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Plane-Wave Pseudopotential Density Functional Theory

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Density Functional Theory

- ★ Hohenberg-Kohn theorems
  - o For a given configuration of nuclei, the electronic energy is uniquely determined by the electron density $\rho(r)$
  - o The "true" electron density minimizes this energy

- ★ Kohn-Sham construction
  - o The electron density can be expanded in terms of one-electron orbitals

$$\rho(\vec{r}) = \sum_i |\psi_i(\vec{r}_i)|^2$$

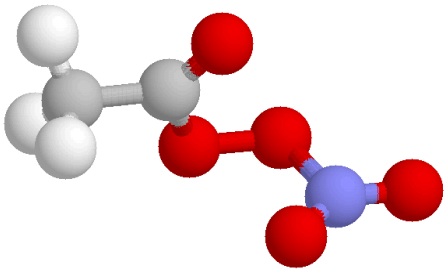
  - o The orbitals are determined by coupled, <u>one electron</u> equations

$$\left[-\tfrac{1}{2}\nabla^2 + \upsilon_{ext}(\vec{r}) + \upsilon_{Coul}[\rho] + \upsilon_{XC}[\rho]\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

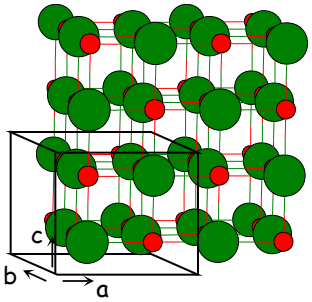
- ★ Adopt some approximation for the "exchange-correlation" interaction $\upsilon_{XC}[\rho]$:
  - o LDA, GGA, BLYP, PW91, PBE, etc.

Supercell Models

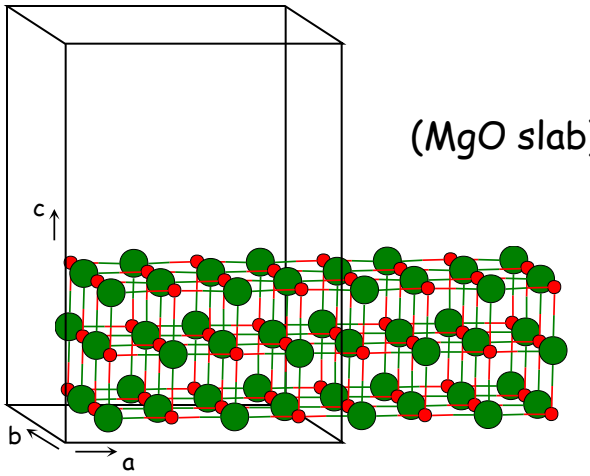
(peroxyacetyl nitrate)



(MgO bulk)



(MgO slab)



"cluster" models
Isolated molecule in vacuum
(or dielectric continuum)

Gas-phase
Solution-phase
"Localized" chemistry

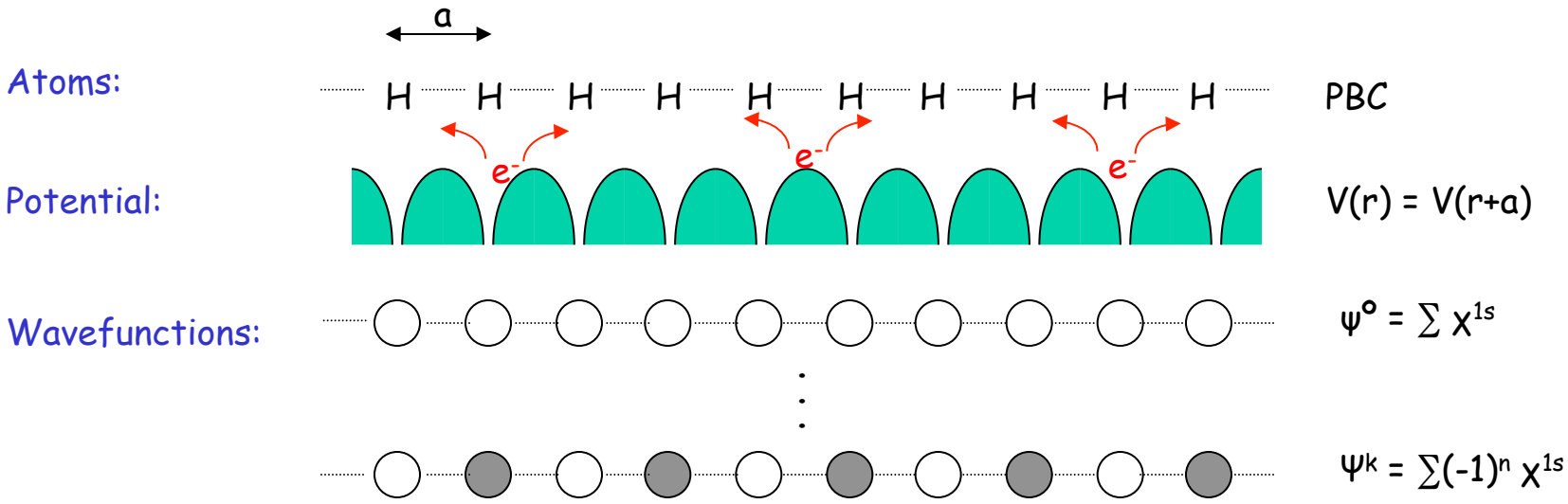
Amenable to highly
accurate calculations

"supercell" models
3-D periodic boundary conditions
applied to atomic configuration

Bulk solids
Bulk liquids
Surfaces and Interfaces
"Delocalized" chemistry

Amenable to highly
efficient calculations

Bloch's Theorem

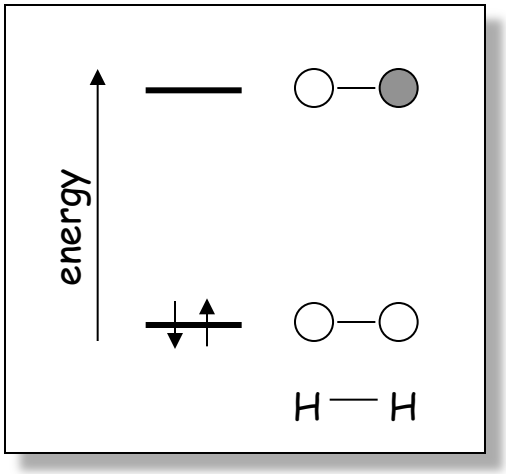


$$\psi^k(r) = \psi^\circ(r)\, e^{ikr}\ ,\ |k| < \pi/a$$

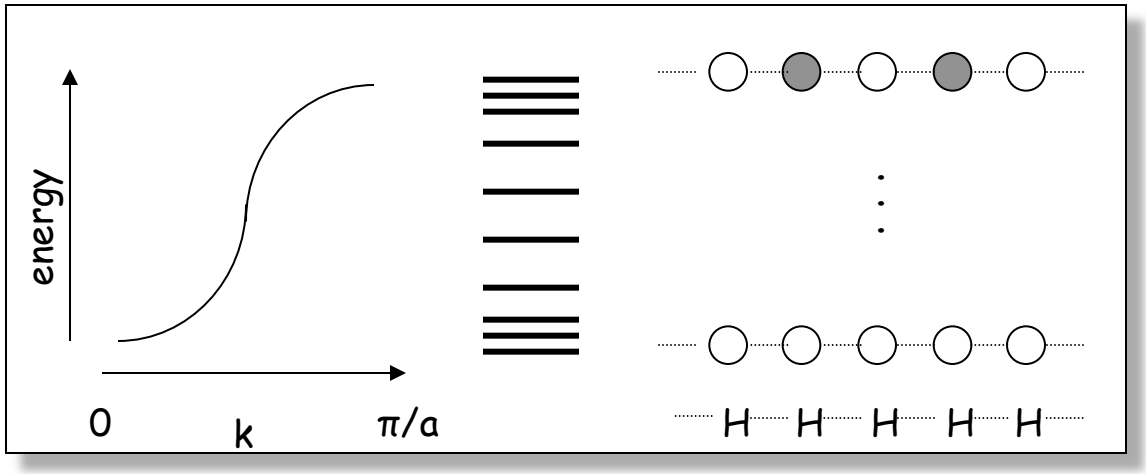
(recall e^{ikr} is like a cosine function)

- ★ Wavefunctions can be written as product of unit-cell-invariant part (1s function here) and cell-periodic part
  - o Readily extensible to three dimensions (real k → vector k)
- ★ Domain of k called "first Brillouin zone"
  - o "Special" k points assigned names, e.g. k = 0 called "Γ point"

Band Structure



Molecular orbital diagram

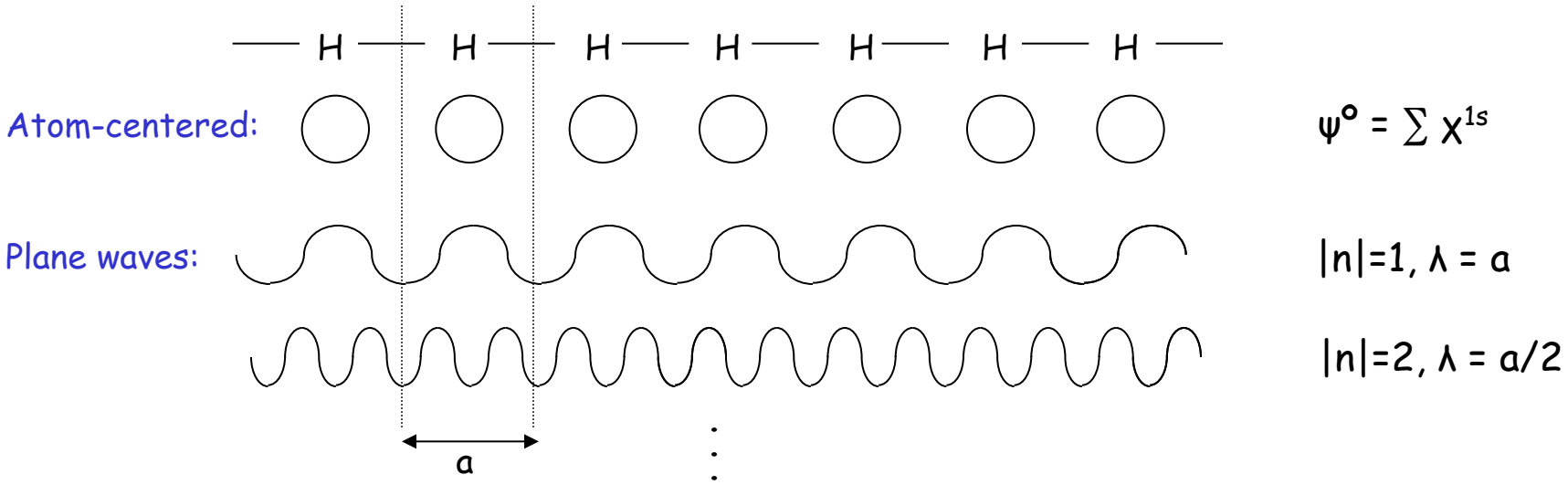


Band structure diagram

- ★ Discrete orbital energies become continuous band of energies, indexed by k
- ★ Width ("dispersion") of band determined by overlaps between neighboring cells
  - o Larger supercells → smaller dispersion
- ★ In practice, sufficient to determine orbitals at a discrete number of k points
  - o "k-point" sampling
  - o Monkhorst-Pack algorithm used for choosing efficient k-point mesh

Basis Sets

- ★ How to represent $\Psi^o(r)$ <u>within</u> the supercell?
- ★ <u>Atom-centered functions</u>:
  - o Gaussians, slaters, numerical orbitals
  - o Compact basis, but difficult to construct and to evaluate Hamiltonian
  - o Implemented in Crystal, DMol, and ADF codes
- ★ <u>Plane-wave functions</u>:
  - o "Particle-in-a-box" basis, especially suited to freely propagating electrons
  - o Not very "atom-like", but extremely easy to construct and to evaluate Hamiltonian
  - o Implemented in Vasp, CASTEP, CPMD, …



Plane-wave Basis

- ★ Expand $\psi^o(r)$ in plane-waves (Fourier expansion)
  - o Periodic boundary conditions restrict allowable plane wave frequencies

    $$\psi^o(r) = \Sigma_G c_G e^{iGr}, \quad G = 2\pi n/a, \quad n \in I$$

  - o Coefficients c_G determined by variational principle

- ★ Kohn-Sham equations assume convenient form
  - o Kinetic energy term diagonal

    $$\langle e^{iGr} | -\tfrac{1}{2}\nabla^2 | e^{iG'r} \rangle = \tfrac{1}{2}G^2 \delta_{GG'}$$

  - o Potential energy term given by Fourier transform of V(r)

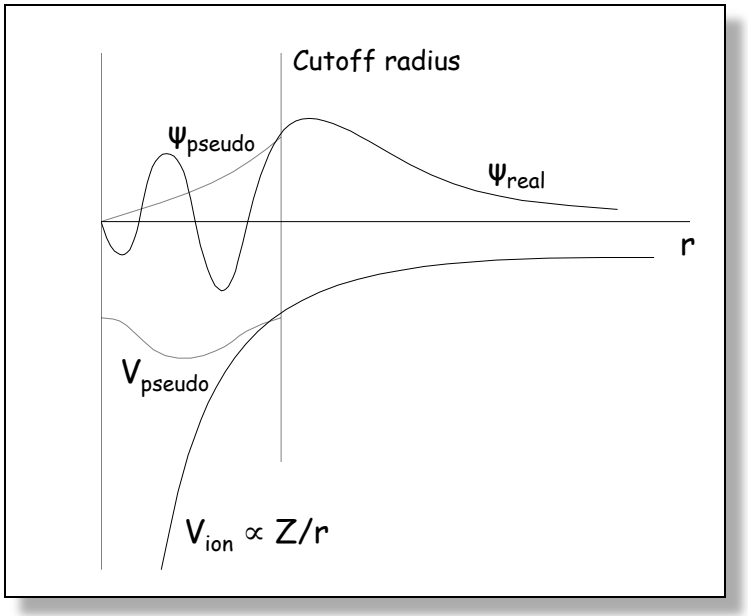
    $$\langle e^{iGr} | V(r) | e^{iG'r} \rangle = V(G - G')$$

  - o Solve (# k-points) Kohn-Sham matrices of dimension (# PW) x (# PW)
    - o direct diagonalization or iterative techniques

- ★ "Kinetic energy cutoff" (single parameter!) determines # plane waves
  - o n_{max} chosen such that $\hbar^2 G_{max}^2/2m_e < KE_{cutoff}$
  - o $n_{max} \sim 10^5 - 10^6$

Pseudopotentials

- ★ Plane waves are poor choice for treating wavefunctions near atomic cores
  - o Rapid oscillations → high kinetic energy → "high n" plane waves
- ★ Replace core electrons and potential with "pseudopotential"
  - o Establish radial cutoff between core and valence regions
  - o Choose specific atomic configurations
  - o Construct PP to go smoothly into real potential outside of cutoff radius
  - o Preserves phase and shape of valence wavefunctions outside cutoff

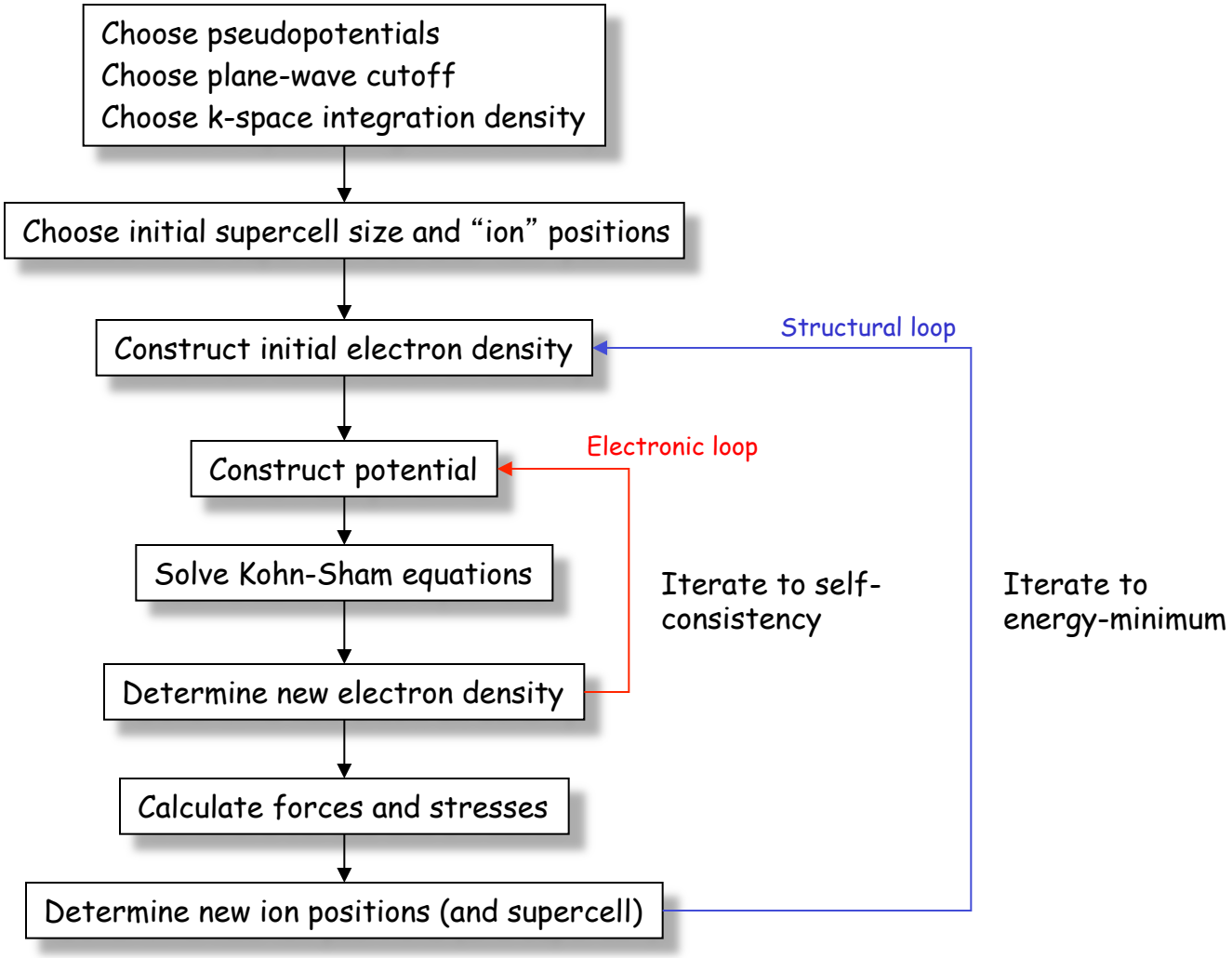


Pseudopotential Jargon

- ★ Transferability
  - o Ability of PP to be applied in different chemical environments
- ★ Local vs. non-local
  - o Spherically symmetric (local) vs. l-dependent (non-local)
- ★ Norm-conserving
  - o Preserving $|\psi|^2$ of valence wavefunctions
- ★ Soft vs. hard
  - o Hard: closer to true atomic potential, requiring large KE cutoff
  - o Soft: larger perturbation on atomic potential, allowing smaller KE cutoff
- ★ "Ultrasoft" (Vanderbilt)
  - o Approach which relaxes norm-conservation by introducing "augmentation charges"
  - o Permits significantly lower KE cutoffs

- ★ Appropriate selection of pseudopotentials one of the key challenges in successful PW-PP calculations!

Algorithm


Choose pseudopotentials
Choose plane-wave cutoff
Choose k-space integration density
Choose initial supercell size and "ion" positions
Construct initial electron density
Structural loop
Construct potential
Electronic loop
Solve Kohn-Sham equations
Iterate to self-consistency
Iterate to energy-minimum
Determine new electron density
Calculate forces and stresses
Determine new ion positions (and supercell)

Implementations

- ★ VASP (Hafner group, U. Vienna)
- ★ CASTEP (Payne group, Cambridge, and MSI)
- ★ CPMD (Parrinello group, Stuttgart, and IBM)
- ★ DACAPO (Nørskov group, Technical University Denmark)

- ★ Highly parallelized and efficient
- ★ Extensive pseudopotential libraries
  - o Incl. ultrasoft PPs
- ★ Local and non-local exchange correlation potentials
- ★ Multiple electronic and structural relaxation algorithms
  - o Car-Parrinello particularly efficient combination of these two

- ★ Varying analysis capabilities and levels of user friendliness

Applications at Ford Research Lab

Bulk materials properties:

- ★ Phase stability and microstructure of Al alloys
  - o Wolverton, *Modelling Simul. Mater. Sci. Eng.* **2000**, *8*, 323
- ★ Al and H siting and thermodynamics of bulk γ-aluminas
- ★ Ionic transport in mixed-valence oxides

Surface chemical processes:

- ★ Water adsorption and dissociation on α-alumina (0001)
  - o Car-Parrinello dynamics simulations, in collaboration with IBM
  - o Hass et al., *Science* **1998**, *282*, 265
- ★ NO reactions on metal surfaces
- ★ NO_x/SO_x storage on base metal oxides

Base Metal Oxide Adsorbents for Automotive Catalysis

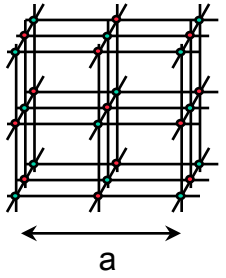
- ★ Overall objective
  - o To understand the intermediates, the thermodynamics, and the kinetics of adsorption, oxidation, and bulk accommodation of NO_x and SO_x on metal oxides of potential interest for automotive catalysis

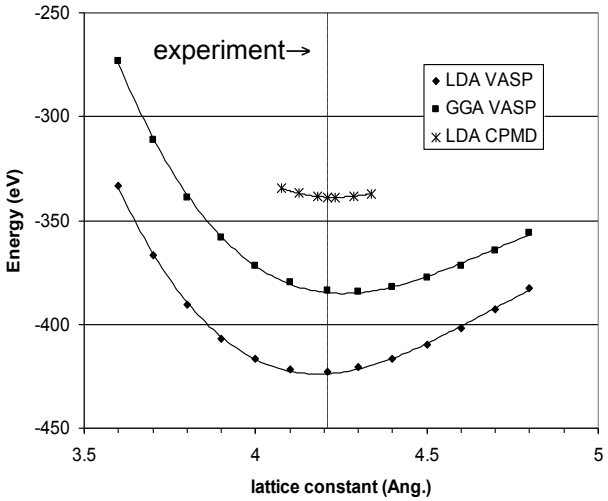
- ★ Work to-date
  - o Initial stages of adsorption and oxidation of SO_x on basal planes, steps, and at point defects on the representative oxides *MgO* and *BaO*

- ★ Approach
  - o Periodic supercell, plane-wave simulations
  - o (Mostly) local density functional theory
  - o (Mostly) ultrasoft pseudopotentials
  - o VASP (and some CPMD)

MO (M = Mg, Ba) Bulk Structures

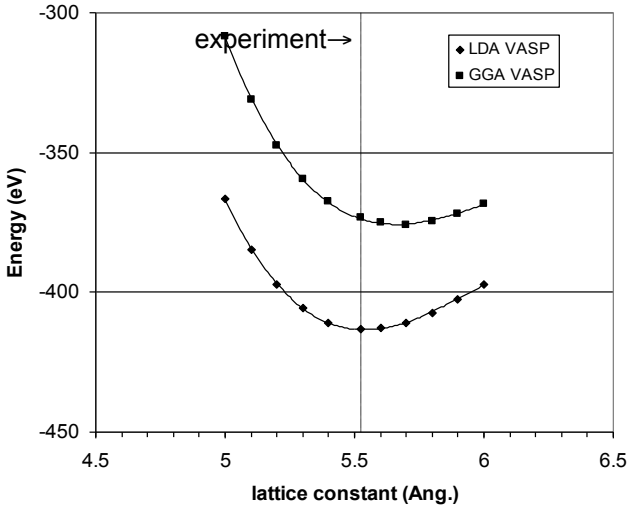
- ★ Simple cubic lattice, 64 atoms/supercell (4 x 4 x 4)
- ★ 2x2x2 k-point integration (1 symmetry unique point)
- ★ 270 eV kinetic energy cutoff
- ★ ~10000 plane waves
- ★ ~< 1000 s/point, 8 node SP2





MgO

Exp't	4.212 Å
LDA Vasp	4.182
GGA Vasp	4.255
LDA CPMD	4.240

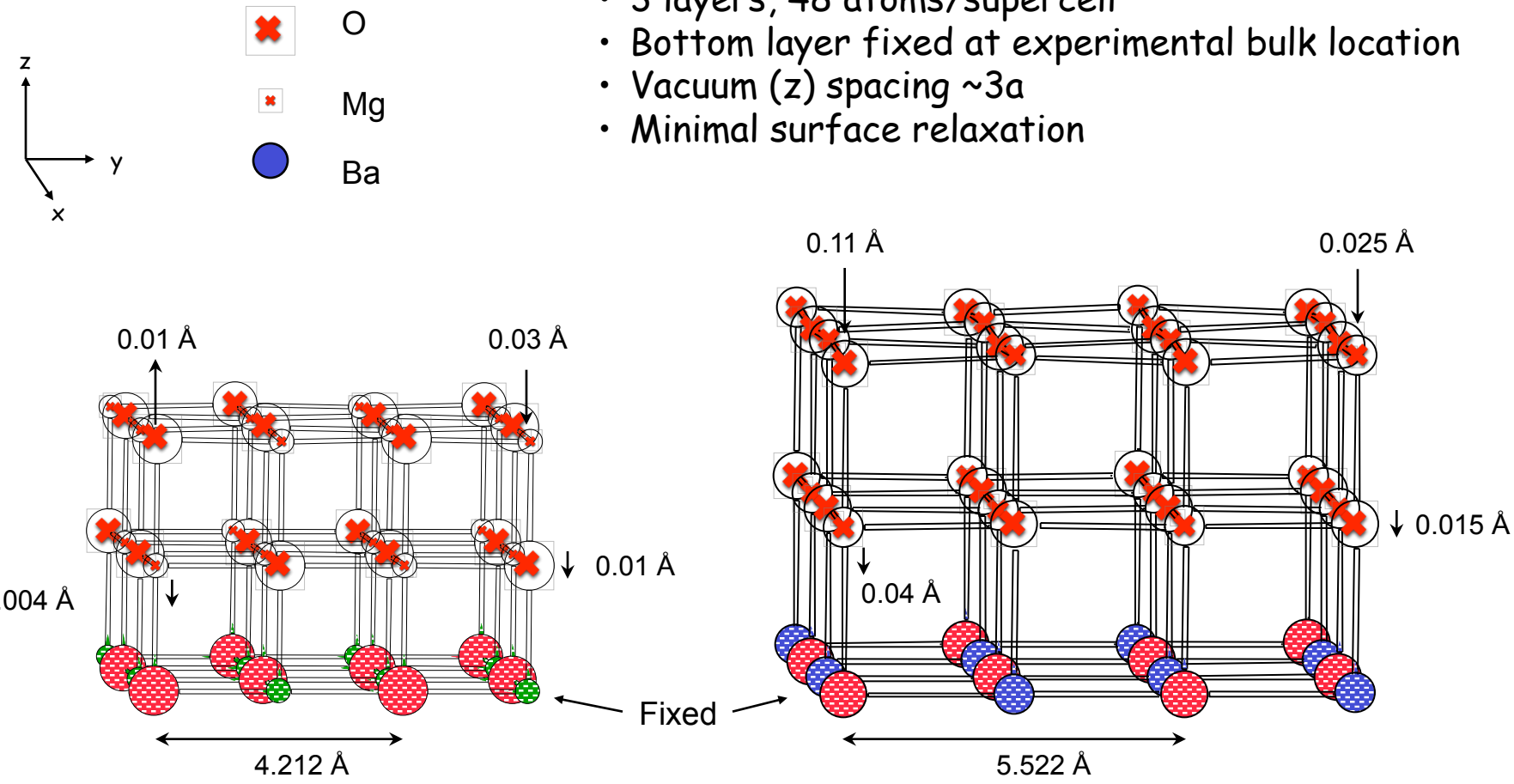


BaO

Exp't	5.522 Å
LDA Vasp	5.538
GGA Vasp	5.661

MO (001) Surface Models

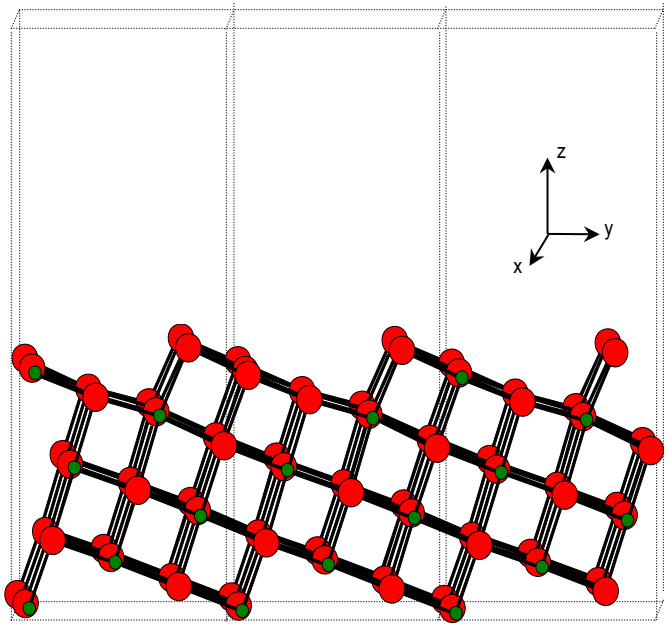
- 2×2 unit cell surface
- 3 layers, 48 atoms/supercell
- Bottom layer fixed at experimental bulk location
- Vacuum (z) spacing ~3a
- Minimal surface relaxation

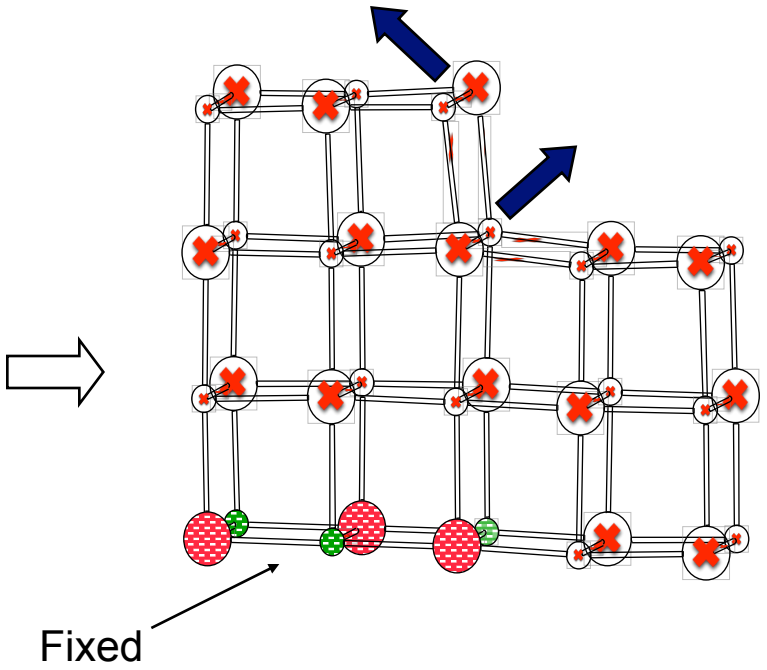


MgO
0.02 J/m^2 relaxation

BaO
0.04 J/m^2 relaxation

MO Step Defect Models



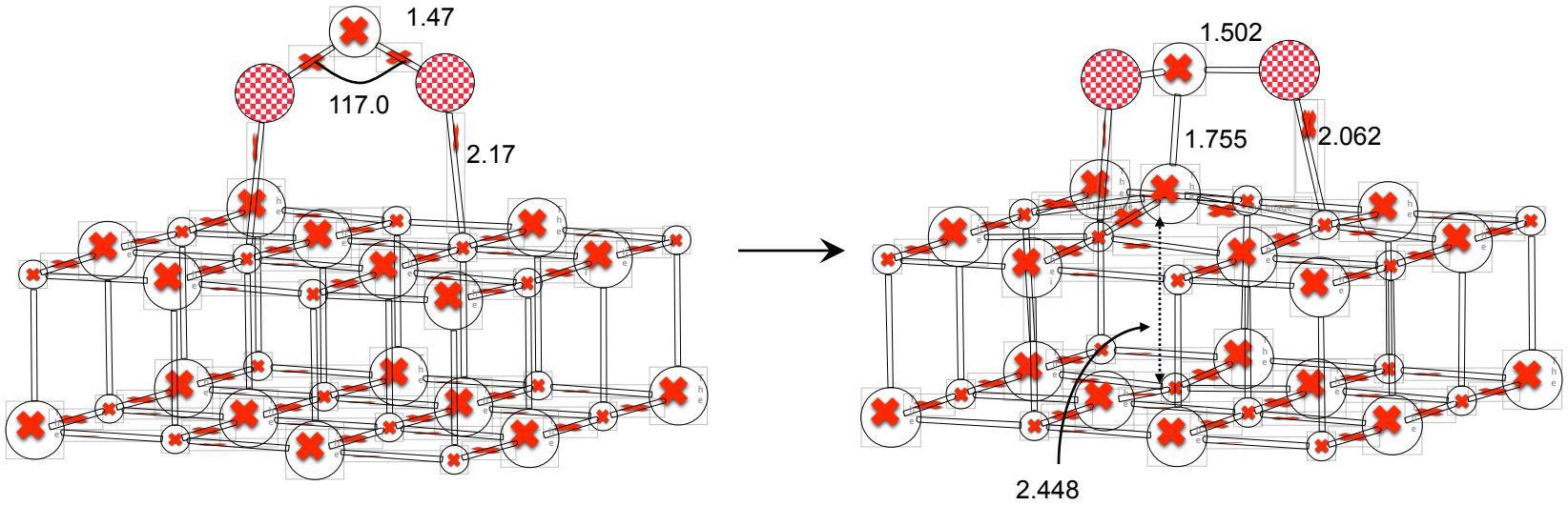


MgO (103) supercells

MgO (103) step relaxations

★ Monatomic step defects modeled using (103) surface
- 48 atoms/supercell; bottom layer fixed at experimental bulk locations
- Primary relaxations at step edge
- 0.30 J m^{-2} surface relaxation energy

$MgO\ (001) + SO_2$

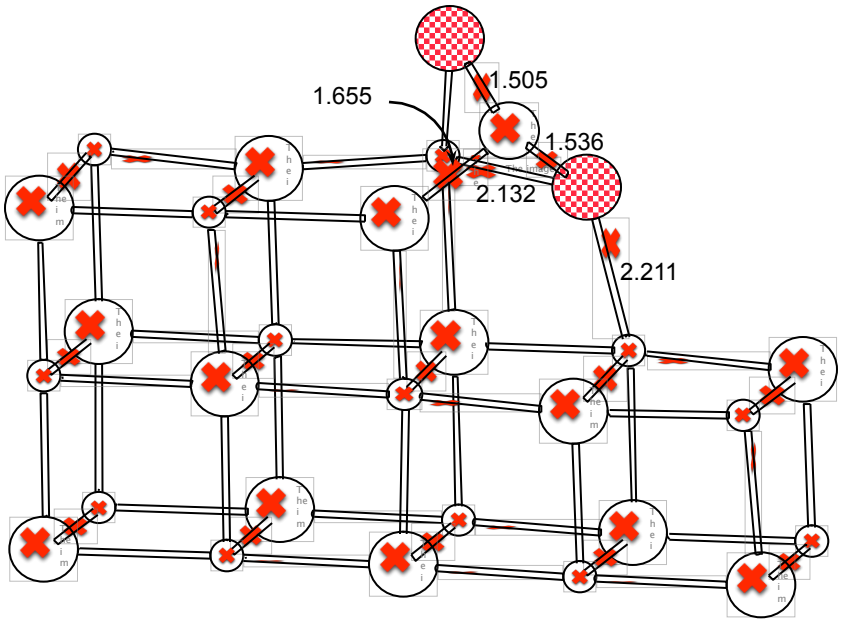


Physisorbed SO_2
-16 kcal mol^{-1} LDA

Chemisorbed SO_2
-42 kcal mol^{-1} LDA

- ★ Metastable dipolar physisorption
  - o Only structure found in cluster simulations
  - o Converts to chemisorbed at ~200 K in MD simulations ($E_a \approx 0.5$ kcal mol^{-1})
- ★ Strong "sulfite"-like chemisorption ($MgO + SO_2 \rightarrow MgO{\cdot}SO_2$)
  - o Specific $S–O_s$ and $O–Mg_s$ interactions; significant charge transfer to adsorbate
  - o Pronounced local lattice distortion, dies off over short range

$MgO\ (103) + SO_2$

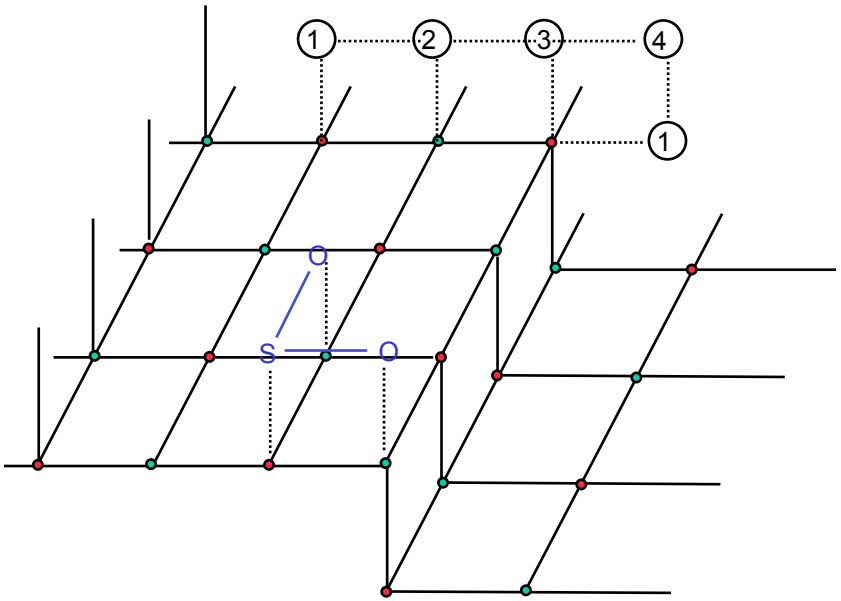


Chemisorbed SO_2
-62 kcal mol^{-1} LDA

★ SO_2 chemisorbs preferentially on coordinatively unsaturated edge ions

- Similar sulfite-like adsorption geometry
- SO_2 oxygen fill vacant lattice sites
- Introduces pronounced lattice distortions along step edge

SO_2 Chemisorption on MgO



BE, kcal mol^{-1}

	S	O_1	O_2	LDA	GGA
(100)				-37	-25
(103)	4	1	3	-62	-46
	1	1	3	-60	
	3	3	2	-59	
	1	1	2	-52	
	2	1	2	-46	
	2	3	2	-34	
(104)	4	1	3	-62	
corner				-92	-81

★ Multiple SO_2 chemisorption sites
- o SO_2 fills "virtual" lattice sites
- o Adsorption energy tracks with lattice ion coordinative unsaturation

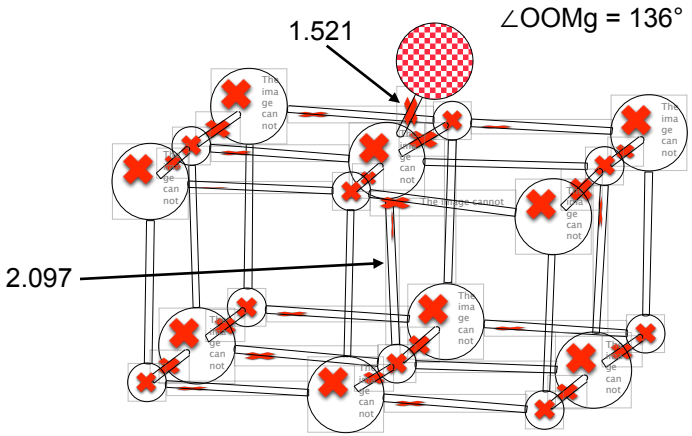
MgO + SO_x Vibrational Spectroscopy

S-O Stretch Frequencies (cm^{-1})

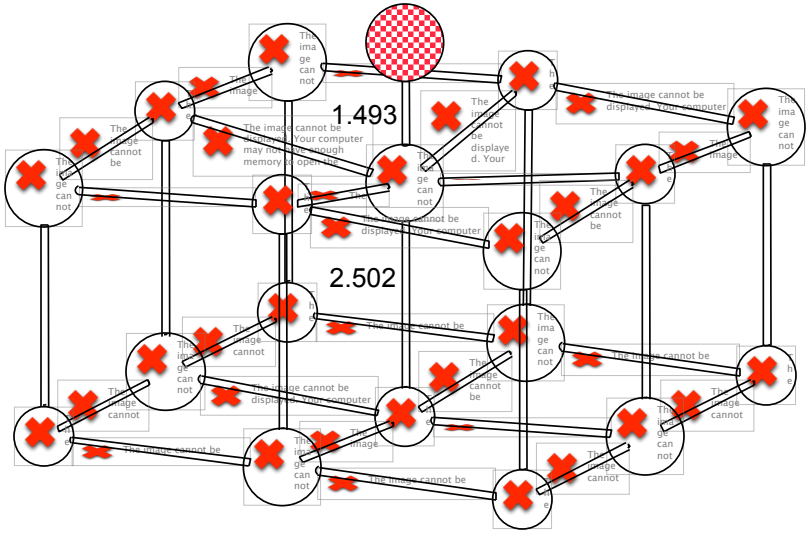
	calc'd (LDA, CPMD)			exp't		
	ν_{asym}	ν_{sym}		ν_{asym}	ν_{sym}	
SO_2	1318	1119		1362	1151	
MgO(100) + SO_2	1100	1024		1040-1070	895-975	
MgO(103) + SO_2	1041	962		"	"	
	$\nu_{e'}$	$\nu_{e'}$	$\nu_{a'}$	$\nu_{e'}$	$\nu_{e'}$	$\nu_{a'}$
SO_3	1345	1345	1026	1345	1345	1060
MgO(100) + SO_3	1239	1204	999	1240-1290	1170	1015-1025
MgO(103) + SO_3	1274	1094	955	"	1100	"

MgO + SO_2: Schoonheydt and Lunsford, *J. Catal.* **1972**, *26*, 261-271
MgO + SO_3: Lavelley et al., *J. Phys. Chem.* **1989**, *93*, 6581-6582

Point Defects: O Adatoms



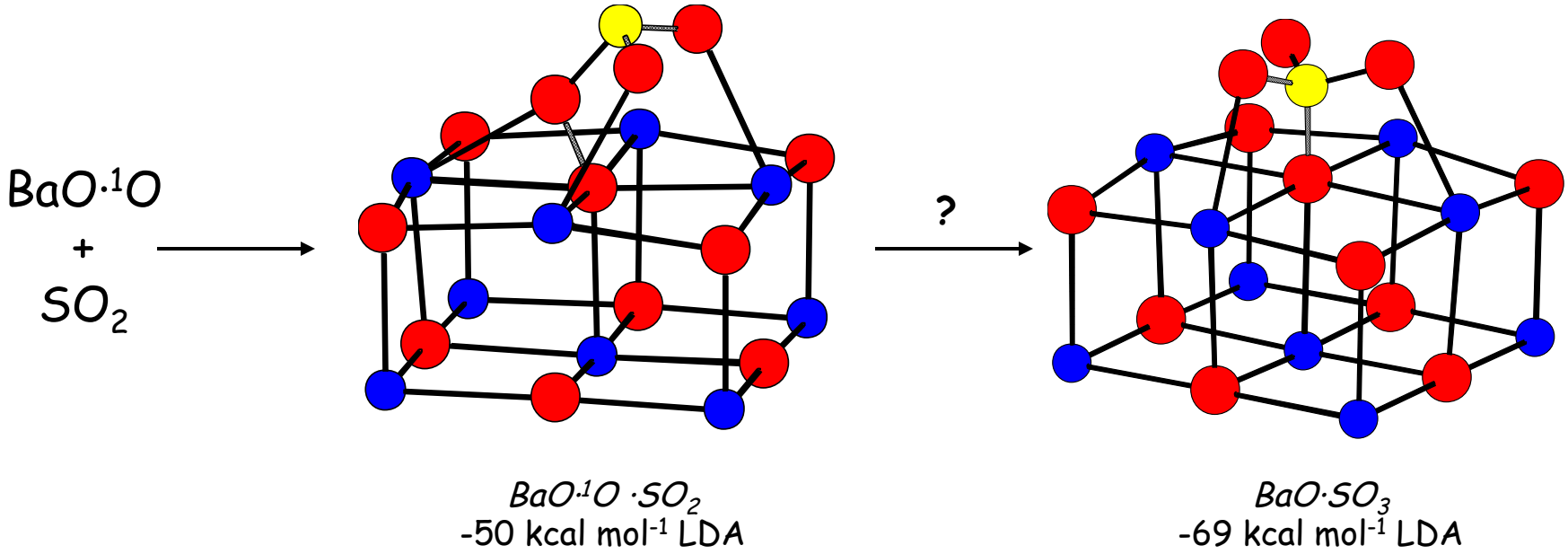
MgO (001) + ½ O_2 → *MgO·^{1}O*
+1 kcal mol^{-1} LDA



BaO (001) + ½ O_2 → *BaO·^{1}O*
-31 kcal mol^{-1} LDA

★ Oxygen adatoms chemisorb preferentially on oxygen ion sites
- ^{1}O adatoms → "peroxide"-like (O_2^{2-}) binding (Kantorovich et al., *Surf. Sci.* **1997**, *374*, 373)
- Chemisorption energy comparable to O_2 BDE (118 kcal mol^{-1})
- Chemisorption energy coverage-independent on BaO up to 1 ML

O Adatoms + SO_2: Sulfur Oxidation



- ★ SO_2 chemisorbs strongly at O adatoms
  - o Similar energetics on MgO and BaO
- ★ Probable intermediate for SO_2 insertion into O-O bond
- ★ Special approaches required for transition state searches
  - o Gradient-only based, e.g. nudged elastic band

Conclusions

- ★ Plane-wave pseudopotential DFT is a powerful technique for studying bulk and surface properties of materials
- ★ PW-PP approach is an extremely useful complement to traditional local orbital approaches to electronic structure
- ★ Improvements in computer speed and algorithms, and wider availability of software, promise to make PW-PP approach increasingly popular

Acknowledgments

- Ford "CAMS" team
  - Ken Hass
  - Chris Wolverton
  - Alex Bogicevic

- IBM collaborators
  - Wanda Andreoni
  - Alessandro Curioni