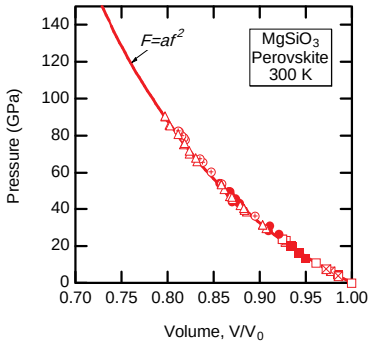
Electronic Structure and First Principles Theory

7/25/04 CIDER/ITP Short Course

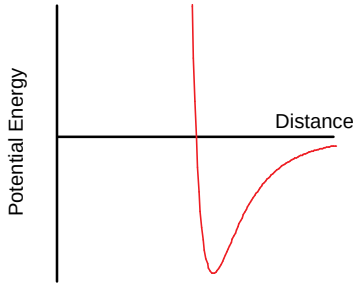
Equation of State

- Start from fundamental relation
- Helmholtz free energy
  - $F=F(V,T,N_i)$
- Isotherm, fixed composition
  - $F=F(V)$
- Taylor series expansion
- Expansion variable must be V or a function of V
  - $F=af^2 + bf^3 + \ldots$
- $f = f(V)$ Eulerian finite strain



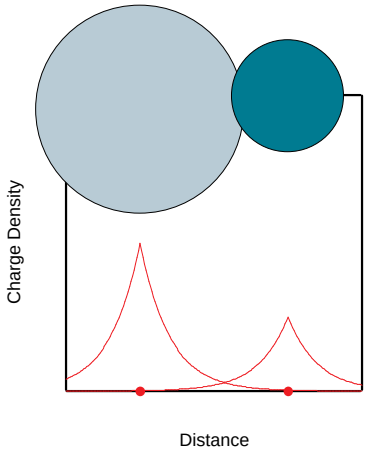
Microscopic Picture 1
Pair Potential

- Assume pairwise interactions
- Assume simple functional form
  - $V(r) = \exp(-r/\rho) + Z_1 Z_2 e^2/r$
- Advantages
  - Fast
- Fundamental inadequacies
  - $C_{12}=C_{44}$
- Empirical inadequacies
  - N+1th observation
  - More complex functional forms and/or parameters depend on
    - Pressure
    - Temperature
    - Structure

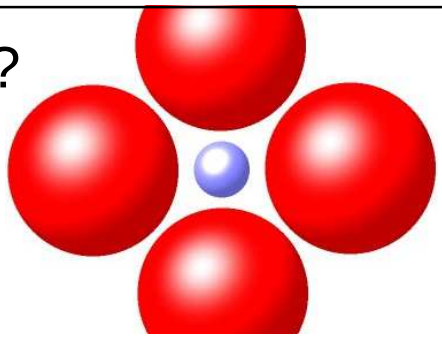


Microscopic Picture 2
Gordon-Kim

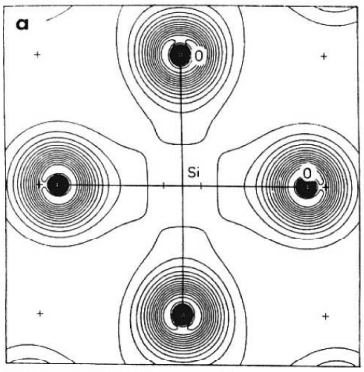
- Assume charge density of crystal = that of overlapping, spherical, fully charged, ions
- Assume charge density of ions = that in free state
- Advantage
  - Ab initio
- Problems
  - Only ionic bonding
  - Cauchy violations
  - O^{2-} not stable in free state
- Partial solution
  - Breathing



Ions or electrons?



- Pauling/Goldschmidt Model
  - Hard fully charge spheres
  - Rationalize/predict low pressure structures
- High pressure?
  - P_{bond}~eV/Å^3=160 GPa~P_{mantle}
  - Ions change
    - Size
    - Shape
    - Charge



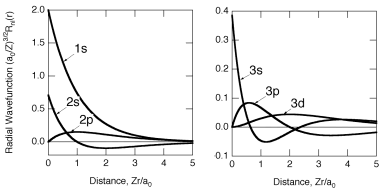
The one electron atom

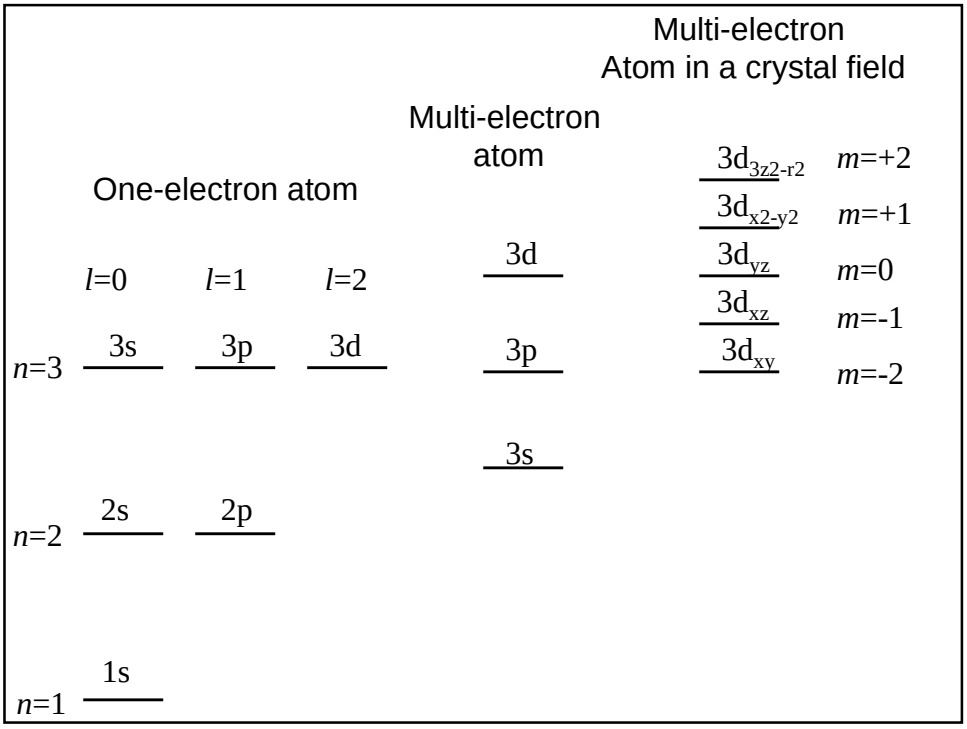
- Exactly soluble

  ψ_i: wave function of state i

  ψ can have either sign
- Charge density, $\rho(\ )$ = square of wave function
- E_i Energy of state i
- States described by three quantum numbers (+ spin)

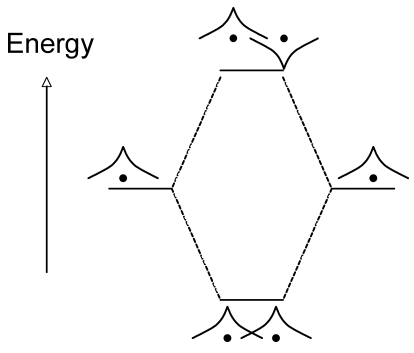
$$\left[\nabla^2 - Z/r\right]\psi_i = E_i\psi_i$$





Molecules

- Isolated Atoms
  - One energy level
- Molecule
  - Two energy levels
    - Bonding
    - Anti-bonding
  - Population
    - Energy difference
    - Temperature



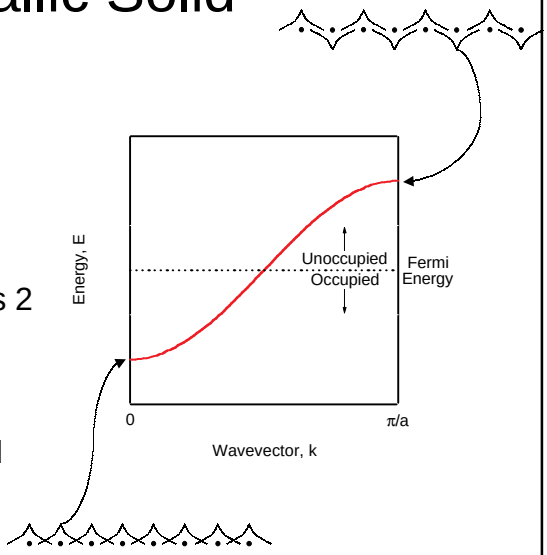
Metallic Solid

- Asymptotically continuous band of N states

$$\psi_k = \cos(kx)\,u(x)$$

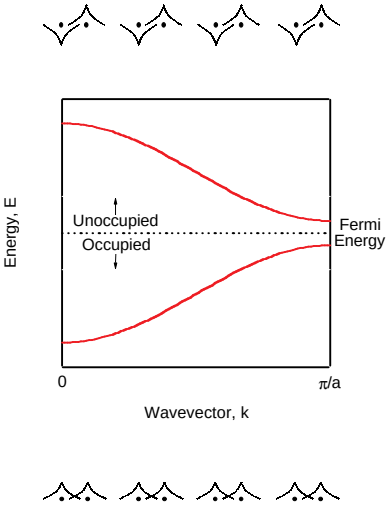
$$E_k = -\Delta\cos(kx)$$

- Each state accommodates 2 electrons
- Half-filled band
- Fermi energy separates occupied from unoccupied states
- No gap



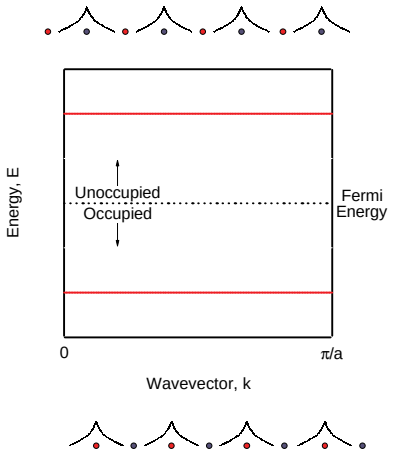
Covalent Solid

- Doubled unit cell
- Halved Brillouin zone
- Folding
- Gap



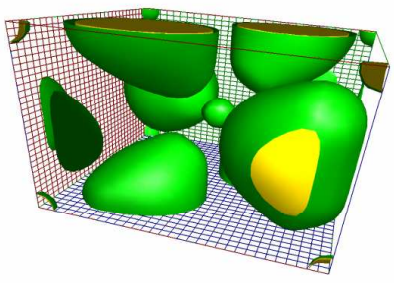
Ionic Solid

- Cation and Anion
- Lower energy state: valence electrons on anion
- ~Flat bands: localized states
- Gap



Density functional theory

- No assumption about charge density, type of bonding, …
- No experimental input, i.e. no free parameters
- Positions and charges of nuclei.
- Assumption of nuclear positions is generally relaxed
- Not exact



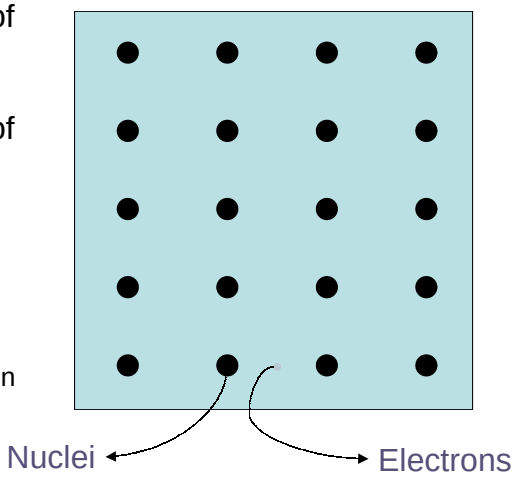
Cohen, 1992

Uniform Charge Density

- Uniform distribution of atoms
  - $P=RTn_A$
- Uniform distribution of electrons
  - Kinetic

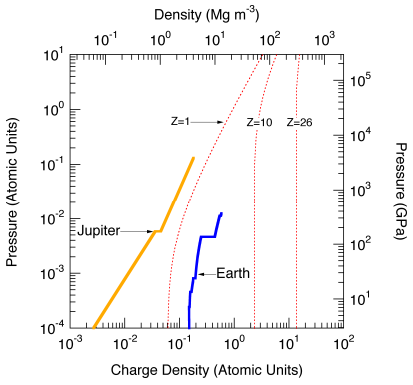
$$P = \frac{\hbar^2}{5m}\left(3\pi^2\right)^{2/3} n_e^{5/3}$$

  - Exchange
  - Correlation
  - Ion-electron interaction



Uniform Charge Density

- EOS depends on Z
  - Jupiter, Z~1
  - Mantle, Z~10
  - Core, Z~26
- Calculated density too high
- Screening



Density Functional Theory

- Kohn,Sham,Hohenberg
- Ground State Internal Energy a unique functional of the charge density
- Approximations
  - Essential
    - Exchange-Correlation Functional
      - Local density approximation
  - Convenient
    - Pseudopotential approximation

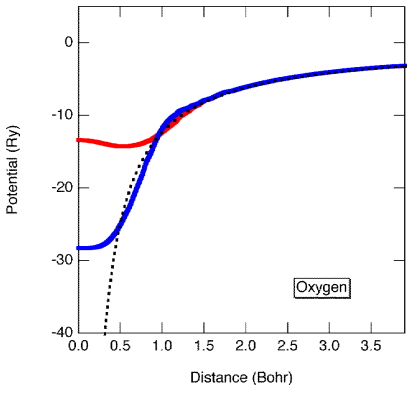
Density Functional Theory

$$\left[-\nabla^2 + V_{KS}\left[\rho(\vec{r})\right]\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

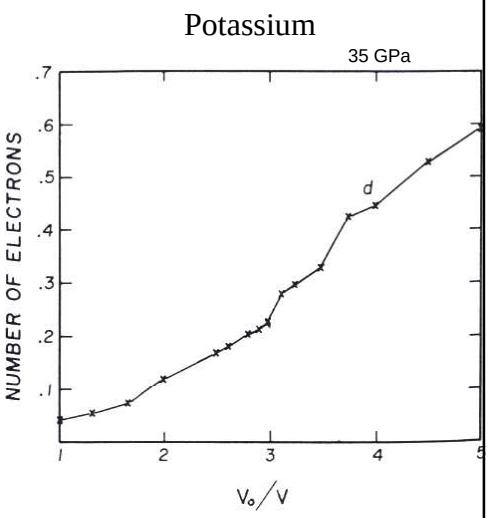
$$V_{KS}\left[\rho(\vec{r})\right] = V_N(\vec{r}) + \int\frac{\rho(\vec{r}\,')}{\vec{r}-\vec{r}\,'}d\vec{r}\,' + V_{XC}\left[\rho(\vec{r})\right]$$

Computational Methods

- Pseudopotential
- Nuclear potential is hard!
- Replace with that of nucleus + core electrons
- Represent valence electrons with plane wave basis set

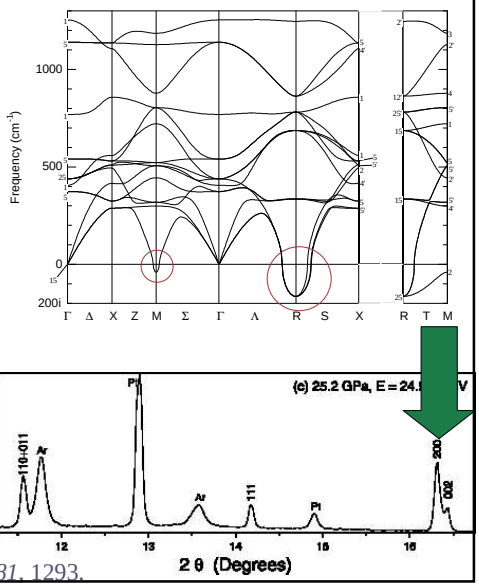


Electronic transition in Potassium



Bukowinski (1976) *GRL 3*, 491

Phase transition in $CaSiO_3$ perovskite

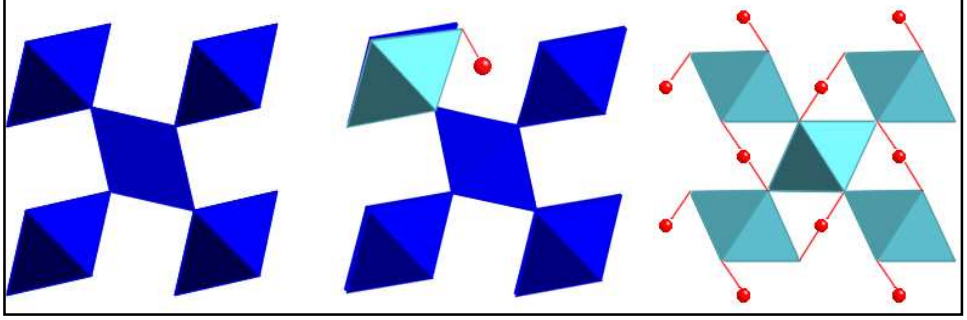


Shim, Jeanloz, Duffy (2002) *GRL 29*, 016148
Stixrude, Cohen, Yu, Krakauer (1996) *Am. Min. 81*, 1293.

Physics of hydrogen bond at high pressure

- Low pressure asymmetric O-H…O
- High pressure symmetric O-H-O
- Implications for
  - Elasticity, transport, strength, melting

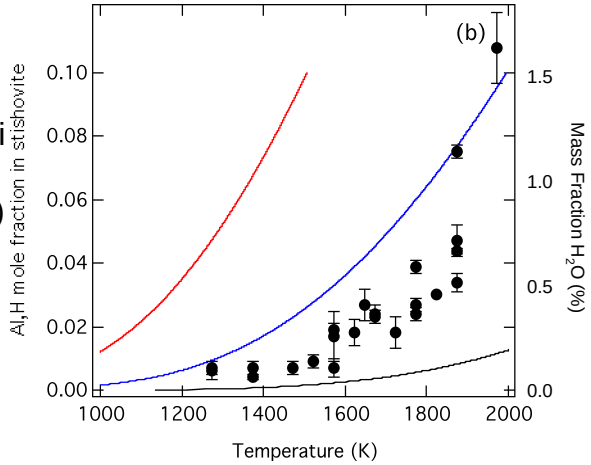
Panero & Stixrude (2004) EPSL



Nominally anhydrous phases

- Primary reservoir of water in mantle?
- Incorporation of H requires charge balance
- Investigate Al+H for Si in stishovite
- End-member (AlOOH) is a stable isomorph
- Enthalpy and entropy of solution

➔Solubility



Panero & Stixrude (2004) EPSL