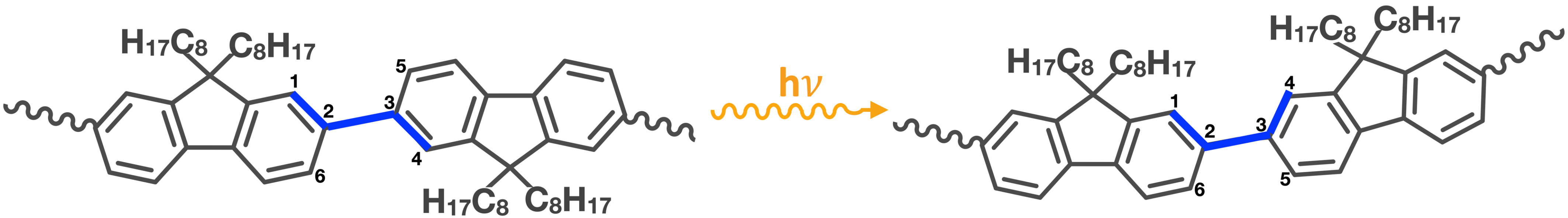
Trans-cis isomerization in the ground and excited states using PLUMED

Collective variable: The dihedrals rotating under light irradiation

Force field derived in the ground and excited states to describe the dihedral rotation



Trans-cis isomerization in the ground and excited states using PLUMED

Different parallel bias metadynamics replica in ground and excited states.
To allow an energy overlaps in each electronic free-energy surfaces Replica Exchange Methods can be used and each replica can exchange its torsional potential.

Fortino, Cozza, Bonomi, Pietropaolo, J. Chem. Phys. 2021, 154, 174108.
Special collection in honor of women in Chemical Physics and Physical Chemistry.

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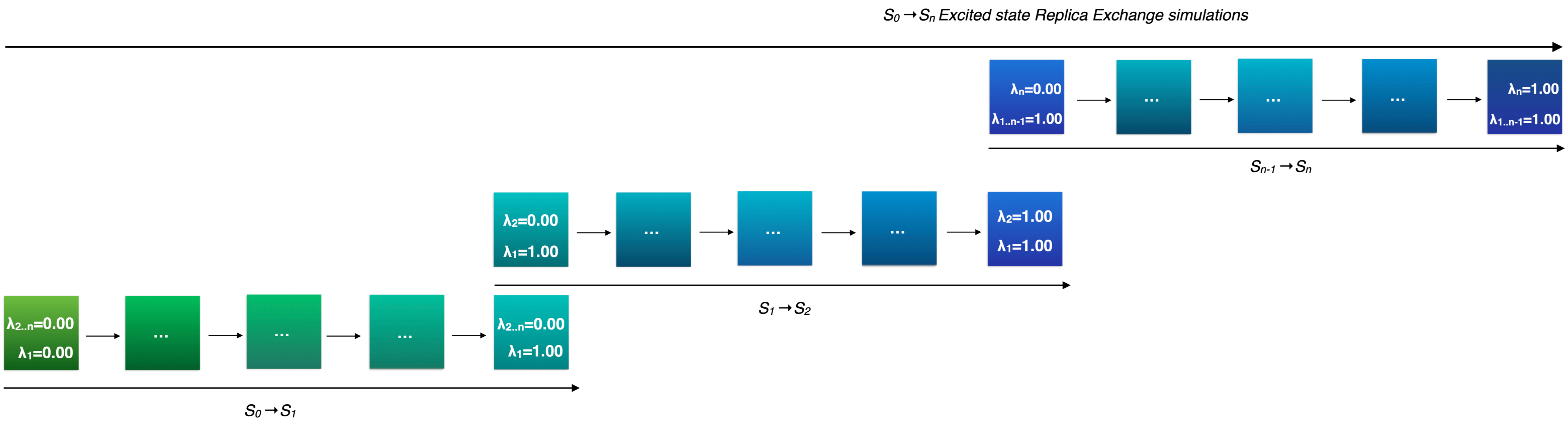
Replica Exchange Methods can be used and each replica can exchange its torsional potential.

$$V_\lambda(\varphi) = \sum_{m=1}^{N} \left[(1-\lambda_1)V^{S_0}(\varphi_m) + \lambda_1(1-\lambda_2)V^{S_1}(\varphi_m) + \cdots \lambda_{n-1}(1-\lambda_n)V^{S_{n-1}}(\varphi_m) + \lambda_n V^{S_n}(\varphi_m)\right]$$



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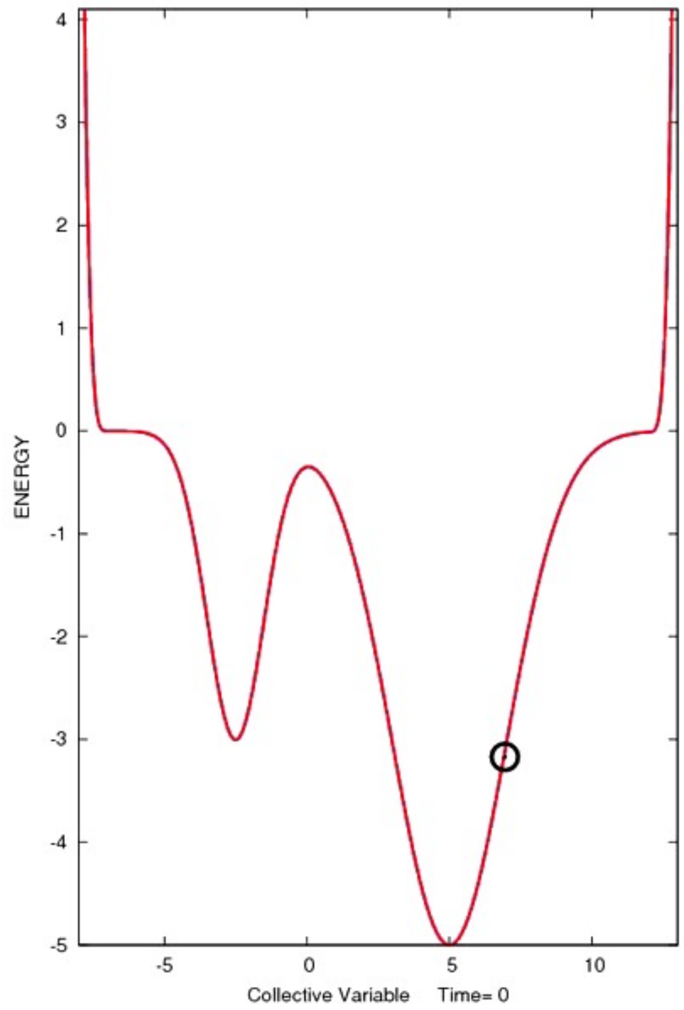
Parallel bias Metadynamics workflow can be used adding multiple mono-dimensional metadynamics bias potentials on specific CVs.

$$V_{PB}(\varphi_1, \dots \varphi_N; t) = -\frac{1}{\beta}\log\left(\sum_{i=1}^{N} e^{-\beta V_G(\varphi_i;t)}\right)$$

$$V_G(\varphi_i; t) = \int_{\mathbf{0}}^{\boldsymbol{t}} dt' \;\; \omega(t') \cdot \exp\left(-\frac{\left(\varphi_i(\boldsymbol{r}) - \varphi_i\left(\boldsymbol{r}(t')\right)\right)^2}{2\sigma_i^2}\right)$$



Laio, Parrinello PNAS 2002, 99 ,12562-12566

Pfaendtner, Bonomi J. Chem. Theory Comput. 2015, 11, 11, 5062–5067

Trans-cis isomerization in the ground and excited states using PLUMED

Finally, Free-energy perturbation was used together with Replica exchange and Parallel bias metadynamics to estimate the free-energy difference between ground and excited states.

$$\Delta F^{(\lambda_i+\Delta\lambda)} = -\frac{1}{\beta}\log\langle e^{-\beta(V_{\lambda_i+\Delta\lambda}-V_{\lambda_i})}\rangle_{\lambda_i}$$

$$\Delta F^{S_i \rightarrow S_{i+1}} = \sum_i \Delta F^{(\lambda_i+\Delta\lambda)}$$