wavefunctions for 6-electron 5-centre bonding units

1. VII = I \leftrightarrow VIII \leftrightarrow IX \leftrightarrow X

With Heitler-London wave-functions for electron-pair \( \pi \)-bonds, the variationally-best wave-function for the \( p \) electrons of \( \Psi_{VII} \) is obtained from

\[
\Psi_{VII} = \Psi_I + C_1 \Psi_{VIII} + C_2 \Psi_X, \quad (A1)
\]

where \( C_1 \) and \( C_2 \) are two independent variational parameters.

When \( b^a b^j \) of eq. (1) is replaced by \( \psi' c^b \psi' c^d \beta + \psi' c^d \psi' c^b \beta + \psi' c^b \psi' c^d + \psi' c^d \psi' c^b \), in which \( \psi' c^b = b + k \), \( \psi' c^d = d + k \), an equivalent \( S = 0 \) spin wave-function with two variational parameters is obtained for \( \psi_{VII} \).

2. I \equiv I \leftrightarrow 2 \leftrightarrow \cdots \leftrightarrow 8 \leftrightarrow 9 \quad (c.f. Table 2)

In Table 2, there are six non-equivalent types of Lewis structures, and therefore the variationally-best linear combination of the wave-functions \( \Psi_I - \Psi_9 \) involves five independent variational parameters.

With localized MOs used to accommodate the bonding N-N \( \pi \)-electrons of structure I, one way to formulate a wave-function with five variational parameters for the \( \pi \)-electrons of this structure involves use of the MOs of eq. (A2),

\[
\begin{align*}
(i) & \quad \psi'_{ab} = a + k b, \quad \psi''_{ba} = b + k' a, \\
& \quad \psi'_{de} = d + k e, \quad \psi''_{ed} = d + k'e,
(ii) & \quad \psi'_{cd} = c + k' d, \quad \psi''_{dc} = d + k' c,
(iii) & \quad \psi'_{bc} = b + k a, \quad \psi''_{cb} = b + k a,
& \quad \psi''_{de} = d + k c, \quad \psi'_{ed} = e + k d,
& \quad \psi'_{ab} = a + k b, \quad \psi'_{de} = d + k e,
\end{align*}
\]

(A2)

to construct three \( S = 0 \) spin configurations, and to combine them linearly according to eq. (A3).

\[
\begin{align*}
\Psi_1^{(LMO)} &= \mu \left[ (\psi'_{ab}^a \psi''_{ba}^\beta + \psi''_{ba}^a \psi'_{ab}^\beta) \psi'_{de}^a \psi''_{ed}^\beta c^\alpha c^\beta \right] \\
&\quad + \left[ (\psi'_{cd}^a \psi''_{dc}^\beta + \psi''_{dc}^a \psi'_{cd}^\beta) \psi'_{bc}^a \psi''_{cb}^\beta c^\alpha c^\beta \right] \\
&\quad + \mu \left[ (\psi'_{ab}^a \psi''_{ab}^\beta) \psi''_{ed}^\alpha \psi''_{ed}^\beta \right]. \\
&\quad (A3)
\end{align*}
\]

The \( c \) AO is doubly-occupied, and the variation parameters are \( k, k', l, \) and \( \mu \).

Localized MO wave-functions may be similarly constructed for the \( \pi \)-electrons of each of the Lewis structures II and III, and the increased-valence structure VII, so that they correspond to the variationally-best linear combinations of the appropriate canonical Lewis structures which are displayed in Tables 2 and Figs. 2 and 3.

3. Delocalized MO Configuration

When localized MOs are used to accommodate the six \( \pi \)-electrons of increased-valence structure VII, as in \( (\psi_{ab}^a)^2 (\psi_{bc}^a)^2 (\psi_{cd}^a)^2 \), the \( S = 0 \) spin configuration for these electrons is given by the "covalent" wave-function, \( \Psi_{\text{cov}} \) of eq. (A4).

\[
\begin{align*}
\Psi_{\text{cov}} &= \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right| \\
&\quad + \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right| \\
&\quad + \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right|. \\
&\quad (A4)
\end{align*}
\]

We can also construct the "ionic" configurations of eq. (A5).

\[
\begin{align*}
\Psi_{\text{ion}} &= \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right| \\
&\quad + \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right| \\
&\quad + \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right|. \\
&\quad (A5)
\end{align*}
\]

From \( \Psi_{\text{cov}} + \Psi_{\text{ion}} \), we obtain the \( \Psi \) (MO) of eq. (A6).

\[
\begin{align*}
\Psi_{\text{cov}} + \Psi_{\text{ion}} &= \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right| \\
&\quad + \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right| \\
&\quad + \left| \psi_{ab}^a \psi_{ab}^\beta \psi_{ed}^a \psi_{ed}^\beta \psi_{bc}^a \psi_{bc}^\beta \right|. \\
&\quad (A6)
\end{align*}
\]

Here the delocalized MOs are given by eq. (A7).

\[
\begin{align*}
\psi_1 &= \psi_{ab} + \psi_{de} + \lambda (\psi_{bc} + \psi_{cd}) \\
\psi_2 &= \psi_{ab} + \psi_{de} \\
\psi_3 &= \psi_{bc} + \psi_{cd} - \lambda^* (\psi_{ab} + \psi_{de}) \\
&\quad (A7)
\end{align*}
\]

The \( \lambda^* \) parameter can be chosen so that \( \psi_3 \) is orthogonal to \( \psi_1 \). Because the antibonding localized MOs
ψ_{ab}, ψ_{bc}, ψ_{cd} and ψ_{de} do not contribute to these MOs, they do not correspond to the Hartree-Fock canonical MOs.

[30] In ref. [25], change “1.24 Å” to “1.20 Å”, and in line 8 below Fig. 1, change “F2NO2” to “F2N2O2”. (d) R. D. Harcourt, P. P. Wolynec, J. Phys. Chem. A 105, 4974 (2001).