THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

RT-"NEO"-TDDFT for Coupled Quantum Dynamics of Electrons and Protons

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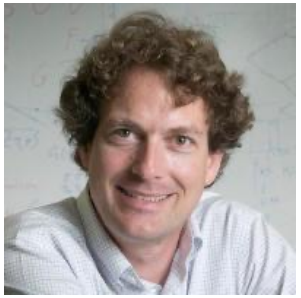
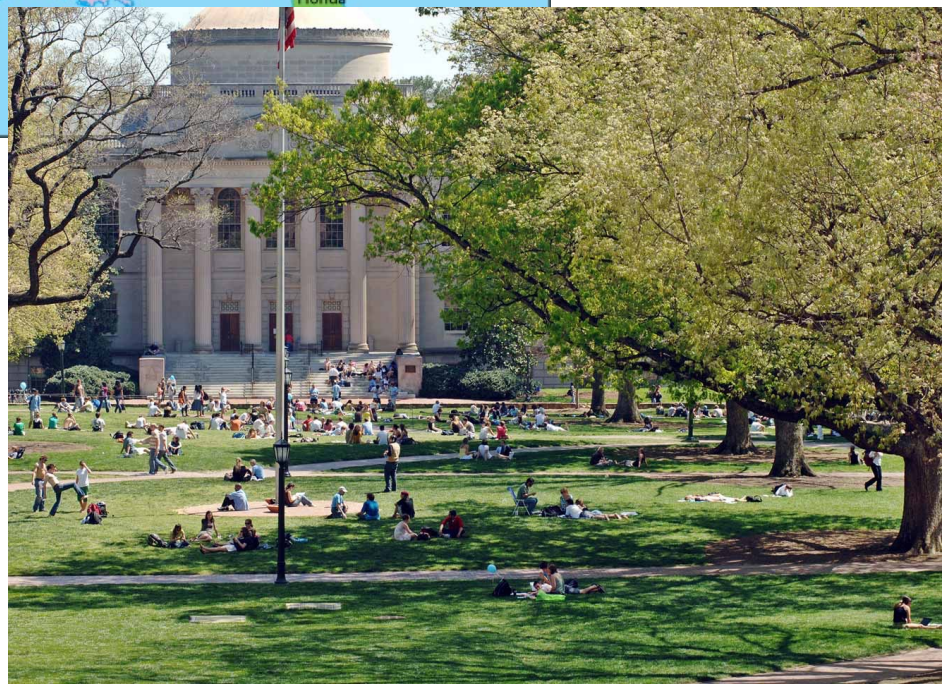


Volker Blum (Duke)

We are here!



Research Triangle of NC

- Univ. of North Carolina at Chapel Hill (UNC)
- Duke University
- North Carolina State University

UNC: Oldest public university in the US (1789)

Kanai Group @ UNC

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

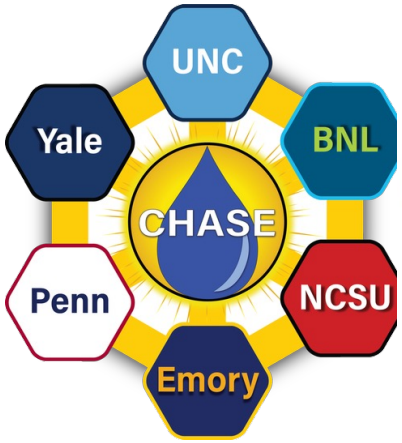
CHASE
Center for Hybrid Approaches in Solar Energy to Liquid Fuels

Dr. JC Wong
Dr. Jianhang Xu
Chris Shepard
Sampreeti Bhattacharya
Ruiyi Zhou
John Bost
Tom Carney
Nicolas Boyer

NSF

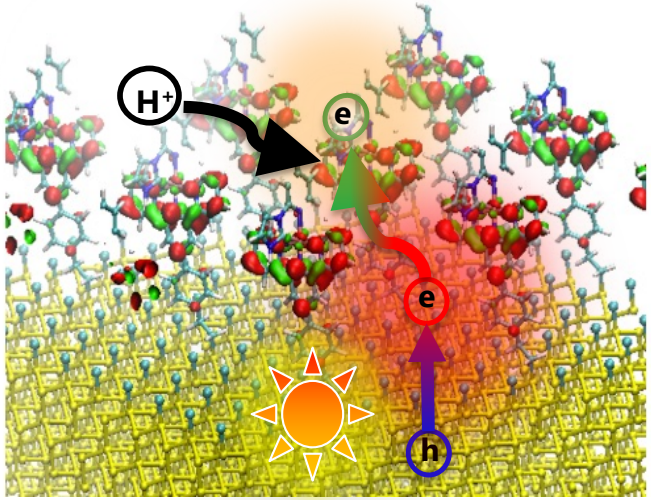
DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA ·

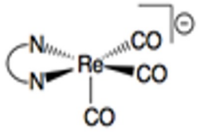
Scientific Motivation : Coupled Dynamics of Electrons and Protons



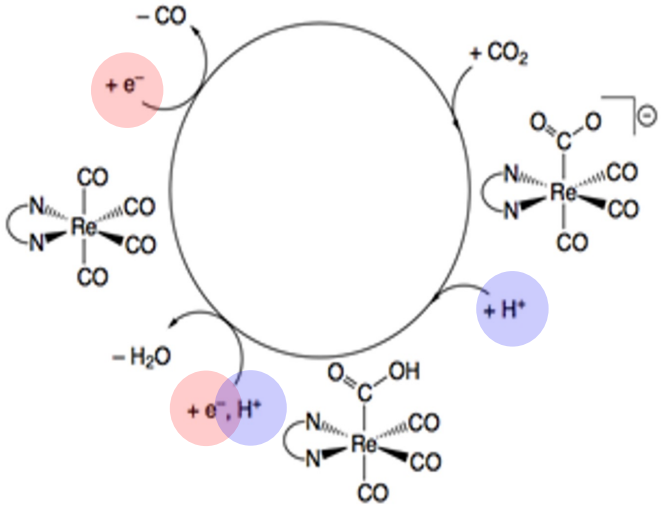
CHASE

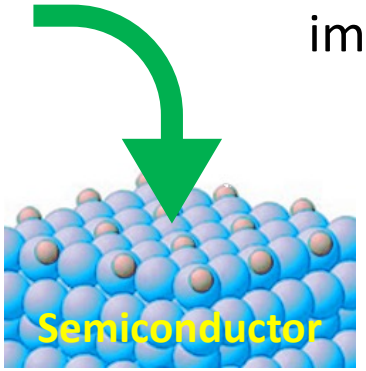
Center for Hybrid Approaches in Solar Energy to Liquid Fuels





CO_2 reduction catalyst





How are H^+/e^- transfer steps in catalysis impacted when adsorbed on a surface?

NEO to KS-DFT for Periodic System

Multicomponent DFT

$$E[\rho^{e},\rho^{p}] = E_{\mathrm{ref}}[\rho^{e},\rho^{p}] + E^{e}_{XC}[\rho^{e}] + E^{p}_{XC}[\rho^{p}] + E_{EPC}[\rho^{e},\rho^{p}]$$

"Non-Born–Oppenheimer Density Functional Theory of Molecular Systems"

J. F. Capitani, R. F. Nalewajski, and R. G. Parr, J. Chem. Phys. 76, 568 (1982)

"Multicomponent Density-Functional Theory for Electrons and Nuclei"

T. Kreibich and E. K. U. Gross, Phys. Rev. Lett. 86, 2984 (2001)

Nuclear Electronic Orbital (NEO) method

F. Pavosevic, T. Culpitt, S. Hammes-Schiffer, Chem. Rev. **120**, 4222 (2020)

NEO to KS-DFT for periodic systems

J. Xu, R. Zhou, Z. Tao, C. Malbon, V. Blum, S. Hammes-Schiffer, Y. Kanai, J. Chem. Phys. 156, 224111 (2022)

$$\psi^{e}_{i,\mathbf{k}}(\mathbf{r}^{e}) = \sum_{\mu} c_{i\mu,\mathbf{k}} \sum_{N} e^{i\mathbf{k}\cdot\mathbf{T}(\mathbf{N})} \phi^{e:NAO/GTO}_{\mu}\left(\mathbf{r}^{e} - \mathbf{R}_{\mu} + \mathbf{T}(\mathbf{N})\right)$$

$$\psi^{p}_{i}(\mathbf{r}^{p}) = \sum_{m} c_{im} \sum_{N} \phi^{p:GTO}_{m}\left(\mathbf{r}^{p} - \mathbf{R}_{m} + \mathbf{T}(\mathbf{N})\right)$$

Atom-centered basis functions

$$\hat{H}^{e}_{\mathbf{k}} = -\frac{1}{2}\nabla^{2}_{e} + v_{ext}(\mathbf{r}^{e}) + v^{e}_{es}(\mathbf{r}^{e}) - v^{p}_{es}(\mathbf{r}^{e}) + \frac{\delta E^{e}_{XC}[\rho^{e}]}{\delta\rho^{e}} + \frac{\delta E_{EPC}[\rho^{e},\rho^{p}]}{\delta\rho^{e}}$$

$$\hat{H}^{p} = -\frac{1}{2M^{p}}\nabla^{2}_{p} - v_{ext}(\mathbf{r}^{p}) - v^{e}_{es}(\mathbf{r}^{p}) + v^{p}_{es}(\mathbf{r}^{p}) + \frac{\delta E^{p}_{XC}[\rho^{p}]}{\delta\rho^{p}} + \frac{\delta E_{EPC}[\rho^{e},\rho^{p}]}{\delta\rho^{p}}$$

Resolution-of-Identity (RI)-LVL scheme

$$\rho^p(\mathbf{r}^p) = \sum_{m,n}\sum_i c^*_{mi}\, c_{ni}\phi_m(\mathbf{r}^p)\phi_n(\mathbf{r}^p) = \sum_\mu c_\mu \Phi_\mu(\mathbf{r}^p) = \sum_\mu c_\mu N_\mu r^{l_\mu} e^{-\alpha_\mu r^2} Y_{l_\mu m_\mu}(\theta,\phi)$$

Auxiliary basis functions

$$c_\mu = \sum_{m,n}\sum_i c^*_{mi}\, c_{ni} C^\mu_{mn} \qquad C^\mu_{mn} = \sum_v (mn|v)(v|\mu)^{-1}$$

$$(mn|v) = \iint \phi_m(\mathbf{r}^p)\phi_n(\mathbf{r}^p)\frac{1}{|\mathbf{r}^p-\mathbf{r}^{p\prime}|}\Phi_v(\mathbf{r}^{p\prime})d\mathbf{r}^p d\mathbf{r}^{p\prime}$$

$$(v|\mu) = \iint \Phi_v(\mathbf{r}^p)\frac{1}{|\mathbf{r}^p-\mathbf{r}^{p\prime}|}\Phi_\mu(\mathbf{r}^{p\prime})d\mathbf{r}^p d\mathbf{r}^{p\prime}$$

RI-LVL scheme : $\Phi^K_\mu(\mathbf{r}^p)$ centered on atom K

$$C^\mu_{mn} = \begin{cases} \sum_v (mn|v)[(v|\mu)^{\mathrm{IJ}}]^{-1} & \text{if } \phi^I_m \text{ or } \phi^J_n \text{ is centered on atom K.} \\ 0 & \text{otherwise} \end{cases}$$

$$(ij|kl) = \sum_{\substack{\mu\lambda\in IJ \\ \nu\sigma\in KL}} (ij|\lambda)\mathbf{L}^{\mathrm{IJ}}_{\lambda\mu}\mathbf{V}_{\mu\nu}\mathbf{L}^{\mathrm{KL}}_{\nu\sigma}(\sigma|kl)$$

Ihrig, et al. New J. Phys. 17, 093020 (2015)

Electrostatic Potential from Quantum Protons

$$v_{es}^{p}(\mathbf{r}) = \sum_{\mu} U_{\mu}(\mathbf{r} - \mathbf{r}_{I_\mu})$$

in spherical coordinate

$$U_{\mu}\left(\mathbf{r} - \mathbf{r}_{I_\mu}\right) = \frac{4\pi}{2l_\mu + 1}\left[r^{l_\mu} p_\mu(r) + \frac{q_\mu(r)}{r^{l_\mu+1}}\right] Y_{l_\mu,m_\mu}(\theta,\phi)$$

$$p_\mu(r) = c_\mu N_\mu \frac{1}{2\alpha_\mu} e^{-\alpha_\mu r^2}$$

$$q_\mu(r) = c_\mu N_\mu \int_0^r r'^{2l_\mu+2}\, e^{-\alpha_\mu r'^2} dr'$$

All quantities are readily available with Φ_μ

For sufficiently large r, it reduces to

$$U_{\mu}(\mathbf{r}) = \frac{4\pi}{2l_\mu + 1} \frac{O_\mu}{r^{l+1}} Y_{l_\mu,m_\mu}(\theta,\phi)$$

$$O_\mu = c_\mu N_\mu \frac{\sqrt{\pi}}{2\sqrt{\alpha}} \frac{(2l+1)!}{(2\alpha)^{l+1}}$$

r^{l+1} can be obtained using Ewald summation, etc.

Proton XC and EPC

$$E_{XC}^{p}[\rho^{p}] \rightarrow K^{p}\left[\left\{\psi_{j}^{p}\right\}\right]$$

$$K_{mn}^{p} = \sum_{k,l}\sum_{i} c_{ki}^{*}\, c_{li}(mk|nl)$$

$$(mn|nl) = \int \phi_m(\mathbf{r}^p)\phi_k(\mathbf{r}^p)\frac{1}{|\mathbf{r}^p-\mathbf{r}^{p\prime}|}\phi_n(\mathbf{r}^p)\phi_l(\mathbf{r}^p)d\mathbf{r}^p d\mathbf{r}^{p\prime}$$

$$= \sum_{\mu,v}(mk|\mu)(\mu|v)^{-1}(v|nl) = \sum_{\mu,v} C_{mk}^{\mu}(\mu|v)C_{nl}^{v}$$

$$E_{EPC}[\rho^{e},\rho^{p}] \approx E_{epc17-2}[\rho^{e},\rho^{p}]$$

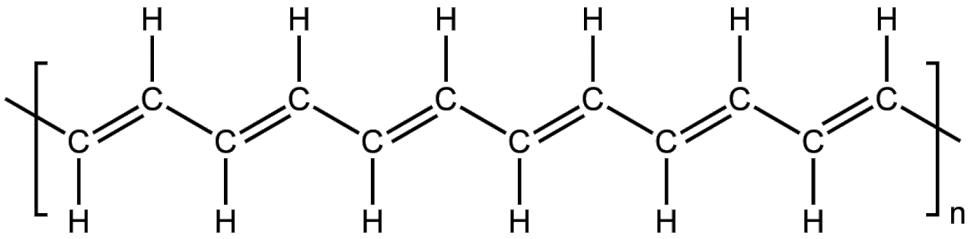
Colle-Salvetti formalism

Yang, et al., J. Chem. Phys. **147**, 114113 (2017)

$$= -\int d\mathbf{R}\,\frac{\rho^{p}(\mathbf{R})\rho^{e}(\mathbf{R})}{a - b\rho^{p}(\mathbf{R})^{\frac{1}{2}}\rho^{e}(\mathbf{R})^{\frac{1}{2}} + c\rho^{p}(\mathbf{R})\rho^{e}(\mathbf{R})}$$

$$a = 2.35, b = 2.4, c = 6.6$$

Proof-of-Principle Demonstration : C_2H_2 polymer



B3LYP for electrons
cc-pVTZ GTO electronic basis set
PB4-D protonic basis set*

Development of nuclear basis sets for multicomponent quantum chemistry methods Q. Yu, F. Pavosevic, S. Hammes-Schiffer, J. Chem. Phys. 152, 244123 (2020)

Zero-Point Energy (ZPE) per proton

No. of k-points	1	2	3	4	8	16
$\Delta E^{\mathrm{NEO}}/n_p$	0.361	0.458	0.463	0.461	0.461	0.461
No. of unit cells	1	2	3	4	8	16
$\Delta E^{\mathrm{NEO}}/n_p$	0.361	0.458	0.463	0.461	0.461	0.461

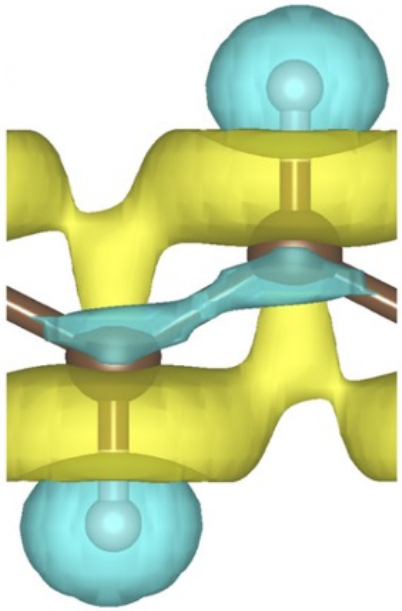
ZPE in C_2H_2 molecule : 0.332 eV

ZPE in C_2H_2 polymer : 0.461 eV

Proof-of-Principle Demonstration : C_2H_2 polymer

NEO-induced Electron Density difference

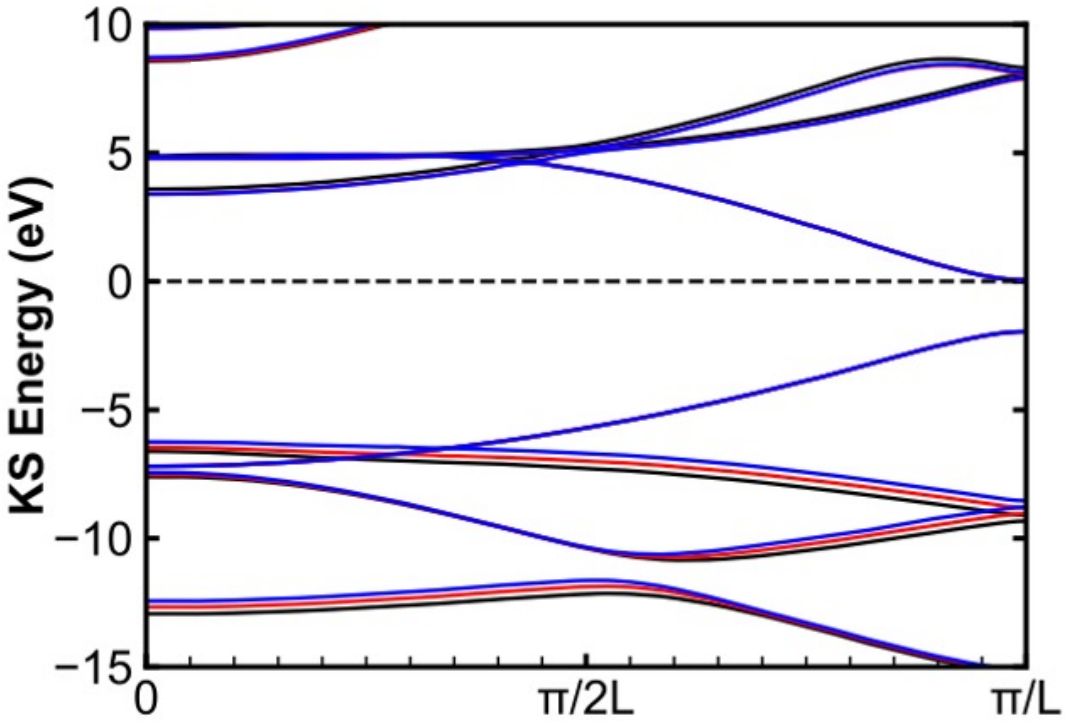
$$\Delta\rho^e(\mathbf{r})$$



(+) change
(-) change

Isosurface @ 1.7 x 10^{-2} Ang^{-3}

Band Structure

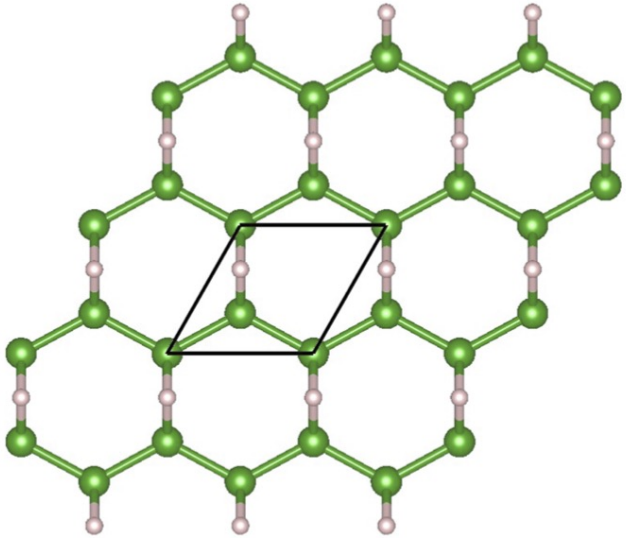


Brillouin Zone

DFT
NEO-DFT, no epc
NEO-DFT, epc17-2

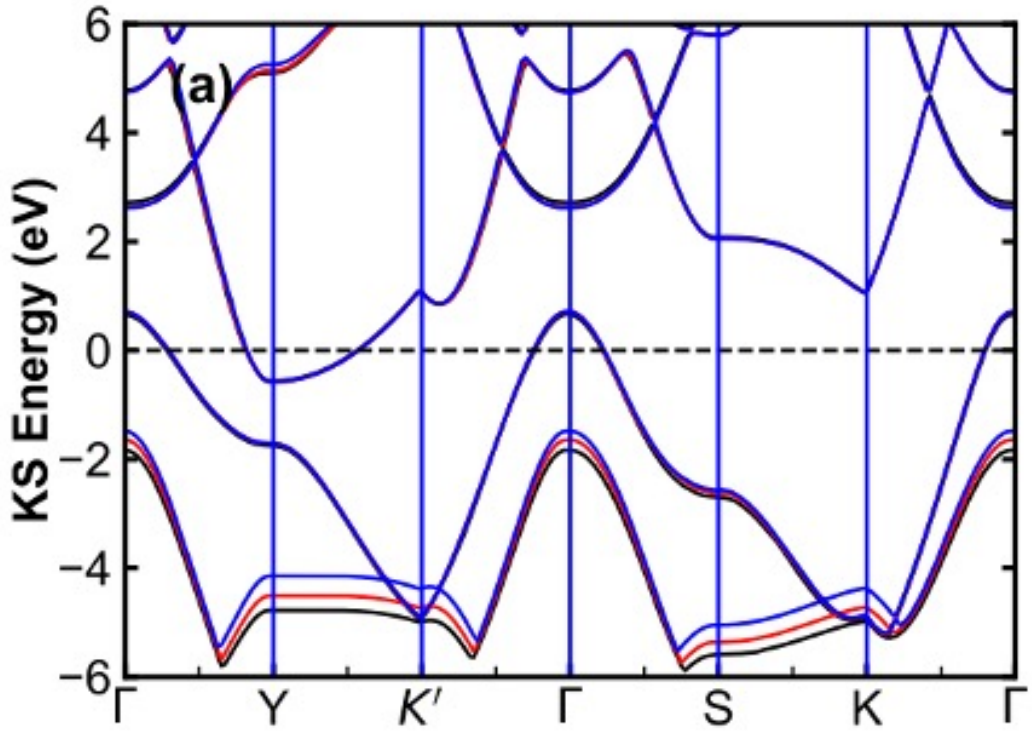
Proof-of-Principle Demonstration : 2D Boron Hydride

Y. Jiao, et al. Angewandte Chemie, 55, 35 (2016)



PBE for electrons : 16 x 16 k-points
cc-pVTZ GTO electronic basis set
PB4-D protonic basis set

Band Structure



Brillouin Zone

DFT
NEO-DFT, no epc
NEO-DFT, epc17-2

Proof-of-Principle Demonstration : 2D Boron Hydride

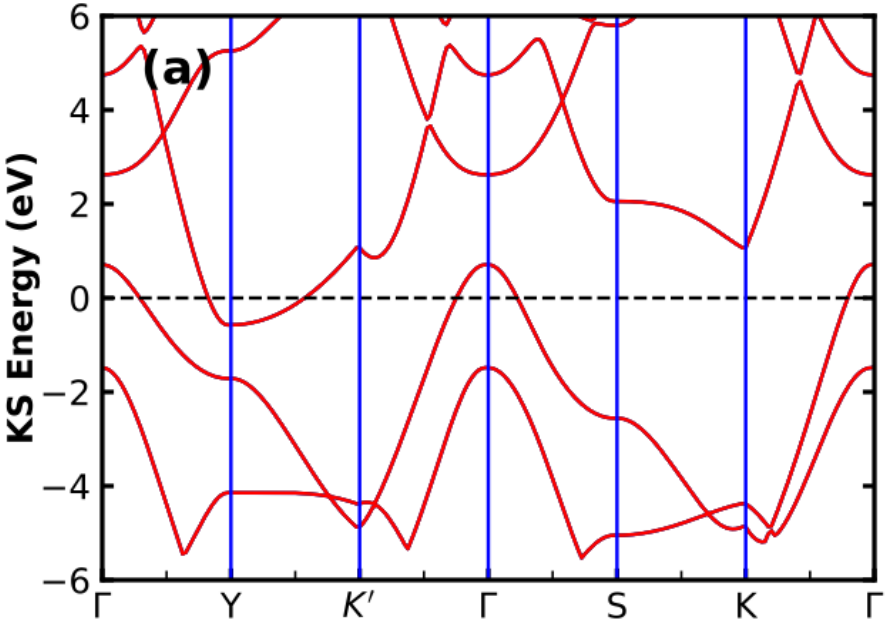
RI-LVL convergence of Auxiliary basis functions

	Total Energy (eV)
8ET	-1382.30466
10ET	-1382.17019
10ET+g	-1382.17016
14ET	-1382.16982

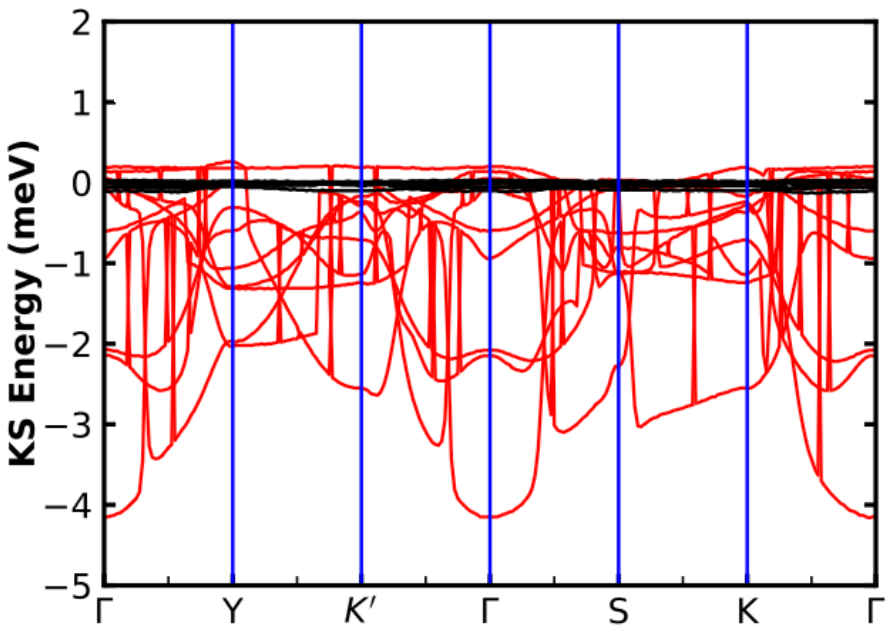
e.g.
8ET: 8s8p8d8f even-tempered Gaussians with the exponents from 2sqrt(2) to 32.

R. Bardo and K. Ruedenberg, JCP, 60, 918 (1974)

Band Structure

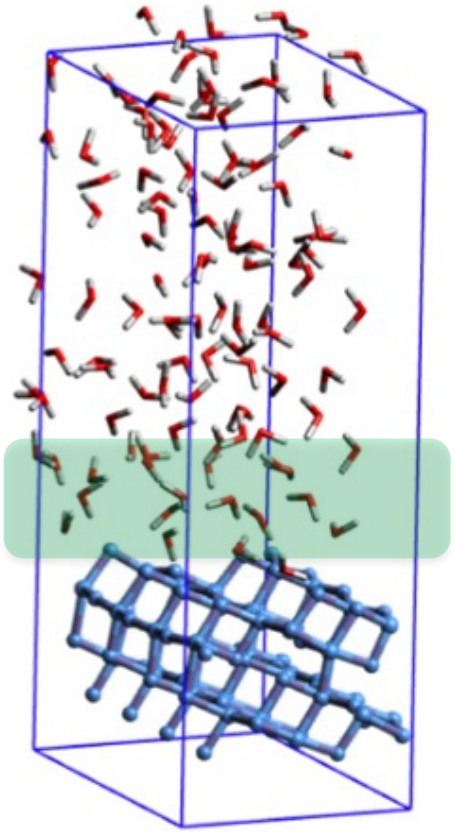


Red : Difference between 8ET and 10ET
Black : Difference between 10ET and 14ET



Proof-of-Principle Demonstration : Water at TiO_2(101) surface

FPMD trajectory snapshot

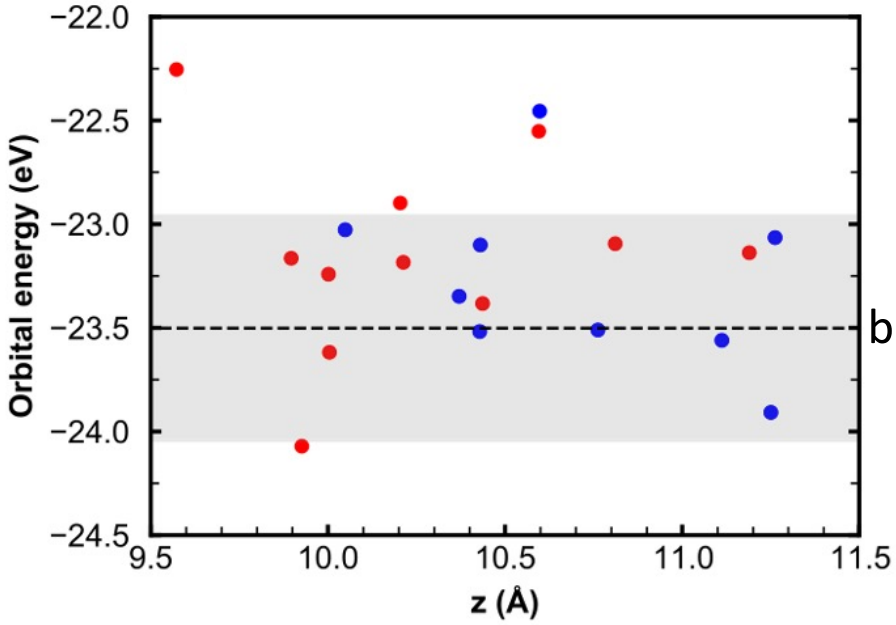


20 H^+ quantized

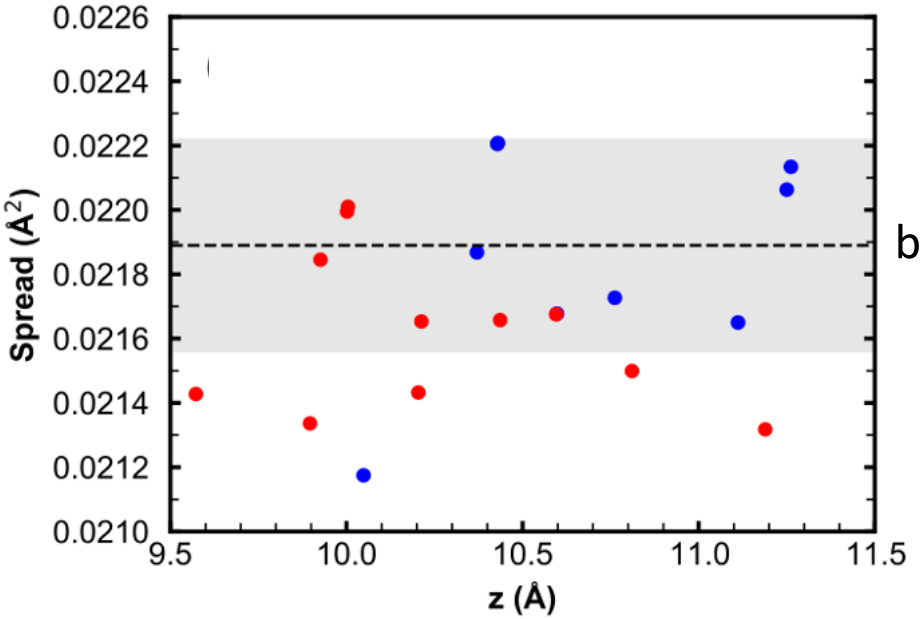
ZPE : 0.33 eV

ZPE in bulk water : 0.31 eV

PBE for electrons : Gamma k-point
cc-pVTZ GTO electronic basis set
PB4-D protonic basis set



bulk water



bulk water

Going "Time-Dependent"

NEO-DFT method with periodic systems

Nuclear-Electronic Orbital Approach to Quantization of Protons in Periodic Electronic Structure Calculations
J. Xu, R. Zhou, Z. Tao, C. Malbon, V. Blum, S. Hammes-Schiffer, Y. Kanai
J. Chem. Phys. 156, 224111 (2022)

RT-TDDFT Implementation

All-electron real-time and imaginary-time time-dependent density functional theory within a numeric atom-centered basis function framework
J. Hekele, Y. Yao, Y. Kanai, V. Blum, P. Kratzer
J. Chem. Phys. 155, 154801 (2021)

Periodic RT-NEO-TDDFT method for studying coupled electron-proton dynamics in heterogeneous systems.

First-Principles Approach to Coupled Quantum Dynamics of Electrons and Protons in Heterogeneous Systems
J. Xu, R. Zhou, V. Blum, T. E. Li, S. Hammes-Schiffer, Y. Kanai
Under Review

Dynamics : Lagrangian for our KS System

Coupled dynamics of electrons and protons with classical nuclei

$$L(t) = \int d\mathbf{r}^e \int d\mathbf{k} \sum_j [\psi^e_{j\mathbf{k}}(\mathbf{r}^e,t)]^* \left[i\frac{\partial}{\partial t} + \frac{1}{2m^e}\nabla^2_{\mathbf{r}^e} \right] \psi^e_{j\mathbf{k}}(\mathbf{r}^e,t)$$

$$- \frac{1}{2}\iint d\mathbf{r}^e\, d\mathbf{r}^{e\prime} \frac{e^2}{|\mathbf{r}^e - \mathbf{r}^{e\prime}|} \rho^e(\mathbf{r}^e,t)\rho^e(\mathbf{r}^{e\prime},t) - E^e_{XC}[\rho^e]$$

$$+ \int d\mathbf{r}^p \sum_j [\psi^{p*}_j(\mathbf{r}^p,t)]^* \left[i\frac{\partial}{\partial t} + \frac{1}{2M^p}\nabla^2_{\mathbf{r}^p} \right] \psi^p_j(\mathbf{r}^p,t)$$

$$- \frac{1}{2}\iint d\mathbf{r}^p\, d\mathbf{r}^{p\prime} \frac{e^2}{|\mathbf{r}^p - \mathbf{r}^{p\prime}|} \rho^p(\mathbf{r}^p,t)\rho^p(\mathbf{r}^{p\prime},t) - E^p_{XC}[\rho^p]$$

$$+ \frac{1}{2}\iint d\mathbf{r}^e\, d\mathbf{r}^p \frac{e^2}{|\mathbf{r}^e - \mathbf{r}^p|} \rho^e(\mathbf{r}^e,t)\rho^p(\mathbf{r}^p,t) - E_{EPC}[\rho^e,\rho^p]$$

$$+ \sum_I \frac{1}{2} M_I \left[\frac{d}{dt}\boldsymbol{R}_I(t) \right]^2 - \sum_{I<J} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I(t) - \boldsymbol{R}_J(t)|}$$

$$- \int d\mathbf{r}^p\, \rho^p(\mathbf{r}^p,t) \sum_I \frac{Z_I e^2}{|\mathbf{r}^p - \boldsymbol{R}_I(t)|} + \int d\mathbf{r}^e\, \rho^e(\mathbf{r}^e,t) \sum_I \frac{Z_I e^2}{|\mathbf{r}^e - \boldsymbol{R}_I(t)|}$$

See. e.g. Kramer and Saraceno, “Geometry of the Time-Dependent Variational Principle” (Springer, Berlin, 1981).

TD-KS equations for RT-NEO-TDDFT

Electrons:

$$i\frac{\partial}{\partial t}\psi^{e}_{i,\mathbf{k}}(\mathbf{r}^{\mathrm{e}},t)=\left[-\frac{1}{2}\nabla_i^2+v^{e}_{\mathrm{DFT-KS}}(\mathbf{r^e})-v^{p}_{\mathrm{es}}(\mathbf{r}^{\mathrm{e}})+\frac{\delta E_{\mathrm{EPC}}[\rho^{\mathrm{e}},\rho^{\mathrm{p}}]}{\delta\rho^{e}}\right]\psi^{e}_{i,\mathbf{k}}(\mathbf{r}^{\mathrm{e}},t)$$

All-electron real-time and imaginary-time time-dependent density functional theory within a numeric atom-centered basis function framework J. Hekele, Y. Yao, Y. Kanai, V. Blum, P. Kratzer
J. Chem. Phys. 155, 154801 (2021)

RT-TDDFT

Protons:

$$i\frac{\partial}{\partial t}\psi^{p}_{I}(\mathbf{r}^{\mathrm{p}},t)=\left[-\frac{1}{2M^{p}}\nabla_I^2+v^{p}_{\mathrm{DFT-KS}}(\mathbf{r}^{\mathrm{p}})-v^{e}_{\mathrm{es}}(\mathbf{r}^{\mathrm{p}})+\frac{\delta E_{\mathrm{EPC}}[\rho^{\mathrm{e}},\rho^{\mathrm{p}}]}{\delta\rho^{p}}\right]\psi^{p}_{I}(\mathbf{r}^{\mathrm{p}},t)$$

$$\psi^{p}_{i}(\mathbf{r}^{p},t)=\sum_{m}c_{im}(t)\sum_{N}\phi^{p:GTO}_{m}\left(\mathbf{r}^{p}-\mathbf{R}_{m}+\mathbf{T(N)}\right)$$

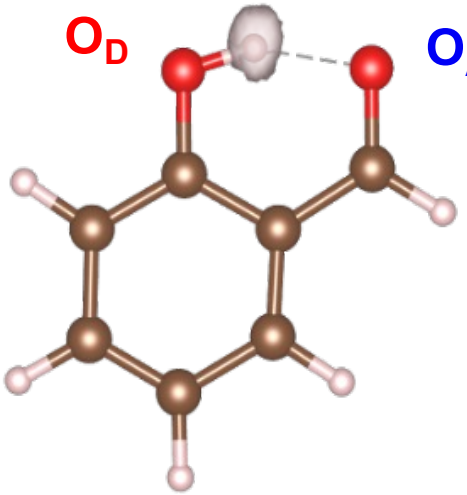
$$\frac{d}{dt}\mathbf{C}(t)=-i\mathbf{S}^{-1}\mathbf{H_{KS}}(t)\mathbf{C}(t)$$

$$\mathbf{C}(t+\Delta t)=\mathbf{S}^{-\frac{1}{2}}\exp\left(-i\Delta t\mathbf{S}^{-\frac{1}{2}}\mathbf{H_{KS}}\left(t+\tfrac{\Delta t}{2}\right)\mathbf{S}^{-\frac{1}{2}}\right)\mathbf{S}^{\frac{1}{2}}\mathbf{C}(t)$$

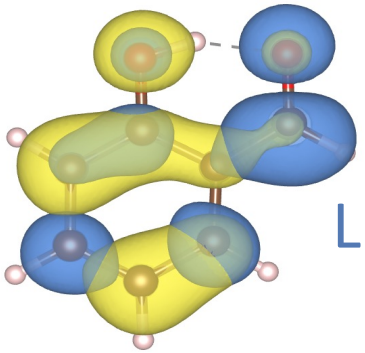
$$\exp(\mathbf{A})=\mathbf{V}\mathrm{diag}\left(e^{\lambda_1},e^{\lambda_2}\ldots e^{\lambda_n}\right)\mathbf{V}^{-1}$$

Electronic Excitation Induced Intra-Molecular Proton Transfer

oHBA molecule

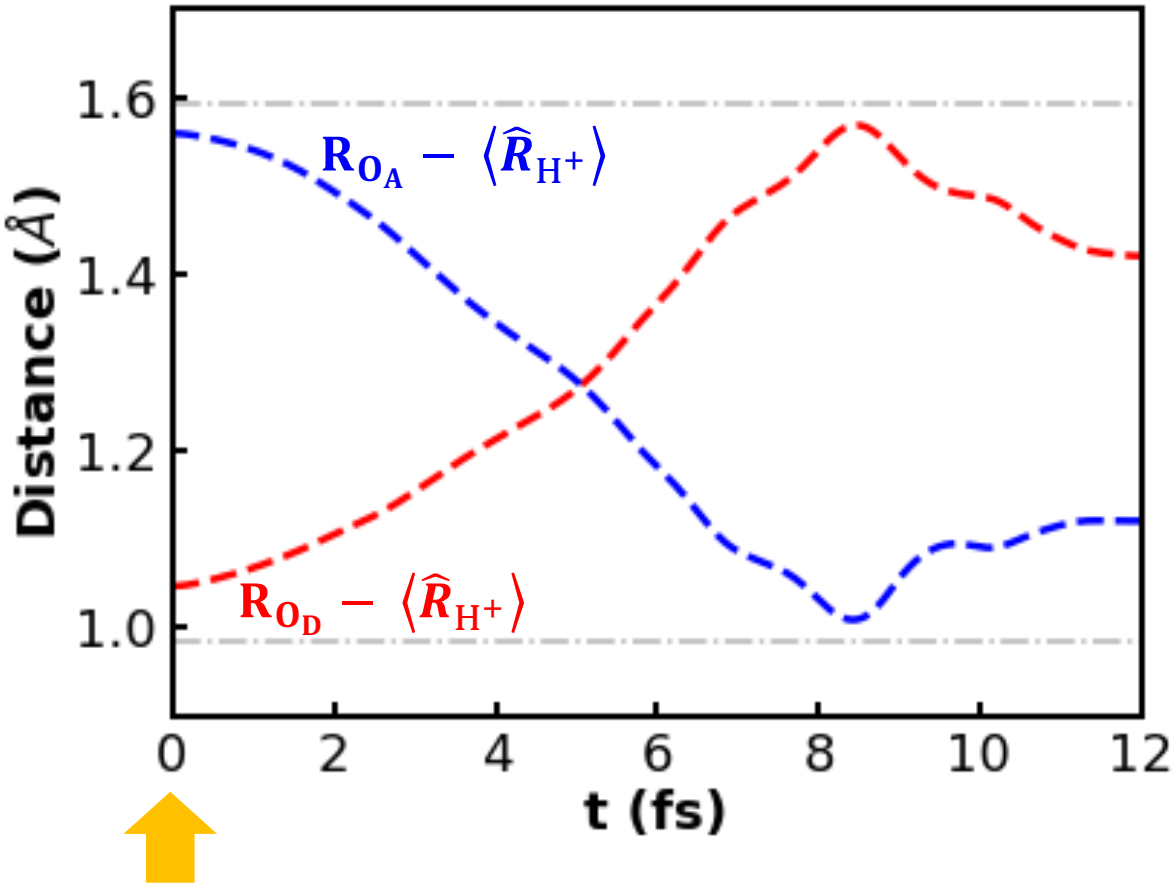


HOMO



LUMO

Electrons: PBE + Tier2 NAO basis
Protons: Hartree-Fock + 4s 4p basis w/ 3 "ghost" atoms
EPC: epc-17-2



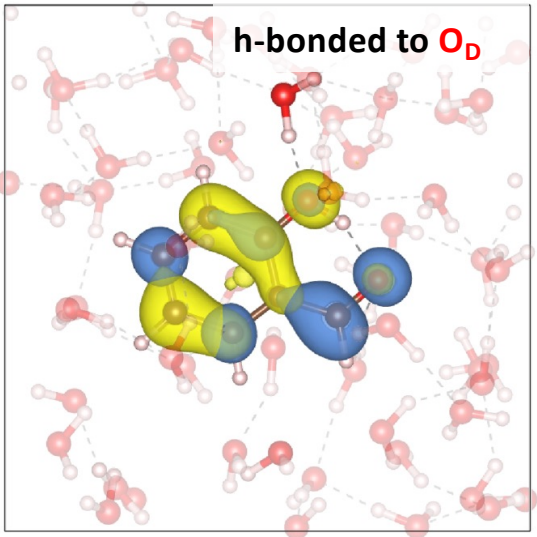
Electronic Excitation (HOMO → LUMO)

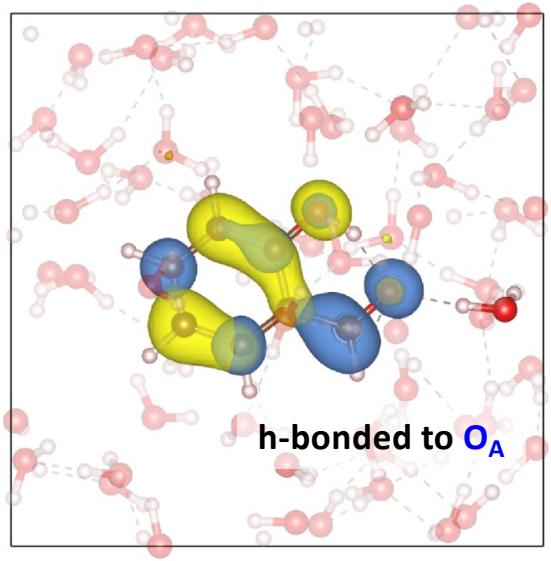
L. Zhao, et al., J. Phys. Chem. Lett. **11**, 4052 (2020)

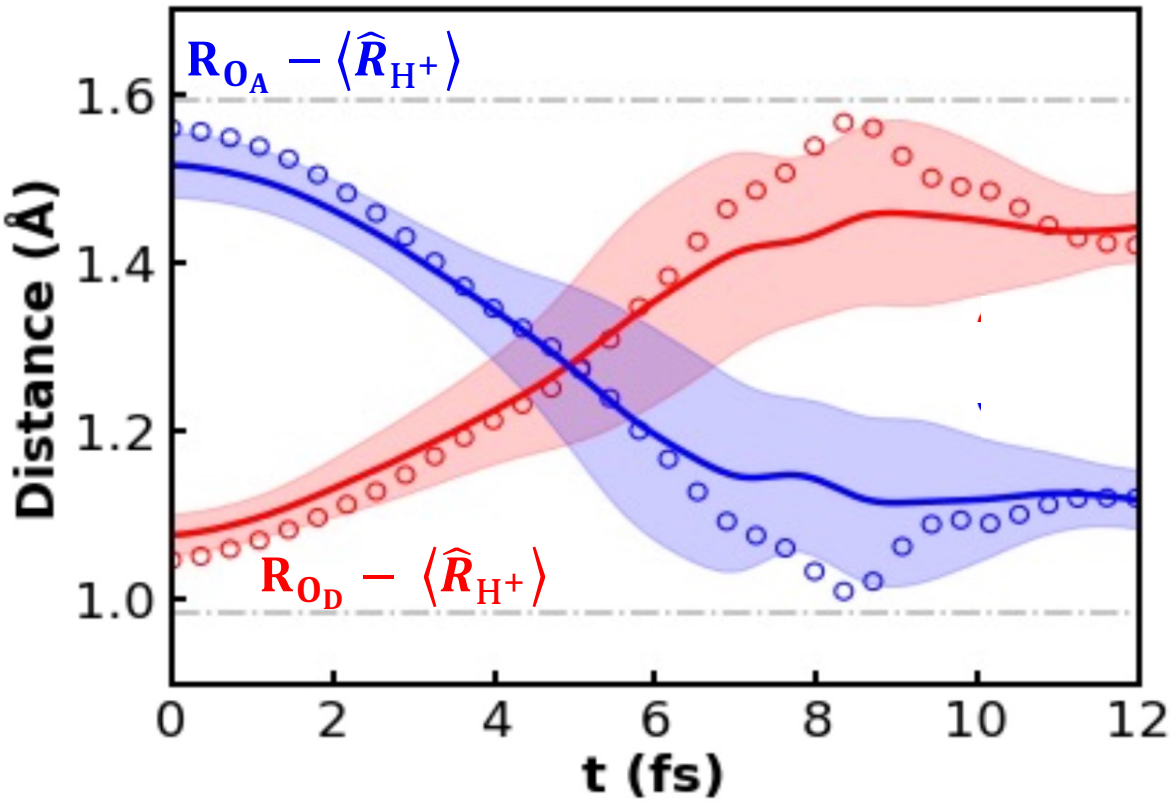
Role of Water Solvation

6 snapshots from 300 K FPMD (SCAN) simulation of oHBA molecule w/ 64 H_2O molecules

h-bonded H_2O could potentially transfer a proton (quantized) to oHBA molecule.





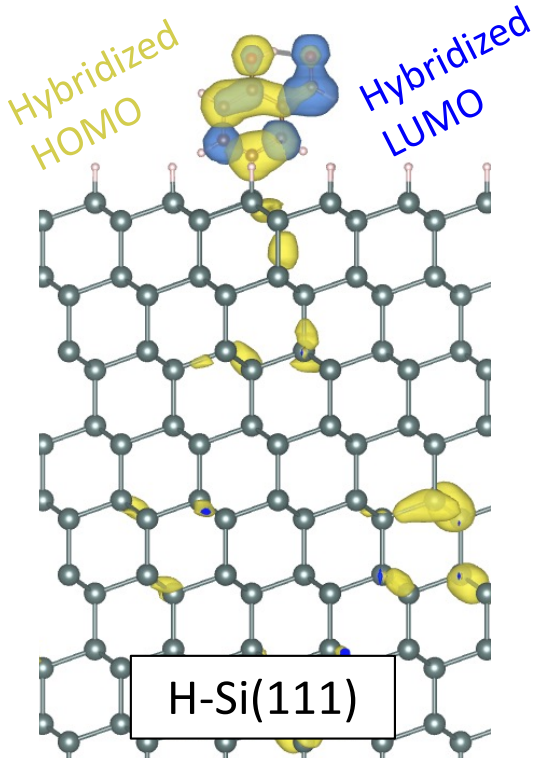


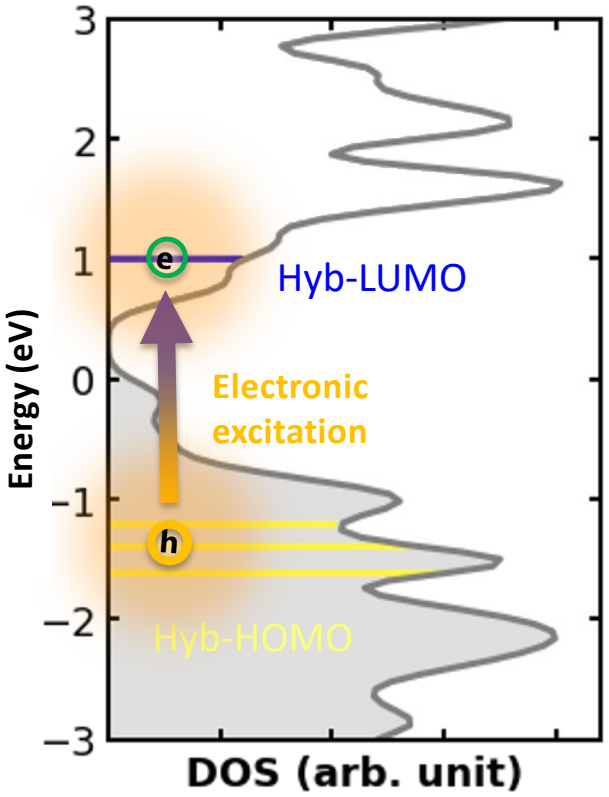
∘ ∘ ∘ Gas Phase ——— In water

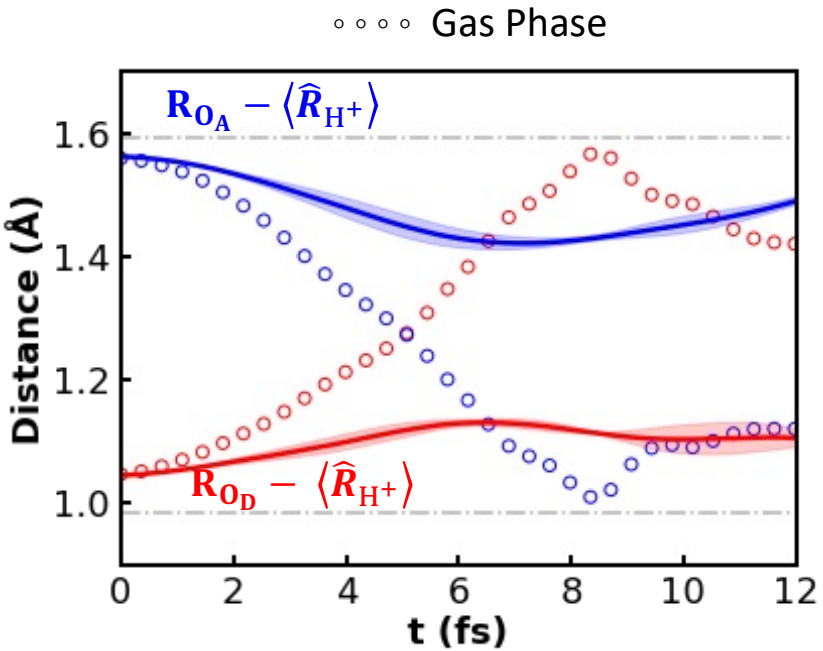
Excitation-induced H^+ transfer still takes place.

Chemisorption on Semiconductor Surface

oHBA





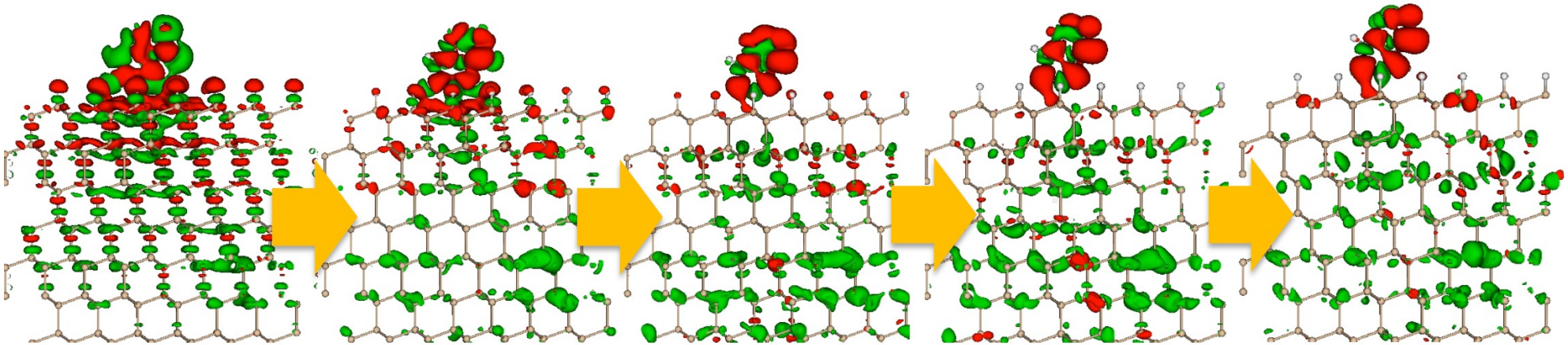


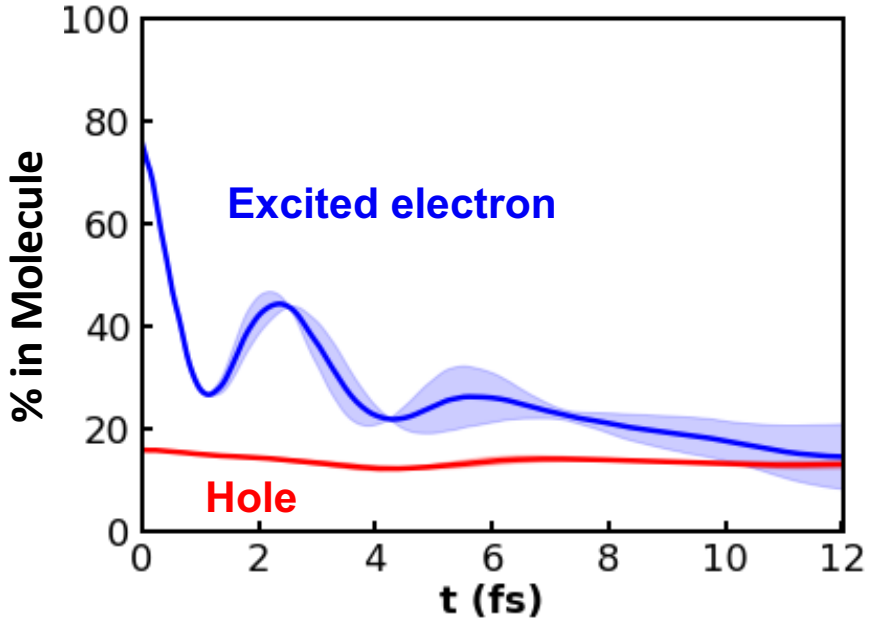
~3700 electrons.

H^+ transfer does NOT take place!

Electron Density Changes at Interface

Electron density change : $\Delta\rho^e(\mathbf{r},t)$ Increases / Decreases

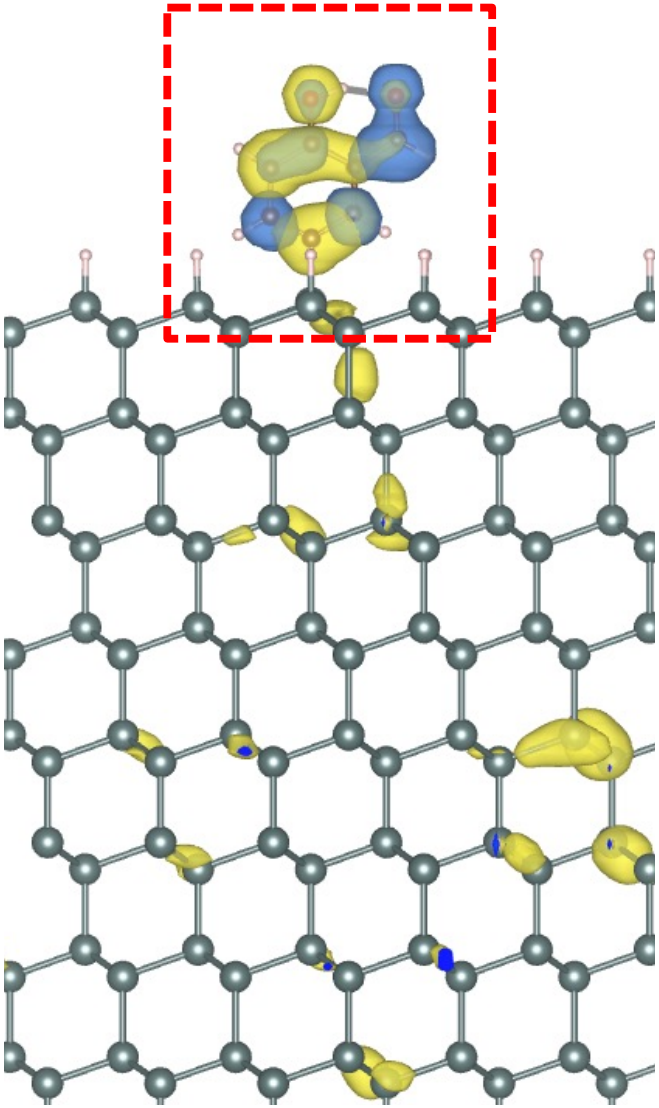


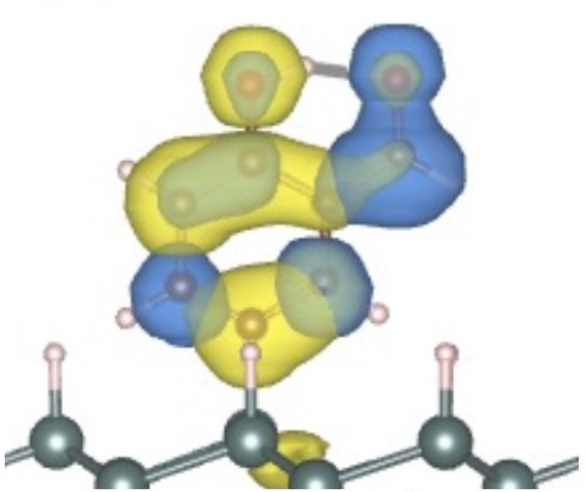


Ultrafast transfer of excited electron to semiconductor surface.

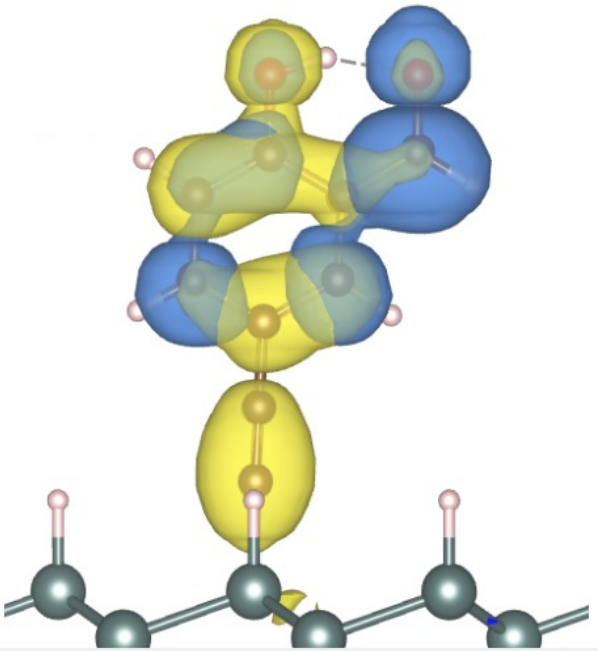
No driving force for the intra-molecular H^+ transfer.

Role of Excited Electron Transfer

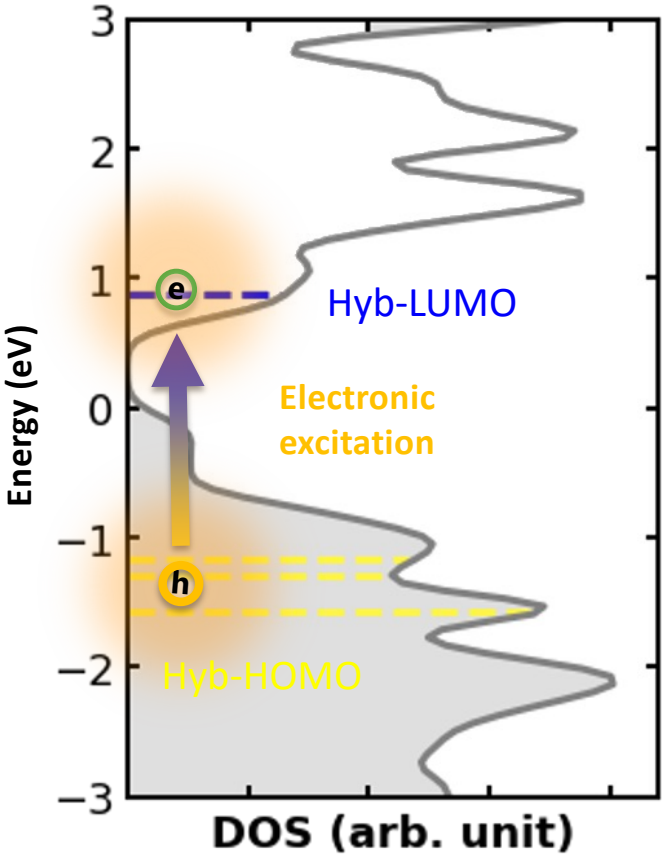


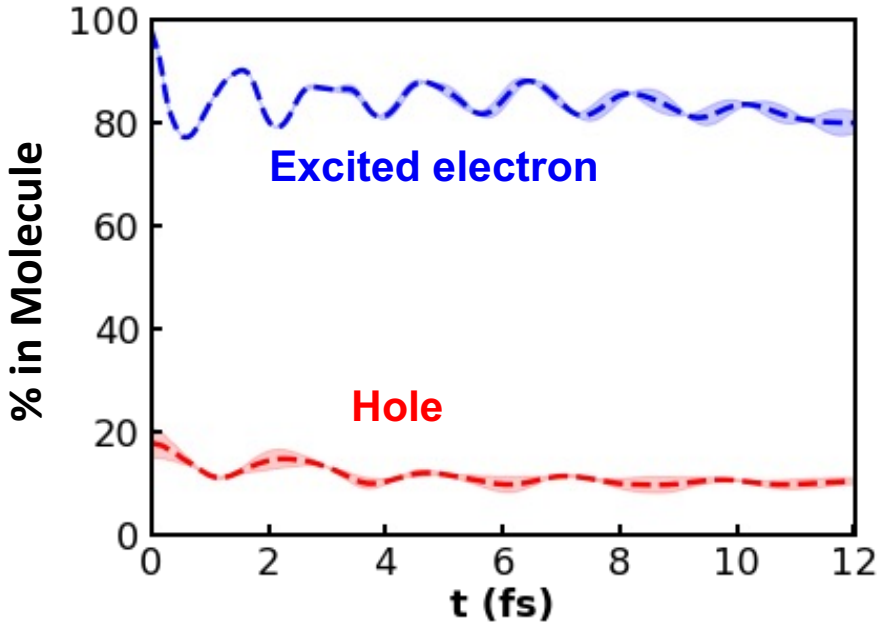


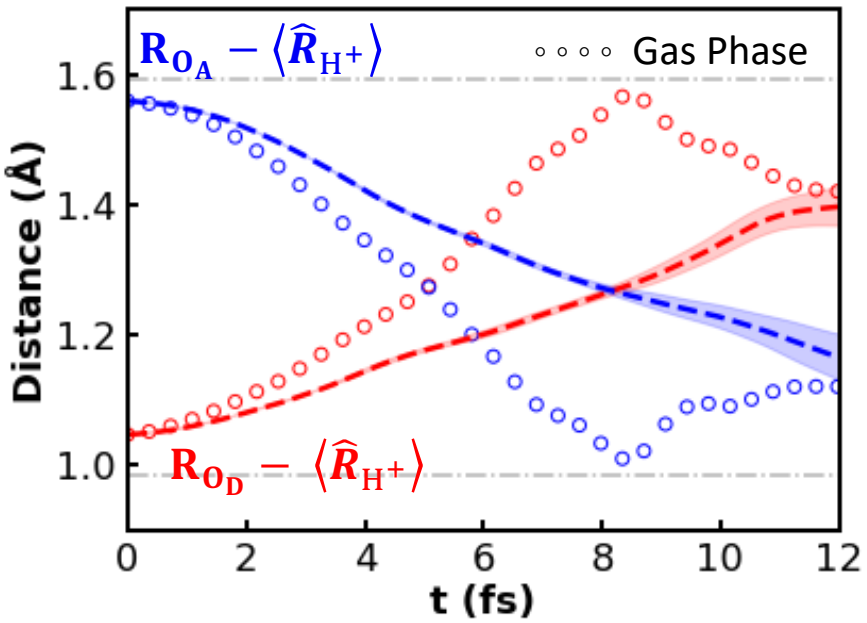
$-\mathbf{C} \equiv \mathbf{C} -$ **Linker**



Controlling Electron Transfer w/ Linker Group



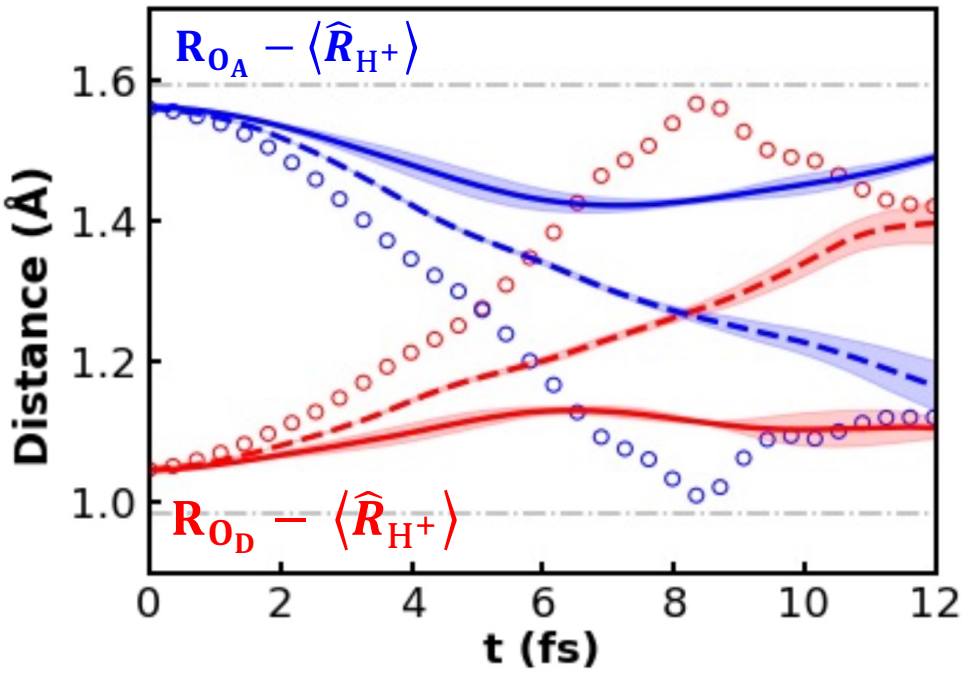


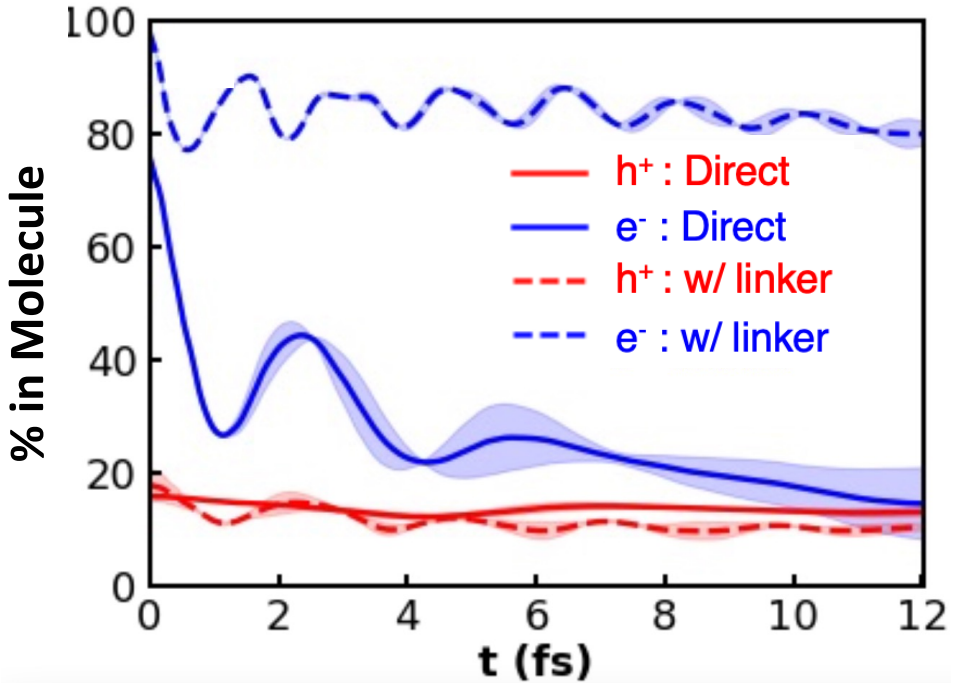


Excited electron transfer to the semiconductor is significantly slower with the linker group.

Excitation-induced H^+ transfer takes place!

Dependence on the surface attachment



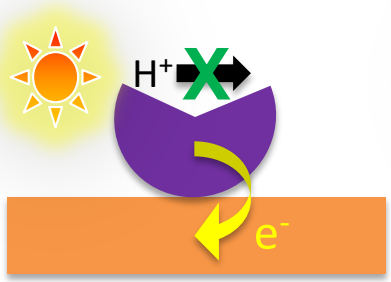


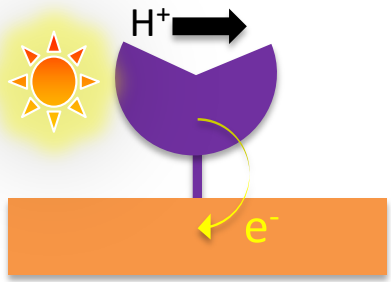
Gas Phase

on Surface (Direct)

on Surface w/ linker

Surface attachment controls intra-molecular H^+ transfer via interfacial excited electron transfer.





Summary and Future/Current Directions

- NEO-DFT method was extended to periodic systems.

  Nuclear-Electronic Orbital Approach to Quantization of Protons in Periodic Electronic Structure Calculations
  J. Xu, R. Zhou, Z. Tao, C. Malbon, V. Blum, S. Hammes-Schiffer, Y. Kanai
  J. Chem. Phys. 156, 224111 (2022)

- Periodic RT-NEO-TDDFT method was implemented and demonstrated to study coupled electron-proton dynamics in heterogeneous systems.

  First-Principles Approach to Coupled Quantum Dynamics of Electrons and Protons in Heterogeneous Systems
  J. Xu, R. Zhou, V. Blum, T. E. Li, S. Hammes-Schiffer, Y. Kanai
  Submitted

Periodic RT-TDDFT with hybrid XC needs to be implemented.

Ehrenfest RT-NEO-TDDFT

- Classical degrees of freedom *and* proton basis set centers are propagated in time

Applications

- Coupled proton-electron dynamics for CO_2 reduction at semiconductor-catalyst interface

Thank you for listening!