

DynEMol code

Dynamics of Electrons in Molecules



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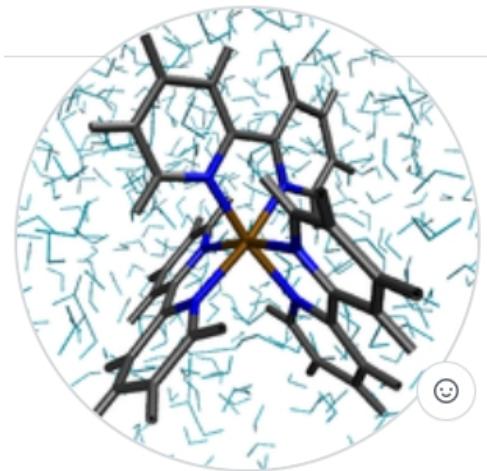
Dynemol Tutorial

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Dynemol: general information

github.com/lgrego/Dynemol



DynEMol: Dynamics of Electrons in Molecules
lgrego

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master 3 branches 0 tags

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Branches Tags

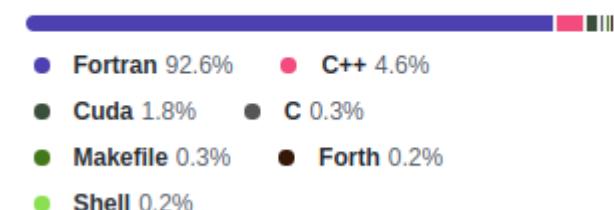
✓ master default

SingleNode

alpha-SO

[View all branches](#)

Languages



Dynemol: general information

Supported branches:

- **Master**: hybrid MPI / openMP / GPU version
- **SingleNode**: openMP / GPU version
- **Alpha-SO**: alpha version of SingleNode with focus in Spin effects

Compiling Dynemol

OS of choice: Linux

Compiler of choice:

Intel oneAPI 2022 = Base Toolkit + HPC Toolkit

Compilation options:

make (*dynemol*) - standard compilation

make *safe* - compilation with safe features

make *debug* - adds flag -g for debugging

make *serial* - remove all parallelization flags

make *gdb* - prepare code to GDB (equivalent to debug + serial) analysis

make *vtune* - prepare code to intel-Vtune analysis

make + *edit CUDA configurations in the makefile*

Running Dynemol

Setup environment variables:

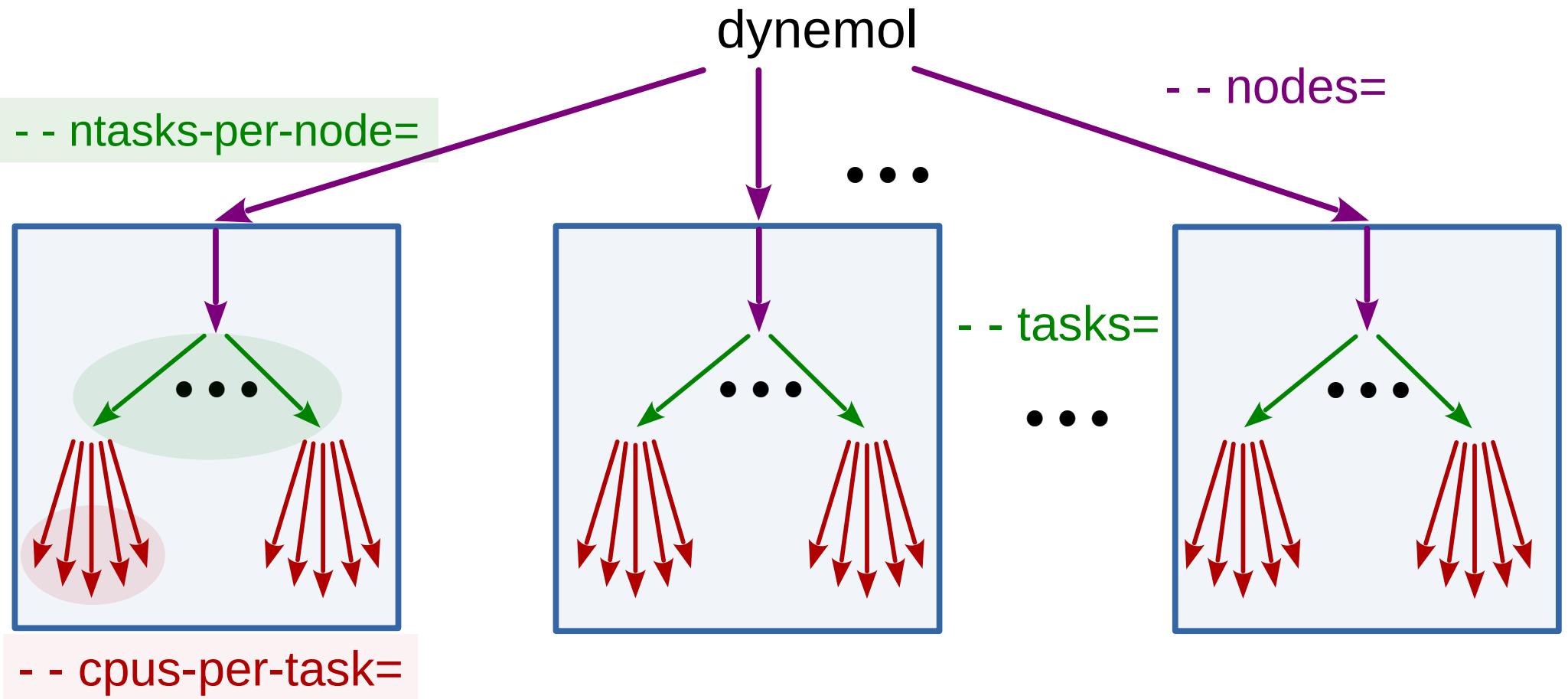
```
export DYNEMOLDIR= "path to dynemol executable directory"
```

```
export DYNEMOLWORKDIR= $(pwd)
```

In directory \$DYNEMOLWORKDIR:

- have the appropriate input files for the job
- for execution directions: edit file ***card.inpt***
- Run \$DYNEMOLDIR/dynemol

Hybrid MPI + openMP mode on SLURM



```
> export OMP_NUM_THREADS=$SLURM_CPUS_PER_TASK
```

```
> srun $DYNEMOLDIR/dynemol
```

card.inpt

- Check the file “\$DYNEMOLDIR/card_file_formats” for guidance

For instance:

```
|-----|  
| EXECUTION CONTROL |  
|-----|  
| DRIVER =           ! <== q_dynamics , avrg_configs , Genetic_Algo , diagnostic , slice_{Cheb, A0, FSSH, CSDM} , MM_Dynamics  
| Survival          =           ! <== .TRUE. for any dynamics simulation  
| DP_Moment         =           ! <== .TRUE. or .FALSE. ; dipole moment fragment must be specified ad-hoc  
| QMMM              =           ! <== .TRUE. for Non-Adiabatic simulations; couples electronic and nuclear dynamics  
| OPT_parms          =           ! <== .TRUE. for reading OPT_basis parameters from "opt_eht_parms.input"  
| ad_hoc             =           ! <== .TRUE. for using ad hoc tuning of parameters  
| Band_structure     =           ! <== .TRUE. for static band-structure calculations  
|-----|  
| STRUCTURE-FILE   input  FORMAT |  
|-----|  
| nuclear_matter    =           ! <== solvated_sys , extended_sys , MDynamics  
| file_type          =           ! <== structure or trajectory ; default = structure  
| file_format        =           ! <== xyz , pdb or vaspr ; default = pdb  
|-----|  
| generate copies of the system by reflection |  
|-----|  
| nnx = 0  ; nny = 0       ! <== (nnx,nny) = (extended) REAL copies on each side  
|                         ! Integers, keep format ; default = (0,0)  
|-----|  
| Periodic Boundary Conditions |  
|-----|  
| PBC = [ 0 , 0 , 0 ]       ! <== PBC replicas : 1 = yes , 0 = no  
|                         ! Integers, keep format , default = (0,0,0)
```

card.inpt

- Check the file “\$DYNEMOLDIR/card_file_formats” for guidance

For instance:

```
|-----|  
| QDynamics parameters |  
|-----|  
t_i = ! <== default = 0.d0  
t_f = ! <== final time in PICoseconds (Real)  
n_t = ! <== number of time steps (Integer)  
  
n_part = ! <== # of particles to be propagated: default is e=1 , e+h=2 ; default = 2  
  
hole_state = char*3:Integer ! <== char*3 = 3-letter fragment or residue ; Integer = M0 of frag/res  
! <== GROUND STATE calcs = 0 (ZERO)  
! <== case STATIC & DP_calcs = hole state of special FMO  
! <== case DYNAMIC = intial M0 for < HOLE > wavepacket in DONOR fragment  
  
electron_state = char*3:Integer ! <== char*3 = 3-letter fragment or residue ; Integer = M0 of frag/res  
! <== case STATIC & DP_calcs = excited state of special FMO  
! <== case DYNAMIC = intial M0 for < ELECTRON > wavepacket in DONOR fragment  
  
LCMO = ! <== .TRUE. for initial wavepackets as Linear Combination of Molecular Orbitals (LCMO)  
! <== default = .FALSE.  
|-----|  
| SAMPLING parameters and SECURITY COPY |  
|-----|  
CT_dump_step = ! <== step for saving El&H1 survival charge density (Integer); default = 1  
frame_step = ! <== step for avrg_configs and time-slice dynamics ; frame_step <= size(trj) ; default = 1  
restart = ! <== .TRUE. for restarting dynamics  
step_security = ! <== step for saving backup files  
! <== default = 100 (QMMM) ; 1000 (MM)
```

card.inpt

- Check the file “`$DYNEMOLDIR/card_file_formats`” for guidance

For instance:

card.inpt

- Check the file “\$DYNEMOLDIR/card_file_formats” for guidance

For instance:

```
|-----  
|      DOS calculations  
|  
| sigma =           ! <== Gaussian broadening of DOS peaks in eV (Real) ; default = 0.04  
|  
| DOS_range = real_interval( min , max ) ! <== (min,max) Real values; defines energy range of DOS calculations  
|-----  
|      SPECTRUM calculations  
|  
| occupied = real_interval( min , max ) ! <== (min,max) Real values; defines energy range of occupied MOs  
| empty    = real_interval( min , max ) ! <== (min,max) Real values; defines energy range of empty MOs
```

```
|-----  
|      Genetic_Alg and CG OPTIMIZATION parameters  
|  
| Pop_Size      = Integer          ! <== Population size of candidate solutions for Genetic-Algorithm (Integer)  
| N_generations = Integer          ! <== number of iterations (Integer)  
| Pop_range     = Real             ! <== range of variation of parameters [0:1] (Real)  
| selection_by   =                 ! <== option = {roullete,ranking,sorting}; fitness selection method  
| Mutation_rate = Real             ! <== range of variation of parameters [0:1] (Real)  
| Adaptive_      = Logical          ! <== true -> Adaptive GA method; gradually tights cost function on-the-fly (Logical)  
| Mutate_Cross   = Logical          ! <== false -> pure Genetic Algorithm ; prefer false for fine tuning! (Logical)  
| CG_            = Logical          ! <== for using CONJUGATE GRADIENT method on Top_Selection after genetic algorithm (Logical)  
| Top_Selection  = Integer          ! <== top selection to undergo CG  
| profiling      = Logical          ! <== generates analysis of the optimization process
```

card.inpt

- Check the file “\$DYNEMOLDIR/card_file_formats” for guidance

For instance:

```
!-----  
| MOLECULAR MECHANICS parameters  
|-----  
|  
| SYSTEM INFO  
|  
| N_of_molecules = ! <== total number of molecules (Integer)  
| N_of_species = ! <== total number of species (Integer)  
|-----  
! repeat the following information filling for all the different species ...  
attention: KEEP FORMAT  
!  
species(1) % residue = ! <== Residue label for species 1 ; character(len3)  
species(1) % N_of_molecules = ! <== Number of molecules of species (Integer)  
species(1) % N_of_atoms = ! <== Number of atoms comprising a single molecule of species i (Integer)  
species(1) % flex = ! <== .TRUE. for Flexible ; .FALSE. for rigid  
  
species(2) % residue = ! <== Residue label for species 2 ; character(len3)  
species(2) % N_of_molecules = ! <== Number of molecules of species (Integer)  
species(2) % N_of_atoms = ! <== Number of atoms comprising a single molecule of species i (Integer)  
species(2) % flex = ! <== .TRUE. for Flexible ; .FALSE. for rigid  
. . .  
. . .  
species(n) % residue = ! <== Residue label for species n ; character(len3)  
species(n) % N_of_molecules = ! <== Number of molecules of species (Integer)  
species(n) % N_of_atoms = ! <== Number of atoms comprising a single molecule of species i (Integer)  
species(n) % flex = ! <== .TRUE. for Flexible ; .FALSE. for rigid  
  
Selective_Dynamics = ! <== .TRUE. for ad_hoc_MM_tuning of MegaMass to selected atoms ; default = .FALSE.
```

card.inpt

- Check the file “\$DYNEMOLDIR/card_file_formats” for guidance

For instance:

```
!-----  
| ENVIRONMENT parameters  
|  
thermostat =           ! <== choose from { Berendsen, Nose_Hoover, Microcanonical }  
  
temperature =          ! <== Bath Temperature (K) , (Real) ; default = 300  
pressure =             ! <== Pressure in atm , (Real) ; default = 1  
  
thermal_relaxation_time = ! <== Temperature coupling term with the bath (Real)  
                           ! <== SMALL = STRONG coupling ; use "infty" to decouple  
                           ! <== picosecond ; default 0.25  
  
pressure_relaxation_time = ! <== Pressure coupling term (Real)  
                           ! <== SMALL = STRONG coupling ; use "infty" to decouple  
                           ! <== picosecond ; default = infty  
  
cutoff_radius =        ! <== Cut off radius (Angs.) for electrostatic and LJ interactions (Real) ; default = 50.  
damping_Wolf =         ! <== damping parameter (Angs.^{-1}) ; default value = 0.001  
                       ! <== Wolf's method damping parameter (length^{-1}) ; (J. Chem. Phys. 1999; 110(17):8254)  
                       ! <== relevant quantity: R_c*Wolf ~ ....  
!  
| EXECUTION INFO  
|  
driver_MM      =           ! <== choose from { MM_Dynamics , MM_Optimize , NormalModes , Parametrize }  
  
read_velocities =          ! <== .TRUE. for reading the initial velocities : T_ , F_ ; default = .TRUE.  
  
MM_input_format =          ! <== choose from { GMX, NAMD, GAFF } ; GMX = OPLS , GAFF and NAMD = Amber  
  
MM_log_step     =          ! <== step for saving MM results & parameters (Integer) ; default = 50  
  
MM_frame_step   =          ! <== step for saving MM results & parameters (Integer) ; default = 50  
  
Units_MM       =          ! <== choose OUTPUT energy units: eV or kj-mol ; default = eV
```

card.inpt

- Check the file “\$DYNEMOLDIR/card_file_formats” for guidance

For instance:

```
!-----  
!  
!-----  
AD-HOC settings  
(ad_hoc = true)  
  
ad_hoc:QM_MM:feature(start:end) = fixing           ! <== QM_MM = QM or MM (apply settings to either realm)  
ad_hoc:QM_MM:feature(start:end) = fixing           ! <== feature = {residue , nr , fragment , V_shift , etc ...}; check types  
ad_hoc:QM_MM:feature(start:end) = fixing           ! <== (start:end) range of change, end >= start; atom index  
ad_hoc:QM_MM:feature(start:end) = fixing           ! <== fixing, depends on feature: 3-letter label, int_value, or real_value  
.  
.  
.  
!  
!-----
```

Running Dynemol

In directory \$DYNEMOLWORKDIR:

- have the appropriate input files for the job:

(* mandatory)

- card.inpt *
- input.pdb * <== system coordinates
- velocity.inpt
- force-field related files
- opt_eht_parms.inpt

Running Dynemol

In directory \$DYNEMOLWORKDIR:

- the execution script run-SN.sh (basic model of script)

```
#!/bin/bash

#####
#Script Name    : run-SN.sh
#Description   : execute Dynemol from pwd using local dynemol src files
#Args          : none
#Author        : Luis G C Rego
#####
#!/bin/bash

export DYNEMOLWORKDIR=$(pwd)
export DYNEMOLDIR=/home/lrego/QMMM/development/dynemol-dir

$DYNEMOLDIR/dynemol
```

- On the terminal run
> ./run-SN.sh

Running Dynemol

In directory \$DYNEMOLWORKDIR:

- Outputs , results , log-files , security-files , etc. are stored in:
 - \$DYNEMOLWORKDIR/ancillary.trunk/
 - \$DYNEMOLWORKDIR/dos.trunk/
 - \$DYNEMOLWORKDIR/dyn.trunk/
 - \$DYNEMOLWORKDIR/log.trunk/
 - \$DYNEMOLWORKDIR/MO.trunk/
 - \$DYNEMOLWORKDIR/opt.trunk/
- *which are deleted and made anew at every execution.*
- *each directory gets a copy of card.inpt for future reference.*

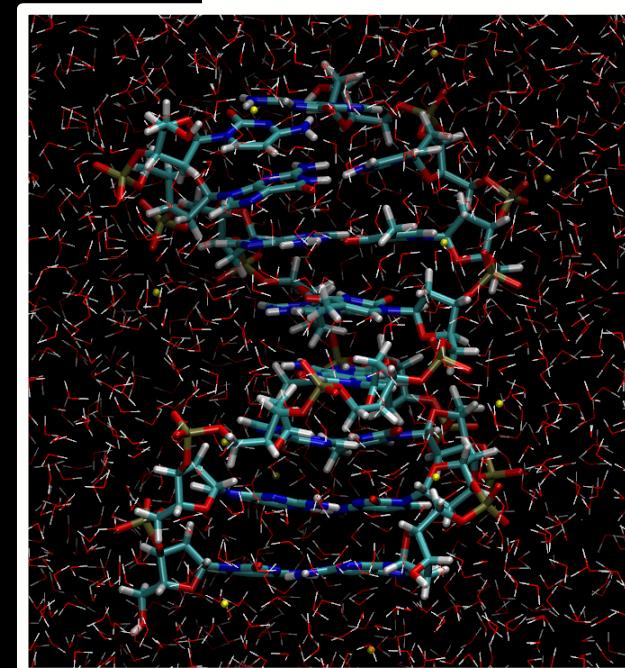
Setting Up the System in card.inpt

Example: DNA strand in water + counter ions

```
!-----  
! Periodic Boundary Conditions  
  
PBC = [ 1 , 1 , 1 ]                                ! <== PBC replicas : 1 = yes , 0 = no  
!  
!  
!-----  
! SYSTEM INFO  
  
N_of_molecules = 2452                               ! <== total number of molecules  
N_of_species   = 3                                  ! <== total number of species  
  
species(1) % residue      = DNA                  ! <== Residue label for species 1  
species(1) % N_of_molecules = 1                    ! <== Number of molecules of species  
species(1) % N_of_atoms    = 506                 ! <== Number of atoms comprising a single molecule of species i  
species(1) % flex          = true                 ! <== .TRUE. for Flexible  
  
species(2) % residue      = Na+                  ! <== Residue label for species 2  
species(2) % N_of_molecules = 14  
species(2) % N_of_atoms    = 1  
species(2) % flex          = true  
  
species(3) % residue      = H2O                  ! <== Residue label for species n  
species(3) % N_of_molecules = 2437  
species(3) % N_of_atoms    = 3  
species(3) % flex          = true  
!  
!-----  
! AD-HOC settings  
(ad_hoc = true)  
  
ad_hoc:QM:QMMM(507:520)  = false  
ad_hoc:QM:QMMM(521:2452) = false  
!  
!  
!-----  
! EXECUTION INFO  
  
driver_MM = MM_Dynamics  
  
MM_input_format = GAFF                         ! <== choose from {GMX, NAMD, GAFF}; GMX = OPLS, GAFF and NAMD = Amber
```

Files:

- input.pdb
- DNA.psf
- Na+.psf
- H2O.psf
- input.prm



Setting Up the System in card.inpt

Example: DNA strand in water + counter ions

H2O.psf

```
PSF

      1 !NTITLE
REMARKS segment TIP

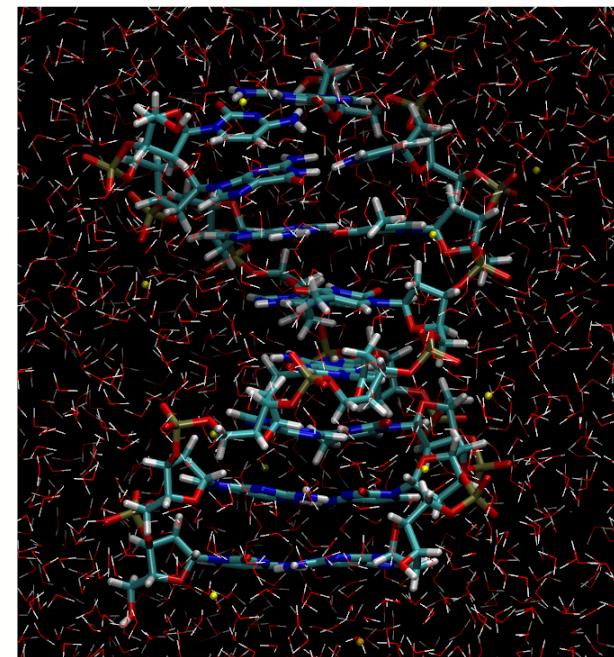
      3 !NATOM
      1 SYS      1       TIP3    OH2      OW      -0.834000    16.0000
      2 SYS      1       TIP3    H1       HW      0.417000     1.0080
      3 SYS      1       TIP3    H2       HW      0.417000     1.0080

      3 !NBOND: bonds
      2           1           3           1           3           2

      0 !NTHETA: angles
      0 !NPHTA: dihedrals
      0 !NIMPHI: impropers
      0 !NDON: donors
      0 !NACC: acceptors
      0 !NNB
```

Files:

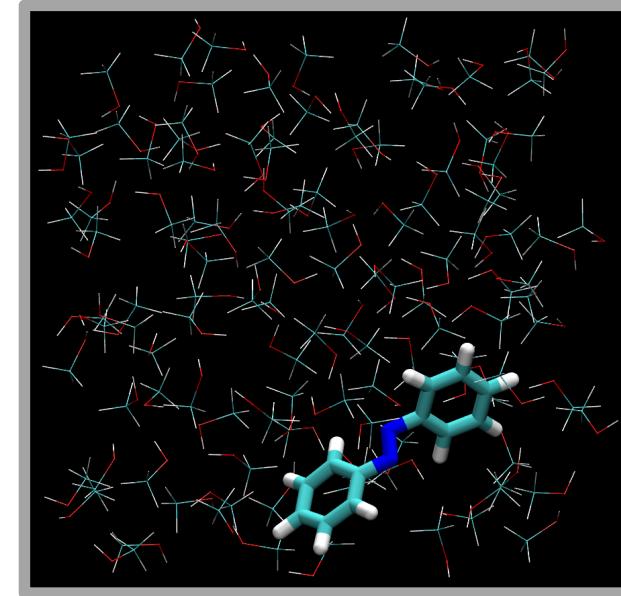
- input.pdb
- DNA.psf
- Na+.psf
- H2O.psf
- input.prm



Photochemistry in Solution

Example: Azobenzene Molecule in Ethanol

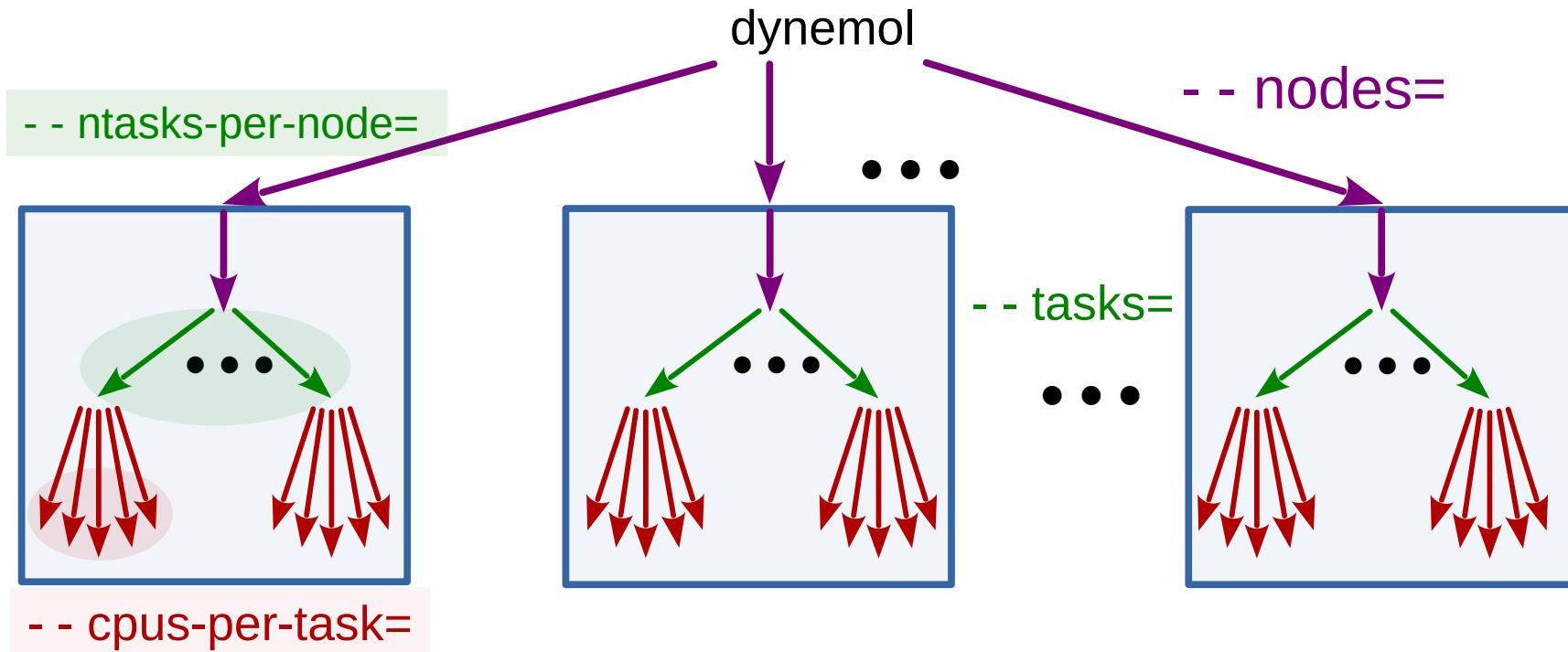
```
!-----  
!----- ACTION flags  
  
DRIVER = slice_A0  
  
QMMM      = true  
nuclear_matter = MDynamics  
file_type   = structure  
file_format  = pdb  
  
PBC = [ 1 , 1 , 1 ]  
  
electron_state = AZO:35  
hole_state     = AZO:33  
  
t_f  = 1.0d0          ! <== final time in PICoseconds  
n_t  = 100000  
  
!----- SYSTEM INFO  
  
N_of_molecules = 119           ! <== total number of molecules  
N_of_species   = 2             ! <== total number of species  
  
species(1) % residue      = COH    ! <== Residue label for species 1  
species(1) % N_of_molecules = 118    ! <== Number of molecules of species 1  
species(1) % N_of_atoms    = 6       ! <== # of atoms in a molecule of species 1  
species(1) % flex          = true    ! <== Flexible : true , false  
  
species(2) % residue      = AZO    ! <== Residue label for species 2  
species(2) % N_of_molecules = 1  
species(2) % N_of_atoms    = 24  
species(2) % flex          = true  
  
!----- AD-HOC settings  
  
OPT_parms = true  
ad_hoc    = true  
ad_hoc:QM:QMMM(1:708)=MM  
  
!----- ENVIRONMENT parameters  
  
thermostat   = Microcanonical ! <== Berendsen, Nose_Hoover, Microcanonical  
  
cutoff_radius = 9.d0           ! <== Cut off radius (Angs.) for LR interactions  
damping_Wolf   = 0.0032d0       ! <== damping parameter (Angs.^-1)  
  
!----- GENERAL INFO  
  
driver_MM      = MM_Dynamics  
read_velocities = true  
MM_input_format = GMX
```



Input Files:

- input.pdb
- AZO.itp
- COH.itp
- topol.top
- velocity.inpt
- opt_eht_parms.input

Hybrid MPI + openMP mode on SLURM



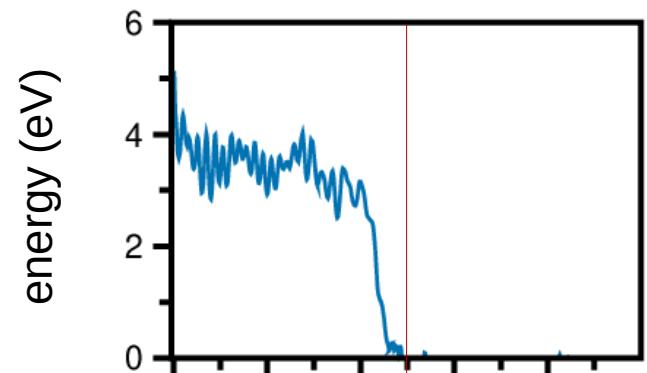
Example: Azobenzene Molecule in Ethanol

# cpus (cores)	nodes	ntasks/node	ntasks	cpus/task	Time/(1000 iteration steps)
96	4	1	4	24	144 seconds
96	4	2	8	12	85.7 seconds
96	4	3	12	8	77.4 seconds

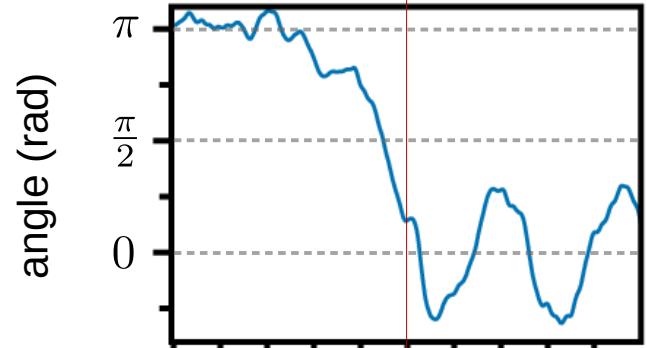
Photochemistry in Solution

Example: Azobenzene Molecule in Ethanol

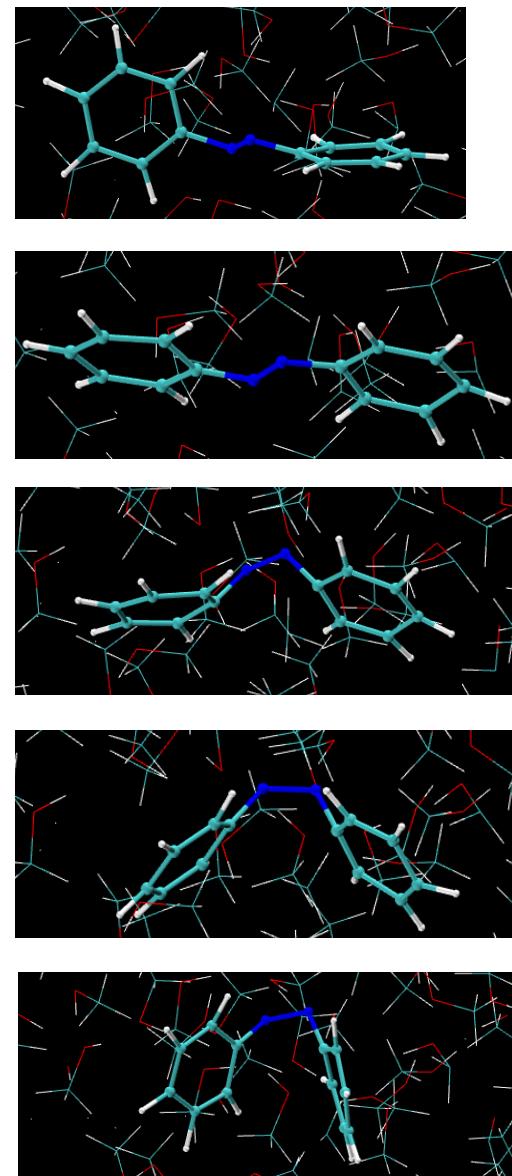
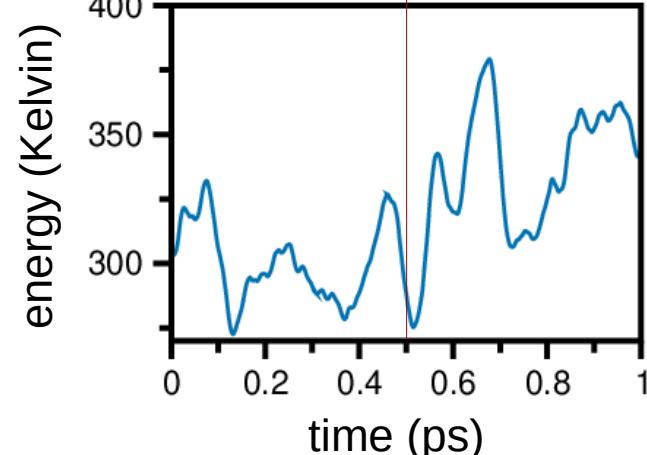
El - H₁ excitation energy



CNNC dihedral angle



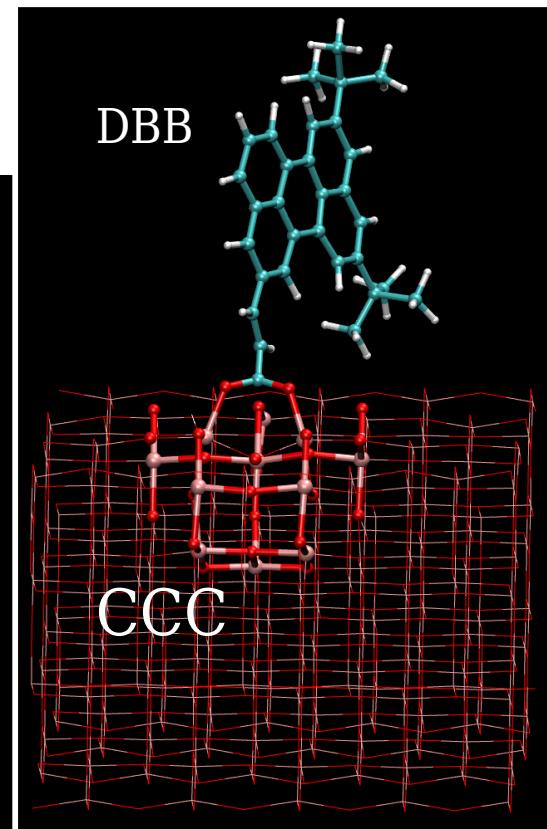
AZ0+EtOH
 E_{kinetic}



Setting Up the System in card.inpt

Example: Dye-sensitized semiconductor

```
!----- ACTION flags -----!  
DRIVER      = MM_Dynamics  
  
nuclear_matter = MDynamics  
file_type      = structure          ! <== structure or trajectory  
file_format     = pdb               ! <== xyz , pdb or vasp  
  
PBC = [ 1 , 1 , 0 ]  
  
t_f  = 50.0                      ! <== final time in PICOseconds  
n_t  = 100000                     ! <== number of time steps  
  
!----- SYSTEM INFO -----!  
  
N_of_molecules = 2                ! <== total number of molecules  
N_of_species   = 2                ! <== total number of species  
  
species(1) % residue      = DBB  ! <== Residue label for species 1  
species(1) % N_of_molecules = 1    ! <== Number of molecules of species i  
species(1) % N_of_atoms    = 64   ! <== # of atoms comprising a single molecule of species i  
species(1) % flex          = true ! <== Flexible : true , false  
  
species(2) % residue      = CCC  ! <== Residue label for species 2  
species(2) % N_of_molecules = 1    !  
species(2) % N_of_atoms    = 479  !  
species(2) % flex          = false
```



Files:

- input.pdb
- DBB.psf
- CCC.psf
- input.prm

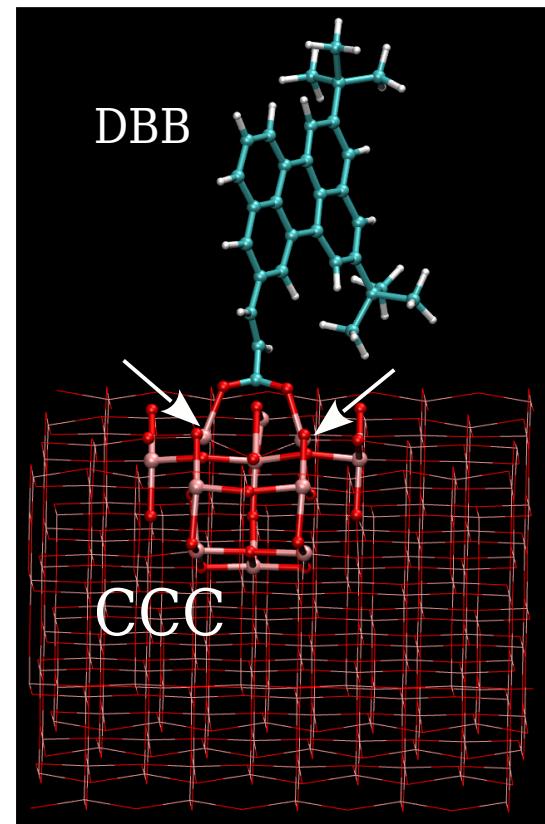
Setting Up the System in card.inpt

Example: Dye-sensitized semiconductor

DBB.psf

```
1 !NTITLE
REMARKS DBB=Perylene_Dye_typeB_tert-Butyl

64 !NATOM
 1 SYS    1      DBB    CA     CA      0.108060   12.011
 2 SYS    1      DBB    CA     CA     -0.256800   12.011
 3 SYS    1      DBB    CA     CB      0.015126   12.011
 .
 .
 .
 .
 .
 .
 61 SYS   1      DBB    HC     HC      0.041699   1.008
 62 SYS   1      DBB    HC     HC      0.038063   1.008
 63 SYS   1      DBB    TI     TI      2.1960    47.8671
 64 SYS   1      DBB    TI     TI      2.1960    47.8671
```



Files:

- input.pdb
- DBB.psf
- CCC.psf
- input.prm

Setting Up the System in card.inpt

Example: Dye-sensitized semiconductor

CCC.psf

```
1 !NTITLE
REMARKS CCC=TiO2 cluster

479!NATOM
1   SYS    1   CCC    TI    TI    2.1960  47.8671
2   SYS    1   CCC    TI    TI    2.1960  47.8671
.
.
.
.
.
.
478   SYS    1   CCC    0     0    -1.0980  15.9994
479   SYS    1   CCC    0     0    -1.0980  15.9994
```

0 !NBOND: bonds

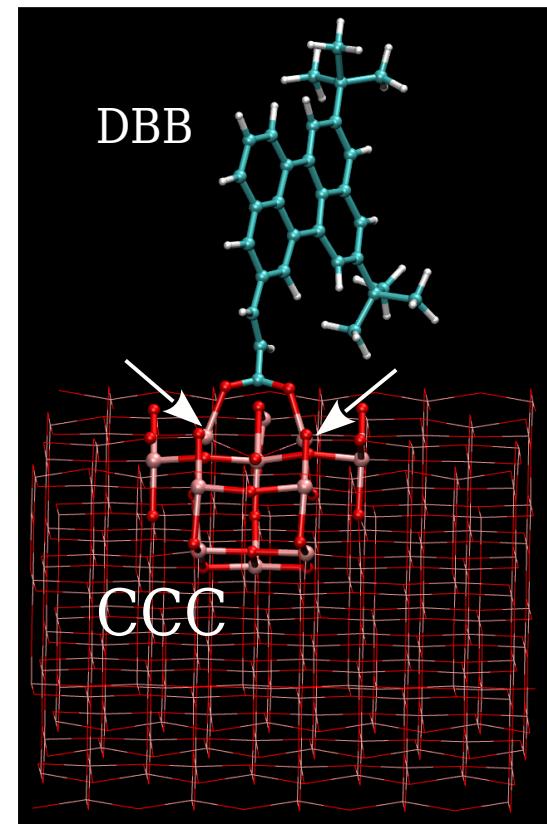
0 !NTHETA: angles

0 !NPHI: dihedrals

0 !NIMPHI: impropers

31 !AD-HOC: flex

```
74    TI  true
136   0   true
204   0   true
71    TI  true
192   0   true
132   0   true
78    TI  true
326   0   true
266   0   true
.
.
.
.
.
.
111   TI  true
424   0   true
265   0   true
```



Files:

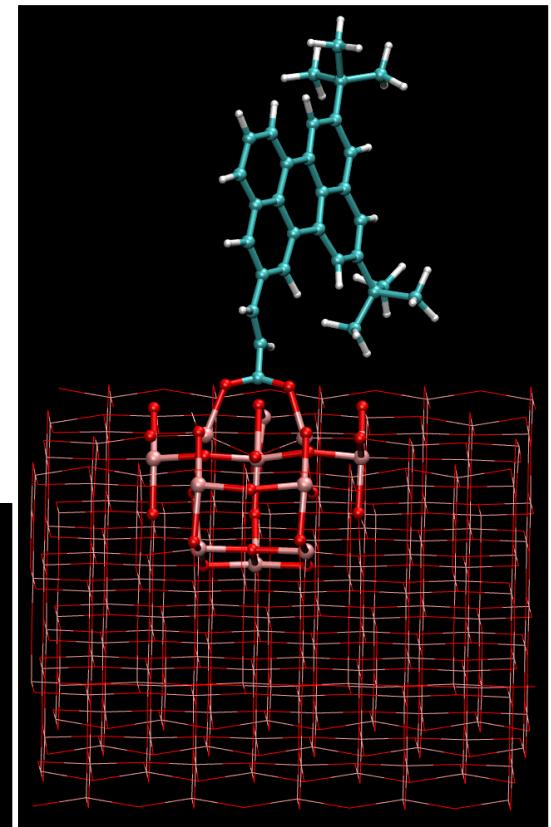
- input.pdb
- DBB.psf
- CCC.psf
- input.prm

Setting Up the System in card.inpt

Example: Dye-sensitized semiconductor

Files:

- input.pdb
- DBB.psf
- CCC.psf
- input.prm



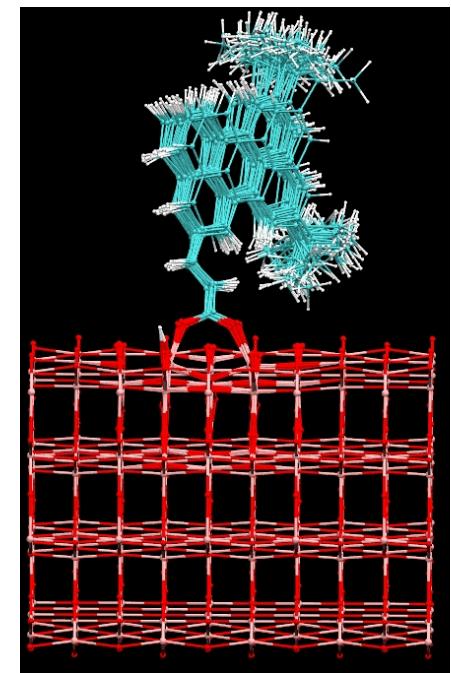
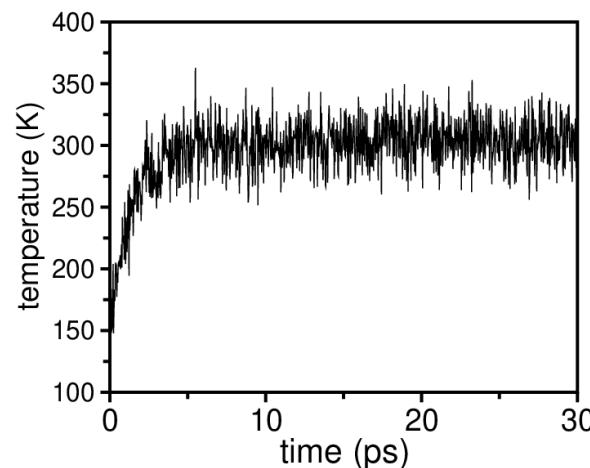
```
|-----  
|           ENVIRONMENT parameters ...  
|  
thermostat      = Microcanonical ! <== Berendsen, Nose_Hoover, Microcanonical  
temperature       = 300.d0          ! <== Bath Temperature (K)  
thermal_relaxation_time = 5.d-1    ! <== Temperature coupling term with the bath  
                                    ! <== SMALL = STRONG ; use "= infinity" to decouple  
cutoff_radius     = 50.d0          ! <== Cut off radius (Angs.) for electrostatic and LJ interactions  
damping_Wolf      = 0.0005         ! <== damping parameter (Angs.^-1)  
|-----  
|           GENERAL INFO ...  
|  
driver_MM        = MM_Dynamics   ! <== MM_Dynamics , MM_Optimize , NormalModes , Parametrize  
read_velocities   = true          ! <== reads the initial velocities : T_ , F_  
MM_input_format  = GAFF          ! <== GMX, NAMD, GAFF  
MM_log_step       = 50            ! <== step for saving MM results & parameters  
MM_frame_step     = 100           ! <== step for saving MM results & parameters
```

Thermalization

Example: Dye-sensitized semiconductor

```
thermostat      = Berendsen      ! <== Berendsen, Nose_Hoover, Microcanonical
temperature      = 300.d0        ! <== Bath Temperature (K)
thermal_relaxation_time = 7.d-1   ! <== Temperature coupling term with the bath
                                    ! <== SMALL = STRONG ; use "= infinity" to decouple
read_velocities  = false         ! <== reads the initial velocities : T_ , F_
```

> \$DYNEMOLDIR/dynemol



```
thermostat      = Microcanonical  ! <== Berendsen, Nose_Hoover, Microcanonical
read_velocities = true           ! <== reads the initial velocities : T_ , F_
```

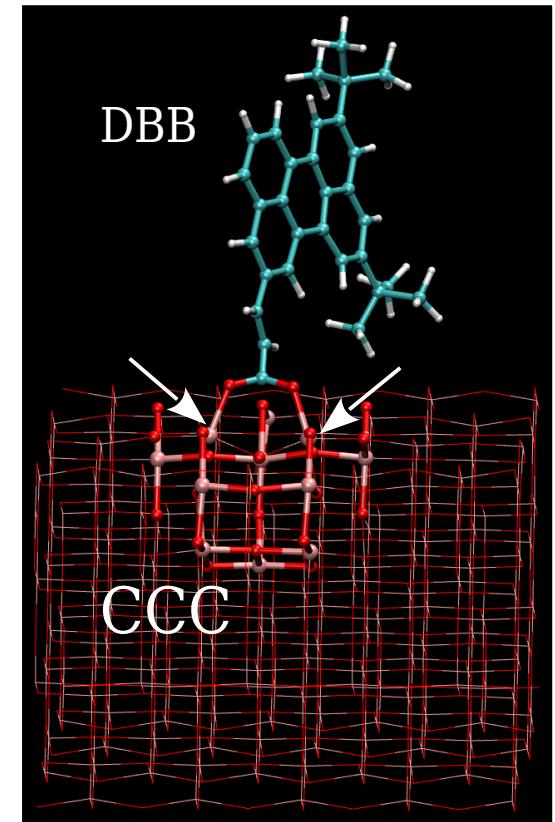
> mv velocity_MM.out velocity_MM.inpt
> \$DYNEMOLDIR/dynemol resume

Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

- Photoinduced electron transfer from DBB:LUMO → TiO₂ cluster
- Photoexcited electron to DBB:LUMO
- Hole in DBB:HOMO
- Atoms at fixed positions
- PBC in the (x,y) plane

```
!-----  
!           ACTION   flags  
  
!-----  
DRIVER = q_dynamics  
  
survival      = true  
nuclear_matter = extended_sys  
file_type      = structure          ! <= structure or trajectory  
file_format    = pdb               ! <= xyz , pdb or vasp  
  
PBC = [ 1 , 1 , 0 ]  
  
electron_state = DBB:84  
hole_state     = DBB:83  
  
t_f  =  0.5d0                      ! <= final time in PIC0oseconds  
n_t  =  1000  
!-----  
!  
!           AD-HOC settings  
  
!-----  
OPT_parms = true  
ad_hoc = true  
ad_hoc:QM:residue(63:64)=CCC  
ad_hoc:QM:nr(63:64)=2  
ad_hoc:QM:V_shift(1:62)=0.6  
!-----  
!  
!           DOS settings  
  
sigma      =  0.040d0                !  
DOS_range = real_interval( -15.d0 , 0.d0 )
```

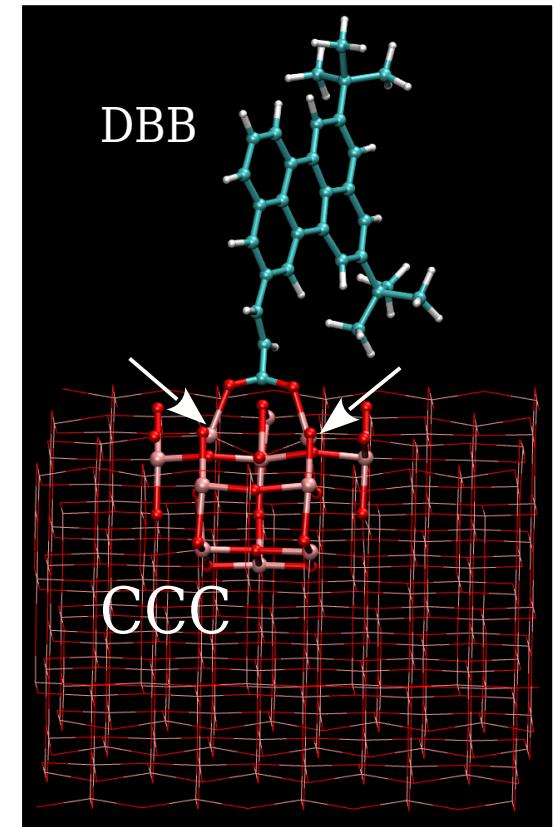


Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

- Ad-hoc settings:
 - Dynemol reads opt_eht_parms.input
 - Ti atoms 63:64 belong to TiO₂ cluster (CCC)
 - Energy offset (V_shift) of DBB fragment orbitals with respect to CCC

```
!----- ACTION flags -----!  
!  
DRIVER = q_dynamics  
  
survival      = true  
nuclear_matter = extended_sys  
file_type      = structure          ! <= structure or trajectory  
file_format     = pdb               ! <= xyz , pdb or vasp  
  
PBC = [ 1 , 1 , 0 ]  
  
electron_state = DBB:84  
hole_state     = DBB:83  
  
t_f  =  0.5d0                      ! <= final time in PIC0oseconds  
n_t  =  1000  
!  
!----- AD-HOC settings -----!  
  
OPT_parms = true  
ad_hoc = true  
ad_hoc:QM:residue(63:64)=CCC  
ad_hoc:QM:nr(63:64)=2  
ad_hoc:QM:V_shift(1:62)=0.6  
!  
!----- DOS settings -----!  
  
sigma      =  0.040d0                !  
DOS_range = real_interval( -15.d0 , 0.d0 )
```

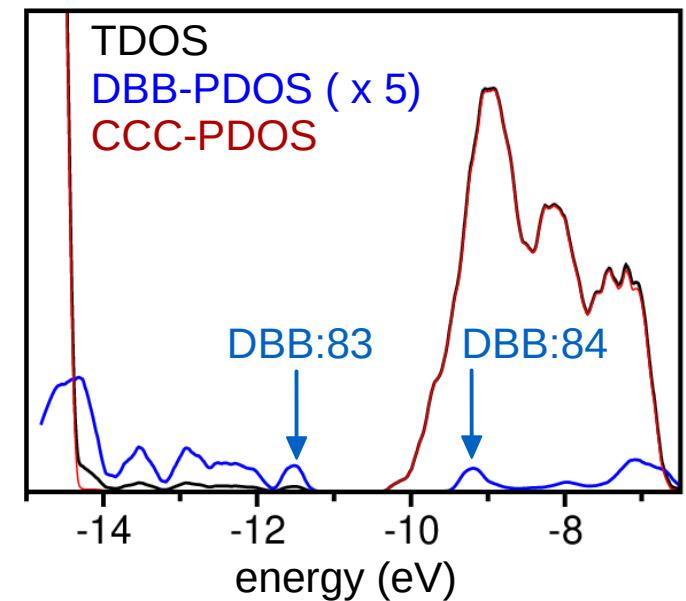
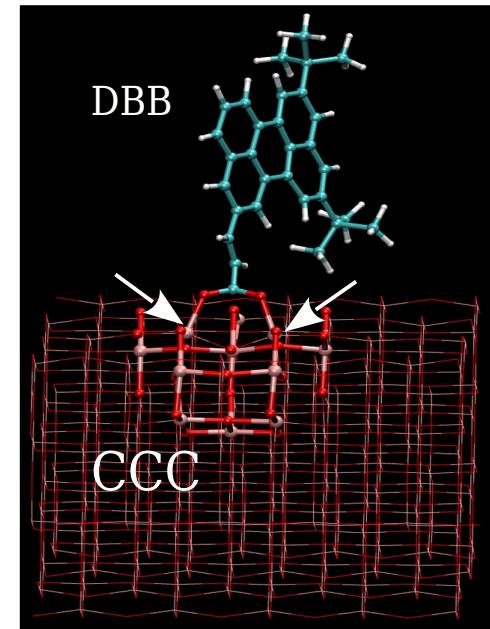


Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

- Energy DOS settings:
 - calculates Total DOS (TDOS.dat)
 - calculates DOS projected on residues (“resname”-PDOS.dat)
 - results written in dos.trunk

```
!-----  
!           ACTION   flags  
  
! DRIVER = q_dynamics  
  
survival      = true  
nuclear_matter = extended_sys  
file_type      = structure          ! <= structure or trajectory  
file_format     = pdb               ! <= xyz , pdb or vasp  
  
PBC = [ 1 , 1 , 0 ]  
  
electron_state = DBB:84  
hole_state     = DBB:83  
  
t_f  =  0.5d0                      ! <= final time in PIC0oseconds  
n_t  =  1000  
!  
!           AD-HOC settings  
  
OPT_parms = true  
ad_hoc = true  
ad_hoc:QM:residue(63:64)=CCC  
ad_hoc:QM:nr(63:64)=2  
ad_hoc:QM:V_shift(1:62)=0.6  
!  
!           DOS settings  
  
sigma      = 0.040d0  
DOS_range = real_interval( -15.d0 , 0.d0 )  
!
```

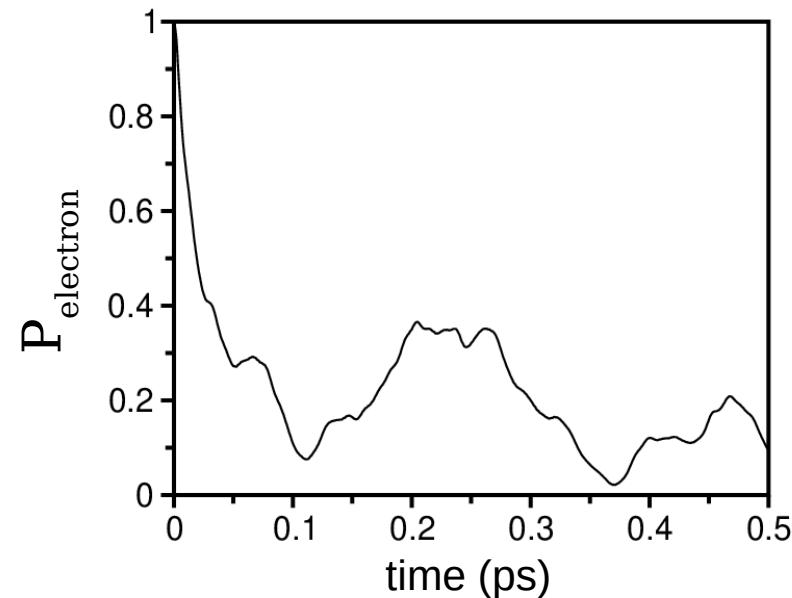
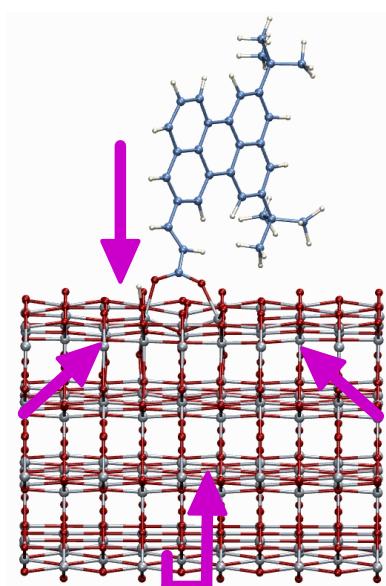


Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Finite-Size Spurious Artifacts

```
!-----  
!  
ACTION      flags  
  
DRIVER = q_dynamics  
  
survival      = true  
nuclear_matter = extended_sys  
file_type      = structure          ! <== structure or trajectory  
file_format    = pdb                ! <== xyz , pdb or vasp  
  
PBC = [ 1 , 1 , 0 ]  
  
electron_state = DBB:84  
hole_state     = DBB:83
```



Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Nnx=0;nny=0

Finite-Size Spurious Artifacts

Nnx=1;nny=0

Nnx=0;nny=1

```
!                                         ACTION   flags
!
! DRIVER = q_dynamics

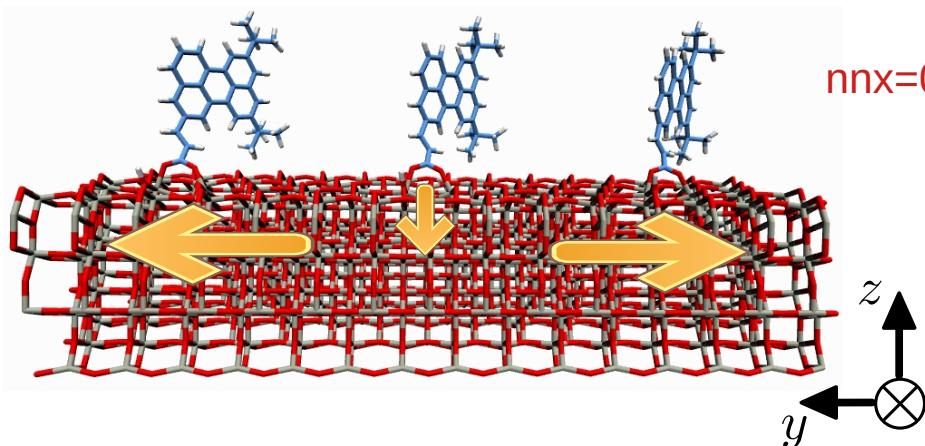
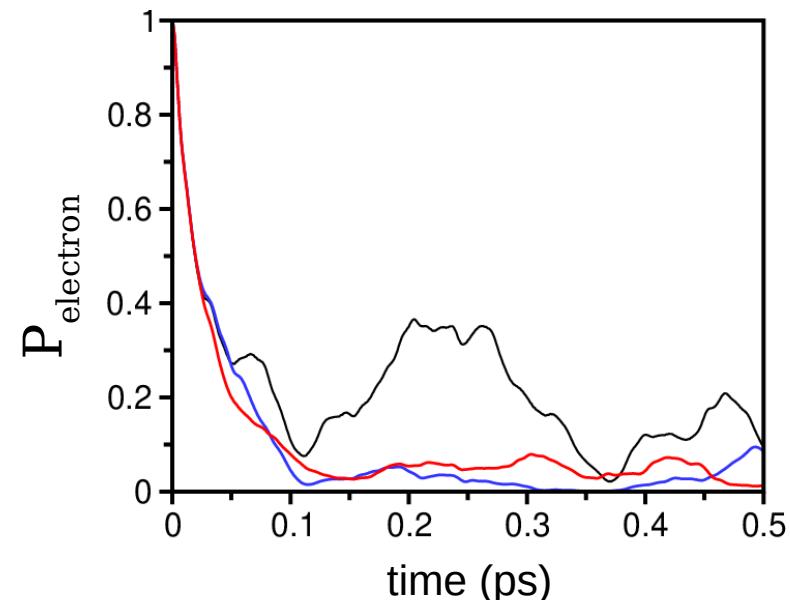
survival      = true
nuclear_matter = extended_sys
file_type      = structure          ! <== structure or trajectory
file_format    = pdb               ! <== xyz , pdb or vasp

nnx = 0 ; nny = 1

PBC = [ 1 , 1 , 0 ]

electron_state = DBB:84
hole_state     = DBB:83

t_f  = 0.5d0                      ! <== final time in PICoseconds
n_t  = 1000
```

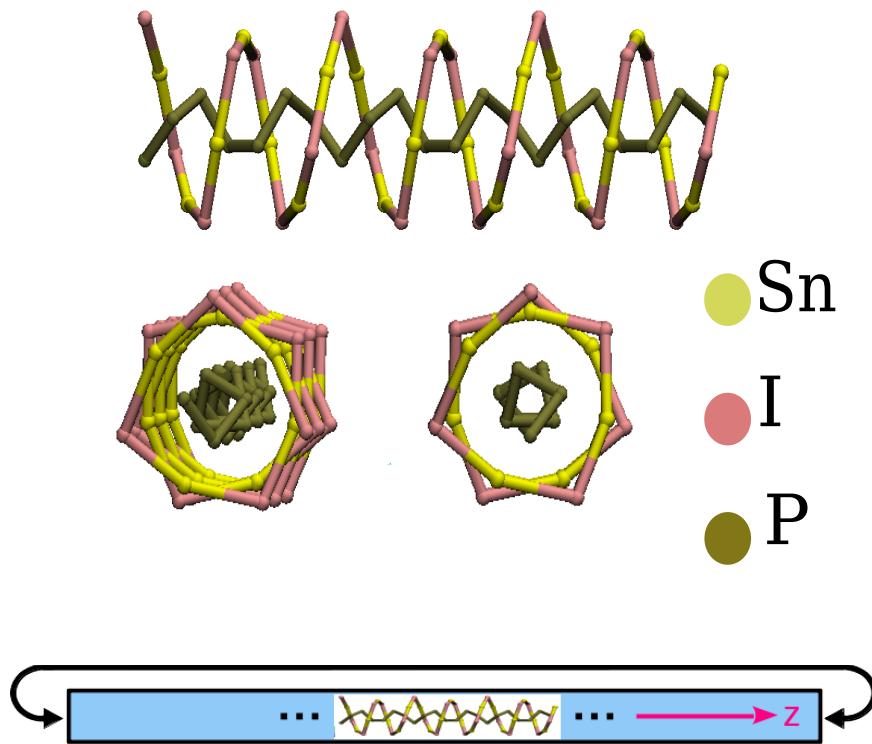


nnx=0,nny=1

Notice: not cost-effective

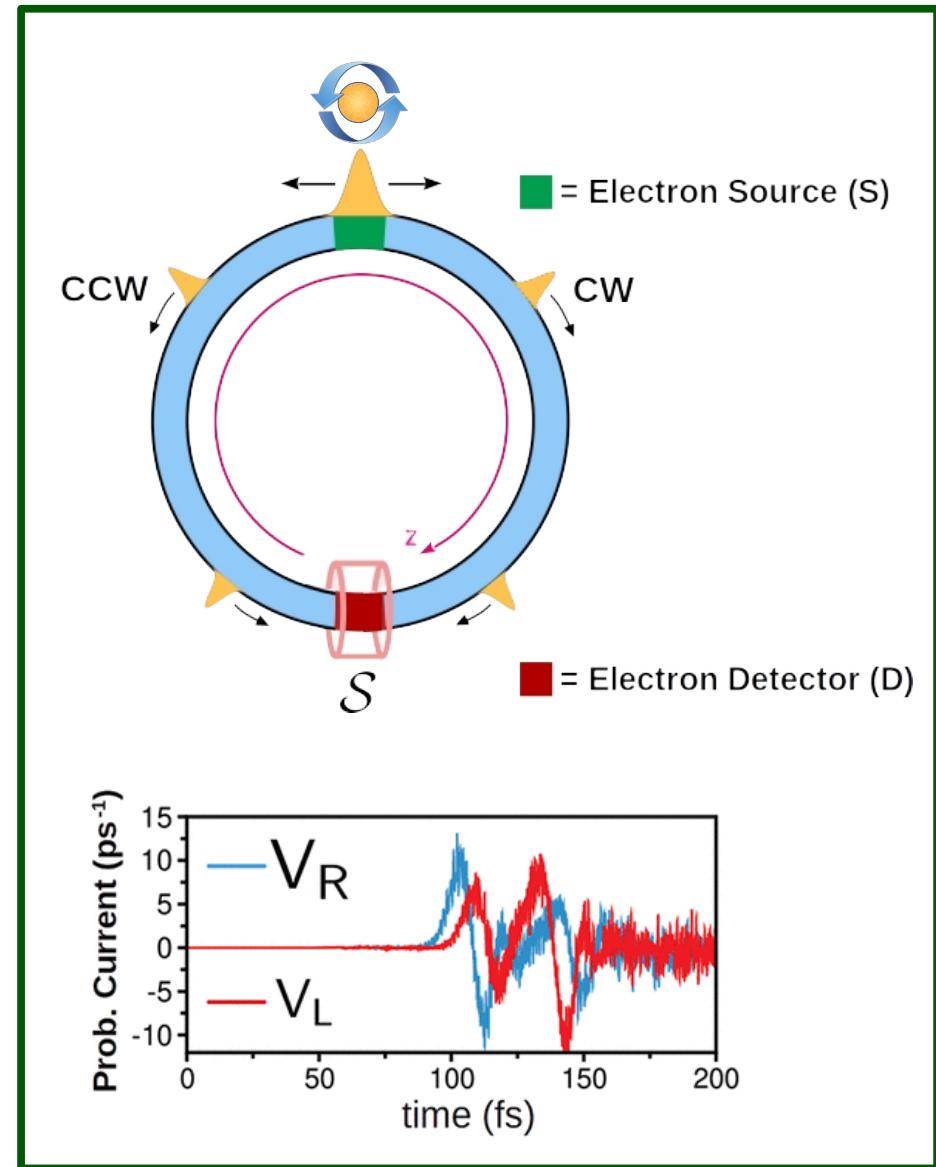
Electron Propagation in Chiral nanowire

Inorganic Double Helices in Semiconducting SnIP



$$nnz = N_{\text{cell}}$$

$$\text{PBC} = [0, 0, 1]$$



Setting Up the System in card.inpt

Example: Dye-sensitized semiconductor

Orbital Rendering of Charge Dynamics

```
!----- ACTION flags
! DRIVER = q_dynamics

survival      = true
nuclear_matter = extended_sys
file_type     = structure          ! <== structure or trajectory
file_format    = pdb               ! <== xyz , pdb or vasp

nnx = 0 ; nny = 0

PBC = [ 1 , 1 , 0 ]

electron_state = DBB:79
hole_state     = DBB:78

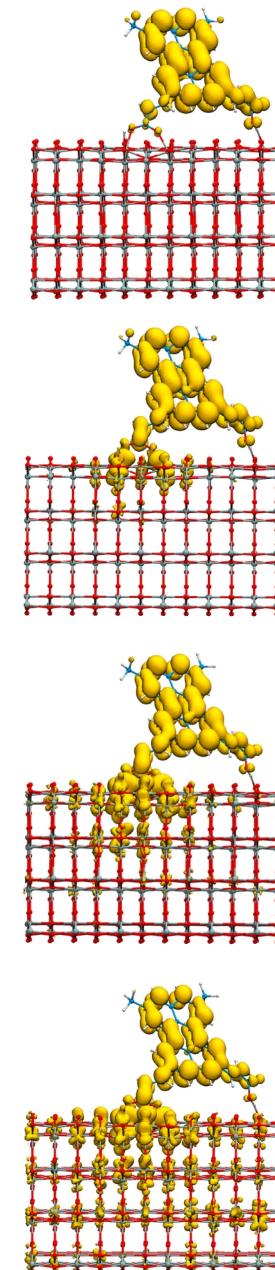
t_f  =  0.2d0                      ! <== final time in PICoseconds
n_t  =  200

!----- AD-HOC settings

OPT_parms = true
ad_hoc = true
ad_hoc:QM:residue(52:53)=CCC
ad_hoc:QM:nr(52:53)=2
ad_hoc:QM:V_shift(1:51)=0.6

!----- VISUALIZATION flags

GaussianCube    =  true   ! <== generating cube files for MO visualization
GaussianCube_step =  40    ! <== time step for saving Gaussian Cube files
```



Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Average over conformations

```
!----- ACTION flags
DRIVER = avrg_configs

survival      = true
nuclear_matter = extended_sys
file_format    = pdb          ! <= xyz , pdb or vasp
file_type      = trajectory   ! <= structure or trajectory
frame_step     = 1            ! <= step for avrg_configs ;
                             frame_step <= size(trj) ; default = 1

nnx = 1 ; nny = 0

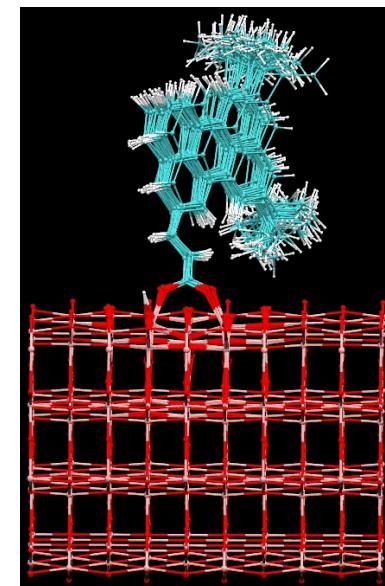
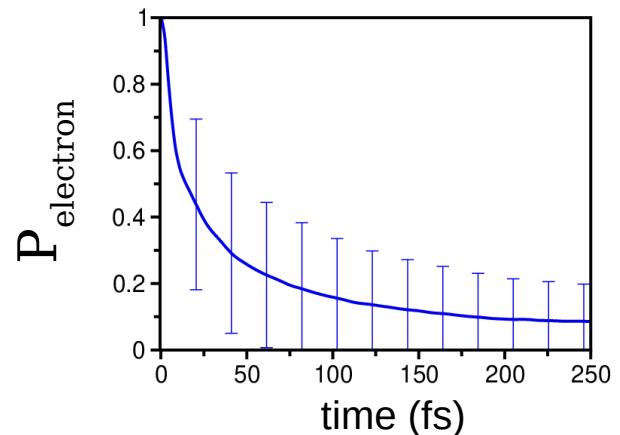
PBC = [ 1 , 1 , 0 ]

electron_state = DBB:84
hole_state     = DBB:83

t_f  =  0.5d0           ! <= final time in PICoseconds
n_t  =  1000

!----- AD-HOC settings
OPT_parms = true
ad_hoc = true
ad_hoc:QM:residue(63:64)=CCC
ad_hoc:QM:nr(63:64)=2
ad_hoc:QM:V_shift(1:62)=0.6

!----- DOS settings
sigma      = 0.040d0
DOS_range = real_interval( -15.d0 , 0.d0 )
```



Input File:

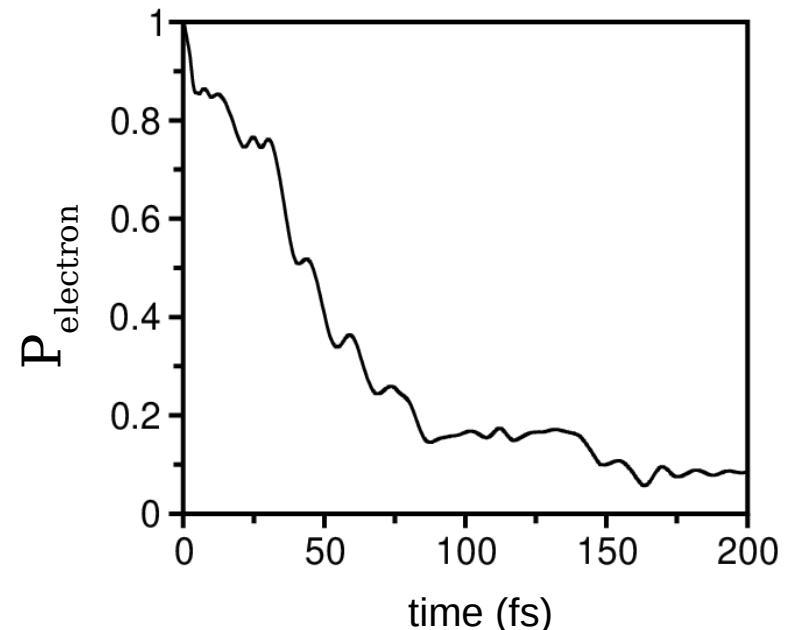
- frames.pdb

Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Non-adiabatic Electron Transfer Dynamics

```
!-----  
!           ACTION   flags  
!<== Ehrenfest QMMM  
DRIVER      = slice_A0  
QMMM        = true  
survival    = true  
  
nuclear_matter = MDynamics  
file_type     = structure  
file_format   = pdb  
  
PBC = [ 1 , 1 , 0 ]  
  
electron_state = DBB:66  
hole_state     = DBB:65  
  
t_f  =  0.20          ! <== final time in PICoseconds  
n_t  = 10000  
!  
!-----  
!           SYSTEM INFO  
N_of_molecules = 2          ! <== total number of molecules  
N_of_species   = 2          ! <== total number of species  
  
species(1) % residue       = DBB  ! <== Residue label for species 1  
species(1) % N_of_molecules = 1  ! <== # of molecules of species 1  
species(1) % N_of_atoms    = 45  ! <== # of atoms in a molecule of species 1  
species(1) % flex           = true ! <== Flexible : true , false  
  
species(2) % residue       = CCC ! <== Residue label for species 2  
species(2) % N_of_molecules = 1  
species(2) % N_of_atoms    = 479  
species(2) % flex           = false  
!  
!           AD-HOC settings  
OPT_parms = true  
ad_hoc = true  
ad_hoc:QM:residue(45:46)=CCC  
ad_hoc:QM:nr(45:46)=2  
ad_hoc:QM:V_shift(1:44)=0.6
```



Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Non-adiabatic Electron Transfer Dynamics

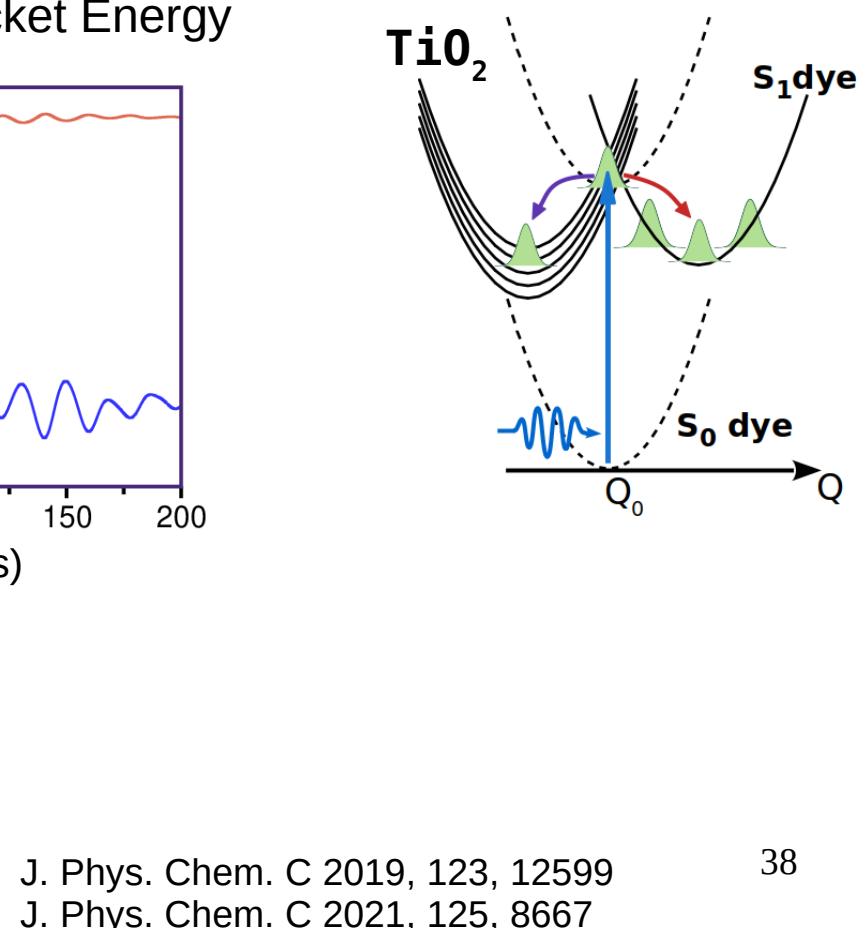
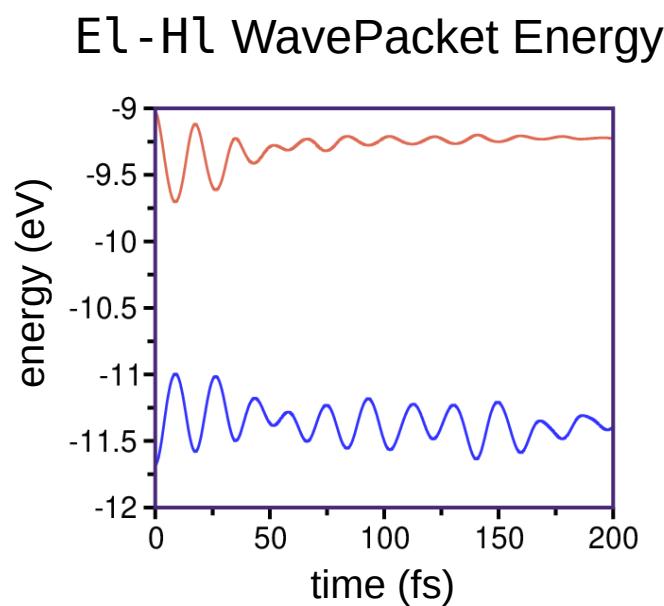
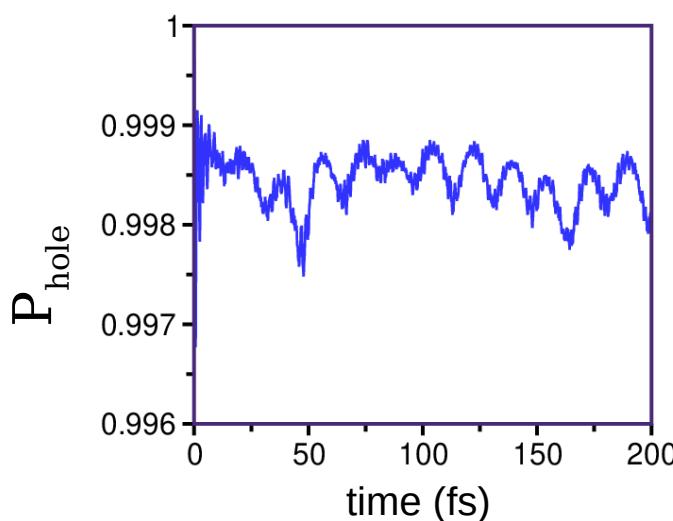
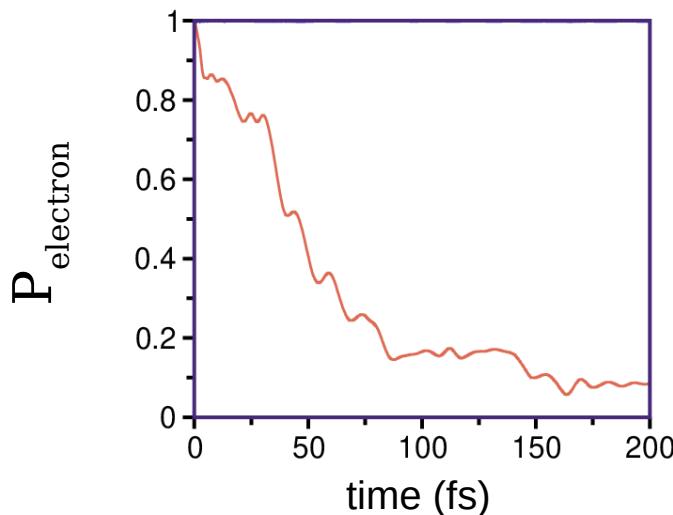
```
!-----  
!           ENVIRONMENT parameters  
  
thermostat      = Microcanonical ! <== Berendsen, Nose_Hoover, Microcanonical  
  
cutoff_radius   = 50.d0          ! <== Cut off radius (Angs.) for electrostatic  
damping_Wolf    = 0.0005         ! <== damping parameter (Angs.^-1)  
  
driver_MM       = MM_Dynamics   ! <== MM_Dynamics , MM_Optimize , NormalModes , Parametrize  
  
read_velocities = true  
  
MM_input_format = GAFF          ! <== GMX, NAMD, GAFF
```

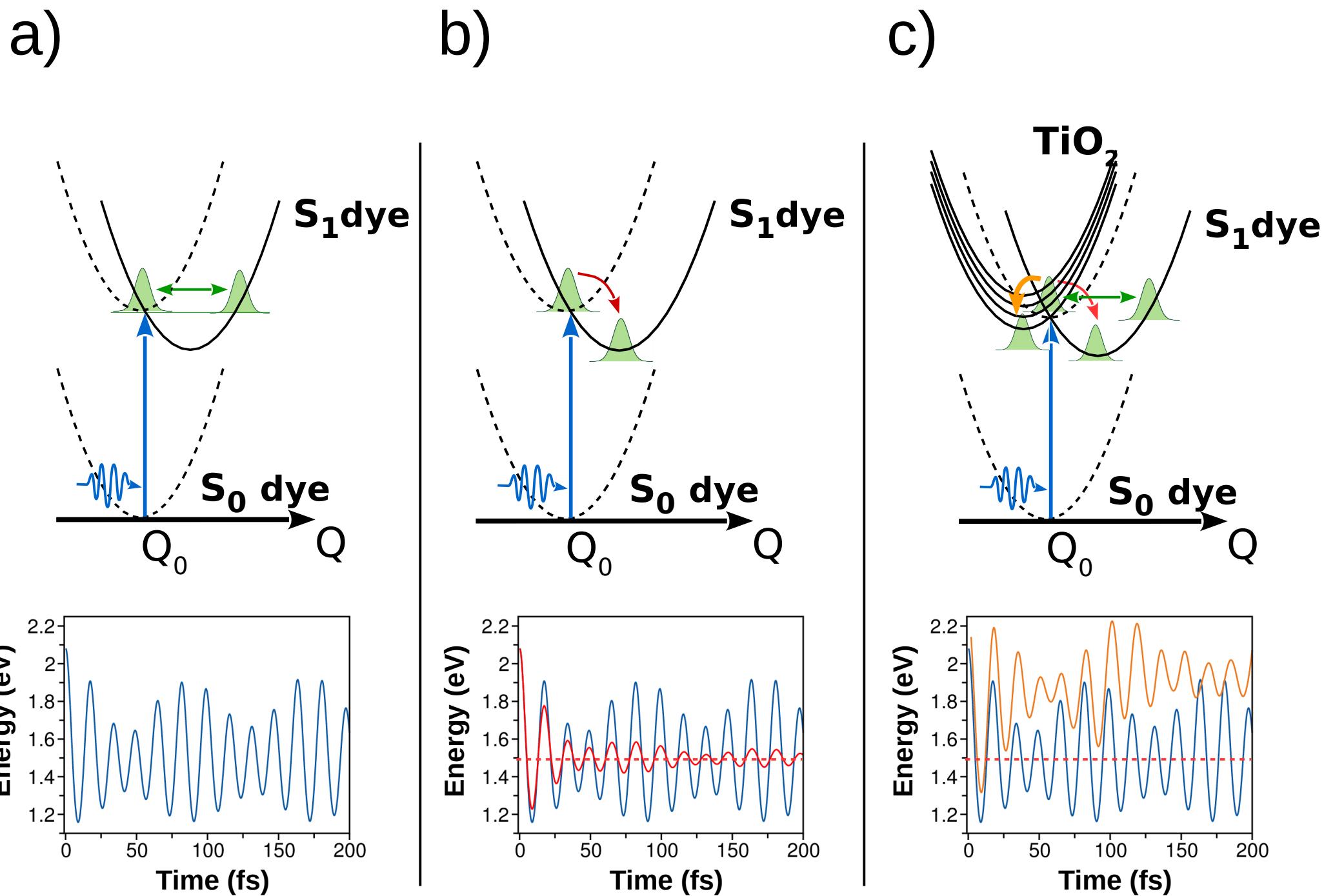


Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Non-adiabatic Electron Transfer Dynamics



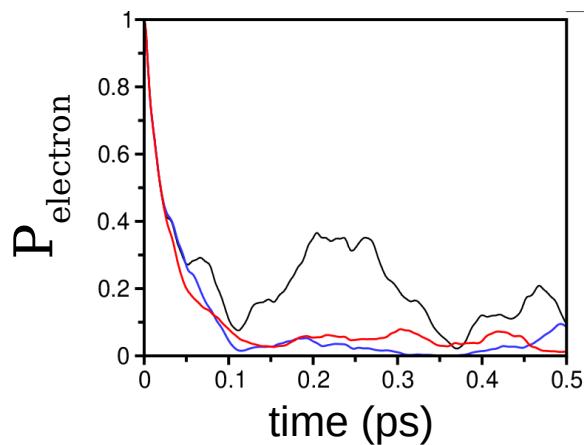


Interfacial Electron Transfer

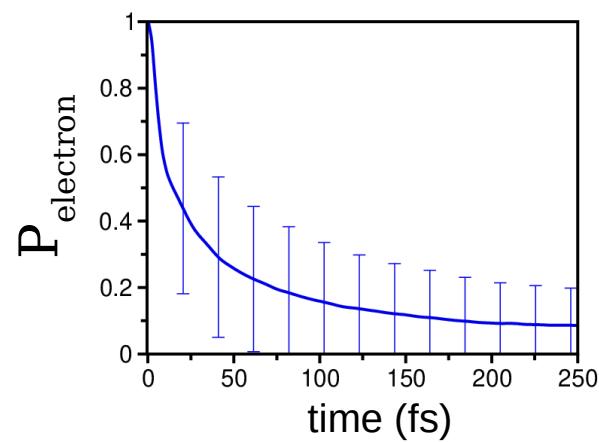
Example: Dye-sensitized semiconductor

Non-adiabatic Electron Transfer Dynamics on **rigid** structures

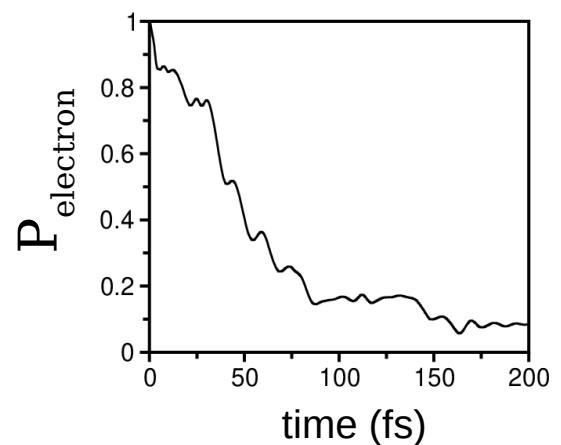
DRIVER = q_dynamics



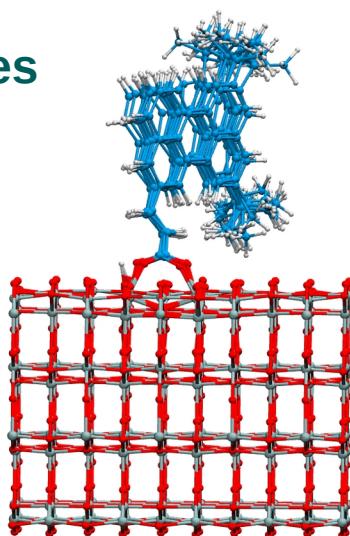
avrg_configs



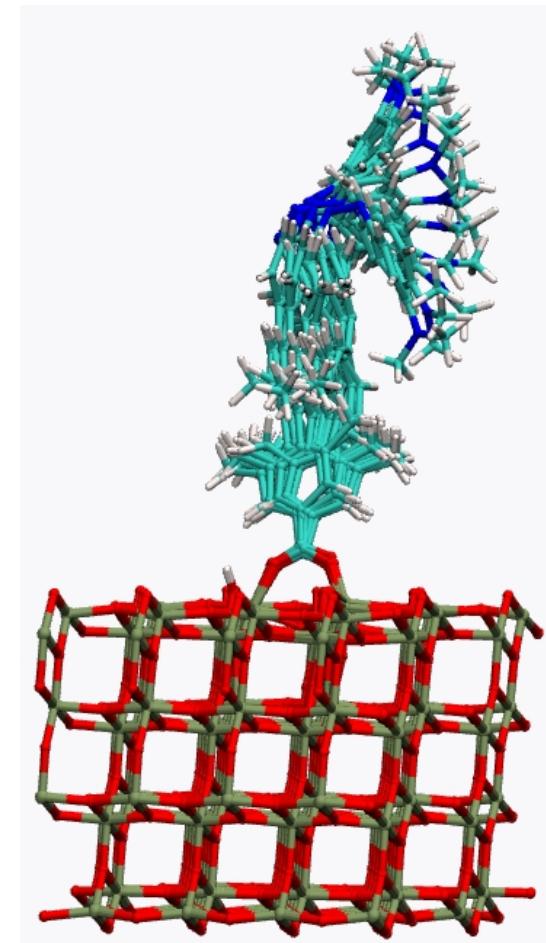
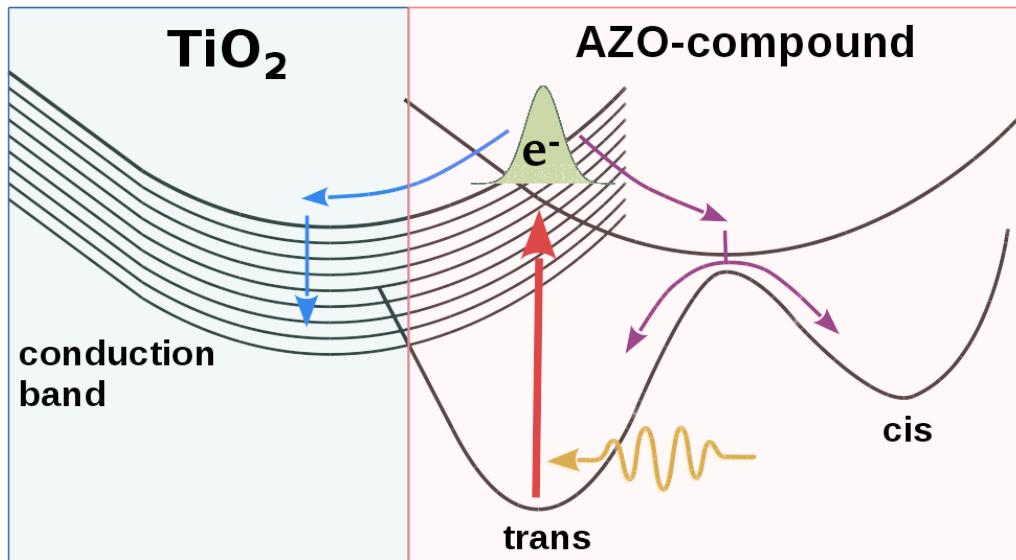
Ehrenfest



Similar behavior for rigid structures



Charge Transfer *vs* Structural Relaxation



J. Phys. Chem. Lett. 2018, 9, 5926.
J. Phys. Chem. C 2019, 123, 5692.
J. Phys. Chem. Lett. 2015, 6, 2393.

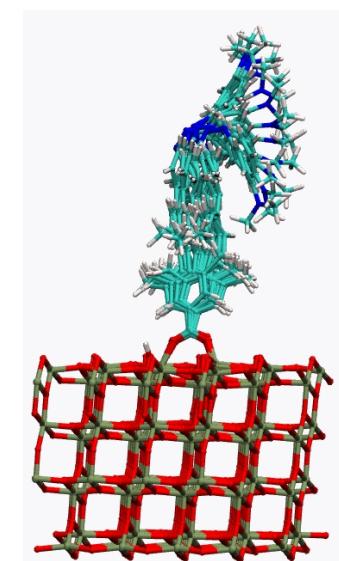
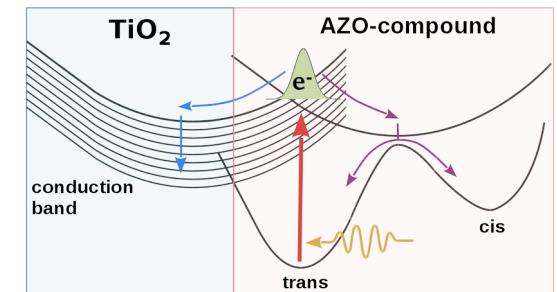
Charge Transfer vs Structural Relaxation

Sample card.inpt

```

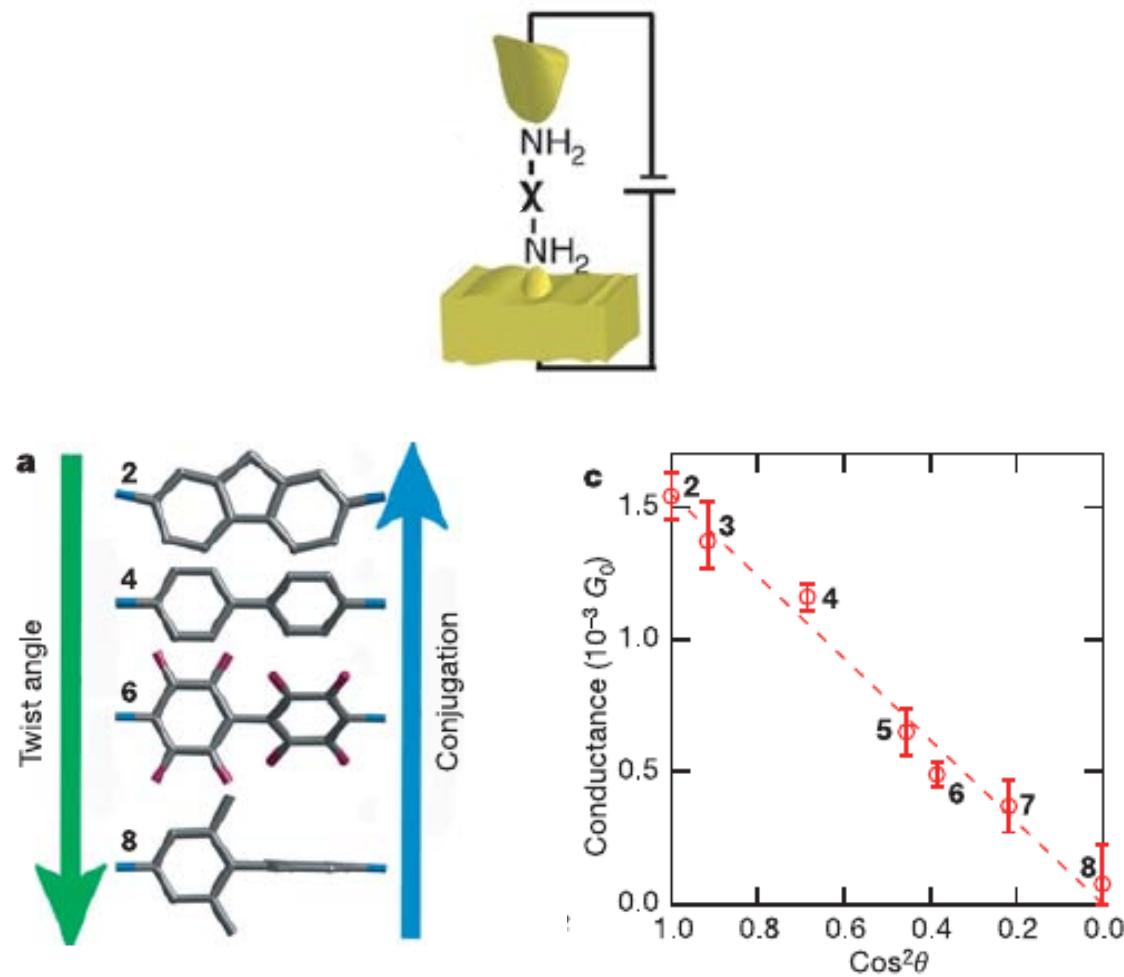
!
!----- ACTION flags
!----- DRIVER = slice_Cheb           ! <== slice_[Cheb, AO, FSSH, CSDM]
!----- QMMM      = true
!----- survival   = true
!----- nuclear_matter = MDynamics
!----- file_type   = structure          ! <== structure or trajectory
!----- file_format  = pdb               ! <== xyz , pdb or vasp
!----- PBC = [ 1 , 1 , 0 ]
!----- electron_state = AZD:92
!----- hole_state    = AZD:89
!----- t_f = 1.50                      ! <== final time in PIC0oseconds
!----- n_t = 75000
!
!----- SYSTEM INFO
!----- N_of_molecules = 2             ! <== total number of molecules
!----- N_of_species   = 2             ! <== total number of species
!----- species(1) % residue       = AZD      ! <== Residue label for species 1
!----- species(1) % N_of_molecules = 1      ! <== # of molecules of species 1
!----- species(1) % N_of_atoms    = 68     ! <== # of atoms in a molecule of species 1
!----- species(1) % flex         = true     ! <== Flexible : true , false
!----- species(2) % residue       = CCC      ! <== Residue label for species 2
!----- species(2) % N_of_molecules = 1      ! <== # of molecules of species 2
!----- species(2) % N_of_atoms    = 383    ! <== # of atoms in a molecule of species 2
!----- species(2) % flex         = false
!
!----- AD-HOC settings
!----- OPT_parms = true
!----- ad_hoc   = true
!----- ad_hoc:QM:residue(67:68)=CCC
!----- ad_hoc:QM:nr(67:68)=2
!
!----- ENVIRONMENT parameters ...
!----- thermostat        = Microcanonical ! <== Berendsen, Nose_Hoover, Microcanonical
!----- cutoff_radius      = 50.0d0          ! <== Cut off radius (Angs.) for electrostatic
!----- damping_Wolf       = 0.001           ! <== damping parameter (Angs.^-1)
!----- driver_MM          = MM_Dynamics    ! <== MM_Dynamics , MM_Optimize , NormalModes , Parametrize
!----- read_velocities    = true            ! <== reads the initial velocities : T_ , F_
!----- MM_input_format    = GMX             ! <== GMX, NAMD, GAFF

```

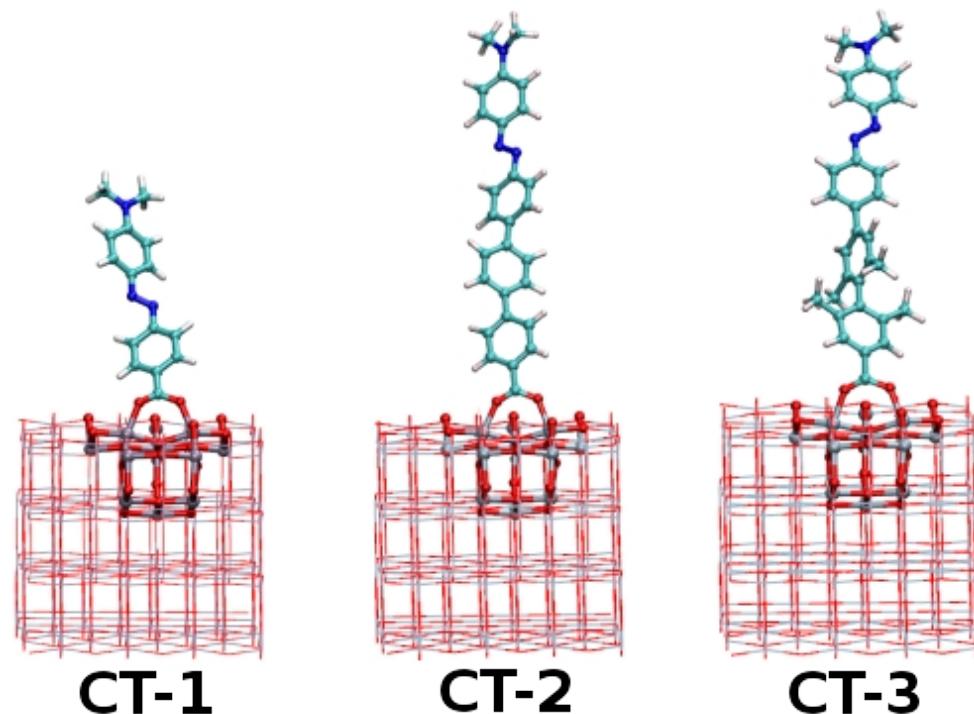
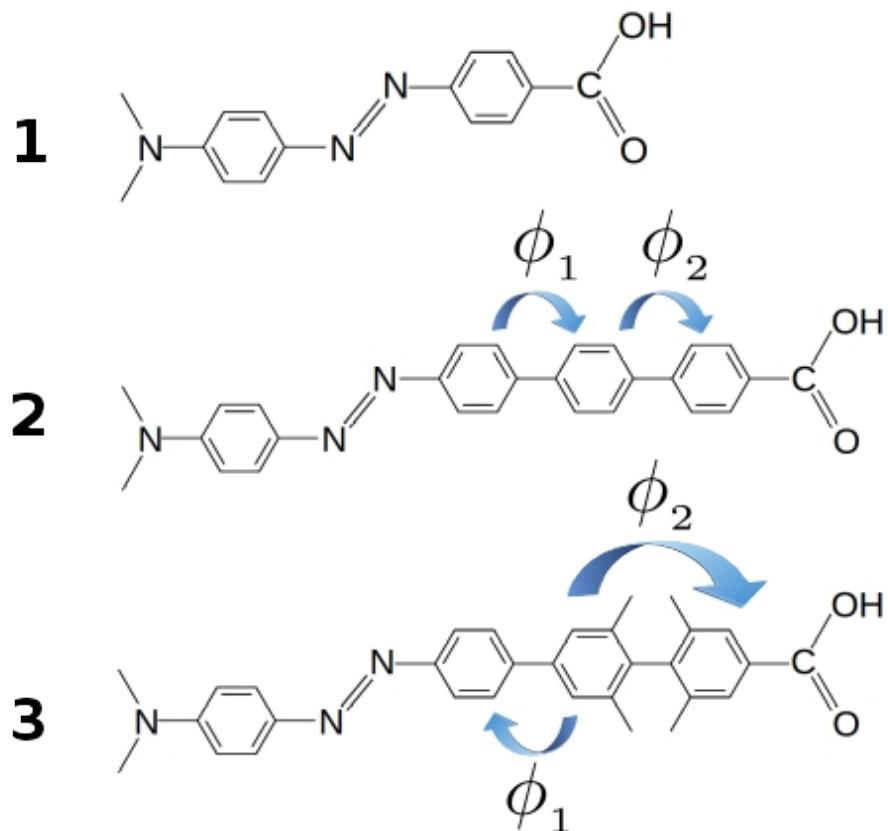


Dependence of single-molecule junction conductance on molecular conformation

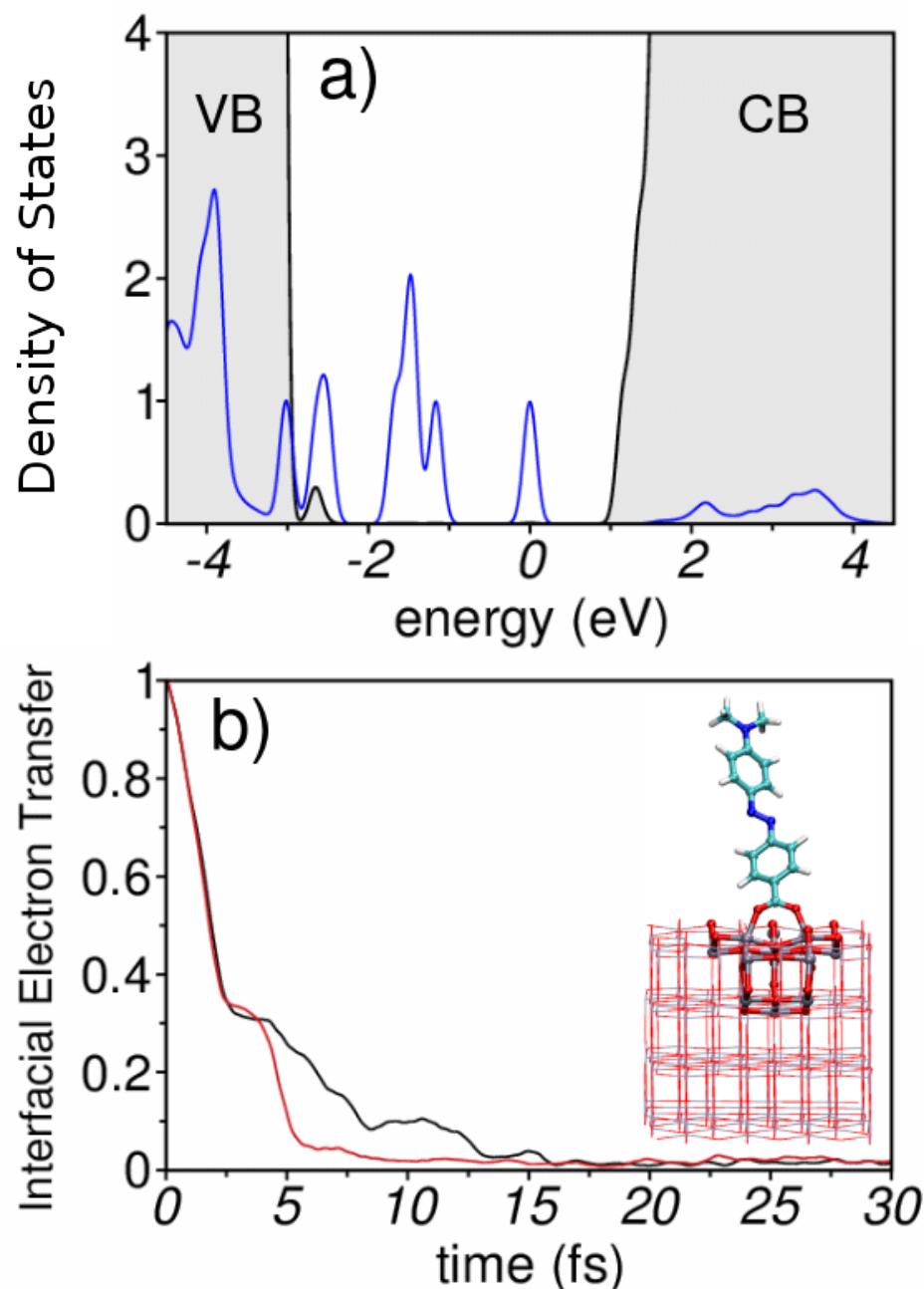
Latha Venkataraman^{1,4}, Jennifer E. Klare^{2,4}, Colin Nuckolls^{2,4}, Mark S. Hybertsen^{3,4} & Michael L. Steigerwald²



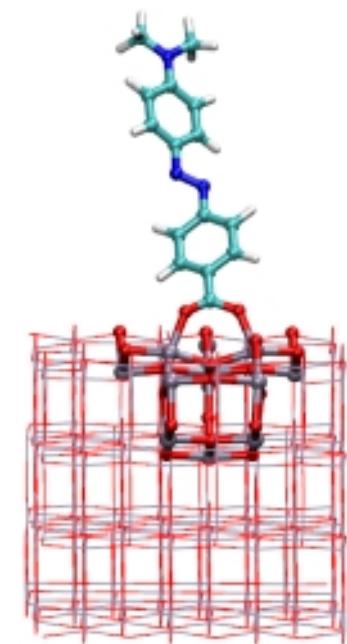
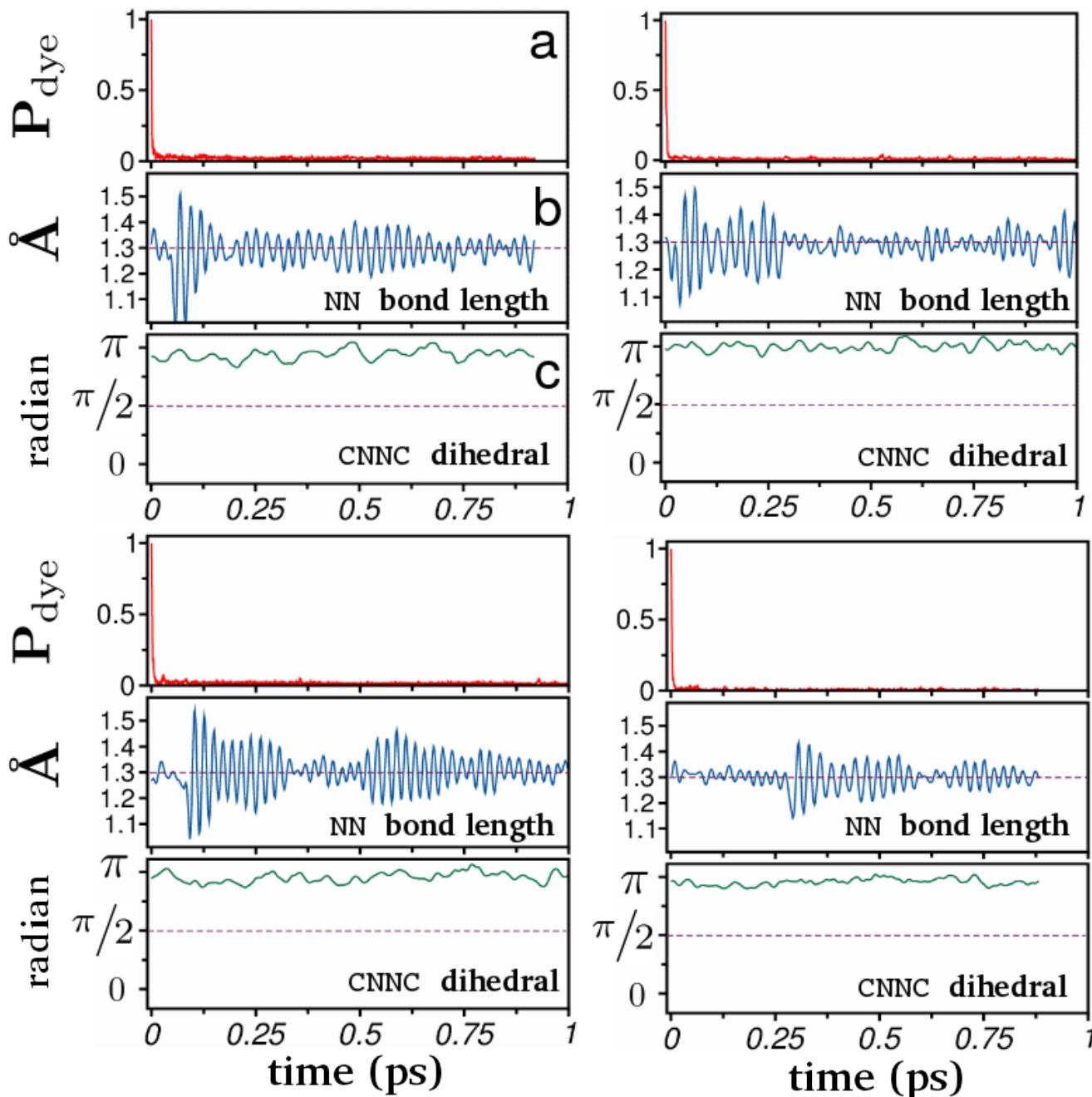
Charge Transfer *vs* Structural Relaxation



Charge Transfer *vs* Structural Relaxation

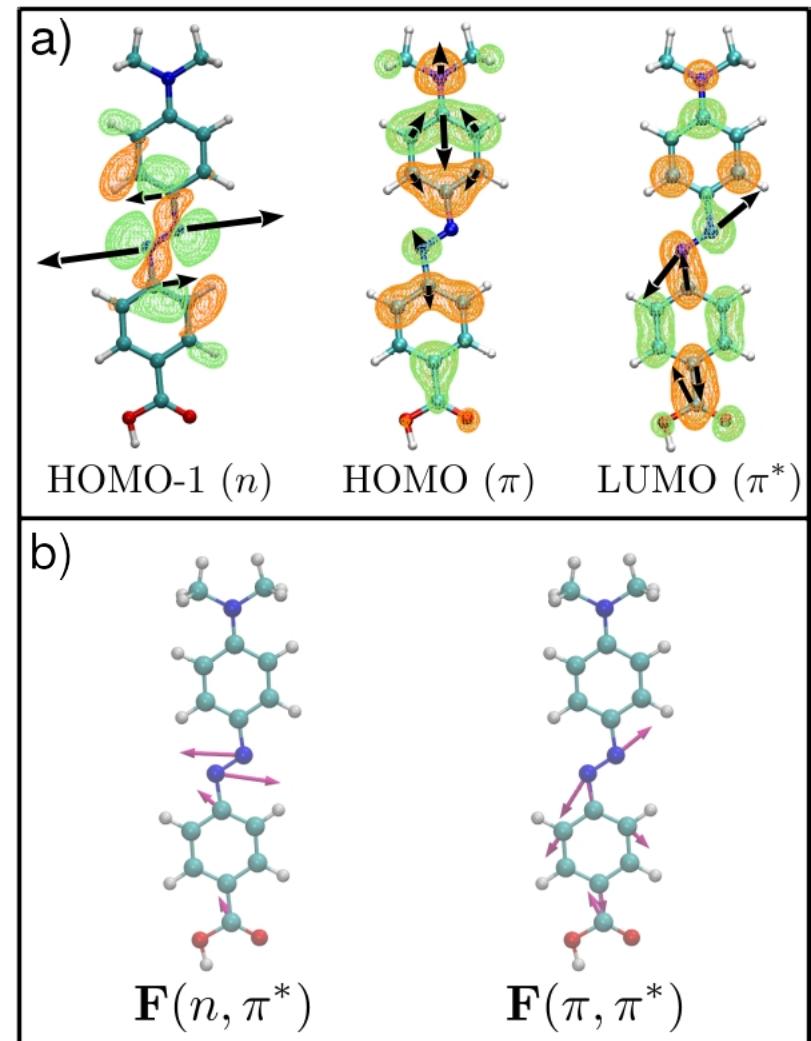
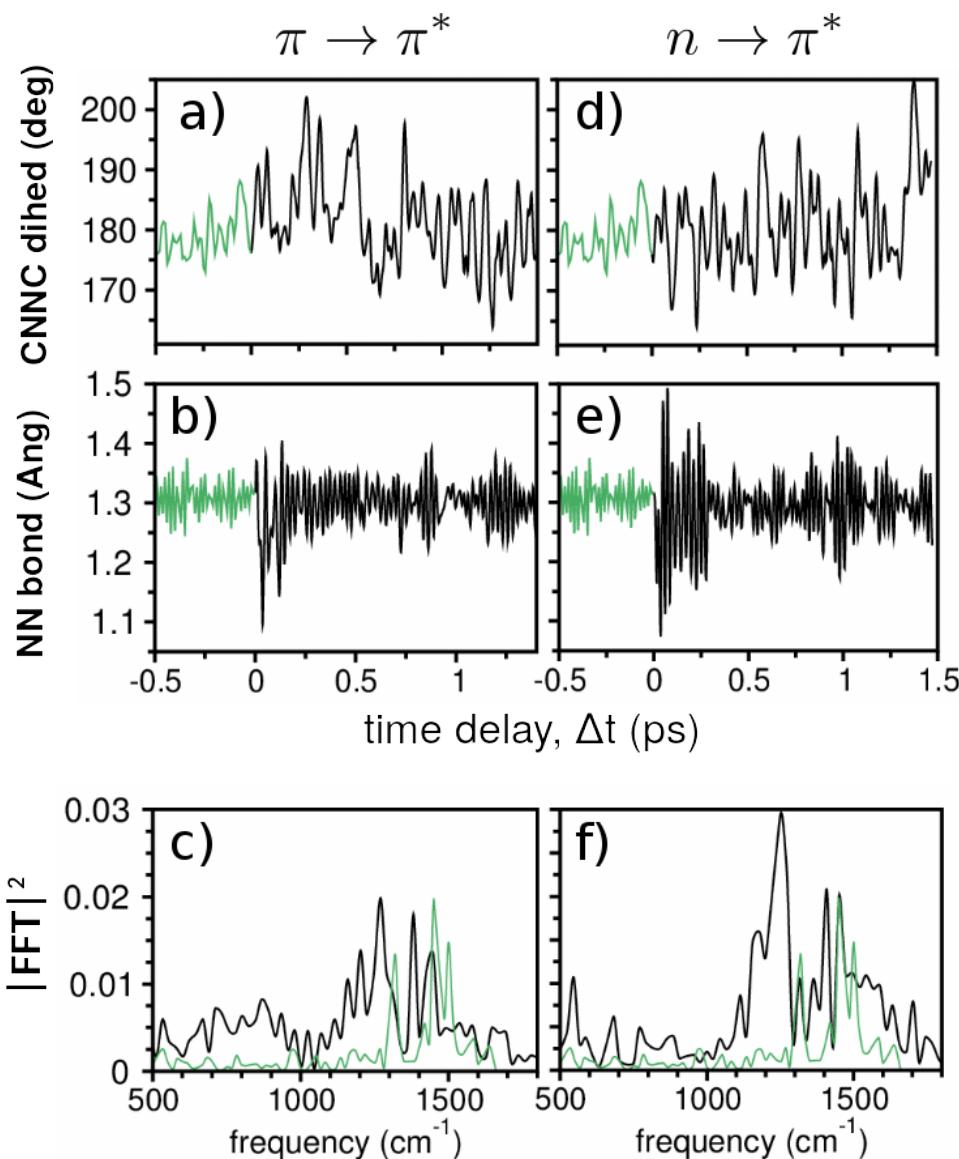


Charge Transfer *vs* Structural Relaxation

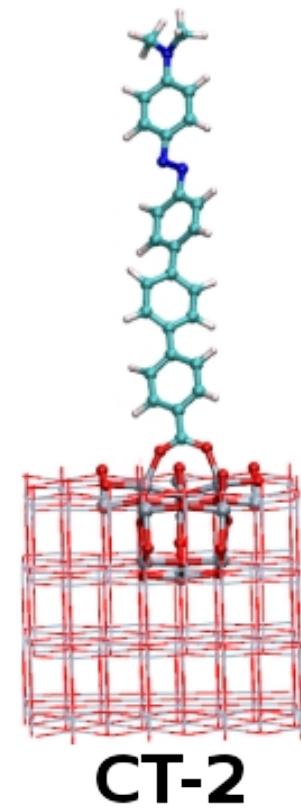
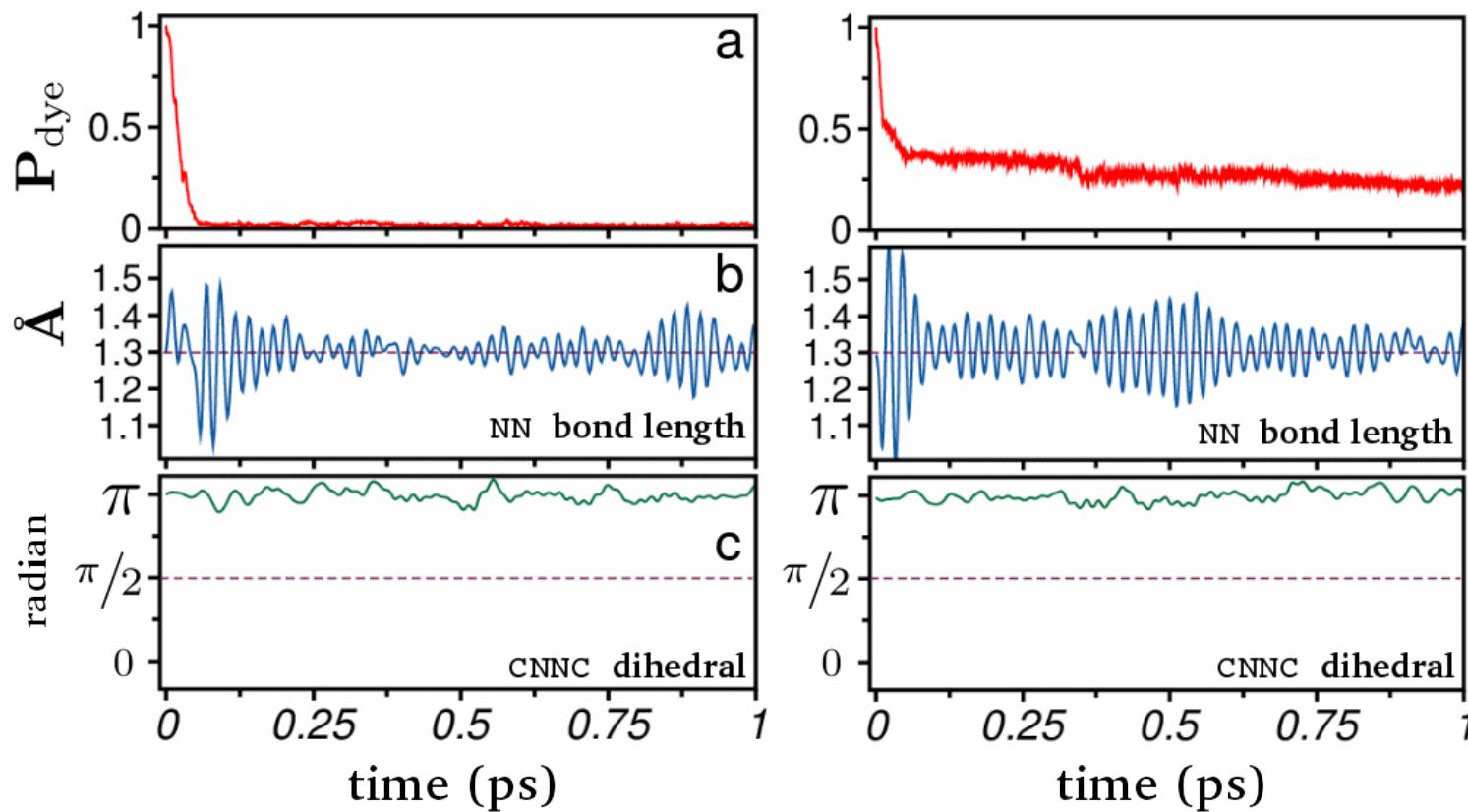


CT-1

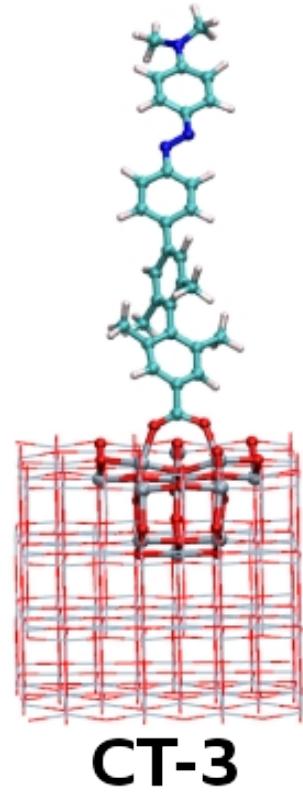
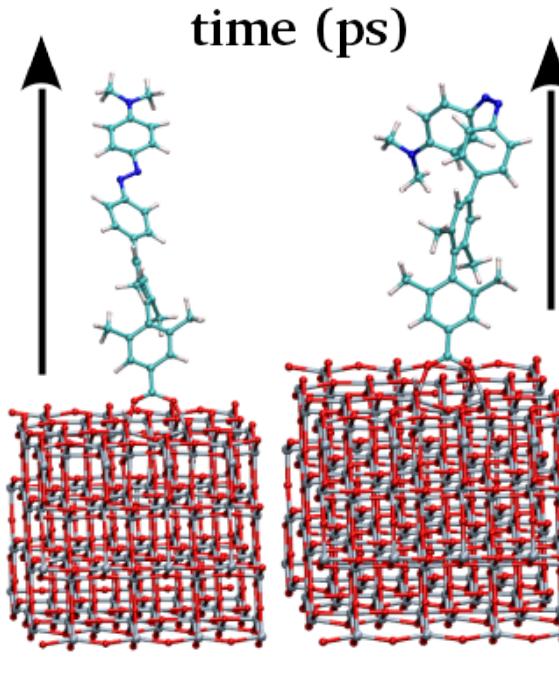
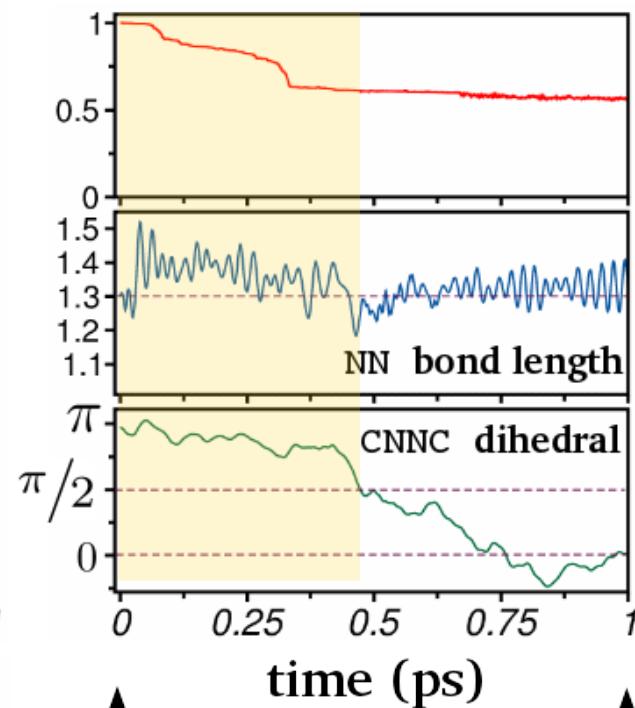
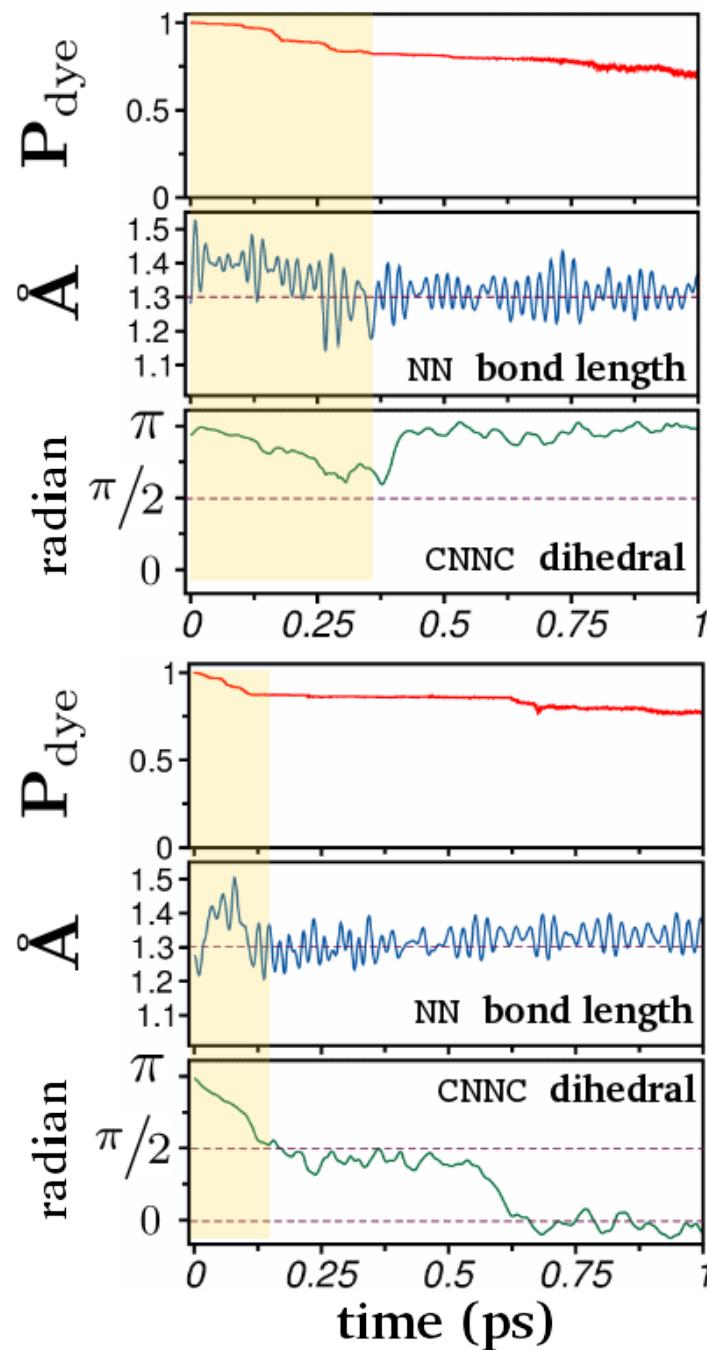
Charge Transfer *vs* Structural Relaxation



Charge Transfer *vs* Structural Relaxation

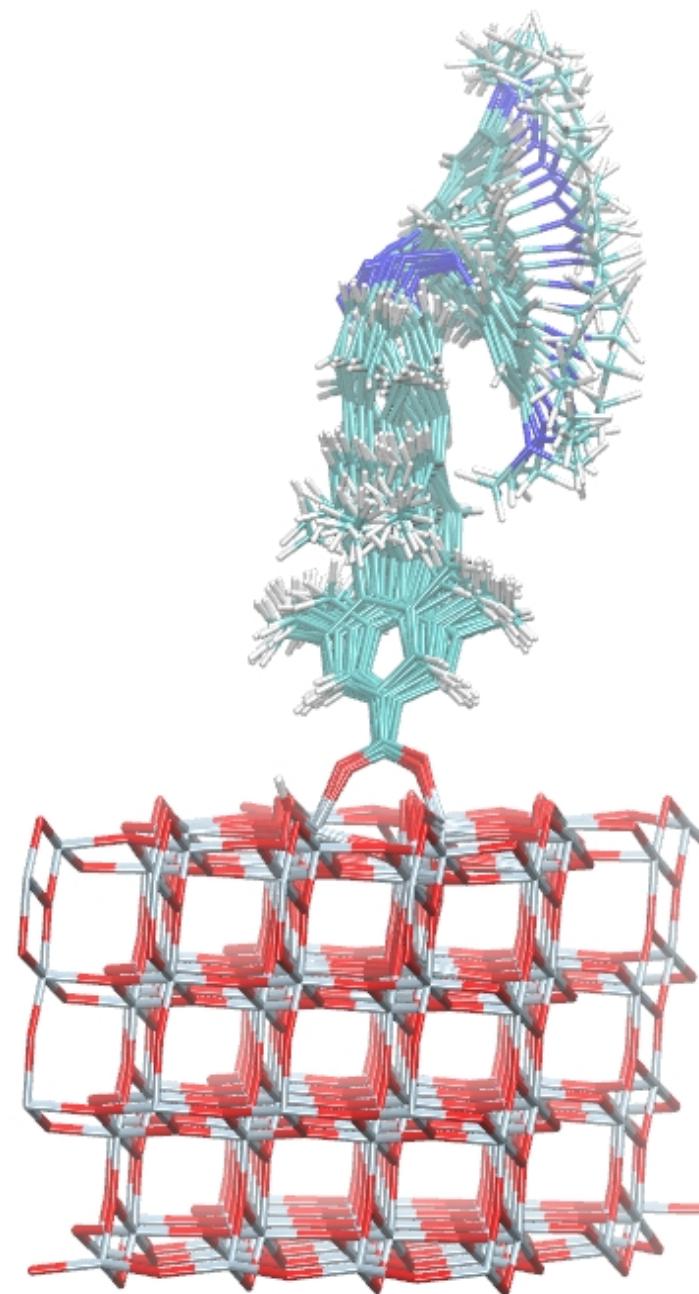
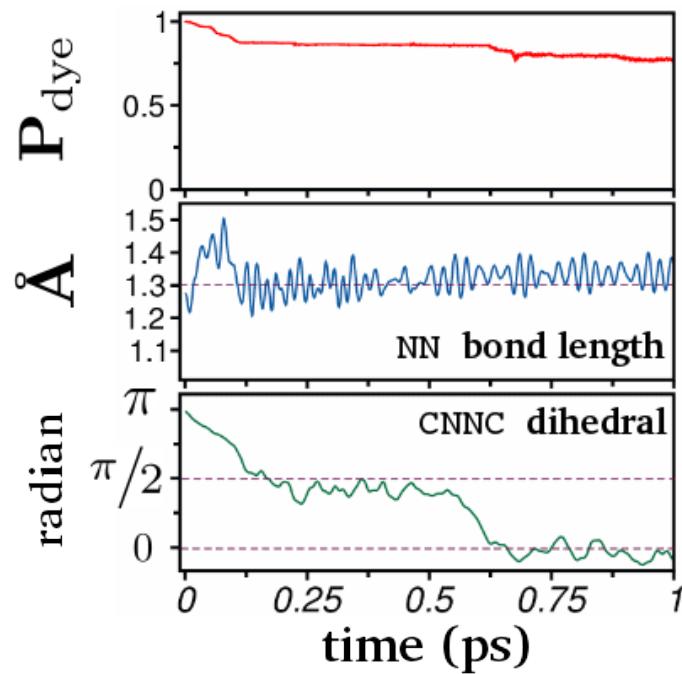


Charge Transfer *vs* Structural Relaxation



CT-3

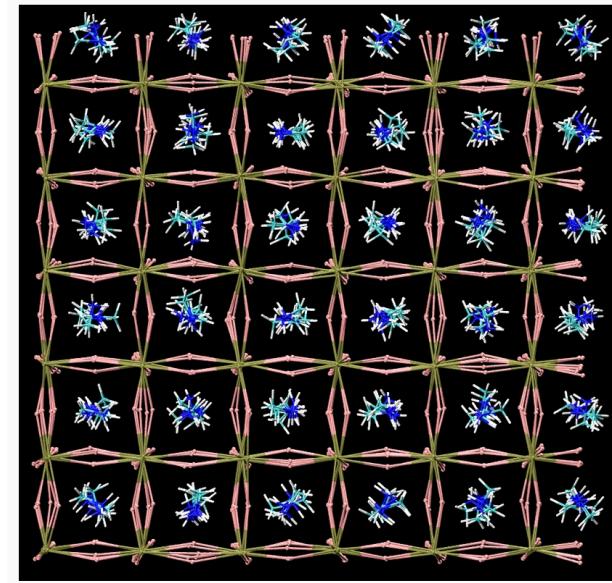
Charge Transfer *vs* Structural Relaxation



MAPbI₃ Hybrid Perovskite: Setting Up the System in card.inpt

input.pdb

6x6x6										
CRYST1	38.914	38.914	38.860	90.00	90.00	90.00	P	1	1	
ATOM	1	HP	MA+	1	5.050	4.890	2.080	1.00	0.00	H 0.0000
ATOM	2	HP	MA+	1	3.960	4.930	3.310	1.00	0.00	H 0.0000
ATOM	3	HP	MA+	1	4.990	3.660	3.170	1.00	0.00	H 0.0000
ATOM	4	N3	MA+	1	4.430	4.320	2.650	1.00	0.00	N 0.0000
ATOM	5	CT	MA+	1	3.440	3.610	1.800	1.00	0.00	C 0.0000
ATOM	6	HC	MA+	1	3.950	2.960	1.080	1.00	0.00	H 0.0000
ATOM	7	HC	MA+	1	2.770	3.000	2.410	1.00	0.00	H 0.0000
ATOM	8	HC	MA+	1	2.830	4.330	1.240	1.00	0.00	H 0.0000
ATOM	9	HP	MA+	2	5.030	4.880	8.420	1.00	0.00	H 0.0000
ATOM	10	HP	MA+	2	4.040	5.000	9.730	1.00	0.00	H 0.0000
ATOM	11	HP	MA+	2	5.140	3.780	9.630	1.00	0.00	H 0.0000
ATOM	12	N3	MA+	2	4.500	4.350	9.100	1.00	0.00	N 0.0000
ATOM	13	CT	MA+	2	3.480	3.500	8.410	1.00	0.00	C 0.0000
ATOM	14	HC	MA+	2	3.980	2.790	7.740	1.00	0.00	H 0.0000
ATOM	15	HC	MA+	2	2.910	2.930	9.150	1.00	0.00	H 0.0000
ATOM	16	HC	MA+	2	2.790	4.120	7.830	1.00	0.00	H 0.0000
ATOM	17	HP	MA+	3	5.000	4.870	14.880	1.00	0.00	H 0.0000
ATOM	18	HP	MA+	3	4.030	4.980	16.200	1.00	0.00	H 0.0000
ATOM	19	HP	MA+	3	5.100	3.740	16.080	1.00	0.00	H 0.0000
ATOM
ATOM
ATOM	1726	HC	MA+	216	36.637	35.367	33.840	1.00	0.00	H 0.0000
ATOM	1727	HC	MA+	216	35.387	35.337	35.110	1.00	0.00	H 0.0000
ATOM	1728	HC	MA+	216	35.327	36.567	33.830	1.00	0.00	H 0.0000
ATOM	1729	Pb	PBI	217	0.720	0.700	5.550	1.00	0.00	Pb 0.0000
ATOM	1730	Pb	PBI	217	0.720	0.700	12.020	1.00	0.00	Pb 0.0000
ATOM	1731	Pb	PBI	217	0.720	0.700	18.500	1.00	0.00	Pb 0.0000
ATOM	1732	I	PBI	217	0.580	0.620	2.250	1.00	0.00	I 0.0000
ATOM	1733	I	PBI	217	3.900	0.590	5.440	1.00	0.00	I 0.0000
ATOM	1734	I	PBI	217	0.640	3.870	5.470	1.00	0.00	I 0.0000
ATOM	1735	I	PBI	217	0.580	0.620	8.720	1.00	0.00	I 0.0000
ATOM	1736	I	PBI	217	3.900	0.590	11.920	1.00	0.00	I 0.0000
ATOM
ATOM
ATOM	2580	I	PBI	217	26.577	36.297	37.840	1.00	0.00	I 0.0000
ATOM	2581	Pb	PBI	217	33.157	33.127	24.980	1.00	0.00	Pb 0.0000
ATOM	2582	Pb	PBI	217	33.157	33.127	31.450	1.00	0.00	Pb 0.0000
ATOM	2583	Pb	PBI	217	33.157	33.127	37.930	1.00	0.00	Pb 0.0000
ATOM	2584	I	PBI	217	33.017	33.047	21.680	1.00	0.00	I 0.0000
ATOM	2585	I	PBI	217	36.327	33.027	24.870	1.00	0.00	I 0.0000
ATOM	2586	I	PBI	217	33.067	36.297	24.900	1.00	0.00	I 0.0000
ATOM	2587	I	PBI	217	33.017	33.047	28.150	1.00	0.00	I 0.0000
ATOM	2588	I	PBI	217	36.327	33.027	31.350	1.00	0.00	I 0.0000
ATOM	2589	I	PBI	217	33.067	36.297	31.370	1.00	0.00	I 0.0000
ATOM	2590	I	PBI	217	33.017	33.047	34.630	1.00	0.00	I 0.0000
ATOM	2591	I	PBI	217	36.327	33.027	37.820	1.00	0.00	I 0.0000
ATOM	2592	I	PBI	217	33.067	36.297	37.840	1.00	0.00	I 0.0000
MASTER	0	0	0	0	0	0	0	2592	0	2592
END										



Relevant entries:

- PBC box vectors
- MM atom types
- residue name
- residue number
- {x,y,z}

Cartesian coords in Angs.

Files:

- input.pdb
- MA+.psf
- PbI.psf
- input.prm

MAPbI₃ Hybrid Perovskite: Setting Up the System in card.inpt

Example: Classical MD of 6x6x6 MAPbI₃ Hybrid Perovskite

card.inpt

```
! ACTION flags

DRIVER      = MM_Dynamics

nuclear_matter = MDynamics
file_type      = structure
file_format    = pdb
                                         ! <== structure or trajectory
                                         ! <== xyz , pdb or vasp

PBC = [ 1 , 1 , 1 ]                                ! Periodic Boundary Conditions on {x,y,z} directions

t_f  = 10.d00
n_t  = 20000
                                         ! <== final time in PIC0oseconds

VDOS = true
                                         ! velocity-DOS is calculated on the fly

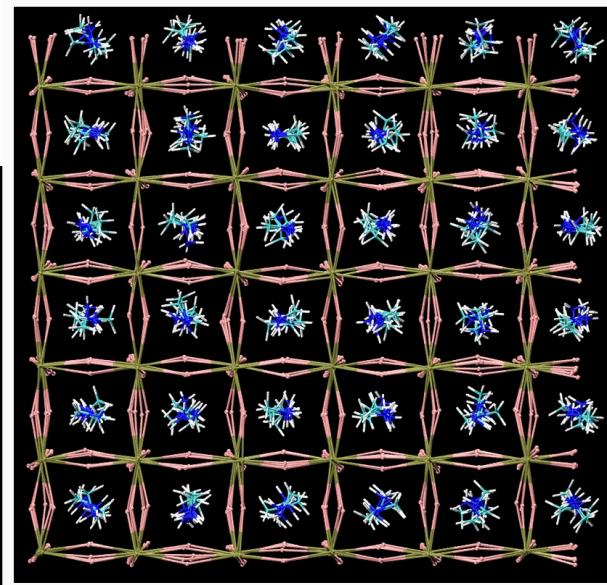
! SYSTEM INFO

N_of_molecules = 217
N_of_species   = 2
                                         ! <== total number of molecules
                                         ! <== total number of species

! repeat the following information filling for all the different species ...

species(1) % residue      = MA+       ! <== Residue label for species 1
species(1) % N_of_molecules = 216
species(1) % N_of_atoms    = 8        ! <== Number of molecules of species 1
                                         ! <== Number of atoms comprising a single molecule of species 1
species(1) % flex          = true     ! <== Flexible : true , false

species(2) % residue      = PbI       ! <== Residue label for species 2
species(2) % N_of_molecules = 1
species(2) % N_of_atoms    = 864
species(2) % flex          = true
```



Files:

- input.pdb
- MA+.psf
- PbI.psf
- input.prm

MAPbI₃ Hybrid Perovskite: Setting Up the System in card.inpt

Example: Classical MD of 6x6x6 MAPbI₃ Hybrid Perovskite

MA+.psf

```
REMARKS methylammonium cation (CH3NH3)+

8 !NATOM
 1 SYS      1       MA+      H      HP      0.540000    1.0080
 2 SYS      1       MA+      H      HP      0.540000    1.0080
 3 SYS      1       MA+      H      HP      0.540000    1.0080
 4 SYS      1       MA+      N      N3     -1.100000   14.011
 5 SYS      1       MA+      C      CT      0.771000   12.011
 6 SYS      1       MA+      H      HC      0.023000    1.0080
 7 SYS      1       MA+      H      HC      0.023000    1.0080
 8 SYS      1       MA+      H      HC      0.023000    1.0080

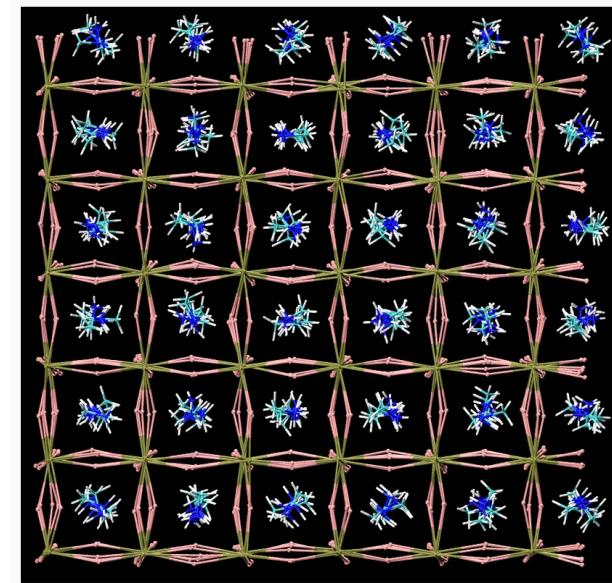
7 !NBOND: bonds
 5   6           5   7           5   8           4   1
 4   2           4   3           4   5

12 !NTHETA: angles
 7   5   8           6   5   7           6   5   8
 3   4   5           2   4   3           2   4   5
 1   4   2           1   4   3           1   4   5
 4   5   6           4   5   7           4   5   8

9 !NPHI: dihedrals
 3   4   5   6           3   4   5   7
 3   4   5   8           2   4   5   6
 2   4   5   7           2   4   5   8
 1   4   5   7           1   4   5   8
 1   4   5   6

0 !NIMPHI: impropers

0 !AD-HOC: flex
```



Files:

- input.pdb
- MA+.psf
- Pbl.psf
- input.prm

MAPbI₃ Hybrid Perovskite: Setting Up the System in card.inpt

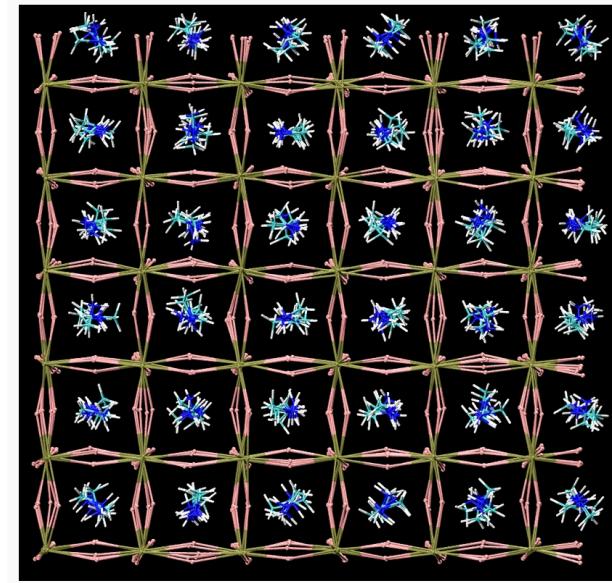
Example: Classical MD of 6x6x6 MAPbI₃ Hybrid Perovskite

PbI.psf

```
REMARKS PbI cage

 864!NATOM
 1  SYS   1      PBI    Pb    Pb    2.0300  207.20
 2  SYS   1      PBI    Pb    Pb    2.0300  207.20
 3  SYS   1      PBI    Pb    Pb    2.0300  207.20
 4  SYS   1      PBI    I     I    -1.1300  126.90
 5  SYS   1      PBI    I     I    -1.1300  126.90
 .
 .
 .
 .
 .
 .
 850 SYS   1      PBI    I     I    -1.1300  126.90
 851 SYS   1      PBI    I     I    -1.1300  126.90
 852 SYS   1      PBI    I     I    -1.1300  126.90
 853 SYS   1      PBI    Pb    Pb    2.0300  207.20
 854 SYS   1      PBI    Pb    Pb    2.0300  207.20
 855 SYS   1      PBI    Pb    Pb    2.0300  207.20
 856 SYS   1      PBI    I     I    -1.1300  126.90
 857 SYS   1      PBI    I     I    -1.1300  126.90
 858 SYS   1      PBI    I     I    -1.1300  126.90
 859 SYS   1      PBI    I     I    -1.1300  126.90
 860 SYS   1      PBI    I     I    -1.1300  126.90
 861 SYS   1      PBI    I     I    -1.1300  126.90
 862 SYS   1      PBI    I     I    -1.1300  126.90
 863 SYS   1      PBI    I     I    -1.1300  126.90
 864 SYS   1      PBI    I     I    -1.1300  126.90

 0 !NBOND: bonds
 0 !NTHETA: angles
 0 !NPHI: dihedrals
 0 !NIMPHI: impropers
 0 !AD-HOC: flex
```



Files:

- input.pdb
- MA+.psf
- PbI.psf
- input.prm

MAPbI₃ Hybrid Perovskite: Setting Up the System in card.inpt

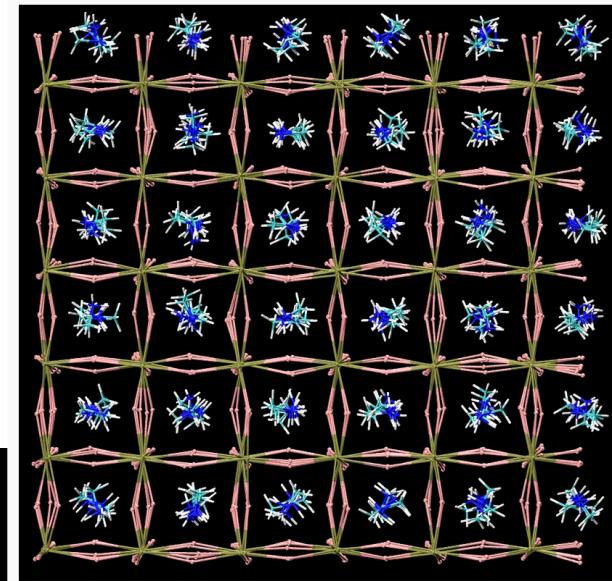
Example: Classical MD of 6x6x6
MAPbI₃ Hybrid Perovskite

card.inpt, continued.

already thermalized

Files:

- input.pdb
- MA+.psf
- PbI.psf
- input prm



```
!-----  
! ENVIRONMENT parameters ...  
  
thermostat      = Berendsen          ! <== Berendsen, Nose_Hoover, Microcanonical  
temperature       = 300.d0            ! <== Bath Temperature (K)  
thermal_relaxation_time = 3.d00        ! <== Temperature coupling term with the bath  
                                      ! <== SMALL = STRONG coupling ; use "infty" to decouple  
cutoff_radius     = 25.d0             ! <== Cut off radius (Angs.) for electrostatic and LJ interactions  
damping_Wolf      = 0.005             ! <== Wolf's method damping parameter (length^{-1});  
                                      ! (J. Chem. Phys. 1999; 110(17):8254)  
!  
! GENERAL INFO ...  
!  
driver_MM         = "MM_Dynamics"    ! <== MM_Dynamics , MM_Optimize , NormalModes , Parametrize  
read_velocities   = true              ! <== reads the initial velocities : T_ , F_  
MM_input_format   = GAFF             ! <== GMX, NAMD, GAFF  
MM_log_step        = 1                ! <== step for saving MM results & parameters  
MM_frame_step      = 25               ! <== step for saving MM results & parameters
```

MAPbI₃ Hybrid Perovskite: Setting Up the System in card.inpt

```
*>>> CHARMM Parameter file <<<
FF-sets
! comb-rule      SCNB      SCEE
    2           2.0       1.2

ATOMS
MASS   12 CT     12.01000
MASS   20 HC     1.00800
MASS   24 HP     1.00800
MASS   00 N3    14.01000

BONDS
!
!V(bond) = Kb(b - b0)**2
!Kb: kcal/mole/A**2
!b0: A
!
!atom type    Kb      b0
CT     HC     338.70  1.0910  *
CT     N3     293.60  1.4990  *
N3     HP     369.00  1.0330  *

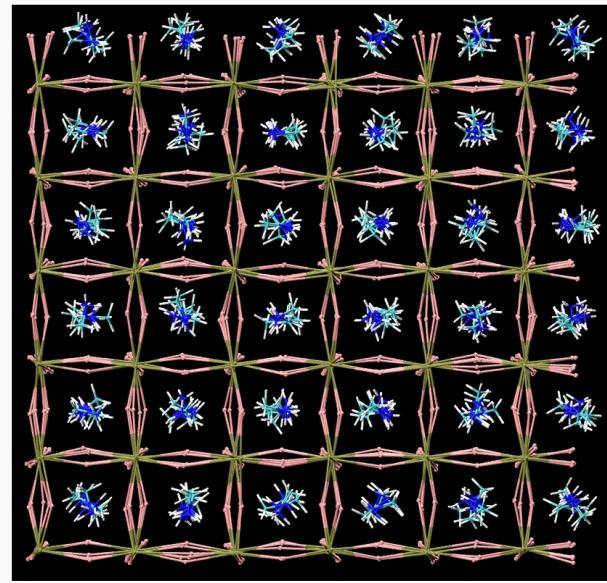
ANGLES
!
!V(angle) = Ktheta(Theta - Theta0)**2
!Ktheta: kcal/mole/rad**2
!Theta0: degrees
!Kub: kcal/mole/A**2 (Urey-Bradley)
!
!atom types      Ktheta   Theta0   Kub   S0
HC     CT     HC     39.00  110.74  *
HP     N3     CT     46.20  110.11  *
HP     N3     HP     40.50  108.11  *
N3     CT     HC     49.00  107.91  *

DIHEDRALS
!
!V(dihedral) = Kchi(1 + cos(n(chi) - delta))
!Kchi: kcal/mole
!n: multiplicity
!delta: degrees
!
!atom types          Kchi   n     phase
X     N3     CT     X     0.1556  3     0.00  *
                                         *
```

⇐ input.prm

Intra-molecular
Bonding FF parameters

Relevant entries highlighted



Example: Classical MD of 6x6x6 MAPbI₃ Hybrid Perovskite

Files:

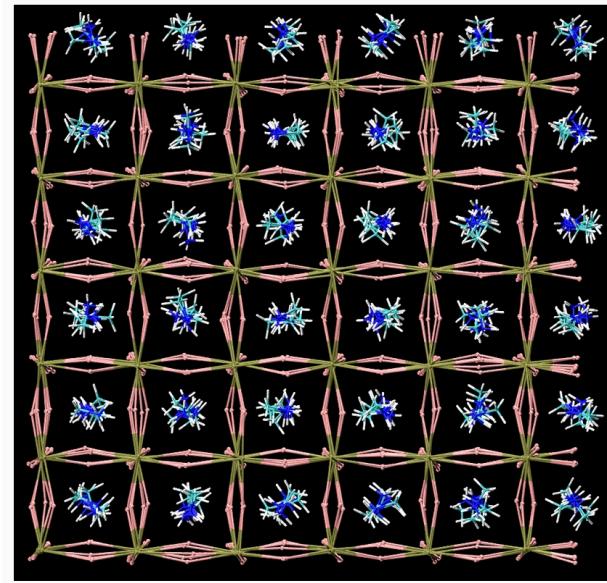
- input.pdb
- MA+.psf
- Pbl.psf
- input.prm

MAPbI₃ Hybrid Perovskite: Setting Up the System in card.inpt

NONBONDED

```
!
!V(Lennard-Jones) = Eps,i,j[(Rmin,i,j/ri,j)**12 - 2(Rmin,i,j/ri,j)**6]
!epsilon: kcal/mole, Eps,i,j = sqrt(eps,i * eps,j)
!Rmin/2: A, Rmin,i,j = Rmin/2,i + Rmin/2,j
!
!atom    type      epsilon      Rmin/2      eps,1-4      Rmin/2,1-4
CT      LJ       -0.109400     1.908000    -0.054700     1.908000
HC      LJ       -0.015700     1.100000    -0.007850     1.100000
N3      LJ       -0.170000     1.824000    -0.085000     1.842000
HP      LJ       -0.015700     0.600000    -0.007850     0.600000
!
!V(Buckingham) = A*exp(-rij/B) - C/rij**6
!A: kcal/mole, Aij = sqrt(Ai * Aj)
!B^-1: Angstrom, 1/Bij = (1/Bi + 1/Bj)/2
!C: kcal/mole, Cij = sqrt(Ci * Cj)
!
!atom    type      A          B          C
Pb      buck   70359906.63  0.131258  0.0000
I       buck   22793.3385   0.482217  696.949542
```

⇐ input.prm
(continued)



SPECIALPAIRS

```
!
!V(Lennard-Jones) = Eps,i,j[(Rmin,i,j/ri,j)**12 - 2(Rmin,i,j/ri,j)**6]
!epsilon: kcal/mole, Eps,i,j = sqrt(eps,i * eps,j)
!Rmin/2: A, Rmin,i,j = Rmin/2,i + Rmin/2,j
!
!atom1 atom2    type      epsilon      Rmin/2      eps,1-4      Rmin/2,1-4
Pb      HP      LJ       -0.014000     1.27093    -0.007000     1.27093
Pb      HC      LJ       -0.014000     1.52088    -0.007000     1.52088
I       HP      LJ       -0.057400     1.54338    -0.028700     1.54338
I       HC      LJ       -0.057400     1.73982    -0.028700     1.73982
!
!V(Buckingham) = A*exp(-rij/B) - C/rij**6
!A: kcal/mole, Aij = sqrt(Ai * Aj)
!B: Angstrom, 1/Bij = (1/Bi + 1/Bj)/2
!C: kcal/mole, Cij = sqrt(Ci * Cj)
!
!atom1 atmo2    type      A          B          C
Pb      Pb      buck   70359906.63  0.131258  0.0000
I       I       buck   22793.3385   0.482217  696.949542
Pb      I       buck   103496.1330   0.321737  0.000000
Pb      N3     buck   32690390.93   0.150947  0.000000
Pb      CT      buck   32690390.93   0.150947  0.000000
I       N3     buck   112936.7142   0.342426  0.000000
I       CT      buck   112936.7142   0.342426  0.000000
```

Non-Bonding FF parameters

Relevant entries highlighted

Files:

- input.pdb
- MA+.psf
- Pbl.psf
- input.prm

Density of Vibrational states (VDOS)

velocity power spectrum (**VelPS.dat**) for stationary state:

$$\sum_i^N |\mathbf{v}_i(\omega)|^2 = \sum_i^N \int_{-\infty}^{\infty} \left(\int_{-\infty}^{\infty} \mathbf{v}_i(t + \tau) \cdot \mathbf{v}_i(\tau) d\tau \right) e^{i\omega t} dt$$

$$\text{VelPS}(\omega) \equiv \sum_i^N |\mathbf{v}_i(\omega)|^2 = \sum_i^N \int_{-\infty}^{\infty} \langle \mathbf{v}_i(\tau + t) \cdot \mathbf{v}_i(t) \rangle_{\tau} e^{i\omega t} dt$$

Vibrational Density of States (**VDOS.dat**):

$$VACF_{mw}(t) = \frac{\sum_i m_i \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle}{\sum_i m_i \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle} = \frac{\sum_i m_i \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle}{3Nk_B T}$$

$$\dot{\mathbf{r}}_k(t) = \mathbf{v}_k = \sum_s^{modes} \mathbf{Q}_{sk}(-i\omega_s) e^{-i\omega_s t} \quad \xrightarrow{\text{thermal equil. + eqiupartition}} \quad m_k |\mathbf{Q}_{sk}|^2 \omega_s^2 = 3k_B T$$

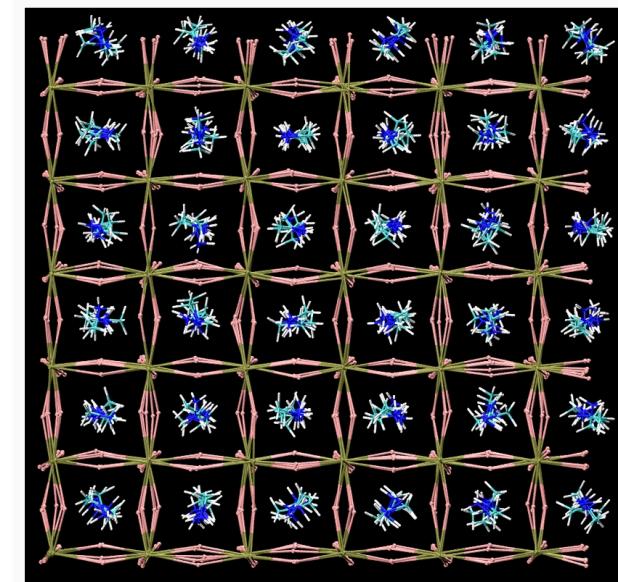
$$\sum_i^N m_i |\mathbf{v}_i(\omega)|^2 = \sum_s \sum_{k=1}^N \int_{-\infty}^{\infty} m_k |\mathbf{Q}_{sk}|^2 \omega_s^2 e^{i(\omega + \omega_s)t} dt = 3Nk_B T \sum_s \delta(\omega + \omega_s)$$

$$\begin{aligned} \text{VDOS}(\omega) \equiv \rho(\omega) &= \sum_s \delta(\omega + \omega_s) \\ &= \frac{\sum_i^N m_i |\mathbf{v}_i(\omega)|^2}{3Nk_B T} = \frac{1}{3Nk_B T} \int_0^{\infty} \sum_i^N m_i \langle \mathbf{v}_i(\tau + t) \cdot \mathbf{v}_i(t) \rangle_{\tau} e^{i\omega t} dt \end{aligned}$$

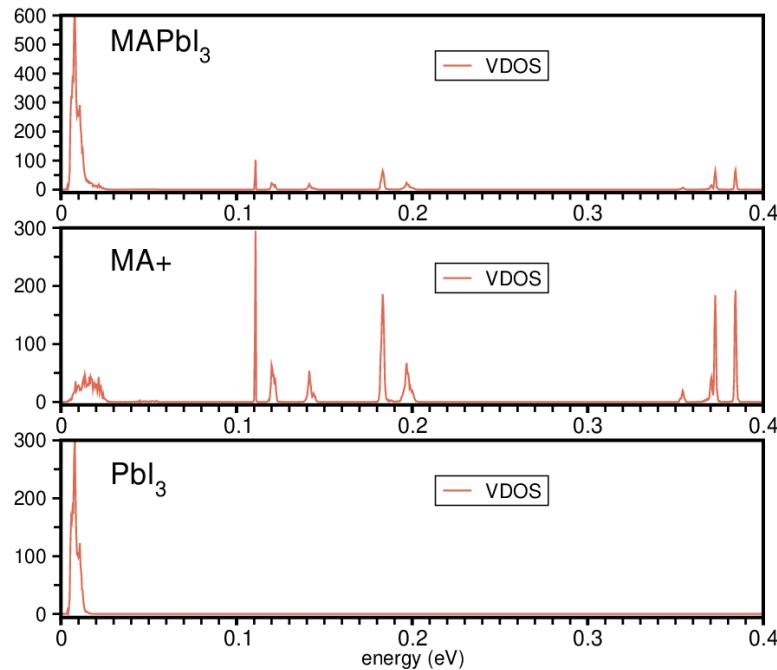
Density of Vibrational states (VDOS)

card.inpt

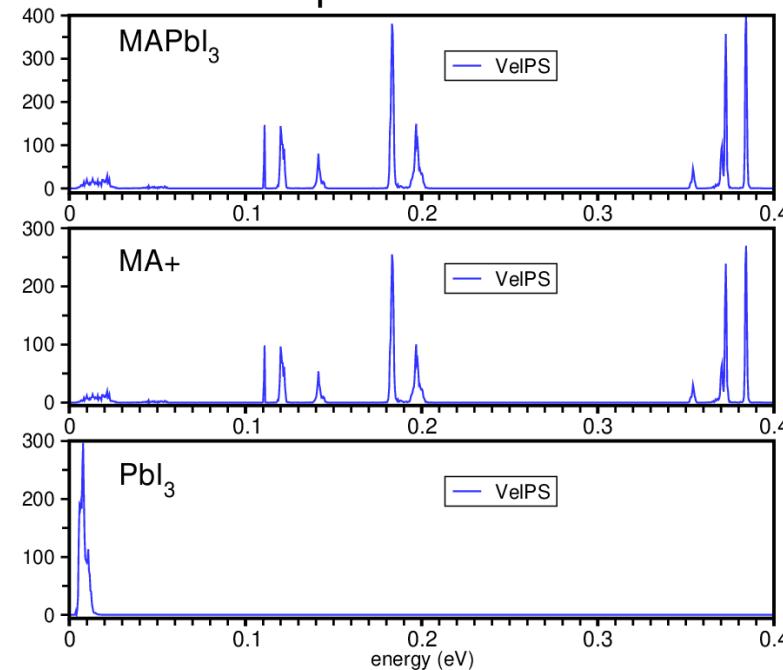
```
!-----  
! ACTION      flags  
  
DRIVER        = MM_Dynamics  
  
nuclear_matter = MDynamics  
file_type      = structure  
file_format    = pdb  
  
PBC = [ 1 , 1 , 1 ]  
          ! <= structure or trajectory  
          ! <= xyz , pdb or vasp  
  
t_f  = 10.d00  
          ! Periodic Boundary Conditions on {x,y,z} directions  
n_t  = 20000  
          ! <= final time in PIC0oseconds  
  
VDOS = true  
          ! velocity-DOS is calculated on the fly
```



Vibrational DoS



Power Spectrum of velocities



Running Dynemol

Setup of environment variables:

```
export DYNEMOLDIR= "path to dynemol executable directory"
```

```
export DYNEMOLWORKDIR= $(pwd)
```

Must have in work-directory \$DYNEMOLWORKDIR:

- the appropriate input files for the job
- file with execution directions: *card.inpt*
- Execution script (e.g., run-SN.sh, for Single-Node execution)

Running Dynemol

In directory \$DYNEMOLWORKDIR:

- the execution script run-SN.sh (basic model of script)

```
#!/bin/bash

#####
#Script Name    : run-SN.sh
#Description   : execute Dynemol from pwd using local dynemol src files
#Args          : none
#Author        : Luis G C Rego
#####
#!/bin/bash

export DYNEMOLWORKDIR=$(pwd)
export DYNEMOLDIR=/home/lrego/QMMM/development/dynemol-dir

$DYNEMOLDIR/dynemol
```

- On the terminal run
> ./run-SN.sh

Running Dynemol

In directory \$DYNEMOLWORKDIR:

- Outputs , results , log-files , security-files , etc. are stored in:
 - \$DYNEMOLWORKDIR/ancillary.trunk/
 - \$DYNEMOLWORKDIR/dos.trunk/
 - \$DYNEMOLWORKDIR/dyn.trunk/
 - \$DYNEMOLWORKDIR/log.trunk/
 - \$DYNEMOLWORKDIR/MO.trunk/
 - \$DYNEMOLWORKDIR/opt.trunk/
- *which are deleted and made anew at every execution.*
- *each directory gets a copy of card.inpt for future reference.*

Acknowledgements

Have contributed to the DynEMol Project:

- Robson O. Silva
- Alberto Torres
- Diego Hoff
- Grazielle Bertolini
- João V. Meyer

