Ab-initio quantum simulations of complex photocatalytic reactions

With:

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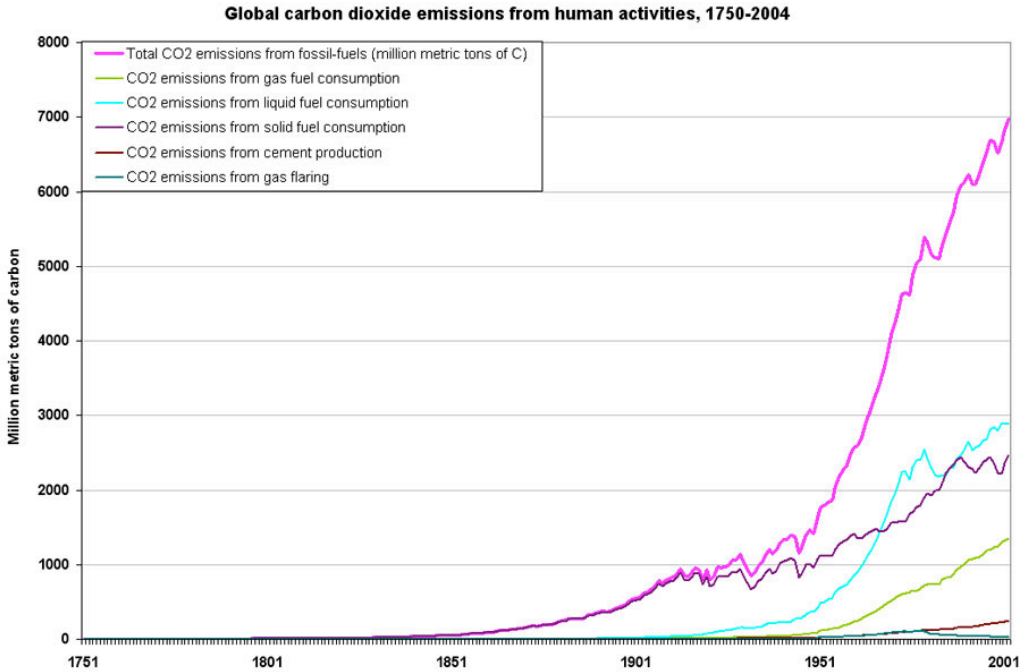
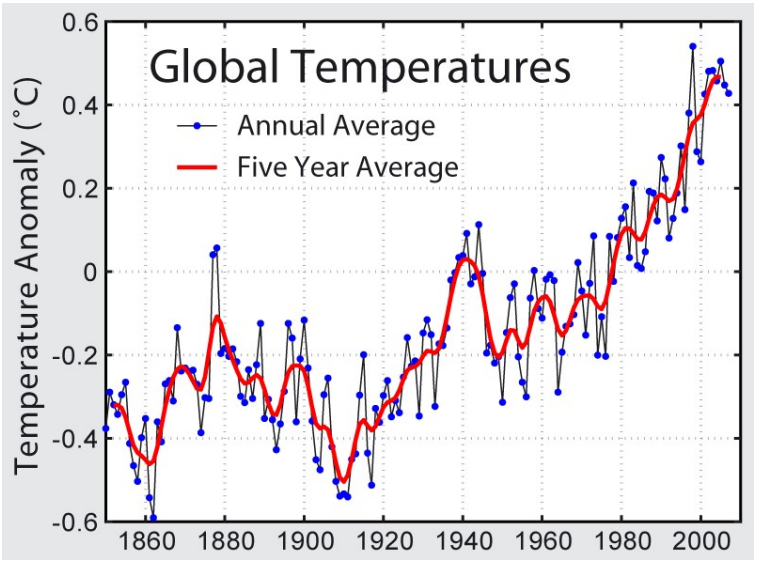
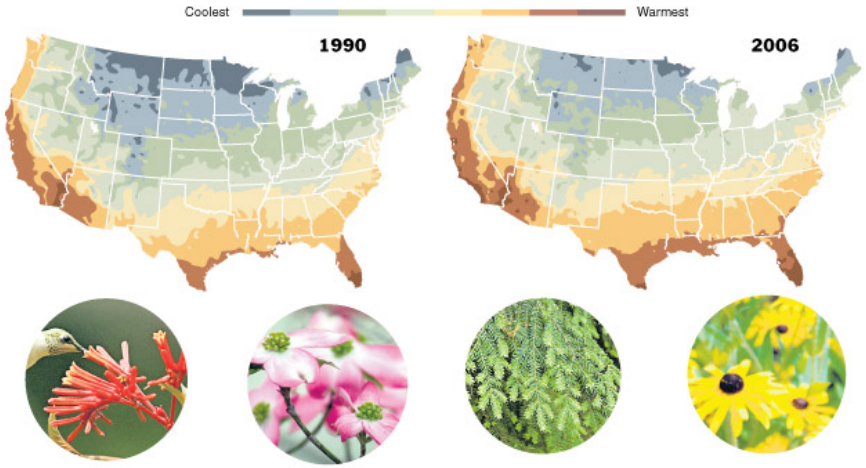
Motivation: The need for alternative energy sources





The zones in the maps correspond to low temperatures. As warmer zones cover more of the United States, different types of plants will grow in many areas.



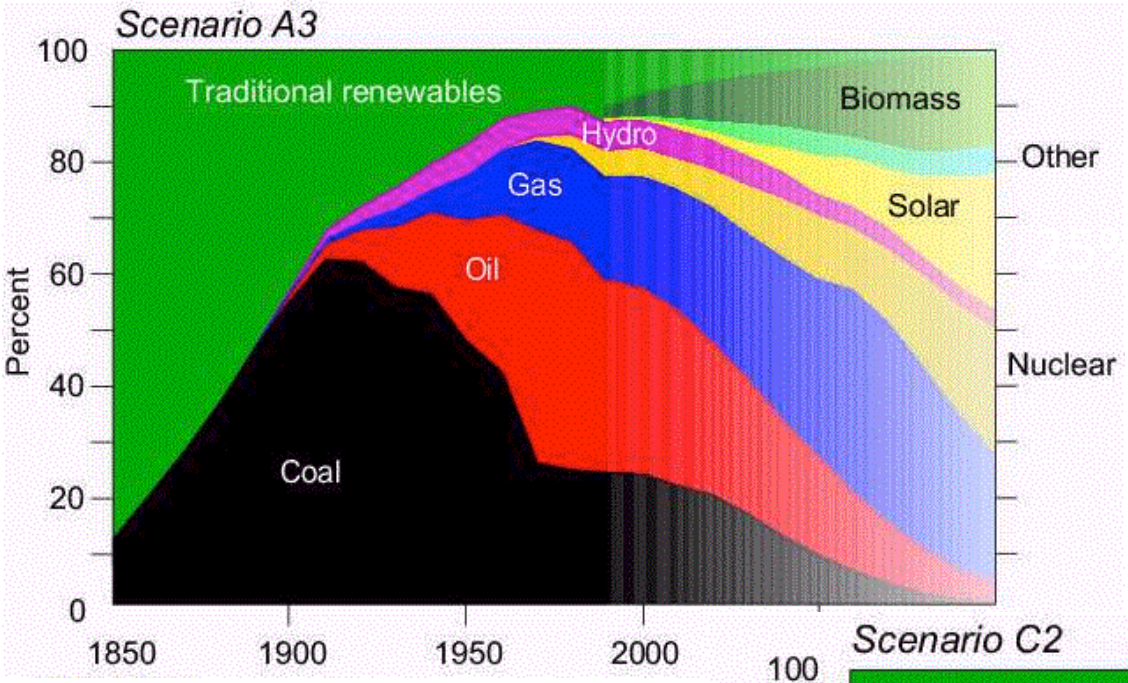
1990 zones are by the United States Department of Agriculture. 2006 zones are by the National Arbor Day Foundation.

Sources: National Arbor Day Foundation; National Wildlife Federation

The New York Times

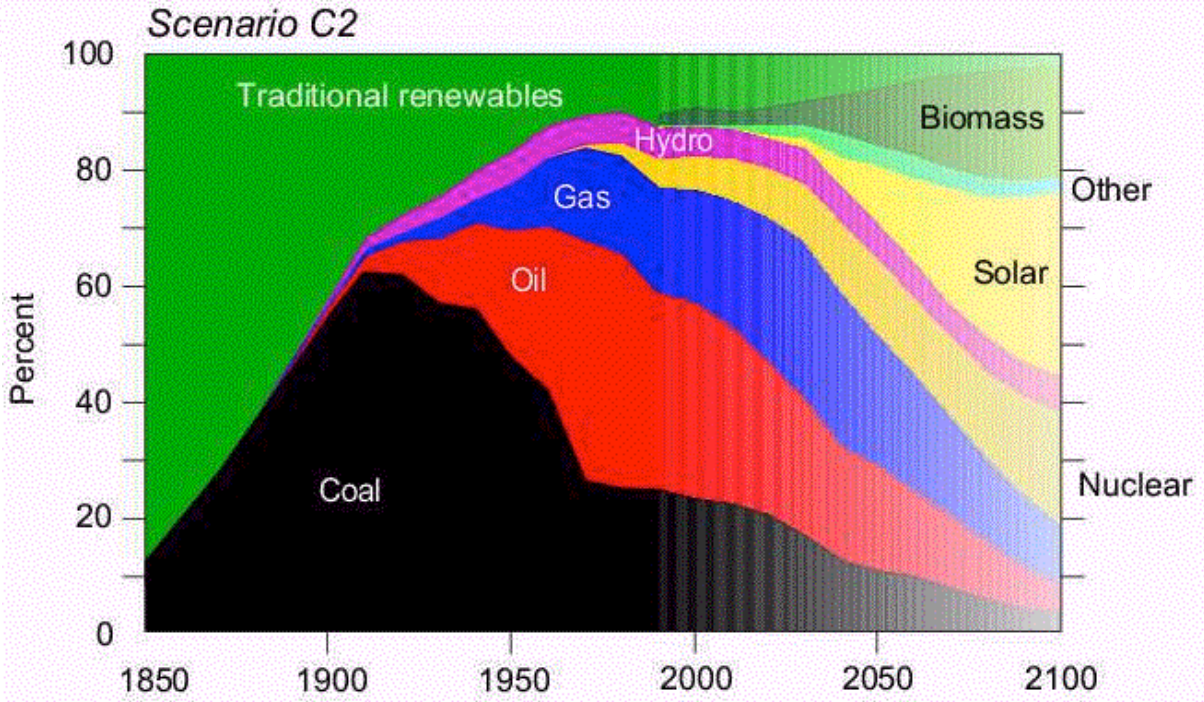
http://www.celsias.com/2007/03/20/channel-4-distances-itself-from-global-warming-documentary/

The challenge of sustainable energy sources

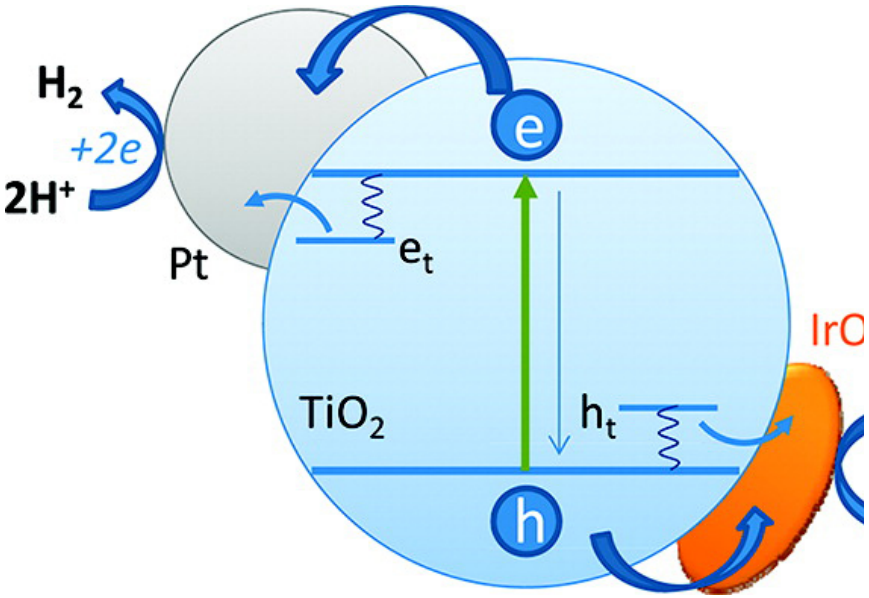


Time and resources running out – fundamental science can play key role in enabling technology

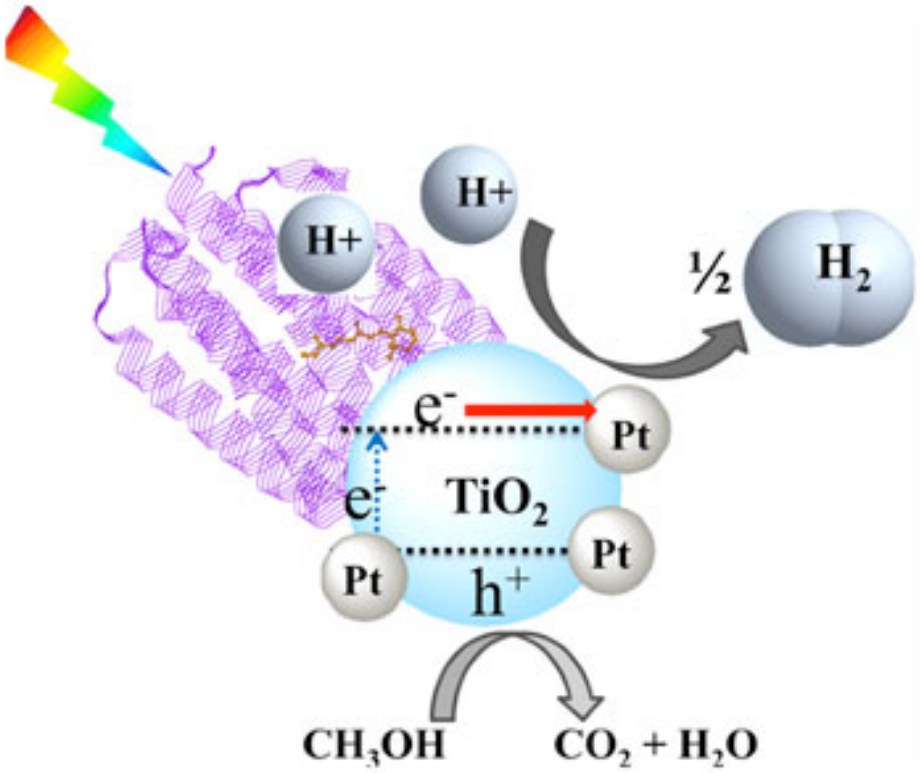
Report of Intergovernmental Panel on Climate Change



Water splitting



Photocatalytic water splitting system utilizing $Pt/TiO_2/IrO_2$:
TiO_2 is light absorber, Pt is the hydrogen evolution catalyst, and IrO_2 is the oxygen evolution catalyst.
(P. Kamat, U. Notre Dame)



H_2 production from organic molecules using TiO_2 nano-particles as photo-catalysts
(Argonne National Lab)

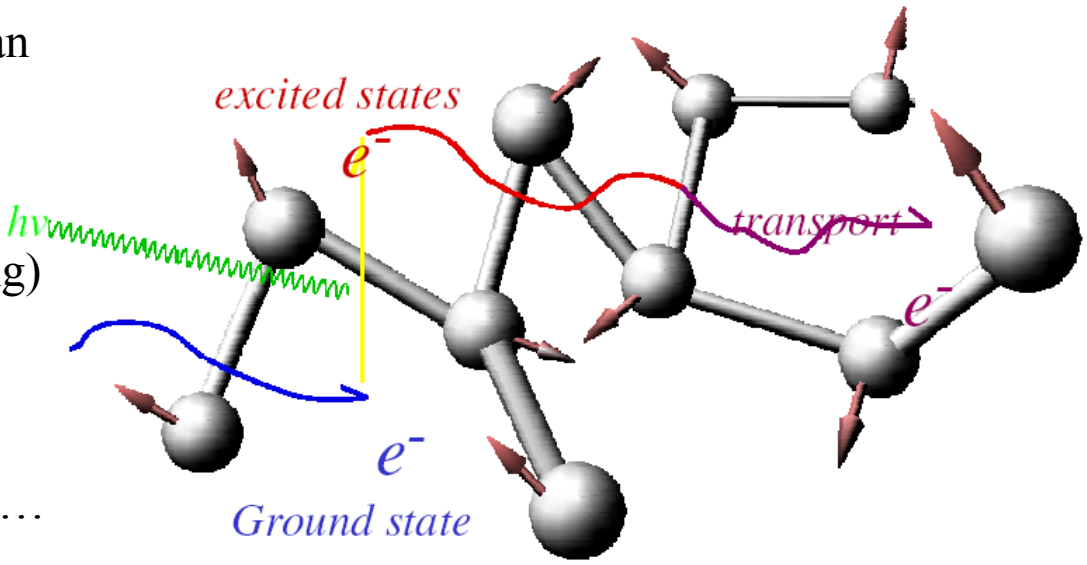
Main issue: coupled electron-ion dynamics

Previous work:

-Schroedinger eq. with model Hamiltonian
Thoss, Miller, Stock, JCP (2000);
Rego& Batista, JACS (2003);…

-semiempirical Hamiltonian (tight-binding)
Allen et al., JMO (2003);…

-ground state DFT + TDDFT
Prezhdo et al., PRL (2005); JACS (2007)…



Our method:

TDAP: self-consistent TDDFT with atomic motion

Coupled electron-ion dynamics without empirical parameters

Meng & Kaxiras, J. Chem. Phys. (2008).

Similar in spirit to: Miyamoto *et al.*; Rubio *et al.*; Tavernelli *et al.*.

Main issue: coupled electron-ion dynamics

$$i\hbar\frac{\partial\phi_j(\mathbf{r},t)}{\partial t} = \underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} + v_{ext}(\mathbf{r},t) + \int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}^d_I|} + v_{xc}[\rho](\mathbf{r},t)\right]}_{H_{\mathrm{DFT}}}\phi_j(\mathbf{r},t)$$

$$M_J\frac{d^2\mathbf{R}^d_J(t)}{dt^2} = -\nabla_{\mathbf{R}^d_J}\left[V^J_{ext}(\mathbf{R}^d_J,t) - \int\frac{Z_J\rho(\mathbf{r},t)}{|\mathbf{R}^d_J-\mathbf{r}|}d\mathbf{r} + \sum_{I\neq J}\frac{Z_JZ_I}{|\mathbf{R}^d_J-\mathbf{R}^d_I|}\right]$$

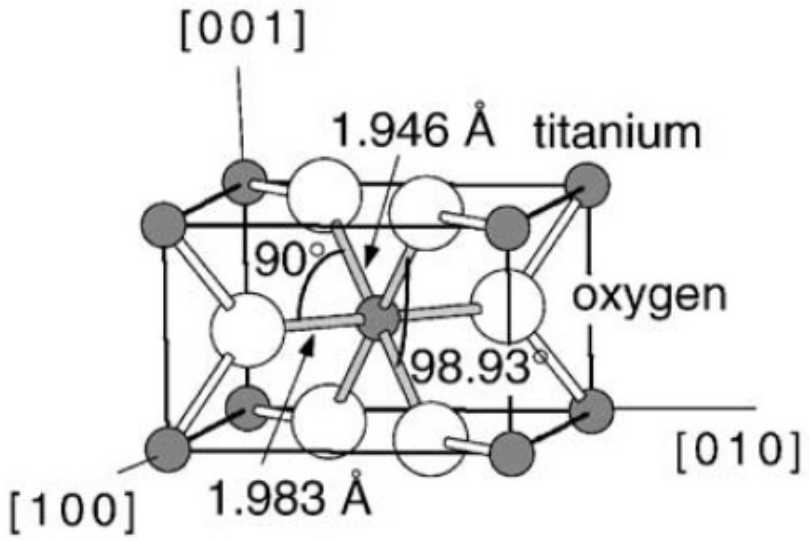
DFT Hamiltonian at each time step

See talks this afternoon by
Kieron Burke (plenary, 14:00)
Leeor Kronik (15:45)

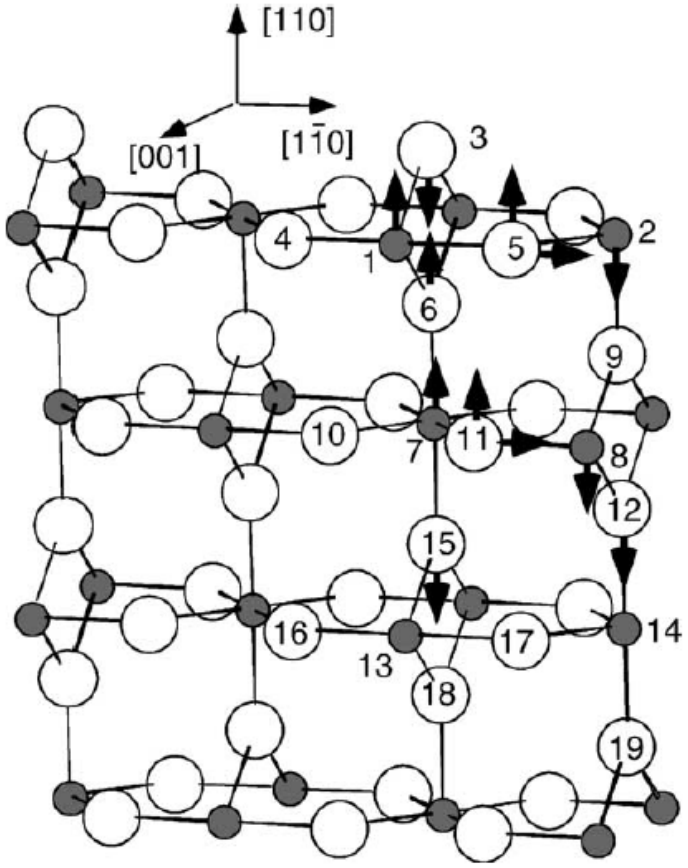
Rutile TiO_2 (110) – a model photocatalyst

Titania (TiO_2) – prototypical surface for studying photocatalysis [1]

Bulk Oxygen – 3 sigma bonds, 1 "lone pair"
Surface Oxygen – 2 sigma bonds, 1 dangling bond, 1 "lp"



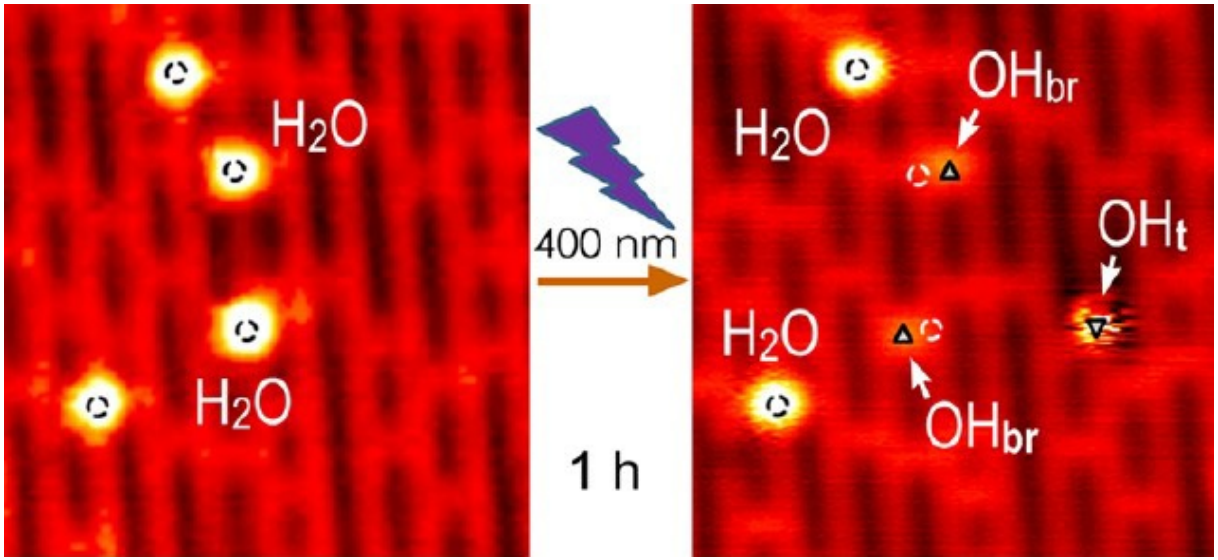
Rutile bulk crystal



1- A. Fujishima, K. Honda. Nature, 238:37-38 (1972)
2- U. Diebold, Surf. Sci. Rep., 48:53-229 (2003)

Experimental evidence for water photo-oxidation (?)

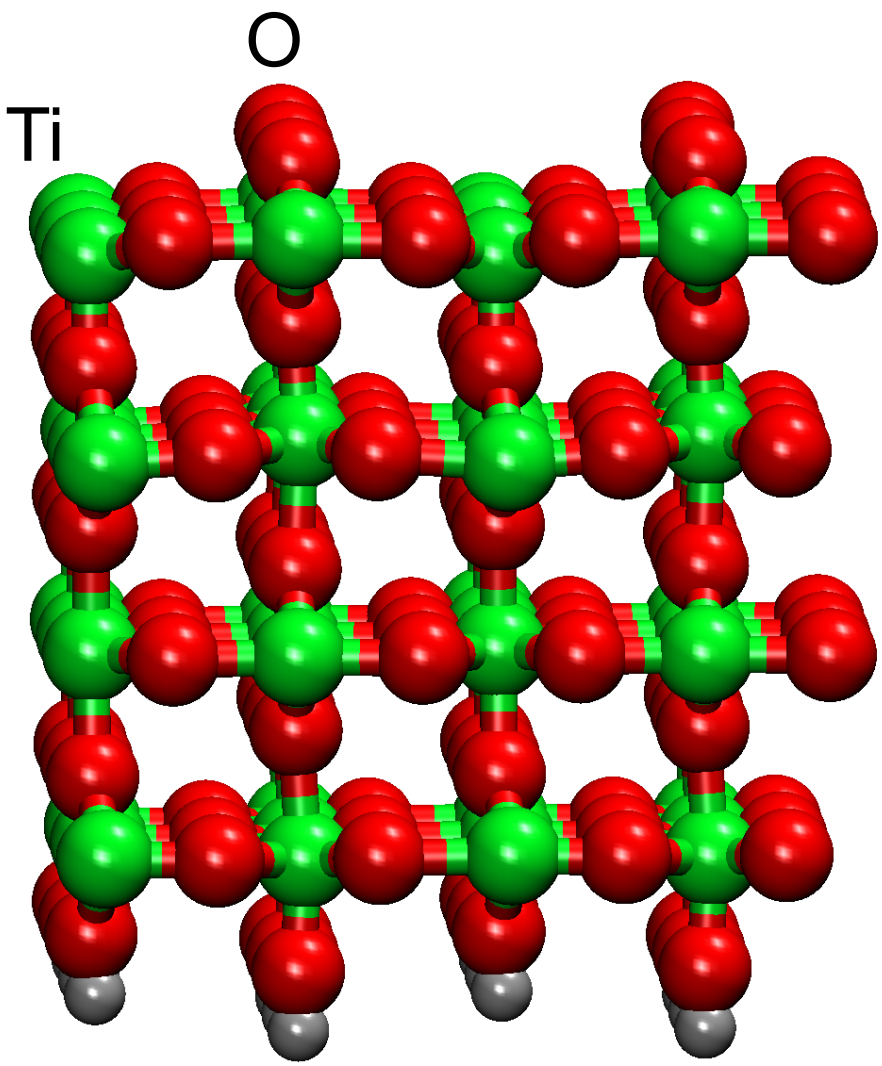
Water might undergo photodissociation in ultra-high vacuum study [1] (has not been reproduced by others).



Our goal: confirm or disprove through real-time simulation of the first step of the water photo-oxidation.

1 – S. Tan et al., JACS. 134:9978-9985 (2012)

Simulation methodology



Slab (4 - 6 layers thick)

DFT: GGA-PBE, GPAW code [1], Including DFT+U correction

ΔSCF approach for simulation of excitation

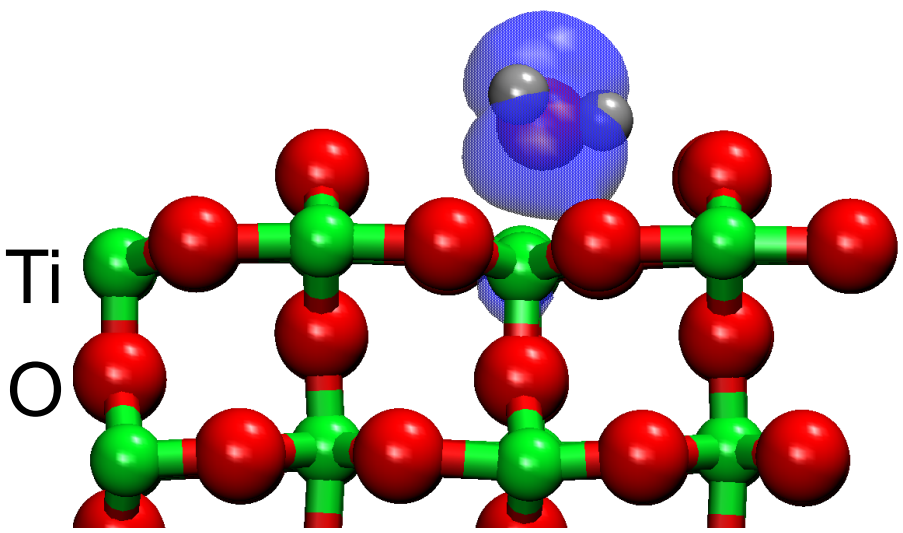
Ehrenfest dynamics for time propagation

1 – J. Enkovaara et al., J. Phys. Cond. Mat. 22:253202 (2010)

Dynamics of electron–hole pair on clean (110) surface

Hole on water non-bonding orbital

Excitation energy 9.3 eV



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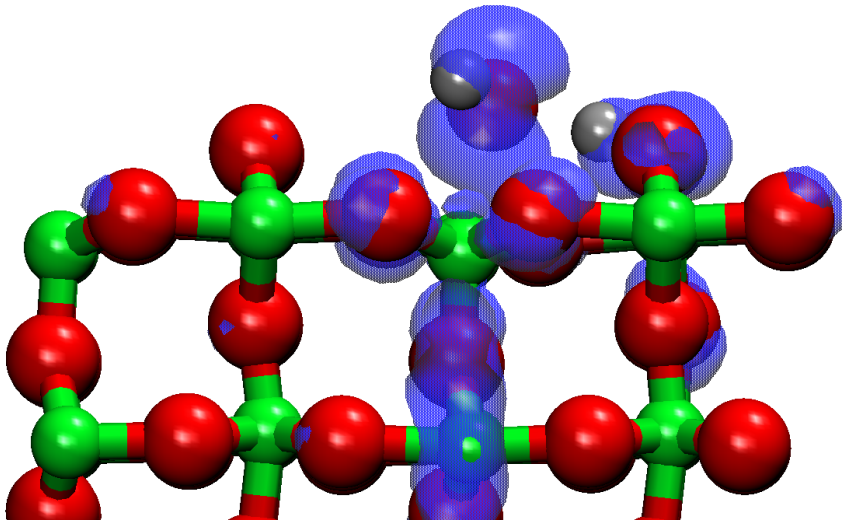


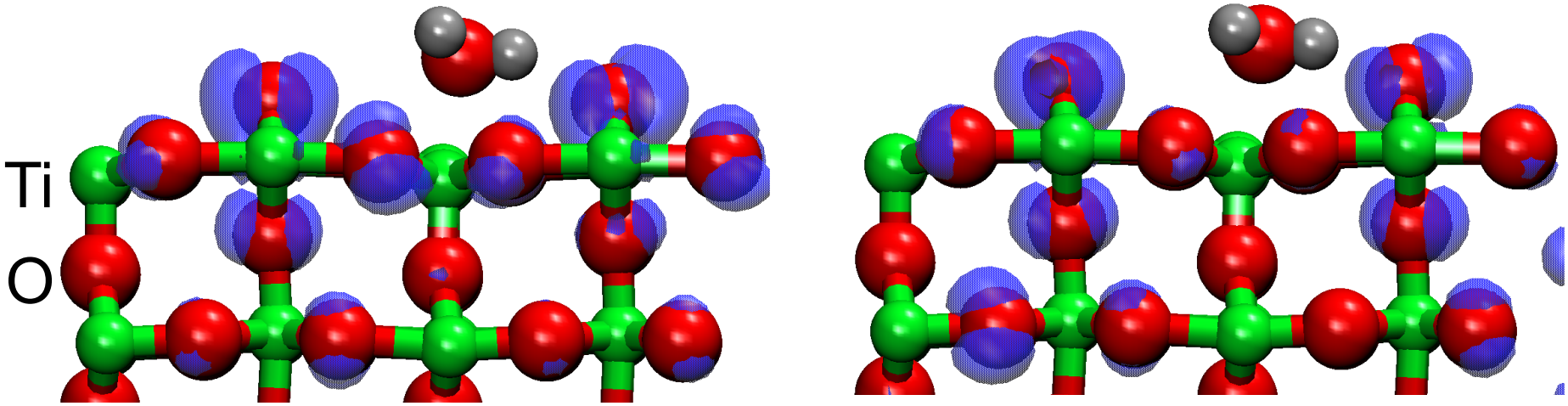
< 10 fs

WATER SPLITS!

Dynamics of electron–hole pair on clean (110) surface

Hole on surface localized slab eigenstate

Excitation energy 3.5 eV



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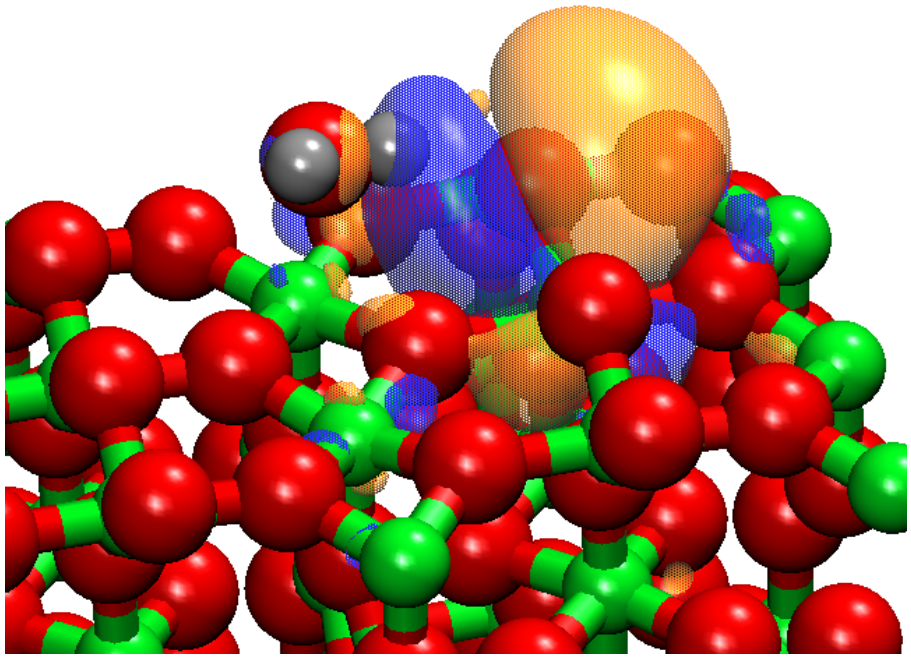
NO SPLITTING

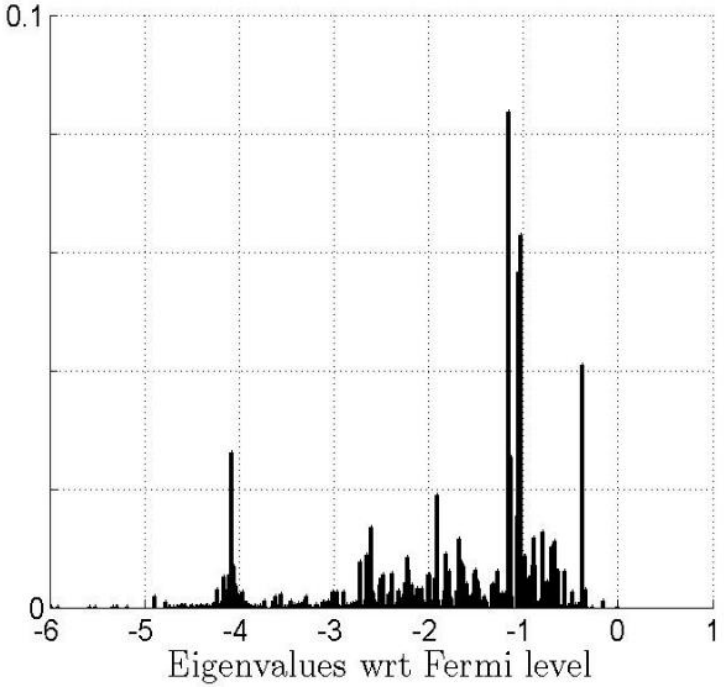
Dynamics of electron–hole pair on clean (110) surface

Hole on a MLWF (O-p_z orbital)

Excitation energy 3.8 eV

Maximally Localized Wannier Functions, computed using the *Wannier90* code [1]





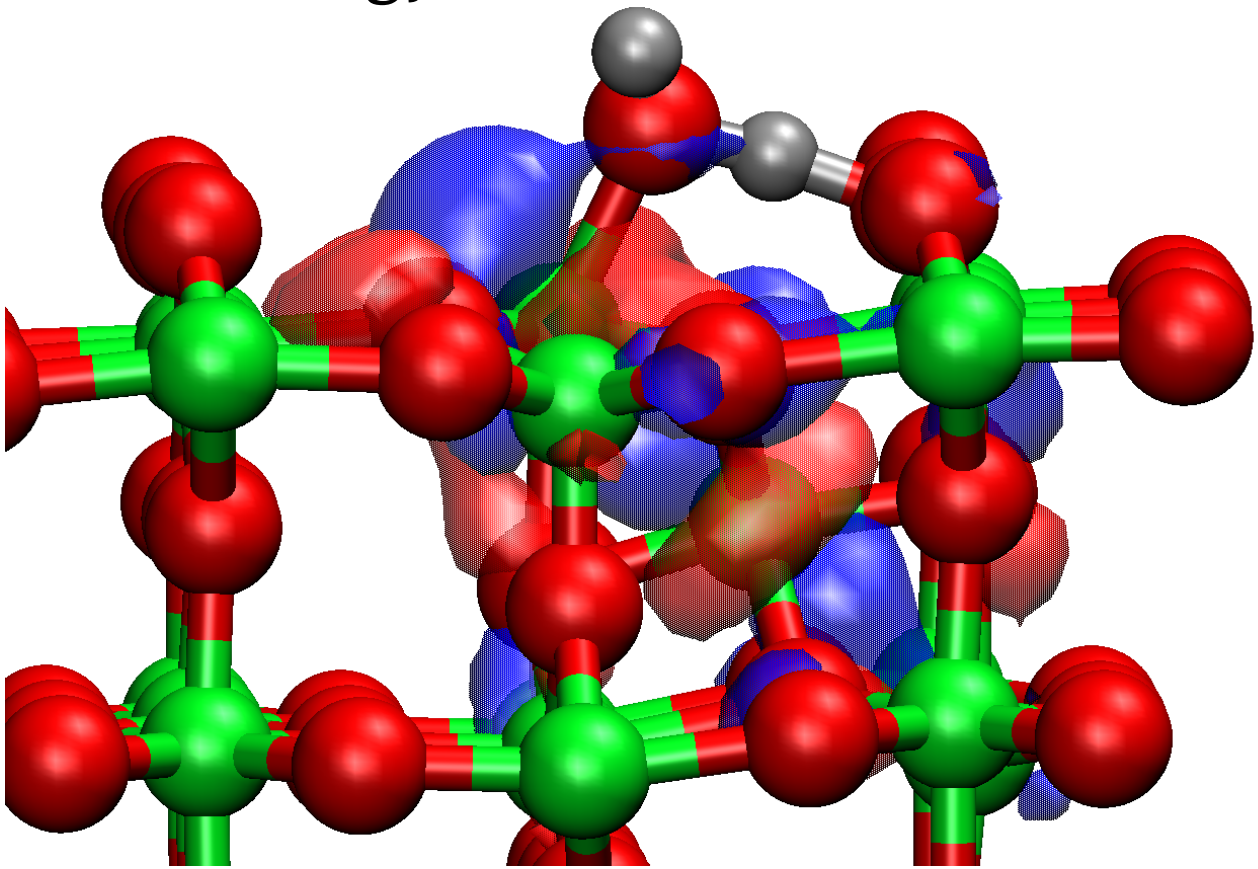
NO SPLITTING

[1] A. Mostofi *et al.* Comput. Phys. Commun. 178:685 (2008)

Interstitial titanium atom defect level

Hole on interstitial defect level

Excitation energy 1.7 eV



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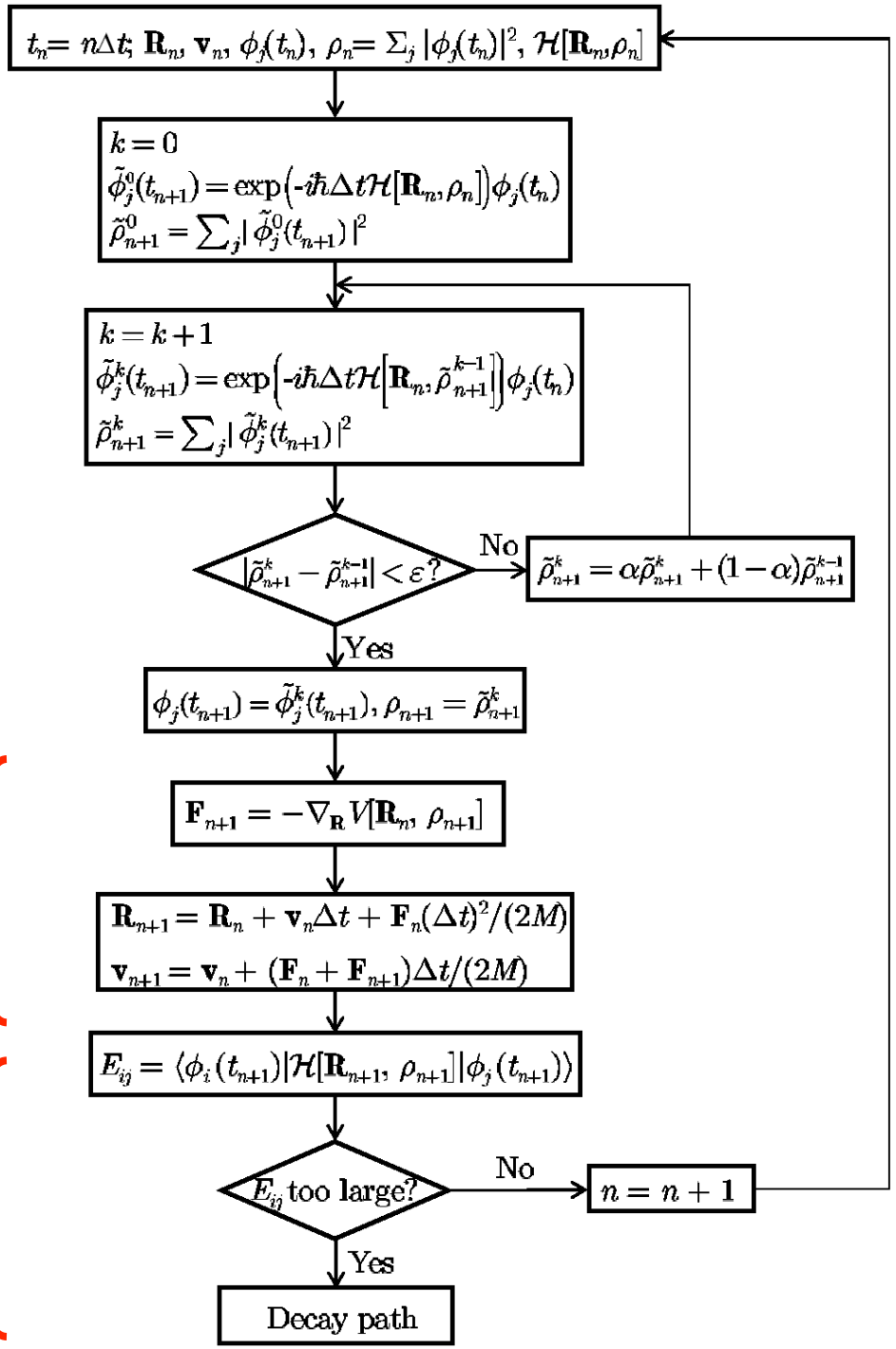
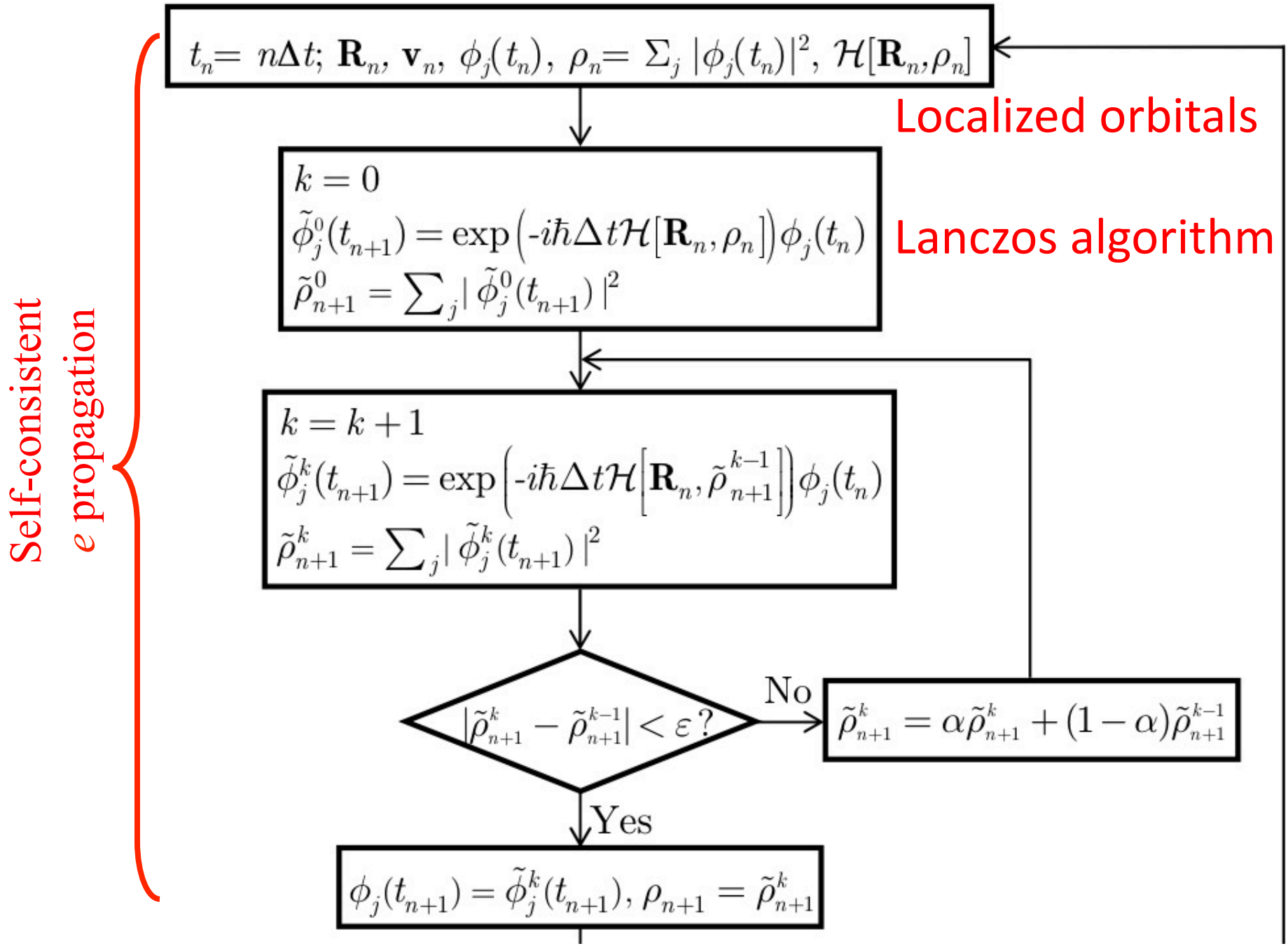
TDAP: an improved TDDFT scheme (computationally efficient) w/ Ehrenfest dynamics

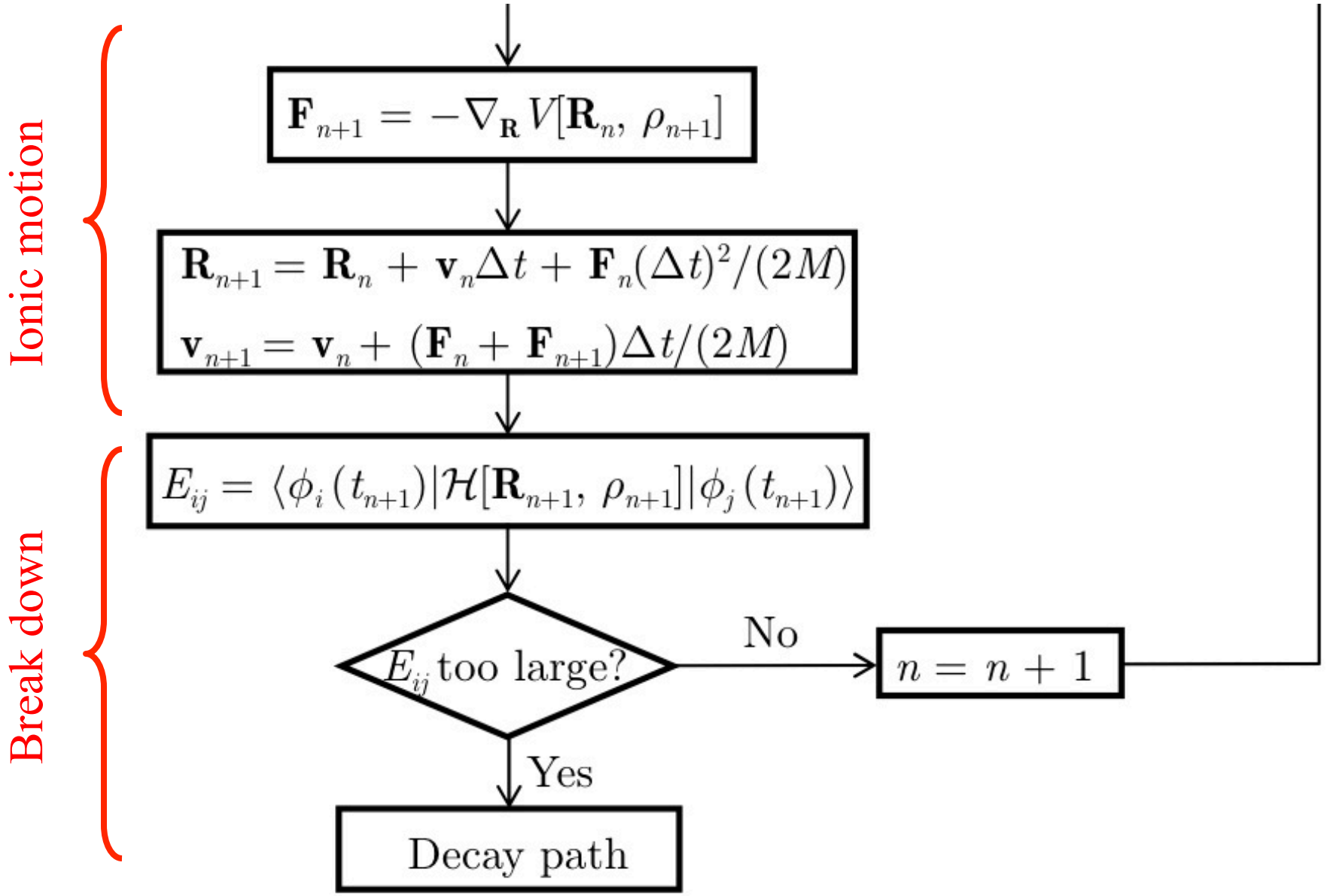
Self-consistent *e* propagation

Ionic motion

Break down

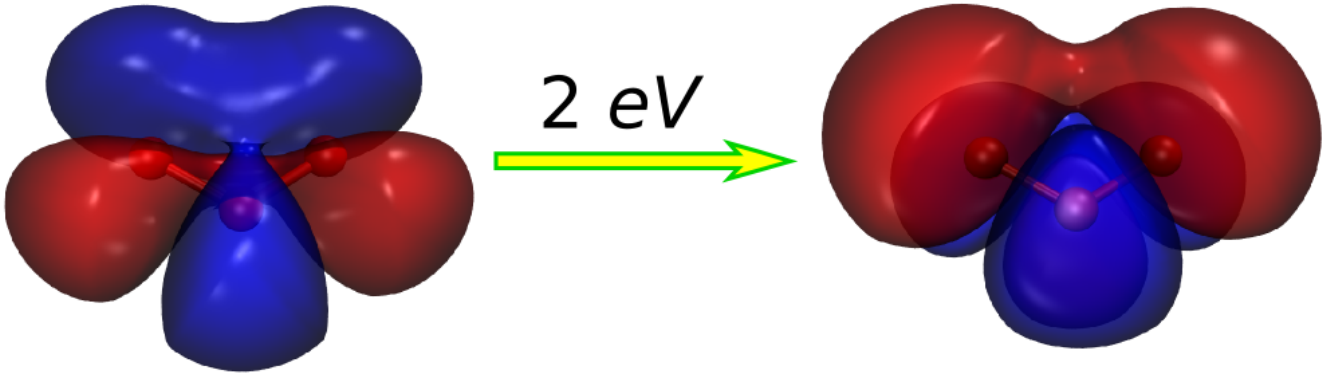



$t_n = n\Delta t;\ \mathbf{R}_n,\ \mathbf{v}_n,\ \phi_j(t_n),\ \rho_n = \Sigma_j\ |\phi_j(t_n)|^2,\ \mathcal{H}[\mathbf{R}_n,\rho_n]$
Localized orbitals
$k = 0$
$\tilde{\phi}_j^0(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}[\mathbf{R}_n,\rho_n]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^0 = \sum_j |\tilde{\phi}_j^0(t_{n+1})|^2$
Lanczos algorithm
$k = k+1$
$\tilde{\phi}_j^k(t_{n+1}) = \exp\left(-i\hbar\Delta t\mathcal{H}\left[\mathbf{R}_n,\tilde{\rho}_{n+1}^{k-1}\right]\right)\phi_j(t_n)$
$\tilde{\rho}_{n+1}^k = \sum_j |\tilde{\phi}_j^k(t_{n+1})|^2$
$|\tilde{\rho}_{n+1}^k - \tilde{\rho}_{n+1}^{k-1}| < \varepsilon ?$
No
$\tilde{\rho}_{n+1}^k = \alpha\tilde{\rho}_{n+1}^k + (1-\alpha)\tilde{\rho}_{n+1}^{k-1}$
Yes
$\phi_j(t_{n+1}) = \tilde{\phi}_j^k(t_{n+1}),\ \rho_{n+1} = \tilde{\rho}_{n+1}^k$
Self-consistent
e propagation


Ionic motion
Break down
$\mathbf{F}_{n+1} = -\nabla_{\mathbf{R}} V[\mathbf{R}_n, \rho_{n+1}]$
$\mathbf{R}_{n+1} = \mathbf{R}_n + \mathbf{v}_n \Delta t + \mathbf{F}_n (\Delta t)^2/(2M)$
$\mathbf{v}_{n+1} = \mathbf{v}_n + (\mathbf{F}_n + \mathbf{F}_{n+1}) \Delta t/(2M)$
$E_{ij} = \langle \phi_i(t_{n+1}) | \mathcal{H}[\mathbf{R}_{n+1}, \rho_{n+1}] | \phi_j(t_{n+1}) \rangle$
E_{ij} too large?
No
$n = n + 1$
Yes
Decay path

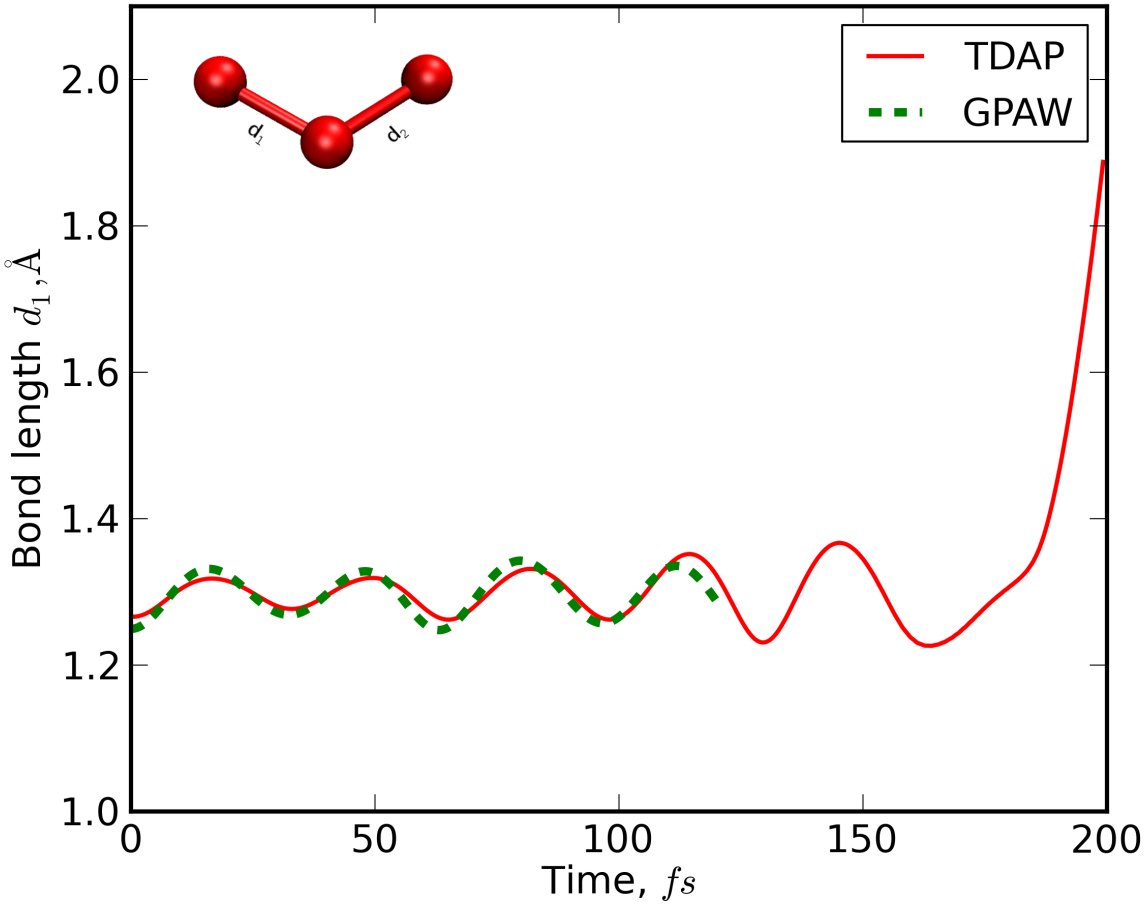
Example: ozone photolysis

- Excitation HOMO to LUMO: slow dissociation



Matsumi, Y. & Kawasaki, M. Photolysis of atmospheric ozone in the ultraviolet region. *Chemical reviews* **103**, 4767–4782 (2003).

1st excited state trajectory



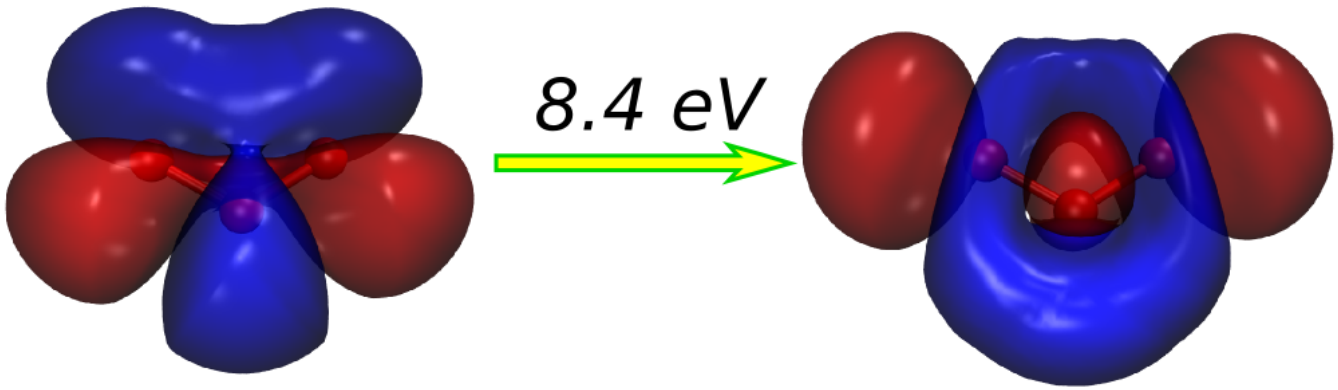
GPAW computation time 37 days (4 cores)

TDAP: 1 hour

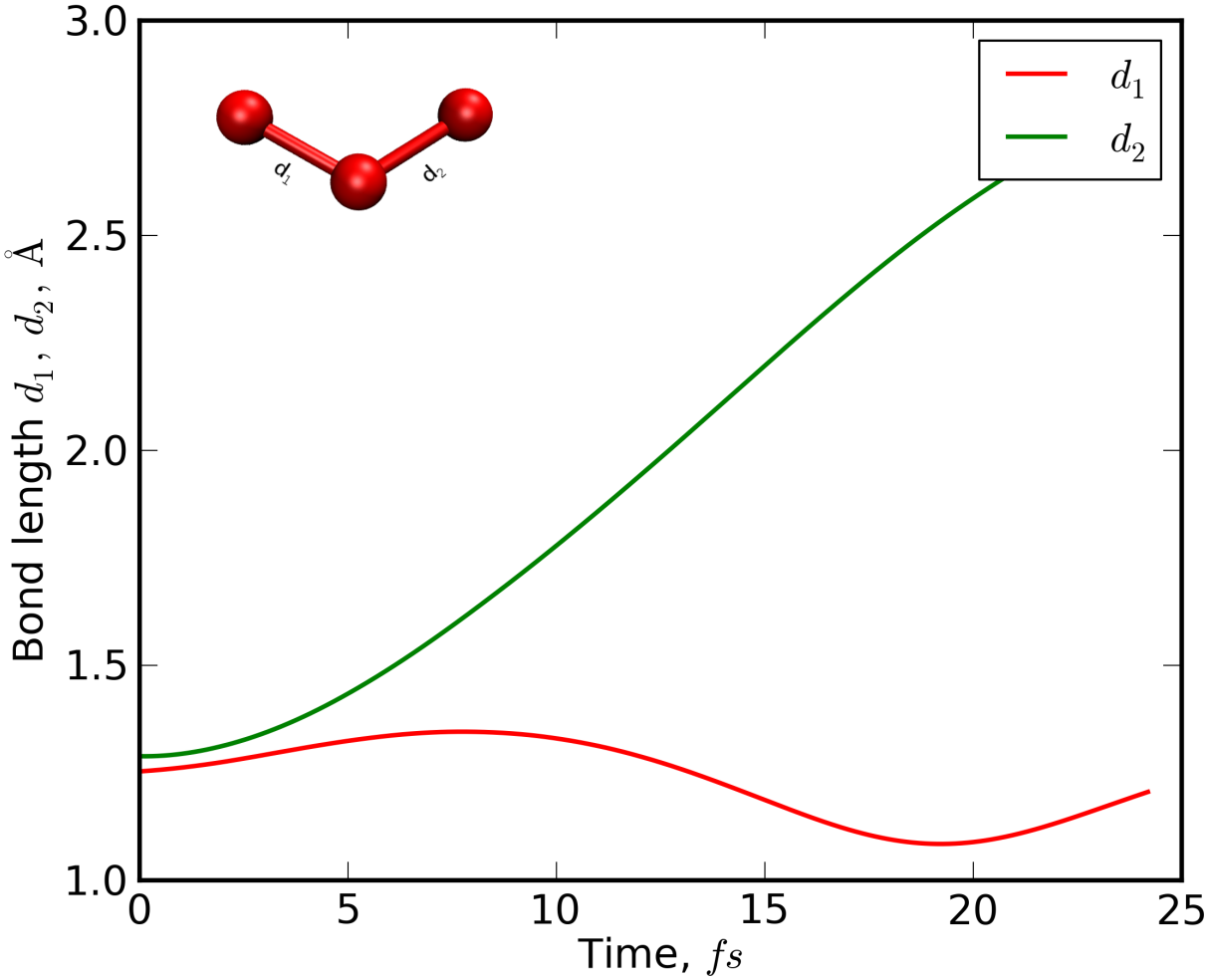
Time step: 5 attosec (both)

Example: ozone photolysis

- Excitation HOMO to LUMO+1: quick dissociation



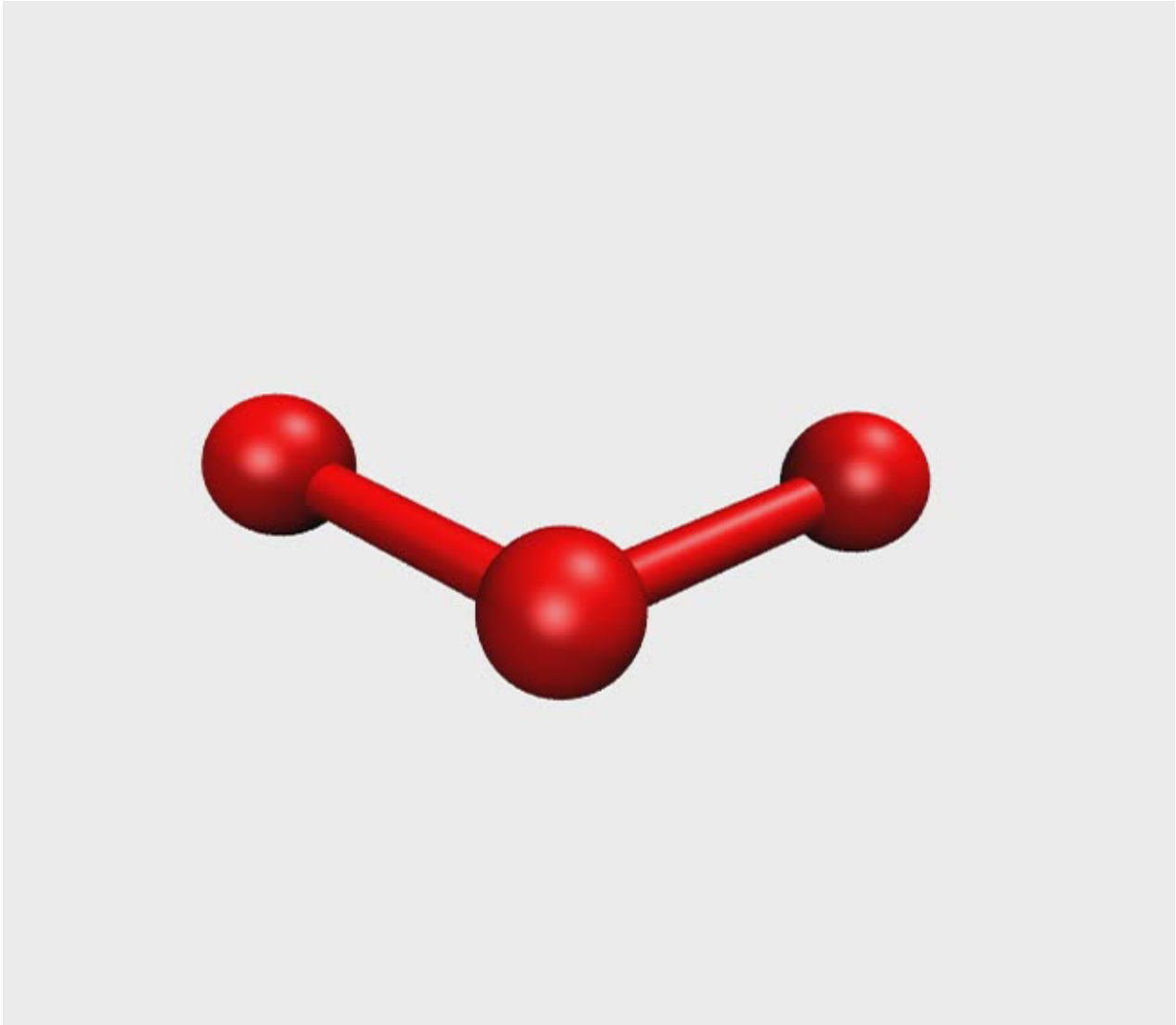
2nd excited state trajectory



2^{nd} excited state trajectory

- Movie:

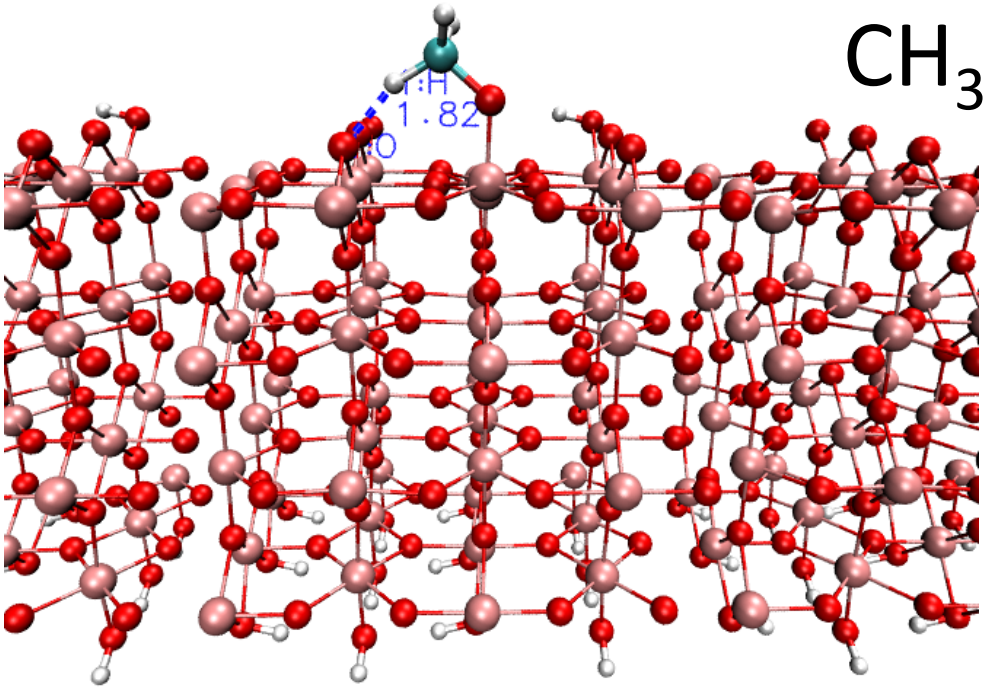
o3split.mov



Methoxy splitting on TiO_2 surface

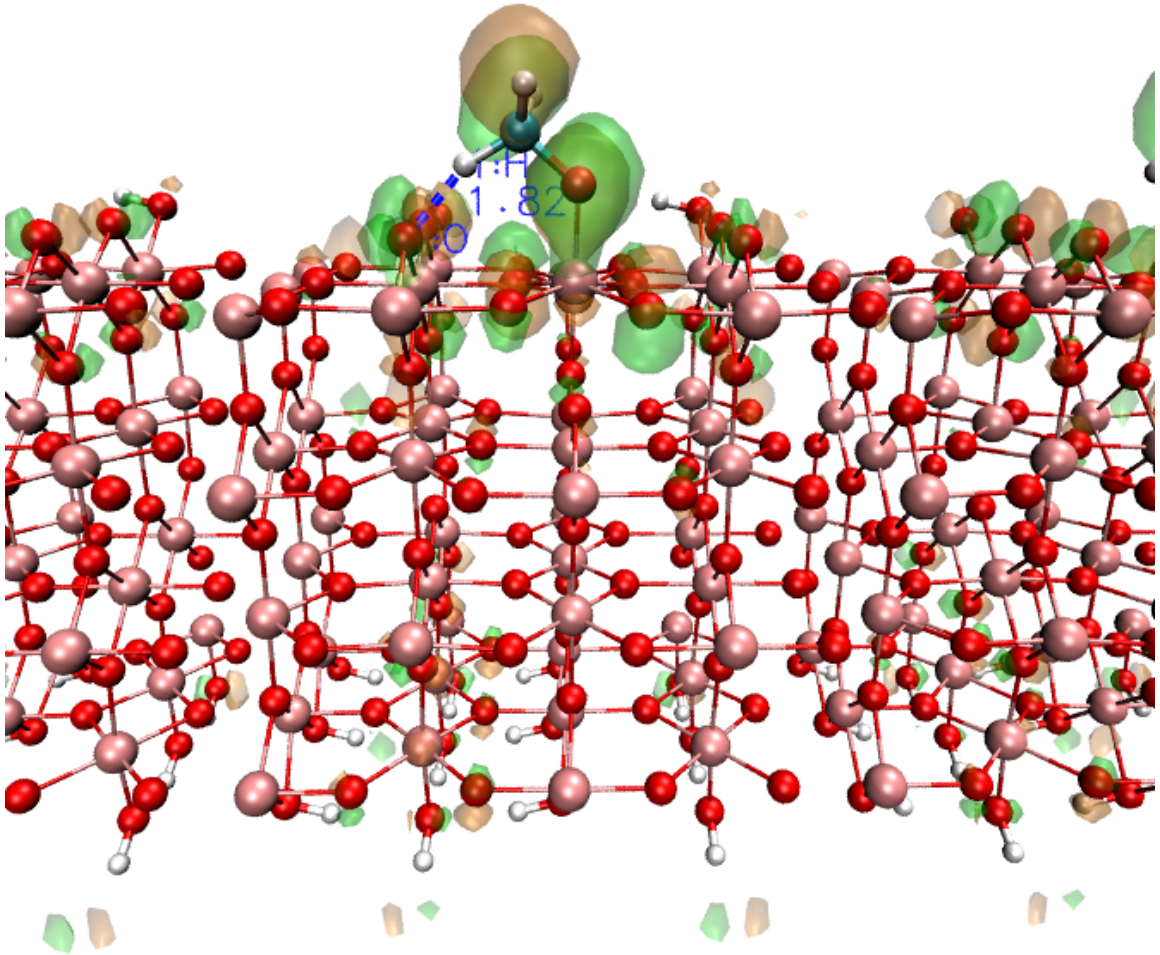
- Formaldehyde was photochemically produced from methoxy on TiO_2 (110) surface

$$CH_3OH + h\nu \rightarrow CH_2O + H_2$$

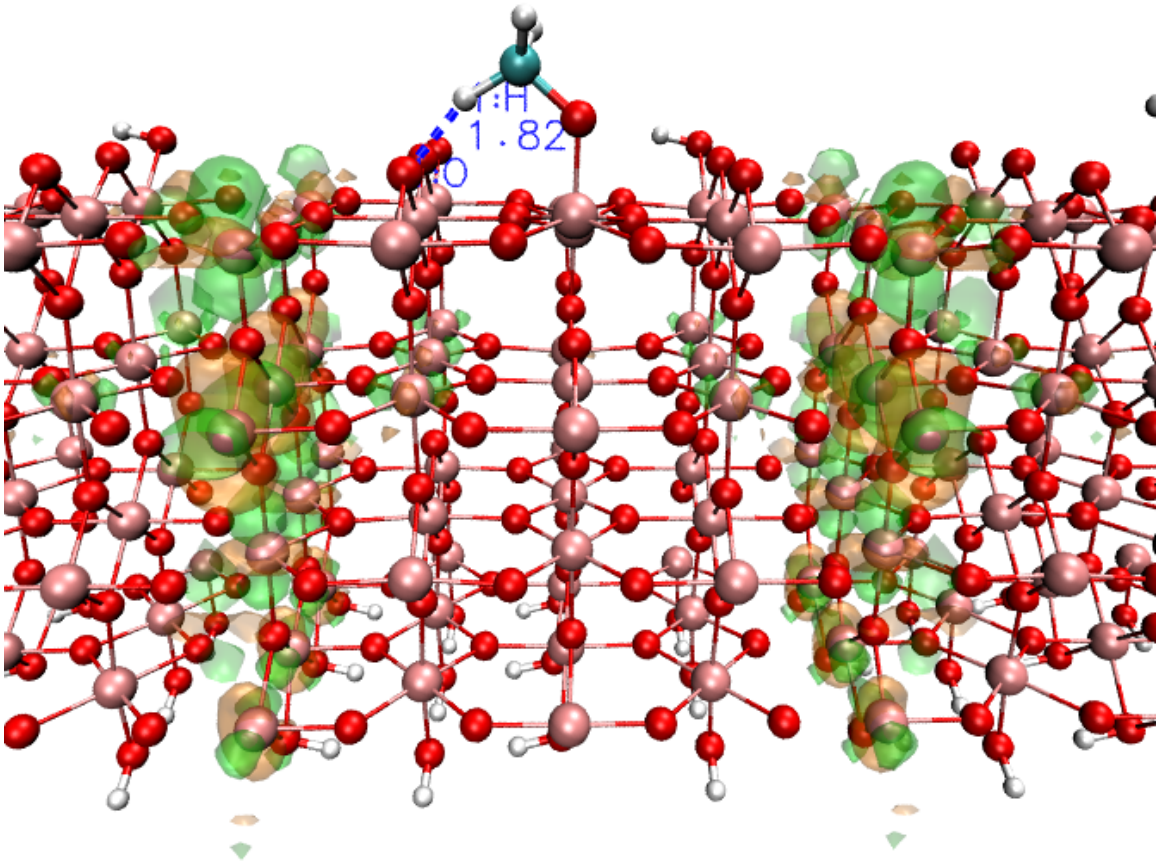


Phillips, K. R., Jensen, S. C., Baron, M., Li, S.-C. & Friend, C. M. Sequential photo-oxidation of methanol to methyl formate on TiO2 (110). *Journal of the American Chemical Society* **135**, 574–577 (2013).

Hole: HOMO-4 State



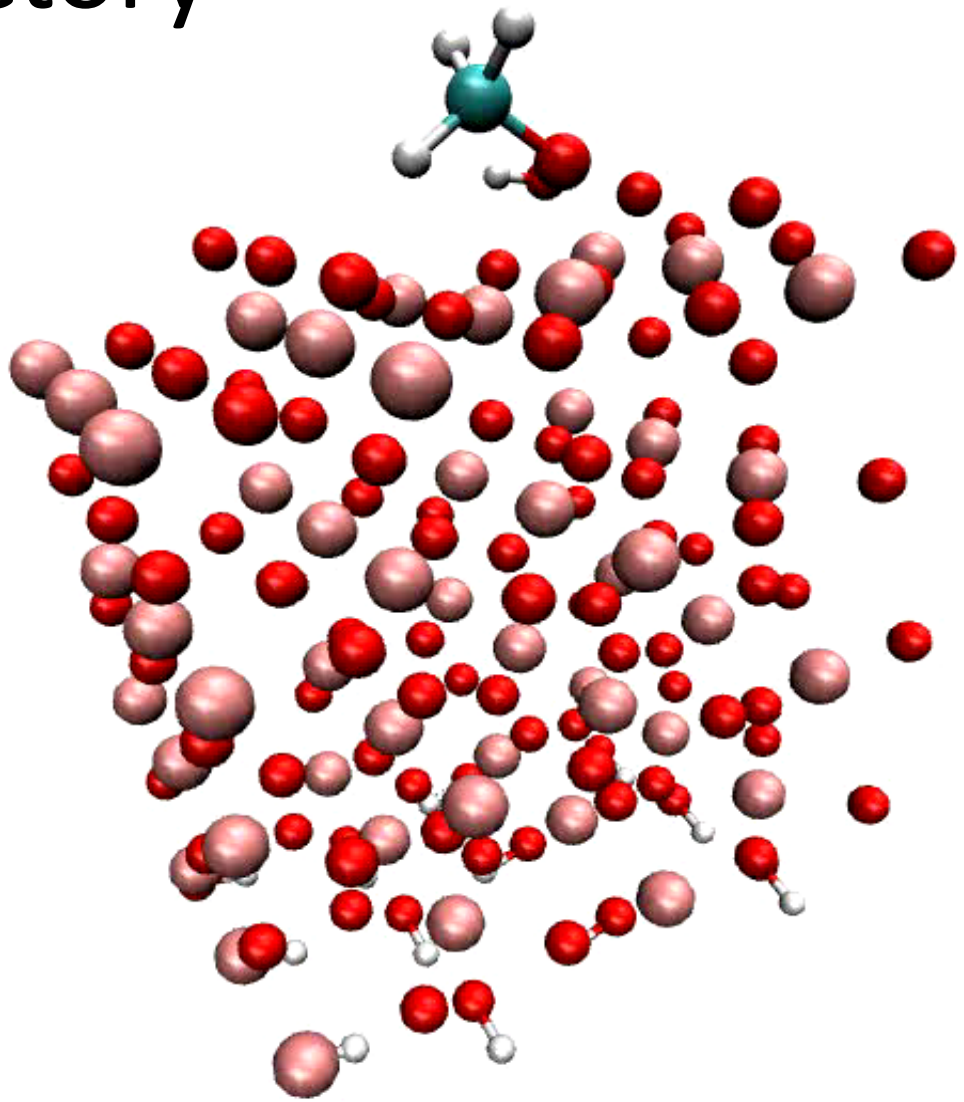
Electron: LUMO state



TDDFT trajectory

- Movie:

mxsplit.mpg



Conclusions and outlook

Encouraging results:

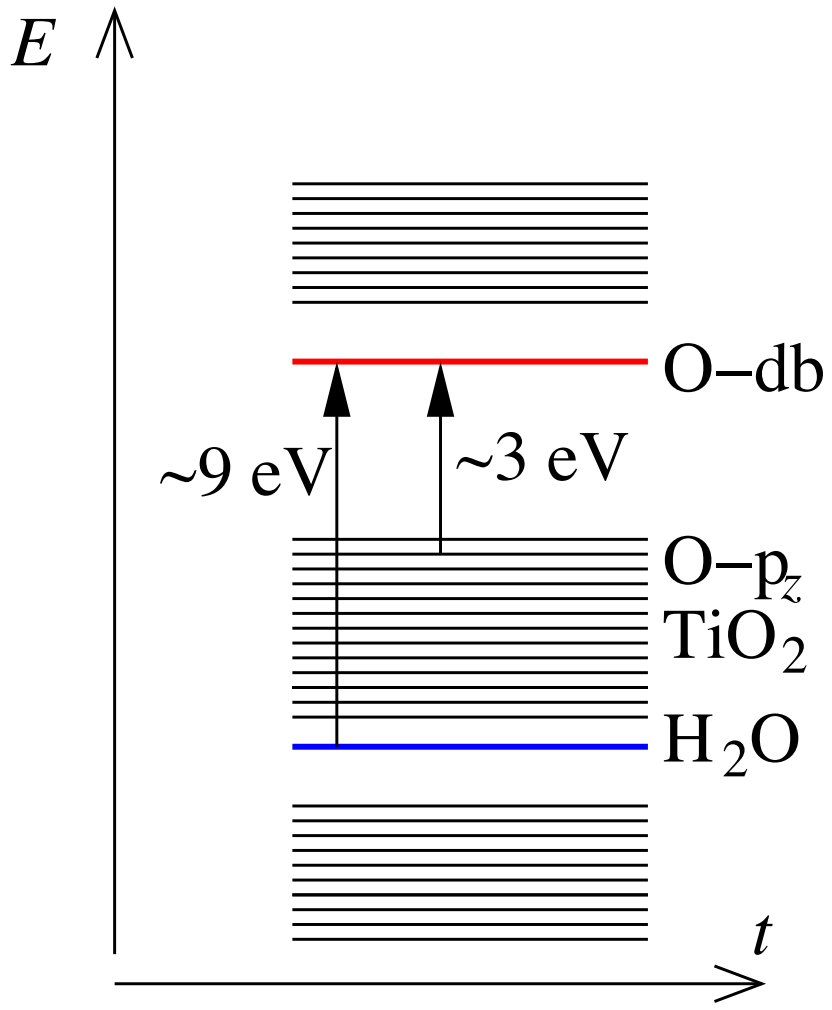
- Clear distinction between systems that show reaction and systems that don't
- Issue of simulation duration

"Behind the scenes": Dozens of simulations with varying initial conditions:

- Hole localization
- Initial configuration
- Initial velocities of nuclei, etc.

Additional features that may be necessary for quantitative comparison to experiment:

- Adsorbate – adsorbate interactions
- Presence of water and changes in the dielectric constant of the environment
- Presence of types of defects, or complex interplay between defects of different types on surface
- Other reactive sites (steps, kinks), other surface orientations (facets)


E
O–db
~9 eV
~3 eV
O–p$_z$
TiO$_2$
H$_2$O
t

Computational setup

- Excitation: promoting electron from HOMO-4 to LUMO to model hole on methoxy group
- In experiment 3-6 eV UV band was used

	E_{gap}, *eV* Bulk TiO_2	**E_{gap}, *eV* Methoxy on (110) TiO_2**
Experiment	3.03	-
SIESTA DFT+U	2.8	2.6
TDAP, ΔSCF	-	2.9

TDAP: improved TDDFT (computationally efficient) + Ehrenfest dynamics

Electrons are propagated according to time-dependent Kohn-Sham equations

$$i\hbar\frac{\partial\phi_j(\mathbf{r},t)}{\partial t}=\hat{H}_{KS}\phi_j \qquad \rho(\mathbf{r},t)=\sum_j|\phi_j(\mathbf{r},t)|^2$$

Nuclei are propagated classically

$$M_J\frac{d^2\mathbf{R}_J^{cl}(t)}{dt^2}=-\nabla_{\mathbf{R}_J^{cl}}\left[V_{ext}^J(\mathbf{R}_J^{cl},t)-\int\frac{Z_J\rho(\mathbf{r},t)}{|\mathbf{R}_J^{cl}-\mathbf{r}|}d\mathbf{r}+\sum_{I\neq J}\frac{Z_JZ_I}{|\mathbf{R}_J^{cl}-\mathbf{R}_I^{cl}|}\right]$$

$$\rho_J(\mathbf{R},t)=|\psi_J(\mathbf{R},t)|^2=\delta\left(\mathbf{R}-\mathbf{R}_J^{cl}\right)$$