DynEMol code
Dynamics of Electrons in Molecules

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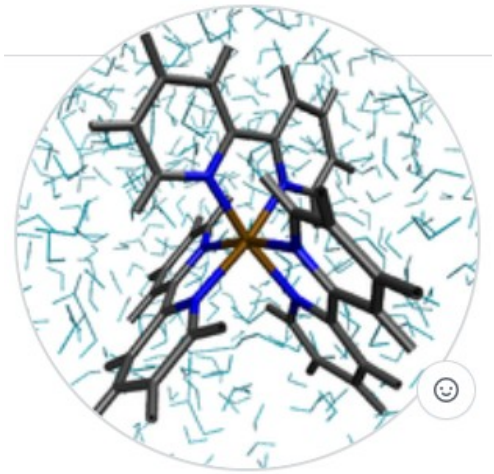
Dynemol: general information

github.com/lgcrego/Dynemol



DynEMol: Dynamics of Electrons in Molecules

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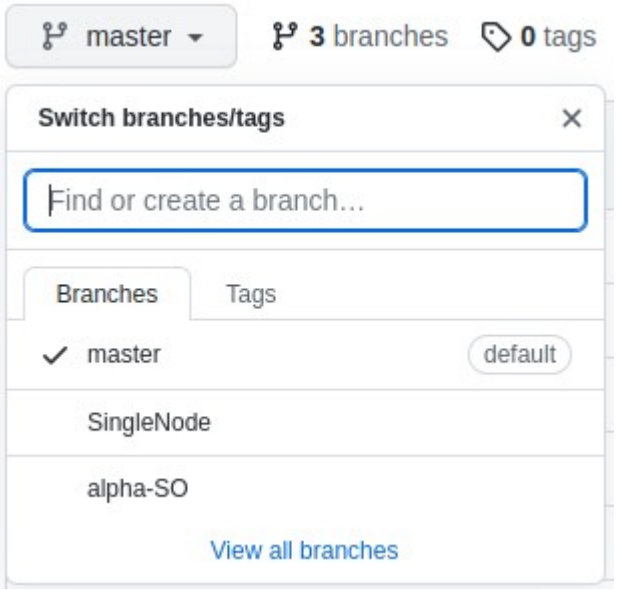


Languages

Fortran 92.6% **C++** 4.6%

Cuda 1.8% **C** 0.3%

Makefile 0.3% **Forth** 0.2%

Shell 0.2%

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:

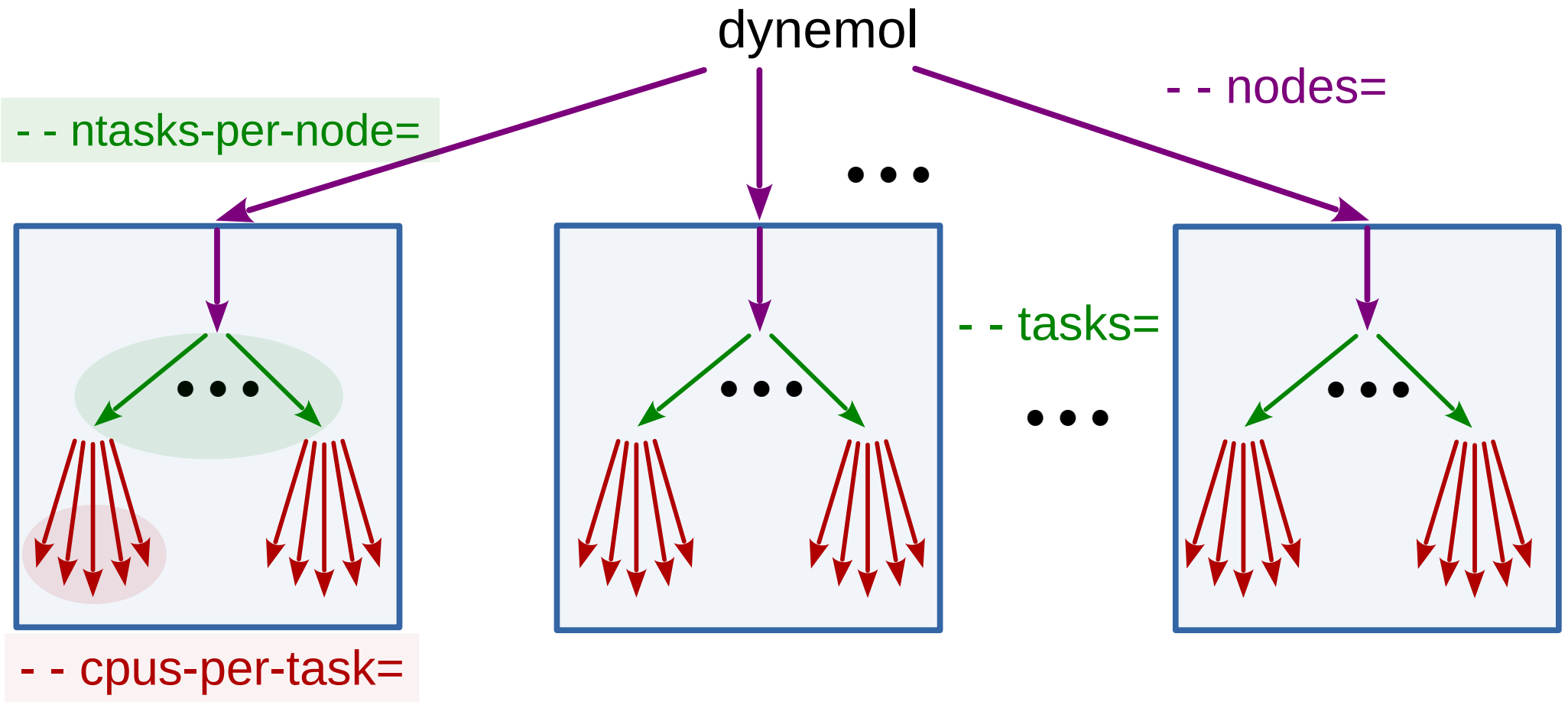
export DYNEMOLDIR= “path to dynemol executable directory”

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_confgs , Genetic_Alg , diagnostic , slice_{Cheb, AO, FSSH, CSDM} , MM_Dynamics

 Survival       =          ! <== .TRUE. for any dynamics simulation
 DP_Moment      =          ! <== .TRUE. or .FALSE. ; dipole moment fragment must be especified ad-hoc
 QMMM           =          ! <== .TRUE. for Non-Adabatic 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 vasp ; 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 = MO of frag/res

                            ! <== GROUND STATE calcs     = 0 (ZERO)
                            ! <== case STATIC & DP_calcs = hole state of special FMO
                            ! <== case DYNAMIC           = intial MO for < HOLE > wavepacket in DONOR fragment

  electron_state = char*3:Integer    ! <== char*3 = 3-letter fragment or residue ; Integer = MO of frag/res

                            ! <== case STATIC & DP_calcs = excited state of special FMO
                            ! <== case DYNAMIC           = intial MO 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&Hl survival charge density  (Integer); default = 1

  frame_step    =           ! <== step for avrg_confgs 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:

```
!-------------------------------------------------------------------
!           DIAGNOSTIC & DATA-ANALYSIS & VISUALIZATION flags
!
  HFP_Forces         =        ! <== .TRUE._for QMMM calcs and .FALSE. otherwise; Hellman-Feynman-Pulay forces

  SPECTRUM           =        ! <== .TRUE. for absorption spectrum calculations
  Alpha_Tensor       =        ! <== .TRUE. for polarizability calcs; Embeded Finite Field Polarizability

  GaussianCube       =        ! <== .TRUE. for generating cube files for MO visualization
  GaussianCube_step  =        ! <== time step for saving Gaussian Cube files (Integer)

  NetCharge          =        ! <== .TRUE. for dumping charge Occupancy in pdb format
  CH_and_DP_step     =        ! <== time step for saving charge and Induced DP values (Integer)
                              ! <== pdb format: charge --> Occupancy ; DP --> next to occupancy

  DensityMatrix      =        ! <== .TRUE. for generating data for postprocessing with manipulate program
  AutoCorrelation    =        ! <== .TRUE. for generating data for postprocessing with manipulate program
  VDOS_              =        ! <== .TRUE. velocity DOS data for postprocessing with manipulate program
!-------------------------------------------------------------------
!           POTENTIALS
!
  EnvField_     =             ! <== .TRUE. for using electrostaic Potential produced by Environment ; default = .FALSE.
  Environ_Type =              ! <== choose from { Ch_MM , DP_QM , DP_MM };
                              ! <== Ch_MM = point charges ; dipoles: { DP_QM , DP_MM } ...
                              ! <== DP_MM = dipole moment from classical point charges
                              ! <== DP_QM = dipole moment from quantum MO

  Environ_step =              ! <== step for updating EnvField (Integer) ; default = 5

  Coulomb_      =             ! <== .TRUE. for dipole potential for solvent molecules ; default = .FALSE.

  Induced_      =             ! <== .TRUE. for induced dipole potential
```

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 tunning! (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 comprosing 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 comprosing 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 comprosing 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
  .                                                 ! <== 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:

- 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.*

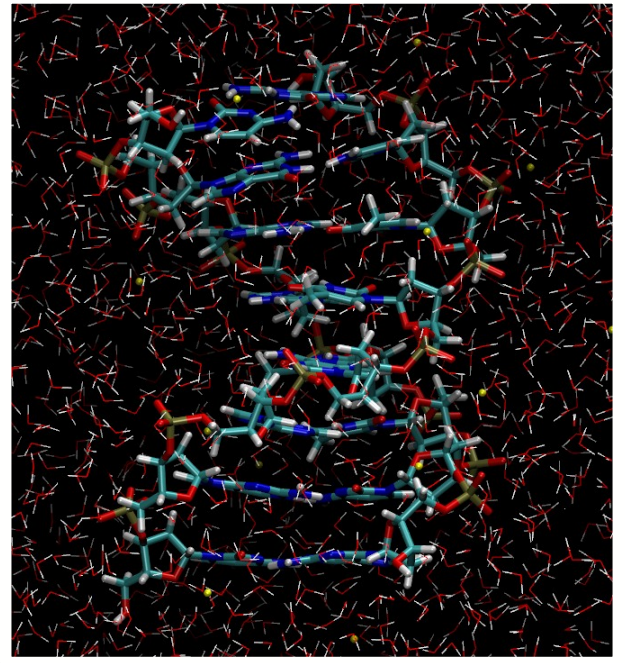
Setting Up the System in card.inpt

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 comprosing 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

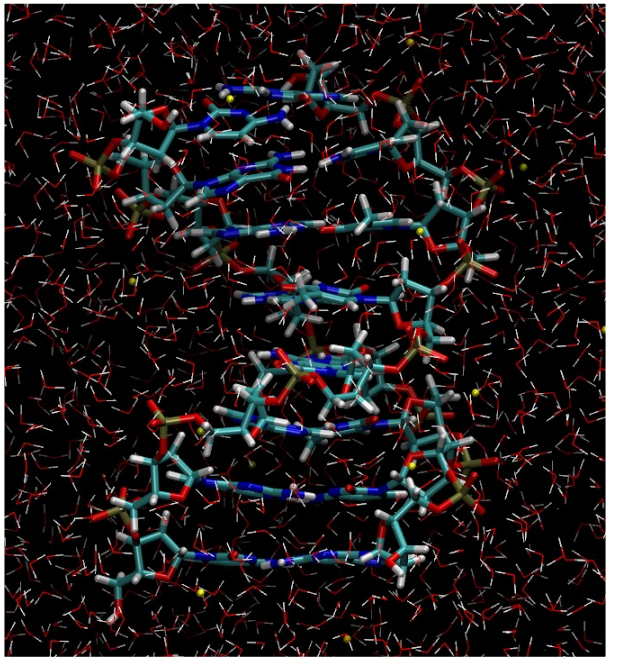
Example: DNA strand in water + counter ions

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 !NPHI: dihedrals

     0 !NIMPHI: impropers

     0 !NDON: donors

     0 !NACC: acceptors

     0 !NNB
```

Files:

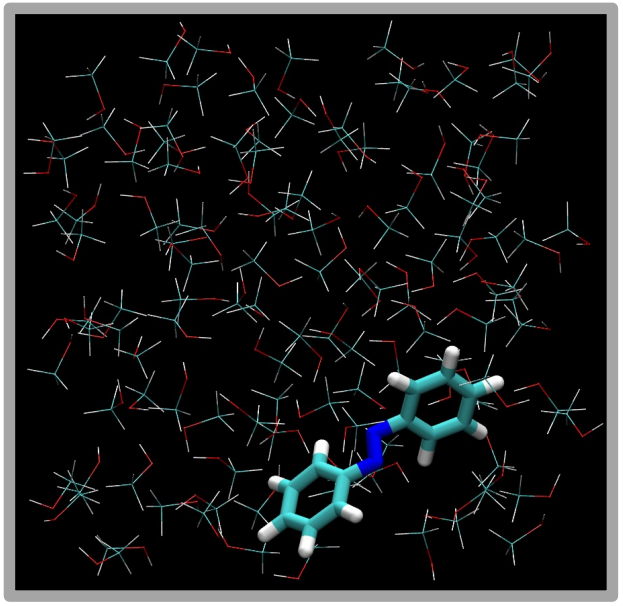
- input.pdb
- DNA.psf
- Na+.psf
- H2O.psf
- input.prm



Photochemistry in Solution

Example: Azobenzene Molecule in Ethanol

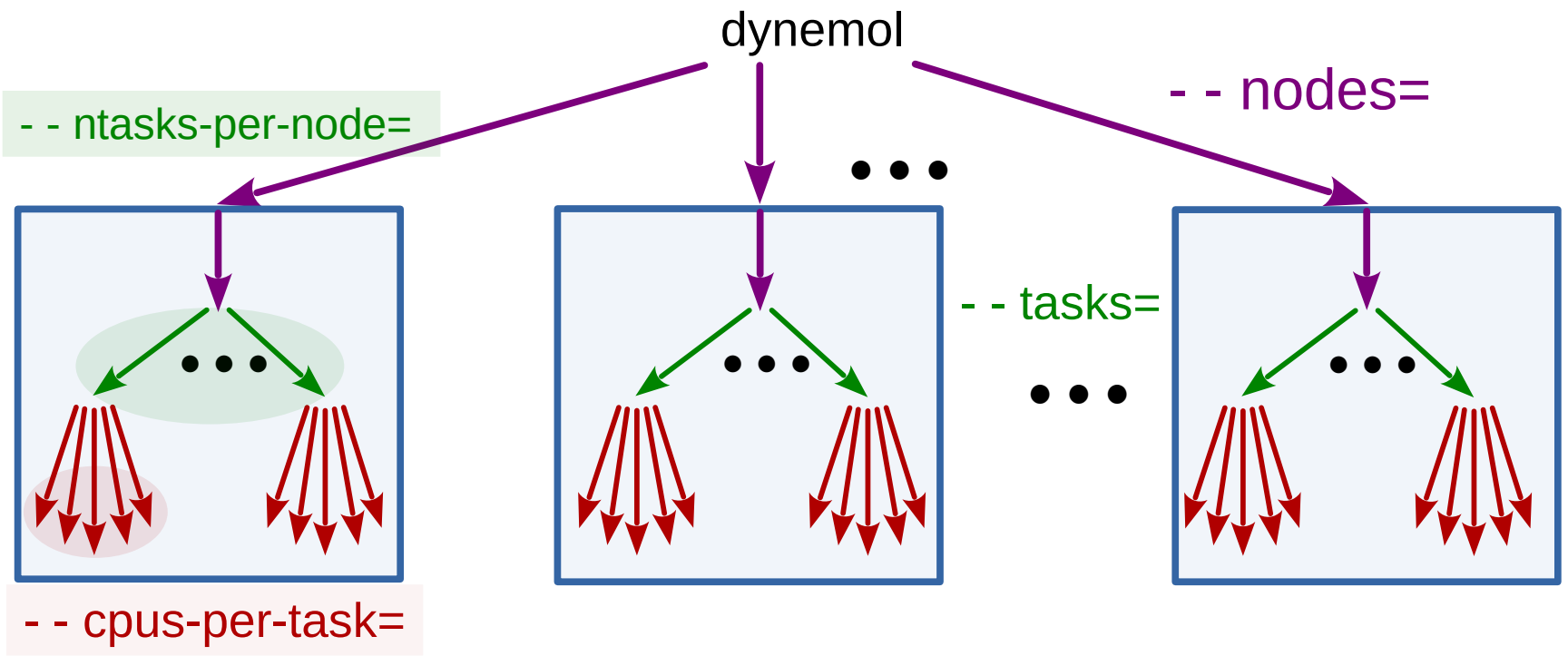
```
!--------------------------------------------------------------------
!                          ACTION flags
  DRIVER = slice_AO

  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

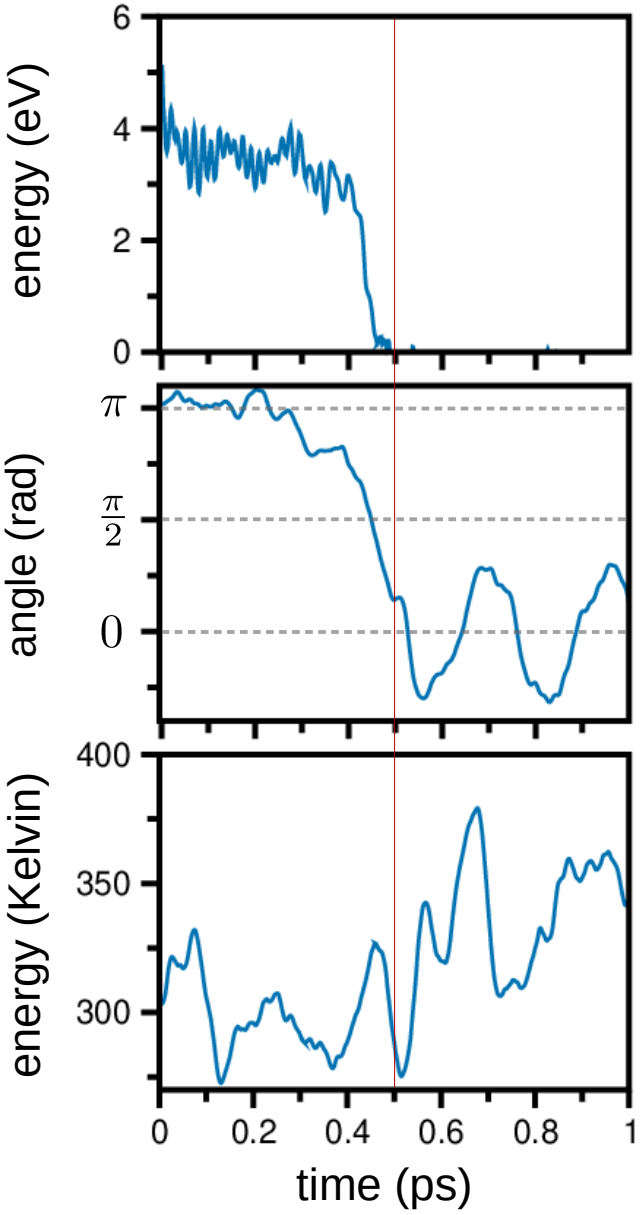
Photochemistry in Solution

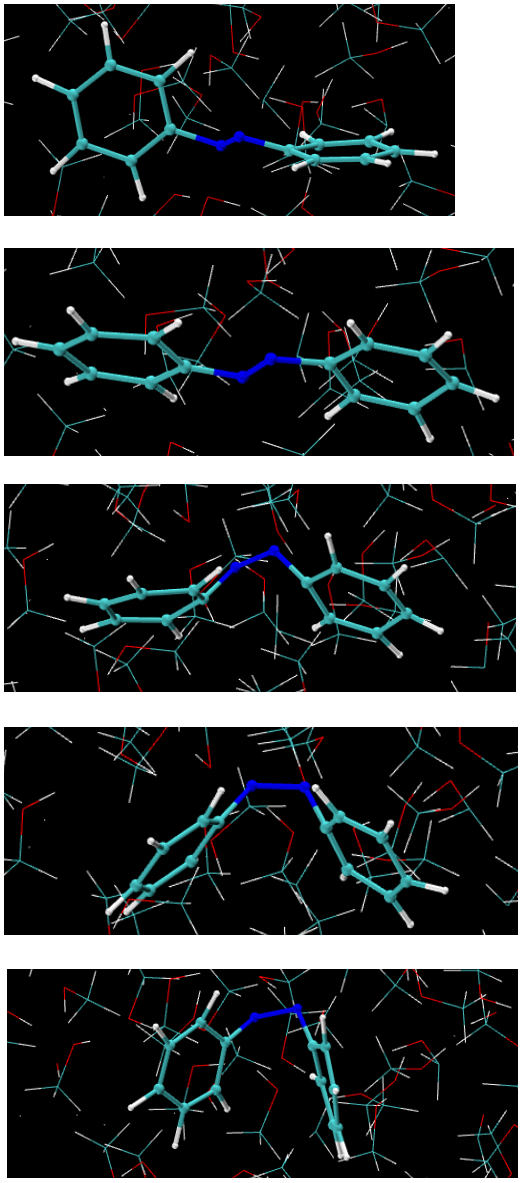
Example: Azobenzene Molecule in Ethanol

El-Hl excitation energy

CNNC dihedral angle

AZO+EtOH $E_{kinetic}$



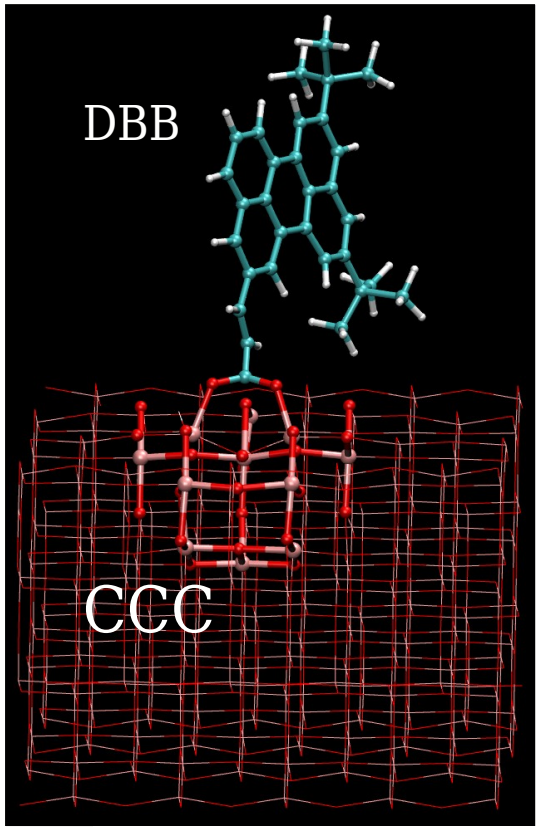


J. Phys. Chem. C 2016, 120, 27688
J. Phys. Chem. C 2011, 115

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 comprosing 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:

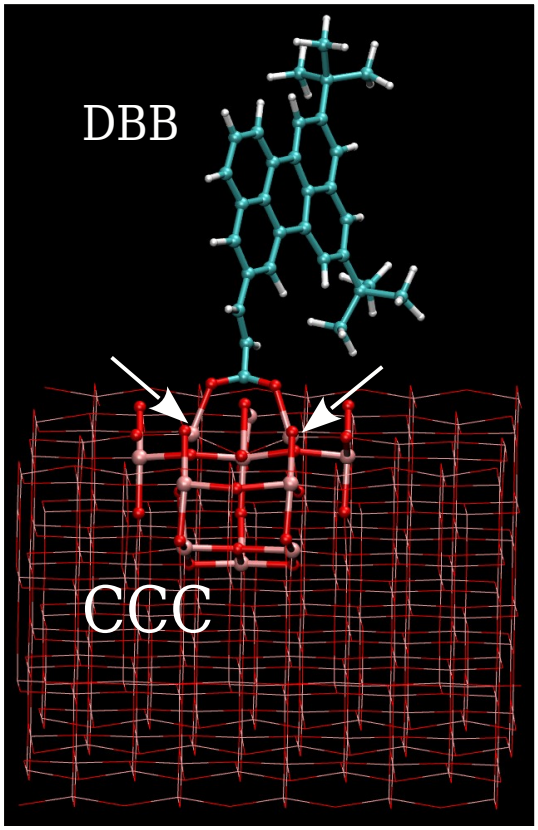
- input.pdb
- DBB.psf
- CCC.psf
- input.prm

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:

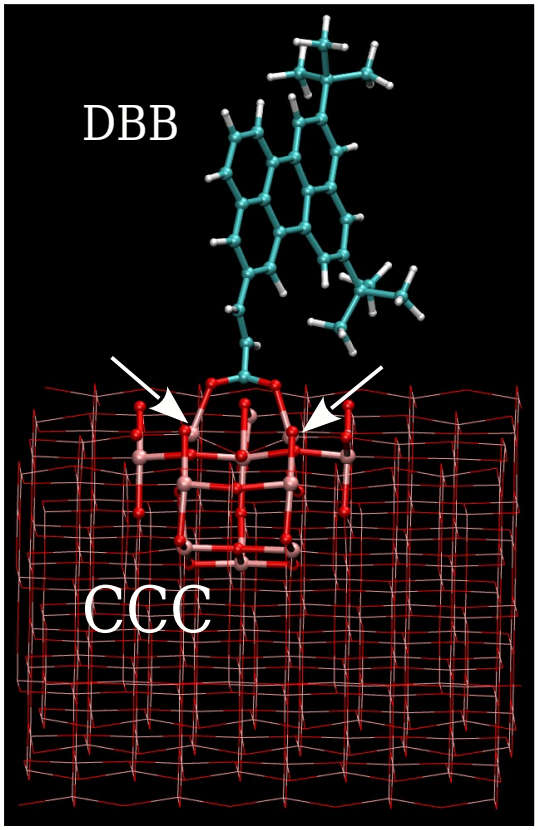
- input.pdb
- DBB.psf
- CCC.psf
- input.prm

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:

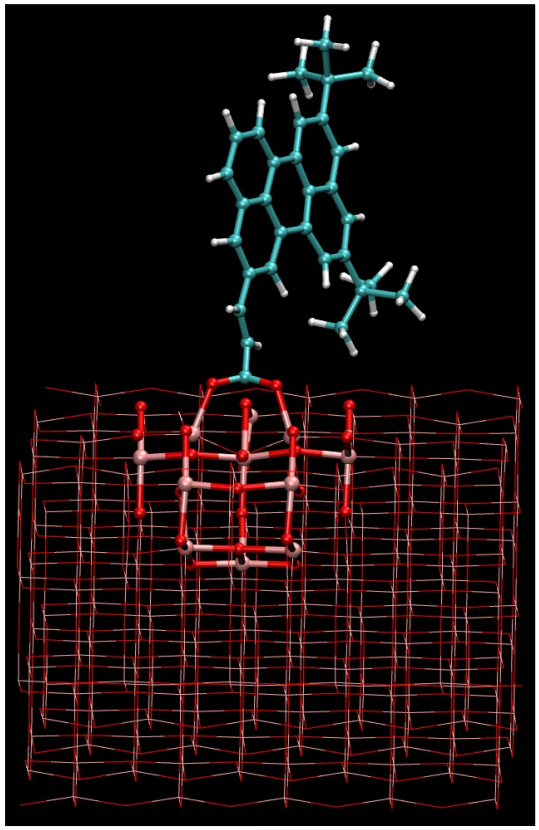
- input.pdb
- DBB.psf
- CCC.psf
- input.prm

Setting Up the System in card.inpt

Example: Dye-sensitized semiconductor

Files:

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



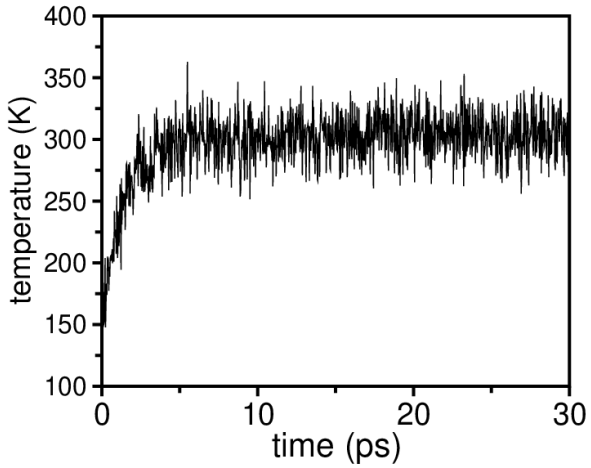
```
!-------------------------------------------------------------------------
!                              ENVIRONMENT parameters ...
!
 thermostat              = Microcanonical   ! <== Berendsen, Nose_Hoover, Microcanonical

 temperature             = 300.d0           ! <== Bath Temperature (K)

 thermal_relaxation_time = 5.d-1            ! <== Temperature coupling term with the bath
                                            ! <== SMALL = STRONG ; use "= infty" 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
```

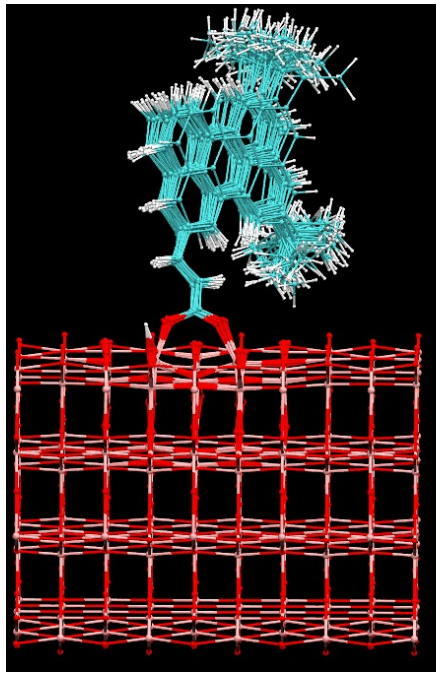
Thermalization

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 "= infty" 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_
```

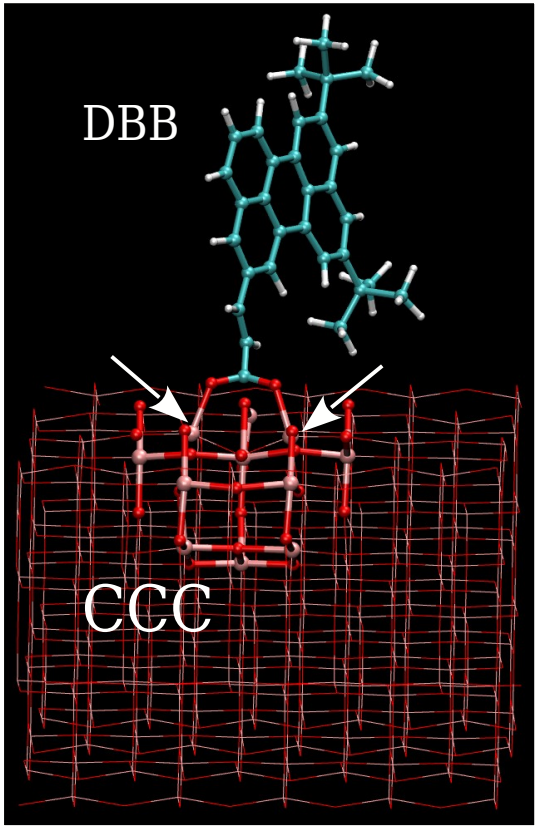
> mv velocity_MM.out velocity_MM.inpt
> $DYNEMOLDIR/dynemol resume

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

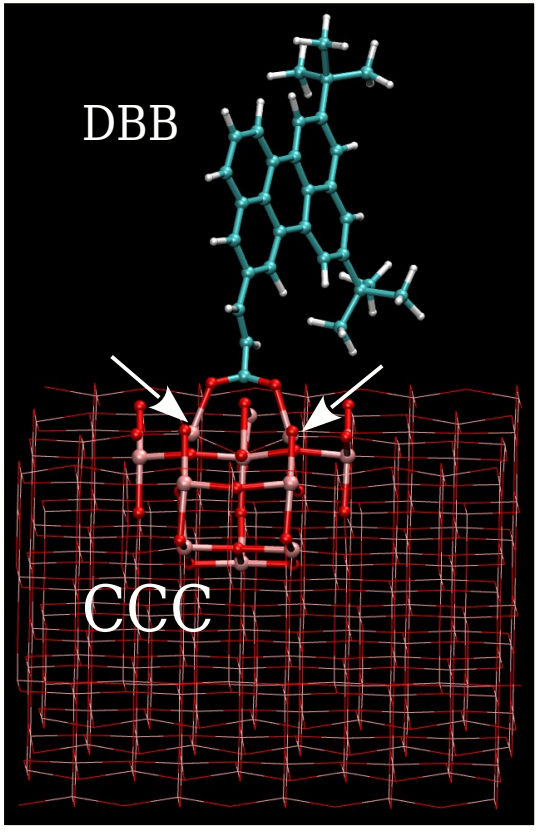
```
!-------------------------------------------------------------------
!                            ACTION   flags
!
  DRIVER = q_dynamics

  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 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 )
```



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

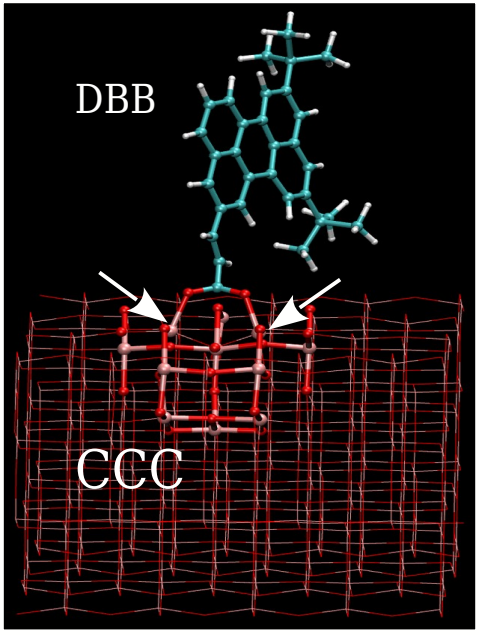



```
!-------------------------------------------------------------------
!                            ACTION   flags
!
  DRIVER = q_dynamics

  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 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 )
```

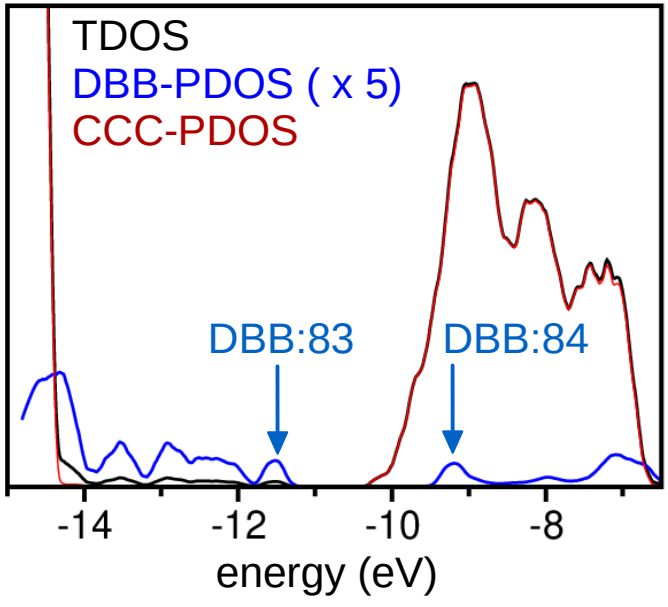
Interfacial Electron Transfer

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 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 )
```

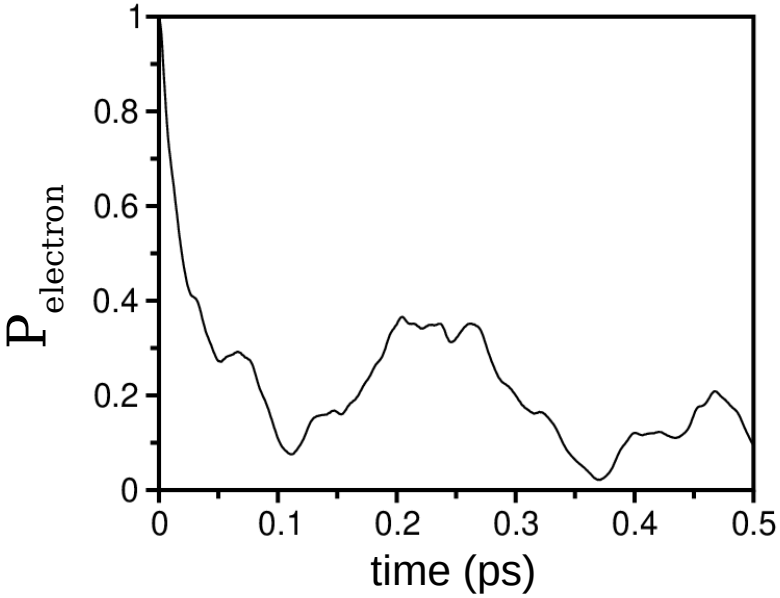


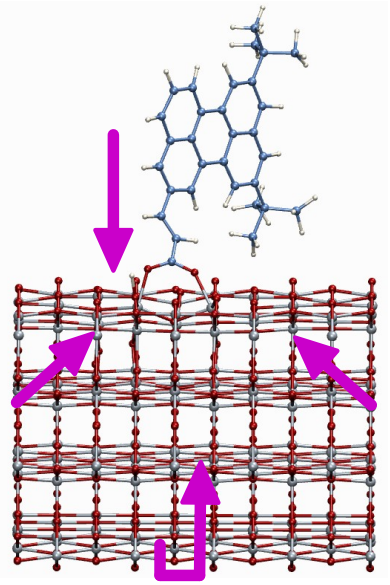
Interfacial Electron Transfer

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

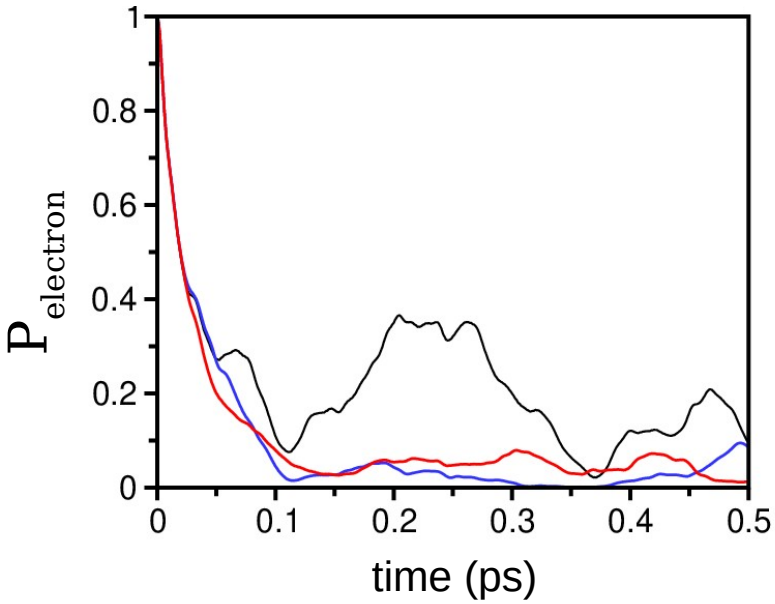
Finite-Size Spurious Artifacts

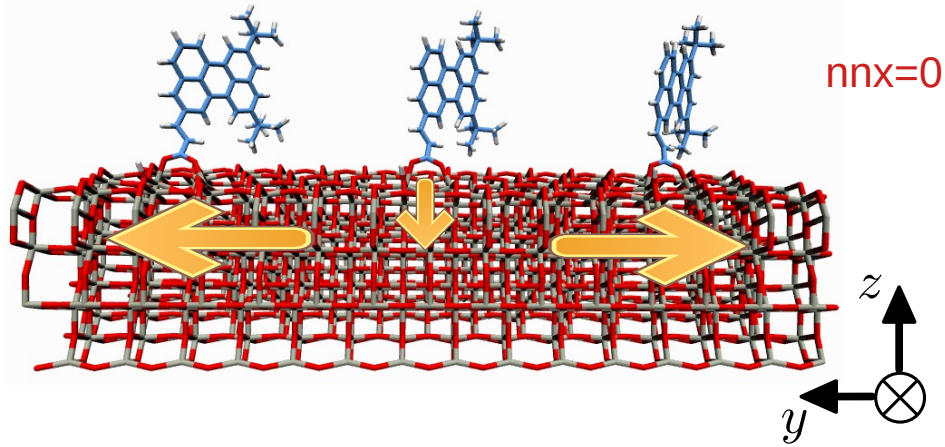
```
!-------------------------------------------------------------------
!                              ACTION   flags
!
  DRIVER = q_dynamics

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

  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=0

Nnx=1;nny=0

Nnx=0;nny=1



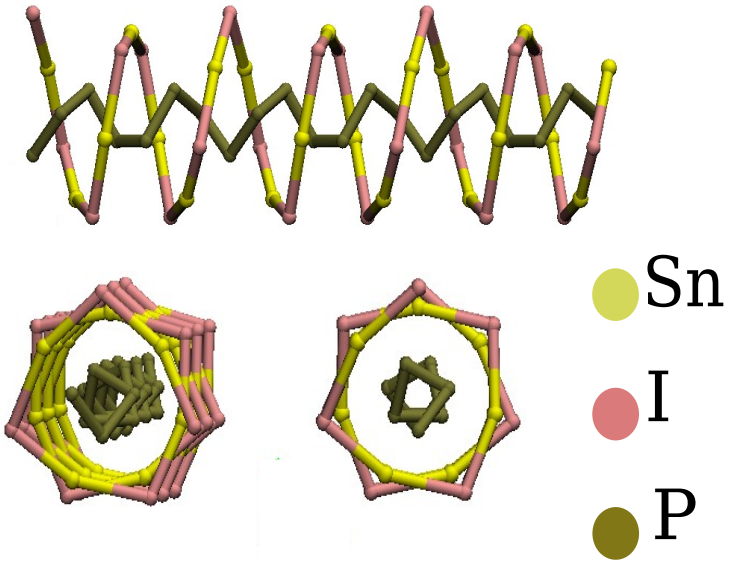


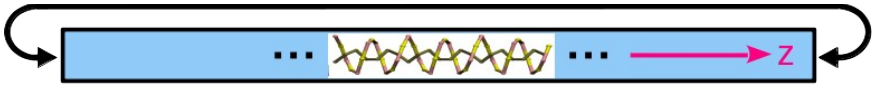
nnx=0,nny=1

Notice: not cost-effective

Electron Propagation in Chiral nanowire

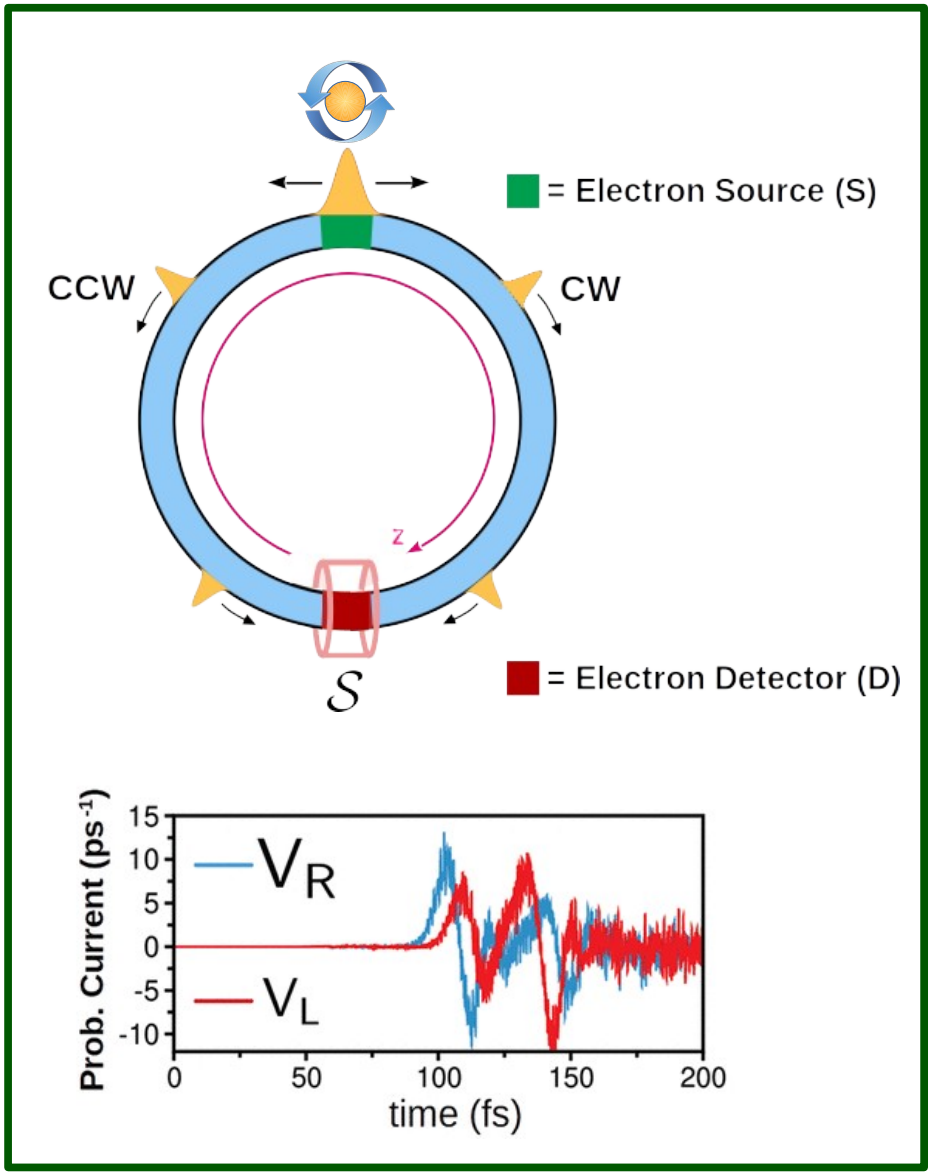
Inorganic Double Helices in Semiconducting SnIP





nnz = N_{cell}

PBC = [0 , 0 , 1]



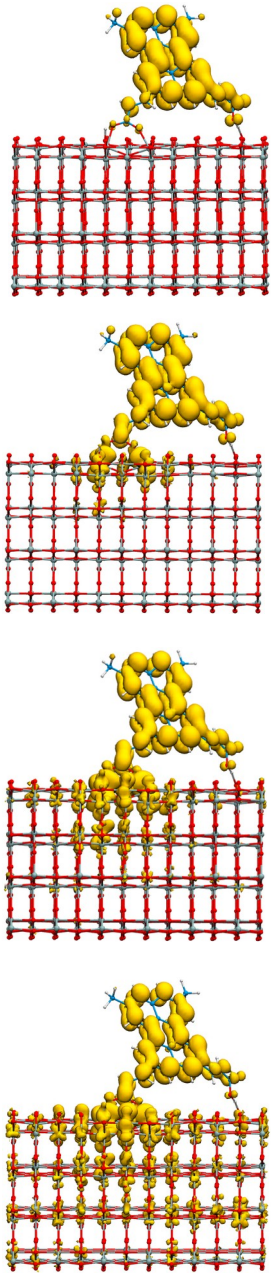
"Chirality-Induced Propagation Velocity Asymmetry", Nano Lett., 2021.

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
```



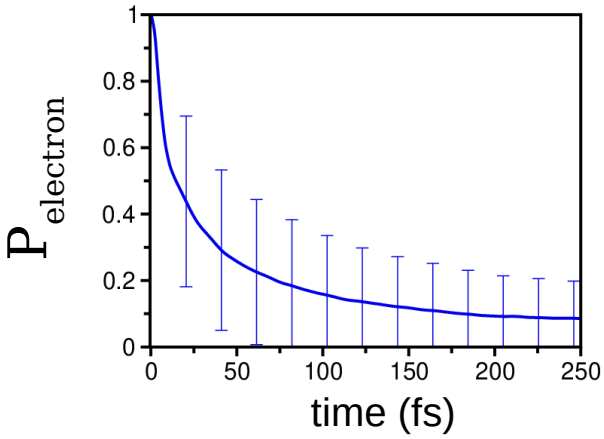
J. Phys. Chem. C 2021, 125, 8667

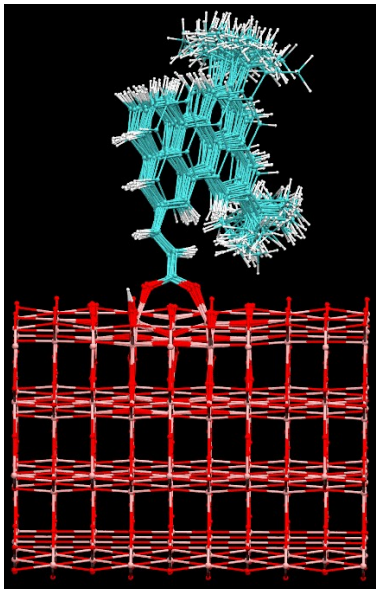
Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Average over conformations

```
!-------------------------------------------------------------------
!                              ACTION   flags
 DRIVER = avrg_confgs

 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_confgs ;
                                        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:

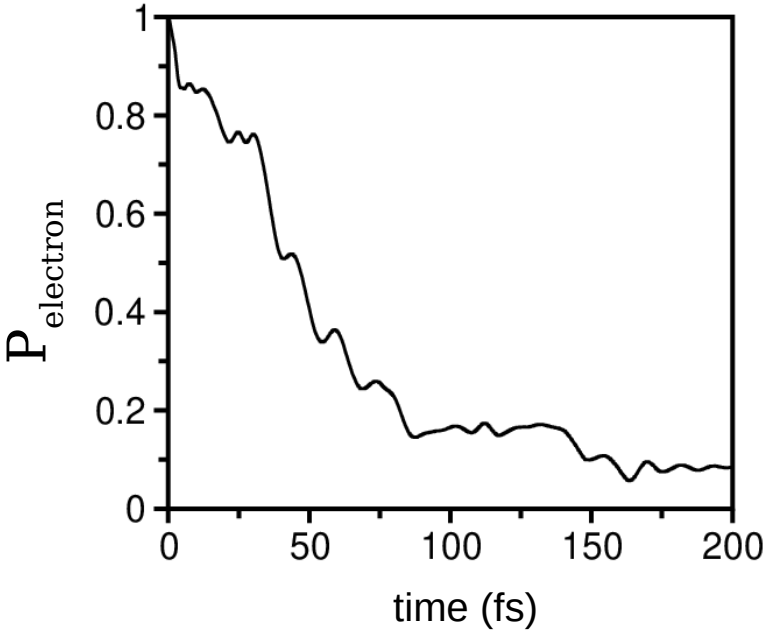
- frames.pdb

Interfacial Electron Transfer

Example: Dye-sensitized semiconductor

Non-adiabatic Electron Transfer Dynamics

```
!-------------------------------------------------------------------
!                        ACTION   flags
  DRIVER       = slice_AO              ! <== Ehrenfest QMMM

  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

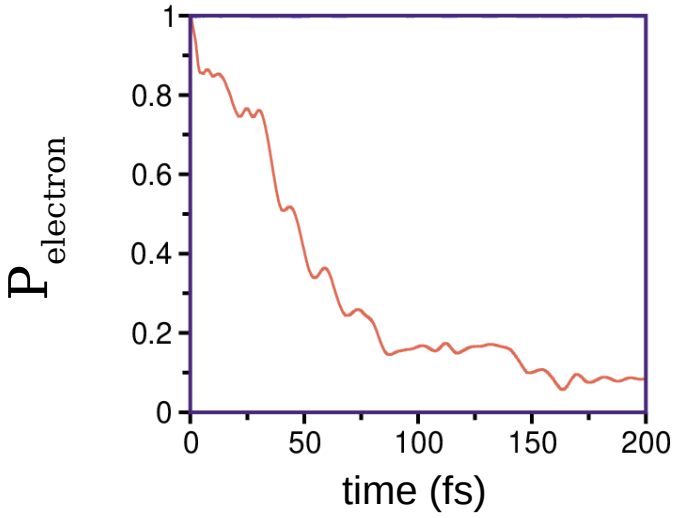
Non-adiabatic Electron Transfer Dynamics

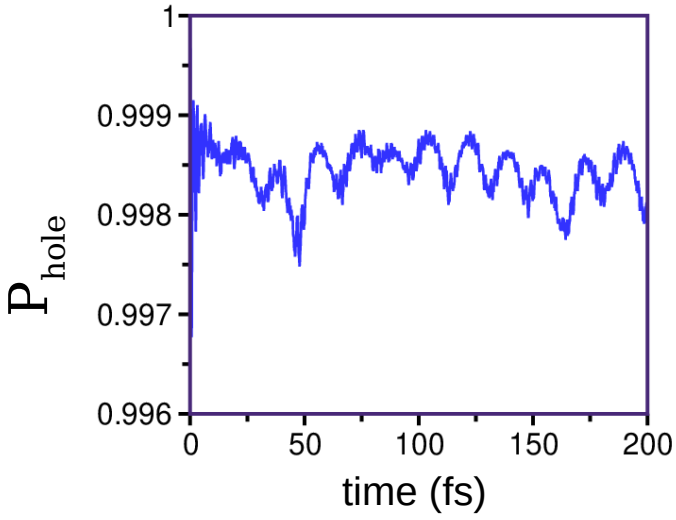
```
!-------------------------------------------------------------------------
!                      ENVIRONMENT parameters

 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
```

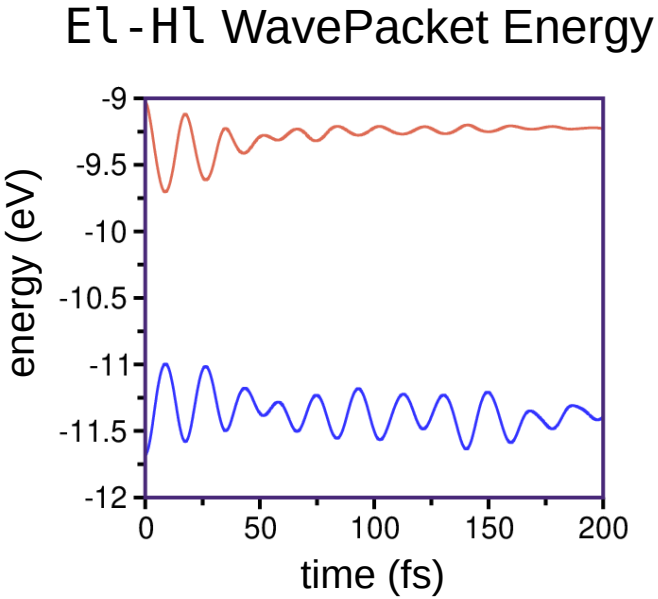
Interfacial Electron Transfer

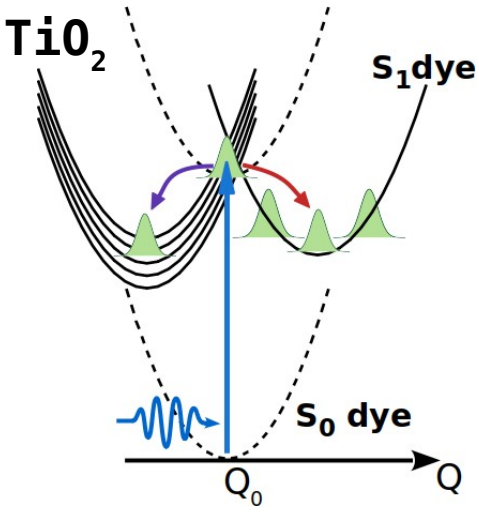
Example: Dye-sensitized semiconductor

Non-adiabatic Electron Transfer Dynamics

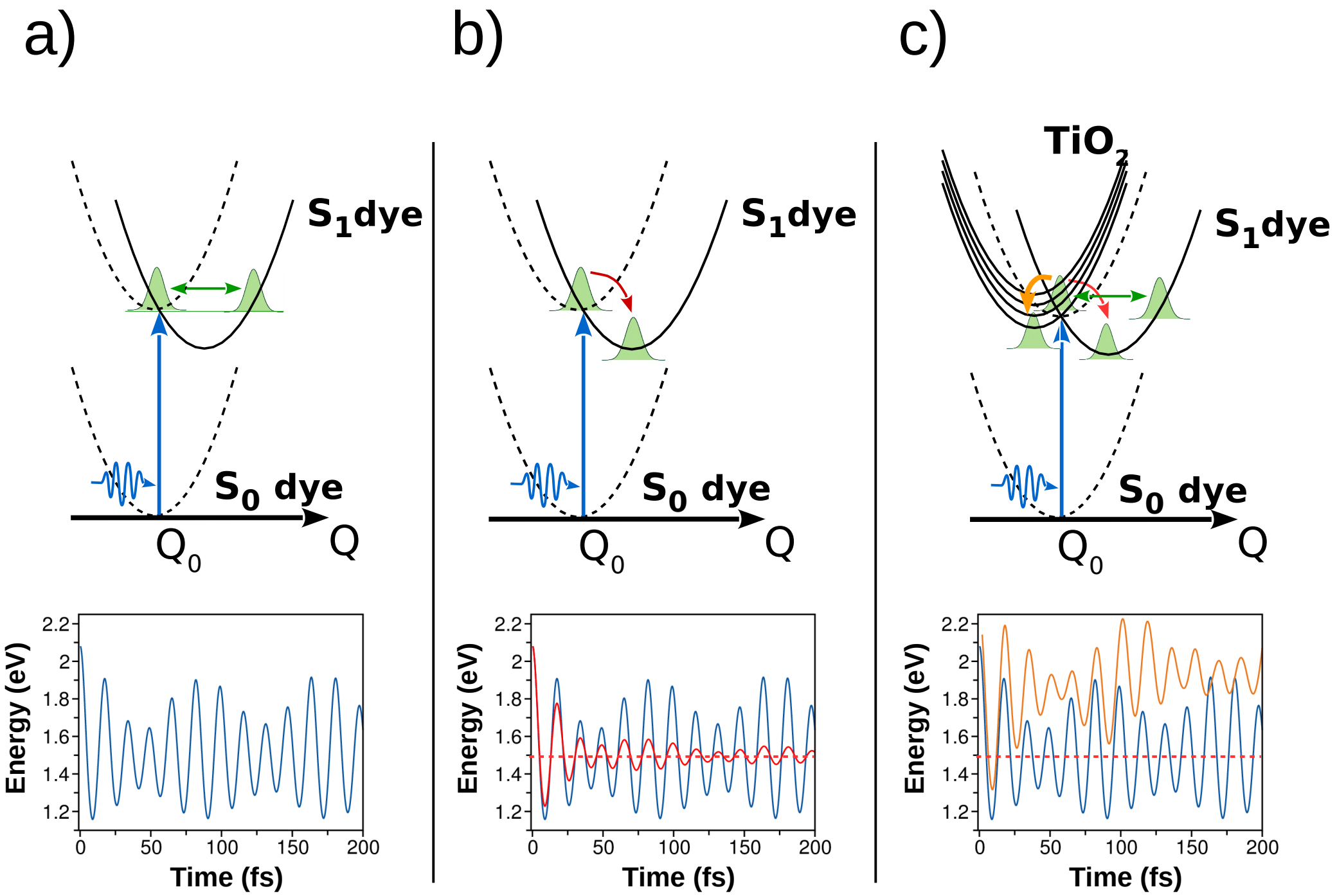








J. Phys. Chem. C 2019, 123, 12599
J. Phys. Chem. C 2021, 125, 8667

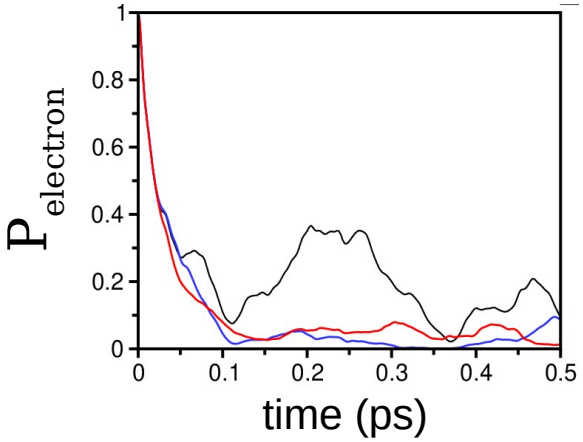

a)
b)
c)
TiO2
S1dye
S0 dye
Q0
Q
Energy (eV)
Time (fs)
2.2
2
1.8
1.6
1.4
1.2
0
50
100
150
200

Interfacial Electron Transfer

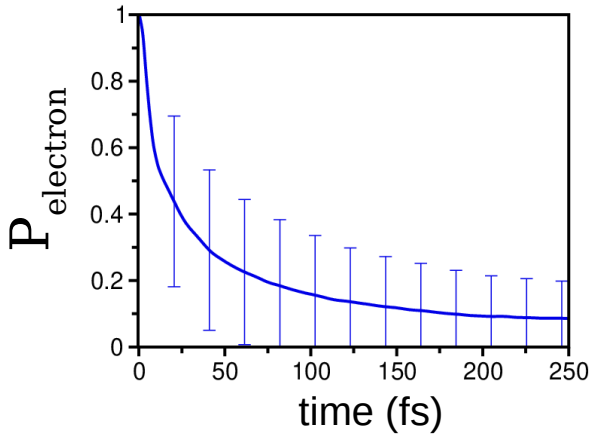
Example: Dye-sensitized semiconductor

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

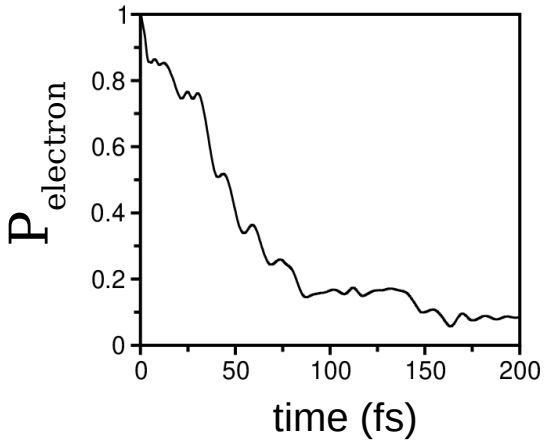
DRIVER = q_dynamics



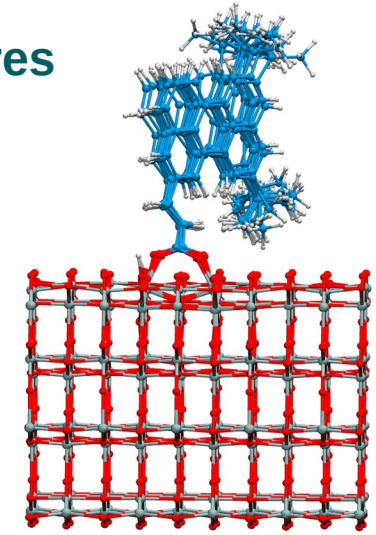
avrg_confgs



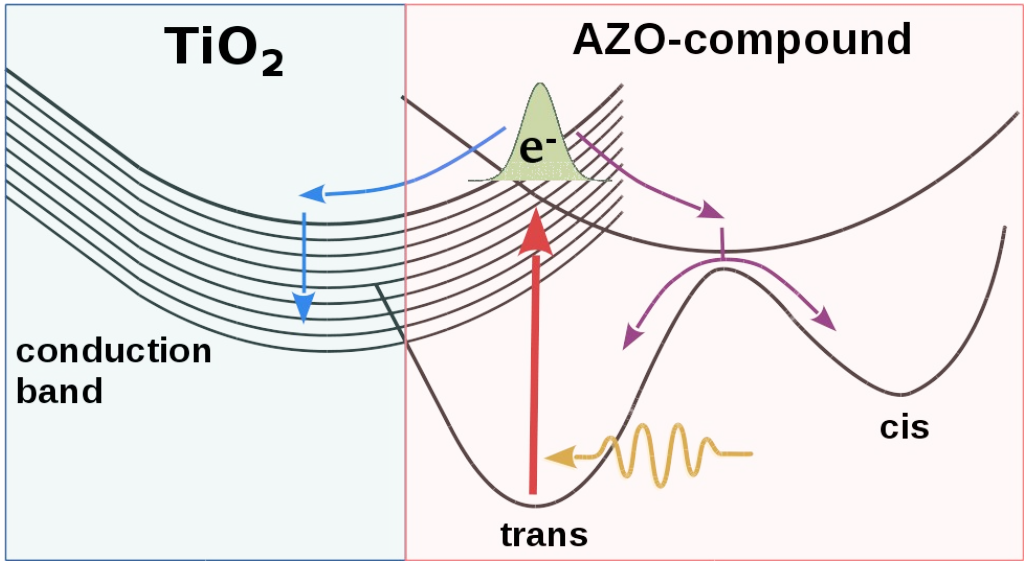
Ehrenfest

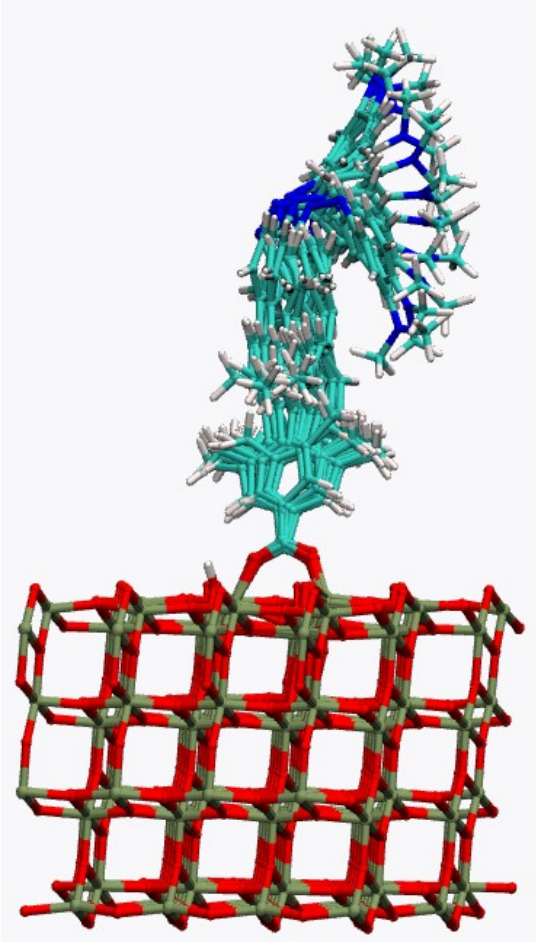


Similar behavior for rigid structutures



Charge Transfer *vs* Structural Relaxation



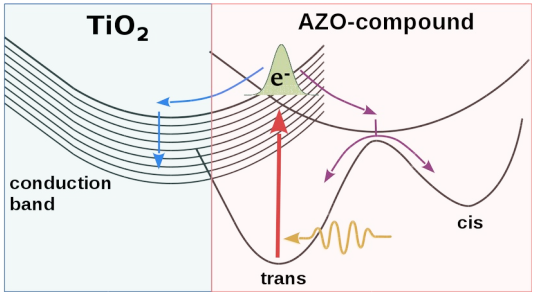


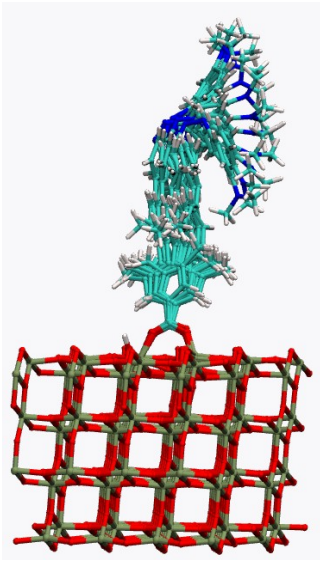
J. Phys. Chem. Lett. 2018, 9, 5926.
J. Phys. Chem. C 2019, 123, 5692.
J. Phys. Chem. Lett. 2015, 6, 2393.

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 PICOseconds
 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
 species(2) % N_of_atoms      = 383
 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.d0           ! <== 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
```

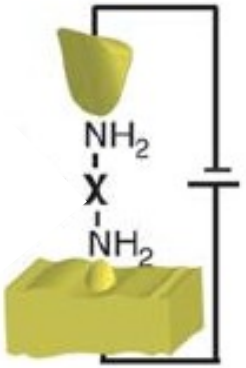


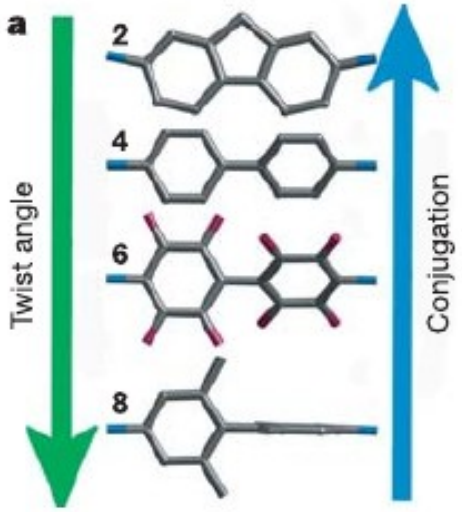


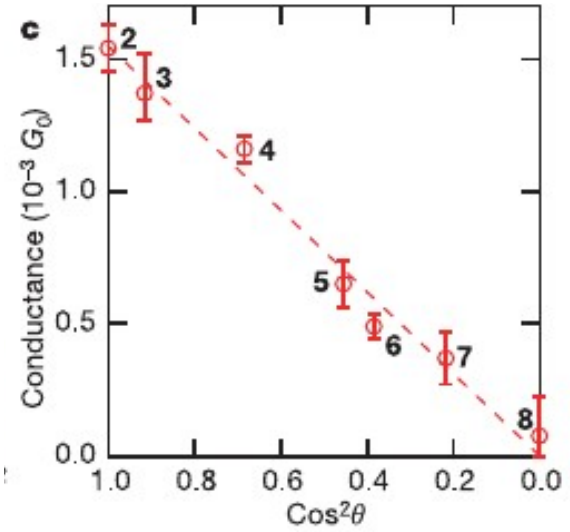
nature Vol 442|24 August 2006|doi:10.1038/nature05037

Dependence of single-molecule junction conductance on molecular conformation

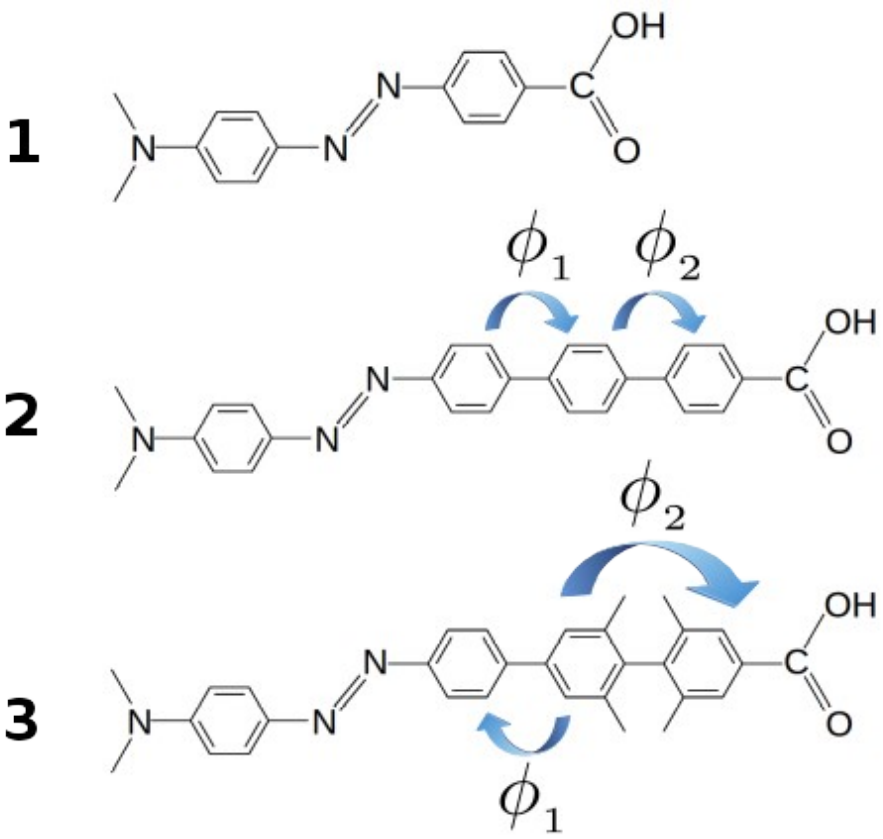
Latha Venkataraman[1,4], Jennifer E. Klare[2,4], Colin Nuckolls[2,4], Mark S. Hybertsen[3,4] & Michael L. Steigerwald[2]

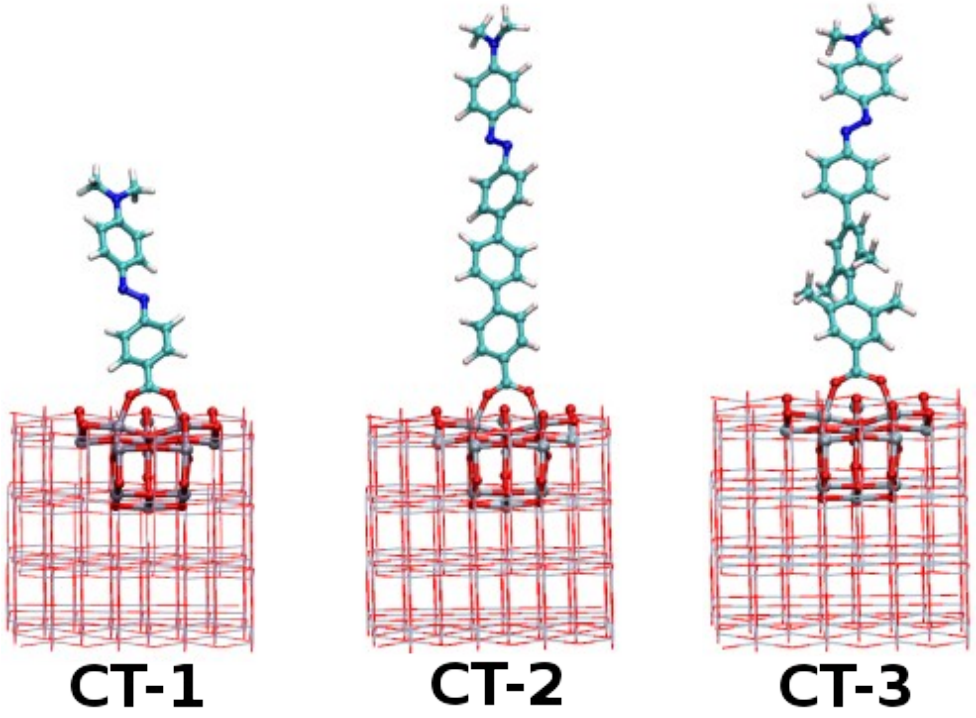






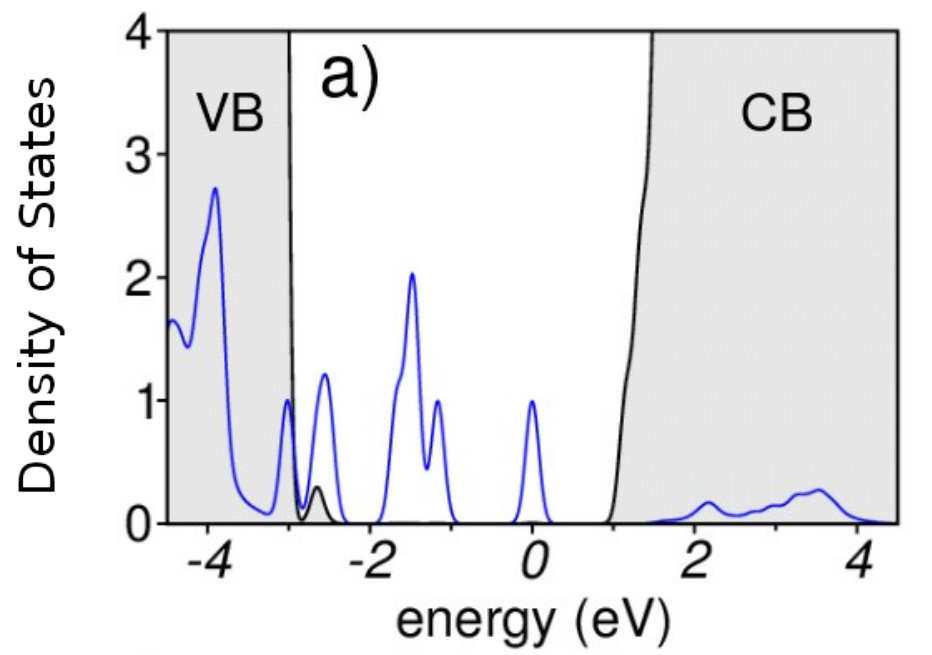
Charge Transfer *vs* Structural Relaxation

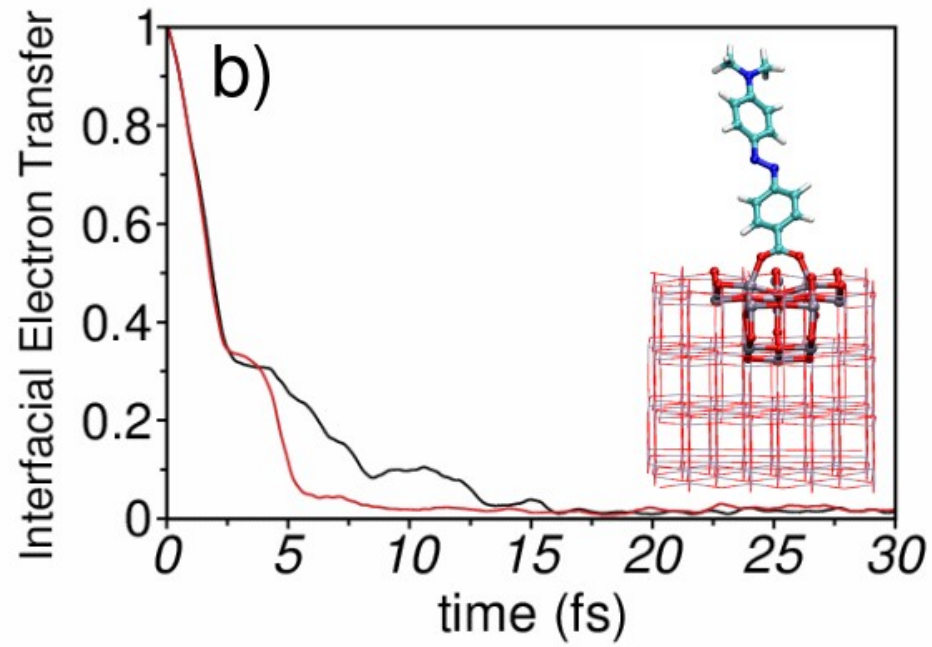




J. Phys. Chem. C, 2019.

Charge Transfer *vs* Structural Relaxation





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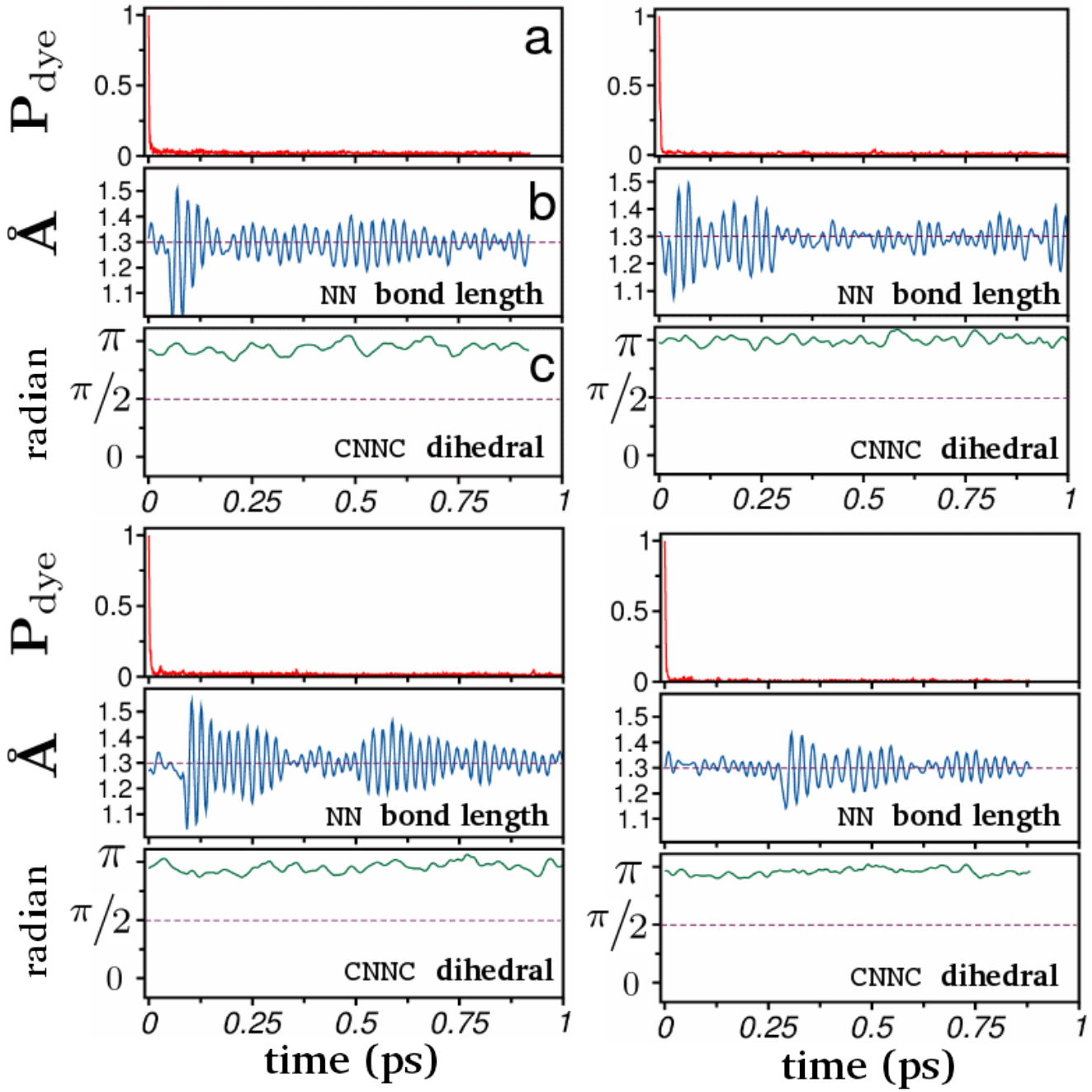
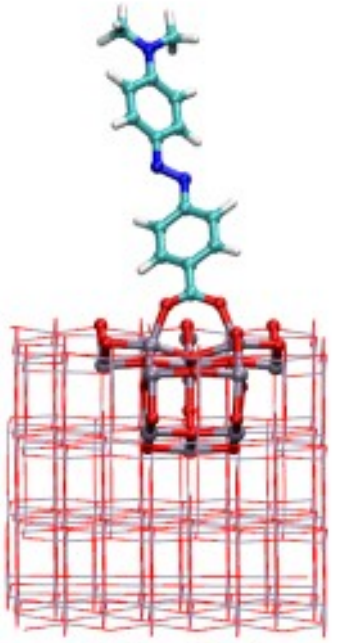
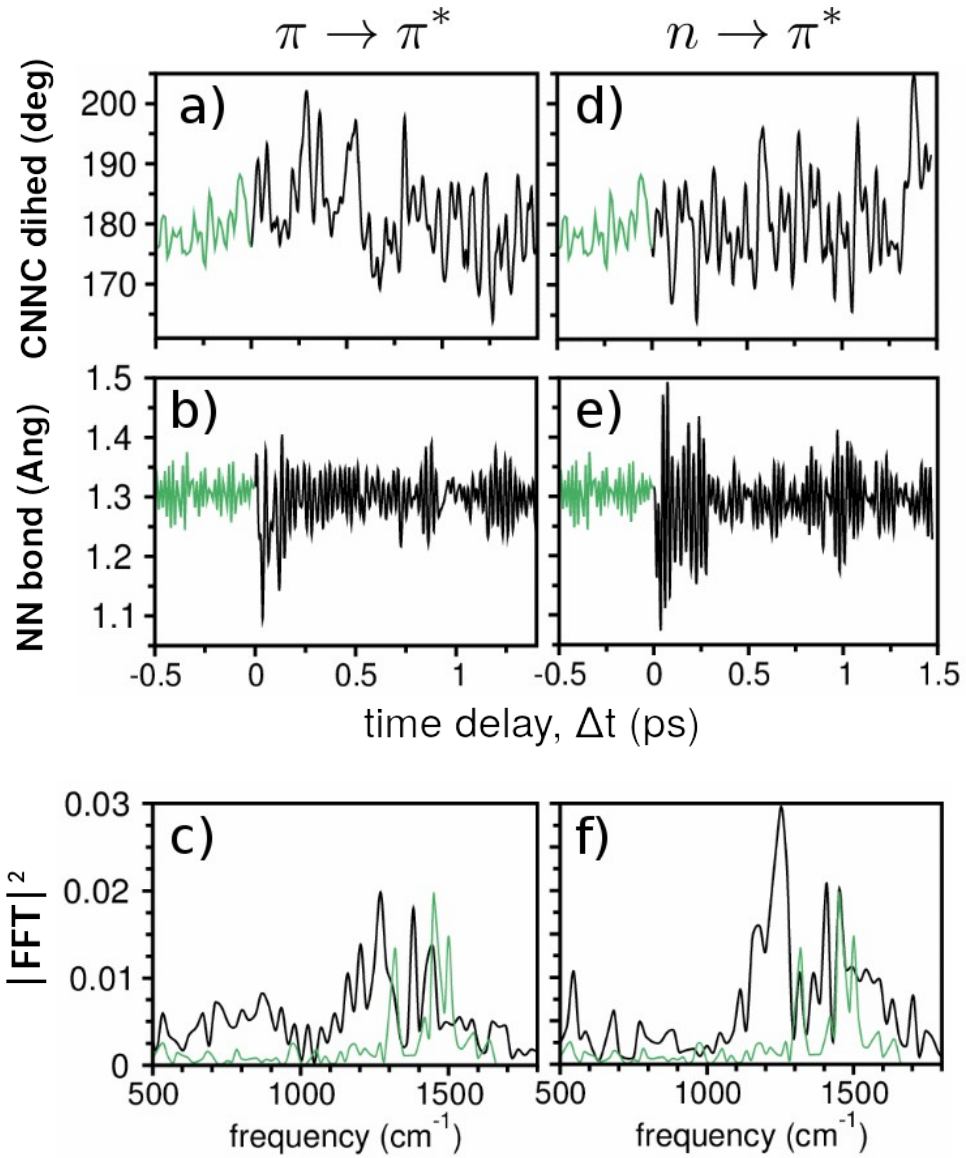
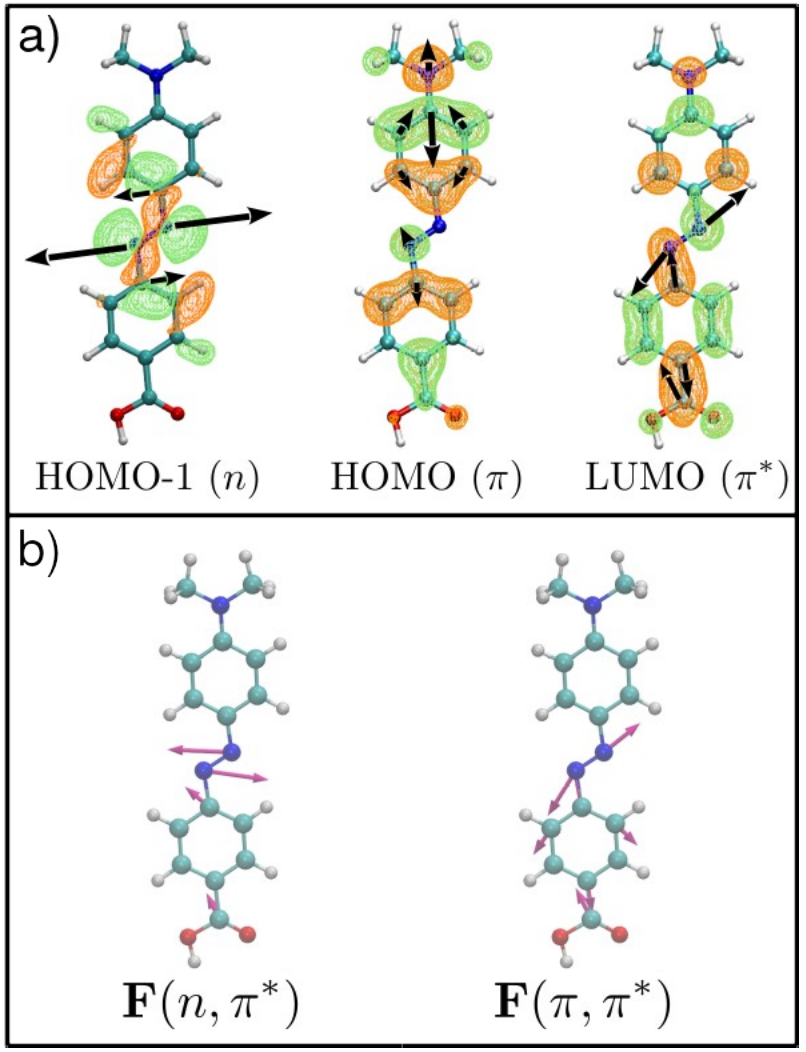




CT-1

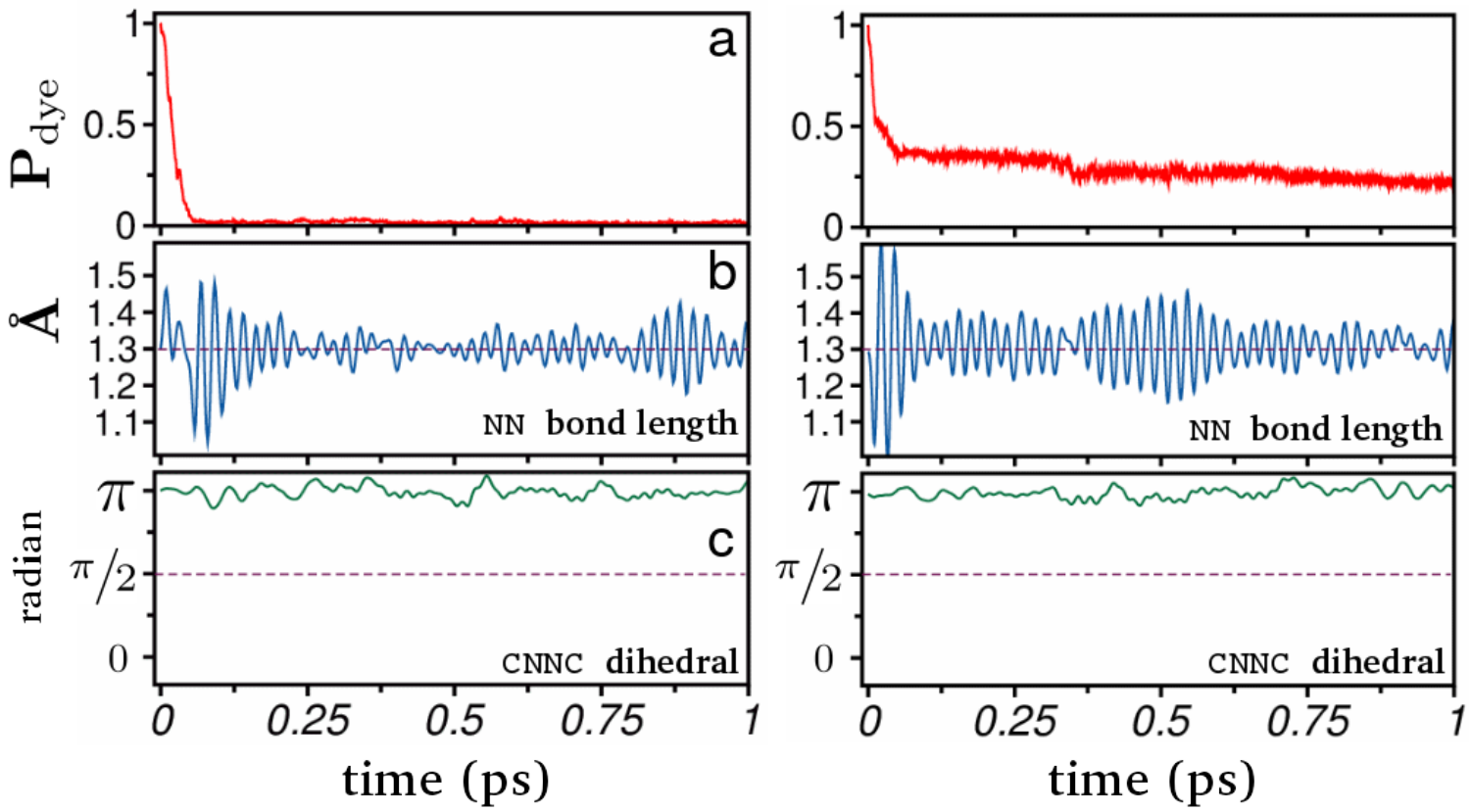
Charge Transfer *vs* Structural Relaxation

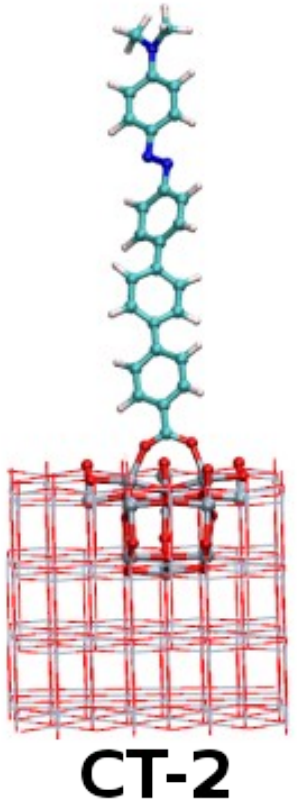




JPC Lett., 2018, **9**, 5926.

Charge Transfer *vs* Structural Relaxation





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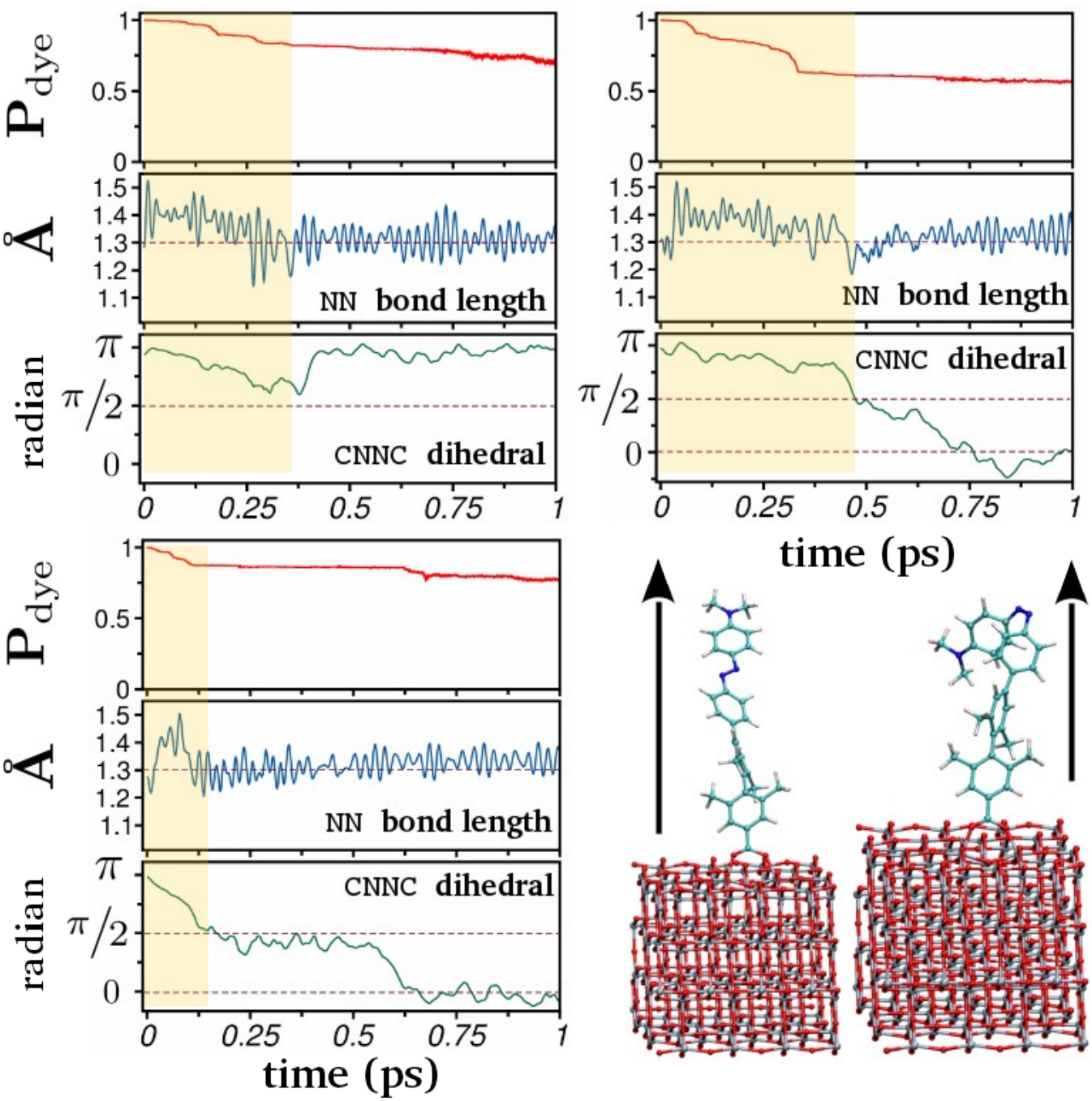

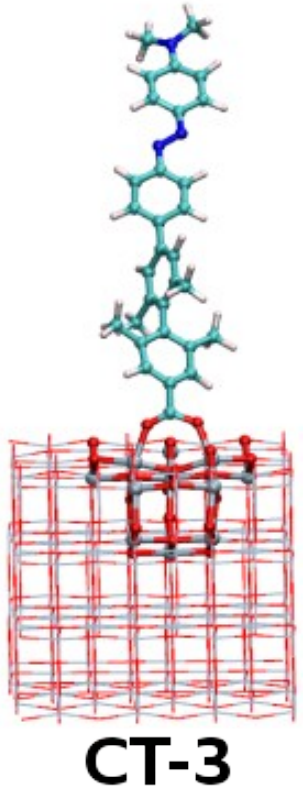

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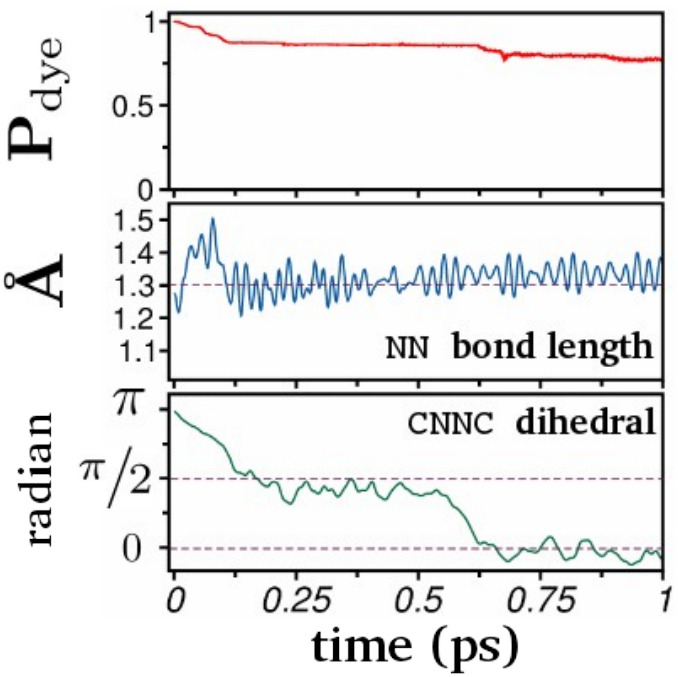

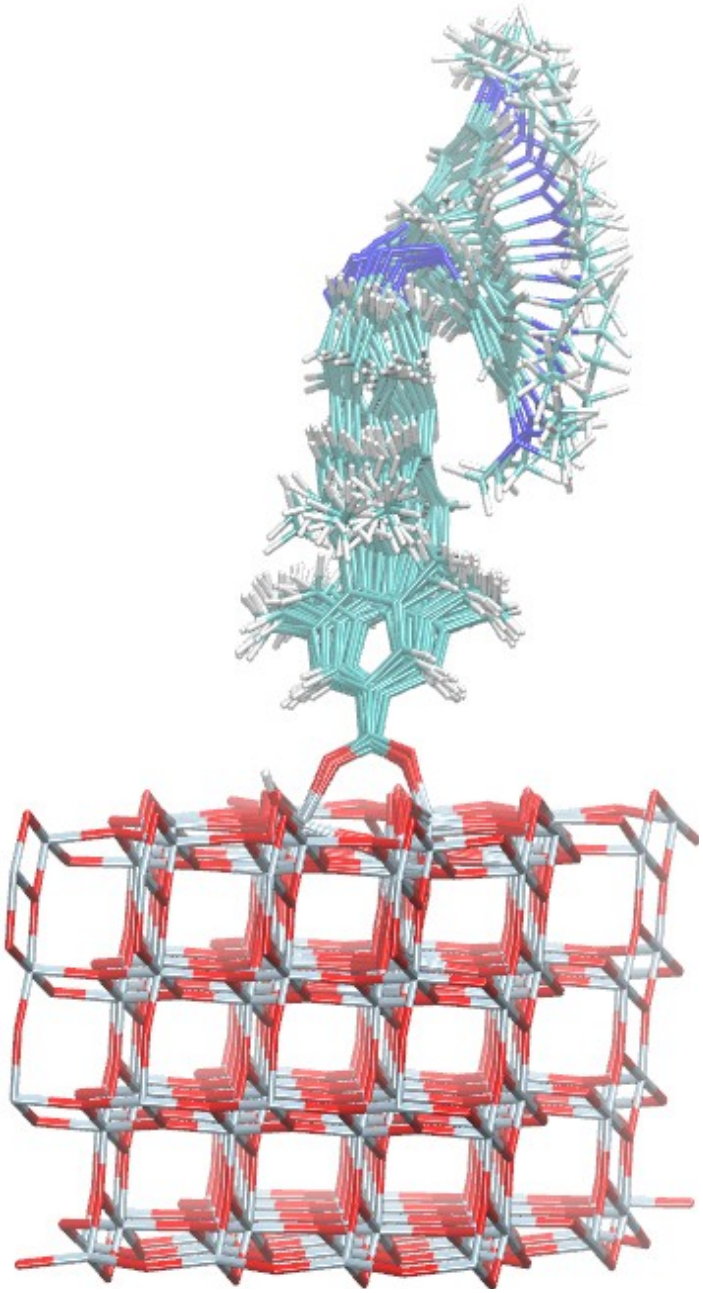

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