# Analytical Excited State Gradients for Time Dependent Density Functional Theory plus Tight Binding (TDDFT+TB)

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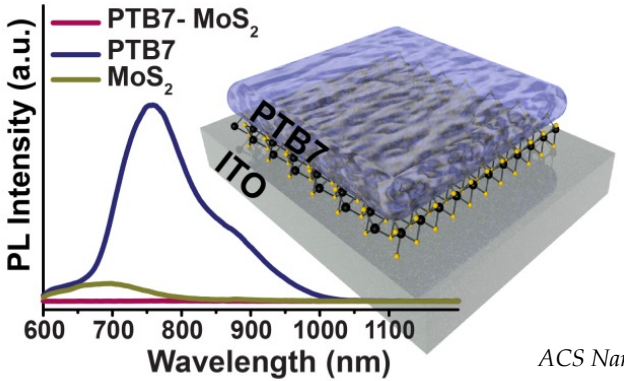
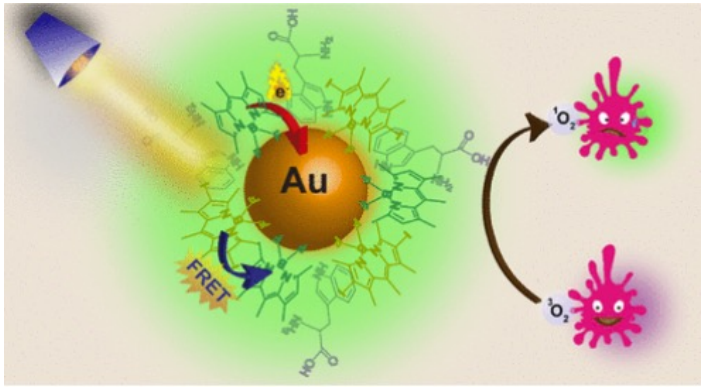
# Applications of Photoluminescence

Photoluminescence can predict the maximum voltage in solar cell absorbers (Photovoltaics)




*ACS Nano.*, **2016**, 10, 11, 10573–10579

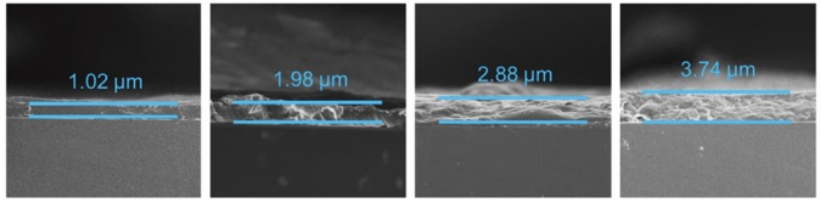



Fluorescent Nanocomposites (Bioimaging)
Photoinduced electron transfer allows efficient generation of singlet oxygen (PDT)

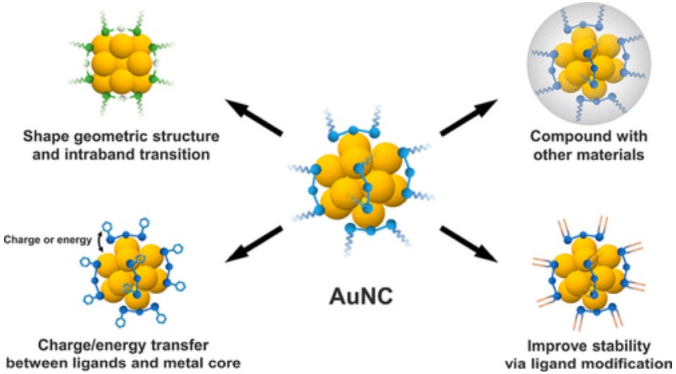
*ACS Appl. Nano Mater.*, **2022**, 5, 5, 6532–6542

Tunable RTP light-emitting colors upon UV light, and white-light-emitting phosphorescence due to the ordered micro/nanostructure of the RTP films (Optoelectronics)

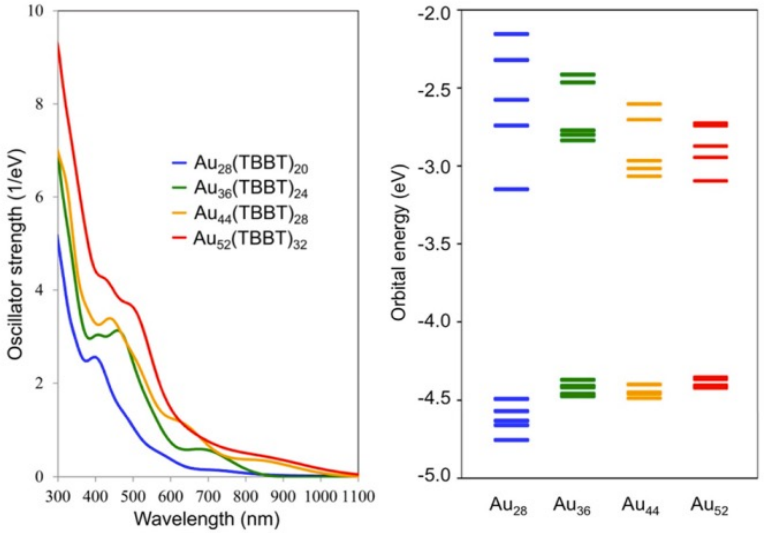
*J. Mater. Chem. C*, **2018**, 6, 4444-4449



# Structure-Property Relationships




*ACS Omega.*, **2020**, 5, 36, 22702-22707




*J. Am. Chem. Soc.*, **2016**, 138, 12, 3950–3953

Theoretically understand structure-property relationships in noble metal nanoclusters so that they can be tuned for specific applications in a plethora of fields

# Time-dependent Density Functional Theory

- Ground state DFT calculation to obtain orbital energies
- Forms EOM → square matrices of virtual to occupied orbital transitions, with excitation and de-excitation vectors in a specific Hilbert space[3]
- A symmetric eigenvalue problem is then set up where eigenvalue is the vertical excitation energy of the system[4]

$$\begin{pmatrix} \boldsymbol{A}+\boldsymbol{B} & 0 \\ 0 & \boldsymbol{A}-\boldsymbol{B} \end{pmatrix} \begin{pmatrix} \vec{X}_I+\vec{Y}_I \\ \vec{X}_I-\vec{Y}_I \end{pmatrix} = \Delta_I \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} \vec{X}_I+\vec{Y}_I \\ \vec{X}_I-\vec{Y}_I \end{pmatrix}$$

Understand change in electronic density from a perturbation[1,2]

$$\rho(\vec{r},t) = \rho^0(\vec{r}) + \delta\rho(\vec{r},t)$$

This simplifies to the **Casida Equations**[4] $\quad \Omega\vec{F}_I = \Delta_I^2\vec{F}_I$

**Coupling Matrix:**

$$K_{ia\sigma,jb\tau} = K^{\mathrm{H}}_{ia\sigma,jb\tau} + K^{\mathrm{xc}}_{ia\sigma,jb\tau}$$

$$K^{\mathrm{H}}_{ia\sigma,jb\tau} = \int \mathrm{d}^3\vec{r} \int \mathrm{d}^3\vec{r}\,' \, \phi^*_{i\sigma}(\vec{r})\phi_{a\sigma}(\vec{r}) \, \frac{1}{|\vec{r}-\vec{r}\,'|} \, \phi^*_{b\tau}(\vec{r}\,')\phi_{j\tau}(\vec{r}\,')$$

$$K^{\mathrm{xc}}_{ia\sigma,jb\tau} = \int \mathrm{d}^3\vec{r} \int \mathrm{d}^3\vec{r}\,' \, \phi^*_{i\sigma}(\vec{r})\phi_{a\sigma}(\vec{r}) \, f^{\mathrm{xc}}_{\sigma\tau}(\vec{r},\vec{r}\,') \, \phi^*_{b\tau}(\vec{r}\,')\phi_{j\tau}(\vec{r}\,')$$

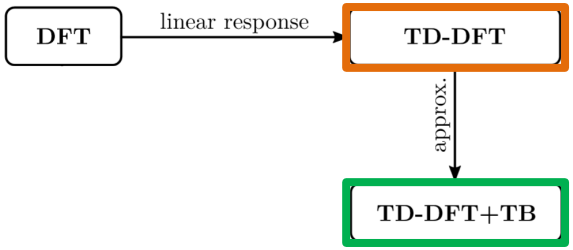
$$\Delta_I = \epsilon_a - \epsilon_i$$

i,j,k,… → Occupied MOs
a,b,c,… → Virtual MOs




1. *Phys. Rev. Lett.*, **1985**, 55, 2850-2852
2. *Phys. Rev. Lett.*, **1986**, 57, 923
3. *J. Mol. Struct. Theochem.*, **2009**, 914, 3-18
4. *World Scientific.*, **1995**, 1, 155-192.

# Time-dependent DFT plus tight-binding (TDDFT+TB)




$$K_{ia\sigma,jb\tau} = K^{\mathrm{H}}_{ia\sigma,jb\tau} + K^{\mathrm{xc}}_{ia\sigma,jb\tau}$$

$$K^{\mathrm{H}}_{ia\sigma,jb\tau} = \int \mathrm{d}^3\vec{r} \int \mathrm{d}^3\vec{r}\,' \, \phi^*_{i\sigma}(\vec{r})\phi_{a\sigma}(\vec{r}) \, \frac{1}{|\vec{r} - \vec{r}\,'|} \, \phi^*_{b\tau}(\vec{r}\,')\phi_{j\tau}(\vec{r}\,')$$

$$K^{\mathrm{xc}}_{ia\sigma,jb\tau} = \int \mathrm{d}^3\vec{r} \int \mathrm{d}^3\vec{r}\,' \, \phi^*_{i\sigma}(\vec{r})\phi_{a\sigma}(\vec{r}) \, f^{\mathrm{xc}}_{\sigma\tau}(\vec{r},\vec{r}\,') \, \phi^*_{b\tau}(\vec{r}\,')\phi_{j\tau}(\vec{r}\,')$$

*World Scientific.*, **1995,** 1, 155-192.

Approximation → Multipole expansion of transition density to the first order (monopole approximation)

$$K_{ia,jb} = \sum_{\mathcal{AB}} q_{ia,\mathcal{A}} \tilde{\gamma}_{\mathcal{AB}} q_{jb,\mathcal{B}}$$

Löwdin partial charge analysis

$$q_{ia,\mathcal{A}} = \sum_{\mu \in \mathcal{A}} c'_{\mu i} c'_{\mu a} \quad \text{with} \quad \boldsymbol{C}' = \boldsymbol{S}^{\frac{1}{2}} \boldsymbol{C}$$

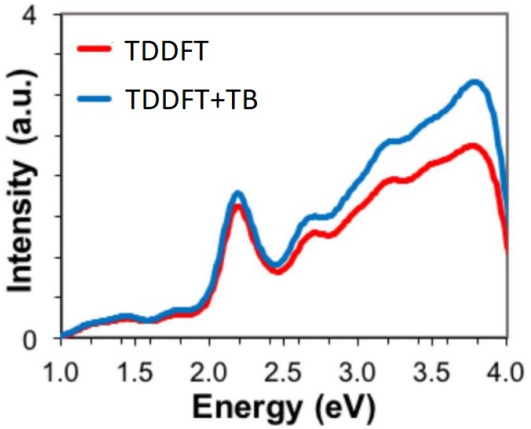
Function based on chemical hardness and internuclear distance

$$\gamma_{\mathcal{AB}} = \gamma_{\mathcal{AB}} \left( \eta_{\mathcal{A}}, \eta_{\mathcal{B}}, \left| \vec{R}_{\mathcal{A}} - \vec{R}_{\mathcal{B}} \right| \right)$$

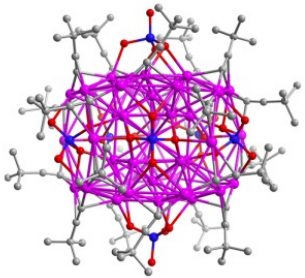
*J. Chem. Phys.*, **2016**, 144, 184103

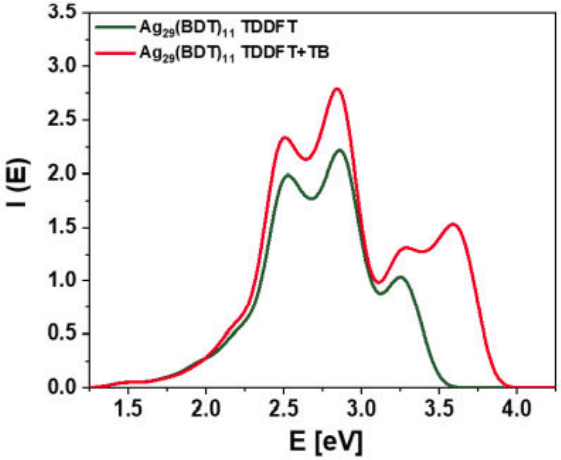
# Time-dependent DFT plus tight-binding (TDDFT+TB)

$Ag_{48}(C{\equiv}C^tBu)_{20}(CrO_4)_7$




*J. Am. Chem. Soc.*, **2019**, 141, 4460-4467

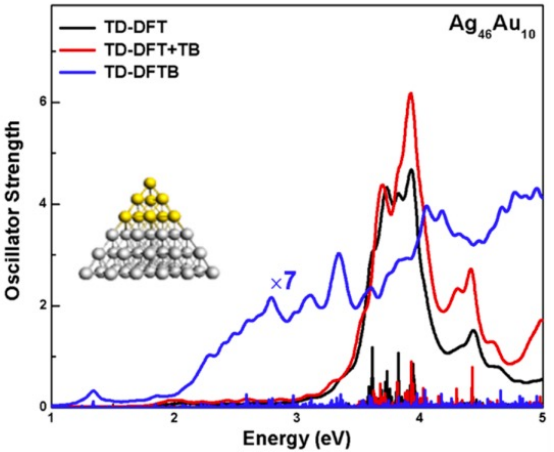





$Ag_{29}(BDT)_{11}DHLA$

TDDFT:
25 hours, 22 cores, 21.08 gb, 500 states

TDDFT+TB:
1 hour, 16 cores, 6.23 gb, 1000 states

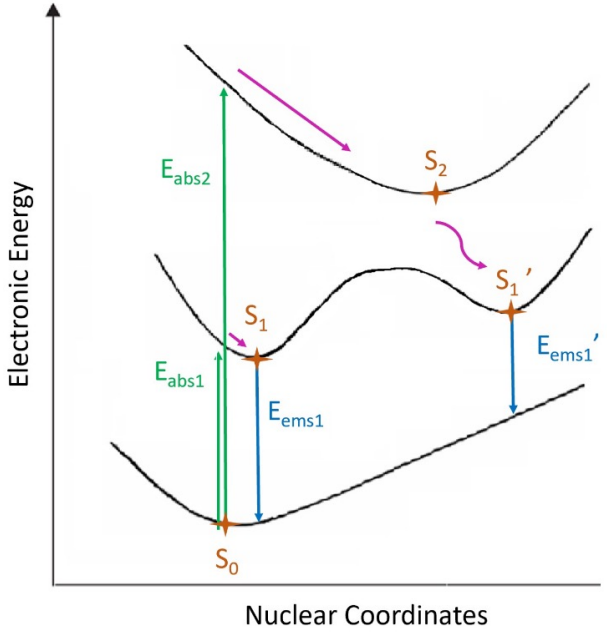



*J. Phys. Chem. C*, **2020**, 124, 7946–7955

Havenridge and Coworkers.
*J. Am. Chem. Soc.*, **2021**, 143, 25, 9405-9414

# Dual Emission of $Au_{14}Cd(S\text{-}Adm)_{12}$

## PL Properties – Analytical TDDFT Gradients (Xα/DZ)



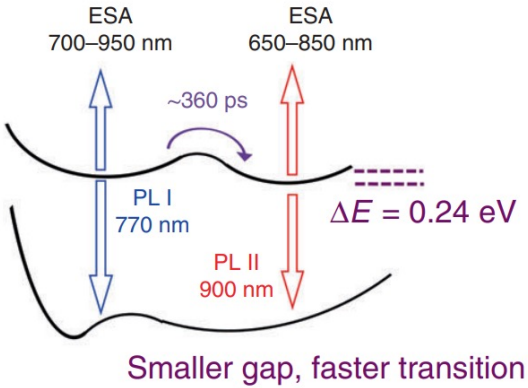

Two emissive states on $S_1$ surface:

$Abs_1$ = 1.59 eV

$E_{ems1}$ = 1.09 eV  $SS_1$ = 0.50 eV

$E_{ems1'}$ = 0.86 eV  $SS_{1'}$ = 0.73 eV

**$\Delta E_{ems}$ = 0.23 eV**



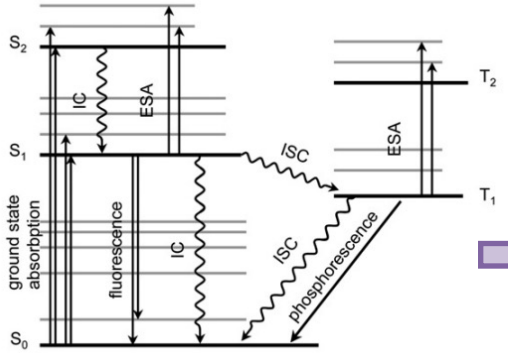

$SS_1$ = 0.64 eV

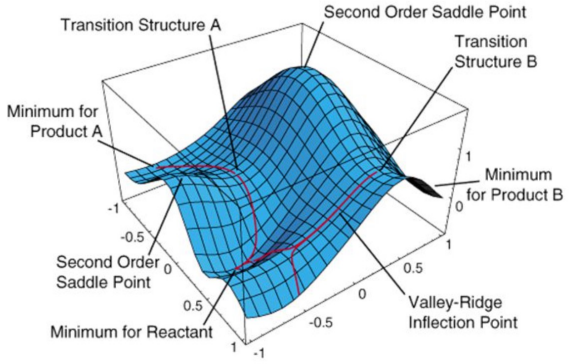
$SS_{1'}$ = 0.87 eV

*Nature Comm.*, **2020**, 11, 2897, 1-9

Two emissive points →
Minima on $S_1$ state or two different minimum points on two different states?

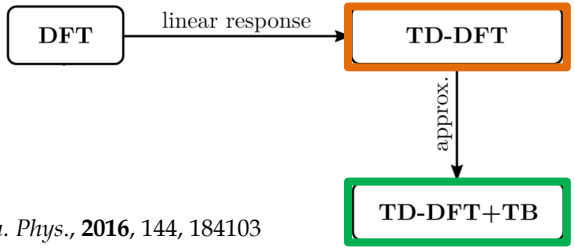
# Analytical Excited State Gradients for TDDFT+TB




*Phys. Chem. Chem. Phys.*, **2003**, 5, 2964-2969

*J. Comp. Chem.*, **2003**, 24, 12, 1514-1527




*J. Chem. Phys.*, **2016**, 144, 184103

## Derivation:

1. Define an energy functional that is equivalent to the vertical excitation energy of that system
2. Set up an energy functional that is stationary with respect to the molecular orbital coefficients
3. Solve the Lagrange multipliers after the constraints have been defined
4. Take the full derivative of each term

# Analytical Excited State Gradients for TDDFT+TB

1. Define an energy functional that is equivalent to the vertical excitation energy

$$G[X,Y,\Omega] = \frac{1}{2}\begin{pmatrix} X+Y \\ X-Y \end{pmatrix}|\Lambda|\begin{pmatrix} X+Y \\ X-Y \end{pmatrix} - \frac{1}{2}\Omega\left(\begin{pmatrix} X+Y \\ X-Y \end{pmatrix}|\Delta|\begin{pmatrix} X+Y \\ X-Y \end{pmatrix} - 2\right)$$

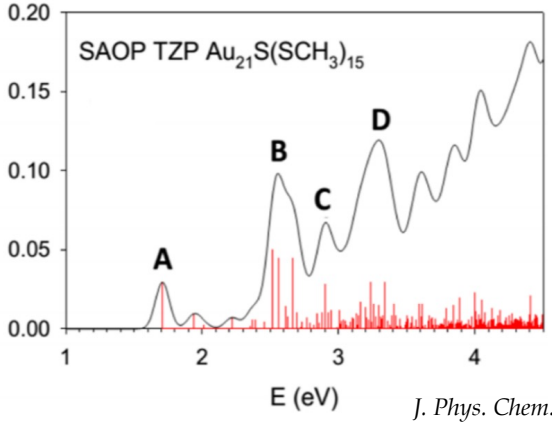
$$\Lambda = \begin{pmatrix} A+B & 0 \\ 0 & A-B \end{pmatrix} \qquad \Delta = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

*J. Chem. Phys.*, **2002,** 117, 7433

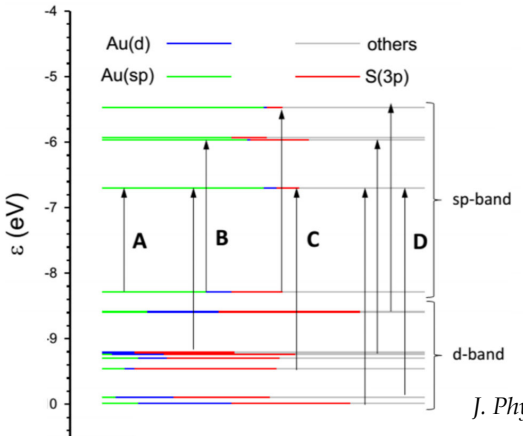
$$\psi_i = \sum_{\mu=1}^{\#AOs} C_{i,\mu}\,\phi_\mu$$

An MO — AOs

*Comput. Chem.*, **2007,** 28, 2589-2601




*J. Phys. Chem. Lett.* **2017**, 8, 457-462




*J. Phys. Chem. Lett.* **2017**, 8, 457-462

# Analytical Excited State Gradients for TDDFT+TB

2. Set up an energy functional that is stationary with respect to the molecular orbital coefficients (Lagrange approach)

$$L[X, Y, \Omega, C, Z, W] = G[X, Y, \Omega] + \sum_{ia} Z_{ia} F_{ia} - \sum_{pq, p \leq q} W_{pq}(S_{pq} - \delta_{pq})$$

*J. Chem. Phys.*, **2002,** 117, 7433

3. Solve the Lagrange multipliers after the constraints have been defined

Functional to be stationary with respect to Lagrange multipliers

$$\frac{\partial L}{\partial Z_{ia}} = F_{ia} = 0$$

$$\frac{\partial L}{\partial W_{pq}} = S_{pq} - \delta_{pq} = 0$$

MOs to be orthonormal and satisfy the ground state DFT equations → Restrict transformation of MO coefficients

$$\frac{\partial L}{\partial C_{\mu p}} = 0$$

$$\sum_{\mu} \frac{\partial G[X, Y, Z]}{\partial C_{\mu p}} C_{\mu q} + \sum_{ia} Z_{ia} \sum_{\mu} \frac{\partial F_{ia}}{\partial C_{\mu p}} C_{\mu q} = \sum_{rs, r \leq s} W_{rs} \sum_{\mu} \frac{\partial S_{rs}}{\partial C_{\mu p}} C_{\mu q}$$

# Analytical Excited State Gradients for TDDFT+TB

$$U_A = \sum_{ia} (X+Y)_{ia} q_{ia,A}$$

$$\Xi_A = \sum_B \gamma_{AB} U_B$$

## 4. Take the full derivative of each term

$$L[X,Y,\Omega,C,Z,W] = G[X,Y,\Omega] + \sum_{ia} Z_{ia}F_{ia} - \sum_{pq,p\leq q} W_{pq}(S_{pq} - \delta_{pq})$$

$$\frac{dL^{S/T}}{dR_A} = \frac{dG^{S/T}}{dR_A} + \sum_{ia} Z_{ia}\frac{dF_{ia}}{dR_A} - \sum_{pq,p\leq q} W_{pq}\frac{dS_{pq}}{dR_A}$$

$$= \sum_{pq} \frac{dF_{pq}}{dR_A}P_{pq} + 2\sum_{iajb} \frac{K^{S/T}_{iajb}}{dR_A}(X+Y)_{ia}(X+Y)_{jb} - \sum_{pq,p\leq q} W_{pq}\frac{dS_{pq}}{dR_A}$$

$$2\sum_{\mu\in A,\nu\notin A} \frac{dh_{\mu\nu}}{dR_A}P_{\mu\nu} + 2\sum_{\mu\in A,\nu\notin A} \frac{d(\mu\nu|rs)}{dR_A}P_{\mu\nu} +$$

$$2\sum_{\mu\in A,\nu\notin A} \frac{dV^{XC}_{\mu\nu}}{dR_A}P_{\mu\nu} +$$

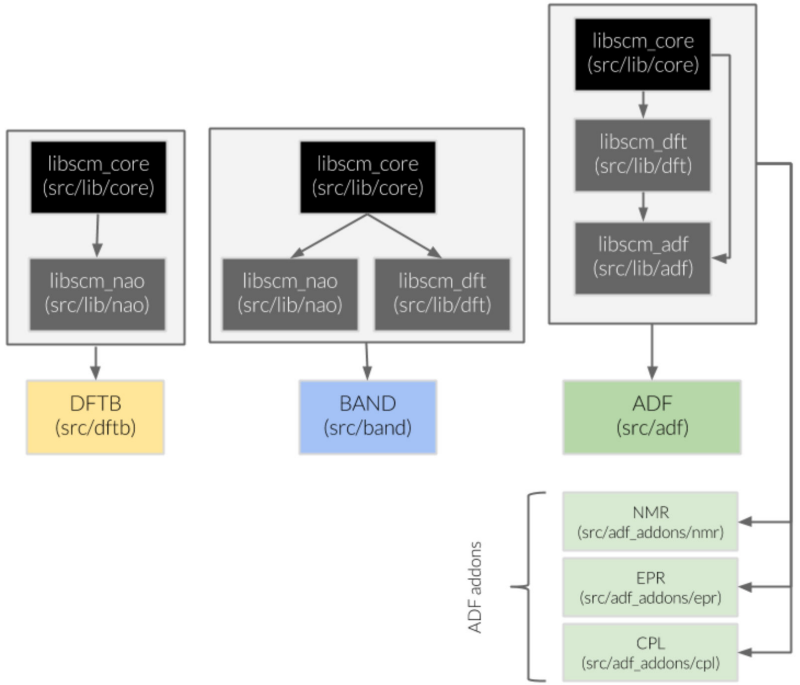
$$2\sum_{\mu\in A,\nu\notin A} S^{1/2}_{\mu\nu}\frac{dS^{1/2}_{\mu\nu}}{dR_A}(\Xi_A + \Xi_B)U_{\mu\nu} +$$

$$4\sum_{\mu\in A,\nu\notin A} \frac{d\gamma_{AB}}{dR_A}U_A U_B - \sum_{\mu\in A,\nu\notin A} \frac{dS_{\mu\nu}}{dR_A}W_{\mu\nu}$$

# Analytical Excited State Gradients for TDDFT+TB

Amsterdam Modelling Suite
2023 Release
ADF Engine

Scalar Relativistic Effects
Dispersion
Singlet-Singlet & Singlet-Triplet
Variety of Basis Sets
Variety of Pure XC Functionals






https://wiki.scm.com/index.php/ADFHOME_Directory_Structure

Havenridge, Rüger and Aikens. *J. Chem. Phys.* **2023**, 158, 224103

# TDDFT+TB Emission Energies

## TDDFT vs. TDDFT+TB $S_n$ Optimization

60 total chemical systems:
9 diatomic molecules
26 small organic molecules[1]
1 gold nanocluster core
10 ligand protected noble metal nanoclusters
14 molecular chromophores[2]

RMS value:
1.04 eV → Diatomic molecules
0.21 eV → Organic molecules
0.03 eV→ LPNMNCs
0.08 eV → Chromophores
0.09 eV → Singlet-Triplet Excitations in Chromophore Set

| Molecule | Method | Runtime | Emission Energy (eV) |
|---|---|---|---|
| LiH | TDDFT | 00:01:00 | 2.31 |
| | TDDFT+TB | 00:00:42 | 2.24 |
| Octatetraene | TDDFT | 00:19:03 | 3.63 |
| | TDDFT+TB | 00:05:08 | 3.65 |
| Cytosine | TDDFT | 00:15:55 | 1.23 |
| | TDDFT+TB | 00:04:59 | 1.21 |
| $Au_7^{3+}$ | TDDFT | 01:10:13 | 1.76 |
| | TDDFT+TB | 00:17:00 | 1.73 |
| $Au_{22}(PA)_{18}$ | TDDFT | 17-06:40:45 | 1.19 |
| | TDDFT+TB | 6-13:20:19 | 1.21 |



1. *J. Chem. Phys.*, **2008**, 128, 134110
2. *J. Chem. Theory Comput.* **2015**, 11, 1102–1109

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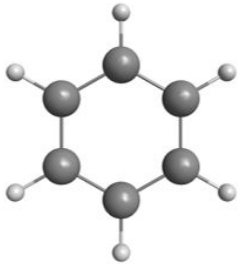
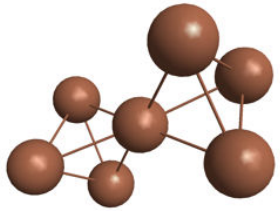
# TDDFT+TB Optimized $S_1$ Geometry

**Bond Lengths TDDFT vs. TDDFT+TB (Å) –**



**Benzene ($C_6H_6$)**

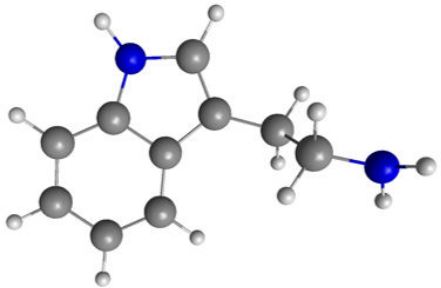
| | | |
|---|---|---|
| Average C-C: | | |
| 1.440 | | 1.439 |
| Average C-H: | | |
| 1.090 | | 1.090 |



**Gold Core ($Au_7^{3+}$)**

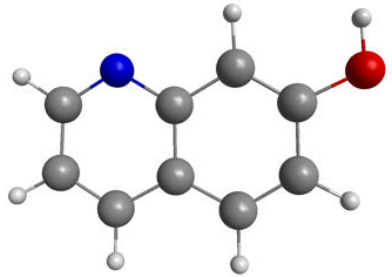
| | | |
|---|---|---|
| Average Au center – Au core: | | |
| 2.775 | | 2.772 |
| Average Au core – Au core: | | |
| 2.785 | | 2.785 |

| | | |
|---|---|---|
| Average C-N: | | |
| 1.408 | | 1.408 |
| Average C-C: | | |
| 1.446 | | 1.446 |
| C-N Terminal: | | |
| 1.488 | | 1.488 |



**Tryptamine ($C_{10}H_{12}N_2$)**

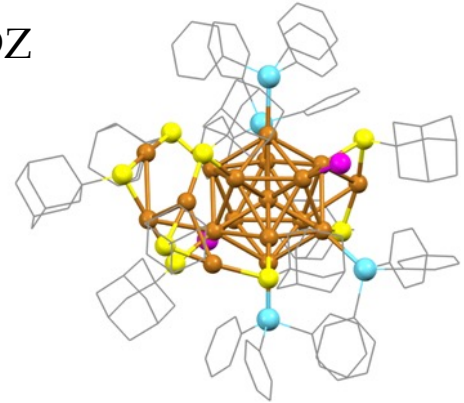
| | | |
|---|---|---|
| Average C-N: | | |
| 1.350 | | 1.356 |
| Average C-O: | | |
| 1.416 | | 1.417 |
| Average C-C: | | |
| 1.420 | | 1.418 |



**7-hydroxyquinoline ($C_9H_7NO$)**

# Example – $Au_{18}$

BP86/DZ



$Au_{18}(S\text{-}Adm)_8(SbPh_3)_4Br_2$
364 Atoms

Average Au core =
2.902 ± 0.074 Å
HL Gap = 1.62 eV

TDDFT+TB →

6 days
70 Geometry Steps
$E_{ems}$ = 1.16 eV
Average Au core = 2.912 ± 0.098 Å
HL Gap = 1.14 eV

TDDFT →

12 days
68 Geometry Steps
$E_{ems}$ = 1.18 eV
Average Au core = 2.912 ± 0.098 Å
HL Gap = 1.14 eV

# Acknowledgements

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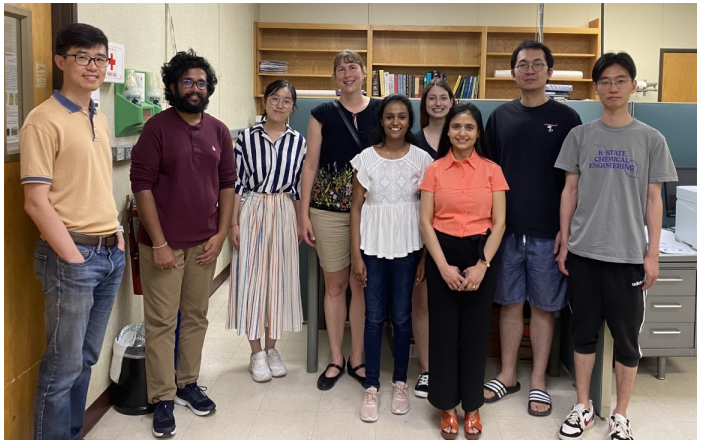

Dr. Stan van Gisbergen
Dr. Olivia Hull

Past and present group members at
Kansas State University