Quantum Matter Institute
THE UNIVERSITY OF BRITISH COLUMBIA

SOLVATION AND POLARIZABILITY BRAINSTORMING SESSION

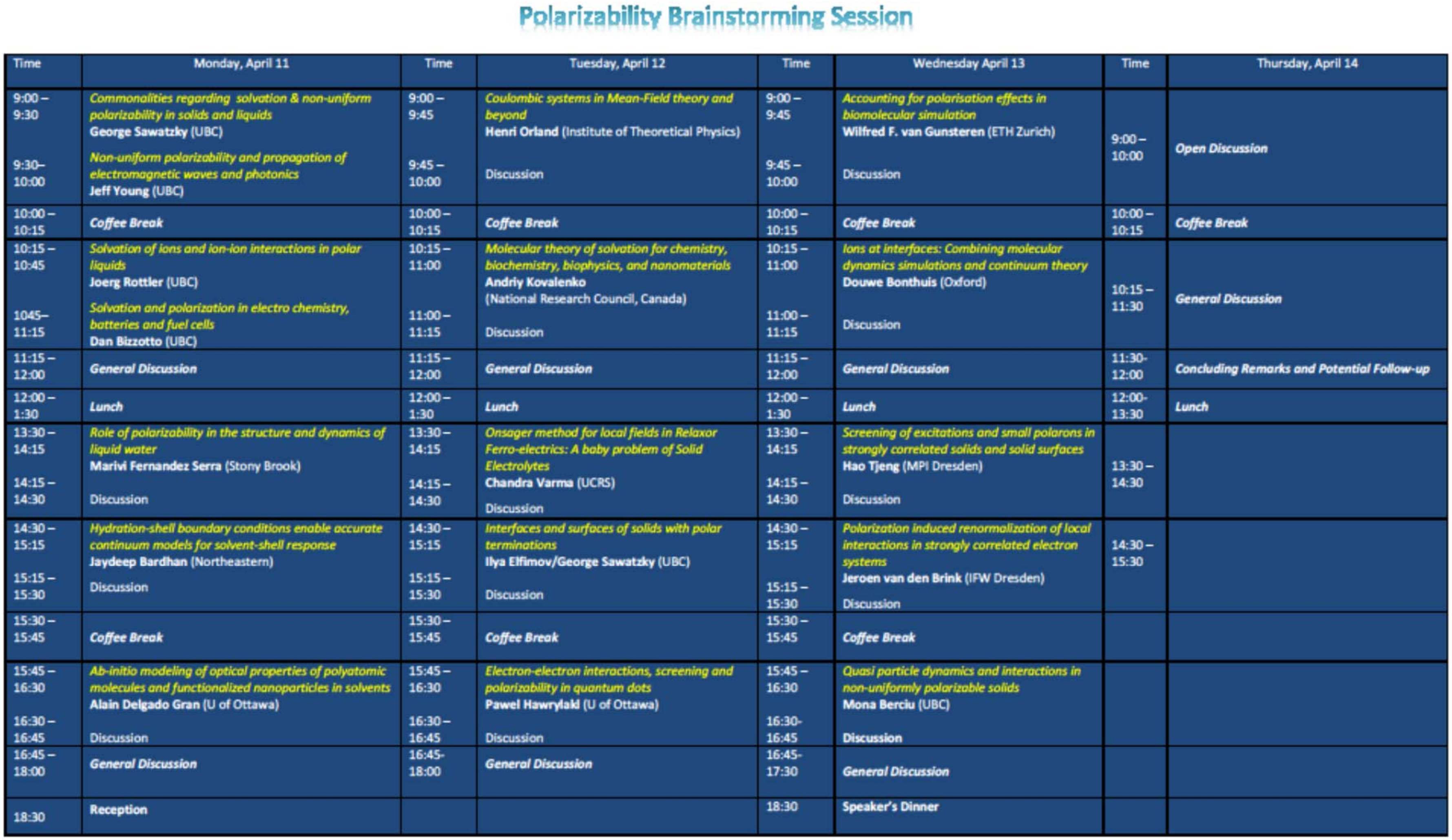
SUPPORTED BY THE Quantum Matter Institute and by the Max Planck/UBC Center for Quantum Materials

George Sawatzky

Importance of SOlvation and polarizability In:

- Life sciences
- electro chemistry
- Batteries and fuel cells
- photo chemistry
- Photonics
- Metamaterials
- Non uniformly polarizable solids
- Structure of water
- Interfaces between materials

SOLVATION AND POLARIZABILITY BRAINSTORMING SESSION

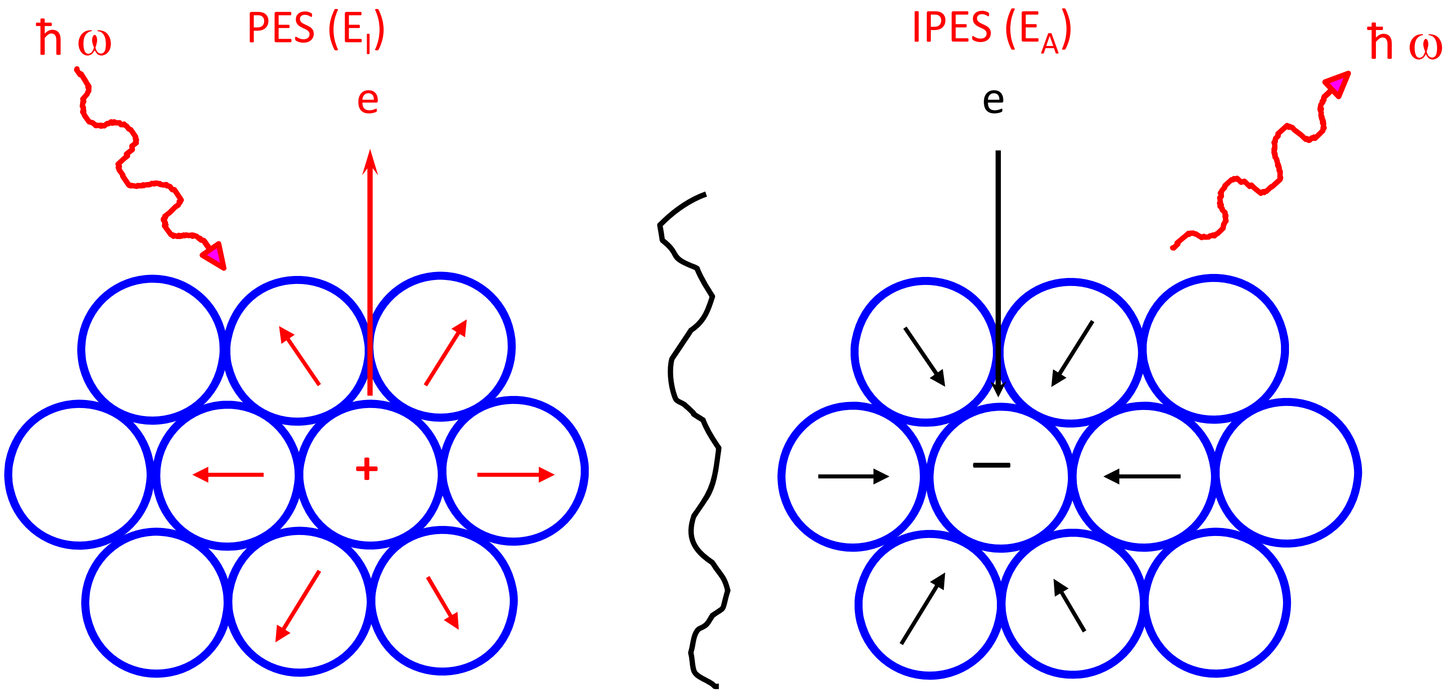


Polarizability Brainstorming Session

Time	Monday, April 11	Time	Tuesday, April 12	Time	Wednesday April 13	Time	Thursday, April 14
9:00 – 9:30 9:30– 10:00	*Commonalities regarding solvation & non-uniform polarizability in solids and liquids* **George Sawatzky** (UBC) *Non-uniform polarizability and propagation of electromagnetic waves and photonics* **Jeff Young** (UBC)	9:00 – 9:45 9:45 – 10:00	*Coulombic systems in Mean-Field theory and beyond* **Henri Orland** (Institute of Theoretical Physics) Discussion	9:00 – 9:45 9:45 – 10:00	*Accounting for polarisation effects in biomolecular simulation* **Wilfred F. van Gunsteren** (ETH Zurich) Discussion	9:00 – 10:00	***Open Discussion***
10:00 – 10:15	***Coffee Break***	10:00 – 10:15	***Coffee Break***	10:00 – 10:15	***Coffee Break***	10:00 – 10:15	***Coffee Break***
10:15 – 10:45 1045– 11:15	*Solvation of ions and ion-ion interactions in polar liquids* **Joerg Rottler** (UBC) *Solvation and polarization in electro chemistry, batteries and fuel cells* **Dan Bizzotto** (UBC)	10:15 – 11:00 11:00 – 11:15	*Molecular theory of solvation for chemistry, biochemistry, biophysics, and nanomaterials* **Andriy Kovalenko** (National Research Council, Canada) Discussion	10:15 – 11:00 11:00 – 11:15	*Ions at interfaces: Combining molecular dynamics simulations and continuum theory* **Douwe Bonthuis** (Oxford) Discussion	10:15 – 11:30	***General Discussion***
11:15 – 12:00	***General Discussion***	11:15 – 12:00	***General Discussion***	11:15 – 12:00	***General Discussion***	11:30- 12:00	***Concluding Remarks and Potential Follow-up***
12:00 – 1:30	***Lunch***	12:00 – 1:30	***Lunch***	12:00 – 1:30	***Lunch***	12:00- 13:30	***Lunch***
13:30 – 14:15 14:15 – 14:30	*Role of polarizability in the structure and dynamics of liquid water* **Marivi Fernandez Serra** (Stony Brook) Discussion	13:30 – 14:15 14:15 – 14:30	*Onsager method for local fields in Relaxor Ferro-electrics: A baby problem of Solid Electrolytes* **Chandra Varma** (UCRS) Discussion	13:30 – 14:15 14:15 – 14:30	*Screening of excitations and small polarons in strongly correlated solids and solid surfaces* **Hao Tjeng** (MPI Dresden) Discussion	13:30 – 14:30	
14:30 – 15:15 15:15 – 15:30	*Hydration-shell boundary conditions enable accurate continuum models for solvent-shell response* **Jaydeep Bardhan** (Northeastern) Discussion	14:30 – 15:15 15:15 – 15:30	*Interfaces and surfaces of solids with polar terminations* **Ilya Elfimov/George Sawatzky** (UBC) Discussion	14:30 – 15:15 15:15 – 15:30	*Polarization induced renormalization of local interactions in strongly correlated electron systems* **Jeroen van den Brink** (IFW Dresden) Discussion	14:30 – 15:30	
15:30 – 15:45	***Coffee Break***	15:30 – 15:45	***Coffee Break***	15:30 – 15:45	***Coffee Break***		
15:45 – 16:30 16:30 – 16:45	*Ab-initio modeling of optical properties of polyatomic molecules and functionalized nanoparticles in solvents* **Alain Delgado Gran** (U of Ottawa) Discussion	15:45 – 16:30 16:30 – 16:45	*Electron-electron interactions, screening and polarizability in quantum dots* **Pawel Hawrylakl** (U of Ottawa) Discussion	15:45 – 16:30 16:30- 16:45	*Quasi particle dynamics and interactions in non-uniformly polarizable solids* **Mona Berciu** (UBC) **Discussion**		
16:45 – 18:00	***General Discussion***	16:45- 18:00	***General Discussion***	16:45- 17:30	***General Discussion***		
18:30	**Reception**			18:30	**Speaker's Dinner**		

We are alive because of sOlvation!!

Solvation of ions in polarizable media



Full polarization develops if Dynamic Response is fast

ΔE > W ; ΔE ≈ energy scale of pol. medium , i.e MO splitting, plasma frequency in metals--- ΔE ---AS HIGH AS 5-20 eV

Solvation in electro chemistry

- Take Na in NH3 (Ammonia) well know that Na ionizes because of the lowering of the ionization potential in a polarizable medium and becomes solvated
- Also the electron which hangs around for charge neutrality will be Solvated lowering its energy from that of the vacuum level.
- The solvated Na or electron will propagate as a polaron carrying the solvation cloud along with it.
- Similarly for NaCl dissolved in water.

Coulomb Interactions in non-Uniformly polarizable media

Homogeneous Maxwell Equations

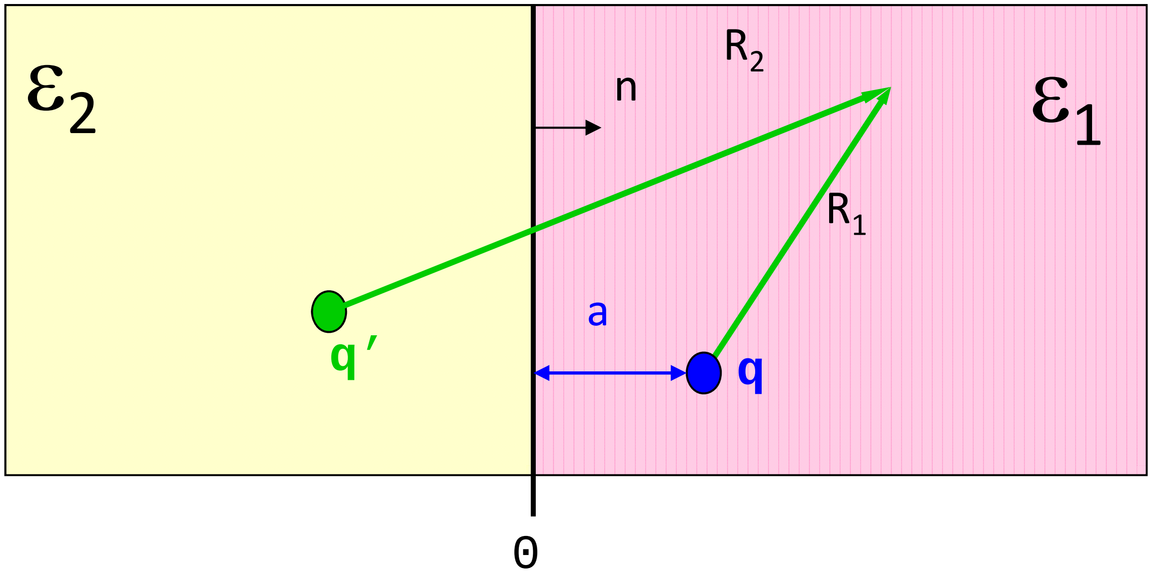
$$\varepsilon(r,r') \longrightarrow \varepsilon(r-r') \longrightarrow \varepsilon(q)$$

Ok if polarizability is uniform Or for q close to zero corresponding to large distances

$$V(q) = \frac{V^0(q)}{\varepsilon(q)}$$

In most correlated electron systems and molecular solids the polarizability is Very NONUNIFORM

Potential of a point charge in the neighbourhood of a dielectric in general



$$(D_1 - D_2)\bullet n = 4\pi\sigma$$

$$(E_1 - E_2)\times n = 0$$

σ - *surface charge*

$$\varepsilon_1 \nabla \bullet E = 4\pi \cdot l \quad z > 0$$

$$\varepsilon_2 \nabla \bullet E = 0 \qquad z < 0$$

$$\nabla \times E = 0$$

$$\phi = \frac{1}{\varepsilon_1}\left(\frac{q}{R_1} + \frac{q'}{R_2}\right) \qquad q' = -\frac{(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_2 + \varepsilon_1)}q$$

Energy to create a charge q at a :

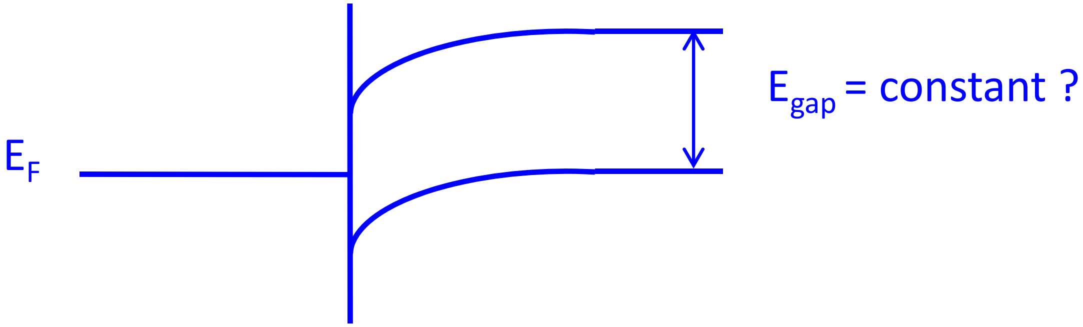
$$E = -\int_o^Q \frac{1}{\varepsilon_1 2a}\left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1}\right) q\,dq = \frac{Q^2}{4\varepsilon_1 a}\left[\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right]$$

Note for a metallic region 2 this is the effect of an effective image charge Note also that the energy reduction to produce a charge goes as Q squared . This is a correlation effect not a simple potential!

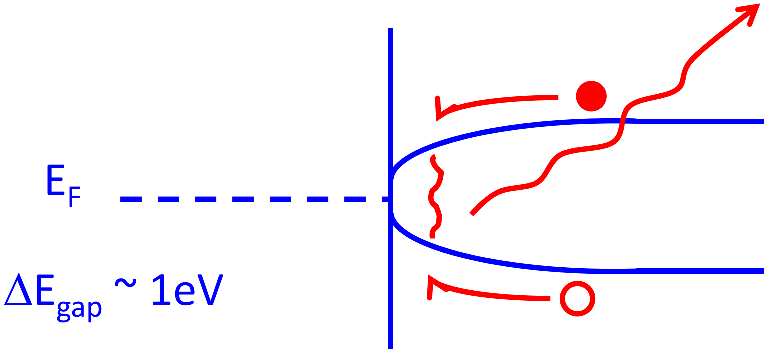
Formal conductivity gap in solids

- **Given by the Ionization potential minus the electron affinity E(I) –E(A)**
- **So for a narrow band semiconductor in contact with a metal the band gap of the semiconductor could strongly decrease at the interface because of the polatizability of the metal**
- **Very important for organic solar cells with narrow band widths!! And very different from band bending in large band width semiconductors like Si**

Conventional wide band semiconductor –metal interface
Results in band bending at the interface: Response time is
Slow compared to the band width in Si



Narrow band semiconductor –metal interface results
in band gap closing at the interface i.e. molecular or strongly
Correlated electron systems



Reduction of also a correlation gap

For Ionic materials like TM oxides use polarizable atoms or ions

- The polarizability of an ion is roughly equal to its volume. The radius of anions like O2- is much larger than for cations like Cu2+. So to calculated the TM 3d U we need to determine the ionization potential and electron affinity in the presence of polarizable O2- ions.

Ionic solids with polarizable anions (α ≅ Volume of the ION)

TM or RE surrounded by Z anions

$$\overrightarrow{P_i} = \alpha \overrightarrow{E_i}$$

$$EI = EI^0 - \frac{1}{2}\sum_i \alpha_i \overrightarrow{E_i} * \overrightarrow{E_i}$$

$$\mathrm{E}_j = \frac{e}{R_j^2}$$

$$U = U^0 - \sum_j \frac{\alpha_j e^2}{R_j^4}$$

Whats the importance of As or P?

- Electronic polarizabilities roughly equal to volume

$\alpha(O^{2-}) \approx 1-3$ $\alpha(P^{3-}) \approx 8$

$\alpha(Se^{2-}) \approx 8$ $\alpha(As^{3-}) \approx 10$

In units of Angstroms cubed

Reduction of U due to polarizability of As 3- in the Fe Pnictides (ELECTRONIC SOLVATION)

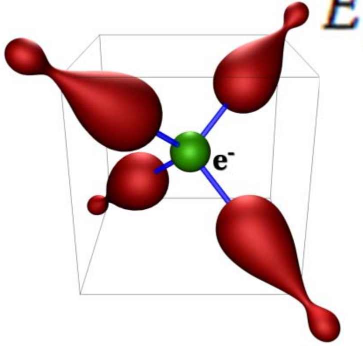
$$\boxed{U = E_I^{TM} - E_A^{TM} \; -2Epol}$$

E_I ionization energy

E_A electron affinity energy

$Epol=\frac{1}{2}\sum_i \sum$

$$E_I = E_I^0 - \sum_i \frac{1}{2}\alpha_i F_i^2 \qquad E_A = E_A^0 + \sum_i \frac{1}{2}\alpha_i F_i^2$$

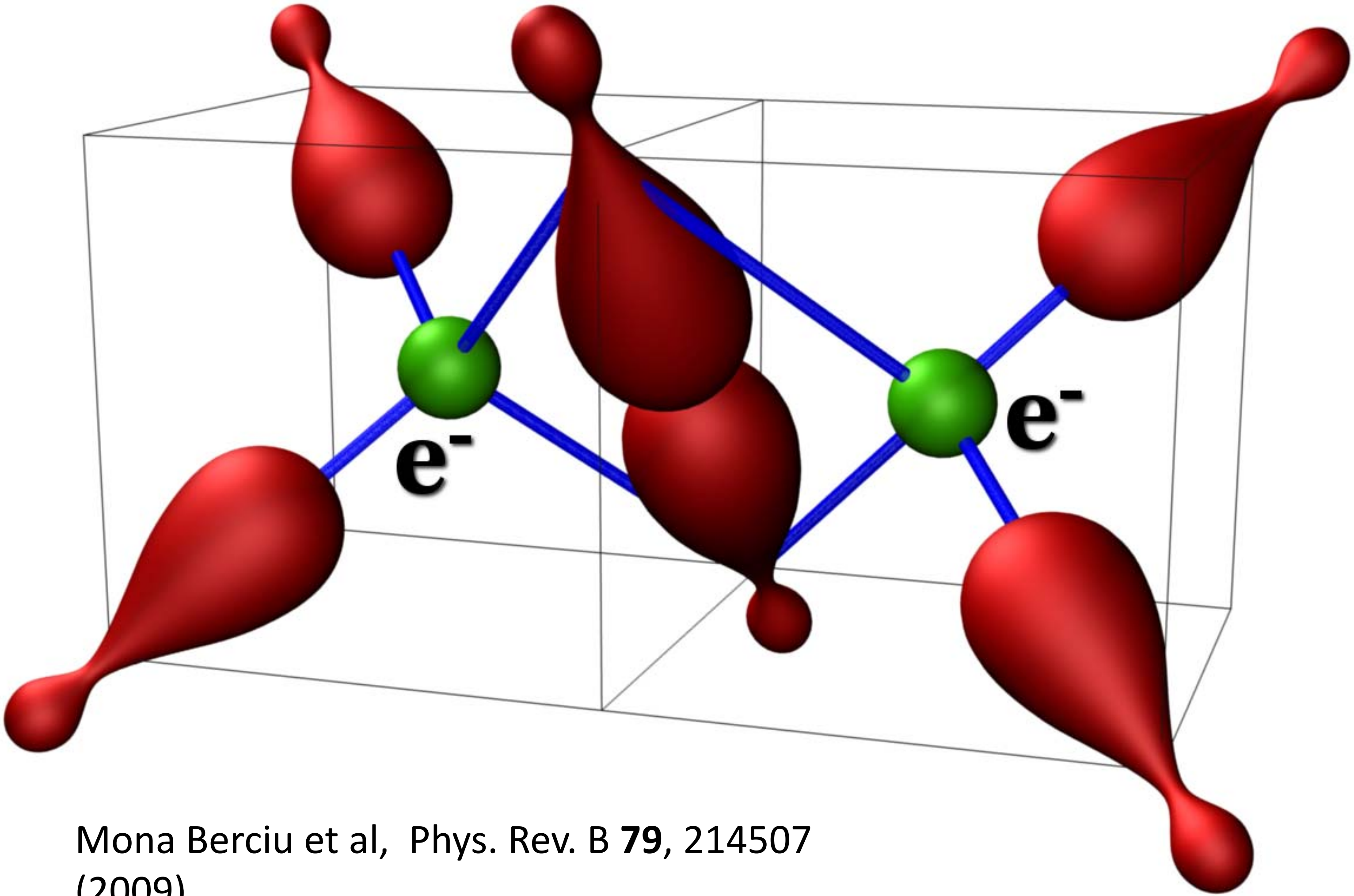


$$Epol = 2\sum_i \frac{1}{2}\alpha_i F_i^2$$

For 4 nn As3- ~ 20 eV

Taking α(As3-) to be 10 $\mathring{A}^3$

Polarization cloud For Two charges on Neighboring Fe



Mona Berciu et al, Phys. Rev. B **79**, 214507 (2009)

$$V = V_0 - \frac{1}{2} \sum_{common} \alpha[(\mathbf{E}_1 + \mathbf{E}_2)^2 - E_1^2 - E_2^2],$$

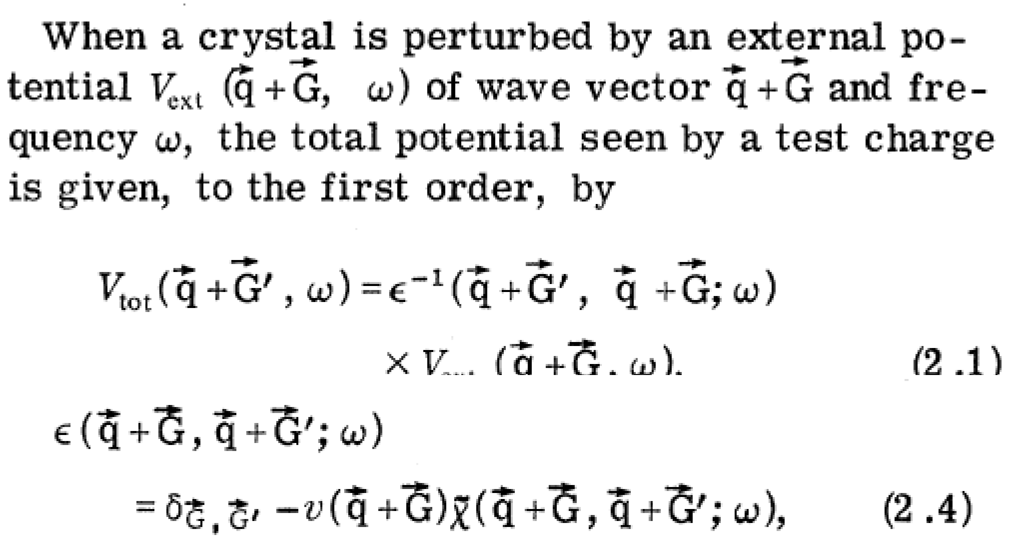
$$V = V_0 - 2\alpha E^2 \cos(\theta)$$

Theta is the Fe-As-Fe bond angle~ 70 degrees for NN and 120 degrees for NNN

Strongly reduced for NN by ~ 4-5eV and increase repulsion for NNN

Hanke and Sham PRB 12, 4501 (1975) Adler phys rev.126, 413 (1962) And 129, 62 (1963) Crystal local field corrections

CLFC



When a crystal is perturbed by an external potential $V_{\mathrm{ext}}(\vec{q}+\vec{G}, \omega)$ of wave vector $\vec{q}+\vec{G}$ and frequency ω, the total potential seen by a test charge is given, to the first order, by

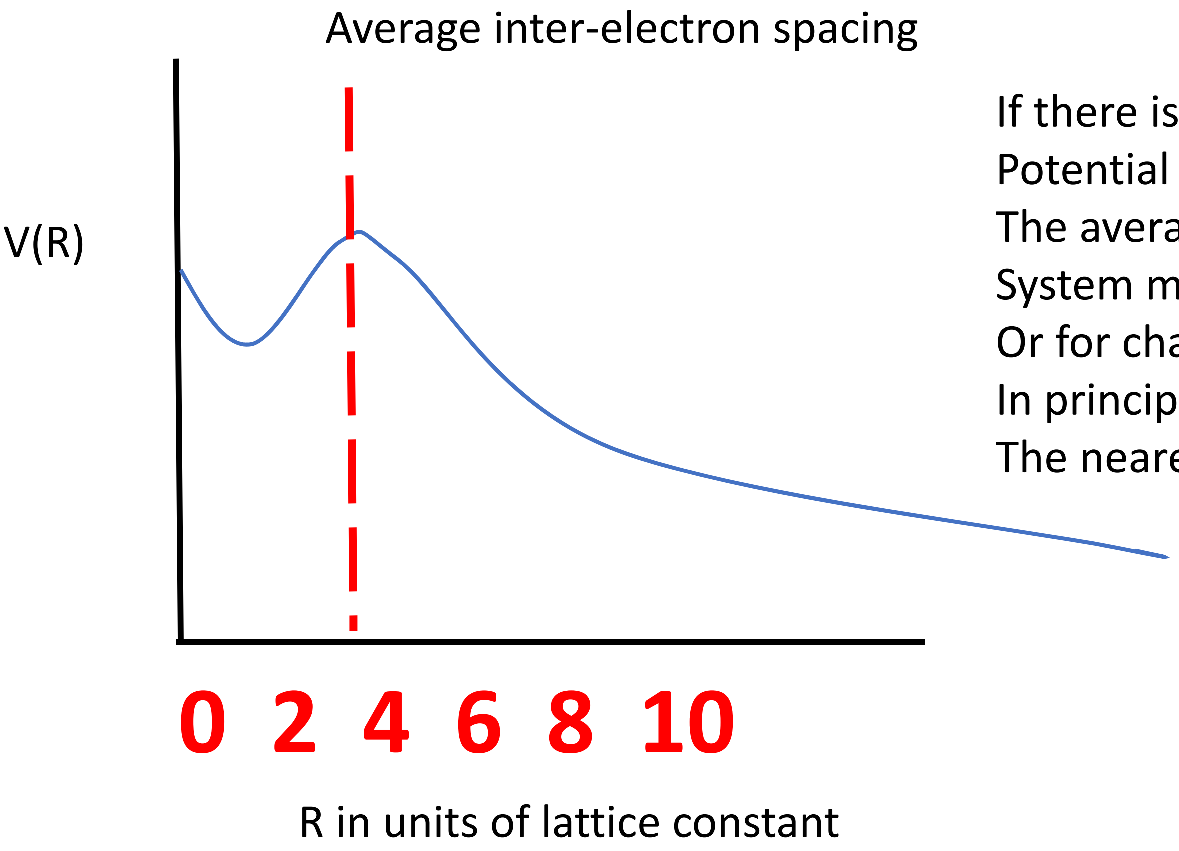
$$V_{\mathrm{tot}}(\vec{q}+\vec{G}', \omega)=\epsilon^{-1}(\vec{q}+\vec{G}', \vec{q}+\vec{G}; \omega) \times V_{\mathrm{ext}}(\vec{q}+\vec{G}, \omega). \qquad (2.1)$$

$$\epsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) = \delta_{\vec{G},\vec{G}'} - v(\vec{q}+\vec{G})\tilde{\chi}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega), \qquad (2.4)$$

“ –Coulomb interactions Involve an inversion of the dielectric matrix. The non diagonal Elements provide “local field effect”

Local field effects are especially important for short range Interactions like U and nn V.

Could non uniform polarizability result in superconductivity?

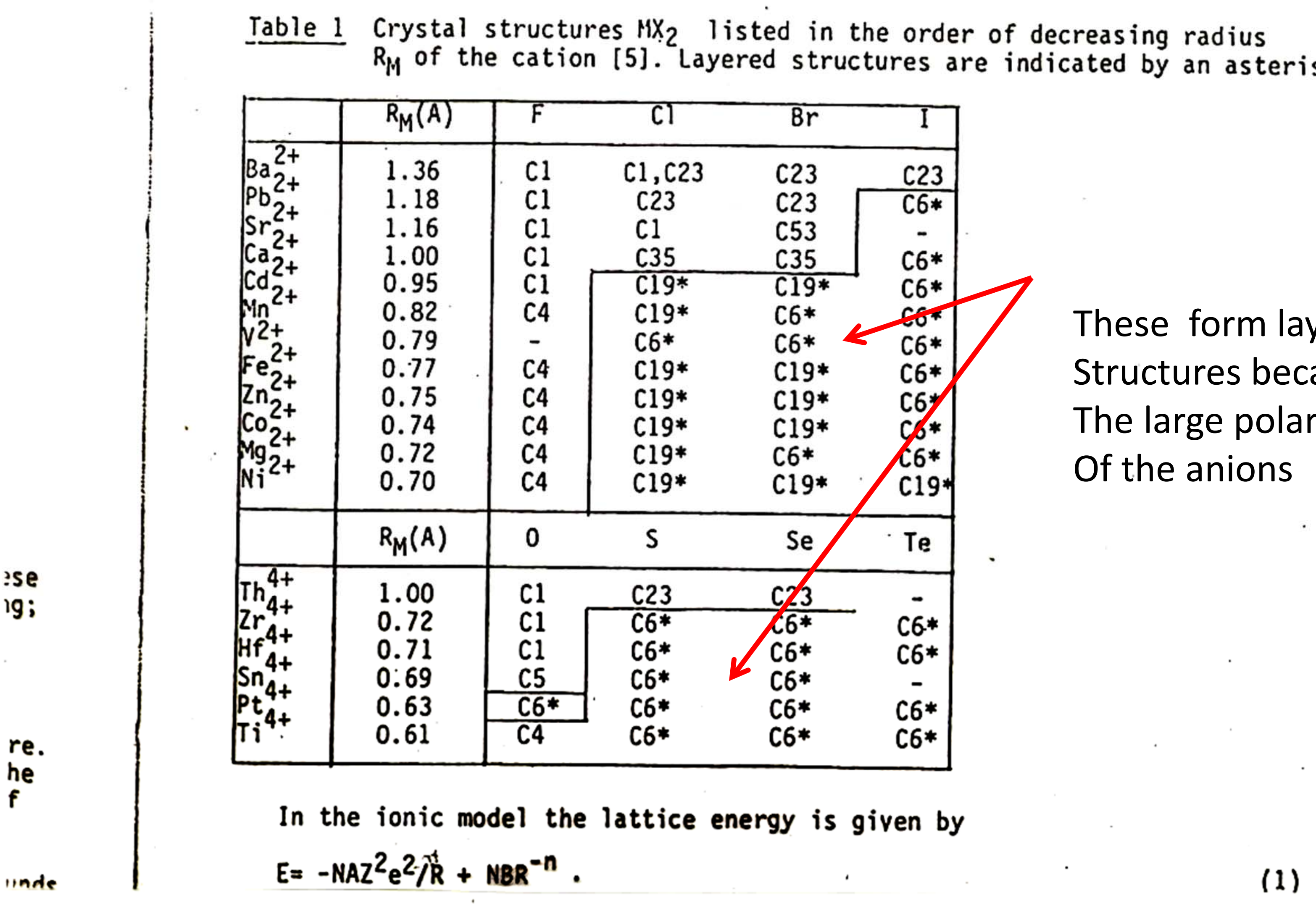


If there is a minimum in the Potential at a distance less than The average electron spacing the System may change to phase separate Or for charge density waves or In principle pairs if the minum is at The nearest neighbor distance.

Influence of polarizability on the crystal structure

- Ionic compounds are often cubic to maximize the Madelung energy i.e. negative charged ions surrounded by positive ones and visa versa
- Strongly polarizable ions could contribute with dipole –monopole interactions provided that they are asymmetrically coordinated as in layered compounds like TiS2 or MoS2
- They consist of a positive cation layer sandwiched between two polarizable anion layers.

Haas in Physics of intercalation compunds springer 1981



ese
ng;
re.
he
f
unds

Table 1 Crystal structures MX_2 listed in the order of decreasing radius R_M of the cation [5]. Layered structures are indicated by an asterisk

	R_M(A)	F	Cl	Br	I
Ba^{2+}	1.36	C1	C1,C23	C23	C23
Pb^{2+}	1.18	C1	C23	C23	C6*
Sr^{2+}	1.16	C1	C1	C53	-
Ca^{2+}	1.00	C1	C35	C35	C6*
Cd^{2+}	0.95	C1	C19*	C19*	C6*
Mn^{2+}	0.82	C4	C19*	C6*	C6*
V^{2+}	0.79	-	C6*	C6*	C6*
Fe^{2+}	0.77	C4	C19*	C19*	C6*
Zn^{2+}	0.75	C4	C19*	C19*	C6*
Co^{2+}	0.74	C4	C19*	C19*	C6*
Mg^{2+}	0.72	C4	C19*	C6*	C6*
Ni^{2+}	0.70	C4	C19*	C19*	C19*

	R_M(A)	O	S	Se	Te
Th^{4+}	1.00	C1	C23	C23	-
Zr^{4+}	0.72	C1	C6*	C6*	C6*
Hf^{4+}	0.71	C1	C6*	C6*	C6*
Sn^{4+}	0.69	C5	C6*	C6*	-
Pt^{4+}	0.63	C6*	C6*	C6*	C6*
Ti^{4+}	0.61	C4	C6*	C6*	C6*

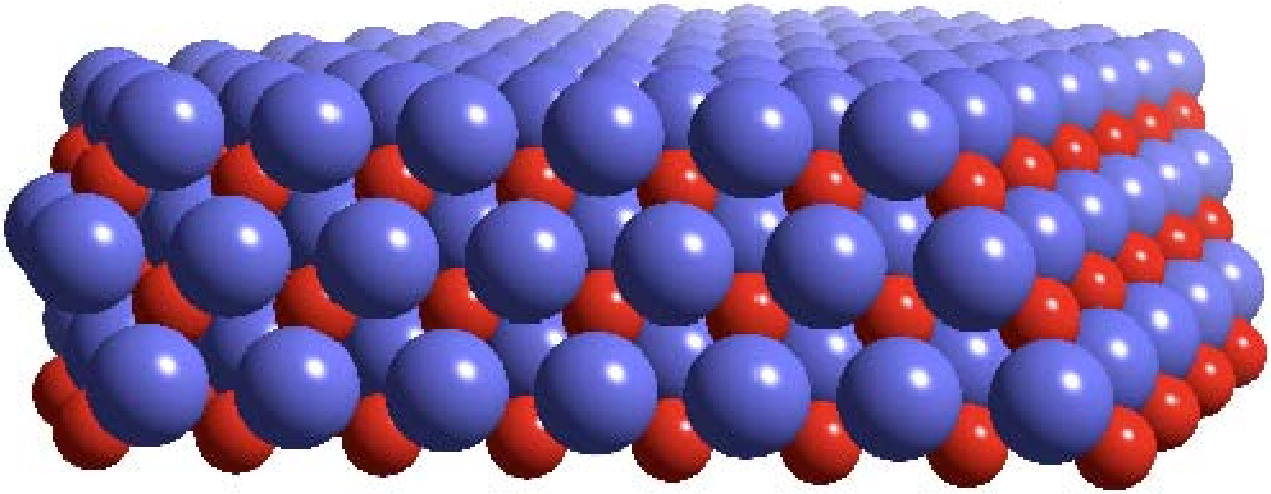
In the ionic model the lattice energy is given by

$$E = -NAZ^2e^2/R + NBR^{-n} . \qquad (1)$$

These form layered
Structures because of
The large polarizability
Of the anions

What happens if we have a polar surface?

- Take the NaCl Rock salt structure as in NiO, CaO, MgO, MnO etc

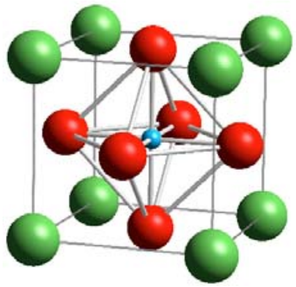


Alternating layers of +2 ,-2 charges in the ionic limit.

Classification of Ionic Crystals Surfaces

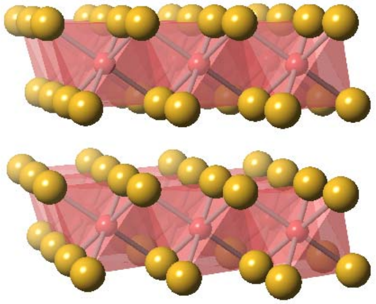
Type 1 : all planes are charge neutral

(001) surface of tetravalent perovskites $SrTiO_3$ ...

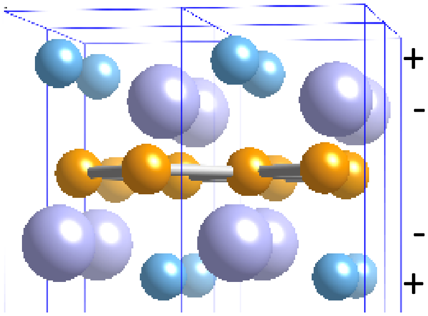


Type 2 : planes are charged but there is no dipole in repeat unit

TiS_2

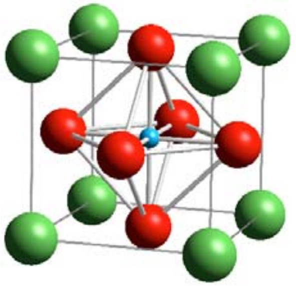


LiFeAs



Type 3 : planes are charged and there is dipole in repeat unit

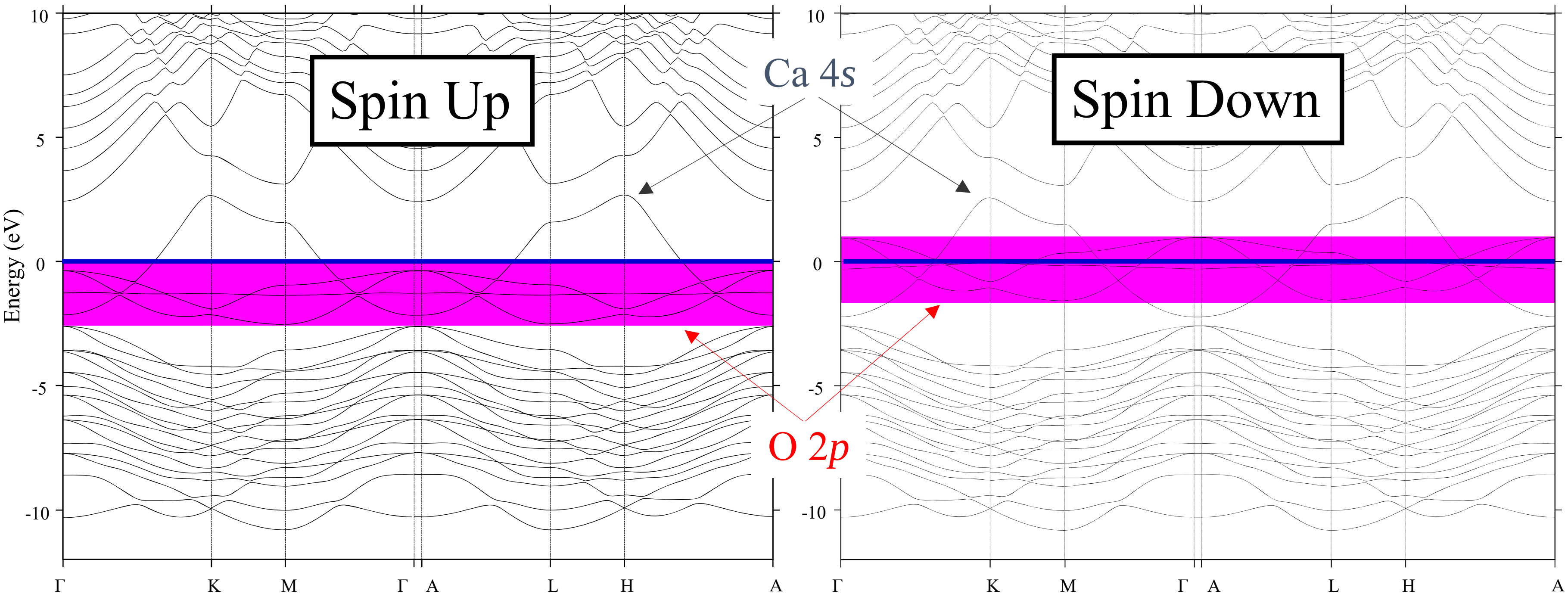
(001) surface of trivalent perovskites $LaAlO_3$, $LaMnO_3$ ...



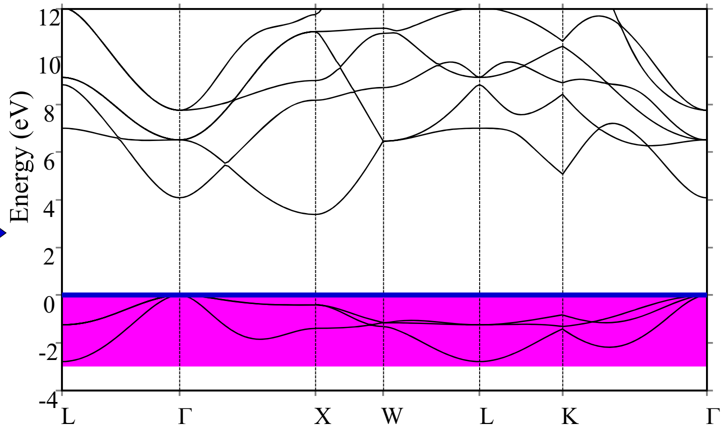
P.W. Tasker, J. Phys. C **12**, 4977 (1979)

Thanks to Ilya Elfimov

LSDA Band Structure of CaO (111) Slab terminated with Ca and O



Note:
Bulk material
(no surface)
is an insulator



But surface is metallic! And ferromagnetic! half metallic ferromagnet in DFT

A lot more will be said about each of these topics in the talks that follow