New Tools for Computational Photochemistry: Wavefunction Analysis and Dynamics

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Introduction

Computational Photochemistry

- Going beyond standard quantum chemistry
- ? What really happens to the electrons after photoexcitation
- \rightarrow Wavefunction analysis









- 7 Time-resolved description
- \rightarrow Nonadiabatic dynamics





Photophysics of interacting nucleobases

- What happens after DNA is excited by UV light
- Energy transfer¹
- Electron transfer and exciplex formation²

Starting point: UV absorption

- Localized/delocalized excitations
- Charge transfer states



 $^1 \rm D.$ Onidas, T. Gustavsson, E. Lazzarotto, D. Markovitsi, PCCP 2007, 9, 5143. $^2 \rm T.$ Takaya, C. Su, et al., PNAS 2008, 105, 10285.

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Polyadenine (single stranded)

- QM/MM calculation
 - 8 nuclebases in the QM region
- CAM-B3LYP/SV(P) excitation energies
 - GPU-based Terachem code
- ▶ 100 MD snapshots × 60 excited states
- Bow do we analyze **6000** excited states?



¹J. J. Nogueira, FP, L. González, *Chem. Sci.* **2017**, 8, 5682.

Leading configurations

$\begin{array}{c} \bullet S_1 \text{ state} \\ H-2 \rightarrow L+1 \\ H-2 \rightarrow L \\ H-2 \rightarrow L+1 \end{array}$	1 (-0.70) (-0.47) 10 (0.29)
$\begin{array}{c} \bullet S_2 \text{ state} \\ \text{H-2} \rightarrow \text{L+1} \\ \text{H-2} \rightarrow \text{L+2} \\ \text{H-2} \rightarrow \text{L+2} \end{array}$	10 (-0.45) 1 (-0.40) 2 (0.35)

Tedious work
Possible ambiguities



Compact Visualization

- Natural transition orbitals¹
- Singular value decomposition of the transition density matrix
- S₁ state
- Locally excited state (L_a)
- Only one important configuration



- © Resolves (some) ambiguities
- Still tedious work

¹R. L. Martin, J. Chem. Phys. **2003**, 118, 11.

Excited states in multichromophoric systems



- O Where the excitation comes from "hole"
- Where the excitation goes to "electron"
- Connection between electron and hole decisive
- 1 2-dimensional picture

Quantitative Description

Transition density matrix (1TDM)

 $D^{0I}_{\mu\nu} = \langle \Psi_0 | \, \hat{a}^{\dagger}_{\mu} \hat{a}_{\nu} \, | \Psi_I \rangle$

 Ψ_0, Ψ_I Ground and excited state wavefunctions $\hat{a}^{\dagger}_{\mu}, \hat{a}_{\nu}$ Creation and annihilation operators

- 2-dimensional population analysis
- ightarrow Charge transfer numbers Ω_{AB}
- Consider individual adenine molecules A1, A2, A3, A4, ...
- Locally excited contributions (diagonal)
- CT contributions (off-diagonal)

Transition density matrix



¹FP, H. Lischka, *JCTC* **2012**, 8, 2777.

²FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

Statistical Analysis

Delocalization length

? How many fragments contribute to the excitation

ightarrow Count the number of non-vanishing Ω_{AB} values

Delocalization Length $DL = \frac{\Omega^2}{\sum_A \left(\sum_B \frac{\Omega_{AB} + \Omega_{BA}}{2}\right)^2}$

DL=1 Locally excited state (only one molecule involved) DL>1 Delocalized exciton or charge transfer state

Polyadenine

Delocalization length (DL)

- Decomposition of the spectrum
- Analysis of 6000 excited states
- Main contribution: DL=2
- Nearest neighbor interactions
- Additionally: DL=1, DL=3
- No significant contributions > 4



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¹J. J. Nogueira, FP, L. González, Chem. Sci. **2017**, 8, 5682.

Polyadenine

Charge transfer (CT)

- Local and Frenkel exciton states (CT < 0.1)
- $\rightarrow~51\%$ of the spectral intensity
- $\rightarrow~{\sf CT}$ admixture for remaining states
- States with significant CT character (CT> 0.3)
- ightarrow Low intensity, high energies



¹J. J. Nogueira, FP, L. González, *Chem. Sci.* **2017**, 8, 5682.

Oligothiophene

Oligothiophene



- Prototypical conjugated polymer
- CAM-B3LYP computations
- ? How to analyse the states
- ${}^{\scriptsize \ensuremath{{\odot}}}$ Just many delocalized π and π^* orbitals
- Plot matrix of CT numbers
- \rightarrow Electron-hole correlation plot

Oligothiophene

Electron-hole correlation plots



- Excitonic structure visible
 - Different nodal planes
- More intuitive visualization

Transition density matrix (real space)

$$\gamma^{0I}(r_h, r_e) = \sum_{\mu\nu} D^{0I}_{\mu\nu} \chi_{\mu}(r_h) \chi_{\nu}(r_e)$$

 $\begin{array}{l} \gamma^{0I}(r_h,r_e) \ \, \mbox{Transition density matrix (real space)} \\ D^{0I}_{\mu\nu} \ \, \mbox{Transition density matrix (matrix representation)} \\ \chi_{\mu} \ \, \mbox{Atomic orbital} \end{array}$

Conditional density for the excited electron

$$\rho_e^{h:A}(r_e) = \int_A \gamma^{0I}(r_h, r_e)^2 \mathrm{d}r_h$$

 $\rho_e^{h:A}(r_e)$ Conditional density for the hole localized on fragment A





S_1 state

- Overall electron and hole densities delocalized
- Conditional electron density follows hole

¹S. A. Bäppler, FP, M. Wormit, A. Dreuw, *PRA* **2014**, 90, 052521.

²FP, B. Thomitzni et al., *JCC* **2015**, 36, 1609.

Exciton Analysis

Exciton analysis

- ▶ Interpret the 1TDM as the wavefunction χ_{exc} of the electron-hole pair
- Use as a basis for analysis

Exciton wavefunction

$$\chi_{exc}(x_h, x_e) = \sum_{\mu\nu} D^{0I}_{\mu\nu} \chi_{\mu}(x_h) \chi_{\nu}(x_e)$$

Operator expectation value

$$\left\langle \hat{O} \right\rangle = \frac{\left\langle \chi_{exc} \right| \hat{O} \left| \chi_{exc} \right\rangle}{\left\langle \chi_{exc} \right| \chi_{exc} \right\rangle}$$

→ Evaluate using analytic integration techniques

¹S. A. Bäppler, FP, M. Wormit, A. Dreuw, *Phys. Rev. A* **2014**, 90, 052521.

Exciton Analysis

Exciton size

Exciton size

$${d_{exc}}^2 = \left< (r_e - r_h)^2 \right>$$

- Average separation of the electron and hole quasi-particles
- 🙂 No fragment definition
- No population analysis

¹S. A. Bäppler, FP, M. Wormit, A. Dreuw, *Phys. Rev. A* **2014**, 90, 052521.



S_1 state

- Overall electron and hole densities delocalized
- Conditional electron density follows hole

Further statistics^{1,2}

- ► d_{exc} = 5.7 Å
- e-h correlation coeff. 0.45



¹S. A. Bäppler, FP, M. Wormit, A. Dreuw, *PRA* **2014**, 90, 052521.
²FP, B. Thomitzni et al., *JCC* **2015**, 36, 1609.

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S_2 state

- Overall electron and hole densities similar to S₁
- Stronger correleations between electron and hole

Further statistics

- ► d_{exc} = 4.9 Å
- e-h correlation coeff. 0.74





S_3 state

- Negative correleations between electron and hole
- \rightarrow Large e-h separation
- Nodal plane on probe thiophene

Further statistics

- ► d_{exc} = 8.9 Å
- e-h correlation coeff. -0.24



Summary

- Excited state wavefunction analysis tools
 - Visualization
 - Quantitative analysis
- \rightarrow Automatization
- \rightarrow Rigorous discussion
- ightarrow New qualitative insight

Software

Extended wavefunction analysis toolbox.

TheoDORE - Theoretical Density, Orbital Relaxation and Exciton analysis¹

- Program package for wavefunction analysis
- Interfaces to various quantum chemistry programs: Columbus, Turbomole, Orca, GAMESS, Gaussian, ADF, Terachem, ...
- Open-source
- libwfa An open-source wavefunction analysis tool library²
 - Q-Chem: Single-reference methods
 - MOLCAS: Multireference methods

¹http://theodore-qc.sourceforge.net

²https://github.com/libwfa/libwfa

Nonadiabatic dynamics

- ? How can we extend the scope of nonadiabatic dynamics methods
- New electronic structure methods
- Speed up the computation of nonadiabatic interaction terms
- Application of model potentials

Electronic structure

?) What electronic structure method should we use

- Multireference theory¹
- Difficult to use
- Computationally expensive
- Time-dependent density functional theory
- ② Dependence on functionals
- Correlated single-reference methods
- ADC(2) / CC2
- 🙂 Easy, cheap, well-defined

¹H. Lischka et al., Chem. Rev. **2018**, 118, 7293–7361.

ADC(2)/CC2

- ADC(2)/CC2 dynamics
- Turbomole/NX interface¹
- Nonadiabatic coupling through overlaps of approximate wavefunctions
- \rightarrow Internal conversion processes
- Turbomole/SHARC interface²
- Spin-orbit coupling through Turbomole/ORCA interface
- \rightarrow Intersystem crossing + internal conversion

¹FP, R. Crespo-Otero, M. Pederzoli, et al., *JCTC* **2014**, 10, 1395.

²S. Mai, FP, M. Pabst, F. Neese, A. Köhn, L. González, *JCP* **2017**, 147, 184109.

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Overlaps

Wave function overlaps

$$S_{IJ} = \langle \Psi_I(\mathbf{R}) | \Psi_J(\mathbf{R}') \rangle$$

Many-electron wave functions

Expansion into Slater determinants

$$\left|\Psi_{I}\right\rangle = \sum_{k=1}^{n_{CI}} d_{kI} \left|\Phi_{k}\right\rangle$$

Expansion into MOs

- α and β spin

$$|\Phi_k\rangle = |\varphi_1 \dots \varphi_{\mathbf{n}_{\alpha}} \bar{\varphi}_{\mathbf{n}_{\alpha}+1} \dots \bar{\varphi}_{\mathbf{n}}|$$

Overlaps

Overlap as double sum over Slater determinant overlaps

$$S_{IJ} = \langle \Psi_I | \Psi'_J \rangle = \sum_{k=1}^{n_{CI}} \sum_{l=1}^{n'_{CI}} d_{kI} d'_{lJ} \langle \Phi_k | \Phi'_l \rangle$$

• Computed as determinant over MO overlaps $\langle \Phi_k | \Phi_l' \rangle =$

$$\begin{vmatrix} \langle \varphi_1 | \varphi'_1 \rangle & \dots & \left\langle \varphi_1 | \varphi'_{n_{\alpha}} \right\rangle \\ \vdots & \vdots & \vdots & \mathbf{0} \\ \langle \varphi_{n_{\alpha}} | \varphi'_1 \rangle & \dots & \left\langle \varphi_{n_{\alpha}} | \varphi'_{n_{\alpha}} \right\rangle \\ & & & \left\langle \bar{\varphi}_{n_{\alpha}+1} | \bar{\varphi}'_{n_{\alpha}+1} \right\rangle & \dots & \left\langle \bar{\varphi}_{n_{\alpha}+1} | \bar{\varphi}'_{l(n)} \right\rangle \\ \mathbf{0} & & \vdots & \ddots & \vdots \\ & & & \left\langle \bar{\varphi}_n | \bar{\varphi}'_{n_{\alpha}+1} \right\rangle & \dots & \left\langle \bar{\varphi}_n | \bar{\varphi}'_n \right\rangle \end{aligned}$$

▶ Formal scaling: O(n_{CI}n'_{CI}n³_{el})
▶ Simplifications?

<u>Overlaps</u>

• Two independent factors for α and β spin

$$\begin{split} \langle \Phi_{k} | \Phi_{l}^{\prime} \rangle &= \\ \begin{vmatrix} \langle \varphi_{1} | \varphi_{1}^{\prime} \rangle & \dots & \left\langle \varphi_{1} | \varphi_{n_{\alpha}}^{\prime} \right\rangle \\ \vdots & \ddots & \vdots \\ \langle \varphi_{n_{\alpha}} | \varphi_{1}^{\prime} \rangle & \dots & \left\langle \varphi_{n_{\alpha}} | \varphi_{n_{\alpha}}^{\prime} \right\rangle \end{vmatrix} \times \begin{vmatrix} \left\langle \bar{\varphi}_{n_{\alpha}+1} | \bar{\varphi}_{n_{\alpha}+1}^{\prime} \right\rangle & \dots & \left\langle \bar{\varphi}_{n_{\alpha}+1} | \bar{\varphi}_{l(n)}^{\prime} \right\rangle \\ \vdots & \ddots & \vdots \\ \left\langle \bar{\varphi}_{n} | \bar{\varphi}_{n_{\alpha}+1}^{\prime} \right\rangle & \dots & \left\langle \bar{\varphi}_{n} | \bar{\varphi}_{n}^{\prime} \right\rangle \\ &= \mathcal{S}_{\mathbf{k} \mathbf{l}} \bar{\mathcal{S}}_{\mathbf{k} \mathbf{l}} \end{split}$$

- Spin-factors reappear
- **Strategy**: Precompute and store these factors

Overlaps



Performance



Uniform performance

- Over 7 orders of magnitude in problem size
- For various wave function models
- 2-3 orders of magnitude faster than previous code (X)

Overlaps

- Integration into the SHARC dynamics code¹
- Interface to various electronic structure codes

Multireference methods **Time-dependent DFT** ADF, Dalton, Gaussian **Coupled cluster**

Columbus. Molcas Turbomole

Photoelectron spectra / Dyson orbitals²

Wave function analysis³

²M. Ruckenbauer, S. Mai, P. Marquetand, L. González, Sci. Rep. 2016, 6, 35522.

³F. Plasser, L. González, J. Chem. Phys. **2016**, 145, 021103.

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¹FP, M. Ruckenbauer, S. Mai, M. Oppel, P. Marquetand, L. González, *JCTC* **2016**, 12, 1207.

Formalism

Linear Vibronic Coupling Model

$$\mathbf{H}_{el} = V_0 \mathbf{1} + \mathbf{W}$$

H_{el} *Diabatic* Hamiltonian matrix

 V_0 (Harmonic) ground state potential - *the same* for all states

W Coupling terms - *different* among states

- Separation of ground- and excited state contributions
- Construction possible from computations at one geometry

Formalism

Intrastate coupling terms

$$W^{n,n} = \epsilon_n + \sum_i \kappa_i^{(n)} Q_i \qquad \qquad \kappa_i^{(n)} = \langle \Psi_n | \frac{\partial H_{el}}{\partial Q_i} | \Psi_n \rangle$$

 $\begin{array}{l} \epsilon_n \ \, \mbox{Constant term - } \textit{vertical excitation energy} \\ \kappa_i^{(n)} \ \, \mbox{Intrastate coupling term for state } n \ \, \mbox{and mode } i \ \, \mbox{gradient} \\ Q_i \ \, \mbox{Normal mode displacement} \end{array}$

Interstate coupling terms

$$\begin{split} W^{m,n} &= \sum_{j} \lambda_{j}^{(m,n)} Q_{j} \\ \lambda_{i}^{(n,m)} &= \left\langle \Psi_{n} \right| \frac{\partial \hat{H}}{\partial Q_{i}} \left| \Psi_{m} \right\rangle = \left(\epsilon_{m} - \epsilon_{n} \right) \left\langle \Psi_{n} \right| \partial Q_{i} \left| \Psi_{m} \right\rangle \end{split}$$

 $\lambda_i^{(n,m)}$ Interstate coupling term for states n,m and mode i - nonad. coupling, wavefunction overlap or excited state Hessians

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Parameterisation

- If nonadiabatic coupling vectors are available available
- $\rightarrow\,$ All parameters from one single point computation at the Franck-Condon geometry
- With wavefunction overlaps
- \rightarrow **3N** computations¹

¹M. Fumanal, F. Plasser, S. Mai, C. Daniel, E. Gindensperger, *JCP* **2018**, 148, 124119.

SO2

Example SO₂



¹FP, S. Gómez, M. F. S. J. Menger, S. Mai, L. Gonzlez, *PCCP* **2019**, 21, 57.

Adenine vs 2-aminopurine

- Comparison of adenine and 2-aminopurine
- Adenine
- \rightarrow Ultrafast decay
- 2-aminopurine
- ightarrow Longer lifetime in S_1



Exciton model

- QM/MM exciton model
- Monomer calculations combined via exciton model
- Electrostatic embedding scheme
- \rightarrow Applied to surface hopping dynamics



¹M. F. S. J. Menger, F. Plasser, B. Mennucci, L. González, *JCTC* **2018**, 14, 6139.

Summary

- Nonadiabatic dynamics
- Enhance applicability through small improvements
 - Dynamics at the ADC(2)/CC2 level
- Wavefunction overlaps
- Model potentials

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