Analysis of Electronic Transitions as the Difference of Electron Attachment and Detachment Densities

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A new method for analyzing calculations of vertical electronic transitions in molecules is proposed. The one-electron difference density matrix between the two states is decomposed into the negative of a "detachment density" describing removal of charge from the initial state plus an "attachment" density describing its new arrangement in the excited state. This approach relates closely to the simple picture of excited states as electron promotions from occupied to unoccupied orbitals, and yet it can be applied to arbitrarily complex wave functions. The trace of the attachment and detachment densities is a measure of the number of electrons promoted in a transition. Attachment and detachment densities are calculated and analyzed for electronic transitions in formaldehyde and the nitromethyl radical.

1. Introduction

Ab initio electronic structure calculations have become a widely used tool for probing the structure and relative energies of molecules in their ground states over the past two decades.[1] The present state of the art for small molecules has reached the stage where chemical accuracy for heats of reactions is attainable via the use of G2 theory[2] or alternative approaches.[3] However, calculations of this type involve typically millions or even billions of configurations in the wave function, and therefore as the computational sophistication increases, so too does the difficulty of ascribing any chemical meaning to details of the wavefunction. The analysis of chemical bonding and reactivity via orbital models[4] has provided much insight at the mean field Hartree—Fock level. One promising extension of the orbital picture to correlated calculations is the atom-adapted and chemically adapted orbitals from full optimized reaction space multiconfigurational wave fuctions.[5] More commonly, to obtain chemical insight from higher level calculations, schemes which focus on the electron density are used,[6,7] ranging from the calculation of effective atomic charges by any of a myriad of choices, to direct plots of surfaces of the electron density, to partitioning of the density into physically motivated regions such as atomic basins. While this is an area still deserving of further research, these approaches are valuable and widely used.

Electronic excited states can now also be calculated to considerable accuracy for medium sized organic and inorganic molecules. In particular, multireference-based approaches, combined with either supplementary configuration interaction[8] or a perturbational estimate of dynamical correlation,[9] have been shown to yield electronic excited states to within 0.25 eV for a wide range of species. A very promising alternative is single reference singles and doubles coupled cluster theory (CCSD) for excited states, which is known equivalently as linear response (LR),[10,11,12] or equations-of-motion (EOM) CCSD[13] and is also identical with symmetry-adapted cluster configuration interaction (SAC-CI)[14] when no terms are neglected. Excited state CCSD also achieves 0.25 eV accuracy for excited states that are essentially single electron promotions from the ground state

(although it is far poorer for states which are primarily double-electron promotions[15]). The simplest excited state methods such as single excitation configuration interaction (CIS) are primarily of qualitative value.[16] However, when CIS is corrected via a recently proposed second-order perturbation theory, CIS(D), errors in excitation energies are typically reduced by a factor of 2.[17] Given the availability of these excited state methods, ab initio calculations of electronic excited states appear poised to become much more routine than they are at present.

This raises the question which we seek to address in this paper: how should excited state calculations be analyzed for chemical meaning? At present the following approaches are in widespread use:

(1) The first approach is direct analysis of the excited state wave function. Analyzing details of the excited state wavefunction is subject to practical difficulties at least equal to those encountered when directly examining ground state wave functions, since it is method dependent, atomic orbital basis set dependent, and dependent on the choice of molecular orbitals. Nevertheless, it is the only approach which does not work with the diminished information content (in the sense of integrating over most electron coordinates to obtain the one-particle density or an operator expectation value) that is implicit in the following simpler alternatives. As an illustration, it has been fairly common practice to report the few largest configuration interaction coefficients to roughly characterize an excited state.

(2) This approach applies the same density analysis techniques discussed above for ground states to excited states. While this will yield detailed information on bonding in the excited state, one drawback is that they give at best indirect information about the nature of the electronic transition and the differences in chemical bonding between ground and excited states. Since ground state bonding is often well understood, there is considerable value in considering differences between states.

(3) The nature of the electronic transition can often be clarified by studying the *difference* density between ground and excited states, as has been used recently by Wiberg and co-workers for example.[18,19] Valence and Rydberg states can be clearly distinguished, and the nature of the transition (e.g. $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ for planar molecules, charge transfer versus localized, etc.) is often apparent for simple organic species. However, the difference density is a complicated function often with intricate nodal surfaces, and for larger molecules its analysis

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is therefore problematical. Finally, there are some types of electronic transition which cannot be adequately characterized in this way, a point to which we return later in the paper.

(4) The analysis of the one-electron transition density between the two states gives information on the electronic transition.[20-22] This represents the *product* of the initial and final orbitals in a simple orbital transition model, which is complementary to the difference density. Clearly for complicated transitions, deconvolution of the transition density to describe an electronic transition is awkward and follows more naturally from the difference density. By contrast, analysis of the one-electron transition density readily provides valuable information on the way in which one-electron operators couple two different states (for strong coupling, the transition density matrix and the operator matrix must "look the same"[22]) and permits straightforward assignment of symmetry in transitions involving degenerate orbitals. The difference density is not helpful for either of these problems.

(5) The calculation of judiciously chosen observable properties can also provide insight into the character of excited states. For example, an excited state can often be characterized as valence or Rydberg based on the expectation value of R^2. Additionally, a charge transfer excited state is indicated by a large change in dipole moment between initial and final states. The main advantage is that the target quantities are physical observables and are hence unambiguously defined, but they convey relatively indirect information about the features of the transition and the changes in bonding which occur on promoting from ground to excited state.

Here we propose a new way of analyzing the results of electronic excited state calculations relative to the ground state which we believe may give the best possible one-electron characterization of electronic transitions. We first define a "detachment density", which corresponds to the removal of electron density from the ground state density distribution. This can be akin to the difference between the electron density of a radical cation and the neutral if the excited state is a "one-electron" promotion, although it will be slightly larger because there will also be small associated changes in the orbits of the other electrons. In other words, excited states are collective properties of all electrons of the molecule, and the "one-electron promotion" is an orbital-based idealization, albeit a valuable one. We next define an "attachment density", which is the replacement of the detachment density in the modified distribution appropriate to the excited state of interest. The sum of the detachment and attachment densities is the difference density. Hence, this is a decomposition of the difference density into two parts, which it must be emphasized is not equivalent to simply examining positive and negative regions of the difference density separately.

There are two main difficulties with a proposal of this type which can be brought up even before any further details are presented. First, since it is a decomposition of the difference density into a detachment and an attachment density, the two components cannot be physically observable, and hence it is possible that they cannot be well-defined. We show in section 2.1 that there is a single definition for the detachment and attachment densities which applies to all excited state methods that yield a one particle density matrix. The second difficulty is that the difference density is a one-electron quantity and may not always be adequate to characterize an electronic transition, which is of course a collective property of all electrons in a molecule. The analysis can only be as good as the information content in the difference density, which we discuss in section 2.2 for some simple ground to excited state transitions and in section 2.3 for the single-excitation CI (CIS) method. On this

basis, it will be clear that the analysis will potentially be valuable for large classes of problems, and the types of cases where it is insufficient should also be evident.

The primary advantage of characterizing an electronic transition as detachment density $\rightarrow$ attachment density is that it reduces the complexity of analyzing difference densities, because the detachment and attachment density are everywhere positive. Many fine details in the difference density could be due to constructive versus destructive addition of the two components. Compare for example the ease of studying the density associated with a nonbonding orbital and the density associated with a π^* orbital separately versus plotting their difference. A second advantage of the analysis is that integration of either the detachment or attachment densities over all space yields an effective "promotion number" for the number of electrons promoted. This gives a connection to the simple orbital picture even for the case of much more complicated excited state wave functions. In section 3, two case studies are presented to see to what extent these advantages can be realized in practice. We focus first on formaldehyde, as a simple example, where the electronic transitions are well-known, and second on several transitions in the nitromethyl radical which are not so well characterized. Elsewhere, we have employed attachment/ detachment density plots to compare the excited states of chlorine nitrate and nitric acid.[23]

2. Theory

2.1. Definition and Properties of Attachment and Detachment Densities. We seek a general definition of the attachment and detachment densities which depends only on the one-particle density matrices of the initial and final states of interest, $\mathbf{P}_1$ and $\mathbf{P}_2$. For convenience, we will assume they are represented in a finite orthogonal basis of spin-orbitals, such as the molecular orbital basis. Since this basis will be used to represent the density matrices of both states, it follows that the same finite one-particle basis should be used for both states, and both states should be at the same geometry. Subtracting these matrices gives the difference density Δ in the orthogonal basis:

$$\Delta = \mathbf{P}_1 - \mathbf{P}_2 \qquad (1)$$

The eigenvectors and eigenvalues of the one-particle density matrix $\mathbf{P}$ describing a single state are the natural orbitals and their occupation numbers. They provide the best orbital description that is possible for the state, in the sense that a configuration interaction expansion using the natural orbitals as the single particle basis is most compact. The basis of our analysis of electronic transitions is to consider what might be termed "natural orbitals of the electronic transition" and their "occupation numbers", which we define as the eigenvectors $\mathbf{U}$ and eigenvalues of the difference density:

$$\mathbf{U}^{\dagger}\Delta\mathbf{U} = \delta \qquad (2)$$

The sum of the occupation numbers δ_p of these orbitals must be zero in an electronic transition which does not involve ionization or electron attachment. However, it is also possible to consider difference densities resulting from ionization or electron attachment in which case the trace of the difference density is nonzero. Therefore, in general we have

$$\mathrm{Tr}(\Delta) = \sum_{p=1}^{N} \delta_p = n \qquad (3)$$

where n is the net gain or loss of electrons in the transition.

A positive semidefinite quantity, which we will term the detachment density $\mathbf{D}$, is then defined as the sum of all natural

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orbitals of the difference density with negative occupation numbers, weighted by the absolute value of their occupations. Thus, if $\mathbf{d}$ is a diagonal matrix with elements

$$d_p = -\min(\delta_p, 0) \qquad (4)$$

Then

$$\mathbf{D} = \mathbf{U}\mathbf{d}\mathbf{U}^\dagger \qquad (5)$$

This detachment density could be considered as a hole density, although not in general corresponding to removal of an integral number of electrons. Another positive semidefinite matrix, which we will term the attachment density, is the sum of all terms in eq 1 with positive occupation numbers.

$$a_p = \max(\delta_p, 0) \qquad (6)$$

$$\mathbf{A} = \mathbf{U}\mathbf{a}\mathbf{U}^\dagger \qquad (7)$$

This corresponds to the electron density associated with the particle levels occupied in the electronic transitions. The difference between these two positive semidefinite quantities, the attachment and detachment densities, yields the original difference density matrix:

$$\Delta = \mathbf{A} - \mathbf{D} \qquad (8)$$

Some properties and observations regarding the attachment density and detachment densities are listed below:

(a) The detachment density is a definition of the density associated with single particle levels vacated in an electronic transition (hole density), while the attachment density corresponds to single particle levels occupied in the transition (particle density).

(b) For complicated wave functions, there can be numerous significant particle and hole levels whose weights are the magnitudes of the eigenvalues in eqs 4 and 6. The transition natural orbitals are the most compact basis for representing an electronic transition, since we know that only orbitals with nonnegligible eigenvalues need to be retained. The distribution of detachment density and attachment density eigenvalues conveys information about the character of the electronic transition.

(c) The decomposition is independent of the direction of the transition. That is, if the difference density is reversed in sign (i.e., we consider the transition $2 \to 1$ rather than $1 \to 2$, then what was formerly the attachment density becomes the detachment density and what was formerly the detachment density becomes the attachment density.

(d) Attachment and detachment densities are most generally defined in the spin-orbital basis. This leads to separate matrices for alpha and beta spin, which is the appropriate form of analysis for radicals, while for spin-conserving transitions from a closed shell ground state, the alpha and beta matrices are identical and can be summed together.

(e) Key invariances and symmetry properties of the original difference density are preserved. If the ground and excited state wave functions are invariant to certain classes of unitary transformation, such as among orbitals occupied or unoccupied in the Hartree–Fock determinant, then so too are the attachment and detachment densities and their eigenvalues. If the difference density transforms as the totally symmetric irreducible representation of the molecular point group, then so do $\mathbf{A}$ and $\mathbf{D}$, while their eigenvectors transform as any of the irreducible representations, akin to conventional natural orbitals.

(f) The trace of the attachment and detachment density defines scalars $p_A = \mathrm{Tr}(\mathbf{A})$ and $p_D = \mathrm{Tr}(\mathbf{D})$ associated with an electronic transition, where both are between zero and the number of electrons. In an electronic transition which does not involve gain or loss of electrons, $p_A = p_D \equiv p$, which we suggest is a measure of the number of electrons promoted in the transition (promotion number). p can often be viewed as the sum of an (integer) number of electrons directly promoted and a contribution which can be loosely associated with the extent of relaxation of other orbitals in the new effective field. This will be discussed further in the following section. In an ionization process, p_A is a measure of the extent of relaxation of other electrons. In an electron attachment process, p_D may be interpreted similarly.

2.2. Interpretation of Attachment and Detachment Densities. The attachment and detachment densities defined above are one-electron quantities which characterize an electronic transition as $\mathbf{D} \to \mathbf{A}$. The detachment density is that part of the ground state electron density which is removed and rearranged as the attachment density in the electronic transition. The remaining (core) electron density is common between the initial and final state. To illustrate the key properties of the attachment and detachment density analysis, it is useful to consider some simple model transitions.

The first example we shall consider is a transition from a ground state which is described by a single determinant, Φ_0, to a singlet excited state, $(1/\sqrt{2})(\Phi_i^a + \Phi_{\bar{i}}^{\bar{a}})$, by replacement of an occupied orbital i by a virtual orbital a (with bars indicating beta spin). In this case, the difference density in the spatial molecular orbital basis is diagonal with only two nonzero elements, $\Delta_{ii} = -1$ and $\Delta_{aa} = 1$. From the definitions it immediately follows that the attachment and detachment density matrices each have just a single nonzero element: $\Delta_{ii} = 1$ and $A_{aa} = 1$. Therefore, the attachment and detachment densities correspond to the density associated with the orbital being occupied and the orbital being vacated in the transition, and their trace (the promotion number) is 1 as we would intuitively expect.

A second example is a transition from the single determinant Φ_0 to a doubly excited determinant $\Phi_{i\bar{i}}^{a\bar{a}}$, where again bars indicate beta spin. The attachment and detachment densities can be calculated in the molecular spatial orbital basis in which case each has only a single nonzero element, which are readily shown to be $D_{ii} = 2$ and $A_{aa} = 2$. Hence, the promotion number p is two as expected for a pure double excitation. These first two examples show that, in the limit of single- or double-orbital replacements, the attachment/detachment density analysis recovers the simple orbital transition picture. In the case where a transition occurs from a single determinant to an excited state that is a linear combination of single, double, and higher substitutions, p will be the weighted average of these different contributions and will characterize the mean number of electrons excited.

Our third example explores the behavior of the attachment/detachment density analysis for a case where there is no simple orbital excitation picture. Suppose the ground state of a molecule involves two nearly degenerate configurations, and the excited state is the other orthogonal linear combination of the two determinants:

$$\Psi_1 = a_0\Phi_0 + a_{i\bar{i}}^{a\bar{a}}\Phi_{i\bar{i}}^{a\bar{a}} \qquad (9a)$$

$$\Psi_2 = a_{i\bar{i}}^{a\bar{a}}\Phi_0 - a_0\Phi_{i\bar{i}}^{a\bar{a}} \qquad (9b)$$

$$(a_{i\bar{i}}^{a\bar{a}})^2 + (a_0)^2 = 1 \qquad (9c)$$

In this case (which reduces to our second example when $a_0 = 1$), the difference density in the spatial molecular orbital basis

is diagonal with two nonzero elements:

$$\Delta_{aa} = -\Delta_{ii} = 2[(a_0)^2 - (a_{ii}^{a\bar{a}})^2]   \qquad (10)$$

Therefore, again the attachment and detachment densities each have a single nonzero element, which is equal to the promotion number, p:

$$p = 2|(a_0)^2 - (a_{ii}^{a\bar{a}})^2| \qquad (11)$$

Thus, the promotion number depends on the extent of configuration interaction in the ground and excited states.

p can range between an upper limit of 2 when $a_0 = 1$ and a lower limit of zero when $a_0 = a_{ii}^{a\bar{a}} = 2^{-1/2}$. A promotion number approaching zero indicates that, within the one-electron attachment and detachment density picture, nothing changes in the transition. Since the transition is a collective property of all electrons, rather than just a single electron, this situation can happen. In such cases, analysis of the transition must include properties of at least two electrons simultaneously. It is certainly possible to define two particle attachment and detachment densities from diagonalization of the two-particle difference density, but since a function of six dimensions poses formidable analysis problems, we shall not pursue this further.

A second caution can be derived from this last example. Note that in the case where $a_0 = \sqrt{3}/2$ and $a_{ii}^{a\bar{a}} = {}^1/_2$ the promotion number is 1, and both p and the attachment and detachment densities are indistinguishable from the first example of the one-electron transition. Thus, a promotion number of 1 has at least two possible origins: first from a pure one-electron transition between single configurations and second from a transition between states which involve differing mixtures of configurations that are related to each other by a double excitation. This is not a failure of the model in any sense but serves as another reminder that a one-electron picture of a many-electron property must be applied judiciously, in conjunction with other techniques for characterizing the transition and the excited state. There is not a 1:1 mapping between promotion numbers and the wave functions for ground and excited states! Exactly the same remark applies to analysis of the difference density, the transition density, or other properties of reduced numbers of electron coordinates.

We anticipate that the primary value of attachment and detachment density analysis will be for characterizing the nature of vertical electronic transitions in molecules. For most molecules, the ground state at its equilibrium geometry is quite well-described as a single determinant, meaning that the overlap between the Hartree—Fock determinant and the exact ground state is typically greater than 0.9. In such cases, we are close to the limit in which attachment and detachment densities are due to electron promotions from a single-determinant ground state to an excited state which is a mixture of orthogonal determinants. The interpretation of the promotion number p is then unambiguous, and this procedure should be valuable.

2.3. Single-Excitation Configuration Interaction. Single-excitation configuration interaction is probably the simplest excited state theory in broad use, within the context of both ab initio and semiempirical molecular orbital calculations. It is of interest to obtain and study explicit expressions for the attachment and detachment densities. Employing spin-orbital notation, the CIS excited state is a linear combination of all single substitutions Φ_i^a constructed from a Hartree—Fock reference determinant Φ_0 by replacing an occupied orbital i by an unoccupied orbital a:

$$\Psi_{CIS} = \sum_{ia} a_i^a \Phi_i^a   \qquad (12)$$

From standard manipulations it follows that the difference density between the one-particle density matrix for the CIS excited state and the HF ground state has nonzero contributions in only the occupied—occupied and virtual—virtual blocks, when expressed in the basis of HF molecular orbitals:

$$\Delta_{ij} = -\sum_a a_i^a a_j^a   \qquad (13a)$$

$$\Delta_{ab} = +\sum_i a_i^a a_i^b   \qquad (13b)$$

The occupied—virtual blocks are zero.

Inspection of eqs 13 suggests that eq 13a might be associated with the negative of the detachment density, since it concerns only the occupied orbitals of the initial HF ground state density matrix. Correspondingly, eq 13b should be associated with the attachment density as it involves only the virtual orbitals which are unpopulated in the ground state. Diagonalization of the difference density matrix via the procedure of section 2.1 yields precisely this result also. All eigenvalues of the occupied—occupied block are negative and define the detachment density via eqs 4 and 5. All eigenvalues of the virtual—virtual block are positive and define the attachment density via eqs 6 and 7. Proof of the sign of the eigenvalues follows from the fact that the eigenvalues of a matrix multiplied by its transpose are always positive.

By taking the trace of eqs 13b, we obtain the effective number of electrons promoted in an electronic transition by the CIS method. From normalization of the CIS wave function, the promotion number is identically 1, as should be expected. CIS represents the minimum generalization of the single transition approximation necessary to correctly describe excited states when highest occupieds or lowest unoccupieds are degenerate, for example. The definition of attachment and detachment densities we have given permits electronic transitions in the CIS method to be visualized and analyzed more or less as if the transition was just a single-orbital replacement, regardless of the extent of configurational mixing that occurs in the excited state wave function and regardless of how inappropriate the molecular orbitals are for describing a transition in such terms.

The extent to which this is actually true can be deduced from the eigenvalue spectrum of the detachment and attachment densities. If the largest eigenvalue of both attachment and detachment densities approaches one, then in the basis of their eigenvectors (note that CIS attachment density mixes only virtual orbitals, and the detachment density mixes only occupied orbitals which leaves the HF and CIS energies unaltered) the excited state can be expressed as a single transition.

There is an existing alternative proposal for finding orbitals appropriate for a compact description of the CIS wave function. Cioslowski[24] has defined single-excitations-adapted molecular orbitals (SEAMO's) as separate unitary transformations of the HF occupied and virtual orbitals which maximize the sum of the squares of the diagonal elements of the singles—singles block of the Hamiltonian. This yields a compact representation of CIS wave functions in terms of one or several dominant configurations, much like our present approach, although the definitions are not in fact mathematically equivalent. However, the SEAMO's were defined exclusively for the CIS method, by contrast with the attachment/detachment density analysis which can be applied to any excited state calculation that yields a one-particle difference density.

Remarkably, in the simple CIS method, the nonzero eigenvalues of the attachment and detachment densities are identical. Proof of this fact follows immediately from the defining relations 13, which show that $D = C^+C$ and $A = CC^+$ where C is the

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TABLE 1: Vertical Excitation Energies (eV) and Attachment/Detachment Density Analysis for Formaldehyde at the CIS/6-311(2+)G*//MP2/6-31G* Level of Theory[a]

state	ω/eV	p_{1PDM}	$p_{relaxed}$	$\lambda(A)_{1PDM}$	$\lambda(A)_{relaxed}$	$\lambda(D)_{1PDM}$	$\lambda(D)_{relaxed}$
$^1A_2$	4.48	1.00	1.28	0.997	1.004	0.997	0.998
$^1B_2$	8.63	1.00	1.61	0.992	0.993	0.992	0.995
					0.292		0.292
					0.105		0.111
$^1B_2$	9.36	1.00	1.61	0.989	0.989	0.989	0.991
					0.276		0.276
					0.115		0.120
					0.110		0.110
$^1A_1$	9.48	1.00	1.28	0.506	0.532	0.506	0.531
				0.464	0.501	0.464	0.512
$^1A_1$	9.70	1.00	1.34	0.582	0.614	0.582	0.596
				0.397	0.467	0.397	0.480
$^1A_2$	9.78	1.00	1.65	0.996	0.996	0.996	0.998
					0.290		0.288

[a] This optimized geometry was reported in ref 19. Promotion numbers p for the CIS one-particle density matrix (1PDM) and the relaxed density are in units of electronic charge, as are the largest eigenvalues, λ, of the attachment (A) and detachment (D) density matrices. Only eigenvalues greater than $0.1e$ are shown.

CIS amplitude matrix of dimension number of virtual orbitals (V) by number of occupied orbitals (O). Suppose x is an eigenvector of D belonging to eigenvalue λ: $Dx = \lambda x$. Then

$$A(Cx) = (CC^\dagger)(Cx) = C(C^\dagger C)x = CDx = \lambda Cx \quad (14)$$

which shows that Cx is an eigenvector of the attachment density with the identical eigenvalue λ. Since $Tr(A) = Tr(D) = 1$, the matrix of larger dimension will have extra zero eigenvalues. This result means that the CIS wave function is optimized such that the transition occurs from a single occupied orbital of the ground state HF wave function to exactly the same extent as it goes to a single unoccupied orbital. Note of course that these orbitals are both transition natural orbitals rather than the canonical orbitals obtained from a ground state HF calculation.

The absence of orbital relaxation in the CIS wave function (i.e., its failure to satisfy the Hellman–Feynman theorem) means that excited state properties calculated from the CIS wave function are relatively poor. In particular, it has been noted that CIS dipole moments calculated from the expectation value of the wave function are significantly poorer than those calculated as the derivative of the energy with respect to an applied electric field. Since the Hellman–Feynman theorem is not satisfied, these expressions are not equivalent definitions of the dipole moment. The gradient expression[16] yields an "effective" or "relaxed" density, which comprises eqs 13, but also an additional term in the occupied–virtual blocks:

$$\Delta_{ia} = \Delta_{ai} = z_i^a \quad (15)$$

where z is the solution of the CIS z-vector equation. The fact that the solution of the z-vector equations incorporates orbital relaxation in the presence of the field has been given as the reason for the superior dipole moments calculated by the energy derivative approach.

Attachment–detachment density analysis gives some insight into the nature of the "orbital relaxation", by considering the effect of eq 15 on the unrelaxed attachment and detachment densities. Since eq 15 couples the occupied–occupied and virtual–virtual blocks, we can no longer directly write down the solution for the attachment and detachment densities. However, we can analyze the general effect of the coupling. Treating eq 14 as a perturbation first affects the eigenvalues of the difference density in second order, with all negative eigenvalues becoming more negative and all positive eigenvalues becoming more positive. From the interleaving theorem for eigenvalues of symmetric matrices,[25] the same result can be

established in general: the promotion number for the relaxed CIS density rigorously satisfies $p \geq 1$.

The proposed definitions of attachment and detachment densities thus give a picture of electronic transitions which seems pleasingly consistent for single-excitation CI (CIS). Working directly from the CIS one-particle density matrix (1PDM) yields a one-electron transition, while inclusion of orbital relaxation effects via the CIS effective density increases the net number of electrons promoted in the transition. The difference between these two numbers is a direct measure of the extent of relaxation effects.

Finally, while in this section we have treated only the CIS method, very similar results can be established for the random phase approximation (RPA).[26] The RPA 1PDM also yields a transition number of 1, and orbital relaxation effects as defined by RPA gradient theory again increase the effective number of electrons involved in the transition. For more sophisticated excited state theories, explicit expressions for attachment and detachment densities cannot be obtained, but the general procedure of section 2.1 suffices.

3. Applications

3.1. Formaldehyde. The excited states of formaldehyde have been among the most intensively studied of any small organic species, and therefore it is a good candidate for a trial application of the new attachment–detachment density analysis. We choose to study vertical excitations in formaldehyde by the CIS method[16] using the 6-311(2+)G* basis at the ground state MP2/6-31G* geometry, to permit direct comparison with the careful and comprehensive study by Wiberg et al. using the same conditions.[19] Our objective is to investigate the effectiveness of the analysis rather than to obtain results of higher numerical quality than those already available.[17,27]

In Table 1, we report formaldehyde CIS/6-311(2+)G* vertical excitation energies and also the promotion number p and the larger eigenvalues of the attachment and detachment densities calculated by both the unrelaxed and relaxed definitions as discussed in section 2.3. All calculations were performed with the Q-Chem program.[28] In Figure 1, the unrelaxed attachment and detachment densities are plotted to illustrate the character of these transitions. A number of interesting points regarding both the nature of the CIS excited states and the electronic transitions can be made from Table 1 and Figure 1.

First, from Table 1, a number of these excitations can be considered single transitions to an excellent approximation. The largest eigenvalue is greater than 0.98 in the three lowest excited states for example. Therefore, the attachment and detachment
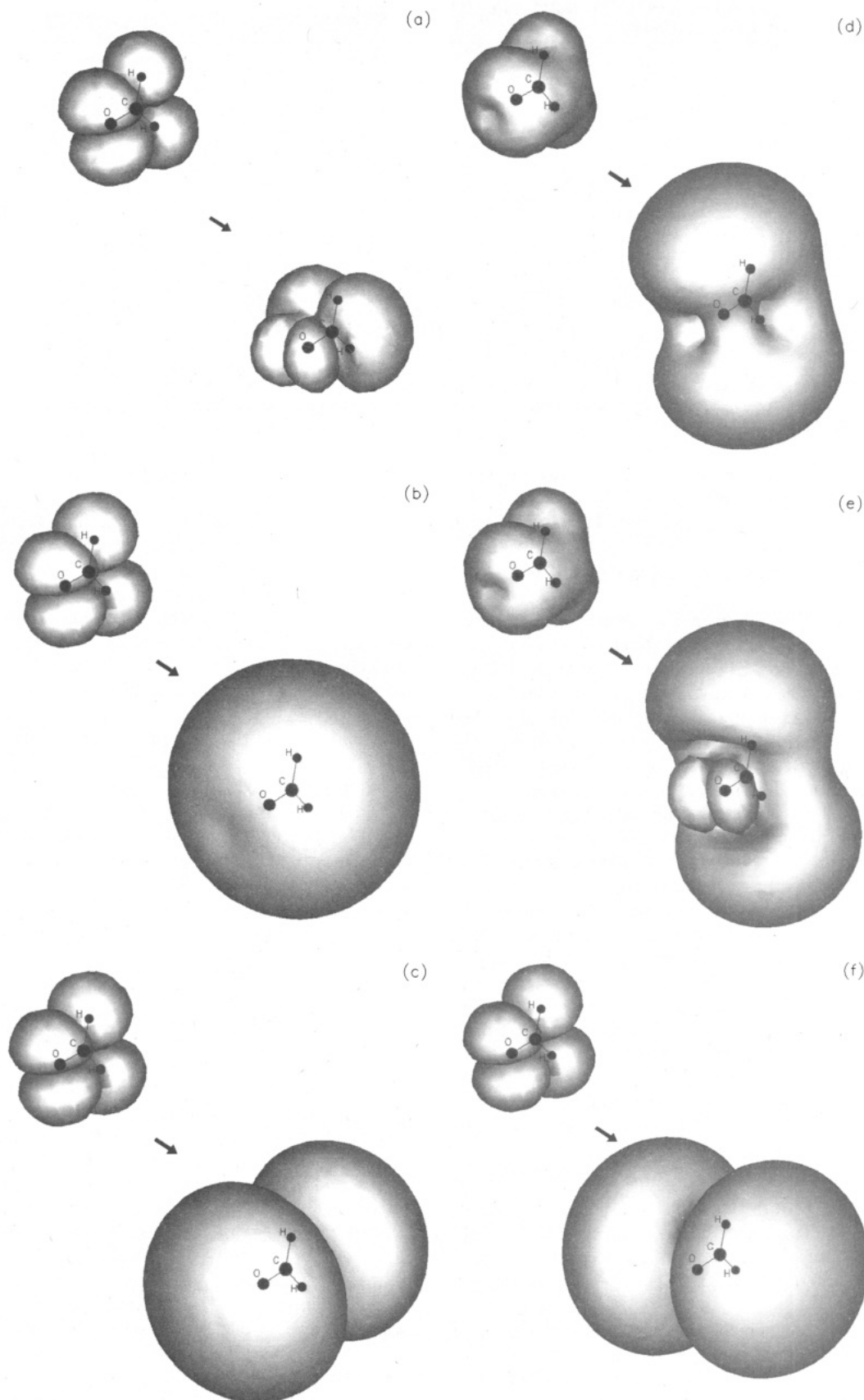
Figure 1. Isosurface plots of the attachment and detachment densities for six of the lowest singlet electronic transitions in formaldehyde, calculated at the CIS/6-311(2+)G*//MP2/6-31G* level of theory using the one-particle (unrelaxed) difference density matrix. The states plotted in panels a–f correspond to those listed in Table 1. The integrated value of the attachment and detachment densities over all space (defined as the promotion number) is identically 1 at this level of theory. The plotted surfaces correspond to a value of 0.0001 e bohr^{-3}.

densities can be directly interpreted as the promotion of an electron from an orbital which is the eigenvector belonging to this single dominant eigenvalue to an orbital which is the eigenvector belonging to same eigenvalue of the attachment

density. This observation *could not be drawn* from previous analysis of the difference density or the dominant configurations. Many significant configurations contribute to each excited state, but this is merely because the CIS wave function is expanded

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in a less-than-appropriate orbital basis: that of the molecular orbitals. From the plots in Figure 1, the character of these single transitions can be readily assigned: the lowest excited state is of n $\rightarrow$ π^* character, while the next two excited states are promotions from the same nonbonding level to 3s and 3p Rydberg levels. This is the interpretation given previously from difference density plots, but it is more apparent from our attachment and detachment density plots.

From Table 1, we also see two states (2^1A_1 and 3^1A_1) which are not single transitions, as evidenced by two significant eigenvalues of the attachment and detachment densities. The only way this result can occur within CIS calculations is if there is significant mixing between two different excitations in these excited states. In these states, a valence $\pi \rightarrow \pi^*$ transition mixes with an n $\rightarrow$ 3p Rydberg transition. The nature of these levels follows straightforwardly from the symmetries of the eigenvectors of **A** and **D**. Due to this extensive mixing, the plots of attachment and detachment densities for these two states are not as readily interpreted in chemical terms. In cases where there are several significant eigenvalues, they can be plotted separately if necessary to unravel the nature of the electronic transition.

We turn next to a comparison of the results using the relaxed density with those obtained from the unrelaxed density, which we had discussed more formally in section 2.3. We compare the promotion numbers for the relaxed density with those for the unrelaxed density to obtain a measure of the importance of orbital relaxation in describing the excited state density. The promotion number for unrelaxed CIS densities is identically one, while the relaxed density has $p \geq 1$ due to inclusion of orbital relaxation terms that are effectively contributions from double substitutions and higher as discussed in section 2.3. From Table 1 it is evident that promotion numbers are increased by between 28% and 60% upon use of the relaxed density. The largest increases in promotion number are for Rydberg states. We believe this reflects the greater rearrangement of the "spectator electrons" due to the creation of a positively charged core in such excitations. By contrast, excitations with valence character show the smaller increases. In summary, for the well-studied excited states of formaldehyde, the attachment and detachment density analysis provides a more direct and insightful approach to characterizing the states than was previously possible.

3.2. Nitromethyl Radical. The excited states of nitromethyl are of interest because of the rich photodissociation dynamics of this radical,[29] which is an intermediate in the combustion of nitromethane. The low-lying vertical electronic transitions are not well-characterized although there have been several previous calculations.[30,31,32] We will use attachment–detachment density analysis to study the electronic transitions. At the C_{2v} MP2/6-31G* geometry of the ground state,[31] we obtained the lowest state of each symmetry using unrestricted single and double quadratic configuration interaction (UQCISD)[33,34] with the 6-31G* basis. This basis is adequate for low-lying valence excited states and permits direct comparison with earlier calculations.[32] QCISD describes dynamical and even nondynamical electron correlation effects quite effectively[34] and eliminates the leading spin contaminant. The one-particle density matrices are defined by QCISD gradient theory and were calculated with the Gaussian 92 program[35] on the NERSC Cray C-90. Attachment/detachment density analysis according to eqs 1–10 was performed locally.

The ground state of the nitromethyl radical is of $^2B_1$ symmetry. UQCISD/6-31G* vertical excitation energies to the lowest excited states of B_2, A_1, and A_2 symmetry are shown in Table 2, together with the results of the attachment/detachment density analysis. From the promotion numbers for alpha and

TABLE 2: Vertical Excitation Energies (eV) and Attachment/Detachment Density Analysis for the Nitromethyl Radical at the UQCISD/6-31G* Level of Theory[a]

state	ω/eV	p_α	p_β	$\lambda(A)_\alpha$	$\lambda(D)_\alpha$	$\lambda(A)_\beta$	$\lambda(D)_\beta$
$^2B_2$	2.219	0.652	1.214	0.372	0.389	0.917	0.935
$^2A_2$	2.289	0.932	1.145	0.582	0.608	0.943	0.925
$^2A_1$	2.750	0.566	1.175	0.335	0.351	0.923	0.933

[a] All calculations were performed at the UMP2/6-31G* optimized geometry of the $^2B_1$ ground state (ref 31), and employ the frozen core approximation. Attachment–detachment analysis is performed separately in the alpha and beta spin spaces since they are inequivalent for radicals. Promotion numbers, p, are in units of electronic charge, as are the largest eigenvalues, λ, of the attachment (**A**) and detachment (**D**) density matrices (all omitted eigenvalues are less than 0.1 e).

beta electrons, and the largest few eigenvalues of the alpha and beta attachment and detachment density matrices in Table 2, we can characterize the excitations in terms of promotions from the $^2B_1$ ground state. To leading order, we regard the excitations as occurring from a single-determinant, restricted open-shell Hartree–Fock ground state.

From Table 2, we see that there are significant differences between the alpha and beta promotion numbers for all three excited states, indicating that excitations either into or out of the singly occupied b_1 orbital are important. The unpaired electron was of alpha spin in our calculations. Therefore, since the beta promotion number is larger than the alpha promotion number, promotions of a beta electron from a doubly occupied level (d) into the singly occupied orbital (s) of b_1 symmetry are dominant relative to promotions of the alpha electron from the singly occupied orbital (s) to unoccupied levels (v). In the single-determinant ground state picture, this implies that the promotion of at least 0.6 electrons is associated with this d $\rightarrow$ s excitation for the transition to the lowest $^2B_2$ state and the lowest $^2A_1$ state. By contrast, as few as only 0.2 electrons are promoted in this way to the lowest $^2A_2$ state.

A second important feature of the data in Table 2 is that the sum of the alpha and beta promotion numbers is much larger than one. This indicates that double excitations and higher are playing a significant role in addition to single excitations. A fraction of the double and triple substitutions are due to relaxation of pairs of electrons which are essentially inactive in the electronic transition (akin to the effect of the relaxed density in the CIS calculations of the previous section). This is responsible for roughly 0.4 electrons for each of the three excitations, based on the contributions from eigenvalues which are small, which leaves roughly 0.8 electrons to account for in the $^2B_2$ state and the $^2A_1$ state and about 1.2 electrons for the $^2A_2$ state.

The remaining single promotions are spin-adapted excitations from orbitals which are doubly occupied to orbitals which are vacant (as the SOMO and LUMO are both of b_1 symmetry, these will be from the same levels as the d $\rightarrow$ s transitions discussed above)

$$^2\Phi(d \rightarrow v) = \frac{1}{\sqrt{2}}(\Phi_d^v + \Phi_{\bar{d}}^{\bar{v}}) \qquad (16)$$

It is impossible to form a normalized wave function that can account for the promotions via eq 16. Therefore, double excitations must be significant. The lowest energy double excitations are spin-adapted single promotions from doubly occupied levels to vacant levels involving the singly occupied level as a "virtual state":

$$^2\tilde{\Phi}(d \rightarrow v) = \frac{1}{\sqrt{6}}(\Phi_d^v - \Phi_{\bar{d}}^{\bar{v}}) - \sqrt{\frac{2}{3}}\Phi_{sd}^{v\bar{s}} \qquad (17)$$
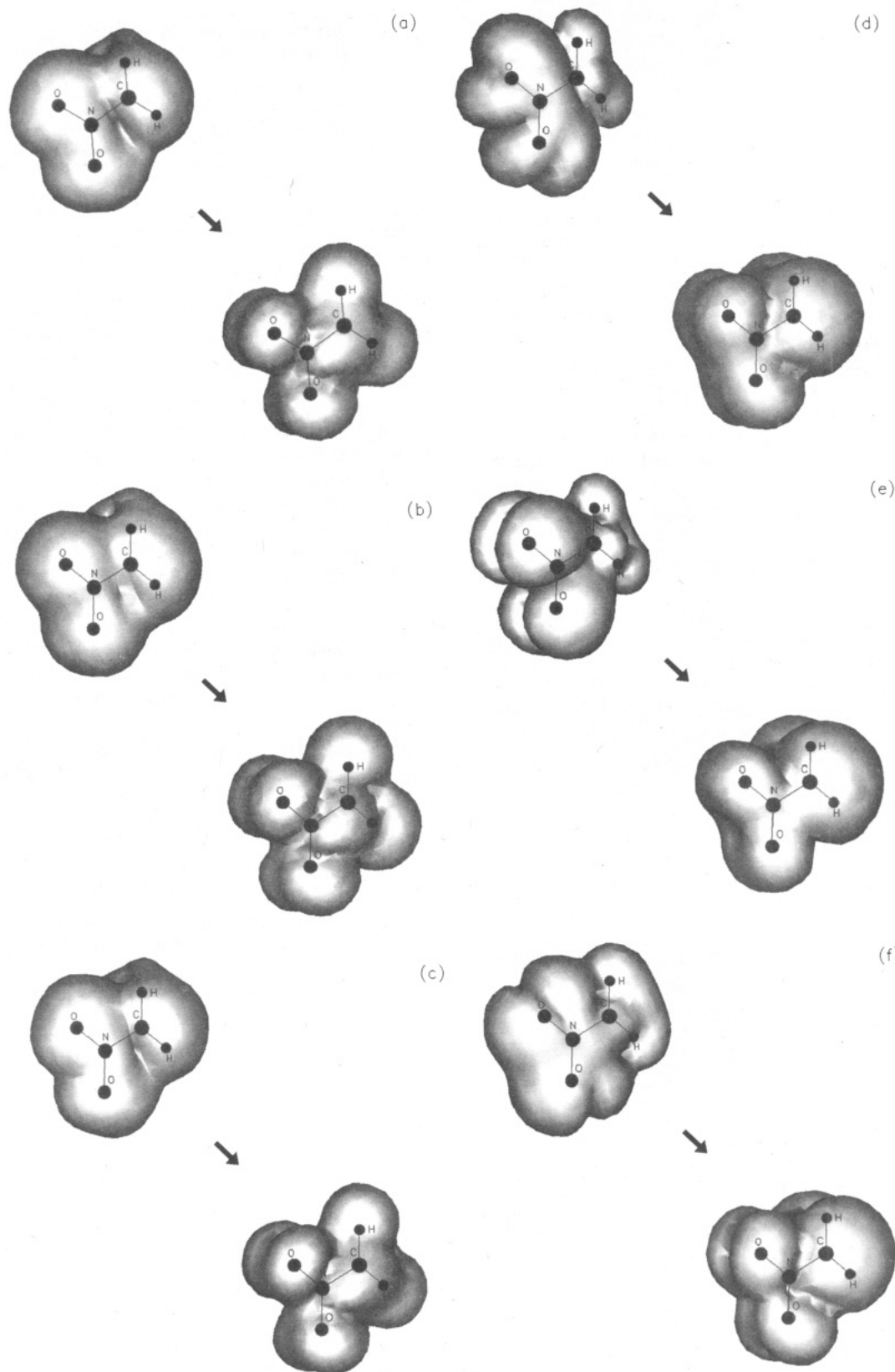
Figure 2. Isosurface plots of the attachment and detachment densities for transitions from the $^2B_1$ ground state of nitromethyl radical to the lowest excited states of $^2B_2$, $^2A_2$ and $^2A_1$ symmetry. The alpha and beta attachment and detachment densities are plotted separately for transitions to the $^2B_2$, $^2A_2$, and $^2A_1$ states in panels a–c and d–f, respectively. The alpha and beta promotion numbers (integrals of the attachment or detachment density over all space) for each transition are given in Table 2. The plotted surfaces correspond to a value of 0.0001 e bohr^{-3}.

This configuration contains much double-excitation character (it promotes $^5/_3$ electrons) and may account for most of the remaining promoted electrons. Using the electron counts, we estimate that eq 17 is predominant for the $^2A_2$ state and slightly less important than the d → s transition for the other two states.

Given this interpretation of the promotion numbers, we can

now examine plots of the alpha and beta attachment and detachment densities shown in Figure 2 for transitions to these three excited states. Let us consider the alpha attachment and detachment densities shown in Figure 2a–c first. It is striking that they appear almost identical for each of the three excitations. Why is this so when the symmetry of each excited state is

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TABLE 3: Vertical Excitation Energies (eV) to the Lowest Excited States of $^2B_2$, $^2A_2$, and $^2A_1$ Symmetry of the Nitromethyl Radical from the $^2B_1$ Ground State at Various Levels of Theory; All Calculations Employ the Frozen-Core Approximation

	$^2B_2$	$^2A_2$	$^2A_1$
MR-CI/6-31G* [a]	1.272	1.778	9.670
ROCIS/6-31G* [b]	4.557	6.183	4.688
UQCISD/6-31G* [c]	2.219	2.289	2.750
composite[d]	1.990	2.476	2.473

[a] Multireference configuration interaction calculations performed at the UHF/6-31G* optimized geometry of the $^2B_1$ ground state, from ref 32. [b] Restricted open-shell single-excitation configuration interaction calculations, performed at the UMP2/6-31G* optimized ground state geometry. [c] Unrestricted QCISD calculations used for attachment–detachment density analysis in Table 2. [d] Composite calculations using Gaussian-2 methodology (ref 2) with two differences. First, all calculations are performed at the UMP2/6-31G* optimized geometry of the $^2B_1$ ground state, and second, no zero-point energy contributions are included.

different? This points to the important role that the configuration shown in eq 17 plays in these excited states. In the alpha space, the promotion associated with the double excitation in eq 17 is *identical* for each of the three states. The detachment density is approximately the density associated with the singly occupied b_1 orbital, while the attachment density is the density associated with the LUMO, which is also of b_1 symmetry.

Turning to the beta attachment and detachment densities shown in Figure 2d–f, we see that all three attachment densities are similar but the detachment densities differ. The two most significant transitions, $\Phi(d{\rightarrow}s)$ and $\tilde{\Phi}(d{\rightarrow}v)$, eq 17, both involve predominantly attachment into the singly occupied orbital. This accounts for the similarity of the attachment densities. Furthermore, the resemblance between the alpha detachment densities and these beta attachment densities is also consistent with this interpretation. This resemblance is particularly striking between parts b and e of Figure 2 for the $^2A_2$ state, where eq 17 is most significant based on our earlier discussion. The beta detachment densities are the density of the beta spin levels vacated in each transition, which to a first approximation is the highest orbital of a_2, b_2, and a_1 symmetry for transitions to the $^2B_2$, $^2A_2$, and $^2A_1$ states, respectively.

Inspection of the attachment and detachment density plots in Figure 2 gives some insight into the changes in bonding between the ground state and these low-lying excited states. We note first that all three electronic transitions are substantially delocalized over the molecular framework. None can be considered local to the nitro group or the C–N bond. Returning to the alpha plots, we note that the alpha attachment densities in each case strengthen the CN bond and weaken the NO bonds. However, from the promotion numbers in Table 2, the promotions in the beta space are most significant. The beta attachment densities and the alpha detachment densities are all essentially nonbonding in the CN bond. Differences in excited state bonding therefore emerge largely from differences in the beta detachment densities. In each case, the detachment densities have bonding character between C and N, and therefore this bond length will increase relative to ground state. In this respect they more closely resemble the nitromethyl anion than the ground state of the neutral.

In Table 3 we report two additional sets of calculations we have performed at the same MP2/6-31G* geometry employed for the QCISD calculations and also summarize previous literature values for these excitation energies. The first additional set of results are restricted open-shell CIS calculations[36] at the ROCIS/6-31G*//MP2/6-31G* level. Their purpose is to test the correctness of our picture of the electronic transitions.

The fact that excitation energies at this simple level of theory are significantly too high is consistent with the fact that ROCIS omits double excitations of the form entering eq 17. The ROCIS excitation energy to the $^2A_2$ state is most poorly given, which matches our inference that it is likely to have the largest contribution from double substitutions. The ROCIS calculations thereby support the view that the electronic transitions are largely a mixture of (d → s) single excitations and double excitations via eq 17.

Comparison of the excitation energies in Table 3 with existing literature values shows that the positions of the QCISD/6-31G* vertical excitations to the $^2B_2$ state and the $^2A_2$ state are in rough agreement with previous multireference CI (MR-CI) calculations.[32] Since these calculations also employed the 6-31G* basis, and were at the UHF/6-31G* ground state geometry which differs only slightly from the MP2/6-31G* geometry we use, agreement of this level or better is expected. Surprisingly, we find a dramatic discrepancy of almost 7 eV in the position of the vertical excitation energy to the lowest $^2A_1$ state, which was calculated to lie at 9.67 eV in the calculations of Cai.[32]

Inspection of the significant configurations in the $^2A_1$ MR-CI wave function shows that the zero-order configurations are completely different from those we have established as significant for the lowest $^2A_1$ state. The leading MR-CI configuration is the lowest energy s → v excitation in the alpha space. The d → v double excitation, eq 17, is omitted in the reference, as is the d → s single excitation. Accordingly, the character of the lowest $^2A_1$ state found in the MR-CI calculations is completely different from the state we predict to be of lowest energy. The enormous difference in the calculated excitation energies illustrates vividly the necessity for having a qualitatively correct description of the state in the MR-CI reference function.

The second additional set of calculations in Table 3 is performed with the G2 procedure[2] with two exceptions: zero-point energy is omitted, and all calculations are at the ground state MP2/6-31G* geometry. This way vertical excitation energies are obtained. These results are the highest level calculations reported hitherto on the vertical excitation energies to these states of the nitromethyl radical and are usually accurate to a few tenths of an electronvolt. We note that the $^2A_2$ state exhibited substantial spin contamination. Overall, these calculations are qualitatively similar to the UQCISD/6-31G* calculations analyzed in detail above. In summary, our calculations and attachment/detachment density analysis have elucidated the nature of three of the low-energy electronic excitations in nitromethyl. This clarifies the origin of the dramatic failure of a previous calculation[32] for the $^2A_1$ state and the cause of the very large errors obtained via single-excitation configuration interaction calculations.

4. Conclusions

We have proposed and investigated a simple new procedure for the analysis of electronic transitions in terms of "attachment" and "detachment" densities. Subtracted, these two quantities yield the one particle difference density for the electronic transition. We believe that this decomposition will be valuable for many problems and note the following key points:

(1) There is an unambiguous definition of the detachment density matrix **D** as being the density associated with eigenvectors belonging to negative eigenvalues of the one-electron difference density matrix, weighted by the eigenvalue. **D** can be interpreted as the hole density of levels vacated in a transition. The attachment density matrix **A** is associated with eigenvectors belonging to positive eigenvalues, weighted by the eigenvalues also, and is to be interpreted as the density associated with single particle levels occupied in the transition.

(2) The attachment and detachment densities are an effective way to analyze electronic transitions obtained by high level calculations in a manner which is closely analogous to the simple picture of electron promotions from orbital to orbital. This decomposition yields a one-electron picture of an electronic transition as detachment density → attachment density, which can be analyzed to characterize the transition. We note that analysis of the one-electron transition density yields valuable complementary information.

(3) The eigenvalues and eigenvectors of the difference density can be regarded as an analog of natural orbitals for electronic transitions. The eigenvalue structure conveys information about the electronic transition. In particular, the trace of the attachment and detachment densities defines a promotion number, p, which indicates the effective number of electrons excited in an electronic transition.

(4) For single excitation configuration interaction (CIS), a number of properties of the attachment and detachment densities were established. For excitations from a Hartree—Fock ground state to a CIS excited state, $p = 1$. The nonzero eigenvalues of the CIS attachment and detachment densities are identical. The so-called relaxed CIS density satisfies $p \geq 1$. These results all have interesting physical interpretations.

(5) We have considered two examples. For formaldehyde, where the transitions are already well-known, the analysis yields clear insight into the character of the transitions which is intrinsically single transition to some states versus mixed valence—Rydberg in others. For nitromethyl, attachment—detachment density analysis was applied to transitions from the ground state to the lowest excited state of each different symmetry, showing that such transitions cannot be viewed as one-electron promotions. Improved values are obtained for the vertical excitation energy to three low-lying excited states.

(6) Attachment—detachment density analysis may be the best possible one-electron picture of an electronic transition from the ground to an excited state. The interpretation is quite straightforward and physically insightful for cases where the ground state is well described as a single configuration. One-electron analysis of any kind must however be used with care when the ground state has strong multiconfigurational character. For such cases it is also possible, although much less practical, to define two-electron detachment and attachment densities.

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