

**ASSC2006 (Spokane, Sept. 2006)**  
**ONE-ELECTRON PROPERTIES**



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## QM STUDIES

SCHRÖDINGER EQUATION:  $H\psi = E\psi$ APPROXIMATIONS: BORN-HOPPENHEIMER  
1e HAMILTONIAN (mean field)BASIS SET: ATOMIC ORBITALS:  $\{\chi\}$ SECULAR EQUATION:  $HC = SCE$ EIGENSTATES:  $\psi_q = \sum_p c_{pq} \chi_p$

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CRYSTALLINE SOLIDS:  
FACTORISATION IN RECIPROCAL SPACE,  $\mathbf{k}$

SECULAR EQUATION:  $\mathbf{H}(\mathbf{k})\mathbf{C}(\mathbf{k})=\mathbf{S}(\mathbf{k})\mathbf{C}(\mathbf{k})\mathbf{E}(\mathbf{k})$

BASIS SET: BLOCH FUNCTIONS

$$\{\chi_p(\mathbf{R}_p+\mathbf{r})\} \rightarrow \{\Phi_p(\mathbf{k})\}$$

LINKED BY FOURIER TRANSFORM TO AOs  $\chi$

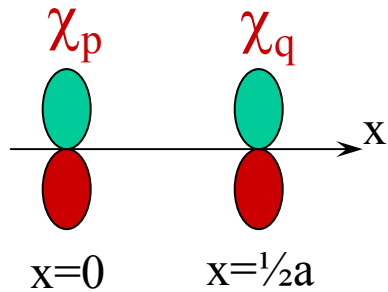
$$\Phi_p(\mathbf{k}) = 1/\sqrt{N} \sum_{\mathbf{g}} \chi_p(\mathbf{R}_p+\mathbf{r}+\mathbf{g}) e^{i\mathbf{k}(\mathbf{R}_p+\mathbf{g})}$$

$\Phi_p(\mathbf{k})$  EXTENDS OVER THE INFINITE SOLID

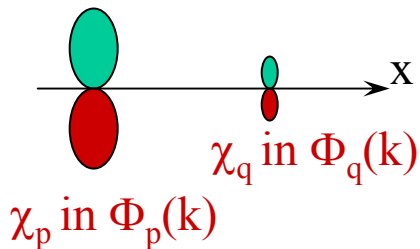
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## k-DEPENDENCE IN BLOCH FCTS

$$\Phi_p(\mathbf{k}) = \sum_g \chi_p(\mathbf{R}_p + \mathbf{r} + \mathbf{g}) e^{i\mathbf{k}(\mathbf{R}_p + \mathbf{g})}$$



$$k_x = 0; e^{ikRq} = 1$$



$$0 < k_x < 1/2; |e^{ikRq}| < 1$$

In the Bloch fct  $\Phi_q(\mathbf{k})$ ,  $\chi_q$  appears smaller

USING DIFFERENT  $\mathbf{k}$  POINTS WE HIGHLIGHT DIFFERENT AOs IN THE STRUCTURE AROUND A REFERENCE POINT

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## DIRECT AND RECIPROCAL SPACES (NUMERICAL) FOURIER TRANSFORM in each SCF cycle

DIR → REC  $H(k)C(k) = S(k)C(k)E(k)$  factorise  $\infty$  problem into a series of finite ones

### CALCULATE EIGENVALUES/EIGENVECTORS

REC → DIR

DENSITY OPERATOR:

MOLECULE 
$$\rho = \sum_1^{\text{occ}} n_1 |\Psi_1\rangle\langle\Psi_1|$$

SOLID 
$$\rho^g = \int_{\text{IBZ}} \sum_1^{\text{occ}} n_1 |\Psi_1(k)\rangle\langle\Psi_1(k)| e^{ikg} dk$$

INTEGRAL  $\int_{\text{IBZ}}$  REPLACED BY FINITE  $\sum_{k=1}^n w_k$

DENSITY MATRIX (SOLID):

$$P_{pq}^g = \int_{\text{IBZ}} \sum_1^{\text{occ}} n_1 c_{pl}(k) c_{ql}^*(k) e^{ikg} dk$$

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QM SOLUTION CONTAINS MORE INFORMATION THAN  
THE ENERGY. CAN BE EXTRACTED WITH APPROPRIATE  
ANALYSIS METHODS

DIRECT AND RECIPROCAL SPACES



ANALYSIS OF THE QUANTUM MECHANICAL  
SOLUTION FOR SOLIDS CAN BE DONE IN

DIRECT SPACE: 1-electron density  $\rho(\mathbf{r})$   
similar to molecular systems

RECIPROCAL SPACE: eigenvalues  $\epsilon_1(\mathbf{k})$   
unique to solids

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ANALYSIS OF THE ELECTRONIC DENSITY  $\rho(\mathbf{r})$   
DIRECT SPACE

-VISUAL: 2D and 3D PLOTS (ECHG, ECH3)

-NUMERICAL: POPULATION ANALYSIS  
MULLIKEN (PPAN)  
HIRSHFELD

-TOPOLOGICAL ANALYSIS: BADER's AIM

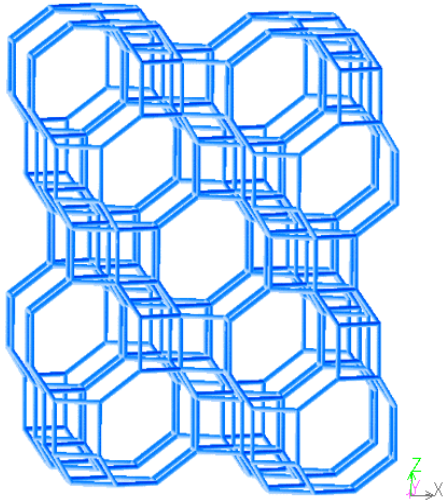
-WANNIER FUNCTIONS; NATURAL ORBITALS

TIP: ALWAYS CHOOSE A SUITABLE  
REFERENCE TO COMPARE WITH!

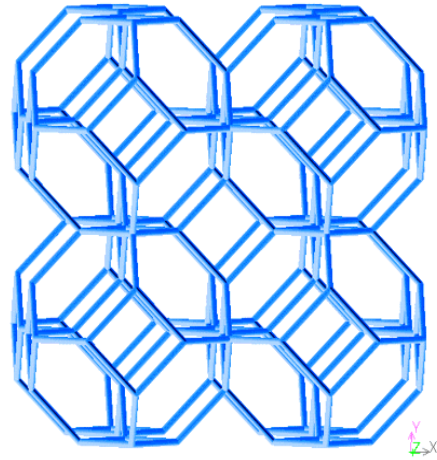


# EXAMPLE: FRAMEWORK PROPERTIES OF ZEOLITES ( $\text{SiO}_2$ ) AND ALPOs ( $\text{AlPO}_4$ )

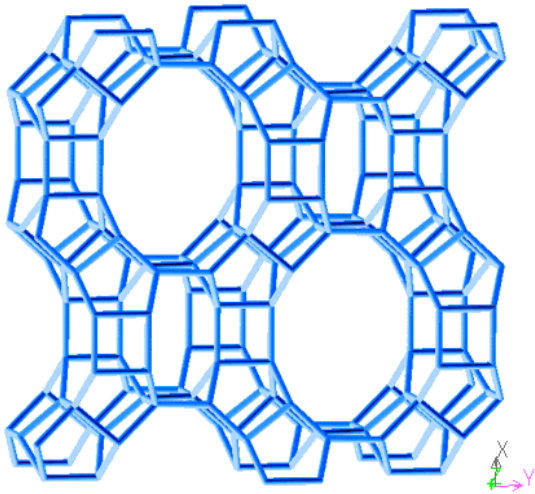
CHA



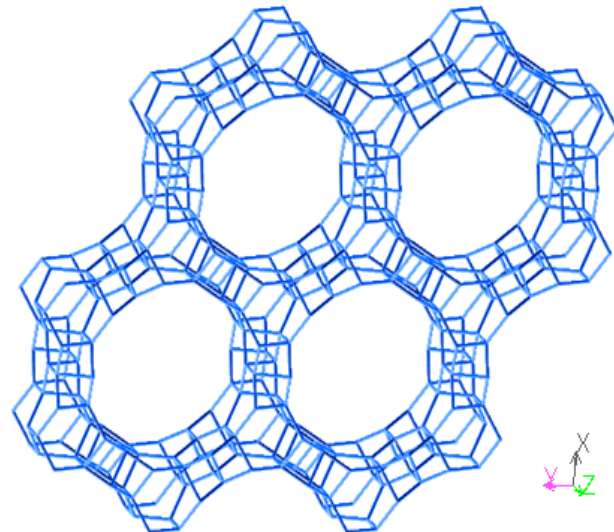
SOD



MOR



VFI



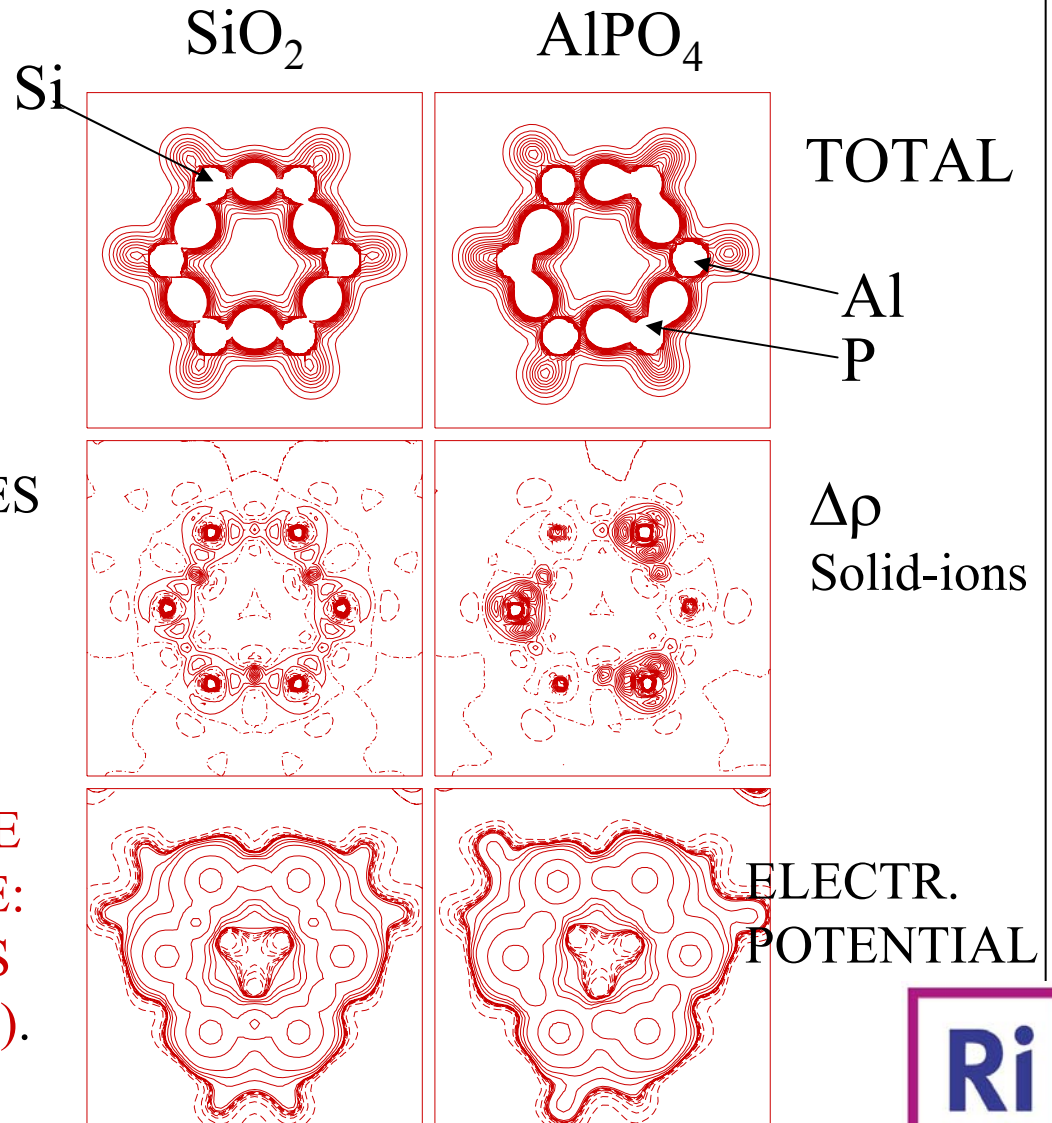


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VISUAL ANALYSIS  
OF  $\rho(r)$   
2D PROJECTION

FRAMEWORK PROPERTIES  
OF ZEOLITES AND AIPOs

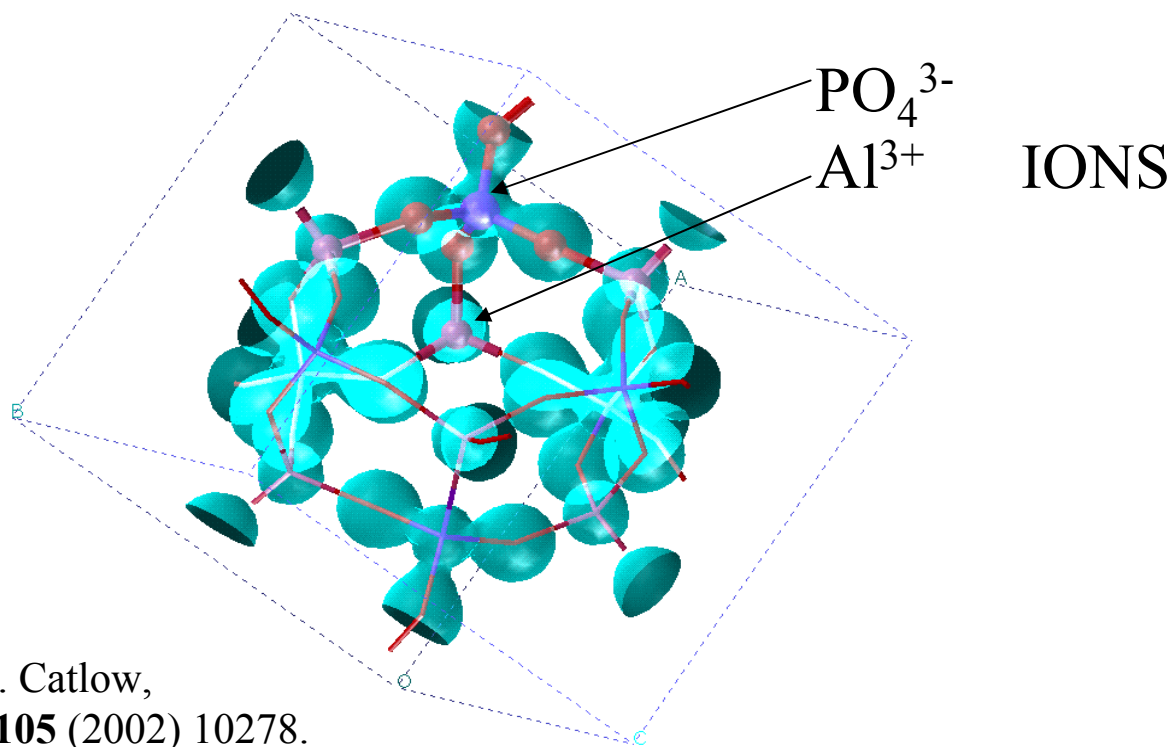
- 1) SELECT A REPRESENTATIVE PLANE
- 2) SUITABLE REFERENCE: ISOLATED FORMAL IONS (SPHERICAL SYMMETRY).



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# VISUAL ANALYSIS OF $\rho(r)$ 3D PROJECTION

FRAMEWORK PROPERTIES OF AlPO<sub>5</sub>  
ISODENSITY LEVEL



F. Corà and C.R.A. Catlow,  
*J. Phys. Chem.*, **B 105** (2002) 10278.

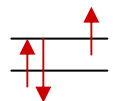
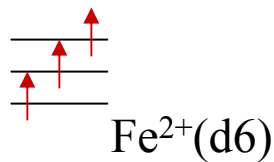


# Ri

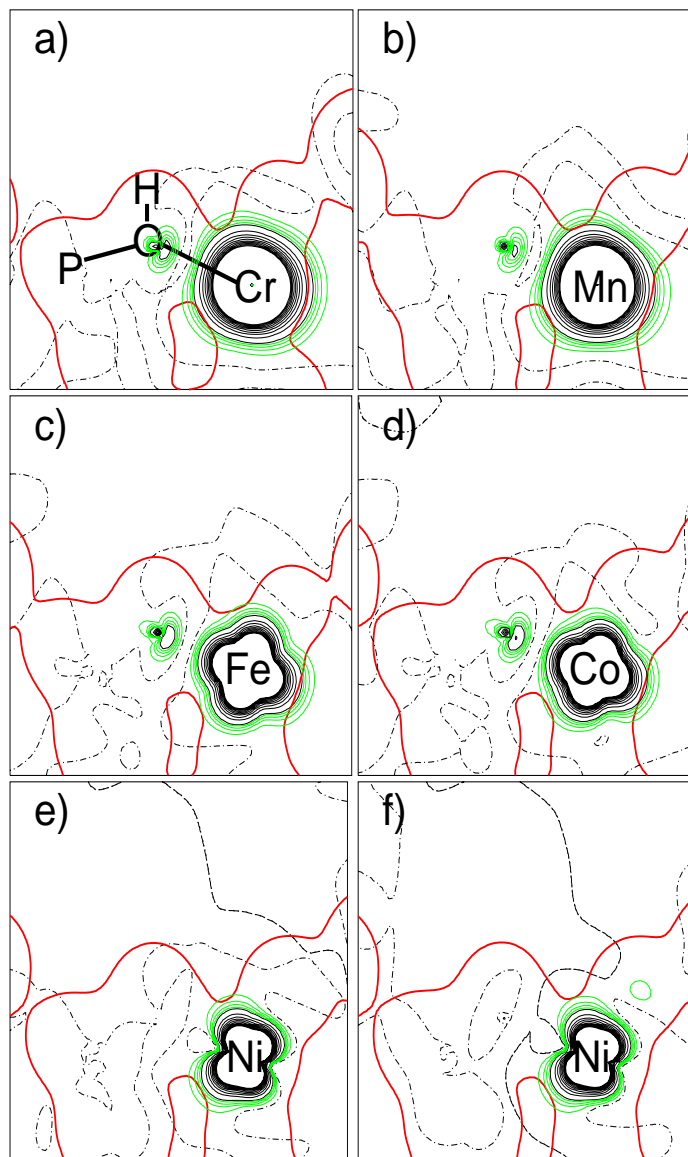
## LEWIS ACIDITY of TRANSITION METAL DOPED ALUMINOPHOSPHATES

spin density ( $\rho^\alpha - \rho^\beta$ ) of the TM  
ion  
compared to the  
framework size

SUITABLE REFERENCE:  
MINORITY SPIN DENSITY



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



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## NUMERICAL ANALYSIS OF THE ELECTRONIC DENSITY $\rho(\mathbf{r})$

MULLIKEN DEFINITION OF CHARGES (PPAN)  
representation of  $\rho(\mathbf{r})$  in the basis set  $\{\chi_p\}$  chosen

$$M_{pq}^g = P_{pq}^g \cdot S_{pq}^g \quad \text{Mulliken matrix}$$

ORBITAL CHARGE:

$$q_p = \sum_{g,q} M_{pq}^g$$

ATOMIC CHARGE:

$$q_A = \sum_{p \in A} q_p$$

BOND CHARGE:

$$q_{AB} = 2 \sum_{p \in A, q \in B} M_{pq}$$



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## MULLIKEN ANALYSIS (local AO basis set)

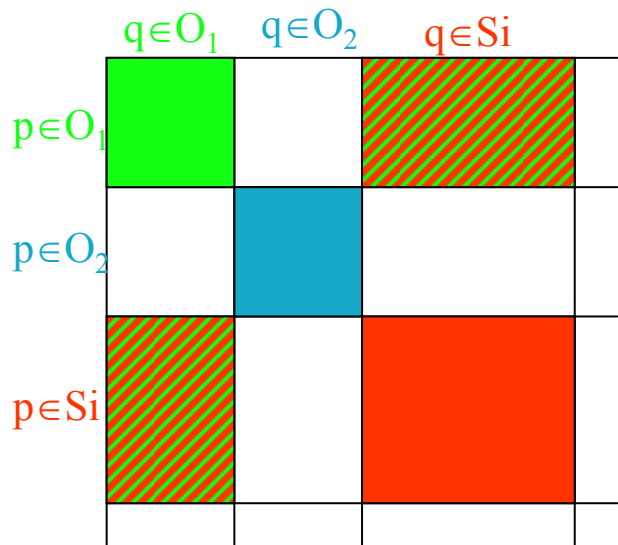
Each atom A is associated an 'atomic' basis set  $\{\chi_{p \in A}\}$

Define the matrix  $M^g = P^g \cdot S^g$

$$(M^g_{pq} = P^g_{pq} \cdot S^g_{pq})$$

Attribute the charge  $P_{p \in A, q \in B}$  to the atoms A,B

Example: SiO<sub>2</sub>



	T	Q(T)	Q(O)	$q_b(T-O)$
SiO <sub>2</sub>	Si	+2.08	-1.04	0.29
AlPO <sub>4</sub>	P	+2.85	-1.26	0.27
	Al	+2.19	-1.26	0.14
GaPO <sub>4</sub>	P	+2.87	-1.30	0.27
	Ga	+2.33	-1.30	0.11

Out-of-diagonal terms: bond population  $q_b(O_1-Si)$  

Diagonal terms: attributed to 1 atom  $q(O_1)$  

Atomic charges:  $Q(A) = q(A) + \frac{1}{2} \sum_{B \neq A} q_b(A-B)$ ; orbital charge:  $q_p = \sum_{q,g} M^g_{pq}$



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# NUMERICAL ANALYSIS OF THE ELECTRONIC DENSITY $\rho(\mathbf{r})$

## HIRSHFELD DEFINITION OF CHARGES comparison of $\rho(\mathbf{r})$ with atomic references

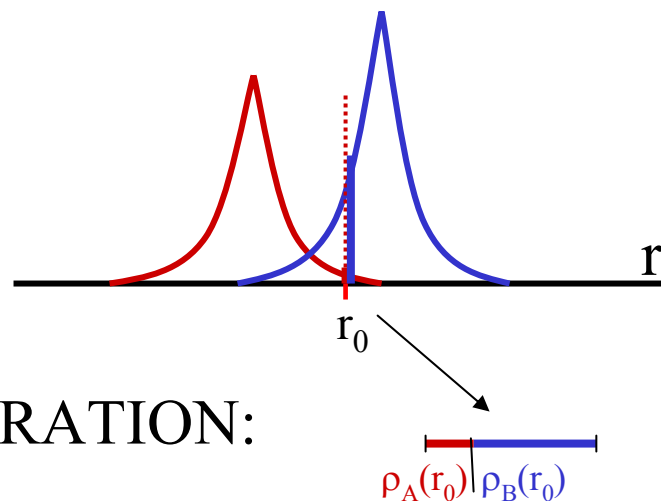
ATOMIC WEIGHTS:  $W_A(\mathbf{r})$

$$W_A(\mathbf{r}) = \rho_A(\mathbf{r}) [\sum_B \rho_B(\mathbf{r})]^{-1}$$

ATOMIC CHARGES BY INTEGRATION:

$$q_A = \int \rho_d(\mathbf{r}) W_A(\mathbf{r}) d\mathbf{r}$$

$$\rho_d(\mathbf{r}) = \rho(\mathbf{r}) - \sum_A \rho_A(\mathbf{r})$$



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## BADER ANALYSIS

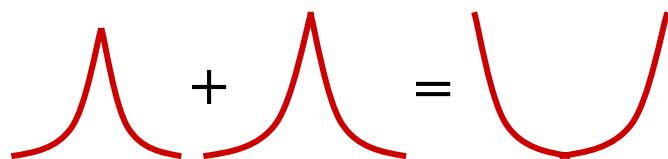
Calculate the Laplacian of  $\rho(\mathbf{r})$ :  $L = \nabla^2 \rho(\mathbf{r})$

in zones of covalent interaction:  $L < 0$

in zones of ionic interaction:  $L > 0$

Electron-density profile along bonds

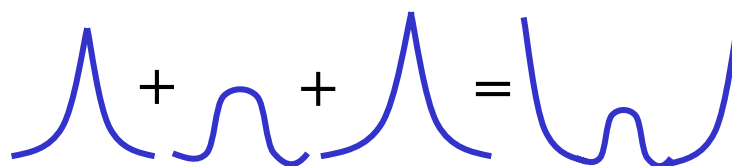
IONIC interaction



Curvature  $> 0$

$L > 0$

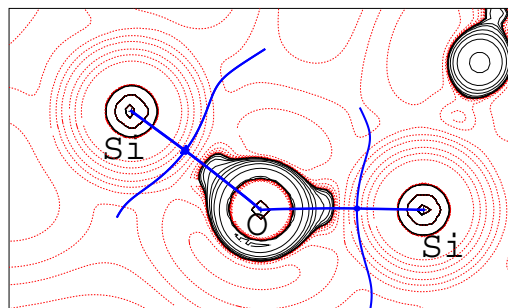
COVALENT interaction



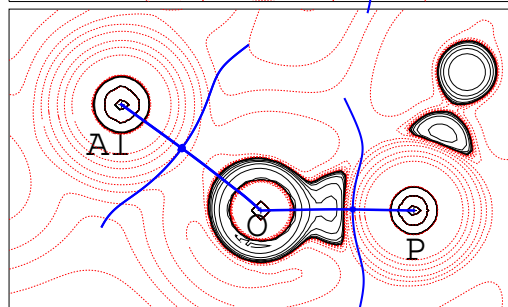
Curvature  $< 0$

$L < 0$

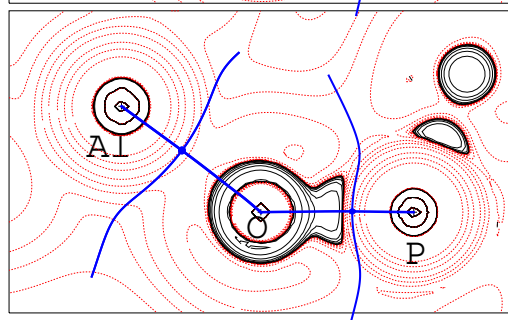
## BADER ANALYSIS

FRAMEWORK PROPERTIES  
OF ZEOLITES AND ALPOS

Si-O-Si bond, silica  
Hartree-Fock density



Al-O-P bond, AIPO  
Hartree-Fock density



Al-O-P bond, AIPO  
DFT-GGA density

LAPLACIAN  $L = \nabla^2 \rho(\mathbf{r})$

**RED:  $L > 0$  ZONES OF IONIC**

**INTERACTION IN THE SOLID**

**BLACK:  $L < 0$  ZONES OF COVALENT**

**INTERACTION IN THE SOLID**

**BLUE: MOLECULAR GRAPHS**

**DELIMIT ATOMIC BASINS**

F. Corà and C.R.A. Catlow,  
*J. Phys. Chem.*, **B 105** (2002) 10278.

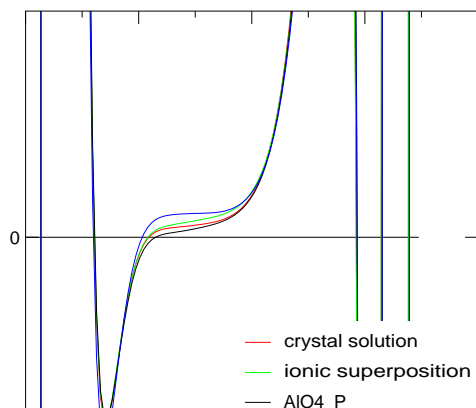




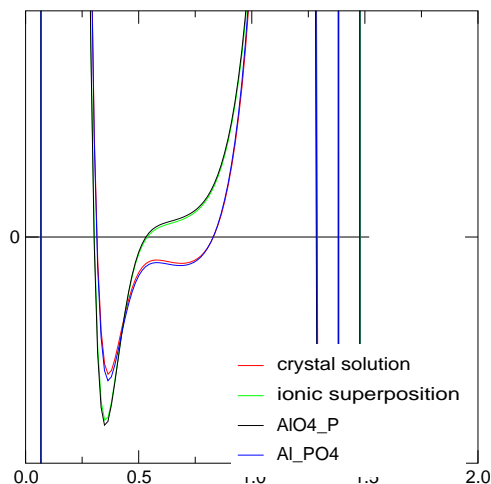
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## BADER ANALYSIS

$\nabla^2\rho(r)$   
along  
Al-O  
bond



$\nabla^2\rho(r)$   
along  
P-O  
bond



FRAMEWORK PROPERTIES  
OF ALPOS

LAPLACIAN  $L = \nabla^2\rho(r)$

$L > 0$  ZONES OF IONIC  
INTERACTION IN THE SOLID

$L < 0$  ZONES OF COVALENT  
INTERACTION IN THE SOLID

REFERENCE: ISOLATED IONS  
OR  $\text{AlO}_4/\text{PO}_4$  GROUPS



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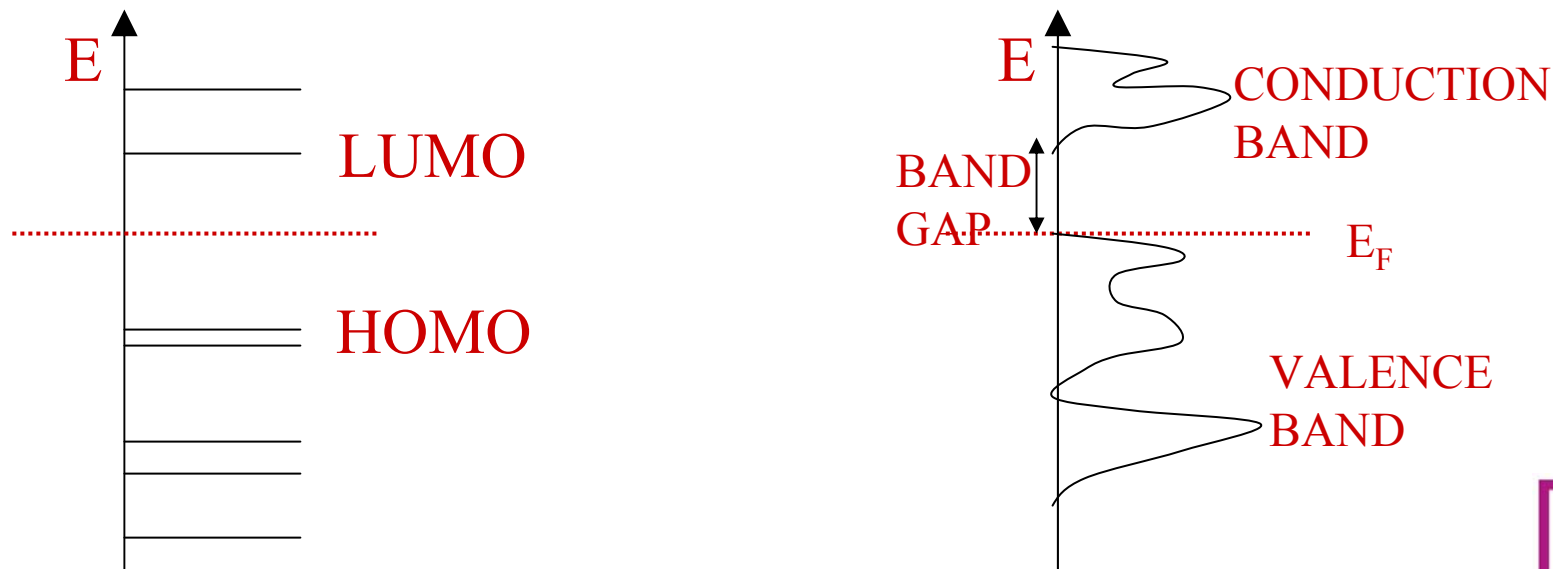
RECIPROCAL SPACE PROPERTIES  
K-DEPENDENCE OF THE SOLUTION

$$H(k)C(k)=S(k)C(k)E(k)$$

SPECTRUM OF one-electron ENERGY LEVELS

MOLECULE

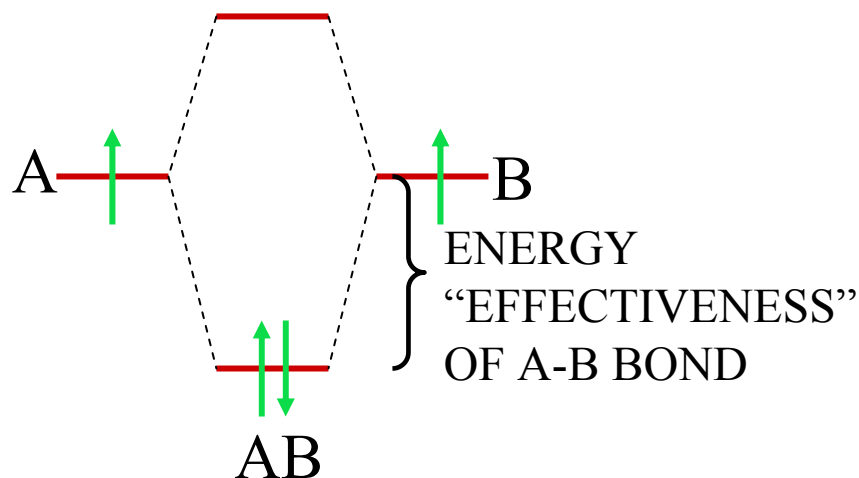
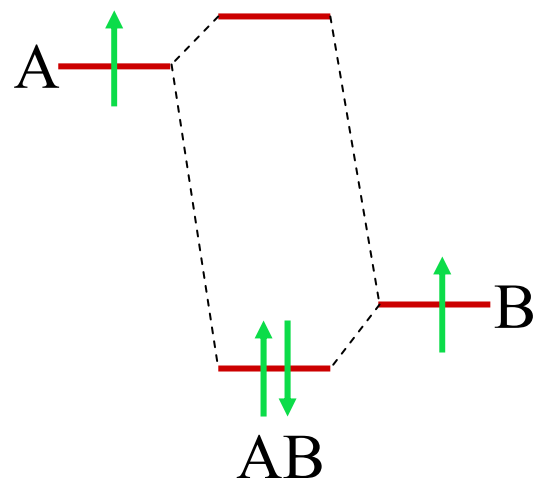
SOLID



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## CHEMISTRY FROM ENERGY LEVELS

## REFERENCE TO MO DIAGRAMS FOR MOLECULES

Example: H<sub>2</sub>

Example: Li-F

Energetic effectiveness of covalence in the A-B bond

How similar are the MO to the starting AO's?

(AO=Atomic or ionic orbitals)

Equivalent information for a solid? BAND STRUCTURE



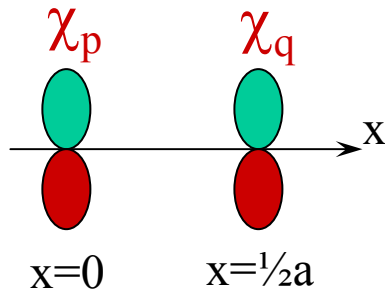
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## CHEMISTRY FROM ENERGY LEVELS

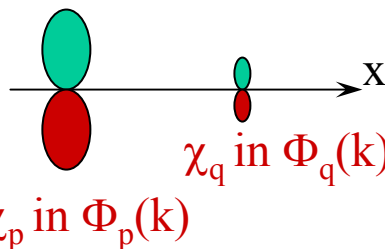
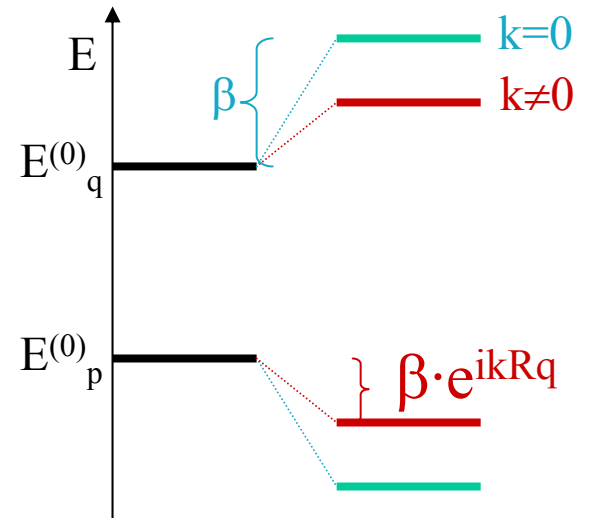
EXPLOIT THE  $k$ -DEPENDENCE IN BLOCH FCTS

$$H(k)C(k) = S(k)C(k)E(k); H_{pq}(k) = \langle \Phi_p(k) | H | \Phi_q(k) \rangle$$

$$\Phi_p(k) = \sum_g \chi_p(R_p + r + g) e^{ik(R_p + g)}$$



$$k_x = 0; e^{ikRq} = 1$$



$$0 < k_x < 1/2; |e^{ikRq}| < 1$$

In the Bloch fct  $\Phi_q(k)$ ,  $\chi_q$  appears smaller

RESULT: DISPERSION OF EIGENVALUES IN  $k$ -SPACE



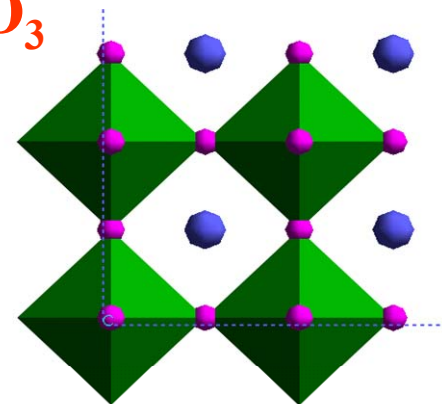
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## PEROVSKITE STRUCTURE: $AMO_3$

For more informaton:

F. Corà and C.R.A.Catlow, Faraday Discussions 114 (1999) 421

F. Corà et al., *'The performance of hybrid density functionals in solid state chemistry'*, Structure and Bonding, Vol. 113, page 171-232



**ALL IONS (M,O) TOPOLOGICALLY EQUIVALENT**

**Network of corner-sharing  $MO_6$  octahedra**

**Dodecahedral interstices A (can be empty)**

**2 cationic sites: different partition of charge possible**

**$LaMnO_3$  (3-3)**

**$BaTiO_3$  (2-4)**

**$KNbO_3$  (1-5)**

**$WO_3$  (0-6)**

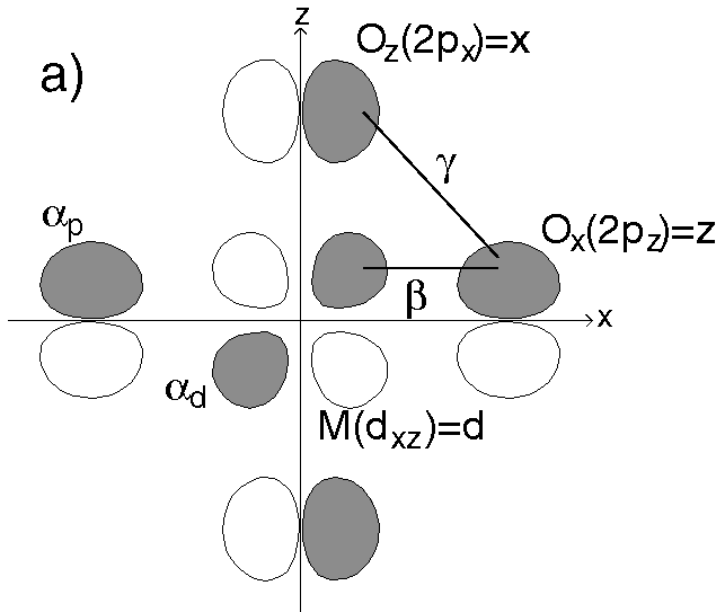
**Does this affect the solution?**



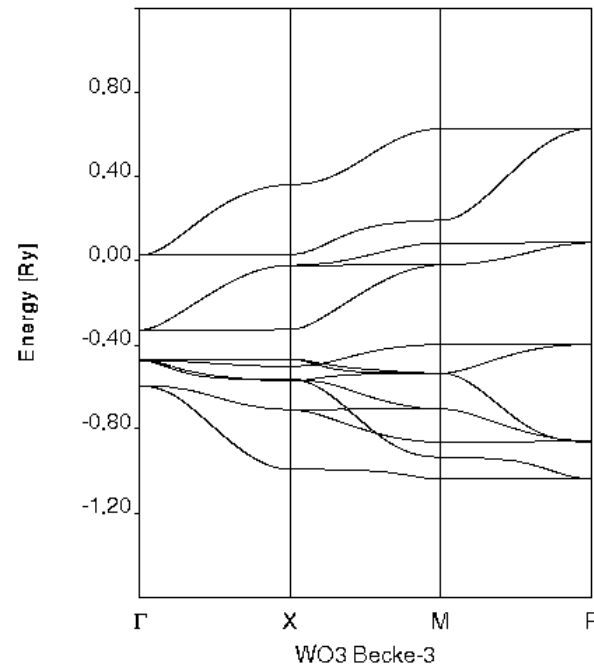
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# FEATURES OF THE QM SOLUTION – CUBIC PHASE

## FRONTIER AO's



## BAND STRUCTURE



Solution modulated by a wave  $e^{ikR}$   
 Different in different k points



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CUBIC PHASE -A COMPARISON OF DIFFERENT PEROVSKITES

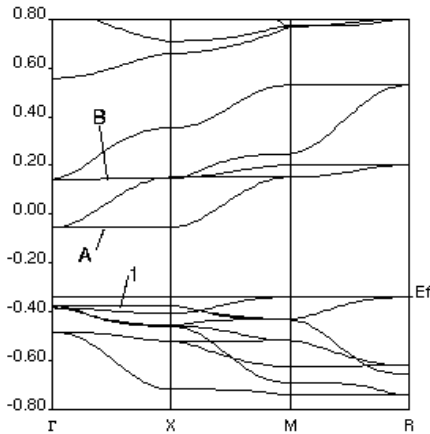
CHARGE  
PARTITION

(6-0)

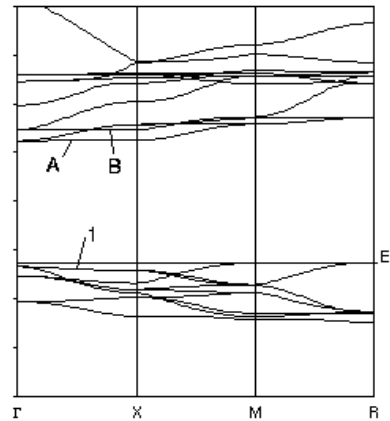
(5-1)

(4-2)

Material	a	Q(O)	$\Delta\alpha$	$\beta$	$\gamma*10$	$\beta^2/\Delta\alpha$
MoO <sub>3</sub>	3.78	-0.998	0.2995	0.1263	-0.162	0.053
WO <sub>3</sub>	3.77	-1.362	0.3173	0.1301	-0.168	0.053
LiNbO <sub>3</sub>	3.96	-1.385	0.4125	0.1166	-0.161	0.033
NaNbO <sub>3</sub>	3.98	-1.374	0.3998	0.1140	-0.157	0.032
KNbO <sub>3</sub>	4.03	-1.395	0.3915	0.1087	-0.151	0.030
CaTiO <sub>3</sub>	3.88	-1.582	0.5148	0.1205	-0.204	0.028
SrTiO <sub>3</sub>	3.93	-1.609	0.5052	0.1162	-0.195	0.027
BaTiO <sub>3</sub>	4.02	-1.571	0.4748	0.1017	-0.188	0.022



WO<sub>3</sub>



CaTiO<sub>3</sub>

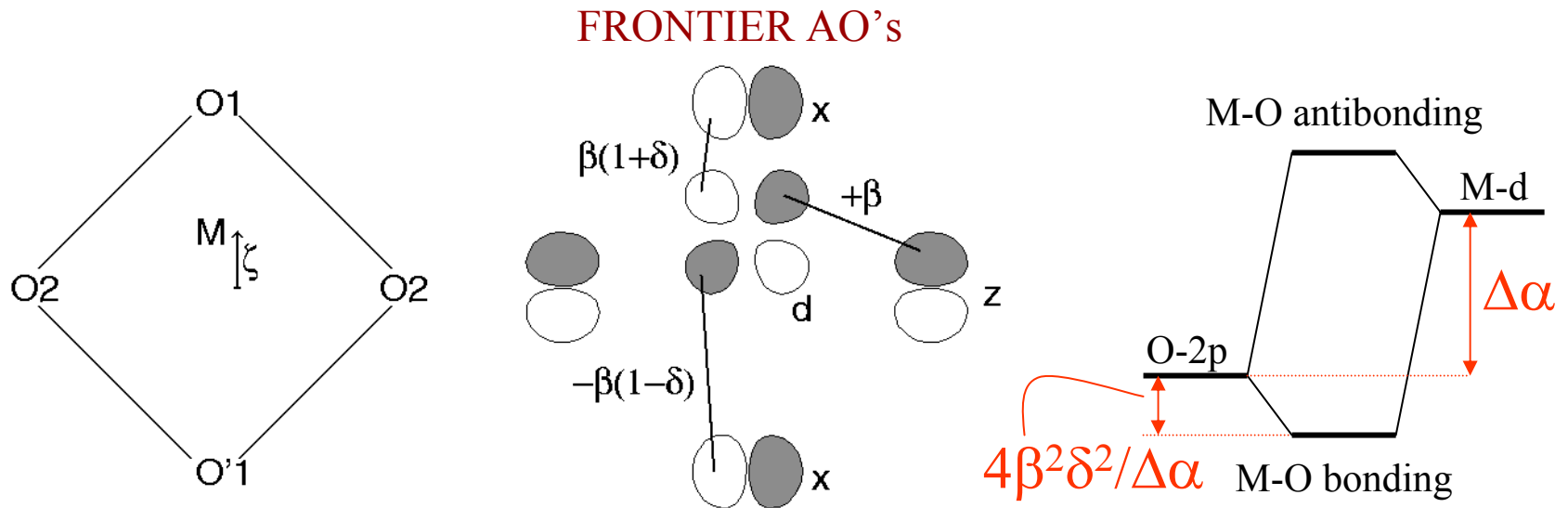
THE HIGHER THE FORMAL CHARGE OF M,  
THE LOWER THE BAND GAP,  
THE HIGHER COVALENCE

SUITABLE REFERENCE:  
SYSTEM WITH EXTREME  
BEHAVIOUR



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## FEATURES OF THE DISTORTED (FE) PHASE



M-O COVALENCE NO LONGER SYMMETRY-FORBIDDEN  
 M-O NON BONDING LEVELS HYBRIDISE INTO BONDING/ANTIBONDING PAIR  
 EFFECTIVENESS PROPORTIONAL TO  $\beta^2/\Delta\alpha$  AND M OFF-CENTERING

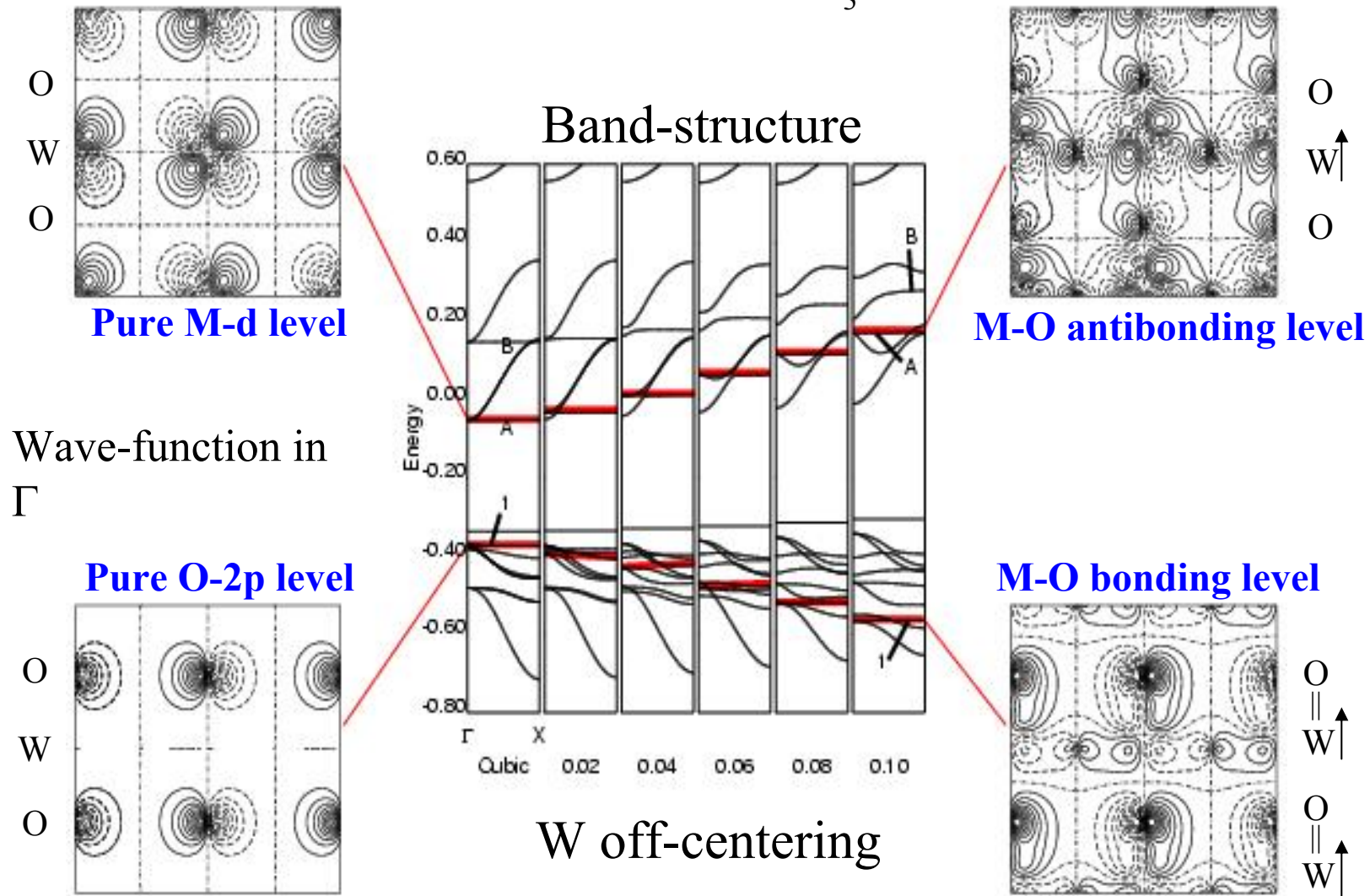
SAME TREND WITH FORMAL CHARGE OF M (see cubic phase) APPLIES HERE



# FERROELECTRIC DISTORTION IN PEROVSKITES

The case of  $\text{WO}_3$

Furio Cora - DFRL



Cubic phase: M-O interactions are symmetry-forbidden

FE distortion forms M-O bonding-antibonding pair

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DOS, PDOS (INTEGRAL OF BAND STRUCTURE OVER  $k$ )  
How many levels available at each energy,  $N(e)$

BASED ON MULLIKEN PARTITION OF CHARGES

ORBITAL PDOS:

$$N_p(e) = 1/V_B \int_{IBZ} \sum_{q,l,g} n_l(k) S_{pq}(k) c_{pl}(k) c_{ql}^*(k) e^{ikg} \delta[e - e_l(k)] dk$$

ATOMIC PDOS:

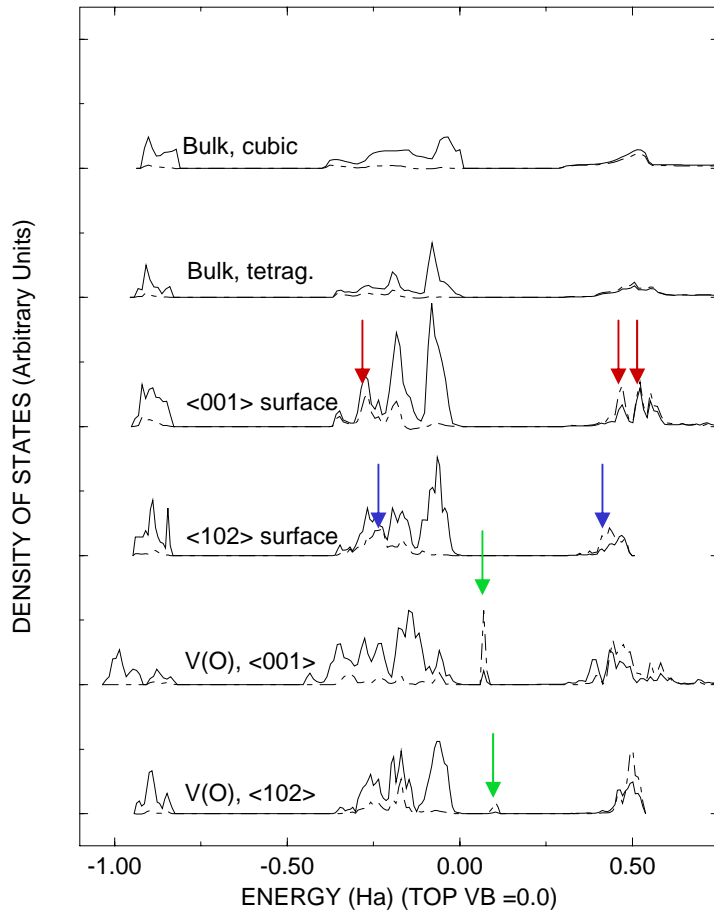
$$N_A(e) = \sum_{p \in A} N_p(e)$$

TOTAL DOS:

$$N_{tot}(e) = \sum_A N_A(e)$$

In the integration we lose information; DOS less informative of the band structures, but simpler for big systems.

DOS, PDOS (How many levels available at each energy,  $N(e)$ )



WO<sub>3</sub>: bulk, surfaces, defects

Surface states

kink states

defect states

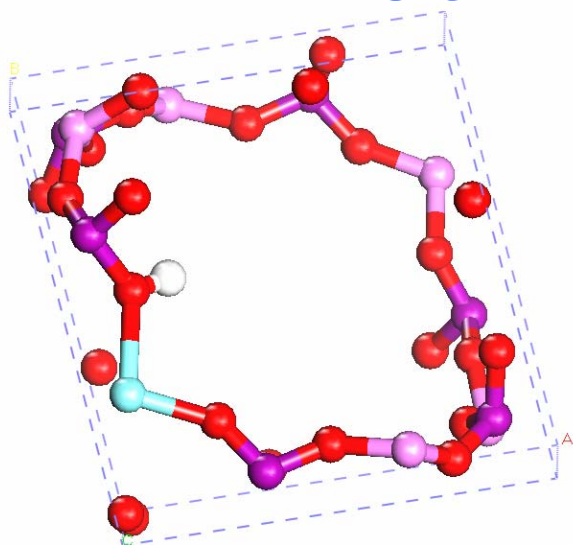
~200 atoms; impossible to  
Highlight in band-structure.



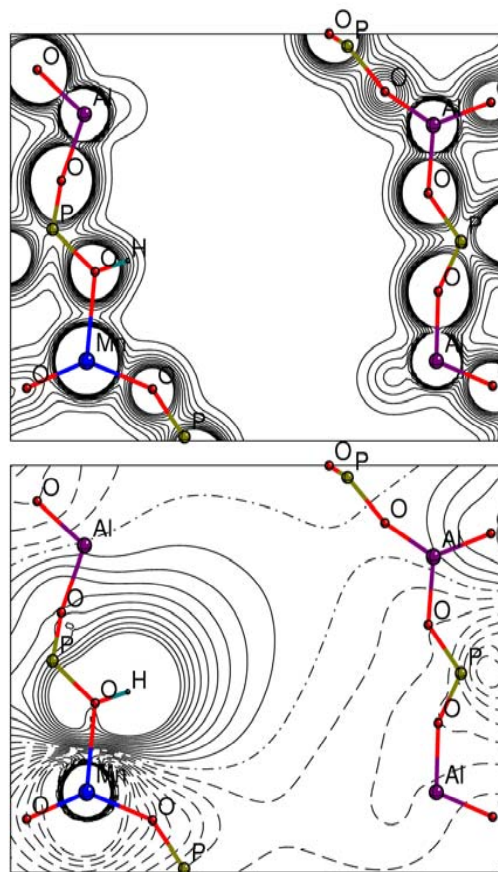
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# (DIFFERENCE) ELECTROSTATIC POTENTIAL

## Mn<sup>II</sup>-HAIPO-34



SUITABLE REFERENCE:  
UNDOPED SYSTEM  
 $\Delta V(\text{MnAlPO}-\text{AlPO})$



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



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## NEW PROPERTIES FROM CRYSTAL03

**LOCALWF**: Wannier functions; localised orbitals

**SPOLWF**: macroscopic polarisation of low symmetry crystals

**PIEZOWF**: piezoelectric constants

**DIELEC**: high-frequency dielectric constants  
(electronic polarisability of the solid)

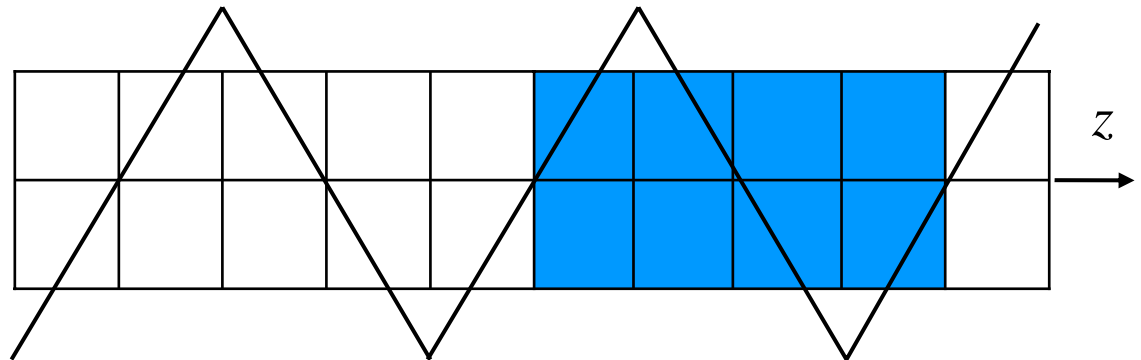
High-frequency diel. const.  $\epsilon_\infty$

Poisson's  
equation

$$\frac{\partial^2 \bar{V}(z)}{\partial z^2} = -4\pi \bar{\rho}(z)$$

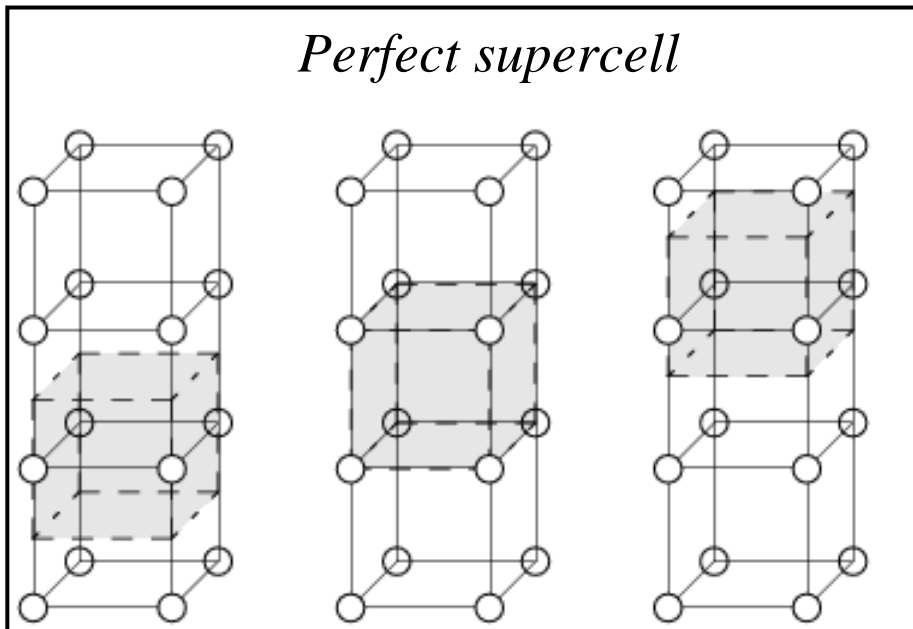
$$\frac{\partial \bar{V}(z)}{\partial z} = -\bar{E}(z)$$

$$\frac{\partial \bar{E}_r(z)}{\partial z} = 4\pi \bar{\rho}(z)$$



Sawtooth external potential

*Perfect supercell*



$$\epsilon_\infty = \lim_{E_0 \rightarrow 0} \frac{E_0}{E_0 + E_r}$$

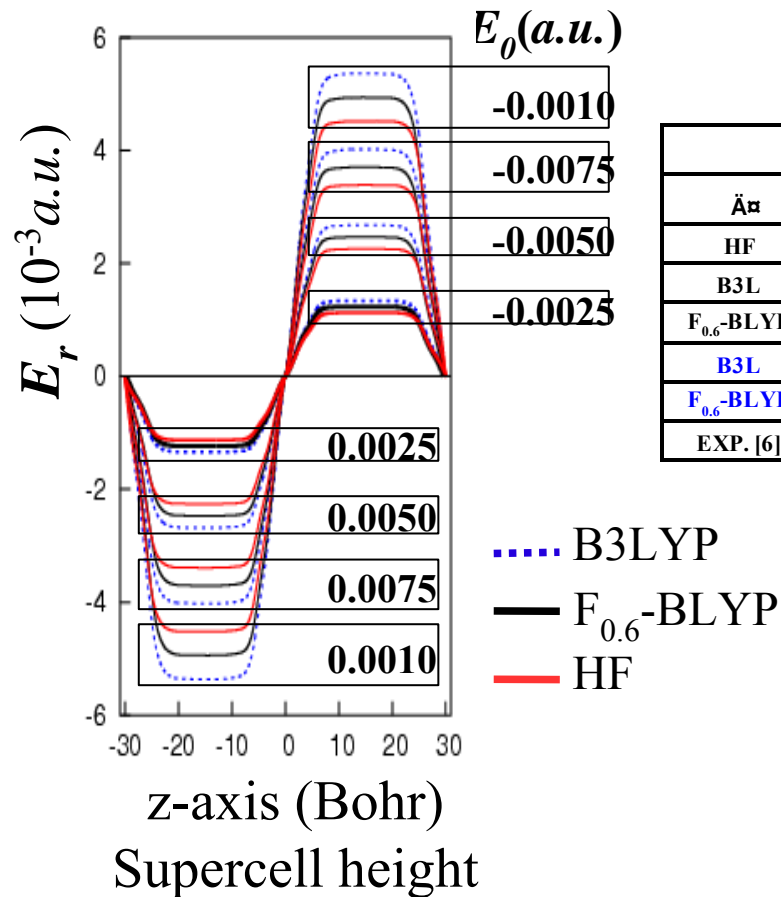
$E_0$  applied electric field

$E_r$  macroscopic response field

UCL

DIELEC: high-frequency dielectric constants,  $\text{CaSO}_4$ 

## Macroscopic electric field response

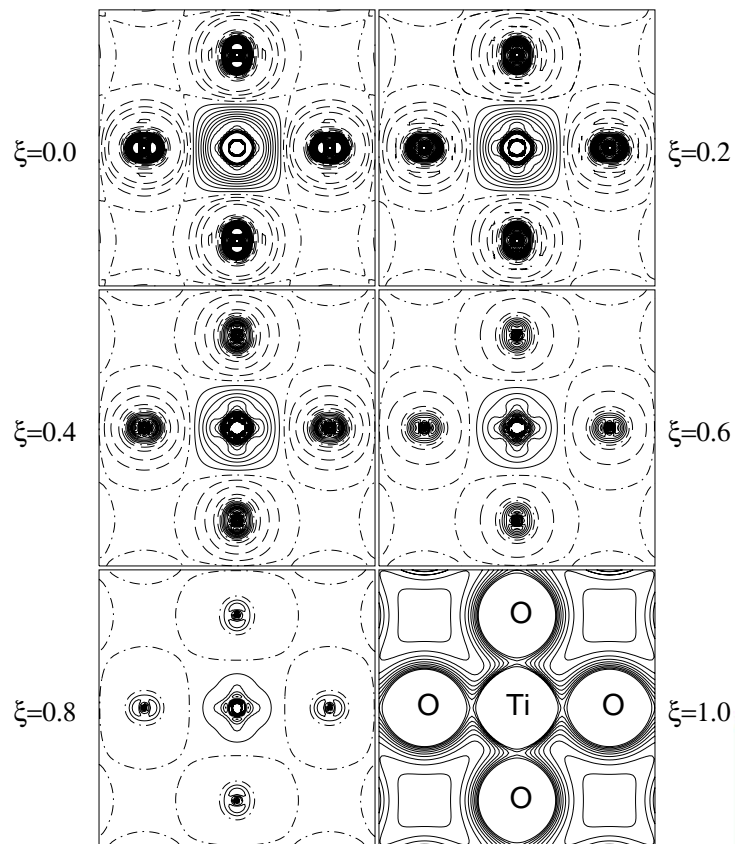


$\hat{A}\alpha$	HEXAGONAL STRUCTURE		ORTHORHOMBIC STRUCTURE		
	A	C	A	B	C
HF	1.721	1.826	1.867	1.872	1.956
B3L	1.956	2.160	2.169	2.165	2.337
F <sub>0.6</sub> -BLYP	1.834	1.978	2.015	2.015	2.137
<b>B3L</b>	<b>1.721</b>	<b>2.125</b>	<b>2.374</b>	<b>2.200</b>	<b>2.532</b>
<b>F<sub>0.6</sub>-BLYP</b>	<b>1.972</b>	<b>2.125</b>	<b>2.192</b>	<b>2.200</b>	<b>2.312</b>
EXP. [6]	2.265	2.396	2.461	2.480	2.601

G.Mallia, R.Dovesi, F.Cora',  
Phys Stat Sol B (2006) in press.



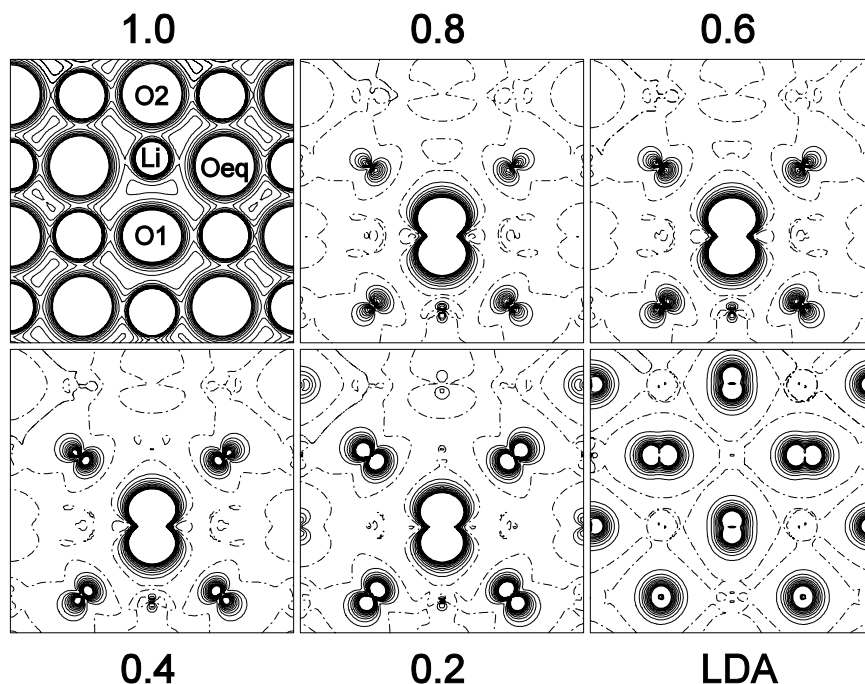
UCL

2D PROJECTION OF  $\rho(r)$ COMPARISON OF HAMILTONIANS: BaTiO<sub>3</sub>  
HYBRID EXCHANGE FUNCTIONALSSUITABLE REFERENCE:  
STANDARD HAMILTONIAN  
(HF or LDA).

F.Cora', Molec. Phys., 103 (2005) 2483.





**SPIN DENSITY** Li-hole in MgOCOMPARISON OF HAMILTONIANS:  
HYBRID EXCHANGE FUNCTIONALSTOTAL ( $a_x=1.0$ )  
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.

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



**FURIO CORA'**

**EPSRC-Advanced Research Fellow**

**University College London, Chemistry**  
**and**

**Davy-Faraday Research Laboratory**

**The Royal Institution**

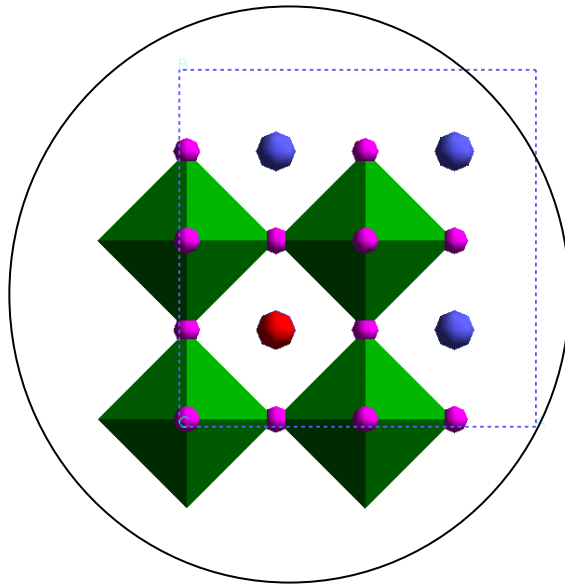
**f.cora@ucl.ac.uk; furio@ri.ac.uk**

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DEFINITION OF THE PROBLEM

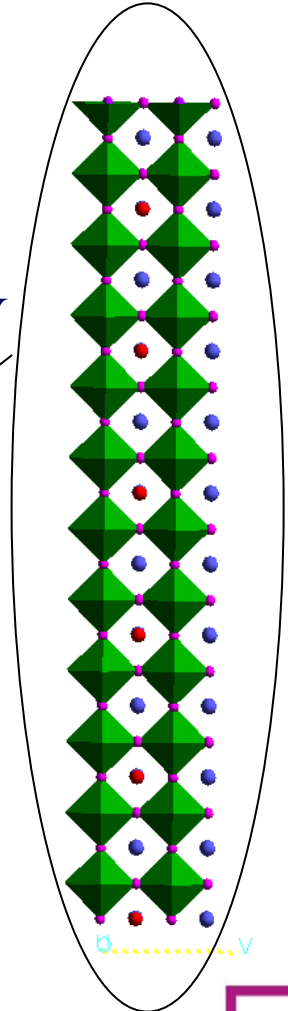
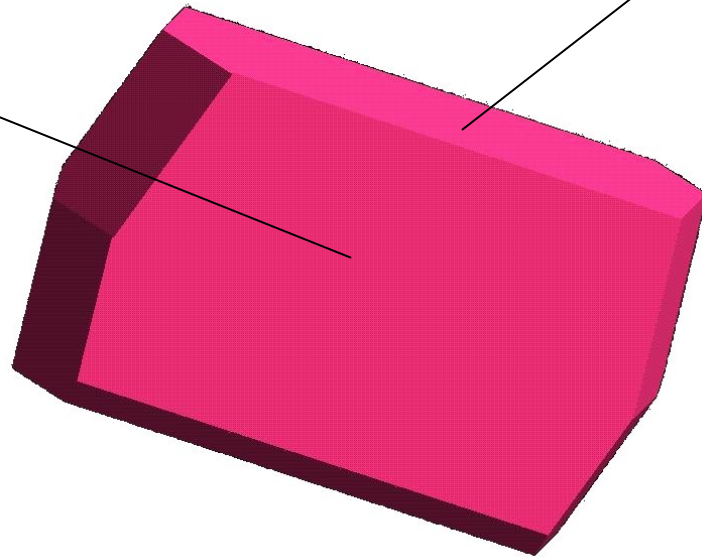
$$N_A \text{ ATOMS} \rightarrow O(10^{23})$$

LOCAL/COLLECTIVE PROPERTIES



BULK PROPERTY

SURFACE PROPERTY

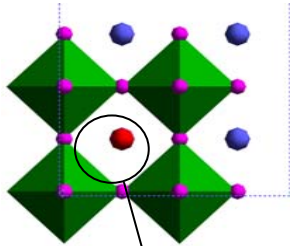


DEFECTS IN BULK/SURFACE



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



DEFECT

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

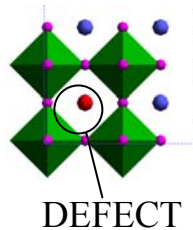
-COLLECTIVE:

ELASTIC CONSTANTS (BULK MOD)  
CONDUCTIVITY  
RESPONSE TO EXTERNAL FIELDS



## CHOICE OF COMPUTATIONAL SETTINGS

### 1) THE MODEL OF THE DEFECTIVE SOLID



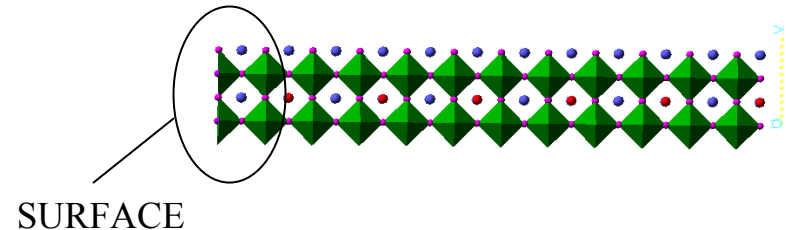
CLUSTER

PERIODIC BOUNDARY CONDITIONS (SUPERCELL)

EMBEDDED CLUSTERS

SLAB

PERIODIC SLAB



### 2) HAMILTONIAN

### 3) CODE-SPECIFIC PARAMETERS

BASIS SET

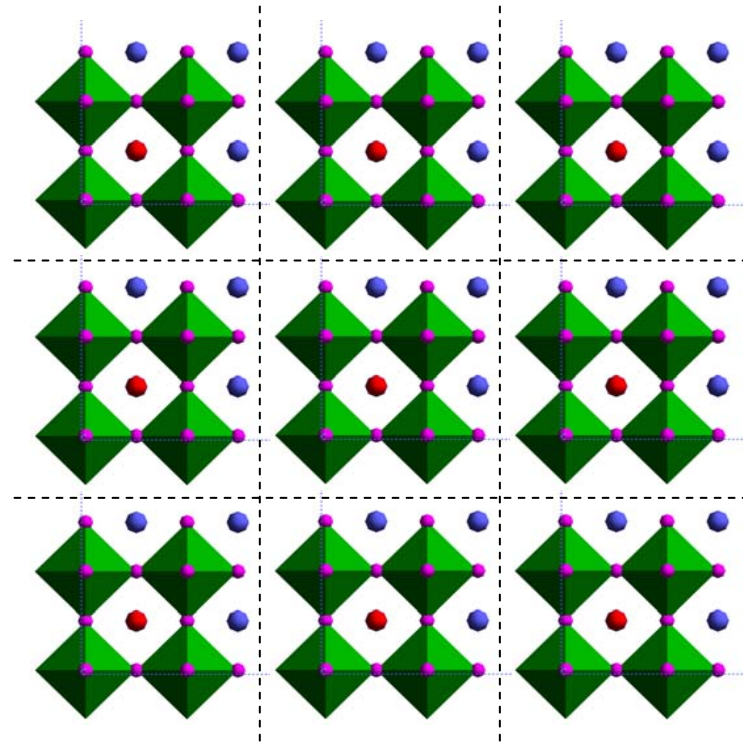
# MODEL OF THE SOLID IN DEFECT STUDIES

## 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

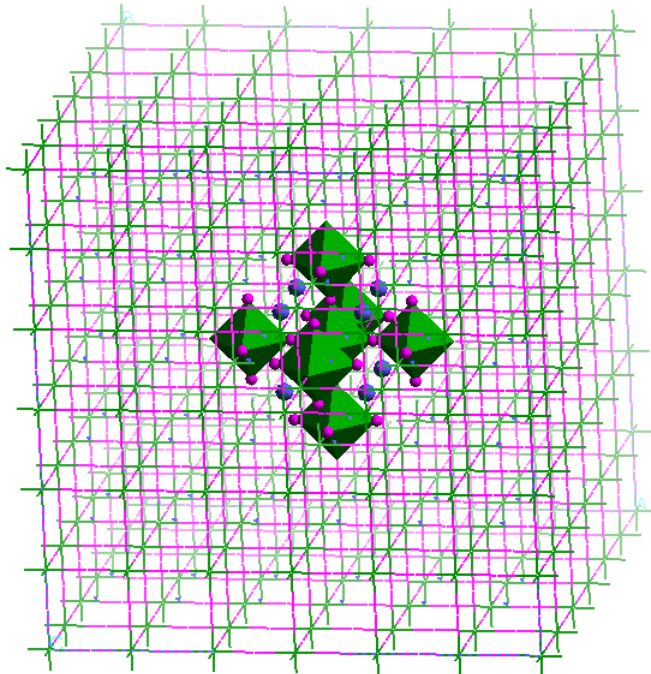
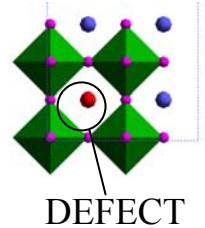


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## MODEL OF THE SOLID IN DEFECT STUDIES

ISOLATED and EMBEDDED CLUSTER

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

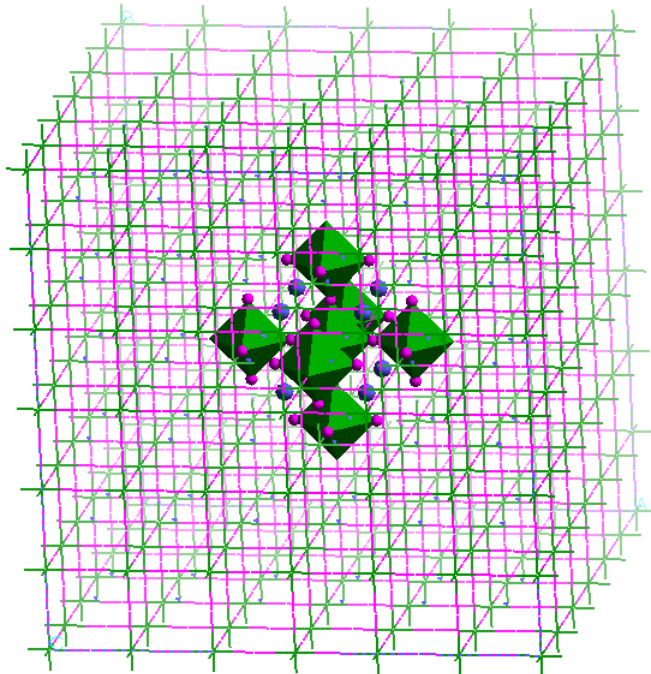
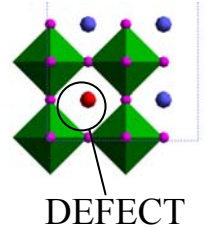


DISCARD (more or less explicitly)  
THE EXTENDED NATURE OF THE  
SOLID; TRY TO RECOVER AS MUCH  
AS POSSIBLE MAKING MODEL  
MORE SOPHISTICATED

# 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**)

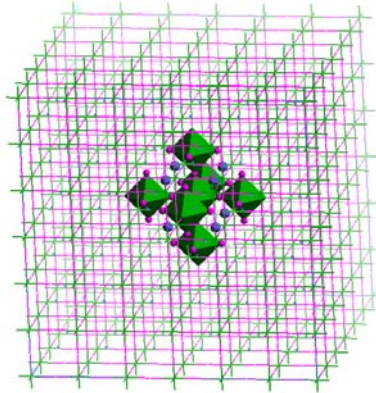
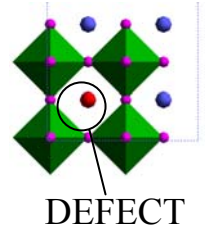


Zone 1	Zone2	Model name
QM	QM	Green's functions
QM	IP	QM/MM
QM	Charges	Embedded cluster
QM	Bond saturation	Embedded cluster
QM	None	Isolated cluster
IP	continuum	Mott-Littleton
QM	Finite cluster	ONIOM



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# ISOLATED and EMBEDDED CLUSTER

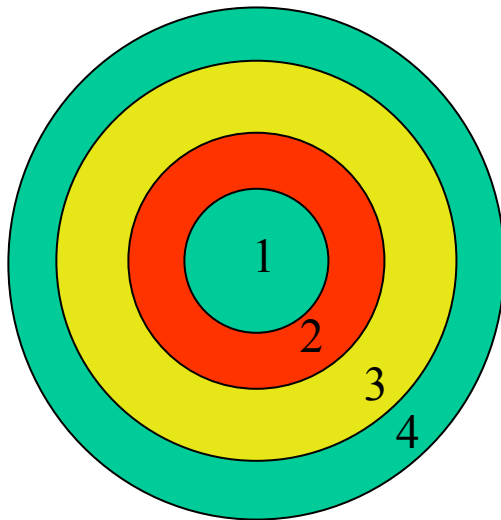
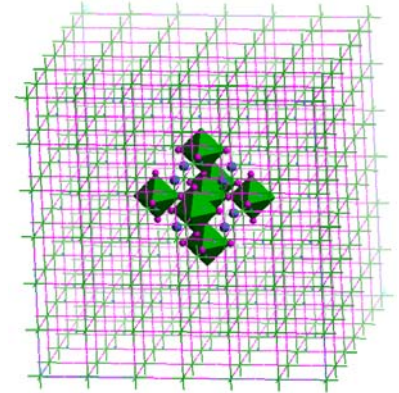


	Zone 1	Zone2	Made-lung field	Long-range relax.	Steric constraints	Delocalised electronic states
	QM	QM	√	√,X	√	√
	QM	IP	√	X	√	X
	QM	Charges	√	X	X	X
	QM	Bond saturation	X	X	X	X
	QM	None	X	X	X	X
	IP	continuum	√	√	√	X



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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

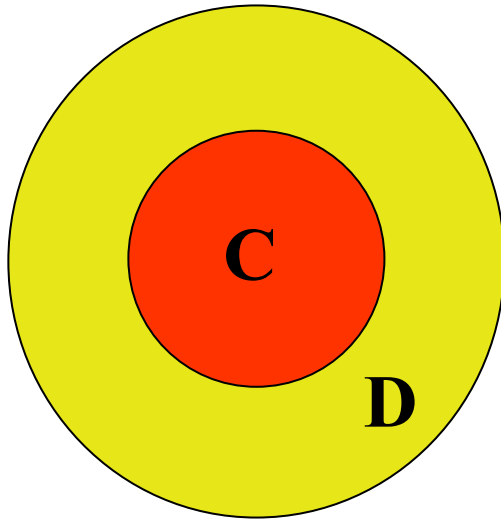
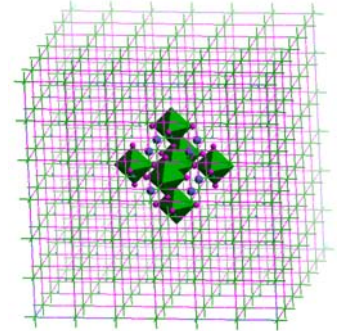
ONIOM:  $E_{TOT} = E_1(\text{HIGH}) + E_2(\text{LOW}) - E_1(\text{LOW})$   
 or  $E_1(\text{HIGH}) + E_2(\text{MED}) - E_1(\text{MED}) + E_3(\text{LOW}) - E_2(\text{LOW})$   
 etc

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;

$P, H \equiv$	<b>CC</b>	<b>CD</b>
	<b>DC</b>	<b>DD<sup>(f)</sup></b>

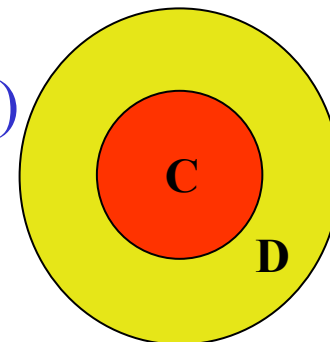
USE PERFECT CRYSTAL SOLUTION (f)  
FOR BLOCK DD; CLUSTER SOLUTION  
FOR CC; COUPLING FOR CD/DC



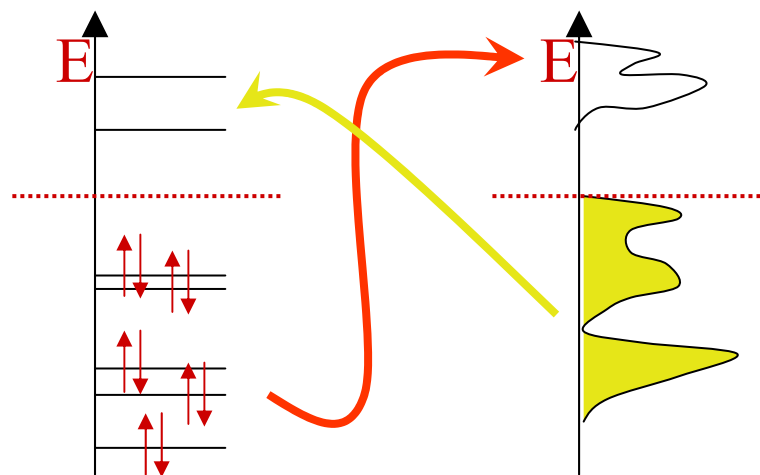
## UCL

# 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

# 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

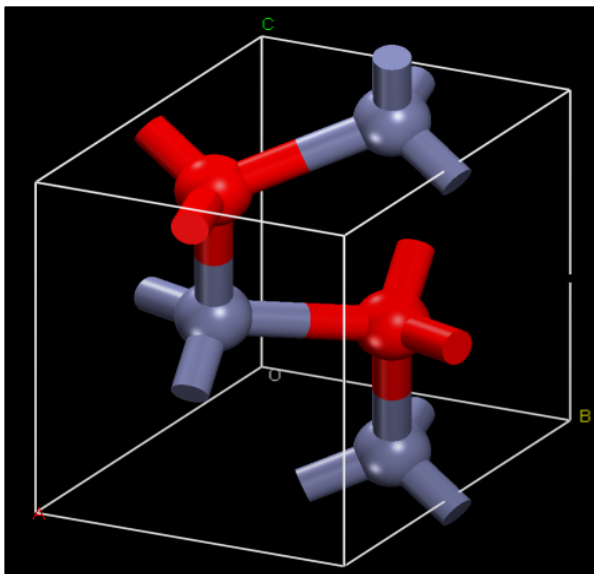
ICI/Synetix

Richard Catlow

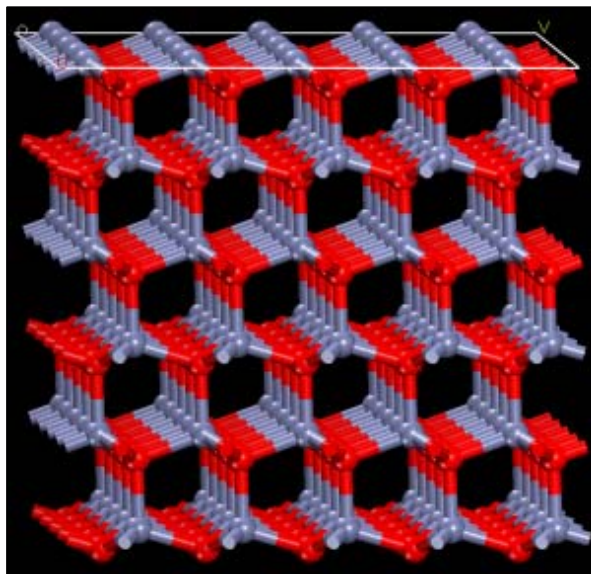
**European Commission Esprit Project (EP 25047) & Industry**

# QM/MM surface embedding

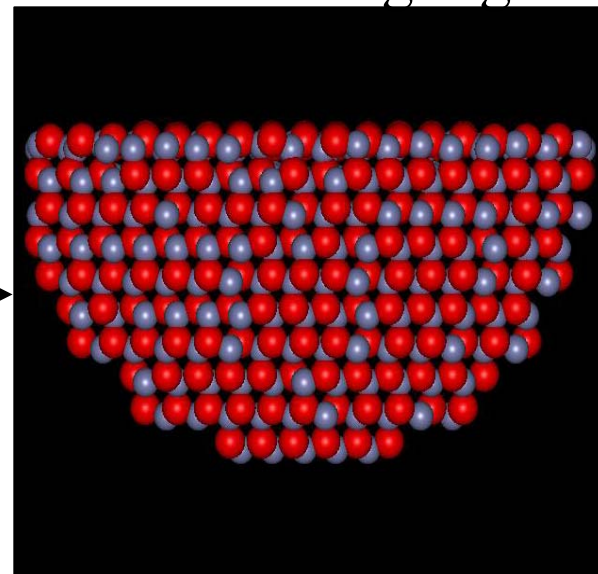
MM bulk



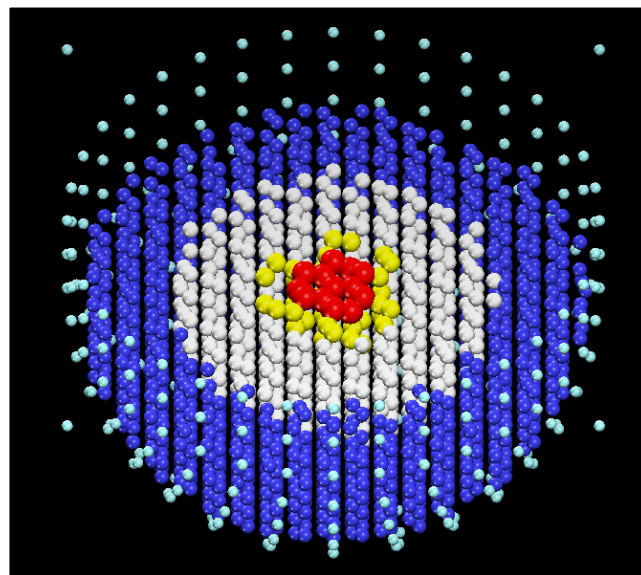
MM surface



MM embedding region



User Input  
Required to  
Choose QM  
region

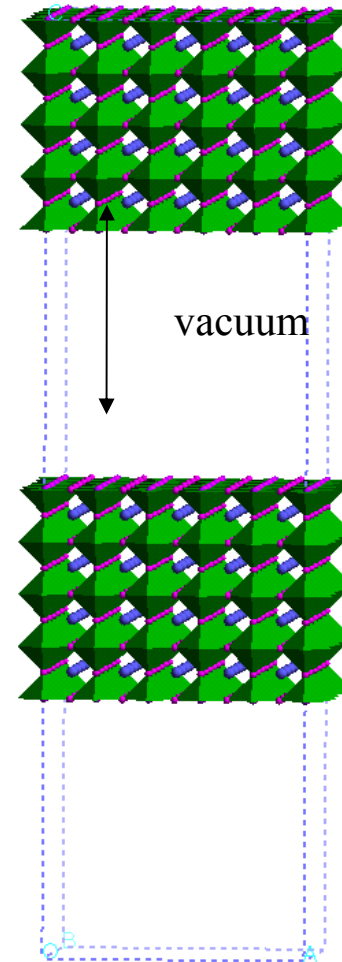
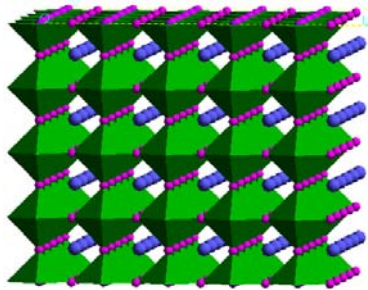


Ready to  
Run

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## MODELS OF A DEFECTIVE SURFACE

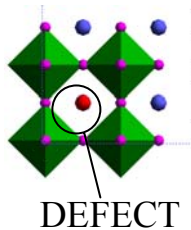
SINGLE or PERIODIC SLAB  
OF **FINITE THICKNESS**  
(vacuum layer thickness)



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:



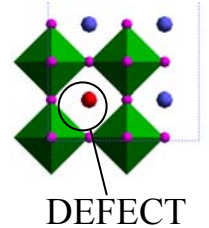
ELASTIC CONSTANTS, BULK MOD  
DIELECTRIC CONSTANTS  
PHONON SPECTRUM  
FERROELECTRIC POLARISATION  
PIEZOELECTRIC CONSTANTS

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

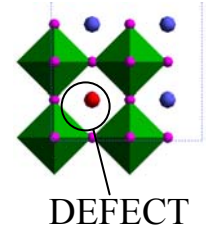
**TIP: USE GEOMETRY-EDITING OPTIONS AVAILABLE  
RETAIN MAXIMUM NUMBER OF SYMMETRY ELEMENTS!**

AVAILABLE KEYWORDS: Manual, page 24 ff

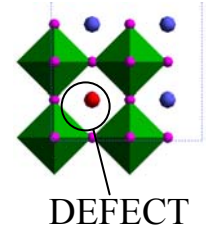
- SUPERCELL
- ATOMDISP, ATOMINSE, ATOMREMO, ATOMSUBS, etc
- DEFINITION OF CLUSTER
- CLUSTER, HYDROSUB, etc

## 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 results

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  $\text{LaCoO}_3$  ( $2\text{Me}^{2+}/\text{La}^{3+} + \text{V}_\text{o}^{2+}$ )

- 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

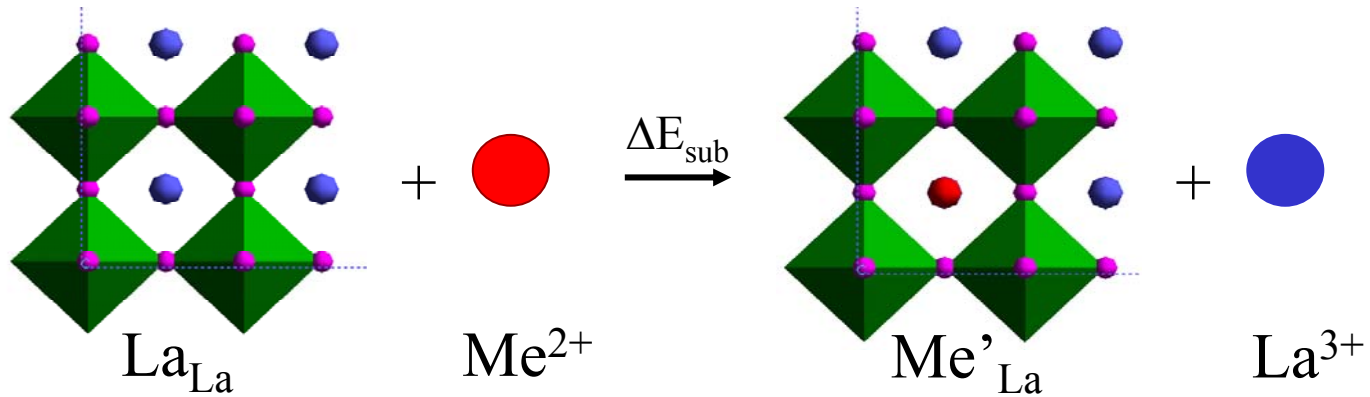
Studied with interatomic potentials; complex structures are still expensive with QM methods, but definitions are the same.

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

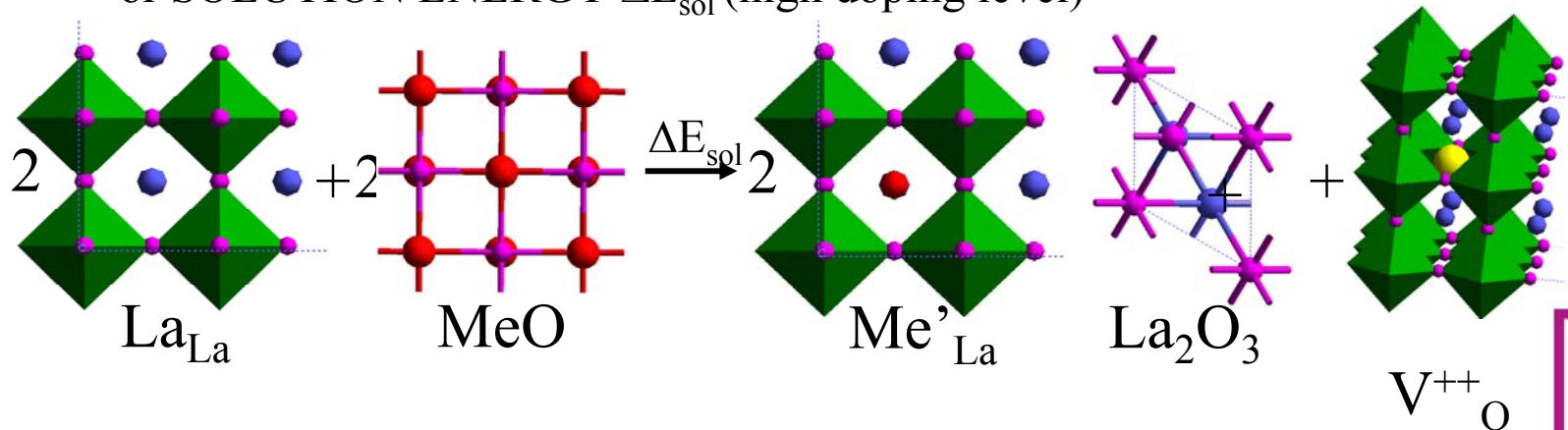
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# 1) DOPING IN $\text{LaCoO}_3$ - $\text{Me}^{2+}$ SOLUBILITY

ANSWER: DEFECT FORMATION ENERGY  $\Delta E_{\text{sub}}$  (low doping level)

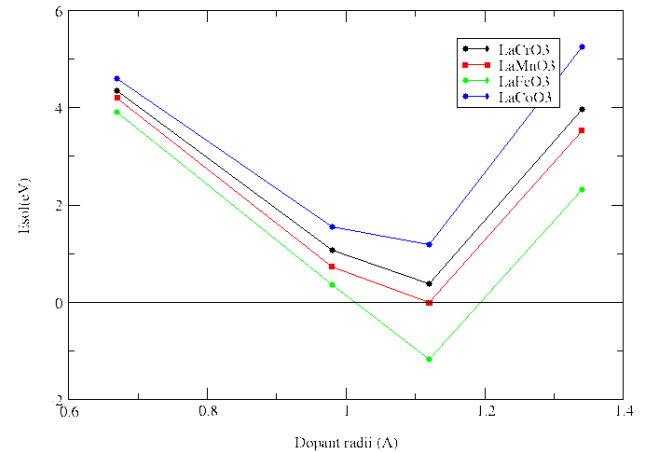


or SOLUTION ENERGY  $\Delta E_{\text{sol}}$  (high doping level)



# 1) DOPING IN $\text{LaMO}_3$ - $\text{Me}^{2+}$ SOLUBILITY

## RESULTS

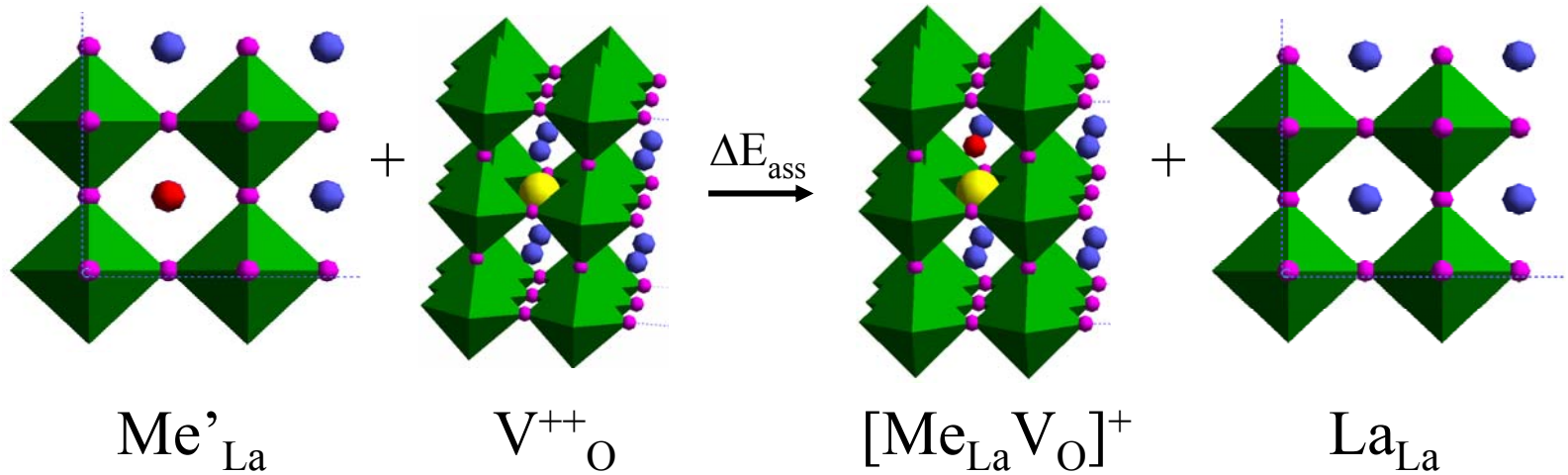


**SIZE MATTERS!!!**  
**SIZE COMPATIBILITY**  
**HOST/DOPANT**

Compound	$E_{\text{sol}}(\text{eV}/\text{dopant})$			
	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Sr}^{2+}$	$\text{Ba}^{2+}$
$\text{LaCrO}_3$	4.35	1.06	0.37	3.97
$\text{LaMnO}_3$	4.20	0.73	-0.01	3.53
$\text{LaFeO}_3$	3.92	0.35	-1.17	2.31
$\text{LaCoO}_3$	4.60	1.54	1.18	5.26

## 2) DOPING IN $\text{LaMO}_3$ – DEFECT ASSOCIATION

ANSWER: DEFECT ASSOCIATION ENERGY  $\Delta E_{\text{ass}}$



RESULTS:

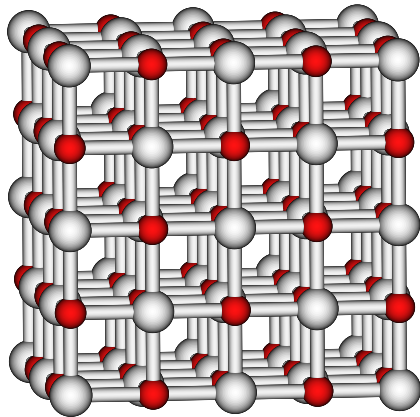
Host Dopant	$\text{LaGaO}_3$	$\text{LaCrO}_3$	$\text{LaMnO}_3$	$\text{LaFeO}_3$	$\text{LaCoO}_3$
Mg/M	-1.37				-0.94
Ca	-0.19				-0.30
Sr	-0.02	0.03	0.35	1.10	-0.19





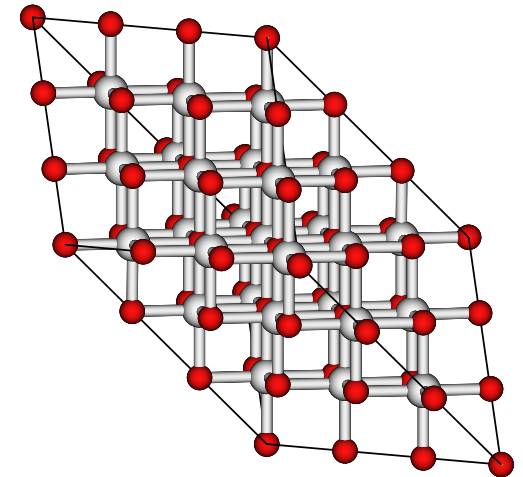
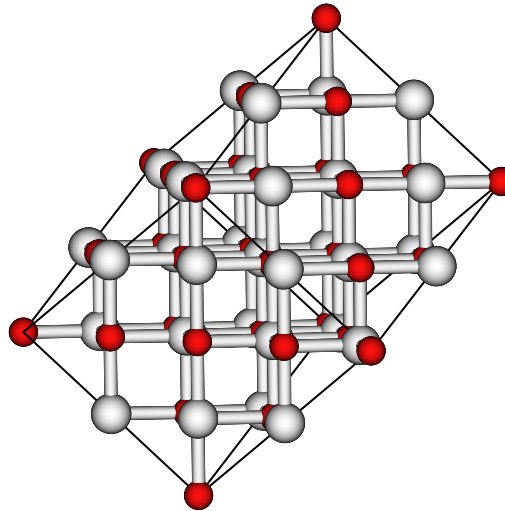
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Li-doping in MgO; charge-balanced by 1 hole  
Possible supercells:



$n \times n \times n$  crystallographic cell  
8,64,216 atoms

$2n \times 2n \times 2n$  double cell  
32,256 atoms



$n \times n \times n$  primitive cell  
8,16,54,128,250 atoms

Check convergence of results



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Li-MgO convergence of results

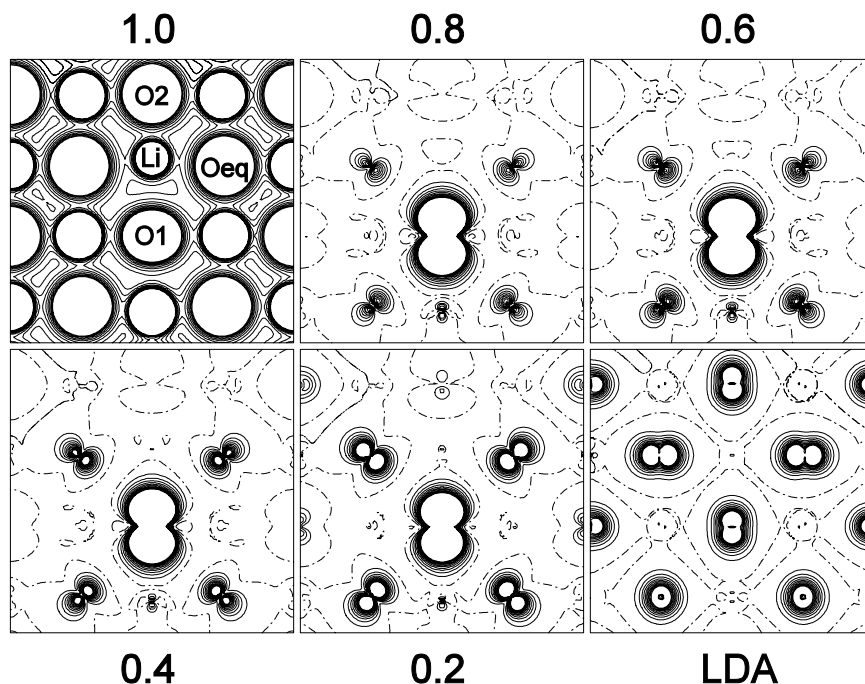
FORMATION ENERGY:

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

					<sup>7</sup> Li	EPR	
<i>n</i>	$\Delta E$	q(Li)	Q(O <sup>-</sup> )	$\mu(\text{O}^-)$	<i>a</i>	<i>b</i>	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.

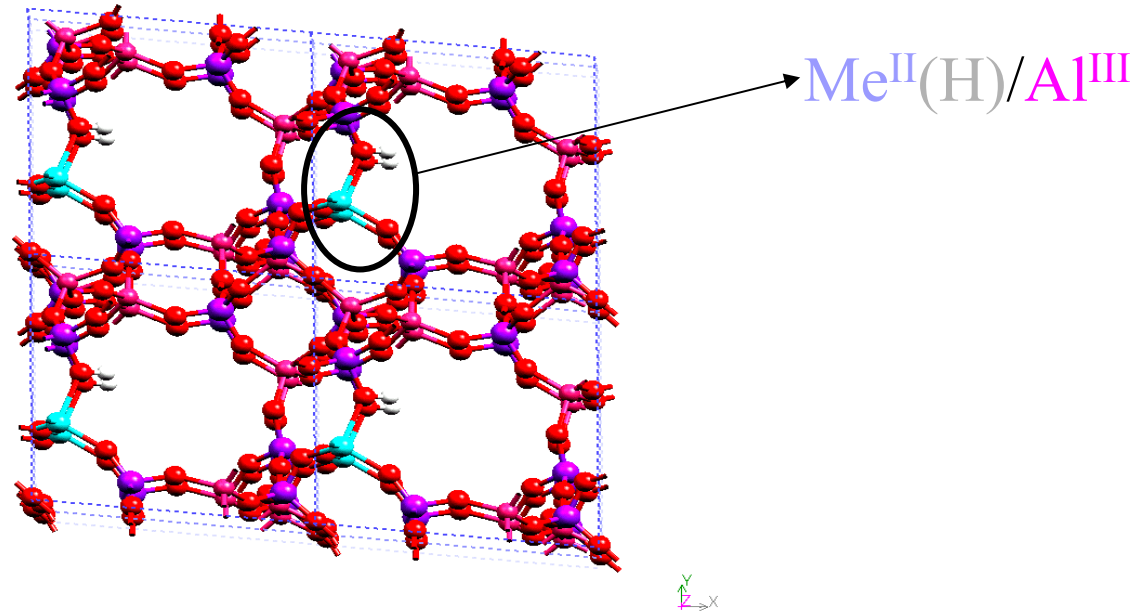
**TRANSITION METAL DOPED  
ALUMINOPHOSPHATES -  
IMPLICATIONS FOR CATALYSIS**

**Furio Corà, Iman Saadoune, Richard**

**Catlow**

*The Royal Institution of G.B.  
Davy-Faraday Research Laboratory  
email: [furio@ri.ac.uk](mailto:furio@ri.ac.uk)*

# SUPERCELL MODEL OF DEFECT CENTRES SUBSTITUTIONAL (DOPANT) IONS



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

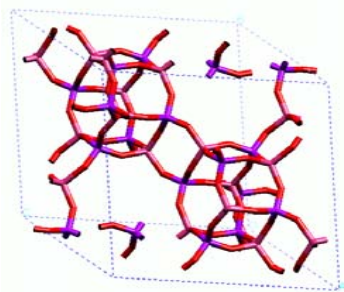
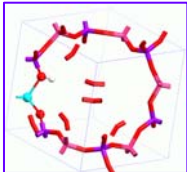
Dopants examined:  $\text{M}^{2+}(\text{H}^+)/\text{Al}^{3+}$  in AlPO-34: Cr, Mn, Fe, Co, Ni, Zn; Be, Mg, Ca, Sr

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

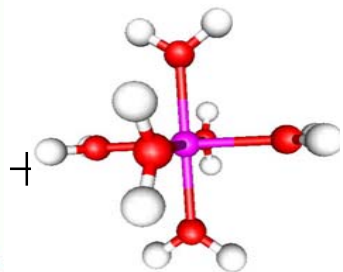
$\text{M}^{3+}(\text{H}^+)/\text{Si}^{4+}$  in Chabasite Cr, Mn, Fe, Co; B, Al, Ga

# Substitutional energy of a framework Al with Me<sup>II</sup>dopants

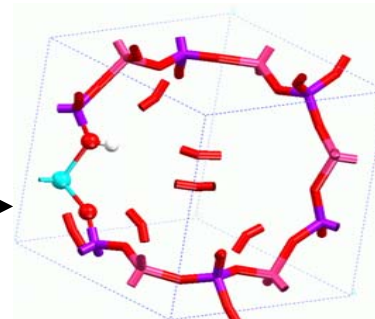
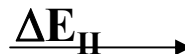
## HYDROTHERMAL SYNTHESIS



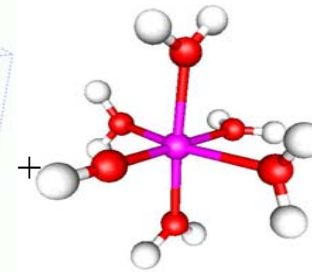
Pure AlPO-34



$[Me^{II}(H_2O)_6]^{2+}$



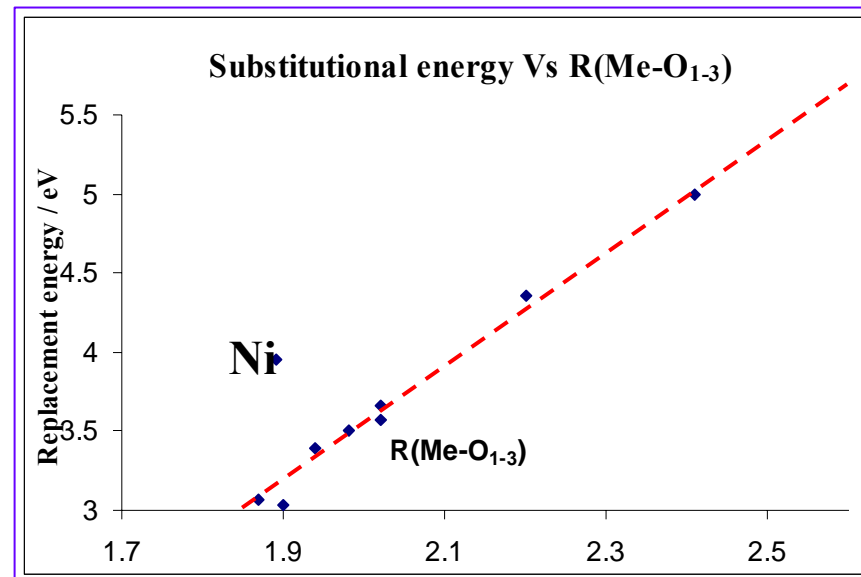
$Me^{II}AlPO-34$



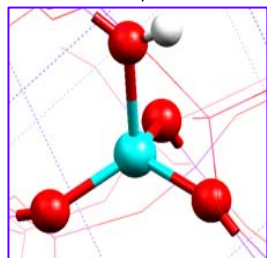
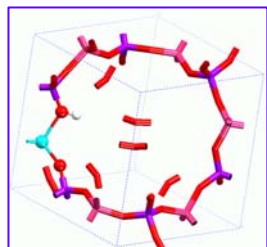
$[Al(H_2O)_5(OH)]^{2+}$

Me <sup>II</sup>	Mg <sup>II</sup>	Ca <sup>II</sup>	Cr <sup>II</sup>	Mn <sup>II</sup>	Fe <sup>II</sup>	Co <sup>II</sup>	Ni <sup>II</sup>	Zn <sup>II</sup>	Sr <sup>II</sup>
$\Delta E_{II} / eV$	3.067	4.351	3.576	3.660	3.508	3.393	3.948	3.038	4.996

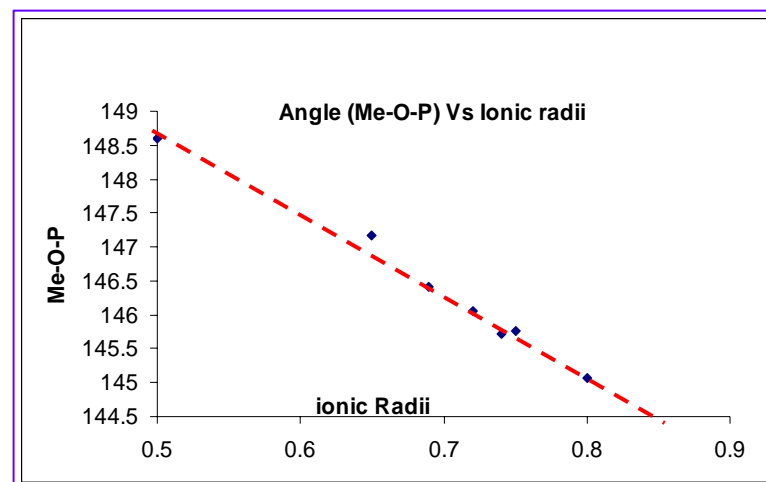
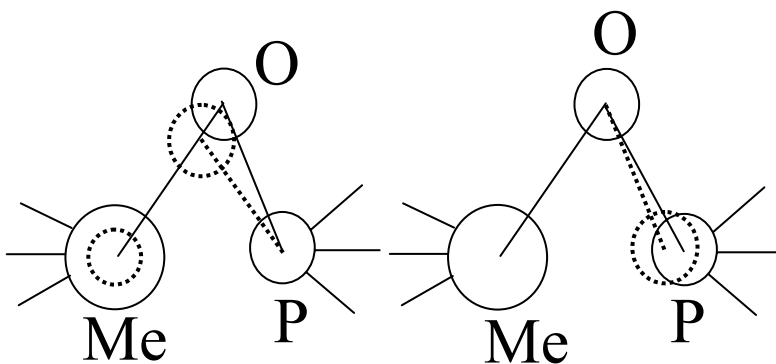
- With the exception of Ni<sup>II</sup>, which is unstable in tetrahedral coordination, the replacement energy increases linearly as a function of the Me-O bond distance.
- The larger the size of the metal dopant, the more difficult its inclusion in the AlPO framework



# EQUILIBRIUM STRUCTURE



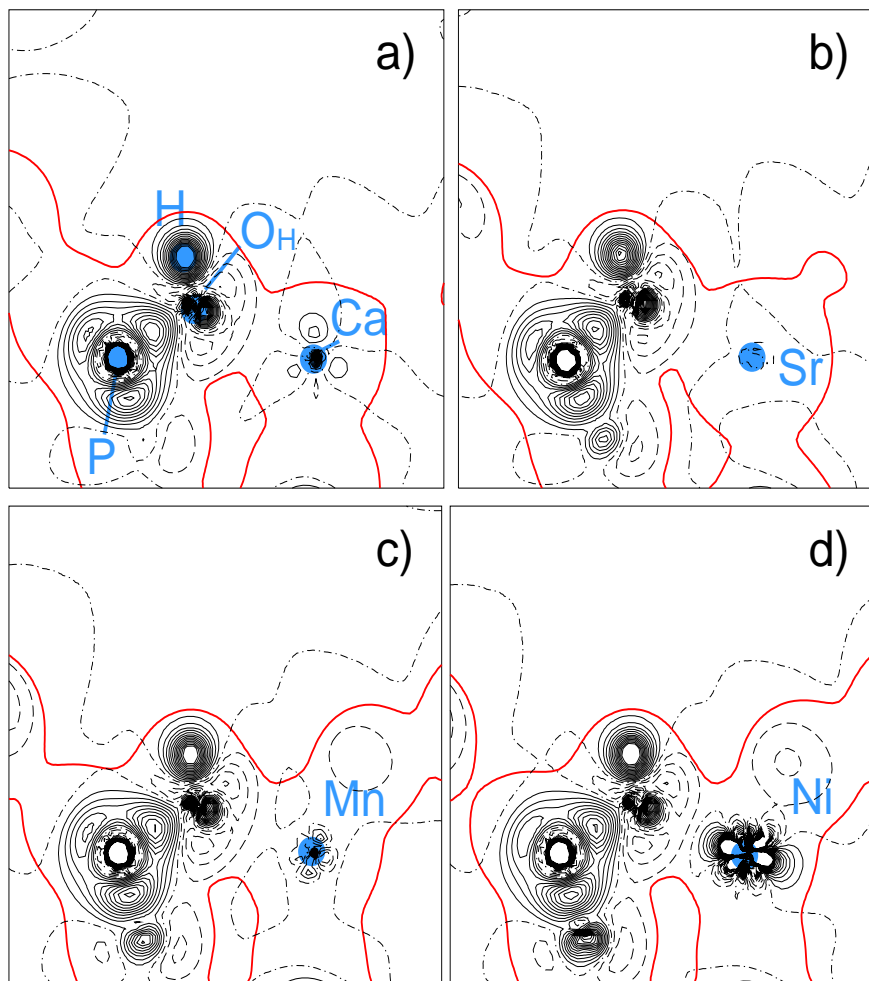
Me <sup>II</sup>	r(Me <sup>II</sup> -O <sub>1</sub> )	r(Me <sup>II</sup> -O <sub>2</sub> )	r(Me <sup>II</sup> -O <sub>3</sub> )	r(Me <sup>II</sup> -O <sub>4</sub> H)	AVG r(Me <sup>II</sup> -O)	Exp ± 0.02 EXAFS
Mg <sup>II</sup>	1.85	1.87	1.91	2.08	1.93	1.94
Ni <sup>II</sup>	1.91	1.92	1.93	2.11	1.98	1.99
Zn <sup>II</sup>	1.90	1.90	1.91	2.18	1.99	1.96
Cr <sup>II</sup>	1.99	2.03	2.04	2.35	2.11	-
Co <sup>II</sup>	1.95	1.94	1.94	2.14	1.99	1.94
Fe <sup>II</sup>	1.99	1.97	1.98	2.19	2.01	-
Mn <sup>II</sup>	2.02	2.04	2.01	2.26	2.08	2.02
Ca <sup>II</sup>	2.17	2.19	2.24	2.40	2.25	-
Sr <sup>II</sup>	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 Saadoun, F. Corà and C.R.A. Catlow,  
*J. Phys. Chem. B*, 2003, 107, 3003.

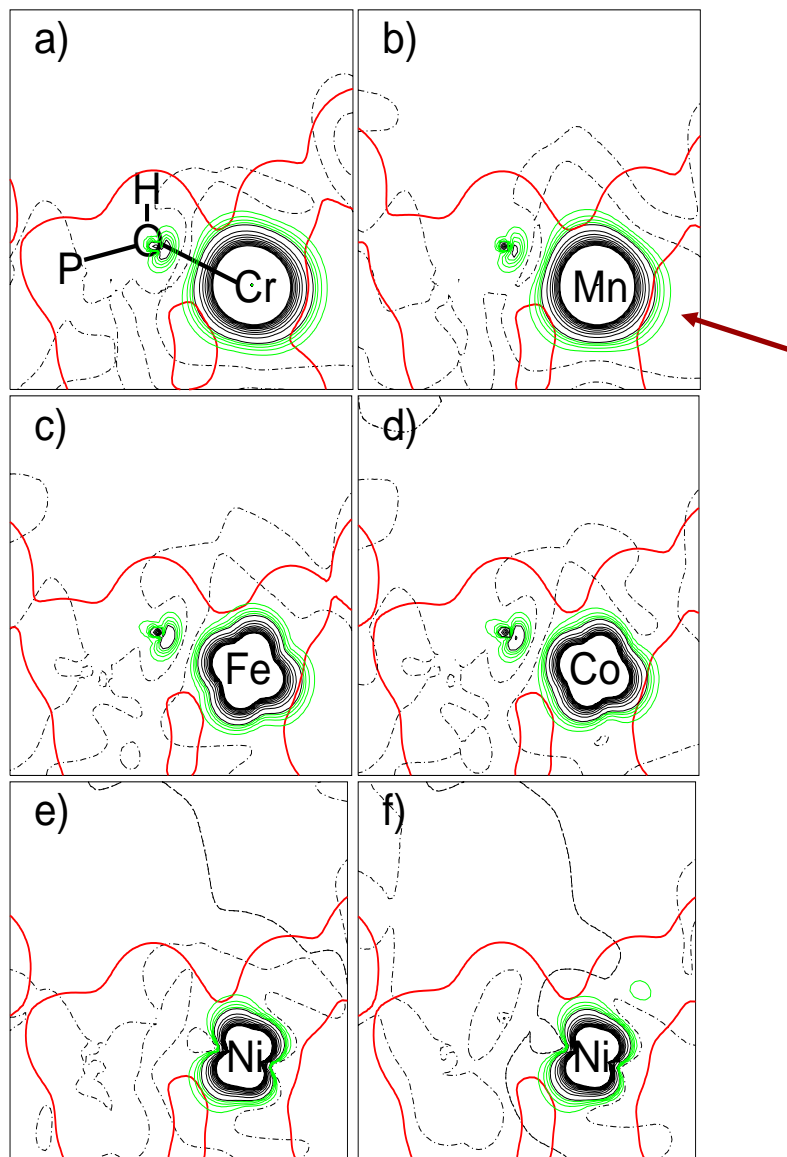


## LEWIS ACIDITY of TRANSITION METAL DOPED ALUMINOPHOSPHATES

spin density of the TM ion  
compared to the  
framework size

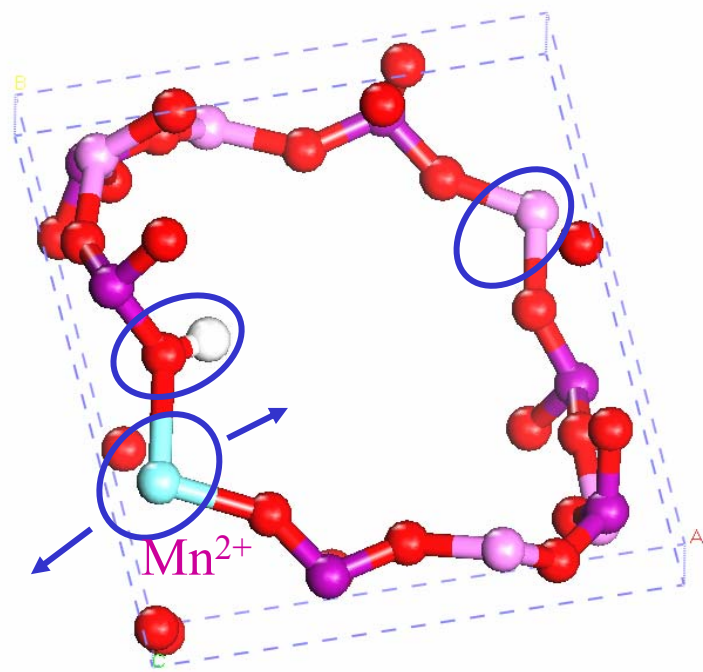
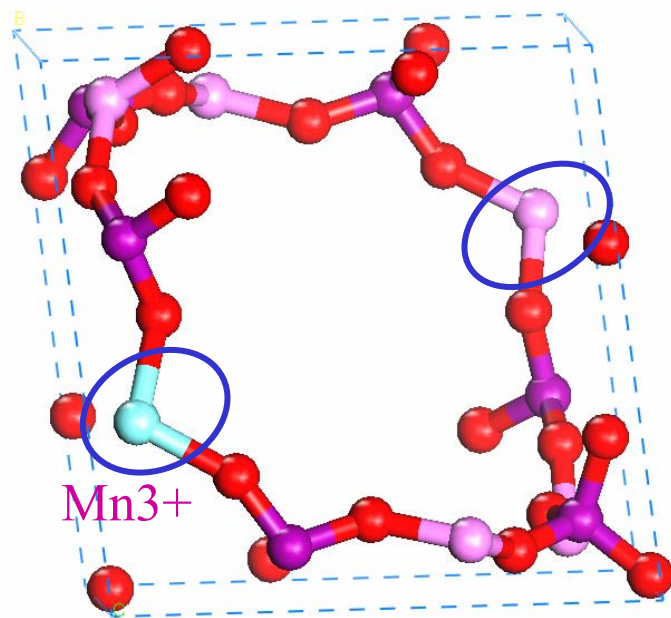
Most effective **from behind**  
the proton

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



# Water adsorption in Mn-doped AlPO-34 catalysts

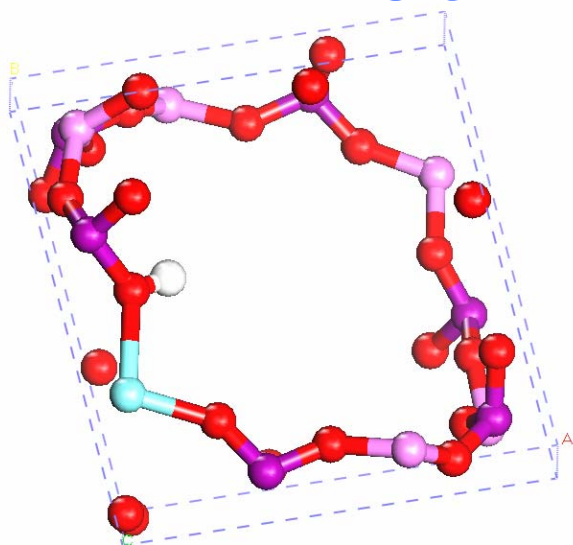
- How does hydration modify the structure and electronic properties of the Mn dopant, and the framework stability ?



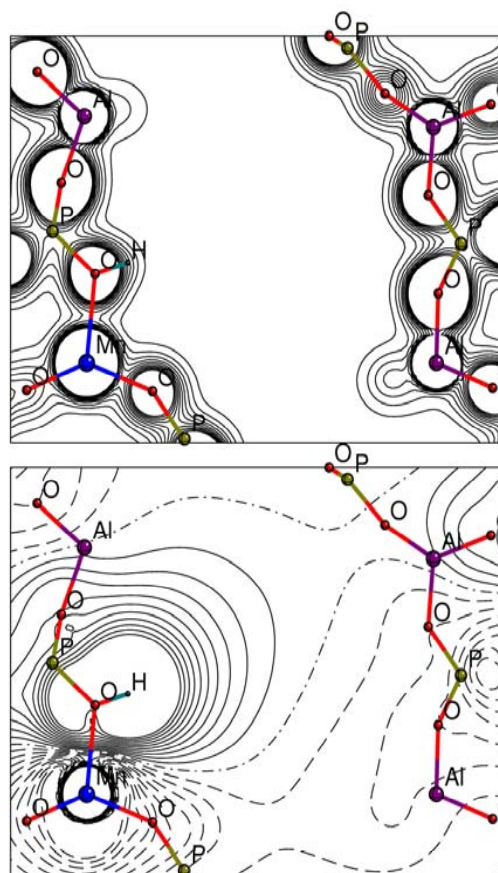
UCL

# WATER ADSORPTION

## Mn<sup>II</sup>-HAIPO-34



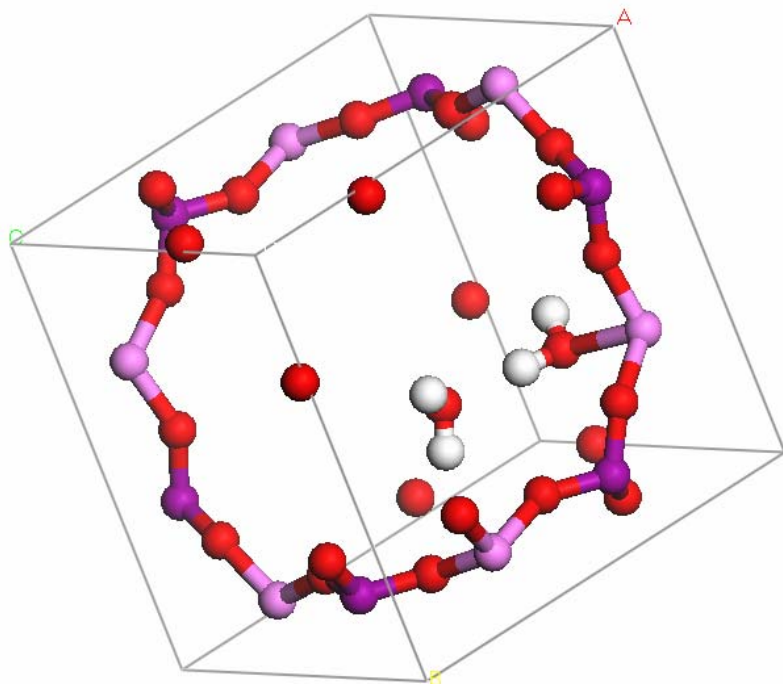
(DIFFERENCE)  
ELECTROSTATIC  
POTENTIAL  
 $\Delta V(\text{MnAlPO}-\text{AlPO})$



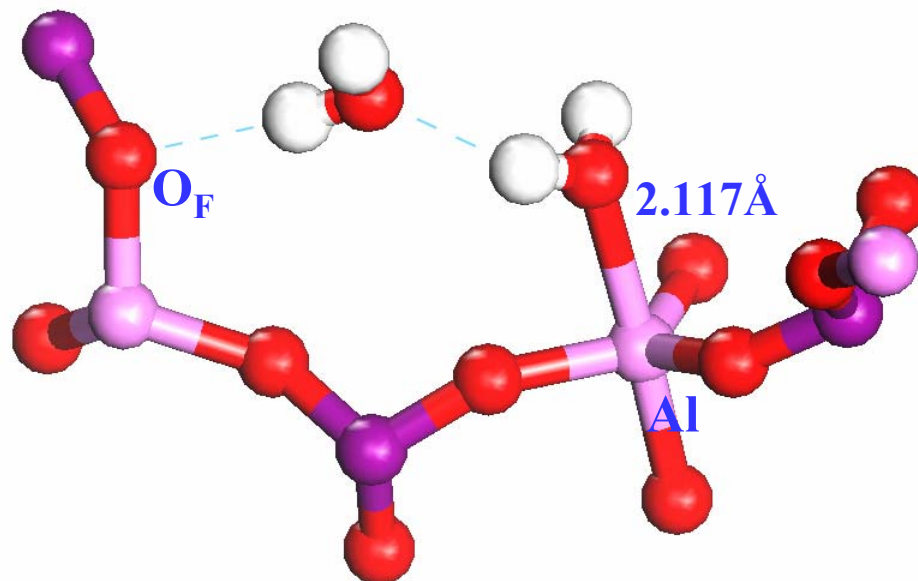
I.Saadoune, C.R.A.Catlow, K.Doll,  
F.Corà, Molec. Simul., 30 (2004) 607.



# Water interaction with Pure AlPO-34



*AlPO-34, 2H<sub>2</sub>O*



$$\Delta E_{ad} = E(\text{AlPO-34, 2H}_2\text{O}) - [E(\text{AlPO-34}) + E(\text{Dimer})]$$

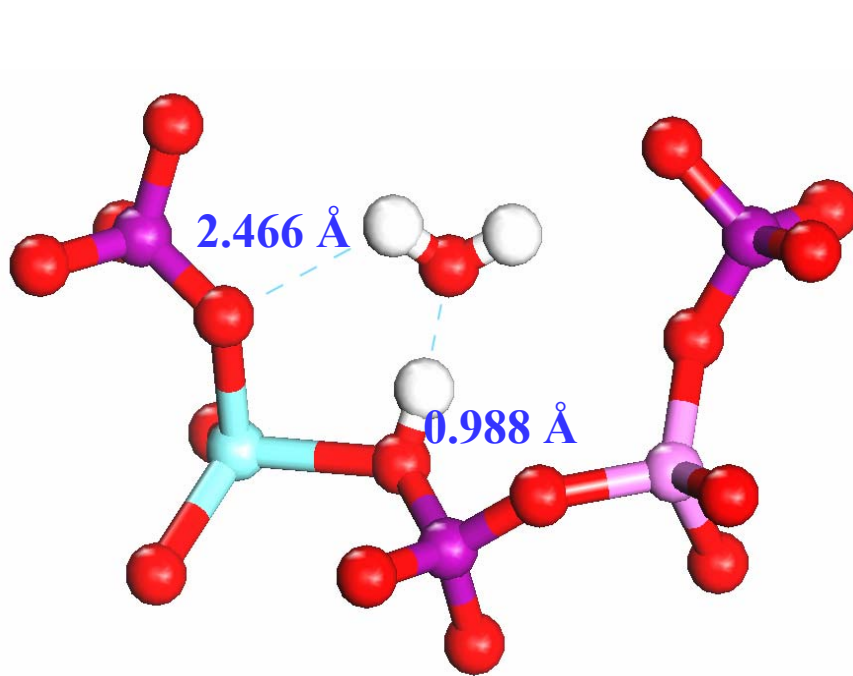
$$\Delta E_{ad} = -0.39 \text{ eV}$$

Hydrophilic nature of the AlPO framework

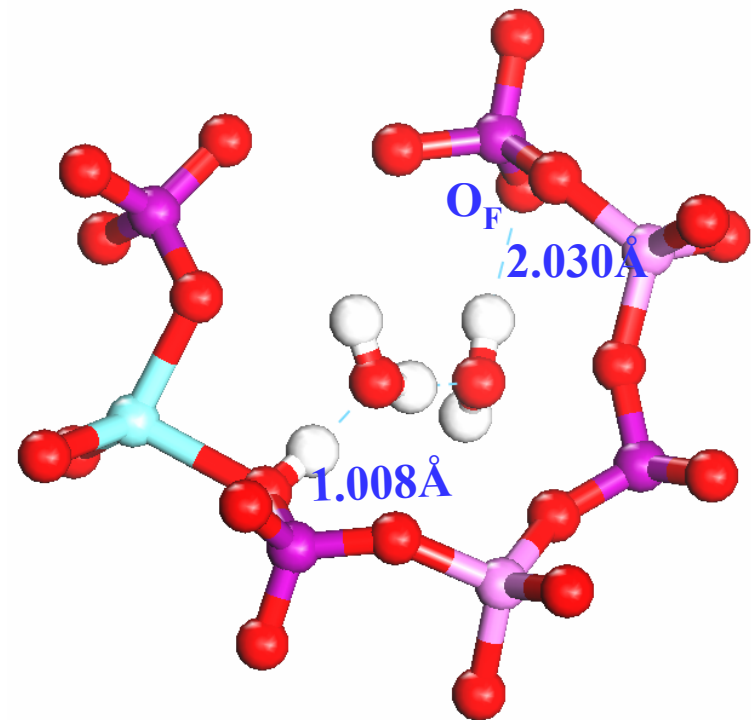
FRAMEWORK INVOLVEMENT → EXTENDED REGION PERTURBED

# Water interaction with Mn<sup>II</sup>-doped AlPO-34

## Water adsorption on the Acid site (OH)

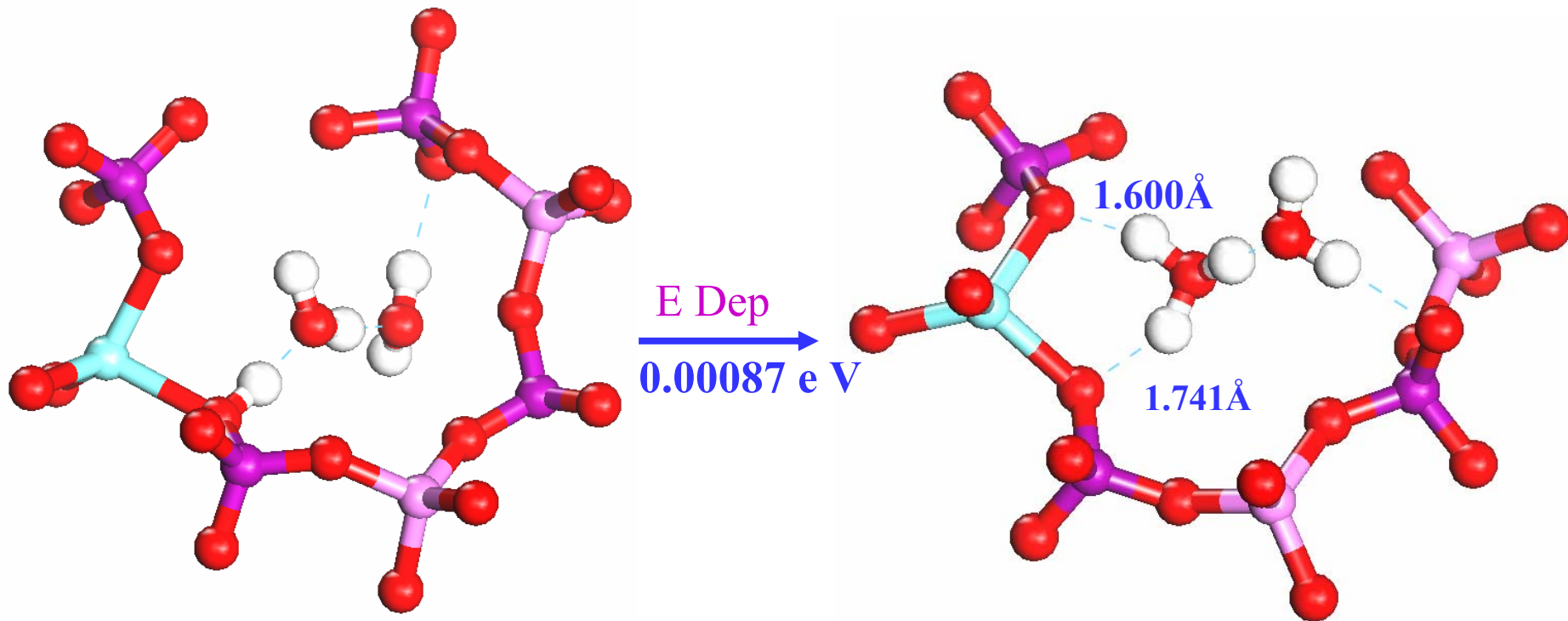


$$\Delta E_{\text{ad}} = -0.93 \text{ eV}$$



$$\Delta E_{\text{ad}} = -1.19 \text{ eV}$$

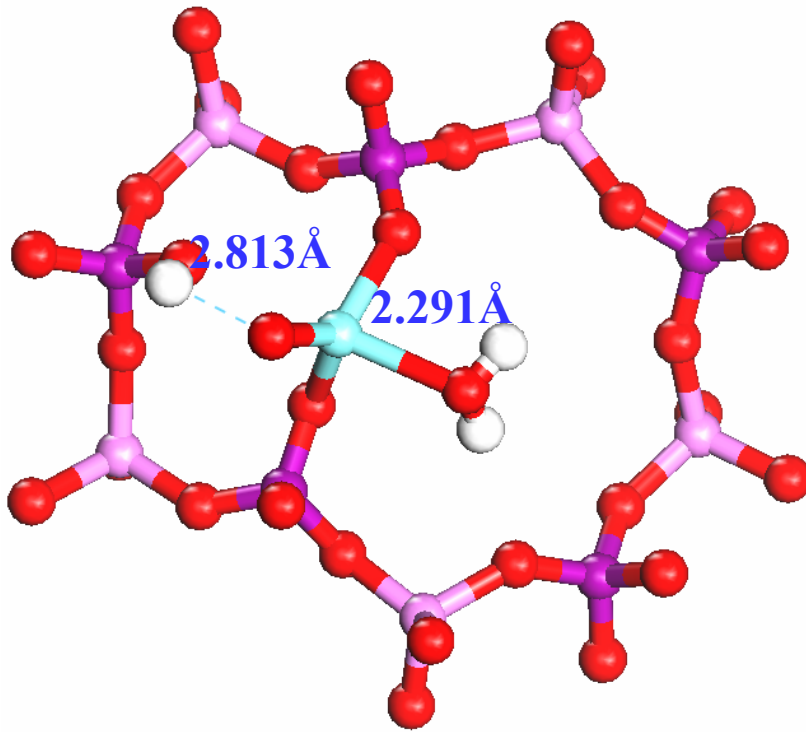
# Framework Deprotonation



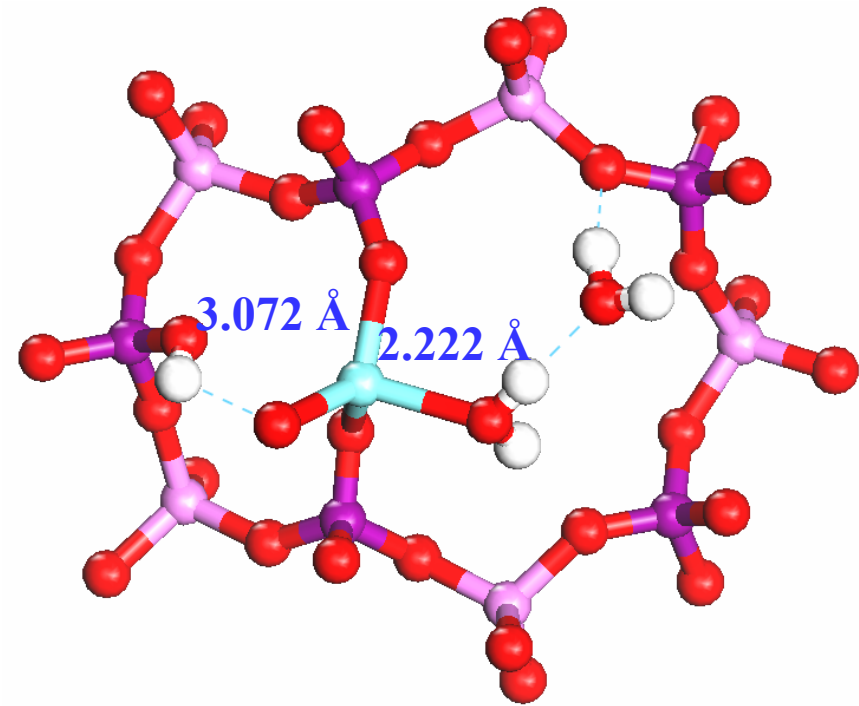
H-BONDED NETWORK INVOLVING THE FRAMEWORK  
EXTENDS UP TO  $\sim 9\text{\AA}$  AWAY FROM DOPANT  
CLUSTER MODELS FAIL TO REPRODUCE IT

# Water adsorption on the Mn<sup>II</sup> site

*The side opposite the acid proton (Attack from behind)*



$$\Delta E_{\text{ad}} = -0.84 \text{ eV}$$



$$\Delta E_{\text{ad}} = -1.17 \text{ eV}$$

*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