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Spring College on Computational Nanoscience

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Calculation of Mechanical and Electro-Mechanical Properties of Materials

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ICTP, Trieste, Italy, 17 to 28 May 2010

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Degrees of Freedom that describe the Structure

- Mechanical properties are determined by the energy as a function of the positions of the atoms including any external forces.

- A system with N atoms has 3N degrees of freedom, however the energy depends only upon the relative positions of the atoms.

- Thus for a system with more than 1 atom the energy is a function of 3N – 3 (translation) – 2 (rotation) = 3N – 5 variables.

- These principles apply to all systems, but let us consider the appropriate ways to deal with the structures of molecules, solids, and nanoscale systems.

Degrees of Freedom that describe the Structure

- What is this analysis good for?

- If we have an expression for the energy defined in terms of realtive coordinates all conditions are satisfied

- However, if have a problem like in electronic structure where there are forces on the nuclei are due to electrons, it is not so clear.
  - The two systems are treated differently - one needs to be more careful
  - One way is to make use of another way to state the requirement -

    The sum of forces to be zero

    Called the “acoustic sum rule because it guarantees that the frequencies of the acoustic modes go to zero for infinite wavelength

    If one simply adds a force to every nucleus so the sum is zero, the fundament requirements are met, but this can introduce quantitaive errors

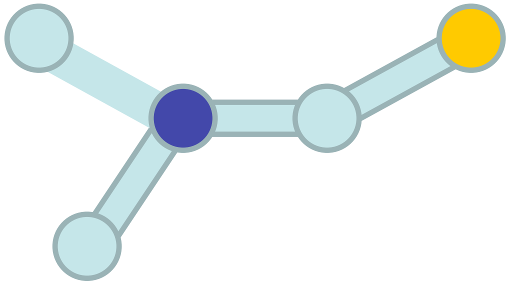
Degrees of Freedom that describe the Structure

- What is the gradients good for?

- The force on any nucleus is $F_i = - dE/dX_i$
  - Hellman-Feynman theorem (force theorem) --- Baroni's talk
  - Notice any possible problem?
    - Suppose the system is not at the exact variational minimum (it never is!) are errors – and violations of the sum rules!

- Molecular dynamics – F=Ma
- Relaxation of positions to find the equilibrium structure
  - Smart ways and dumb ways
    - Suppose I am a dumb American I might just go downhill (Steepest descent) – works but VERY slow in many cases
- We will concentrate on
  - Relaxation
  - Displacements with external forces

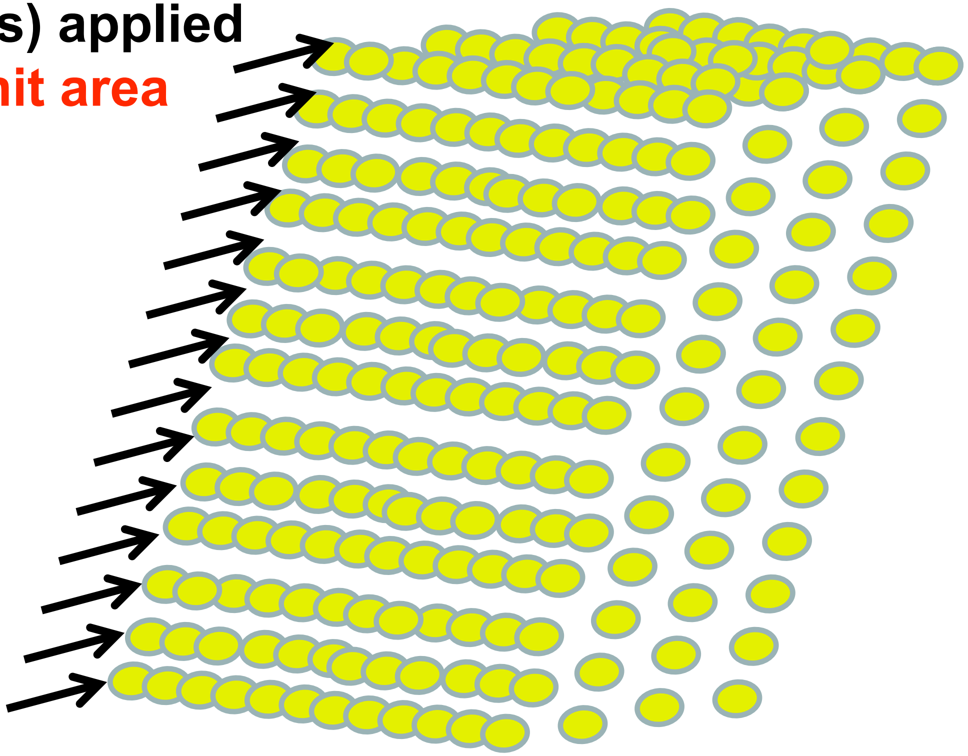
A Small Molecule



- In principle, very simple – just move the atoms given the forces
  - Better and worse ways but any way is finally OK

A crystal

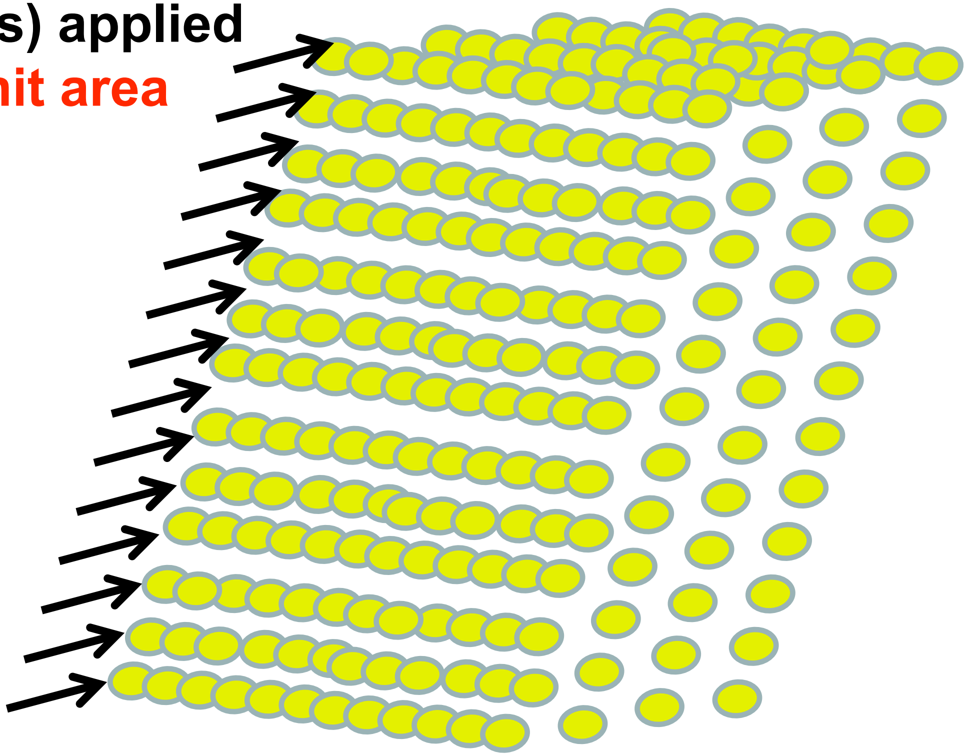
- Consider pressure (stress) applied to a surface – force per unit area



- The effect is transmitted into the sample by one atom pushing on the next – until every atom adjusts and zero net force on it
- Is this the best way calculate the resulting strain in a crystal of 10^{23} atoms?

A crystal

- Consider pressure (stress) applied to a surface – force per unit area



- The final result is a 1) uniform strain inside (ε_{ij} – 9 elements that are often related by symmetry) an 2) distortions on the surface
- The problem divides into two parts:

Elastic constants depend on on strain and stress

A surface scientist s cares about 2

The Stress Theorem

- Just the generalization of the force theorem

$$\sigma = dE/d\varepsilon$$

- But it has some theory to work it out

  generalization of the virial theorem

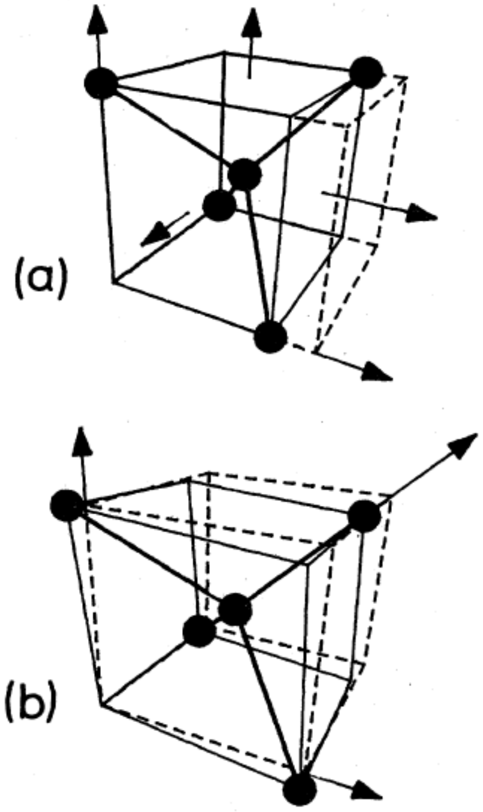
  Involves kinetic and potential energies

  in the bulk –

  not only potential terms

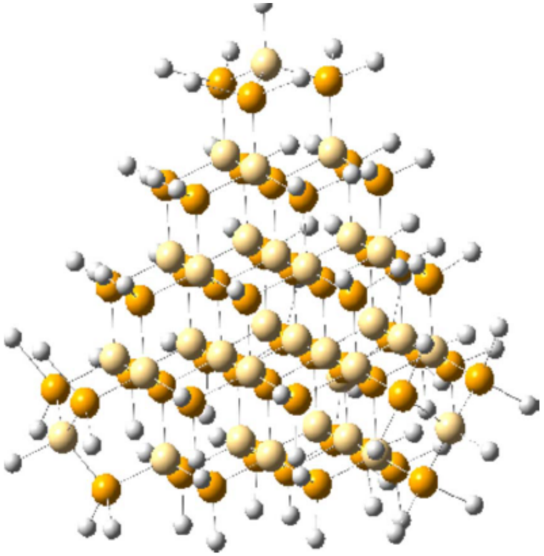
- It can be viewed as “stretching of space”

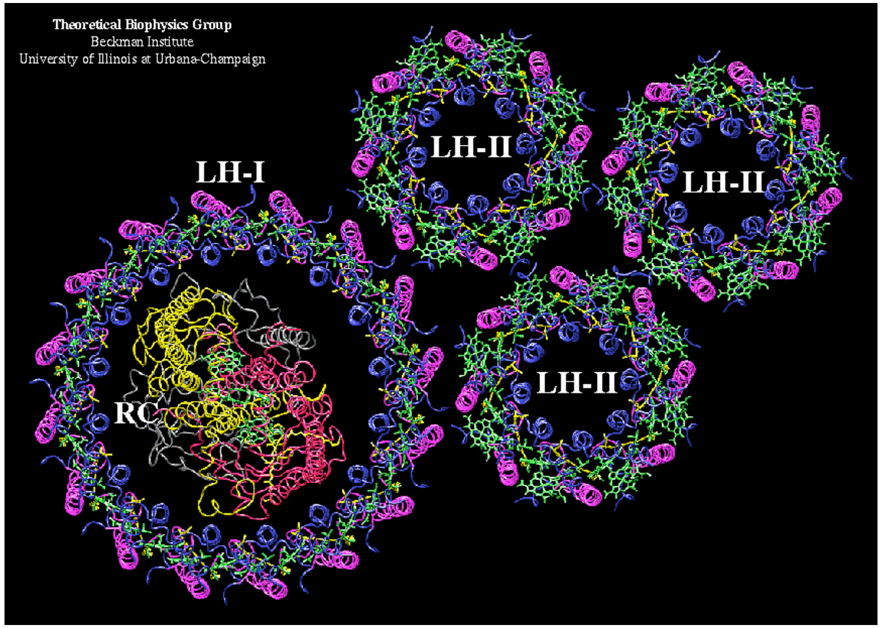
- Clearly this is the appropriate variable



A nanostructure (or a large molecule)

- What do we do?
- A large molecule – treat just like a small molecule?
- Divide the problem into interior and surface?





Theoretical Biophysics Group
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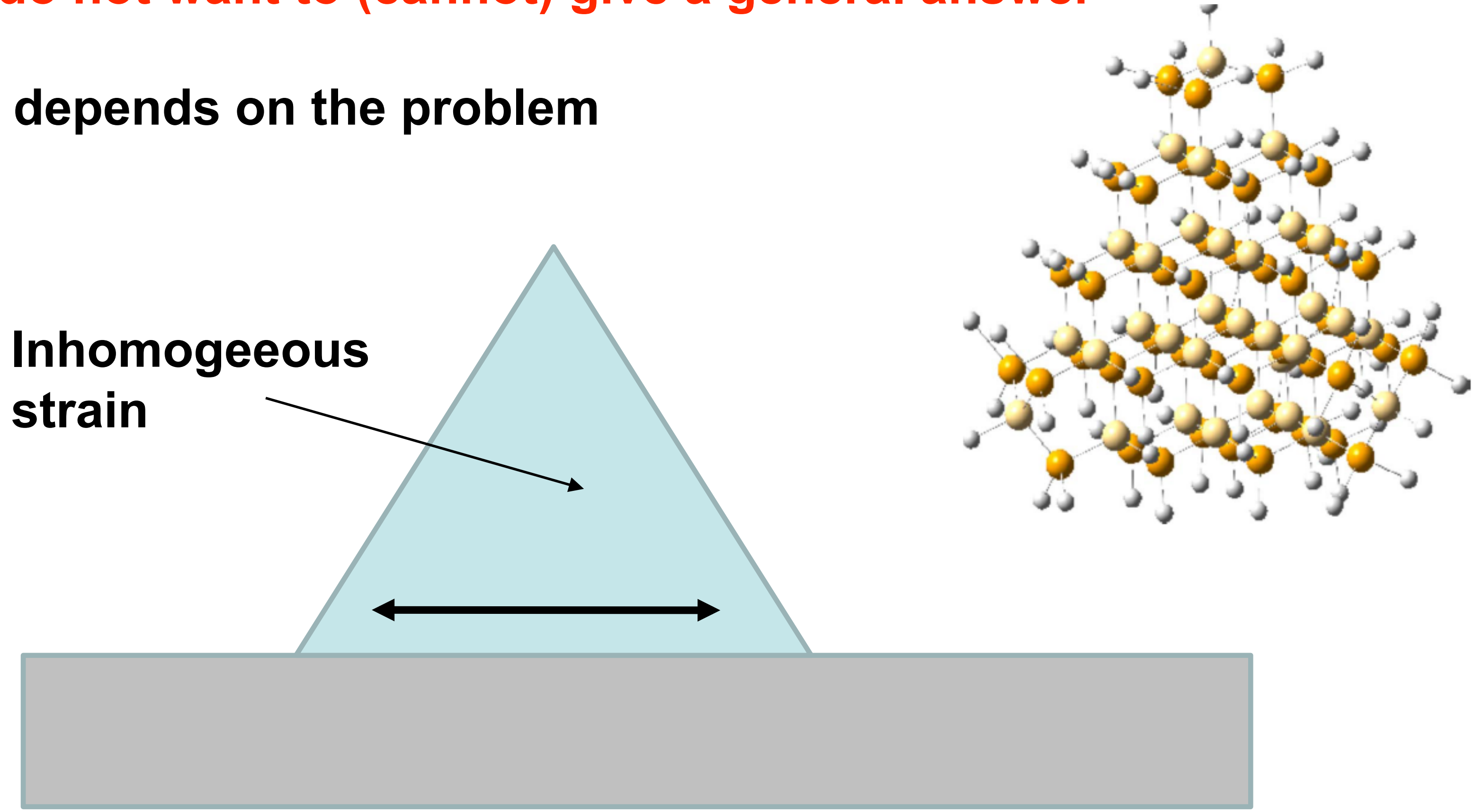
University of Illinois at Urbana-Champaign

What if this is a cluster of 10,000 atoms?
What if it is on a substrate?

A nanostructure (or a large molecule)

- I do not want to (cannot) give a general answer

- It depends on the problem



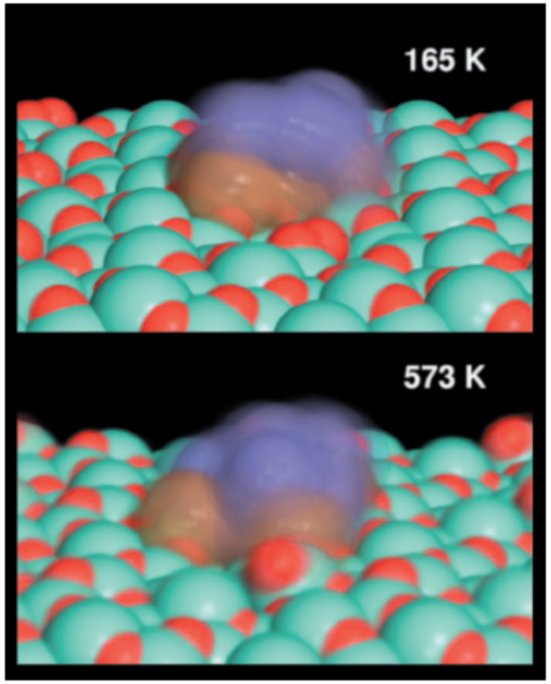
What if this is a cluster of 10,000 atoms?
Lattice mismatch leads to strain

A nanostructure (or a large molecule)

Pt Clusters – DFT MD – related to catalysis

For small systems forces are the way to go

Especially for finite T MD on a small cluster



PHYSICAL REVIEW B **78**, 121404(R) (2008)

Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

F. Vila,[1] J. J. Rehr,[1,*] J. Kas,[1] R. G. Nuzzo,[2] and A. I. Frenkel[3]

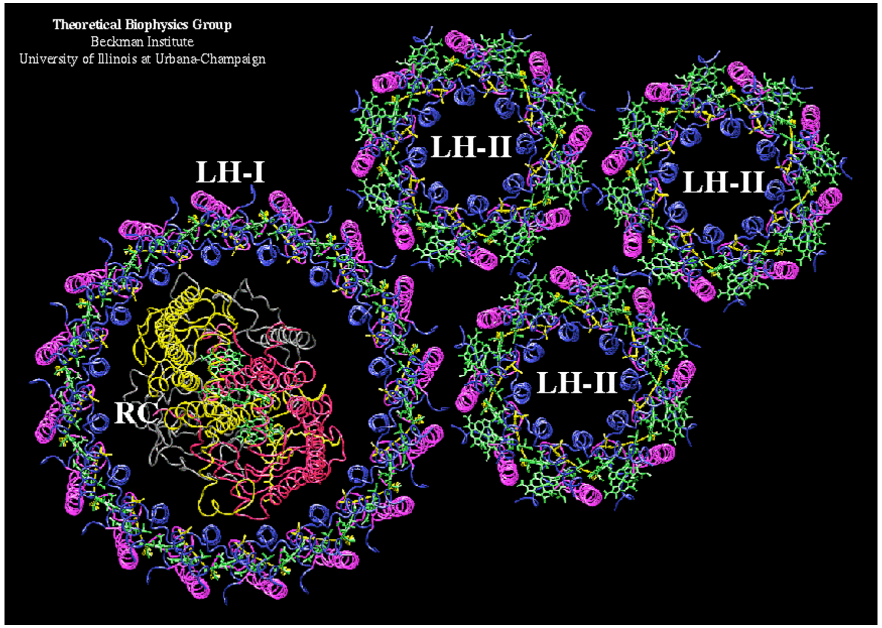
A nanostructure (or a large molecule)

- I do not want to (cannot) give a general answer

- It depends on the problem

In a large molecule, there may
\not be an “inside”
A polymer?
DNA?
Protein

What to do?



A nanostructure (or a large molecule)

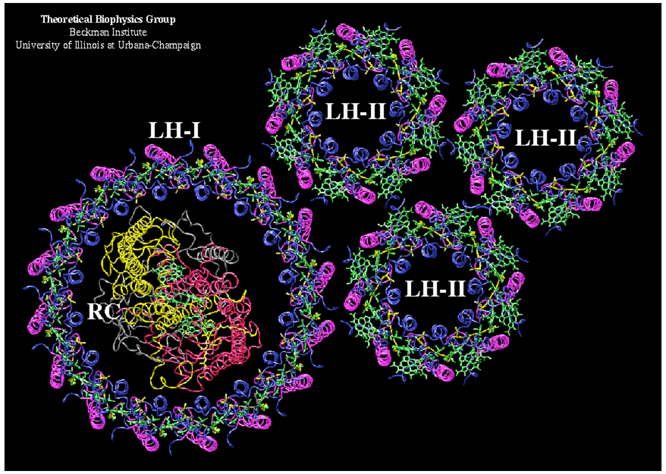
- What to do?

- Go to the web and look up Peter Pulay
- Pulay has found methods that are exceptionally clever and fast

- "Pulay Forces" result from coupled degrees of freedom, that add terms to the force theorem

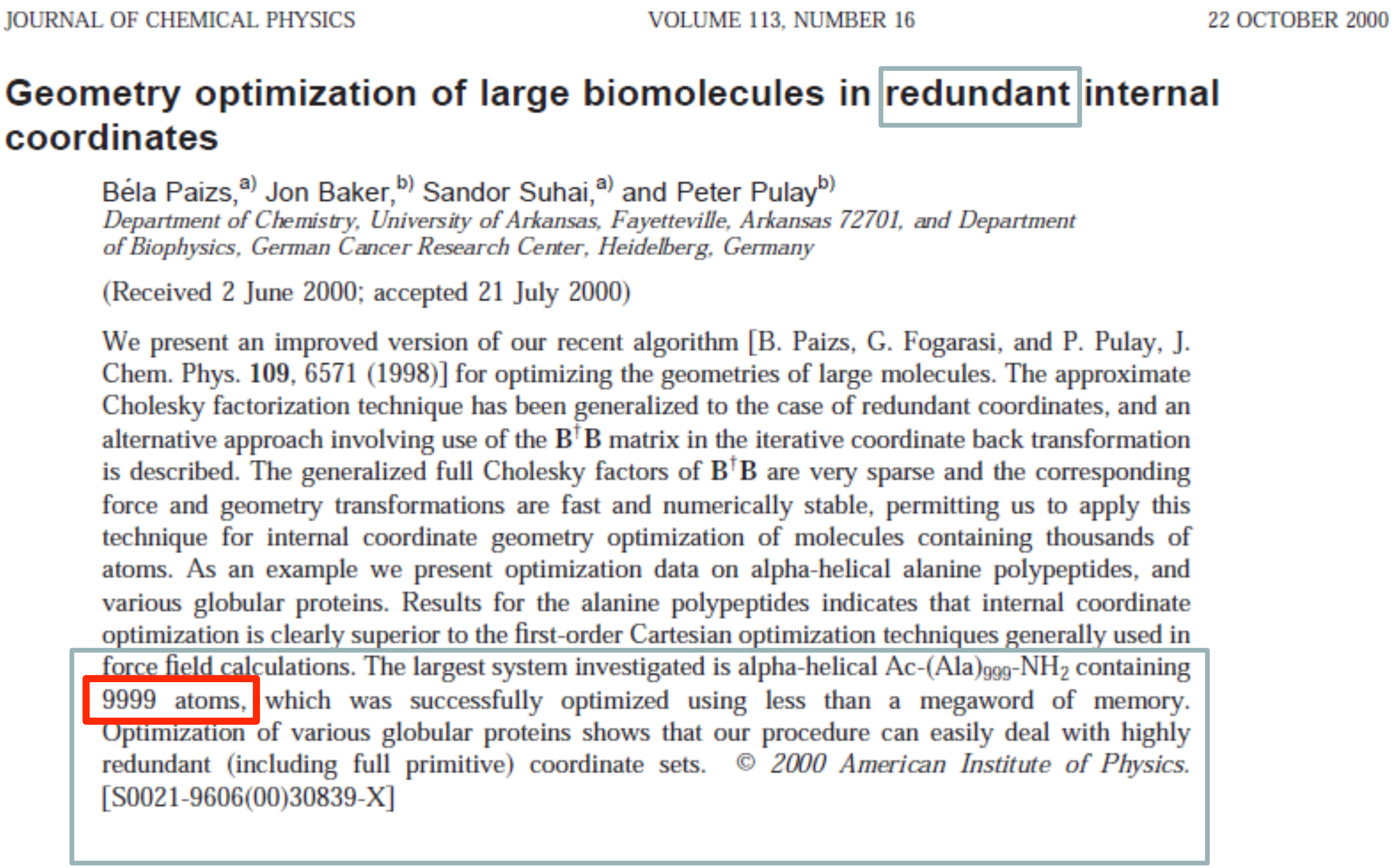
- The basic problem is to identify the best generalized coordinates – by information from the Hessian - second derivatives

- Pulay - and many others! - have derived clever ways for find the Hessian from information generated in the course of the iterations



These are the methods also used in electronic structure methods!

A Large Molecule



JOURNAL OF CHEMICAL PHYSICS VOLUME 113, NUMBER 16 22 OCTOBER 2000

Geometry optimization of large biomolecules in redundant internal coordinates

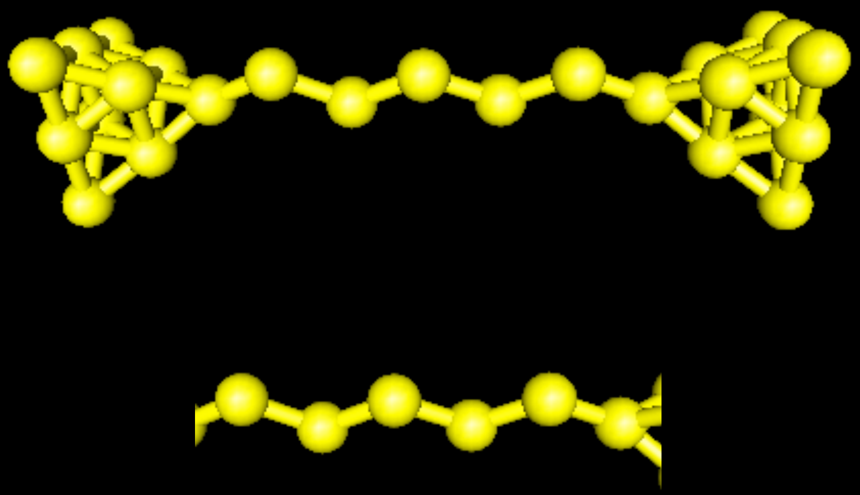
Béla Paizs,[a] Jon Baker,[b] Sandor Suhai,[a] and Peter Pulay[b]
Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, and Department of Biophysics, German Cancer Research Center, Heidelberg, Germany

(Received 2 June 2000; accepted 21 July 2000)

We present an improved version of our recent algorithm [B. Paizs, G. Fogarasi, and P. Pulay, J. Chem. Phys. **109**, 6571 (1998)] for optimizing the geometries of large molecules. The approximate Cholesky factorization technique has been generalized to the case of redundant coordinates, and an alternative approach involving use of the $\mathbf{B}^{\dagger}\mathbf{B}$ matrix in the iterative coordinate back transformation is described. The generalized full Cholesky factors of $\mathbf{B}^{\dagger}\mathbf{B}$ are very sparse and the corresponding force and geometry transformations are fast and numerically stable, permitting us to apply this technique for internal coordinate geometry optimization of molecules containing thousands of atoms. As an example we present optimization data on alpha-helical alanine polypeptides, and various globular proteins. Results for the alanine polypeptides indicates that internal coordinate optimization is clearly superior to the first-order Cartesian optimization techniques generally used in force field calculations. The largest system investigated is alpha-helical Ac-$(\mathrm{Ala})_{999}$-NH_2 containing 9999 atoms, which was successfully optimized using less than a megaword of memory. Optimization of various globular proteins shows that our procedure can easily deal with highly redundant (including full primitive) coordinate sets. [S0021-9606(00)30839-X]

Simulation of a Au “wire”

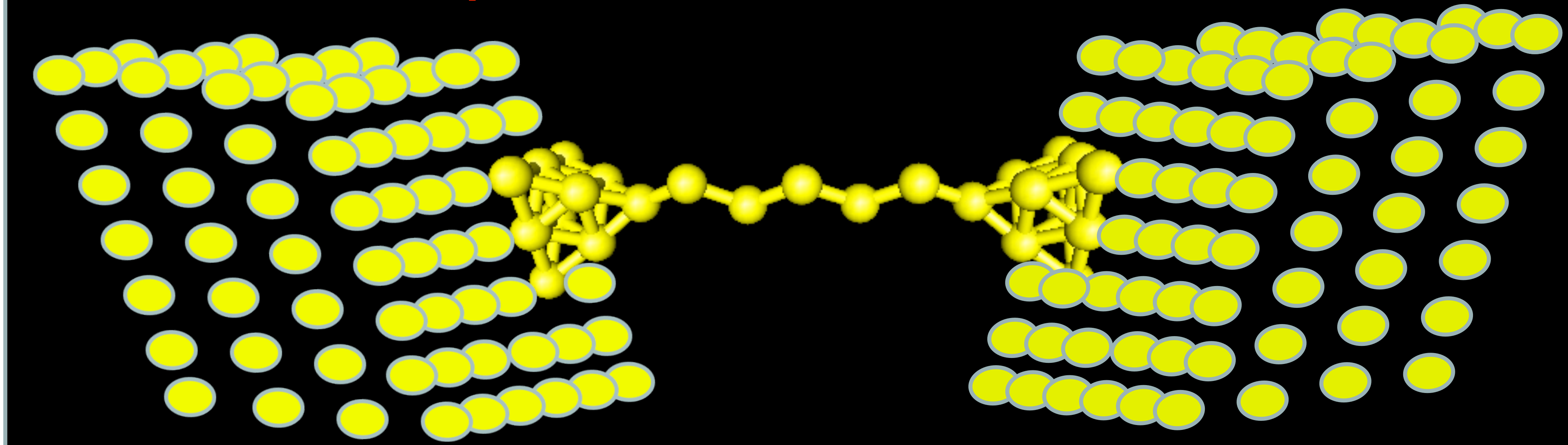
- Molecular dynamics simulation of a gold nanowire one atom thick pulled between two gold tips



- “Molecule” with external forces

Example of Simulation

- The real problem



- Molecular dynamics for wire and part of tip
- Rest of crystal\ provides a net static external forces

Electro – mechanical properties

Electro – mechanical properties

Dipole Moments

Piezoelectricity

Ferrolectricity

Interface charged sheets
(polarization)
(conductivity in the interface)

All have some general principles in common

Final consequence depends critically on the problem

Electro – mechanical properties

All have some general principles in common

Final consequence depends critically on the problem

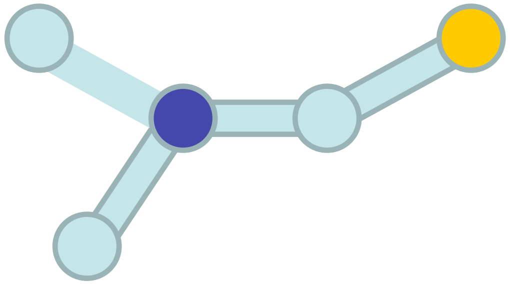
You have had this in first-year physics

Remember the difference between the
relation of polarization and electric field:

A “needle” – a long thin object
A slab – like in a capacitor
A sphere

With a computer you can work out other shapes

A Small Molecule



No problem to calculate a dipole moment in a finite system – like a molecule

$$\mathbf{d} = e \int d\mathbf{r}\; n(\mathbf{r})\, \mathbf{r}$$

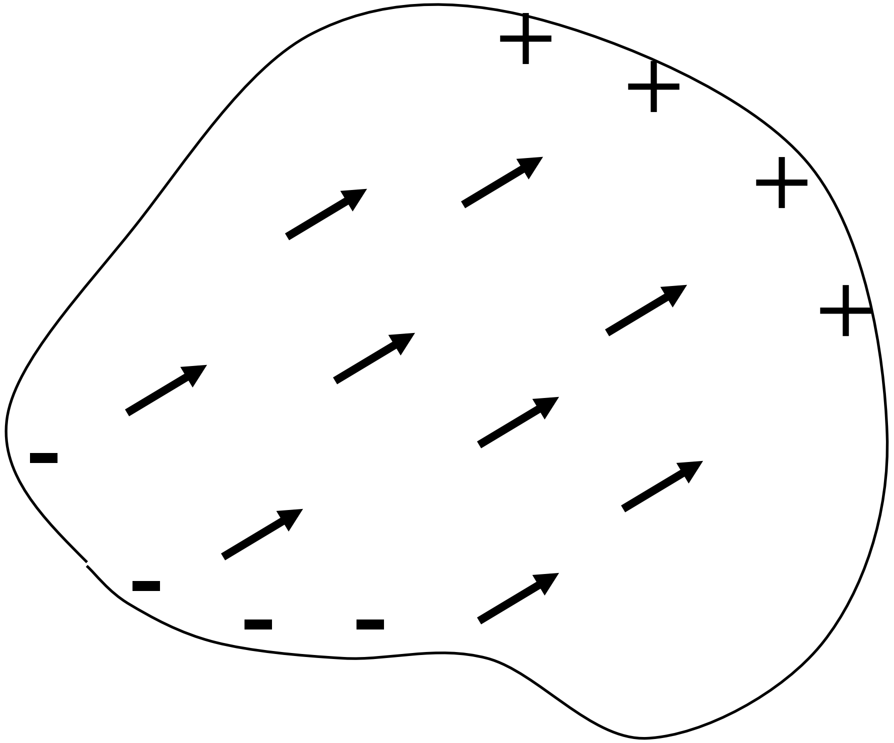
$$n(\mathbf{r}) = n^{+}(\mathbf{r}) + n^{-}(\mathbf{r})$$

protons → $n^{+}(\mathbf{r})$

electrons → $n^{-}(\mathbf{r})$

A Cluster or Large Molecule

No problem to calculate a dipole moment so long as it is regarded as a finite system taking into account all parts interior and surface



$$d = e \int dr \; n(r) \; r$$

$$n(r) = n^{+}(r) + n^{-}(r)$$

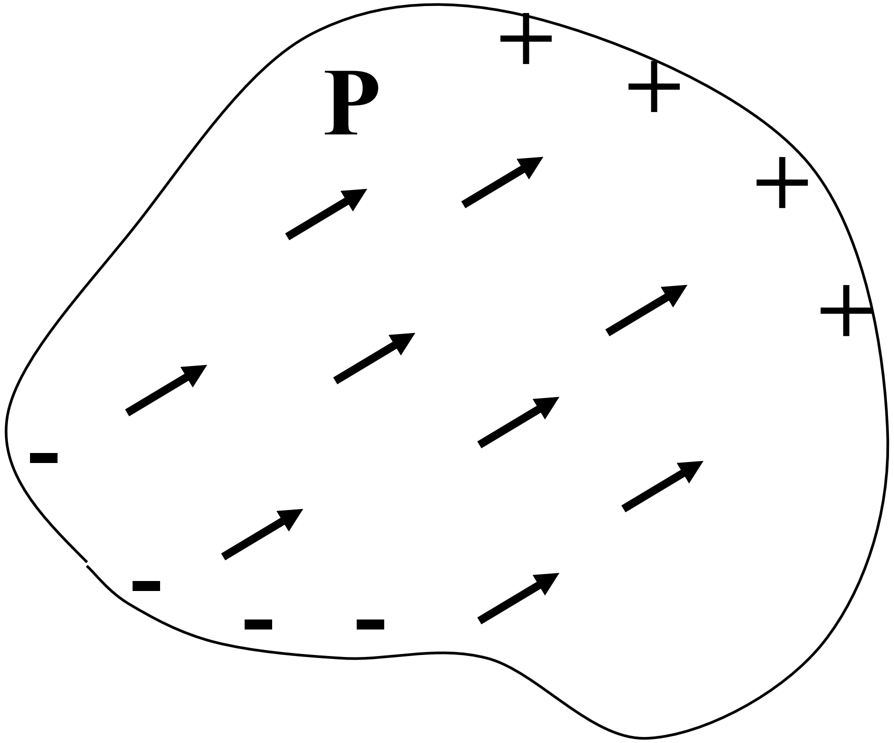
protons

electrons

The problem in a crystal

P_{av} = dipole moment per unit volume V

$$P_{av} = \frac{d}{V}$$



$$d = e \int dr\, n(r)\, r$$

$$n(r) = n^{+}(r) + n^{-}(r)$$

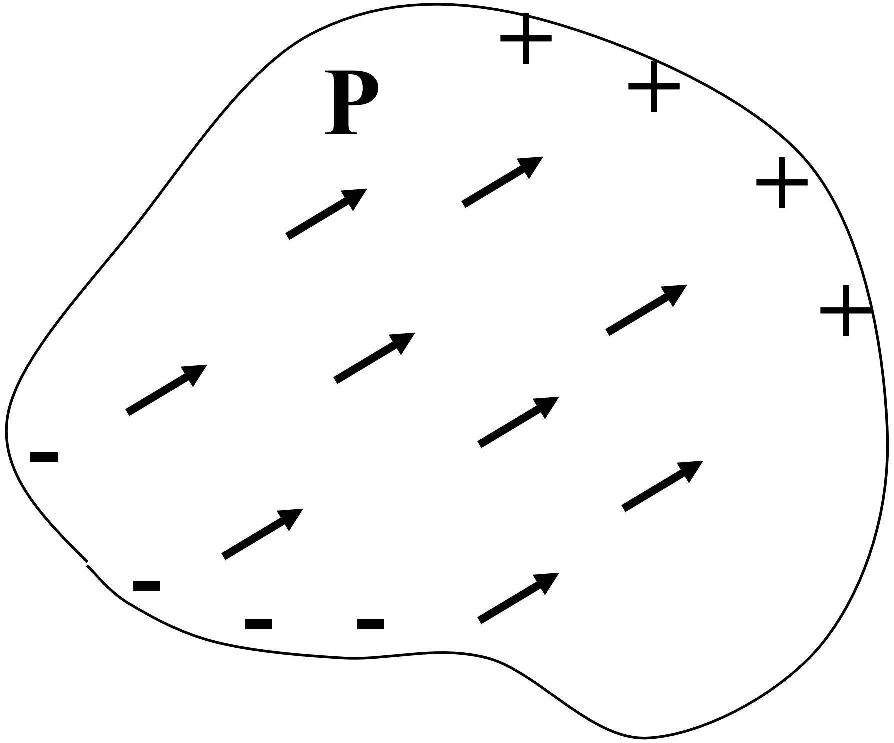
protons

electrons

But this is not well defined in the limit of large size

The surface term does not do to zero

The resolution in a crystal



$$\nabla P(\mathbf{r}) = -n(\mathbf{r})$$

$$(d/dt)P(\mathbf{r}) = j(\mathbf{r})$$

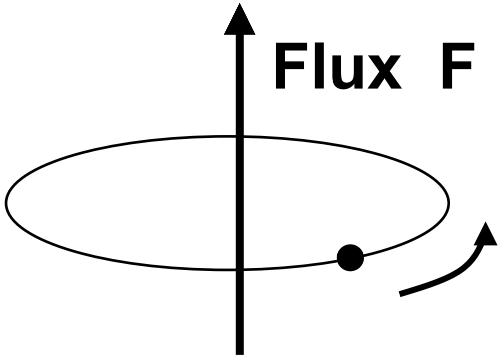
$$\Delta P = \int dt \int dr\, j(r,t)$$

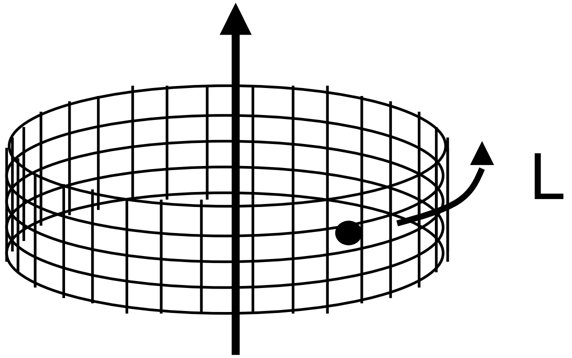
- The current j(r) is a well-defined measurable quantity inside the material – does not depend on the surfaces!
- Only Changes are meaning full
- Changes in P can be determined from the time integral of the current

The resolution in a crystal

- **This leads to the famous "Berry phase expressions"**
- **That are in all the major computer codes!**

King-Smith and Vanderbilt -- 1993





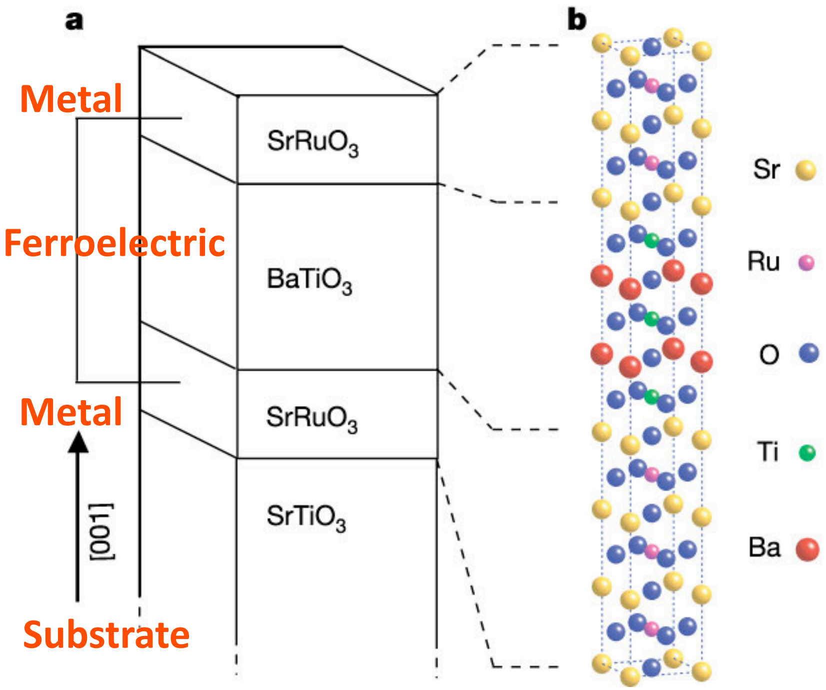
- **Aharonov-Bohm Effect:**
- Transport a charge (a current) around the magnetic flux
- **Displacement of charge in an infinite crystal with periodic boundary conditions**

Electro – mechanical properties

Back to finite systems where there are no such problems

At what layer thickness does ferroelectricity disappear

- **Example** – **Ferroelectric/metallic oxide epitaxial structure - Prediction of the reduction in ferroelectric moment – no transition for less than 6 atomic layers – J. Junquera, et al., Nature (2004).**



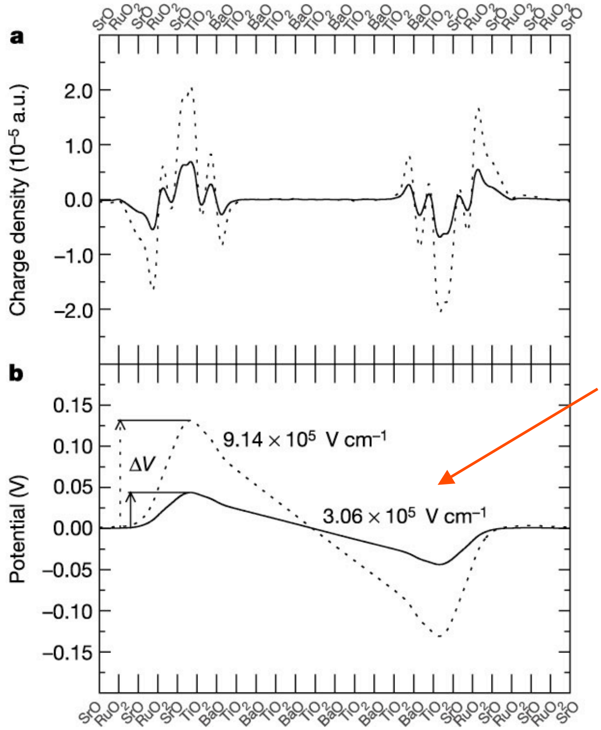
Metal

Ferroelectric

Metal

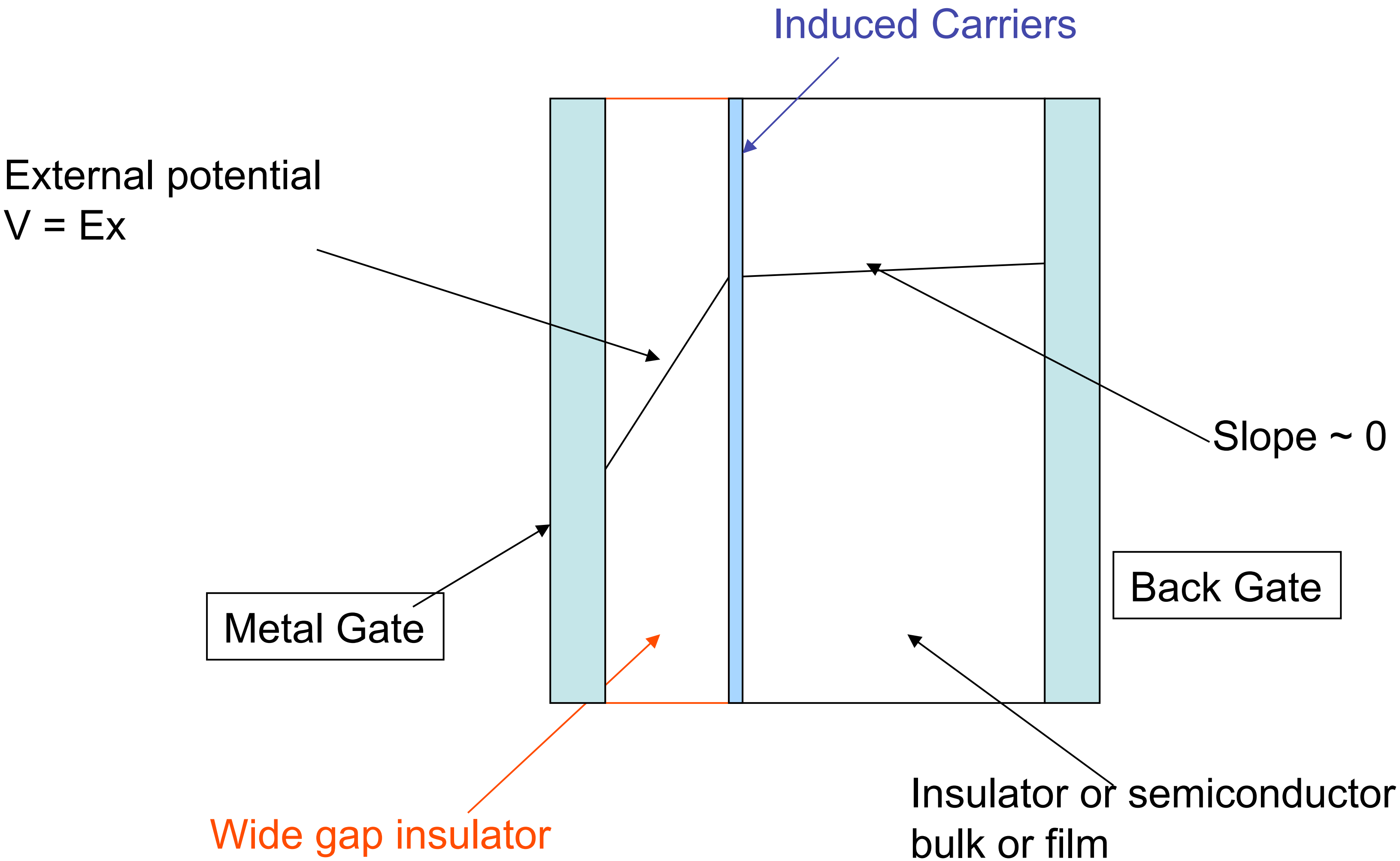
Substrate

Electron density and interface fields



Controls
relative energies
of electronic states

Field effect devices – general idea



Induced Carriers

External potential
V = Ex

Slope ~ 0

Back Gate

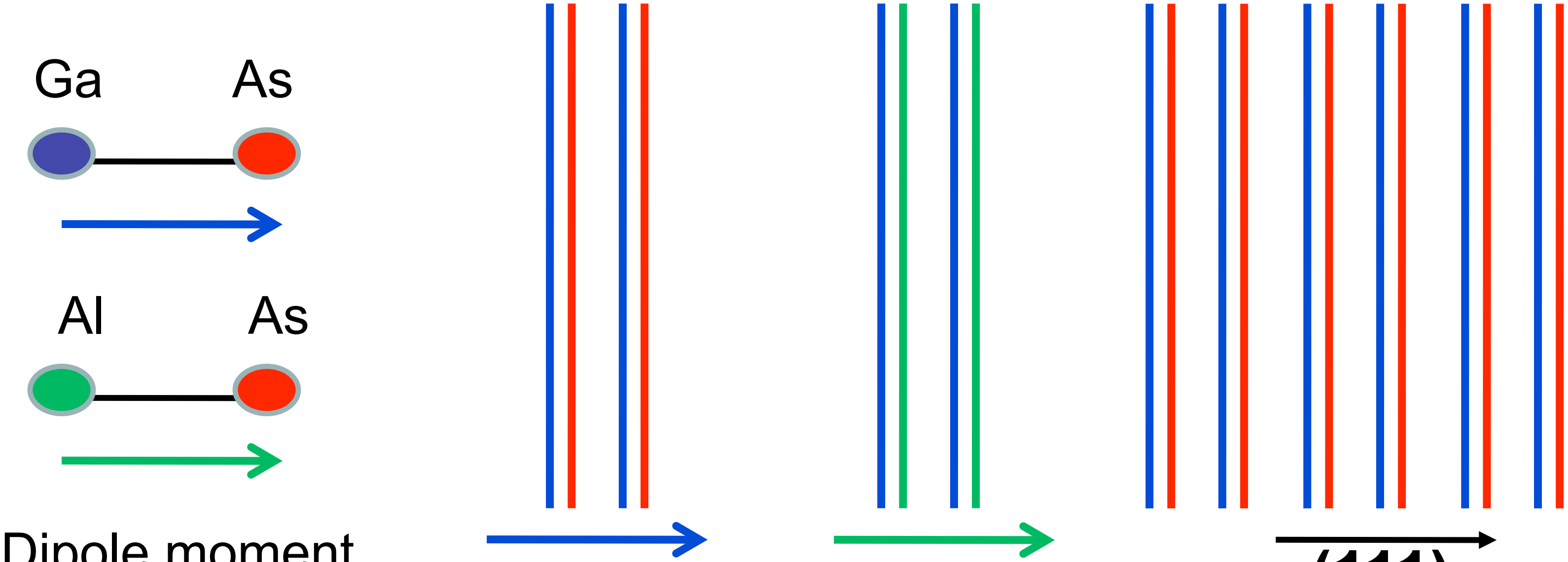
Metal Gate

Wide gap insulator

Insulator or semiconductor
bulk or film

Polarization in nanoscale systtems
Eexample of a semiconductor structure

Example- GaAs/AlAs



Molecule has
Dipole moment

Dipole moment
Different for
GaAs and AlAs

Layers have
Dipole moment

Dipole moment
Different for
GaAs and AlAs

Bulk is NOT Ferroelectric
(Same for GaAs and AlAs

Why?
Next Slide

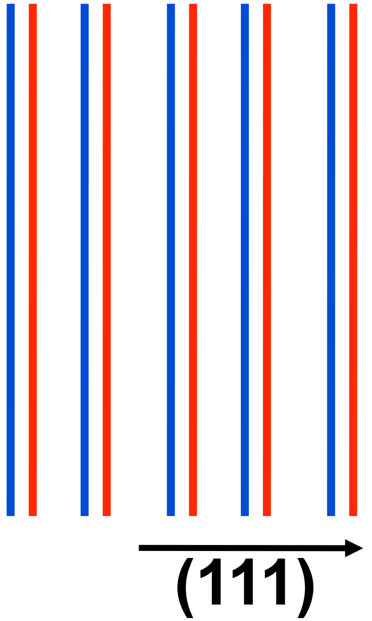
Not Ferroelectric

Nanoscale Different from bulk!

Polarization in nanoscale systtems
Eexample of a semiconductor structure

Example- GaAs/AlAs

Bulk is NOT Ferroelectric
(Same for GaAs and AlAs



CONFUSING!!
But finally clear if you look at it the right way

(-1-1-1) surfaces are different
It is a fact surface experiments show this clearly

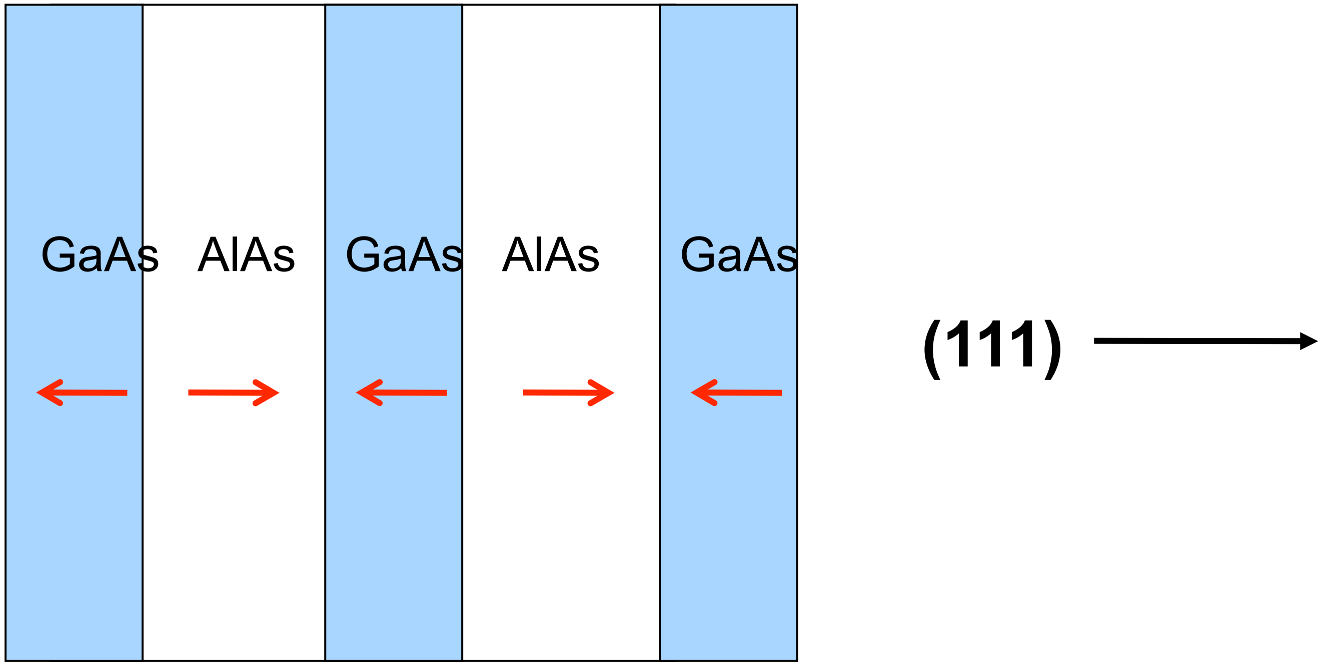
The DEFINITION of bulk is ZERO internal E field
This actually happens because charges
accumulate on the surface and cancel fields!
An experimental fact! Lowers the energy!

Different from the bulk!

IF we can make nanoscale systems in which this cancelation does NOT occur!

Built-in electric fields in a quantum well

Example- GaAs/AlAs



Different from the bulk!

Nanoscale systems ARE MADE in which this cancelation does NOT occur

because the interface is well-controlled –
No extrinsic effects

Energy Density

Construct an energy density e(**r**)*

$$E = T + E_{cc} + E_{xc} + \sum_R E_{nl} = \int e(\mathbf{r})\, d\mathbf{r}$$

$$\boxed{e(\mathbf{r}) = t(\mathbf{r}) + e_{cc}(\mathbf{r}) + e_{xc}(\mathbf{r}) + E_{nl}\,\delta(\mathbf{r}\text{-}\mathbf{R})}$$

Kinetic Energy Density

$$t^{(a)}(\mathbf{r}) = -\tfrac{1}{2}\psi^*(\mathbf{r})\nabla^2\psi(\mathbf{r})$$

$$t^{(s)}(\mathbf{r}) = \tfrac{1}{2}|\nabla\psi(\mathbf{r})|^2$$

$$gauge\ dep.(\mathbf{r}) = -\tfrac{1}{4}\nabla\cdot(\nabla\rho(\mathbf{r}))$$

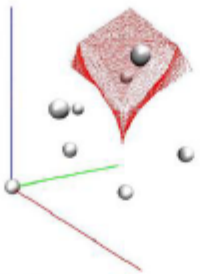
Classical Coulomb Energy Density

$$e_{cc}^{(a)}(\mathbf{r}) = -\tfrac{1}{8\pi}V(\mathbf{r})\nabla^2 V(\mathbf{r})$$

$$e_{cc}^{maxwell}(\mathbf{r}) = \tfrac{1}{8\pi}|\nabla V(\mathbf{r})|^2$$

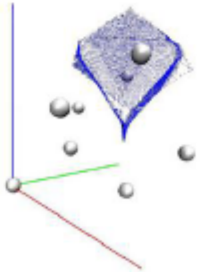
$$gauge\ dep.(\mathbf{r}) = -\tfrac{1}{8\pi}\nabla\cdot(V(\mathbf{r})\nabla V(\mathbf{r}$$

Unique when integrated over the “Bader Volume”



Bader volume.

“Zero-flux” surfaces = no gauge dep.



Charge neutral volume.
(different from Bader Volume)

* N. Chetty, and R. M. Martin, Phys. Rev. B 45, 6074 (1992);

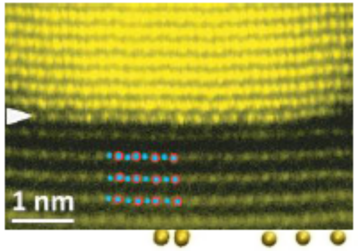
Unique for a surface or interface
Unique and useful in some nanosystems

Not known if it wil really be useful on an atom-by-atom basis

Min Yu, UIUC, unpublished

Energy Density

Interface of Au (111) // TiO_2(110)

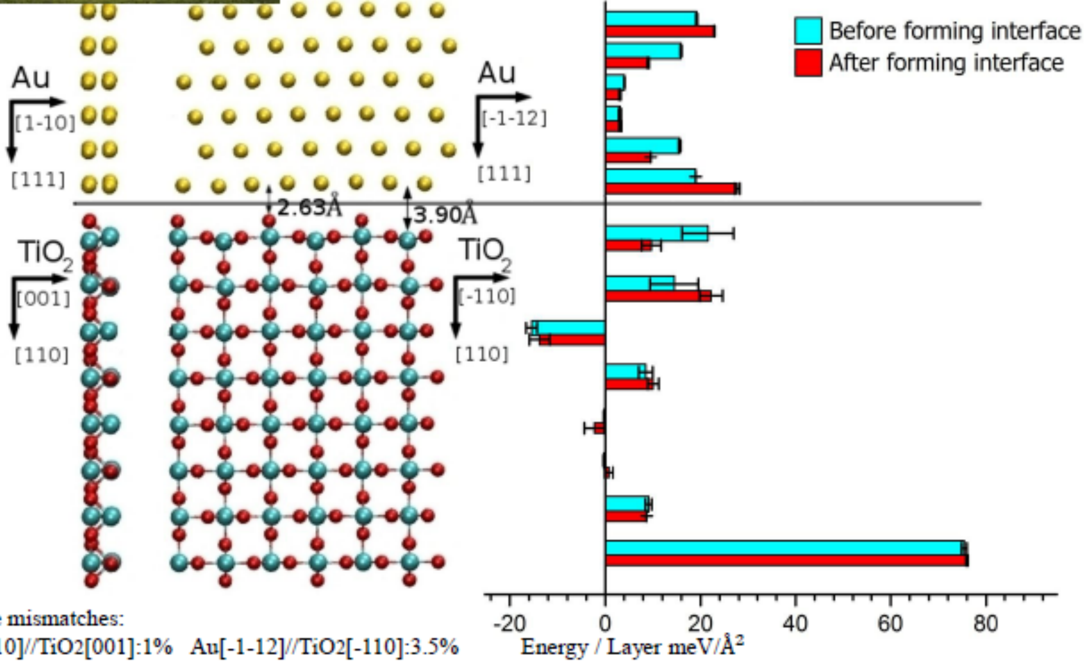


VASP*: PAW-PBE Au: 5d10 6s1; Ti: [Ne]3s2 3p6 4s2 3d2; O:[He]2s2 2p4

* G. Kresse, et.al . Phys. Rev. B 59,1758 (1999).

Work of Adhesion

Total Energy Calc.: $\frac{1}{A}(E_{Au} + E_{TiO_2} - E_{Au\text{-}TiO_2})$	**7 meV/Å²**
Energy Density Calc.: Integrate 2L Au + 4L TiO_2	4 ± 2 meV/Å²



Lattice mismatches:
Au[1-10]//TiO_2[001]:1%   Au[-1-12]//TiO_2[-110]:3.5%

Surface

Not known if it wil really be useful on an atom-by-atom basis

Min Yu, UIUC, unpublished

Conclusions

•Nanosystems can have different be different from (small) molecules and crystals

•Small molecules - straightforward
•Crystals – straightforward for things like elastic constants (but some interesting aspects)\
•Crystals – only recently discovered how to deal with polarization

•Mechanical behavior may be very complicated in naosystems – but the principles are clear – and symmetry can give great simplications

•Electric behavior can be very different from bulk

•Energy density – gives unique results for different parts of a system –remains too be seen how useful it is for properties of systems with inhomogeneous variations