

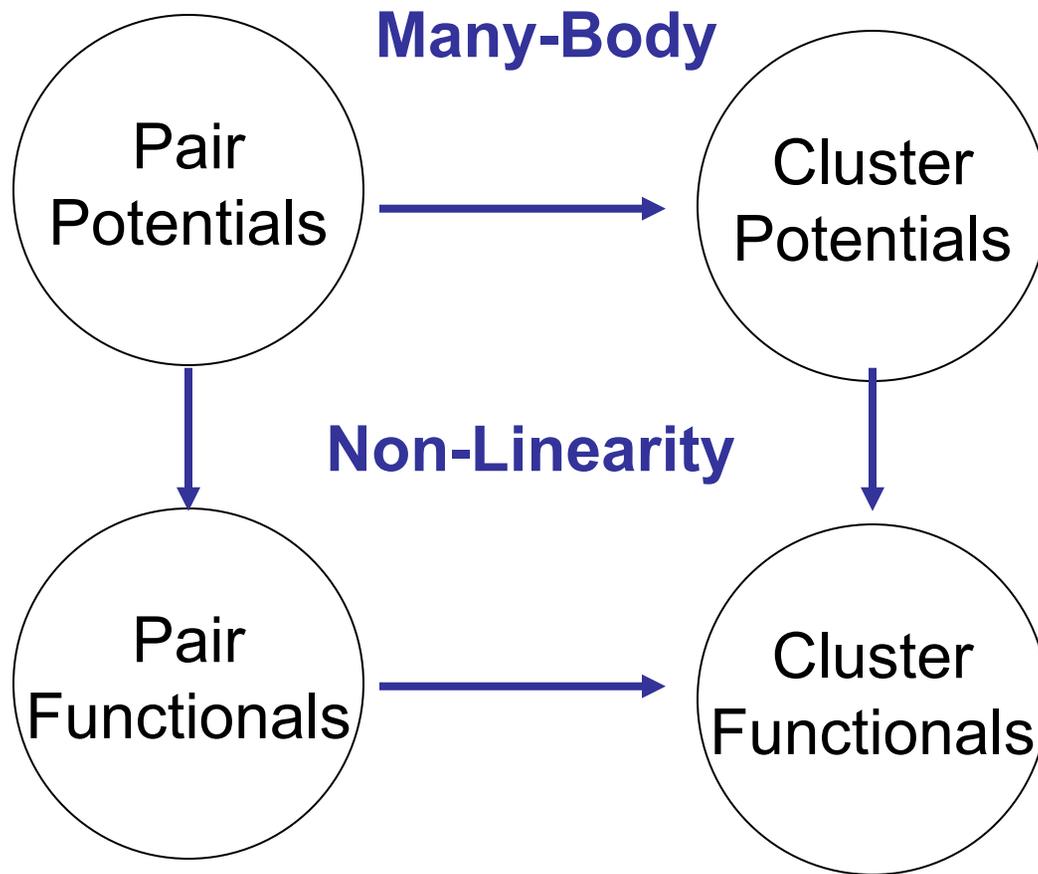
# Atomistic Modeling of Materials

## Potentials for Organic Materials and Oxides

3.320 Lecture 3a (2/8/05)



## How to Fix Pair Potential Problem ?



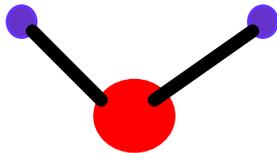
# Organic Molecules and Polymers

Distinguish between **BONDED** and **NON-BONDED** interactions

*Along covalent bonds*

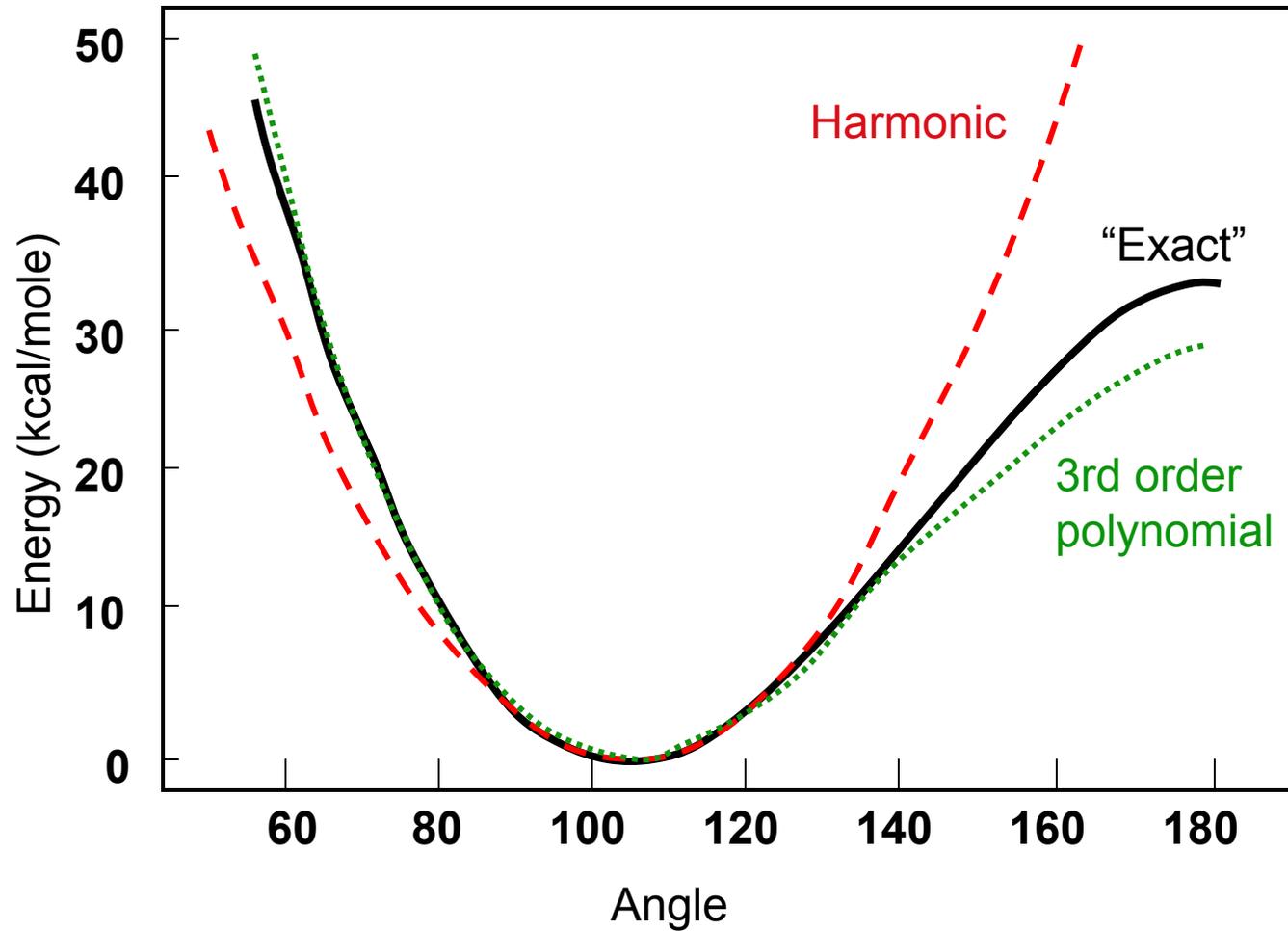
*Between atoms that are not bonded*

**Example:** A Potential for H<sub>2</sub>O: Relevant Energy Terms



*In class exercise: please take notes*

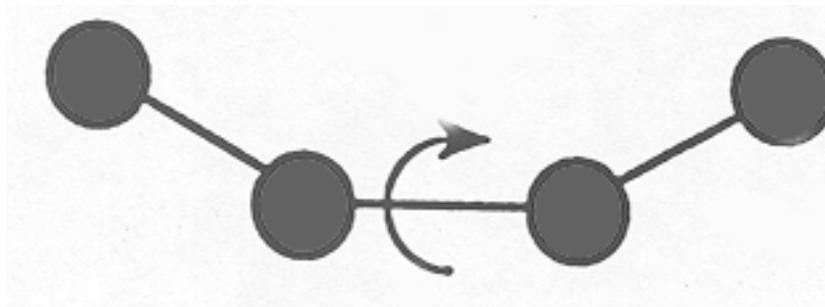
## Bending term for H<sub>2</sub>O



## More complicated molecules

**Example:** Ethane: Staggered versus Eclipsed configuration has different energy:

→ *Need four-body potential*

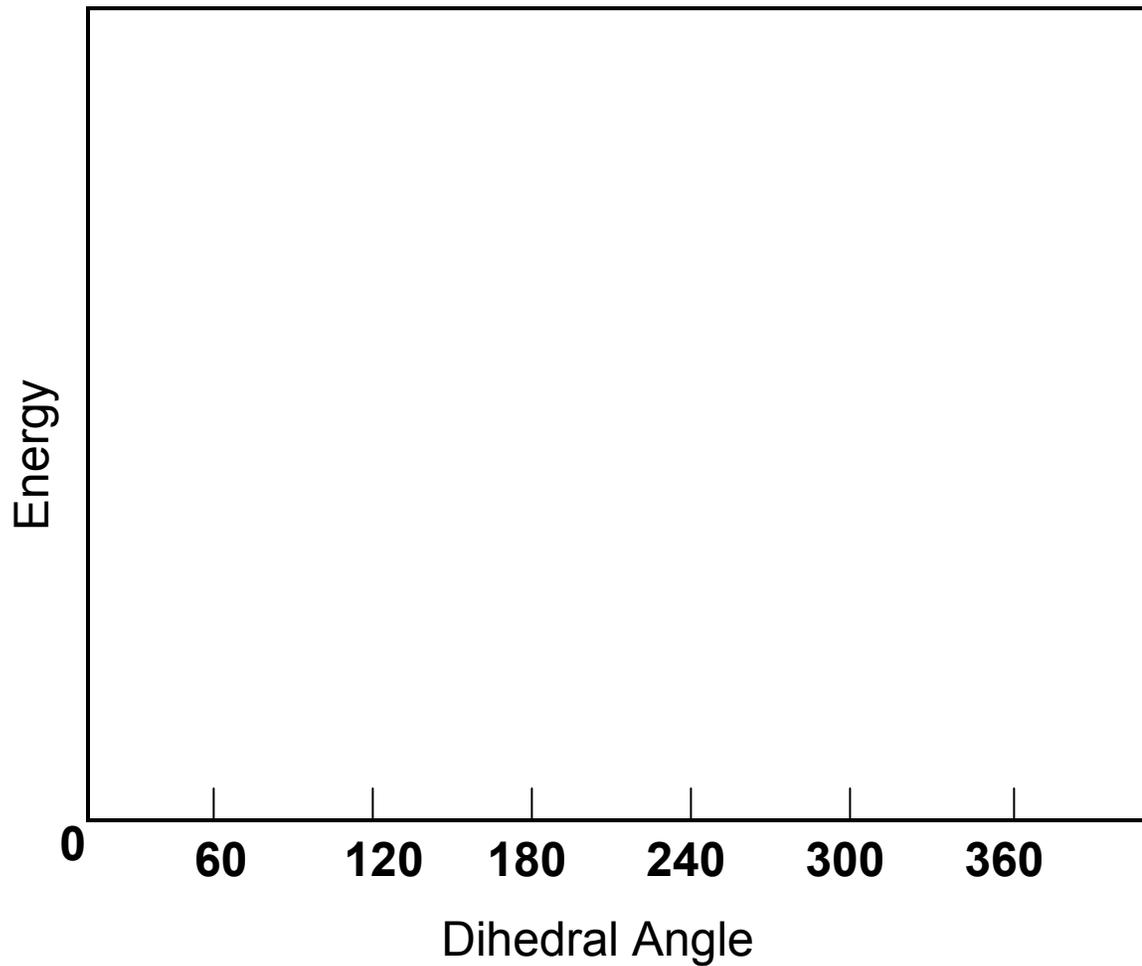


**Periodicity requirements:** e.g for ethane configurations repeat after 120 degrees torsion

$$V_{\text{torsion}} = K \cos(3\omega)$$

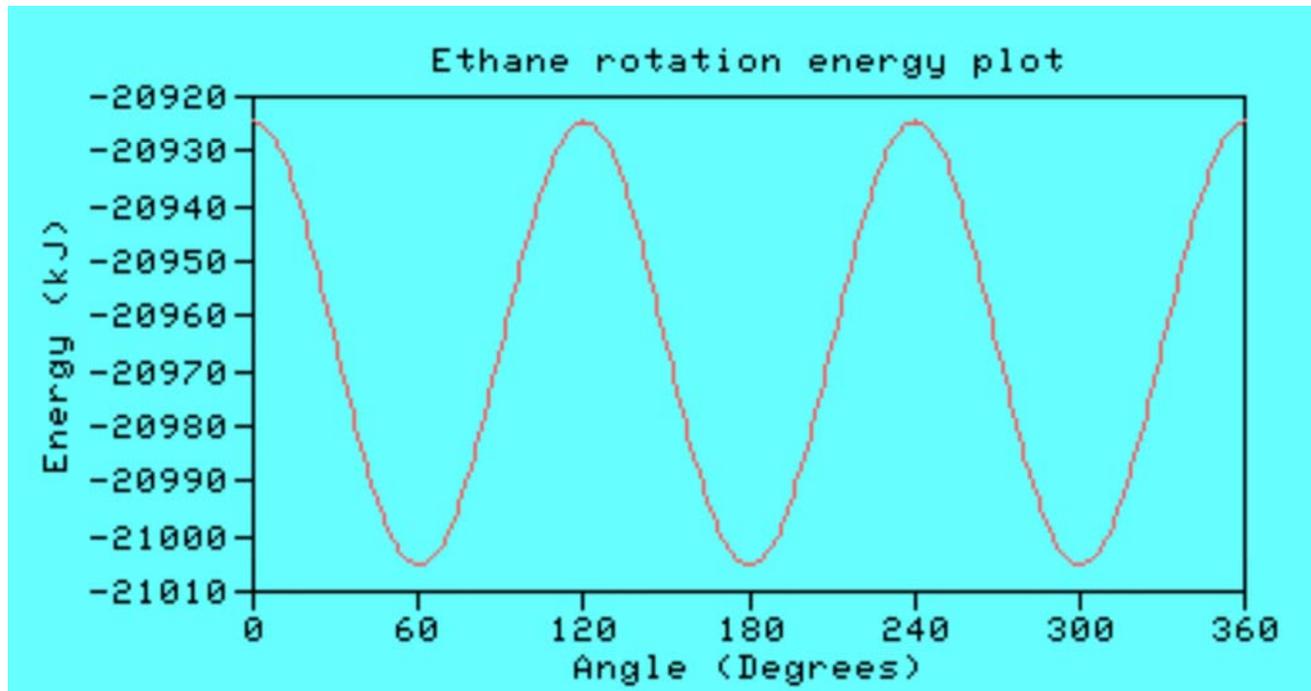
*torsion angle* →

# Torsion Potential has Periodicity

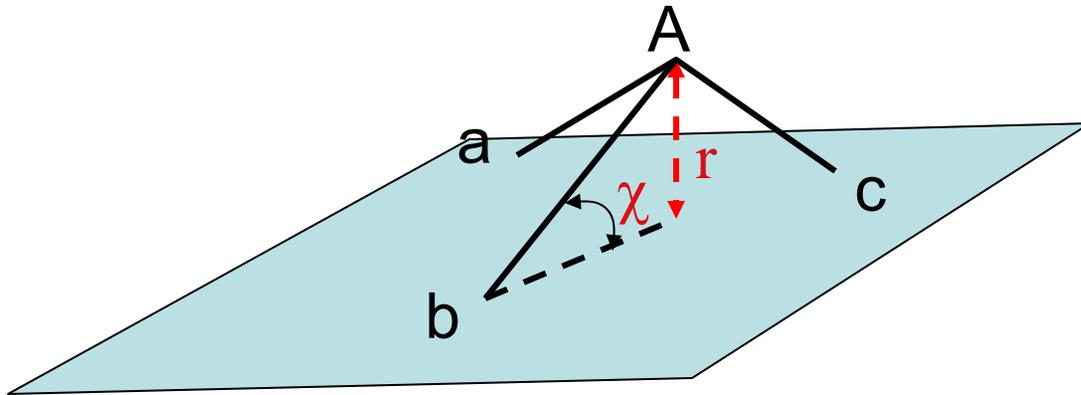


Draw  $\cos(2\omega)$   
and  $\cos(3\omega)$

# Torsion Potential has Periodicity



## Out-of-Plane or Improper Torsion



Used when the four atoms defining the torsion are “not in sequence”

## A real example: Poly-Hydroxybenzoic Acid

$$U = \sum_{\text{chains}} \left\{ \sum_{ijk} \mathcal{U}_{\text{valence},ijk} + \sum_{ijkl} \mathcal{U}_{\text{torsion},ijkl} + \sum_{ijkl} \mathcal{U}_{\text{improper torsion},ijkl} + \frac{1}{2} \sum_{ij} \mathcal{U}_{\text{vdW},ij} + \frac{1}{2} \sum_{ij} \mathcal{U}_{\text{Coulomb},ij} \right\}$$

where

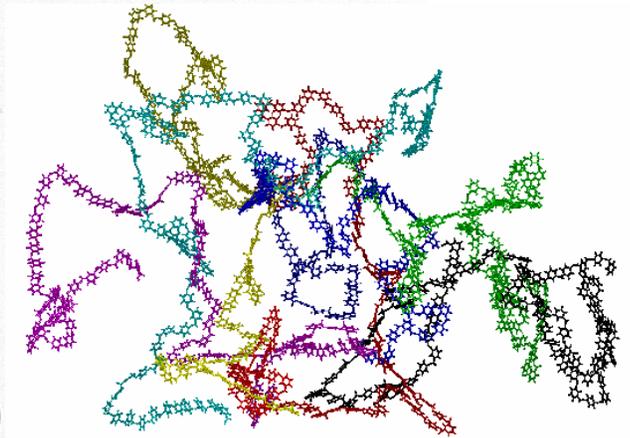
$$\mathcal{U}_{\text{valence},ijk} = \frac{1}{2} k_v (\theta_{ijk} - \theta_{ijk,0})$$

$$\mathcal{U}_{\text{torsion},ijkl} = \sum_{m=1}^4 H_{m\phi} (1 - \cos(m\phi_{ijkl}))$$

$$\mathcal{U}_{\text{improper torsion},ijkl} = H_{2\Phi} (1 - \cos(2\Phi_{ijkl}))$$

$$\mathcal{U}_{\text{vdW},ij} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

$$\mathcal{U}_{\text{Coulomb},ij} = (4\pi\epsilon_0 r_{ij})^{-1} q_i q_j$$



## Why do potentials work so well in organics ?

One given potential does not deal with changes in the coordination of covalent bonds. Changes in coordination are done by changing the potential ! ->

Hence: different potentials for  $sp^2$ ,  $sp^3$   $sp$  carbon ...

### Potentials good for:

- Conformation (configuration) of molecules
- Packing of molecules
- Barriers between various conformations

### Potentials not good for:

- Chemical reactions (bond breaking)

Potentials lack polarization

**Many general potential  
parameterizations for  
common organic molecules**

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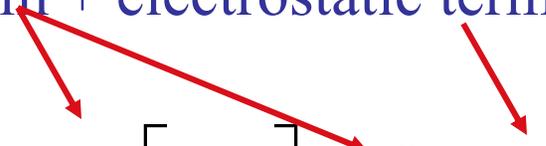
a set of good links for empirical  
models in chemistry

<http://www.msg.ku.edu/~msg/MGM/links/ffield.html>

## Empirical Models in Oxides

Well developed field. Relatively successful

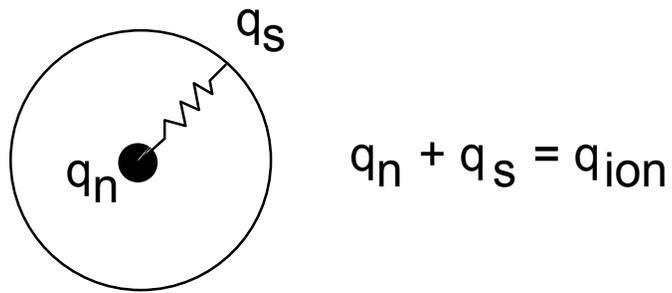
Typically, Buckingham + electrostatic term is used

$$V(r) = A \exp\left[-\frac{r}{\rho}\right] - \frac{C}{r^6} + \frac{q_1 q_2}{r}$$


long-ranged electrostatic part is summed by Ewald method

**Polarization:** induced dipole from electrical field from other ions

## Shell Model



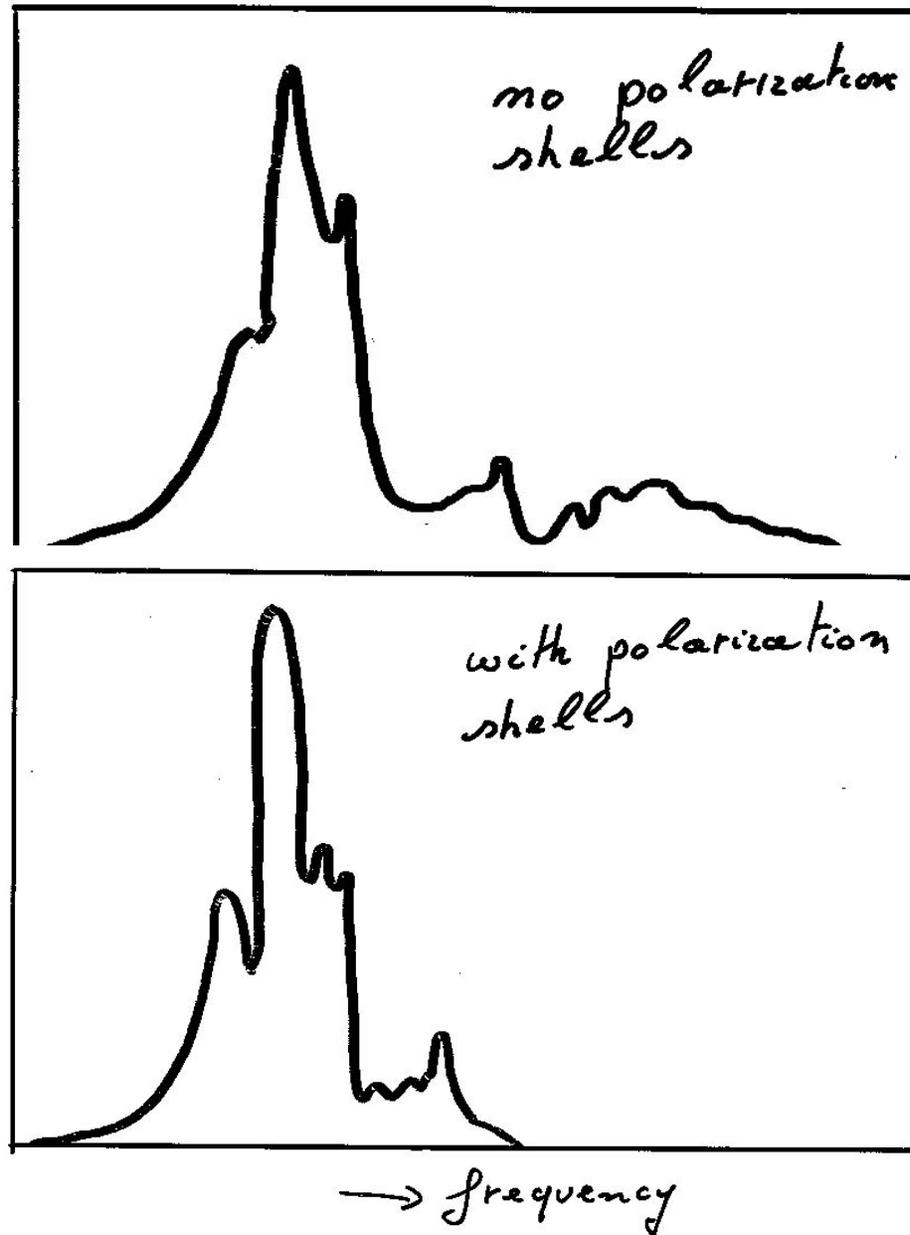
Two particles used per ion: **core** and **shell**, connected by a spring

- Shell interacts with other shells through potentials
- Cores and shells interact electrostatically
- Core and shell of one atom are coupled through a spring

$$V_{ion} = k\Delta r^2$$

spring constant  $k$  relates to polarizability of the ion

# Phonon density of states of MgO



## A good source for potentials in oxides

### Self-Consistent Interatomic Potentials for the Simulation of Binary and Ternary Oxides

Bush, T. S., J. D. Gale, R. A. Catlow, and P. D. Battle, 1994: . *Journal of Materials Chemistry*, **4**, 831-837.

*A consistent set of pair potentials has been derived empirically by fitting to the experimentally measured lattice properties of a series of binary metal oxide. In contrast to previous strategies, the potential parameters were optimized concurrently, utilizing residuals from all structures in the series, each calculated from the energy-minimized geometry. A more reliable determination of ion polarisabilities can thus be made.*

Good source for oxide potentials on the web collected by Woodley:

[http://www.ri.ac.uk/DFRL/research\\_pages/resources/Potential\\_database/index.html](http://www.ri.ac.uk/DFRL/research_pages/resources/Potential_database/index.html)

# Limitations of Pair Potentials in Oxides

## Oxygen Breathing Effects

oxygen ion changes size as function of its environment

## Variable Charge Effects

Especially transition metal ions have charge state dependent on environment

## Multibody Bonding Effects

# Evaluation of Potentials

## For metals

Bond energy depends very much on the number of bonds already made to an atom. Such an effect is absent in pair potentials, which are by definition environment-independent.

As a result, whenever bond-breaking in covalent materials is involved, the result of a potential model should be interpreted cautiously.

## For organic molecules

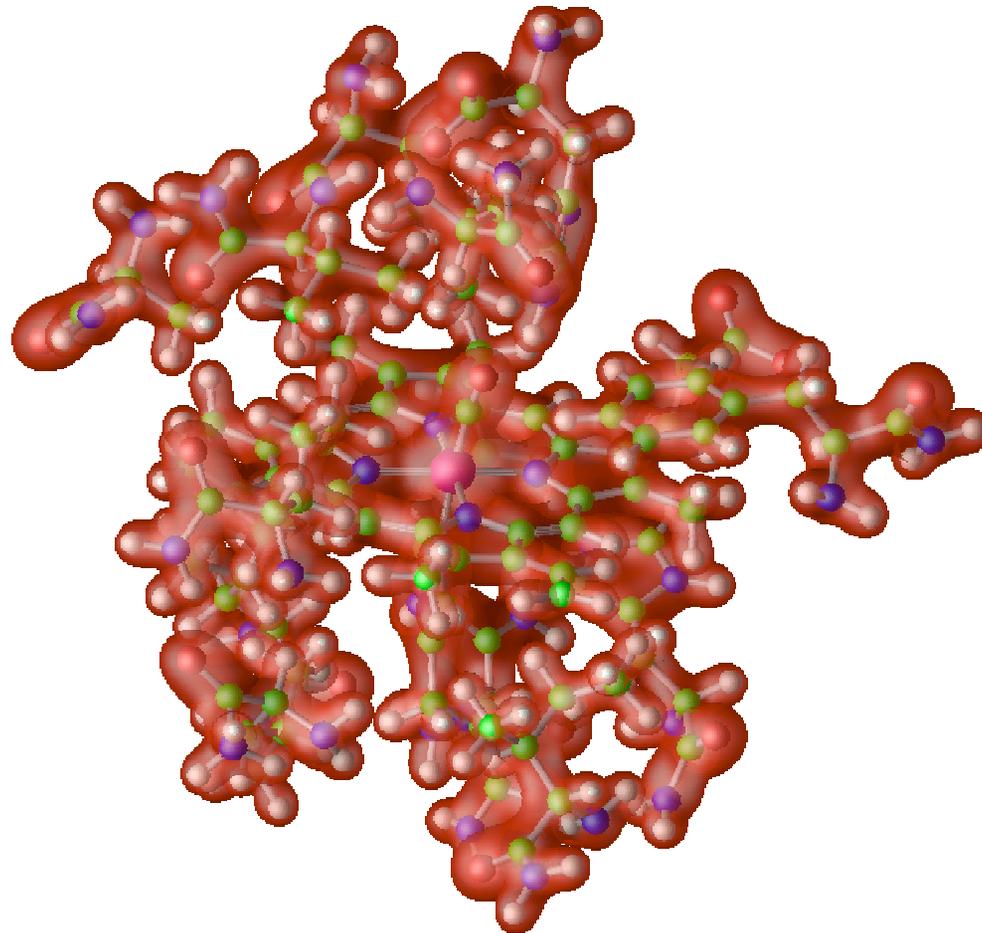
Very good potentials have been fit to C-H and C-C bonds in various bonding arrangements. These can be used to model conformational arrangements of polymeric systems (where no bond-breaking is involved)

## For oxides

In highly ionic oxides, qualitatively reasonable results can be expected with empirical potential models (+ electrostatic energy). Accuracy is mainly limited by the oxygen “breathing” effect. The more covalent the oxide, the more difficult it will be to find potentials that reproduce the materials behavior in a wide range of environments. Shell polarization is essential in low symmetry environments.

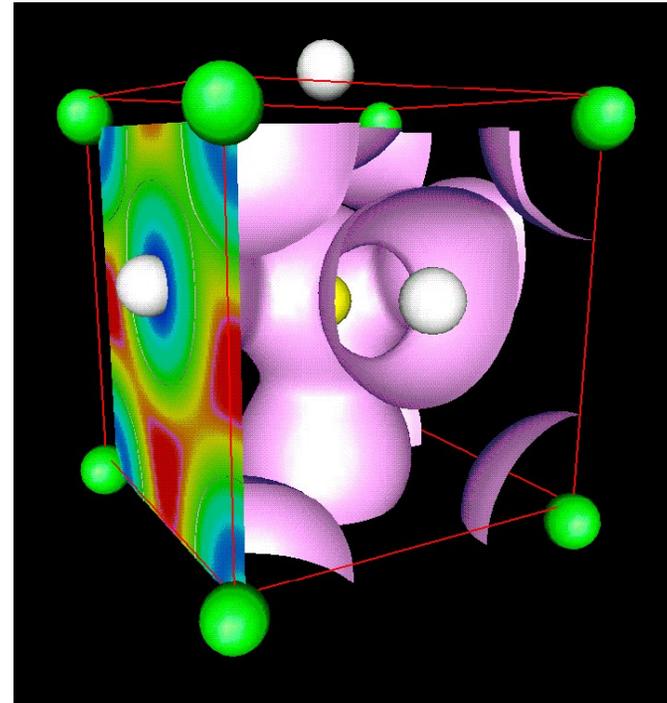
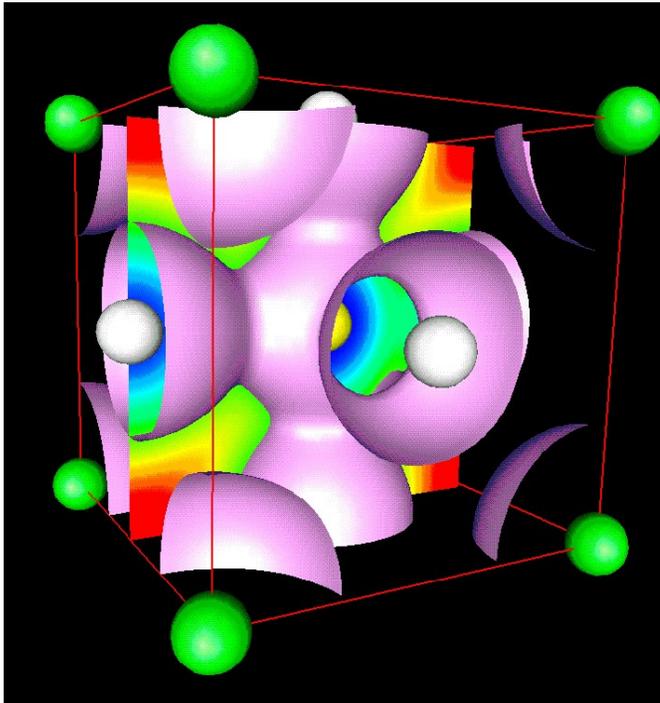
## 3.320: Lecture 3b (Feb 8 2005)

# IT'S A QUANTUM WORLD !



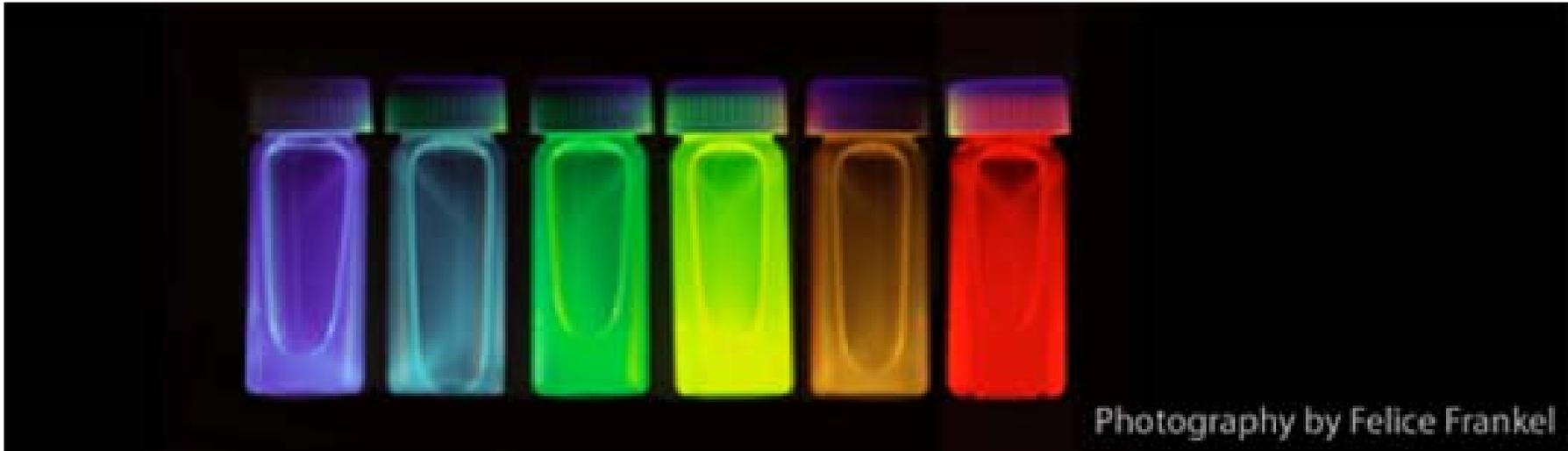
# Why do we need quantum mechanics ?

## 1) Bonding and Structure



Paraelectric (cubic) and ferroelectric (tetragonal) phases of  $\text{PbTiO}_3$

## 2) Electronic, optical, magnetic properties



Courtesy of Felice Frankel. Used with permission.

# 3) Dynamics, chemistry

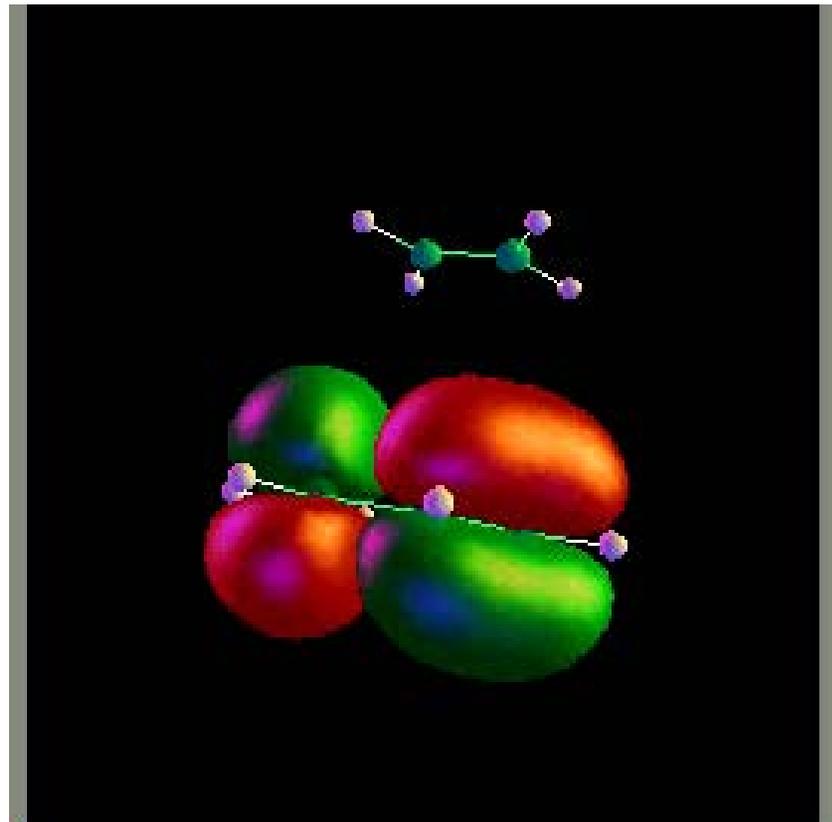
Diels-Alder Reaction:

1,3-butadiene + ethylene  $\rightarrow$  cyclohexene



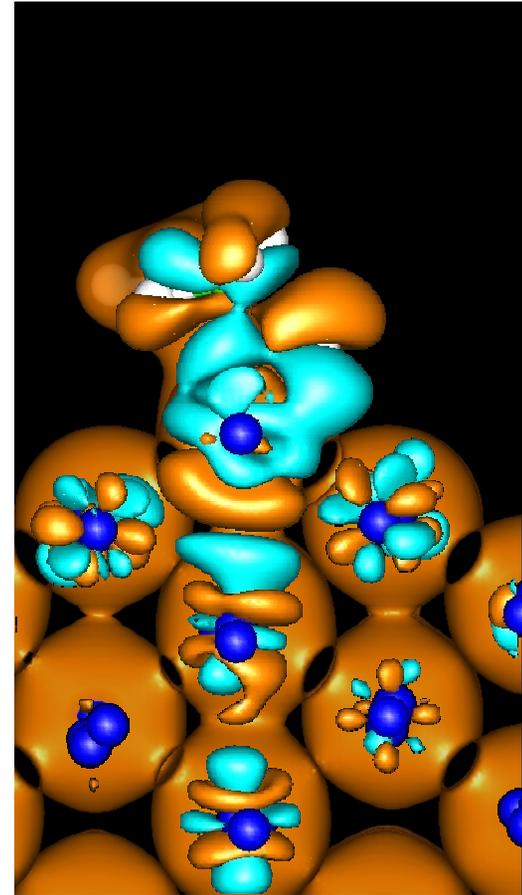
<http://www.wag.caltech.edu/home-pages/jim/>

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# Standard Model of Matter

- Atoms are made by massive, point-like nuclei (protons+neutrons)
- Surrounded by tightly bound, rigid shells of core electrons
- Bound together by a glue of valence electrons



# Material Properties From First-Principles

- Energy at our living conditions (300 K): **0.04 eV**  
(kinetic energy of an atom in an ideal gas:  $3/2 k_B T$ ).
- Differences in bonding energies are within one order of magnitude of **0.29 eV** (hydrogen bond).
- Binding energy of an electron to a proton (hydrogen):  
**13.6058 eV = 1 Rydberg (Ry) = 0.5 Hartree (Ha) = 0.5 a.u**

# Bibliography

- Richard M. Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge University Press (2004).
- Mike Finnis, *Interatomic Forces in Condensed Matter*, Oxford University Press (2003).
- Efthimios Kaxiras, *Atomic and Electronic Structure of Solids*, Cambridge University Press (2003).

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*"Reducing expectations for over 20 years!"*

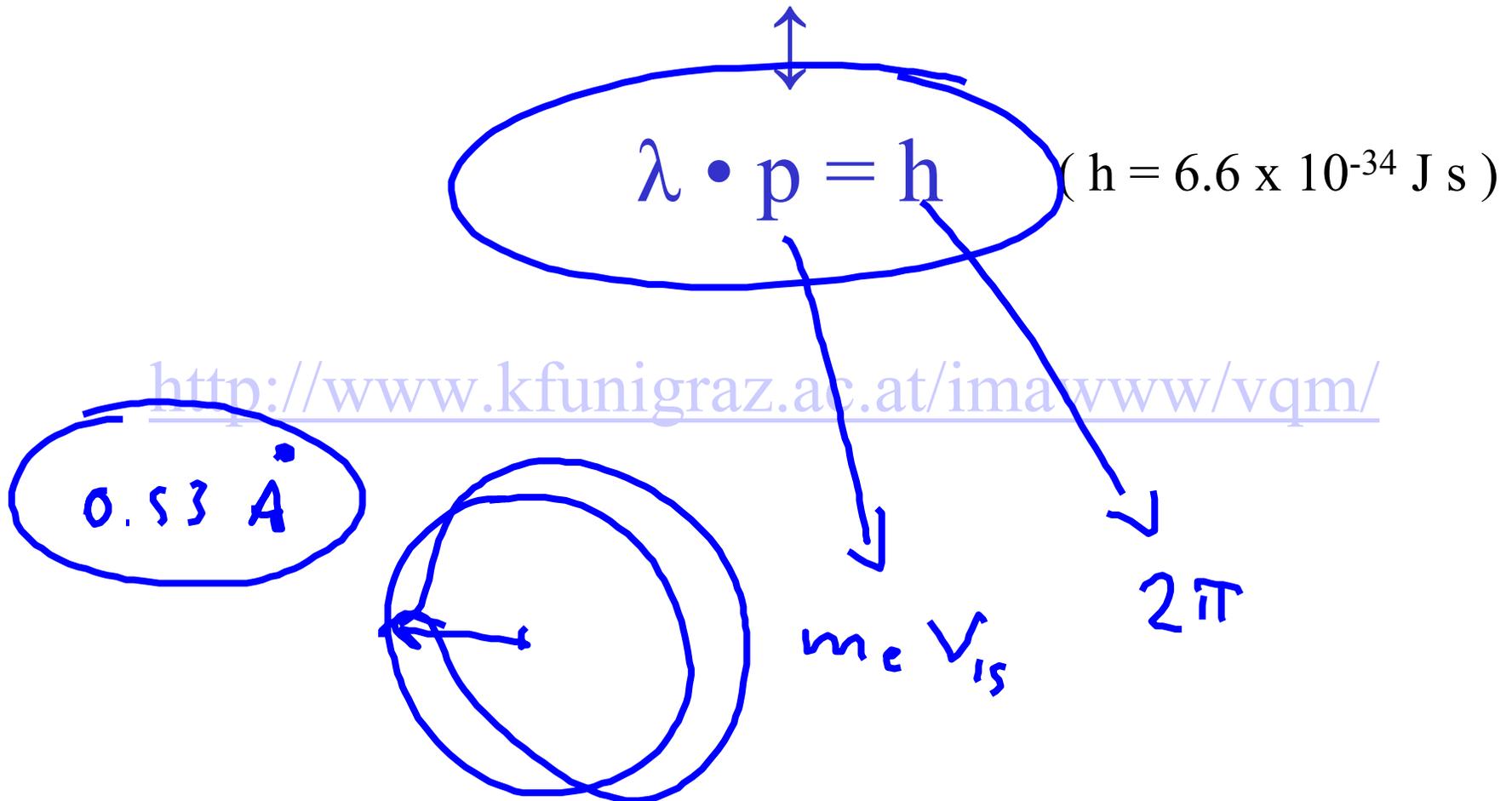
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# Wave-particle Duality

- *Waves have particle-like properties:*
  - *Photoelectric effect: quanta (photons) are exchanged discretely*
  - *Energy spectrum of an incandescent body looks like a gas of very hot particles*
- **Particles have wave-like properties:**
  - Electrons in an atom are like standing waves (harmonics) in an organ pipe
  - Electrons beams can be diffracted, and we can see the fringes

# When is a particle like a wave ?

Wavelength • momentum = Planck



# Quantum effects in the nuclear motion

“The nature of the hydrated excess proton in water”,  
Marx, D., Tuckermann, M. E., Hutter, J., & Parrinello,  
M. (1999). Nature (London) 397, 601-604

Pair of graphs removed for copyright reasons.  
Source: Marx et al, Nature 1999 as above.

“Effect of Quantum Fluctuations on Structural Phase Transitions  
in SrTiO<sub>3</sub> and BaTiO<sub>3</sub>”, W. Zhong and David Vanderbilt,  
Phys.Rev. B 53, 5047 (1996)

# So, What Is It ? A Misnomer...

It's the mechanics of **waves**, instead of **classical particles**



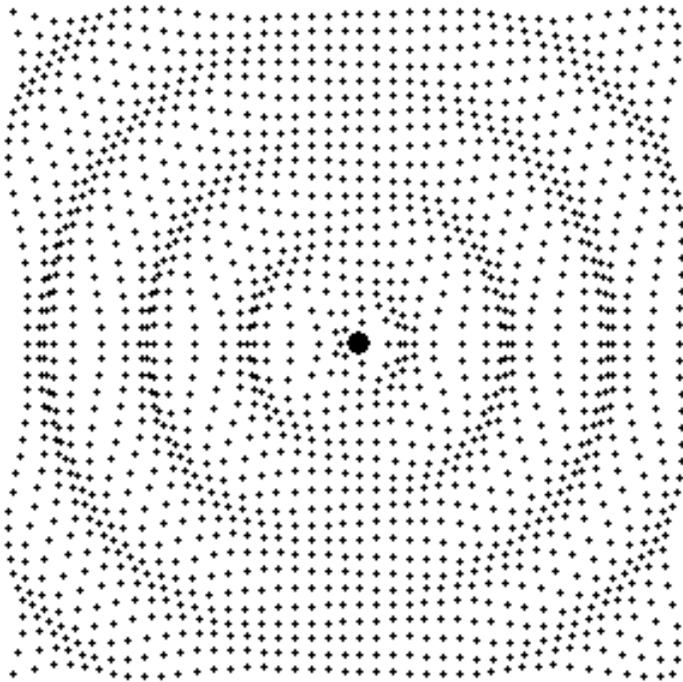
# Mechanics of a Particle

$$m \frac{d^2 \vec{r}}{dt^2} = \vec{F}(\vec{r}) = -\vec{\nabla} V(\vec{r}) \quad \longrightarrow \quad \begin{array}{c} \vec{r}(t) \\ \vec{v}(t) \end{array}$$

The sum of the kinetic and potential energy is conserved

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Cannon firing a cannonball.

# Description of a Wave



The wave is an excitation (a vibration): we need to know the amplitude of the excitation at every point and at every instant

$$\Psi = \Psi(\vec{r}, t)$$

# Time-dependent Schrödinger's equation

(Newton's 2<sup>nd</sup> law for quantum objects)

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, t) \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

1925-onwards: E. Schrödinger (wave equation), W. Heisenberg (matrix formulation), P.A.M. Dirac (relativistic)

# Stationary Schrödinger's Equation (I)

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, *) \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

# Stationary Schrödinger's Equation (II)

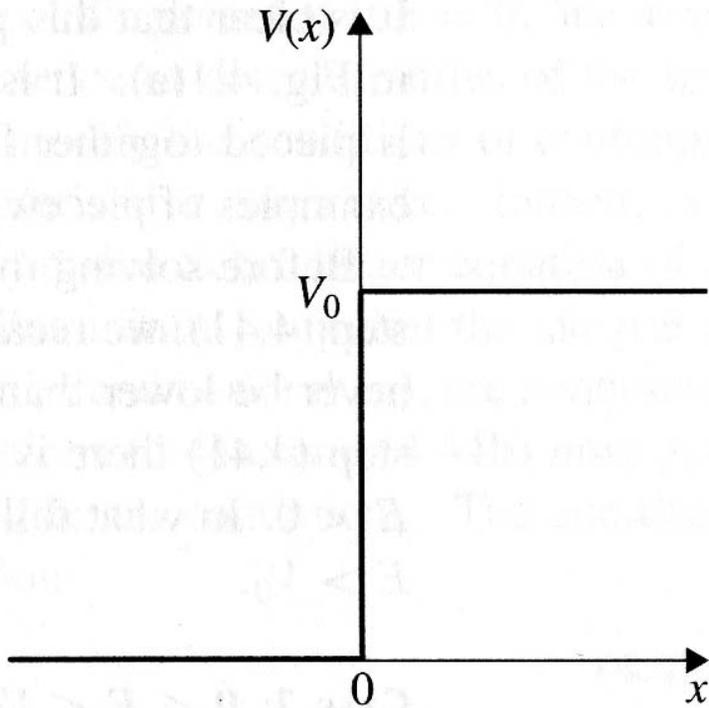
$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi(\vec{r}) = E \varphi(\vec{r})$$

# Interpretation of the Quantum Wavefunction (Copenhagen)

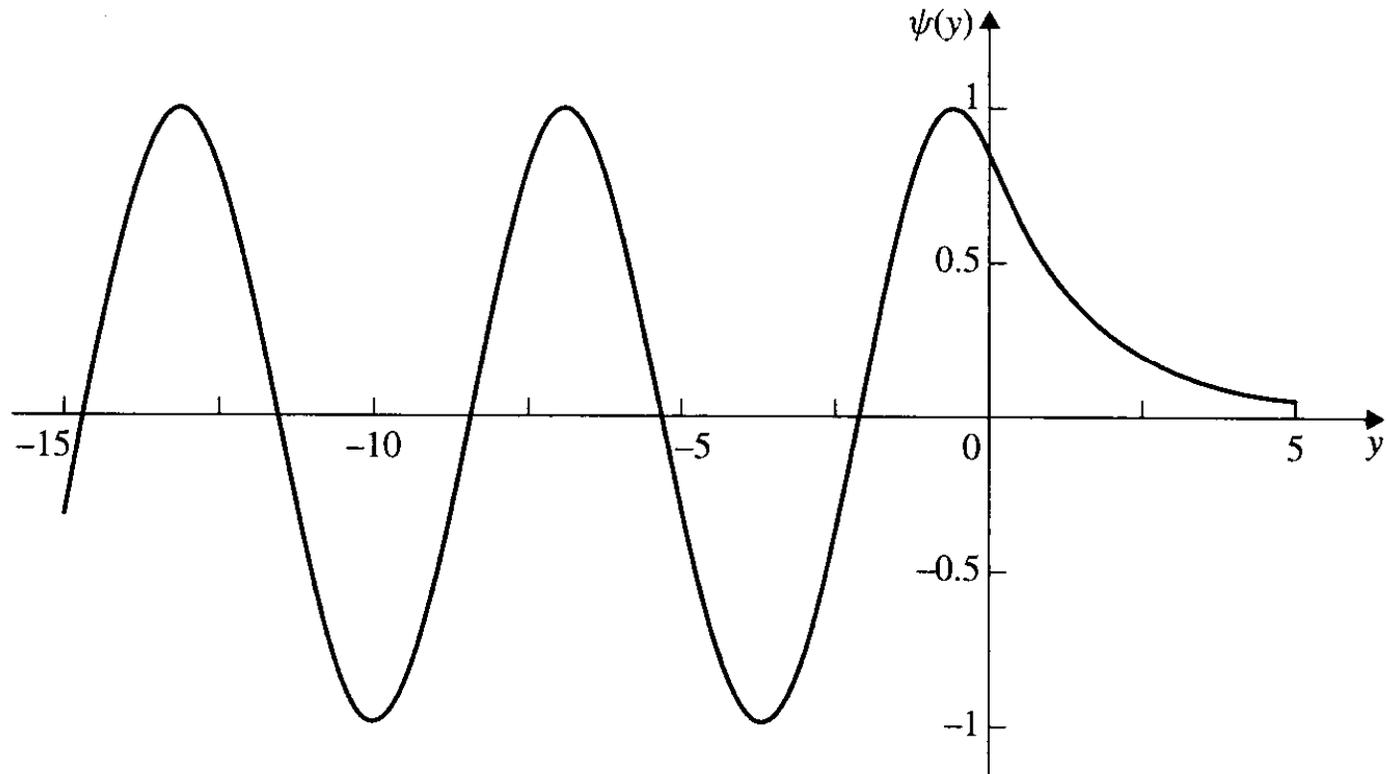
$\|\Psi(\vec{r}, t)\|^2$  is the probability of finding an electron in  $r$  and  $t$

$$\left\| \varphi(\vec{r}) \exp\left(-\frac{i}{\hbar} Et\right) \right\|^2 = \|\varphi(\vec{r})\|^2$$

# Metal Surfaces (I)

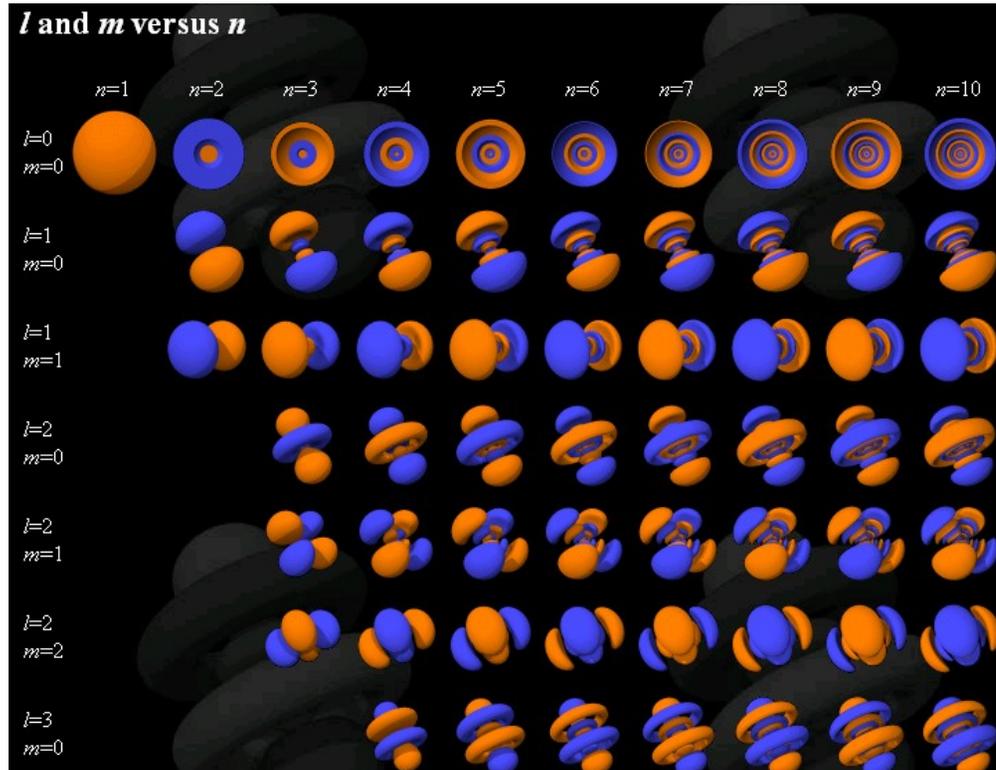


# Metal Surfaces (II)



# Solutions in a Coulomb Potential: the Periodic Table

<http://www.orbitals.com/orb/orbtable.htm>



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