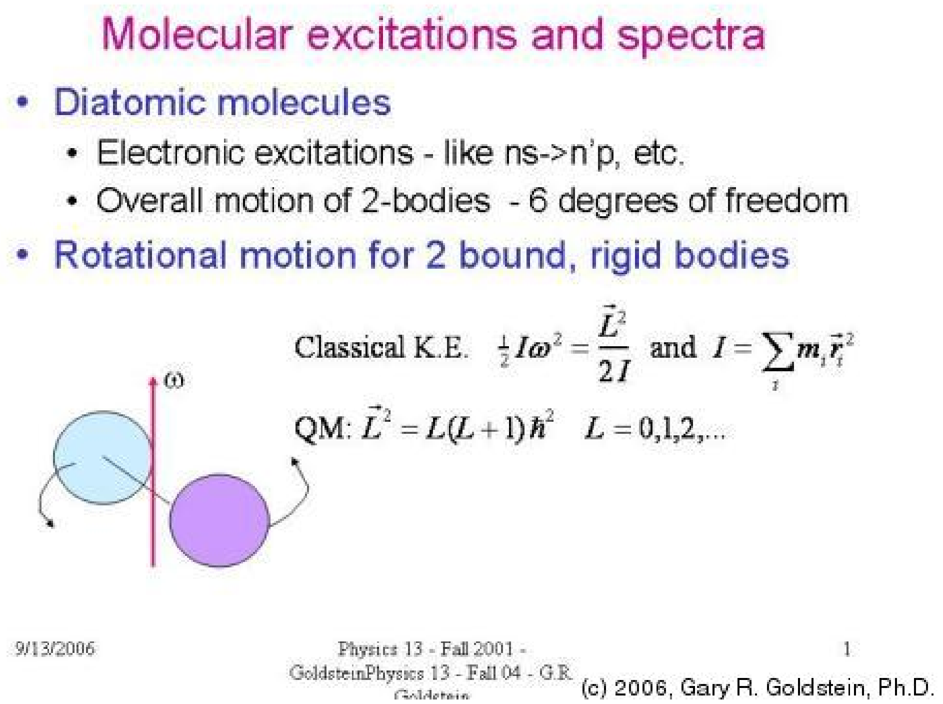
1. Molecular excitations and spectra



Molecular excitations and spectra

- Diatomic molecules
  - Electronic excitations - like ns->n'p, etc.
  - Overall motion of 2-bodies - 6 degrees of freedom
- Rotational motion for 2 bound, rigid bodies

Classical K.E. $\frac{1}{2}I\omega^2 = \frac{\vec{L}^2}{2I}$ and $I = \sum_i m_i \vec{r}_i^{\,2}$

QM: $\vec{L}^2 = L(L+1)\hbar^2 \quad L = 0,1,2,\ldots$

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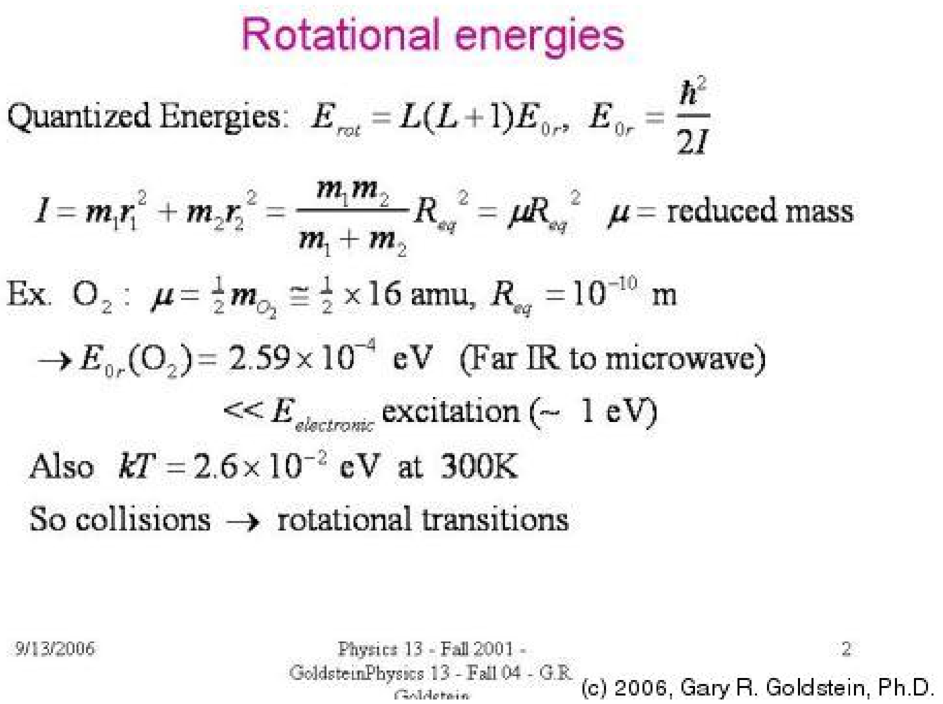
2. Rotational energies



Rotational energies

Quantized Energies: $E_{rot} = L(L+1)E_{0r}, \; E_{0r} = \frac{\hbar^2}{2I}$

$I = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} R_{eq}^{\;2} = \mu R_{eq}^{\;2} \quad \mu =$ reduced mass

Ex. O_2 : $\mu = \frac{1}{2} m_{O_2} \cong \frac{1}{2} \times 16$ amu, $R_{eq} = 10^{-10}$ m

$\rightarrow E_{0r}(O_2) = 2.59 \times 10^{-4}$ eV (Far IR to microwave)

$<< E_{electronic}$ excitation (~ 1 eV)

Also $kT = 2.6 \times 10^{-2}$ eV at 300K

So collisions → rotational transitions

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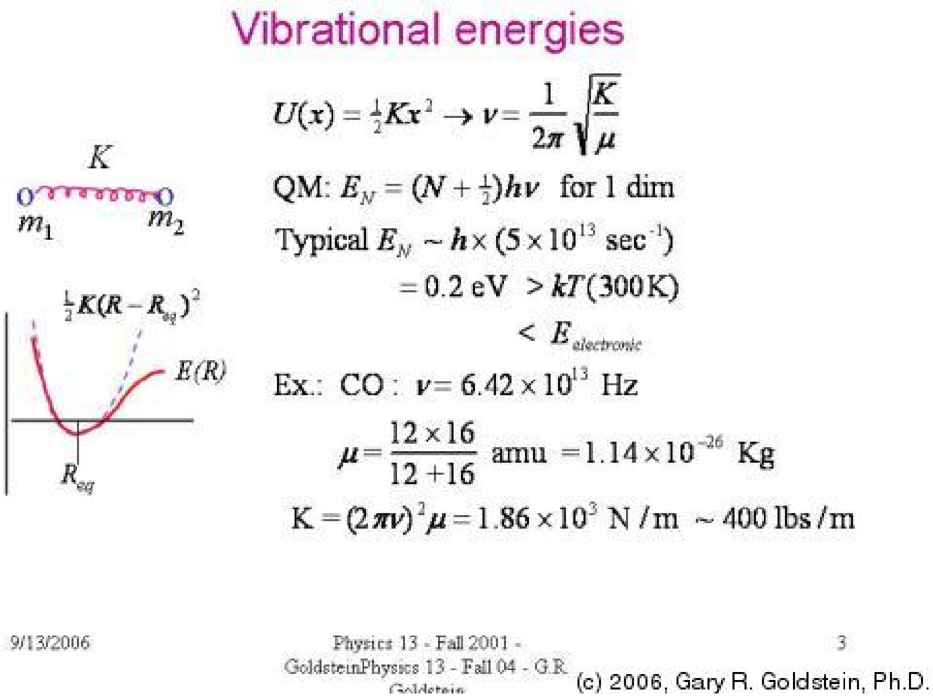
3. Vibrational energies



Vibrational energies

$U(x) = \frac{1}{2}Kx^2 \rightarrow \nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$

QM: $E_N = (N+\frac{1}{2})h\nu$ for 1 dim

Typical $E_N \sim h \times (5\times10^{13}\ \text{sec}^{-1})$

$= 0.2\ \text{eV} > kT(300\text{K})$

$< E_{electronic}$

Ex.: CO : $\nu = 6.42\times10^{13}$ Hz

$\mu = \frac{12\times16}{12+16}$ amu $= 1.14\times10^{-26}$ Kg

$K = (2\pi\nu)^2\mu = 1.86\times10^3$ N/m ~ 400 lbs/m

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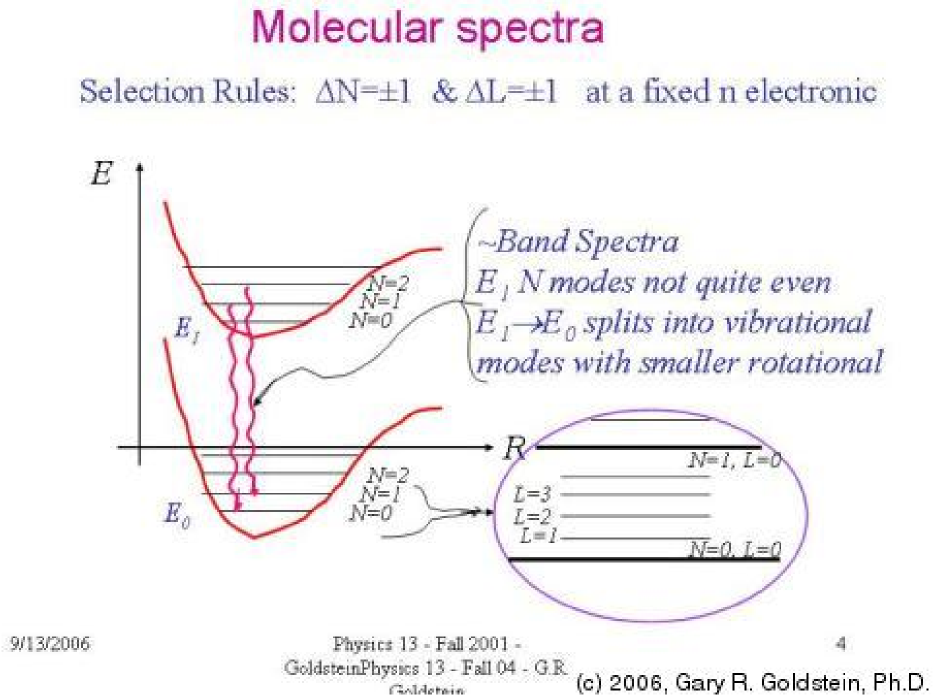
4. Molecular spectra



Molecular spectra

Selection Rules: ΔN=±1 & ΔL=±1 at a fixed n electronic

~Band Spectra
E_1 N modes not quite even
$E_1 \rightarrow E_0$ splits into vibrational
modes with smaller rotational

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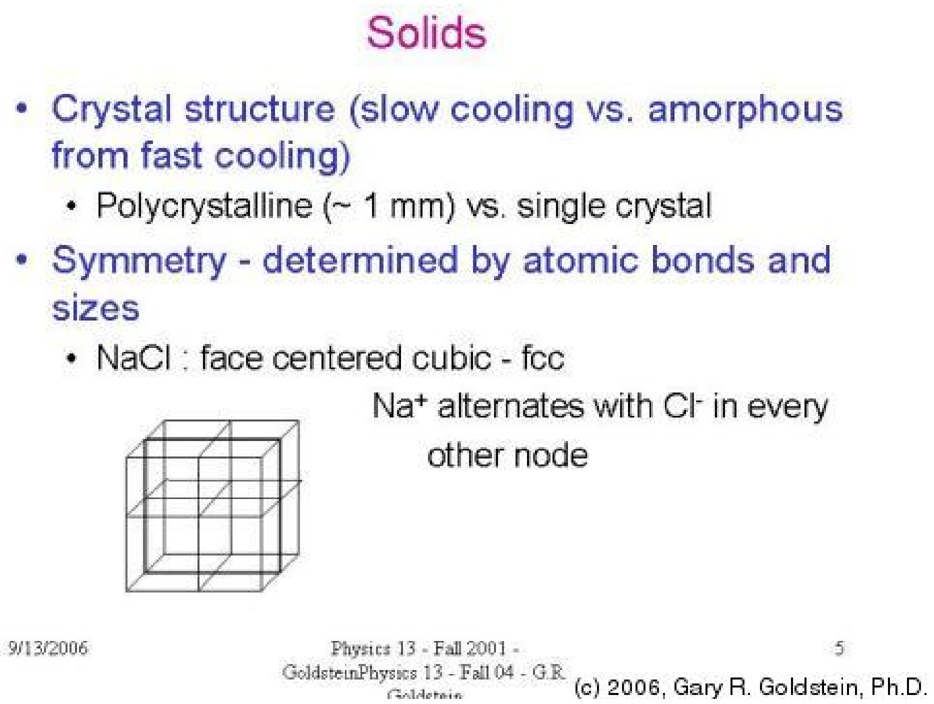
5. Solids



Solids

- Crystal structure (slow cooling vs. amorphous from fast cooling)
  - Polycrystalline (~ 1 mm) vs. single crystal
- Symmetry - determined by atomic bonds and sizes
  - NaCl : face centered cubic - fcc

Na$^+$ alternates with Cl$^-$ in every other node

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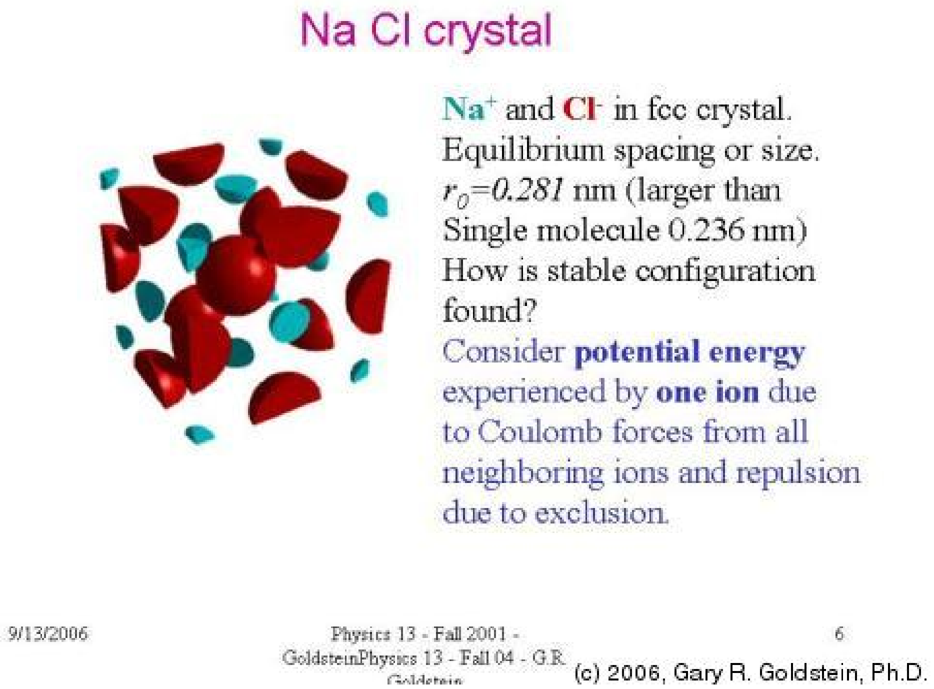
6. Na Cl crystal



Na Cl crystal

Na$^+$ and **Cl$^-$** in fcc crystal. Equilibrium spacing or size. $r_0=0.281$ nm (larger than Single molecule 0.236 nm) How is stable configuration found?

Consider **potential energy** experienced by **one ion** due to Coulomb forces from all neighboring ions and repulsion due to exclusion.

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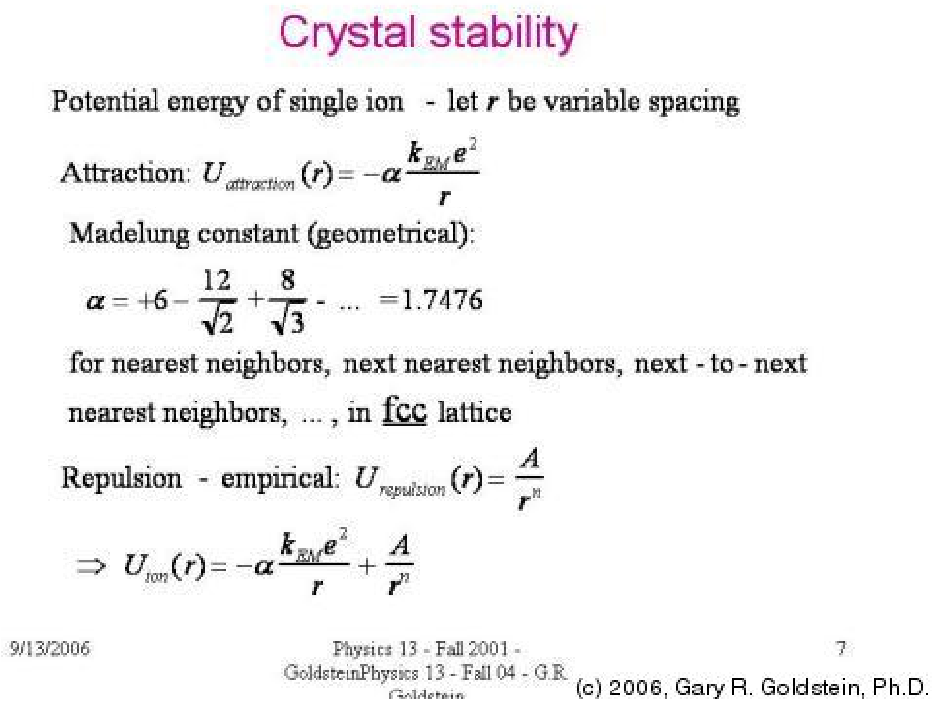
7. Crystal stability



Crystal stability

Potential energy of single ion - let r be variable spacing

Attraction: $U_{attraction}(r) = -\alpha \frac{k_{EM} e^2}{r}$

Madelung constant (geometrical):

$$\alpha = +6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \ldots = 1.7476$$

for nearest neighbors, next nearest neighbors, next - to - next nearest neighbors, ... , in <u>fcc</u> lattice

Repulsion - empirical: $U_{repulsion}(r) = \frac{A}{r^n}$

$$\Rightarrow U_{ion}(r) = -\alpha \frac{k_{EM} e^2}{r} + \frac{A}{r^n}$$

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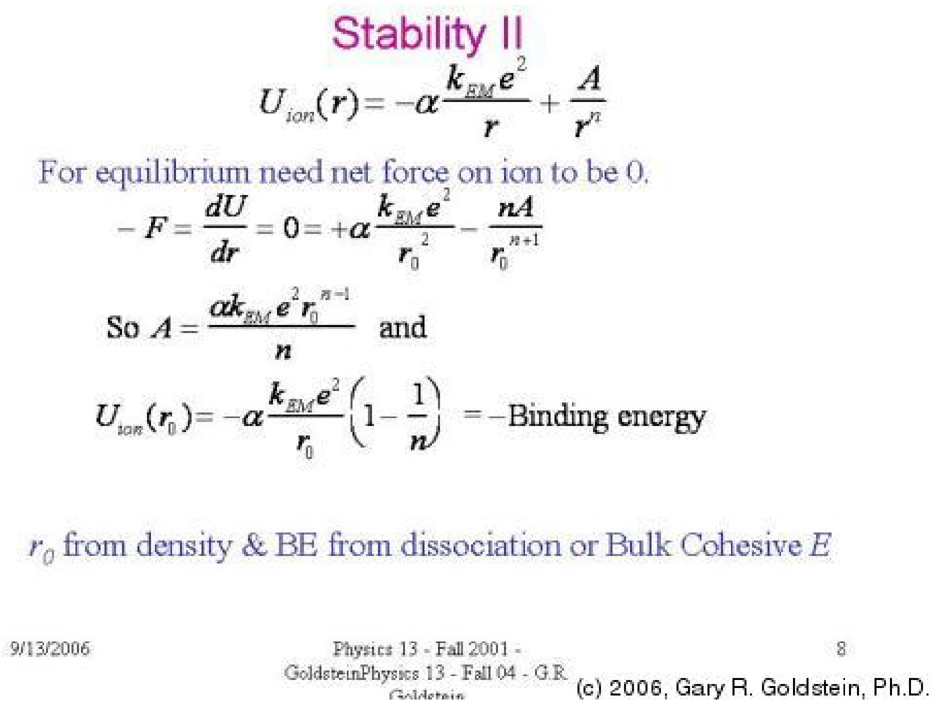
8. Stability II



Stability II

$$U_{ion}(r) = -\alpha \frac{k_{EM} e^2}{r} + \frac{A}{r^n}$$

For equilibrium need net force on ion to be 0.

$$-F = \frac{dU}{dr} = 0 = +\alpha \frac{k_{EM} e^2}{r_0^2} - \frac{nA}{r_0^{n+1}}$$

So $A = \frac{\alpha k_{EM} e^2 r_0^{n-1}}{n}$ and

$$U_{ion}(r_0) = -\alpha \frac{k_{EM} e^2}{r_0} \left(1 - \frac{1}{n}\right) = -\text{Binding energy}$$

r_0 from density & BE from dissociation or Bulk Cohesive E

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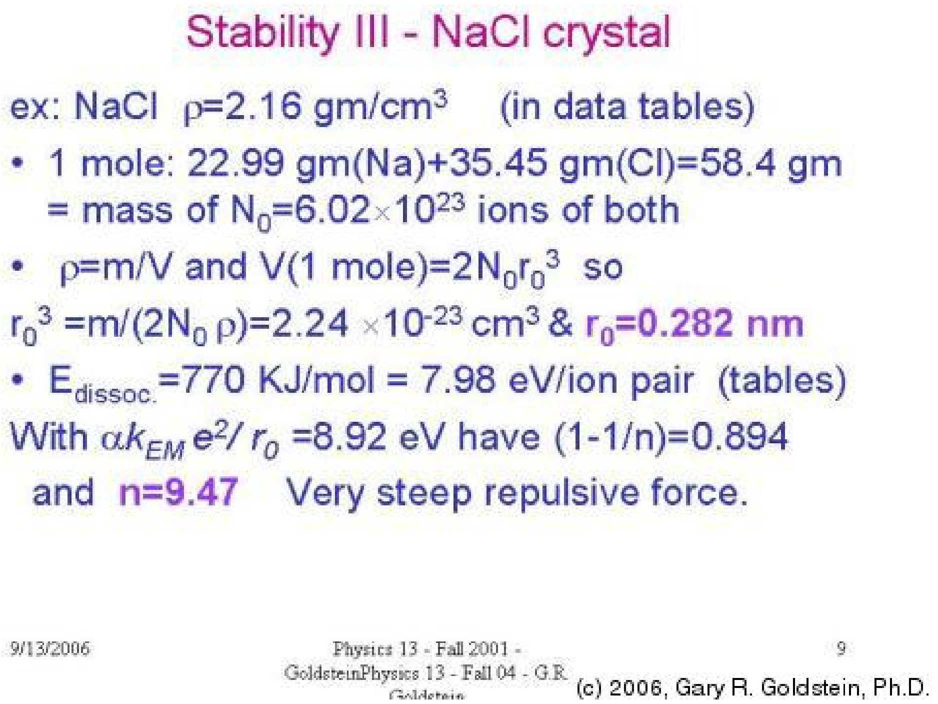
9. Stability III - NaCl crystal



Stability III - NaCl crystal

ex: NaCl $\rho=2.16$ gm/cm^3 (in data tables)

- 1 mole: 22.99 gm(Na)+35.45 gm(Cl)=58.4 gm = mass of $N_0=6.02\times10^{23}$ ions of both
- $\rho=m/V$ and $V(1 \text{ mole})=2N_0r_0^3$ so

$r_0^3=m/(2N_0\,\rho)=2.24\times10^{-23}$ cm^3 & $r_0=0.282$ nm

- $E_{dissoc.}$=770 KJ/mol = 7.98 eV/ion pair (tables)

With $\alpha k_{EM}\,e^2/\,r_0=8.92$ eV have $(1-1/n)=0.894$

and $n=9.47$ Very steep repulsive force.

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10. Other crystals

Other crystals

- fcc for many **Ionic crystals**: LiF, KF, KCl, KI, AgCl, & Au, Si, Al, Ca, Cu, Ni, Pb
- body centered cubic (bcc): CsCl & Ba, Cs, Fe, K, Li, Mb, Na $\alpha=1.7627$ 8 nearest

Cl^- gold + Cs^+ teal

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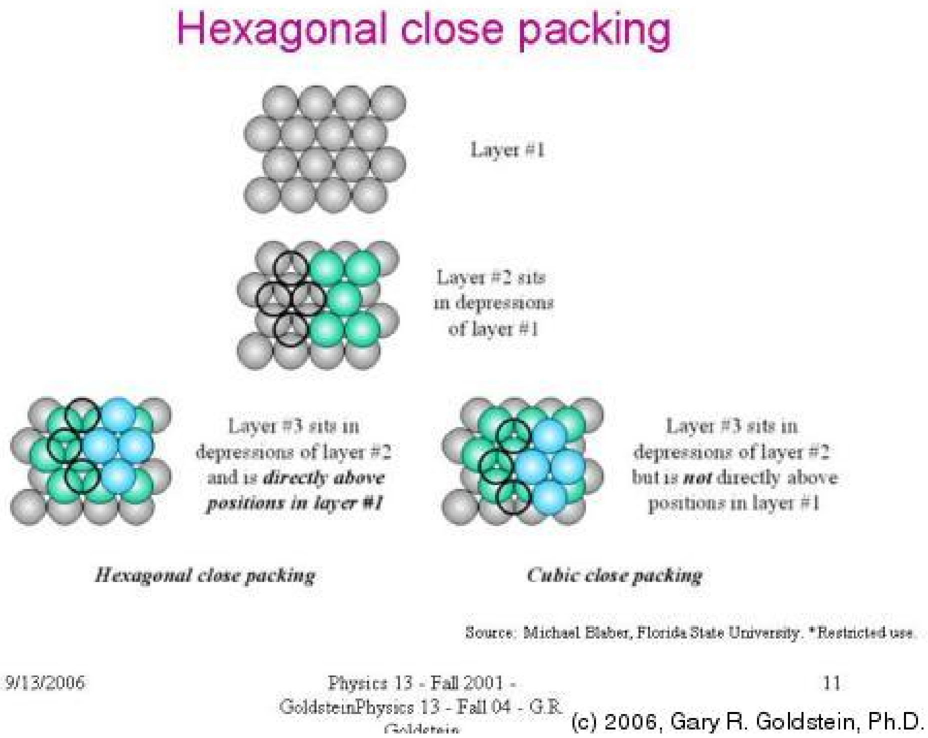
11. Hexagonal close packing



Hexagonal close packing

Source: Michael Blaber, Florida State University. *Restricted use.

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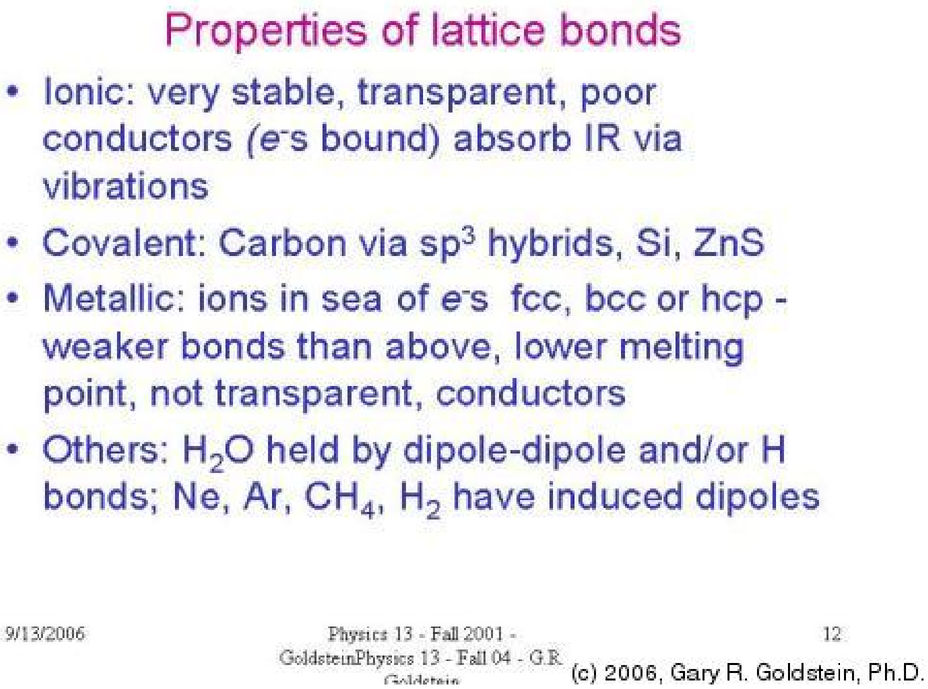
12. Properties of lattice bonds



Properties of lattice bonds

- Ionic: very stable, transparent, poor conductors (*e*$^-$s bound) absorb IR via vibrations
- Covalent: Carbon via sp^3 hybrids, Si, ZnS
- Metallic: ions in sea of *e*$^-$s fcc, bcc or hcp - weaker bonds than above, lower melting point, not transparent, conductors
- Others: H_2O held by dipole-dipole and/or H bonds; Ne, Ar, CH_4, H_2 have induced dipoles

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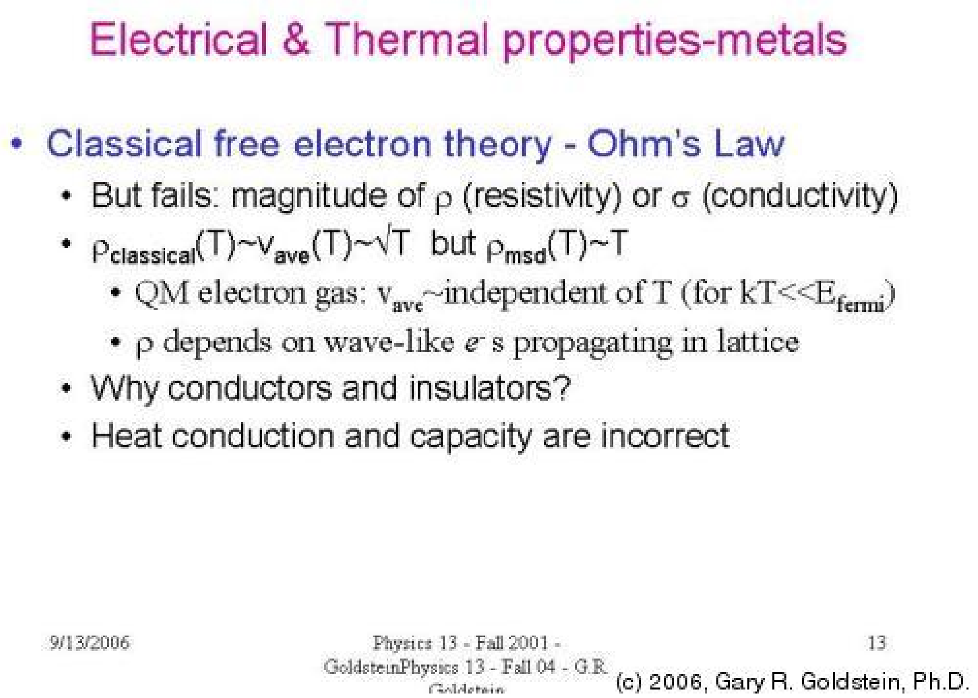
13. Electrical & Thermal properties-metals



Electrical & Thermal properties-metals

- Classical free electron theory - Ohm's Law
  - But fails: magnitude of ρ (resistivity) or σ (conductivity)
  - $\rho_{classical}(T) \sim v_{ave}(T) \sim \sqrt{T}$ but $\rho_{msd}(T) \sim T$
    - QM electron gas: v_{ave}~independent of T (for $kT << E_{fermi}$)
    - ρ depends on wave-like e^- s propagating in lattice
  - Why conductors and insulators?
  - Heat conduction and capacity are incorrect

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