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技術を社会へ−Integration for Innovation

First principles simulation for photo-excitation and carrier splitting in condensed maters

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Acknowledgements

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outline

1. Requirements on simulations (designing photovoltaic material)→Photo-absorption vs. carrier splitting
2. Theoretical approach(real-time propagation TDDFT)
3. Photo-induced increase of dipole moment in Polar crystal and TTF/TCNQ dimer (DA pair)
4. One technical note on effect of UV light
5. Summary

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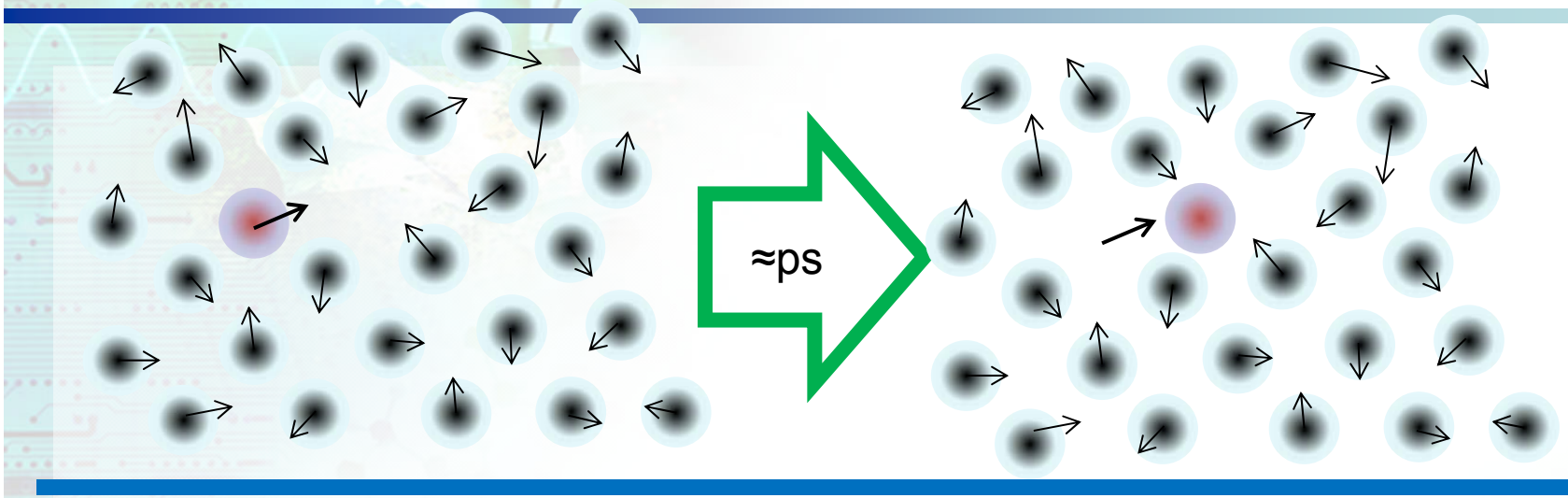
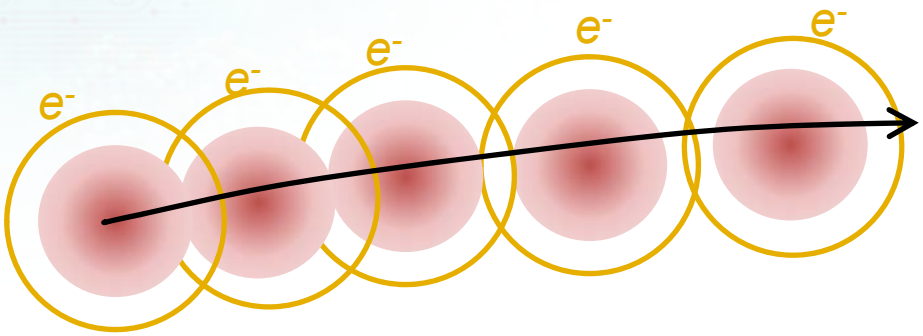
Equilibrium condition was





Equilibrium cases:

Electrons running around immediately follow ion motion and remain their ground states!

$$H\psi_n = \varepsilon_n \psi_n$$

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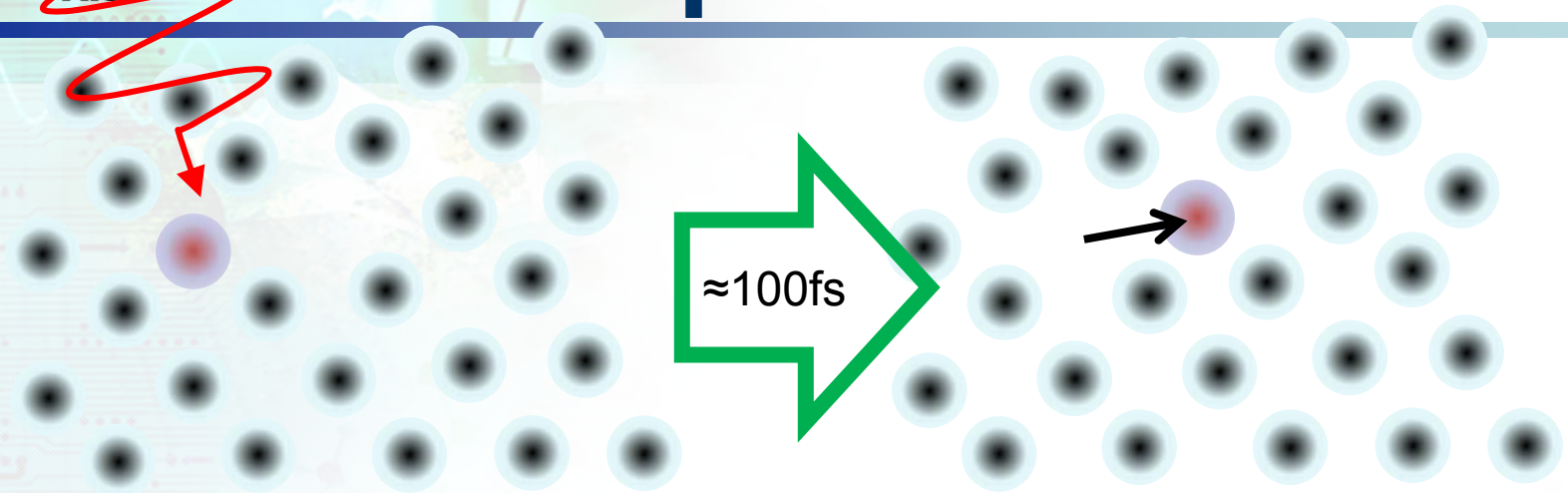
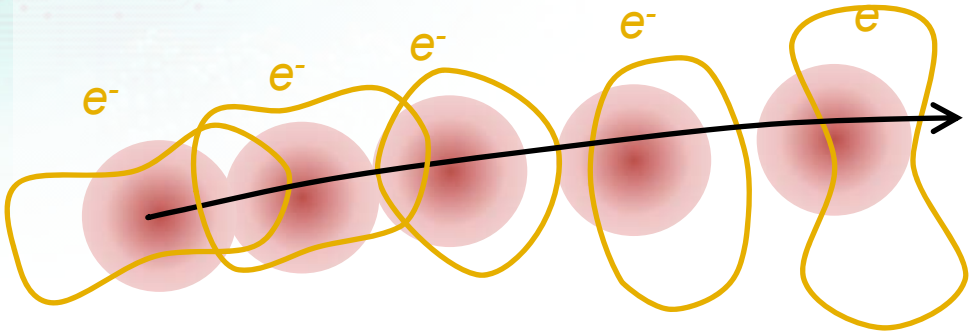
Non-equilibrium condition





Electrons running around are excited and does not follow ion motion and remain their excited states for a while!

$$H\psi_n = i\hbar\frac{d}{dt}\psi_n$$

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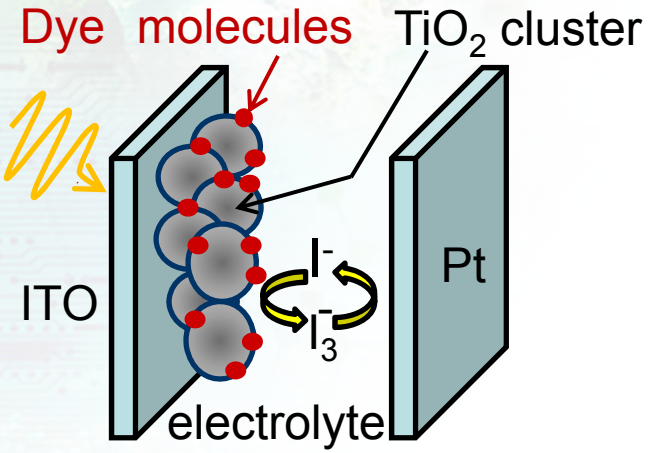
Equilibrium *vs* non-equilibrium Phenomena in different time-scale

Wet: using electrolyte



→ Redox dynamics and recombination rate govern the efficiency
(Electron transport from dye to TiO_2 → fast)
Requirements
Theoretical approach must be the thermo-dynamical approach

Solid (NW, Q-dot): using p-n junction

Carrier dynamics govern the photovoltaic process:
Photo-absorption rate vs. e-h splitting rate
→ What is required for theoretical approach?

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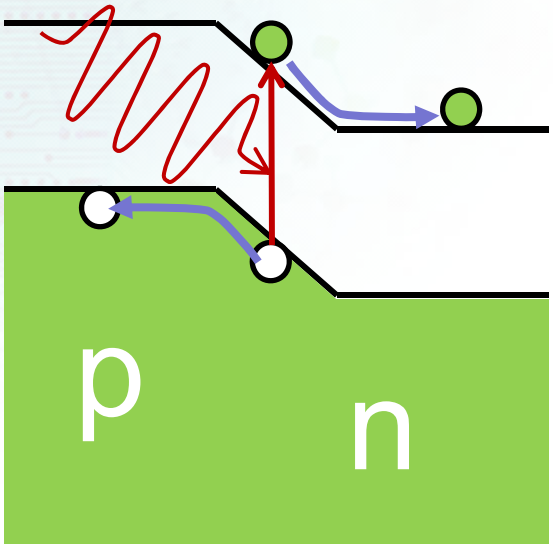
Necessity of solving electron dynamics in fast-process

- Electrons and holes are no-longer steady states



Need of direct simulation for electron dynamics by solving time-dependent Schrödinger equation

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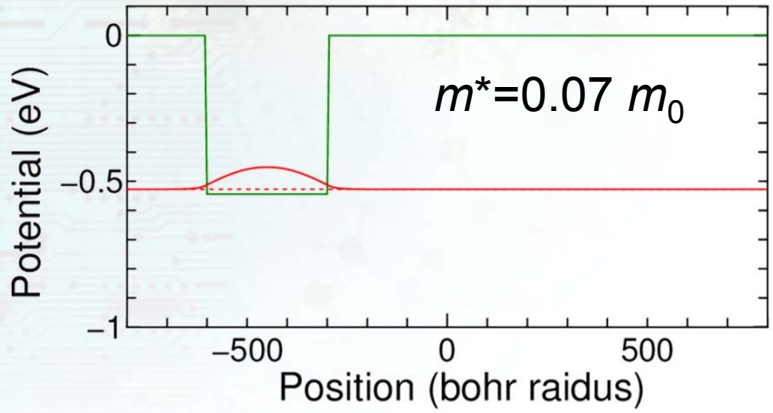
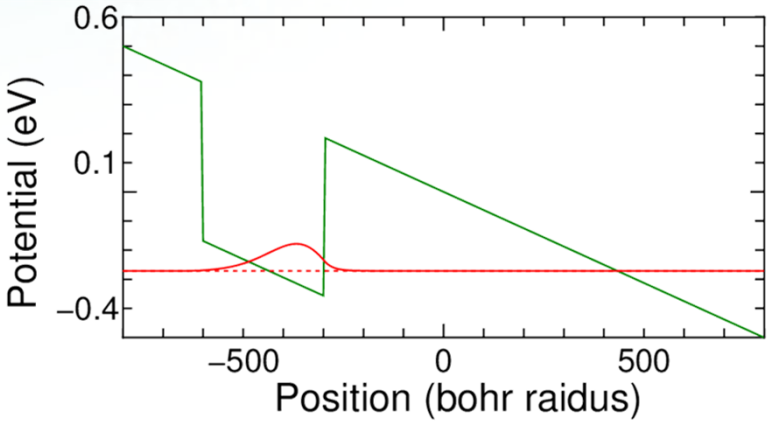
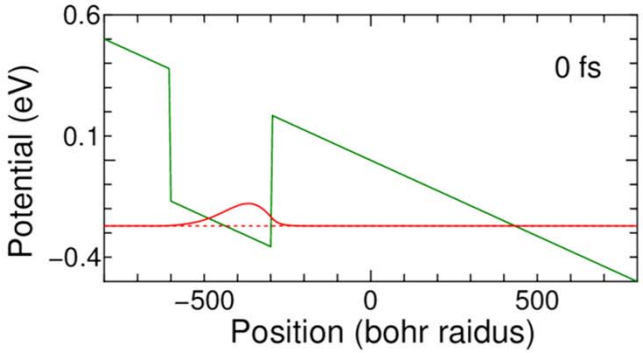
Thought from simple 1D model

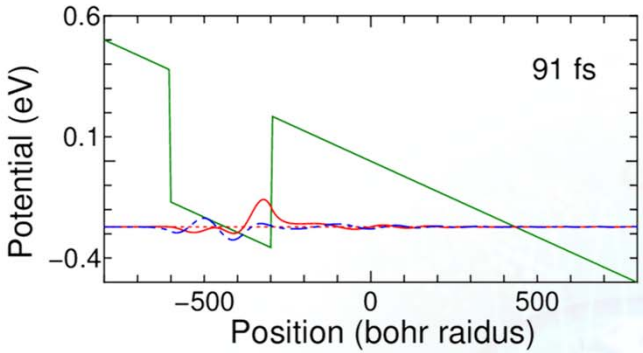
Collaboration with Mr. Arora (IIT)

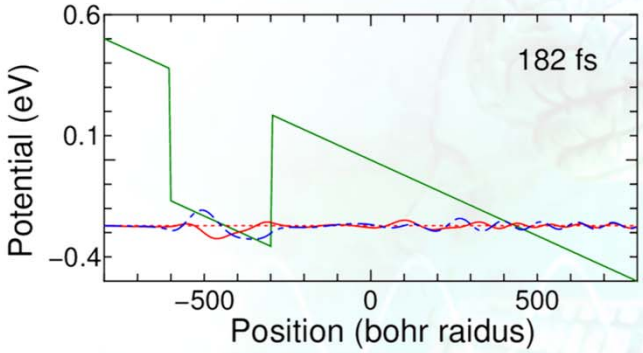
$$H\psi = E\psi \quad \Rightarrow \quad i\hbar\frac{d\psi}{dt} = (H + E \cdot x \cdot sin(\omega t))\,\psi$$











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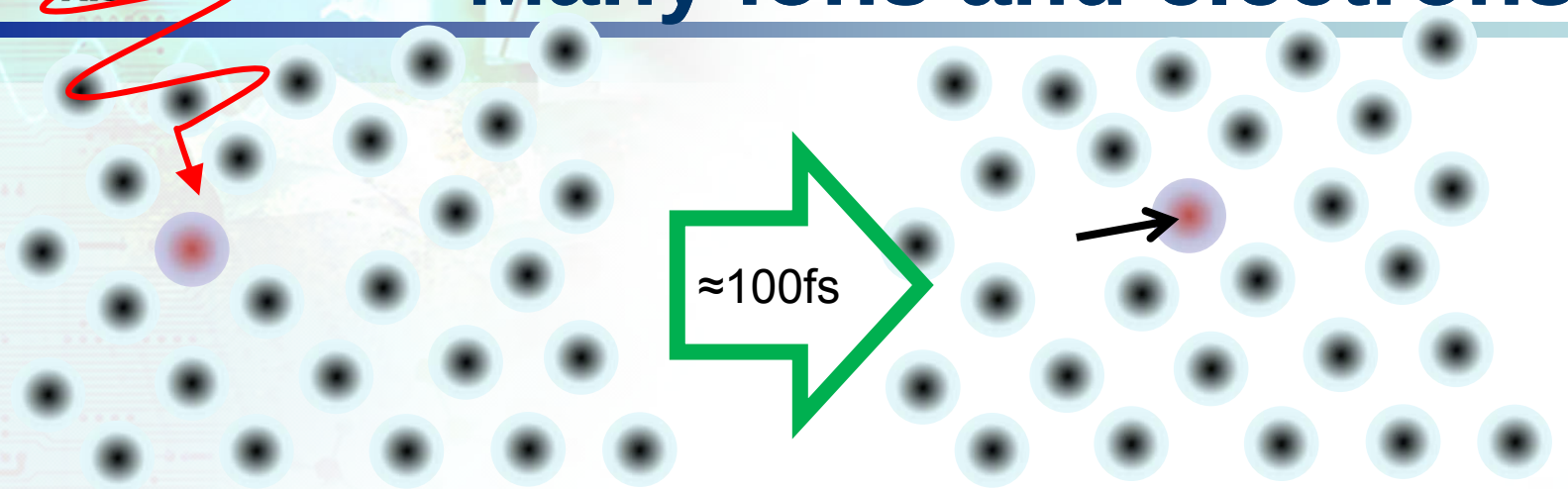
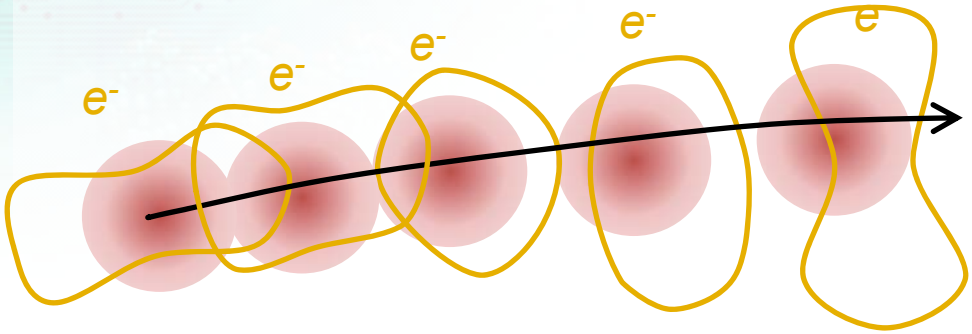
For real materials
Many ions and electrons





Applying the time-dependent density functional theory and Ehrenfest dynamics

$$H_{KS}\psi_n^{KS} = i\hbar\frac{d}{dt}\psi_n^{KS}$$

$$F_I = M_I\frac{d^2R_I}{dt^2}$$

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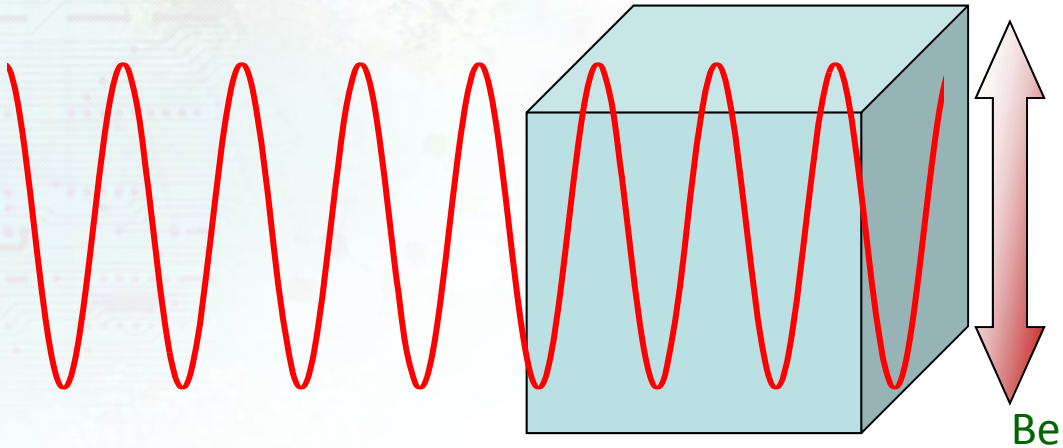
Computational methods(1)

Pioneering works by time-dependent density functional theory (TDDFT): Prof. Yabana's group

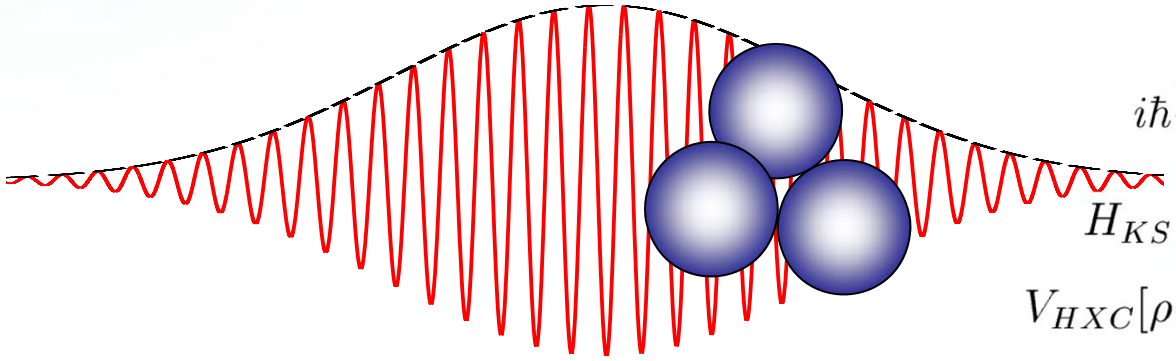


$$i\hbar\frac{d\psi_{n,k}(\mathbf{r},t)}{dt} = H_{KS}\left[\rho(\mathbf{r},t)\right]\psi_{n,k}(\mathbf{r},t)$$

$$H_{KS}\left[\rho(\mathbf{r},t)\right] \Rightarrow H_{KS}\left[\rho(\mathbf{r},t),\mathbf{A}(t)\right]$$

$$\frac{1}{2m}\left(\mathbf{P}-\frac{1}{c}\mathbf{A}(t)\right)^2$$

Bertsch, et al., PRB62 7998, (2000).



$$i\hbar\frac{d\psi_{n,k}(\mathbf{r},t)}{dt} = H_{KS}\left[\rho(\mathbf{r},t)\right]\psi_{n,k}(\mathbf{r},t)$$

$$H_{KS}\left[\rho(\mathbf{r},t)\right] \Rightarrow H_{KS}\left[\rho(\mathbf{r},t),V_{ext}(\mathbf{r},t)\right]$$

$$V_{HXC}[\rho(\mathbf{r},t)] \Rightarrow V_{HXC}[\rho(\mathbf{r},t)] + V_{ext}(\mathbf{r},t)$$

Castro et al., Eur. Phys. J. D 28, 211 (2004).

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Computational methods(2)

Energy conservation rule in TDDFT-MD

$$\sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \frac{1}{2} \int\int \frac{\rho(\mathbf{r}',t)\rho(\mathbf{r},t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$
$$+ \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r} + \sum_I Z_I \left(\int \frac{\rho(\mathbf{r},t)}{|\mathbf{R}_I(t)-\mathbf{r}|} d\mathbf{r} + \sum_{J\neq I} \frac{Z_J}{|\mathbf{R}_I(t)-\mathbf{R}_J(t)|} \right) \equiv E_{tot}^{DFT}(\mathbf{r},t)$$

MD simulation must conserve

$$U(t) = \sum_I \frac{M_I}{2} \left(\frac{d\mathbf{R}_I}{dt} \right)^2 + E_{tot}^{DFT}(\mathbf{r},t)$$

TDDFT term

$$\frac{dU(t)}{dt} = \sum_I \frac{d\mathbf{R}_I(t)}{dt} \cdot \left(M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{dE_{tot}^{KS}(\mathbf{r},t)}{d\mathbf{R}_I(t)} \right) + \sum_i \left(\frac{d\psi_i^*(\mathbf{r},t)}{dt} \frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} + C.C. \right)$$

$$M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} = -\frac{dE_{tot}^{DFT}(\mathbf{r},t)}{d\mathbf{R}_I(t)}$$
$$\frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} = H_{KS}(\mathbf{r},t)\psi_i(\mathbf{r},t) = i\hbar \frac{d\psi_i(\mathbf{r},t)}{dt}$$

$= 0$

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Computational methods(3)

Energy conservation rule in TDDFT-MD (continued)

$$\sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \frac{1}{2} \int\int \frac{\rho(\mathbf{r}',t)\rho(\mathbf{r},t)}{|\,\mathbf{r}-\mathbf{r}'\,|} d\mathbf{r}' d\mathbf{r}$$
$$+ \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r} + \sum_I Z_I \left(\int \frac{\rho(\mathbf{r},t)}{|\,\mathbf{R}_I(t)-\mathbf{r}\,|} d\mathbf{r} + \sum_{J\neq I} \frac{Z_J}{|\,\mathbf{R}_I(t)-\mathbf{R}_J(t)\,|} \right) \equiv E_{tot}^{DFT}(\mathbf{r},t)$$

With time-varying external field

$$V_{ext}(\mathbf{r},t) = \int \frac{\rho_{ext}(\mathbf{r}',t)}{|\,\mathbf{r}'-\mathbf{r}\,|} d\mathbf{r}'$$

$$E_{tot}^{DFT}(\mathbf{r},t)$$
$$= \sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r}$$
$$+ \frac{1}{2} \int\int \frac{(\rho(\mathbf{r}',t)+\rho_{ext}(\mathbf{r}',t))\,(\rho(\mathbf{r},t)+\rho_{ext}(\mathbf{r},t))}{|\,\mathbf{r}-\mathbf{r}'\,|} d\mathbf{r}' d\mathbf{r}$$
$$+ \sum_I Z_I \left(\int \frac{(\rho(\mathbf{r},t)+\rho_{ext}(\mathbf{r},t))}{|\,\mathbf{R}_I(t)-\mathbf{r}\,|} d\mathbf{r} + \sum_{J\neq I} \frac{Z_J}{|\,\mathbf{R}_I(t)-\mathbf{R}_J(t)\,|} \right)$$

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Computational methods(4)

$E_{tot}^{DFT}(\mathbf{r},t)$

Miyamoto, Zhang, Phys. Rev. B77, 165123 (2008)

$$= \sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r}$$

$$+ \frac{1}{2} \int\int \frac{(\rho(\mathbf{r}',t) + \rho_{ext}(\mathbf{r}',t))\,(\rho(\mathbf{r},t) + \rho_{ext}(\mathbf{r},t))}{|\,\mathbf{r} - \mathbf{r}'\,|} d\mathbf{r}' d\mathbf{r}$$

$$+ \sum_I Z_I \left(\int \frac{(\rho(\mathbf{r},t) + \rho_{ext}(\mathbf{r},t))}{|\,\mathbf{R}_I(t) - \mathbf{r}\,|} d\mathbf{r} + \sum_{J \neq I} \frac{Z_J}{|\,\mathbf{R}_I(t) - \mathbf{R}_J(t)\,|} \right)$$

$$U(t) = \sum_I \frac{M_I}{2} \left(\frac{d\mathbf{R}_I}{dt} \right)^2 + E_{tot}^{DFT}(\mathbf{r},t)$$

Goes to zero!

$$\frac{dU(t)}{dt} = \sum_I \frac{d\mathbf{R}_I(t)}{dt} \cdot \left(M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{dE_{tot}^{KS}(\mathbf{r},t)}{d\mathbf{R}_I(t)} \right) + \sum_i \left(\frac{d\psi_i^*(\mathbf{r},t)}{dt} \frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} + C.C. \right)$$

$$+ \int \frac{d\rho_{ext}(\mathbf{r},t)}{dt} \left(\int \frac{(\rho(\mathbf{r}',t) + \rho_{ext}(\mathbf{r}',t))}{|\,\mathbf{r}' - \mathbf{r}\,|} d\mathbf{r}' + \sum_I Z_I \frac{1}{|\,\mathbf{R}_I(t) - \mathbf{r}\,|} \right) d\mathbf{r}$$

Time integral=W, so U-W=Conserved quantity

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Computational methods(5)

- Time-dependent density functional theory for real-time propagation of electron wave functions *[Sugino, Miyamoto, PRB59, 2579 (1999).]*
- Adding scalar potential $V_{ext}(r,t)$ to $H_{KS}(r,t)$ for optical E-field satisfying the energy conservation rule *[Miyamoto, Zhang, PRB77, 165123 (2008).]*

$$i\hbar \frac{d\psi_n(\mathbf{r},t)}{dt} = \{\ H_{KS}(\mathbf{r},t) + V_{ext}(\mathbf{r},t)\ \}\psi_n(\mathbf{r},t)$$

- Plane wave basis (60 Ry), norm-conserving pseudopotential, LDA

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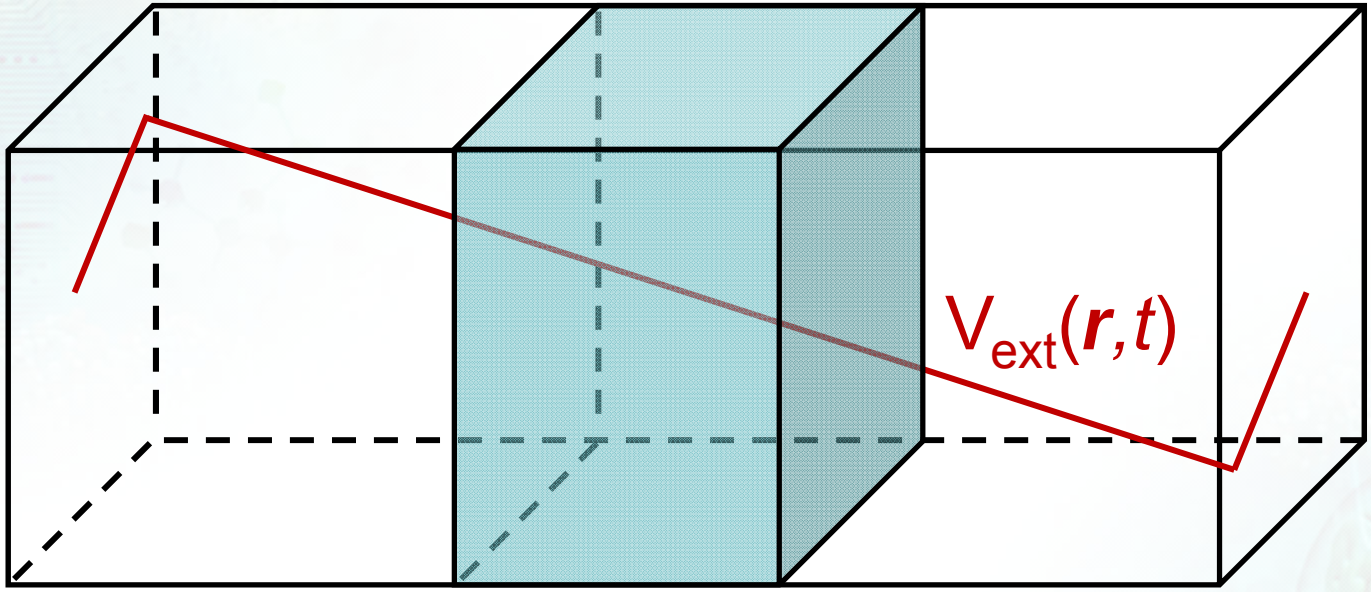
Computational methods(6)

Periodic boundary conditions



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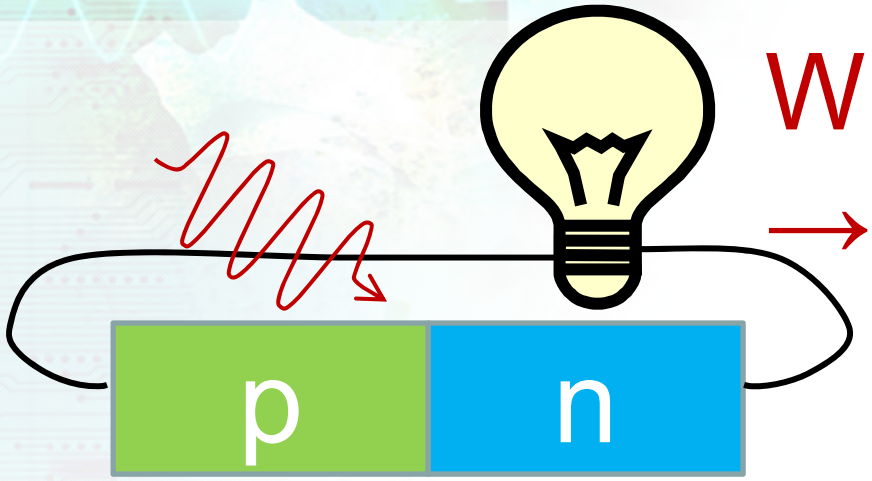
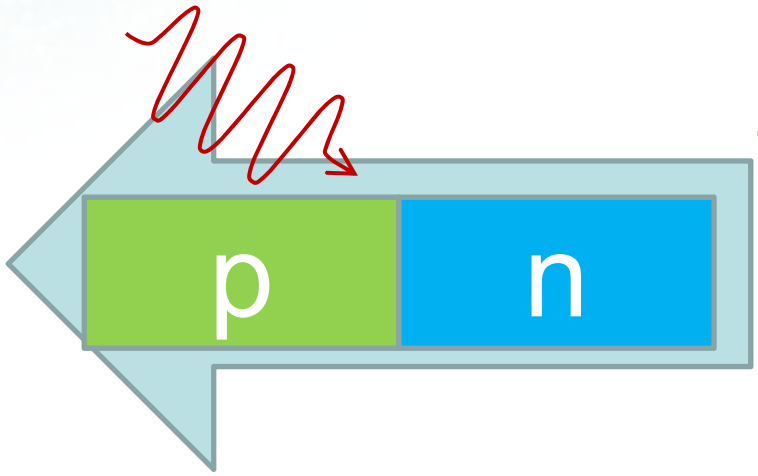
e-h splitting *as* dipole moment



With circuit
→Induction of current



Without circuit
→Increase of dipole moment

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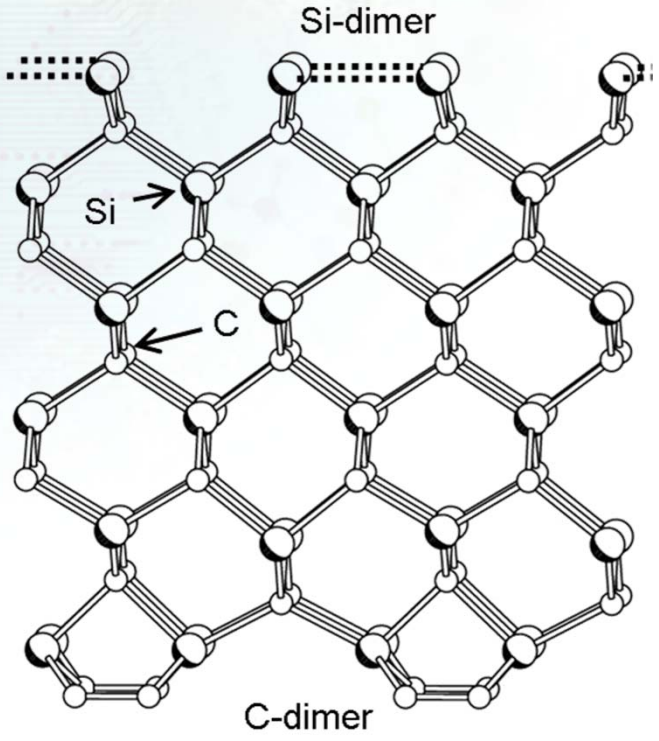
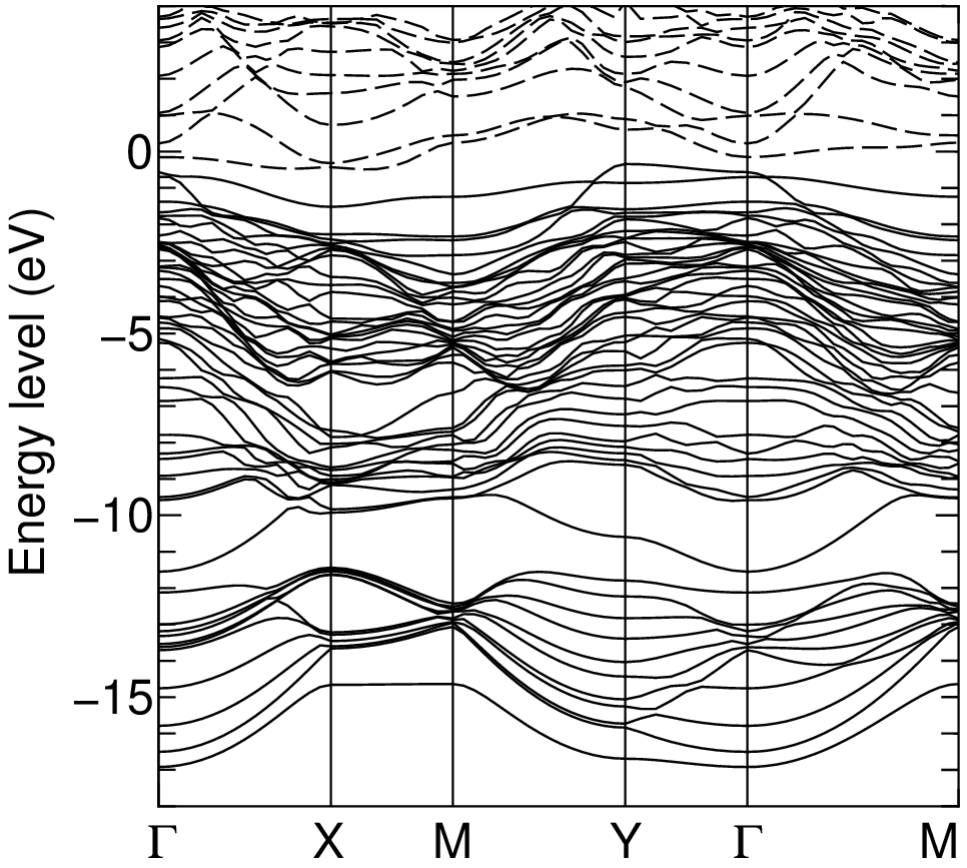
Case study 1: polar crystal

SiC(001) polar surface





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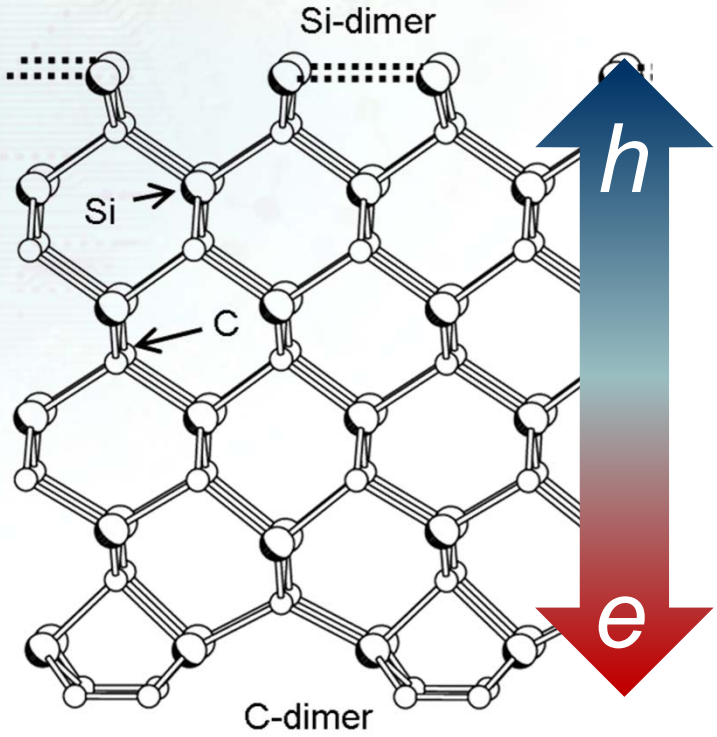
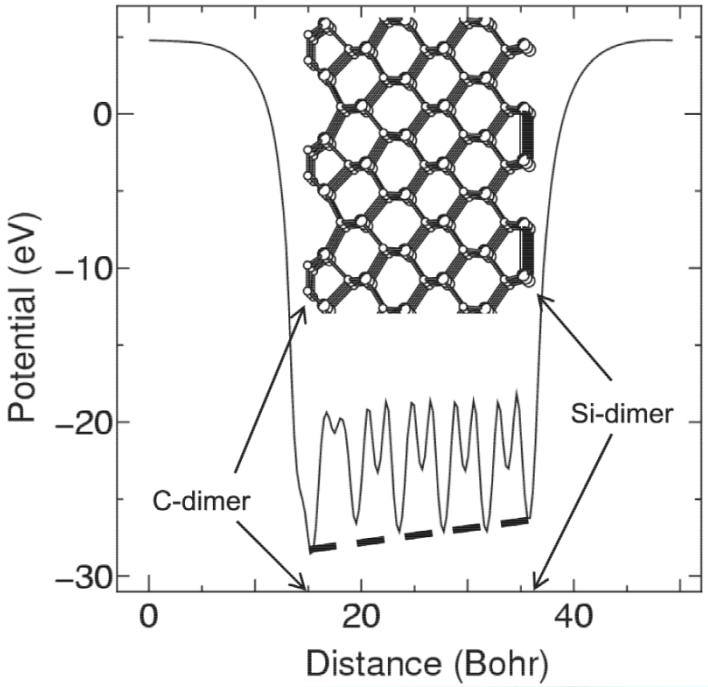
Case study 1: polar crystal

SiC(001) polar surface



90 degree



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Procedure of calculations

- Compute time-propagation of electrons under the light (direct solution of time-dependent Schrödinger equation.)

$$i\hbar\frac{d\psi_1(\mathbf{r},t)}{dt} = \{\ H_{KS}(\mathbf{r},t) + V_{ext}(\mathbf{r},t)\ \}\psi_1(\mathbf{r},t)$$

$$\rho(\mathbf{r},t) = \sum_{n=occ} \psi_n(\mathbf{r},t)^*\psi_n(\mathbf{r},t)$$

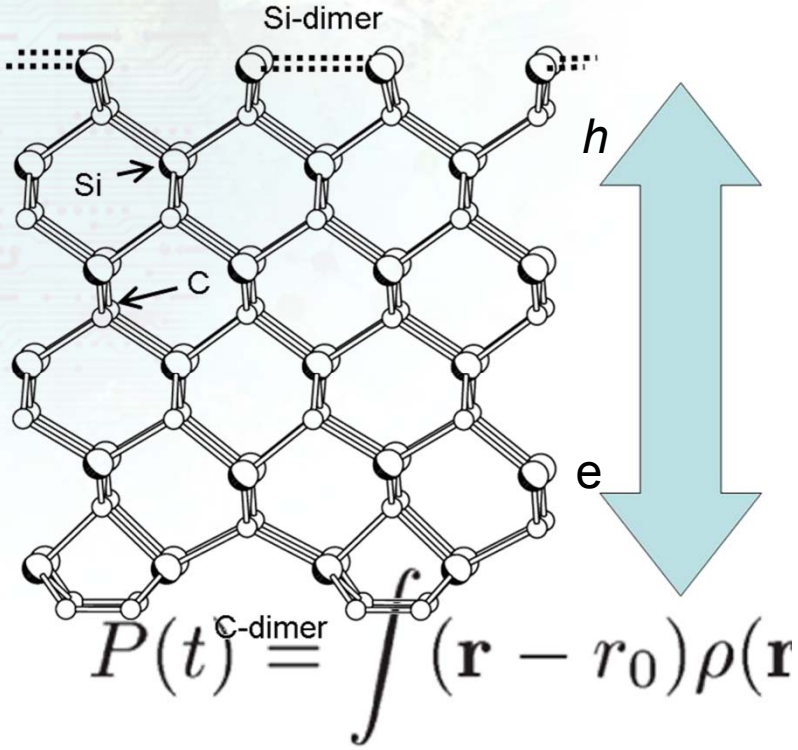
$$i\hbar\frac{d\psi_2(\mathbf{r},t)}{dt} = \{\ H_{KS}(\mathbf{r},t) + V_{ext}(\mathbf{r},t)\ \}\psi_2(\mathbf{r},t)$$

$$P(t) = \int (\mathbf{r}-r_0)\rho(\mathbf{r},t)d\mathbf{r}$$

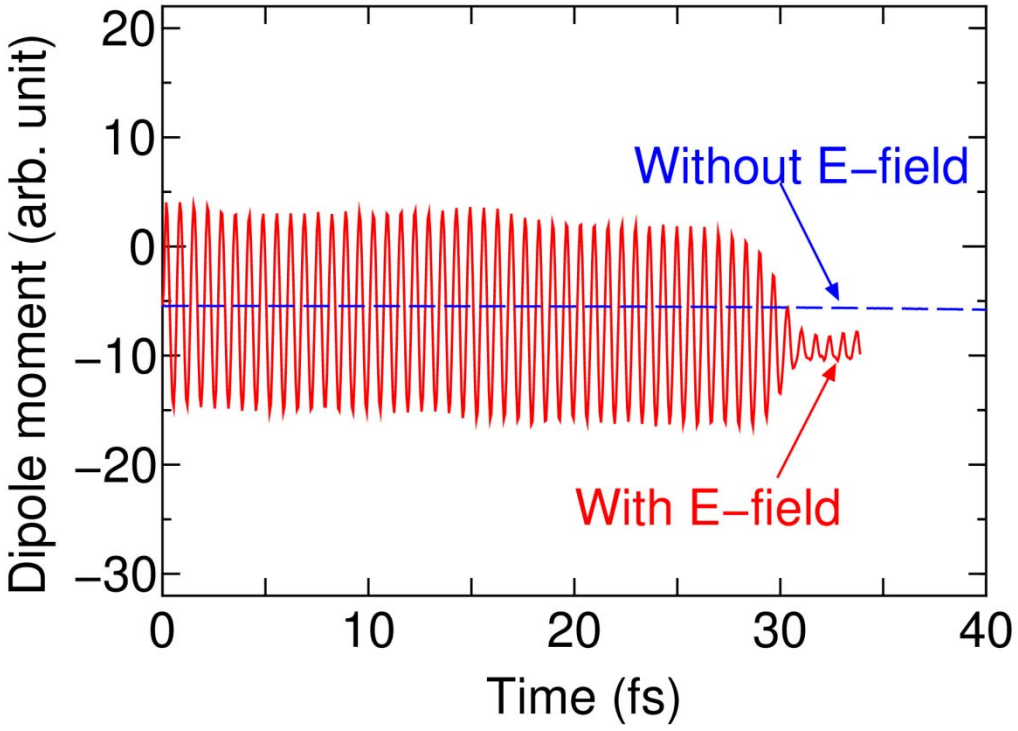
$$i\hbar\frac{d\psi_3(\mathbf{r},t)}{dt} = \{\ H_{KS}(\mathbf{r},t) + V_{ext}(\mathbf{r},t)\ \}\psi_3(\mathbf{r},t)$$

$$i\hbar\frac{d\psi_n(\mathbf{r},t)}{dt} = \{\ H_{KS}(\mathbf{r},t) + V_{ext}(\mathbf{r},t)\ \}\psi_n(\mathbf{r},t)$$

SiC(001) polar surface



$$P(t) = \int (\mathbf{r} - r_0)\rho(\mathbf{r}$$



In this case, the optical E-field and dipole moment are parallel. YM, APEX **3**, 047202 (2010).

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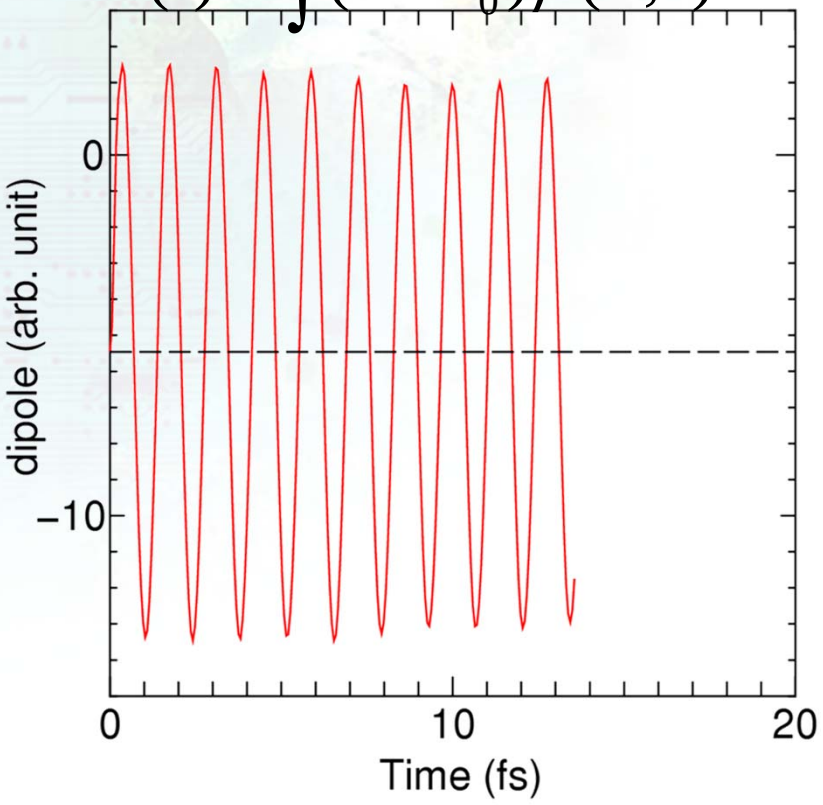
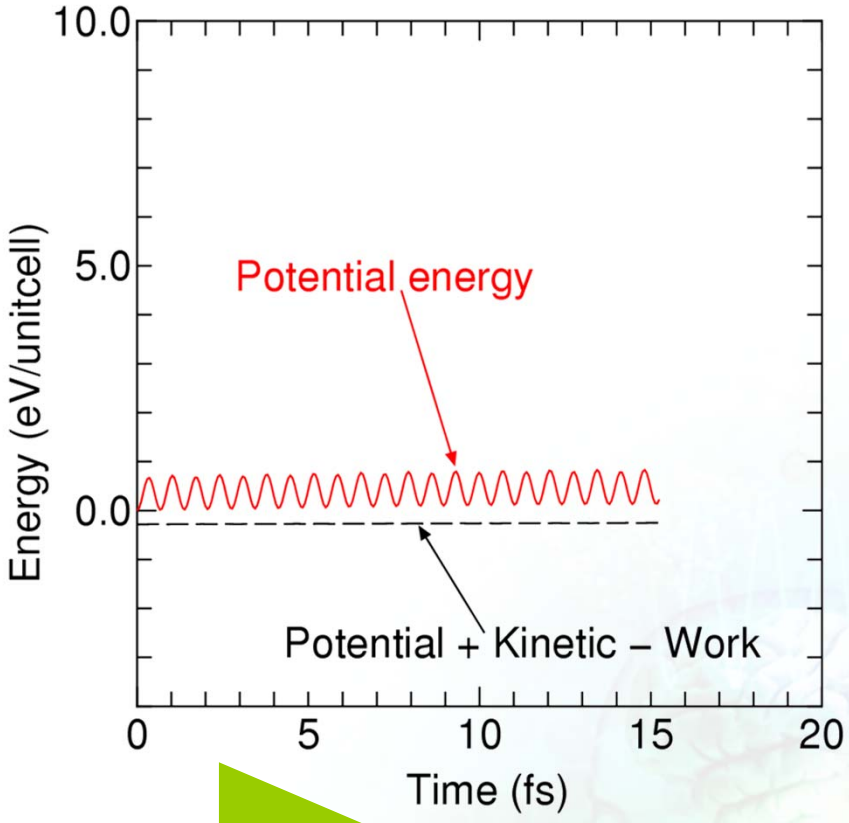
How could we find the optical frequency?: In case of off-resonance

$$P(t) = \int (z - z_0)\rho(\vec{r}, t)d\vec{r}$$





FT of P(t) gives peak frequency at 6 eV

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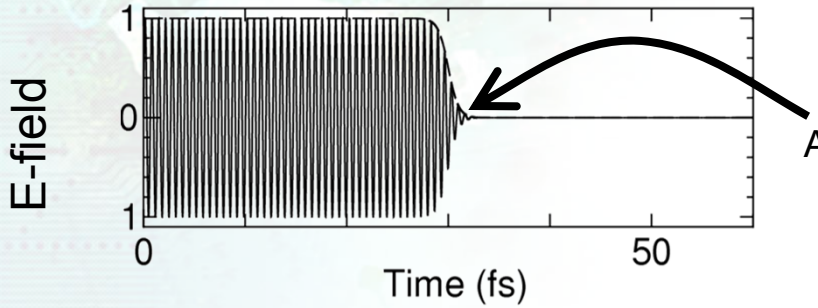
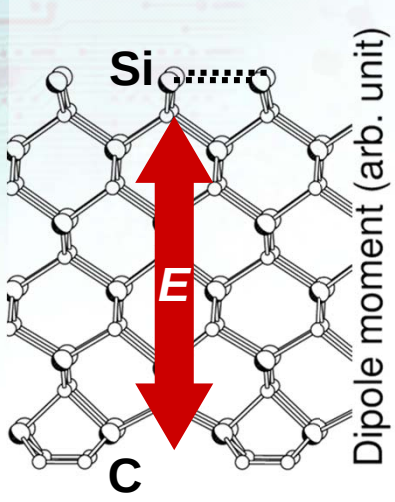
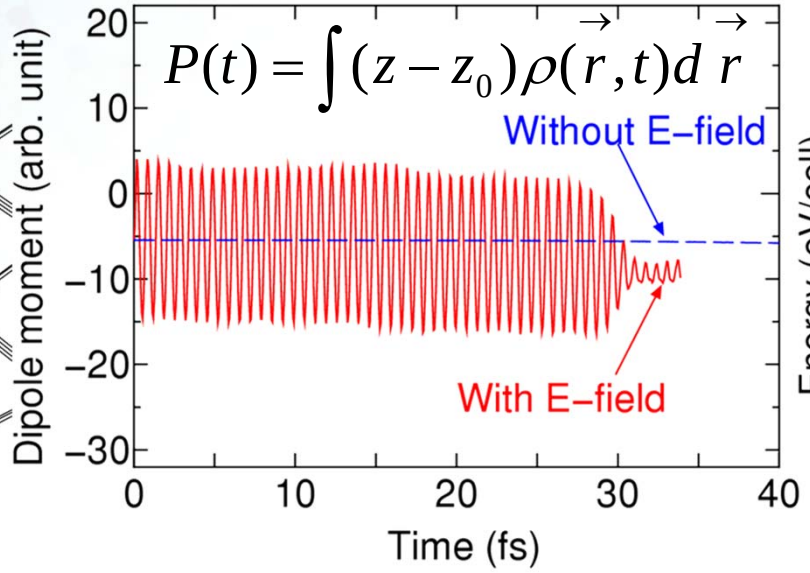
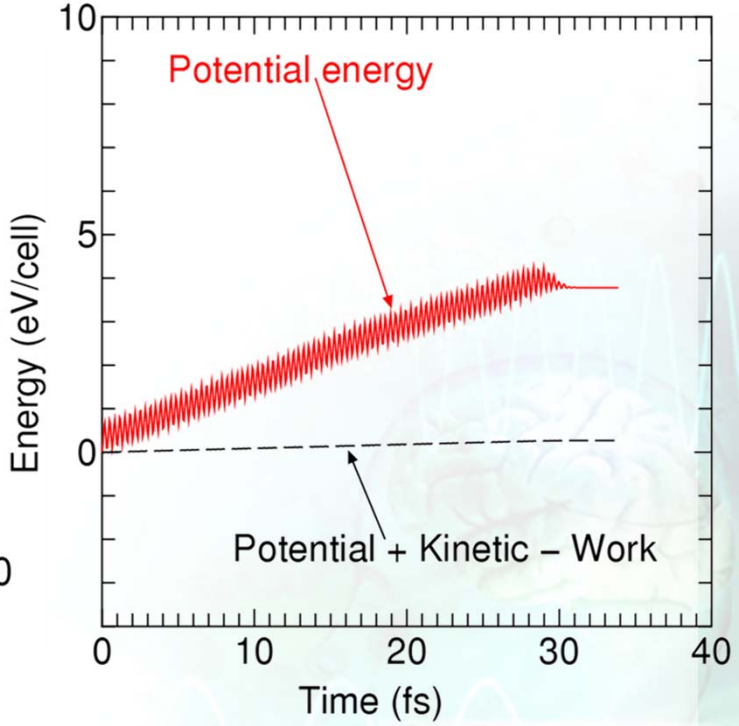
At the resonance



Attenuation of light at 30 fs, hv=6eV







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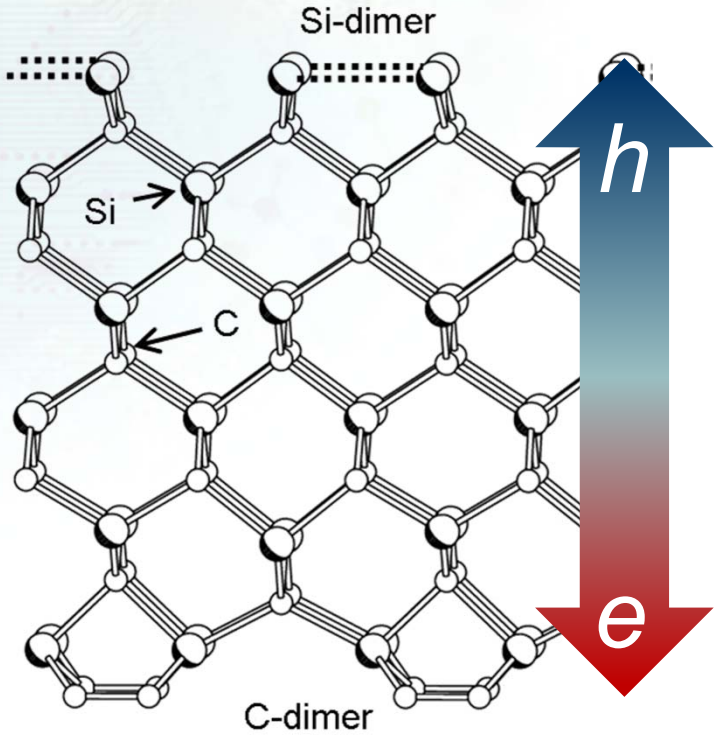
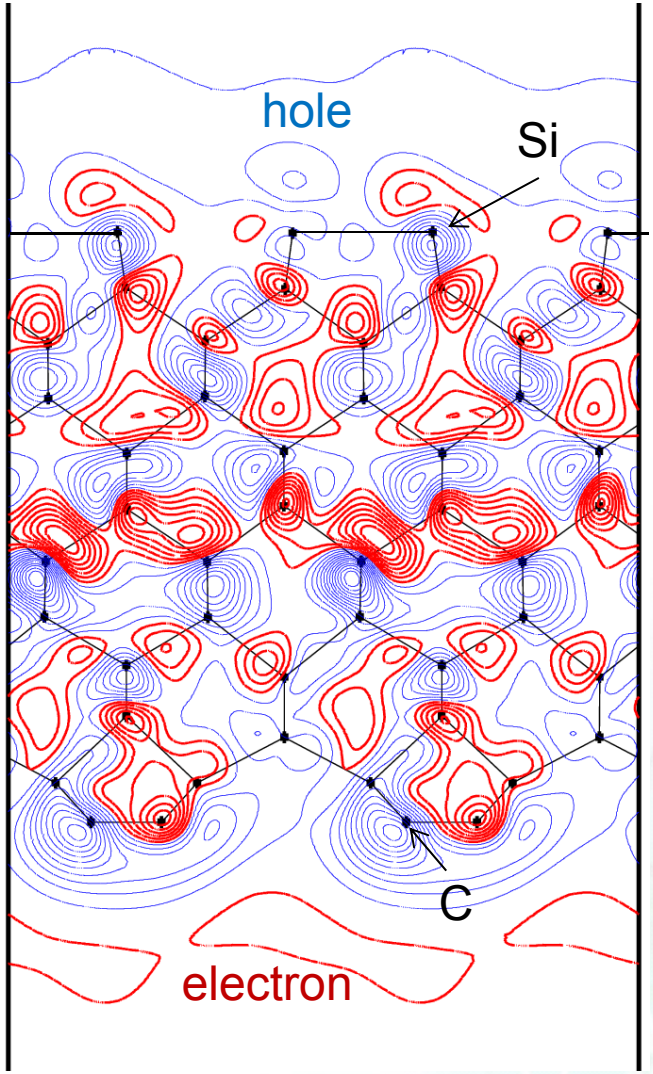
Snap shot of charge density

SiC(001) polar surface





Compared with no light

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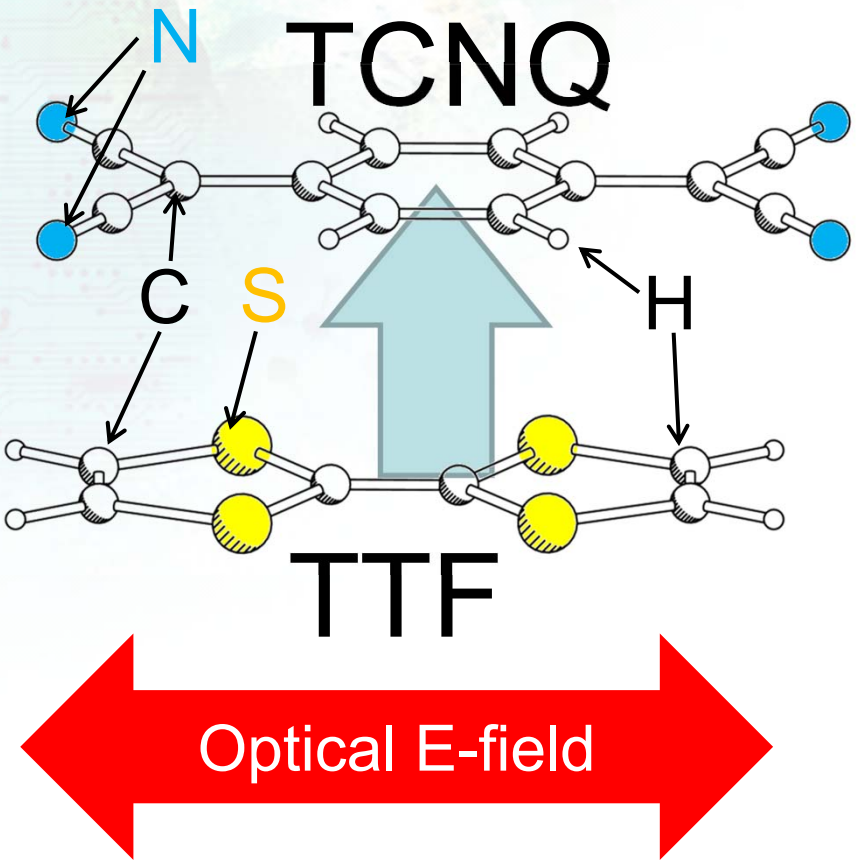
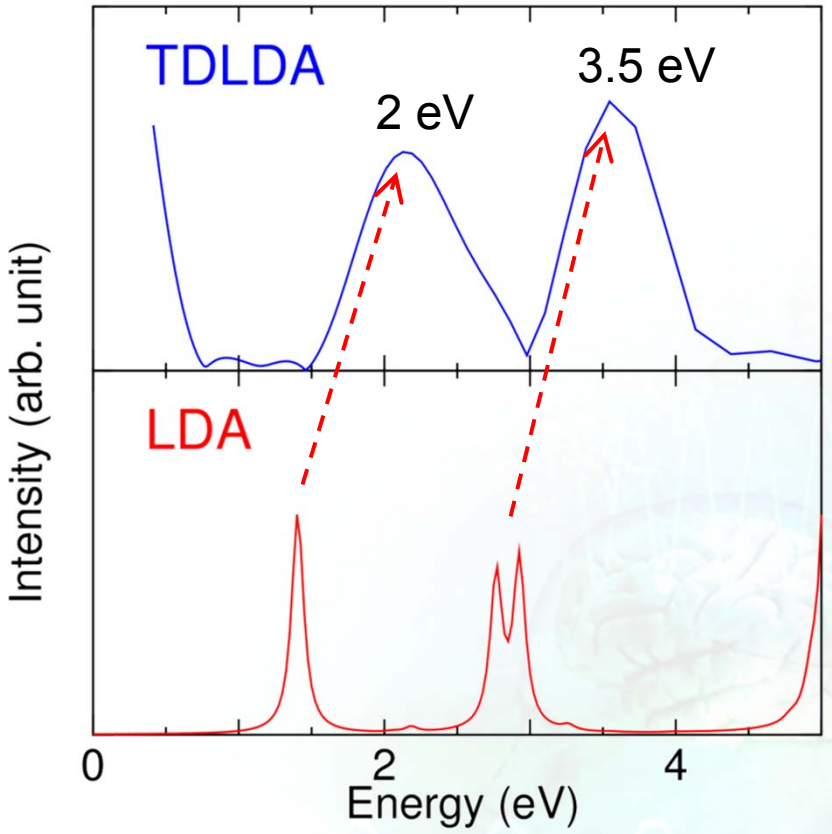
Organic dimer (TTF/TCNQ) as analogy of *pn*-junction





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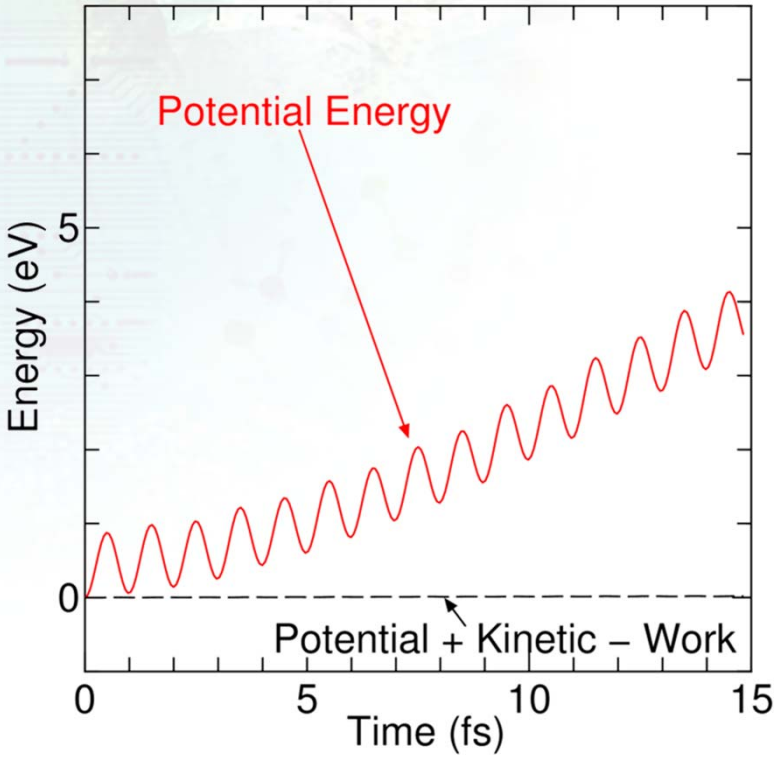
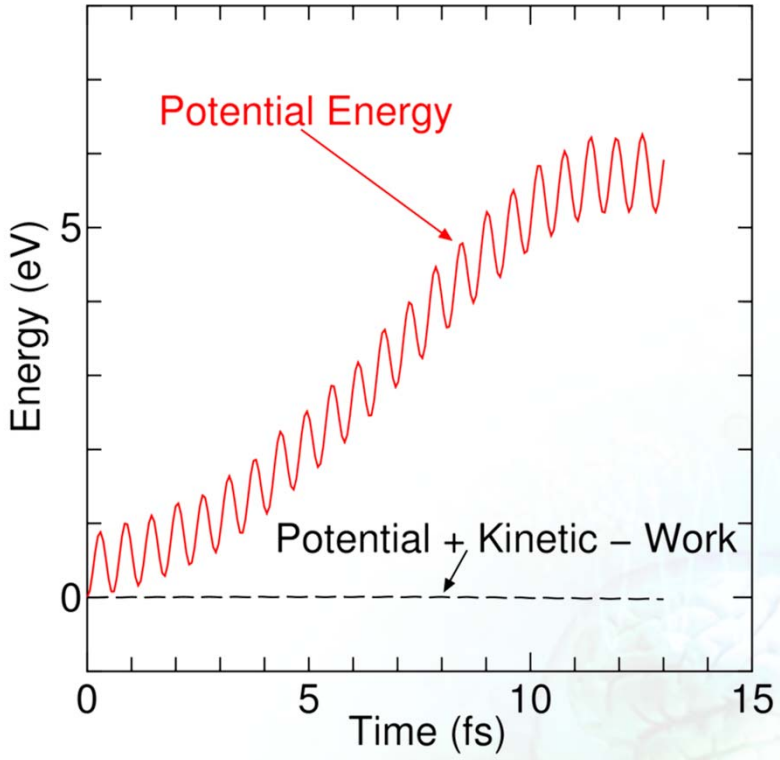
Accumulation of energy with resonant frequencies of lights

$\hbar\omega = 2.00eV$ Period 2.07 fs



$\hbar\omega = 3.50eV$ Period 1.18 fs



Following the energy-conservation rule by Miyamoto, Zhang, Phys. Rev. B**77**, 165123 (2008).

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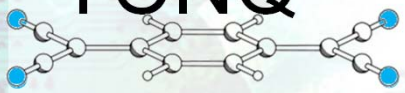
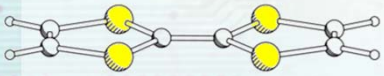
Increase of dipole moment

TCNQ

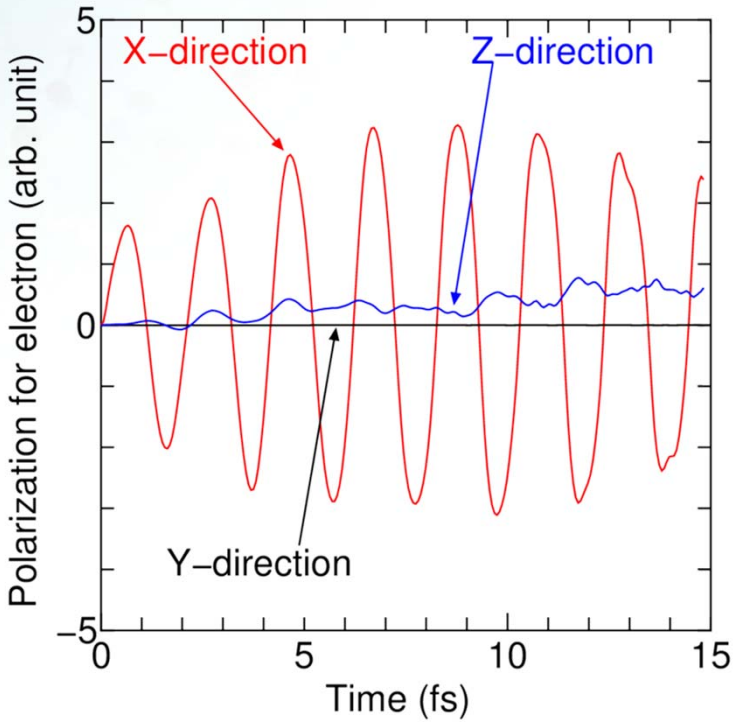


TTF

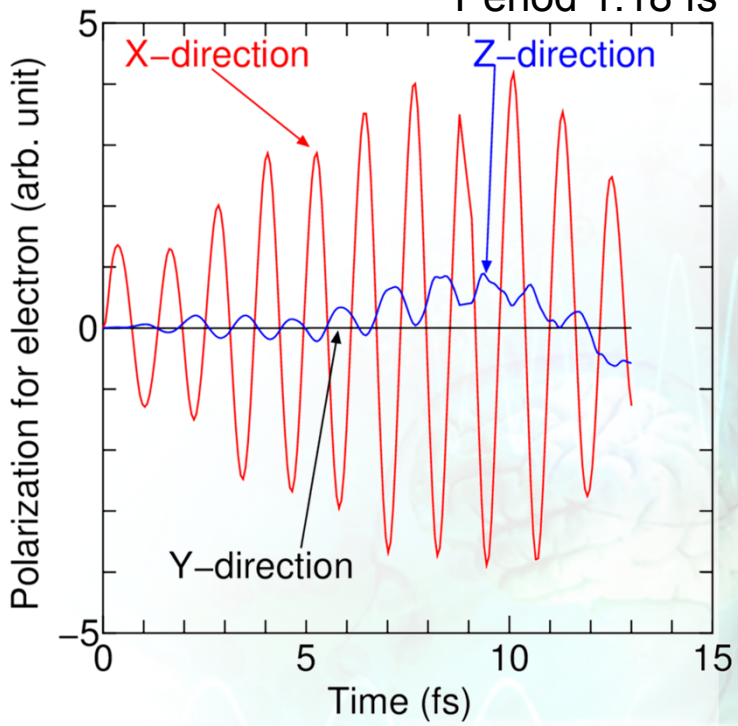


$$P(t)_{\{x,y,z\}} - P(t=0)_{\{x,y,z\}}$$

$\hbar\omega = 2.00eV$ Period 2.07 fs



$\hbar\omega = 3.50eV$ Period 1.18 fs



M. Yoon, Y. Miyamoto, M. Scheffler, New J. Phys. **13**, 073039 (2011).

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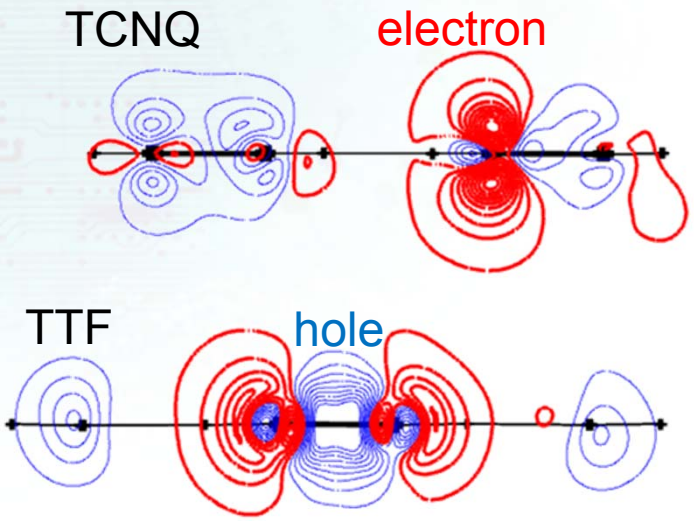
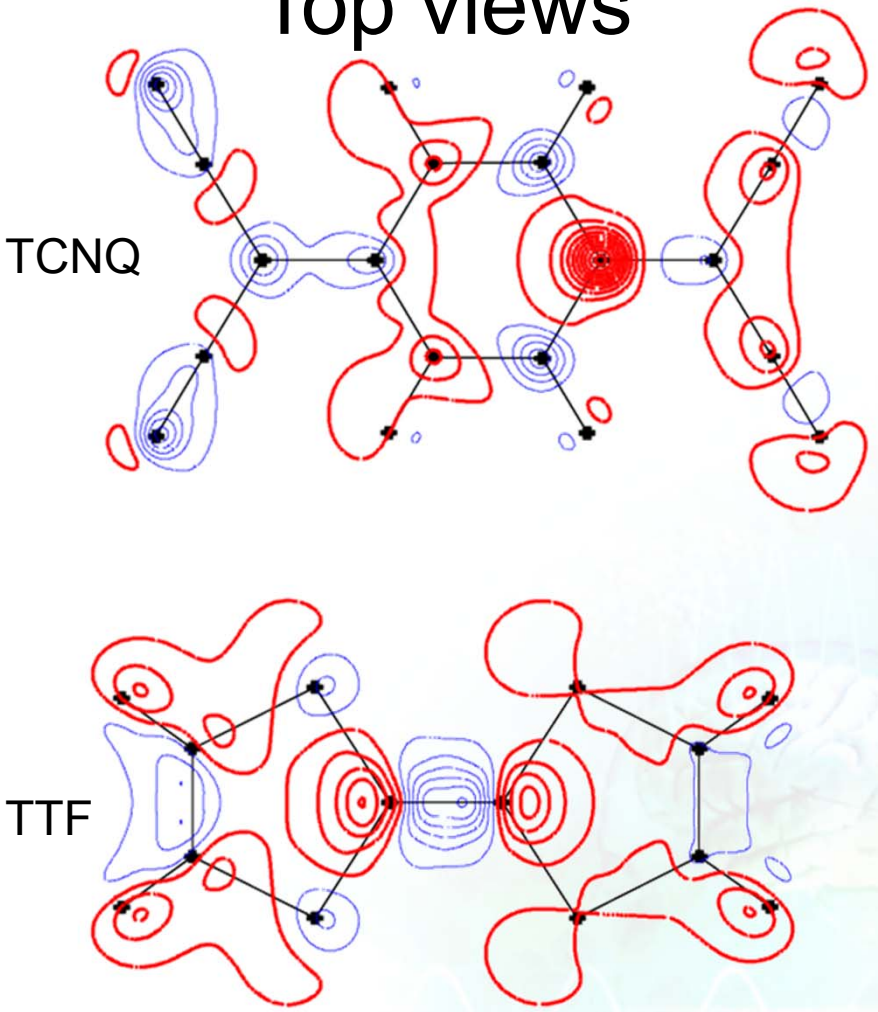
Analysis of molecular orbitals (intra- and inter-molecular CT)

Snapshot at t = 12.7 fs with *hv*= 2 eV

Side view



Top views



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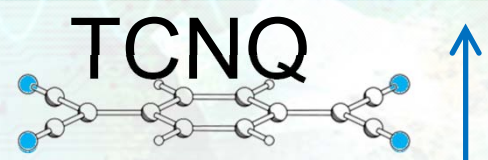
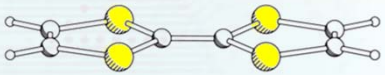
Possible photovoltaic devices





TTF

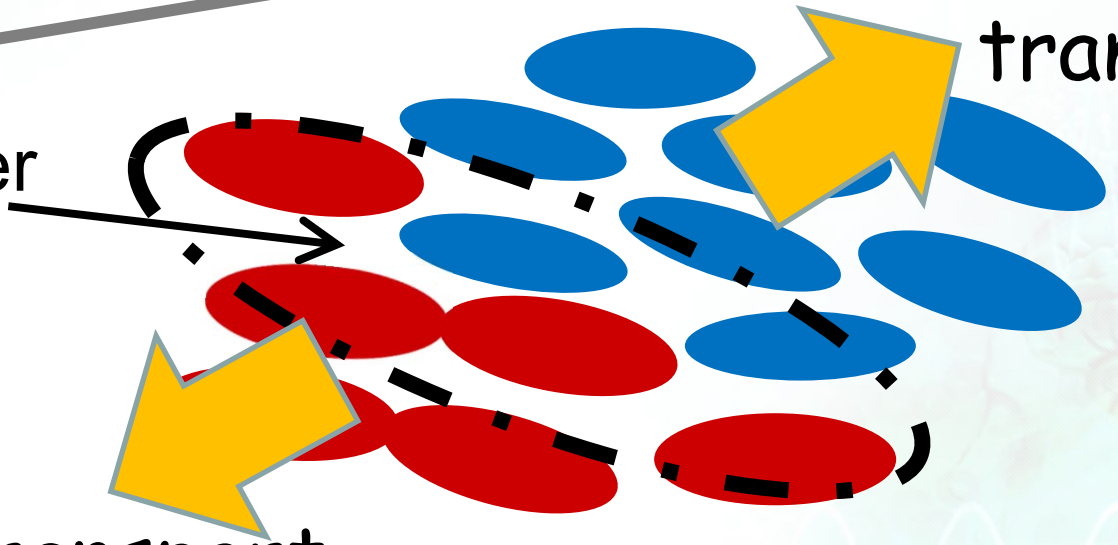
TCNQ

TTF

These molecules are unsolvable

Electron transport

Photo-carrier generation



Hole transport

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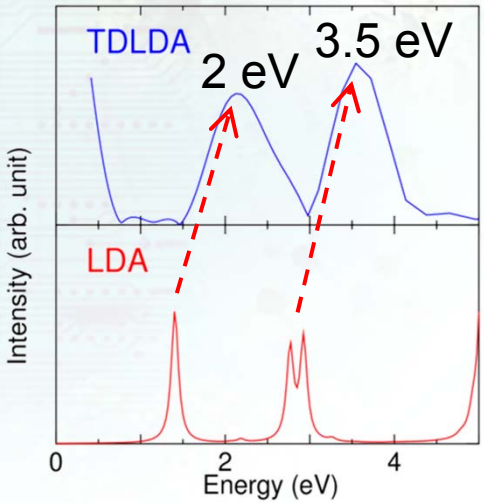
One technical note (effect of UV)

Absorption peak on organic molecules: visible + UV



UV absorption is useless for photovoltaic unless you create multi-excitons

Can we eliminate UV peak?

One of possibilities: make mixture with wide HOMO-LUMO gap molecules

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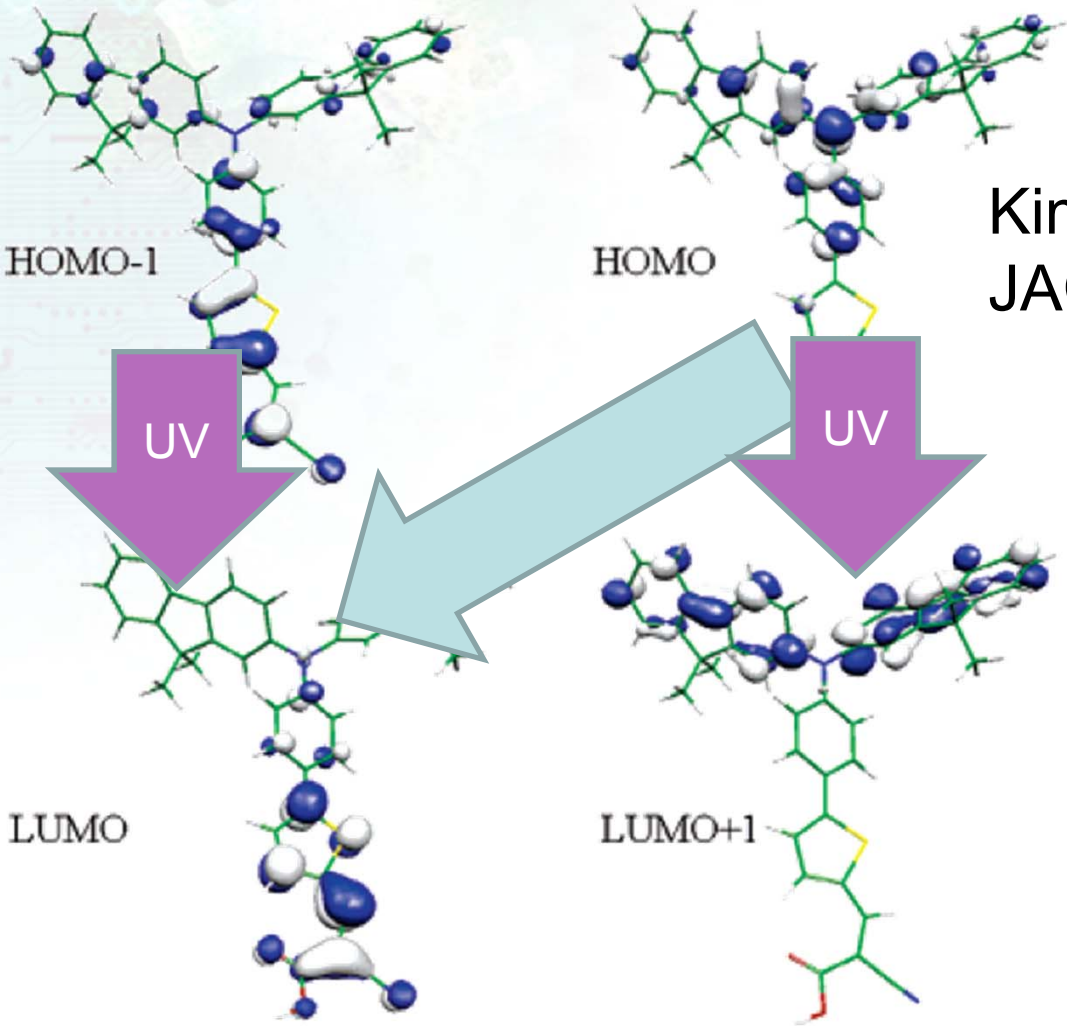
General note for optical property



Kim et al., (Grätzel group)
JACS 128, 16701 (2006)

Need of additional molecules which interfere HOMO-1 and LUMO-1

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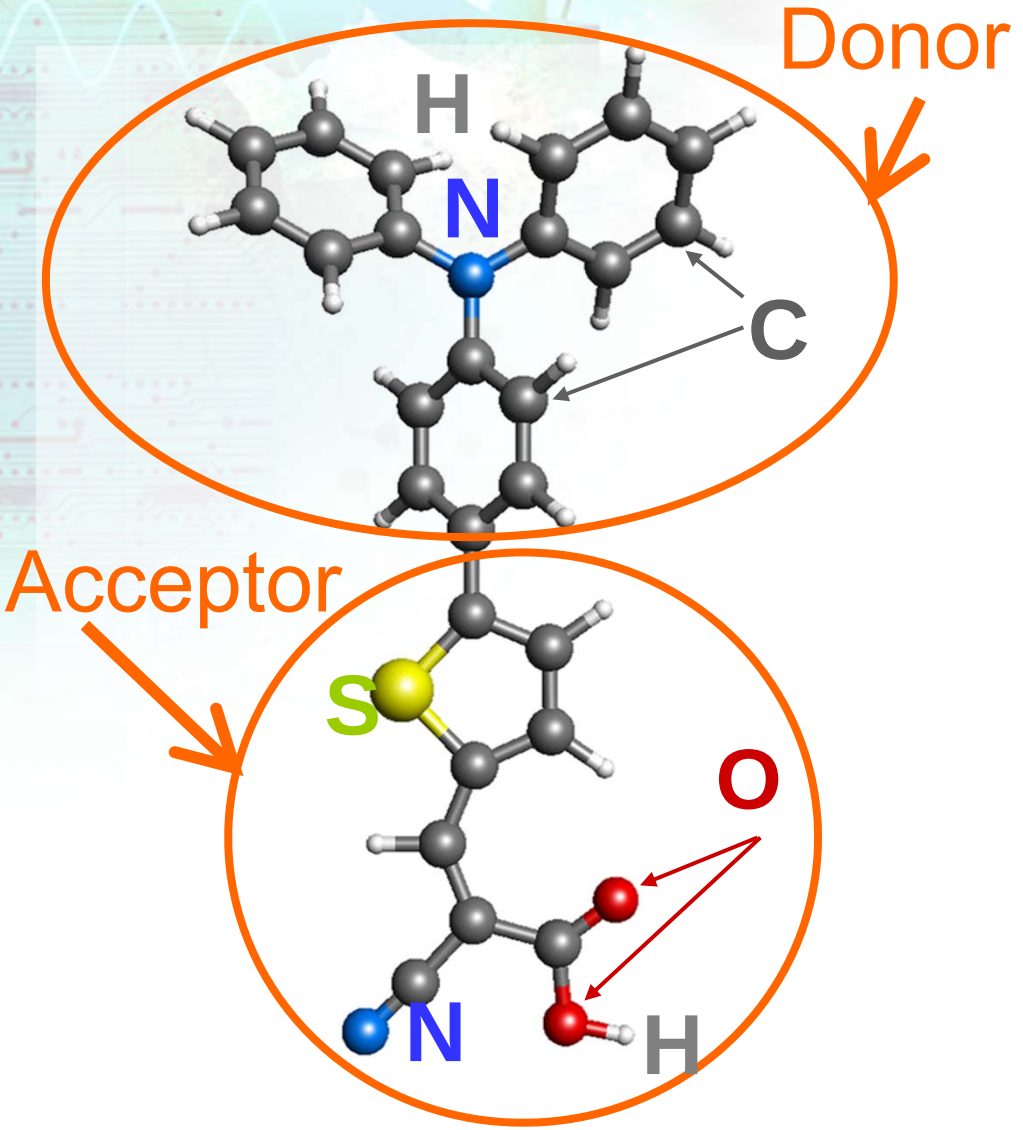
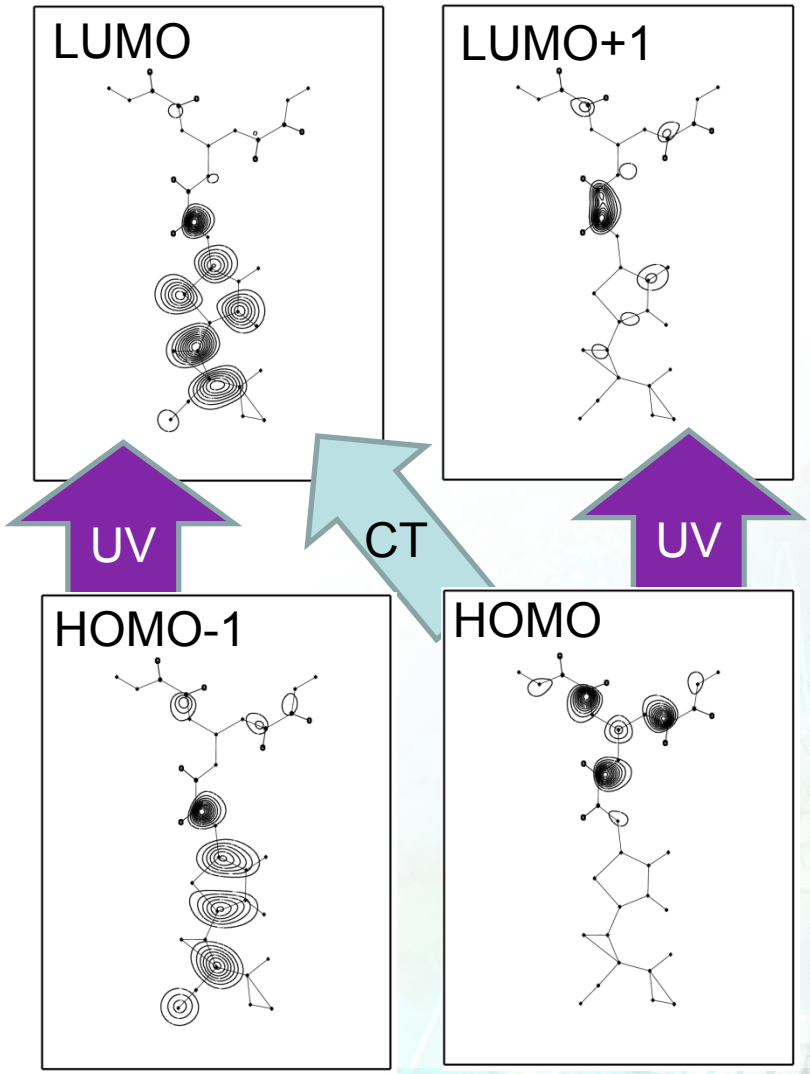
One hypothetical model





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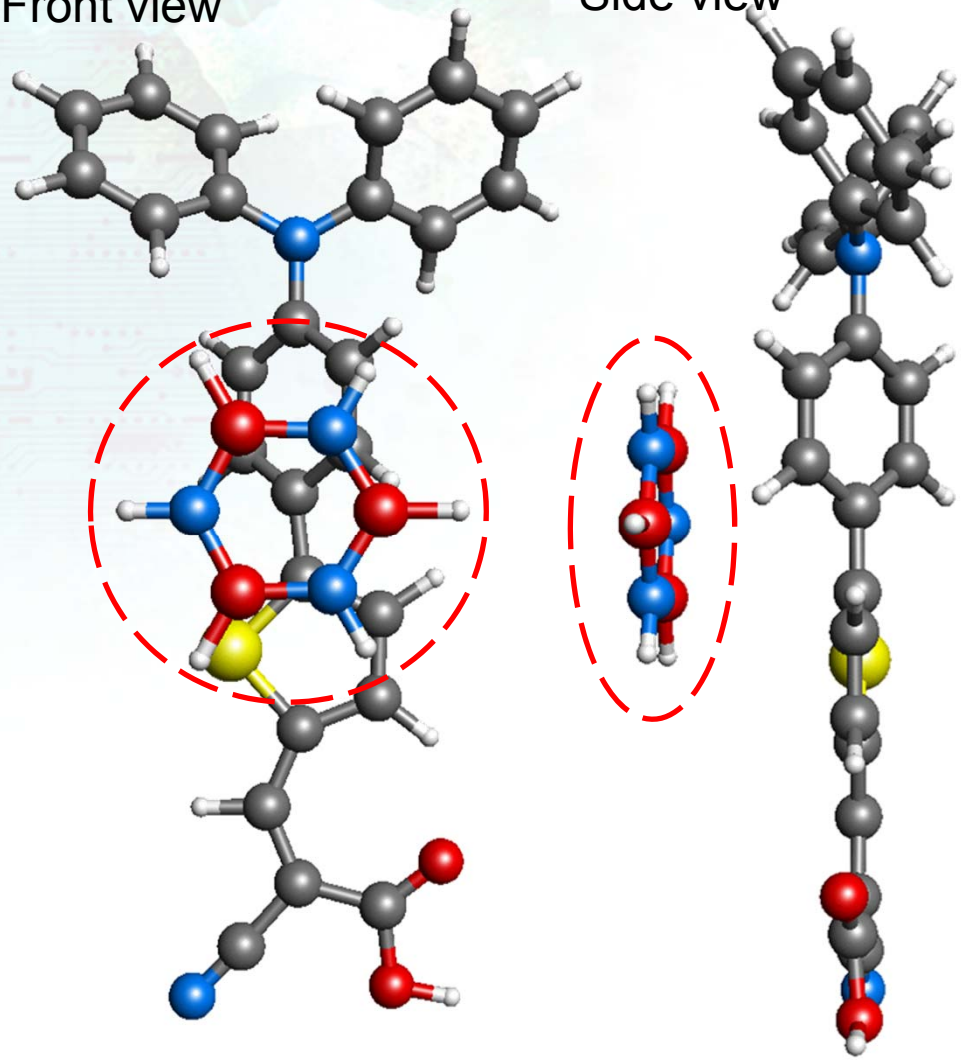
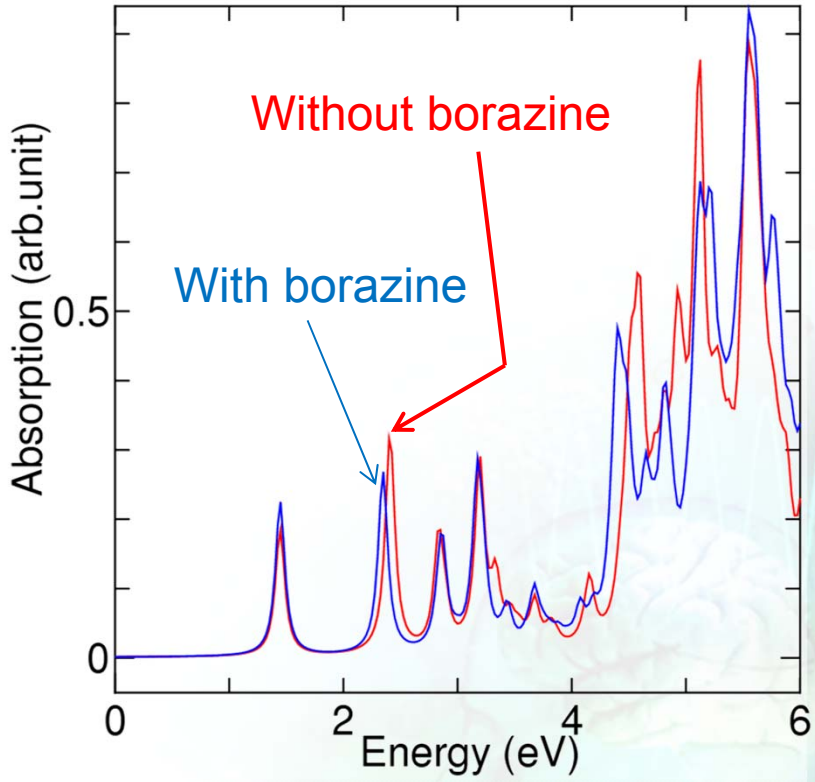
Mixture with borazine ($B_3N_3H_6$)

Front view

Side view





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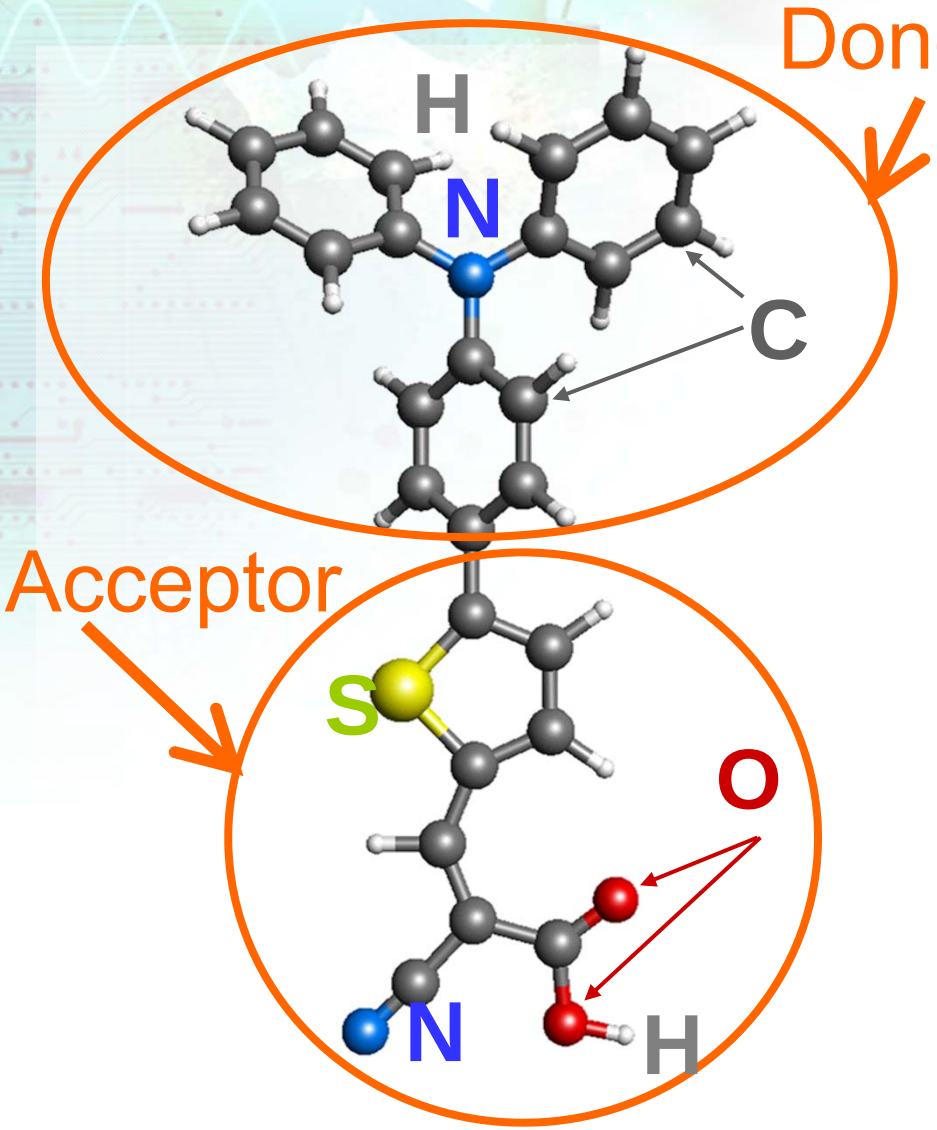
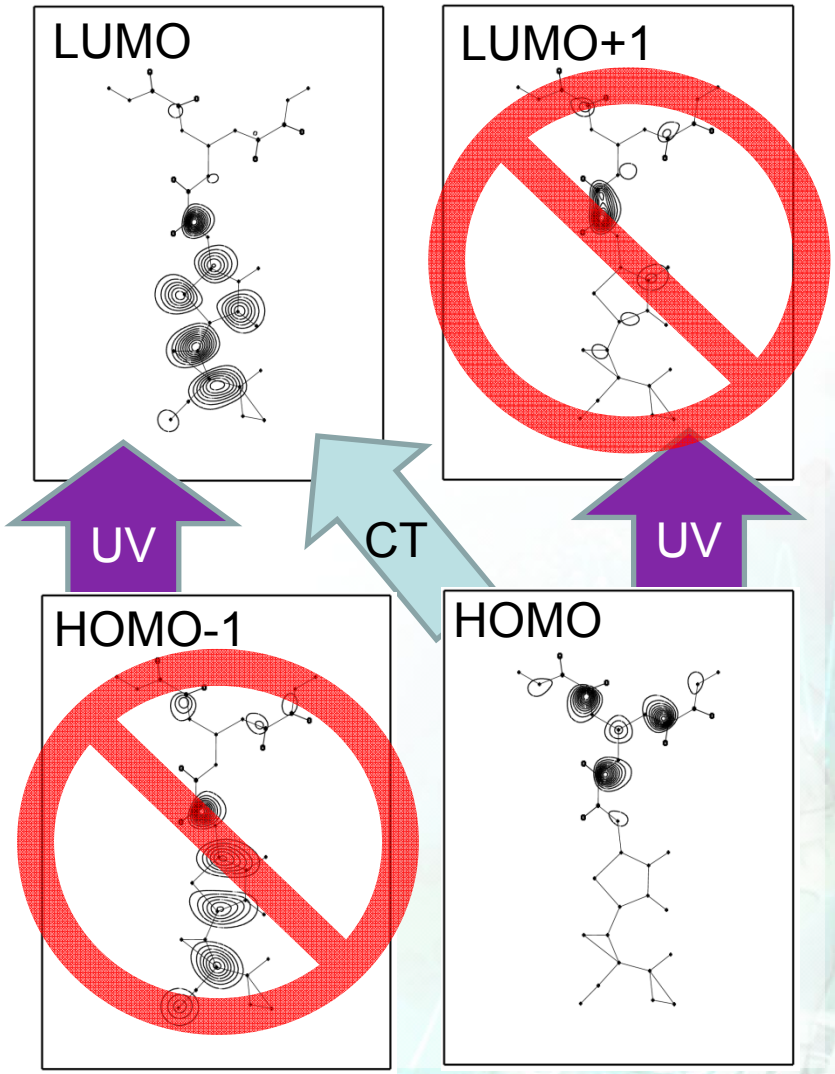
One hypothetical model





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Other required simulations

1. Time-constant data extracted from fast dynamics plugged in in master-equation
2. Combined with carrier transport simulation
3. Structural change of photovoltaic material during photo-electro conversion
   →Longer time TDDFT-MD simulation for aging

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Summary

1. Theoretical method to explore photovoltaic material (monitoring time-dependence of dipole moment that mimics photo-excited *e*-*h* separation)
2. A TTF/TCNQ dimer shows increase of dipole moment upon illumination of light at 2.00 eV and 3.50 eV.
3. Practical simulation for photovoltaic devices (multi-scale theory for fast and slow dynamics is needed)