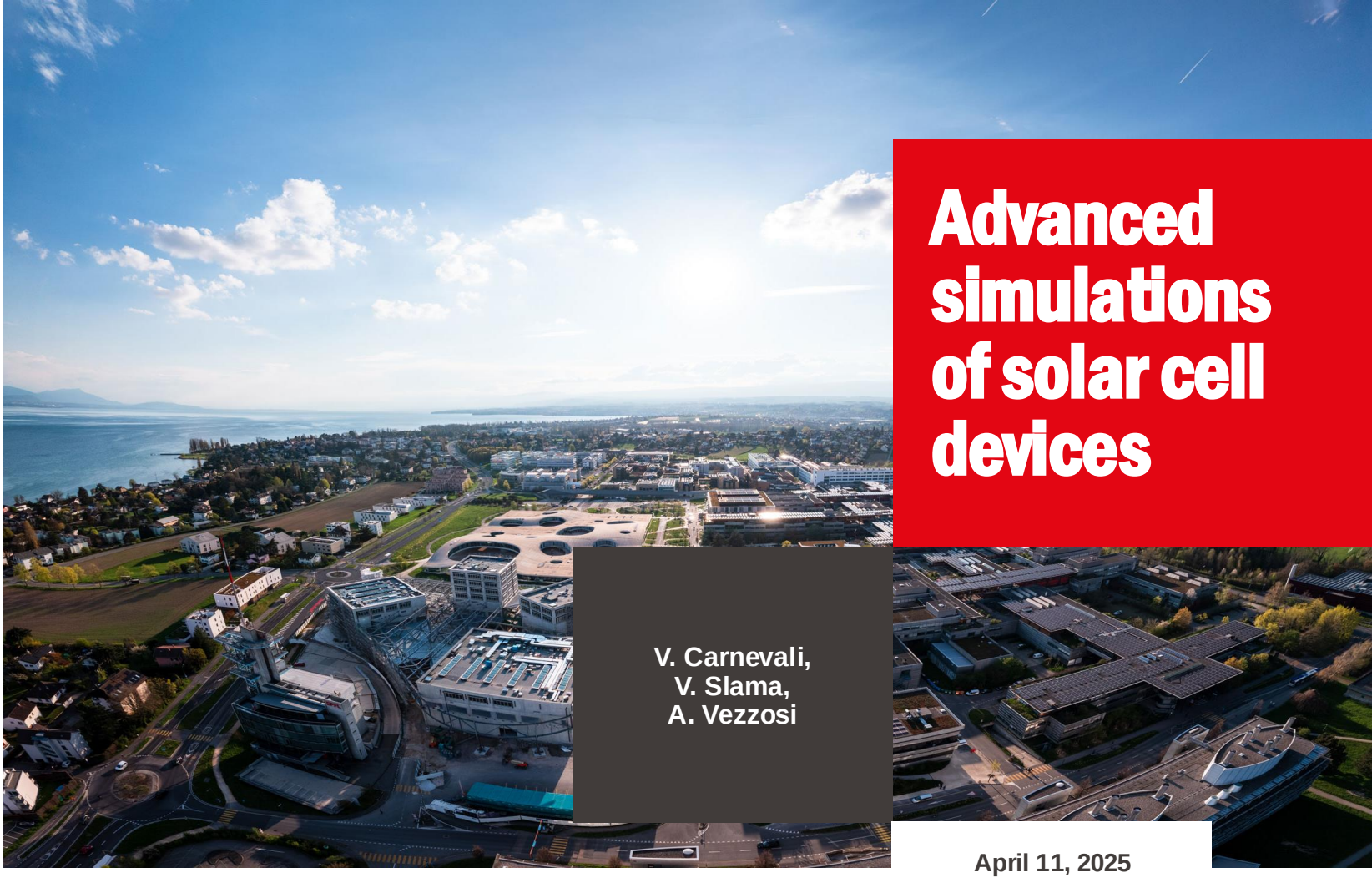
Advanced simulations of solar cell devices



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Creating surface from bulk

- Open bulk structure in the VMD (***vmd FAPbI3_2x2x2.pdb***)
- Visualize periodic box of the system – in TkConsole: ***pbc box***
- Get periodic boundary conditions dimensions: ***pbc get***

```
>Main< (Downloads) 2 % pbc get
{12.814000 12.532000 12.676000 90.000000 90.000000 90.000000}
```

- We plan to create surface in z dimension - need to create thicker layer in the z dimension to have bulk-like properties in the middle of the layer => need to extend box in z dimension: ***pbc set {12.814000 12.532000 50.000}***
- Move the system up along the z axis: ***set sel [atomselect top "all"] $sel moveby {0.0 0.0 15.0}***
- Save the structure e.g ***FAPbI3_2x2x2_surf1.pdb***
- Move the system in along the same axis by the same distance as in bulk: ***$sel moveby {0.0 0.0 12.676}***
- Save the structure in new file e.g. ***FAPbI3_2x2x2_surf2.pdb***
- Exit vmd

Creating surface from bulk

- Combine two files in the single pdb file (text editor or linux terminal:
  cat FAPbI3_2x2x2_surf2.pdb FAPbI3_2x2x2_surf1.pdb > FAPbI3_2x2x4_surf.pdb
- Remove lines with **END** and **CRYST1** in the middle of the merged FAPbI3_2x2x4_surf.pdb file (either in vmd or text editor)

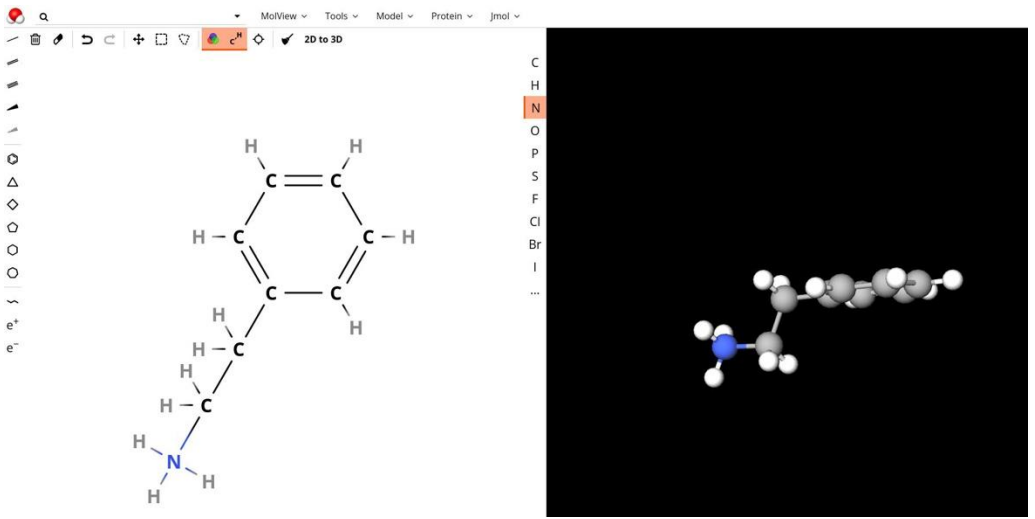
```
ATOM     94  I   UNL X  16       9.611  12.434  40.352  0.00  0.00           I
ATOM     95  I   UNL X  15       6.407   9.167  40.352  0.00  0.00           I
ATOM     96  I   UNL X  16       6.407  12.029  37.183  0.00  0.00           I
END
CRYST1   12.814   12.532   50.000  90.00  90.00  90.00 P 1           1
ATOM      1  C   UNL X   1       3.204   3.262  18.169  0.00  0.00           C
ATOM      2  N   UNL X   1       4.368   2.667  18.169  0.00  0.00           N
ATOM      3  N   UNL X   1       2.039   2.667  18.169  0.00  0.00           N
```

Lines to be removed

Surface passivation – building molecule

- Create passivation molecule for example using online molview online tool

  https://molview.org/



- Convert the .mol file format to pdb

  https://www.cheminfo.org/Chemistry/Cheminformatics/FormatConverter/index.html

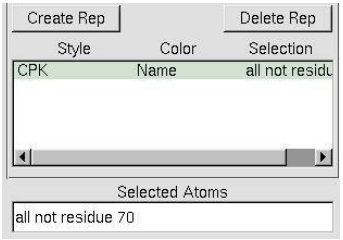
  - Remove all the **CONNECT** and **MASTER** lines from the pdb file.

Surface passivation

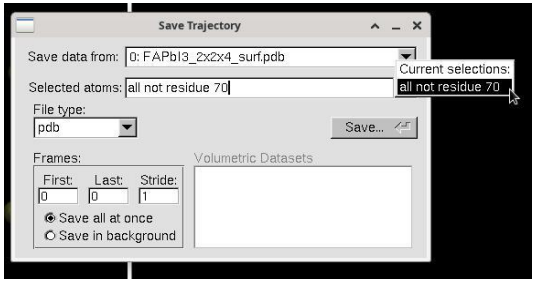
- Open 2D system in vmd and remove single FA molecule from the surface
  - Get the FA index
    - Mouse → Label → Atoms and click on FA to be removed)
    - In the vmd terminal window you should see information about residue

```
Info) molecule id: 0
Info) trajectory frame: 0
Info) name: C
Info) type: C
Info) index: 168
Info) residue: 70
Info) resname: UNL
Info) resid: 13
Info) chain: X
Info) segname:
Info) x: 9.611000
Info) y: 9.528000
Info) z: 18.169001
Info) Added new Atoms label UNL13:C
```

Selected residue

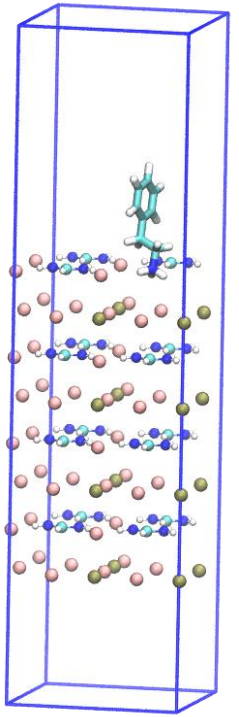


  - Create representation with the single FA missing
  - Save the structure of the specified representation with new name e.g. ***FAPbI3_2x2x4_surf_prep.pdb***



Surface passivation

- Open 2D system in vmd and remove single FA molecule from the surface
- Load the passivating molecule (structure.pdb) and reorient to NH3 group replacing missing FA
  - File → Load Molecule load structure.pdb
  - Mouse → Move → Molecule and using mouse orient the passivating molecule in desired way
  - Save coordinates of the shifted molecule (e.g. as structure_shifted.pdb)
- Close vmd and combine files of the surface without single FA and the passivating molecule: ***cat FAPbI3_2x2x4_surf_prep.pdb structure_shifted.pdb > FAPbI3_2x2x4_passivated.pdb***
- Remove lines with **END** and **CRYST1** in the middle of the merged file
- Check the final structure in vmd

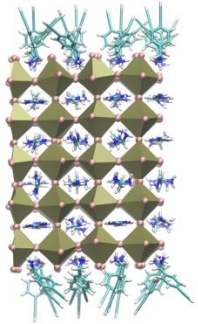


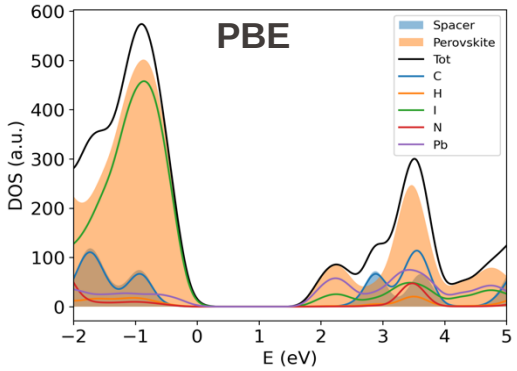
PDOS of the passivated and multilayer systems

- Requirements for the good passivating layer:
  - Protection from the moisture
    - perovskites are ionic materials → dissolved by water
  - Defect passivation
    - Usually with NH_3^+ group and I^- counter ions – passivation of iodide vacancies
  - Larger binding energy than FA (to replace FA molecules and stabilize the surface)
  - Not to block charge extraction from active layer to ETL/HTL layers
    - Smaller molecules
    - **Electroactive molecules** → enhancing charge transport or selective for holes/electrons

PDOS of the passivated and multilayer systems

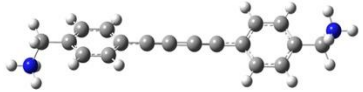
BMAA

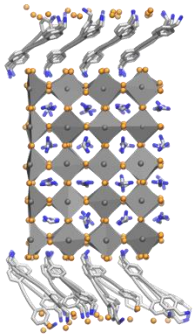


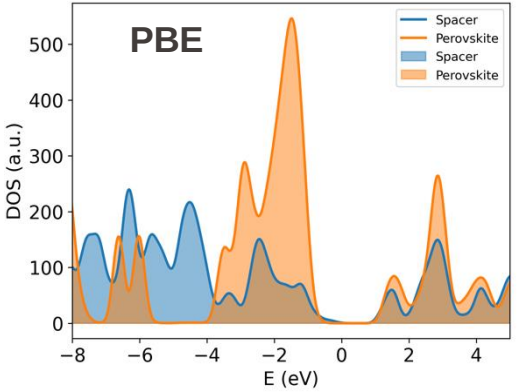


- Surface protection from moisture and defect passivation
- No active role in charge transport

BDAA



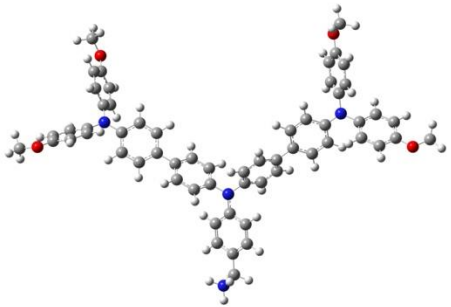


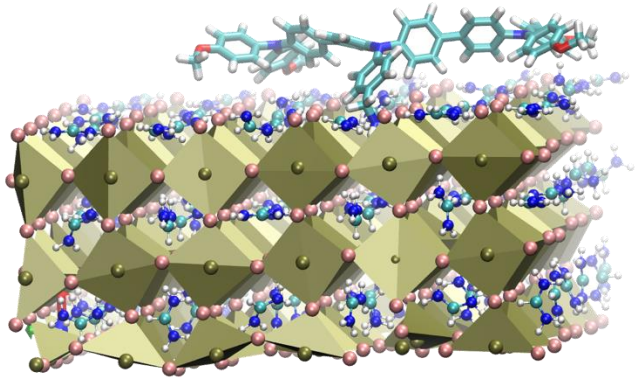


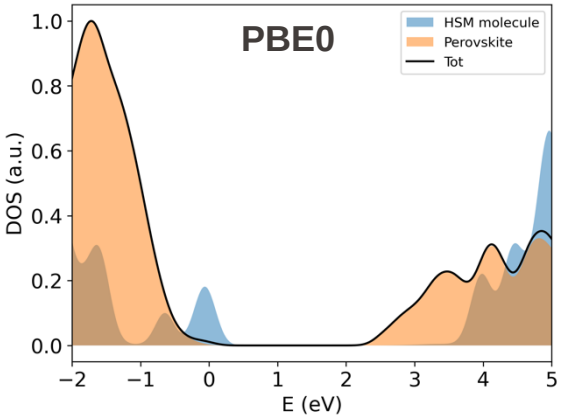
- Surface protection from moisture and defect passivation
- Good alignment with conduction and valence band → active charge transport of both electrons and holes

PDOS of the passivated and multilayer systems

Hole shuttle molecule (HSM)



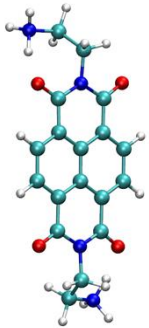


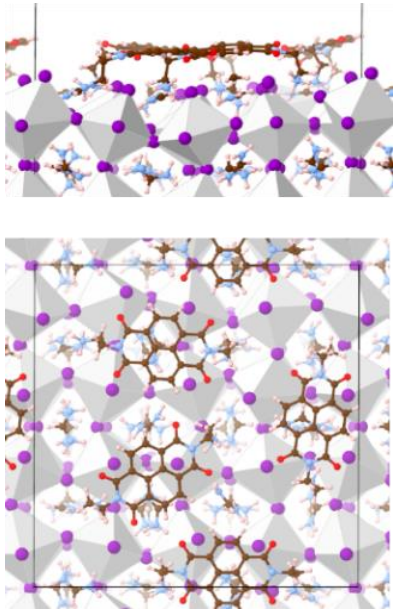


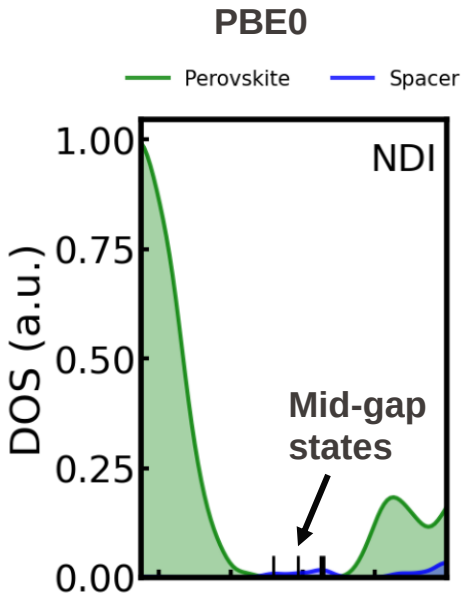
- Good for hole selective transport (transporting holes and blocking the electrons)

PDOS of the passivated and multilayer systems

Naphtalene diimide (NDI)



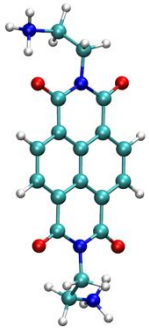


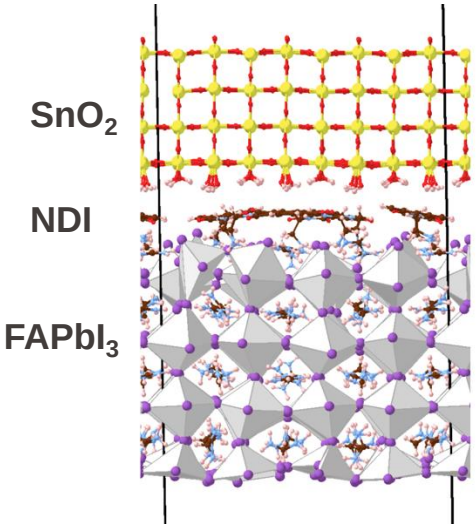


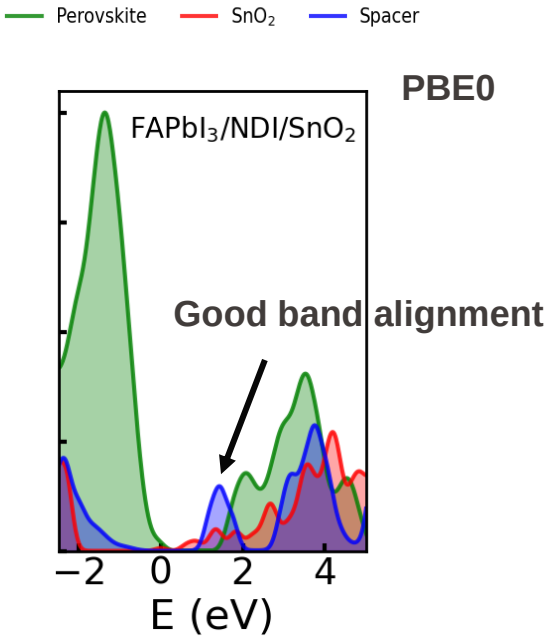
- Additives can introduce localized trap-states within the gap (not good for electron transport)

PDOS of the passivated and multilayer systems

Naphtalene diimide (NDI)







- However, in the actual device the energy levels of the molecules shift and have good selective carrier transport properties.

PDOS of the passivated and multilayer systems

BMAA, BDAA, HSM inputs: 8Lect_shared

Compute the PDOS alignment restarting the calculation from the wavefunctions included in the folders (the calculations will converge after a few steps)

```
&SCF
  EPS_SCF 5.0E-6
  SCF_GUESS RESTART
  ...
```

Be sure to have it in the &SCF section to have the calculation restart from the wavefunctions.

!!!Do not change the prefix in the input, otherwise cp2k will not recognize the wavefunctions!!!