Deciphering excited state properties utilizing algebraic diagrammatic construction schemes of decreasing order

Marvin Hoffmann | Andreas Dreuw

Abstract

Excited state properties are difficult to trace back to the common molecular orbital picture when the excited state wavefunction is a linear combination of two or more Slater determinants. Here, a theoretical methodology is introduced based on the algebraic diagrammatic construction scheme for the polarization propagator (ADC(n)) that allows to make this connection and to eventually derive structure–function relationships. The usefulness of this approach is demonstrated by an analysis of the transition dipole moments of the low-lying 1B3u and 2B3u states of anthracene and (1,4,5,8)-tetraazaanthracene.

KEYWORDS

ab initio calculations, computational photochemistry, electronic structure analysis, excited electronic states, optical spectra

1 | INTRODUCTION

Optical properties and molecular photochemistry is determined by the electronic structure of the excited electronic states involved. Hence, analysis of their electronic structure is a prerequisite for understanding molecular photochemistry in general.1–4 The most straightforward analysis consists of simply inspecting the molecular orbitals involved in an electronic excitation.5,6 However, this quickly falls short when multiple molecular orbital pairs are needed to describe the transition into an excited electronic state. Alternatively, the difference between ground (P0) and excited state (PI) one-electron density matrices

\[ \Delta \alpha = P_1 - P_0, \]

that is, the difference density matrix \( \Delta \alpha \), can be analyzed. Diagonalization and splitting of its eigenvalues into electron detachment (negative sign) and attachment (positive sign) contributions offers an even more transparent picture of the electronic structure of the excited state.7,8 Alternatively, one can obtain information by analyzing the one-particle transition density matrix \( \gamma_{\alpha} \):

\[ \gamma_{\alpha}(r_e,r_h) = \int \cdots \Psi_0(r_1,r_2,...,r_N)\Psi_I(r_e,r_2,...,r_N)dr_2...dr_N. \] (2)

Here, \( r_e \) and \( r_h \) describe the coordinates of the excited electron and hole, respectively.7,10 By performing a singular value decomposition of the transition density matrix, one obtains the so-called natural-transition orbitals which in contrast to the simple molecular orbitals allow a more concise visualization of the electronic transition.11–13 Moreover, the transition density can be identified as an exciton wavefunction

\[ \chi_{\text{exc}}(r_e,r_h) = \gamma_{\alpha}(r_e,r_h), \] (3)

and used to calculate physical properties of the exciton as expectation values, such as electron–hole distance, exciton size and correlation coefficient.14–18

Although the density- and exciton wavefunction descriptors yield valuable physical insight into excitation character and properties of excited electronic states, the connection to the canonical molecular orbital picture, the current natural language of chemists, gets lost. This
happens immediately when already two singly excited determinants \( \psi \) constitute the excited state wavefunctions, for example,

\[
\psi_{1/2} = c_1 \phi_{H+1}^L + c_2 \phi_{H+1}^{L+1},
\]

(Equation 4)

with \( \phi_{H+1} \) describing a single electron transition from the HOMO to the LUMO+1 and \( \phi_{H+1}^{L+1} \) from the HOMO-1 to the LUMO. This is by no means unusual and this pattern (Equation 4) typically occurs in polyenes and related aromatic compounds.\textsuperscript{19-21} Going to densities and integration over the individual MO contributions eventually limits the interpretability and usefulness of quantum chemical results for synthesis in particular, since its rules are practically all based on the molecular orbital picture.

To return to a molecular orbital interpretation once the correlated excited state wavefunction has been calculated, the molecular factors determining the expansion coefficients \( c \) (Equation 4) as well as the individual properties of the determinants need to be known. This can be achieved by exploiting the systematic structure of ADC schemes for the polarization propagator with decreasing order of perturbation theory, that is, by analyzing the contributions of individual excited states at different orders. The methodological procedure will be outlined in the following and its usefulness demonstrated by explaining the differences in the absorption spectra of anthracene and (1,4,5,8)-tetraazaanthracene.

**2 | PRELIMINARY THEORETICAL CONSIDERATIONS**

Considering the simplest case consisting of the linear combination of two singly excited determinants according to Equation (4) allows one to construct a two-state model Hamiltonian to analyze the factors governing the expansion coefficients \( c \). Within this two-state model the effective Hamiltonian matrix is given as

\[
H_{\text{eff}} = \begin{pmatrix}
E & V \\
V & E + \Delta E
\end{pmatrix}
\]

(Equation 5)

with \( E \) being the energy of one p-h basis state and \( (E + \Delta E) \) being the energy of the second basis state, \( \Delta E \) is thus the energy difference between the two p-h basis states and \( V \) the coupling between them. The resulting eigenvalues after diagonalization are the energies of the excited states given as

\[
\lambda_{1/2} = \frac{1}{2} (\Delta E + 2E \pm \sqrt{\Delta E^2 + 4V^2})
\]

(Equation 6)

with their energetic splitting being

\[
\Delta \lambda = \sqrt{\Delta E^2 + 4V^2}.
\]

(Equation 7)

The corresponding non-normalized eigenvectors are given as

\[
v_{1,2} = \begin{pmatrix}
c_1 \\
c_2
\end{pmatrix} = -\frac{\Delta E \pm \sqrt{\Delta E^2 + 4V^2}}{2V}
\]

(\( V \))

(Equation 8)

whose elements determine the expansion coefficients \( c \) of the basis functions in the final state vectors. Considering the case of both basis states being equal in energy (\( \Delta E = 0 \)) results in the elements of the eigenvectors (i.e., the expansion coefficient \( c \) of the corresponding linear combination) to be independent from the coupling \( V \) and the resulting normalized eigenvectors are

\[
v_{1,2} = \frac{1}{\sqrt{2}} \begin{pmatrix}
\pm 1 \\
1
\end{pmatrix}
\]

(Equation 9)

Thus, both p-h basis states contribute equally to the resulting excited state in either symmetric (same sign) or asymmetric (opposite sign) manner. In the limit of \( \Delta E \) approaching infinity the resulting normalized eigenvectors are

\[
v_1 = \begin{pmatrix}
0 \\
1
\end{pmatrix}, v_2 = \begin{pmatrix}
1 \\
0
\end{pmatrix}
\]

(Equation 10)

Consequently, the two basis states decouple in the limit of an infinitely large energy gap and the resulting excited states are thus no longer linear combinations of two p-h basis states.

Understanding the molecular causes for the energetic splitting between two p-h basis states directly explains the degree of mixing between the basis states and the properties of the resulting excited states. While the difference in excitation energies of the resulting two excited states is trivial, getting the energetic splitting of two individual p-h basis states is not straightforward.

**3 | ALGEBRAIC-DIAGRAMMATIC CONSTRUCTION SCHEME FOR THE POLARIZATION PROPAGATOR**

The algebraic diagrammatic construction scheme for the polarization propagator (ADC) in its intermediate state representation offers an unique opportunity, since in analogy to the aforementioned two-state model, a Hermitian eigenvalue problem

\[
MY = Y\Omega,
\]

(Equation 11)

involving the ADC secular matrix \( M \) is solved which gives access to the diagonal matrix of vertical excitation energies \( \alpha_n \) and the excitation vectors \( y_n \). Here, the connection between the ADC matrix and the effective Hamiltonian of the two-state model (Equation 5) is of interest. The ADC secular matrix \( M \) has a block like structure and is build up from the correlated intermediate basis states which correspond to singly- (p-h), doubly- (2p-2h) and so forth excited configurations. The p-h, p-h block is always expanded to the maximum order, deterministically large energy gap and the resulting excited states are thus no

\[
Y_{\alpha} = \begin{pmatrix}
Y_1 \\
Y_2
\end{pmatrix}, Y_{\alpha} = \begin{pmatrix}
Y_1 \\
Y_2
\end{pmatrix}
\]

(Equation 12)

thus, both p-h basis states contribute equally to the resulting excited state in either symmetric (same sign) or asymmetric (opposite sign) manner. In the limit of \( \Delta E \) approaching infinity the resulting normalized eigenvectors are

\[
Y_{\alpha} = \begin{pmatrix}
0 \\
1
\end{pmatrix}, Y_{\alpha} = \begin{pmatrix}
1 \\
0
\end{pmatrix}
\]

(Equation 13)

Consequently, the two basis states decouple in the limit of an infinitely large energy gap and the resulting excited states are thus no longer linear combinations of two p-h basis states.

Understanding the molecular causes for the energetic splitting between two p-h basis states directly explains the degree of mixing between the basis states and the properties of the resulting excited states. While the difference in excitation energies of the resulting two excited states is trivial, getting the energetic splitting of two individual p-h basis states is not straightforward.
its diagonal elements which correspond to the energies of the two molecular orbitals involved in the particle-hole excitation state is simply given as the difference between the orbital energies diagonal element, that is, the energy of the p-h intermediate basis states in Equation (5). In zeroth-order perturbation theory the diagonal elements of the corresponding ADC(0) matrix, yield the energy of the individual intermediate basis states. Due to the hierarchical nature of the ADC(n) schemes, 795 terms for the diagonal elements of the singles block of the ADC(3) matrix, 28 whose explicit expressions can be found in the literature. 29,30

Calculating the ADC secular matrix using different orders of perturbation theory (ADC(0), ADC(1), ADC(2), etc.) allows by simple subtraction of the diagonal elements to obtain the individual contributions to the particle-hole intermediate basis state energy. For example

\[ D_{ia}^{\text{ADC}(0)} = (\epsilon_a - \epsilon_i) - \langle i | a | i \rangle. \] (12)

The indices \( i, j, k, \ldots \) denote occupied orbitals and \( a, b, c, \ldots \) virtual orbitals. Expanding the energy of the p-h intermediate basis state in first-order perturbation theory, the expression for the diagonal element of the particle-hole intermediate basis state within ADC (1) reads

\[ D_{ia}^{\text{ADC}(1)} = (\epsilon_a - \epsilon_i) - \langle i | a | i \rangle. \] (13)

The antisymmetrized integral \( \langle i | a | i \rangle \) which is now subtracted from the previous zeroth-order expansion (Equation 12) corresponds to the electron–hole Coulomb and exchange interaction and generally leads to a reduction of the energy for the p-h intermediate basis state in first order. While the orbital energy difference corresponds to IP – EA at the level of Koopman’s theorem, that is, the electric/band gap, \( D_{ia}^{\text{ADC}(1)} \) (Equation 13) now corresponds to an excitation energy and relates thus to an optical gap. Contributions of correlation effects to the intermediate basis state energy are first incorporated at second order. In total three additional second-order terms arise

\[
\begin{aligned}
&\frac{1}{2} \sum_{ck,ab} \langle ac|k|ck|ac\rangle \\
&\frac{1}{2} \sum_{ck,ab} \langle cd|k|cd\rangle \\
&- \sum_{ck,ab} \langle ac|k|ac\rangle
\end{aligned}
\] (14)

The first two terms describing the correlation effects due to the individual electron and hole orbital, respectively, whereas the third term describes electron–hole pair correlation, reminiscent of the second-order Møller–Plesset expression for the ground state. Therefore, in the case of ADC(2) where the intermediate basis states are constructed based on the MP2 ground state, the diagonal element of the singles block additionally contains these second-order terms. In a canonical orbital basis the explicit expression of the diagonal element of the particle-hole intermediate basis state of the ADC(2) matrix thus reads

\[
D_{ia}^{\text{ADC}(2)} = (\epsilon_a - \epsilon_i) - \langle i | a | i \rangle + \frac{1}{2} \sum_{ck,ab} \langle ac|k|ck|ac\rangle + \frac{1}{2} \sum_{ck,ab} \langle cd|k|cd\rangle - \sum_{ck,ab} \langle ac|k|ac\rangle
\] (15)

Expanding up to third-order perturbation theory, yields additional 29 terms for the diagonal elements of the singles block of the ADC (3) matrix, 28 whose explicit expressions can be found in the literature. 29,30

Geometric optimizations as well as frequency calculations were conducted with MP2 using the resolution-of-identity approximation (RI) and the def2-TZVP basis set 31 within the Psi4 software package...
in version 1.4. Subsequent ADC calculations in conjunction with the def2-SVPD basis set were performed using adcc in version 0.15.1 together with PySCF for the SCF procedure. Molecular structures were drawn using MarvinSketch.

5 | CASE STUDY: EXCITED STATES OF HETEROACENES

Acenes and polycyclic aromatic hydrocarbons in general possess two low-lying excited $\pi\pi^*$ states which are observed in the low-energy region of experimental UV/VIS absorption spectra. These states have been termed previously according to Platt as $1L_u$ and $1L_e$ states. Recently, an alternative nomenclature was proposed for the low-lying excited $\pi\pi^*$ states based on the physical properties of the corresponding exciton. The $1L_e$ state was shown to consistently exhibit a more strongly correlated electron–hole pair than the $1L_u$ state and was thus labeled as the $1L_s$ (strongly correlated) state next to the $1L_w$ (weakly correlated) state. This nomenclature was highlighted to be more strictly applicable independent of substitution patterns and the point group symmetry of nitrogen substituted acenes.

In the absorption spectrum of anthracene, for example, the $1L_w$ ($1B_{2u}$) state is visible at 3.67 eV, whereas the $1L_s$ ($1B_{3u}$) state has practically no oscillator strength at an excitation energy of 3.89 eV at the theoretical level of ADC(2) (Figure 2). However, when acenes are chemically modified by substitution or, as is the case here, by heteroatom introduction, the intensity of the $1L_s$ state increases. Focusing only on the $1L_s$ ($1B_{3u}$) state, this effect is here demonstrated for (1,4,5,8)-tetraazaanthracene (Figure 1), for which the computed absorption spectrum shows an increase of the intensity of the corresponding energetically higher-lying $2B_{3u}$ state compared to anthracene (Figure 2).

The origin of this effect is not understood at an electronic structure level and no guidelines exist for synthetic chemists how to modify the molecular structure to modulate the intensity of an absorption band, for example. For the latter an understanding in terms of molecular orbitals would be desirable, however, this is washed out when densities are used for interpretation.

Starting with anthracene, the two $1B_{3u}$ and $2B_{3u}$ states correspond to linear combinations of the $H−1−L$ and $H−L+1$ p−h intermediate basis states in analogy to Equation (4) (but here we take the squared expansion coefficients), that is

$$1B_{3u} = 0.44\%\phi_{H−1,L−1}^{1} − 0.42\%\phi_{H,L}^{1+1}$$  \hspace{1cm} (18)$$

and

$$2B_{3u} = 0.42\%\phi_{H−1,L+1}^{1} + 0.44\%\phi_{H,L}^{L+1}.  \hspace{1cm} (19)$$

Consequently, both p−h intermediate states contribute almost equally to the resulting $1B_{3u}$ and $2B_{3u}$ excited states. At the ADC(2)/def2-SVPD level of theory, $2B_{3u}$ possesses a substantial transition dipole moment of 4.27 a.u. (osc. strength: 2.43) in contrast to the $1B_{3u}$ state (Table 1) with a transition dipole moment of 0.06 a.u. (osc. Strength: 3.28×10^{-6}). Furthermore, the diagonal elements (i.e., energies) of both p−h intermediate basis states in the ADC (2) matrix before diagonalization are merely 0.01 eV apart in energy (Table 2). In analogy to a possible two-state coupling model, reminiscent of excitonic coupling of two degenerate chromophores, one excited state gets all the transition dipole moment whereas the other gets none.

In order to validate the applicability of the two-state model proposed earlier, the corresponding model Hamiltonian can be set up using the ADC(2) values ($\Delta E = \Delta D^{ADC(2)} = 0.01$ eV, $E = D_{H−L+1}^{ADC(2)} = 4.64$ eV, $\Delta \epsilon = 1.54$ eV):

$$H_{eff} = \begin{pmatrix} 4.64 & 0.77 \\ 0.77 & 4.64 + 0.01 \end{pmatrix}$$  \hspace{1cm} (20)$$

Note that the coupling $V$ can be calculated via rearranging Equation (7). Calculating the normalized eigenvectors (Equation 8) leads to squared expansion coefficients of the basis states in the eigenvectors.

FIGURE 1  Anthracene (1) and (1,4,5,8)-tetraazaanthracene (2)

FIGURE 2  Calculated electronic absorption spectra of anthracene and (1,4,5,8)-tetraazaanthracene at the ADC(2)/def2-SVPD level. Highlighted in gray are the two coupled $1B_{3u}$ and $2B_{3u}$ states for both molecules. Note the shift of intensity to the lower $1B_{3u}$ ($1L_u$) state at 3.8 eV when going from anthracene to tetraazaanthracene.
of 0.495 and 0.505 respectively, in agreement with the coefficient mixing ratio (0.51/0.49) in the ADC(2) vectors.

This demonstrates the general validity of the two-state model and identifies $\Delta D$ as the key factor determining the coefficients and subsequent mixing ratio of the eigenvectors. Therefore, the physical properties, for example, transition dipole moments, of the resulting excited states are mostly determined by the difference of the diagonal elements of the ADC matrix before diagonalization. ADC schemes offer now the opportunity to identify the chemical reasons for the energy difference of the diagonal elements $\Delta E$. This is achieved by utilizing decreasing orders of ADC schemes to calculate the individual perturbation theoretical corrections (Equation (16) of the p-h basis states which correspond to specific exciton properties as outlined above. Indeed, the differences in exciton properties dictate the observed variations in diagonal elements $\Delta D$ (Equation (17)) in the ADC matrices going from ADC(2) to ADC(1) and ADC(0). Following Equation (17), the diagonal element difference found within the ADC (2) matrix before diagonalization (0.01 eV, see Table 2) results from the sum of the three contributions (Table 3) $\Delta^{(2)}$ (0.05 eV), $\Delta^{(3)}$ ($-0.08$ eV) and $\Delta^{(2)}$ (0.04 eV).

By going from ADC(2) to ADC(1) and thereby removing electron correlation, $\Delta^{(2)}$, in the description of both p-h states results in a $\Delta D^{ADC(1)}$ of 0.03 eV (Table 2). Using the corresponding ADC(1) values in the two-state model Hamiltonian, the resulting squared normalized coefficients are practically unaffected due to the small change in diagonal element difference with values of 0.496 and 0.504 respectively.

Last, removing also electron–hole interaction by going to ADC (0) and thus only accounting for the difference in the energy gap between the respective virtual (electron) and occupied (hole) molecular orbitals leads to a diagonal element difference of 0.05 eV (Table 2). It is thus recognized that the differences in electron–hole interaction ($\Delta^{(0)}$) and correlation ($\Delta^{(2)}$) are in magnitude never significantly different from the difference in energy gap of the involved molecular orbitals ($\Delta^{(0)}$). Consequently, the mixing ratio stays almost constant with 0.5 throughout different orders of ADC schemes (Figure 3).

Examining now the transition dipole moments of the individual uncoupled p-h intermediate basis states at the ADC(0) level, reveals both to be very similar with 3.76 and 3.80 a.u., respectively (Table 1). Since the two eigenstates $1B_{3u}$ and $2B_{3u}$ are the difference and the sum of the two basis functions $\phi_{1/1}^{1/1}$ and $\phi_{1/1}^{2/1}$, it is clear that $1B_{3u}$ exhibits no transition dipole moment while $2B_{3u}$ has a larger transition dipole moment. Eventually, we were thus able to translate the excited state properties of the $1B_{3u}$ and $2B_{3u}$ states computed at the ADC (2) level. This also provides a suggestion for a recipe how to modulate the excited state properties of the $1B_{3u}$ and $2B_{3u}$ states by chemical modifications: the energies of the contributing orbitals need to change differently to module $\Delta E$ which appears to be the dominating term influencing the composition of the excited state wavefunctions, as will be demonstrated with the next example.

In (1,4,5,8)-tetraazaanthracene the $1B_{3u}$ (1L) state exhibits a significantly enhanced transition dipole moment of 1.24 a.u. (osc. strength: 0.15) compared to the unsubstituted anthracene (see Table 1). The enhanced transition dipole moment goes in hand with a considerable degree of de-mixing of both p-h basis states as seen by the coefficients for the excited states at the ADC(2) level:

$$1B_{3u} = -0.63\%\phi_{1/1}^{1/1} + 0.23\%\phi_{1/1}^{2/1}$$
Δcorresponding terms are determined by the differences in their exciton properties. The basis state mixing ratio of the resulting excited states is indicated by a vertical bar.

**TABLE 4** Particle-hole intermediate basis state energies $D$ of $\phi_{H-1}$ and $\phi_{H}^{+1}$ resulting difference ($\Delta D^{adc(n)}$) at different ADC(n) levels for (1,4,5,8)-tetraazaanthracene

| p-h State | $D$ (eV) |
|-----------|----------|
| $\phi_{H-1}$ | ADC(2) | ADC(1) | ADC(0) |
| 4.59 | 4.87 | 9.33 |
| $\phi_{H}^{+1}$ | 5.00 | 5.99 | 10.75 |
| $\Delta D^{adc(n)}$ | 0.41 | 1.12 | 1.42 |

Abbreviation: ADC, algebraic diagrammatic construction.

\[
2B_{3u} = 0.23\%\phi_{H-1} + 0.63\%\phi_{H}^{+1} \tag{22}
\]

Most notably, the energy difference $\Delta D^{adc(2)}$ of the two p-h basis states $\phi_{H-1}$ and $\phi_{H}^{+1}$ amounts to 0.41 eV (Table 4) and is therefore drastically larger compared to anthracene (0.01 eV). Calculating the squared normalized expansion coefficients using again the two-state model ($E = D^{adc(2)} = 4.59$ eV, $\Delta E = \Delta D^{adc(2)} = 0.41$ eV, $\Delta \epsilon = 1.59$ eV) results in a predicted mixing ratio of 0.63/0.37 ($\nu_1$) and 0.37/0.63 ($\nu_2$) respectively, which agrees well with the coefficient mixing ratio of the two p-h basis states within the ADC(2) excited states (0.62/0.38). Note, that the sum of both p-h basis state coefficients being not equal to 1 due to numerous insignificant minor contributions from other p-h basis states at ADC(2) level, which are not contained in the two-state model.

Nevertheless, the differences of the diagonal elements $\Delta D^{adc(2)}$ of the $\phi_{H-1}$ and $\phi_{H}^{+1}$ basis states prior to diagonalization is again determined by the differences in their exciton properties. The corresponding terms are $\Delta^{(2)} = -1.42$ eV, $\Delta^{(1)} = 0.30$ eV and $\Delta^{(3)} = 0.71$ eV, referring to differences in orbital energy gap, exciton Coulomb attraction and exchange repulsion, and in exciton correlation, respectively. The energy gap difference between the respective electron (virtual) and hole (occupied) molecular orbitals constitutes the largest term in magnitude, with the orbital energy gap ($\epsilon_v - \epsilon_h$) of the $\phi_{H-1}$ p-h basis state being significantly smaller (9.33 eV) compared to the $\phi_{H}^{+1}$ p-h basis state (10.75 eV). Even though $\Delta^{(3)}$ is the dominating term, $\Delta^{(2)}$ and $\Delta^{(1)}$ counteract due to their opposite sign and result in a lowering of $\Delta D$ at ADC(2) level. Obviously, the $\phi_{H}^{+1}$ p-h basis state exhibits a larger electron–hole interaction as well as electron–hole correlation (Table 5). This results in an increase of mixing of $\phi_{H}^{+1}$ and $\phi_{H-1}$ when going from ADC(0) to ADC(1) and ADC(2) (see Figure 4).

From a different perspective, removing correlation effects $\Delta^{(2)}$ in the p-h basis states leads to an increase in energy splitting from $\Delta D^{adc(2)} = 0.41$ eV to $\Delta D^{adc(1)} = 1.12$ eV and leads to a demixing in the resulting excited states. This is corroborated by the calculated mixing ratio using the ADC(1) values in the two-state model (Equation 8) which amounts to 0.79/0.21. Also the removal of electron–hole attraction and exchange repulsion $\Delta^{(1)}$ further increases the energy splitting between the p-h basis states.

**TABLE 5** Contributions to the diagonal elements $D$ of both p-h intermediate basis states $\phi_{H-1}$ and $\phi_{H}^{+1}$ of (1,4,5,8)-tetraazaanthracene as well as the resulting differences $\Delta^{(m)}$ at each perturbation theoretical order

| Term | (2) (eV) | (1) (eV) | (0) (eV) |
|------|---------|---------|---------|
| $\phi_{H-1}$ | -0.29 | -4.46 | 9.33 |
| $\phi_{H}^{+1}$ | -0.98 | -4.76 | 10.75 |
| $\Delta^{(m)}$ | -0.71 | -0.30 | 1.42 |

**FIGURE 3** Energies of the diagonal elements $D$ of both p-h basis states ($\phi_{H-1}, \phi_{H}^{+1}$) and resulting excited states (1B$_{3u}$, 2B$_{3u}$) after diagonalization $\omega$ of the respective ADC matrix in the case of anthracene. The basis state mixing ratio of the resulting excited states is indicated by a vertical bar.

**FIGURE 4** Energies of the diagonal elements $D$ of both p-h basis states ($\phi_{H-1}, \phi_{H}^{+1}$) and resulting excited states (1B$_{3u}$, 2B$_{3u}$) after diagonalization $\omega$ of the respective ADC matrix in the case of (1,4,5,8)-tetraazaanthracene. The resulting mixing ratio of the basis states in the final excited states is given as a vertical bar.
Let us now return to the question why the $1B_{2u}$ state acquires transition dipole moment and thus larger oscillator strength in (1,4,5,8)-tetraazaanthracene than in the parent anthracene. Both intermediate basis states $\phi_{H,L}^{1}$ and $\phi_{H,H}^{1}$ were symmetrically mixed in the $1B_{3u}$ and $2B_{3u}$ states of anthracene due to their energetic degeneracy, which resulted in an all-or-nothing distribution of the transition dipole moment between both excited states: $1B_{3u}$ nothing and $2B_{3u}$ all. In contrast in (1,4,5,8)-tetraazaanthracene, the introduction of the nitrogen atoms lead to an energetic splitting of $\phi_{H,L}^{1}$ and $\phi_{H,H}^{1}$ and consequently to their de-mixing in the corresponding $1B_{3u}$ and $2B_{3u}$ states. This breaks the all-or-nothing distribution of the transition dipole moment and thus $1B_{3u}$ gains some oscillator strength while $2B_{3u}$ loses some. Hence, the energetic splitting of the intermediate basis states determines the distribution of their properties, here the transition dipole moment, over the excited states.

Investigation of the involved molecular orbitals and their relative change in energy upon nitrogen substitution helps to illustrate the observed changes in physical properties (Figure 4). The MOs (Figure 5) can be grouped into whether the nitrogen atoms are included within the MO (H/L) or on a nodal plane (H – 1/L + 1). The energy of the HOMO and LUMO decrease more than HOMO – 1 and LUMO + 1, leading to an increase in $\Delta \epsilon_1$ for the $\phi_{H,H}^{1}$ p-h basis state and a decrease in $\Delta \epsilon_1$ for the $\phi_{H,L}^{1}$ p-h basis state, respectively. Therefore, the zeroth-order term difference ($\Delta^{(0)}$) increases leading to the observed decoupling of the p-h states.

As we have demonstrated above by going from ADC(2) to ADC(1) and ADC(0) allows analyzing the difference of the specific exciton properties with the zeroth-order contribution $\Delta^{(0)}$ being the dominant contribution in magnitude. Since $\phi_{H,L}^{1}$ and $\phi_{H,H}^{1}$ correspond to distinct molecular orbitals, the excited state properties can now be specifically modified by tuning the p-h basis state energies, in particular the molecular orbital energy gap as demonstrated above, by chemical substitution or heteroatom introduction into the parent molecule.

**ACKNOWLEDGMENTS**

Marvin Hoffmann acknowledges support by the Heidelberg Graduate School of Mathematical and Computational Methods for the Sciences, University of Heidelberg (GSC 220) as well as the Deutsche Forschungsgemeinschaft for funding within the Sonderforschungsbereich “N-Heteropolyzyklen als Funktionsmaterialien” (SFB 1249). Furthermore, Marvin Hoffmann thanks Maximilian Scheurer for support regarding adcc. Open access funding enabled and organized by Projekt DEAL. WOA Institution: Ruprecht Karls Universität Heidelberg. Blended DEAL: Projekt DEAL.

**ORCID**

Marvin Hoffmann https://orcid.org/0000-0001-6786-8291
Andreas Dreuw https://orcid.org/0000-0002-5862-5113

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How to cite this article: Hoffmann M, Dreuw A. Deciphering excited state properties utilizing algebraic diagrammatic construction schemes of decreasing order. J Comput Chem. 2021;42:793–800. https://doi.org/10.1002/jcc.26499