Lecture 3:
A closer look into electronic wavefunctions

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Excited State Phenomenology

- **Intramolecular excitations**
  - Valence states: $\pi\pi^*$, $n\pi^*$, $\pi\sigma^*$
  - Rydberg states

- **Intermolecular excitations**
  - Charge transfer states
  - Excitonic states

- **One-electron excited states (single excitations)**

- **Two-electron excited states (double excitations)**
Valence states

Bonding / non-bonding orbital → antibonding orbital

- Excitation within the valence space
- Bonding → antibonding orbital: $\pi\pi^*$, $\pi\sigma^*$, $\sigma\sigma^*$
- Lone pair → antibonding orbital: $n\pi^*$
Valence states

$\pi\pi^*$ states

- $\pi$-orbital: nodal plane in the molecular plane
- Typical UV absorbing states
Valence states

$n\pi^*$ states

- Usually "dark"
Valence states

\[ \pi\sigma^*, \sigma\sigma^* \] states

- Can lead to dissociation of the molecule
Rydberg states

- Excitations into diffuse orbitals
- Molecular ion circled by an electron

→ Similar to "Rydberg series" of the hydrogen atom
Rydberg states

Diffuse p-orbitals
Rydberg states

Rydberg states - in practice

Cutoff 0.04
Cutoff 0.03
Cutoff 0.02
Charge Transfer States

- Electron transfer between two chromophores
- Approximate energy

\[ E_{CT} \approx IP + EA - \frac{1}{R} \]

- Strong dependence on the intermolecular separation!
Excitons

- Excited states in larger systems
- Coupled local excitations
  - many orbitals involved
- Alternative viewpoint: *electron-hole* pair
  - two-body wavefunction
    \[ \chi_{\text{exc}}(x_h, x_e) \]
How to move from a computation to a phenomenological description?
Many-electron wavefunctions

Starting point:

\[
\hat{H} \Psi_0(x_1, x_2, \ldots) = E_0 \Psi_0(x_1, x_2, \ldots)
\]
\[
\hat{H} \Psi_I(x_1, x_2, \ldots) = E_I \Psi_I(x_1, x_2, \ldots)
\]

- How to describe the many-electron function \( \Psi_0(x_1, x_2, \ldots) \)?
- How to discuss changes between \( \Psi_0(x_1, x_2, \ldots) \) and \( \Psi_I(x_1, x_2, \ldots) \)?

→ Systematic complexity reduction through reduced density matrices
Density Matrices

Integrate out all the coordinates except for one

1-Electron reduced density matrix (1DM)

\[ \gamma(x, x') = n \int \ldots \int \Psi(x, x_2, \ldots, x_n) \Psi(x', x_2, \ldots, x_n) dx_2 \ldots dx_n \]

1DM in second quantization

\[ D_{\mu\nu} = \langle \Psi | \hat{a}_\mu^\dagger \hat{a}_\nu | \Psi \rangle \]
\[ \gamma(x, x') = \sum_{\mu\nu} D_{\mu\nu} \chi_\mu(x) \chi_\nu(x') \]

\( \gamma(x, x') \) Coordinate representation of the 1DM

\( D_{pq} \) Matrix representation of the 1DM

\( \chi_\mu, \chi_\nu \) Atomic orbitals

\( \hat{a}_\mu^\dagger, \hat{a}_\nu \) Creation and annihilation operators
Density Matrix

Physical meaning

Expectation value of a 1-electron operator

\[ \langle \Psi | \hat{O}_1 | \Psi \rangle = n \int \ldots \int \Psi(x_1, x_2, \ldots, x_n) \hat{O}_1 \Psi(x_1, x_2, \ldots, x_n) \, dx_1 \, dx_2 \ldots \, dx_n \]

Dipole moment, angular momentum, kinetic energy, ...

Using the 1DM

\[ \langle \Psi | \hat{O}_1 | \Psi \rangle = \sum_{\mu \nu} D_{\mu \nu} \int \chi_{\mu}(x_1) \hat{O}_1 \chi_{\nu}(x_1) \, dx_1 \]

- Many-electron integral reduced to a summation over 1-electron integrals
- All wavefunction-specific information contained in the 1DM
→ Logical starting point for wavefunction analysis
Electron Density

\[ \rho(x) = \gamma(x, x) \]
\[ \rho(x) = n \int \ldots \int \Psi(x, x_2, \ldots, x_n)^2 dx_2 \ldots dx_n \]

- Description of the overall electron distribution

Adenine

- Ground state
- \( n\pi^* \) state
- \( \pi\pi^*(L_b) \) state
- \( \pi\pi^*(L_a) \) state

- Not really helpful ...

F. Plasser  
Electronic Wavefunctions  
19 / 54
**Next step:** Divide the electron density into contributions of different atoms

- There is no unique way to do so!
Population Analysis

Mulliken population of atom A

\[ n(A) = \sum_{\mu \in A} (DS)_{\mu\mu} \]

- Summation over diagonal 1DM elements
- Correction for non-orthonormality of the AOs

Löwdin population of atom A

\[ n(A) = \sum_{\mu \in A} (S^{1/2}DS^{1/2})_{\mu\mu} \]

\( S \) AO-overlap matrix
Population Analysis

Many other options exist

- Atoms in molecules decomposition of the density\(^1\)
- Hirshfeld charges
  - Comparison with atomic densities
- Natural population analysis\(^2\)
- Fitting to electrostatic potential
- ...

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Population Analysis

- Different states of Adenine
- ADC(2)/cc-pVDZ
- Mulliken charges of the N-atoms

<table>
<thead>
<tr>
<th>gr. st.</th>
<th>$N_1$</th>
<th>$N_3$</th>
<th>$N_7$</th>
<th>$N_9$</th>
</tr>
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<tbody>
<tr>
<td>$n\pi^*$</td>
<td>-0.28</td>
<td>-0.27</td>
<td>-0.25</td>
<td>-0.17</td>
</tr>
<tr>
<td>$\pi\pi^*(L_b)$</td>
<td>-0.21</td>
<td>-0.21</td>
<td>-0.23</td>
<td>-0.16</td>
</tr>
<tr>
<td>$\pi\pi^*(L_a)$</td>
<td>-0.28</td>
<td>-0.27</td>
<td>-0.27</td>
<td>-0.15</td>
</tr>
</tbody>
</table>
Natural Orbitals

Diagonalization of the 1DM

Natural orbitals

\[ \mathbf{D} = \mathbf{T} \times \text{diag}(n_1, n_2, \ldots) \times \mathbf{T}^T \]

- **\( \mathbf{T} \)**: Natural orbital coefficients
- **\( n_i \)**: Occupation numbers
  - Closed shell orbitals (\( n_i = 2 \))
  - Open shell / active orbitals (\( 0 < n_i < 2 \))
  - Unoccupied orbitals (\( n_i = 0 \))
NaI

- $S_3$ state at 7.0 Å separation
- Closed-shell state
- $\text{Na}^+ + \text{I}^-$

$n_i = 0.00$

$n_i = 2.00$

$n_i = 2.00$

$n_i = 2.00$
Natural orbitals

NaI

- $S_0$ state at 7.0 Å separation
- Biradical state
- Na · + · I
- Only small covalent interaction

Hint: Use a smaller cutoff value (0.03)

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>I</th>
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<tbody>
<tr>
<td>$n_i$ = 0.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_i$ = 1.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_i$ = 2.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_i$ = 2.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Transition Density Matrices

Comparison of two wavefunctions $\Psi_0$ and $\Psi_I$

1-Electron transition density matrix (1TDM)

\[
\gamma_{0I}(x_h, x_e) = n \int \cdots \int \Psi_0(x_h, x_2, \ldots, x_n) \Psi_I(x_e, x_2, \ldots, x_n) \, dx_2 \cdots dx_n
\]

1TDM in second quantization

\[
D_{\mu\nu}^{0I} = \langle \Psi_0 | \hat{a}_\mu^\dagger \hat{a}_\nu | \Psi_I \rangle
\]

\[
\gamma_{0I}(x_h, x_e) = \sum_{\mu\nu} D_{\mu\nu}^{0I} \chi_\mu(x_h) \chi_\nu(x_e)
\]

$\gamma_{0I}(x_h, x_e)$ Coordinate representation of the 1TDM

$D_{\mu\nu}^{0I}$ Matrix representation of the 1TDM

$x_h, x_e$ Coordinates of the excitation hole and excited electron
Transition Density Matrix

Physical meaning

**Transition property of a 1-electron operator**

\[
\langle \Psi_0 | \hat{O}_1 | \Psi_I \rangle = \sum_{\mu \nu} D_{\mu \nu}^{0I} \langle \chi_\mu | \hat{O}_1 | \chi_\nu \rangle
\]

- Transition moments, oscillator strength
Transition Density

\[ \rho_0 I(x) = \gamma_0 I(x, x) \]

Adenine

- \( n\pi^* \) state
- \( \pi\pi^*(L_b) \) state
- \( \pi\pi^*(L_a) \) state

- Physical meaning: transition moments
- Interaction with light
- **But**: no intuitive interpretation
Natural Transition Orbitals

Singular value decomposition of the 1TDM

\[ \mathbf{D}^{0I} = \mathbf{U} \times \text{diag}(\sqrt{\lambda_1}, \sqrt{\lambda_2}, \ldots) \times \mathbf{V}^T \]

- \( \mathbf{U} \) *Hole* orbital coefficients
- \( \lambda_i \) Transition amplitudes
- \( \mathbf{V} \) *Electron* orbital coefficients

- Compact representation of the excitation
- Important for large basis sets

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Natural Transition Orbitals

- Adenine: ADC(3)/aug-cc-pVDZ
- $S_4$ state
- Canonical orbitals, 5 dominant transitions
  - LUMO+6 $\uparrow-0.39$
  - LUMO+11 $\uparrow-0.36$
  - LUMO+13 $\uparrow+0.21$
  - LUMO+10 $\uparrow-0.20$
  - LUMO+14 $\uparrow-0.13$

- Low energy virtual orbitals are very diffuse (quasi-continuum)
Natural Transition Orbitals

- Individual orbitals do not have a physical meaning
- Canonical orbitals can be misleading
- Decisive: 1TDM $\gamma_{0I}(x_h, x_e)$
- Optimal representation through natural transition orbitals
Natural Transition Orbitals

- Adenine: ADC(3)/aug-cc-pVDZ
- Natural transition orbitals
- One dominant transition
  - Compact valence state
- Diffuse orbitals were only artifacts!

$\uparrow 97\%$
**Linear combination** of the orbitals

\[
-0.39 \times + 0.21 \times -0.13 \times -0.26 \times -0.20 \times
\]

Natural Transition Orbitals
Statistical Analysis

Analysis of the distribution of the hole/electron in space

**Hole density**

\[ \rho_h(x_h) = \int \gamma_0 I(x_h, x_e) dx_e \]

**(Excess) electron density**

\[ \rho_e(x_e) = \int \gamma_0 I(x_h, x_e) dx_h \]

- Analysis of statistical moments
  - Centroids
  - Root-mean-square size \( \sigma_h, \sigma_e \)
Statistical Analysis

- Adenine, ADC(3)/aug-cc-pVDZ
- Statistical moments

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$ (eV)</th>
<th>Osc. Str.</th>
<th>$\sigma_h(\sigma_{h,z})$</th>
<th>$\sigma_e$</th>
<th>Character</th>
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<tbody>
<tr>
<td>$S_1$</td>
<td>5.23</td>
<td>0.138</td>
<td>2.09(0.75)</td>
<td>2.27</td>
<td>$\pi\pi^*$</td>
</tr>
<tr>
<td>$S_2$</td>
<td>5.41</td>
<td>0.142</td>
<td>2.17(0.73)</td>
<td>2.39</td>
<td>$\pi\pi^*$</td>
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<tr>
<td>$S_3$</td>
<td>5.53</td>
<td>0.010</td>
<td>2.19(0.75)</td>
<td><strong>4.11</strong></td>
<td>Rydberg</td>
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<tr>
<td>$S_4$</td>
<td>5.62</td>
<td>0.002</td>
<td>1.98(0.43)</td>
<td>2.23</td>
<td>$n\pi^*$</td>
</tr>
<tr>
<td>$S_5$</td>
<td>5.90</td>
<td>0.000</td>
<td>2.20(0.75)</td>
<td><strong>4.73</strong></td>
<td>Rydberg</td>
</tr>
</tbody>
</table>
Difference Density Matrices

Subtract the density matrices of the ground state and excited state

1-Electron difference density matrix (1DDM)

\[ \Delta^{0I} = D^{II} - D^{00} \]

Adenine

- \( n\pi^* \) state
- \( \pi\pi^* (L_b) \) state
- \( \pi\pi^* (L_a) \) state

- Physical meaning: changes in one-electron properties during the excitation process
- **But**: Not very intuitive
Attachment/detachment analysis

Natural difference orbitals

\[
D^{II} - D^{00} = W \times \text{diag}(\kappa_1, \kappa_2, \ldots) \times W^T
\]

- **W** Natural difference orbital coefficients
- **\(\kappa_i < 0\)** Detachment eigenvalues, \(d_i\)
- **\(\kappa_i > 0\)** Attachment eigenvalues, \(a_i\)

- Weighted sum over all positive (negative) eigenvalues leads to the attachment (detachment) densities\(^1\)

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Attachment/Detachment Densities

**Adenine, ADC(2)/cc-pVDZ**

- $n\pi^*$ state
- $\pi\pi^*(L_b)$ state
- $\pi\pi^*(L_a)$ state
Phenomenology 1DM 1TDM/1DDM Exciton TheoDORE C

Natural Difference Orbitals

- Adenine, ADC(2)/cc-pVDZ, $n\pi^*$ state
- Comparison of transition and difference DMs

### NTOs

<table>
<thead>
<tr>
<th></th>
<th>NTOs</th>
<th>NDOs</th>
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<tr>
<td></td>
<td><img src="image1" alt="NTO1" /></td>
<td><img src="image2" alt="NTO2" /></td>
</tr>
<tr>
<td>$\lambda_1$</td>
<td>0.84</td>
<td>$a_1$</td>
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<tr>
<td></td>
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<td><img src="image4" alt="NTO4" /></td>
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<tr>
<td>$\lambda_1$</td>
<td>0.84</td>
<td>$d_1$</td>
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### NDOs

<table>
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<th>NDOs</th>
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<tbody>
<tr>
<td></td>
<td><img src="image5" alt="NDO1" /></td>
<td><img src="image6" alt="NDO2" /></td>
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<tr>
<td>$a_2$</td>
<td>0.07</td>
<td>$d_2$</td>
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<tr>
<td></td>
<td><img src="image7" alt="NDO3" /></td>
<td><img src="image8" alt="NDO4" /></td>
</tr>
<tr>
<td>$a_3$</td>
<td>0.06</td>
<td>$d_3$</td>
</tr>
</tbody>
</table>

- Main transition the same
- But additional contributions in the 1DDM
- **Orbital relaxation**
Exciton Analysis

Main idea

- Interpret the 1TDM as the wavefunction $\chi_{exc}$ of the electron-hole pair
- Use as a basis for analysis

**Exciton wavefunction**

$$\chi_{exc}(x_h, x_e) = \sum_{\mu\nu} D_{\mu\nu}^{0I} \chi_\mu(x_h) \chi_\nu(x_e)$$
Exciton Analysis

Charge transfer numbers

\[ \Omega_{AB} = \int_A dx_h \int_B dx_e \chi_{exc}(x_h, x_e) \]

- **A** Fragment where the hole is localized
- **B** Fragment where the electron is localized
- \(\Omega_{AB}\) Probability

- Pseudocolor matrix plot of the \(\Omega_{AB}\) matrix

(a) \(-\)

(b) \(+\)

(c) \(\chi_{exc}\)
Exciton Analysis

- Example: Poly(para phenylene vinylene)
- ADC(2)/SV(P)

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Exciton Analysis

Singlet

$1^1B_u - W(1,1)$

$2^1A_g - W(1,2)$

$2^1B_u - W(1,3)$

$3^1A_g - W(1,4)$

$7^1B_u - W(1,5)$

$10^1A_g - W(1,6)$

$4^1A_g - W(2,1)$

$3^1B_u - W(2,2)$

$8^1A_g - W(2,3)$

$9^1B_u - W(2,4)$

$11^1A_g - W(2,5)$

$10^1B_u - W(3,1)$
**Exciton Analysis**

**Triplet**

- $1^3B_u - W(1,1)$
- $1^3A_g - W(1,2)$
- $2^3B_u - W(1,3)$
- $2^3A_g - W(1,4)$
- $3^3B_u - W(1,5)$
- $3^3A_g - W(1,6)$
- $4^3B_u - W(1,7)$
- $4^3A_g - W(1,8)$
- $5^3B_u - W(1,9)$
- $6^3A_g - W(1,10)$
- $5^3A_g - W(2,1)$
- $9^3B_u - W(2,2)$
TheoDORE - **Theoretical Density, Orbital Relaxation and Exciton analysis**

- Program package for wavefunction analysis
- Interfaces to a number of quantum chemistry programs: Molcas, Turbomole, Columbus, Orca, GAMESS, ...
- Open-source: http://theodore-qc.sourceforge.net
Main scripts

- **theoinp**
  Input generation

- **analyze_sden.py**
  - Analysis of state/difference density matrices
  - Population analysis
  - Attachment/detachment analysis

- **analyze_tden.py**
  - Analysis of transition density matrices
  - Natural transition orbitals
  - Electron-hole correlation plots
libwfa - A wavefunction analysis library

- State/transition/difference DM analysis methods
- Orbitals + densities
- Different population analyses
- Also tools in coordinate space
- Available in **Q-Chem**: TDDFT, EOM-CC, ADC
- Interface to **MOLCAS** in progress: CASSCF, CASPT2
Conclusions

Analysis of electronic wavefunctions - why?

1. Make things easier
   - Compact orbital representations
   - Automatization

2. Give specific quantitative results
   - Charge transfer character
   - Delocalization
   - Spatial extent
   - Double excitation character

3. Provide new physical insight
   - Orbital relaxation
   - Exciton correlation

There is more to wavefunctions than meets the eye!
Density matrices

- Other textbooks ...

Basic analysis techniques