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TDDFT in Chemistry and Biochemistry

Lecture 2: Molecular Properties
BENASQUE 9th TDDFT: Prospects and Applications

Shane M. Parker
Case Western Reserve University
Department of Chemistry
shane.parker@case.edu
quantumparker.com

Photochemistry

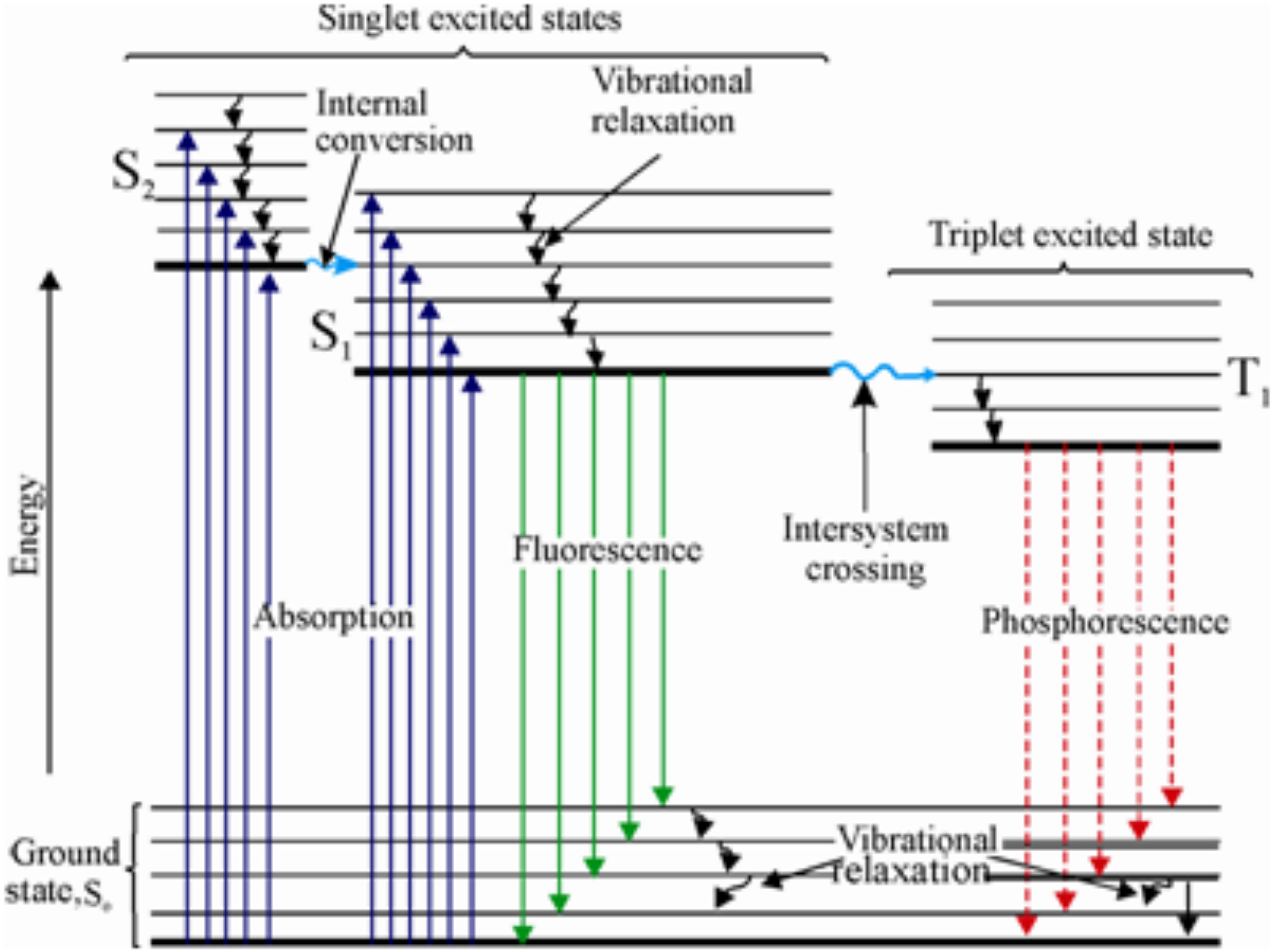


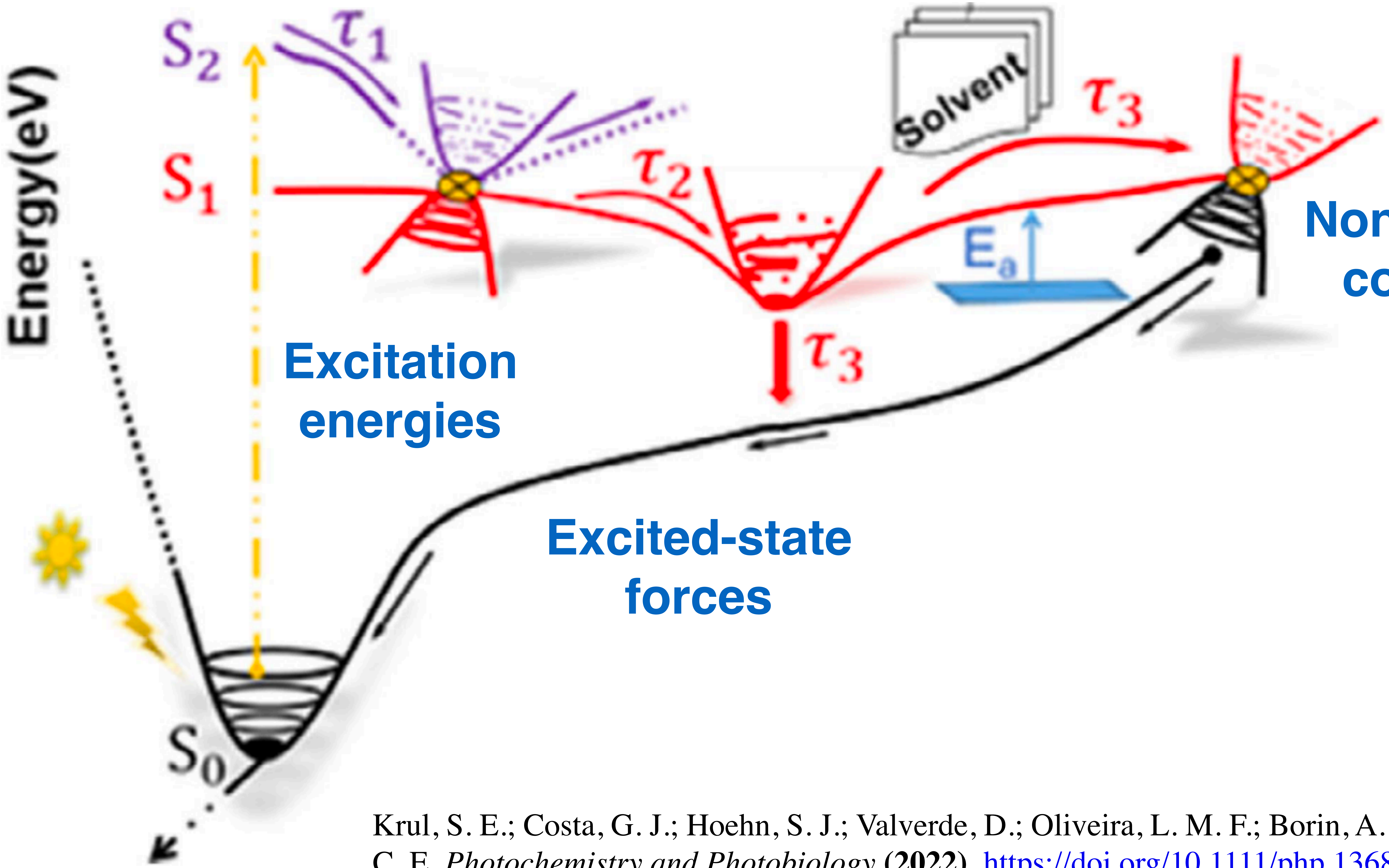
image from quora.com

Use TDDFT to determine

- **identities of the states involved? properties?**
- photochemical pathway? timescales?

Sun, Q.; Mosquera-Vazquez, S.; Lawson Daku, L. V. M.; Gu n e, L.; Goodwin, H. A.; Vauthey, E.; Hauser, A. *J. Am. Chem. Soc.* **2013**, *135* (37), 13660–13663.

Photochemistry requires, TDDFT provides



Excitation energies

Excited-state forces

Nonadiabatic couplings

Krul, S. E.; Costa, G. J.; Hoehn, S. J.; Valverde, D.; Oliveira, L. M. F.; Borin, A. C.; Crespo-Hernández, C. E. *Photochemistry and Photobiology* **(2022)**. https://doi.org/10.1111/php.13688.

Disclaimer: I am a Chemist

density is $\rho(x,t)$

space-spin $x \rightarrow (\vec{r},\sigma)$

1 particle density matrix is $\rho(x,x',t)$ or $\gamma(x,x')$

assuming the **adiabatic approximation to the XC functional** is useful

typically think about **isolated or solvated molecules**

hybrid density functionals preferred

Action Lagrangian

The requisite properties

Photochemistry of Thymine

Interpreting Excited States

Action functional

Convenient to define time-dependent quantum mechanical properties through the **action functional**

$$\mathcal{S}[\Phi] = \langle\!\langle \Phi | \hat{H}(t) - \mathrm{i}\frac{\partial}{\partial t} | \Phi \rangle\!\rangle$$

with

$$\langle\!\langle u | v \rangle\!\rangle \equiv \frac{1}{T}\int_0^T \mathrm{d}t \langle u(t) | v(t) \rangle$$

Stationarity of the action yields the Schrödinger equation

$$\frac{\delta \mathcal{A}}{\delta \langle\!\langle \Phi |} = \left(\hat{H}(t) - \mathrm{i}\frac{\partial}{\partial t} \right) | \Phi \rangle\!\rangle = 0$$

Differentiating the action yields properties

$$\frac{\delta \mathcal{A}}{\delta v(x,t)} = \mathbf{\Pi}^{(1)}(x,t) = \rho(x,t)$$

Action Lagrangian for time-periodic perturbations

Time-periodic potential means

$$\Phi(t+T) = e^{\mathrm{i}\alpha}\Phi(t)$$

Purely periodic part treated through **action Lagrangian**

$$\mathcal{A}[\Phi,\varepsilon] = \langle\!\langle \Phi | \hat{H}(t) - \mathrm{i}\frac{\partial}{\partial t} | \Phi \rangle\!\rangle - \varepsilon(\langle\!\langle \Phi | \Phi \rangle\!\rangle - 1)$$

Reduces to *quasi-energy* at stationary point

$$\mathcal{A}[\Phi,\varepsilon]|_{\mathrm{stat}} = \varepsilon$$

and energy eigenvalues in time-independent case

$$\mathcal{A}^{(0)}[\Phi,\varepsilon]|_{\mathrm{stat}} = E_n$$

Exact response properties

Define Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \hat{v}(t)$$

$$\hat{v}(t) = \int \mathrm{d}x v(t,x)\hat{\rho}(x)$$

$$v(t,x) = \sum_{\alpha} v_{\alpha}(x)\mathrm{e}^{-\mathrm{i}\omega_{\alpha}t} + v_{-\alpha}(x)\mathrm{e}^{\mathrm{i}\omega_{\alpha}t}$$

And assume ground state is initial state

$$|\Psi\rangle\!\rangle\big|_{v=0} \equiv |\Psi^{(0)}\rangle\!\rangle = |0\rangle$$

Differentiate, make stationary, evaluate at *v*=0

$$f^{(\alpha\beta\ldots)} \equiv f^{(\alpha\beta\ldots)}(x_1, x_2, \ldots) \equiv \left.\frac{\delta^n f}{\delta v_{\alpha}(x_1)\delta v_{\beta}(x_2)\ldots}\right|_{\mathrm{stat},v=0}$$

Exact static properties

Differentiate

$$\begin{aligned}\mathcal{A}^{(\alpha)} =& \langle\!\langle \cancel{\Psi^{(\alpha)} | \hat{H}_0 - E_0 - \frac{\partial}{\partial t} | \Psi^{(0)}} \rangle\!\rangle \\ &+ \langle\!\langle \cancel{\Psi^{(0)} | \hat{H}_0 - E_0 - \frac{\partial}{\partial t} | \Psi^{(\alpha)}} \rangle\!\rangle \\ &+ \langle\!\langle \Psi^{(0)} | \hat{\rho}(x) \mathrm{e}^{-\mathrm{i}\omega_\alpha t} - \cancel{\varepsilon^{(\alpha)}} | \Psi^{(0)} \rangle\!\rangle + \cancel{\varepsilon^{(\alpha)}}\end{aligned}$$

Make stationary

$$\frac{\delta \mathcal{A}^{(\alpha)}}{\delta \langle\!\langle \Psi^{(\alpha)} |} = (\hat{H}_0 - E_0 - \frac{\partial}{\partial t}) | \Psi^{(0)} \rangle\!\rangle = 0$$

$$| \Psi^{(0)} \rangle\!\rangle = | 0 \rangle$$

Evaluate

$$\Pi^{(1)}(x) = \varepsilon^{(\alpha)} = \rho^{00}(x) \quad \longrightarrow \quad \bar{\rho}(x) = \hat{\rho}(x) - \rho^{00}(x)$$

Exact linear response

Differentiate

$$\mathcal{A}^{(\alpha\beta)} = \cancel{\langle\!\langle\Psi^{(\alpha)}|\hat{H}_0 - E_0 - \mathrm{i}\frac{\partial}{\partial t}|\Psi^{(\beta)}}\rangle\!\rangle + \cancel{\langle\!\langle\Psi^{(\beta)}|\hat{H}_0 - E_0 - \mathrm{i}\frac{\partial}{\partial t}|\Psi^{(\alpha)}}\rangle\!\rangle$$

$$+ \cancel{\langle\!\langle\Psi^{(\alpha)}|\bar{\rho}(x_2)\mathrm{e}^{-\mathrm{i}\omega_\beta t}|\Psi^{(0)}\rangle\!\rangle} + \langle\!\langle\Psi^{(0)}|\bar{\rho}(x_2)\mathrm{e}^{-\mathrm{i}\omega_\beta t}|\Psi^{(\alpha)}\rangle\!\rangle$$

$$+ \cancel{\langle\!\langle\Psi^{(\beta)}|\bar{\rho}(x_1)\mathrm{e}^{-\mathrm{i}\omega_\alpha t}|\Psi^{(0)}\rangle\!\rangle} + \langle\!\langle\Psi^{(0)}|\bar{\rho}(x_1)\mathrm{e}^{-\mathrm{i}\omega_\alpha t}|\Psi^{(\beta)}\rangle\!\rangle$$

Make stationary

$$\frac{\mathcal{A}^{(\alpha\beta)}}{\delta\langle\!\langle\Psi^{(\beta)}|} = (\hat{H}_0 - E_0 - \mathrm{i}\frac{\partial}{\partial t})|\Psi^{(\alpha)}\rangle\!\rangle + \bar{\rho}(x_1)\mathrm{e}^{-\mathrm{i}\omega_\alpha t}|\Psi^{(0)}\rangle\!\rangle = 0$$

$$|\Psi^{(\alpha)}\rangle\!\rangle = -(\hat{H}_0 - E_0 - \omega_\alpha)^{-1}\bar{\rho}(x_1)|0\rangle\mathrm{e}^{-\mathrm{i}\omega_\alpha t}$$

Evaluate

$$\Pi^{(2)}(\omega, x_1, x_2) = -\Bigg[\langle 0|\bar{\rho}(x_2)(\hat{H}_0 - E_0 - \omega)^{-1}\bar{\rho}(x_1)|0\rangle$$

$$+ \langle 0|\bar{\rho}(x_1)(\hat{H}_0 - E_0 + \omega)^{-1}\bar{\rho}(x_2)|0\rangle\Bigg]$$

Exact linear response: sum-over-states

$$\Pi^{(2)}(\omega, x_1, x_2) = -\left[\langle 0|\bar{\rho}(x_2)(\hat{H}_0 - E_0 - \omega)^{-1}\bar{\rho}(x_1)|0\rangle + \langle 0|\bar{\rho}(x_1)(\hat{H}_0 - E_0 + \omega)^{-1}\bar{\rho}(x_2)|0\rangle\right]$$

Spectral representation of inverse

$$(\hat{H} - z)^{-1} = \sum_n \frac{|\Phi_n\rangle\langle\Phi_n|}{E_n - z}$$

Gives the sum-over-states expression

$$\Pi^{(2)}(\omega, x_1, x_2) = -\sum_{n\neq 0}\left[\frac{\rho^{0n}(x_2)\rho^{n0}(x_1)}{\Omega_{0n} - \omega} + \frac{\rho^{0n}(x_1)\rho^{n0}(x_2)}{\Omega_{0n} + \omega}\right]$$

Exact quadratic response

$$\mathcal{A}^{(\alpha\beta\gamma)} = \mathcal{P}^{(\alpha\beta\gamma)} \langle\!\langle \Psi^{(\alpha)} | \bar{\rho}(x_2) \mathrm{e}^{-\mathrm{i}\omega_\beta t} | \Psi^{(\gamma)} \rangle\!\rangle$$

Insert first-order results

$$\Pi^{(3)}(\omega_\alpha, \omega_\beta, x_1, x_2, x_3) =$$

$$\mathcal{P}^{(\alpha\beta\gamma)} \langle 0 | \bar{\rho}(x_1) (\hat{H}_0 - E_0 + \omega_\alpha)^{-1} \bar{\rho}(x_2) (\hat{H}_0 - E_0 - \omega_\gamma)^{-1} \bar{\rho}(x_3) | 0 \rangle$$

Sum-over-states:

$$\Pi^{(3)}(\omega_\alpha, \omega_\beta, x_1, x_2, x_3) =$$

$$\sum_{\substack{n\neq 0 \\ m\neq 0}} \left[\frac{\rho^{0n}(x_1)\bar{\rho}^{nm}(x_2)\rho^{m0}(x_3)}{(\Omega_{0n} - \omega_\alpha)(\Omega_{0m} + \omega_\gamma)} + \frac{\rho^{0n}(x_1)\bar{\rho}^{nm}(x_3)\rho^{m0}(x_2)}{(\Omega_{0n} + \omega_\alpha)(\Omega_{0m} - \omega_\beta)} \right.$$

$$+ \frac{\rho^{0n}(x_2)\bar{\rho}^{nm}(x_1)\rho^{m0}(x_3)}{(\Omega_{0n} + \omega_\beta)(\Omega_{0m} - \omega_\gamma)} + \frac{\rho^{0n}(x_2)\bar{\rho}^{nm}(x_3)\rho^{m0}(x_1)}{(\Omega_{0n} + \omega_\beta)(\Omega_{0m} - \omega_\alpha)}$$

$$\left. + \frac{\rho^{0n}(x_3)\bar{\rho}^{nm}(x_1)\rho^{m0}(x_2)}{(\Omega_{0n} + \omega_\gamma)(\Omega_{0m} - \omega_\beta)} + \frac{\rho^{0n}(x_3)\bar{\rho}^{nm}(x_2)\rho^{m0}(x_1)}{(\Omega_{0n} + \omega_\gamma)(\Omega_{0m} - \omega_\alpha)} \right]$$

Exact response theory: the big idea

RG justifies only the validity of the time-dependent density

No wavefunction available!

$$\Pi^{(2)}(\omega, x_1, x_2) = -\sum_{n\neq 0}\left[\frac{\rho^{0n}(x_2)\rho^{n0}(x_1)}{\Omega_{0n}-\omega} + \frac{\rho^{0n}(x_1)\rho^{n0}(x_2)}{\Omega_{0n}+\omega}\right]$$

Linear response allows a **definition** of

excitation energies

ground-to-excited state transition densities

$$\Pi^{(3)}(\omega_\alpha, \omega_\beta, x_1, x_2, x_3) = \sum_{\substack{n\neq 0\\ m\neq 0}}\left[\frac{\rho^{0n}(x_1)\bar{\rho}^{nm}(x_3)\rho^{m0}(x_2)}{(\Omega_{0n}+\omega_\alpha)(\Omega_{0m}-\omega_\beta)} + \dots\right]$$

Quadratic response allows a **definition** of

state-to-state transition densities

TDDFT Action Lagrangian

$$\begin{aligned}\mathcal{A}[\boldsymbol{\varphi},\varepsilon] =& \frac{1}{T}\int_0^T \mathrm{d}t \sum_j \Bigg[\int \mathrm{d}x \left(\frac{1}{2} |\nabla \varphi_j(t,x)|^2 - \mathrm{i}\varphi_j^*(t,x) \frac{\partial \varphi_j(t,x)}{\partial t} \right) \\ &+ \int \mathrm{d}x \varphi_j^*(t,x) v(t,x) \varphi_j(t,x) - \sum_k \varepsilon_{jk} \left(\int \mathrm{d}x \varphi_j^*(t,x)\varphi_k(t,x) - \delta_{jk} \right) \Bigg] \\ &+ \mathcal{A}^{\mathrm{HXC}}[\rho]\end{aligned}$$

Stationarity

$$\frac{\delta \mathcal{A}[\varphi,\varepsilon]}{\delta \varphi_j^*(t,x)} = \frac{1}{2}\nabla^2 \varphi_j(t,x) + v^s(t,x)\varphi_j(t,x) - \mathrm{i}\frac{\partial \varphi_j(t,x)}{\partial t} - \sum_k \varepsilon_{jk}\varphi_k(t,x) = 0$$

$$v^s(t,x) = v(t,x) + v^{\mathrm{HXC}}(t,x)$$

$$\mathcal{A}[\varphi,\varepsilon]|_{\mathrm{stat}} = \sum_j \left(\varepsilon_{jj} - v_{jj}^{\mathrm{HXC}}[\rho] \right) + \mathcal{A}^{\mathrm{HXC}}[\rho]$$

TDDFT linear response

Differentiate

$$\mathcal{A}^{(\alpha\beta)} = \int_0^T \mathrm{d}t \int \mathrm{d}x \sum_j \Big[\varphi_j^{*(\alpha)} \left(\hat{h} - \mathrm{i}\frac{\partial}{\partial t}\right) \varphi_j^{(\beta)} + \varphi_j^{*(\beta)} \left(\hat{h} - \mathrm{i}\frac{\partial}{\partial t}\right) \varphi_j^{(\alpha)}$$

$$+ \varphi_j^{*(\alpha)} \bar{\rho}(x_2) \varphi_j \mathrm{e}^{-\mathrm{i}\omega_\beta t} + \varphi_j^{*} \bar{\rho}(x_2) \varphi_j^{(\alpha)} \mathrm{e}^{-\mathrm{i}\omega_\beta t}$$

$$+ \varphi_j^{*(\beta)} \bar{\rho}(x_1) \varphi_j \mathrm{e}^{-\mathrm{i}\omega_\alpha t} + \varphi_j^{*} \bar{\rho}(x_1) \varphi_j^{(\beta)} \mathrm{e}^{-\mathrm{i}\omega_\alpha t} \Big]$$

$$+ \mathcal{A}^{\mathrm{HXC}(\alpha\beta)}[\rho]$$

Using chain rule

$$\mathcal{A}^{\mathrm{HXC}(\alpha\beta)}[\rho] = \int \mathrm{d}\zeta v^{\mathrm{HXC}}[\rho](\tau, y) \rho^{(\alpha\beta)}(\tau, y)$$

$$+ \int \mathrm{d}\zeta_1 \mathrm{d}\zeta_2 f^{\mathrm{HXC}}[\rho](\tau_1 - \tau_2), y_1, y_2) \rho^{(\alpha)}(\tau_1, y_1) \rho^{(\beta)}(\tau_2, y_2)$$

TDDFT linear response

Expand orbitals: $\mathrm{U}(t) = \mathrm{e}^{\boldsymbol{\kappa}(t)}$

$$\varphi_j(t,x) = \phi_j(x) + \sum_a \phi_a(x)\kappa_{ja}(t) + \frac{1}{2}\sum_{ak}\phi_k(x)\kappa_{ja}(t)\kappa_{ak}(t) + \ldots$$

$$\varphi_a(t,x) = \phi_a(x) + \sum_j \phi_j(x)\kappa_{aj}(t) + \frac{1}{2}\sum_{jb}\phi_b(x)\kappa_{aj}(t)\kappa_{jb}(t) + \ldots$$

Make stationary

$$\frac{\partial \mathcal{A}^{(\alpha\beta)}}{\partial \kappa_{ia}^{(\beta)*}} = \frac{1}{T}\int_0^T \mathrm{d}t \Big[\langle\phi_a|\hat{h} + \hat{v}^{\mathrm{HXC}} - \varepsilon_{ii} - \mathrm{i}\frac{\partial}{\partial t}|\varphi_i^{(\alpha)}\rangle + \langle\phi_a|\bar{\rho}(x_1)|\phi_i\rangle \mathrm{e}^{-\mathrm{i}\omega_\alpha t}\Big]$$

$$+ \sum_{pq} f_{pq,ia}^{\mathrm{HXC}} \rho_{pq}^{(\alpha)} = 0$$

Leads to

$$\kappa_{ia}^{(\alpha)} = X_{ia} e^{-\mathrm{i}\omega_\alpha t} \qquad \kappa_{ia}^{(-\alpha)} = Y_{ia} e^{\mathrm{i}\omega_\alpha t}$$

TDDFT linear response (skipping derivation)

Response operator

$$\mathbf{\Pi}^{(2)}_{\mathrm{TDDFT}}(\omega) = \left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} - \omega\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{pmatrix}\right]^{-1}$$

$$\begin{pmatrix}\mathbf{X}^{(\alpha)}\\ \mathbf{Y}^{(\alpha)}\end{pmatrix} = -\mathbf{\Pi}^{(2)}_{\mathrm{TDDFT}}(\omega)\begin{pmatrix}\mathbf{P}^{(\alpha)}\\ \mathbf{Q}^{(\alpha)}\end{pmatrix}$$

Linear Response Function

$$\mathcal{A}^{(\alpha\beta)} = \begin{pmatrix}\mathbf{P}^{(\beta)}\\ \mathbf{Q}^{(\beta)}\end{pmatrix}^{T}\begin{pmatrix}\mathbf{X}^{(\alpha)}\\ \mathbf{Y}^{(\alpha)}\end{pmatrix}$$

$$\mathcal{A}^{(\alpha\beta)} = -\begin{pmatrix}\mathbf{P}^{(\beta)}\\ \mathbf{Q}^{(\beta)}\end{pmatrix}^{T}\mathbf{\Pi}^{(2)}_{\mathrm{TDDFT}}(\omega)\begin{pmatrix}\mathbf{P}^{(\alpha)}\\ \mathbf{Q}^{(\alpha)}\end{pmatrix}$$

TDDFT quadratic response (abbreviated)

Response function

$$\Pi^{(3)}(\omega_\alpha, \omega_\beta) = \left[\mathrm{tr}(\mathbf{K}^{(\alpha\beta)}\mathbf{v}^{(\gamma)}) + \begin{pmatrix}\mathbf{P}^{(\gamma)}\\ \mathbf{Q}^{(\gamma)}\end{pmatrix}^T \Pi^{(2)}_{\mathrm{TDDFT}}(\omega_\alpha + \omega_\beta)\begin{pmatrix}\mathbf{P}^{(\alpha\beta)}\\ \mathbf{Q}^{(\alpha\beta)}\end{pmatrix}\right]$$

Product of first-order densities

$$K_{ij}^{(\alpha\beta)} = -\sum_a X_{ja}^{(\alpha)}Y_{ia}^{(\beta)} + X_{ja}^{(\beta)}Y_{ia}^{(\alpha)}$$

$$K_{ab}^{(\alpha\beta)} = \sum_i X_{ia}^{(\alpha)}Y_{ib}^{(\beta)} + X_{ia}^{(\beta)}Y_{ib}^{(\alpha)}$$

RHS involves hyperkernel

$$g^{\mathrm{XC}\pm}[\rho](x_1, x_2, x_3) \approx \left.\frac{\delta^3 E^{\mathrm{XC}}[\rho]}{\delta\rho^{\pm}(x_1)\delta\rho(x_2)\delta\rho(x_3)}\right|_{\mathrm{ref}}$$

TDDFT quadratic response (abbreviated)

$$\begin{aligned}
(P+Q)^{(\alpha\beta)}_{ia} =& -\frac{1}{2}\sum_{j}\mathcal{P}^{(\alpha\beta)}\left[(X+Y)^{(\beta)}_{ja}U^{+(\alpha)}_{ji} - (X-Y)^{(\beta)}_{ja}U^{-(\alpha)}_{ji}\right] \\
&+\frac{1}{2}\sum_{b}\mathcal{P}^{(\alpha\beta)}\left[(X+Y)^{(\beta)}_{ib}U^{+(\alpha)}_{ab} - (X-Y)^{(\beta)}_{ib}U^{-(\alpha)}_{ab}\right] \\
&+H^{+}_{ai}[\mathbf{K}^{(\alpha\beta)}] + 2g^{\mathrm{HXC}+}_{ai}[\rho^{(\alpha)},\rho^{(\beta)}]\ , \\
(P-Q)^{(\alpha\beta)}_{ia} =& -\frac{1}{2}\sum_{j}\mathcal{P}^{(\alpha\beta)}\left[(X-Y)^{(\beta)}_{ja}U^{+(\alpha)}_{ji} - (X+Y)^{(\beta)}_{ja}U^{-(\alpha)}_{ji}\right] \\
&+\frac{1}{2}\sum_{b}\mathcal{P}^{(\alpha\beta)}\left[(X-Y)^{(\beta)}_{ib}U^{+(\alpha)}_{ab} - (X+Y)^{(\beta)}_{ib}U^{-(\alpha)}_{ab}\right] \\
&-H^{-}_{ia}[\mathbf{K}^{(\alpha\beta)}] + 2g^{\mathrm{HXC}-}_{ai}[\rho^{(\alpha)},\rho^{(\beta)}]
\end{aligned}$$

Hyperkernel

$$g^{\mathrm{XC}\pm}[\rho](x_1,x_2,x_3) \approx \left.\frac{\delta^3 E^{\mathrm{XC}}[\rho]}{\delta\rho^{\pm}(x_1)\delta\rho(x_2)\delta\rho(x_3)}\right|_{\mathrm{ref}}$$

Action Lagrangian

The requisite properties

Photochemistry of Thymine

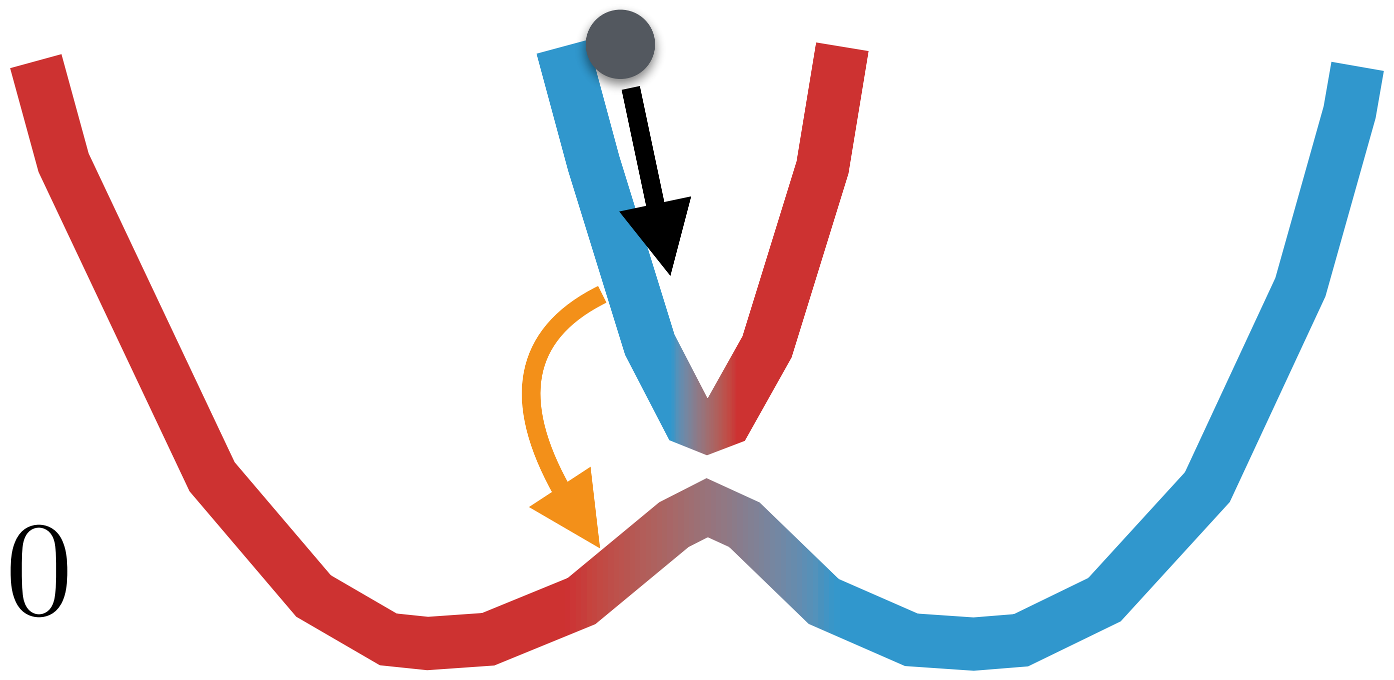
Interpreting Excited States

Energies, forces and couplings

Energies

$$E_n = E_0 + \Omega_n$$

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - \Omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}\right] \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} = 0$$



Forces

$$\nabla E_n = \nabla E_0 + \nabla \Omega_n \neq \frac{\partial}{\partial R} E_n$$

State-to-state properties

$$\langle \Psi_n | \hat{v} | \Psi_m \rangle$$

Derivative couplings

$$\langle \Phi_n | \nabla \Phi_m \rangle$$

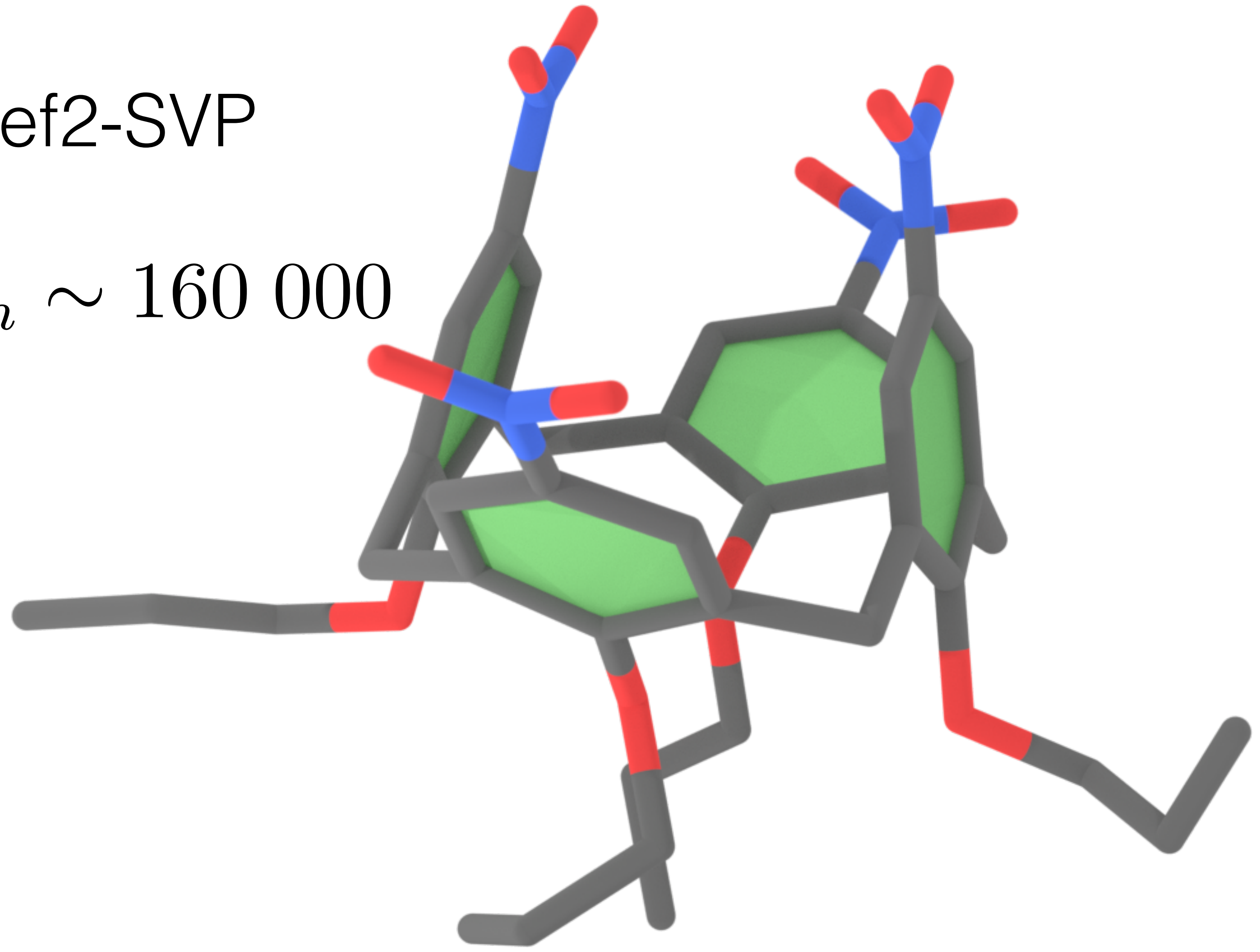
Energies: iterative diagonalization

Storage unfeasible for even medium molecules

~ 400 GB for calix[4]arene

def2-SVP

$N_{ph} \sim 160\,000$



Matrix-vector products

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix} = \begin{pmatrix} \mathbf{u} \\ \mathbf{v} \end{pmatrix}$$

$$D_{\mu\nu} = C_{\mu i} x_{ia} C_{\nu a} + C_{\mu a} y_{ia} C_{\nu i}$$

Compare to Fock-build

$$\Lambda_{\mu\nu}[\mathbf{D}] = \sum_{\kappa\lambda} \{2(\mu\nu|\kappa\lambda) + 2 f^{xc}_{\mu\nu\kappa\lambda} + c_x[(\mu\kappa|\nu\lambda) - (\mu\lambda|\kappa\nu)]\} D_{\kappa\lambda}$$

v.

$$F_{\mu\nu}[\mathbf{D}] = \sum_{\kappa\lambda} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] D_{\kappa\lambda} + v^{XC}_{\mu\nu}[\mathbf{D}]$$

Forces: orbital response

$$\frac{\mathrm{d}E}{\mathrm{d}\mathbf{R}} = \frac{\mathrm{d}E}{\mathrm{d}\mathbf{C}}\frac{\mathrm{d}\mathbf{C}}{\mathrm{d}\mathbf{R}} + \ldots$$

Excitation energies not stationary w.r.t. orbitals

$$\frac{\mathrm{d}E_0}{d\mathbf{C}} \propto \mathbf{F}^{\mathrm{ov}} = 0 \qquad \longleftrightarrow \qquad \frac{d\Omega_n}{d\mathbf{C}} \neq 0$$

Brute force (old school) way: compute orbital response

$$\frac{\mathrm{d}\mathbf{C}}{\mathrm{d}R} = \mathbf{C}\mathbf{U}^R \qquad \qquad \mathbf{\Lambda}\mathbf{U}^R = \mathbf{Q}$$

$$\mathbf{P}^T\mathbf{U}^R = \mathbf{P}^T\mathbf{\Lambda}^{-1}\mathbf{Q} = \mathbf{Z}\mathbf{Q}$$

Better way: **Lagrangian**

Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* **1984**, *81* (11), 5031.

X

Forces: Lagrangian

excitation energy

normalized excitation

$$L = \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix}^T \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix}$$

KS orbitals

Stationarity w.r.t. orbitals

orthonormal orbitals

e.g.

$$L_{pq} = \sum_{\mu} \frac{\partial L}{\partial C_{\mu p}} C_{\mu q} = 0 \longrightarrow \mathbf{D}^n = \begin{pmatrix} \mathbf{T}^{\mathrm{O}} & \mathbf{Z} \\ \mathbf{Z}^T & \mathbf{T}^{\mathrm{V}} \end{pmatrix}$$

$$(\mathbf{A} + \mathbf{B})\mathbf{Z} = -\mathbf{R}$$

After some work

$$\frac{\mathrm{d}\Omega_n}{\mathrm{d}R} = \frac{\partial L}{\partial R} = \langle \mathbf{h}^{(R)} \mathbf{D}^n \rangle + \langle \mathbf{S}^{(R)} \mathbf{W} \rangle + \langle \mathbf{V}^{(R)} \mathbf{\Gamma} \rangle$$

Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117* (16), 7433.

Force Lagrangian: Right-hand-side

$$\Omega_n = \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix}^T \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} = \frac{1}{4} \big[(\mathbf{X}^n + \mathbf{Y}^n)^T (\mathbf{A} + \mathbf{B})(\mathbf{X}^n + \mathbf{Y}^n) \\ + (\mathbf{X}^n - \mathbf{Y}^n)^T (\mathbf{A} - \mathbf{B})(\mathbf{X}^n - \mathbf{Y}^n) \big]$$

$$Q^{\pm}_{kp} = \sum_{\mu} \frac{\partial}{\partial C_{\mu k}} C_{\mu p} \frac{1}{4} \sum_{iajb} (X \pm Y)^n_{ia} (A \pm B)_{iajb} (X \pm Y)^n_{jb}$$

$$(A \pm B)_{iajb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \sum_{\mu\nu\kappa\lambda} C_{\mu i} C_{\nu a} C_{\kappa j} C_{\lambda b} f^{\mathrm{HXC}\pm}_{\mu\nu\kappa\lambda}$$

$$Q_{kp} = \frac{1}{2} \sum_a (X+Y)^n_{ka} H^+_{pa}[X+Y]^n + \frac{1}{2} \sum_a (X-Y)^n_{ka} H^-_{pa}[X-Y]^n$$

Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117* (16), 7433.

X

State-to-state properties

Double residue of $\mathbf{\Pi}^{(3)}$ → $\rho^{0n}(x_1)\bar{\rho}^{nm}(x_3)\rho^{m0}(x_2)$

$\omega_\alpha, \omega_\beta \to -\Omega_n, \Omega_m$

Defines $\boldsymbol{\rho}_{nm} = \begin{pmatrix} \mathbf{K}^{nm}_{\text{occ}} & \mathbf{X}^{nm} \\ (\mathbf{Y}^{nm})^T & \mathbf{K}^{nm}_{\text{virt}} \end{pmatrix}$

$$K^{nm}_{ij} = -\sum_a X^m_{ja} X^n_{ia} + Y^n_{ja} Y^m_{ia} \qquad K^{nm}_{ab} = \sum_i X^m_{ia} X^n_{ib} + Y^n_{ia} Y^m_{ib}$$

$$\begin{pmatrix} \mathbf{X}^{nm} \\ \mathbf{Y}^{nm} \end{pmatrix} = \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - (\Omega_m - \Omega_n) \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]^{-1} \begin{pmatrix} \mathbf{P}^{nm} \\ \mathbf{Q}^{nm} \end{pmatrix}$$

Total cost ~2 TDDFT calculations

- 1 diagonalization per excited state
- 1 polarizability-like solve per amplitude

Derivative coupling: Chernyak-Mukamel

Recall

$$d^R_{nm} = \langle \Phi_n | \nabla^R \Phi_m \rangle$$

$$= \frac{1}{\Omega_{mn}} \int \mathrm{d}\mathbf{x}\; v^{(R)}(\mathbf{x}) \rho^{nm}(\mathbf{x})$$

Hellman-Feyman invalid; back to response theory!

$$\mathcal{A}^{(\alpha\beta)} = \sum_{ia} \langle \phi_i | \hat{v} | \phi_a \rangle X^{(\alpha)}_{ia} + \langle \phi_i | \hat{v}^\dagger | \phi_a \rangle Y^{(\alpha)}_{ia} \qquad \textbf{TDDFT}$$

$$= \langle \Psi_0 | \hat{v} | \Psi^{(\alpha)} \rangle + \langle \Psi_0 | \hat{v}^\dagger | \Psi^{(-\alpha)} \rangle \qquad \textbf{exact}$$

$$|\Psi^{(\alpha)}\rangle = -\sum_n \frac{|\Phi_n\rangle v_{n0}}{\Omega_n - \omega} \quad \longrightarrow \quad \lim_{\omega \to \Omega_n} (\omega - \Omega_n) |\Psi^{(\alpha)}\rangle = |\Phi_n\rangle v_{n0}$$

$$\langle \Phi_0 | \nabla \Phi_n \rangle = -\sum_{ia} (X - Y)^n_{ia} \langle \phi_i | \nabla \phi_a \rangle$$

Chernyak, V.; Mukamel, S. *J. Chem. Phys.* **2000**, *112* (8), 3572.

Derivative couplings efficiently

$$\langle \Phi_0 | \nabla \Phi_n \rangle = -\sum_{ia} (X - Y)^n_{ia} \langle \phi_i | \nabla \phi_a \rangle$$

Becomes $$d^R_{0n} = -\langle (\mathbf{X} - \mathbf{Y})(\mathbf{U}^R + \frac{1}{2}(\mathbf{S}^{(R)} + \mathbf{T}^{(R)})) \rangle$$

$$(\mathbf{A} + \mathbf{B})\mathbf{U}^R = -\mathbf{h}^R$$

Z-vector $$(\mathbf{A} + \mathbf{B})\mathbf{Z} = (\mathbf{X}^n - \mathbf{Y}^n)$$

$$(\mathbf{A} + \mathbf{B})(\mathbf{X}^n + \mathbf{Y}^n) = \Omega_n (\mathbf{X}^n - \mathbf{Y}^n)$$

Final expression

$$d^R_{0n} = \langle \mathbf{h}^{(R)} \mathbf{P} \rangle - \langle \mathbf{S}^{(R)} \mathbf{W} \rangle + \langle \mathbf{V}^{(R)} \mathbf{\Gamma} \rangle$$

Send, R.; Furche, F. *J. Chem. Phys.* **2010**, *132* (4), 044107.

Arbitrary derivative couplings

$$\langle \Phi_n | \nabla \Phi_m \rangle = \sum_{pq} \rho_{pq}^{nm} \langle \phi_p | \nabla \phi_q \rangle$$

Make a Lagrangian

KS orbitals

$$L^{nm} = \sum_{pq} \rho_{pq}^{nm} \langle \phi_p(R_0) | \phi_q(R) \rangle + \sum_{ia} \boxed{Z_{ia}} F_{ia} - \sum_{pq} \boxed{W_{pq}} (S_{pq} - \delta_{pq})$$

orthonormal orbitals

Make stationary

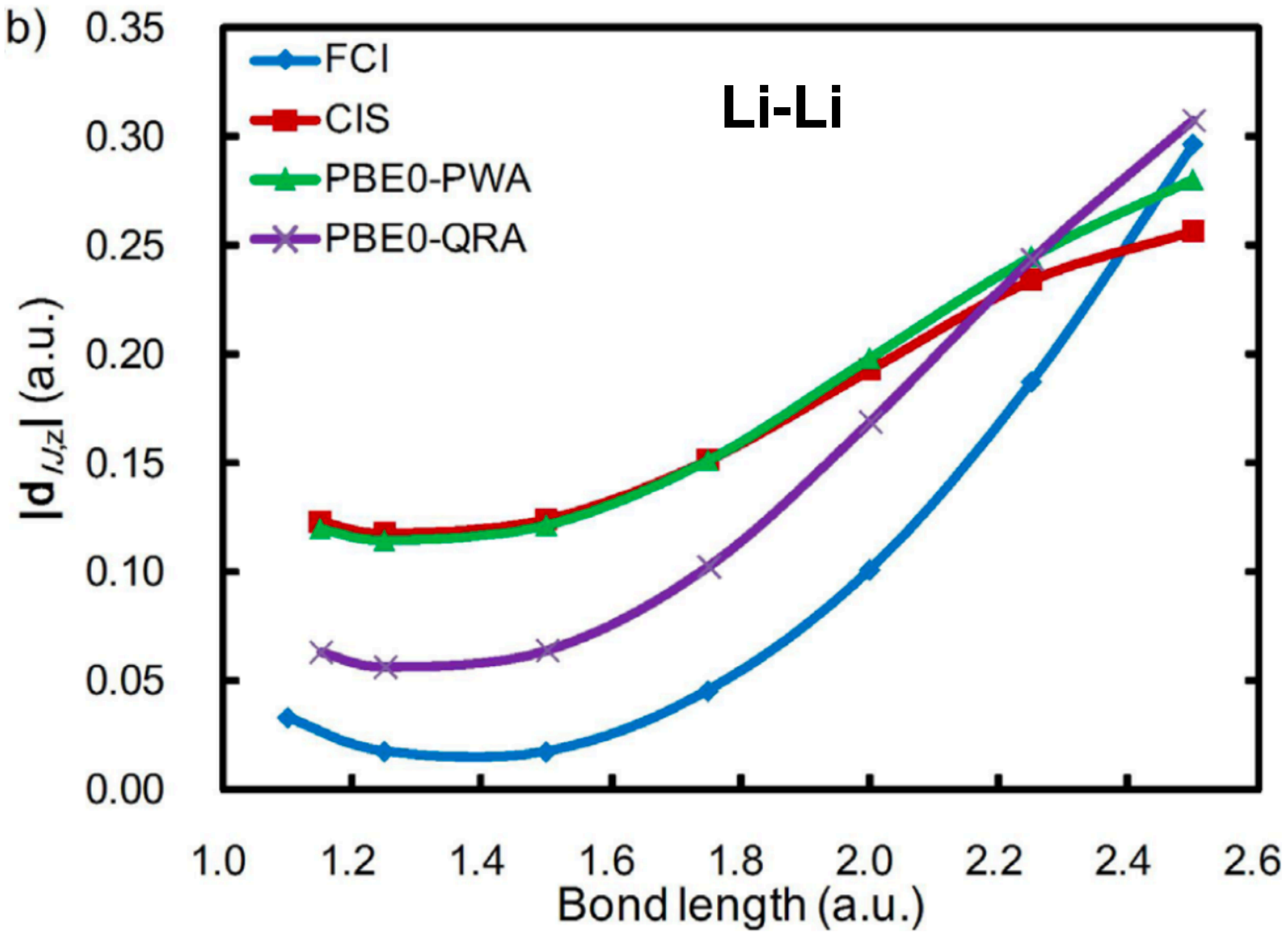
$$d_{nm}^{R} = \frac{\partial L^{nm}}{\partial R} = \langle \frac{\partial \mathbf{h}}{\partial R} \boldsymbol{\rho}^{nm} \rangle + \langle \frac{\partial \mathbf{S}}{\partial R} \mathbf{W}^{nm} \rangle + \langle \frac{\partial \mathbf{V}}{\partial R} \boldsymbol{\Gamma}^{nm} \rangle$$

Send, R.; Furche, F. *J. Chem. Phys.* **2010**, *132* (4), 044107.

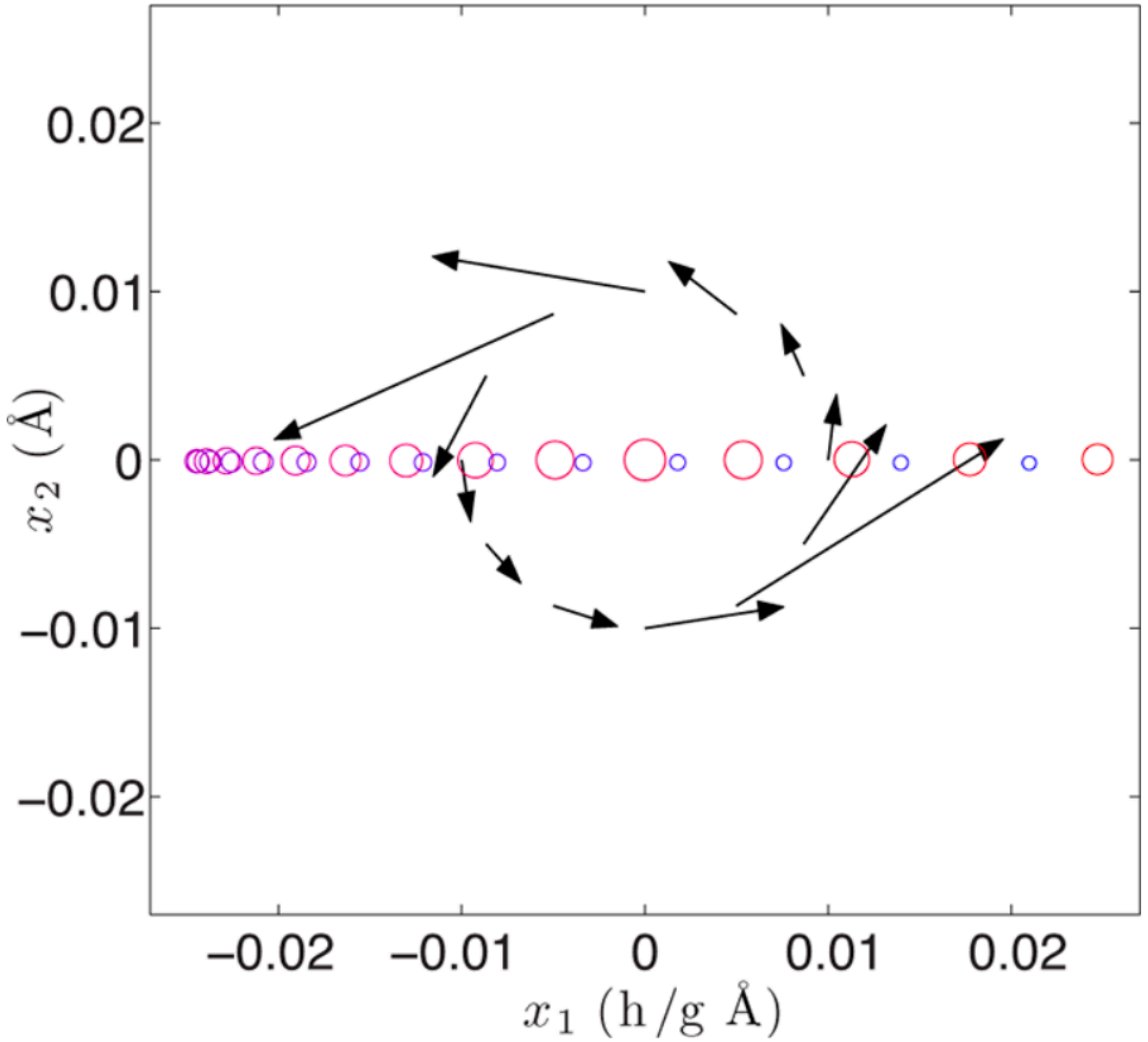
Li, Z.; Liu, W. *J. Chem. Phys.* **2014**, *141* (1), 014110.

Successes: properties reliable when KS TDDFT is sensible

Derivative couplings



State-to-state conical intersections



- correct topology for state-to-state
- “useful” accuracy

Acc. Chem. Res. 2015, 48, 1340−1350

J. Chem. Phys. 142, 064109 (2015)

Challenges: non-real instabilities

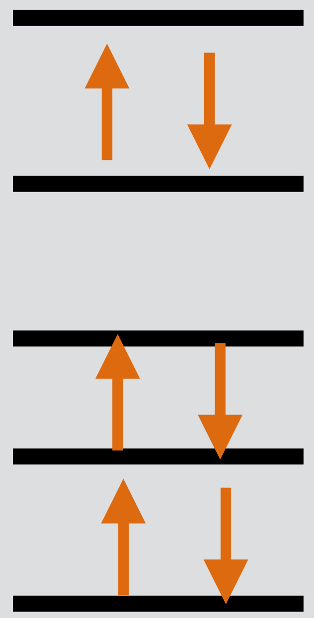
Magnetic orbital rotation Hessian

$$(A - B)_{ia,jb} = \varepsilon_{ab}\delta_{ij} - \varepsilon_{ij}\delta_{ab} + c_x[(ib|ja) - (ij|ab)],$$

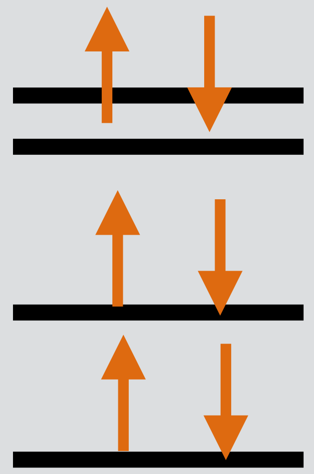
If **A - B** has any negative eigenvalues, the system is said to be “non-real unstable”

$$(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\mathbf{Z} = \Omega_n^2\mathbf{Z}$$

- hard to guarantee real eigenvalues
- what do imaginary energies mean?



Normally okay because for semilocal XC, can only happen with non-Aufbau occupation



Becomes problematic during dynamics because orbital gaps collapse

Solution: Tamm-Dancoff Approximation

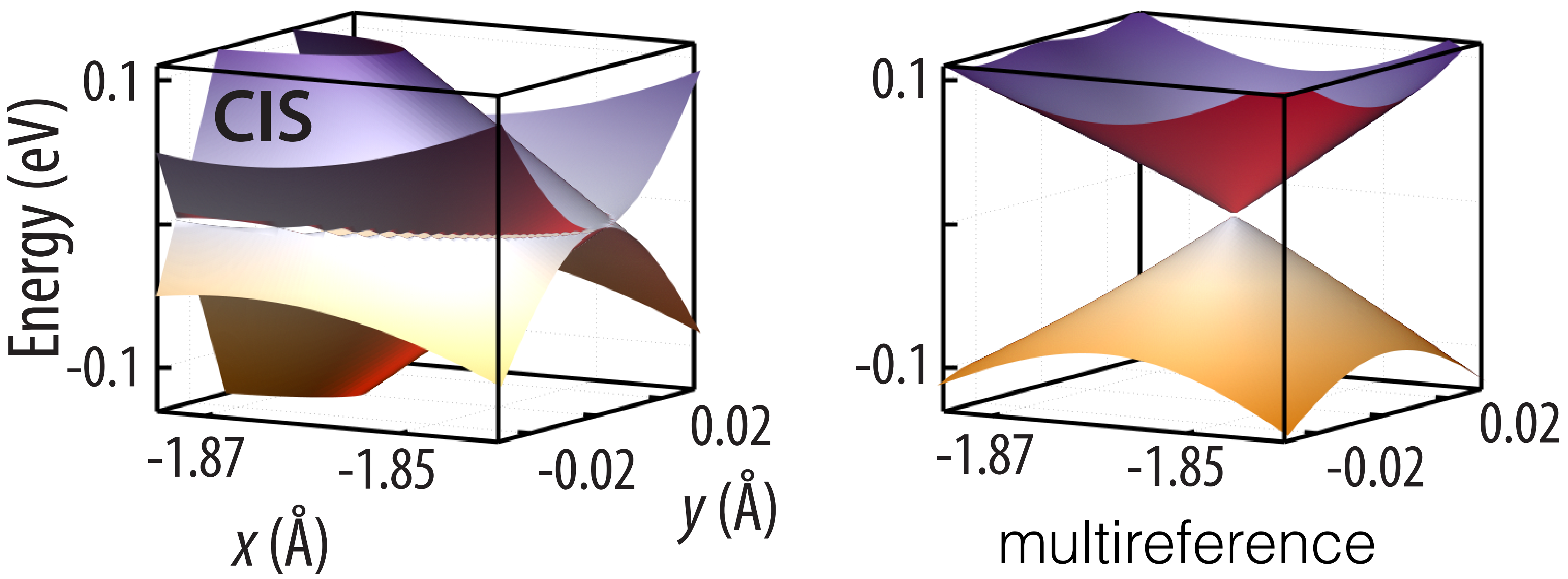
$$\mathbf{AX} = \mathbf{X}\Omega$$

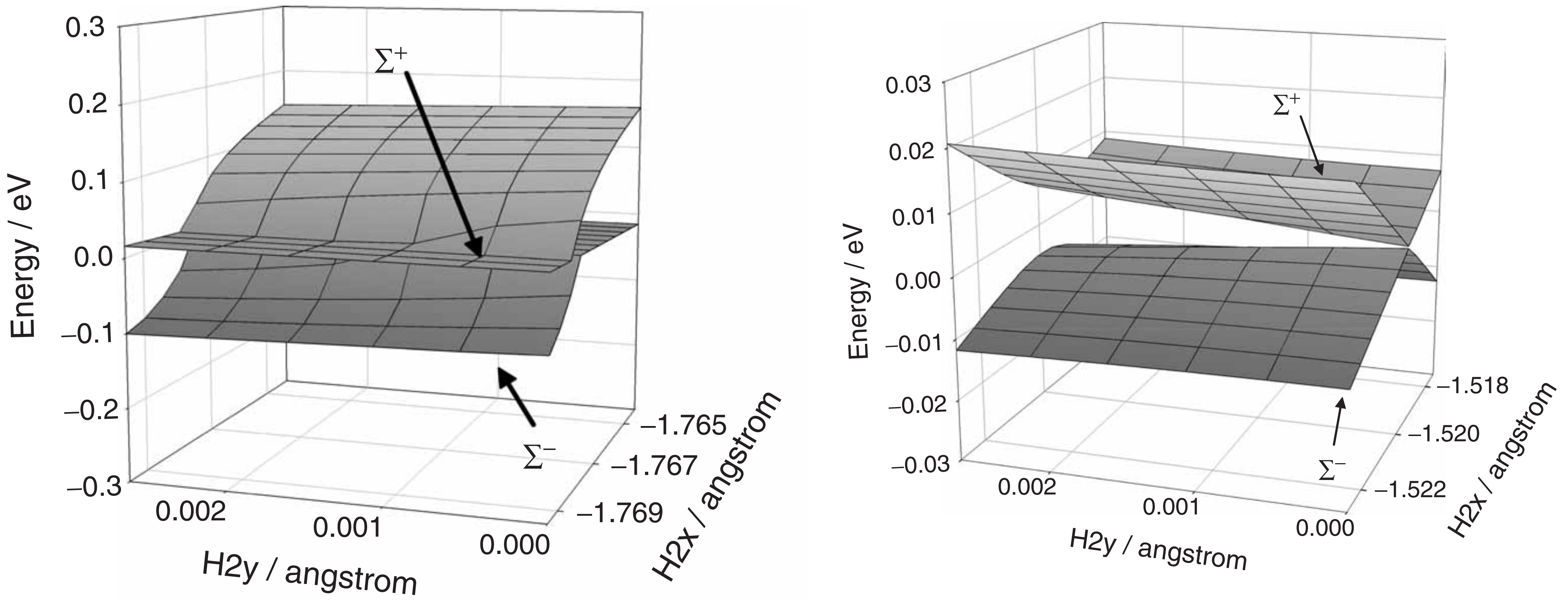
- eigenvalues of Hermitian matrix -> real
- negative even allowed (and okay!)

R. Seeger and J. A. Pople, J. Chem. Phys. 66, 3045 **1977**

Challenges: ground-to-excited conical intersections

Wrong dimensionality





B3LYP SA-CASSCF

Unstable properties

$$\mathbf{D}^n = \begin{pmatrix} \mathbf{T}^{\mathrm{O}} & \mathbf{Z} \\ \mathbf{Z}^T & \mathbf{T}^{\mathrm{V}} \end{pmatrix}$$

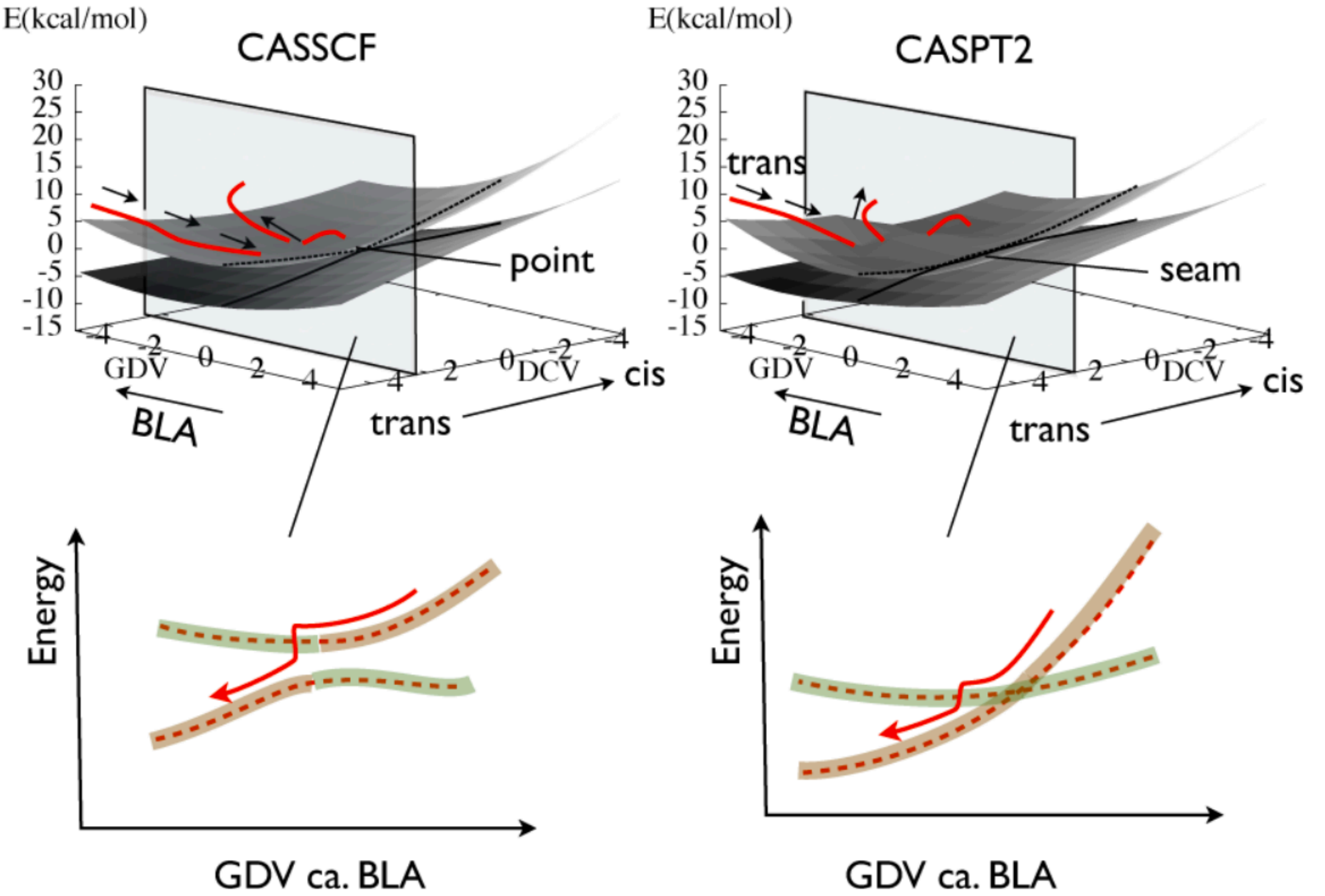
$$\mathbf{Z} = -(\mathbf{A}+\mathbf{B})^{-1}\mathbf{R}$$

$$(\mathbf{A}+\mathbf{B})^{-1} = \sum_n \frac{(\mathbf{X}^n+\mathbf{Y}^n)(\mathbf{X}^n+\mathbf{Y}^n)^\dagger}{\Omega_n}$$

- noninteracting seams instead of cones
- orbital response diverges

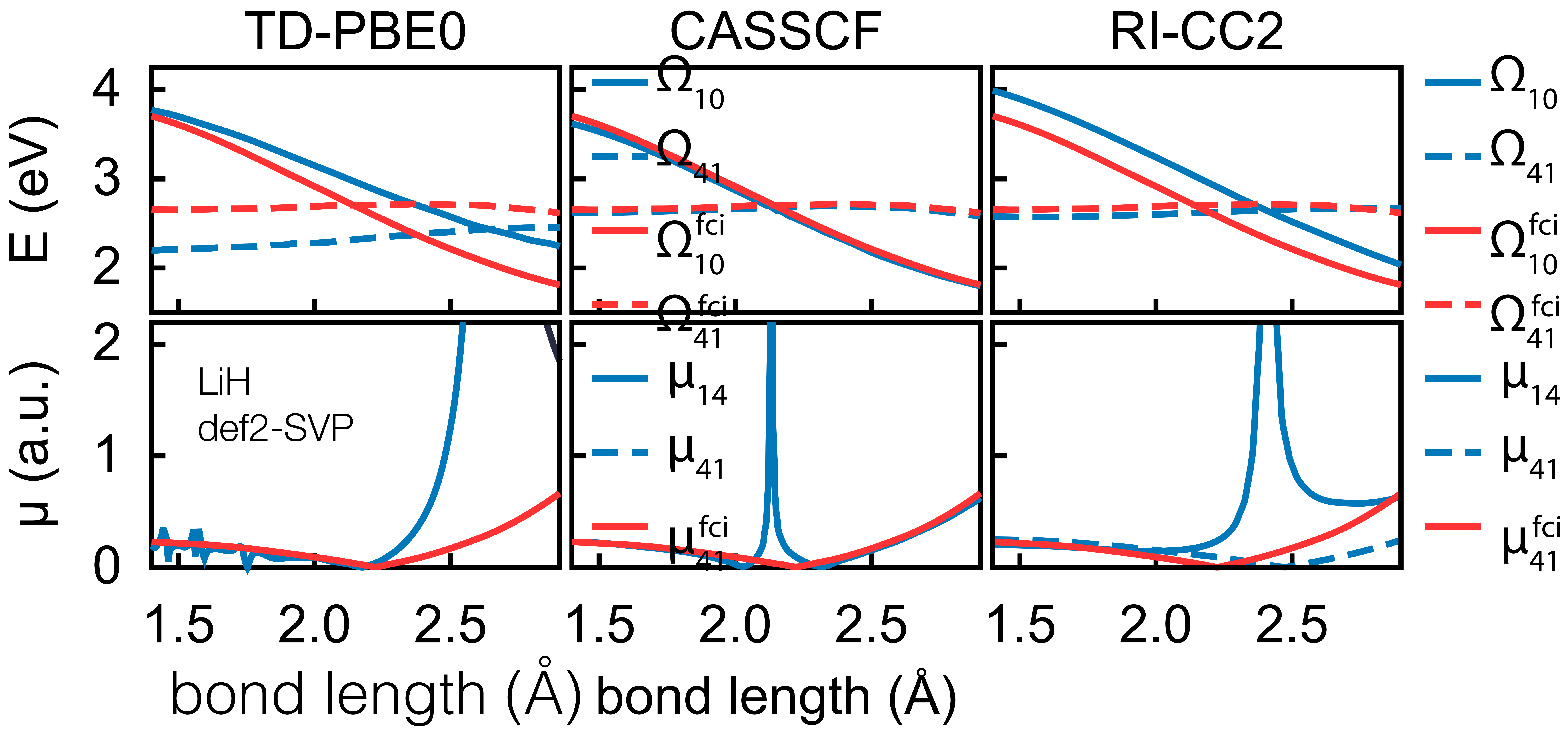
Levine, B. G.; Ko, C.; Quenneville, J.; Martínez, T. J. *Mol. Phys.* **2006**, *104* (5-7), 1039–1051.

… but dynamics may not be terribly sensitive to topology



dx.doi.org/10.1021/ct500154k | J. Chem. Theory Comput. 2014, 10, 3074−3084

Challenges: quadratic response failures hurt state-to-state



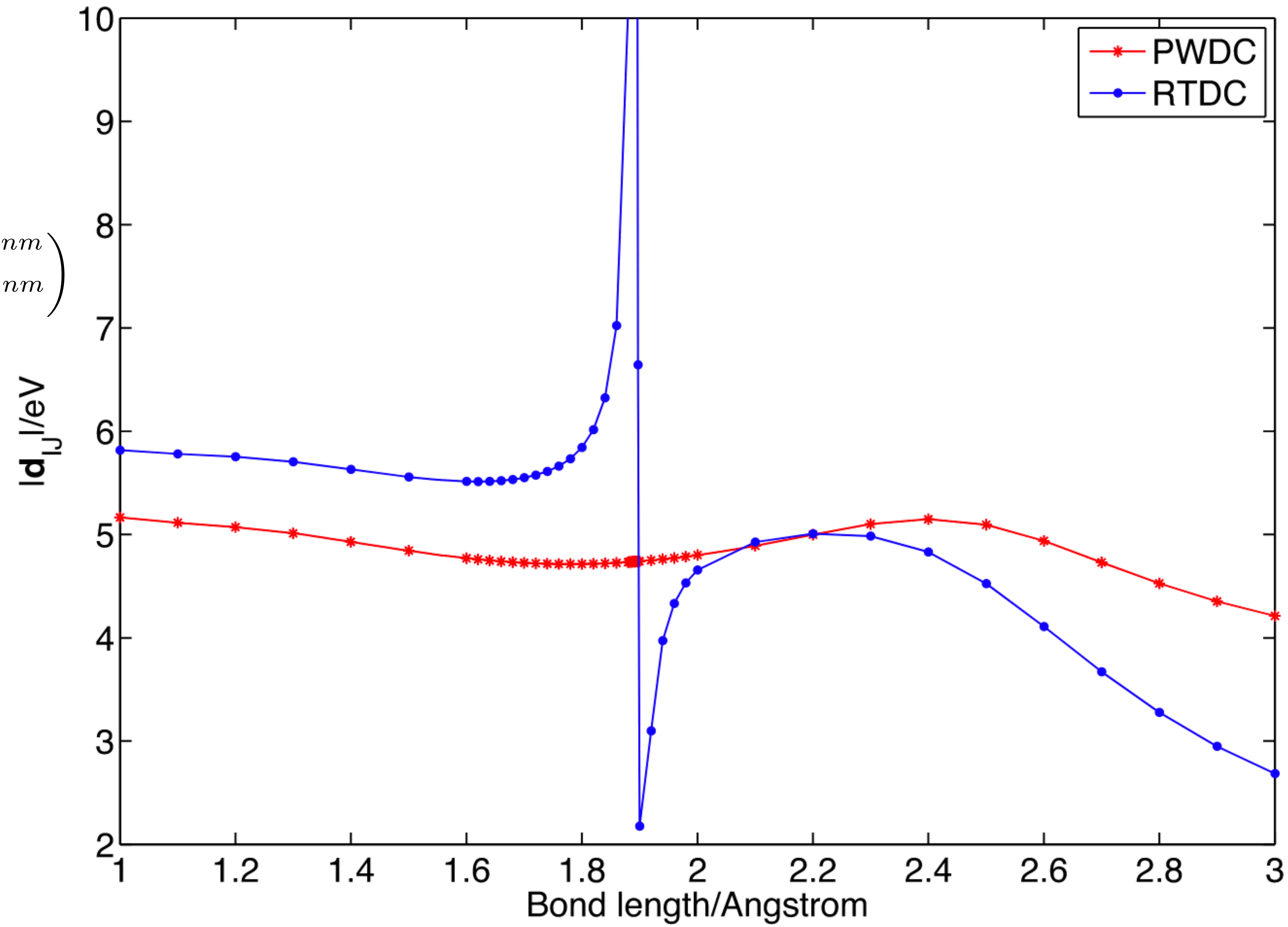
$$\begin{pmatrix} \mathbf{X}^{nm} \\ \mathbf{Y}^{nm} \end{pmatrix} = \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - (\Omega_m - \Omega_n) \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]^{-1} \begin{pmatrix} \mathbf{P}^{nm} \\ \mathbf{Q}^{nm} \end{pmatrix}$$

… but there is a workaround: pseudowavefunction

$$\begin{pmatrix} \mathbf{X}^{nm} \\ \mathbf{Y}^{nm} \end{pmatrix} = \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - \cancel{(\Omega_m - \Omega_n)} \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]^{-1} \begin{pmatrix} \mathbf{P}^{nm} \\ \mathbf{Q}^{nm} \end{pmatrix}$$

$$\Downarrow$$

$$\begin{pmatrix} \mathbf{X}^{nm} \\ \mathbf{Y}^{nm} \end{pmatrix} = - \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{P}^{nm} \\ \mathbf{Q}^{nm} \end{pmatrix}$$



J. Chem. Phys. 142, 064114 (2015)

Properties and couplings: Summary

Success/Failure	Consequence	Can we avoid?	Can we fix?
Tend to work when (TD)DFT works	Already know a lot about where (TD)DFT works	All useful tricks from (TD)DFT	All useful tricks from (TD)DFT
Nonreal instabilities	Imaginary energies?	TDA	Maybe, but not clear
Improper dimensionality of conical intersections	Ground and excited states artificially decoupled	May not have a big effect on dynamics	Need an ensemble ground state
Degenerate ground state	Properties can diverge near degeneracy	In dynamics, hop while we still have a gap	Need an ensemble ground state
Spurious poles in quadratic response	Unphysical divergences in state-to-state coupling	Pseudowavefunction approximation	Memory kernel?

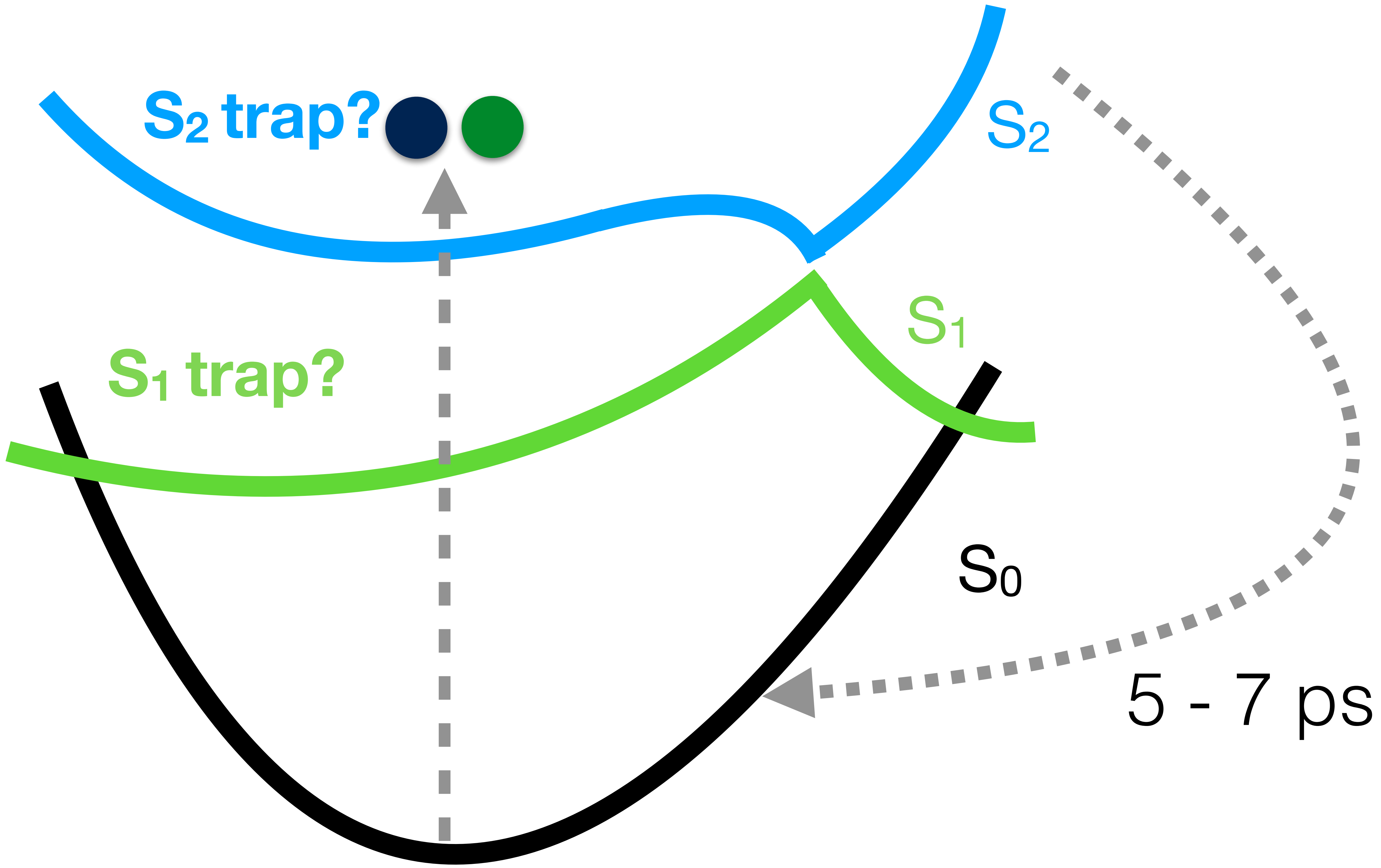
Action Lagrangian

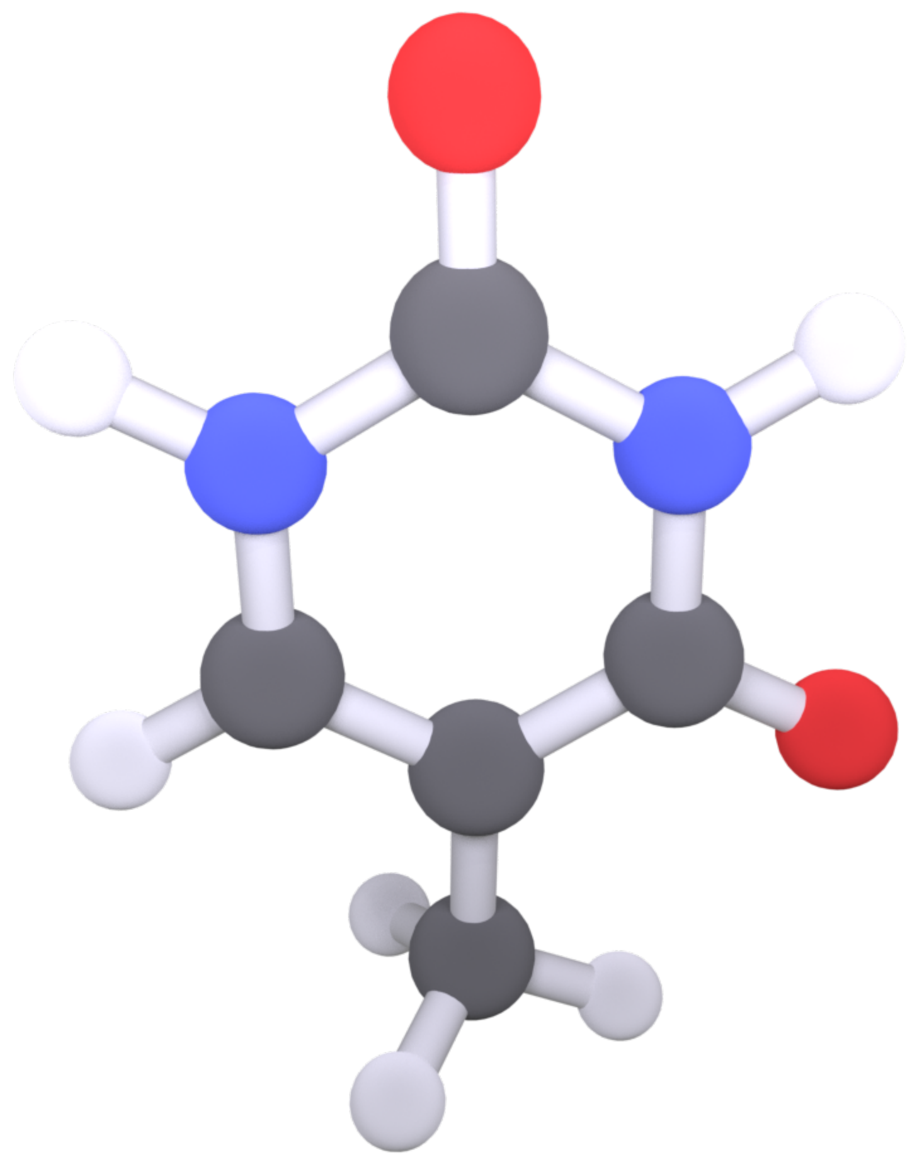
The requisite properties

Photochemistry of Thymine

Interpreting Excited States

Excited-state deactivation of thymine

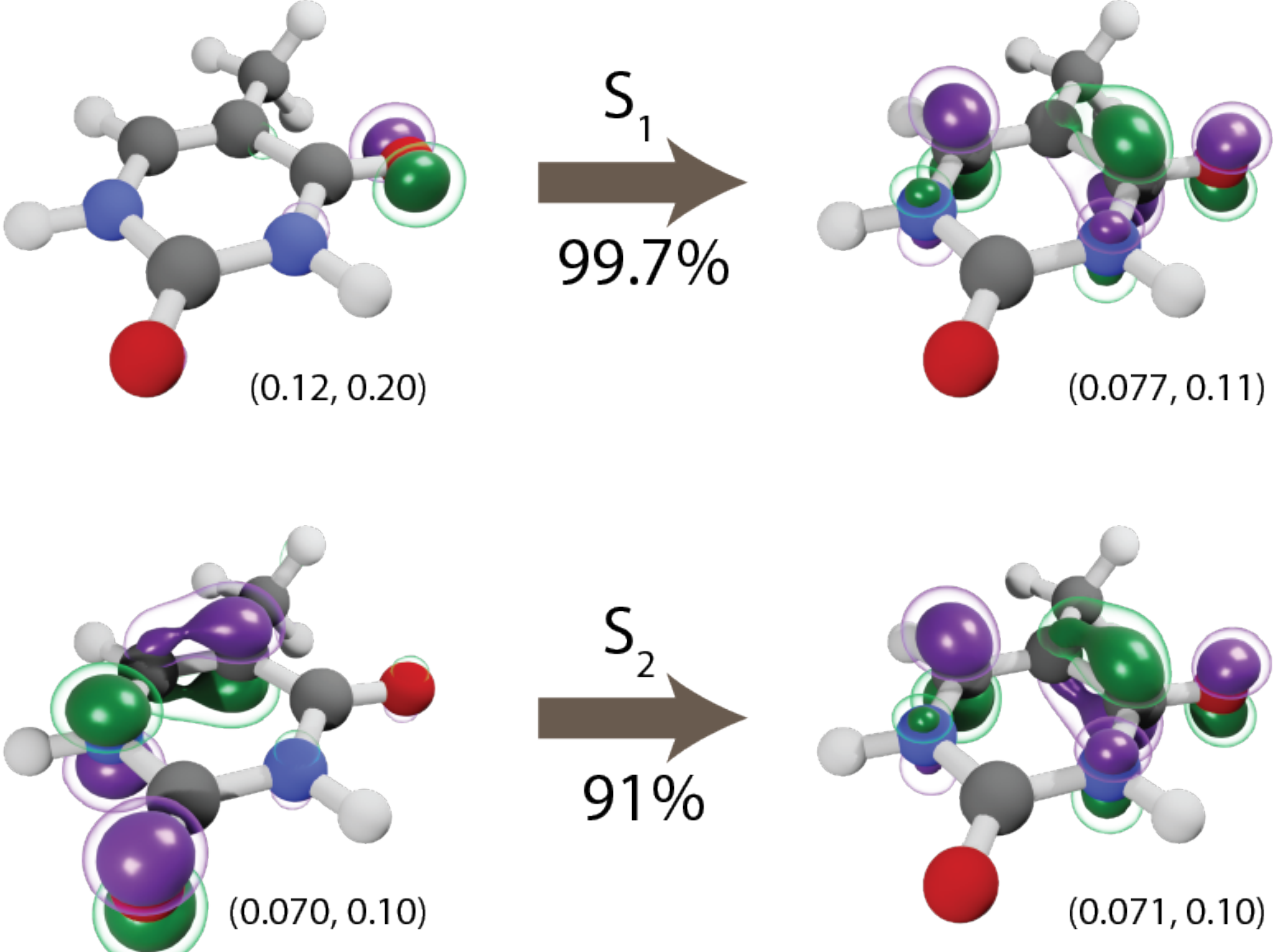




Kang, H.; Lee, K. T.; Jung, B.; Ko, Y. J.; Kim, S. K. *J. Am. Chem. Soc.* **2002**, 124 (44), 12958–12959.
Stojanović, L.; Bai, S.; Nagesh, J.; Izmaylov, A.; Crespo-Otero, R.; Lischka, H.; Barbatti, M. *Molecules* **2016**, 21 (11), 1603.
Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

Thymine: S_1 is dark n-π^*, S_2 is bright π-π^*

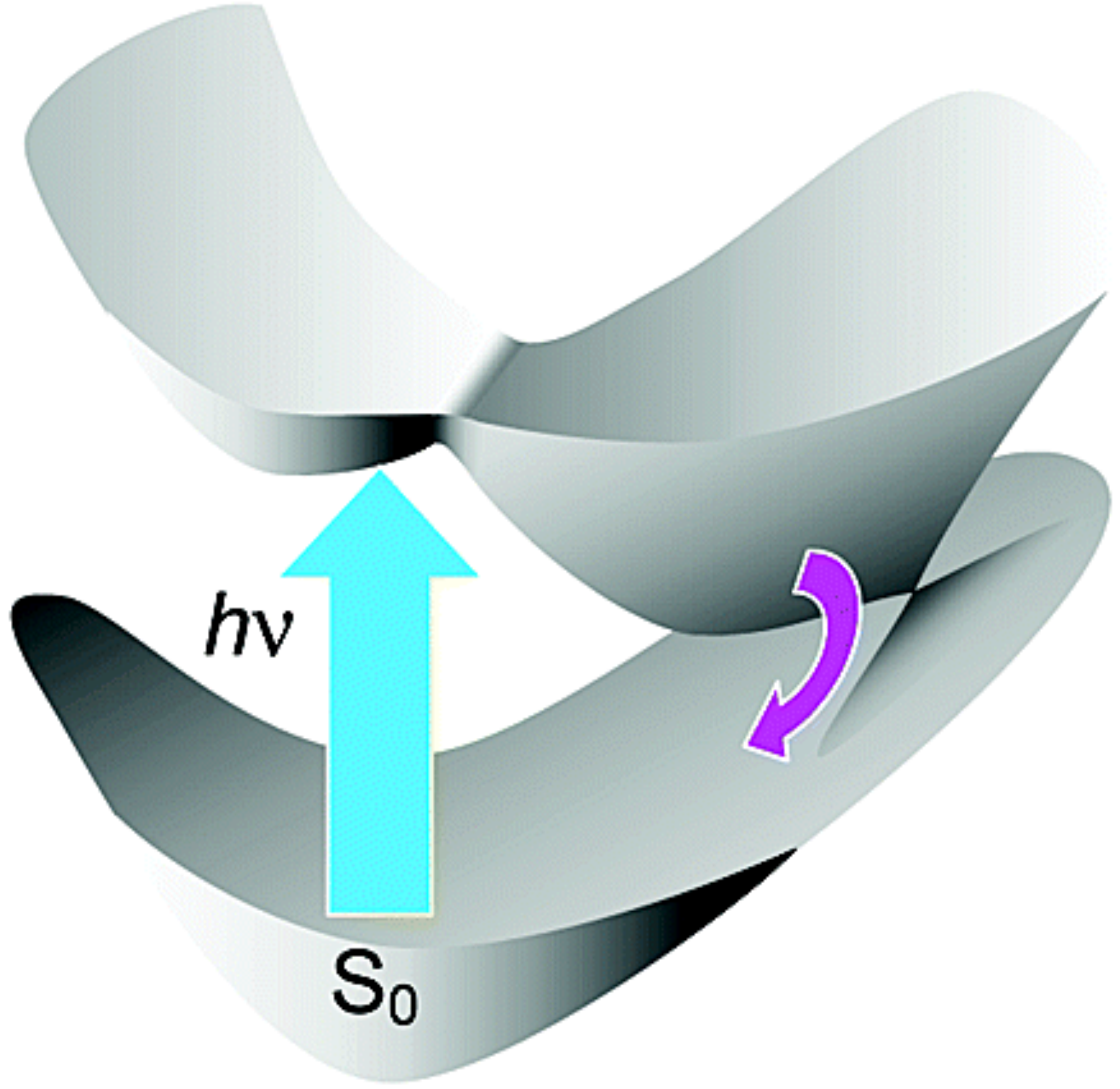
Dominant NTOs
isovals chosen such that
~25%, 50% of total
orbital probability density

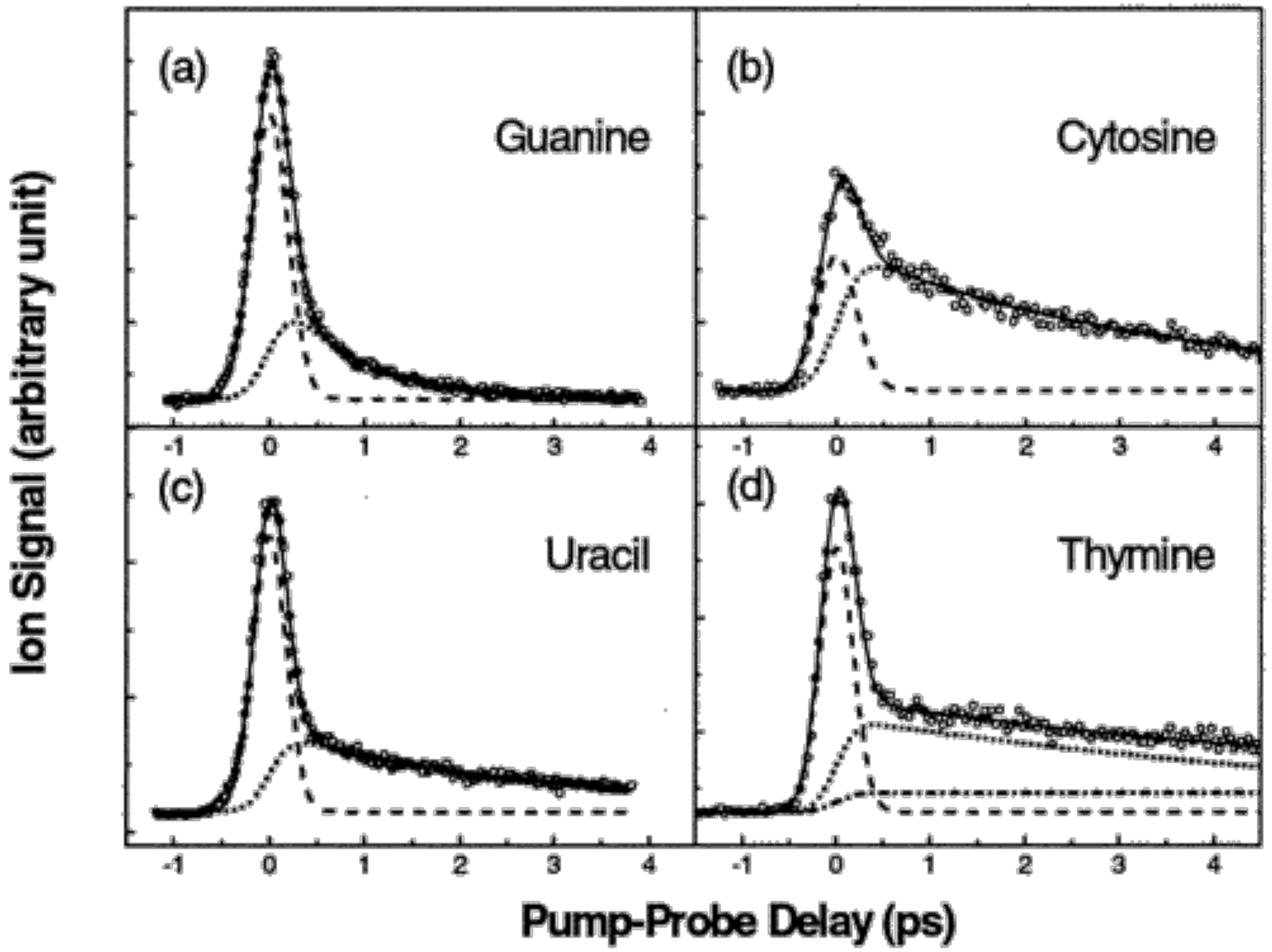


Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

Prior results: fs pump-probe transient ionization

Signal	Timescale
Prompt	100-200 fs
Fast	5-7 ps
Slow	>1 ns





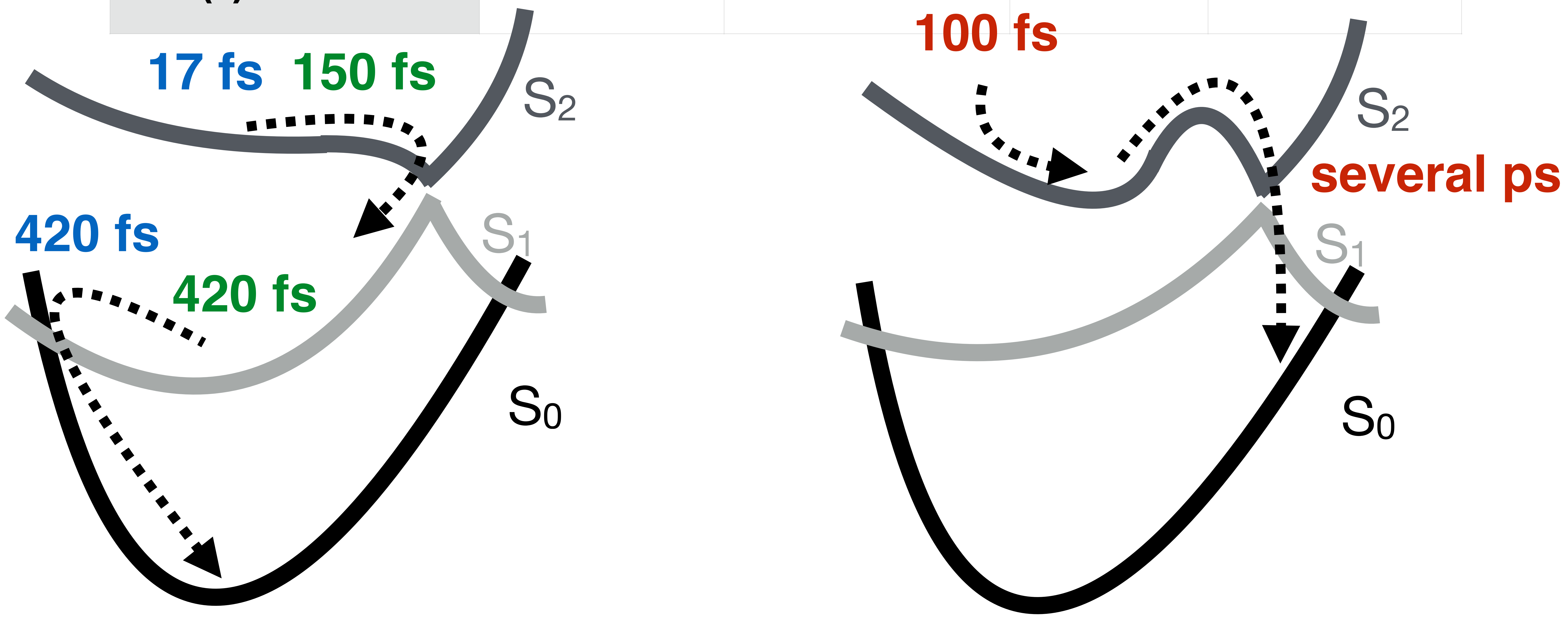
Kang et al J. Am. Chem. Soc. **2002** 124, 12958-12959

Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

Prior results: photochemistry simulations

No qualitative or quantitative agreement on simulated timescales or mechanisms

Method	prompt	assignment	fast	assignment
Semiempirical	17 fs	$S_2 \rightarrow S_1$	420 fs	$S_1 \rightarrow S_0$
CASSCF	100 - 200 fs	$S_{2,FC} \rightarrow S_{1,min}$	2.6 - 5 ps	$S_{2,min} \rightarrow S_1$
ADC(2)	150 - 158 fs	$S_2 \rightarrow S_1$	420 fs	$S_1 \rightarrow S_0$



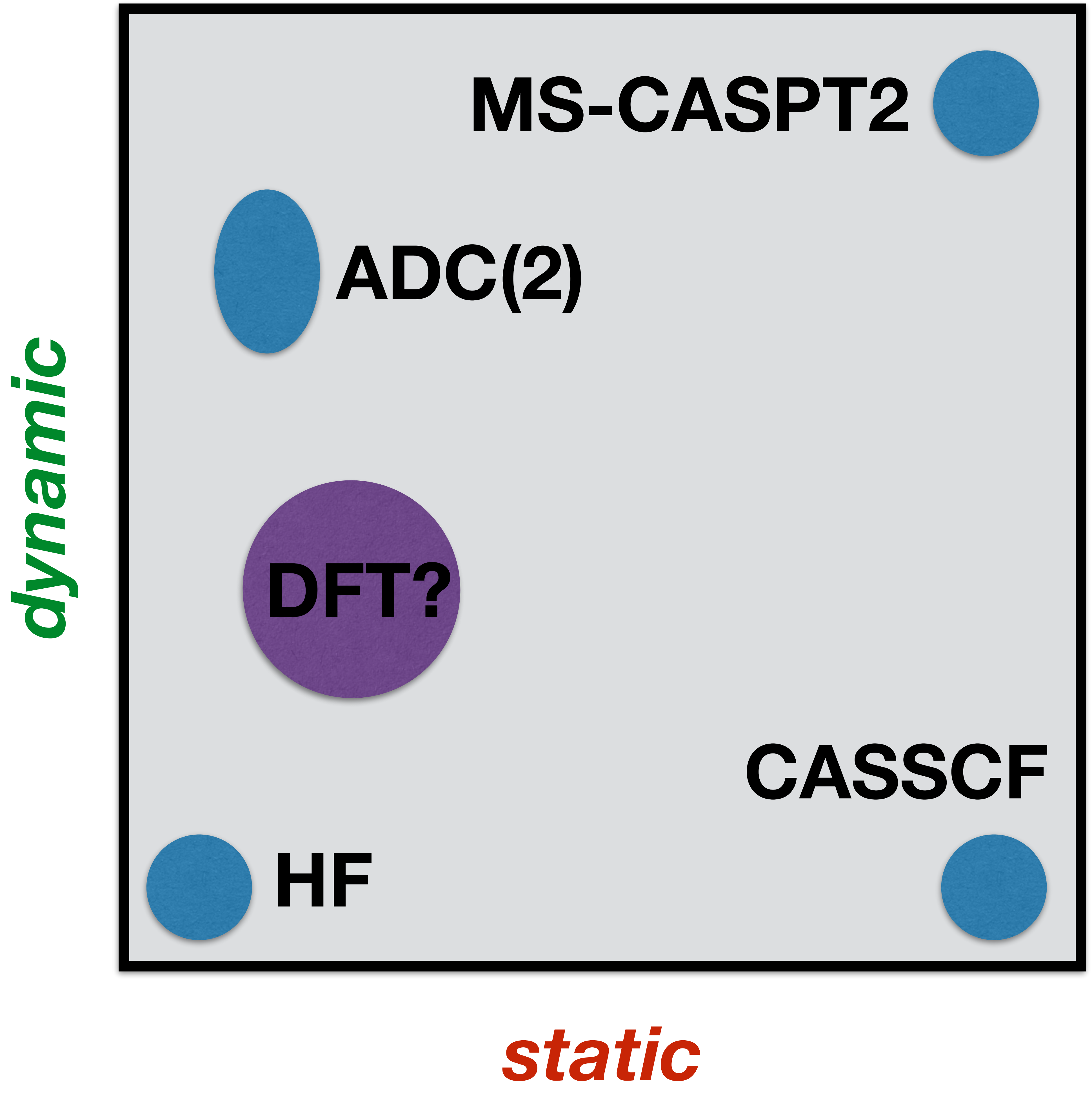
Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

A tale of two types of correlation

Electron correlation often discussed in terms of dynamic/static

Static: important for degenerate ground states (strong correlation)

Dynamic: important for correct state orderings (weak correlation)



x

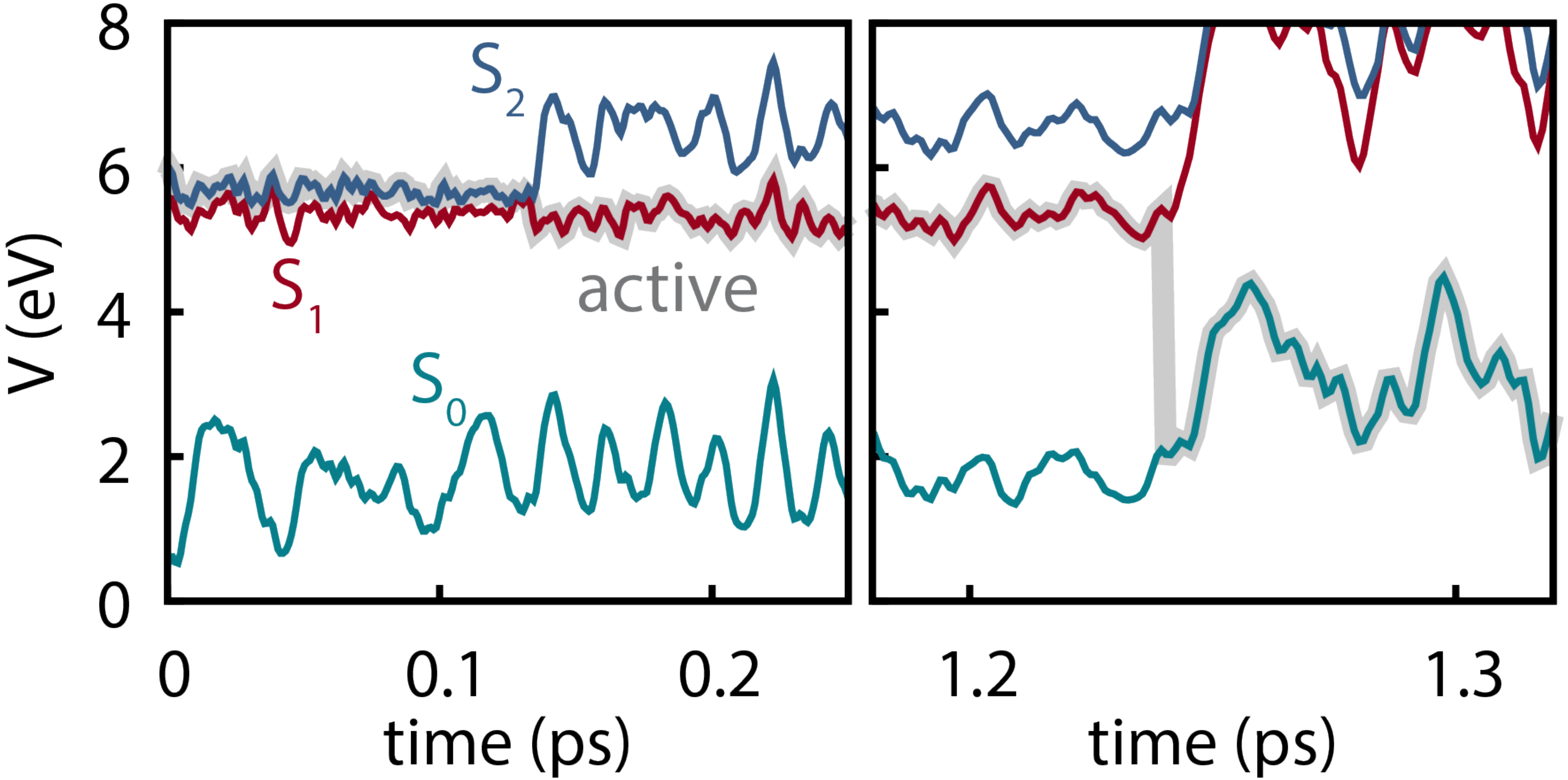
Computed excited-state energies

Method	**S_1 (eV)**	**S_2 (eV)**
PBE0/def2-SVP	4.85	5.44
PBE0/def2-SVPD	4.83	5.24
ADC(2)[52]	4.56	5.06
MS-CASPT2[50]	5.09	5.09
MS-CASPT2[42]	5.23	5.44
CASSCF[50]	5.31	7.12
EEL spectroscopy		4.95[64], 4.9[65], 4.96[66]

Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

Representative dynamics

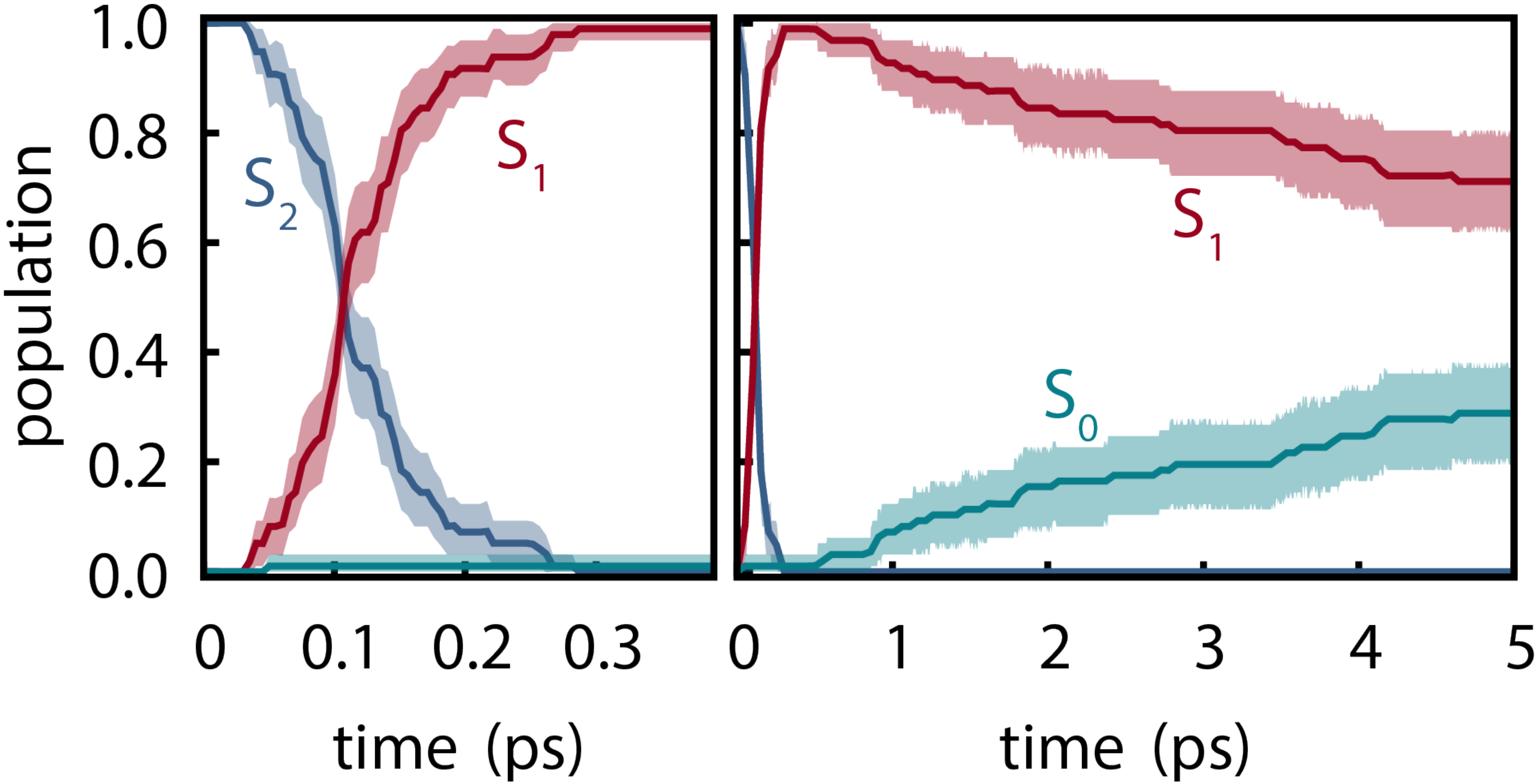
PBE0-D3/def2-SVP



Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

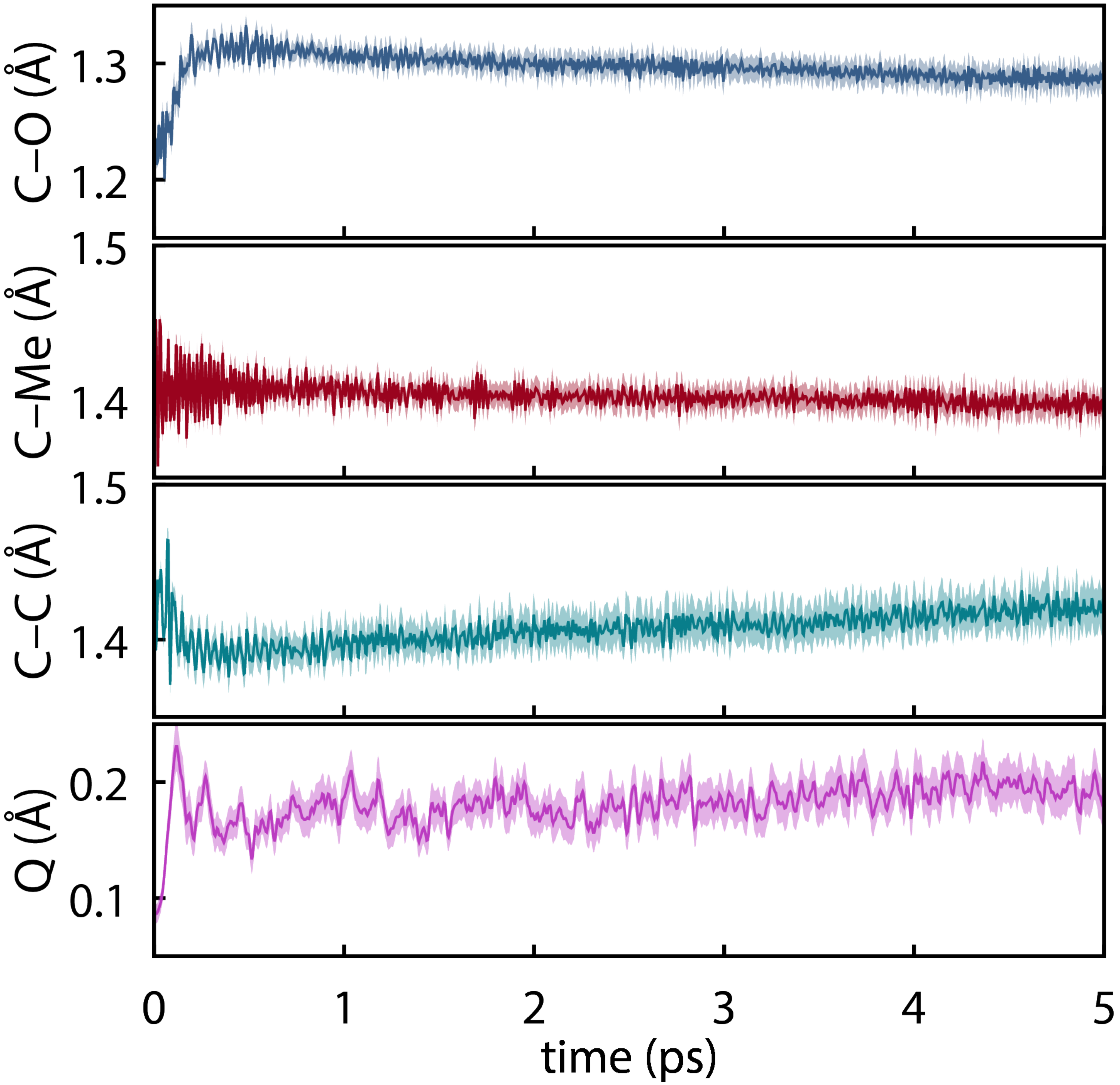
Averaged population dynamics

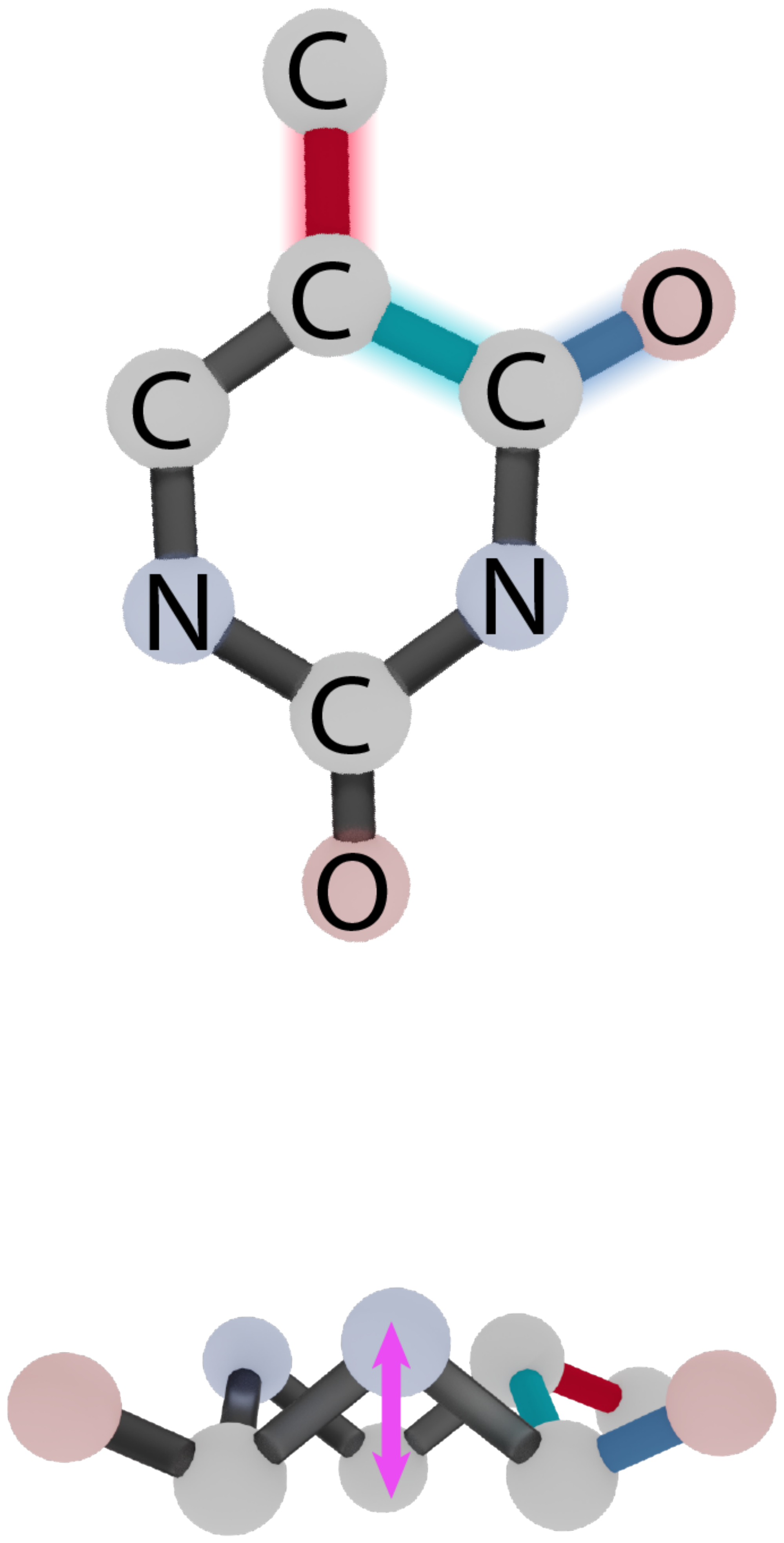
PBE0-D3/def2-SVP



Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

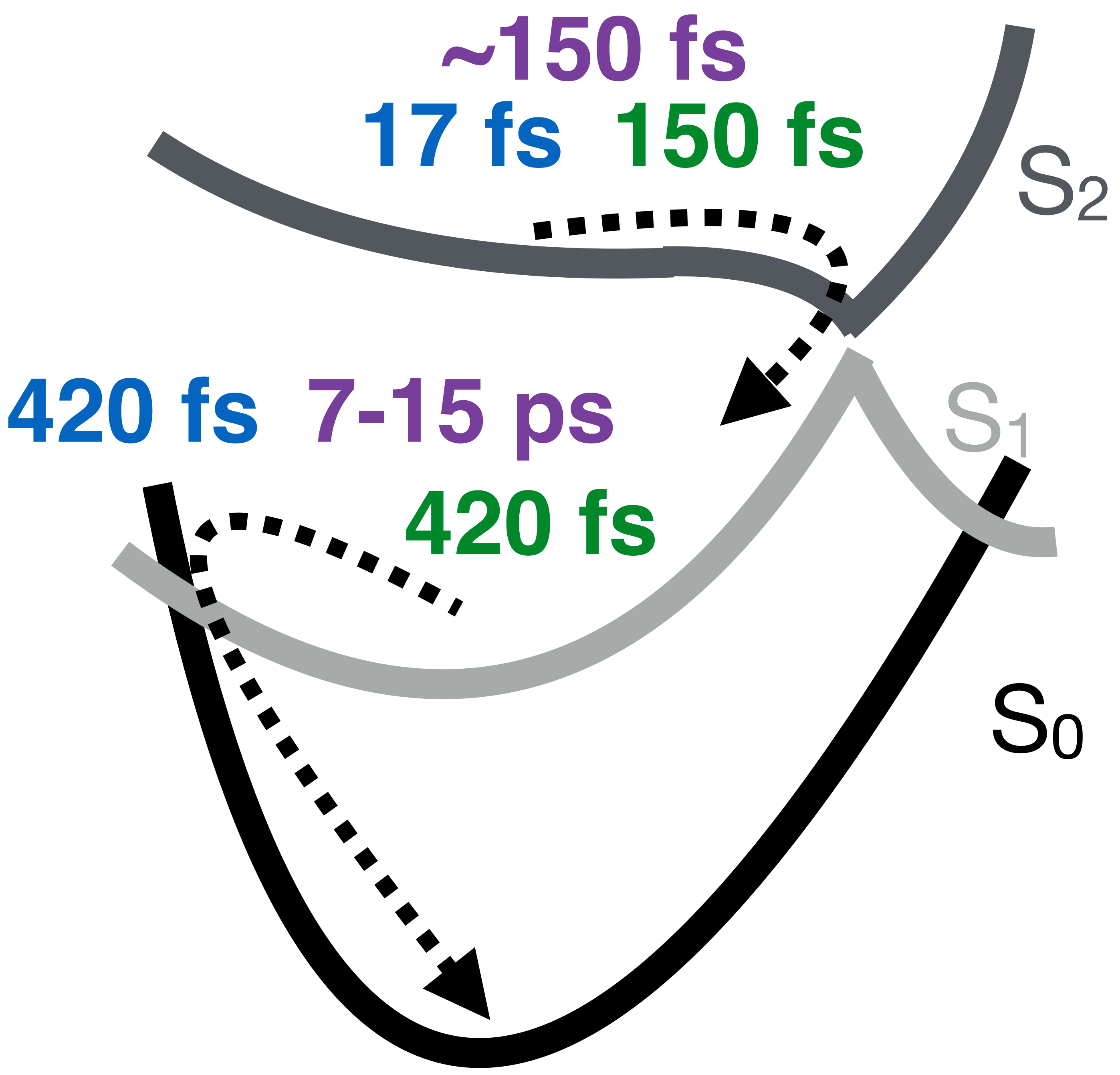
Thymine: structural dynamics

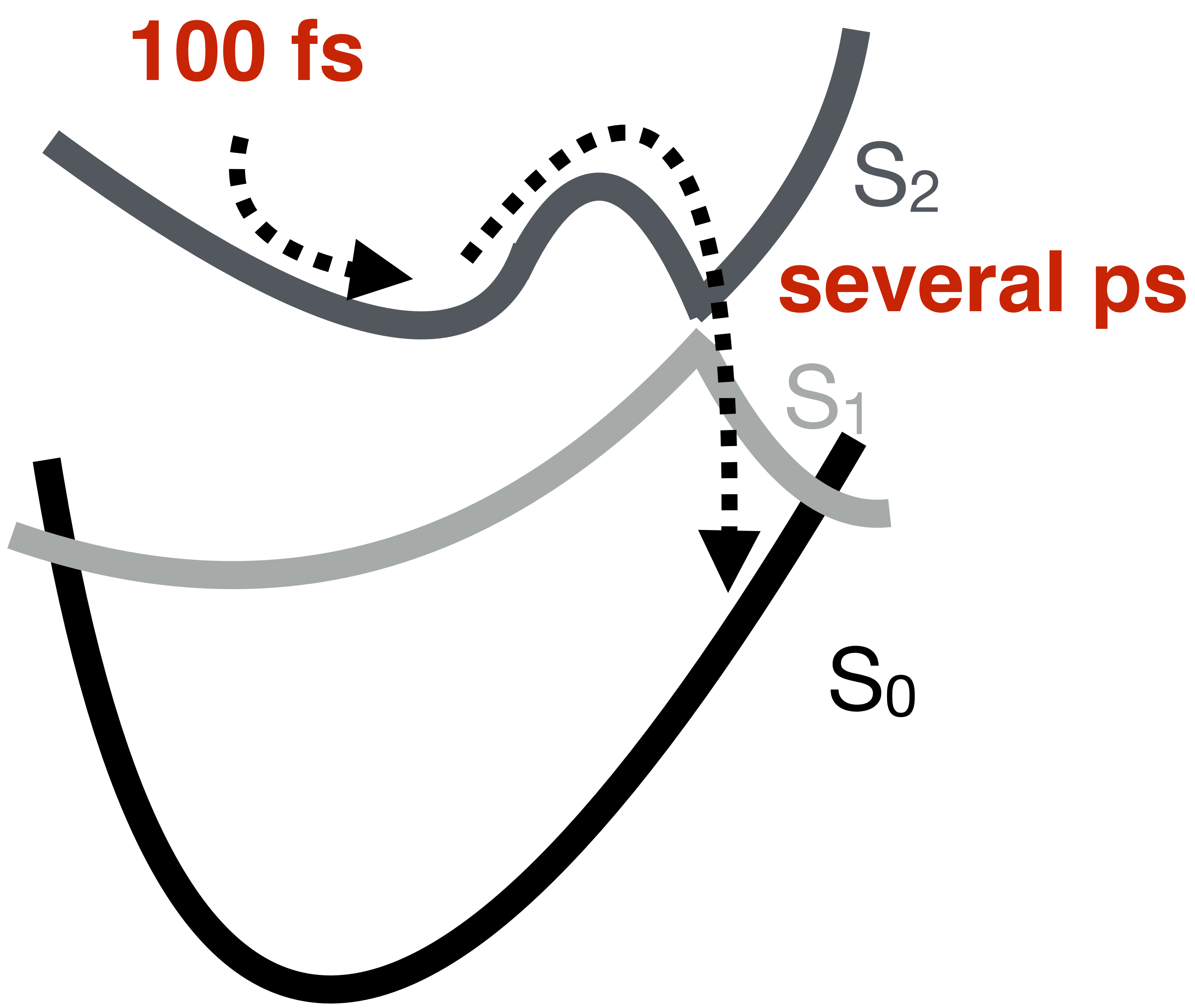




Only SH-TDDFT simulations consistent with experiment

Method	prompt	assignment	fast	assignment
Semiempirical[1]	17 fs	$S_2 \rightarrow S_1$	420 fs	$S_1 \rightarrow S_0$
CASSCF[2]	100 - 200 fs	$S_{2,FC} \rightarrow S_{1,min}$	2.6 - 5 ps	$S_{2,min} \rightarrow S_1$
ADC(2)[3]	150 - 158 fs	$S_2 \rightarrow S_1$	420 fs	$S_1 \rightarrow S_0$
FSSH+PBE0 (this)	140 - 200 fs	$S_2 \rightarrow S_1$	7 - 15 ps	$S_1 \rightarrow S_0$



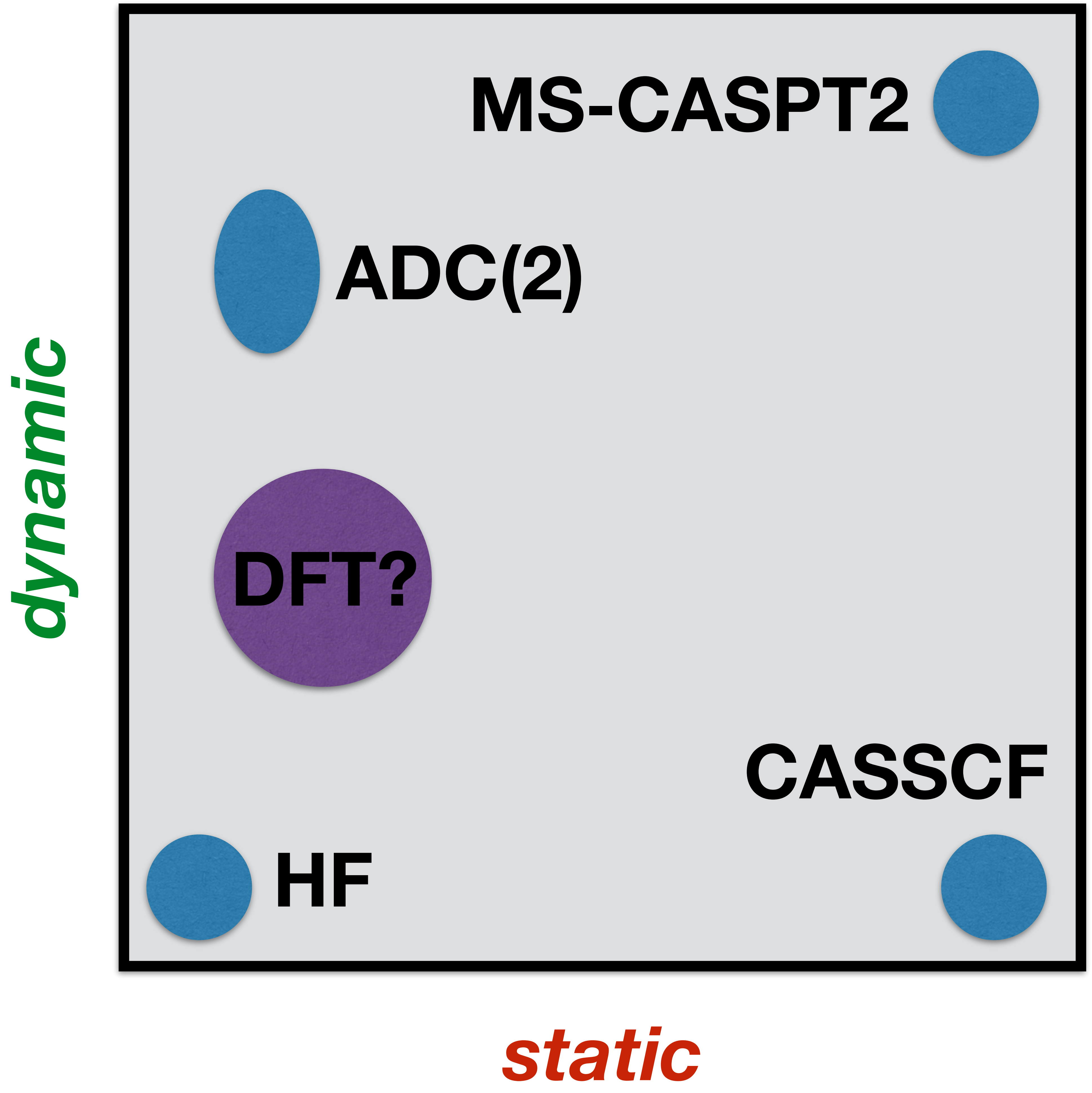


Parker, S. M.; Roy, S.; Furche, F. *PCCP*. **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

Balanced correlation?

Static: important for degenerate ground states (strong correlation)

Dynamic: important for correct state orderings (weak correlation)



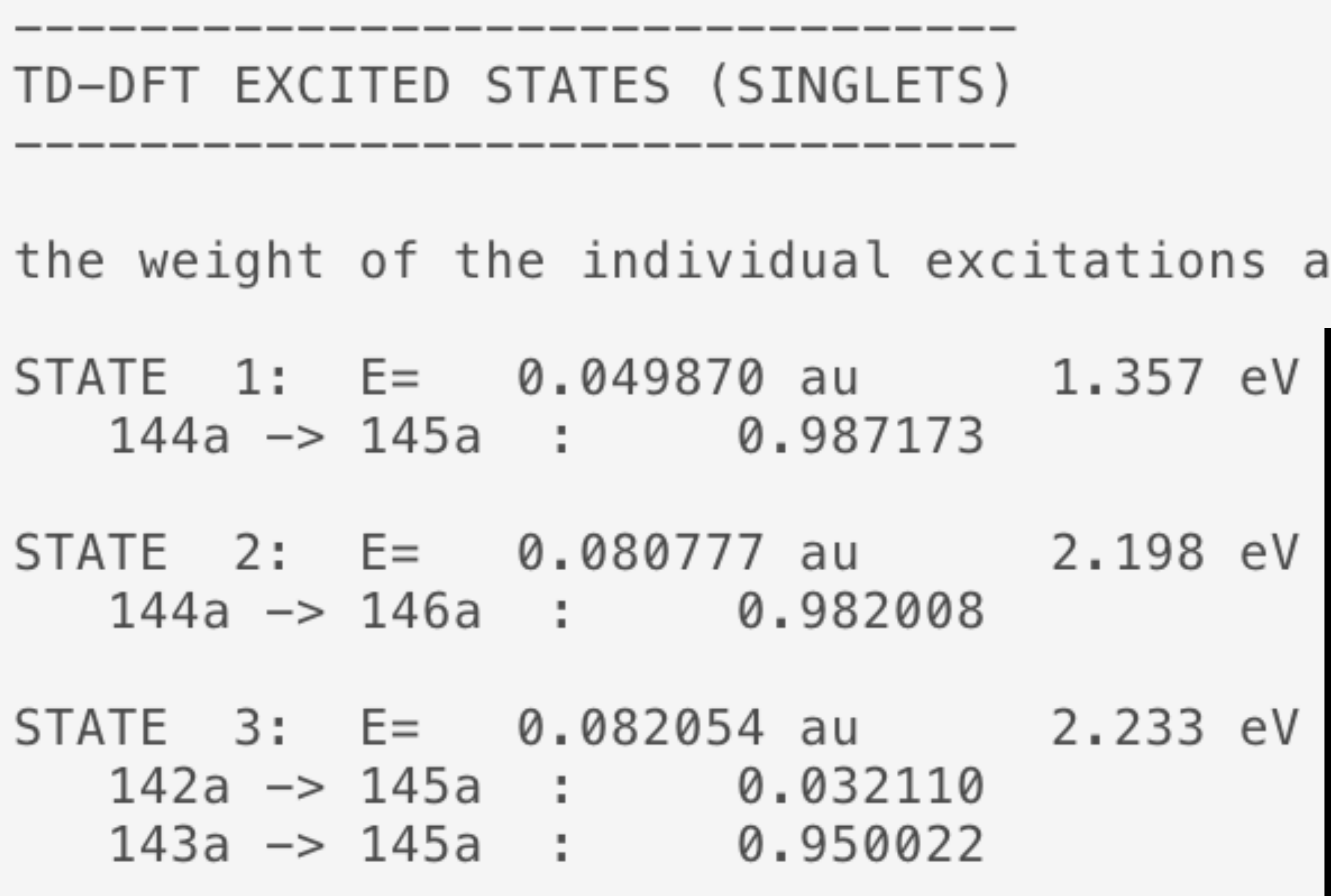
Action Lagrangian

The requisite properties

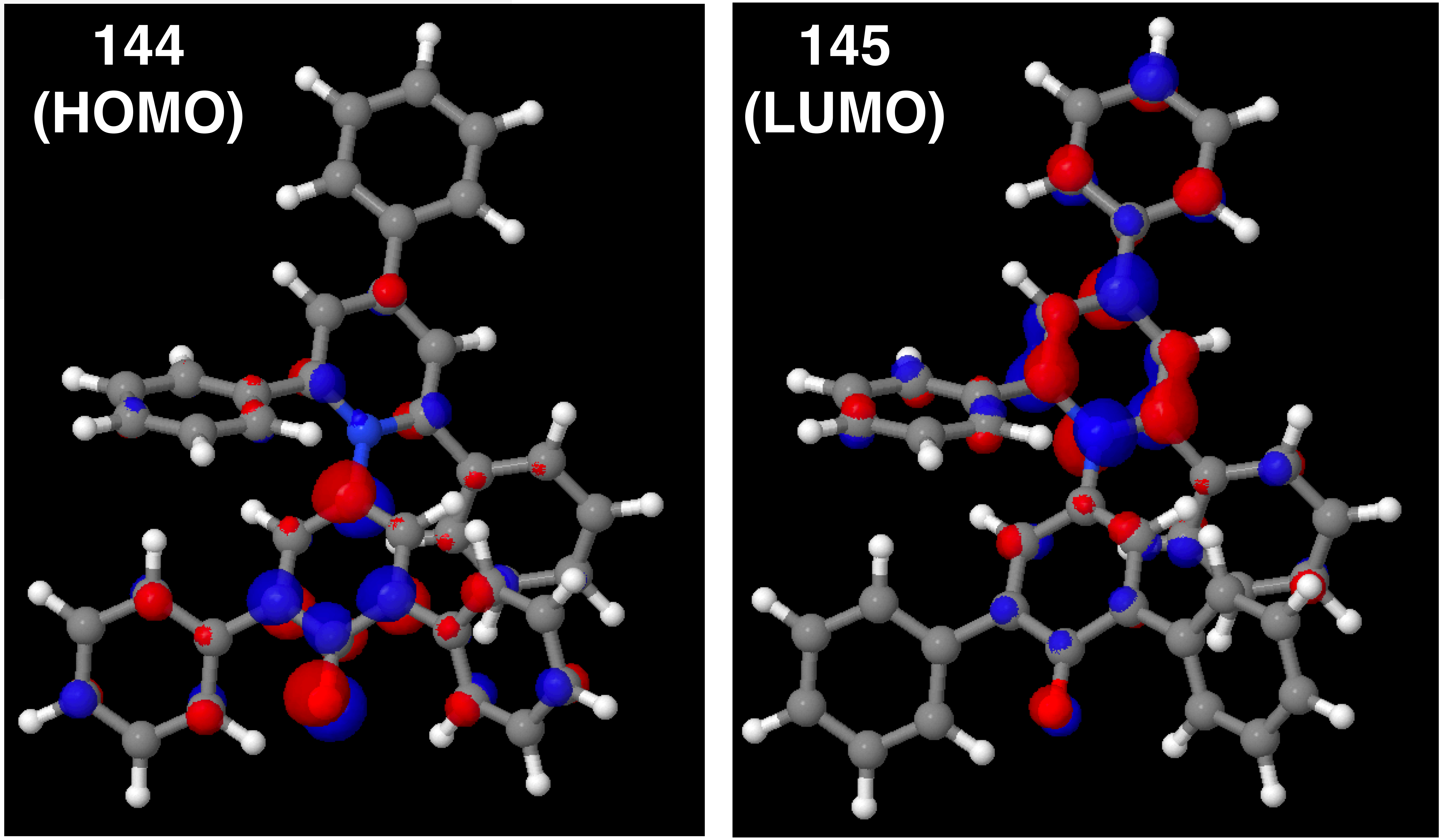
Photochemistry of Thymine

Interpreting Excited States

So you ran some TDDFT calculations. Now what?



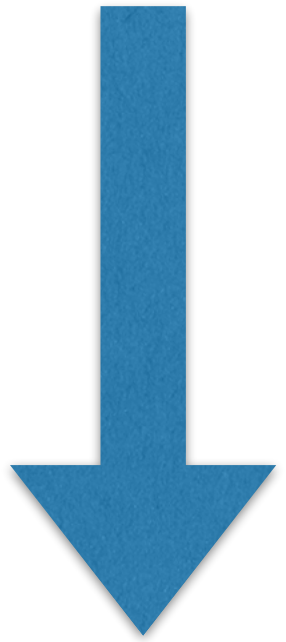
```
--------------------------------
TD-DFT EXCITED STATES (SINGLETS)
--------------------------------

the weight of the individual excitations are printed if larger than 0.01

STATE  1:  E=   0.049870 au      1.357 eV
   144a -> 145a  :     0.987173

STATE  2:  E=   0.080777 au      2.198 eV
   144a -> 146a  :     0.982008

STATE  3:  E=   0.082054 au      2.233 eV
   142a -> 145a  :     0.032110
   143a -> 145a  :     0.950022
```



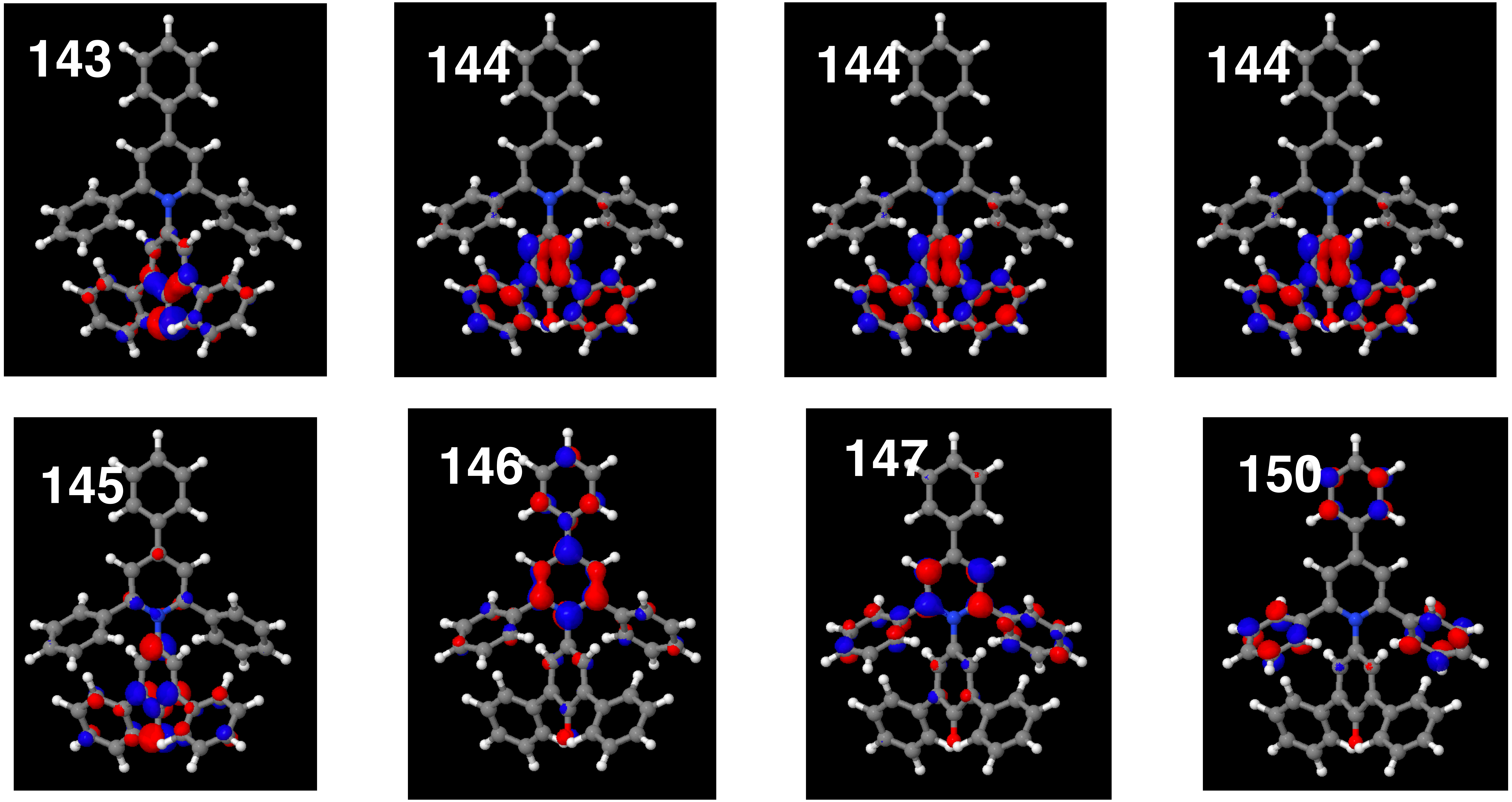
But what if it is more complicated?

```
STATE   3:   E=    0.136955 au       3.727 eV     30058.2 cm**-1 <S**2> =    0.000000
    143a -> 145a  :       0.012034
    144a -> 146a  :       0.248933
    144a -> 147a  :       0.678902
    144a -> 150a  :       0.017086
```

occupied



virtual



Natural Transition Orbitals

Transition vector includes transitions from every possible occupied to every possible virtual

$$X_{ia} \rightarrow \begin{pmatrix} X_{11} & X_{12} & X_{13} & \cdots \\ X_{21} & X_{22} & X_{23} & \cdots \\ X_{31} & X_{32} & X_{33} & \cdots \\ \vdots & \vdots & \vdots & \end{pmatrix}$$

But how relevant are Kohn-Sham orbitals to excited states?

$$\mathbf{X} = \sum_k \vec{U}_k \sigma_k \vec{V}_k^T$$

“occupied”

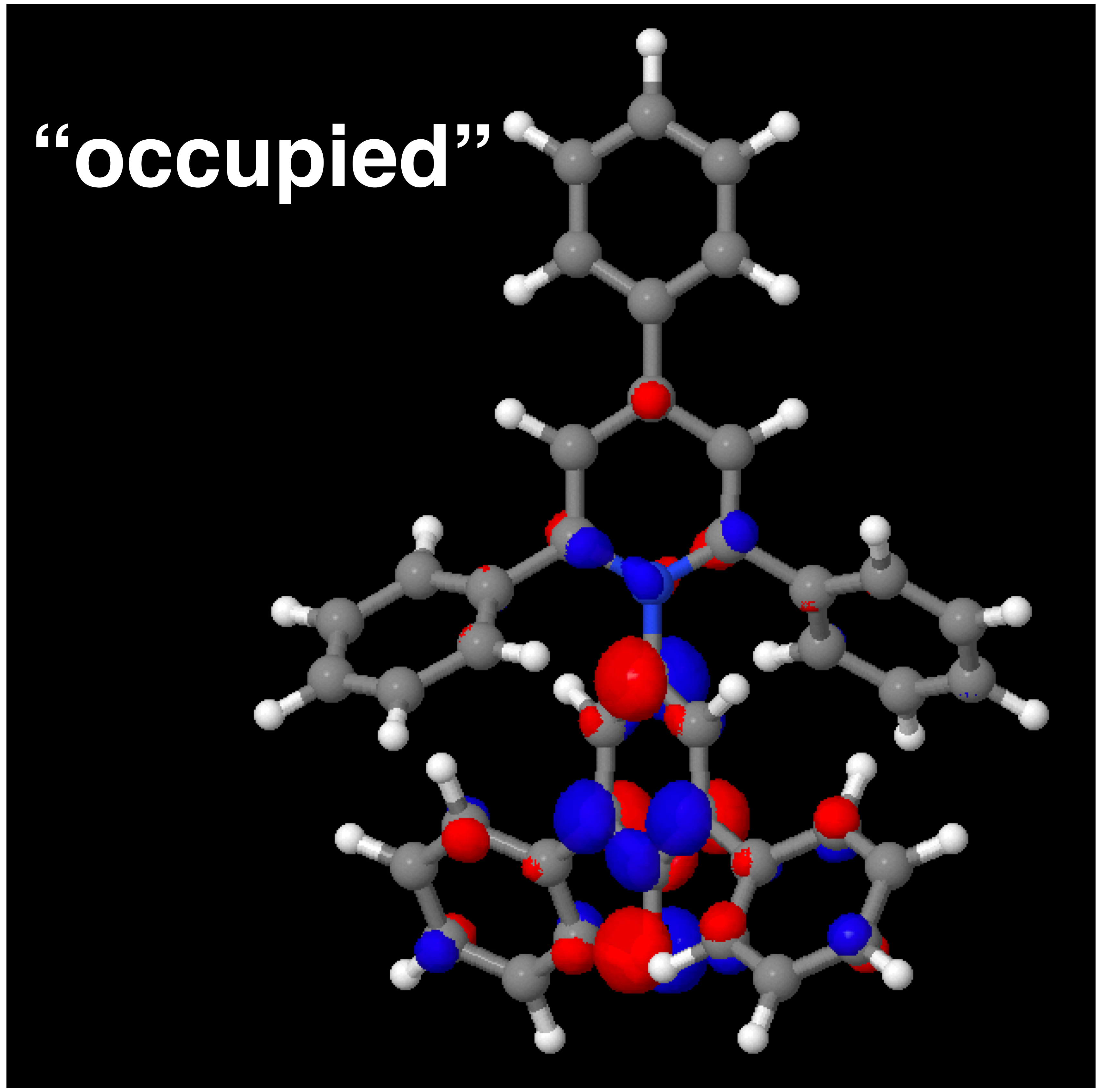
“virtual”

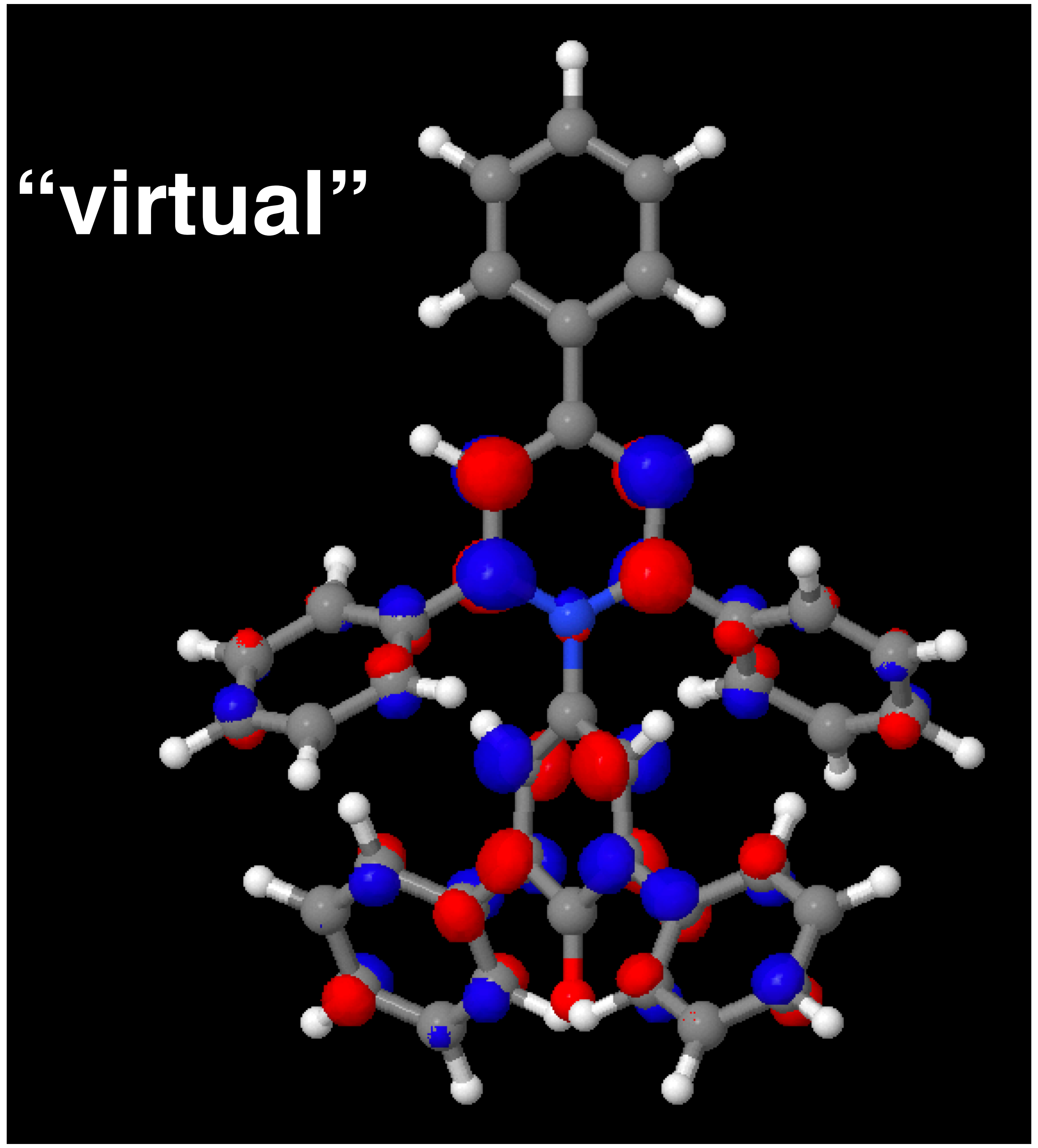
SVD!

Natural Transition Orbitals

```
STATE  3:  E=   0.136955 au      3.727 eV
   143a -> 145a  :      0.012034
   144a -> 146a  :      0.248933
   144a -> 147a  :      0.678902
   144a -> 150a  :      0.017086
```

```
E=    0.136955 au        3.727 eV    30058.2 cm**-1
   144a -> 145a  : n=  0.96425590
   143a -> 146a  : n=  0.02428133
   142a -> 147a  : n=  0.00948078
   141a -> 148a  : n=  0.00197224
   140a -> 149a  : n=  0.00130794
   139a -> 150a  : n=  0.00100346
```





Key takeaways

- **Action Lagrangian** conveniently defines properties
- Response functions are **formal tools** that can be used to **define** properties
- Cost of excited-state calculations similar to ground state
- Generally, **nonlinear properties are accurate when (TD)DFT is accurate**
- Use TDA to avoid non-real instabilities
- Beware ground-to-excited conical intersections
- Use pseudowavefunction approach for state-to-state properties
  - True for nonlinear spectra as well, like excited-state absorption
- Despite misgivings, SH-TDDFT performs excellently for photochemistry (so far)