CP2K Quantum Mechanics / Molecular Mechanics 2D Embedding and Applications

David Z. Gao, Matthew B. Watkins, Filippo Federici-Canova, Alexander L. Shluger

Department of Physics and Astronomy

University College London

Outline

Introduction to QM/MM

- Embedded Cluster Models
- Embedded Island Models
- Embedded Sandwich Models

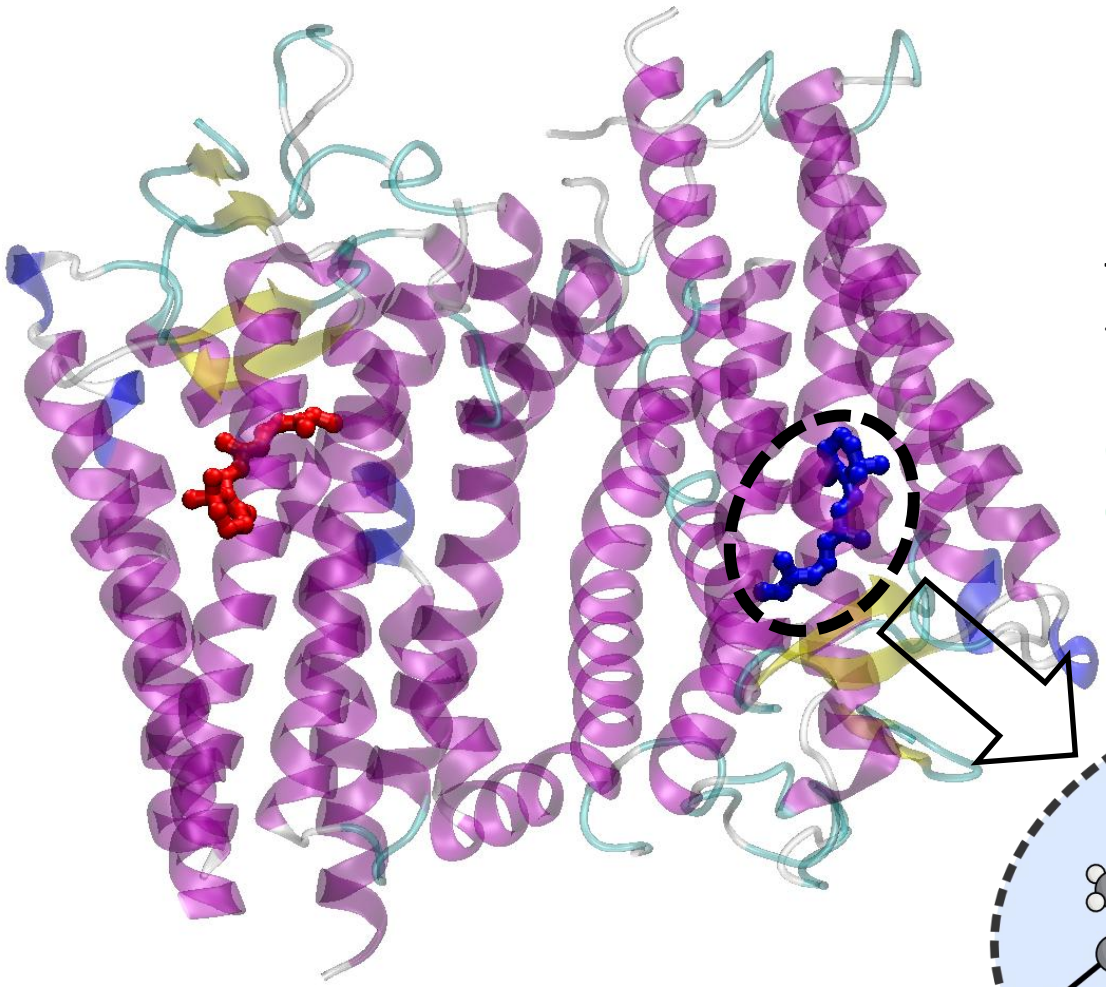
Implementation in CP2K

Application to Molecular Films

- Experimental Overview
- Applying QM/MM
- Common Challenges

Conclusions

Embedded Cluster Methods (Finite Systems)

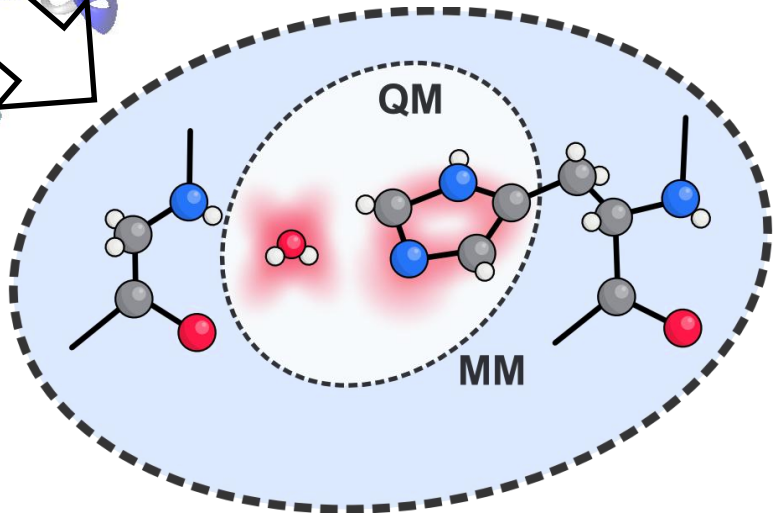


Why Combine QM and MM?

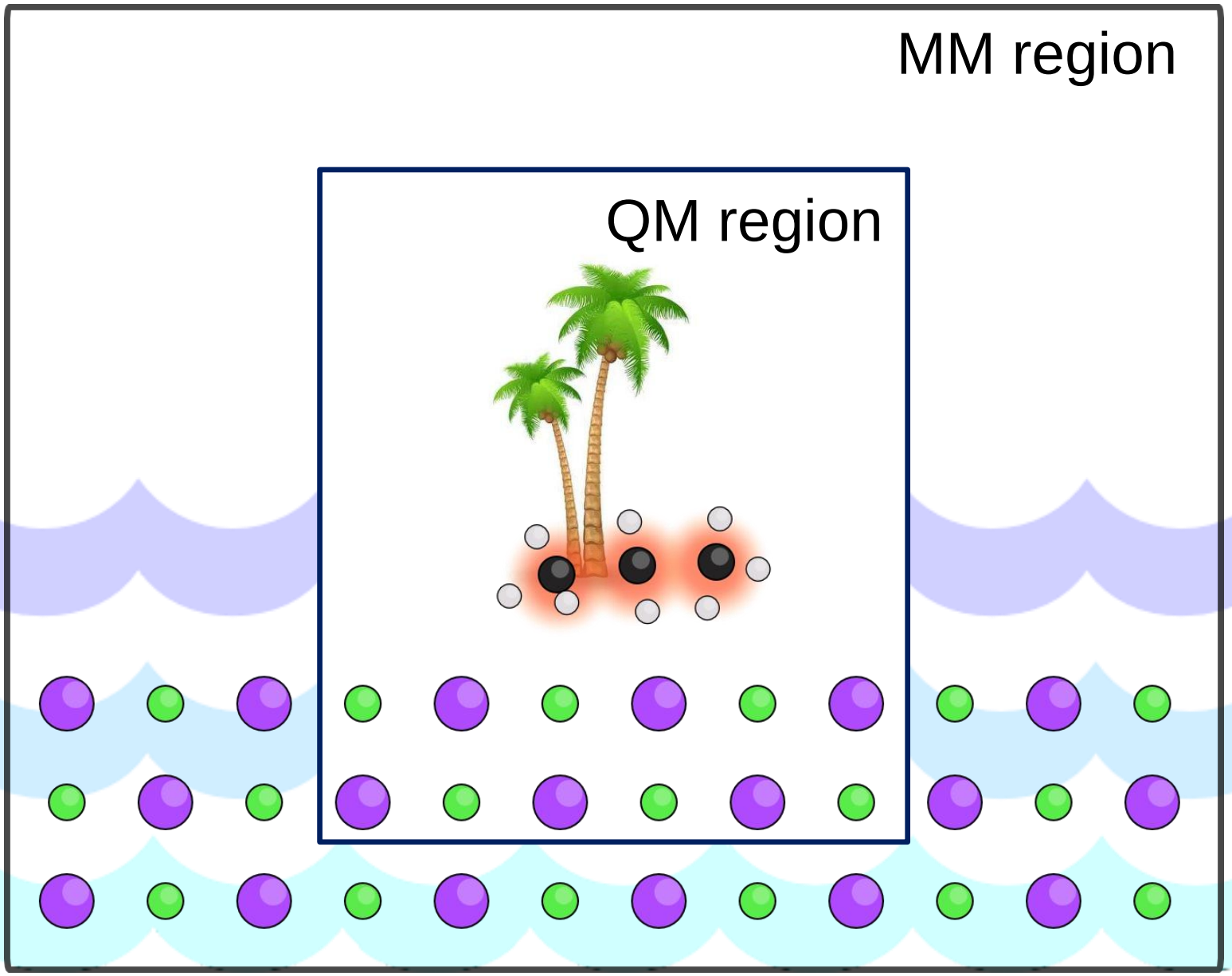
- QM: Electronic Effects
- MM: Wider Environment
- Reduce Computational Cost

Typically too expensive to treat the full system with *ab initio* techniques

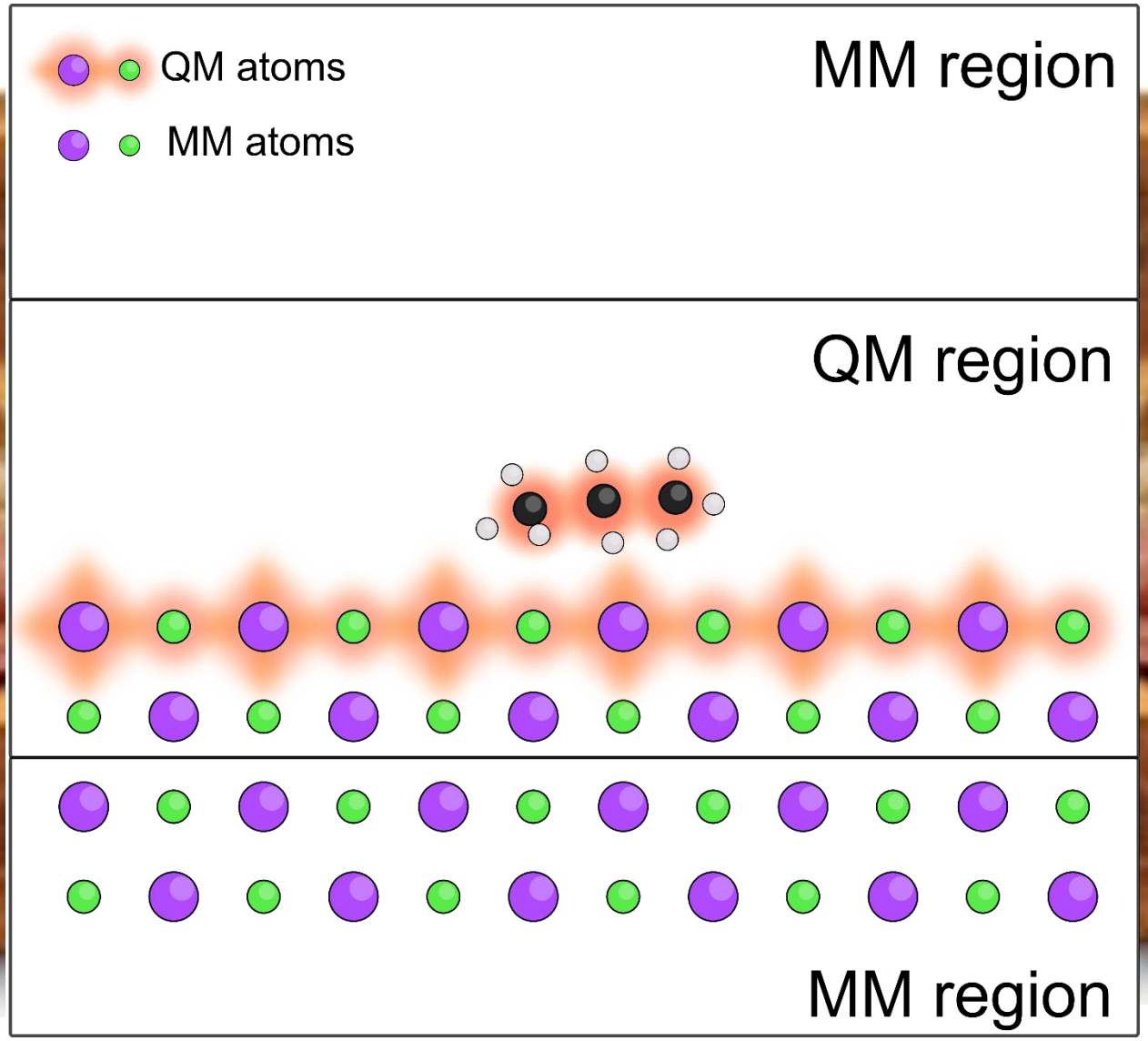
Only part of the system contains critical interactions!



Additional Embedding Schemes in CP2K: Island



Additional Embedding Schemes in CP2K: Sandwich



Periodic in 2 Dimensions: The Infinite Sandwich Model

Additive QM/MM in CP2K

$$E_{\mathrm{TOT}}(\mathbf{r}_\alpha,\mathbf{r}_\mathrm{a}) = E^{\mathrm{QM}}(\mathbf{r}_\alpha) + E^{\mathrm{MM}}(\mathbf{r}_\mathrm{a}) + E^{\mathrm{QM/MM}}(\mathbf{r}_\alpha,\mathbf{r}_\mathrm{a}) \quad (1)$$

Total energy is just the QM part + MM part + interaction between them!
Note: There is also subtractive QM/MM… which is a bit different… (also in CP2K)

$$E^{\mathrm{QM/MM}}(\mathbf{r}_\alpha,\mathbf{r}_\mathrm{a}) = \sum_{\mathrm{a}\in\mathrm{MM}} q_\mathrm{a} \int \frac{\rho(\mathbf{r},\mathbf{r}_\alpha)}{|\mathbf{r}-\mathbf{r}_\mathrm{a}|} d\mathbf{r} + \sum_{\substack{\mathrm{a}\in\mathrm{MM}\\ \alpha\in\mathrm{QM}}} v_{\mathrm{VdW}}(\mathbf{r}_\alpha,\mathbf{r}_\mathrm{a}) \quad (2)$$

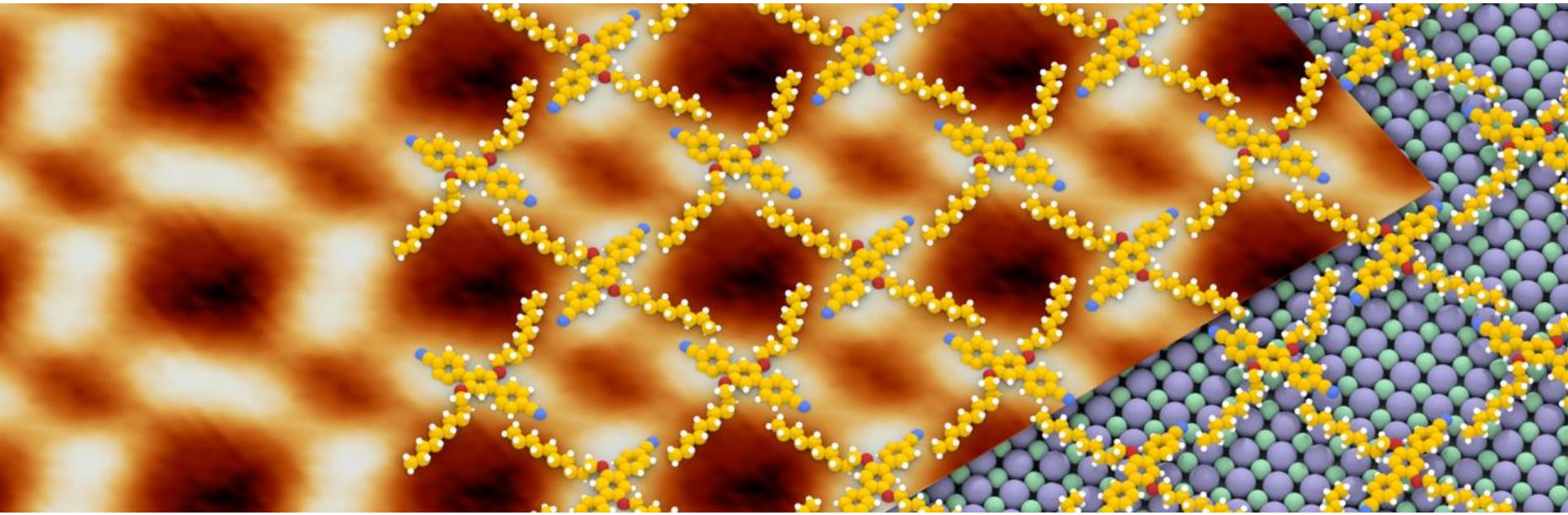
$\mathbf{r}_\mathrm{a}$ = Position of an MM atom with charge q_a

$\rho(\mathbf{r},\mathbf{r}_\alpha)$ = Total electronic and nuclear charge density of the QM system

$v_{\mathrm{VdW}}(\mathbf{r}_\alpha,\mathbf{r}_\mathrm{a})$ = van der Waals interactions between MM and QM atoms

An Example Application:

Molecular Design and Control over the Morphology of Self-Assembled Films on Ionic Substrates

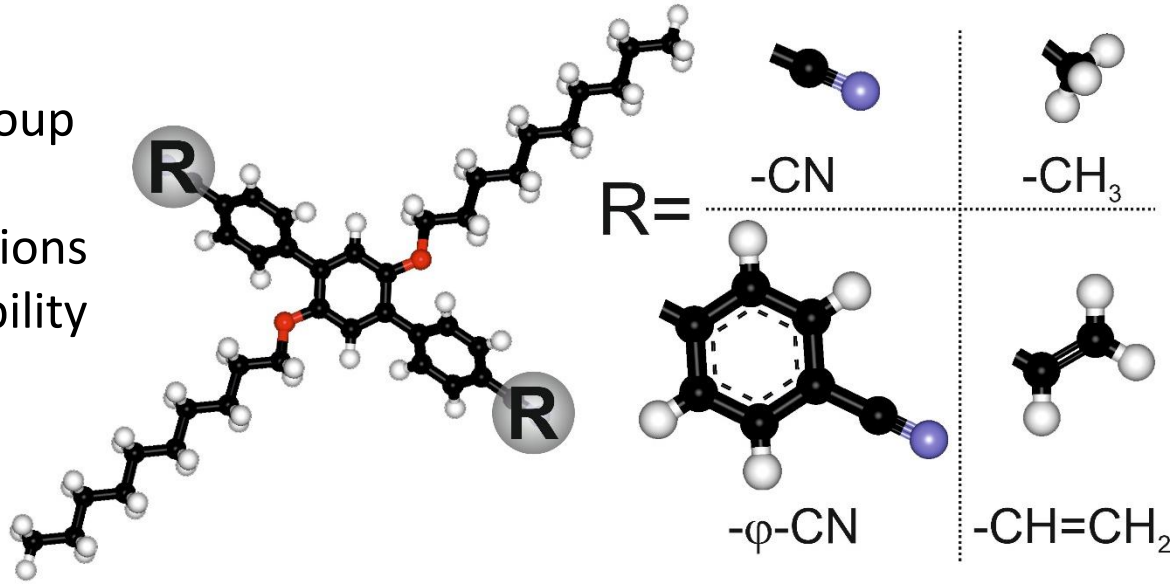


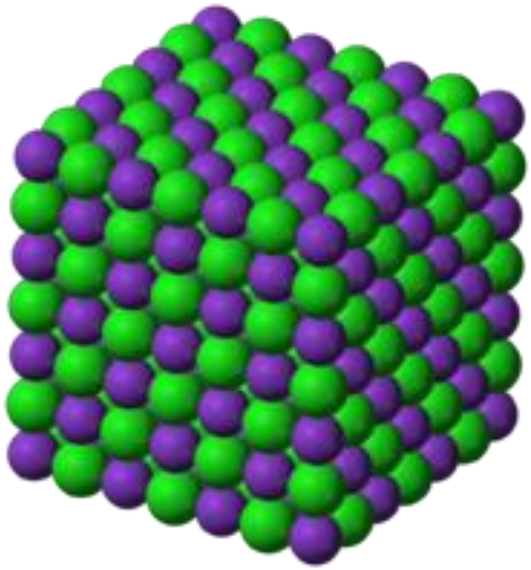
Ania Amrous, Franck Bocquet, Laurent Nony, Franck Para, Christian Loppacher, Simon Lamare, Frank Palmino, Frederic Cherioux, David Z. Gao*,Filippo Federici Canova, Matthew B. Watkins, and Alexander L. Shluger*
Advanced Materials Interfaces, **2004**, 1, 1400414.

The Surface and a Molecule

Molecular Design:

- Anchoring CN Functional Group
- Interchangeable Groups
- Rings for π-Stacking Interactions
- Hydrocarbon Arms for Flexibility





The KCl(001) Substrate:

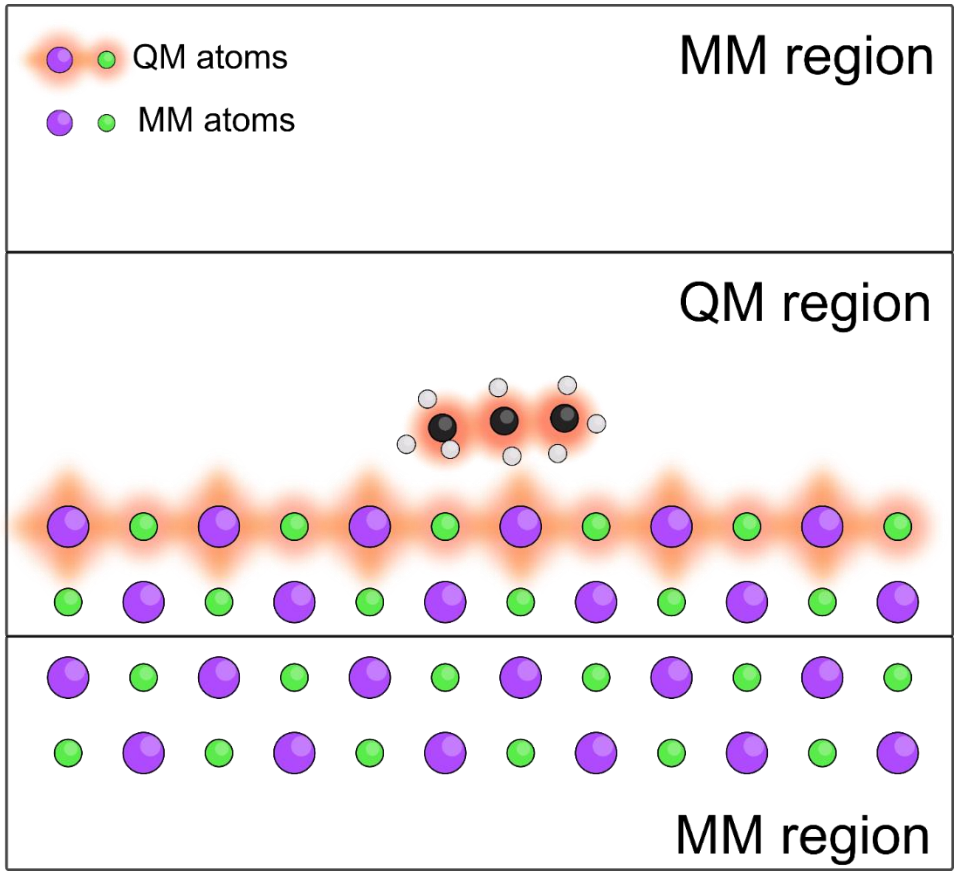
- **Experimentally Limited**: Easily Cleaved, Obtainable, Few Impurities, Etc…
- Simple Cubic Structure
- Simple Step Edges
- Insulator with Anchoring and Repulsive Sites

QM/MM Representation

2D Monolayer Films
2D Sandwich Embedding

DFT for Molecule-Surface Interactions

Classical Force Field for Subsurface KCl Atoms



QM/MM CP2K Input Sections

```
&FORCE_EVAL
 METHOD QMMM (QMMM/FIST/QS)
 @include QS.inc (The usual DFT stuff!)

 &MM (This is from @include MM.inc)
  &FORCEFIELD
   &CHARGE
     ATOM K
     CHARGE 1.0
   &END CHARGE
   &CHARGE
     ATOM Cl
     CHARGE -1.0
   &END CHARGE

   &NONBONDED
    &WILLIAMS
     atoms K   Cl
     A [eV] 4117.9
     B [angstrom^-1] 3.2808
     C [eV*angstrom^6] 0.0
     RCUT [angstrom] 3.0
    &END WILLIAMS
    &WILLIAMS
     atoms Cl  Cl
     A [eV] 1227.2
     B [angstrom^-1] 3.1114
     C [eV*angstrom^6] 124.0
     RCUT [angstrom] 3.0
    &END WILLIAMS
    &WILLIAMS
     atoms K   K
     A [eV] 3796.9
     B [angstrom^-1] 3.84172
     C [eV*angstrom^6] 124.0
     RCUT [angstrom] 3.0
    &END WILLIAMS
   &END NONBONDED
  &END FORCEFIELD
  &POISSON (POISSON section in the MM part)
   &EWALD
     EWALD_TYPE spme
     ALPHA .44
     GMAX  40
   &END EWALD
  &END POISSON
 &END MM
```

QM/MM CP2K Input Sections

```
&QMMM

  &CELL (Size of QS Cell)
    ABC 12.6 15.0 12.6
    PERIODIC XZ
  &END CELL
    ECOUPL GAUSS (Use GEEP)
    NOCOMPATIBILITY
    USE_GEEP_LIB 6
    NOCENTER F
    NOCENTER0 F
  &PERIODIC (Apply periodic potential)
    &MULTIPOLE OFF
    #QM multipole coupling
    #use if XY of MM box =/= QM box
    &END
  &END PERIODIC

  &MM_KIND K (Width of MM Gaussians)
    RADIUS 1.52
  &END MM_KIND
  &MM_KIND Cl
    RADIUS 1.67
  &END MM_KIND
  #should be treated as parameters

  &QM_KIND K
    MM_INDEX 25..32 41..48
  &END QM_KIND
  &QM_KIND Cl
    MM_INDEX 17..24 33..40
  &END QM_KIND

&END QMMM
```

QM/MM CP2K Input Sections

```
&SUBSYS
  &CELL
   ABC 12.6 50 12.6 (Size of Entire System)
   PERIODIC XZ
  &END CELL
  &TOPOLOGY
   COORD_FILE_NAME kcl.xyz
   COORD_FILE_FORMAT XYZ
   &GENERATE
     &ISOLATED_ATOMS (Ignores bonds, dihedrals...)
       LIST 1..48
     &END ISOLATED_ATOMS
   &END GENERATE
  &END TOPOLOGY
  &KIND K
   ELEMENT K
   BASIS_SET DZVP-MOLOPT-SR-GTH
   POTENTIAL GTH-PBE-q9
  &END KIND
  &KIND Cl
   BASIS_SET DZVP-MOLOPT-GTH
   POTENTIAL GTH-PBE-q7
  &END KIND
&END SUBSYS
```

```
&END FORCE_EVAL

&GLOBAL
 FLUSH_SHOULD_FLUSH
 PRINT_LEVEL MEDIUM
 PROJECT KCl
 RUN_TYPE GEO_OPT
&END GLOBAL

&MOTION
 &GEO_OPT
   OPTIMIZER LBFGS
 &END

 &CONSTRAINT
   &FIXED_ATOMS
   LIST 1..16
   EXCLUDE_MM .FALSE.
   EXCLUDE_QM .TRUE.
   &END FIXED_ATOMS
 &END CONSTRAINT
&END MOTION
```

Step 1: Select Individual QM and MM Representations

CP2K with mixed Gaussian and plane wave (GPW) approach

J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, *Comput. Phys. Commun*. **2005** , *167* , 103 .

GGA/PBE with the MOLOPT basis set

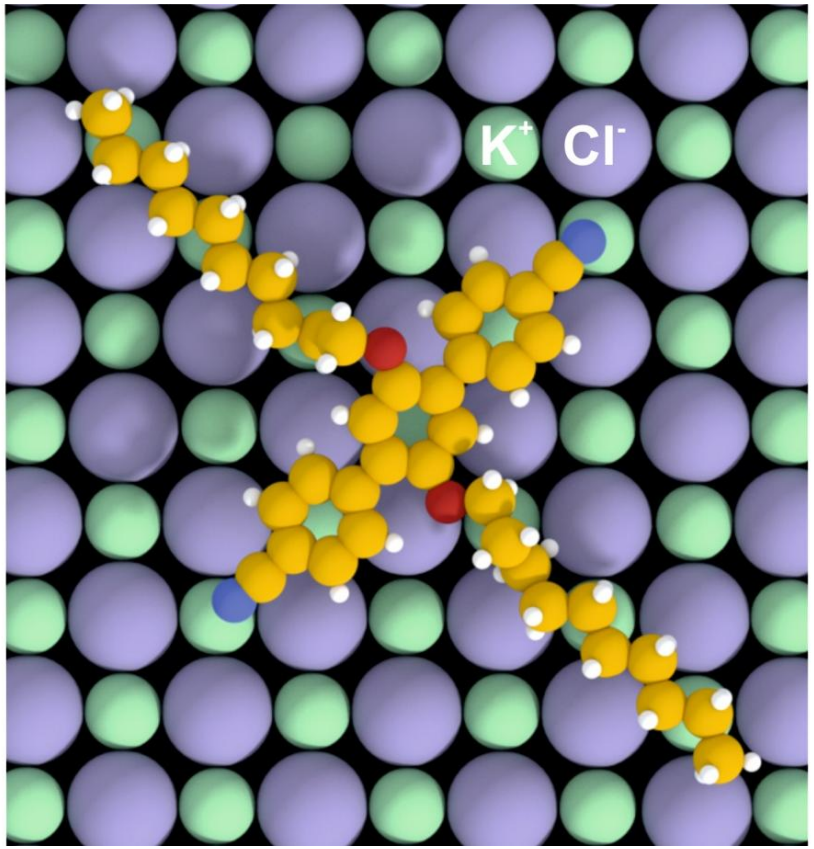
J. VandeVondele, J. Hutter, *J. Chem. Phys.* **2007**, *127*, 114105 .

DFT-D2 dispersion corrections

S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787 .

Calculated Properties:

- Mulliken and Bader analysis indicate **no charge transfer**
- Main interaction to be between **CN and the surface cations**
- **3.1 eV** Adsorption Energy
- DFT Recipe Produces 5.2 eV KCl homo/lumo gap (Exp:7.6 eV)

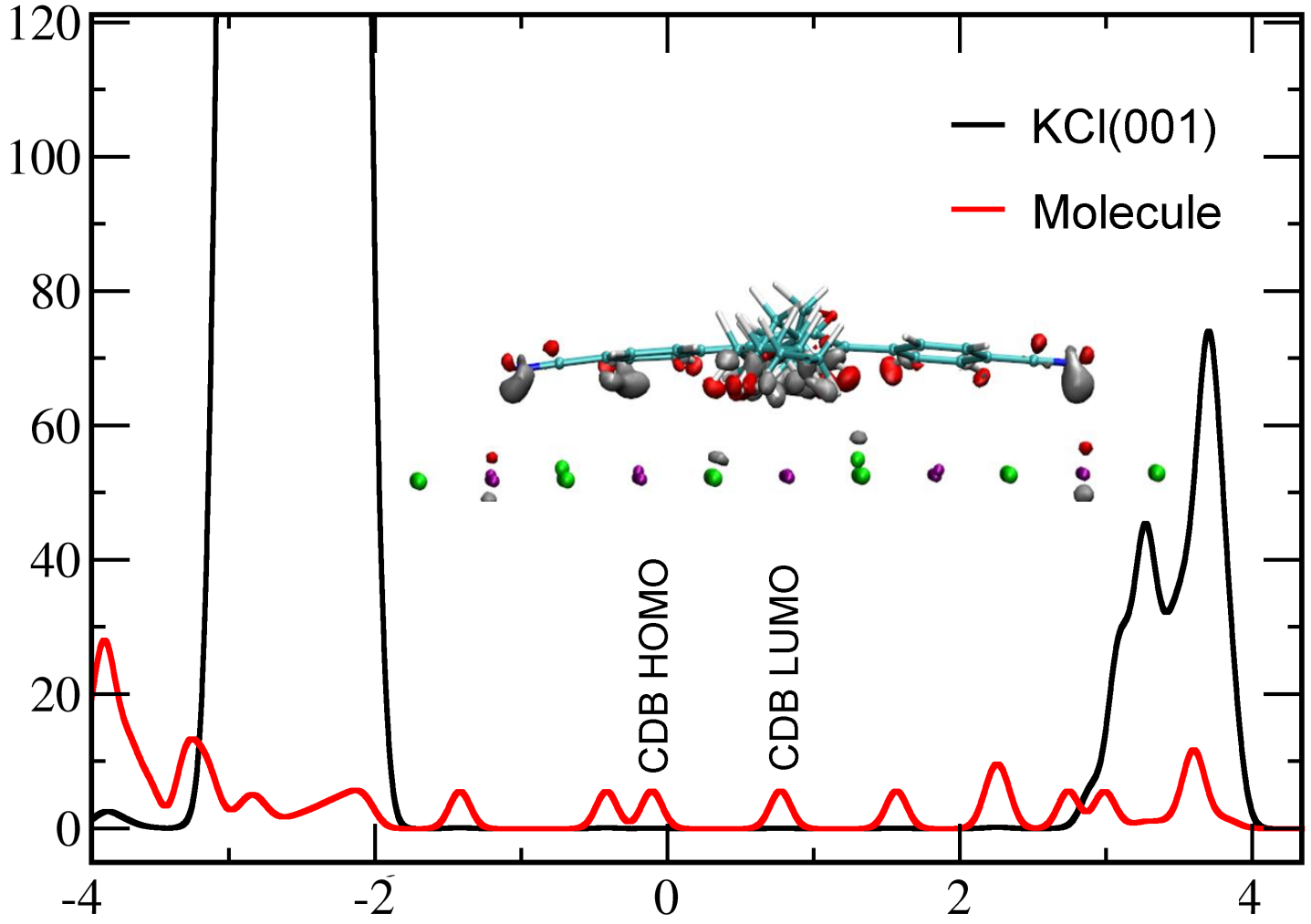


MM Representation of KCl(001): Previously Derived Pair Potentials:
C.R.A. Catlow , K.M. Diller , M.J. Norgett ,
J. Phys. C: Solid State Phys. ***1977, 10, 1395.***

(Note: Fixed Shells to Cores!)

Electronic Properties: CDB on KCl(001)

Full DFT DOS



D.Z. Gao, F. Federici Canova, M.B. Watkins, A.L. Shluger, *Journal of Computational Chemistry*, **2014**, Submitted

Step 2: Evaluate the QM/MM Model

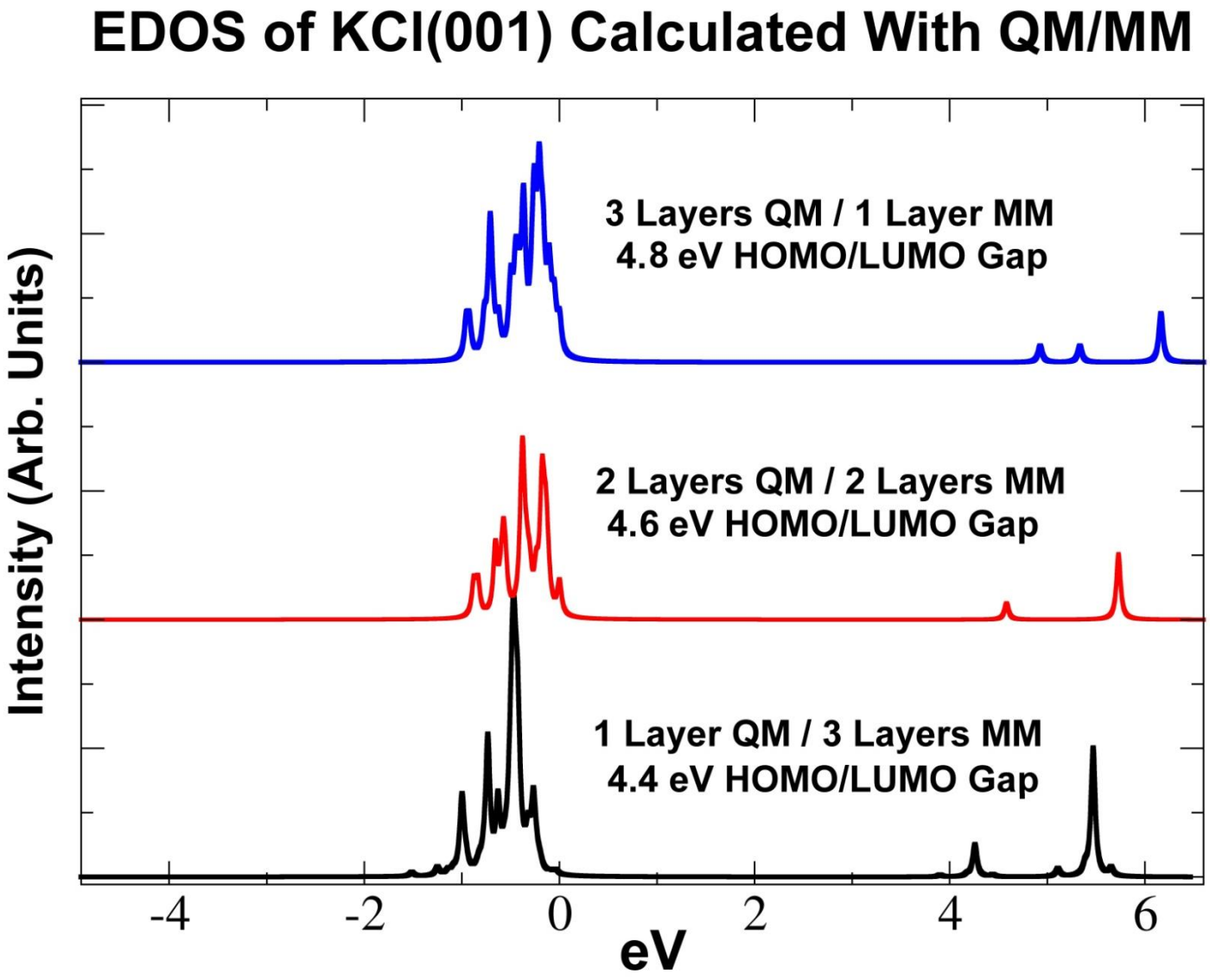
After choosing DFT and classical representations…. Evaluate QM/MM

- Compare known **physical properties** of the various representations
- Compare **electronic structure** of the DFT and QM/MM systems
- Check for some of the **common issues** related to embedding

Starting with some physical properties:
QM/MM indeed seems to work…

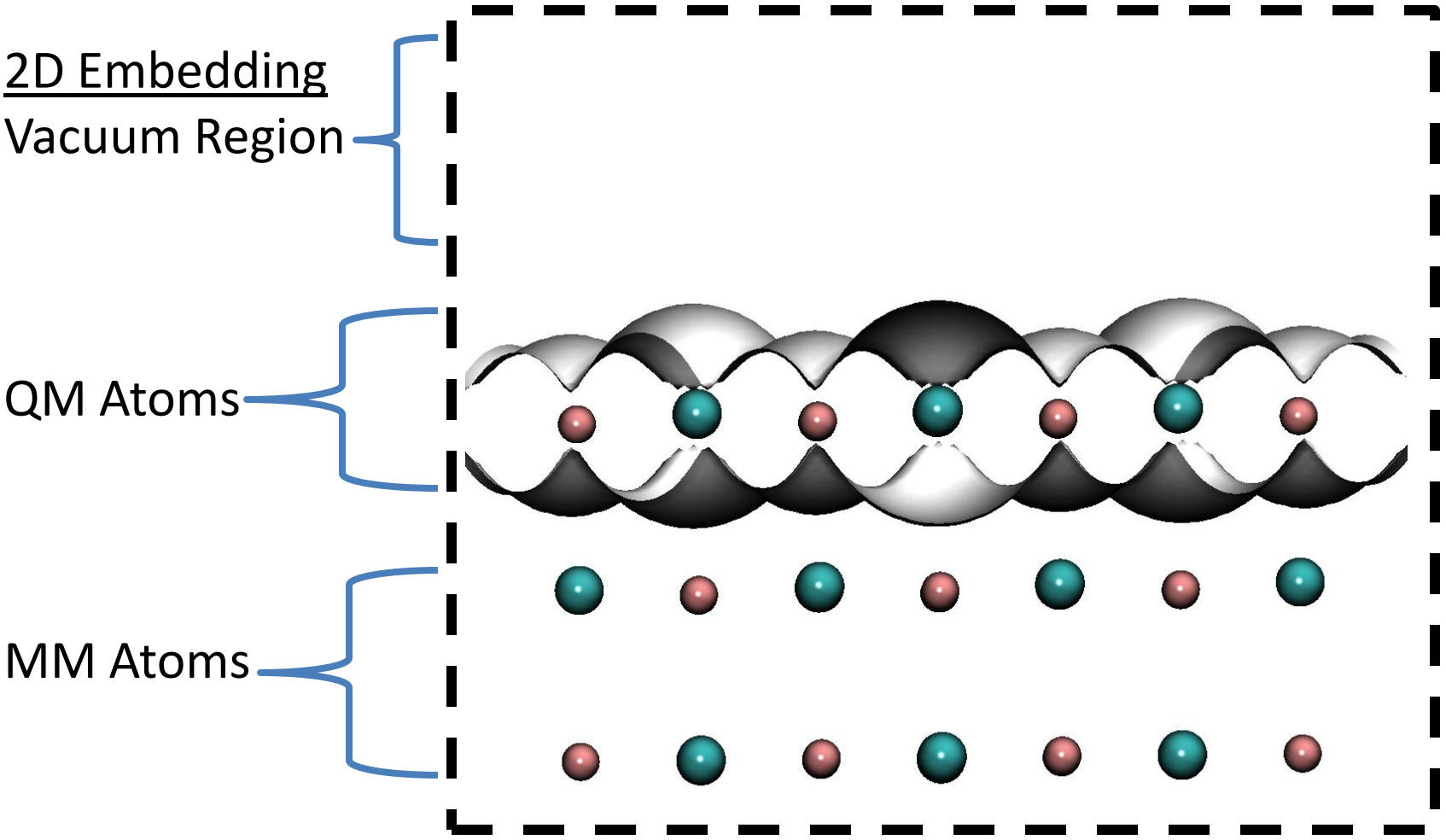
	Lattice Constant	Surface Rumpling	Band Gap
Experiment	6.3 Å	0.03 Å	7.6 eV
DFT (PBE-D2)	6.3 Å	0.03 Å	5.4 eV
1QM/3MM Layers	6.3 Å	0.04 Å	4.4 eV

D.Z. Gao, F. Federici Canova, M.B. Watkins, A.L. Shluger, *Journal of Computational Chemistry*, **2014**, Submitted



D.Z. Gao, F. Federici Canova, M.B. Watkins, A.L. Shluger, *Journal of Computational Chemistry*, **2014**, Submitted

Common Considerations: Electron Leakage



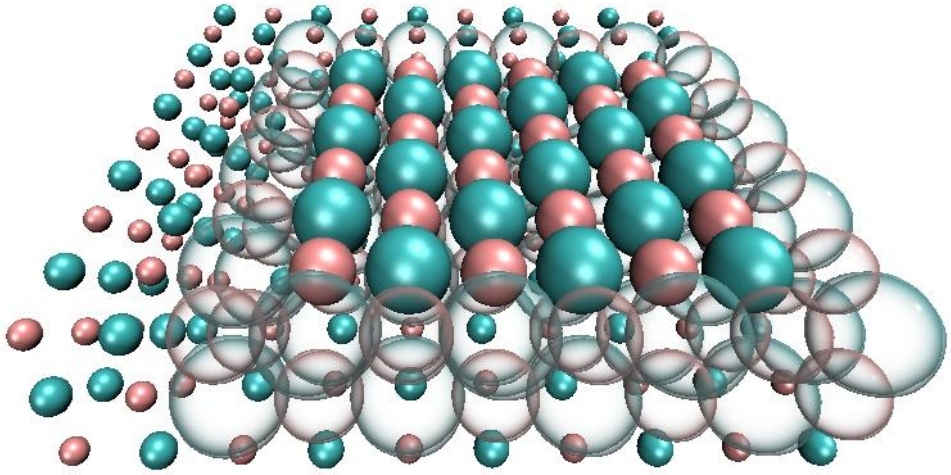
In previous embedded cluster studies charge leakage was an issue:

- Examine the electron density plots of the system
- Less of a problem in ionic materials , looks OK here!

Common Considerations: Border Potentials

QM atoms interact with MM atoms at the border…

- May not be properly represented using the standard force field
- Additive corrective potential may be added to improve the model



Some possible causes:

A. Difference in lattice constant in the QM and MM region
B. More complex interactions at the edge… covalent bonds etc?

Example Solution and Implementation… (for case A)

1. Fix the atoms to the desired positions
2. Optimize an additional set of additive pair potentials
3. Forces on border atoms should reach 0 ideally

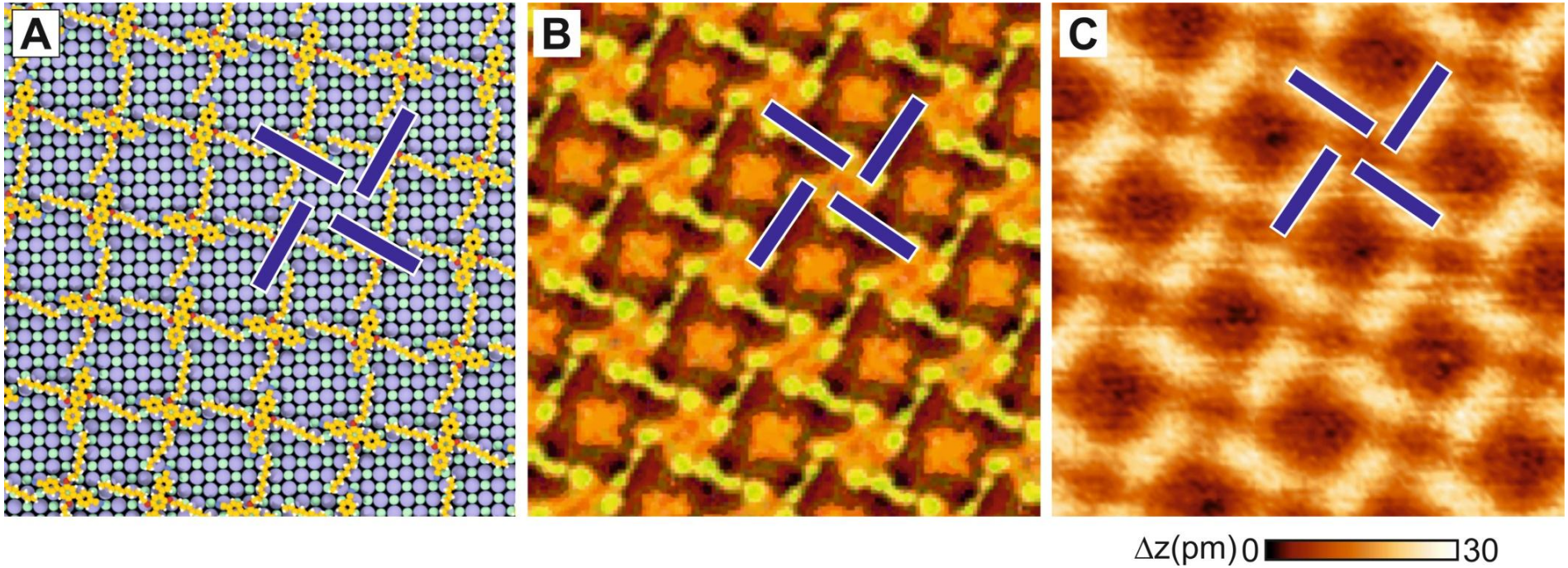
QM/MM CP2K Embedding Potentials Input Example

```
&MM

  &FORCEFIELD
    &CHARGE
      ATOM K
      CHARGE 1.0
    &END CHARGE
    &CHARGE
      ATOM Cl
      CHARGE -1.0
    &END CHARGE
    &CHARGE (border KCl)
      ATOM KZ
      CHARGE 1.0
    &END CHARGE
    &CHARGE
      ATOM ClZ
      CHARGE -1.0
    &END CHARGE
    &NONBONDED
      &WILLIAMS
       (the normal sets of potentials)
      &END WILLIAMS
      &WILLIAMS
          atoms K   ClZ
          A [eV] 4117.9
          B [angstrom^-1] 3.2808
          C [eV*angstrom^6] 0.0
          RCUT [angstrom] 5.0
      &END WILLIAMS
      &WILLIAMS
          atoms KZ  Cl
          A [eV] 4117.9
          B [angstrom^-1] 3.2808
          C [eV*angstrom^6] 0.0
          RCUT [angstrom] 5.0
      &END WILLIAMS
      (all other possible pairings)
    &END NONBONDED
    &END FORCEFIELD

    &POISSON
      &EWALD
        EWALD_TYPE spme
        ALPHA .44
        GMAX  40
      &END EWALD
    &END POISSON

&END MM
```

If you need border potentials for KCl (001) bulk material or some scripts to do this just ask

Periodic Monolayer Structures: CDB on KCl (001)

Advanced Materials Interfaces, **2014**, 1, 1400414.

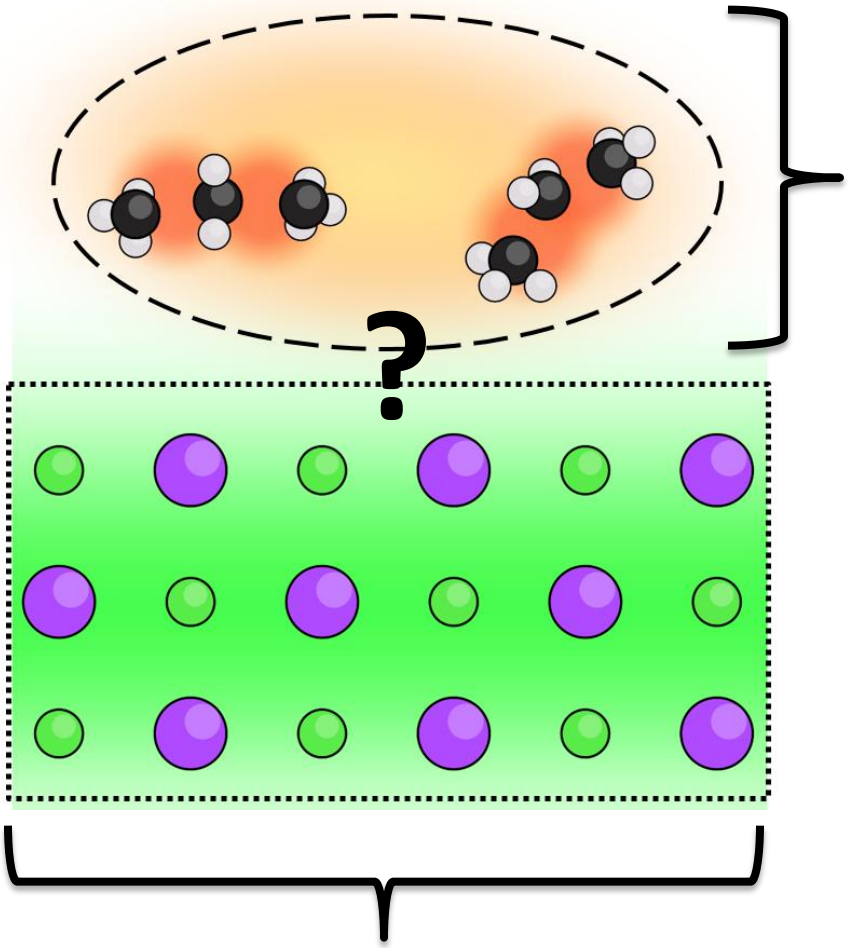


[A] Investigate various possible monolayer configurations

- Constrained using the periodicity of the pattern from experiment
- Enantiomers (i.e. molecules flipped over) result in degenerate patterns
- Adsorption energy **per molecule** increases to 3.4 eV in these configurations

[B] Simulate AFM images to [C] interpret experimental results…

Creating a Force Field for CDB/TCB on KCl (001)



CHARMM Force Field for the molecule

B.R. Brooks, C.L. Brooks, A.D. Mackerell, et al.
J. Comput. Chem. **2009**, 30, 1545-1614.

Classical Representation of KCl(001):

C.R.A. Catlow , K.M. Diller , M.J. Norgett ,
J. Phys. C: Solid State Phys. ***1977, 10, 1395.***

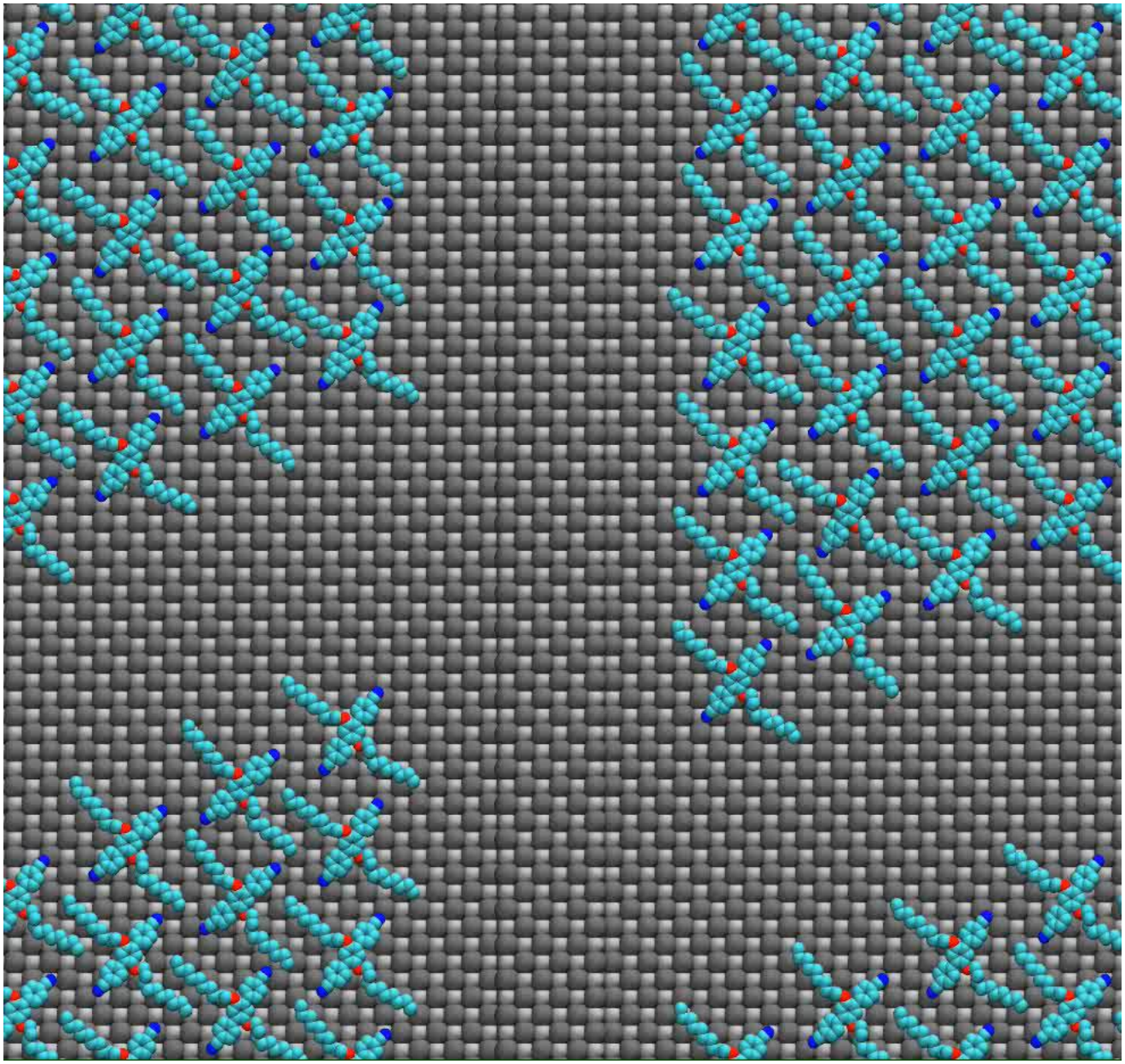
1) Use **QM/MM** to generate fitting data

2) Genetic algorithm to fit large numbers of variables simultaneously

3) Evaluate force field

4) Study dynamics within the system

Molecular Dynamics… a quick example!



Thanks!

UCL

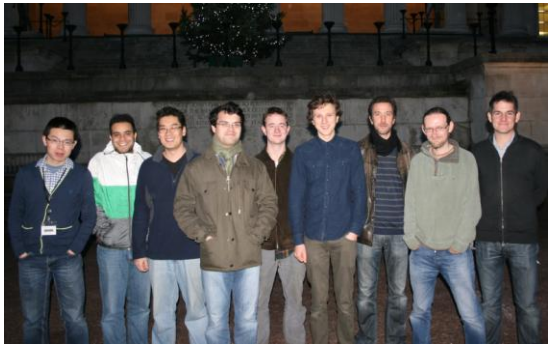
Conclusions

QM/MM can greatly reduce cost if:
•Only some interactions are critical
•MM potentials are available

General Steps:
•Select QM and MM parameters
•Test electronic and physical properties
•Check for some common breakdowns

http://www.cp2k.org/exercises:2014_uzh_molsim:index : Marcella Iannuzzi

http://www.archer.ac.uk/training/course-material/2014/08/CP2K/Slides/QMMM.pdf



LCN LONDON CENTRE FOR NANOTECHNOLOGY

THE THOMAS YOUNG CENTRE TyC

AIMR

nanolayers