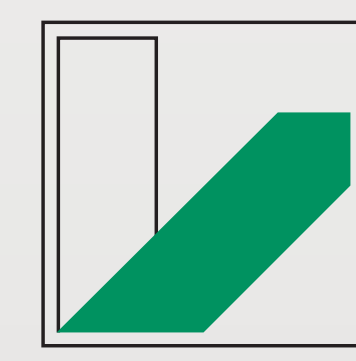


META-GGAs IN TDDFT: IMPORTANCE OF THE CURRENT-DENSITY CORRECTION

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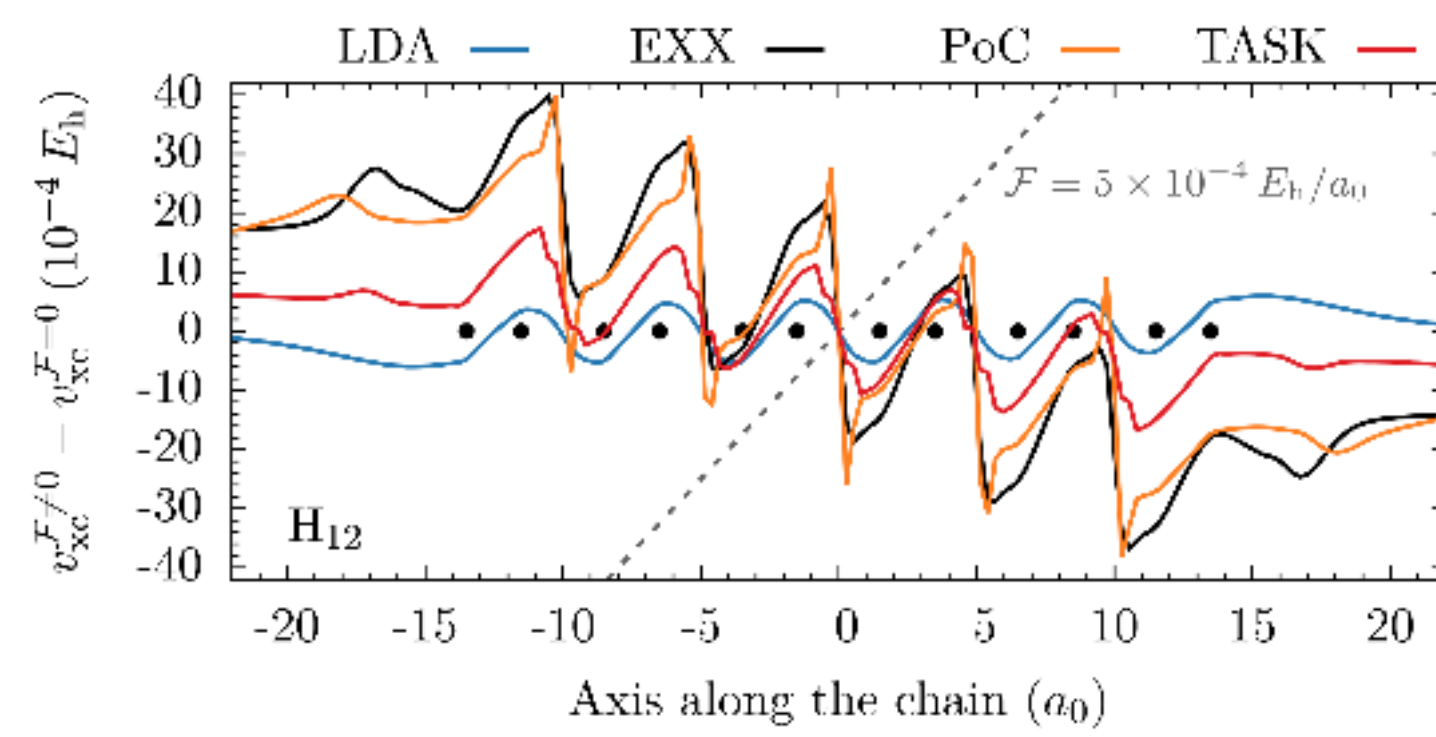


Motivation

- **Meta-GGAs** $E_{xc}^{mGGA}[n, \nabla n, \tau] = \int e_{xc}^{mGGA}(\mathbf{r}, t) d^3r$ can show **(ultra)nonlocality** due to orbital dependence of

$$\tau(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_j |\nabla \varphi_j(\mathbf{r})|^2.$$

- For ground-state calculations meta-GGAs can show similar properties as exact exchange, e.g., a **sizeable derivative discontinuity** $\Delta_x = \left. \frac{\delta E_x}{\delta n(\mathbf{r})} \right|_+ - \left. \frac{\delta E_x}{\delta n(\mathbf{r})} \right|_-$, under semi-local computational costs [1].



- How do modern meta-GGAs (**TASK** and **r²SCAN**) perform in **TDDFT**?
- How to use modern meta-GGAs in **TDDFT**?

Challenges: Meta-GGAs in TDDFT

Gauge Variance

- $\tau(\mathbf{r}, t)$ is **gauge variant**, but v_{xc} should be invariant since exact E_{xc} is only a functional of $n(\mathbf{r}, t)$.

- Gauge transformation with $\Lambda(\mathbf{r}, t)$ of external potentials leads to **time- and position-dependent phase** in all orbitals

$$\varphi_j[\Lambda](\mathbf{r}, t) = \varphi_j(\mathbf{r}, t) \exp\left(-\frac{ie}{\hbar} \Lambda(\mathbf{r}, t)\right).$$

- τ transforms as

$$\tau[\Lambda](\mathbf{r}, t) = \tau(\mathbf{r}, t) - e \nabla \Lambda(\mathbf{r}, t) \cdot \mathbf{j}_p(\mathbf{r}, t) + \frac{e^2}{2m} |\nabla \Lambda(\mathbf{r}, t)|^2 n(\mathbf{r}, t)$$

$$\text{with } \mathbf{j}_p = \frac{\hbar}{m} \sum_j \text{Im}[\varphi_j^*(\mathbf{r}, t) \nabla \varphi_j(\mathbf{r}, t)].$$

Continuity Equation

- Using $\tau(\mathbf{r}, t)$ in time-dependent equations leads to a **violation of the continuity equation**.

- Considering the time-dependent (G)KS equations

$$i\hbar \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = \hat{H}_{\text{GKS}} \varphi_j(\mathbf{r}, t)$$

the continuity equation can be derived as

$$\frac{\partial}{\partial t} |\varphi_j(\mathbf{r}, t)|^2 = \frac{1}{i\hbar} [\varphi_j^*(\mathbf{r}, t) \hat{H}_{\text{GKS}} \varphi_j(\mathbf{r}, t) - \varphi_j(\mathbf{r}, t) \hat{H}_{\text{GKS}} \varphi_j^*(\mathbf{r}, t)]$$

with $\hat{H}_{\text{GKS}} = \hbar^2 / (2m) \nabla^2 + v_{\text{local}} + v_{\tau}^{\text{GKS}}(\mathbf{r}, t)$.

- Summing up over j leads to

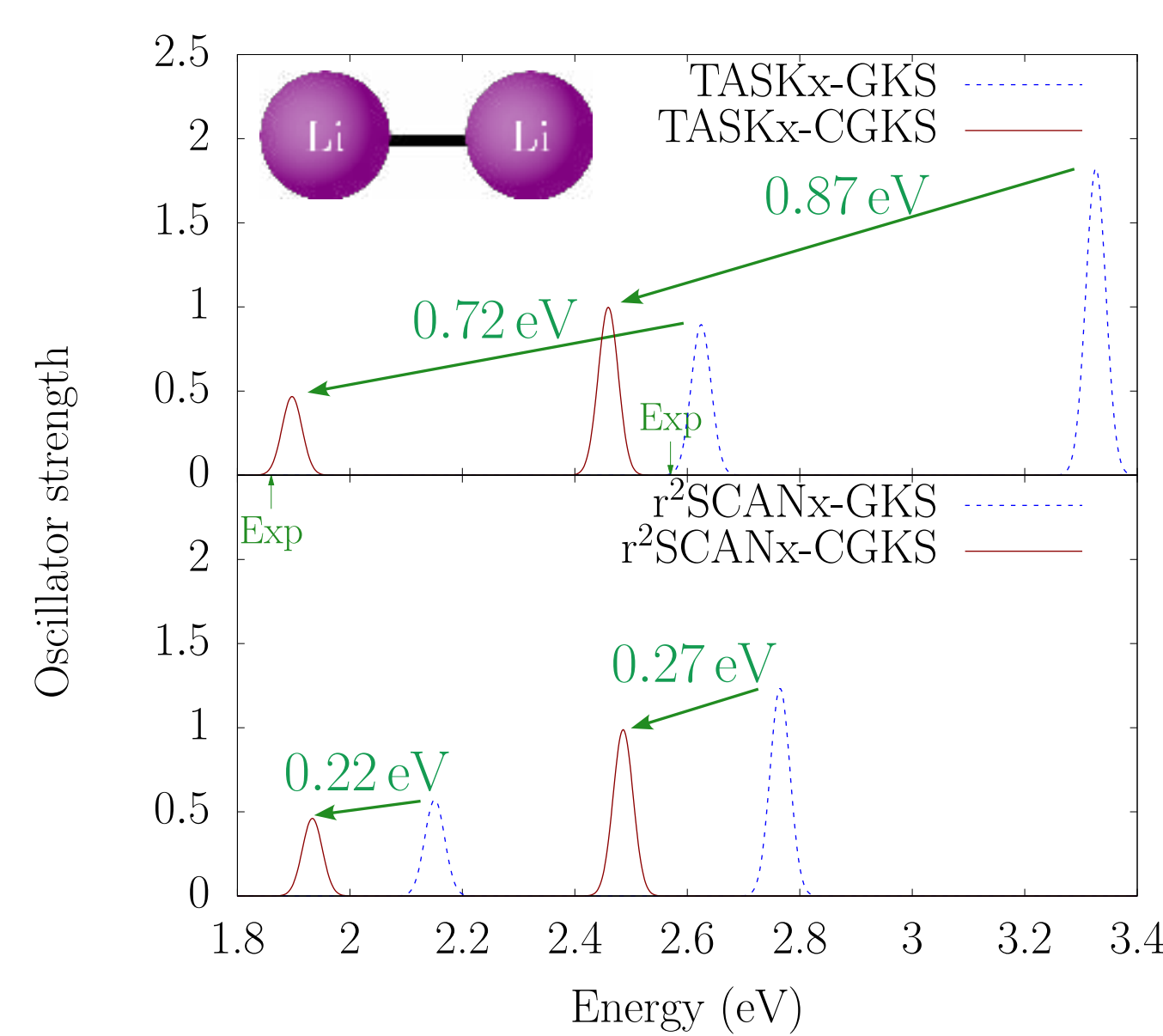
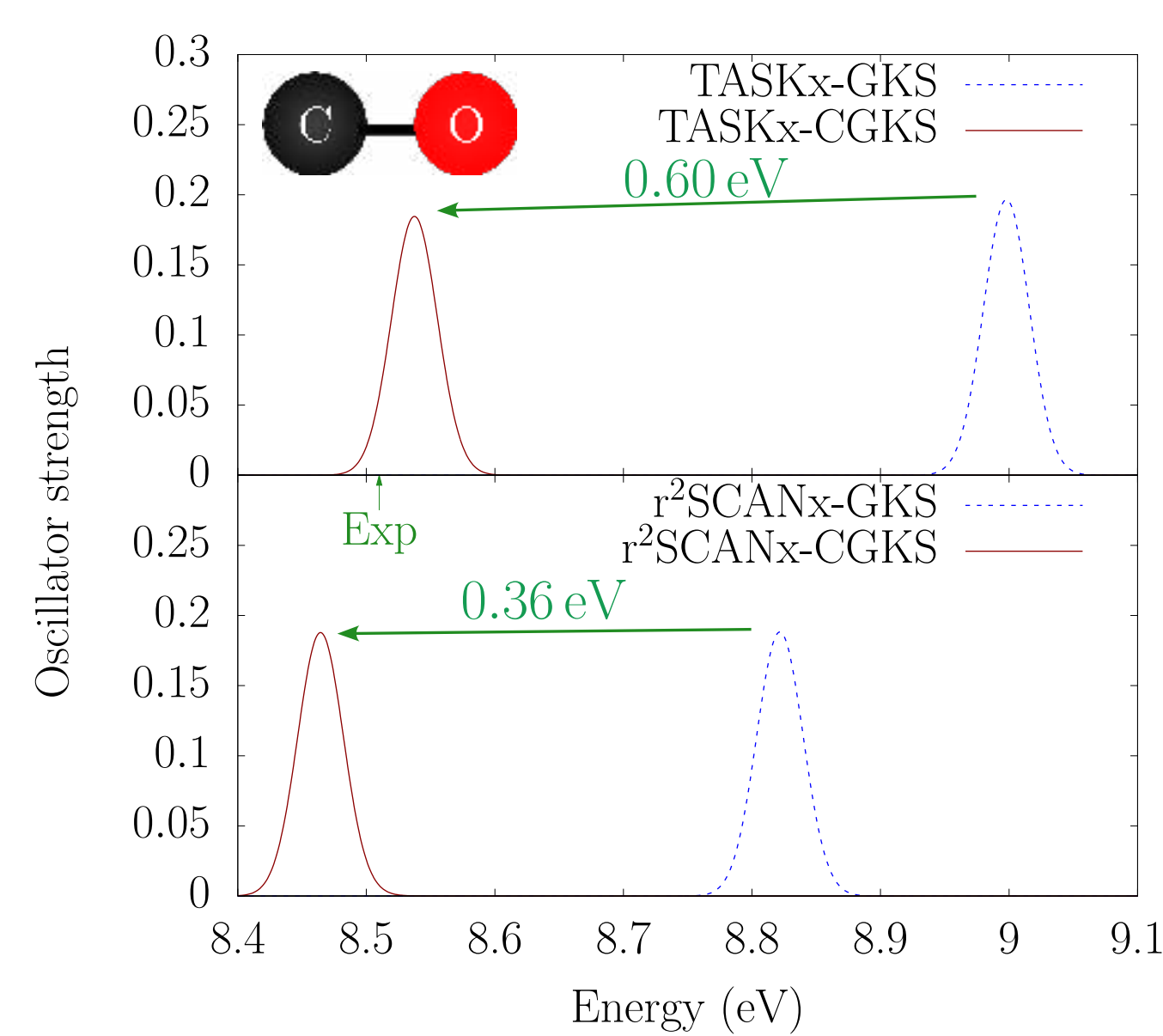
$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \left[\mathbf{j}_p(\mathbf{r}, t) \left(1 + \frac{\partial e_{xc}^{mGGA}}{\partial t}(\mathbf{r}, t) \right) \right].$$

Solution: Current-Density Correction

by Becke [2] and Tao [3]
first applied by Bates, Furche [4]

$$\hat{\tau}(\mathbf{r}, t) = \tau(\mathbf{r}, t) - m \frac{|\mathbf{j}_p(\mathbf{r}, t)|^2}{2n(\mathbf{r}, t)}$$

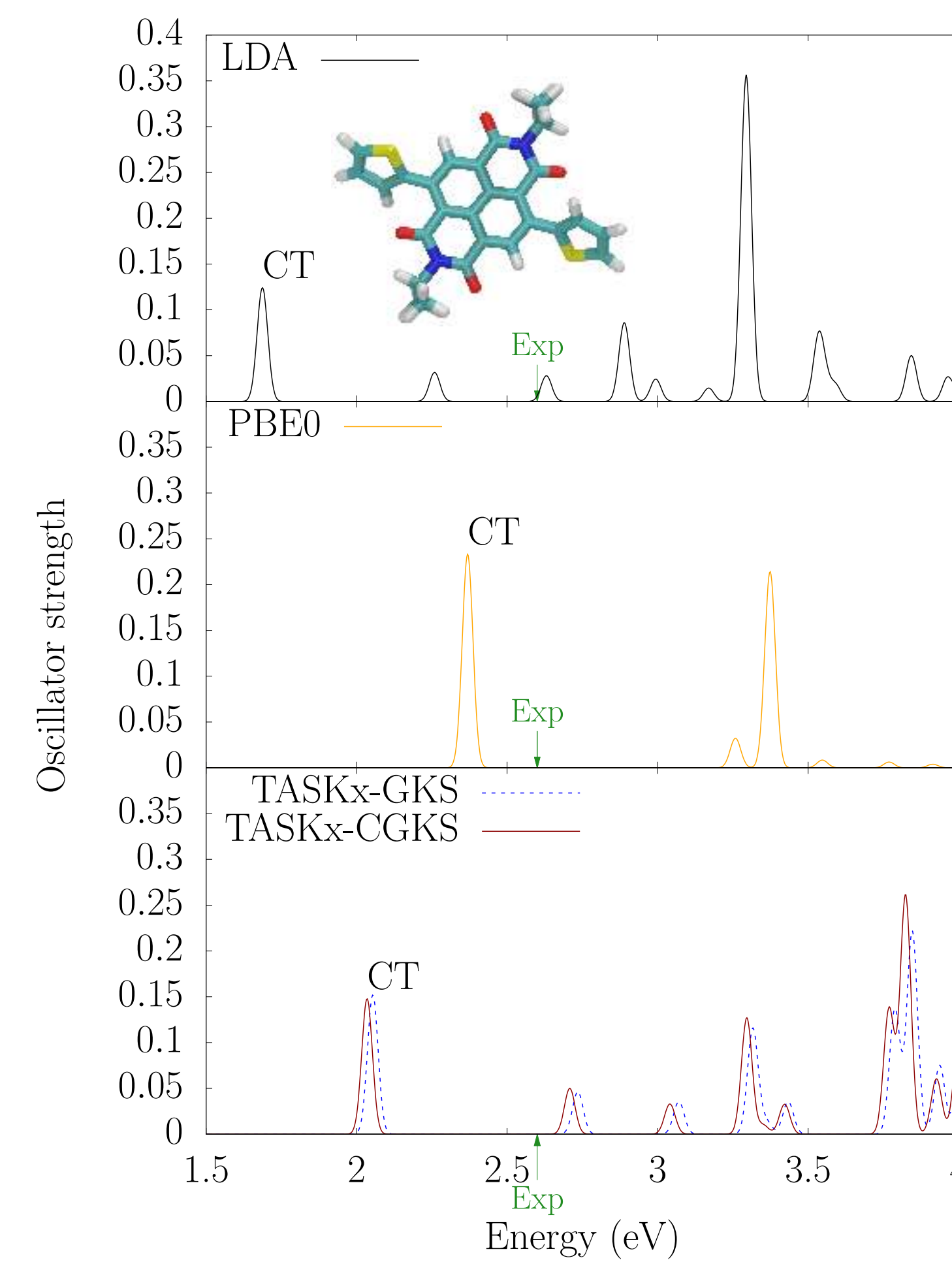
Results for Time Dependent Density Functional Theory



- For **CO** and **Li₂** the influence of $\hat{\tau}$ leads to a **strong redshift** from GKS to CGKS of the excitation lines.
- This is observed for both **TASKx** and **r²SCANx**.
- Propagating with **SCANx** leads to numerical instabilities.

⇒ For both functionals the current-density correction leads to a clearly **better agreement with the experimental value**.

⇒ Not including $\hat{\tau}$ can lead to significant deviations to experimental values!



- Naphtalene diimide (NDI-1): **organic semiconductor** system with CT excitation as lowest spectral line.

⇒ Serves as a model system for the description of CT lines.

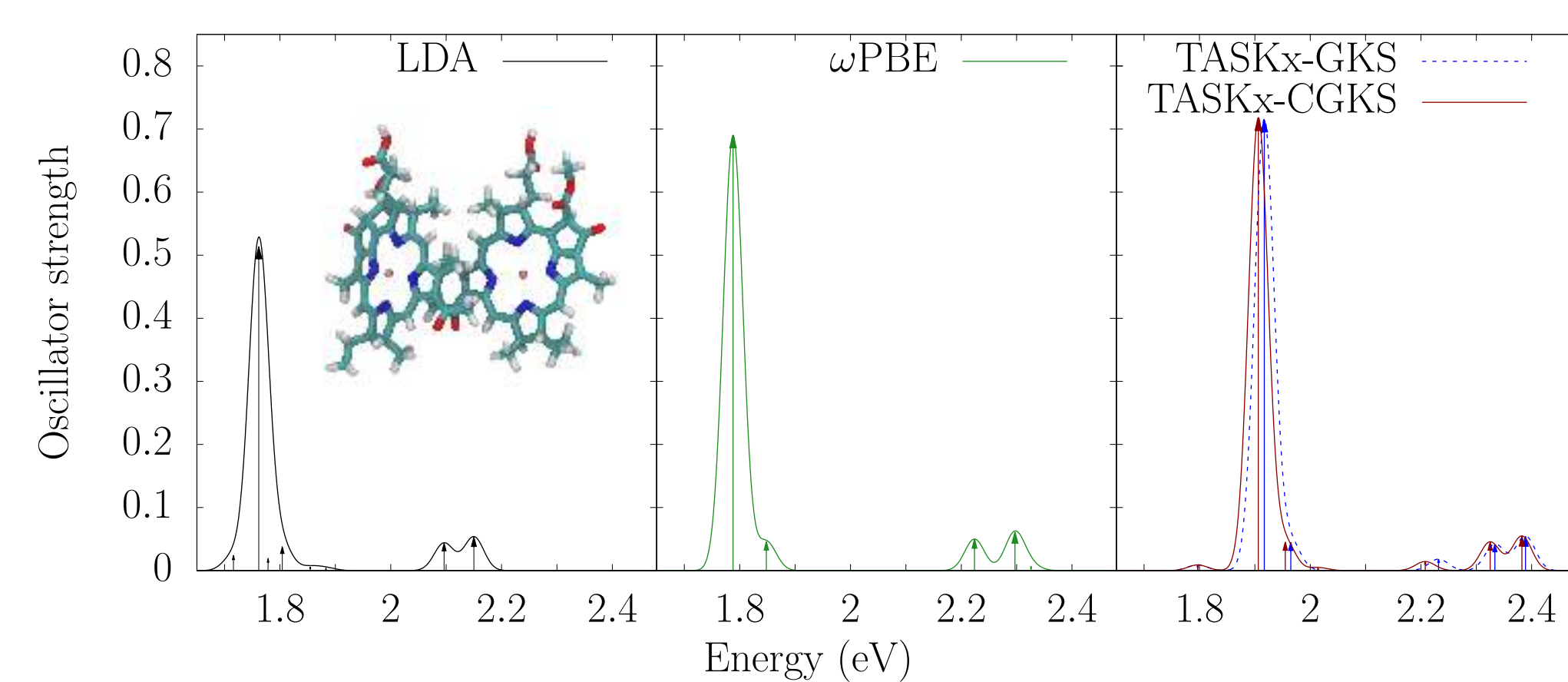
- **LDA** clearly underestimates the position (1.69 eV) of the CT line (experiment: ~ 2.6 eV).

- **PBE0** as global hybrid shifts CT line to a higher energy at 2.37 eV.

- **TASKx-CGKS** shows the first line at 2.03 eV, still **underestimating** the CT excitation energies (2.05 eV for GKS).

- (C)GKS leads to higher energies compared to the linear-response KLI results of Ref. [5] with 1.80 eV.

⇒ TASKx leads to more accurate results than LDA but still cannot compete with the global hybrid PBE0 in this respect.



- Expectation: Coupling as **J-aggregate** of two single Q_Y and Q_X excitations.
- symm. coupling → high oscillator strength; anti-symm. coupling → low oscillator strength

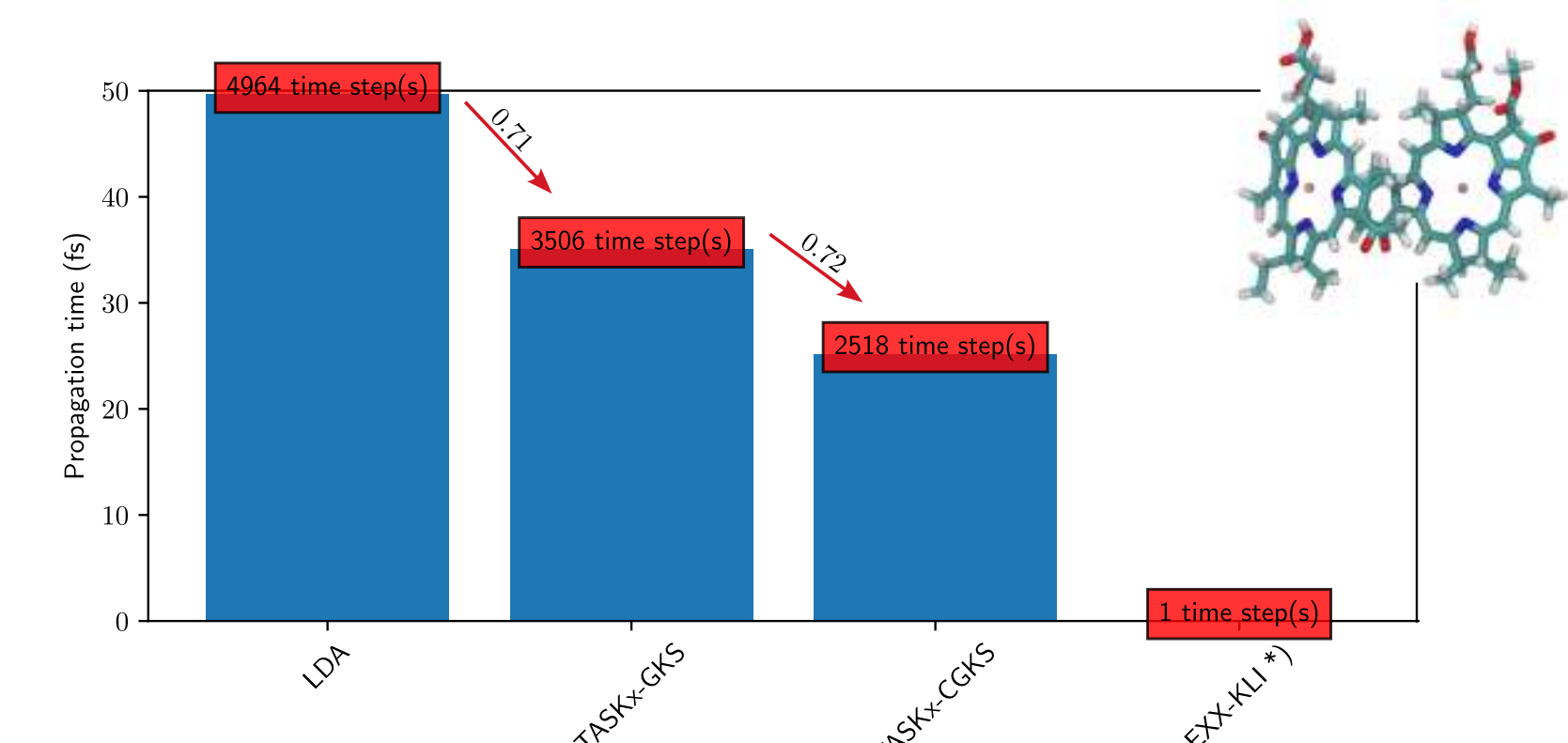
- **LDA** shows significant deficiencies in describing the coupling: several spurious excitations near coupled Q_Y line.

- **omegaPBE** shows the expected results.

- **TASKx** shows 3 spurious lines. However, the positions are (mostly) shifted outside the range of the coupled Q lines.

- Small influence of the current-density correction $\hat{\tau}$.

Comparison of **computation times** with BTDDFT: 24 h wall time



*) estimated value for exact exchange KLI (EXX-KLI) calculation

Conclusion

- We found a **systematic redshift** from GKS to CGKS for all systems.
- The magnitude of the influence of $\hat{\tau}$ **cannot be assessed a priori**.
- For NDI-1 and Bacteriochlorophyll molecules: Small influence of $\hat{\tau}$.
- For CO and Li₂: Strong influence of $\hat{\tau}$ and **better agreement with experimental results for CGKS**.

⇒ Generally include $\hat{\tau}$ for meta-GGA calculations in TDGKS!

- TASKx leads to **improvements in the description of CT excitations** compared to LDA at semi-local computational cost but cannot compete with ω PBE.

References

- [1] T. Aschebrock and S. Kümmel, Physical Review Research **1**, [5] F. Hofmann and S. Kümmel, The Journal of Chemical Physics **033082** (2019).
- [2] A. D. Becke, The Journal of Chemical Physics **117**, 6935 (2002).
- [3] J. Tao, Physical Review B **71**, 205107 (2005).
- [4] J. E. Bates and F. Furche, The Journal of Chemical Physics **137**, [6] T. Schmidt and S. Kümmel, Physical Review B **93**, 165120 (2016).
- [5] S. G. Balasubramani et al., The Journal of Chemical Physics **152**, 184107 (2020).

Interesting Technical Aspects

- Creating consistent meta-GGA PPs is highly demanding.

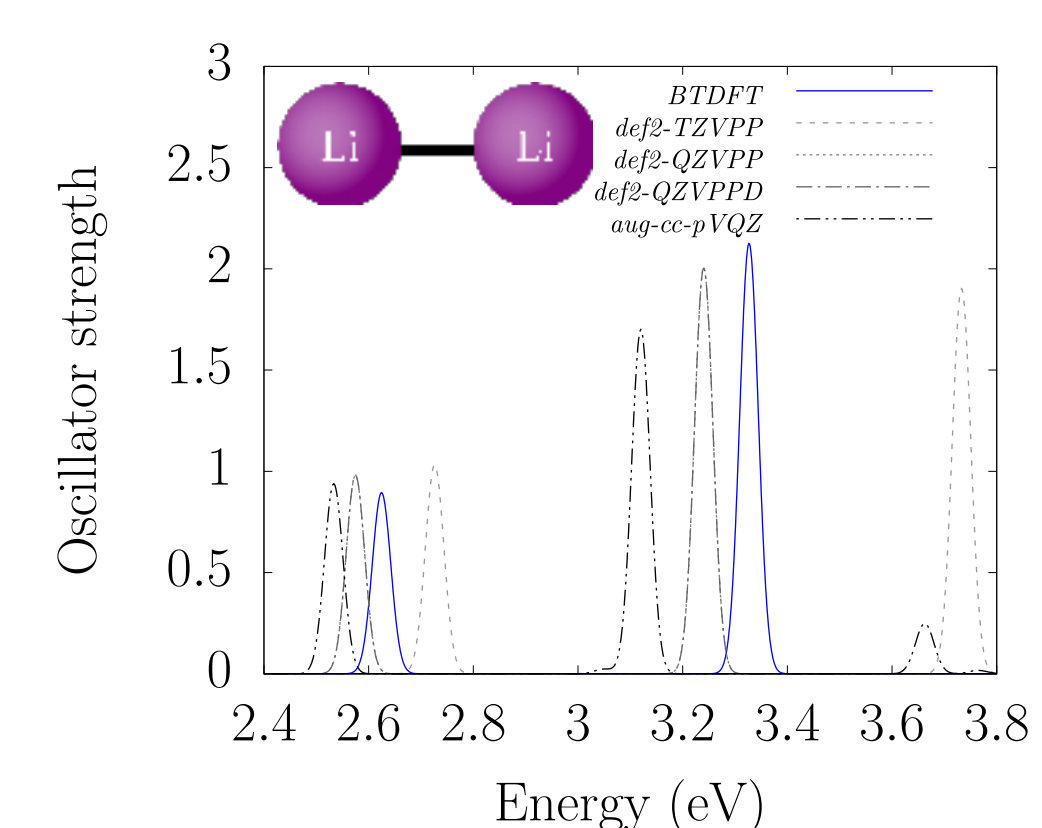
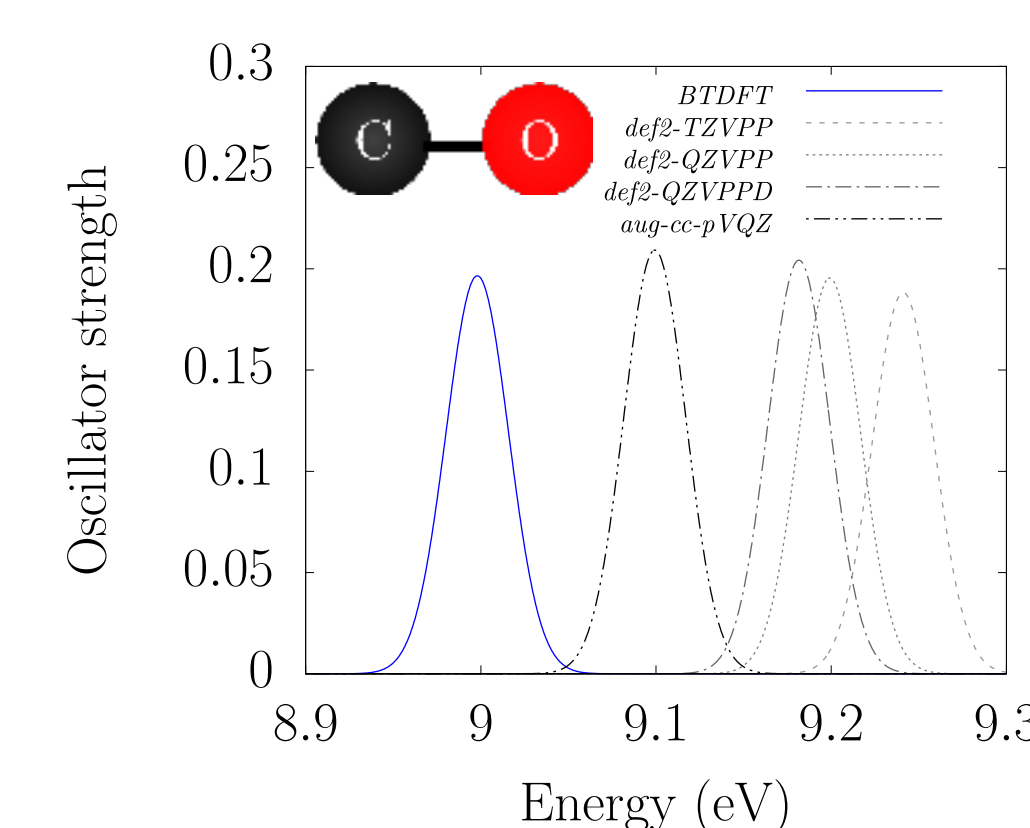
- Many meta-GGAs depend on the **iso-orbital indicator** $\alpha = \frac{\tau - \tau^W}{\tau_{\text{unif}}}$.

- Meta-GGA functionals on top of (semi-)local PPs misinterpret iso-orbital regions compared to all-electron calculations since the core density $n_c(\mathbf{r})$ can have a large influence on α .

- Include core density via **core correction**[6]:

$$\tau = \frac{\hbar^2}{2m} \left\{ \left(\sum_{\text{valence states}} |\nabla \varphi_j^v|^2 \right) + \left| \nabla \left(n_c^{1/2} \right) \right|^2 \right\}.$$

- Exact for atoms with only s -type core orbitals such as N, C, O, and Li.



- Verify **core correction** by comparing our BTDDFT (real-time, real-space) results for **CO** and **Li₂** to Turbomole[7] (all-electron) results using TASKx-GKS (**no** $\hat{\tau}$).

- Increasing the basis set size stepwise leads to better agreement with BTDDFT.

- Linear-response all-electron spectrum shows better agreements for larger basis sets.

⇒ BTDDFT with core-corrected PPs leads to **robust results** compared to all-electron codes.