Chapter 6

Electronic structure and reactivity in double Rydberg anions: characterization of a novel kind of electron pair

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Abstract

A double Rydberg anion (DRA) consists of a stable cationic core and two electrons in a diffuse Rydberg orbital. These anions correspond to a local minimum on a potential energy surface where more stable isomers may exist. Experimental and theoretical works have contributed to a better understanding of the unusual electronic structure of these molecules. With electron propagator calculations and analysis of the electron localization function, some relationships between electronic structure and reactivity in DRAs are considered.

1. Introduction

In a pioneering photoelectron study of the anion–molecule complex $\text{H}^-\text{NH}_3$, workers at Johns Hopkins University discovered a low-energy peak that could not be assigned to a hot band of this anion–molecule complex.$^1$ The invariance of the latter peak’s position with respect to deuteration, which eliminated hot bands of the anion–molecule complex from consideration, led these workers to propose the presence of another isomer in the mass-selected ion sample. They subsequently proposed that this feature pertained to a tetrahedral $\text{NH}_4^-$ anion.$^2$ Perturbative electron propagator calculations provided an accurate assignment of the photoelectron spectrum, ascribing the two principal peaks to a $\text{H}^-\text{NH}_3$ complex and the low-energy peak to a tetrahedral anion.$^3$ The Dyson orbital corresponding to the latter feature has $a_1$ symmetry and exhibits NH antibonding and
HH bonding relationships between diffuse $s$ functions. Such phase relationships and
the predominance of diffuse $s$ functions on hydrogens explained the sharpness of the
corresponding photoelectron peak. This description also validated the use of the term
double Rydberg anion (DRA),$^{2,4}$ for two electrons are found in a Rydberg-like orbital
that is distributed on the periphery of a closed-shell cation, $\text{NH}_4^+$. Several theoretical works were published on other simple hydrides and, in addition
to tetrahedral $\text{NH}_4^-$ DRAs have been found$^5$–$^{13}$ for $C_3v \text{OH}_3^-$ and tetrahedral $\text{PH}_4^-$. Geometry optimizations of $C_3v \text{SH}_3^-$ and linear structures of $\text{FH}_2^-$ and $\text{ClH}_2^-$ encountered
transition states (TS) instead of DRA minima.$^{10}$ The same study provided harmonic
vibrational frequencies for $\text{NH}_4^-, \text{OH}_3^-$, and $\text{PH}_4^-$. Recent calculations on $\text{NH}_3R^-$ and $\text{OH}_2R^-$ anions, where $R = \text{CH}_3, \text{NH}_2, \text{OH},$ and
$\text{F}$, have identified other stable anions of this type.$^{14}$ Here, $\text{AH}_n$ substituents replace
hydrogens from the parent species, tetrahedral $\text{NH}_4^-$, and $C_3v \text{OH}_3^-$. Dyson orbitals
for electron detachments from stable anions such as $\text{NH}_3\text{CH}_3^-$ are delocalized over
the periphery of the entire species. This result extends previous studies where large
molecular cations were found to accommodate a diffuse, Rydberg electron that is spread
over the periphery of the entire cationic kernel.$^{15}$ Covalent and ionic bonding that
involves Rydberg-like orbitals has been explored as well.$^{16}$

Experiments with higher resolution on $\text{N}_2\text{H}_7^-$$^{17}$ were quickly followed by electron
propagator calculations$^{18}$ that confirmed the existence of an anion–molecule complex,
$\text{H}^- (\text{NH}_3)_2$, and two DRAs with vertical electron-detachment energies placed symmet-
rically about the position of the low-energy peak in the $\text{NH}_4^-$ spectrum. One of these
$\text{N}_2\text{H}_7^-$ species is a complex consisting of the tetrahedral DRA and a coordinated amm-
nia molecule. The other features a hydrogen bond between two $\text{N}$ atoms in a structure
that resembles the $\text{N}_2\text{H}_7^+ (\text{NH}_3^+ - \text{NH}_3)$ complex. The Dyson orbital for anion electron
detachment in the latter isomer is localized on the three nonbridging hydrogens attached
to the ammonium fragment’s $\text{N}$ atom. Vibrational satellites of each of the three ver-
tical peaks also were assigned. Agreement of equally high quality was obtained for
vibrational satellites seen in the $\text{NH}_4^-$ spectrum.

These works established the existence of a novel variety of electron pair in DRAs.
Extensions of traditional electron pair concepts are clearly needed for these anions.
The electron localization function (ELF)$^{19}$ is an interesting and robust descriptor of
chemical bonding, which has been successfully applied to a wide variety of molecular
systems.$^{20–24}$ This function, which is based on a topological analysis of a quantum
function related to Pauli repulsion, describes the degree of localization (or delocalization)
of electron pairs within the molecular space.

Section 2 explains the theory behind electron propagator calculations and the
ELF. Section 3.1 contains results of ELF analysis for $\text{NH}_4R^-$ DRAs (with $R = \text{H},$
$\text{CH}_3, \text{NH}_2, \text{OH}$) and molecular complexes of $\text{N}_2\text{H}_7^-$. After validation of the topological
ELF analysis in the characterization of Rydberg electrons, the next step (described in
Section 3.2.) is to study the reaction path that connects a DRA with a global minimum
in the corresponding potential energy surface. In particular, we studied the reaction
profile between tetrahedral $\text{NH}_4^-$ and the $\text{H}^+\text{NH}_3$ complex. Our goal is to find the TS
and determine the activation energy for this reaction. Through electronic structure cal-
culations at different geometries along the energy profile, we expect to find when the
double Rydberg character of $\text{NH}_4^+$ is lost in favor of electronic distributions that are
characteristic of ion–molecule complexes.
2. Theory

2.1. Electron propagator theory

Electron propagator calculations \(^{25-28}\) of electron-binding energies (that is, electron-attachment and -detachment energies) may be based on one-electron equations which read

\[
\left[ F + \Sigma \left( \varepsilon_i^{\text{Dyson}} \right) \right] \phi_i^{\text{Dyson}} = \varepsilon_i^{\text{Dyson}} \phi_i^{\text{Dyson}} \tag{1}
\]

where \(F\), the Fock operator, depends on the first-order density matrix of a reference state, \(\Sigma(\varepsilon)\) is the energy-dependent, nonlocal correlation operator known as the self-energy, \(\varepsilon_i^{\text{Dyson}}\) is a self-consistent eigenvalue and \(\phi_i^{\text{Dyson}}\) is the corresponding eigenfunction known as the Dyson orbital. The eigenvalues equal electron-binding energies, and the Dyson orbitals are defined by the following equations for electron-detachment energies

\[
\phi_i^{\text{Dyson}}(x_1) = \sqrt{N} \int \Psi_N(x_1, x_2, x_3, \ldots, x_N) \times \Psi_{i,N-1}^*(x_2, x_3, \ldots, x_N) dx_2 dx_3 \ldots dx_N \tag{2}
\]

and electron-attachment energies

\[
\phi_i^{\text{Dyson}}(x_1) = \sqrt{N+1} \int \Psi_{i,N+1}(x_1, x_2, x_3, \ldots, x_{N+1}) \times \Psi_N^*(x_2, x_3, \ldots, x_{N+1}) dx_2 dx_3 \ldots dx_{N+1} \tag{3}
\]

where \(x_j\) is the space-spin coordinate of electron \(j\), \(\Psi_N\) is an initial state with \(N\) electrons and \(\Psi_{i,N\pm 1}\) is the \(i\)-th final state with \(N \pm 1\) electrons. Diagonal approximations neglect off-diagonal matrix elements of the self-energy operator in the canonical, Hartree–Fock (HF) basis. Perturbative arguments underlie the second order, third order, P3 and OVGF diagonal approximations of the self-energy operator. The more advanced Brueckner Doubles T1 (BD-T1) method \(^{25}\) does not make the diagonal approximation and includes partial, infinite-order contributions to the self-energy operator. The latter corrections are generated by the use of the Brueckner Doubles coupled-cluster wave function to describe the initial state and by other techniques, which consider final-state orbital relaxation and differential correlation effects. The norm of the Dyson orbital, \(p_i\), reads

\[
p_i = \int |\phi_i^{\text{Dyson}}(x_1)|^2 dx_1 \tag{4}
\]

and is an index of the qualitative validity of the perturbative arguments that are made in the diagonal approximations. In the latter methods, the Dyson orbital equals the square root of the pole strength times a canonical, HF orbital. In contrast, Dyson orbitals generated with nondiagonal methods are expressed as a linear combination of orbitals pertaining to the reference state, which may be of the HF or Brueckner varieties.
2.2. Electron localization function

The ELF function is defined according to

\[ \eta(r) = \left[ 1 + \left( \frac{T(r)}{T_{\text{TF}}(r)} \right)^2 \right]^{-1} \tag{5} \]

and is interpreted as a local measure of Pauli repulsion.\(^{19}\) In this equation, \(T(r)\) represents the difference between the kinetic energy density of the real system and the exact kinetic energy density of a fictitious bosonic system with the same electronic density. Therefore, \(\eta(r)\) measures the degree of electron pairing with respect to a homogeneous electron gas whose kinetic energy density is given by the Thomas–Fermi model, \(T_{\text{TF}}(r)\). ELF values are close to 1 for localized electron pairs, whereas small values of this function \(\eta(r) < 0.5\) correspond to highly delocalized electron density. The topological analysis of the ELF provides a useful partition of molecular space into subsystems, called basins. These nonoverlapping regions are categorized as either core or valence basins, where valence basins are labeled by the number of connections with core basins, or synaptic order. A monosynaptic basin, \(V(X_1)\), typically describes lone pairs that belong to \(X_1\). A disynaptic basin, \(V(X_1, X_2)\), describes bonds between \(X_1\) and \(X_2\) atomic centers. Basins associated with more than three atomic cores are called polysynaptic. Of greatest importance in the following discussion are the asynaptic basins, which describe electrons that are not connected with atomic centers.\(^{21,29}\) Basins provide not only a useful qualitative picture of the electron pairs in a molecule, but they also have well-defined properties.\(^{30}\) For example, electron population of a given basin is obtained by integrating the electron density over its volume \(\Omega_i\),

\[ \tilde{N}_i = \int_{\Omega_i} \rho(r) dr \tag{6} \]

The relative fluctuation of these populations, \(\lambda\), has been suggested as a measure of the degree of electron delocalization.\(^{31}\) It is defined as,

\[ \lambda(\tilde{N}_i) = \frac{\sigma^2(\tilde{N}_i)}{\tilde{N}_i} \tag{7} \]

where \(\sigma^2(\tilde{N}_i)\) is the variance or quantum uncertainty associated with \(\tilde{N}_i\).

2.3. Methods of calculation

The following strategy for electronic structure calculations on DRAs was employed. Geometry optimization and harmonic frequency analysis for the cations were performed at the HF level with a standard Pople basis set.\(^{14,18}\) These structures were used as initial guesses in the optimization of the respective anions, where the 6-311 ++G(d,p) basis set, which includes diffuse functions, was used. By this stage, optimizations and frequency calculations could be refined using a higher level of theory; therefore, MP2 and QCISD calculations were performed for all the molecular systems. The diffuse
nature of the highest occupied molecular orbital in the DRAs requires that the basis
set be supplemented with an additional set of diffuse functions. Exponents for diffuse
Gaussian functions were obtained by multiplying the smallest exponent with a given
angular dependence by 1/3. In this manner, sp functions on nitrogen atoms and addi-
tional s functions on hydrogen were added. The ELF analysis was performed on the electron
density obtained from single point calculations at the MP2 level with a bigger basis set,
6-311++G(2df,2p) augmented with extra diffuse functions, at the anion equilibrium
geometries (see Fig. 1). Gaussian03 was employed for all these calculations, whereas
the ELF analysis was carried out with the TopMod package of programs and Vis5d
software for visualization.

The TS for the internal conversion of the tetrahedral NH$_4^-$ DRA into the H$^-$NH$_3$
complex was obtained at the MP2 level with the usual basis set treatment, and it was
characterized by a unique imaginary frequency (525i cm$^{-1}$). The reaction profile was
obtained by performing an intrinsic reaction coordinate (IRC) calculation upon the
TS structure. Some points on this profile were chosen for a full analysis with electron
propagator methods, including several diagonal self-energy approximations and the
BD-T1 method. Finally, topological analysis of the ELF was performed on various
points along the reaction path.

3. Results and discussion

3.1. ELF analysis of DRA systems

In this section, ELF analysis for NH$_3$R$^-$ systems (with R = H, CH$_3$, NH$_2$, OH) and
molecular complexes of N$_2$H$_7^-$ is presented. The color convention for all pictures is
green for NH bonds, blue for lone pair electrons, and red for Rydberg electrons. Note
that in some figures there are small red dots which correspond to core electrons. These
features will be ignored in tables and in qualitative descriptions.

In general, all the systems analyzed with ELF function show asynaptic basins, which
by definition are associated with none of the atomic cores in the molecule. Because
Rydberg electrons and asynaptic basins are absent in the parent cations, asynaptic
basins can be assigned to Rydberg electrons in the uncharged and anionic species. High
fluctuation values found for these basins reflect a high degree of delocalization.

ELF results for NH$_4^-$ in Table 1 show four equivalent bisynaptic basins correspon-
ding to NH bonds, which are equivalent in tetrahedral symmetry. The electron population
is about 2.0 electrons for each of them, and fluctuation values are in agreement with
typical NH single bonds. Four asynaptic valence basins also are found. With a 0.24
Table 1

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electron population, these basins have a very high $\lambda$ value: 0.89 on a scale of 0 to 1. Figure 2 shows the graphic representations of the ELF analysis for this anion. As has been mentioned above, the ELF function approaches unity for localized electron pairs. $N$ core electrons and NH bonds can be identified clearly at $\eta(r) = 0.8$. Rydberg electrons are highly delocalized when $\eta(r) = 0.3$, and they are located preferentially close to hydrogen atoms (Fig. 2b). A spherical distribution of Rydberg basins around the cation core is observed even with a smaller isosurface where $\eta(r) = 0.20$. Figure 2c is in agreement with the analysis based on the Dyson orbital for electron detachment from the anion.\textsuperscript{18}
For the NH$_3$CH$_3^-$ anion, valence basins describing NH, CH, and NC bonds are found. Three asynaptic basins account for Rydberg electrons. The populations for these basins are slightly higher than their counterparts in the NH$_4^-$ anion, but λ values are smaller.

Figure 3a depicts the ELF topology for this system at different isosurface values. Rydberg basins again are highly delocalized for $\eta(r) = 0.30$ and are located in regions close to H atoms belonging to the NH$_3$ fragment. At lower $\eta(r)$ values, Rydberg basins are expanded until they completely envelop the NH$_3$ portion of the anion.

In NH$_3$NH$_2^-$, a lone electron pair is present which reduces the symmetry of the system. ELF analysis shows three bisynaptic basins corresponding to NH bonds in the NH$_3$ fragment. Only two of them are equivalent in electron population, but all three have the same fluctuation value. There are two NH basins that belong to the NH$_2$ fragment and another bisynaptic region describing the NN bond. Rydberg electrons are contained in a unique asynaptic basin which contains only 1.03 electrons. The fluctuation value assigned to this basin is comparable with those of the NN and NC bonds. Figure 3b shows the corresponding pictures for this system. Rydberg electrons can be identified at $\eta(r) = 0.4$. Exploring the lowest values for the ELF isosurface, it is possible to see how Rydberg electron density encloses the anion and interacts even with the H atoms of the NH$_2$ substituent while leaving free the region around the lone pair.

The NH$_3$OH$^-$ anion behaves similarly. NH bonds, with about the same electron populations and λ values as those of the previous cases, are found. Two monosynaptic
basins describing lone pairs on the oxygen concentrate high electron population, but their fluctuations reveal delocalization. Rydberg electrons in this case are split into two basins. In Figure 3c, the Rydberg basin with larger population is located in the opposite direction with respect to the lone pairs and interacts with H₁ and H₃ of the NH₃ fragment. The remaining asynaptic basin, with a very small population and high delocalization, appears for η(r) = 0.4 – 0.3.

From a general point of view, Figure 3 shows the evolution of the isosurface value for the last three anionic systems. It is clear that the presence of lone pairs has an important effect on the Rydberg electrons’ localization. Repulsions with lone pair electrons distort the Rydberg electrons toward the more positive regions of the anion.

Results for N₂H⁺₇ complexes are summarized in Table 2 and Figure 4. The most stable arrangement corresponds to two ammonia molecules coordinated to a hydride

<table>
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Topological analysis of ELF function for (a) $\text{H}^-(\text{NH}_3)_2$, (b) bridge, and (c) $\text{NH}_4^-$ (NH$_3$) (Fig. 4a). Topological analysis of this ionic structure does not find any asynaptic basin. Therefore, one may conclude that this complex has no Rydberg character. Another minimum that is less stable by 0.5 eV also was found. In this case, the NH$_4^-$ anion is bridged to an ammonia molecule. Three Rydberg basins, with almost the same population and fluctuation, are present. The highly delocalized electrons of these basins can be visualized only when $\eta(r) = 0.2$ or less. Finally, a third structure exhibits coordination between NH$_4^-$ and NH$_3$ fragments. Four asynaptic basins are present in this structure. Two of them, identified as occupying the region between the molecules, are almost equivalent in population and slightly more localized than the other two. The isosurfaces depicted in Figure 4c show how two Rydberg basins appear at $\eta(r) = 0.3$, whereas at $\eta(r) = 0.2$ the NH$_4^-$ molecule is completely covered by Rydberg electron density. From the last picture, one can conclude that this complex corresponds to a NH$_4^-$ DRA coordinated to an ammonia molecule.

**3.2. Transformation of a DRA to an ion–molecule complex**

Figure 5 shows the energy profile for the reaction. A sharp increase of energy is observed in the pathway from the reactant to the TS. Enlargement of the NH bond distance occurs with retention of $C_3v$ symmetry. After the TS, energy decays slowly, but with more drastic geometry changes. The detached H$_4$ atom (see Table 3 for numbering) travels around the NH$_3$ fragment, leaving the $C_3$ axis soon after the TS. Table 3 summarizes the geometries for stationary points on this profile. The TS has geometrical parameters that resemble those of the tetrahedral form of NH$_4^-$, but with an obvious elongation between H$_4$ and the nitrogen atom. The final product is a complex between a hydride anion and an ammonia molecule. The latter species has NH bond lengths that are close to those of
an isolated NH$_3$ molecule, but with HNH angles that are smaller. The activation energy for this reaction, $\Delta E_{\text{act}}$, has been determined to be 0.59 eV (13.58 kcal/mol), whereas the energy difference between reactant and product, $\Delta E_R$, is $-0.68$ eV ($-15.59$ kcal/mol). These values include zero-point energy corrections.

Bowen’s experimental work assigned an electron-detachment energy of 0.47 eV to the tetrahedral NH$_4^-$ anion, whereas the main peak, corresponding to an electron-binding energy of the H$^-$NH$_3$ complex, was determined to be 1.11 eV. Table 4 lists vertical electron-detachment energies (VEDEs) calculated with different approximations of electron propagator theory for the reactant, the product and ten other molecular structures along the reaction path, including the TS. As has been discussed elsewhere, due to strong electron correlation in the DRA, Koopmans values do not agree closely with the experiment. Nevertheless, these values are included in the table as a comparative reference for an uncorrelated method. Propagator calculations within the diagonal self-energy approximation, namely, second and third order, OVGF and P3, provide better descriptions than HF orbital energies, but still do not give an accurate account of the
photoelectron spectrum. For instance, second order and P3 underestimate the VEDE of the H\textsuperscript{+}-NH\textsubscript{3} complex, but third order and OVGF overestimate this transition energy. As for the reactant, second order predicts a higher VEDE, and the remaining methods are below the experimental value. A global inspection of these diagonal methods reveals how the electron-binding energy decreases from the reactant to the TS, reaching a negative value for the latter structure and its neighbors. The OVGF approximation is an exception, for it predicts a small but still positive VEDE at the TS. Pole strengths present interesting trends, for they are mostly around 0.85 in the reactant, decreasing quickly as the reaction evolves to the TS structure. Afterward these values increase again, until they reach 0.9 in the product. The definition of the pole strength parameter in propagator theory implies that when it is close to the unity, Koopmans’s approximation is qualitatively valid. Therefore, the small values obtained around the TS reveal that the overlap between Dyson and occupied HF molecular orbitals is poor in this region, and a better electron correlation treatment is required. Note that the smallest pole strength is placed just before the TS and not on that point as might be expected. The reason for this finding is that the TS structure is no longer a DRA. This hypothesis will be supported in the following discussion of ELF results. Electron-detection energies obtained with the BD reference state merit attention, since this method goes beyond the diagonal self-energy approach and has a more flexible treatment of correlation. For reactant and product, BD-T1 values show an excellent agreement with the experimental spectrum. Binding energies are small around the TS, but are all positive. The lowest ionization energy belongs to the structure previous to the TS, but the minimum value for the pole strength occurs afterward. The pole strength of the reactant is higher than that for the product.

Results of ELF topological analysis are depicted in Figure 6. For simplicity, not all of the calculated structures have been included, but the picture illustrates how the basin distribution varies along the reaction path. Because of the high delocalization of Rydberg electrons, the plots correspond to a small ELF value, \(\eta(r) = 0.25\), in all cases. For the reactant, NH\textsubscript{3}\textsuperscript{+}, four peripheral Rydberg basins around the cation core are found,
just as has been described in previous section. The following structure shows just two red basins, where the Rydberg electrons are polarized along the $C_3v$ axis. As the energy increases, Rydberg electrons are more localized on the leaving H atom and are found finally within a monosynaptic basin that corresponds to a hydride anion. At the TS structure, the asynaptic basins are gone and lone pair electrons on nitrogen appear in blue. The reaction has evolved to the product, where $H^-$ and $NH_3$ fragments may be identified clearly.

4. Conclusions

The present study confirms the existence of a novel variety of electron pair. In contrast to the bonding pairs of Lewis and Langmuir and to the lone pairs of Moffitt, the diffuse electron pairs of $NH_4^-$ and $N_2H^-$ are built chiefly of extravalence atomic functions and occupy the periphery of molecular cations. The concept of a Rydberg electron pair may lead to the prediction or observation of similar species or it may eventually yield to more generalized qualitative concepts of electronic structure.

The reaction profile that is displayed in the figures demonstrates the presence of a considerable barrier to the rearrangement of $NH_4^-$ from a tetrahedral, double Rydberg structure to an anion–molecule complex. In the TS, $C_3v$ symmetry applies as one of the NH distances is markedly longer than the others. An additional reduction of symmetry occurs after the transition state with the formation of the hydride–ammonia complex.

Calculation of accurate electron-detachment energies along the entire reaction path requires the use of a highly correlated electron propagator approximation. Pole strengths associated with these transition energies have a minimum value near the transition state and indicate that correlation effects are largest at these geometries. Dyson orbitals for the electron-detachment energy also differ most from HF orbitals at these structures. The delocalized amplitudes of the Dyson orbital associated with the DRA have become more localized on the leaving hydrogen in the transition state.
Analysis of the electron localization function for geometries of the same reaction path provides an alternative, but compatible, perspective on the evolution of electronic structure. The novel asynaptic basin of the DRA, which represents a pair of electrons that is delocalized over the periphery of the ammonium cation core, is transformed into a conventional, monosynaptic basin that is associated with the departing hydrogen at the geometries near the transition state. After the transition state, the NH$_4^-$ system may be described as a hydride–ammonia complex.

Acknowledgments

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References