Ab Initio Nuclear-Electronic Orbital Ehrenfest Dynamics

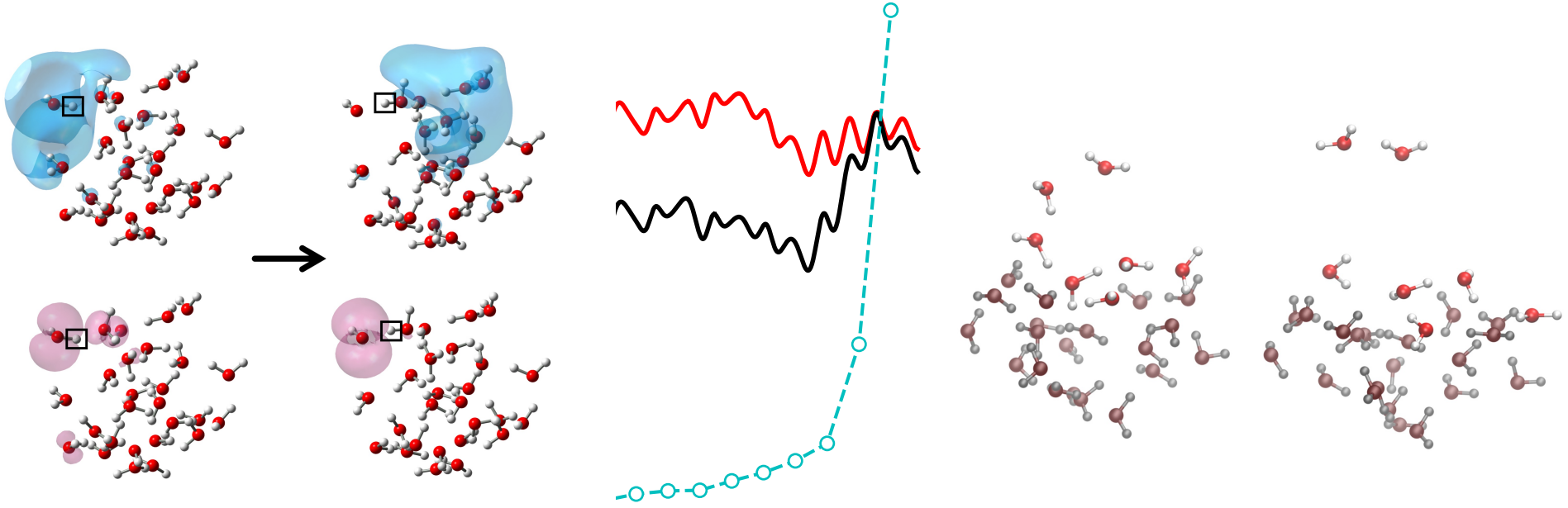
Li Research Group, University of Washington, Seattle UNIVERSITY of WASHINGTON

Photoexcitation Induced Proton Relay

Excited State BOMD

NAMD

Ground BOMD

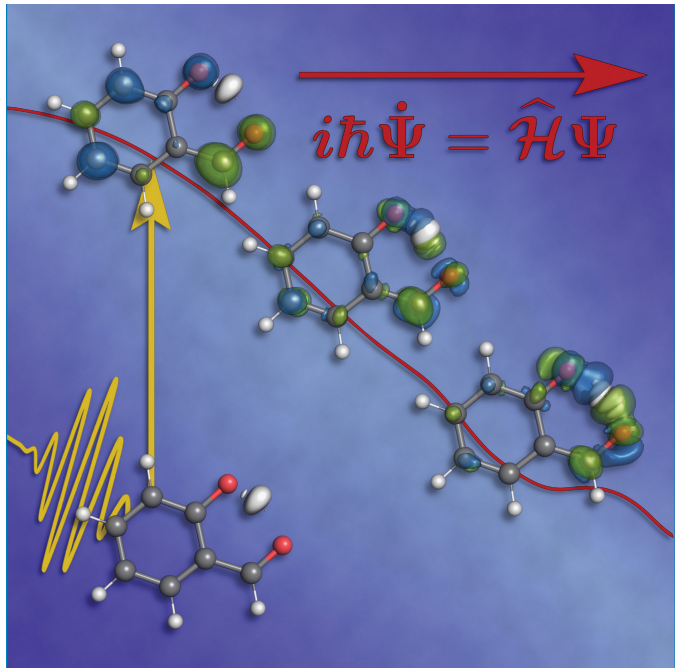


t = 0 fs ~10 fs ~130 fs ~200 fs ~300 fs

The Role of Excited State Proton Relays on the Photochemical Dynamics of Water Nanodroplets, T. F. Stetina, S. Sun, D. B. Lingerfelt, A. Clark, X. Li, J. Phys. Chem. Lett., 2019,*10*,3694-3698

Outline

- Time-Dependent Electronic Structure Theory
- Ab Initio Ehrenfest Dynamics
  - Electron, Hole, and Proton in Photochemical Processes of Water
- Ab Initio Nuclear-Electronic Orbital Ehrenfest Dynamics
  - Excited State Proton Transfer



Time-Dependent Electronic Structure Theory

- Non-relativistic $$i\frac{\partial}{\partial t}\mathbf{P} = [\mathbf{F}(t), \mathbf{P}(t)]$$

- Relativistic (2c) $$i\frac{\partial}{\partial t}\begin{pmatrix}\mathbf{P}_{\alpha\alpha}(t) & \mathbf{P}_{\alpha\beta}(t)\\ \mathbf{P}_{\beta\alpha}(t) & \mathbf{P}_{\beta\beta}(t)\end{pmatrix} = \left[\begin{pmatrix}\mathbf{F}_{\alpha\alpha}(t) & \mathbf{F}_{\alpha\beta}(t)\\ \mathbf{F}_{\beta\alpha}(t) & \mathbf{F}_{\beta\beta}(t)\end{pmatrix}, \begin{pmatrix}\mathbf{P}_{\alpha\alpha}(t) & \mathbf{P}_{\alpha\beta}(t)\\ \mathbf{P}_{\beta\alpha}(t) & \mathbf{P}_{\beta\beta}(t)\end{pmatrix}\right]$$

J. J. Goings, P. J. Lestrange, X. Li, "Real-Time Time-dependent Electronic Structure Theory," WIREs Comput. Mol. Sci., 2018, e1341
X. Li, N. Govind, C. Isborn, E. A. DePrince, K. Lopata, "Real-Time Time-dependent Electronic Structure Theory," Chem. Rev., 2020, 120, 9951.

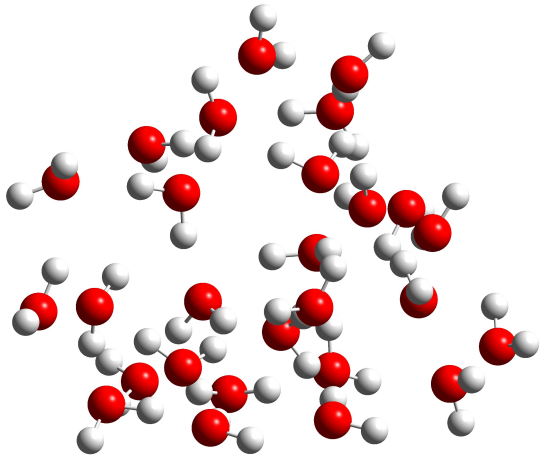
RT-TDDFT

$$\mathbf{C}^\dagger(t_n)\cdot\mathbf{F}(t_n)\cdot\mathbf{C}(t_n) = \boldsymbol{\epsilon}(t_n)$$
$$\mathbf{U}(t_n) = \exp\left[-i\cdot 2\Delta t\cdot\mathbf{F}(t_n)\right]$$
$$= \mathbf{C}(t_n)\cdot\exp\left[-i\cdot 2\Delta t\cdot\boldsymbol{\epsilon}(t_n)\right]\cdot\mathbf{C}^\dagger(t_n)$$
$$\mathbf{P}(t_{n+1}) = \mathbf{U}(t_n)\cdot\mathbf{P}(t_{n-1})\cdot\mathbf{U}^\dagger(t_n)$$

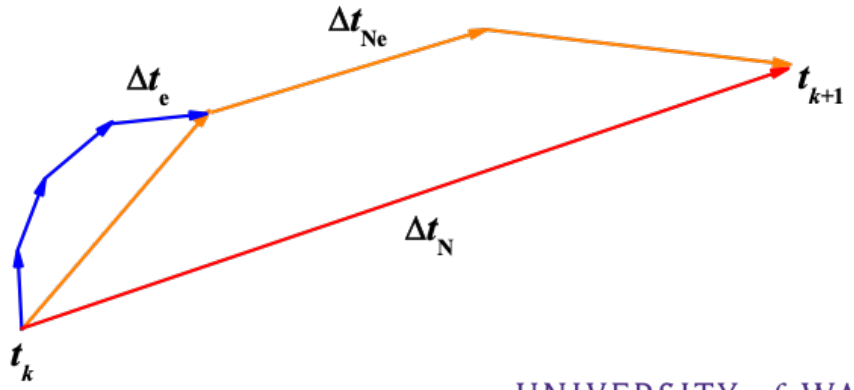
LR-TDDFT

$$\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B}^* & \mathbf{A}^*\end{pmatrix}\begin{pmatrix}X\\ Y\end{pmatrix} = \omega\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}X\\ Y\end{pmatrix}$$
$$A_{ai,bj} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ai||bj) + \frac{\partial^2 E_{\mathrm{xc}}}{\partial P_{\nu\mu}\partial P_{\lambda\kappa}}$$
$$B_{ai,bj} = (ai||jb)$$
$$(ai|bj) = \sum_{\substack{\sigma_1,\sigma_2,\sigma_3,\sigma_4=\alpha,\beta\\ \mu\nu\lambda\delta}} C^{*\sigma_1}_{\mu a}C^{*\sigma_2}_{\nu i}C^{\sigma_3}_{\lambda b}C^{\sigma_4}_{\delta j}(\mu\nu|\lambda\delta)$$

Radiolysis Induced "Hole" Dynamics



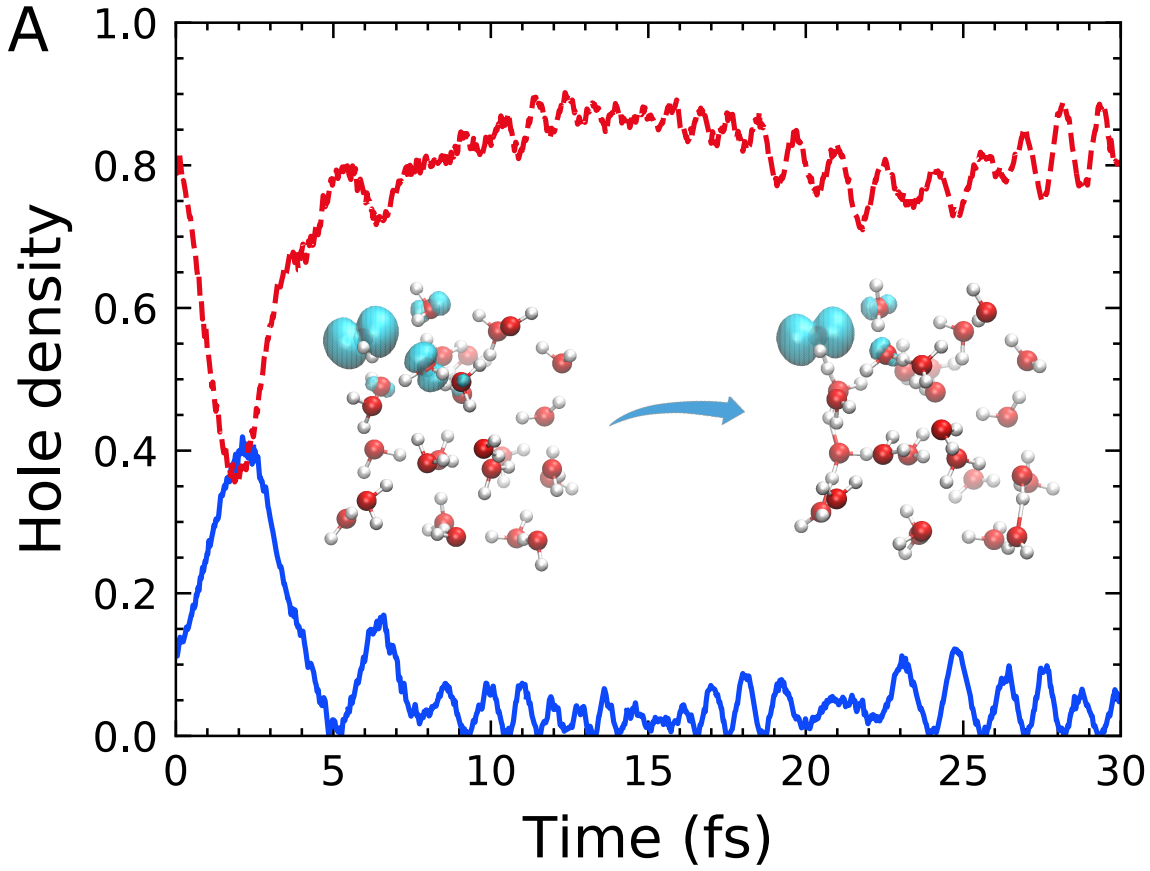
- 21 vibrationally bound initial conditions sampled from a 27-water nanodroplet ground state trajectory;
- Theories and methods
  - Ab initio on-the-fly Ehrenfest dynamics;
    - Triple-split operator method
    - $\Delta t_N = 0.0500$ fs, $\Delta t_{Ne} = 0.0050$ fs, $\Delta t_e = 0.0005$ fs
  - Real-time TDDFT with BH&H functional and 6-31G(d, p) basis
- Photoionization (*i.e.*, vertical ionization)
  - e^- removal from HOMO

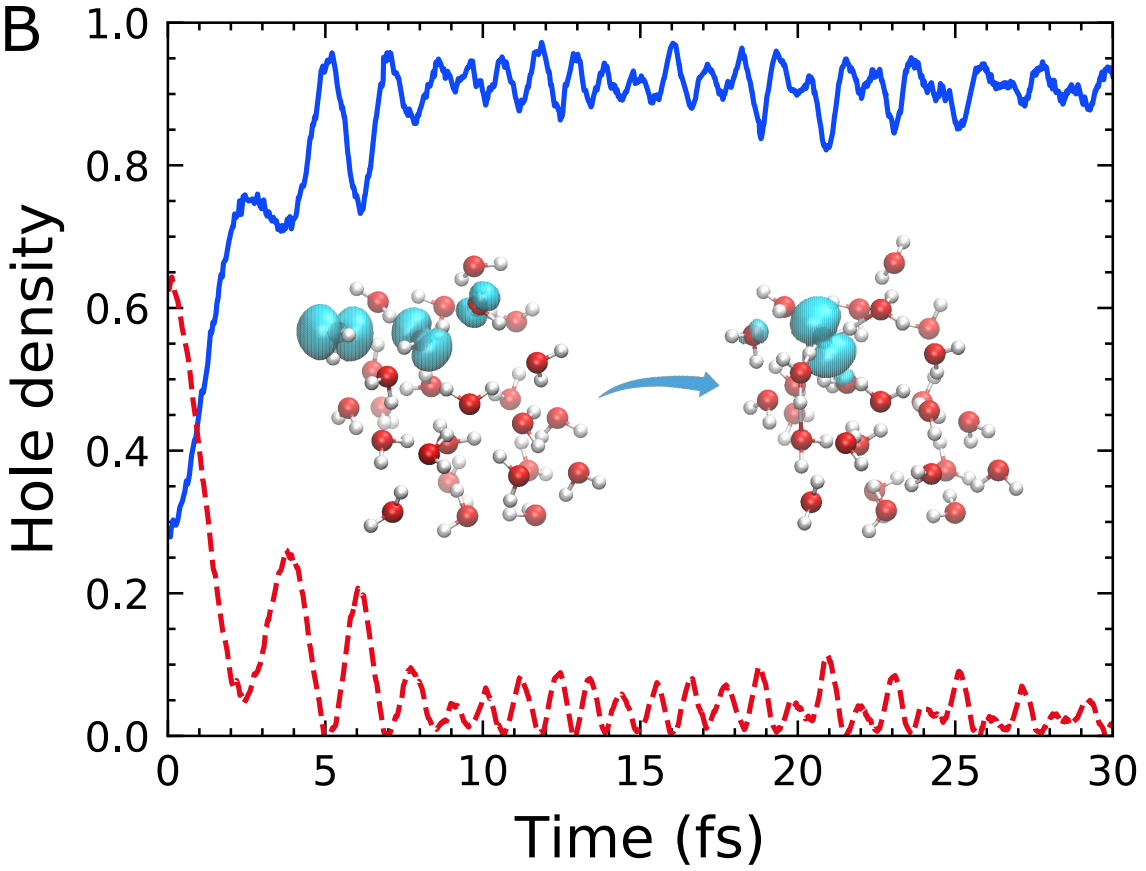


TDHF-Ehrenfest - J. Chem. Phys., 2005, 084106
TDDFT-Ehrenfest - J. Chem. Phys., 2007, 126, 134307
Two-Component Ehrenfest - J. Chem. Phys., 2015, 143, 114105.

“Hole” Dynamics – Trapping vs. Transfer

- Hole localization takes place within 10 fs; irreversible due to molecular motion
- Hole trapping ~70%; Hole transfer ~20%

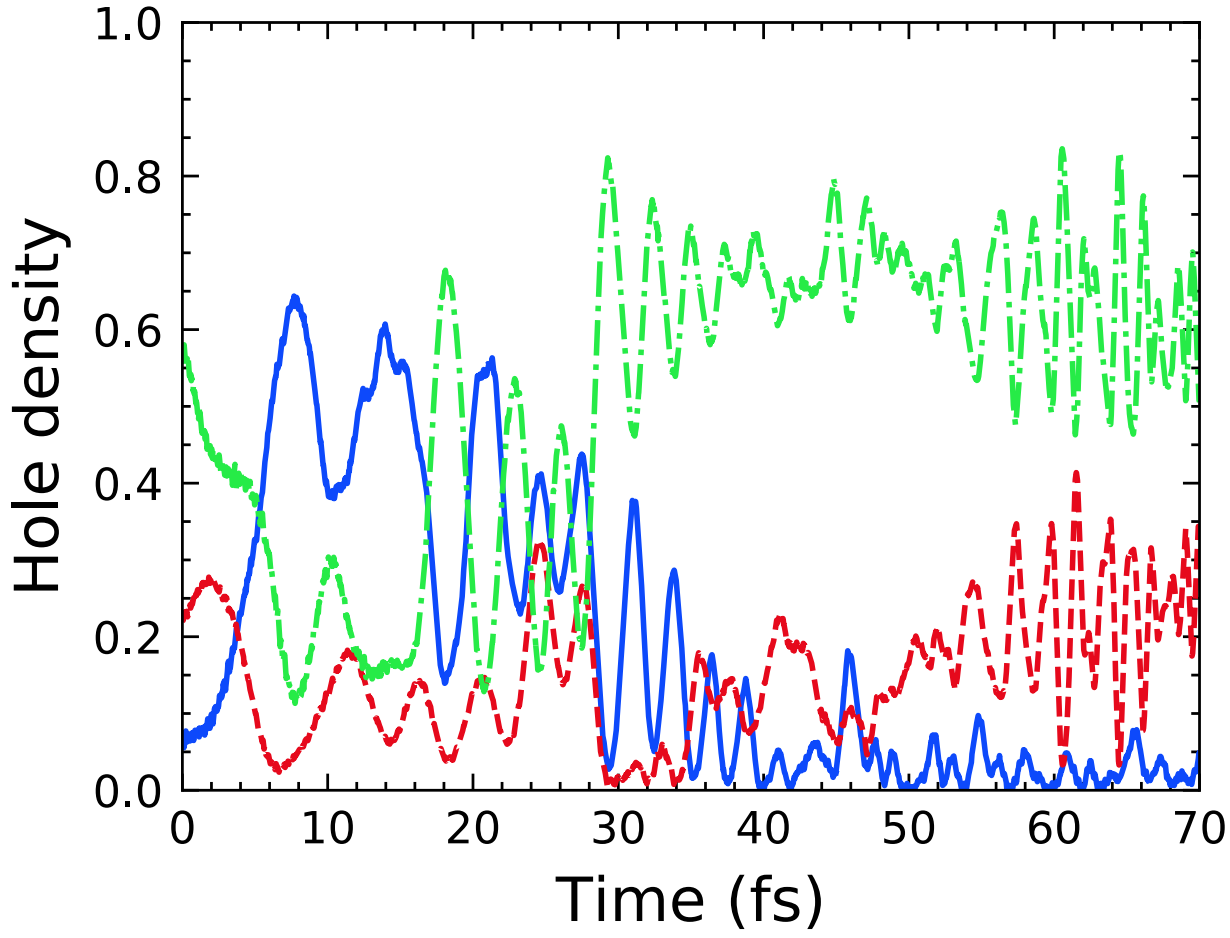




The “Hole” Story in Ionized Water from the Perspective of Ehrenfest Dynamics
Lu, L; Wildman, A; Jenkins, A; Young, L; Clark, A; Li, X, J. Phys. Chem. Lett.2020,*11*,9946-9951

“Hole” Dynamics – Long-lived Coherence

- Two trajectories exhibit long-lived coherence
  - More prominent in low-temperature?



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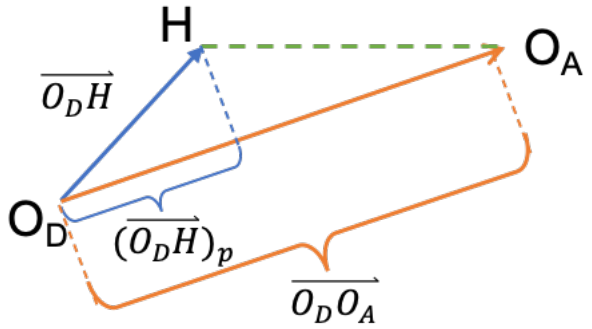
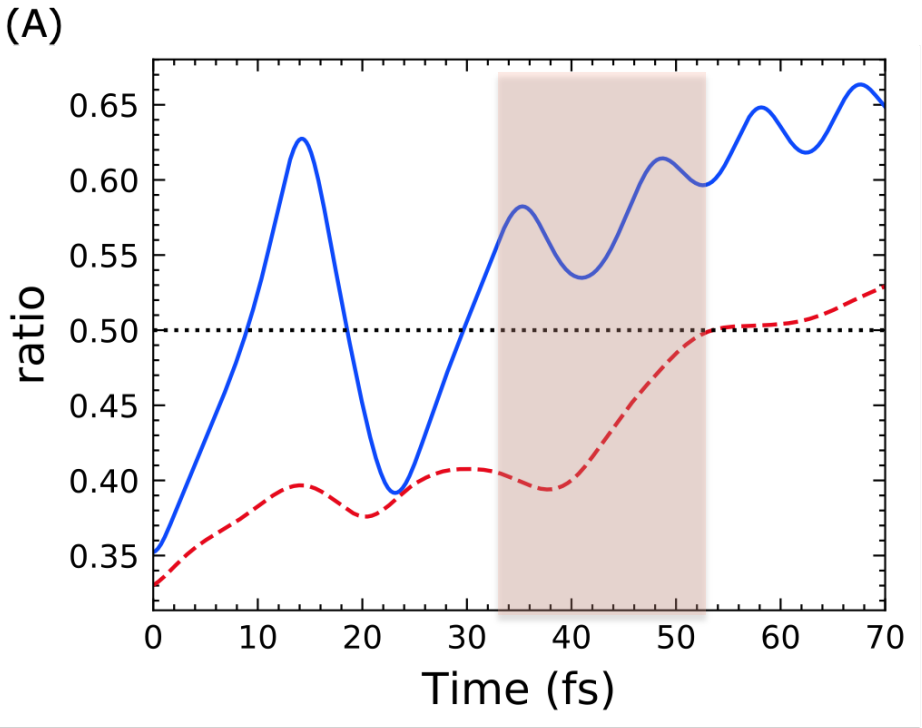
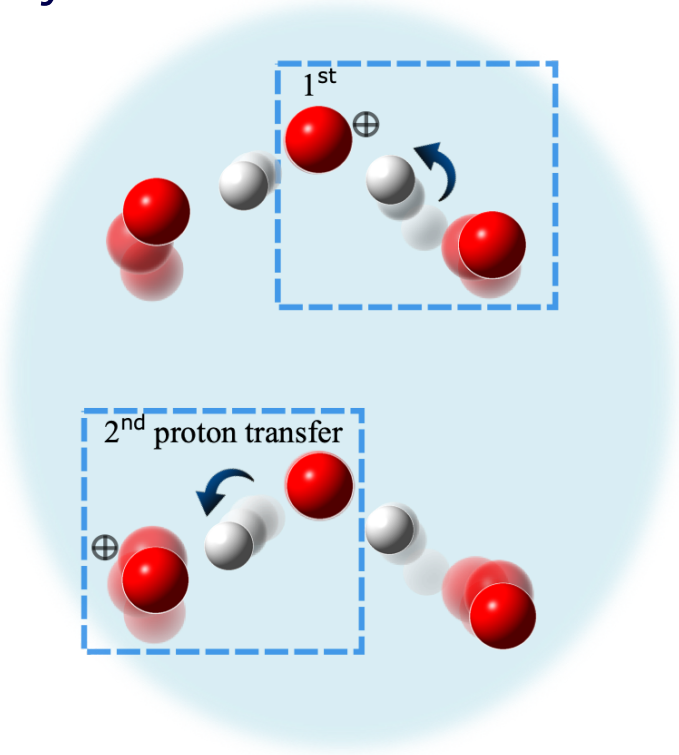
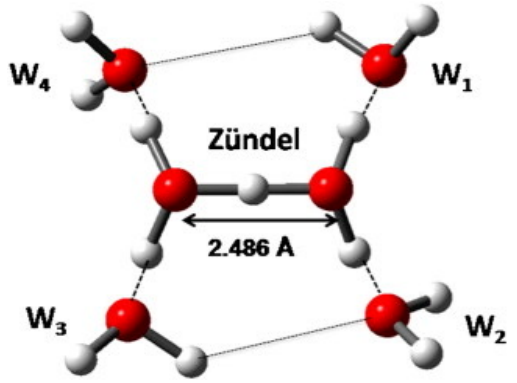
"Hole" Dynamics – Proton Transfer

- Most OH vibrations exhibit larger vibrational amplitude
- Proton transfer ~76% within 30-40 fs
- Radiolysis induced proton relay









Zundel complex formed as intermediate

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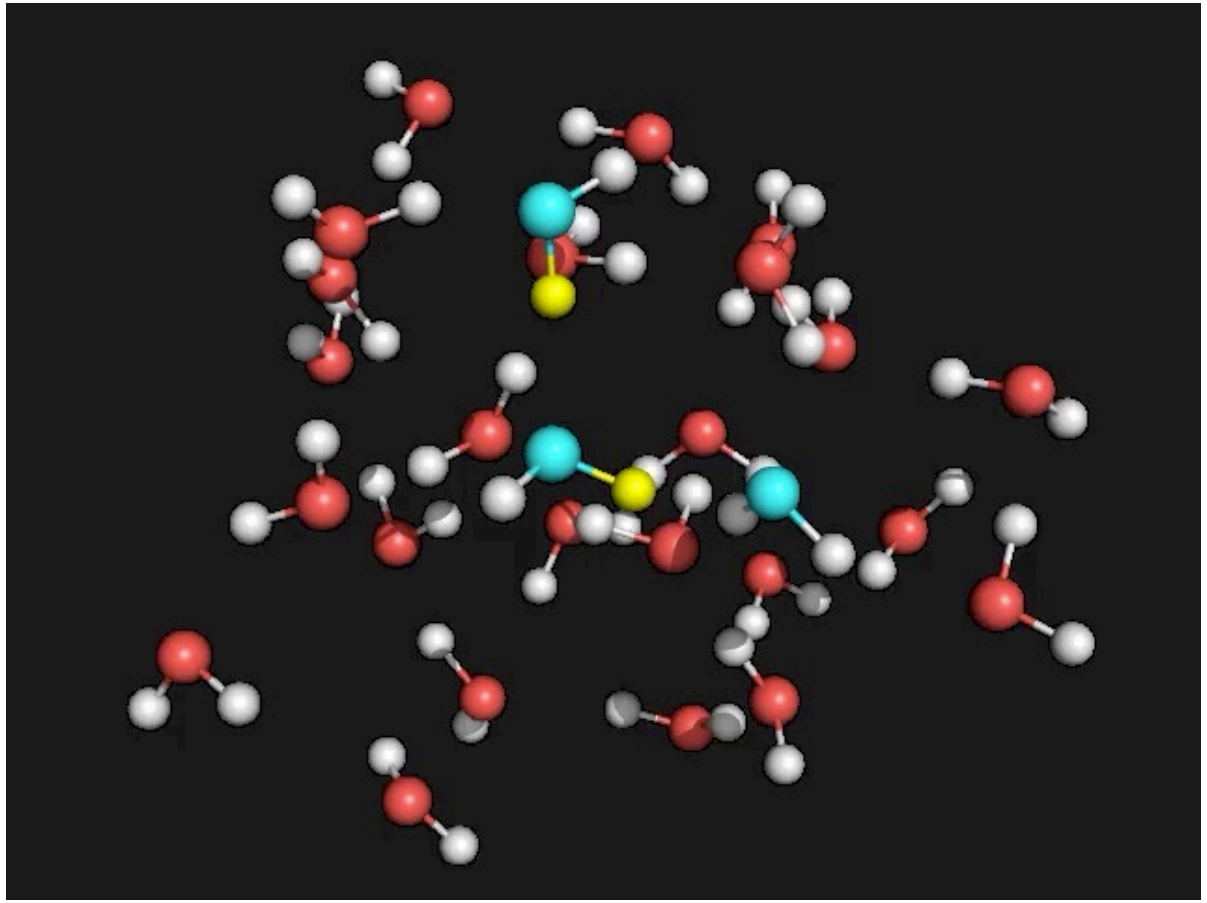
"Hole" Dynamics – Radiolysis Induced Proton Relay

- Radiolysis induced proton relay is asynchronous
  - Photoexcited proton relay is mostly synchronous



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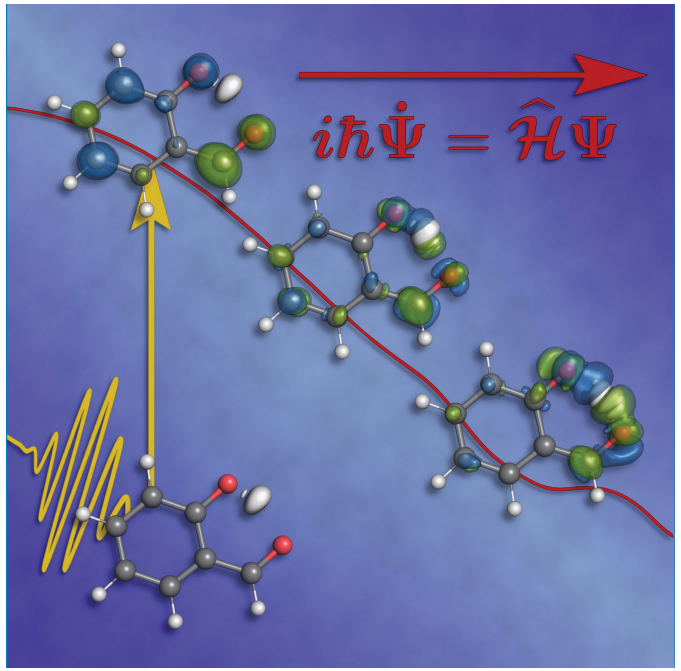


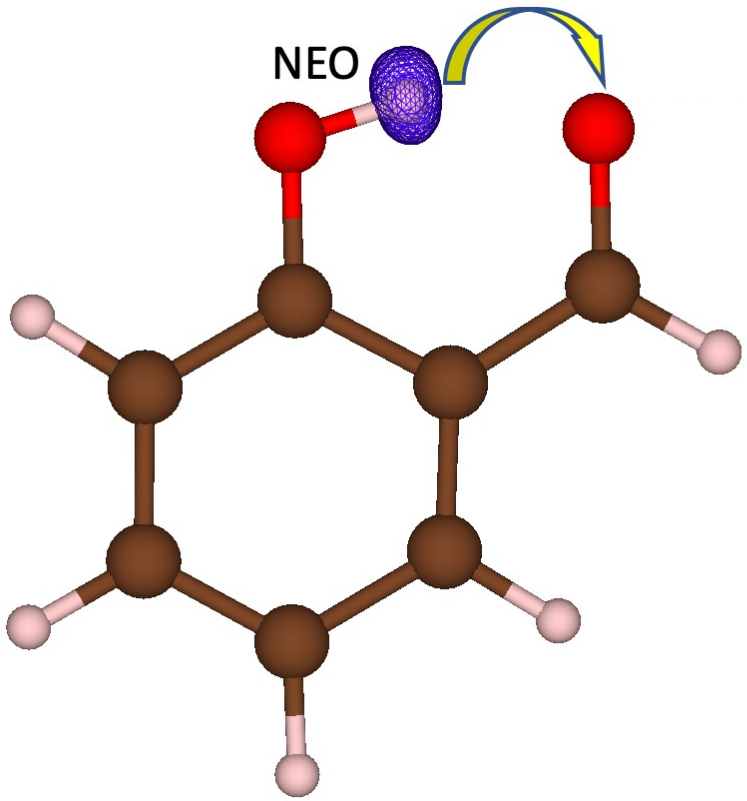
Nuclear-Electronic Orbital (NEO)

– Li/Hammes-Schiffer Collaboration

$$\Psi_{\mathrm{NEO}}(\mathbf{r}^{\mathrm{e}},\mathbf{r}^{\mathrm{p}};t)=\Phi^{\mathrm{e}}(\mathbf{r}^{\mathrm{e}};t)\Phi^{\mathrm{p}}(\mathbf{r}^{\mathrm{p}};t)$$

$$i\hbar\frac{\partial}{\partial t}\Psi_{\mathrm{NEO}}(\mathbf{r}^{\mathrm{e}},\mathbf{r}^{\mathrm{p}};t)=\mathrm{H}(\mathbf{r}^{\mathrm{r}},\mathbf{r}^{\mathrm{p}};t)\Psi_{\mathrm{NEO}}(\mathbf{r}^{\mathrm{e}},\mathbf{r}^{\mathrm{p}};t)$$

$$E=\mathrm{Tr}[\mathbf{h}^{\mathrm{e}\prime}\mathbf{P}^{\mathrm{e}\prime}]+\mathrm{Tr}[\mathbf{h}^{\mathrm{p}\prime}\mathbf{P}^{\mathrm{p}\prime}]+\frac{1}{2}\mathrm{Tr}[\mathbf{J}^{\mathrm{ee}\prime}\mathbf{P}^{\mathrm{e}\prime}]+\frac{1}{4}\mathrm{Tr}[\xi\mathbf{K}^{\mathrm{ee}\prime}\mathbf{P}^{\mathrm{e}\prime}]$$
$$+\frac{1}{2}\mathrm{Tr}[\mathbf{J}^{\mathrm{pp}\prime}\mathbf{P}^{\mathrm{p}\prime}]+\frac{1}{2}\mathrm{Tr}[\mathbf{K}^{\mathrm{pp}\prime}\mathbf{P}^{\mathrm{p}\prime}]-\mathrm{Tr}[\mathbf{J}^{\mathrm{ep}\prime}\mathbf{P}^{\mathrm{p}\prime}]$$
$$+(1-\xi)E_{\mathrm{xc}}^{\mathrm{ee}}[\mathbf{P}^{\mathrm{e}\prime}]+(1-\xi)E_{\mathrm{c}}^{\mathrm{ep}}[\mathbf{P}^{\mathrm{e}\prime},\mathbf{P}^{\mathrm{p}\prime}]+V_{\mathrm{NN}}$$



F. Pavosevic,T. Culpitt, and S.Hammes-Schiffer, "**Multi-component quantum chemistry: Integrating electronic and nuclear quantum effects via the nuclear-electronic orbital method**," Chem. Rev. 120, 4222–4253 (2020)

Time-Dependent NEO Theory

– Li/Hammes-Schiffer Collaboration

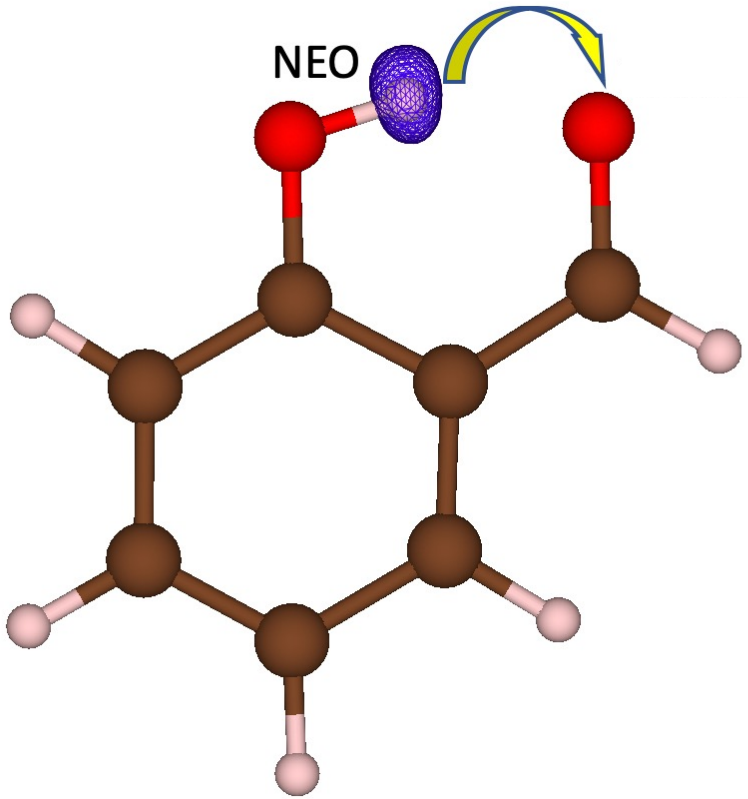
- Multi-component Runge-Gross Theory: There exist a non-interacting, time-dependent electron-proton system that produces the same density as the interacting system at any time *t*.

$$i\hbar\frac{\partial}{\partial t}\mathbf{P}^{\mathrm{e}}(t) = [\mathbf{F}^{\mathrm{e}}(t,\mathbf{P}^{\mathrm{e}}(t),\mathbf{P}^{\mathrm{p}}(t)),\mathbf{P}^{\mathrm{e}}(t)]$$

$$i\hbar\frac{\partial}{\partial t}\mathbf{P}^{\mathrm{p}}(t) = [\mathbf{F}^{\mathrm{p}}(t,\mathbf{P}^{\mathrm{p}}(t),\mathbf{P}^{\mathrm{e}}(t)),\mathbf{P}^{\mathrm{p}}(t)]$$

$$\mathbf{F}^{\mathrm{e}}(t) = \mathbf{H}^{\mathrm{ee}}(t,\mathbf{P}^{\mathrm{e}}(t)) + \mathbf{H}^{\mathrm{ep}}(\mathbf{P}^{\mathrm{e}}(t),\mathbf{P}^{\mathrm{p}}(t))$$

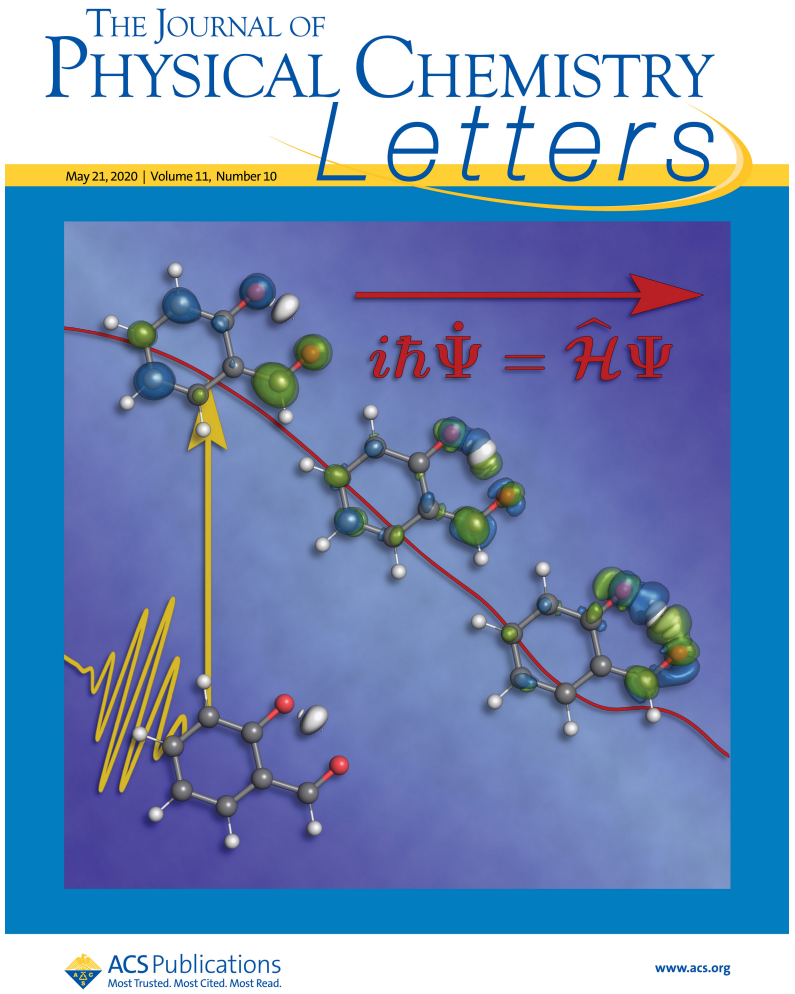
$$\mathbf{F}^{\mathrm{p}}(t) = \mathbf{H}^{\mathrm{pp}}(t,\mathbf{P}^{\mathrm{p}}(t)) + \mathbf{H}^{\mathrm{pe}}(\mathbf{P}^{\mathrm{p}}(t),\mathbf{P}^{\mathrm{e}}(t))$$

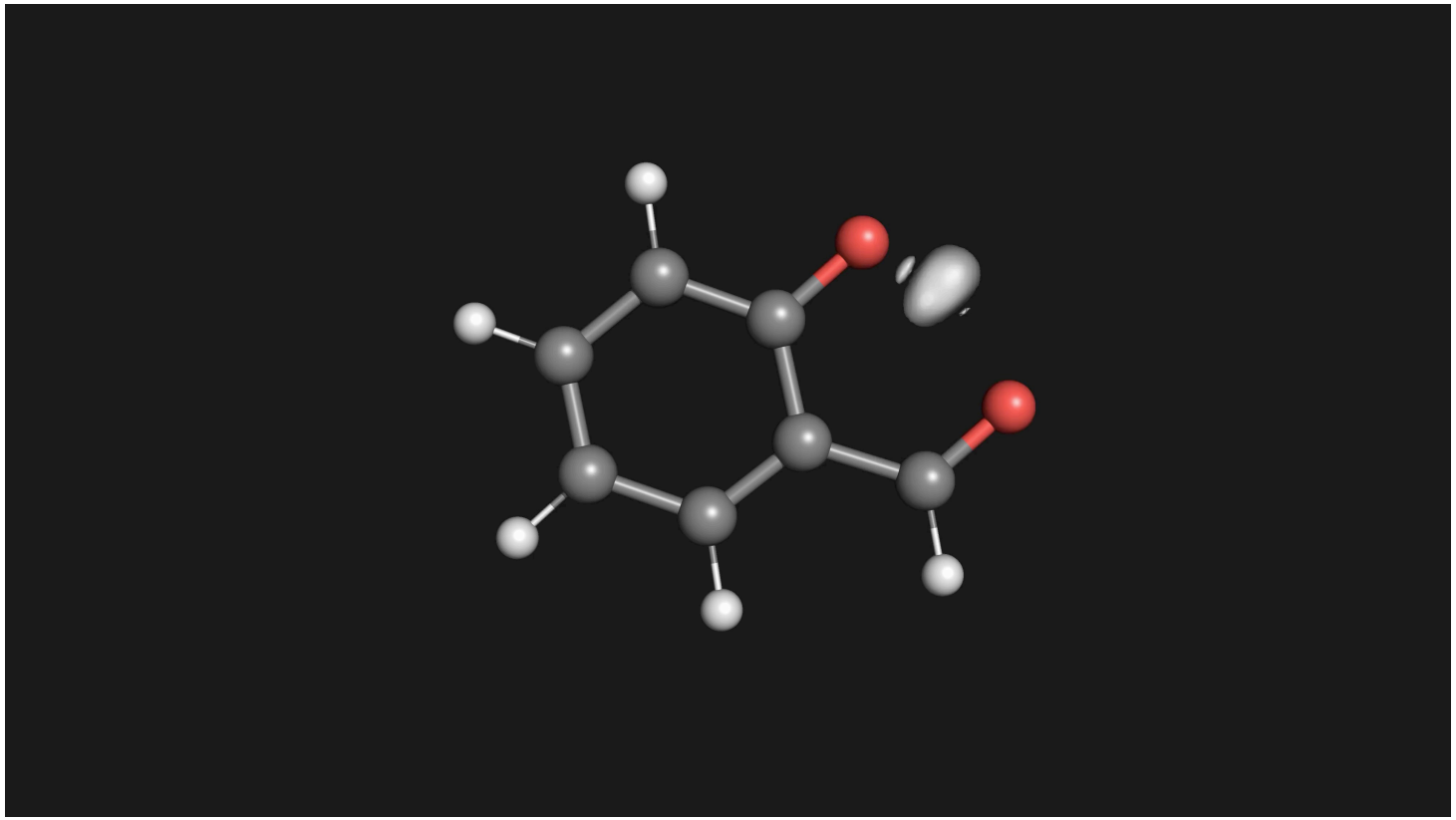


Real-Time Time-Dependent Nuclear-Electronic Orbital Approach: Dynamics Beyond the Born-Oppenheimer Approximation, L. Zhao, Z. Tao, F. Pavosevic, A. Wildman, S. Hammes-Schiffer, X. Li, J. Phys. Chem. Lett., 2020, *11*, 4052-4058

Time-Dependent NEO

– Li/Hammes-Schiffer Collaboration





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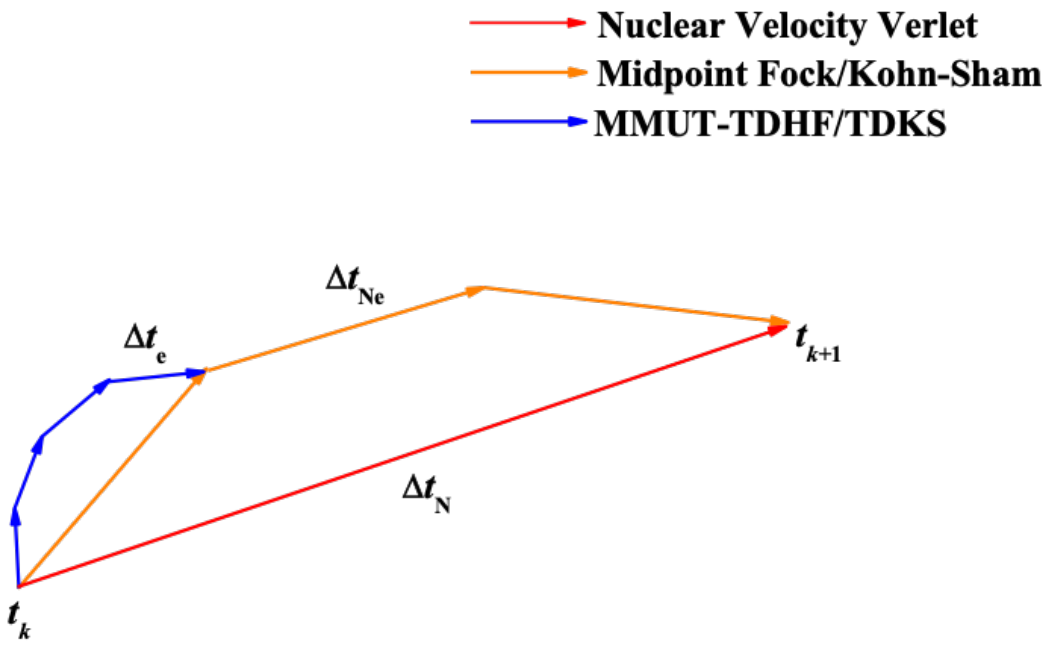
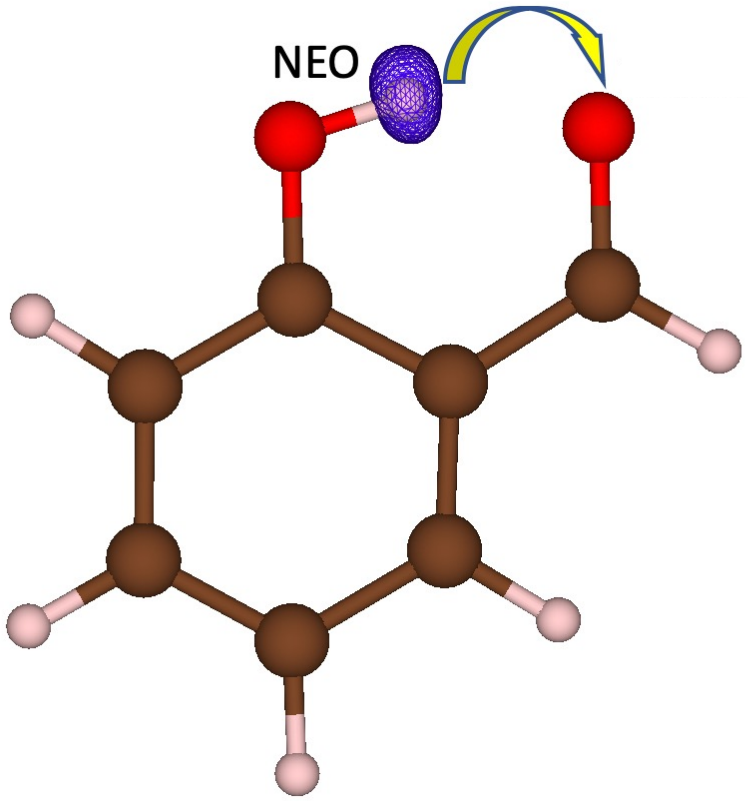
NEO-Ehrenfest Dynamics

– Li/Hammes-Schiffer Collaboration

$$\frac{\partial E}{\partial x_A} = \frac{\partial E}{\partial x_A}\bigg|_{\mathbf{P}^{e\prime},\mathbf{P}^{p\prime}} + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{e\prime}}\bigg|_{\mathbf{P}^{p\prime}} \frac{\partial \mathbf{P}^{e\prime}}{\partial x_A}\right] + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{p\prime}}\bigg|_{\mathbf{P}^{e\prime}} \frac{\partial \mathbf{P}^{p\prime}}{\partial x_A}\right]$$





MMUT Integrator - Phys. Chem. Chem. Phys.2005, *7*,233
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NEO-Ehrenfest Dynamics

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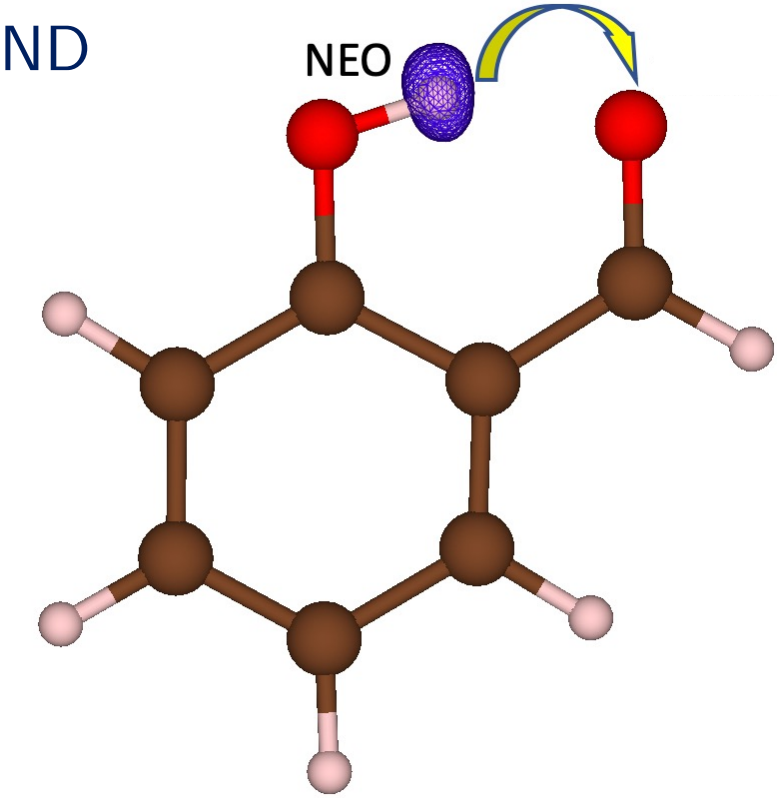
$$\frac{\partial E}{\partial x_A} = \frac{\partial E}{\partial x_A}\bigg|_{\mathbf{P}^{\mathrm{e}\prime},\mathbf{P}^{\mathrm{p}\prime}} + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{\mathrm{e}\prime}}\bigg|_{\mathbf{P}^{\mathrm{p}\prime}} \frac{\partial \mathbf{P}^{\mathrm{e}\prime}}{\partial x_A}\right] + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{\mathrm{p}\prime}}\bigg|_{\mathbf{P}^{\mathrm{e}\prime}} \frac{\partial \mathbf{P}^{\mathrm{p}\prime}}{\partial x_A}\right]$$

- What if we have an adequate number of protonic bases AND know the trajectory of the proton?

$$i\hbar\frac{\partial}{\partial t}\mathbf{P}^{\mathrm{e}}(t) = [\mathbf{F}^{\mathrm{e}}(t,\mathbf{P}^{\mathrm{e}}(t),\mathbf{P}^{\mathrm{p}}(t)),\mathbf{P}^{\mathrm{e}}(t)]$$

$$i\hbar\frac{\partial}{\partial t}\mathbf{P}^{\mathrm{p}}(t) = [\mathbf{F}^{\mathrm{p}}(t,\mathbf{P}^{\mathrm{p}}(t),\mathbf{P}^{\mathrm{e}}(t)),\mathbf{P}^{\mathrm{p}}(t)]$$



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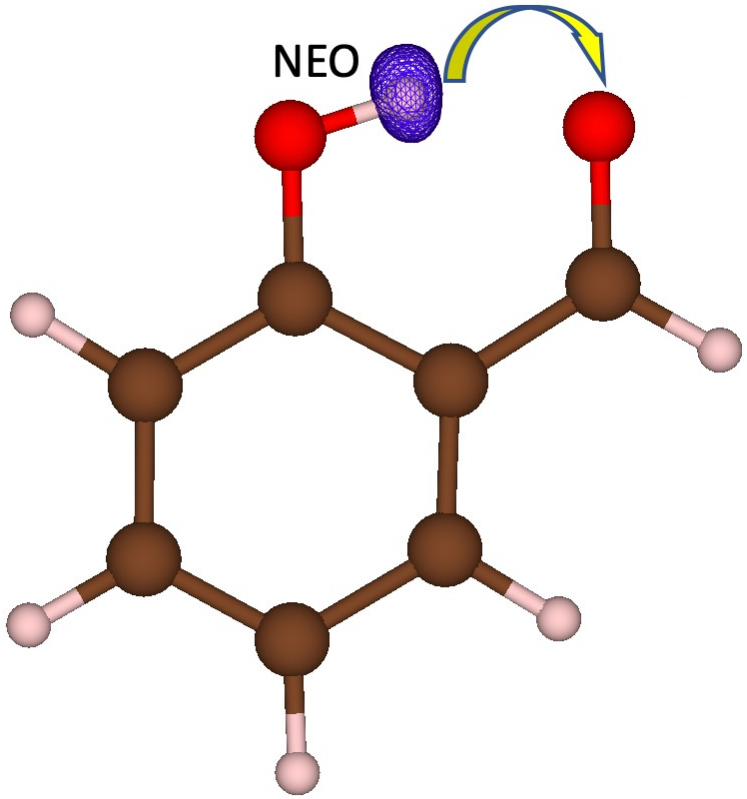
NEO-Ehrenfest Dynamics

– Li/Hammes-Schiffer Collaboration

$$\frac{\partial E}{\partial x_A} = \frac{\partial E}{\partial x_A}\bigg|_{\mathbf{P}^{\mathrm{e}\prime},\mathbf{P}^{\mathrm{p}\prime}} + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{\mathrm{e}\prime}}\bigg|_{\mathbf{P}^{\mathrm{p}\prime}} \frac{\partial \mathbf{P}^{\mathrm{e}\prime}}{\partial x_A}\right] + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{\mathrm{p}\prime}}\bigg|_{\mathbf{P}^{\mathrm{e}\prime}} \frac{\partial \mathbf{P}^{\mathrm{p}\prime}}{\partial x_A}\right]$$

- In reality, it is not possible to predict the long-time evolution of the chemical processes associated with proton.
  - This is also true for electronic degrees of freedom when there is no clear bound of the dynamics.
- What if we can predict the short-time protonic position?



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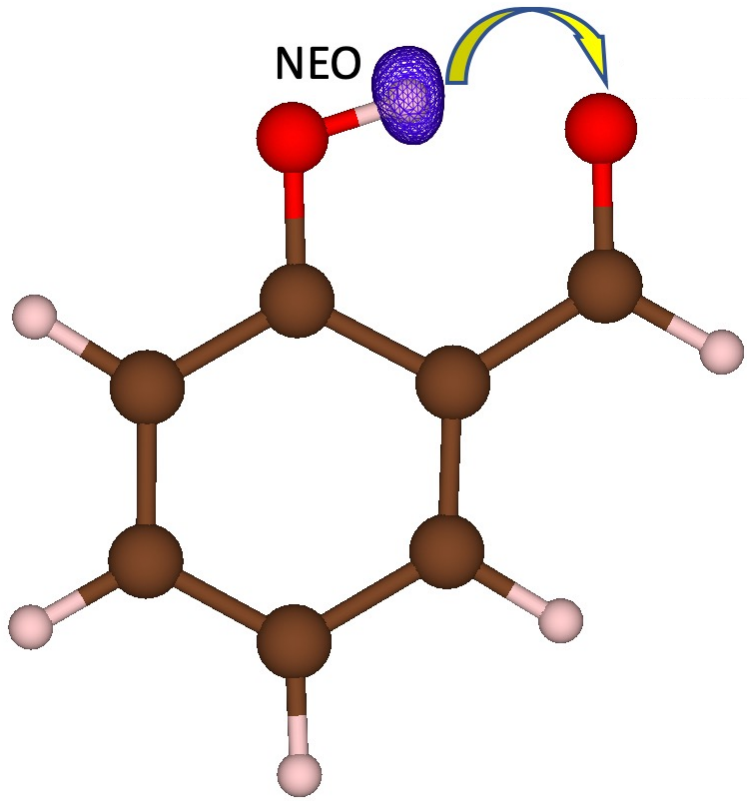
- Travelling Proton Basis (TPB)

$$\begin{aligned} i\frac{\partial}{\partial t}\mathbf{P}^{\mathrm{p}} &= \left(\mathbf{F}^{\mathrm{p}} - i\boldsymbol{\tau}\right)\mathbf{P}^{\mathrm{p}} - \mathbf{P}^{\mathrm{p}}\left(\mathbf{F}^{\mathrm{p}} + i\boldsymbol{\tau}^{\dagger}\right) \\ &= \left[\mathbf{F}^{\mathrm{p}}, \mathbf{P}^{\mathrm{p}}\right] - i\left(\boldsymbol{\tau}\mathbf{P}^{\mathrm{p}} + \mathbf{P}^{\mathrm{p}}\boldsymbol{\tau}^{\dagger}\right) \end{aligned}$$

$$\tau_{QP} = \left\langle \phi_Q^{\mathrm{p}} \middle| \frac{\partial}{\partial t} \middle| \phi_P^{\mathrm{p}} \right\rangle = \sum_{\alpha=x,y,z} \left\langle \phi_P^{\mathrm{p}} \middle| \frac{\partial \phi_Q^{\mathrm{p}}}{\partial \mathcal{R}_Q^{\alpha}} \right\rangle \dot{\mathcal{R}}_P^{\alpha}$$



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NEO-Ehrenfest Dynamics

– Li/Hammes-Schiffer Collaboration

$$\frac{\partial E}{\partial x_A} = \frac{\partial E}{\partial x_A}\bigg|_{\mathbf{P}^{\mathrm{e}\prime},\mathbf{P}^{\mathrm{p}\prime}} + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{\mathrm{e}\prime}}\bigg|_{\mathbf{P}^{\mathrm{p}\prime}} \frac{\partial \mathbf{P}^{\mathrm{e}\prime}}{\partial x_A}\right] + \mathrm{Tr}\left[\frac{\partial E}{\partial \mathbf{P}^{\mathrm{p}\prime}}\bigg|_{\mathbf{P}^{\mathrm{e}\prime}} \frac{\partial \mathbf{P}^{\mathrm{p}\prime}}{\partial x_A}\right]$$

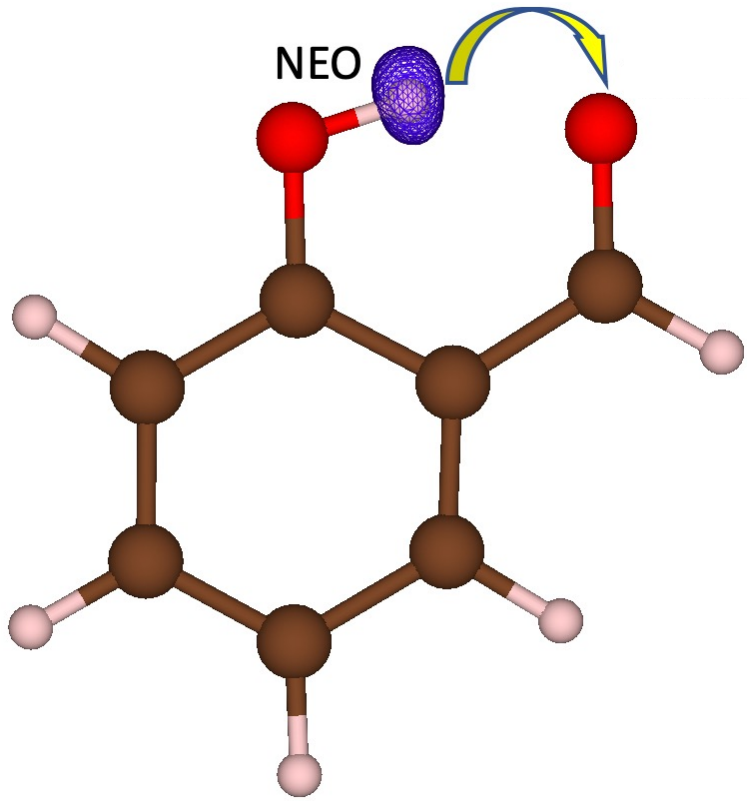
- Travelling Proton Basis (TPB)

$$\tau_{QP} = \left\langle \phi_Q^{\mathrm{p}} \middle| \frac{\partial}{\partial t} \middle| \phi_P^{\mathrm{p}} \right\rangle = \sum_{\alpha=x,y,z} \left\langle \phi_P^{\mathrm{p}} \middle| \frac{\partial \phi_Q^{\mathrm{p}}}{\partial \mathcal{R}_Q^\alpha} \right\rangle \dot{\mathcal{R}}_P^\alpha$$

  - Semi-classical approximation using a fictitious proton mass

$$\tilde{m}_{\mathrm{p}} \ddot{\mathcal{R}} = -\nabla E$$

    - m_{p} = real proton mass



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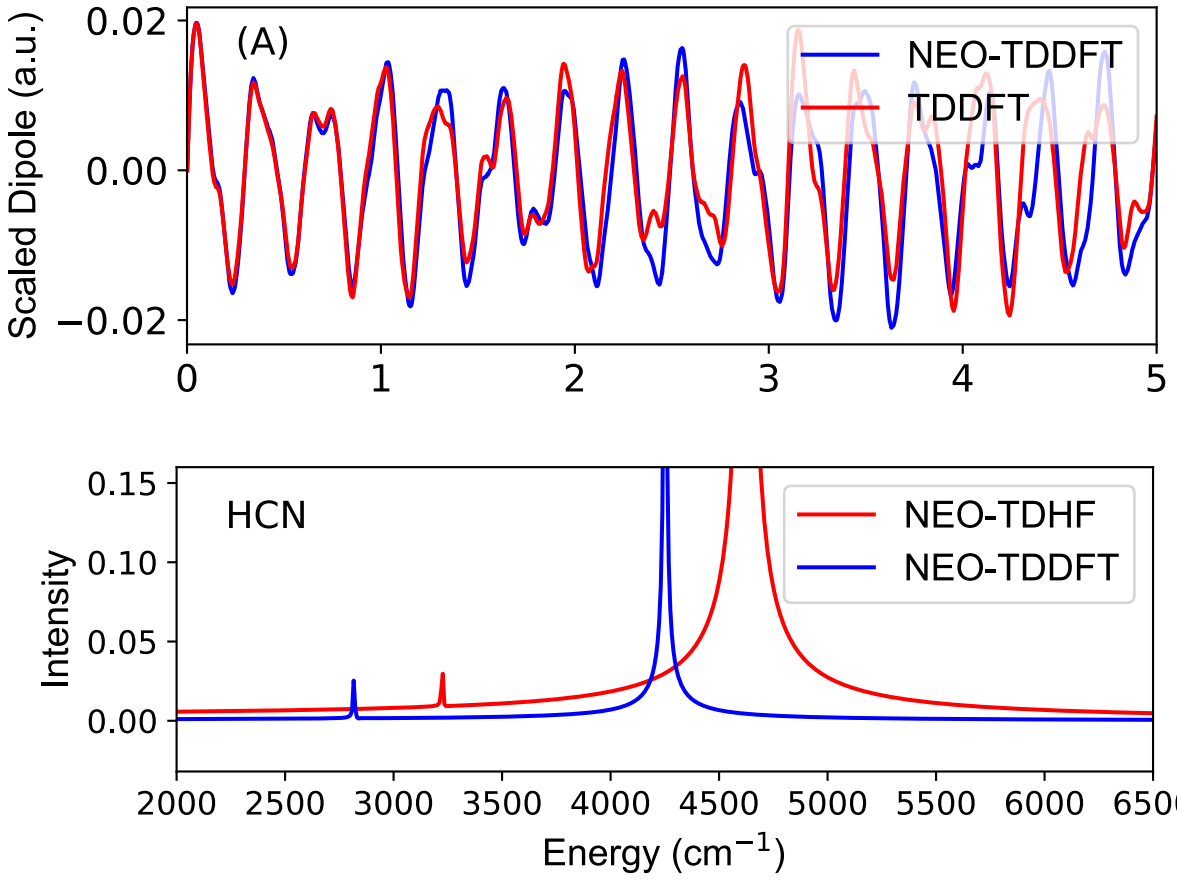
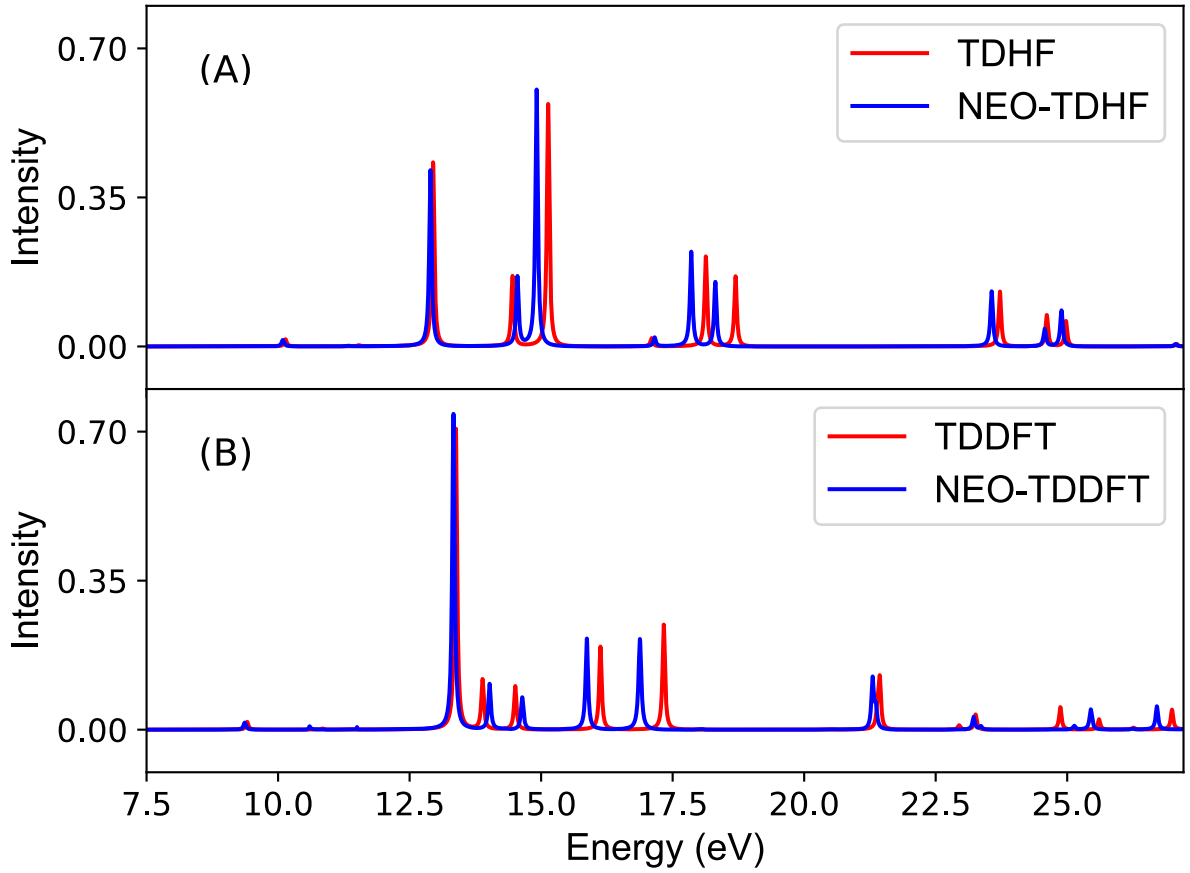
NEO-Ehrenfest Dynamics – Near Equilibrium Condition

– Li/Hammes-Schiffer Collaboration





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NEO-Ehrenfest Dynamics – Near Equilibrium Condition

– Li/Hammes-Schiffer Collaboration

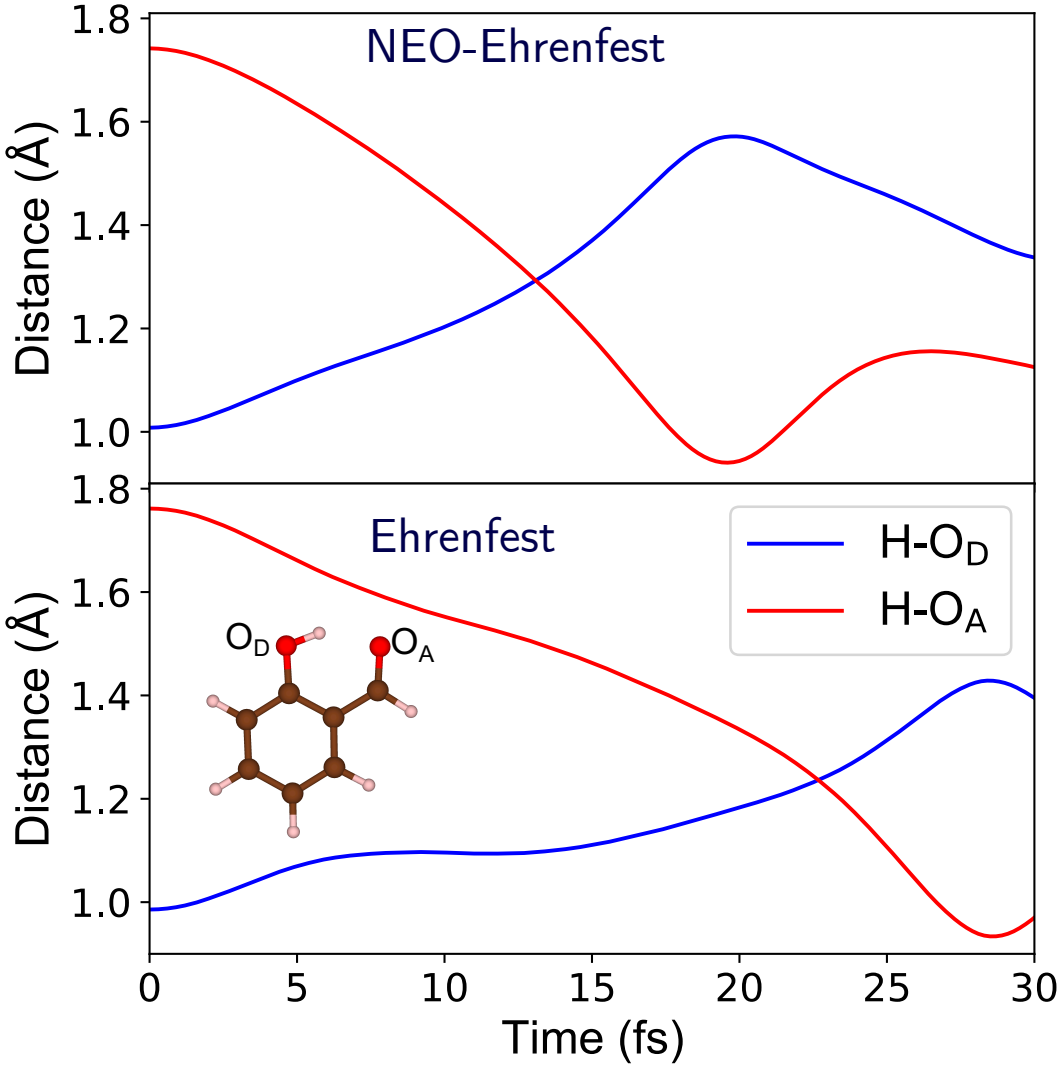
TABLE I. Vibrational frequencies (in cm^{-1}) calculated using NEO-TDHF-Ehrenfest with Fixed Proton Basis (FPB) and Traveling Proton Basis (TPB) functions compared to NEO-HF(V) and VPT2.

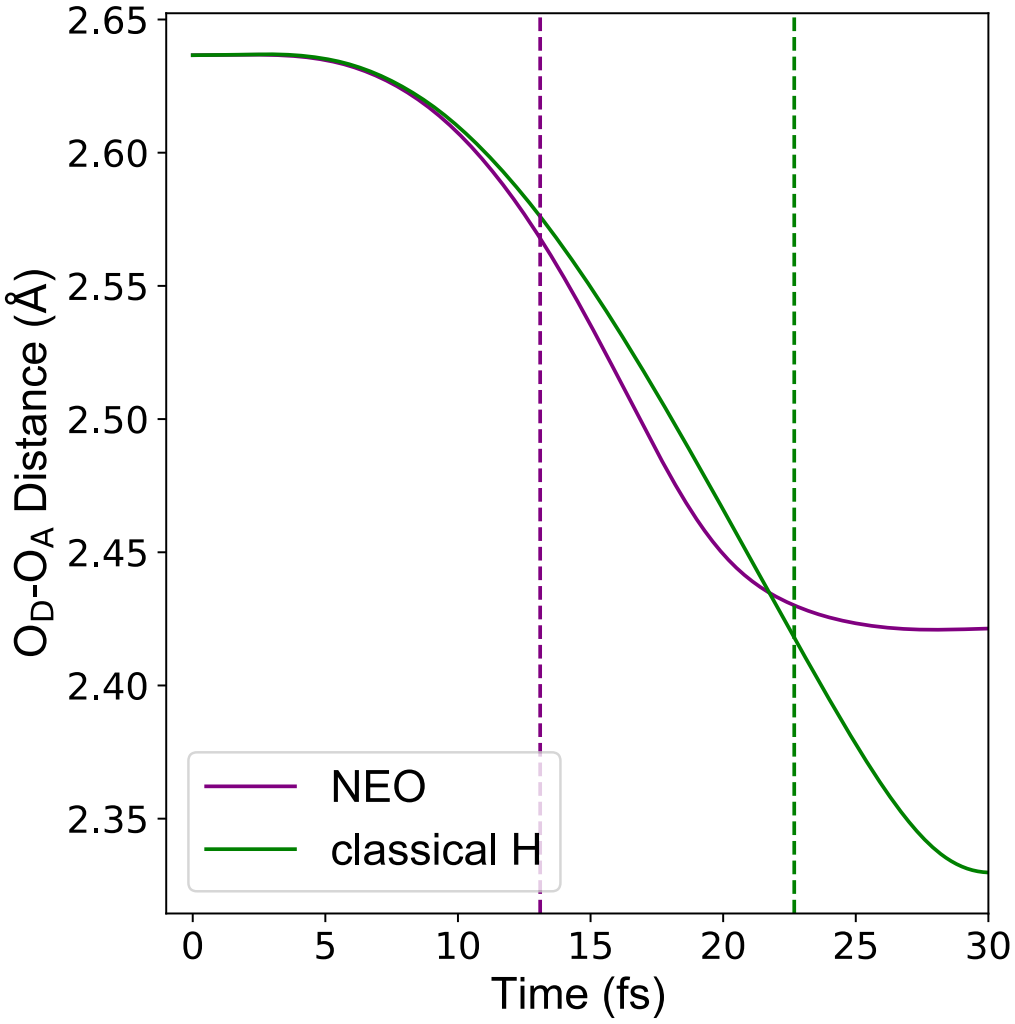
	vibrational mode	FPB	TPB	NEO-HF(V)[a]	NEO-HF(V)-aug[b]	VPT2
HCN	CH stretch	3620	3483	3618	3456	3514
	CH bend	1294	1131	1473	883	846
	CN stretch	2446	2405	2417	2407	2397
HNC	NH stretch	4009	3867	3994	3841	3879
	NH bend	1214	1057	1257	594	485
	NC stretch	2304	2296	2293	2290	2262
FHF^-	FH stretch	1741	1644	1728	1518	1636
	FH bend	1622	1482	1617	1417	1412
	FF stretch	675	689	686	686	548

NEO-Ehrenfest Dynamics, L. Zhao, A. Wildman, Z. Tao, P. Schneider, S. Hammes-Schiffer, and X. Li, J. Chem. Phys., 2020, *153*, 224111

NEO-Ehrenfest Dynamics – Non-Equilibrium Condition

– Li/Hammes-Schiffer/Tully Collaboration





S. Hammes-Schiffer, J. C. Tully, X. Li, in press.

NEO-Ehrenfest Dynamics – Non-Equilibrium Condition

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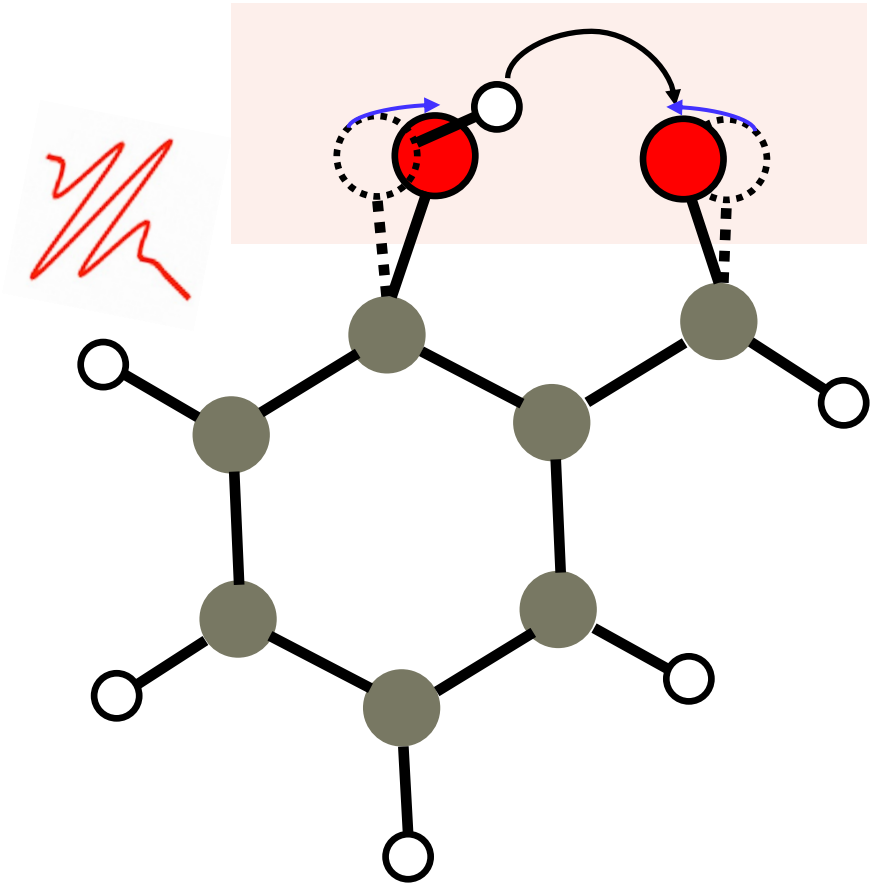

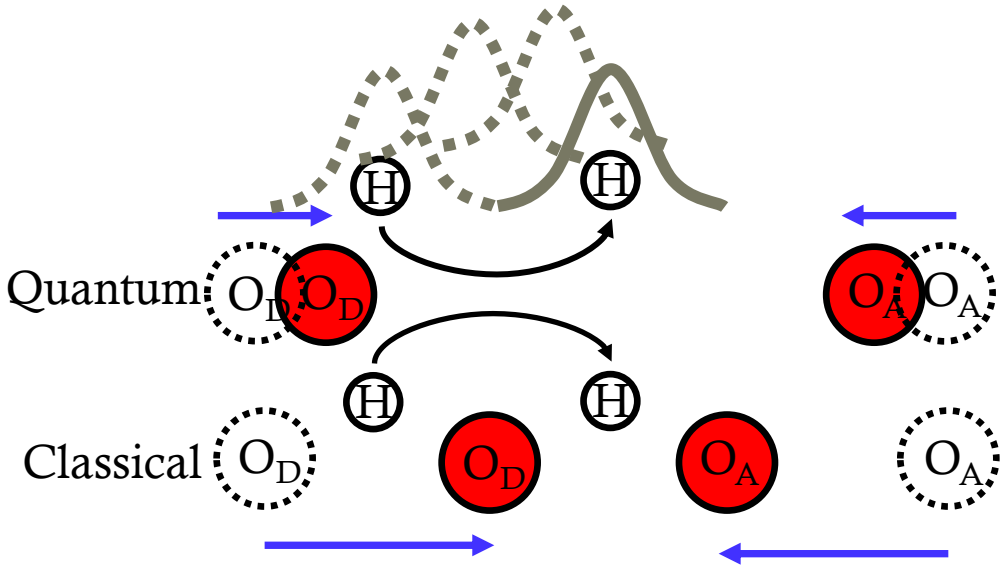

S. Hammes-Schiffer, J. C. Tully, X. Li, in press.

Group Members

- Dr. Andrew Jenkins
- Dr. Yue Huang
- Dr. Chad Hoyer
- Dr. Andrew Valentine
- Dr. Tianyuan Zhang
- Dr. Luning Zhao
- Dr. Ernesto Martinez
- Dr. Shichao Sun
- Dr. Adam Grofe
- Dr. Joshua Goings
- Dr. Prachi Sharma
- Andrew Wildman
- Ryan Beck
- Torin Stetina
- Hang Hu
- Lauren Koulias
- Lixin Lu
- Alexis Mills
- Xiaolin Liu
- Ben Link
- Jordan Ehrman
- Aodong Liu
- Can Liao

Recent Collaborators

- Prof. Ed Valeev (Virginia Tech)
- Dr. Chao Yang (LBNL)
- Prof. Lin X Chen (Argonne & Northwestern)
- Prof. Benedetta Mennucci (U of Pisa)
- Prof. Christine Aikens (Kansas State U)
- Prof. Aurora Clark (Washington State U)
- Dr. Michael Frisch
- Dr. Giovanni Scalmani
- Prof. Daniel Gamelin (UW)
- Prof. David Ginger (UW)
- Prof. Peter Pauzauskie (UW)
- SSI-ChronusQ Team
- EFRC-IDREAM Team
- CCS-SPEC Team