Natural Resonance Theory: III. Chemical Applications

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ABSTRACT: We describe quantitative numerical applications of the natural resonance theory (NRT) to a variety of chemical bonding types, in order to demonstrate the generality and practicality of the method for a wide range of chemical systems. Illustrative applications are presented for 1) benzene and polycyclic aromatics; 2) CO₂, formate, and related acyclic species; 3) ionic and polar compounds; 4) coordinate covalent compounds and complexes; 5) hypervalent and electron-deficient species; 6) noncovalent H-bonded complex; and 7) a model Diels-Alder chemical reaction surface. The examples exhibit the general harmony of NRT weightings with qualitative resonance-theoretic concepts and illustrate how these concepts can be extended to many new types of chemical phenomena at a quantitative ab initio level. © 1998 John Wiley & Sons, Inc. J Comput Chem 19: 628–646, 1998

Keywords: natural resonance theory; resonance theory; bonding; chemical

Introduction

In the two accompanying papers we presented a “natural resonance theory” (NRT) algorithm and the associated definitions of NRT bond order and valency indices. In the present paper, we de-
equivalent Lewis (Kekulé) formulas,

\[
\begin{array}{c}
\text{HH} \\
\text{C} \equiv \text{C} \\
\text{HH} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{HH} \\
\text{C} \equiv \text{C} \\
\text{HH} \\
\end{array} \tag{1.1}
\]

The strongest (“aromatic”) forms of electronic delocalization are sometimes assumed to be restricted to cyclic geometry and symmetry-equivalent resonance structures, as in (1.1), but (as recognized by Pauling and others\(^4\)) similar strong resonance delocalization can occur in species that are acyclic (e.g., \(\text{CO}_2\), formate ion) or have unique leading resonance structures (e.g., amide group, naphthalene). Moreover, the well-known instability of cyclobutadiene [despite the superficial “analogy” to (1.1)]

\[
\begin{array}{c}
\text{H} \quad \text{C} \equiv \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \equiv \text{C} \quad \text{H} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H} \quad \text{C} \equiv \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \equiv \text{C} \quad \text{H} \\
\end{array} \tag{1.2}
\]

demonstrates that cyclic, symmetry-equivalent structures can oppose (rather than promote) resonance stabilization. Thus, a comprehensive theory of quantum-mechanical resonance should describe a wide range of electronic delocalization effects in benzenoid and nonbenzenoid systems, with cyclic or acyclic geometry and equivalent or inequivalent resonance structures.

Several examples of NRT applications to weakly delocalized species (well represented by a conventional Lewis structural formula) were presented in the preceding two papers. In the present paper, we emphasize the applications to strongly delocalized or “anomalous” species whose properties cannot be depicted by a conventional Lewis structural formula. Our goal is to present representative examples of NRT applications for a wide range of bonding types, rather than detailed discussion of individual species, providing a baseline for more detailed future investigations. Furthermore, because the two preceding papers describe the numerical stability and convergence of NRT analysis with respect to improvements in theoretical level (extensions of basis, inclusion of correlation effects, etc.), we shall not emphasize this aspect in the present work. Unless otherwise mentioned, all calculations were carried out with default NRT program options. We employ \textit{ab initio} molecular orbital (MO) wave functions at selected basis levels,\(^5\) with either idealized Pople-Gordon\(^6\) or fully optimized geometry, to demonstrate that the analysis is independent of valence bond (VB)-type wave functions.

The plan of the paper is as follows. The next section describes classical cases of resonance in cyclic aromatic benzenoid systems (benzene, naphthalene, anthracene, phenanthrene) and derivatives (toluene, xylenes, benzyl cation). We then describe \(\text{CO}_2\), formate, and related strongly delocalized acyclic species (OCNH, HNCNH, allene, formamide, HNO\(_2\), HONO). Next we describe ionic bonding and “ionic-covalent resonance” in the series X—F, X—CH\(_3\) (X = Li, CH\(_3\), NH\(_2\), OH, F), examining the transition between covalent and ionic bonding limits. After this we describe coordinate covalent bonding, including Lewis acid-base complexation (BF\(_3\)—NH\(_3\)) and transition metal coordination (Ni—CO). Later we describe “octet-violating” examples of hypervalency (PC\(_3\), SF\(_6\), SF\(_4\)) and electron-deficient hypovalency (B\(_2\)H\(_6\), BF\(_3\), F\(_2\)CO, F\(_2\)N\(_2\)). Following this discussion, the next section describes noncovalent bonding, particularly H-bonded complexes (water dimer, cyclic formamide dimer, FH\(_2\), malonaldehyde), followed by NRT analysis of the potential energy surface for a model Diels-Alder chemical reaction surface, including the “activated complex” transition state. The final section presents a brief summary and conclusions.

**Cyclic Aromatic Systems**

**BENZENE AND BENZENE DERIVATIVES**

A unique feature of benzenoid systems is the cyclic pattern of conjugation allowing each localized \(\pi\) bond to delocalize into two adjacent \(\pi^*\) antibonds in concerted counterrotating triple cycles.

\[
\begin{align*}
\pi_{AB} & \rightarrow \pi_{CD}^*, \pi_{CD} \rightarrow \pi_{EF}^*, \pi_{EF} \rightarrow \pi_{AB}^* \tag{2.1a} \\
\pi_{AB} & \rightarrow \pi_{EF}^*, \pi_{EF} \rightarrow \pi_{CD}^*, \pi_{CD} \rightarrow \pi_{AB}^* \tag{2.1b}
\end{align*}
\]

Such concerted donor-acceptor interactions are inherently cooperative, so that each \(\pi \rightarrow \pi^*\) interaction of benzene is strengthened relative to a corresponding interaction in, e.g., butadiene. In terms of the resonance-theoretic mnemonic [cf. (4.3) in the first paper], the concerted sequence of 2-\(e\) delocalizations (2.1a) or (2.1b) leads to the three-bond shifts that convert one Kekulé structure to another. The NRT program\(^7\) automatically searches for Kekulé-like NBO interaction patterns (2.1) whenever strong delocalizations are encountered and
adds the second Kekulé structure if necessary. Note that the cyclic conjugative patterns (2.1) can in principle occur even if the interacting bonds are not linked by a sigma framework [as might occur, e.g., in the transition from localized (H₂)₃ to delocalized “metallic” H₆ at high pressures], so the reference to a “Kekulé-like” structure has only topological significance.

Table I shows the calculated ab initio NRT weights for benzene (RHF/6-31G**/PG level). The NRT weights confirm the dominance of the leading Kekulé structures (1.1). A slight admixture (<0.01%) of dipolar “singly ionic” structures is associated with individual πᵢ → πᵢ* interactions, according to the standard resonance mnemonic.

In terms of Pauling-Wheland “covalent-ionic resonance,” this structure could be formally associated with a long-bonded “Dewar structure” form, but this association is unjustified and misleading. The weight of actual Dewar structures in the NRT expansion is negligibly small, apparently owing to a type of numerical “redundancy” in the NRT functional (see Appendix). Table I shows that the two Kekulé structures (each 45.8%) essentially dominate the NRT expansion, leading to CC bond orders (b(CC) = 1.494) in excellent agreement with the value (1.4) expected from conventional resonance concepts.

It is interesting to examine the subtle effects of substituents that lift the equivalence of the two leading Kekulé structures and could only be discerned with a quantitative form of resonance theory. From the RHF/6-31G**/PG wave function for toluene, for example, the NRT weights of the two leading resonance structures are found to be (numbers in brackets denote reference structure)

Note that, in all these cases, the energetically preferred rotamer (as shown) allows the in-plane C—H bond of each methyl group to eclipse a π bond of the more highly weighted Kekulé structure. Table II compares the calculated NRT bond orders (for idealized PG geometry) with fully...
TABLE I.  
Summary of NRT Analysis for RHF/6-31G* Benzene (Pople-Gordon Geometry), Showing Leading Resonance Structure Weightings \([w_\alpha]\) with Degeneracies (Deg.), Bond Orders \((b_{CC}, b_{CH})\), and Atomic Valencies \((V_C, V_H)\), with Covalent and Ionic (Electrovalent) Contributions.

<table>
<thead>
<tr>
<th>Structure</th>
<th>(\alpha)</th>
<th>Deg.</th>
<th>(w_\alpha) (%)</th>
<th>Structure</th>
<th>(\alpha)</th>
<th>Deg.</th>
<th>(w_\alpha) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}^-)</td>
<td>12</td>
<td>0.08</td>
<td></td>
<td>(\text{H}^-)</td>
<td>12</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>(\text{H}^+)</td>
<td>12</td>
<td>0.10</td>
<td></td>
<td>(\text{H}^+)</td>
<td>12</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>(\text{H}^\text{+})</td>
<td>12</td>
<td>0.10</td>
<td></td>
<td>(78 others)</td>
<td></td>
<td>4.08</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom X</th>
<th>(b_{XC})</th>
<th>(b_{X^{\text{cov}}}^{\text{(cov)}})</th>
<th>(b_{X^{\text{ion}}}^{\text{(ion)}})</th>
<th>(V_X)</th>
<th>(V_X^{(\text{cov})})</th>
<th>(V_X^{(\text{ion})})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.4941</td>
<td>1.4842</td>
<td>0.0072</td>
<td>3.9706</td>
<td>3.7293</td>
<td>0.2414</td>
</tr>
<tr>
<td>H</td>
<td>0.9878</td>
<td>0.7608</td>
<td>0.2270</td>
<td>0.9878</td>
<td>0.7608</td>
<td>0.2270</td>
</tr>
</tbody>
</table>

optimized \(R_{CC}\) values for the xylene and other benzene derivatives, showing that the actual ring distortions are consistent with the calculated variations in NRT weightings. Figure 1 shows the graphical correlation of \(R_{CC}\) (optimized) with \(b_{CC}\) (PG) for all the neutral aromatic ring bonds (including those discussed in the following subsection), demonstrating the accuracy with which subtle variations of ring geometry [on the order of \(\sigma(10^{-5} \text{ Å})\)] are predicted by quantitative NRT bond orders.

As a further test we examine the benzyl cation, which is expected to exhibit much stronger departures from idealized benzene geometry. At the RHF/6-31G*//PG level,\textsuperscript{14} the leading NRT resonance structures are\textsuperscript{11}

\[
\begin{align*}
\text{CH}_2^+ & \quad \text{CH}_2^+ & \quad \text{CH}_2^+ \\
\text{a. [16.2\%]} & \quad \text{b. [11.6\%]} & \quad \text{c. [11.5\%]} \\
\text{(2)} & \quad \text{(2)} & \quad \text{(2.7)}
\end{align*}
\]

The calculated NRT bond orders predict quinoid-like ring distortion with significant double bond character in the exocyclic CC bond, consistent with experimental findings.\textsuperscript{15} Table II includes comparisons of these bond orders with the optimized.
### TABLE II.
Comparison of Calculated RHF / 6-31G* // PG NRT Bond Orders (\( b_{CC}, b_{CH} \)) and Optimized RHF / 6-31G* Bond Lengths (\( R_{CC}, R_{CH} \); in Å) for Benzene Derivatives [see (2.3) – (2.7)]: Benzene; Toluene; Benzyl Cation; o-, m-, and p-Xylene

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
<th>Benzyl cation&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
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<tr>
<td></td>
<td>( b_{ab}^{(PG)} )</td>
<td>( R_{ab}^{(PG)} )</td>
<td>( b_{ab}^{(PG)} )</td>
</tr>
<tr>
<td>( C_1 )</td>
<td>( C_2 )</td>
<td>1.4941</td>
<td>1.3862</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>( C_3 )</td>
<td>1.4941</td>
<td>1.3862</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>( C_4 )</td>
<td>1.4941</td>
<td>1.3862</td>
</tr>
<tr>
<td>( C_4 )</td>
<td>( C_5 )</td>
<td>1.4941</td>
<td>1.3862</td>
</tr>
<tr>
<td>( C_5 )</td>
<td>( C_6 )</td>
<td>1.4941</td>
<td>1.3862</td>
</tr>
<tr>
<td>( C_6 )</td>
<td>( C_7 )</td>
<td>1.4941</td>
<td>1.3862</td>
</tr>
<tr>
<td>( C_7 )</td>
<td>( C_8 )</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( C_8 )</td>
<td>( H )</td>
<td>0.9878</td>
<td>1.0756</td>
</tr>
<tr>
<td>( C_9 )</td>
<td>( H )</td>
<td>0.9878</td>
<td>1.0756</td>
</tr>
<tr>
<td>( C_{10} )</td>
<td>( H )</td>
<td>0.9878</td>
<td>1.0756</td>
</tr>
<tr>
<td>( C_{11} )</td>
<td>( H )</td>
<td>0.9878</td>
<td>1.0756</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>( H )</td>
<td>0.9878</td>
<td>1.0756</td>
</tr>
<tr>
<td>( C_{13} )</td>
<td>( H )</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>o-Xylene</th>
<th>m-Xylene</th>
<th>p-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( b_{ab}^{(PG)} )</td>
<td>( R_{ab}^{(PG)} )</td>
<td>( b_{ab}^{(PG)} )</td>
</tr>
<tr>
<td>( C_1 )</td>
<td>( C_2 )</td>
<td>1.4542</td>
<td>1.4012</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>( C_3 )</td>
<td>1.4727</td>
<td>1.3874</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>( C_4 )</td>
<td>1.4778</td>
<td>1.3866</td>
</tr>
<tr>
<td>( C_4 )</td>
<td>( C_5 )</td>
<td>1.4935</td>
<td>1.3809</td>
</tr>
<tr>
<td>( C_5 )</td>
<td>( C_6 )</td>
<td>1.4778</td>
<td>1.3866</td>
</tr>
<tr>
<td>( C_6 )</td>
<td>( C_1 )</td>
<td>1.4727</td>
<td>1.3874</td>
</tr>
<tr>
<td>( C_{10} )</td>
<td>( C_x )</td>
<td>1.0076</td>
<td>1.5118</td>
</tr>
<tr>
<td>( C_{2,3,4} )</td>
<td>( C_y )</td>
<td>1.0076</td>
<td>1.5118</td>
</tr>
<tr>
<td>( C_{2} )</td>
<td>( H )</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( C_{3} )</td>
<td>( H )</td>
<td>0.9873</td>
<td>1.0763</td>
</tr>
<tr>
<td>( C_{4} )</td>
<td>( H )</td>
<td>0.9878</td>
<td>1.0756</td>
</tr>
<tr>
<td>( C_{5} )</td>
<td>( H )</td>
<td>0.9878</td>
<td>1.0756</td>
</tr>
<tr>
<td>( C_{6} )</td>
<td>( H )</td>
<td>0.9873</td>
<td>1.0763</td>
</tr>
<tr>
<td>( C_{x} )</td>
<td>( H )</td>
<td>0.9977</td>
<td>1.0835</td>
</tr>
<tr>
<td>( C_{y} )</td>
<td>( H )</td>
<td>0.9977</td>
<td>1.0835</td>
</tr>
<tr>
<td>( C_{y} )</td>
<td>( H )</td>
<td>0.9977</td>
<td>1.0835</td>
</tr>
<tr>
<td>( C_{y} )</td>
<td>—</td>
<td>0.9904</td>
<td>1.0860</td>
</tr>
</tbody>
</table>

<sup>a</sup>Carbon atoms are labelled as shown below.

![Diagram of benzene and its derivatives](image)

\( H_x, H_y, \) respectively, denote in-plane and out-of-plane H atoms (with \( H_c \) cis to \( C_6 \)), and \( C_y \) denotes the second methyl carbon (\( C_{o}, C_{p}, \text{or} \ C_j \)) in the xylenes.

<sup>b</sup>PG geometry.
Figure 1. NRT bond order–bond length correlation for neutral aromatic ring CC bonds of Table II, comparing bond orders of idealized geometry (all $R_{CC} = 1.40 \, \text{Å}$) to the fully optimized bond lengths: benzene (dot), toluene (circles), $\alpha$-xylene (crosses), $m$-xylene (squares), and $p$-xylene (triangles).

Figure 1. NRT bond order–bond length correlation for neutral aromatic ring CC bonds of Table II, comparing bond orders of idealized geometry (all $R_{CC} = 1.40 \, \text{Å}$) to the fully optimized bond lengths: benzene (dot), toluene (circles), $\alpha$-xylene (crosses), $m$-xylene (squares), and $p$-xylene (triangles).

whereas the $\pi^- \rightarrow \pi^*$ interactions of benzene and other aromatics give rise to strong stabilizing delocalizations and alternative resonance structures, the corresponding delocalizations in cyclobutadiene (1.2) are wholly absent. This is due to the fact that the near-rectangular geometry of a hypothetical closed-shell cyclobutadiene molecule necessarily puts the localized $\pi$ and $\pi^*$ orbitals in a nearly parallel arrangement, so that the nodal plane of the antibonding $\pi^*$ leads to effective cancellation of $\pi^- \cdot \pi^*$ overlap (and Fock matrix element, etc.). Hence, the alternative resonance structure shown in (1.2) gains no weighting in the NRT expansion, and the cyclobutadiene molecule gains none of the conjugative delocalization that usually stabilizes species with adjacent double bonds.

**POLYCYCLIC AROMATICS**

We also briefly illustrate application of the NRT method to polycyclic aromatic systems (all calculated at the split valence RHF/3-21G//PG level). For these examples we set NRTTHR = 10 (i.e., increase the threshold for estimated second-order resonance stabilization energy from 1 to 10 kcal/mol) to suppress the many structures associated with weak sigma delocalization.

For naphthalene, the leading NRT weightings are found to be

\[
\begin{align*}
\text{a. } & [29.8\%] & (2) & \quad \text{b. } [27.0\%] \\
\text{c. } & 1.5\% (4) & \quad \text{d. } 1.1\% (4)
\end{align*}
\]

Note that the high weight of the nondegenerate resonance structure (2.8b) implies a significantly higher degree of pi bond fixation in naphthalene than in benzene. Table III compares the calculated NRT bond orders (for the idealized PG geometry with all CC bonds fixed at 1.40 Å) to fully optimized CC bond lengths, which are seen to exhibit the expected pattern of distortions. Graphical representations of these correlations are displayed in Figure 2.

We also consider two fused three-ring C_{14}H_{10} isomers, anthracene and phenanthrene, at the RHF/3-21G//PG level. For anthracene, the leading NRT structures are found to be

\[
\begin{align*}
\text{a. } & [27.5\%] & (2) & \quad \text{b. } [15.3\%] (2) \\
\text{c. } & 3.4\% (2) & \quad \text{d. } 0.8\% (4)
\end{align*}
\]

Similarly, NRT analysis for phenanthrene gives

\[
\begin{align*}
\text{a. } & [22.3\%] (2) & \quad \text{b. } [17.9\%] (2) \\
\text{c. } & [10.6\%] & \quad \text{d. } [9.0\%]
\end{align*}
\]
TABLE III.
Comparison of Calculated RHF / 3-21G // PG NRT Bond Orders ($b_{ij}^{(PG)}$) and Optimized RHF / 3-21G Bond Lengths ($R_{ij}^{(opt)}$, in Å) for C$_i$–C$_j$ Bonds of Naphthalene, Anthracene, and Phenanthrene [See Eq. (2.8)–(2.10)], with the Atom Numberings Shown Below. a

<table>
<thead>
<tr>
<th>Naphthalene</th>
<th>Anthracene</th>
<th>Phenanthrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>j</td>
<td>$b_{ij}^{(PG)}$</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1.6441</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>1.3218</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
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<td>9</td>
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<td>1.3279</td>
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<tr>
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<td>11</td>
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<td>11</td>
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<tr>
<td>12</td>
<td>13</td>
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</tr>
</tbody>
</table>

Note that the CC, CH bonds of polycyclic aromatics are all assumed equal to corresponding benzene values (1.40 Å, 1.08 Å) in idealized PG geometry, so that the calculated $b_{ij}^{(PG)}$ values reflect intrinsic electronic differences rather than variations in bond lengths.

FIGURE 2. Similar to Figure 1, for polycyclic aromatics of Table III: naphthalene (circles), anthracene (squares), and phenanthrene (triangles).

with lesser contributions from many ionic structures. Table III includes comparisons of (idealized PG) NRT bond orders with optimized CC bond lengths for all these species, showing the overall pattern of agreement (despite the severe constraints of ring geometry). Figure 2 exhibits the graphical bond order–bond length correlation for the polycyclic aromatics over the full range of CC variation from near-single to near-double bond character. The NRT results appear to be in satisfactory overall harmony with qualitative resonance-theoretic concepts of organic chemistry, but the NRT weightings bring out many subtleties of resonance delocalization that would not be apparent in the qualitative framework.

Carbon Dioxide, Formate Ion, and Related Acyclic Species

CO$_2$ AND RELATED SPECIES

A particularly interesting type of acyclic strong delocalization is exhibited by the carbon dioxide molecule, which Pauling judged to have equal resonance contributions from the double-bonded and triple-bonded forms. In the nominal Lewis representation (\textsuperscript{3}O=C=\textsuperscript{3}O), there are strong $n_O^{-} \rightarrow \pi^*_{CO}$ delocalizations in the orthogonal pi systems of each of the two (degenerate) NBO Lewis structures. In excellent accordance with Pauling’s description are comparable NRT contributions (RHF/6-31G*//PG level) from double- and
triple-bonded resonance structures,\(^9\)

\[
\text{O} = \text{C} = \text{O} \quad \text{O} = \text{C} \equiv \text{O}^+. \quad \text{a. [} 49.5\% \text{]} \quad \text{b. [} 25.0\% \text{]} \quad (3.1)
\]

The resonance-weighted NRT bond orders \((b_{\text{CO}} = 2,000)\) essentially coincide with classical structural formulas, even though NBO analysis indicates that strong \(n_\text{O} \rightarrow \pi^*_{\text{CO}}\) delocalizations (each estimated at 199 kcal/mol by second-order perturbation theory) make each CO bond quite unlike that of, e.g., formaldehyde.

The strong \(n \rightarrow \pi^*\) delocalizations can be successively removed by “protonating” each lone pair and decreasing nuclear charge to preserve neutrality in the isovalent sequence \(\text{O} = \text{C} = \text{O}, \text{H} \equiv \text{C} = \text{O} \ldots\text{H}_2\text{C} = \text{C} = \text{CH}_2\). Each such replacement diminishes the weight of a triple-bonded form (arising from \(n \rightarrow \pi^*\) delocalization). The first of these “partially localized” analogs, \(\text{HN} = \text{C} = \text{O},\) has NRT weightings

\[
\text{H} = \text{N} = \text{C} = \text{O} \quad \text{N} = \text{C} \equiv \text{O}^+ \quad \text{N} = \text{C} = \text{O}^- \\
\text{a. [} 49.7\% \text{]} \quad \text{b. [} 24.4\% \text{]} \quad \text{c. [} 22.1\% \text{]} \\
(3.2)
\]

reflecting the “symmetry breaking” of the two orthogonal \(\pi\) systems. The next member, \(\text{HN} = \text{C} = \text{NH},\) has a twisted symmetric \((S_2)\) structure with NRT weightings reflecting still higher \(\pi\) localization,

\[
\text{H} = \text{N} = \text{C} = \text{N} \quad \text{H} = \text{N} = \text{C} = \text{N}^+ \quad \text{a. [} 76.9\% \text{]} \quad \text{b. 8.2\%} \\
\text{H} = \text{N} = \text{C} = \text{N}^- \quad \text{c. 8.2\%} \\
(3.3)
\]

Finally in allene, in which the last of the \(n \rightarrow \pi^*\) delocalizations is removed, only the nominal double-bonded resonance structure has significant weighting (91.9\%). Thus, the NRT weightings\(^9\) exhibit the expected successive degrees of localization of the \(\pi\) system in this isovalent sequence.

### Formate Ion and Related Species

It is also interesting to consider the general \(A = B - \ddot{C}\) “keto-enol” resonance motif,

\[
A = B - \ddot{C} \quad \text{↔} \quad \ddot{A}^- - B\equiv C^+ \quad (3.4)
\]

as exemplified by formate ion \((\text{HCOO}^-),\) formamide \((\text{H}_2\text{NCHO}),\) nitrous acid \((\text{HONO}),\) \(\text{HNCO},\) and other species. We describe NRT applications to several such systems at the geometry-optimized RHF/6-31 + G* level of theory.

The formate ion itself is a classic case of strong, symmetric delocalization, with equivalent leading NRT structures

\[
\text{O} = \text{O}^- \quad \text{O} = \text{O}^+ \\
\text{H} \quad \text{H} \\
\text{a. [} 46.4\% \text{]} \quad \text{b. [} 46.4\% \text{]} \\
(3.5)
\]

and equal CO bond orders \((b_{\text{CO}} = 1.524)\) of significant ionic character \((b_{\text{CO}}^{(\text{ion})} = 0.689,\) \(b_{\text{CO}}^{(\text{conv})} = 0.835)\).\(^{20}\)

An analogous neutral pattern is seen in \(\text{HNO}_2,\)

\[
\text{O} = \text{O}^- \quad \text{O} = \text{O}^+ \\
\text{H} \quad \text{H} \\
\text{a. [} 47.0\% \text{]} \quad \text{b. [} 47.0\% \text{]} \\
(3.6)
\]

with similar NO bond orders \((b_{\text{NO}} = 1.518)\) and even higher ionicity \((b_{\text{NO}}^{(\text{ion})} = 1.226,\) \(b_{\text{NO}}^{(\text{conv})} = 0.296)\).

The corresponding nonsymmetric pattern is exemplified by the amide group\(^2\) of formamide, which has leading NRT structures

\[
\text{O} = \text{N} \quad \text{O} \quad \text{H} \\
\text{O}^- \quad \text{N}^+ \quad \text{H} \\
\text{a. [} 65.8\% \text{]} \quad \text{b. [} 28.4\% \text{]} \\
(3.7)
\]

with distinct CO and CN bond orders \((b_{\text{CO}} = 1.744,\) \(b_{\text{CN}} = 1.289)\) and degrees of ionicity \((b_{\text{CO}}^{(\text{ion})} = 0.715,\) \(b_{\text{CN}}^{(\text{ion})} = 1.029,\) \(b_{\text{CO}}^{(\text{conv})} = 0.508,\) \(b_{\text{CN}}^{(\text{conv})} = 0.781)\). Similarly, the NRT weightings for HONO

\[
\text{O} = \text{N} = \text{O}^- \quad \text{O} = \text{N} = \text{O}^+ \\
\text{H} \\
\text{a. [} 87.1\% \text{]} \quad \text{b. 7.2\%} \\
(3.8)
\]
result in nonsymmetric NRT bond orders (protonated $b_{NO} = 1.042$, free $b_{NO} = 1.968$), reflecting the still greater dominance of the leading resonance structure. The greater weighting of the dipolar structure in formamide (3.7b) than in HONO (3.8b) can be attributed to the better donor (Lewis base) character of $n_N$ vs. $n_O$ (i.e., greater electropositivity of N) and better acceptor (Lewis acid) character of $\pi_{CO}^* \text{ vs. } \pi_{NO}^*$ (i.e., greater CO electronegativity difference polarizing the pi antibond toward the central atom), leading to stronger $n_N \rightarrow \pi_{CO}^*$ than $n_O \rightarrow \pi_{NO}^*$ NBO delocalizations. Thus, the relative NRT weights in (3.7) and (3.8) seem to be in agreement with expected chemical trends.

**Ionic Bonding and “Ionic-Covalent Resonance”**

The description of ionic and polar compounds presents a peculiar difficulty in Pauling-Wheland resonance theory, insofar as it was necessary to attribute “covalent” and “ionic” resonance structures to molecules that were conventionally described by a single Lewis structure formula. This difficulty stems from the fact that the Heitler-London VB pair function describes homopolar bonds (“pure covalent” bonding), so that bond polarity must be represented with “ionic-covalent resonance.”

No such difficulty arises in the NBO/NRT formalism; each two-center polar bond (e.g., $\sigma_{ab} = c_a h_a + c_b h_b$) can vary continuously between homopolar ($c_a = c_b$) and ionic ($c_a = 0$ or $c_b = 0$) limits within the framework of a single localized Lewis structure formula.

To illustrate the distinctive treatment of ionic or polar covalent bonding in the NRT framework, we consider two series of molecules,

\[
\begin{align*}
X-F \quad & X = \text{Li}, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F} \\
X-\text{CH}_3 \quad & X = \text{Li}, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}
\end{align*}
\]

As expected, these are all well described by a single NRT structure (>99%). Table IV displays the calculated $X-F$ and $X-C$ bond orders ($b_{XF}$, $b_{XC}$), as well as their ionic ($b_{XF}^{\text{ion}}$, $b_{XC}^{\text{ion}}$) and covalent ($b_{XF}^{\text{cov}}$, $b_{XC}^{\text{cov}}$) components, at the RHF/6-31G* /PG level.

As Table IV shows, the formal $X-F$ or $X-C$ bond order is always close to unity ($1.01 \pm 0.01$), corresponding to the nominal single bond of the conventional Lewis structure. However, the bond type ranges from nearly pure ionic (e.g., $b_{XF}^{\text{ion}} \approx 1, b_{XF}^{\text{cov}} = 0$ for $X = \text{Li}$) to covalent (e.g., $b_{XF}^{\text{ion}} = 0, b_{XF}^{\text{cov}} = 1$ for $X = \text{F}$). The NRT ionic and covalent bond orders are seen to vary smoothly in the manner expected from empirical electronegativity differences.

It is noteworthy that (except for $X = \text{Li}$) the methyl $C-X$ bonds exhibit slight partial double bond character, of the type expected to give rise to torsional barriers. The resonance structures responsible for partial $C = X$ character are associated with hyperconjugative $\sigma \rightarrow \sigma^*$ (or $n \rightarrow \sigma^*$) interactions that were previously identified as the principal origin of barriers to internal rotation in ethane-like molecules. Weak resonance delocalization of the form

\[
\begin{align*}
\text{H} & \quad \text{H}^+ \\
\text{C} & \quad \text{C} = \text{X} \\
\text{H} & \quad \text{H}^-
\end{align*}
\]

(4.2)

can therefore be considered as the resonance-theoretic counterpart of the $\sigma \rightarrow \sigma^*$ “charge transfer” picture. The somewhat surprising ionic contribution to CC bonding in ethane ($b_{CC}^{\text{ion}} = 0.019$, corresponding to about 2% ionic character) can also be attributed to the dipolar hyperconjugative structures in (4.2).

Table IV also shows the variations in NRT covalency ($V_{F}^{\text{cov}}$, $V_{C}^{\text{cov}}$), electrovalency ($V_{F}^{\text{ion}}$, $V_{C}^{\text{ion}}$), and total atomic valency ($V_{F}$, $V_{C}$) for F and C atoms. Consistent with standard valence concepts, fluorine is found to be essentially “univalent” ($V_{F} = 1.00 \pm 0.02$) and carbon “tetravalent” ($V_{C} = 4.00 \pm 0.004$) in all these compounds. The covalency of F (or C) is found to vary steadily with the F—X (or C—X) electronegativity difference in the expected way. Thus, the NRT description of ionic and polar compounds bypasses the problematic “ionic-covalent resonance” of Pauling-Wheland theory but achieves very satisfactory agreement with intuitive electronegativity and valency concepts that underlie Pauling’s classic description of chemical bonding.

**Coordinate Covalent Bonding: Lewis Acid–Base and Organometallic Complexes**

Coordinate covalency (“dative” or “donor-acceptor” bonding) represents a pervasive bonding
motif in many inorganic and organometallic species. Formation of a coordinate bond between a Lewis base “donor” and Lewis acid “acceptor” leads to a special type of polar covalency whose NRT description resembles that of ionic and strong polar covalent bonding, as discussed in the preceding section.

To illustrate the application of NRT to coordinate complexes, we consider the prototype Lewis acid–base adduct BF₃ ⋯ NH₃ (geometry optimized RHF/6-31G* level), whose leading NRT weightings are shown below.

The coordinate B ⋯ N bond is found to have total bond order \( b_{BN} = 0.803 \) of high polarity \( b_{BN}^{(\text{ionic})} = 0.589 \). Note that formation of the final acid–base adduct from its isolated Lewis base \((\text{NH}_3)\) and Lewis acid (BF₃) precursors involves promotion of the B–N bonded resonance structure (5.1a) from a minor secondary structure at large separation to the leading reference structure at equilibrium, so the NRT weightings will exhibit a “discontinuity” (of the type described in the preceding paper) at some intermediate distance unless both structures (5.1a, b) are stipulated as reference structures for all R (cf. penultimate section).

As a second example, we consider the nickel carbonyl complex, NiCO. The wave function was taken to be of RHF/LANL1DZ form (Hay-Wadt double zeta ECP basis), with equilibrium bond lengths \( R_{\text{NiC}} = 1.7696 \) Å and \( R_{\text{CO}} = 1.1483 \) Å. NRT analysis of this wave function leads to the resonance weightings

\[
\text{Ni} - \text{C} \equiv \text{O}: \quad \text{Ni} = \text{C} \equiv \text{O}; \quad \text{Ni} : \text{C} \equiv \text{O}:
\]

\[
a. \ [87.4\%] \quad b. \ [12.4\%] \quad c. \ [0.2\%]
\]

With respect to Ni and CO precursors, structure (5.2a) is due to carbonyl lone pair donation into unfilled Ni valence orbitals and (5.2b) to \( \pi \) back-bonding from metal \( d \) into unfilled carbonyl \( \pi^*_{\text{CO}} \) orbitals. Note that (5.2c) represents the carbonyl moiety as double bonded (formally, “octet violating” at C), rather than the usual triple-bond “free” CO. The calculated NRT bond orders indicate that the coordinate NiC bond (with \( b_{\text{NiC}} = 1.122 \)) has high polarity (86.1% ionic character), and the carbonyl bond order \( b_{\text{CO}} = 2.874 \) is significantly reduced from its value in free CO. These NRT weightings and bond orders appear to be in good overall agreement with conventional concepts of bonding in Werner-type complexes.

**Octet Rule-Violating** Hypervalent and Hypovalent Bonding

The NRT structures of most stable compounds appear to conform well to the Lewis octet rule. However, NRT analysis can also be applied to species exhibiting formal surplus (“hypervalency”) or deficiency (“hypovalency”) of valence electron pairs. In the former case, the NRT program can
recognize hypervalency if the number of formal electron pairs of a candidate structure exceeds the valence shell dimensionality, and multireference weighting (if required) is then carried out in the full NAO basis rather than the restricted valence space. We briefly present numerical examples for each of these exceptional bonding types.

**“HYPERVALENT” SPECIES**

A classical example of hypervalency is “penta-valent” PCl₅, in which P appears to be surrounded by five valence electron pairs. NRT analysis of the geometry-optimized RHF/6-31G* wave function for this species gives the six reference structures shown below.

Each PCl bond [with \( b_{PCl} = 0.744 \) (ax) and 0.849 (eq)] is of rather high ionic character [41.1% (ax), 34.2% (eq)]. As is shown in (6.1), five of the leading resonance structures (accounting for about 67% of the NRT expansion) are found to obey the octet rule, and the calculated atomic valency of phosphorus \( (V_p = 4.036, V_{PCl}^{(cov)} = 2.554) \) appears only slightly exceptional. Evidently, the high ionic character of P—Cl bonding permits high coordination number to phosphorus within the constraint of the octet rule.

Another classical example of apparent hypervalency is given by sulfur hexafluoride, SF₆. At the RHF/6-31G* geometry-optimized level, SF₆ gives rise to the 16(!) reference structures shown below:

Only one of which [(6.2b), approximately 5%] is formally hypervalent. The formal SF bond orders are all equal \( b_{SF} = 0.680 \) and of high polarity \( b_{SF}^{(ion)} = 0.419 \). Although the total atomic valency of sulfur \( (V_S = 4.080) \) is rather unusual, the calculated NRT covalency \( (V_S^{(cov)} = 1.564) \) is actually less than expected for a nominal “divalent” element (and far less than the apparent “hexavalency” of a superficial line formula). With respect to the charge distributions as well as the relative unimportance of \( d \)-orbital participation, the NRT results are quite consistent with the NBO analysis presented by Reed, showing the close connection between these descriptions.

As a final example, we consider SF₄ (“sawhorse” geometry, \( C_{2v} \)). At the geometry-optimized RHF/6-31G* level, the two sets of SF bonds are inequivalent, leading to the five reference structures shown below.

\[
\text{F-} - \text{S} \rightarrow \text{F} \quad \text{F-} - \text{S} \rightarrow \text{F} \quad \text{F} - \text{SF} \rightarrow \text{F} \quad \text{F} - \text{SF} \rightarrow \text{F} \\
\text{a. [21.1%] (2) b. [19.8%] (2) c. [14.0%] (2)} \tag{6.3}
\]

The near-collinear SF bonds have lower total \( b_{SF} \) (0.772 vs. 0.820) but higher \( b_{SF}^{(ion)} \) (0.534 vs. 0.489) than do the two transverse bonds, consistent with an ionic picture of linear three-center hypervalent bonds (also applicable to the bonding in SF₆). Although leading structure (6.3a) is formally hypervalent, the other four reference structures (accounting for about 67% of the NRT expansion) are not, and neither the sulfur total valency \( (V_S = 3.184) \) nor the covalency \( (V_S^{(ion)} = 1.138) \) suggests the five valence electron pairs that might be naively inferred from a line formula. Further aspects of hypervalency in relation to NRT weightings and natural charge distributions are discussed elsewhere.

**“HYPOVALENT” (ELECTRON-DEFICIENT) SPECIES**

A classical example of electron-deficient bonding is diborane, \( \text{B}_2\text{H}_6 \), which leads (at geometry-optimized RHF/6-31G* level) to the NRT weightings shown below.

\[
\text{H-} - \text{BH} \rightarrow \text{H} \quad \text{H-} - \text{BH} \rightarrow \text{H} \\
\text{a. [25.1%] (2) b. [24.3%] (2) \tag{6.4}}
\]

In the NRT representation, the bridging BH bonds have significantly lower bond order \( (b_{BH} = 0.500) \).
and higher polarity \((v_{\text{ion}}^{(\text{CO})}) = 0.221\) than do the “ordinary” flanking BH bonds \((v_{\text{BH}} = 0.995, v_{\text{ion}}^{(\text{BH})}) = 0.024\). Note that this molecule is well described by a single NBO structure with two three-center B—H—B bonds, and the NRT weightings and bond orders from (6.4) are crudely consistent with Pauling’s standard resonance-theoretic treatment of three-center bridge bonds.\(^{33}\) The calculated NRT atomic valency of boron \((V_B = 2.943)\) is in excellent agreement with the empirical trivalency of Group III elements.

A still simpler type of hypovalency is represented by the Lewis acid BF\(_3\) [cf. (5.1)], whose NRT representation (geometry-optimized RHF/6-31G* level) has leading structures

\[
\text{F} \quad \text{F} \quad \text{B} \quad \text{F} \quad \text{F} \quad \text{F} \quad \\text{F}^+ \\
\text{F} \quad \text{F} \quad \text{B} \quad \text{F} \quad \text{F} \quad \text{F} \quad \\text{F}^+ \
\]

\(6.5\)

The dipolar structures in \((6.5)\) lead to B—F bonds with partial double-bond character \((b_{\text{BF}} = 1.050)\) and high ionicity \((v_{\text{ion}}^{(\text{BF})}) = 0.774\). The total natural valency of boron \((V_B = 3.150)\) is seen to be primarily of electrovalent origin \((V_{\text{ion}}^{(\text{BF})}) = 2.201)\), and the leading resonance structure \((6.5a)\) is indeed of “octet-violating” form.

It is interesting to compare BF\(_3\) with the isoelectronic species F\(_2\)CO and F\(_2\)NN (at the same RHF/6-31G* level). The leading NRT structures of F\(_2\)CO are found to be

\[
\text{F} \quad \text{C} \quad \text{F} \\
\text{F} \quad \text{C} \quad \text{F} \
\]

\(6.6\)

with bond orders \((b_{\text{CO}} = 2.335, b_{\text{CF}} = 0.821)\) of relatively high ionic character \((v_{\text{ion}}^{(\text{CO})}) = 1.046, v_{\text{ion}}^{(\text{CF})}) = 0.441)\), having somewhat higher \(b_{\text{CO}}\) than formaldehyde \((2.045)\). The corresponding NRT representation of F\(_2\)NN is

\[
\text{N}^- \quad \text{F} \quad \text{F} \quad \text{N}^+ \\
\text{N}^- \quad \text{F} \quad \text{F} \quad \text{N}^+ \
\]

\(6.7\)

with increased NN triple-bond character \((b_{\text{NN}} = 2.473, b_{\text{NN}}^{(\text{ion}}) = 0.808)\) and weaker NF bonds \((b_{\text{NF}} = 0.742, b_{\text{NN}}^{(\text{ion}) = 0.176})\). Thus, these isoelectronic AXF\(_3\) species illustrate the progressive change in AX bonding from “single” \((A = B, X = F)\) to “double” \((A = C, X = 0)\) to “triple” \((A = X = N)\), in accordance with conventional Lewis structure models.

---

**Noncovalent Bonding: H-Bonded Complexes**

The topic of “noncovalent” hydrogen bonding is of special interest for resonance theory. Pauling\(^{34}\) originally judged that the H-bond was essentially of pure electrostatic rather than “partial divalent” character (as had been suggested by Lewis\(^{35}\)). However, Sidgwick\(^{36}\) applied the theory of resonance to H bonding, and Coulson\(^{37}\) concluded that resonance effects were the leading contributions to H bond attraction. The controversy regarding whether H bonding is primarily of “electrostatic” or “resonance” (partial covalent) nature has continued unabated.\(^{38}\) Although the original resonance picture of A—H···B hydrogen bonding [cf. (3.4)]

\[
A \rightarrow H : B \leftrightarrow A^+ \rightarrow H \rightarrow B^+ \quad (7.1)
\]

was developed by Sidgwick (rather than Pauling and Wheland), we can compare NRT applications with this conventional Pauling-Wheland-like resonance description.

We first consider the elementary example of the water dimer, \((\text{H}_2\text{O})_2\), at the optimized RHF/6-31 + G* level. NRT analysis leads to the leading resonance structures

\[
\text{H} \rightarrow \text{O} \quad \text{O} \rightarrow \text{H} \\
\text{H} \rightarrow \text{O} \quad \text{O} \rightarrow \text{H} 
\]

\(7.2\)

with appreciable O···H bond order \((b_{\text{OH}} = 0.019)\). The appearance of the “ion pair” contribution \((b_{\text{OH}} = 0.19)\) is consistent with the suggestion of significant “charge transfer” character of the H-bonded complex.\(^{39}\)

The H-bonded complex \(F^- \rightarrow \text{HF}\) demonstrates another aspect of intermolecular resonance delocalization, in that the resonating contributions analogous to (7.1) are symmetrically related,

\[
\text{F} \rightarrow \text{H} \quad \text{F}^- \leftrightarrow \text{F}^- \text{H} \rightarrow \text{F}, \quad (7.3)
\]
and the equilibrium geometry is symmetric ($D_{sb}$), suggesting the analogy with CO$_2$, formate ion, and other cases of symmetric strong delocalization. As expected, the NRT expansion for this species (RHF/6-31G* level) is dominated ($50.0\%$ each) by the two structures in (7.3), and both partial FH bonds ($b_{FH} = 0.500$) have significant covalent ($b_{FH}^{(co)} = 0.106$) and ionic ($b_{FH}^{(ion)} = 0.394$) bonding character. As with other symmetric and unsymmetric examples discussed in previous sections, the resonance contributions in (7.2) and (7.3) appear to differ in degree, but not in type.

Another interesting aspect of intermolecular H bond resonance is its ability to couple to intramolecular resonance delocalization. This can be illustrated with the example of the formamide dimer, (NH$_2$CHO)$_2$, cyclically H bonded. At the same RHF/6-31 + G* level used for formamide [cf. (3.7)], the NRT expansion for the cyclic dimer has the leading terms

$$
\begin{align*}
\text{a. } [38.8\%] \\
\text{b. } [18.7\%] \\
\text{c. } 8.3\% \\
\text{d. } 1.1\%
\end{align*}
$$

In addition to the leading H-bonded structure (7.4d), other structures appear in which H-bonding is coupled to the $n_N \rightarrow \pi^*_{CO}$ delocalization (totaling about 3.3%), giving rise to appreciable bond order ($b_{O \cdots H} = 0.027$) in each H bond. As expected, dipolar amide resonance structures (7.4b, c) are the leading delocalizations, but it is noteworthy that their relative weighting is significantly greater than that in the monomer. The calculated dimer bond orders $b_{CN} = 1.307$ and $b_{CO} = 1.718$ (cf. $b_{CN} = 1.292$ and $b_{CO} = 1.744$ for the monomer) also reflect the enhanced amide resonance. From such comparisons one can recognize that amide delocalization is significantly strengthened by dimer formation, i.e., that H bond formation couples with, and enhances, amide resonance (and vice versa). Such coupling effects can be anticipated from the donor-acceptor character of H bonding. 38, 39

Finally, we consider the case of intramolecular H bonding in methylated malonaldehyde 40 (optimized RHF/6-31 + G* level), for which the leading NRT structures are

$$
\begin{align*}
\text{a. } [75.3\%] \\
\text{b. } 7.5\% \\
\text{c. } 6.0\% \\
\text{d. } 2.3\%
\end{align*}
$$
Structures (7.5b, c) are associated with expected pi conjugation ($\pi_{\text{CO}} \rightarrow \pi_{\text{CC}}^\parallel$, $\pi_{\text{CC}} \rightarrow \pi_{\text{CO}}$) and (7.5d, e) with weaker sigma conjugation around the carbonyl group ($n_O \rightarrow \sigma_{\text{CH}}^\parallel$, $n_O \rightarrow \sigma_{\text{CC}}^\parallel$), whereas (7.5f) is the expected H bonding resonance, analogous to that found previously [e.g., (7.2b)] in the intermolecular case. As with (7.4), one would expect that pi-conjugative and H bond resonance would be coupled (and mutually enhanced) as the proton shifts from one oxygen toward the other. [Note, however, that even a symmetrically bridged O $\cdots$ H $\cdots$ O species will exhibit slight differences between the weightings for the two “equivalent” (O $\cdots$ H $\rightarrow$ O $\leftrightarrow$ O $\cdots$ H $\cdots$ O) tautomeric forms, owing to methyl-eclipsing effects analogous to those in (2.3)–(2.6).] Quantitative aspects of the well-known “proton hopping”41 dynamics of malonaldehyde and related species should be reflected in the NRT weightings.

NATURAL RESONANCE THEORY: III

Chemical Transformation on a Potential Energy Surface: Reactant, Product, and Transition Species

As a final example, we consider the NRT representation of a model Diels-Alder chemical reaction,

$$\begin{array}{c}
\text{H} \quad \text{C} \\
\text{H} \quad \text{H} \\
\text{C} = \text{C} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{O} \quad \text{O}
\end{array} + \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} = \text{C} \\
\text{H} \\
\text{H} \\
\text{O} \quad \text{O}
\end{array} \rightarrow \begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{C} = \text{C} \\
\text{H} \\
\text{H} \quad \text{H} \\
\text{O} \quad \text{O}
\end{array},$$

(8.1)

to illustrate the use of user-selected reference structures to compare widely differing reactant ($R$) and product ($P$) systems. We employ a model reaction coordinate ($s$) corresponding to the distance from the ethylene CC midpoint to the point midway between the terminal C atoms of cis-butenadiene in constrained $C_s$ symmetry. For each value of $s$, the remaining bond distances and angles were optimized ($C_s$ constrained) at the RHF/3-21G level. Although several aspects of this model are idealized with respect to actual Diels-Alder reactions, the calculated reaction energy profile (Fig. 3a) shows the expected qualitative features, with the separated reactant state at the left (ethylene $+$ butadiene, initially at $s_R = 3.0$ Å) leading to the final product state at the right (equilibrium cyclohexene, at $s_P = 1.4324$ Å), separated by an activated “transition state” (at $s^t = 2.0945$ Å).

To compare the weightings of reactant-like ($w_R$) and product-like ($w_P$) resonance structures across the entire reaction coordinate, we stipulate (with the $\$NRTSTR$ keylist) that these two resonance structures be considered as reference structures at all $s$ (despite the small weight of $w_R$ in the $P$ region and vice versa). Figure 3b shows the calculated NRT values of $w_R$ and $w_P$ along the reaction coordinate. As expected, the $R$ structure dominates ($w_R = 87.03\%$, $w_P = 0.01\%$) in the reactant-well region near $s_R = 3.0$ Å, whereas the $P$ structure dominates ($w_P = 88.05\%$, $w_R < 0.01\%$) in the product-well region near $s_P$. As one approaches the transition state (TS) region from either side, the weightings $w_R(s)$ and $w_P(s)$ of the two resonance structures gradually approach equality, until they cross ($w_R = w_P$) near the TS. We may designate the crossing point $s^t$ at which

$$w_R(s^t) = w_P(s^t)$$

(8.2)
as the “natural transition state” (NTS), to distinguish it from the corresponding point ($s^t$) at the top of the energy barrier [where the NRT weightings are found to be $w_R(s^t) = 48.4\%$, $w_P(s^t) = 31.3\%$]. In the present case, the NTS is found to occur near $s^t = 2.078$ Å, differing only slightly from $s^t$. On physical and chemical grounds, the approximation $s^t \approx s^t$ would be expected to hold true for many chemical reactions.

Figure 3c shows the corresponding variations of NRT bond orders for the four distinct CC bonds (in conventional cyclohexene numbering, $b_{12}$, $b_{23}$, $b_{34}$, $b_{45}$). Consistent with the expected chemical picture, these evolve continuously from the (1,2,0,2) pattern of the reactant structure to the (2,1,1,1) pattern of the product structure, with an approximate (1.5,1.5,0.5,1.5) pattern at the TS. Although the quantitative values of the NRT bond orders and weightings will be altered in higher level treatments of the reaction profile (particularly, inclusion of correlation effects), the chemically reasonable variations shown in Figure 3a–c.
FIGURE 3. (a) Reaction energy profile for model Diels-Alder reaction, calculated at RHF/3-21G level (see text for geometry and definition of reaction coordinate s). (b) NRT resonance weights for reactant (w_R; triangles) and product (w_P; squares) resonance structures along the model Diels-Alder reaction coordinate. (c) Natural bond order b_{AB} along the reaction coordinate, showing the evolution from reactant (butadiene plus ethylene) to product (cyclohexene) bond patterns. Bond numbering corresponds to cyclohexene labelling (e.g., b_{12} is the final cyclohexene double bond and b_{45} the initial ethylene double bond).

are expected to be preserved at higher theoretical levels.

Figure 4 compares the NRT bond orders to optimized CC bond lengths for all points along the Diels-Alder reaction coordinate. The values of R_{CC} and b_{CC} are highly correlated and appear to lie along a universal smooth curve. The nonlinear "kinks" of this curve are consistent with the expectation [cf. (3.9) in the preceding paper] that a bond order–bond length curve cannot be globally
Summary and Conclusions

The natural resonance theory (NRT) method provides a new, quantitative tool to express the chemical content of numerical wave functions in the familiar and intuitive language of resonance theory. Unlike classical Pauling-Wheland theory, the NRT method makes no reference to "valence bond," multiconfigurational, or other specialized form of wave function. Rather, it employs only the information contained in the first-order reduced density matrix and is therefore applicable to any ab initio or semiempirical quantum chemical procedure (including variational, M"uller-Plesset perturbative, and density functional methods) for which a density matrix is available. The NRT method has been implemented as a general-purpose program\(^7\) (embedded in the general Natural Bond Orbital analysis package\(^6\)) that can be attached to a wide variety of modern electronic structure systems, including Gaussian 9X,\(^{44}\) GAMESS,\(^{45}\) and others.

In the present paper, we have emphasized NRT applications in the framework of ab initio molecular orbital theory in order to demonstrate the practicality of NRT analysis for the most widely used quantum chemical methods and its independence from VB-type wave functions.

The results presented here illustrate the NRT description for a wide variety of chemical species: cyclic and acyclic; neutral and charged; symmetric and nonsymmetric; and hypervalent, hypovalent, normal covalent, ionic, coordinate covalent, and noncovalent bonding types. Emphasis has been placed on some classical applications of resonance theory (benzene, CO\(_2\), amide group, carboxylate ion, etc.) as well as nonconventional applications to subtle bond fixing (Mills-Nixon), torsional, H bonding, and conjugative coupling effects. The former applications serve to demonstrate the broad consistency of NRT analysis with conventional Pauling-Wheland concepts (despite important differences, e.g., in the treatment of "ionic-covalent resonance"). The latter serve to illustrate the many extensions and refinements of resonance-theoretic reasoning that become feasible in the quantitative NRT framework. We have also demonstrated the applicability of NRT analysis to the continuous chemical transformations of a model Diels-Alder reaction, relating the transition state to the competing reactant and product resonance structures. Our emphasis throughout has been on sampling a broad range of NRT applications, rather than investigating particular systems in detail. We believe that these examples provide a useful baseline for future NRT investigations of a wide variety of organic, inorganic, and biochemical systems.

Resonance theory once represented the most dominant influence in theoretical chemistry. We believe it can once again play an active, creative role in modern chemistry, infused with a new degree of quantitative ab initio rigor and generality.

Appendix

The minimum of the NRT variational functional [eq. (4.7) in the first accompanying paper] can be derived exactly for the elementary case of the benzene pi system in a minimal basis (e.g., H"uckel-type) framework, where the pi MOs are determined by symmetry. When these MOs are transformed to a basis of localized bond ($\pi_1$) and
antibond ($\pi_i^*$) NBOs ($i = 1, 2, 3$), it is readily shown that the $\pi_i$ and $\pi_i^*$ occupancies $q_i = \langle \pi_i | \Pi | \pi_i \rangle$, $q_i^* = \langle \pi_i^* | \Pi | \pi_i^* \rangle$ are given by

$$q_1 = q_2 = q_3 = 1/2, \quad q_1^* = q_2^* = q_3^* = 1/3.$$  \hspace{1cm} (A1)

For the usual covalent resonance structures [Kekulé structures $K$ (reference), $K'$; Dewar structures $D_1$, $D_2$, $D_3$], one can readily write out the table of occupancies $q_{ia}$ of $\pi_i$ and $\pi_i^*$ NBOs as shown below.

<table>
<thead>
<tr>
<th>NBO</th>
<th>$K$</th>
<th>$K'$</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_3$</th>
<th>true</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi_1^*$</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>$1/3$</td>
</tr>
<tr>
<td>$\pi_2^*$</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>$1/3$</td>
</tr>
<tr>
<td>$\pi_3^*$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$1/3$</td>
</tr>
<tr>
<td>$\pi_1$</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>$1/3$</td>
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<tr>
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<td>1</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>$2/3$</td>
</tr>
<tr>
<td>$\pi_3$</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>$1/3$</td>
</tr>
</tbody>
</table>

If we choose the weights of the three Dewar structures to be identical ($w_D$), the differences

$$q_i - \sum_\alpha w_\alpha q_{i\alpha}$$

are seen to be

$$\frac{1}{3} - w_K - 2w_D, \text{ for each } \pi_i^* \quad \text{(A2)}$$

$$1/3 - 2w_K - w_{K'} - 4w_D, \text{ for each } \pi_i. \quad \text{(A3)}$$

With the normalization condition $w_K + w_{K'} + 3w_D = 1$, one can eliminate $w_K$ from (A3) to see that (A2) and (A3) are equivalent. Thus, there are two independent unknowns to satisfy a single condition (A2), and the variational minimum $\delta(w_K, w_{K'}, w_D) = 0$ (corresponding to $f(w) = 1$) is achieved for any values of $w_K$, $w_D$ satisfying (A2). In particular, the weights $w_K = \frac{1}{3}$ and $w_{K'} = \frac{1}{3}$ for the two Kekulé structures reproduce the benzene pi occupancies (A1) exactly, with no contribution from Dewar structures ($w_D = 0$).

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**References**

9. Throughout this paper, “formal charge” labels are attached to assist in specifying the complete Lewis structure for cases that may otherwise be ambiguous. We typically omit specification of lone pairs unless highlighted in the discussion. Note that “formal charges” are purely a notational device, only loosely connected to the physical charge distribution as described, e.g., by natural population analysis. Note also that when two electronically distinct “structures” (corresponding, in the case of CO$_2$, to the two twisted orientations of orthogonal pi bonds) map onto a single Lewis diagram, as in (3.1a), the diagram is labelled with their combined weight (49.7%). However, multiple equivalent Lewis diagrams are specified by giving the calculated weighting for one member of the set, followed by the multiplicity in parentheses, as for the two equivalent triple-bonded structures (3.1b).
10. Strong resonance mixing is also observed for non-$D_{5h}$ geometries that break the symmetry equivalence of the two Kekulé structures in (1.1). In contrast, for the cyclobutadiene “analog” (1.2), there is no resonance mixing of the two structures in geometries that differ even infinitesimally from $D_{5h}$ symmetry (corresponding to the fact that $\pi \rightarrow \pi^*$ NBO delocalizations are rigorously absent in this case; see below).
11. For brevity’s sake, in the following, we display only the leading resonance structure contributions, showing all reference structures [bracketed] and, in some cases, the few most important secondary structures. Although the weights of neglected structures are generally significantly smaller than those displayed, their cumulative contribution can be appreciable, as, e.g., in (2.7). Additional details of neglected structures are available from the authors.
In the Pauling-Wheland "covalent-ionic resonance" formalism, each structure in (3.5) would therefore correspond to significant contributions from more highly ionic structures, such as

$$\text{O}^- + \text{C} = \text{O}^-$$

20. A more comprehensive discussion of the important topic of resonance in amides and related groups is reserved for a forthcoming paper.


23. In Pauling-Wheland theory, the origins of internal rotation barriers were not linked to resonance interactions such as (4.2), but instead were attributed to $d$- and $f$-orbital contributions to bonding hybrids (reference 4, pp. 130–134).


constraints, and other factors not directly related to resonance delocalization, and thus not reflected in bond order variations.

