

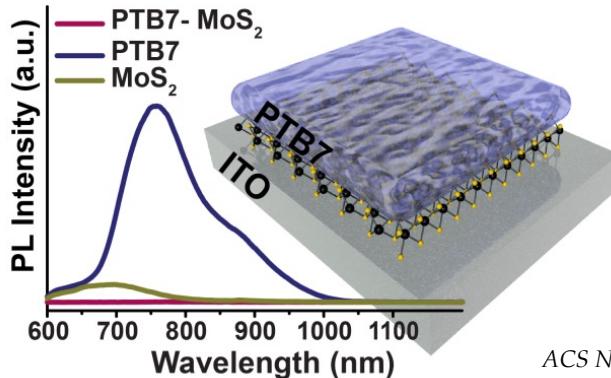


# Analytical Excited State Gradients for Time Dependent Density Functional Theory plus Tight Binding (TDDFT+TB)

Shana Havenridge, Robert Rüger, and  
Christine M. Aikens

# Applications of Photoluminescence

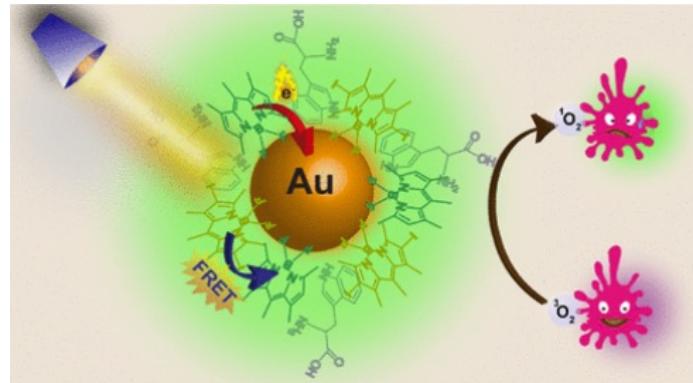
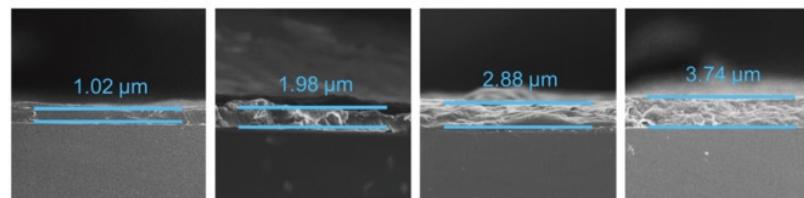
Photoluminescence can predict the maximum voltage in solar cell absorbers (**Photovoltaics**)



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

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

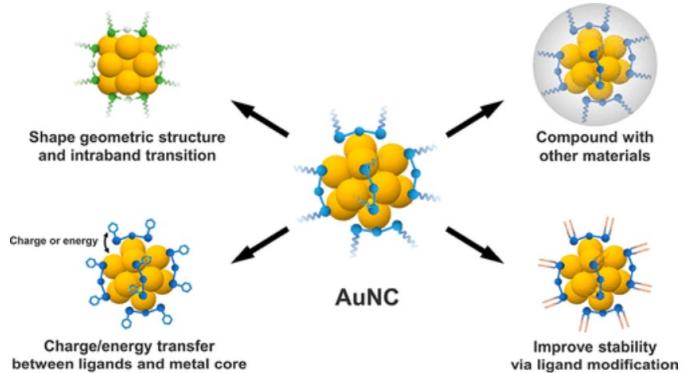
*J. Mater. Chem. C*, 2018, 6, 4444-4449



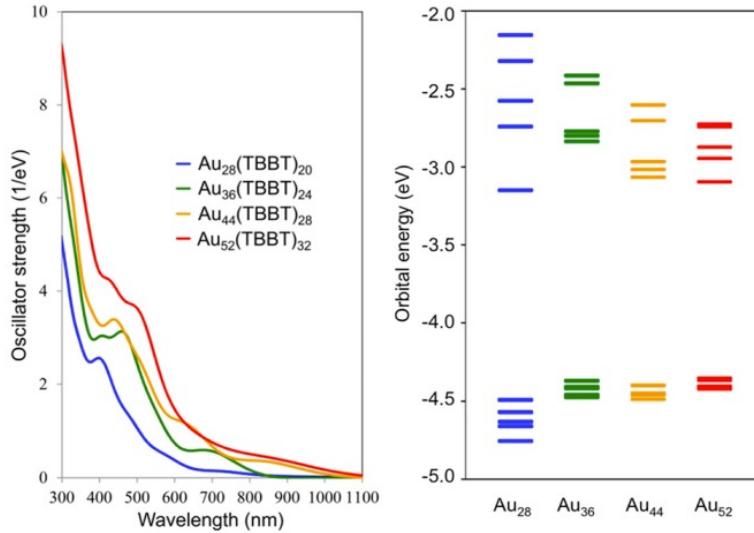
Fluorescent Nanocomposites (**Bioimaging**)  
Photoinduced electron transfer allows efficient generation of singlet oxygen (**PDT**)

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

# 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  $\rightarrow$  square matrices of virtual to occupied orbital transitions, with excitation and de-excitation vectors in a specific Hilbert space<sup>3</sup>
- A symmetric eigenvalue problem is then set up where eigenvalue is the vertical excitation energy of the system<sup>4</sup>

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

This simplifies to the **Casida Equations**<sup>4</sup>     $\Omega \vec{F}_I = \Delta_I^2 \vec{F}_I$

**Coupling Matrix:**

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

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

$$K_{ia\sigma,jb\tau}^{xc} = \int d^3\vec{r} \int d^3\vec{r}' \phi_{i\sigma}^*(\vec{r}) \phi_{a\sigma}(\vec{r}) f_{\sigma\tau}^{xc}(\vec{r}, \vec{r}') \phi_{b\tau}^*(\vec{r}') \phi_{j\tau}(\vec{r}')$$

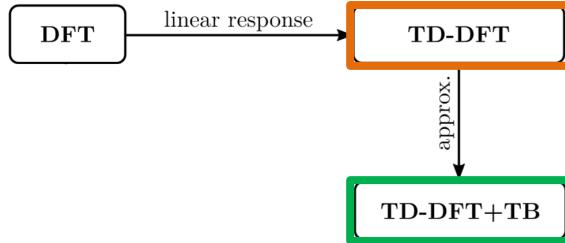
$$\Delta_I = \epsilon_a - \epsilon_i$$

i,j,k,...  $\rightarrow$  Occupied MOs  
a,b,c,...  $\rightarrow$  Virtual MOs

Understand change in electronic density from a perturbation<sup>1,2</sup>

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

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



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

Löwdin partial charge analysis

Function based on chemical hardness  
and internuclear distance

$$K_{ia\sigma,jb\tau} = K_{ia\sigma,jb\tau}^H + K_{ia\sigma,jb\tau}^{xc}$$
$$K_{ia\sigma,jb\tau}^H = \int d^3\vec{r} \int d^3\vec{r}' \phi_{i\sigma}^*(\vec{r}) \phi_{a\sigma}(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \phi_{b\tau}^*(\vec{r}') \phi_{j\tau}(\vec{r}')$$
$$K_{ia\sigma,jb\tau}^{xc} = \int d^3\vec{r} \int d^3\vec{r}' \phi_{i\sigma}^*(\vec{r}) \phi_{a\sigma}(\vec{r}) f_{\sigma\tau}^{xc}(\vec{r}, \vec{r}') \phi_{b\tau}^*(\vec{r}') \phi_{j\tau}(\vec{r}')$$

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

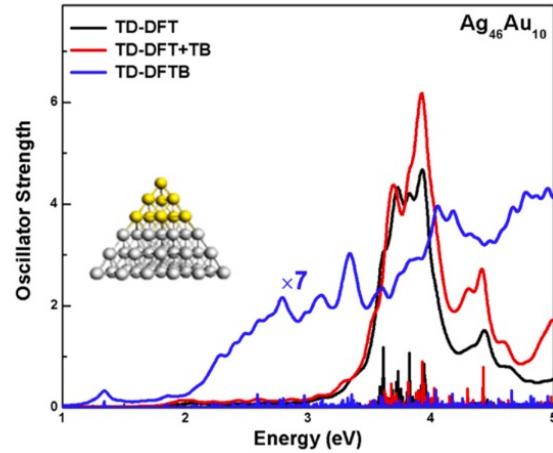
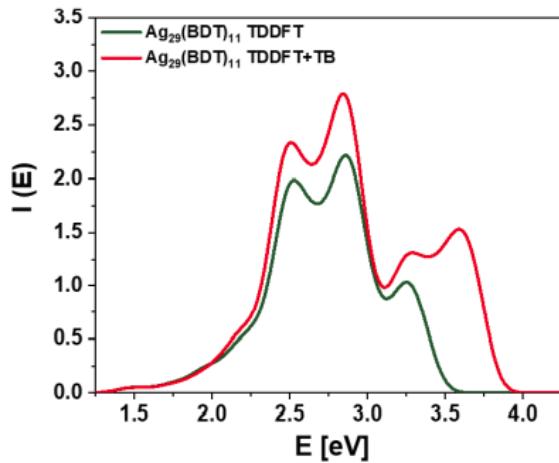
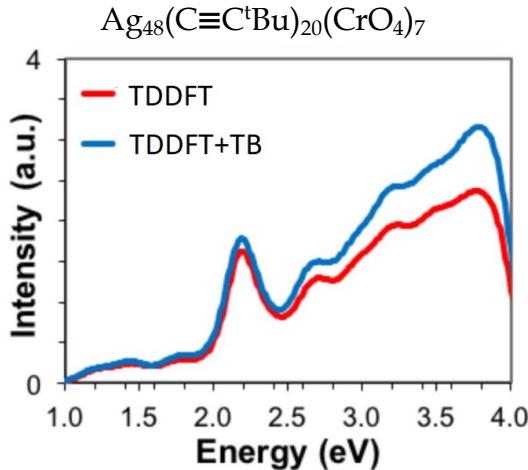
$$K_{ia,jb} = \sum_{\mathcal{A}\mathcal{B}} q_{ia,\mathcal{A}} \tilde{\gamma}_{\mathcal{A}\mathcal{B}} q_{jb,\mathcal{B}}$$

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

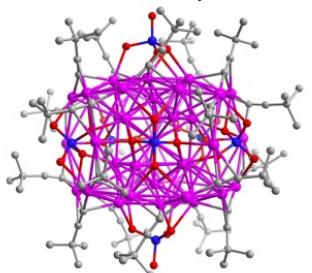
$$\gamma_{\mathcal{A}\mathcal{B}} = \gamma_{\mathcal{A}\mathcal{B}} \left( \eta_{\mathcal{A}}, \eta_{\mathcal{B}}, \left| \vec{R}_{\mathcal{A}} - \vec{R}_{\mathcal{B}} \right| \right)$$

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

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



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



$\text{Ag}_{29}(\text{BDT})_{11}$ DHLA

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

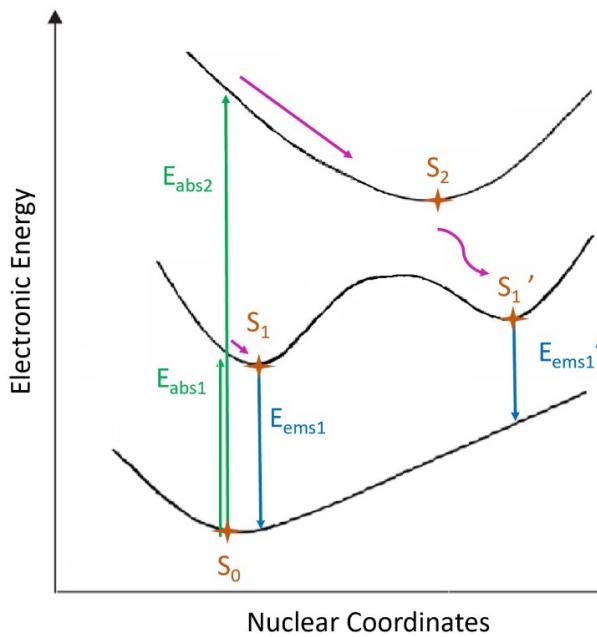
TDDFT+TB:  
1 hour, 16 cores, 6.23 gb, 1000 states

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

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



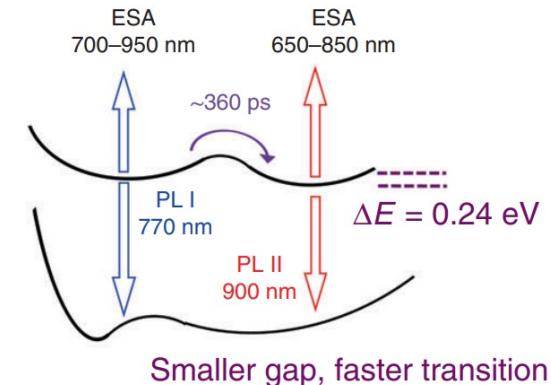
## PL Properties – Analytical TDDFT Gradients (Xα/DZ)



Two emissive states on  $S_1$  surface:

$$\begin{array}{ll} \text{Abs}_1 = 1.59 \text{ eV} & \text{SS}_1 = 0.50 \text{ eV} \\ \text{E}_{\text{ems}1} = 1.09 \text{ eV} & \text{E}_{\text{ems}1'} = 0.86 \text{ eV} \\ \text{SS}'_1 = 0.73 \text{ eV} & \end{array}$$

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

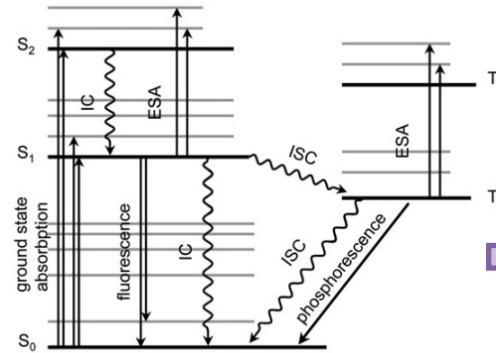


$$\begin{array}{l} \text{SS}_1 = 0.64 \text{ eV} \\ \text{SS}'_1 = 0.87 \text{ eV} \end{array}$$

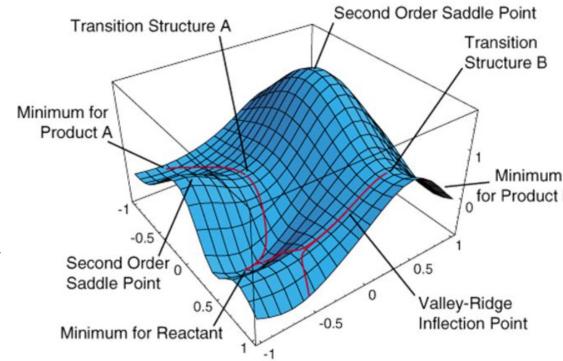
*Nature Comm.*, 2020, 11, 2897, 1-9

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

# Analytical Excited State Gradients for TDDFT+TB



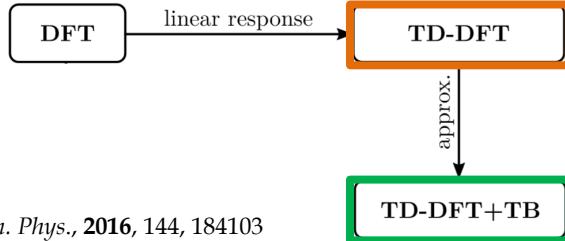
*Phys. Chem. Chem. Phys.*, 2003, 5, 2964-2969



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

## 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



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

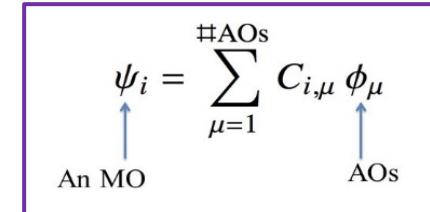
# Analytical Excited State Gradients for TDDFT+TB

- Define an energy functional that is equivalent to the vertical excitation energy

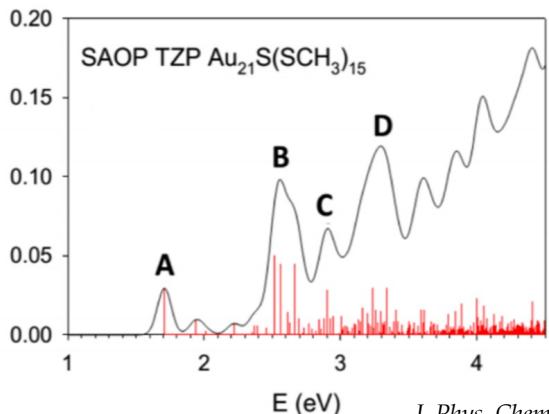
$$G[X, Y, \Omega] = \frac{1}{2} \left\langle \begin{matrix} X + Y \\ X - Y \end{matrix} \middle| \Lambda \right| \begin{matrix} X + Y \\ X - Y \end{matrix} \right\rangle - \frac{1}{2} \Omega \left( \left\langle \begin{matrix} X + Y \\ X - Y \end{matrix} \middle| \Delta \right| \begin{matrix} X + Y \\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

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

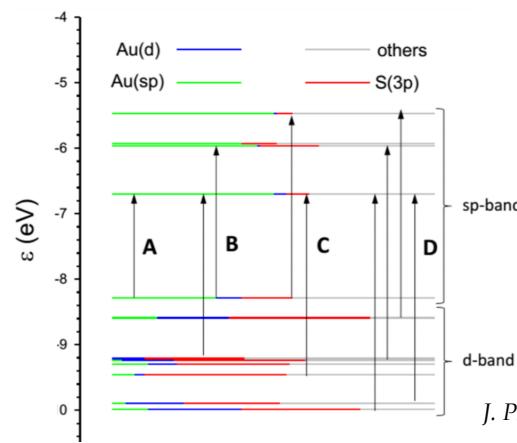
J. Chem. Phys., 2002, 117, 7433



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

- 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

- Solve the Lagrange multipliers after the constraints have been defined

Functional to be stationary with respect to Lagrange multipliers

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

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

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


$$\frac{\partial L}{\partial C_{\mu p}} = 0$$
$$\sum_{\mu} \frac{\partial G[X, Y, Z]}{\partial C_{\mu p}} C_{\mu q} + \sum_{ia} Z_{ia} \sum_{\mu} \frac{\partial F_{ia}}{\partial C_{\mu p}} C_{\mu q} = \sum_{rs, r \leq s} W_{rs} \sum_{\mu} \frac{\partial S_{rs}}{\partial C_{\mu p}} C_{\mu q}$$

# Analytical Excited State Gradients for TDDFT+TB

## 4. Take the full derivative of each term

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

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

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

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

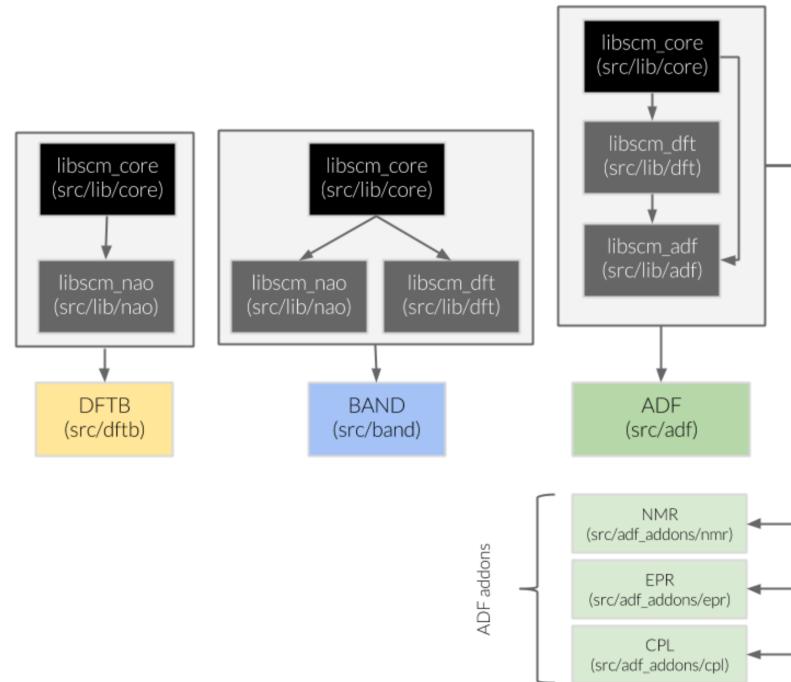
$$\Xi_A = \sum_B \gamma_{AB} U_B$$

$$\begin{aligned} & \frac{2 \sum_{\mu \in A, \nu \notin A} \frac{dh_{\mu\nu}}{dR_A} P_{\mu\nu} + 2 \sum_{\mu \in A, \nu \notin A} \frac{d(\mu\nu|rs)}{dR_A} P_{\mu\nu} +}{2 \sum_{\mu \in A, \nu \notin A} \frac{dV_{\mu\nu}^{XC}}{dR_A} P_{\mu\nu} +} \\ & \frac{2 \sum_{\mu \in A, \nu \notin A} S_{\mu\nu}^{1/2} \frac{dS_{\mu\nu}^{1/2}}{dR_A} (\Xi_A + \Xi_B) U_{\mu\nu} +}{4 \sum_{\mu \in A, \nu \notin A} \frac{d\gamma_{AB}}{dR_A} U_A U_B - \sum_{\mu \in A, \nu \notin A} \frac{dS_{\mu\nu}}{dR_A} W_{\mu\nu}} \end{aligned}$$

# 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



# TDDFT+TB Emission Energies

## TDDFT vs. TDDFT+TB S<sub>n</sub> Optimization

60 total chemical systems:

9 diatomic molecules

26 small organic molecules<sup>1</sup>

1 gold nanocluster core

10 ligand protected noble metal nanoclusters

14 molecular chromophores<sup>2</sup>

RMS value:

1.04 eV → Diatomic molecules

0.21 eV → Organic molecules

0.03 eV → LPNMNCs

0.08 eV → Chromophores

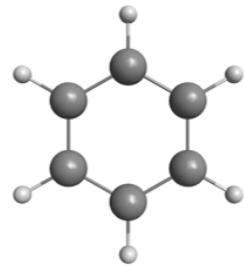
0.09 eV → Singlet-Triplet

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 <sub>7</sub> <sup>3+</sup>	TDDFT	01:10:13	1.76
	TDDFT+TB	00:17:00	1.73
Au <sub>22</sub> (PA) <sub>18</sub>	TDDFT	17-06:40:45	1.19
	TDDFT+TB	6-13:20:19	1.21

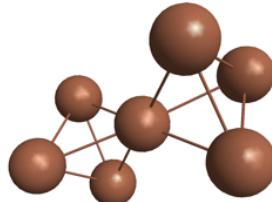
# TDDFT+TB Optimized S<sub>1</sub> Geometry

Bond Lengths TDDFT vs. TDDFT+TB (Å) -



Benzene (C<sub>6</sub>H<sub>6</sub>)

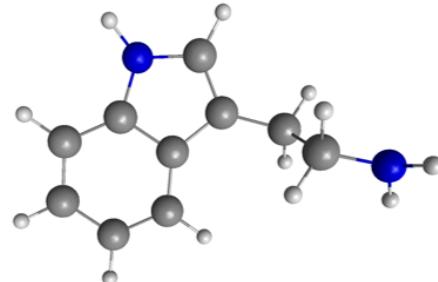
Average C-C:	1.440	1.439
Average C-H:	1.090	1.090



Gold Core (Au<sub>7</sub><sup>3+</sup>)

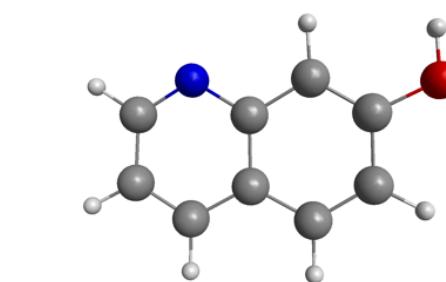
Average Au center - Au core:	2.775	2.772
Average Au core - Au core:	2.785	2.785

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



Tryptamine (C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>)

Average C-N:	1.850	1.856
Average C-O:	1.416	1.417
Average C-C:	1.420	1.418

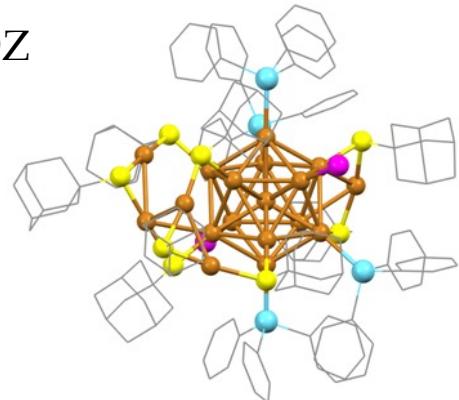


7-hydroxyquinoline (C<sub>9</sub>H<sub>7</sub>NO)

# Example – Au<sub>18</sub>



BP86/DZ



Au<sub>18</sub>(S-Adm)<sub>8</sub>(SbPh<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>  
364 Atoms

Average Au core =  
 $2.902 \pm 0.074 \text{ \AA}$   
HL Gap = 1.62 eV

TDDFT+TB →

6 days  
70 Geometry Steps  
 $E_{\text{ems}} = 1.16 \text{ eV}$   
Average Au core =  $2.912 \pm 0.098 \text{ \AA}$   
HL Gap = 1.14 eV

TDDFT →

12 days  
68 Geometry Steps  
 $E_{\text{ems}} = 1.18 \text{ eV}$   
Average Au core =  $2.912 \pm 0.098 \text{ \AA}$   
HL Gap = 1.14 eV

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