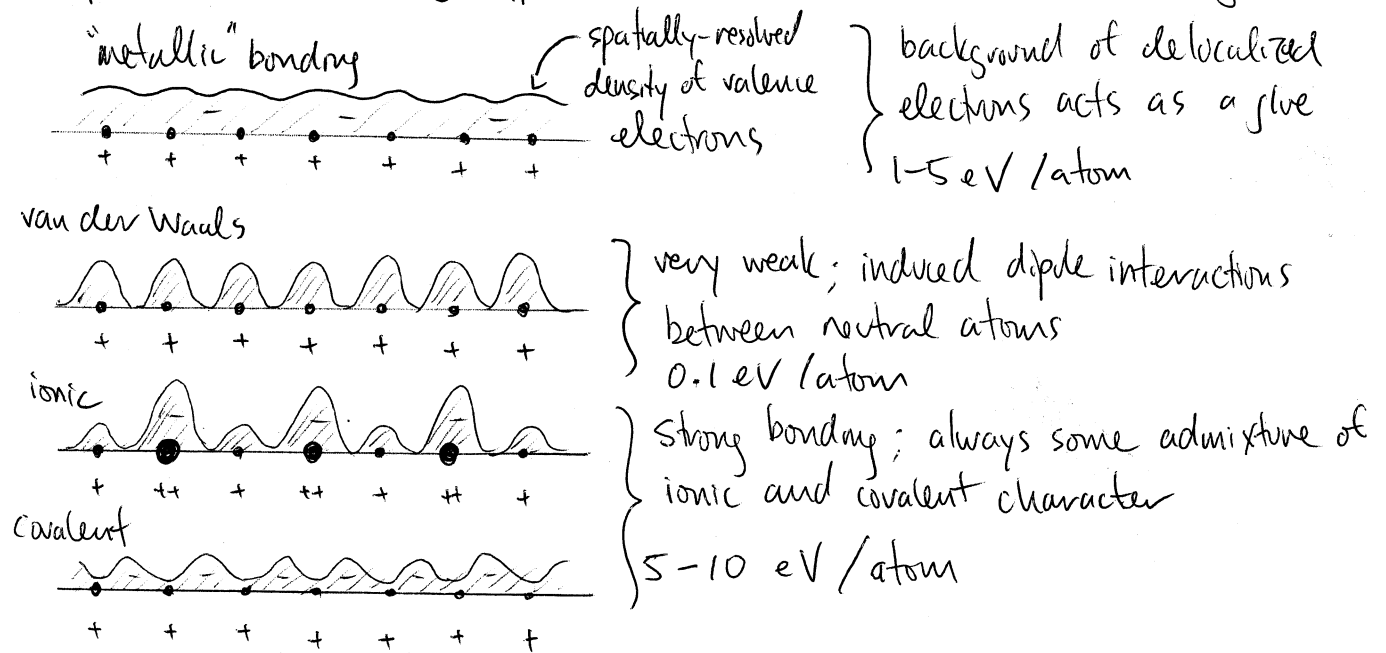


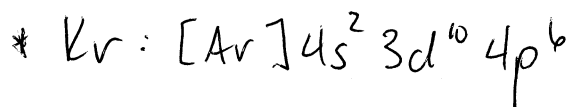
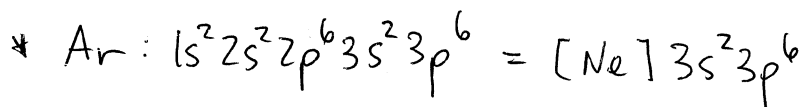
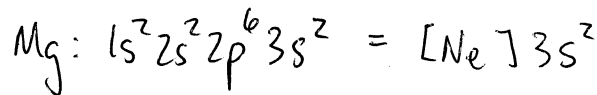
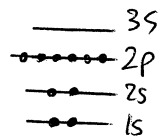
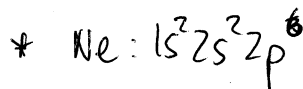
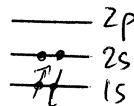
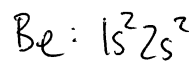
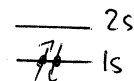
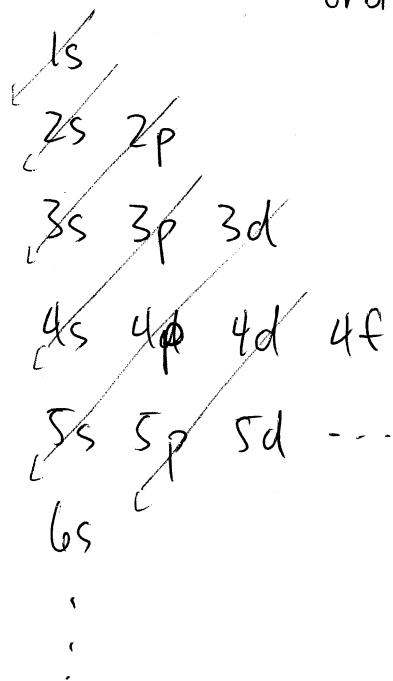
- * agglomerations of matter cohere (i.e. are held together by cohesive forces)
 - a variety of mechanisms but all ultimately Coulombic
 - separate question from whether a material is amorphous or regular, liquid or solid
 - key issue: is there an energy cost (positive chemical potential) to removing one atom or molecule from the system?
 - e.g. for a liquid, yes, but for a gas, no — which explains why only liquids exhibit a surface tension

- * cohesion is a product of chemical bonding
 - attractive electrostatic forces that are strong enough for a collection of atoms to become self-trapping
 - complicated interplay between ionic cores (nucleus + inner shell electrons) and valence electrons
 - spectrum of bonding types that fall into a few broad categories



Electronic structure of atoms

- * isolated neutral atom has Z protons in the nucleus and an equal number of orbiting electrons populating discrete energy levels
 - central \downarrow electrostatic potential
 - electronic wf. is factorizable into radial and angular components
 - allowed states described by radial quantum number $n = 1, 2, 3, \dots$ and AM quantum numbers $l = 0, 1, 2, \dots$ and $m_l = -l, -l+1, \dots, 0, 1, \dots$
 - electrons are fermions with intrinsic angular momentum (spin $1/2$), so each orbital $n(l)$ can accommodate $2 \times (2l+1)$ electrons
 - heuristic filling order with special stability for filled orbitals and "complete" shells

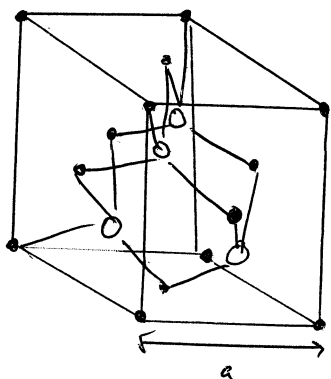


* = noble gas configuration

Extremely covalent materials

* C, Si, and Ge can form in the diamond structure

→ fcc + 2 site basis $\tau_1 = 0$, $\tau_2 = \frac{a}{4}(1,1,1)$



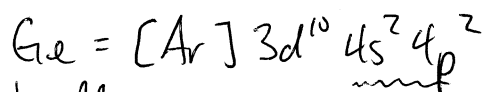
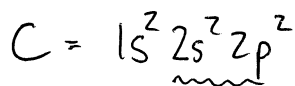
view of the conventional (nonprimitive) unit cell

tetrahedral

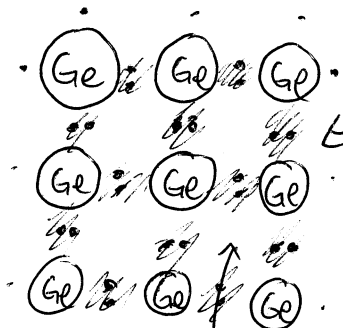
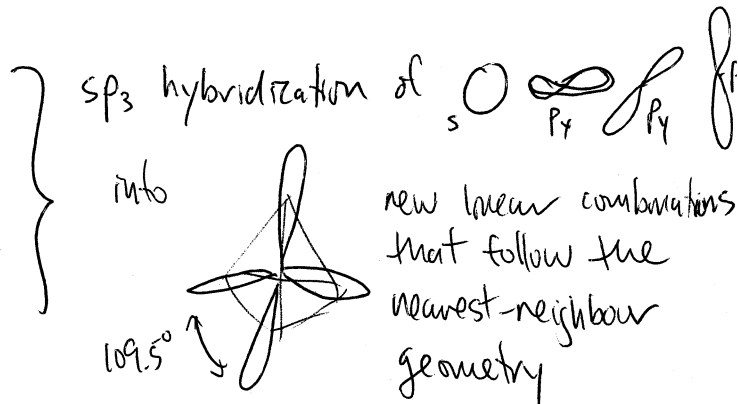
→ each atom 4-fold coordinated with ~~tetrahedral~~ bonding directions

→ bonding occurs via sharing (pairwise with neighbouring atoms)

the four valence electrons:



→ schematically

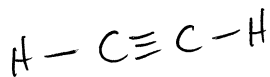
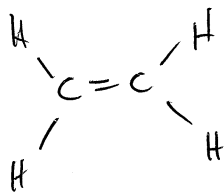


network of highly directional bonds
(crystal is like one gigantic molecule)

lots of open space and far from close packing

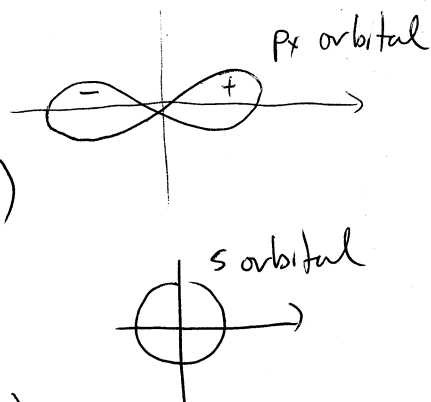
sp hybridization in carbon

- * carbon has a rich variety of sp , sp_2 , sp_3 hybridizations
- * in the molecular context, these give rise to the double and triple carbon bonds



- * the bonding angles are linear (sp), trigonal planar (sp_2), and tetrahedral (sp_3)

e.g. suppose that $\psi_{p_x}(\vec{r}) = f(r)x$
 with $f(r) > 0$ (for large r at least)
 and $\psi_s(\vec{r}) = g(r)$



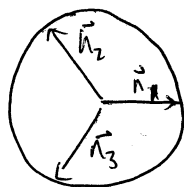
For general direction \vec{n} (unit vector),

$$\psi_{p,\vec{n}} = f(r)\vec{r} \cdot \vec{n}$$

The inner product $\langle \psi_{p,\vec{n}_1} | \psi_{p,\vec{n}_2} \rangle = \sum_{\substack{a=x,y,z \\ b=x,y,z}} n_1^a \underbrace{\langle \psi_{p,a} | \psi_{p,b} \rangle}_{\delta_{a,b}} n_2^b$

$$= \vec{n}_1 \cdot \vec{n}_2$$

Take planar directions



$$\vec{n}_1 = \vec{e}_x$$

$$\vec{n}_2 = -\frac{1}{2}\vec{e}_x + \frac{\sqrt{3}}{2}\vec{e}_y$$

$$\vec{n}_3 = -\frac{1}{2}\vec{e}_x - \frac{\sqrt{3}}{2}\vec{e}_y$$

and define a new set of states that are linear combinations

$$|i\rangle = \alpha |\psi^s\rangle + \beta |\psi_{\vec{n}_i}^p\rangle \quad i=1,2,3$$

By construction $\langle \psi_{p,z} | i \rangle = 0$

and $\langle i | j \rangle = \alpha^2 + \beta^2 \vec{n}_i \cdot \vec{n}_j$

Normalization $\langle i | i \rangle = \alpha^2 + \beta^2 = 1$

Orthogonality $\langle i | j \rangle = \alpha^2 + \beta^2 \vec{n}_i \cdot \vec{n}_j = 0$
 $= -\frac{1}{2}$ for $i \neq j$

Hence, $\alpha^2 = \frac{1}{2} \beta^2$ and $1 = \frac{3}{2} \beta^2$

or $\alpha = \frac{1}{\sqrt{3}}$ and $\beta = \sqrt{\frac{2}{3}}$

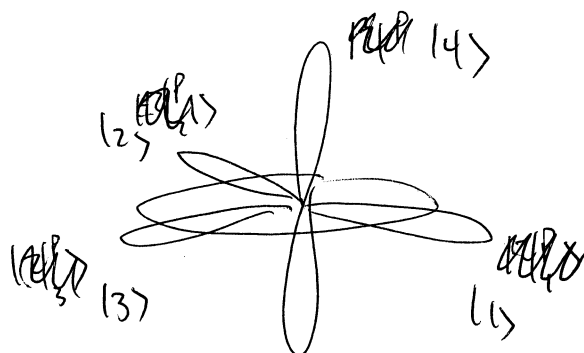
The full basis is

$$|1\rangle = \frac{1}{\sqrt{3}} |\psi^s\rangle + \sqrt{\frac{2}{3}} |\psi_x^p\rangle$$

$$|2\rangle = \sqrt{\frac{1}{3}} |\psi^s\rangle - \sqrt{\frac{1}{6}} |\psi_x^p\rangle + \sqrt{\frac{1}{2}} |\psi_y^p\rangle$$

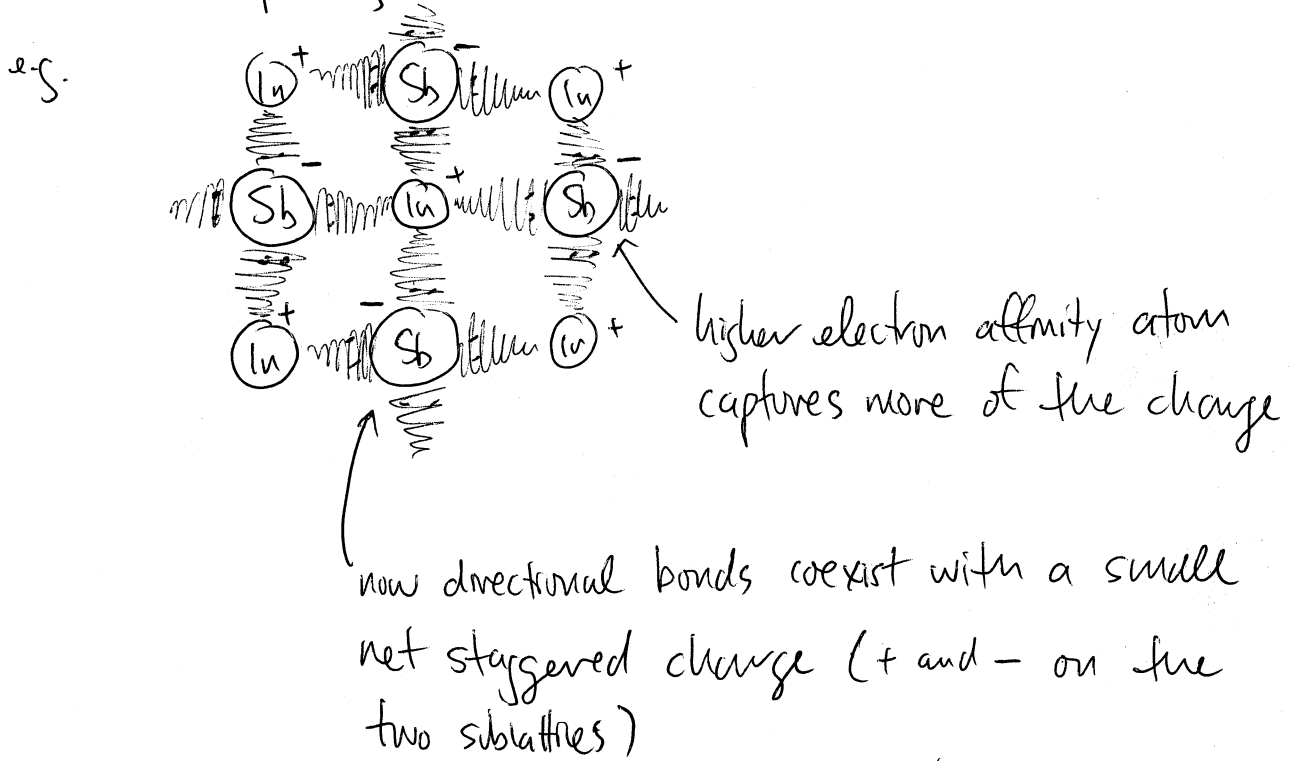
$$|3\rangle = \sqrt{\frac{1}{3}} |\psi^s\rangle - \sqrt{\frac{1}{6}} |\psi_x^p\rangle - \sqrt{\frac{1}{2}} |\psi_y^p\rangle$$

$$|4\rangle = |\psi_z^p\rangle$$

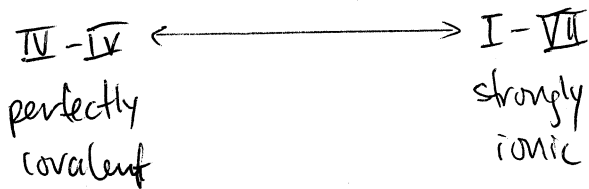


Mixed covalent and ionic character

- * C, Si, Ge follow the IV-IV bonding pattern
- other matches III-V, ..., I-VII also allow for an exact pairing of valence electrons

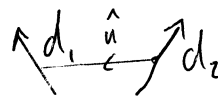
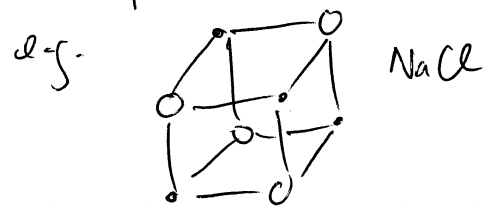
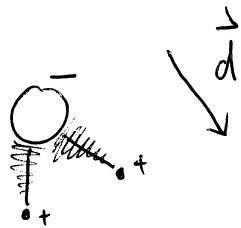


* covalent and ionic character exist in a continuum



- covalent bonding can exist in a variety of geometric structures
- strong ionic bonding is only supported on bipartite lattices
- in individual molecules, electron affinity effects can lead to a permanent dipole moment

e.g. H_2O



↑ all n.n. links connect + and - sites

and long range interactions $\sim \frac{\vec{d}_1 \cdot \vec{d}_2 - 3(\vec{d}_1 \cdot \hat{n})(\vec{d}_2 \cdot \hat{n})}{r^3}$

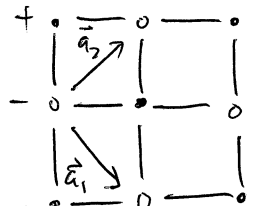
Ewald sums

* Cohesive energy of an ionic solid is related to the total of all pairwise electrostatic interactions

$$\sum_{i < j} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} \leftarrow \text{charges } q_i = Z_i e$$

Sum over site indices that avoids double counting

atomic separations

e.g.  square lattice rotated 45° with a two-site basis:
 charge $-e$ at $\vec{r}_1 = 0$
 charge $+e$ at $\vec{r}_2 = \vec{d} = d\vec{e}_+$

$$E_{\text{coh}} = \sum_{i < j} \frac{\pm e^2}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{2} \sum_{\vec{R}, \vec{r}} \sum_{\vec{R}', \vec{r}'} \frac{q_{\vec{r}} q_{\vec{r}'}}{|\vec{R} + \vec{r} - \vec{R}' - \vec{r}'|} (1 - \delta_{\vec{R} + \vec{r}, \vec{R}' + \vec{r}'})$$

$$= \frac{1}{2} \sum_{\vec{R}, \vec{R}'} \left[\frac{e^2 (1 - \delta_{\vec{R}, \vec{R}'})}{|\vec{R} - \vec{R}'|} - \frac{e^2}{|\vec{R} - \vec{R}' + \vec{d}|} - \frac{e^2}{|\vec{R} - \vec{R}' - \vec{d}|} + \frac{e^2 (1 - \delta_{\vec{R}, \vec{R}'})}{|\vec{R} - \vec{R}'|} \right]$$

$$= \sum_{\vec{R}, \vec{R}'} \left[\frac{e^2 (1 - \delta_{\vec{R}, \vec{R}'})}{|\vec{R} - \vec{R}'|} - \frac{e^2}{|\vec{R} - \vec{R}' + \vec{d}|} \right]$$

$$= \frac{-e^2}{d} \sum_{\vec{R}} \left[\sum_{\substack{\vec{R}' \\ (\neq \vec{R})}} \left(\frac{d}{|\vec{R} - \vec{R}' + \vec{d}|} - \frac{d}{|\vec{R} - \vec{R}'|} \right) + 1 \right]$$

$$= \frac{-e^2 N_{\text{unit cells}}}{d} \left[\sum_{\vec{R} \neq 0} \left(\frac{d}{|\vec{R} + \vec{d}|} - \frac{d}{|\vec{R}|} \right) + 1 \right]$$

by translational symmetry

* After factoring out the energy e^2/d , what remains is the Madelung constant

$$\alpha = \sum_{\vec{R} \neq 0} \left(\frac{d}{|\vec{R} + \vec{d}|} - \frac{d}{R} \right) + 1,$$

a universal, dimensionless value that depends only on the lattice geometry

* These so-called Ewald sums are hard to carry out

→ weak convergence (nearly harmonic subseries that have a delicate cancellation)

→ related to the fact that Coulomb forces (here unscreened) are long-ranged

→ any truncation of the summation is equivalent to establishing a pattern of surface charges on a finite crystal

* Overall attraction is counteracted by a short-range repulsion (the Pauli exclusion hard core)

$$\frac{E_{\text{coh}}}{N_{\text{ion pairs}}} = -\frac{\alpha e^2}{d} + \frac{C}{d^{12}}$$

→ 12 is a phenomenological exponent

→ view as a function of d that is optimized at an equilibrium nearest neighbour separation $d_0 = \left[\frac{12C}{e^2 \alpha} \right]^{1/11}$