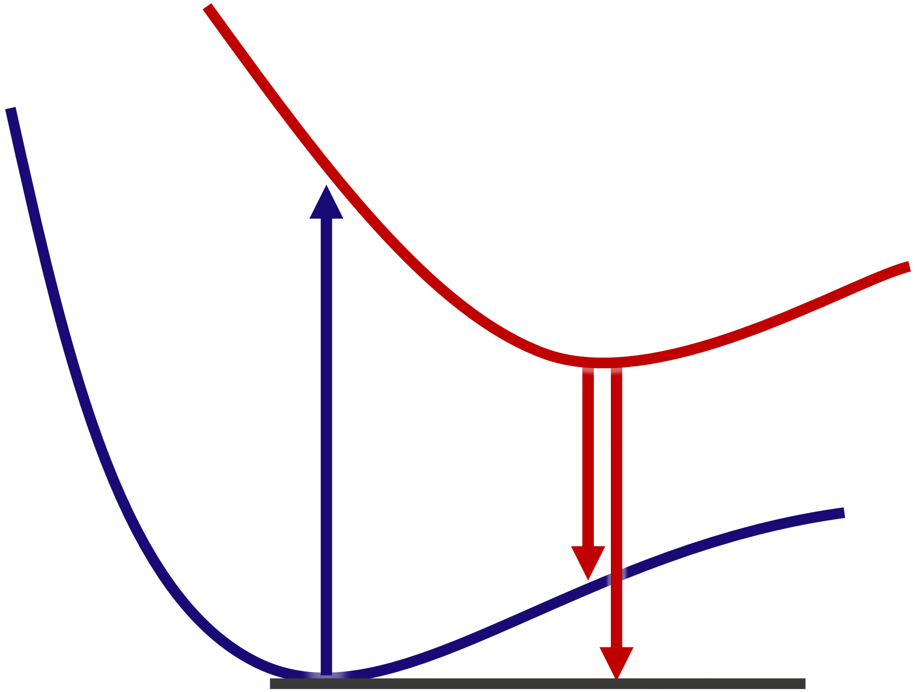
Time-dependent density functional theory

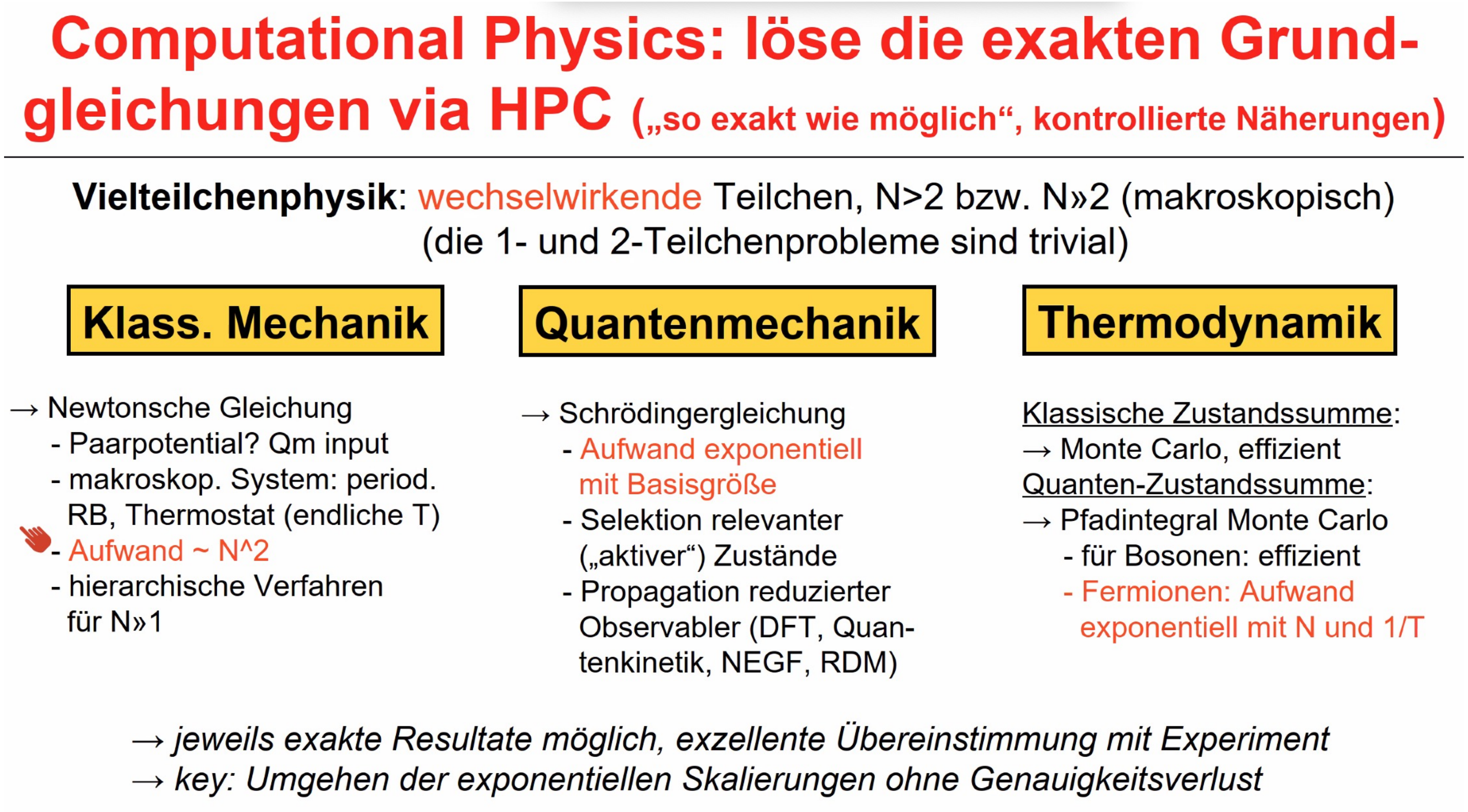
Anna Hehn



Forschungsseminar *Vielteilchen-Theorie*

November 22, 2022

Forschungsseminar Vielteilchentheorie



Computational Physics: löse die exakten Grundgleichungen via HPC („so exakt wie möglich“, kontrollierte Näherungen)

Vielteilchenphysik: wechselwirkende Teilchen, N>2 bzw. N»2 (makroskopisch)
(die 1- und 2-Teilchenprobleme sind trivial)

Klass. Mechanik

→ Newtonsche Gleichung
- Paarpotential? Qm input
- makroskop. System: period. RB, Thermostat (endliche T)
- Aufwand ~ N^2
- hierarchische Verfahren für N»1

Quantenmechanik

→ Schrödingergleichung
- Aufwand exponentiell mit Basisgröße
- Selektion relevanter („aktiver“) Zustände
- Propagation reduzierter Observabler (DFT, Quantenkinetik, NEGF, RDM)

Thermodynamik

Klassische Zustandssumme:
→ Monte Carlo, effizient
Quanten-Zustandssumme:
→ Pfadintegral Monte Carlo
- für Bosonen: effizient
- Fermionen: Aufwand exponentiell mit N und 1/T

→ *jeweils exakte Resultate möglich, exzellente Übereinstimmung mit Experiment*
→ *key: Umgehen der exponentiellen Skalierungen ohne Genauigkeitsverlust*

Motivation: TDDFT in Chemistry

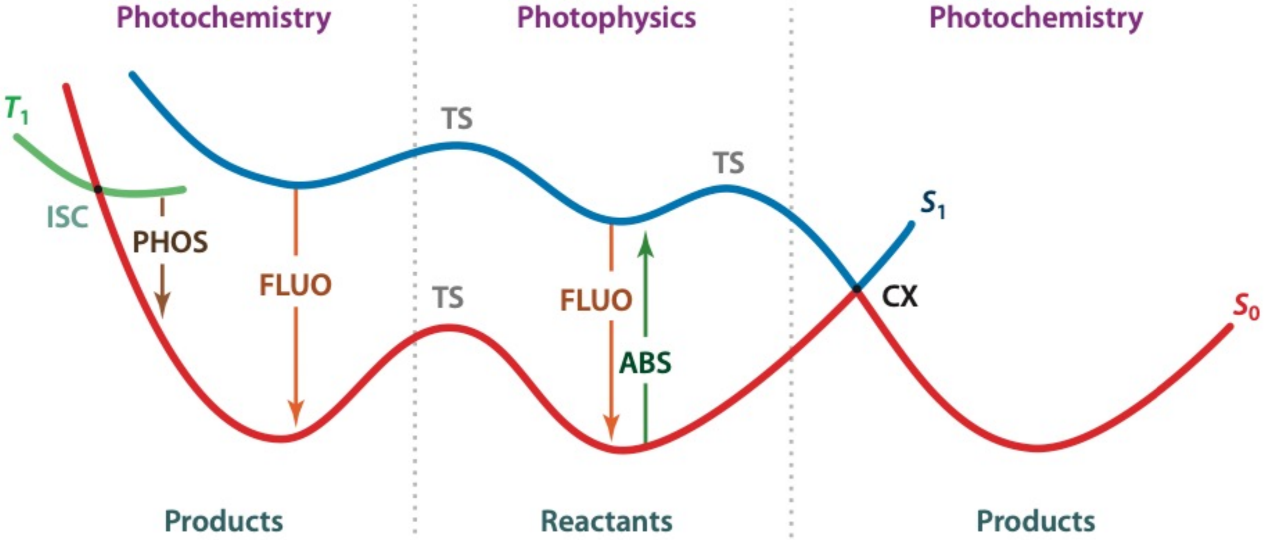
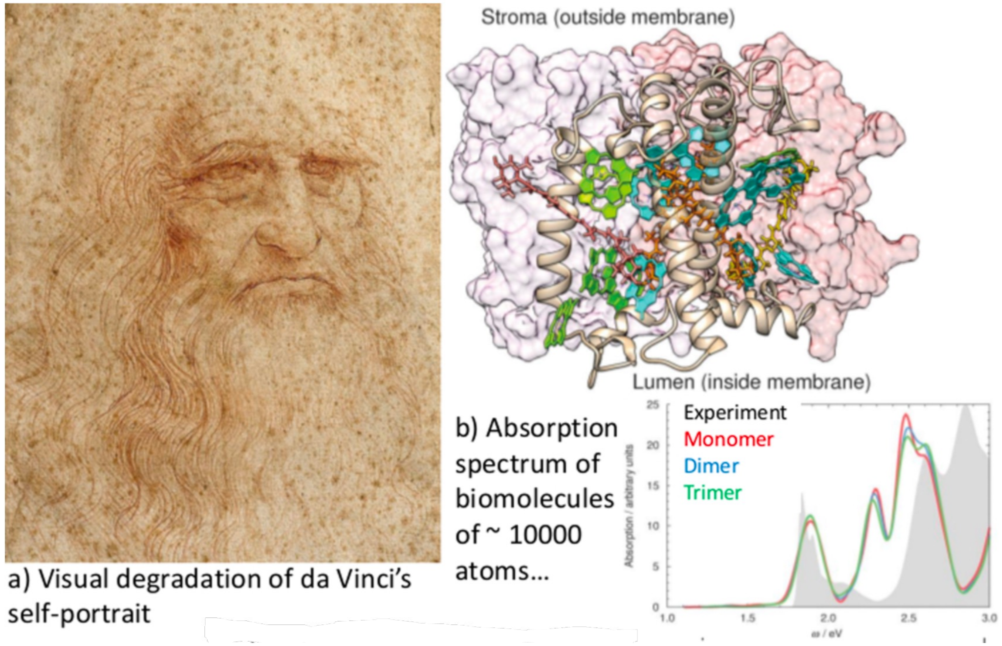


Fig: Potential energy surfaces for photophysical and photochemical processes.

Casida, Huix-Rotllant, *Annu. Rev. Phys. Chem. 63*, 287 **(2012)**.



a) Visual degradation of da Vinci's self-portrait

b) Absorption spectrum of biomolecules of ~ 10000 atoms…

Fig: Range of TDDFT applications for excitations & response.

Maitra, *J. Chem. Phys. 144*, 220901 **(2016)**.

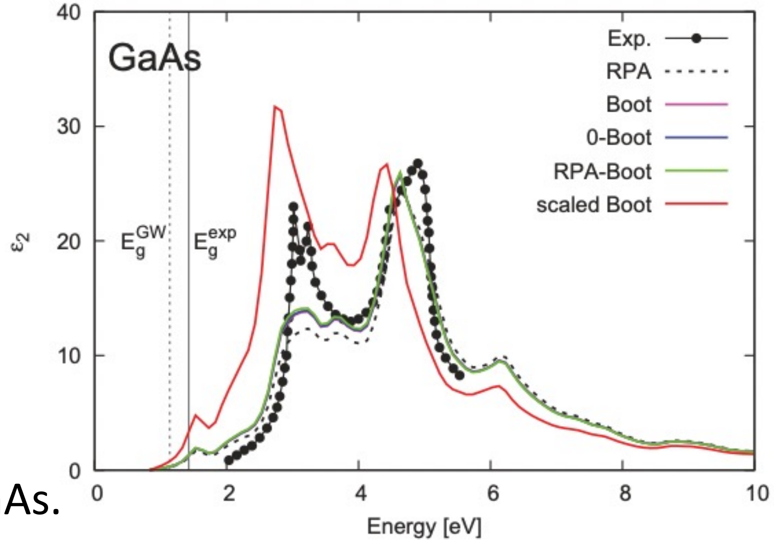


Fig: Optical absorption spectrum of GaAs.

Ullrich *et al.*, *Electron. Struct.* 2, 023002 **(2020)**; Botti *et al*., *Rep. Prog. Phys. 70*, 357 **(2007)**.

Motivation:
TDDFT and machine learning

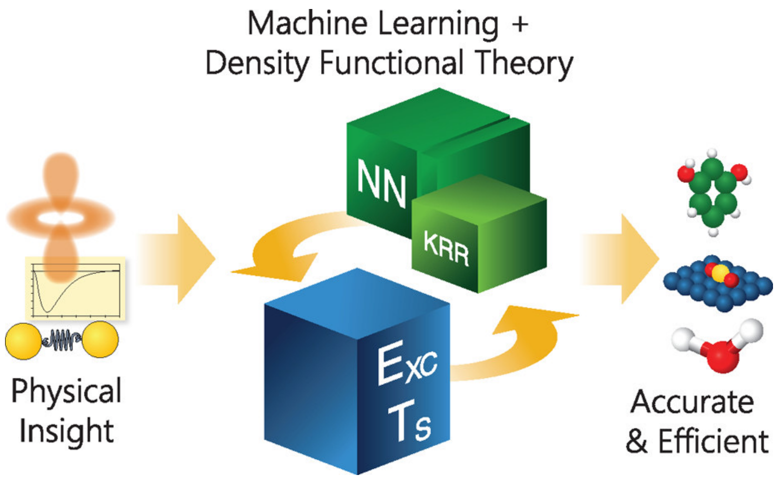


Fig: .

Fig: ML improving DFT.

Burke, *Acc. Chem. Res. 54*, 4 **(2021)**.

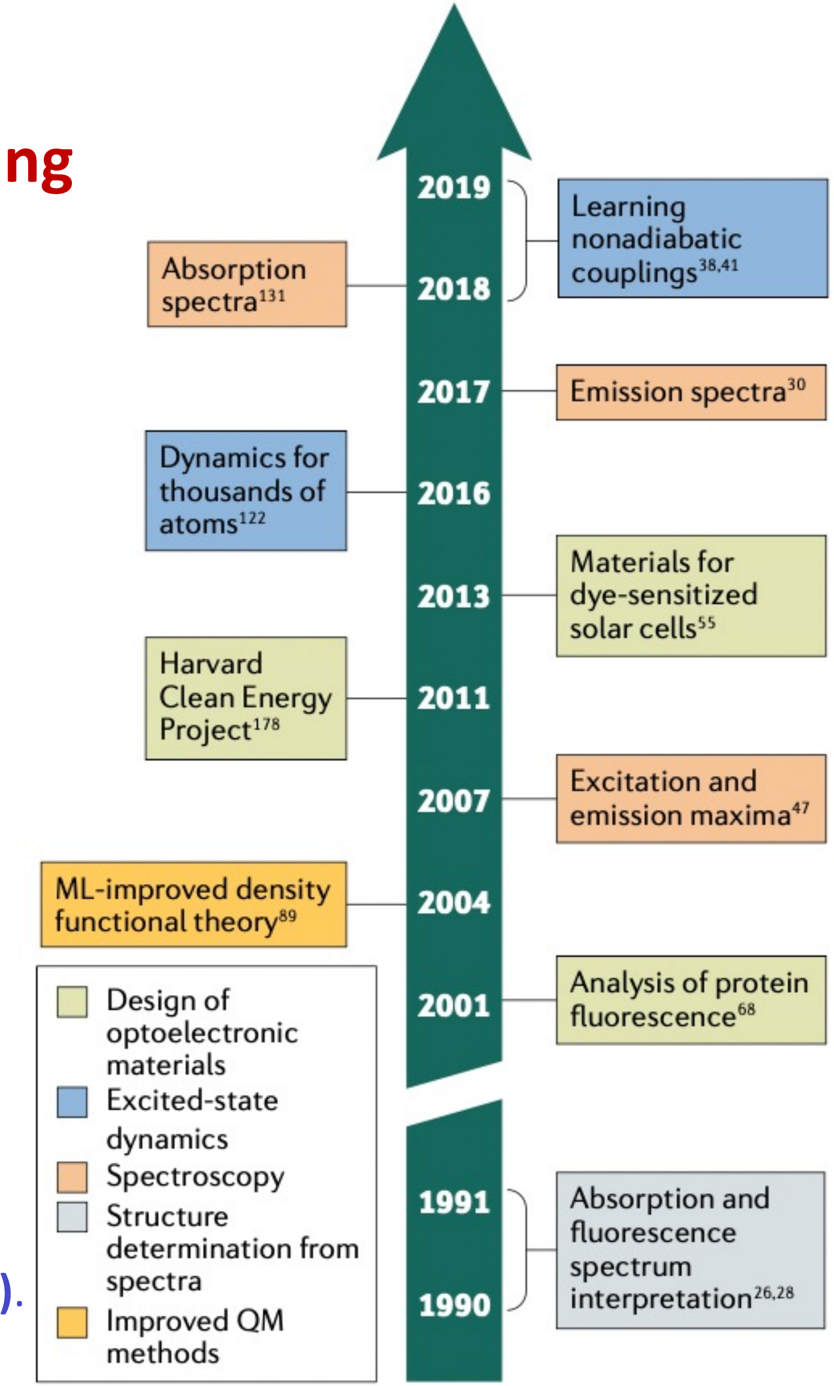


Fig: Pioneering developments in the field of ML and excited-state research.

Dral, Barbatti, *Nat. Rev. Chem. 5*, 388 **(2021)**.

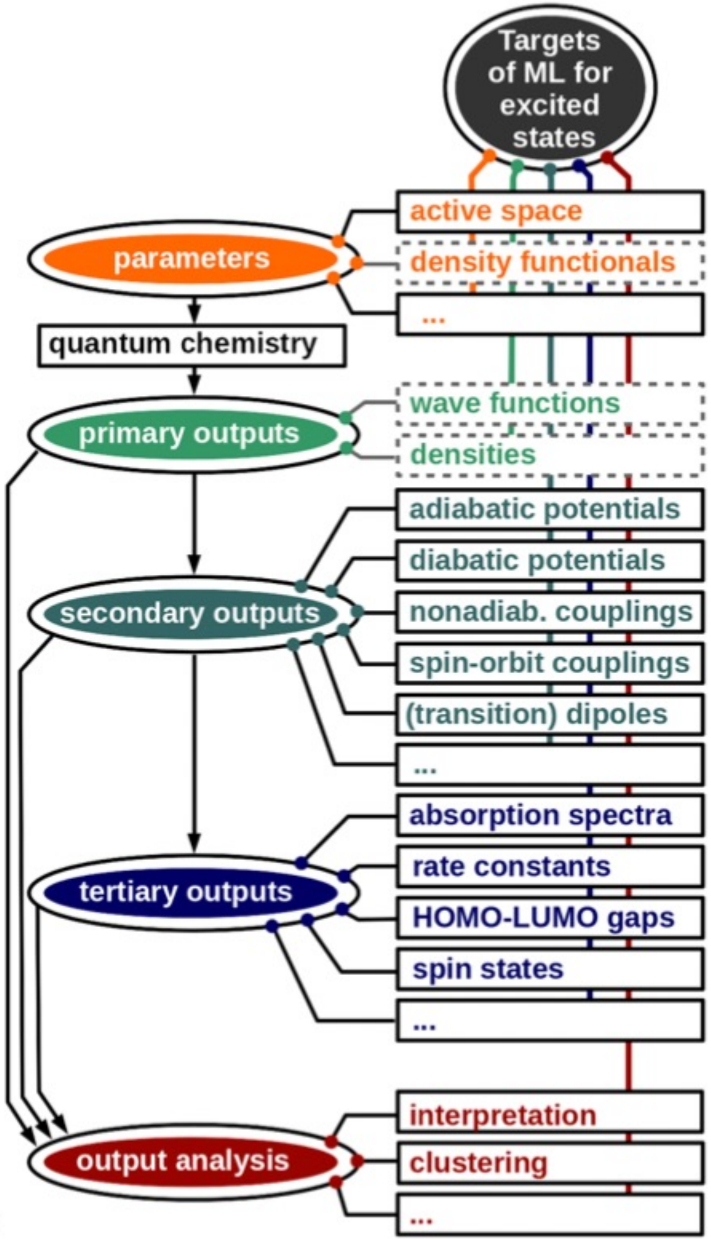


Fig: Targets of ML for excited states.

Marquetand, *Chem. Rev. 121*, 9873 **(2020)**.

The beginnings of TDDFT

1930s: Felix Bloch developed first time-dependent extension of Thomas-Fermi theory

Bloch, *Z. Phys. 81*, 363 **(1933)**.

1970s: First TD-Kohn-Sham computations

Ando, *Solid State Commun. 21*, 133 **(1977);** Peukert, *J. Phys. C: Solid State Phys. 11*, 4945 **(1978).**

1980s: Proofs of one-to-one density-potential mappings for time-periodic potentials

Deb, Gosh, *J. Chem. Phys. 77*, 342 **(1982); Bartolotti**, *Phys. Rev. A 24*, 1661 **(1981);**
Bartolotti, *Phys. Rev. A 26*, 2243 **(1982);**

1984: **Runge-Gross theorem**

Runge, Gross, *Phys. Rev. Lett. 52*, 997 **(1984)**.

1995: **Linear-response framework**

Casida, *Recent Advances in Density Functional Methods*, Part I, ed. Chong, pp. 155-92, Singapore **(1995).**
Petersilka, Grossmann, Gross, *Phys. Rev. Lett. 76*, 1212 **(1996).**

1999: **TDDFT excited-state properties**

Van Caillie, Amos, *Chem. Phys. Lett. 308*, 249 **(1999)**; *Chem. Phys. Lett. 317*, 159 **(2000)**.
Furche, Ahlrichs, *J. Chem. Phys. 117*, 7433 **(2002)**.

Fundamentals of TDDFT: the Runge-Gross theorem (1984)

Runge-Gross theorem proves 1-to-1 density-potential mapping:

$$\rho(\mathbf{r},t) \quad \leftrightarrow \quad v(\mathbf{r},t)+c(t) \quad \leftrightarrow \quad \Psi(\mathbf{r},t)e^{-i\int c(t)\mathrm{d}t}$$

The potential is uniquely defined by the density.

Every observable is defined as a functional of $\rho(\mathbf{r},t)$.

$$O[\rho](t) = \langle\Psi(t)|\hat{O}(t)|\Psi(t)\rangle$$

but complete time evolution is required,
$O[\rho](t)$ depends on the initial wave function.

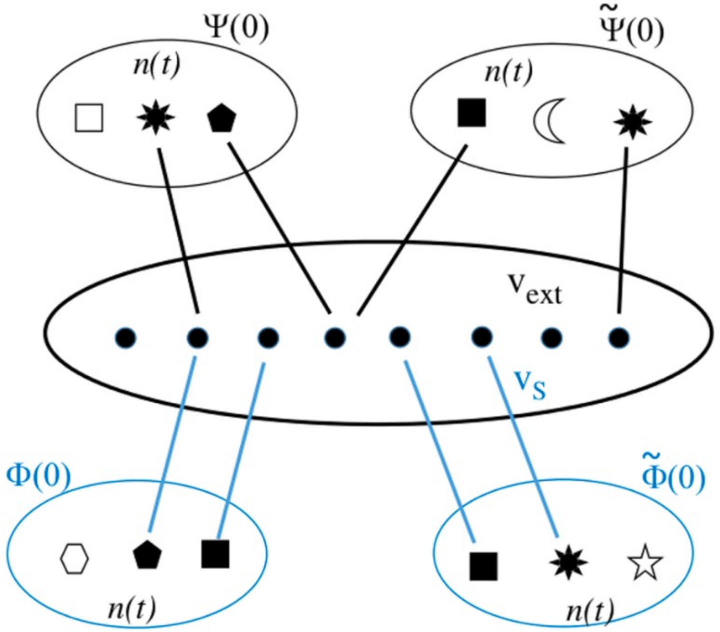


Fig: One-to-one density-potential map.

Maitra, *J. Chem. Phys. 144*, 220901 **(2016)**.

Runge, Gross, *Phys. Rev. Lett. 52*, 997 **(1984);**
Ghosh, Dhara, *Phys. Rev. A 38*, 1149 **(1988);** Vignale, *Phys. Rev. B 70*, 201102 **(2004).**

Fundamentals of TDDFT: the action principle

Energy is not a conserved quantity!

$$\boxed{A[\Psi] = \int_{t_0}^{t_1} dt \langle\Psi(t)| \left[i\frac{\partial}{\partial t} - \hat{H}(t) \right] |\Psi(t)\rangle}$$

$\frac{\partial A[\Psi]}{\partial\langle\Psi(t)|} = 0$ yields $i\frac{\partial}{\partial t}|\Psi(\mathbf{r},t)\rangle = \hat{H}(\mathbf{r},t)|\Psi(\mathbf{r},t)\rangle$

Equivalent formulation with density functional:

$$A[\Psi[\rho,\Psi_0]] = \int_{t_0}^{t_1} \mathrm{dt}\, \langle\Psi[\rho,\Psi_0](\mathrm{t})| \left[\mathrm{i}\frac{\partial}{\partial \mathrm{t}} - \hat{\mathrm{H}}(\mathrm{t}) \right] |\Psi[\rho,\Psi_0](\mathrm{t})\rangle + \phi(\mathrm{t}_1) - \phi(\mathrm{t}_0) = \mathrm{A}[\rho] + \mathrm{const}$$

Exact density via Euler equation: $\frac{\delta A[\rho]}{\delta\rho(\mathbf{r},t)} = 0$

Fundamentals of TDDFT: Time-dependent Kohn-Sham DFT

Introducing orbitals:

$$\boxed{\rho(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2}$$

Exact density via reference system of non-interacting orbitals:

$$i\frac{\partial \phi_j(\mathbf{r},t)}{\partial t} = \left[-\frac{\nabla^2}{2} + v_{\mathrm{S}}[\rho](\mathbf{r},t)\right]\phi_j(\mathbf{r},t)$$

with the potential

$$v_{\mathrm{S}}(\mathbf{r},t) = v_{\mathrm{ext}}(\mathbf{r},t) + v_{\mathrm{H}}(\mathbf{r},t) + v_{\mathrm{XC}}(\mathbf{r},t)$$

$$v_{\mathrm{H}}(\mathbf{r},t) = \int \mathrm{d}^3\mathbf{r}' \, \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} \;\; ; \;\; v_{\mathrm{XC}}(\mathbf{r},t) = \frac{\delta A_{\mathrm{XC}}[\rho]}{\delta \rho(\mathbf{r},t)}$$

Linear Response

Introducing perturbation $\lambda\hat{W}$

$$\boxed{\hat{H}(t) = \hat{H}_0 + \lambda\hat{W}(t)}$$

Time-dependent wave function via time evolution operator $\hat{U}_\lambda$

$$\begin{aligned} |\Psi_\lambda(t)\rangle &= \hat{U}_\lambda(t,t_0)|\Psi_0\rangle \\ &= (1 - i\int_{t_0}^{t} \mathrm{d}t'\, \hat{W}(t') + \ldots)|\Psi_0\rangle \end{aligned}$$

Expectation value of operator $\hat{O}(t)$

$$\begin{aligned} \langle\hat{O}(t)\rangle_\lambda &= \langle\Psi_\lambda(t)|\hat{O}(t)|\Psi_\lambda(t)\rangle \\ &= \langle\Psi_0|\hat{U}_\lambda^\dagger\hat{O}(t)\hat{U}_\lambda|\Psi_0\rangle \\ &= \langle\Psi_0|\hat{O}(t)|\Psi_0\rangle + i\langle\Psi_0|\int_{t_0}^{t} \mathrm{d}t'\, [\hat{W}(t'),\hat{O}(t)]|\Psi_0\rangle + \ldots \end{aligned}$$

Linear Response

$$O^{(1)}(t) = \delta\langle\Psi_\lambda(t)|\hat{O}(t)|\Psi_\lambda(t)\rangle = \frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\Psi_\lambda(t)|\hat{O}(t)|\Psi_\lambda(t)\rangle\Big|_{\lambda=0}$$

$$= i\int_{t_0}^{t}\mathrm{d}t'\,\langle\Psi_0|[\hat{W}(t'),\hat{O}(t)]|\Psi_0\rangle$$

with one-particle operators
$$\lambda\hat{W}(t) = \int \mathrm{d}^3\mathbf{r}\,\hat{\rho}(\mathbf{r},t)w(\mathbf{r},t)$$

$$\hat{O}(t) = \int \mathrm{d}^3\mathbf{r}\,\hat{\rho}(\mathbf{r},t)o(\mathbf{r},t)$$

$$\rho^{(1)}(\mathbf{r},t) = i\int_{t_0}^{t}\mathrm{d}t'\int\mathrm{d}^3\mathbf{r}'\,w(\mathbf{r},t')\langle\Psi_0|[\hat{\rho}(\mathbf{r}',t'),\hat{\rho}(\mathbf{r},t)]|\Psi_0\rangle$$

$$= \int\mathrm{d}t'\int\mathrm{d}^3\mathbf{r}'\,\chi(t-t',\mathbf{r},\mathbf{r}')w(\mathbf{r}',t')$$

$$\boxed{\rho^{(1)}(\mathbf{r},\omega) = \int\mathrm{d}^3\mathbf{r}'\,\chi(\mathbf{r},\mathbf{r}',\omega)w(\mathbf{r}',\omega)}$$

Poles correspond to excitation energies.

The linear response function

$$\rho^{(1)}(\mathbf{r},\omega) = \int \mathrm{d}^3\mathbf{r}'\, \chi(\mathbf{r},\mathbf{r}',\omega) w(\mathbf{r}',\omega)$$

Back to KS ansatz:

$$\underbrace{\frac{\delta v_{\mathrm{KS}}[\rho](\mathbf{r},\omega)}{\delta\rho(\mathbf{r}')}}_{\chi_{\mathrm{KS}}^{-1}} = \underbrace{\frac{\delta v_{\mathrm{ext}}[\rho](\mathbf{r},\omega)}{\delta\rho(\mathbf{r}')}}_{\chi^{-1}} + \underbrace{\frac{\delta v_{\mathrm{H}}[\rho](\mathbf{r},\omega)}{\delta\rho(\mathbf{r}')}}_{\frac{1}{|\mathbf{r}-\mathbf{r}'|}} + \underbrace{\frac{\delta v_{\mathrm{XC}}[\rho](\mathbf{r},\omega)}{\delta\rho(\mathbf{r}')}}_{f_{\mathrm{XC}}[\rho](\omega,\mathbf{r},\mathbf{r}')}$$

Dyson-like equation for χ

$$\chi(\omega,\mathbf{r},\mathbf{r}') = \chi_{\mathrm{KS}}(\omega,\mathbf{r},\mathbf{r}') + \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2\, \chi_{\mathrm{KS}}(\omega,\mathbf{r},\mathbf{r}_1) \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{XC}}(\omega,\mathbf{r}_1,\mathbf{r}_2) \right) \chi(\omega,\mathbf{r}_2,\mathbf{r}')$$

Lehmann representation

$$\chi_{\mathrm{KS}}(\omega,\mathbf{r},\mathbf{r}') = \sum_{ia} \left[\frac{\phi_i^*(\mathbf{r})\phi_a(\mathbf{r}')\phi_i(\mathbf{r})\phi_a^*(\mathbf{r}')}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta} - \frac{\phi_i(\mathbf{r})\phi_a^*(\mathbf{r}')\phi_i^*(\mathbf{r})\phi_a(\mathbf{r}')}{\omega + (\varepsilon_a - \varepsilon_i) + i\eta} \right]$$

Let’s do the same for the density matrix!

Reduced one-particle density matrix

$$\gamma(t,\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N} \phi_i(t,\mathbf{r})\phi_i^*(t,\mathbf{r}')$$

$$\rho(t,\mathbf{r}) = \gamma(t,\mathbf{r},\mathbf{r})$$

Idempotency condition

$$\gamma(t,\mathbf{r},\mathbf{r}') = \int \mathrm{d}\mathbf{r}_1\, \gamma(t,\mathbf{r},\mathbf{r}_1)\gamma(t,\mathbf{r}_1,\mathbf{r}')$$

von-Neumann equation

$$i\frac{\partial}{\partial t}\phi_i(t) = \hat{H}_{\mathrm{KS}}[\rho](t)\phi_i(t) \;\; \rightarrow \;\; \boxed{i\frac{\partial}{\partial t}\gamma(t) = \left[\hat{H}_{\mathrm{KS}}[\rho](t), \gamma(t)\right]}$$

Same as before: Reordering in orders of λ to obtain the first-order response:

$$\gamma^{(n)}(t) = \frac{1}{n!}\frac{\delta}{\delta\lambda}\gamma_\lambda(t)\Big|_{\lambda=0}$$

Furche, *J. Chem. Phys. 114*, 5982 **(2001)**.

Let’s do the same for the density matrix!

0th order: static KS equations $$[\hat{H}^{(0)}_{\mathrm{KS}},\gamma^{(0)}]=0\ ;\ \ \hat{H}^{(0)}_{\mathrm{KS}}\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r})$$

1st order: Linear response $$i\frac{\partial}{\partial t}\gamma^{(1)}=[\hat{H}^{(0)}_{\mathrm{KS}},\gamma^{(1)}]+[\hat{H}^{(1)}_{\mathrm{KS}},\gamma^{(0)}]$$

Furche, *J. Chem. Phys. 114*, 5982 **(2001)**.

Let's do the same for the density matrix!

0th order: static KS equations

$$[\hat{H}^{(0)}_{\mathrm{KS}}, \gamma^{(0)}] = 0 \; ; \; \hat{H}^{(0)}_{\mathrm{KS}} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

1st order: Linear response

$$i \frac{\partial}{\partial t} \gamma^{(1)} = [\hat{H}^{(0)}_{\mathrm{KS}}, \gamma^{(1)}] + [\hat{H}^{(1)}_{\mathrm{KS}}, \gamma^{(0)}]$$

Inserting

$$\hat{H}_{\mathrm{KS}}(t) = \frac{1}{2}\Delta + v_{\mathrm{nuc}}(\mathbf{r}) + v_{\mathrm{H}}[\rho_\lambda](t,\mathbf{r}) + v_{\mathrm{XC}}[\rho_\lambda](t,\mathbf{r}) + \lambda w(t,\mathbf{r})$$

$$\hat{H}^{(1)}_{\mathrm{KS}}(t) = v_{\mathrm{H}}[\rho^{(1)}](t,\mathbf{r}) + u_{\mathrm{XC}}[\rho, \rho^{(1)}](t,\mathbf{r}) + w(t,\mathbf{r})$$

$$u_{\mathrm{XC}}[\rho, \rho^{(1)}](t,\mathbf{r}) = \int \mathrm{d}t' \int \mathrm{d}^3\mathbf{r}' \, \rho^{(1)}(t',\mathbf{r}') f_{\mathrm{XC}}[\rho](t-t',\mathbf{r},\mathbf{r}')$$

$$\boxed{\omega \gamma^{(1)} = [\hat{H}[\rho], \gamma^{(1)}] + [v_{\mathrm{H}}[\rho^{(1)}] + u_{\mathrm{XC}}[\rho, \rho^{(1)}](\omega) + w, \gamma^{(0)}]}$$

Furche, *J. Chem. Phys. 114*, 5982 **(2001)**.

The TDDFT eigenvalue problem: Casida equations I

Formulating the response in terms of static KS orbitals

$$\gamma^{(1)}(\mathbf{r},\mathbf{r}') = \sum_{ia}\left(X_{ia}\phi_a(\mathbf{r})\phi_i(\mathbf{r}') + Y_{ia}\phi_i(\mathbf{r})\phi_a(\mathbf{r}')\right)$$

$$\gamma^{(1)} = \begin{pmatrix} X \\ Y \end{pmatrix} = |X,Y\rangle$$

with corresponding normalization condition

$$\begin{pmatrix} X & Y \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = 1 \qquad \rightarrow \qquad \boxed{\langle X,Y|\Delta|X,Y\rangle = 1}$$

gives TDKS response equation

$$\left[\begin{pmatrix} A & B \\ B & A \end{pmatrix} - \omega\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right]\begin{pmatrix} X \\ Y \end{pmatrix} = -\begin{pmatrix} P \\ Q \end{pmatrix} \qquad \rightarrow \qquad \boxed{(\Lambda - \omega\Delta)\,|X,Y\rangle = -|P,Q\rangle}$$

The TDDFT eigenvalue problem: Casida equations II

Poles and residuals of $(\Lambda - \omega\Delta)^{-1}$:

Casida equations

$$(\Lambda(\Omega_n) - \Omega_n\Delta)\,|X_n, Y_n\rangle = 0$$

$$\langle X_n, Y_n|\Delta|X_n, Y_n\rangle = 1$$

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

$$(A-B)_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$$

$$(A+B)_{iajb} = (A-B)_{iajb} + 2C_{iajb}$$

$$C_{iajb} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\,\phi_i(\mathbf{r})\phi_j(\mathbf{r}')\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{XC}}(\omega, \mathbf{r}, \mathbf{r}')\right)\phi_a(\mathbf{r})\phi_b(\mathbf{r}')$$

Comparison to linear response function

$$\gamma^{(1)}(t,\mathbf{r}_1,\mathbf{r}_1') = \int \mathrm{d}t' \int \mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_2'\,\Xi(t-t',\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')w(t',\mathbf{r}_2,\mathbf{r}_2')$$

$$\Xi(\omega,\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2') = -\langle(\mathbf{r}_1,\mathbf{r}_1')|(\Lambda(\omega)-\omega\Delta)^{-1}|(\mathbf{r}_2,\mathbf{r}_2')\rangle$$

$$\boxed{\chi(\omega,\mathbf{r}_1,\mathbf{r}_2) = \Xi(\omega,\mathbf{r}_1,\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_2)}$$

$$\begin{aligned}
\Lambda &= \Lambda_{\mathrm{KS}} + (\Lambda - \Lambda_{\mathrm{KS}}) \\
(\Lambda(\omega)-\omega\Delta)^{-1} &= (\Lambda_{\mathrm{KS}}-\omega\Delta)^{-1} - (\Lambda_{\mathrm{KS}}-\omega\Delta)^{-1}(\Lambda(\omega)-\Lambda_{\mathrm{KS}})(\Lambda(\omega)-\omega\Delta)^{-1} \\
\chi(\omega,\mathbf{r}_1,\mathbf{r}_1') &= \chi_{\mathrm{KS}}(\omega,\mathbf{r}_1,\mathbf{r}_1') \\
&\quad + \int \mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_2'\,\chi_{\mathrm{KS}}(\omega,\mathbf{r}_1,\mathbf{r}_2)\left(\frac{1}{|\mathbf{r}_2-\mathbf{r}_2'|} + f_{\mathrm{XC}}(\omega,\mathbf{r}_2,\mathbf{r}_2')\right)\chi(\omega,\mathbf{r}_2',\mathbf{r}_1')
\end{aligned}$$

TDDFT in practice: Adiabatic local density approximation (ALDA)

A_{XC} is unknown

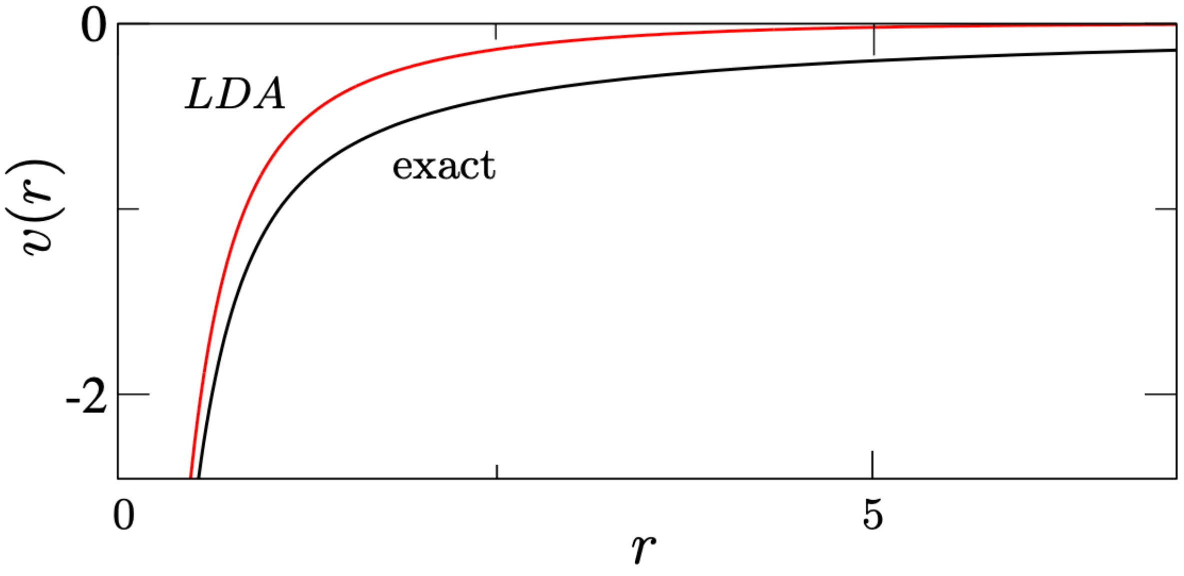
$$v_{\mathrm{XC}}[\rho](\mathbf{r},t) = \frac{\delta A_{\mathrm{XC}}[\rho](\mathbf{r},t)}{\delta\rho(\mathbf{r},t)} \longrightarrow v_{\mathrm{XC}}[\rho(t)](\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[\rho(t)](\mathbf{r})}{\delta\rho(\mathbf{r},t)}$$

$$f_{\mathrm{XC}}[\rho](t-t',\mathbf{r},\mathbf{r}') \longrightarrow f_{\mathrm{XC}}[\rho(t)](\mathbf{r},\mathbf{r}') = \frac{\delta E_{\mathrm{XC}}[\rho(t)](\mathbf{r})}{\delta\rho(t,\mathbf{r})\delta\rho(t,\mathbf{r}')}$$

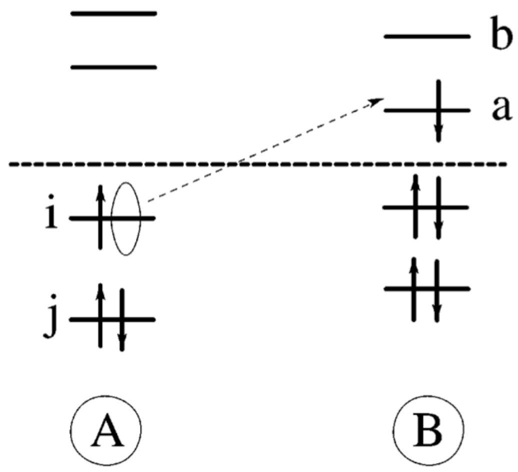
- only depends on the electron density at time t, no “memory” dependence
- same XC functionals as for GS-DFT

Short-comings of TDDFT within the ALDA approximation

- **Wrong asymptotics** due to self-interaction error (excitation energies systematically too small)
  Elliott, Furche, Burke, *Rev. Comp. Chem. 26*, 91 **(2009)**.



- **Charge-transfer states**
  Dreuw, Head-Gordon, *Chem. Rev. 105*, 4009 **(2005);**
  Tozer, *J. Chem. Phys. 119*, 12697 **(2003)**.



$$\lim_{r\to\infty} E_{\mathrm{CT}}(r) = -\frac{1}{r} + \mathrm{IE} - \mathrm{EA}$$

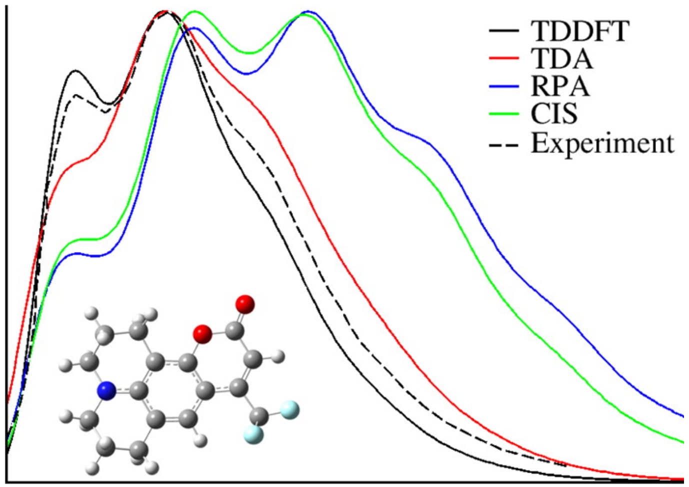
- **Doubly excited states** Maitra *et al., J. Chem. Phys. 120*, 5932 **(2004)**.

- **Multireference ground-states** Furche, *J. Chem. Phys. 114*, 5982 **(2001)**.

TDDFT for periodic systems:
Fast, but accurate hybrid functional approaches

Tamm-Dancoff Approximation (TDA)
adequate model for absorption and fluorescence spectra

Jacquemin et al., *J. Chem. Theory Comput.* 9, 4517, (**2013**).



AO-based formalism

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

Projection to ensure $X_{ij\sigma} = 0$

$$\sum_{\kappa k} \left[F_{\mu\kappa\sigma}\delta_{ik} - F_{ik\sigma}S_{\mu\kappa}\right] X_{\kappa k\sigma} + \sum_{\kappa\lambda} Q^{\dagger}_{\mu\kappa\sigma} K_{\kappa\lambda\sigma}[\mathbf{D}^{\mathrm{X}}] C_{\lambda i\sigma} = \sum_{\kappa} \Omega S_{\mu\kappa} X_{\kappa i\sigma}$$

$$K_{\mu\nu\sigma}[\mathbf{D}^{\mathrm{X}}] = \sum_{\kappa\lambda\sigma'} D^{\mathrm{X}}_{\kappa\lambda\sigma'} \left[(\mu\nu|\kappa\lambda) - a_{\mathrm{EX}}\delta_{\sigma\sigma'}(\mu\kappa|\nu\lambda) + f^{\mathrm{XC}}_{\mu\nu\sigma,\kappa\lambda\sigma'}\right]$$

Coulomb **Exchange** **XC functional**

TDDFT for periodic systems:
Fast, but accurate hybrid functional approaches

TDDFT

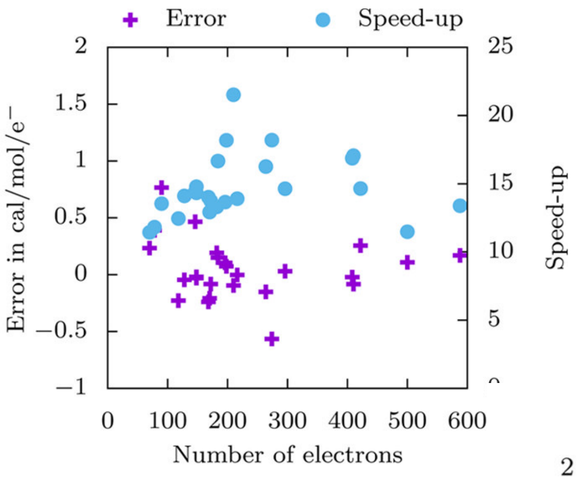
Efficient treatment of exact exchange

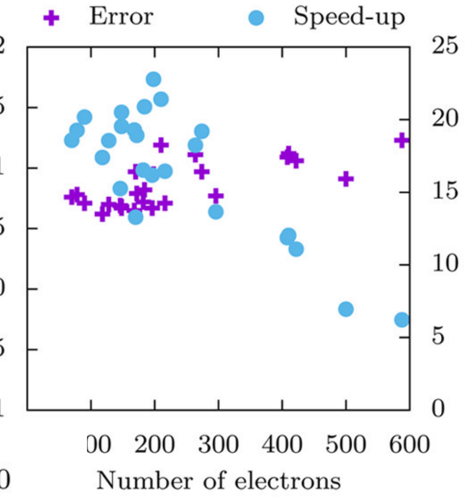
Rebolini *et al.*, *J. Chem. Theory Comput.* (**2016**).

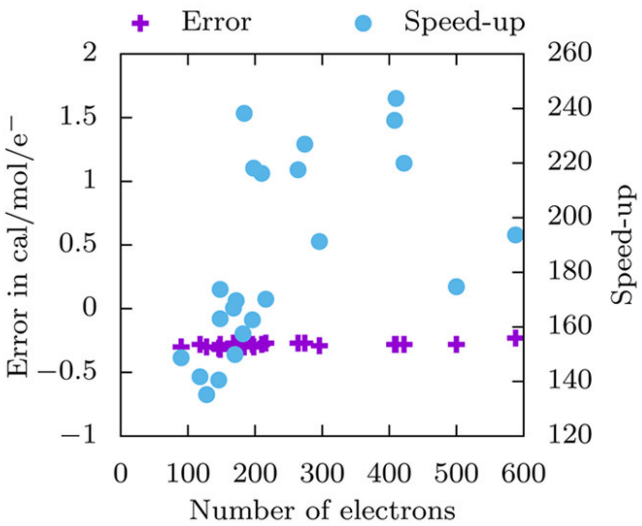
Numerical Integration
Neese, *Chem. Phys.* **(2008)**.

Density fitting
Merlot, *J. Comput. Chem.* **(2013).**

Auxiliary density matrix method (ADMM)
Hutter *et al. J. Chem. Theory Comput.* **(2010).**







TDDFT for periodic systems:
Fast, but accurate hybrid functional approaches

State-of-the-art algorithms to reduce the computational cost of exchange:

→ Numerical integration (COSX) Neese, *Chem. Phys. 356*, 98 **(2008)**.

→ Density fitting (PARI-K) Merlot, *J. Comput. Chem. 34*, 1486 **(2013)**.

→ **Auxiliary density matrix method (ADMM)** Guidon *et al. J. Chem. Theory Comput. 6*, 2348 **(2010).**

$$D^{\mathrm{X}}_{\kappa\lambda\sigma}(\mu\kappa|\nu\lambda) \approx \sum_{\hat{\kappa}\hat{\lambda}}\sum_{\hat{\mu}\hat{\nu}} \hat{D}^{\mathrm{X}}_{\hat{\kappa}\hat{\lambda}\sigma}\hat{U}^{\mathrm{T}}_{\hat{\mu}\mu\sigma}(\hat{\mu}\hat{\kappa}|\hat{\nu}\hat{\lambda})\hat{U}_{\hat{\nu}\nu\sigma}$$

exact exchange with small auxiliary density

$$+\left[\sum_{\kappa\lambda} D^{\mathrm{X}}_{\kappa\lambda\sigma} f^{\mathrm{EX}}_{\mu\kappa\sigma,\nu\lambda\sigma} - \sum_{\hat{\kappa}\hat{\lambda}}\sum_{\hat{\mu}\hat{\nu}} \hat{D}^{\mathrm{X}}_{\hat{\kappa}\hat{\lambda}\sigma}\hat{U}^{\mathrm{T}}{}_{\hat{\mu}\mu\sigma} f^{\mathrm{EX}}_{\hat{\mu}\hat{\kappa}\sigma,\hat{\nu}\hat{\lambda}\sigma}\hat{U}_{\hat{\nu}\nu\sigma}\right]$$

1st order GGA correction term

Possible ADMM variant:
Auxiliary density matrix by projection

$$\hat{\mathbf{D}} = \hat{\mathbf{U}}\mathbf{D}\hat{\mathbf{U}}^{\dagger} \qquad \hat{S}_{\hat{\mu}\hat{\nu}} = \int \hat{\varphi}_{\hat{\mu}}(\mathbf{r})\hat{\varphi}_{\hat{\nu}}(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

$$\hat{\mathbf{U}} = \hat{\mathbf{S}}^{-1}\hat{\mathbf{V}} \qquad \hat{V}_{\hat{\mu}\nu} = \int \hat{\varphi}_{\hat{\mu}}(\mathbf{r})\varphi_{\nu}(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

TDDFT for periodic systems:
Fast, but accurate hybrid functional approaches

dftb.org

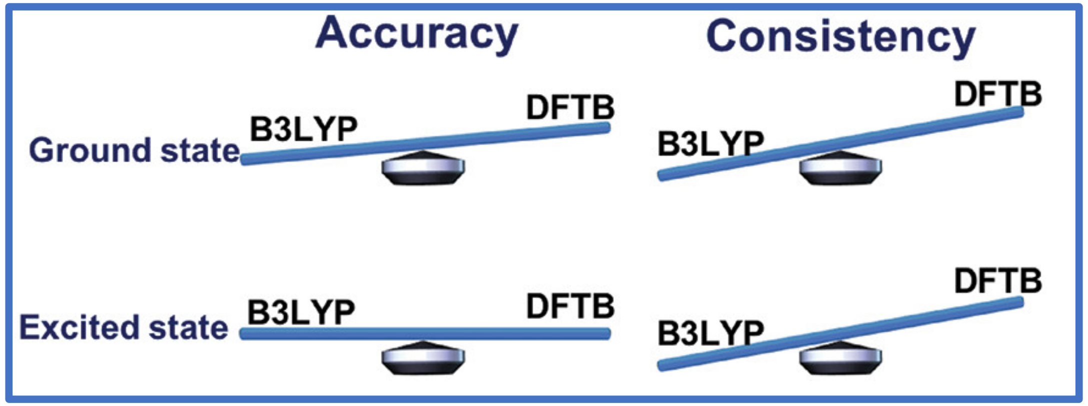
Extensions for excited-state properties

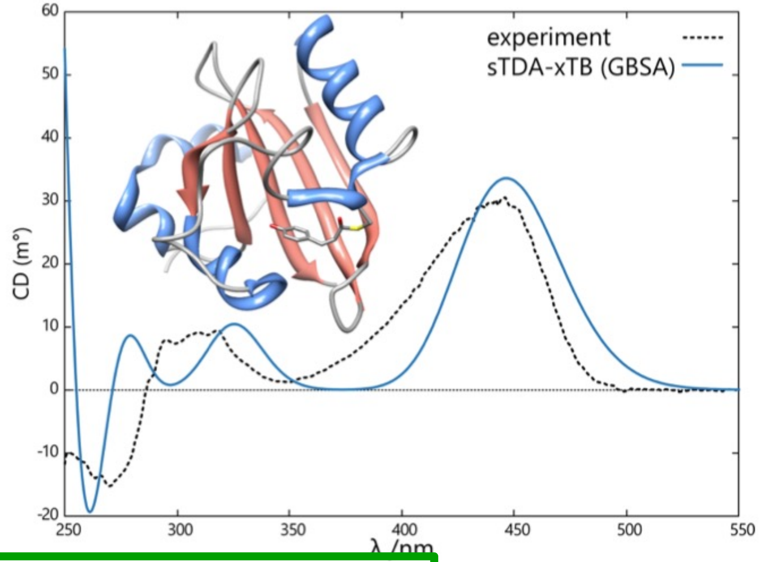
Elstner *et al.*, *J. Chem. Theory Comput.* (**2021**).

1. Semi-empirical tight binding

TDDFTB Benchmarks

Jacquemin *et al.*, *J. Chem. Theory Comput.* (**2019**).





Global parameters only!

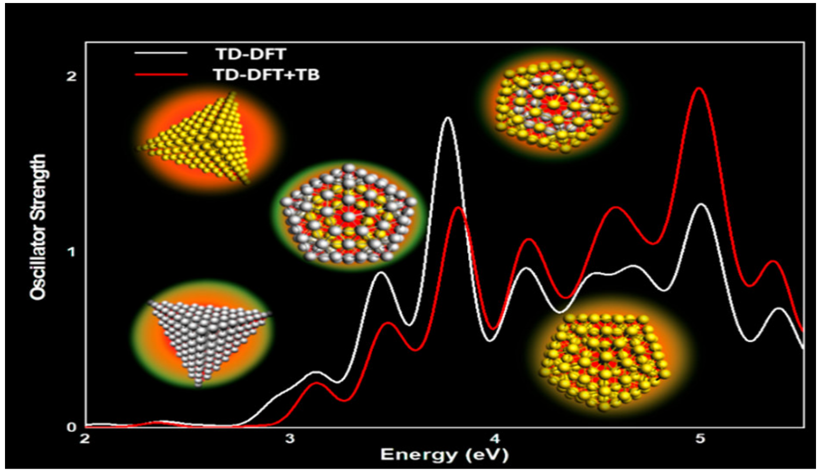
Simplified TDA (sTDA)

Grimme, *J. Chem. Phys.* (**2013**).

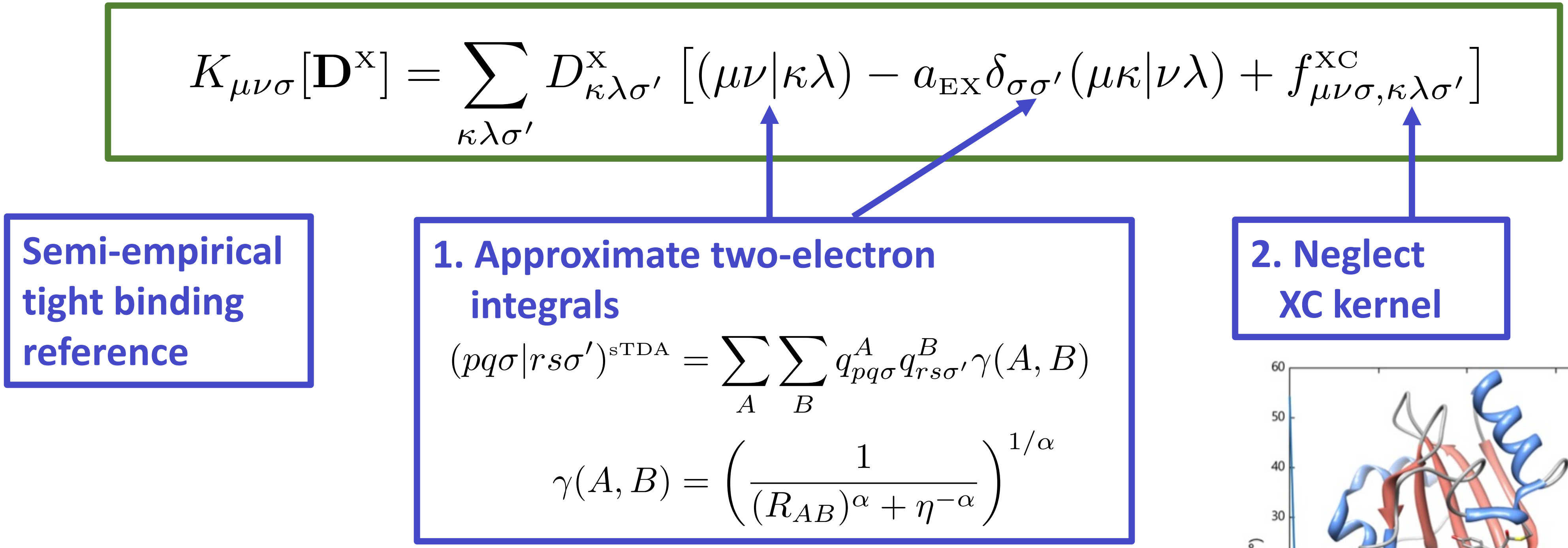
TDDFT+TB

Visscher *et al.*, *J. Phys. Chem. C* (**2020**).

SCM
Software for Chemistry & Materials



TDDFT for periodic systems:
Fast, but accurate hybrid functional approaches



$$K_{\mu\nu\sigma}[\mathbf{D}^{\mathrm{X}}] = \sum_{\kappa\lambda\sigma'} D^{\mathrm{X}}_{\kappa\lambda\sigma'} \left[(\mu\nu|\kappa\lambda) - a_{\mathrm{EX}}\delta_{\sigma\sigma'}(\mu\kappa|\nu\lambda) + f^{\mathrm{XC}}_{\mu\nu\sigma,\kappa\lambda\sigma'} \right]$$

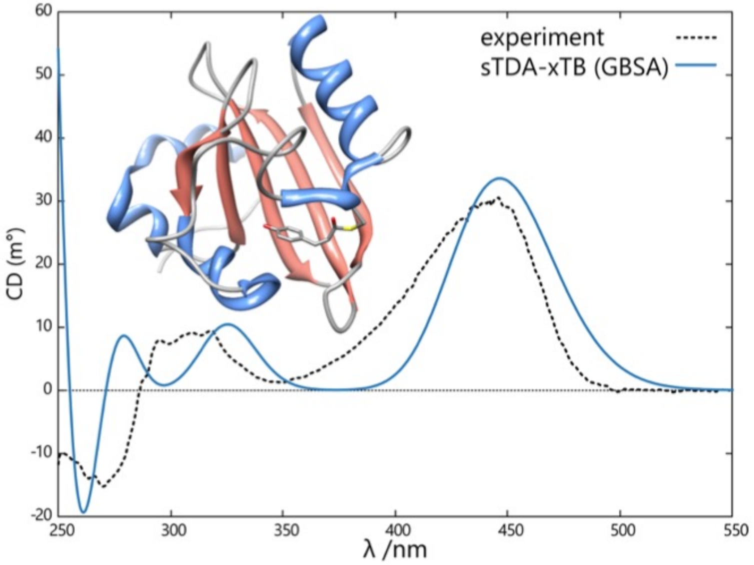
Semi-empirical tight binding reference

1. Approximate two-electron integrals

$$(pq\sigma|rs\sigma')^{\mathrm{sTDA}} = \sum_A \sum_B q^A_{pq\sigma} q^B_{rs\sigma'} \gamma(A,B)$$

$$\gamma(A,B) = \left(\frac{1}{(R_{AB})^{\alpha} + \eta^{-\alpha}} \right)^{1/\alpha}$$

2. Neglect XC kernel



- **Minimal number of global parameters**
- **Correct asymptotics for electron repulsion**
- **System sizes of several hundreds of atoms**

Grimme *J. Chem. Phys.* 138, 244104, **(2013)**.

Excited-state properties

Non-variational wave function $E_{\mathrm{ES}}[\mathbf{X},\mathbf{C},\mathbf{R}] = E_{\mathrm{GS}} + \Omega$

$$\frac{\delta E_{\mathrm{ES}}}{\delta \mathbf{R}} = \frac{\partial E_{\mathrm{ES}}}{\partial \mathbf{R}} + \frac{\partial E_{\mathrm{ES}}}{\partial \mathbf{X}}\frac{\partial \mathbf{X}}{\partial \mathbf{R}} + \frac{\partial E_{\mathrm{ES}}}{\partial \mathbf{C}}\frac{\partial \mathbf{C}}{\partial \mathbf{R}}$$

First-order response needed!

→ Explicit derivation

$$\frac{\partial E_{\mathrm{GS}}}{\partial \mathbf{C}} = 0 \longrightarrow \frac{\partial^2 E_{\mathrm{GS}}}{\partial \mathbf{R}\partial \mathbf{C}} = -\frac{\partial^2 E_{\mathrm{GS}}}{\partial \mathbf{C}^2}\frac{\partial \mathbf{C}}{\partial \mathbf{R}}$$

or

→ Adding constaint to satisfy static KS equations (Brillouin condition)

$$\boxed{\begin{aligned} L(\mathbf{X},\mathbf{C},\mathbf{R},\bar{\mathbf{Z}}) &= E_{\mathrm{GS}} + \Omega + \sum_{ia} \bar{Z}_{ia} F_{ia} \\ F_{ia} &= 0 \end{aligned}}$$

Excited-state properties: a Lagrange functional for TDDFT

$$\boxed{\begin{gathered} L(\mathbf{X},\mathbf{C},\mathbf{R},\bar{\mathbf{Z}}) = E_{\mathrm{GS}} + \Omega + \sum_{ia} \bar{Z}_{ia} F_{ia} \\ F_{ia} = 0 \end{gathered}}$$

→ **(2n+1) rule:** only zeroth-order response needed!

$$\frac{\delta L}{\delta \mathbf{R}} = \frac{\partial E_{\mathrm{ES}}}{\partial \mathbf{R}} + \bar{\mathbf{Z}} \frac{\partial^2 E_{\mathrm{GS}}}{\partial \mathbf{R} \partial \mathbf{C}} = \frac{\partial E_{\mathrm{ES}}}{\partial \mathbf{R}} + \bar{\mathbf{Z}} \frac{\partial \mathbf{F}}{\partial \mathbf{R}}$$

Additional equations for Lagrangian multipliers:

$$\frac{\partial L}{\partial \mathbf{C}} = 0 = \frac{\partial E_{\mathrm{ES}}}{\partial \mathbf{C}} + \bar{\mathbf{Z}} \frac{\partial^2 E_{\mathrm{GS}}}{\partial \mathbf{C}^2}$$

→ **(2n+2) rule / Sternheimer-Dalgarno / Z-vector**

Excited-state properties: a Lagrange functional for TDDFT

Geometry dependence of AOs needs to be taken into account!

$$\mathbf{R} = \mathbf{R}_0 + \Delta\mathbf{R} \quad \Rightarrow \quad \begin{aligned} \phi(\mathbf{R}) &= \mathbf{C}(\mathbf{R}_0)\varphi(\mathbf{R}) \\ \mathbf{S}(\mathbf{R}) &= \langle \phi(\mathbf{R}) | \phi(\mathbf{R}) \rangle \neq \mathbf{1} \end{aligned}$$

Different strategies to ensure orthonormality:

→ **Additional constraint in the Lagrangian**

Furche, Ahlrichs, *J Chem Phys*, 121, 12772 (**2002**).

$$L(\mathbf{X}, \mathbf{C}, \mathbf{R}, \bar{\mathbf{Z}}, \bar{\mathbf{W}}) = E_{\mathrm{GS}} + \Omega + \sum_{ia} \bar{Z}_{ia} F_{ia} - \sum_{p \leq q} \bar{W}_{pq}(S_{pq} - \delta_{pq})$$

→ **Orthogonalized molecular orbitals (OMOs)**

Helgaker, Jorgensen, Handy, *Theor Chim Acta*, 76, 227 (**1989**).

$$\mathbf{C}^{\mathrm{OMO}}(\mathbf{R}) = \mathbf{C}^{\mathrm{UMO}}(\mathbf{R}_0)(\mathbf{S}^{\mathrm{UMO}}(\mathbf{R}))^{-1/2}$$

Not needed when using plane waves Hutter, *J Chem Phys*, 118, 3928 (**2003**).

Excited-state properties for periodic systems: a Lagrangian ansatz for TDDFPT with mixed Gaussian plane waves

Lagrange / Z vector formalism to avoid 1st order response:

1. Excitation energies

$$\mathbf{A}\mathbf{X}_n = \boldsymbol{\Omega}_n \mathbf{S}\mathbf{X}_n \quad \text{with} \quad \mathbf{X}_n^\dagger \mathbf{S}\mathbf{X}_m = \mathbf{1}$$

Lagrangian for state *n*: $L = \Omega + \bar{\mathbf{Z}}\mathbf{F} + \bar{\mathbf{W}}\mathbf{S}$

Geometry dependence of AOs

2. Z vector equation

$$\frac{\partial L}{\partial \mathbf{C}} \rightarrow \mathbf{B}\bar{\mathbf{Z}} = -\mathbf{R}$$

3. Excited-state gradient

$$\frac{\partial L}{\partial \zeta} = \frac{\partial \Omega}{\partial \zeta} + \bar{\mathbf{Z}}\frac{\partial \mathbf{F}}{\partial \zeta} + \bar{\mathbf{W}}\frac{\partial \mathbf{S}}{\partial \zeta}$$

Brillouin condition

$$\sum_{ia\sigma} \bar{Z}_{ia\sigma} F_{ia\sigma} = \sum_{i\mu\nu\sigma} \bar{Z}_{i\nu\sigma} Q^\dagger_{\mu\nu\sigma} F_{\mu i\sigma}$$

$$= \sum_{i\mu\nu\sigma} \bar{Z}_{i\nu\sigma}\left(F_{\nu\mu\sigma} C_{\mu i\sigma} - S_{\nu\mu} C_{\mu i\sigma} \varepsilon_{i\sigma}\right)$$

Furche, Ahlrichs, *J Chem Phys*, 121, 12772 (**2002**); Hutter, *J Chem Phys*, 118, 3928 (**2003**).

Excited-state properties for periodic systems: a Lagrangian ansatz for TDDFPT with mixed Gaussian plane waves

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Transformation rules

$$M^{\mathrm{AO}}_{\mu\nu\sigma} = \sum_{\kappa\lambda kl} S_{\mu\kappa} C^{\mathrm{T}}_{\kappa k\sigma} M^{\mathrm{MO}}_{kl\sigma} C_{l\lambda\sigma} S_{\lambda\nu}$$

$$M^{\mathrm{MO}}_{kl\sigma} = \sum_{\kappa\lambda} C^{\mathrm{T}}_{\kappa k\sigma} M^{\mathrm{AO}}_{\kappa\lambda\sigma} C_{\lambda l\sigma}$$

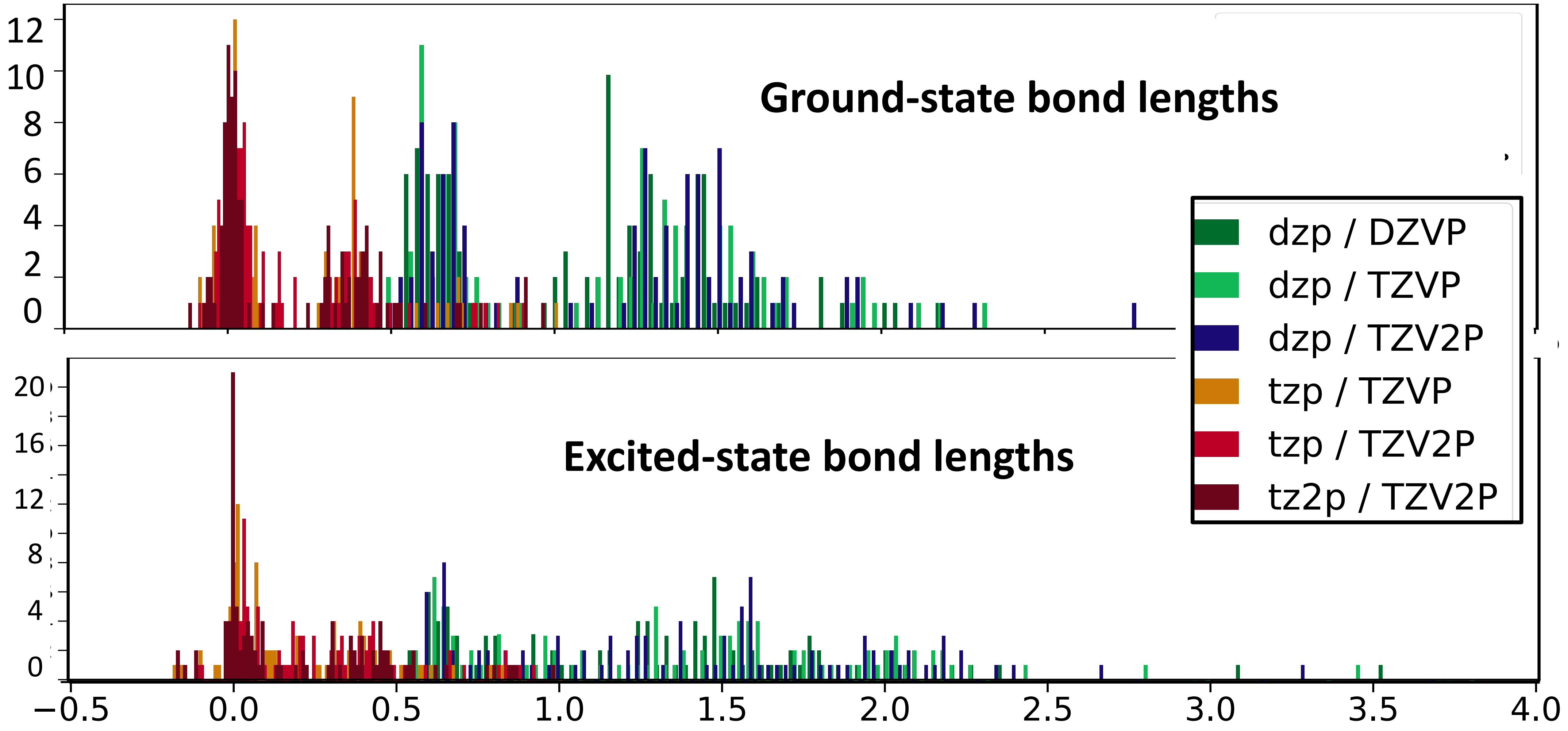
Projection for Lagrange multipliers

$$\frac{\partial L}{\partial \mathbf{C}}\mathbf{C} = 0 \rightarrow \bar{\mathbf{W}} \qquad \frac{\partial L}{\partial \mathbf{C}}\mathbf{Q} = 0 \rightarrow \bar{\mathbf{Z}}$$

Furche, Ahlrichs, *J Chem Phys*, 121, 12772 (**2002**); Hutter, *J Chem Phys*, 118, 3928 (**2003**).

Accuracy benchmarks for molecular systems

ADMM-PBE0 geometries wrt PBE0 reference

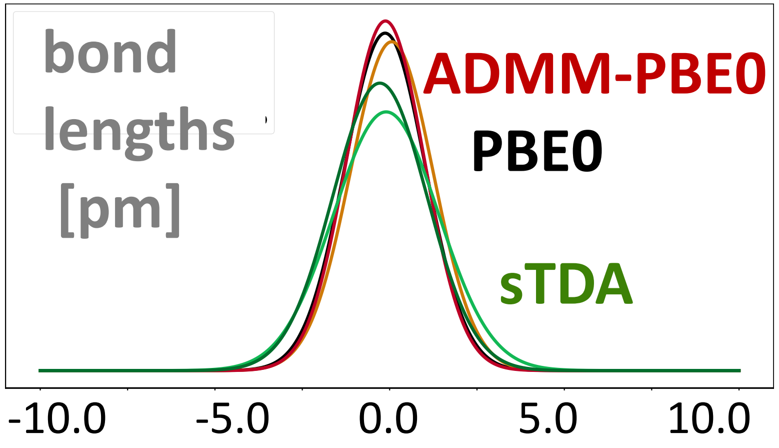


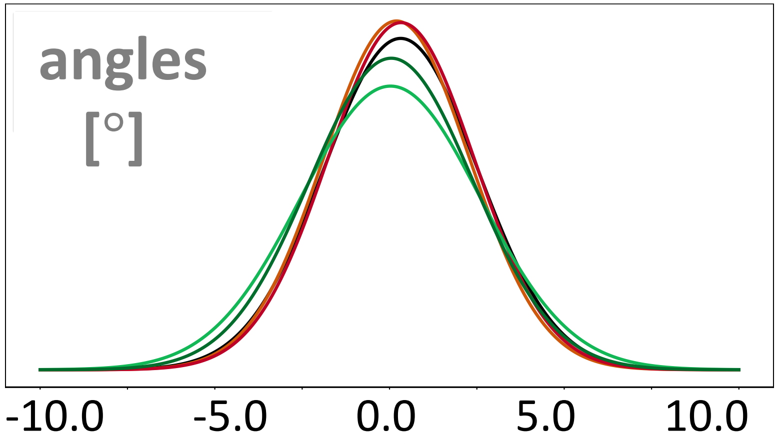
➡ **ADMM error < 0.3 pm | < 0.1° for triple-zeta basis sets**

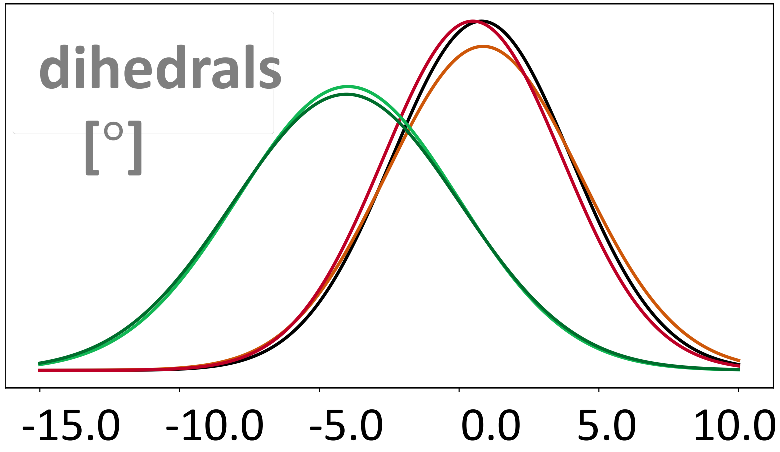
Jacquemin *et al. J. Chem. Theory Comput. 13*, 6237 **(2017)**.

Accuracy benchmarks for molecular systems

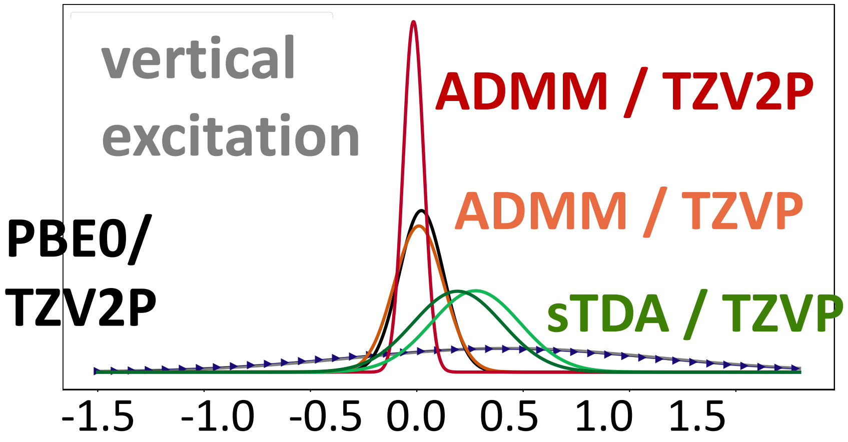
wrt EOM-CCSD reference

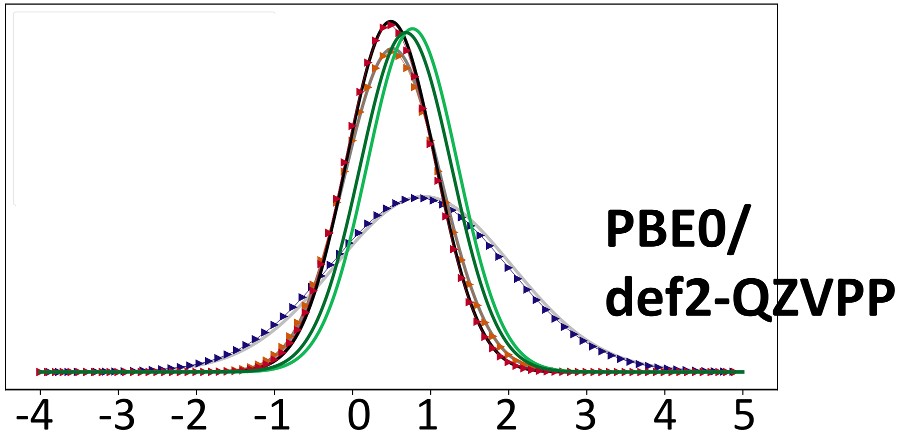






wrt PBE0 reference

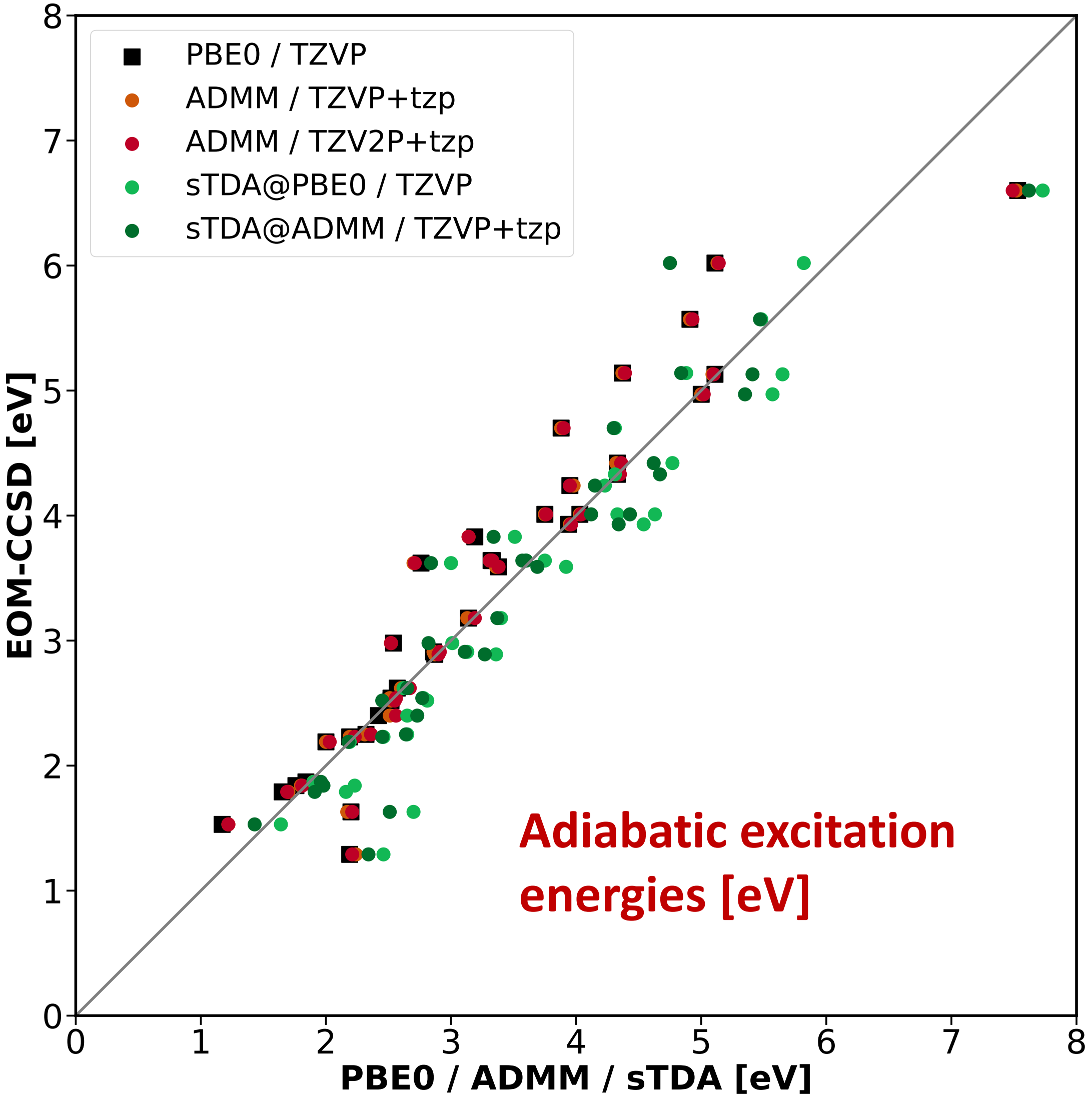




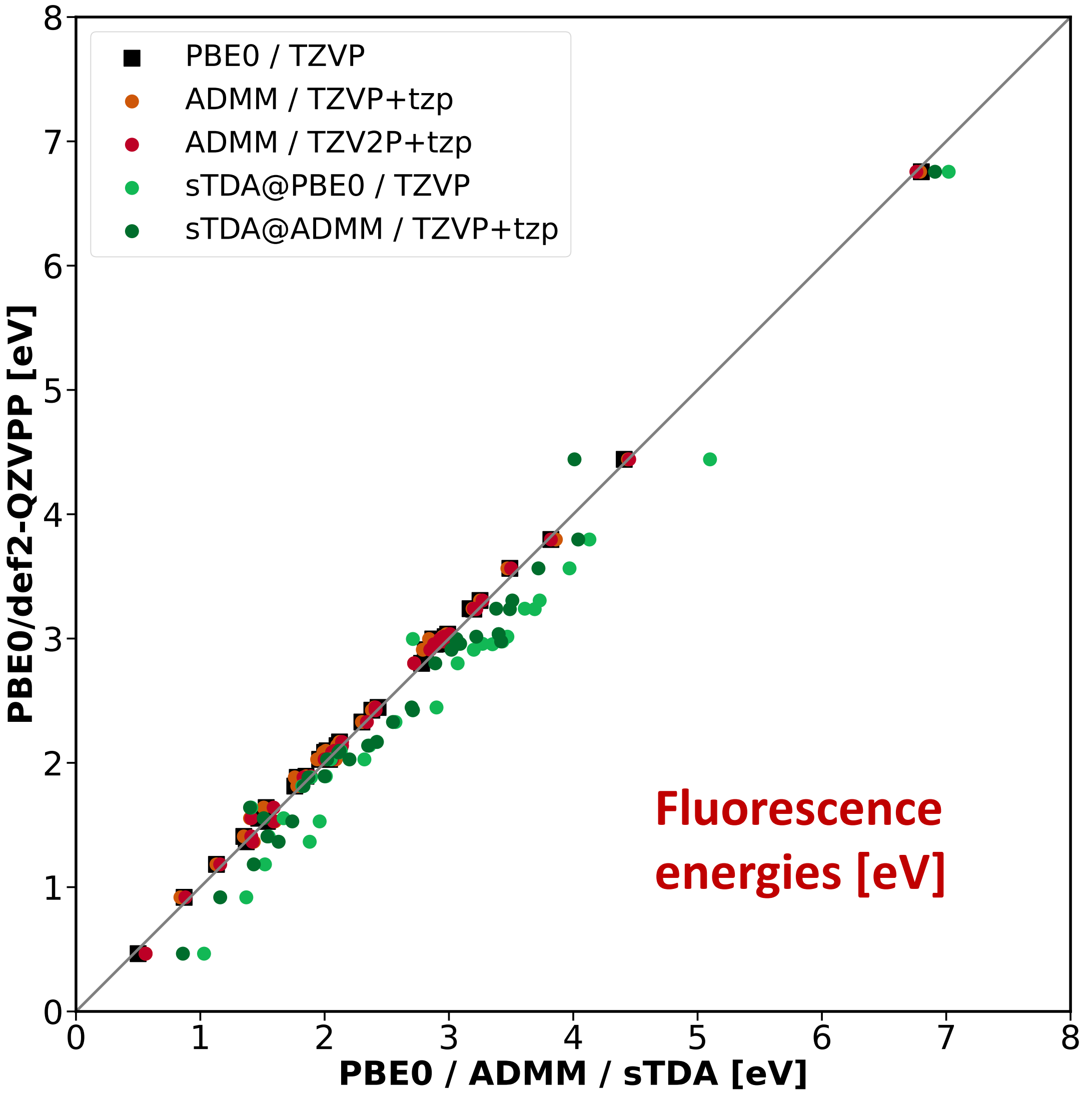
➡ **Error** **sTDA** **< 1.1 pm | < 1.6°** **for triple-zeta basis sets**

PBE0/ADMM **< 0.9 pm | < 1.2°**

Accuracy benchmarks for molecular systems



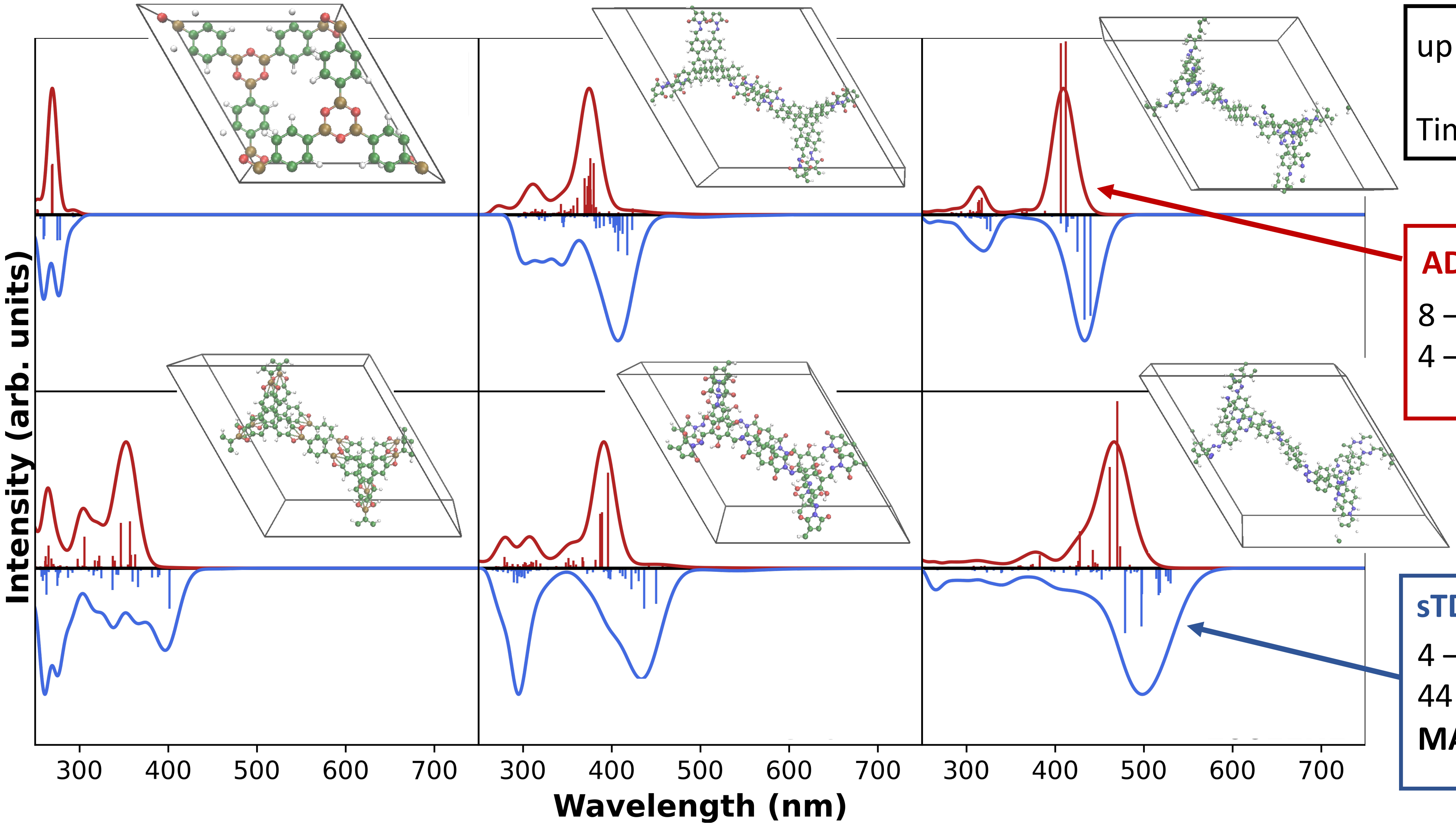
Adiabatic excitation energies [eV]



Fluorescence energies [eV]

Errors in the range of 0.2 – 0.5 eV

Accuracy benchmarks for molecular systems



up to 300 atoms
7440 basis functions
Timings for 2304 cores

ADMM-PBE0

8 – 30 min for ES opt step
4 – 10 hrs for 500 ES

sTDA

4 – 10 min for ES opt step
44 mins for 500 ES
MAD of 0.31 – 0.42 eV

gain in efficiency by at least one order of magnitude

Current research: Excited-state dynamics for periodic systems

Excited-state properties with hybrid functional accuracy

ADMM-TDDFT

Semi-empirical sTDA

Periodic boundary conditions

CP2K + NX

newtonx.org

Adiabatic and Nonadiabatic dynamics

On-the-fly velocity Verlet MD

Fewest switches surface hopping

Local diabatization

Decoherence corrections

Barbatti *et al., WIREs: Comp. Mol. Sci.* 4, 26 (**2014**).

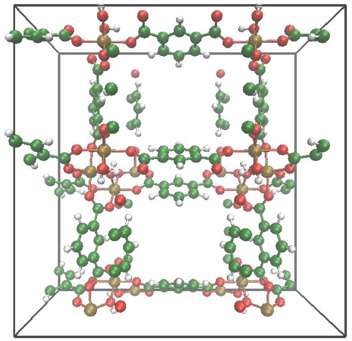
Efficient nonadiabatic couplings

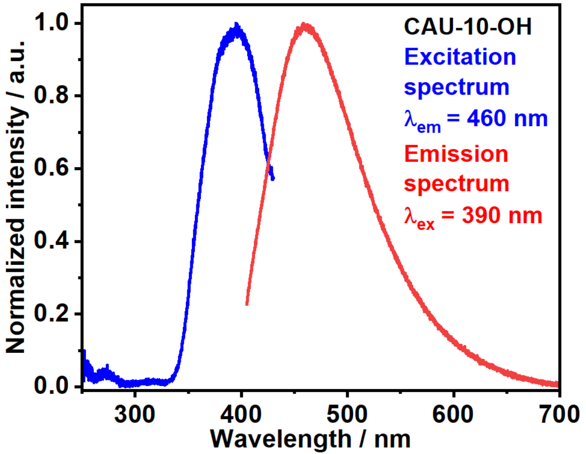
Orbital derivative couplings

Baeck-An couplings

$$\sigma_{MN} \approx \frac{\mathrm{sgn}(\Delta E_{MN})}{2}\sqrt{\frac{1}{\Delta E_{MN}}\frac{\mathrm{d}^2\Delta E_{MN}}{\mathrm{d}t^2}}$$

Fluorescence CAU10-MOFs





Summary

Often used approach in practice: **ALDA and KS-Ansatz**

$$v_{\mathrm{XC}}^{\mathrm{ALDA}}[\rho](\mathbf{r},t) = v_{\mathrm{XC}}[\rho(t)](\mathbf{r})$$

$$\rho(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2$$

Linear response formalism / Casida equations

$$(\Lambda - \Omega\Delta)|X,Y\rangle = 0 \ ; \ \langle X,Y|\Delta|X,Y\rangle = 1$$

Excited-state properties via Lagrange functional

$$L[X,Y,\Omega,C,Z,W] = E_0 + G[X,Y,\Omega] + \sum_{ia} Z_{ia}F_{ia} - \sum_{p\leq q} W_{pq}(S_{pq} - \delta_{pq})$$

Summary

Often used approach in practice: **ALDA and KS-Ansatz** → How to overcome the adiabatic approximation? How to design frequency dependent kernels? Connection to MBPT and more accurate ansätze than TDDFT

$$v_{\mathrm{XC}}^{\mathrm{ALDA}}[\rho](\mathbf{r},t) = v_{\mathrm{XC}}[\rho(t)](\mathbf{r})$$

$$\rho(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2$$

Linear response formalism / Casida equations

$$(\Lambda - \Omega\Delta)|X,Y\rangle = 0 \ ; \ \langle X,Y|\Delta|X,Y\rangle = 1 \longrightarrow$$

Alternatives to LR-TDDFT

Excited-state properties via Lagrange functional

$$L[X,Y,\Omega,C,Z,W] = E_0 + G[X,Y,\Omega] + \sum_{ia} Z_{ia}F_{ia} - \sum_{p\leq q} W_{pq}(S_{pq} - \delta_{pq})$$

→ Machine learning ...

→ Going beyong excited-state properties
What else is needed to perform excited-state dynamices and to calculate excitation spectra?
Efficient ways to do so?