ASSC2006 (Spokane, Sept. 2006)
LOCAL DEFECTS IN SOLIDS

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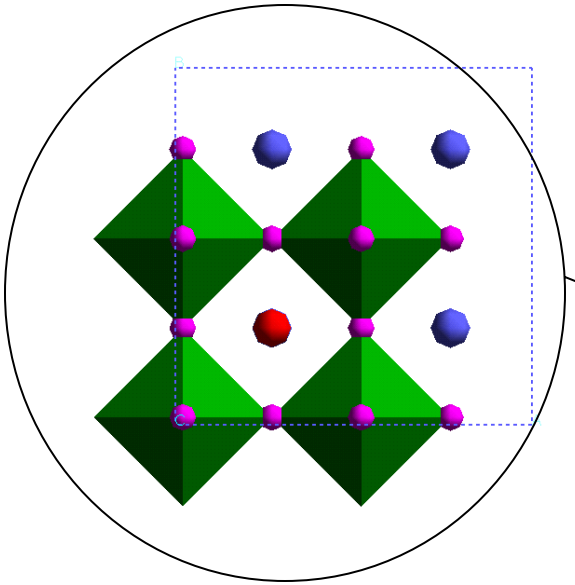
FURIO CORA' 22/09/2006

UCL

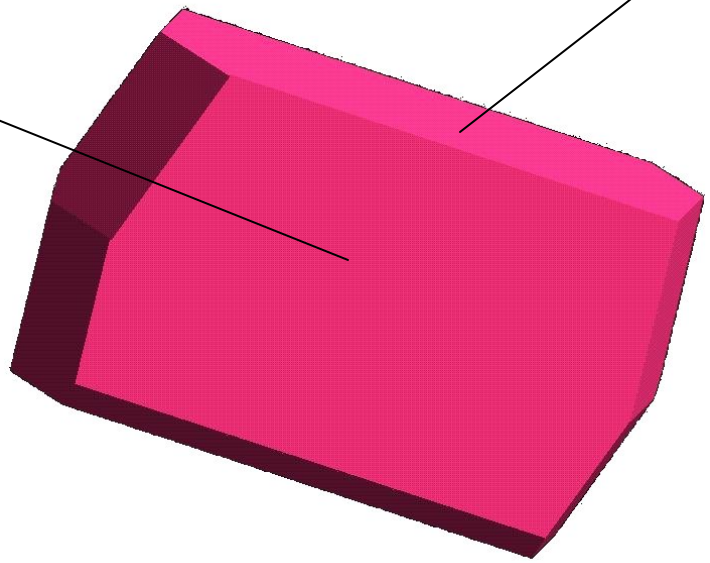
DEFINITION OF THE PROBLEM

N_A ATOMS → O(10^{23})

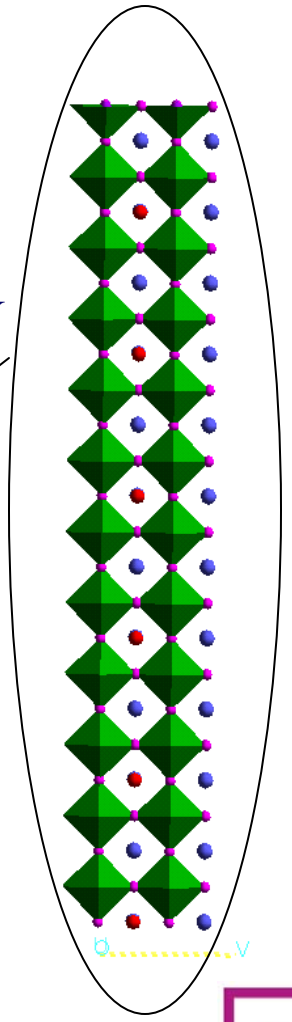
LOCAL/COLLECTIVE PROPERTIES



BULK PROPERTY

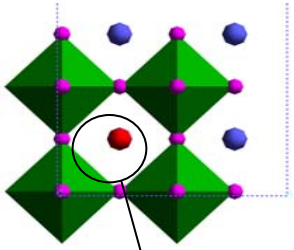


SURFACE PROPERTY



DEFECTS IN BULK/SURFACE

$O(N_A)$ ATOMS → NEED TO BE CLEVER MODEL OF THE REAL SOLID



PARTICULARLY IMPORTANT FOR DEFECTS:
BREAK LOCALLY THE TRANSLATIONAL SYMMETRY OF CRYSTALS

THE CHOICE OF THE MODEL DEPENDS ON THE TYPE OF PROPERTY:

-LOCAL:

BOND BREAKING IN CATALYSIS
MIGRATION OF DEFECTS

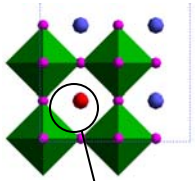
-COLLECTIVE:

ELASTIC CONSTANTS (BULK MOD)
CONDUCTIVITY
RESPONSE TO EXTERNAL FIELDS

Ri

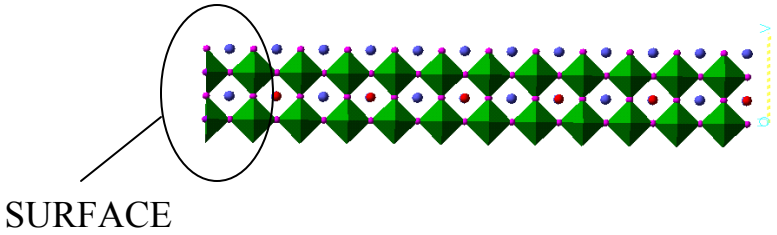
CHOICE OF COMPUTATIONAL SETTINGS

1) THE MODEL OF THE DEFECTIVE SOLID



CLUSTER
PERIODIC BOUNDARY CONDITIONS (SUPERCELL)
EMBEDDED CLUSTERS

SLAB
PERIODIC SLAB



2) HAMILTONIAN

3) CODE-SPECIFIC PARAMETERS

BASIS SET

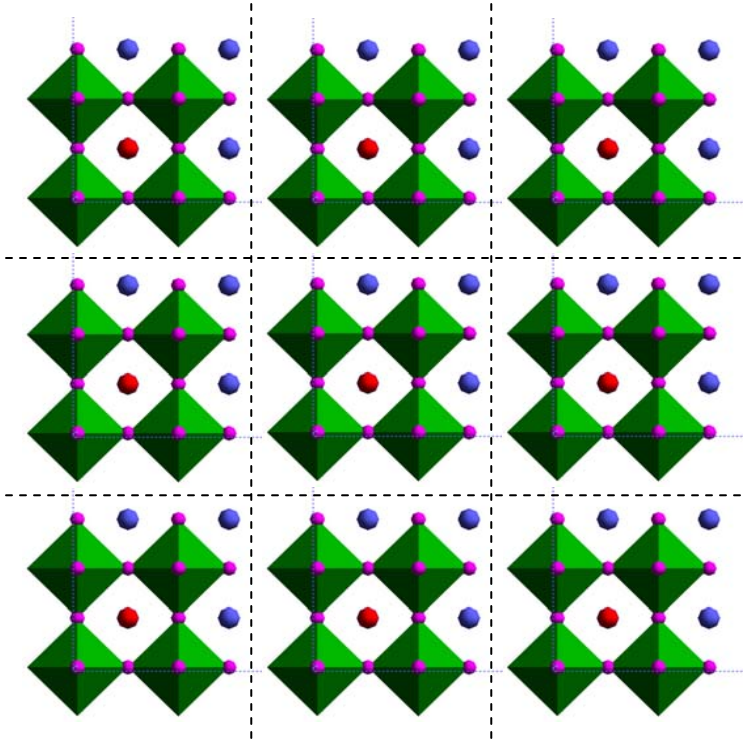
MODEL OF THE SOLID IN DEFECT STUDIES

SUPERCELL APPROACH

Periodic image of the defect centre

Interaction between defects
Treat all ions with same accuracy

Describe properly the extended nature of the solid



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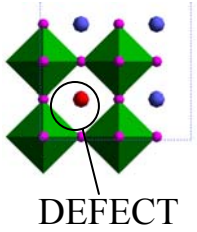
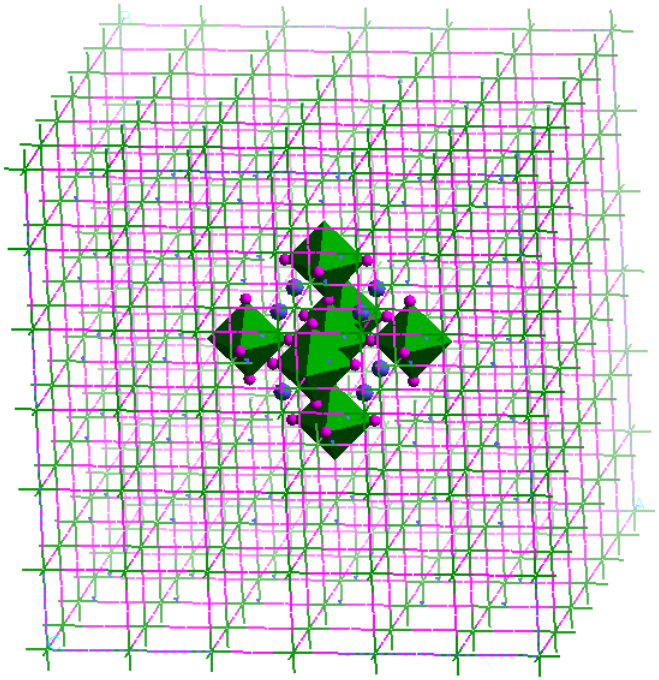
MODEL OF THE SOLID IN DEFECT STUDIES



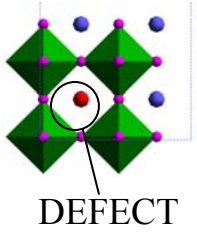
ISOLATED and EMBEDDED CLUSTER

Divide crystal into two or more zones treated with decreasing accuracy (efficient, but introduce interfaces)



DISCARD (more or less explicitely) THE EXTENDED NATURE OF THE SOLID; TRY TO RECOVER AS MUCH AS POSSIBLE MAKING MODEL MORE SOPHISTICATED

MODEL OF THE SOLID IN DEFECT STUDIES



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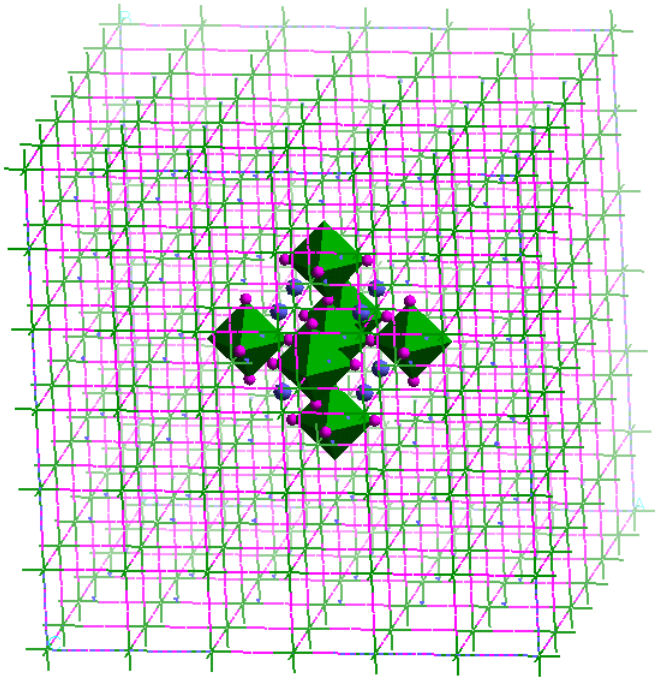
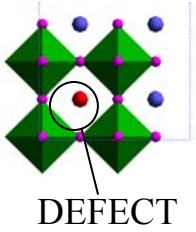
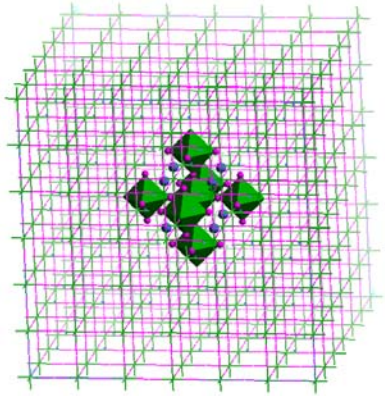


Zone 1	Zone2	Model name
QM	QM	Green's functions
QM	IP	QM/MM
QM	Charges	Embedded cluster
QM	Bond saturation	Embedded cluster
QM	None	Isolated cluster
IP	continuum	Mott-Littleton
QM	Finite cluster	ONIOM

ISOLATED and EMBEDDED CLUSTER





Zone 1	Zone2	Made-lung field	Long-range relax.	Steric constraints	Delocalised electronic states
QM	QM	√	√,X	√	√
QM	IP	√	√,X	√	X
QM	Charges	√	X	X	X
QM	Bond saturation	X	X	X	X
QM	None	X	X	X	X
IP	continuum	√	√	√	X

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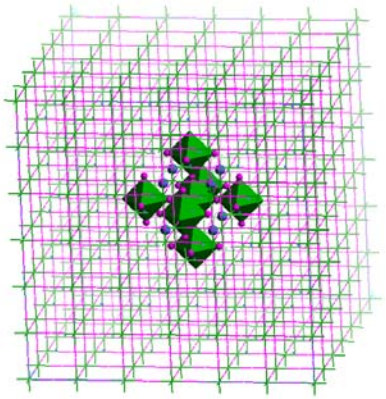
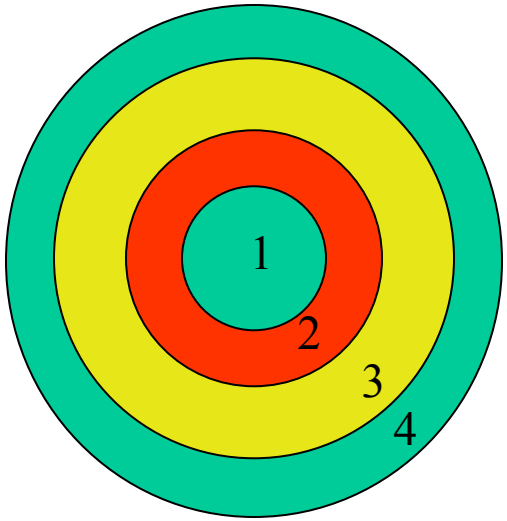
EMBEDDED CLUSTER: ADDITIVE/SUBTRACTIVE SCHEMES





ADDITIVE: EACH ZONE TREATED AT ONLY ONE LEVEL
SUBTRACTIVE: CENTRAL ZONE(S) TREATED AT MORE THAN ONE LEVEL

ONIOM: $E_{TOT}=E_1(HIGH)+E_2(LOW)-E_1(LOW)$
or $E_1(HIGH)+E_2(MED)-E_1(MED)+E_3(LOW)-E_2(LOW)$
etc

CONSISTENCY OF DESCRIPTION WITH DIFFERENT HAMILTONIANS

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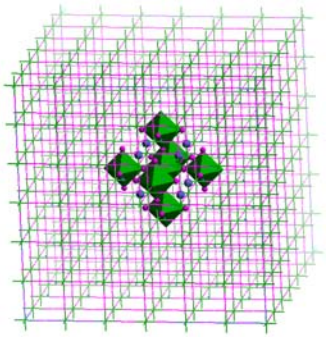
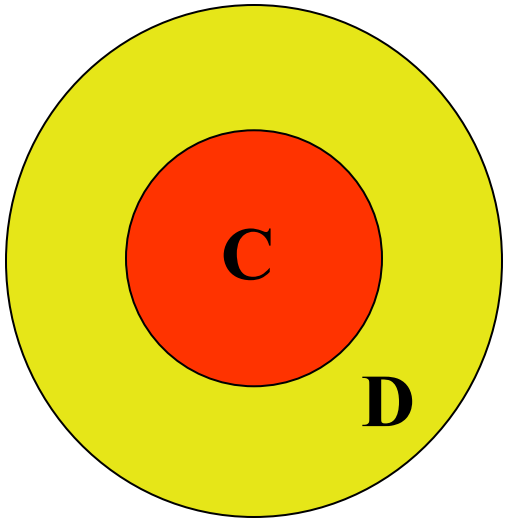
THE PERTURBED CLUSTER THEORY
And the code EMBED (QM/QM embedding)





TWO REGIONS: C,D

PARTITION REPRESENTATIVE MATRICES;

$$P,H \equiv \begin{array}{|c|c|} \hline \textbf{CC} & \textbf{CD} \\ \hline \textbf{DC} & \textbf{DD}^{(f)} \\ \hline \end{array}$$

USE PERFECT CRYSTAL SOLUTION (f) FOR BLOCK DD; CLUSTER SOLUTION FOR CC; COUPLING FOR CD/DC

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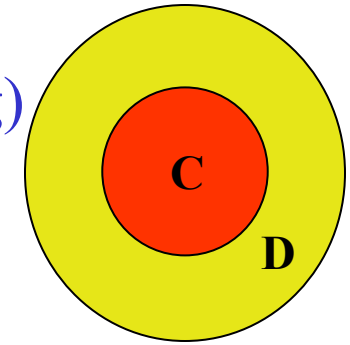
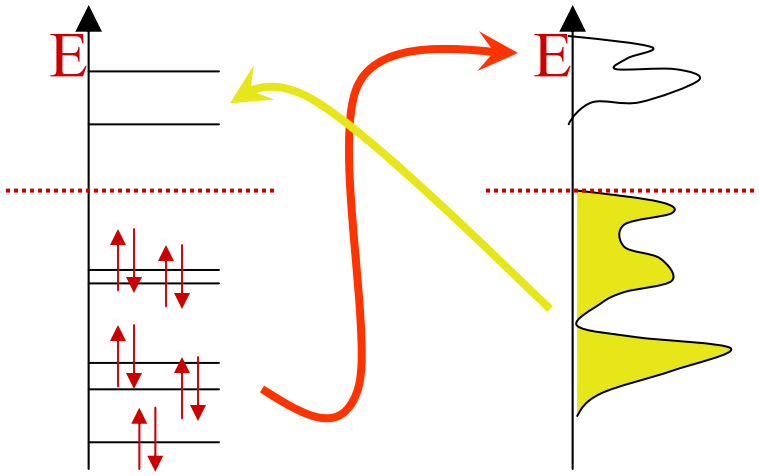
THE PERTURBED CLUSTER THEORY
And the code EMBED (QM/QM embedding)



ELECTRONS IN REGIONS C,D ARE NOT ISOLATED:
COUPLING BETWEEN CLUSTER (C) AND OUTER (D)
SOLUTIONS: OPTIC (energy-dependent) POTENTIAL
BASED ON GREEN'S FUNCTIONS THEORY



CLUSTER SOLUTION

OUTER SOLUTION

EMPTY LEVELS OF C COUPLED WITH FILLED BANDS OF D AND VICE-VERSA.
OPEN SYSTEM FOR ELECTRONS; ELECTRONIC CHEMICAL POTENTIAL

C.Pisani, U.Birkenheuer, S.Casassa, F.Corà,
EMBED01 User's Manual, University of Torino.
www.theochem.unito.it/EMBED/embed.html

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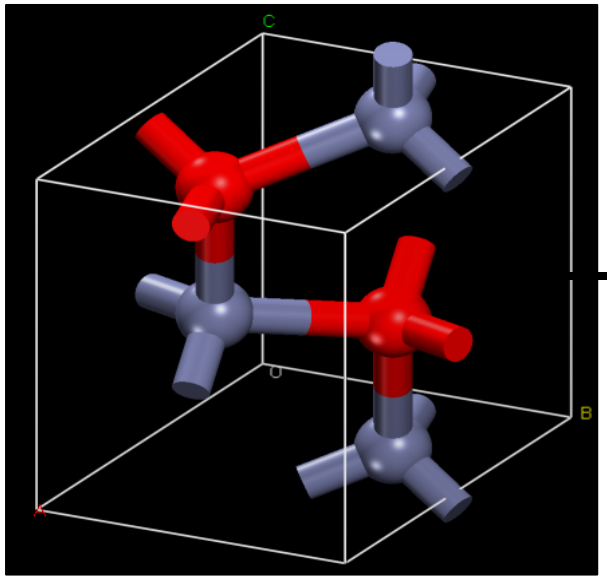
QM/MM EMBEDDING: QUASI / CHEMSHELL

Zeolites	CLRC Daresbury Lab	Norsk Hydro
	Paul Sherwood	
Enzymes	Zurich Technical University	BASF
	Max Planck Institut Muhlheim	
	Walter Thiel	
Metal Oxides	The Royal Institution of Great Britain	ICI/Synetix
	Richard Catlow	

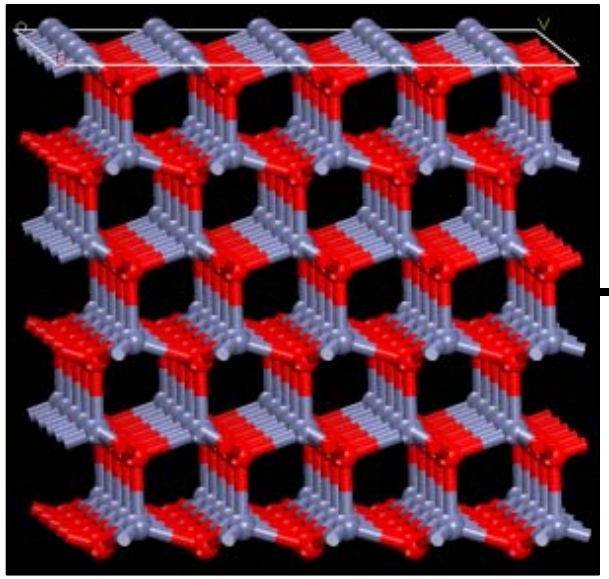
European Commission Esprit Project (EP 25047) & Industry

QM/MM surface embedding

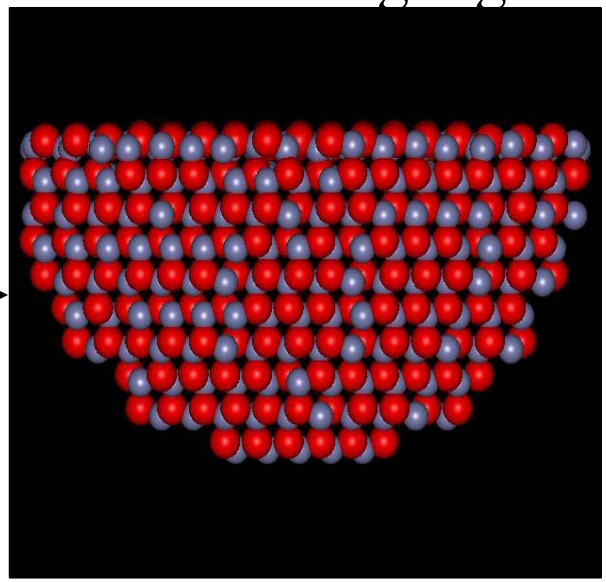
MM bulk



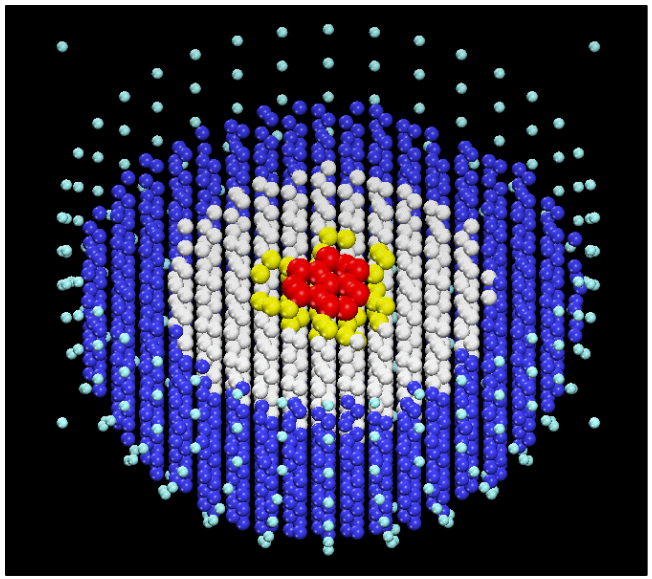
MM surface



MM embedding region



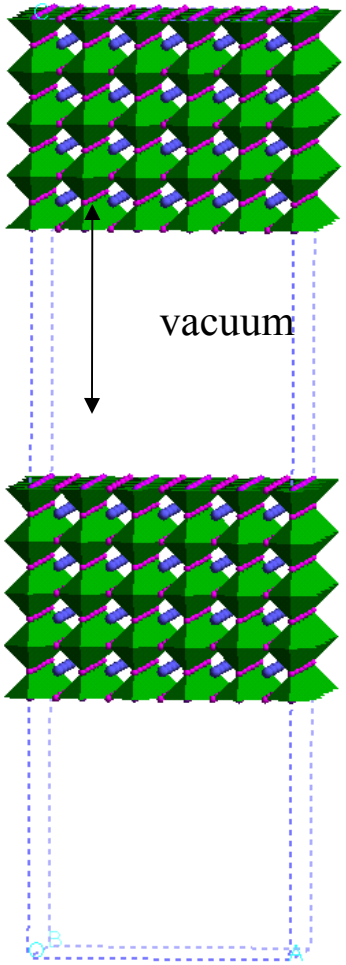
User Input Required to Choose QM region

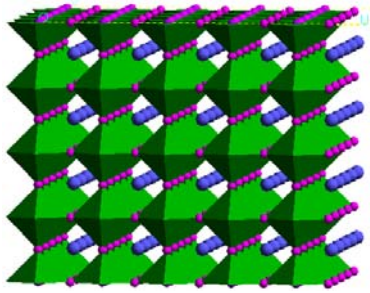


Ready to Run

MODELS OF A DEFECTIVE SURFACE

SINGLE or PERIODIC SLAB
OF FINITE THICKNESS
(vacuum layer thickness)

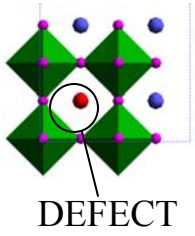




SURFACE DEFECTS:
Combine supercell+slab models

CHOICE OF THE MODEL

WHICH PROPERTY ARE WE INTERESTED IN?
WHICH HOST SYSTEM?



LOCAL:

↓

- POINT DEFECTS
- STRUCTURE AROUND DOPANT
- CHEMICAL REACTIVITY

CLUSTER

PERIODIC BOUNDARY CONDITIONS (SUPERCELL)

EMBEDDED CLUSTERS

COLLECTIVE:

↓

- ELASTIC CONSTANTS, BULK MOD
- DIELECTRIC CONSTANTS
- PHONON SPECTRUM
- FERROELECTRIC POLARISATION
- PIEZOELECTRIC CONSTANTS

PERIODIC MODEL

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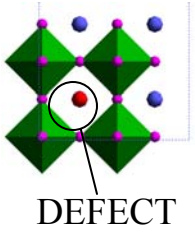
OPTIONS AVAILABLE IN CRYSTAL



-SUPERCELL
-DEFINITION OF CLUSTER FROM A PERIODIC STRUCTURE
(isolated or saturated with H only)
-information for EMBED

TIP: USE GEOMETRY-EDITING OPTIONS AVAILABLE
RETAIN MAXIMUM NUMBER OF SYMMETRY ELEMENTS!

AVAILABLE KEYWORDS: Manual, page 24 ff
-SUPERCELL
ATOMDISP, ATOMINSE, ATOMREMO, ATOMSUBS, etc
-DEFINITION OF CLUSTER
CLUSTER, HYDROSUB, etc

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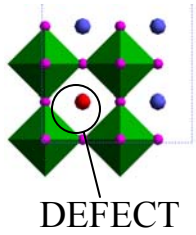
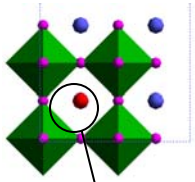
OBSERVABLES OF INTEREST



1) DEFECT FORMATION ENERGY
   feasible? Equilibrium concentration?
2) EQUILIBRIUM STRUCTURE
3) CHEMISTRY AROUND DEFECT
   catalytic activity
   physi/chemi-sorption
   energy levels
4) COLLECTIVE PROPERTIES
   conductivity
   elastic/piezoelectric constants

USEFUL CHECKS (MUST!)



Whether we choose a supercell or cluster-related description of defects, two checks enable us to test the accuracy of our model

1) The self-embedding test:
   The system without defects must reproduce the properties of the periodic host crystal under PBC.
   Important in cluster-based methods: are border atoms the same as atoms in the centre?
2) The size consistency test:
   How stable are the results as a function of increasing system size?
   For instance, how does the observable of interest change if we double the size of the supercell (cluster)?

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DEFECT FORMATION ENERGY

Write a suitable MASS/CHARGE-BALANCED chemical equation that corresponds to the process examined, leading to the creation of the defect.

Always define it in the paper, and refer energies to this equation.

For instance: dopant incorporation in a crystal.

How is it performed experimentally?

Sol-gel? Sintering? Deposition from a precursor? Hydrothermal? Each method corresponds to a different chemical reaction leading to the same defect.

No general rule; use examples

EXAMPLE FROM THE LITERATURE

1) EFFECT OF DOPING ON IONIC CONDUCTION IN $LaCoO_3$ ($2Me^{2+}/La^{3+} + V_o^{2+}$)

- Ionic description: interatomic potentials
- Defect problem: supercell and/or Embedded cluster

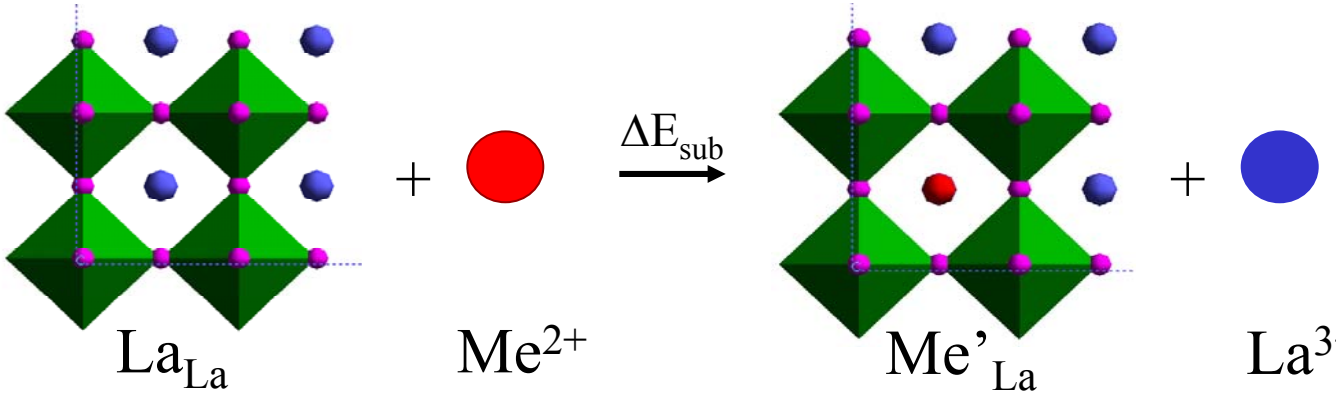
From: M.S.Islam, J. Mater. Chem 10 (2000) 1027
M.S.D. Read et al., J.Mater. Chem 10 (2000) 2298
M.Cherry et al., J. Solid St. Chem. 118 (1995) 125

Studied with interatomic potentials; complex structures are still expensive with QM methods, but definitions are the same.

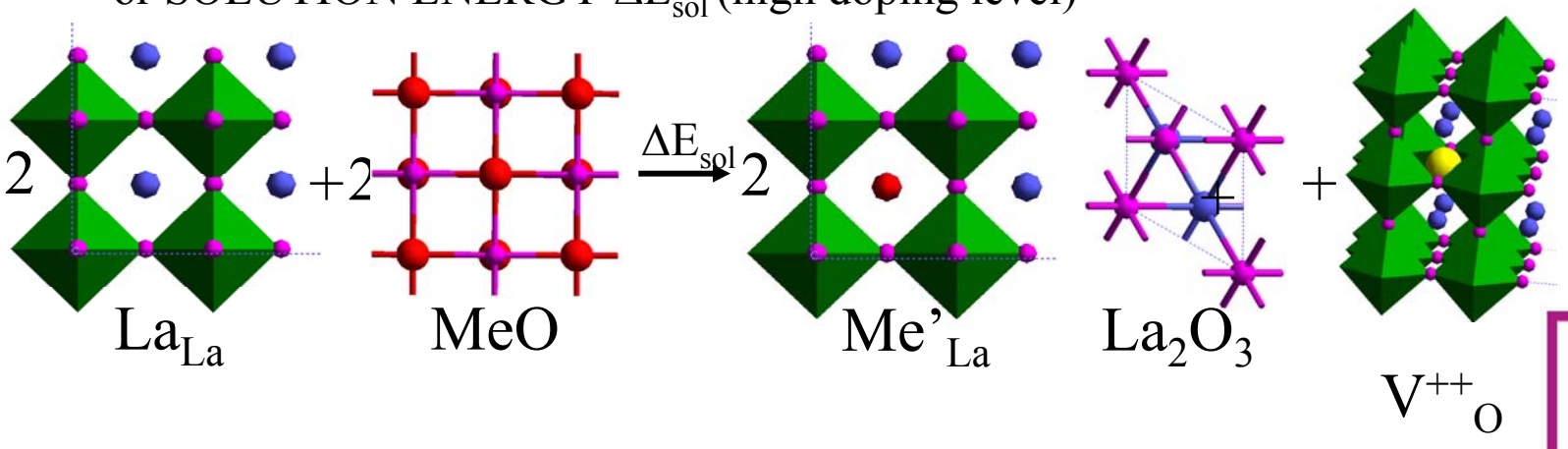
Don't use your F1 on a cross country circuit!

1) DOPING IN $LaCoO_3$ - Me^{2+} SOLUBILITY

ANSWER: DEFECT FORMATION ENERGY ΔE_{sub} (low doping level)

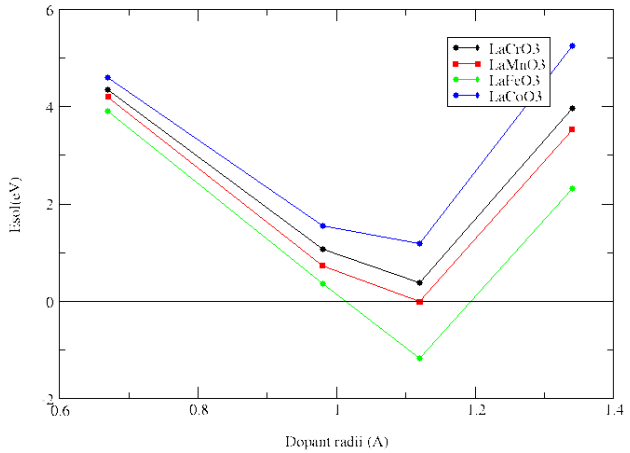


or SOLUTION ENERGY ΔE_{sol} (high doping level)



1) DOPING IN $LaMO_3$ - Me^{2+} SOLUBILITY

RESULTS



	E_{sol}(eV/dopant)			
Compound	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$LaCrO_3$	4.35	1.06	0.37	3.97
$LaMnO_3$	4.20	0.73	-0.01	3.53
$LaFeO_3$	3.92	0.35	-1.17	2.31
$LaCoO_3$	4.60	1.54	1.18	5.26

SIZE MATTERS!!!

SIZE COMPATIBILITY HOST/DOPANT

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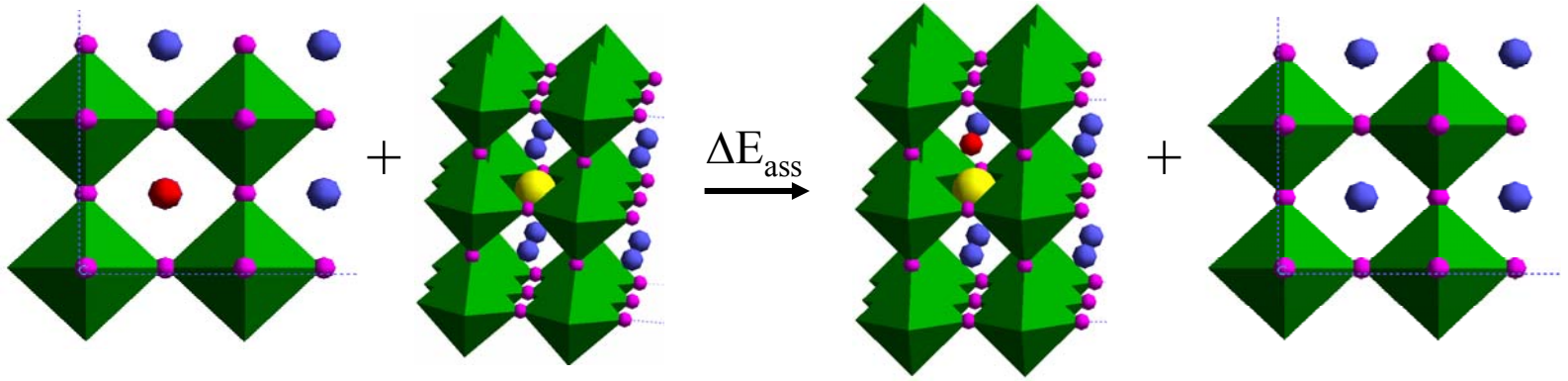
2) DOPING IN $LaMO_3$ – DEFECT ASSOCIATION

ANSWER: DEFECT ASSOCIATION ENERGY ΔE_{ass}

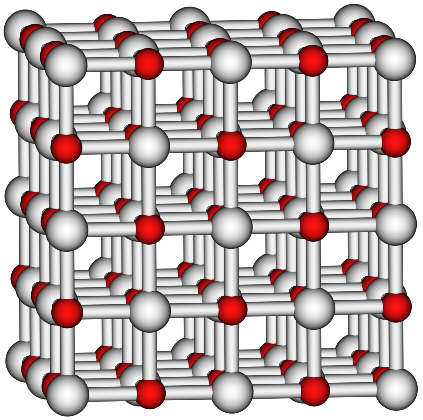


Me'_{La} V^{++}_{O} $[Me_{La}V_O]^+$ La_{La}

RESULTS:

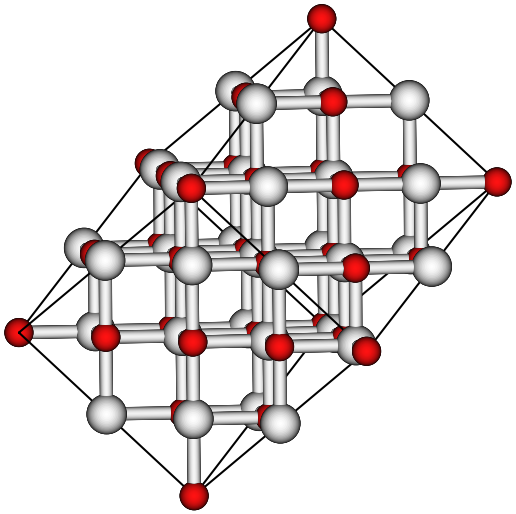
Host / Dopant	$LaGaO_3$	$LaCrO_3$	$LaMnO_3$	$LaFeO_3$	$LaCoO_3$
Mg/M	-1.37				-0.94
Ca	-0.19				-0.30
Sr	-0.02	0.03	0.35	1.10	-0.19

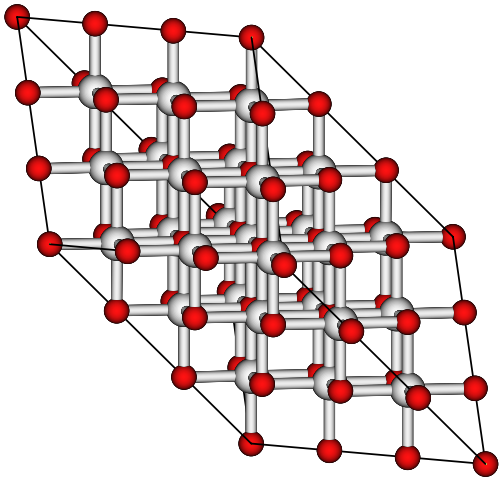
Li-doping in MgO; charge-balanced by 1 hole
Possible supercells:



$n_x n_x n$ crystallographic cell
8,64,216 atoms

$2n_x 2n_x 2n$ double cell
32,256 atoms





$n_x n_x n$ primitive cell
8,16,54,128,250 atoms

Check convergence of results

Li-MgO convergence of results

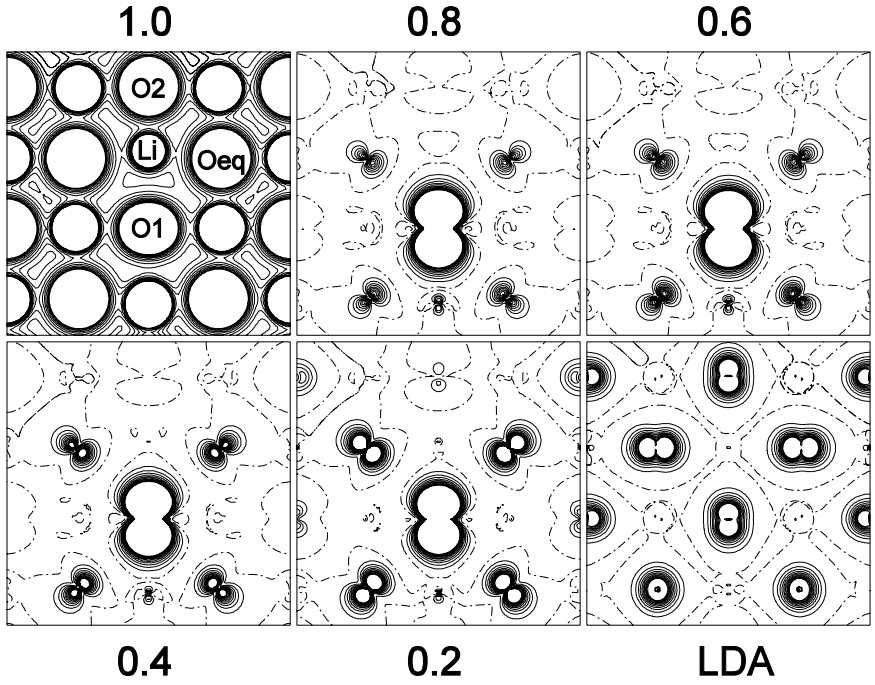
FORMATION ENERGY:

$\Delta E = E(MgO:[Li]^0) - E(MgO) + E(Mg^{at}) - E(Li^{at})$

					^{7}Li	EPR	
n	ΔE	q(Li)	Q(O-)	μ(O-)	*a*	*b*	P
32	0.15102	0.982	-0.979	0.983	0.122	3.180	-0.015
54	0.15108	0.982	-0.977	0.983	-0.385	3.039	-0.014
64	0.15144	0.982	-0.978	0.983	-0.245	3.216	-0.013
128	0.15083	0.982	-0.977	0.983	-0.548	3.022	-0.013
216	0.14993	0.982	-0.977	0.983	-0.820	3.037	-0.013
250	0.15027	0.982	-0.977	0.983	-0.801	3.023	-0.013
256	0.15033	0.982	-0.976	0.983	-0.776	3.023	-0.013

SPIN DENSITY Li-hole in MgO

COMPARISON OF HAMILTONIANS:
HYBRID EXCHANGE FUNCTIONALS



TOTAL (a_x=1.0)
AND
SPIN ELECTRON
DENSITY

F. Corà et al., page 171-232 in J.McGrady and N. Kaltsoyannis (Ed), DFT in Inorganic Chemistry, Structure and Bonding, Vol. 113, Springer-Verlag, Heidelberg, 2004.
F.Corà G. Mallia, in preparation.

Ri

TRANSITION METAL DOPED ALUMINOPHOSPHATES - IMPLICATIONS FOR CATALYSIS

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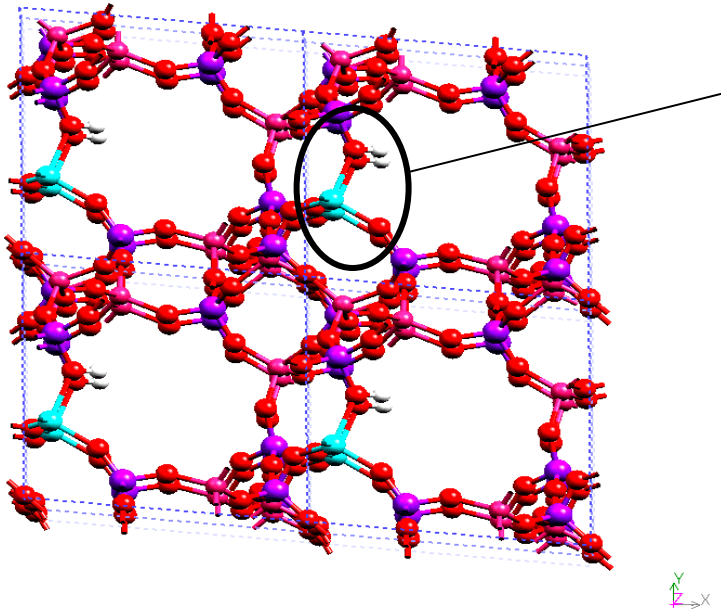
SUPERCELL MODEL OF DEFECT CENTRES
SUBSTITUTIONAL (DOPANT) IONS

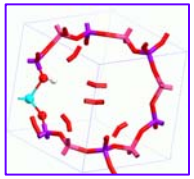


Representation of a Me^{II} substitutional ion, charge –compensated by an acidic proton, in the AlPO-34 framework, described with periodic boundary conditions.

Dopants examined: $M^{2+}(H^{+})/Al^{3+}$ in AlPO-34: Cr, Mn, Fe, Co, Ni, Zn; Be, Mg, Ca, Sr

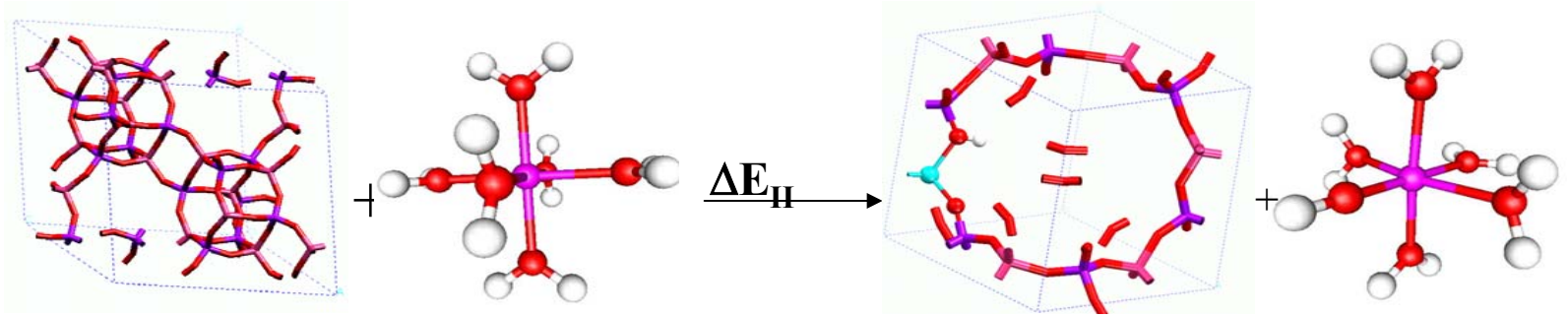
M^{3+}/Al^{3+} Cr, Mn, Fe, Co; B, Ga

$M^{3+}(H^{+})/Si^{4+}$ in Chabasite Cr, Mn, Fe, Co; B, Al, Ga



Substitutional energy of a framework Al with Me^{II}dopants

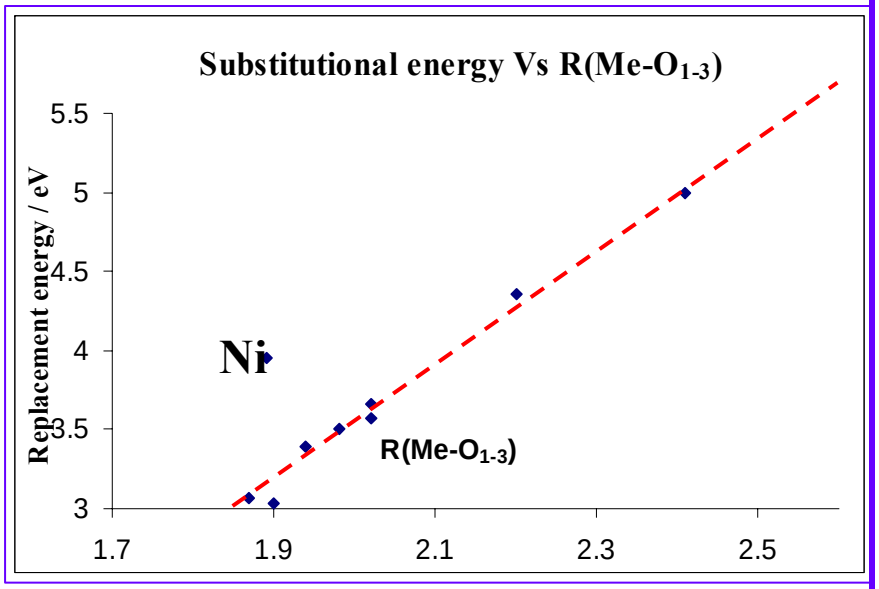
HYDROTHERMAL SYNTHESIS



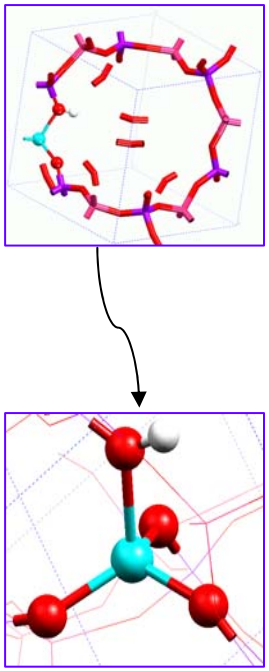
Pure AlPO-34 $[Me^{II}(H_2O)_6]^{2+}$ *Me^{II}AlPO-34* $[Al(H_2O)_5(OH)]^{2+}$

Me^{II}	Mg^{II}	Ca^{II}	Cr^{II}	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Zn^{II}	Sr^{II}
ΔE_{II} /eV	3.067	4.351	3.576	3.660	3.508	3.393	3.948	3.038	4.996

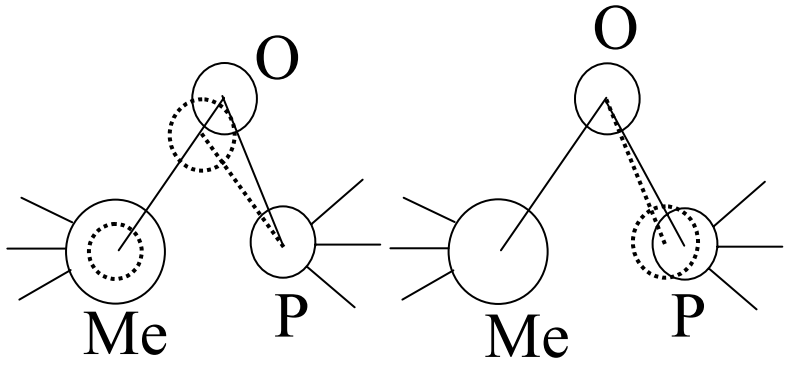
- With the exception of Ni^{II}, which is unstable in tetrahedral coordination, the replacement energy increases linearly as a function of the Me-O bond distance.
- The larger the size of the metal dopant, the more difficult its inclusion in the AlPO framework

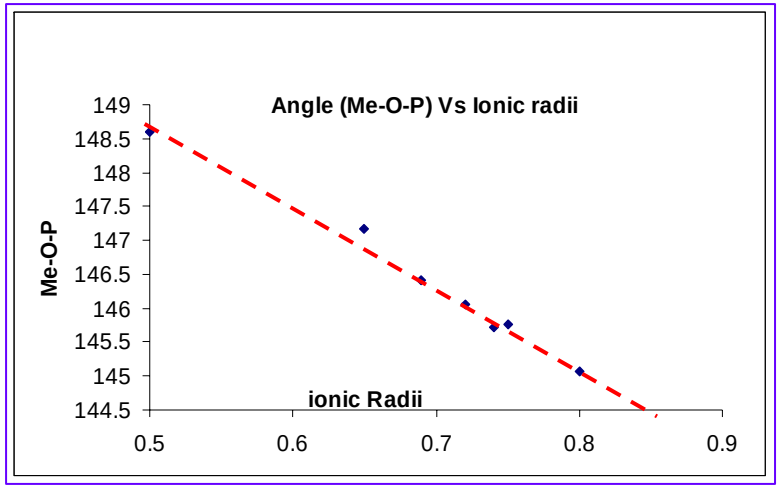


EQUILIBRIUM STRUCTURE



Me^{II}	$r(Me^{II}-O_1)$	$r(Me^{II}-O_2)$	$r(Me^{II}-O_3)$	$r(Me^{II}-O_4H)$	AVG $r(Me^{II}-O)$	Exp ± 0.02 EXAFS
Mg^{II}	1.85	1.87	1.91	2.08	1.93	1.94
Ni^{II}	1.91	1.92	1.93	2.11	1.98	1.99
Zn^{II}	1.90	1.90	1.91	2.18	1.99	1.96
Cr^{II}	1.99	2.03	2.04	2.35	2.11	-
Co^{II}	1.95	1.94	1.94	2.14	1.99	1.94
Fe^{II}	1.99	1.97	1.98	2.19	2.01	-
Mn^{II}	2.02	2.04	2.01	2.26	2.08	2.02
Ca^{II}	2.17	2.19	2.24	2.40	2.25	-
Sr^{II}	2.36	2.42	2.44	2.55	2.44	-

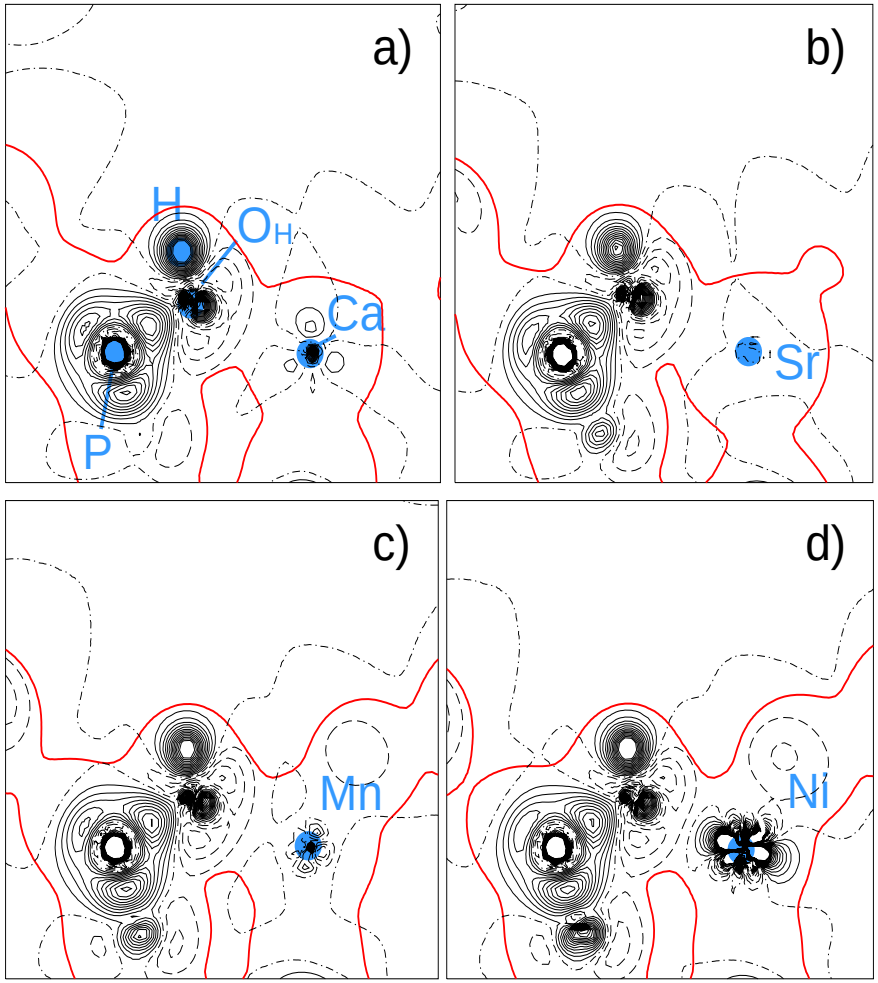




CHEMISTRY

Difference electron density maps (solid - isolated ions) for 2+ dopant ions in AlPO-34

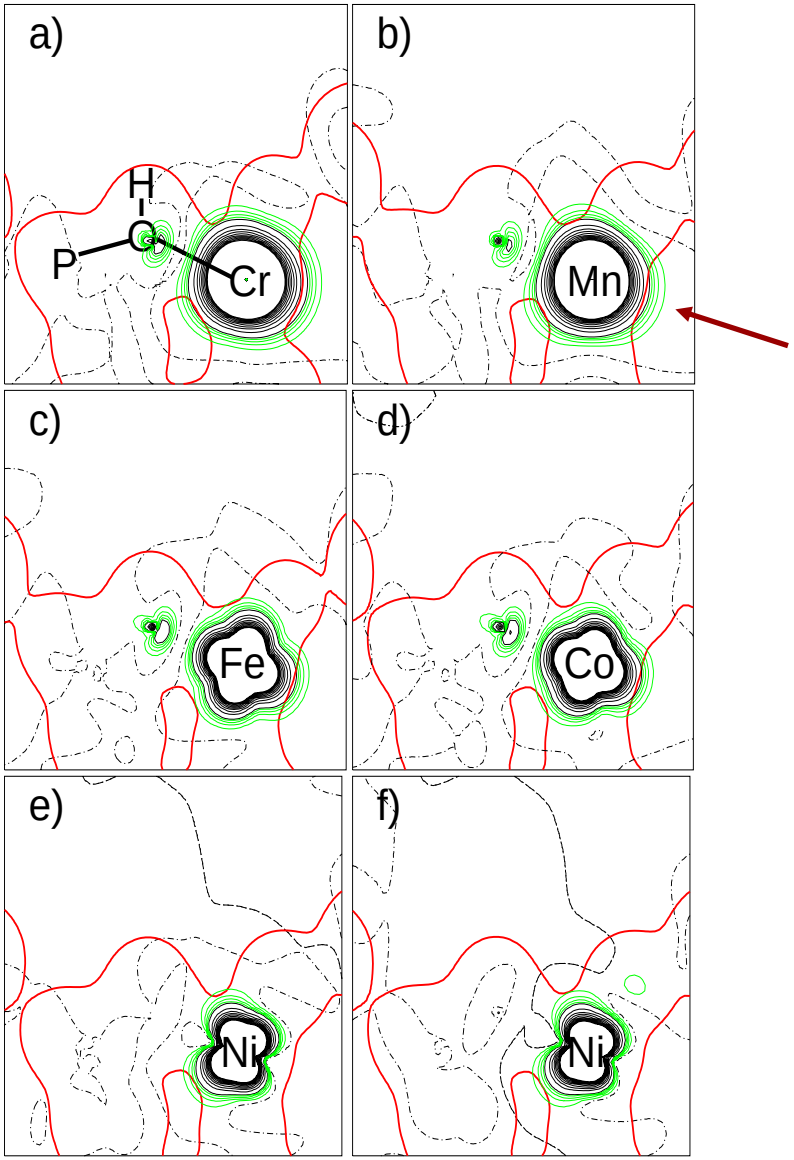
a) Ca-OH-P, b) Sr-OH-P, c) Mn-OH-P, or d) Ni-OH



Continuous and dashed lines correspond to positive and negative densities. The red line indicates the framework size.

I Saadoune, F. Corà and C.R.A. Catlow, *J. Phys. Chem. B*, **2003**, *107*, 3003.

LEWIS ACIDITY of TRANSITION METAL DOPED ALUMINOPHOSPHATES



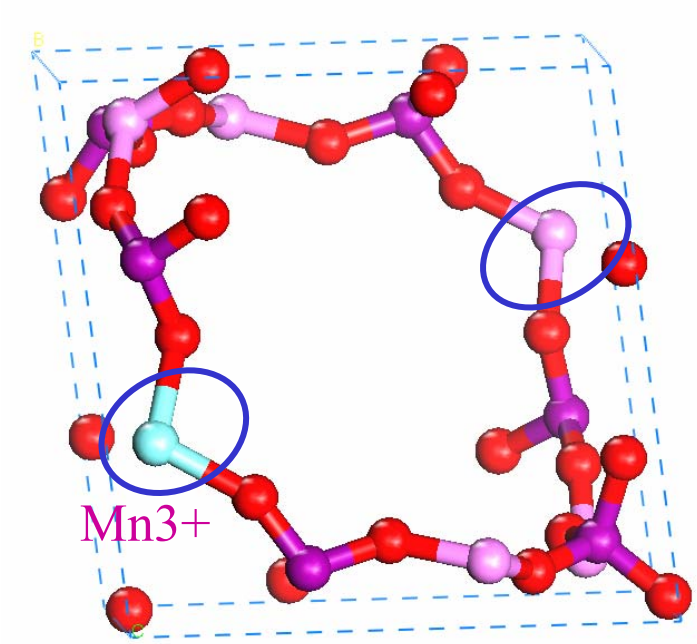
spin density of the TM ion compared to the framework size

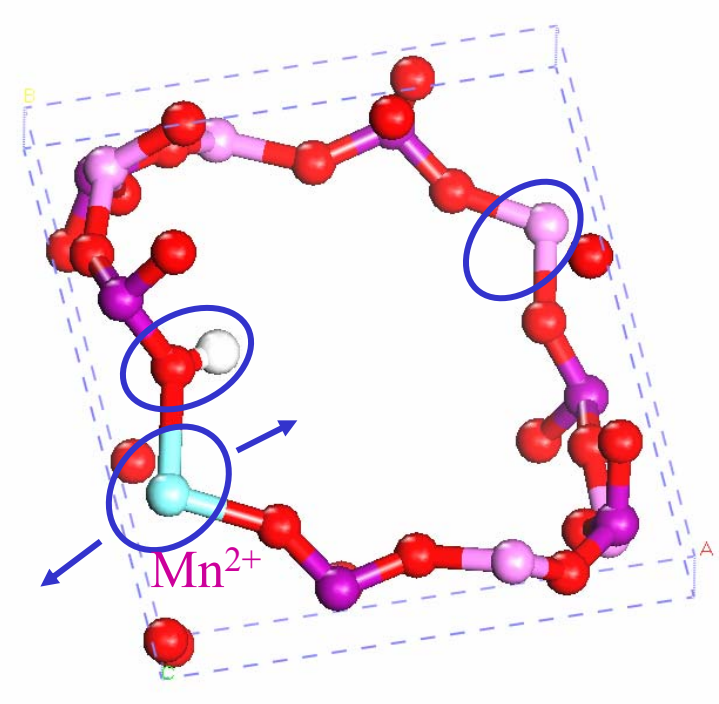
Most effective from behind the proton

F. Corà, I Saadoune and C.R.A. Catlow, *Angew. Chemie*, **41** (2002) 4871.

Water adsorption in Mn-doped AlPO-34 catalysts

- How does hydration modify the structure and electronic properties of the Mn dopant, and the framework stability ?



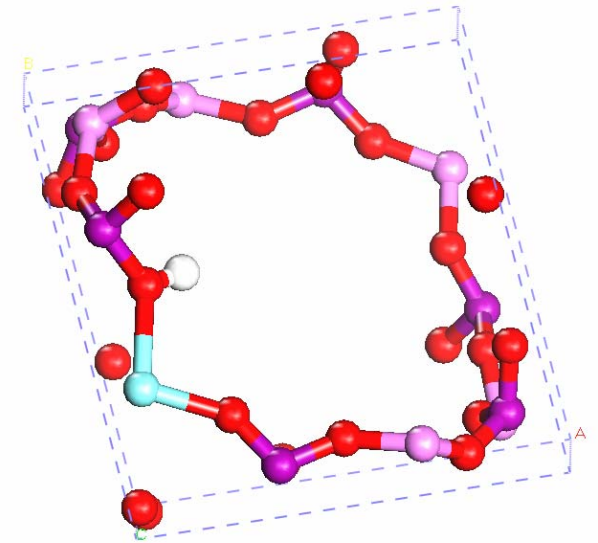


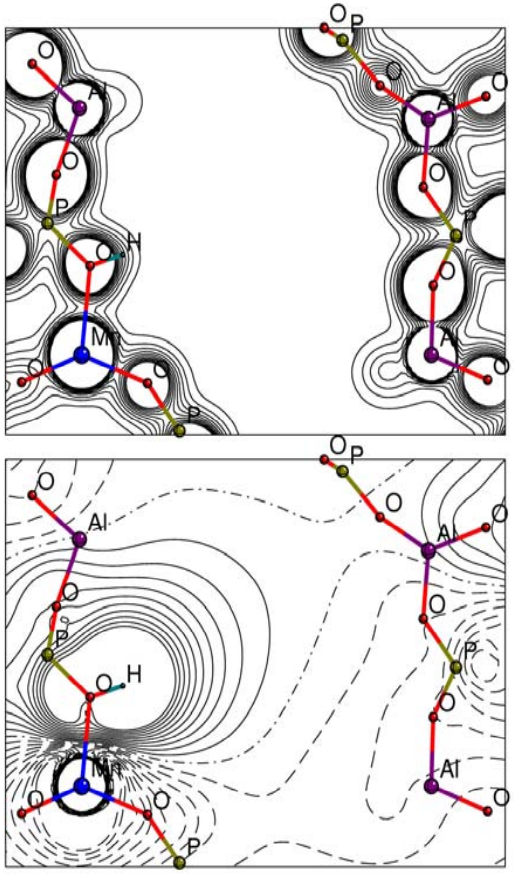
FURIO CORA' 22/9/2006

UCL

WATER ADSORPTION

Mn^{II}-HAlPO-34

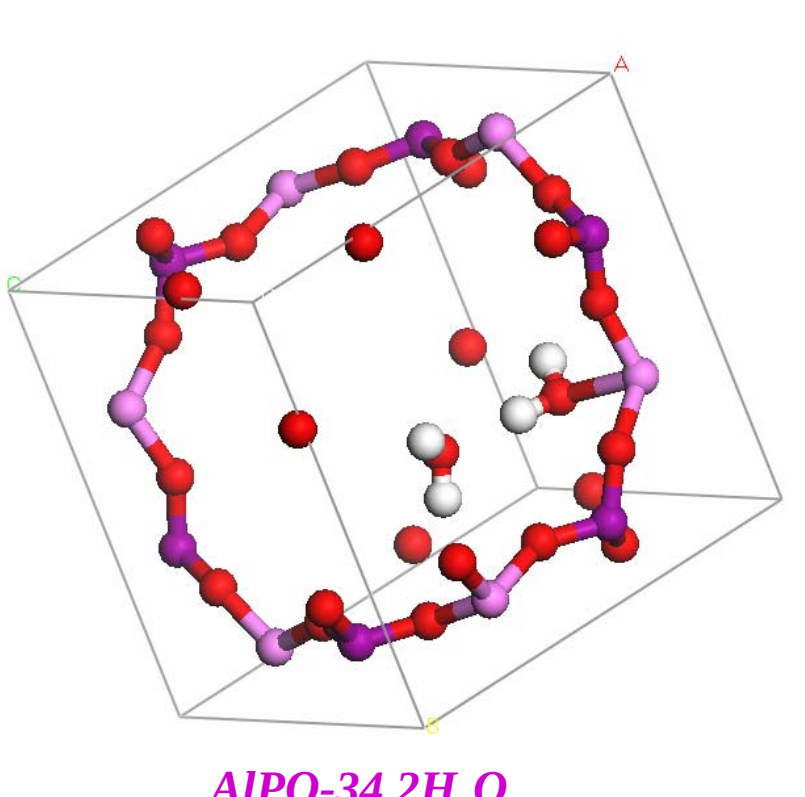




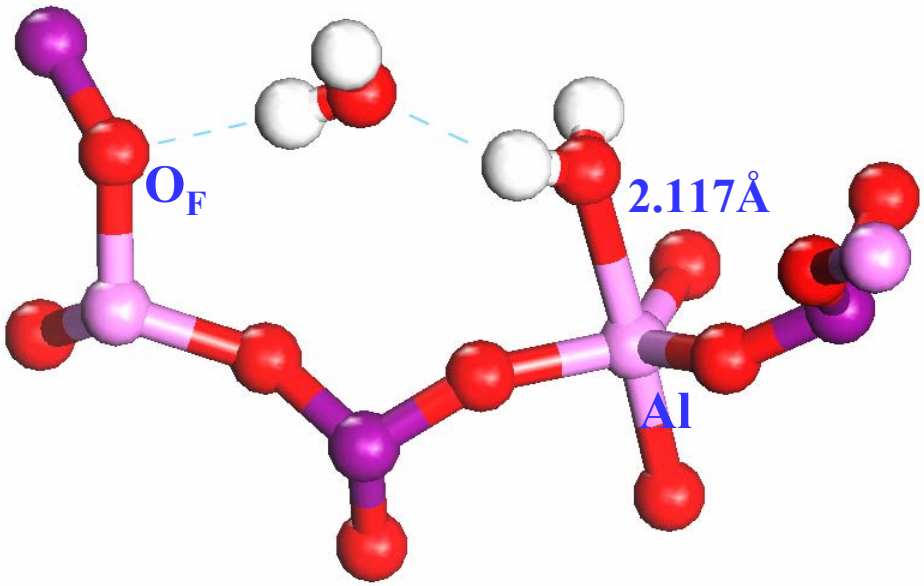
(DIFFERENCE)
ELECTROSTATIC
POTENTIAL
ΔV(MnAlPO-AlPO)

I.Saadoune, C.R.A.Catlow, K.Doll,
F.Corà, Molec. Simul., 30 (2004) 607.

Water interaction with Pure AlPO-34



AlPO-34,2H$_2$O



$\Delta Ead = E(AlPO\text{-}34,2H_2O)-[(AlPO\text{-}34)+E(Dimer)]$

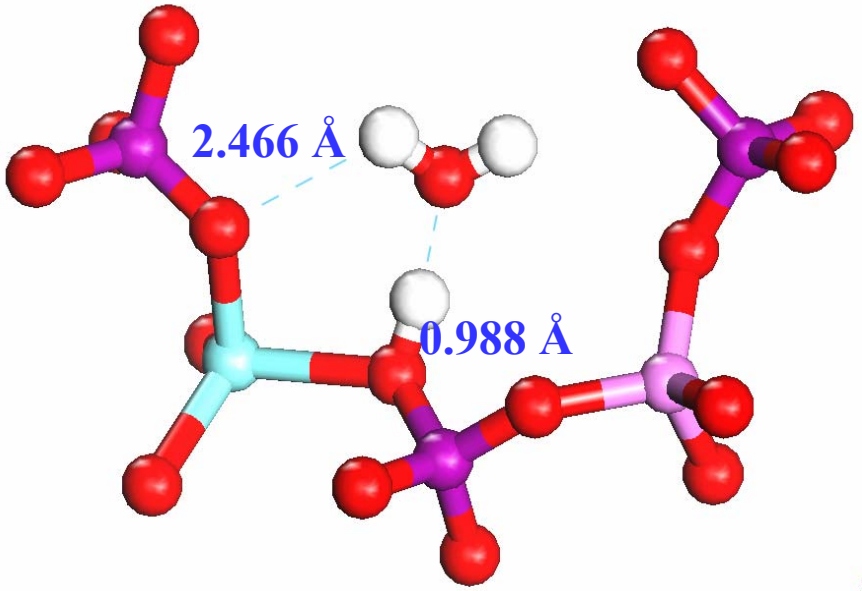
$\Delta Ead = -0.39$ eV

Hydrophilic nature of the AlPO framework

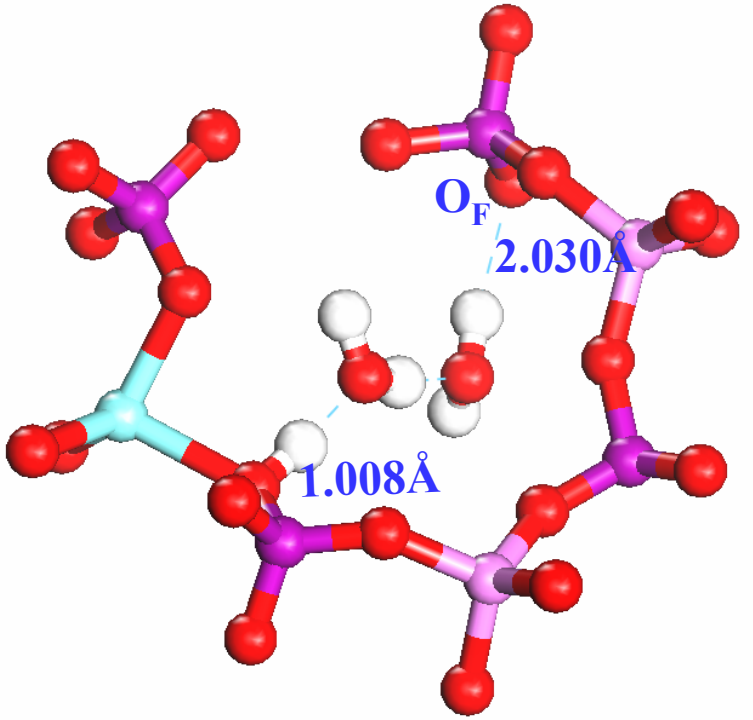
FRAMEWORK INVOLVEMENT → EXTENDED REGION PERTURBED

Water interaction with Mn^{II}-doped AlPO-34

Water adsorption on the Acid site (OH)

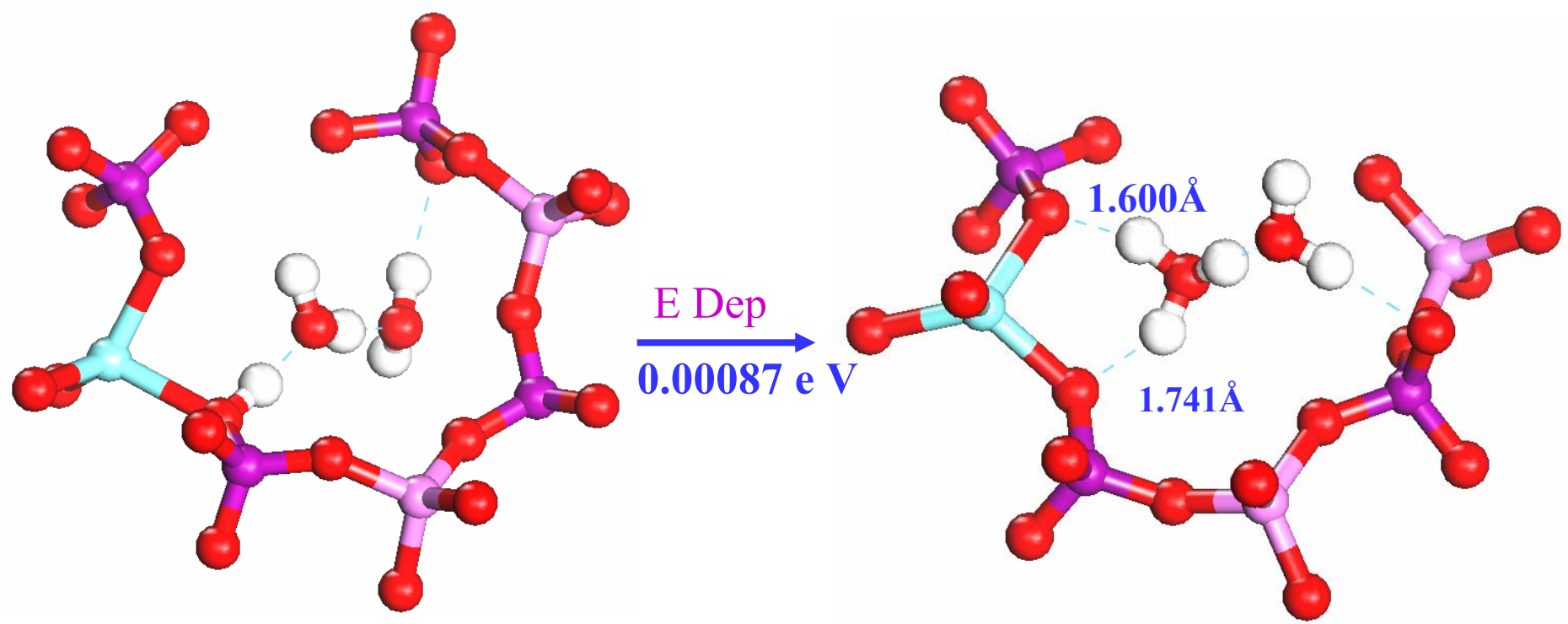


ΔE_{ad} = -0.93 eV



ΔE_{ad} = -1.19 eV

Framework Deprotonation

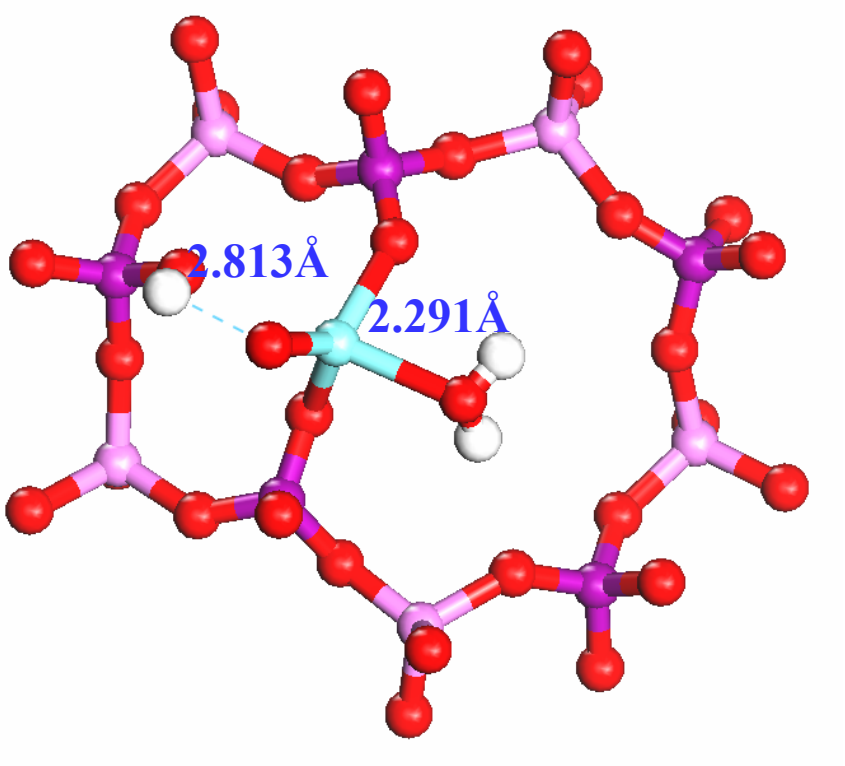


H-BONDED NETWORK INVOLVING THE FRAMEWORK
EXTENDS UP TO ~9Å AWAY FROM DOPANT
CLUSTER MODELS FAIL TO REPRODUCE IT

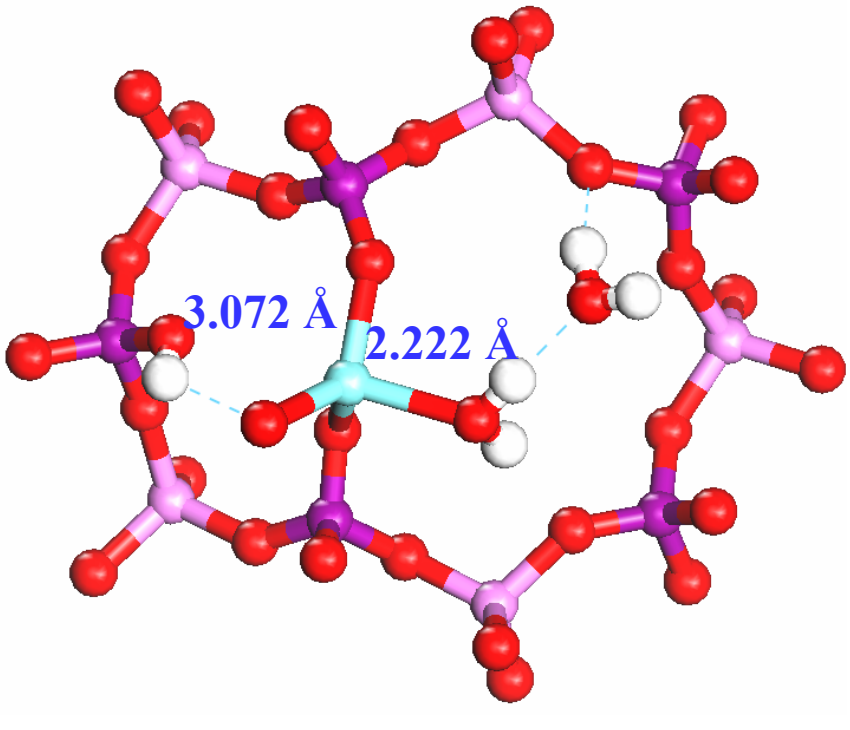
I.Saadoune, C.R.A.Catlow, K.Doll,
F.Corà, Molec. Simul., 30 (2004) 607.

Water adsorption on the Mn^{II} site

The side opposite the acid proton (Attack from behind)



ΔEad = -0.84 eV



ΔEad = -1.17eV

Attack from behind leads to broken framework

FINAL MESSAGES

-SELF-EMBEDDING TEST
-SIZE CONSISTENCY TEST
-WRITE RELEVANT DEFECT FORMATION REACTION
-NOT ALWAYS MORE EXPENSIVE COMPUTATIONAL METHODS
GIVE BETTER RESULTS: BALANCE BETWEEN
HAMILTONIAN, MODEL, COMPUTATIONAL TOLERANCES
-DON'T BE AFRAID OF OVERSIMPLIFYING THE MODEL

-MODELLING WORK SUCCESSFUL IF PROPERTY OF INTEREST
IS EXPLAINED WITH FEW SIGNIFICANT PARAMETERS