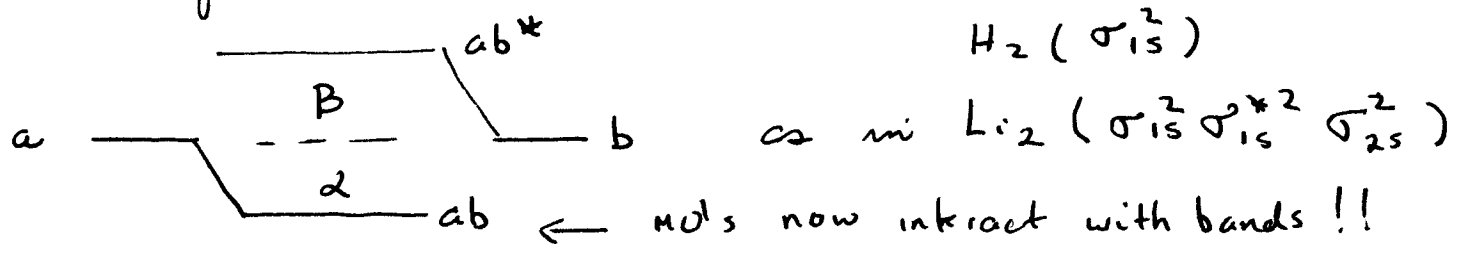


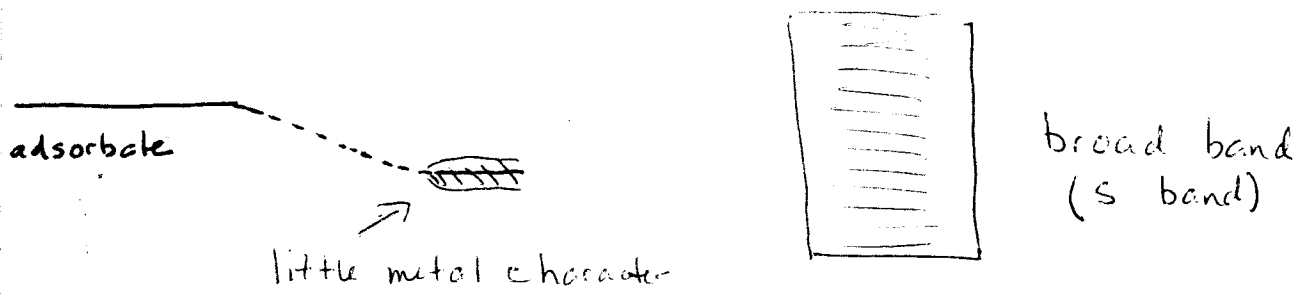
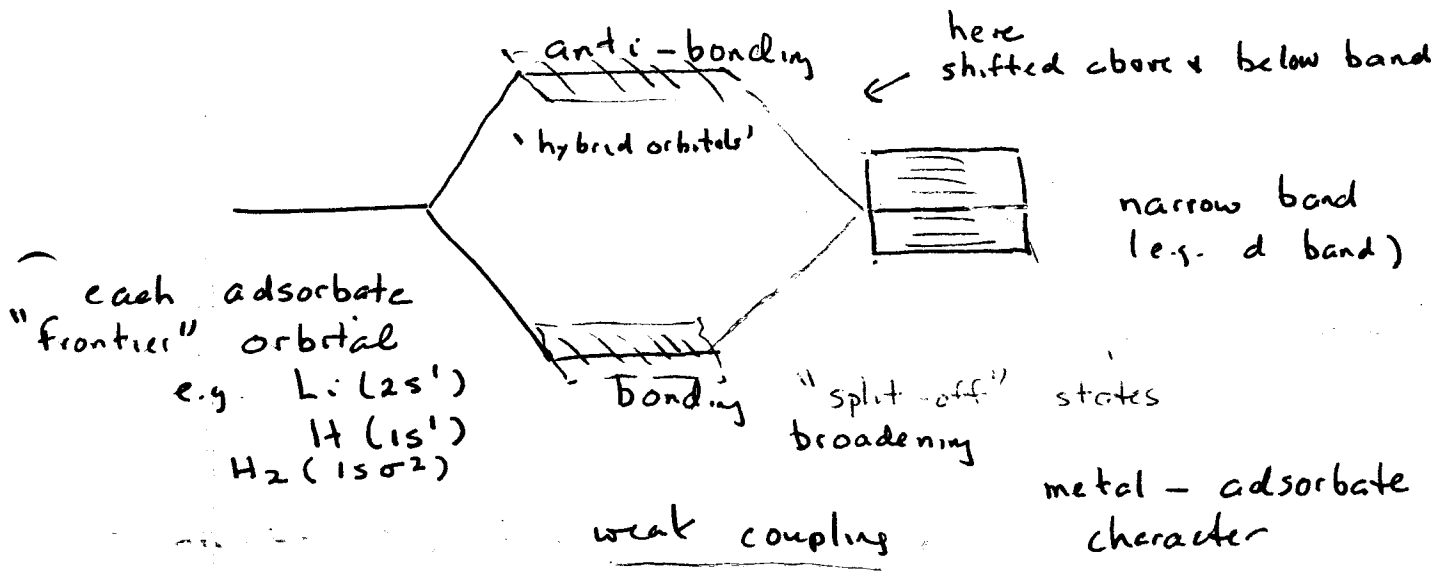
Metal Surfaces cont.

Non-dissociative chemisorption (actual bonding)

MO's from two atomic orbitals:



strong coupling



can depend on plane of substrate }
 as well as adsorbate, substrate }

From coupling to bonding depends on how filled the adsorbate MO's and bands are.

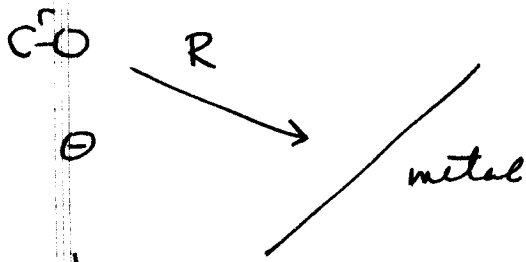
Quantum Chemical Calculations

Calculate total electronic energy as function of position of adsorbate

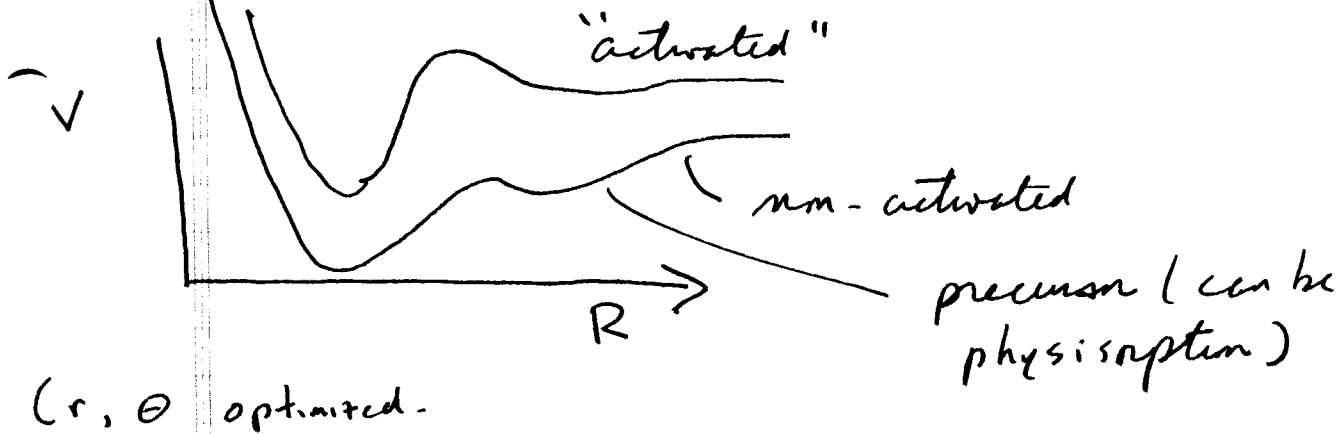
Can mimic solid by repeating unit n as many copies as possible.

$$E_{elec} = V_{nuclei}$$

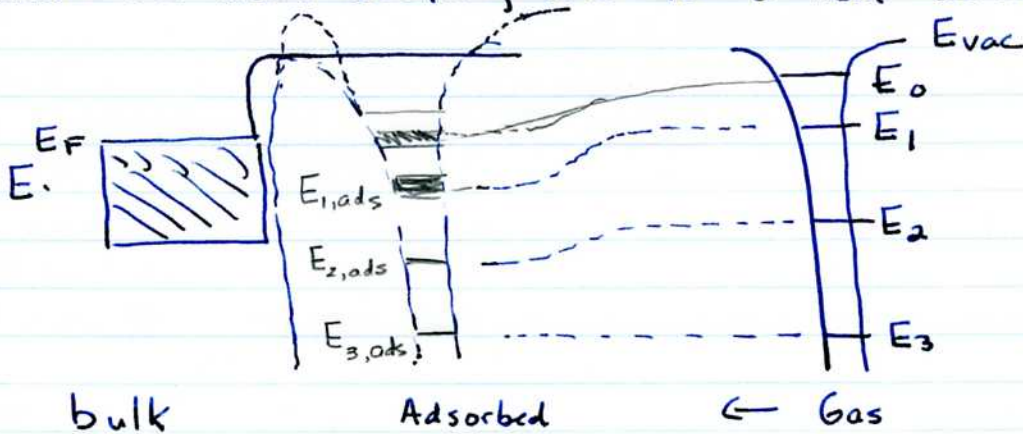
Born-Oppenheimer Approx.



$V(r, R, \theta)$ for each CO orbital.

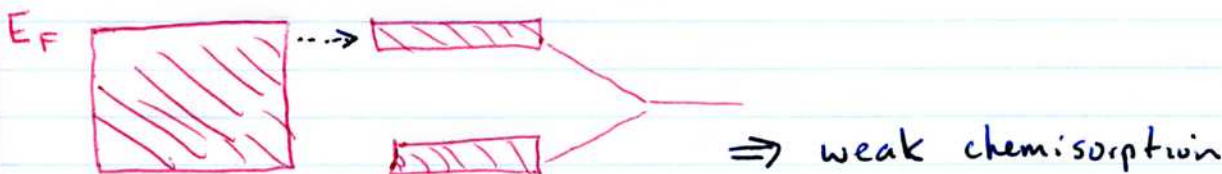
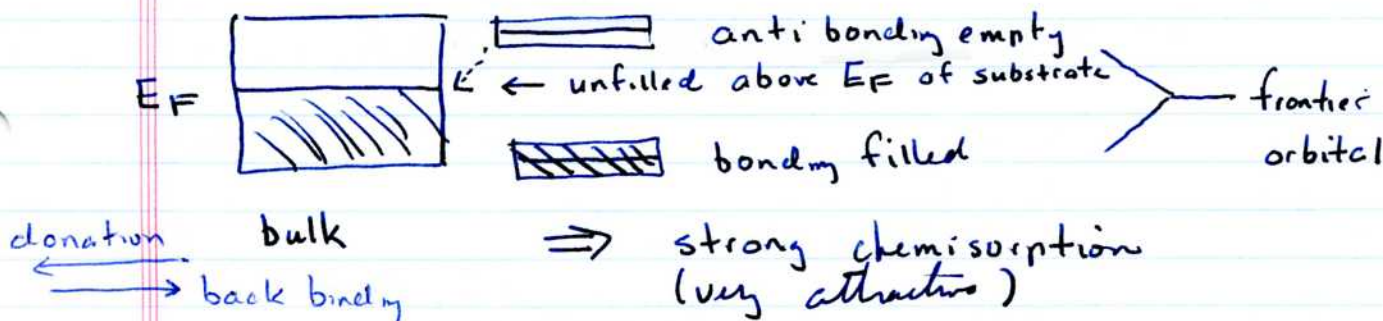


Now consider the weak coupling case for a real adsorbate:



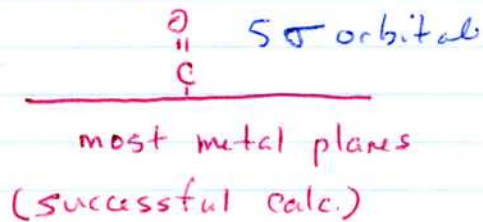
weak binding from $E_{0,ads}$ $E_{1,ads} \Rightarrow$ weak chemisorption

Strong Coupling Cases



can have overlapping bands

Must do detailed calculation.
CO - metals best understood.
hybrid orbitals

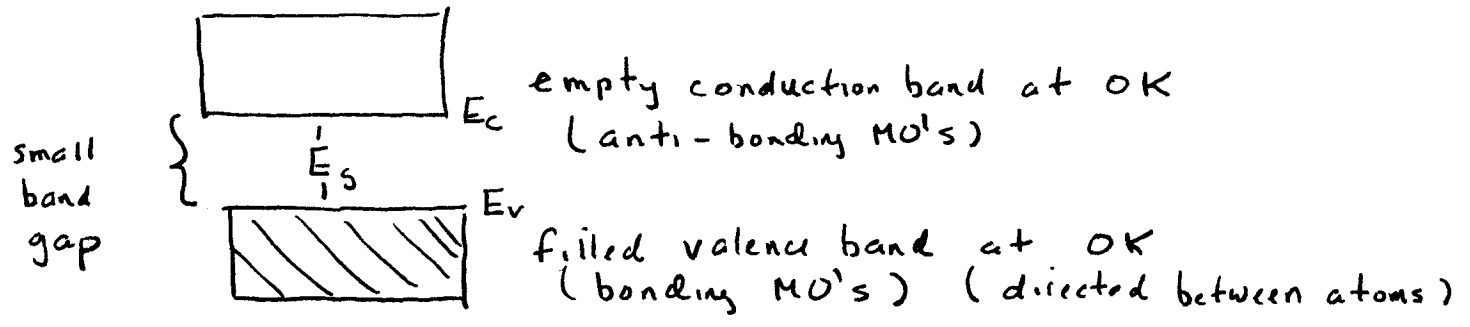


Also related to reactivity.
(related to dissociative chemisorption; more complex)
need 0 activation barrier

Semiconductors (pure + doped) (intrinsic + extrinsic)

- structures largely the result of covalent bond formation (e.g. silicon)

Pure (intrinsic)



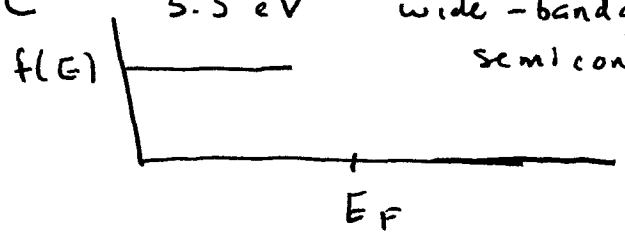
$0 < E_g \leq 3 \text{ eV}$ normally $1 \text{ eV} \sim 10^4 \text{ K}$

Some band gaps:

Si	1.12 eV	} $\gg kT$
Ge	0.74 eV	
GaAs	1.52 eV	
C	5.5 eV	

wide-bandgap semiconductor

$$E_F \equiv \frac{E_c + E_v}{2}$$

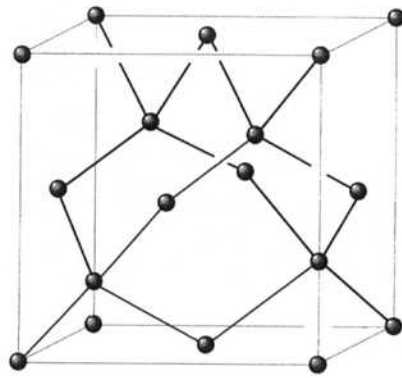


Conductance increases with increasing T (more e^- excitation).
Chemisorption can occur (e.g. H on Si) but can be analyzed in terms of dangling bonds, or MO-band theory

Doped (extrinsic)

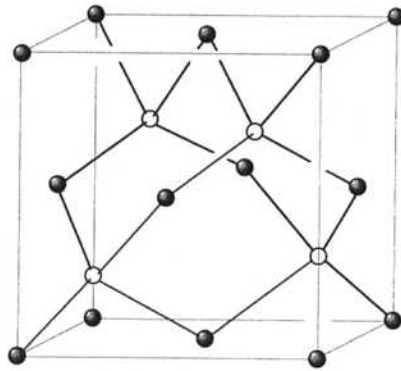
- to increase the number available, we can add impurities to semiconductor to change E_g .

(i) n-type dopant contains electrons to be donated.



(a) Diamond ● - C

sp³ hybridization
 $ns^2 np^2 \rightarrow sp^3$



(b) Zinc blende (α -Zn-S)
 ● - Zn ○ - S

Fig. 2.22 The two most common semiconductor crystal structures: (a) diamond and (b) zinc blende (α -ZnS).

expected to interact significantly. As a result the dispersion curves for 1s, 2s and 2p electrons, the 'core electrons', remain as tightly defined and narrow energy levels. The overlap of the 3s electron charge distributions leads to the expectation that the 3s electrons will 'delocalize' from the atomic cores, thereby losing the discrete character of their energy levels. As discussed for the case of Li, we therefore expect the discrete 3s levels to blend to form a band structure. The resulting dispersion for the 3s level is shown schematically in Fig. 2.24. The Fermi level is indicated and shows that the 3s band is half filled and that, therefore, Na is a good conductor. Good conductivity occurs when only a slight increase in energy is required for the conduction electrons to move into the available vacant energy levels.

ir of many
 across the
 is a steady
 tates at the
 bon should
 n electrical
 e a perfect
 bonding in
 red using a

conductors,
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 rties of the

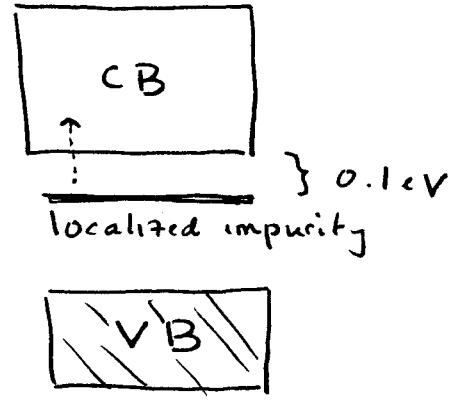
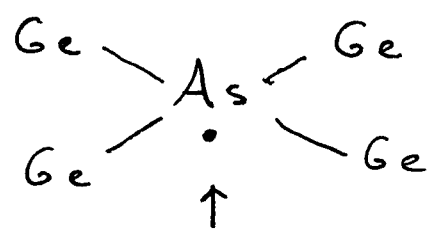
valent bond
 mixing of s
 d. These sp^3
 for bond
 nae (α -ZnS)

o the energy
 nd well with
). If we plot
 the lattice is
 fig. 2.23. This
 rve) and the
 behaviour is
 es, clearly, it
 en found that
 m the s-band
 curve to have
 he dispersion
 ie greater the

ace) and the
 the structure
 ns for the 3s
 is and are not

Example: Ge (Group IV) doped with arsenic (Group V)

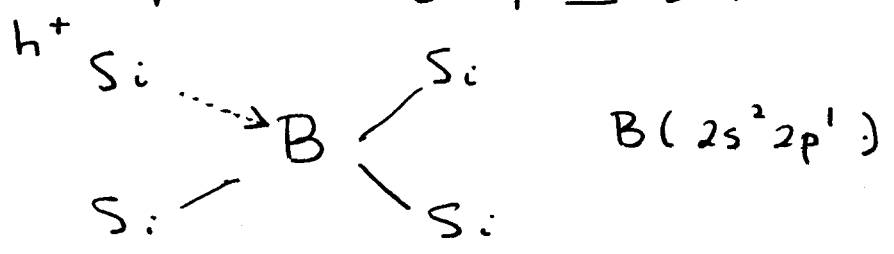
As: 5 valence electrons for bonding ($4s^2 4p^3$) but only 4 are needed. Remaining electron occupies a discrete level about 0.1 eV below conduction band.



or Si doped with P

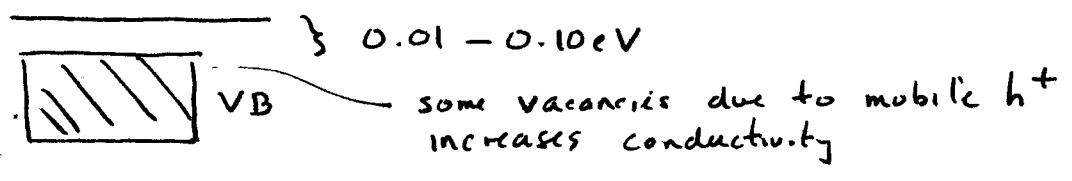
can be promoted into CB upon excitation

(ii) p-type dopant deficient in electrons; e.g. dope with Group III atoms

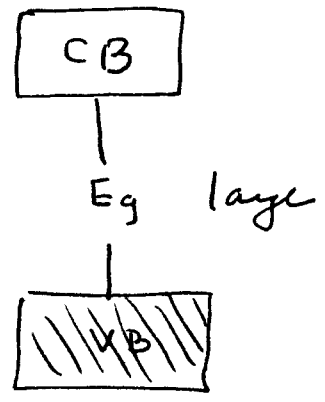


Here a localized impurity state also results, but sits close to the VB:

acceptor state



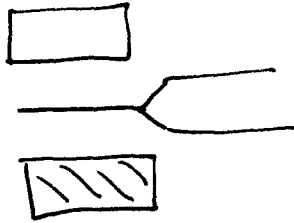
Insulators



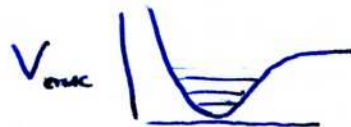
Surface States: Semiconductors

- same as impurities

Si + non-bonding



reconstructed



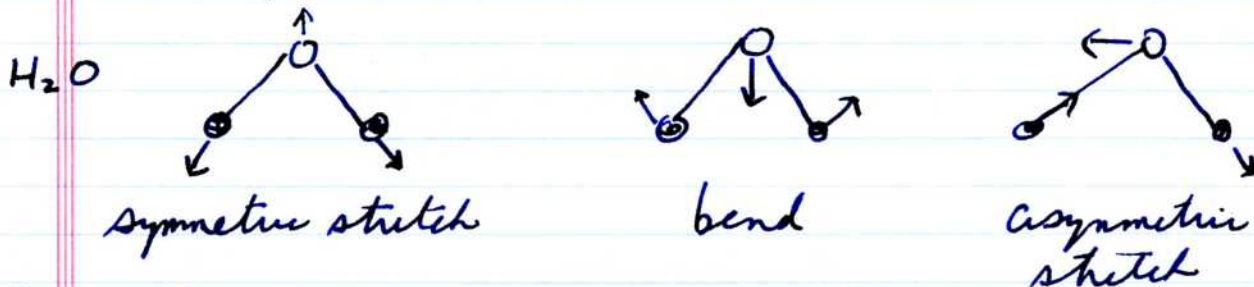
The Vibrations of Solids

Let's first consider a polyatomic molecule of N atoms + $3N$ degrees of freedom.

$3N \rightarrow$ 3 translational degrees
 3(2) rotational degrees Θ, Φ, χ
 $3N - 6(5)$ vibrational degrees

"normal modes of vibration" involve displacements of all atoms + are associated with coordinates Q_k ("normal coordinates") V : sum of springs (SHOs)

$$E = \sum_k E_{v_k} \quad E_{v_k} = h\nu_k (v_k + 1/2) = \hbar \omega_k (v_k + 1/2)$$



For each mode:

2 ——— ← can think of as 2nd excited state
 1 ———
 $v_k = 0$ ———
 OR introduce concept of "phonons" $h\nu \approx \hbar \omega$ (like photons), which are quasi-waves such that

$v=0$ no phonons in mode
 $v=1$ one phonon in mode
 $v=2$ two phonons in mode

The normal mode frequencies are discrete.

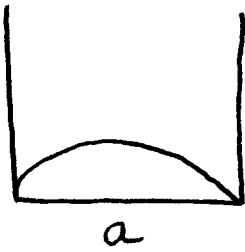
But what about a solid? $N \rightarrow \infty$

The simplest realistic model is the Debye model.

3D Debye Model

Peter Debye reasoned that the vibrational modes can be approximated as elastic waves, or standing waves that vanish at the endpoints. We can also do the calculation for photons and then let $c \rightarrow v$.

Standing Wave Approach



elastic waves: disturbances subject to linear restoring forces.

standing waves: linear combinations
 $n_x (\lambda_x/2) = a \quad n_y (\lambda_y/2) = a$

$n_z (\lambda_z/2) = a$
 n_x, n_y, n_z define modes.

$$\frac{2a}{\lambda_x} = n_x \quad \frac{2a}{\lambda_y} = n_y \quad \frac{2a}{\lambda_z} = n_z$$

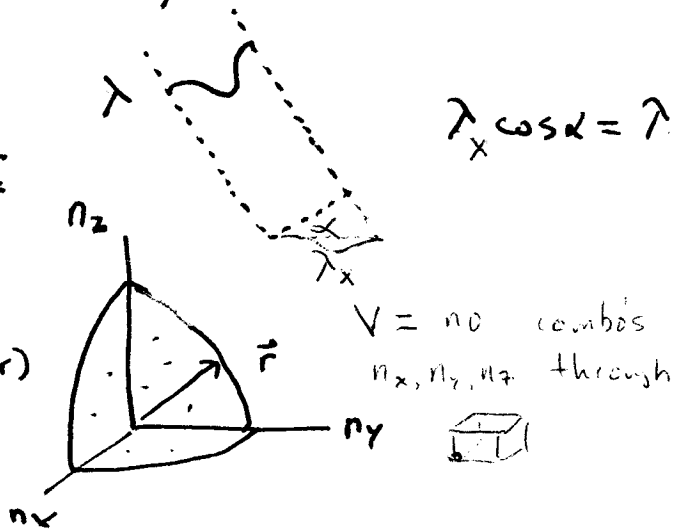
$$4a^2 \left(\frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} + \frac{1}{\lambda_z^2} \right) = n_x^2 + n_y^2 + n_z^2$$

$$\frac{4a^2}{\lambda^2} \left(\underbrace{\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma}_1 \right) = n_x^2 + n_y^2 + n_z^2$$

$$4a^2 / \lambda^2 = n_x^2 + n_y^2 + n_z^2$$

$$v = \lambda \nu \quad 4a^2 \frac{\nu^2}{v^2} = r^2$$

$$\begin{aligned} \text{No. modes (0-r)} &= \frac{1}{8} \frac{4}{3} \pi r^3 = M(r) \\ &= \pi r^3 / 6 \end{aligned}$$



$$r = \frac{2a\nu}{v}$$

$$M(\nu) = \frac{\pi}{6} \left(\frac{2a\nu}{v} \right)^3 = \frac{4}{3} \pi V \frac{\nu^3}{v^3}$$

$$N(\nu) = \frac{dM}{d\nu}$$

density of modes $\nu, \nu + d\nu$
 $N(\nu) d\nu = \frac{4\pi V}{v^3} \nu^2 d\nu$

also same as density states calc. in ?
 particle in a box