Crystalline Solids: Symmetry and Bonding

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PHYS 624: Introduction to Solid State Physics
http://www.physics.udel.edu/~bnikolic/teaching/phys624/phys624.html
Translational Invariance of Crystalline Solids

- The translationally invariant nature of the periodic solid and the fact that the core electrons are very tightly bound at each site (so we may ignore their dynamics) makes approximate solutions to many-body problem $10^{21}$ atoms/cm$^3$ (essentially, a thermodynamic limit) possible.

- The simplest model of a solid is a periodic array of valance orbitals embedded in a matrix of atomic cores. Solving the problem in one of the irreducible elements of the periodic solid (e.g., one of the spheres in the Figure), is often equivalent to solving the whole system.
Translational symmetry of the lattice: There exist a set of basis vectors \((\vec{a}, \vec{b}, \vec{c})\) such that the atomic structure remains invariant under translations through any vector \(\vec{R}_n = n_1\vec{a} + n_2\vec{b} + n_1\vec{c}\) where \((n_1, n_2, n_3) \in \mathbb{Z}\).

One can go from any location in the lattice to an identical location by following path composed of integer multiples of the vectors \(\vec{a}\) and \(\vec{b}\).

NOTE: Keep in mind that basic building blocks of periodic structures can be more complicated than a single atom: e.g., in NaCl, the basic building block is composed of one Na and one Cl ion which is repeated in a cubic pattern to make the NaCl crystalline structure.
The 1D systems can have only discrete translational symmetry.

In 2D and 3D cases, a crystal can also have other symmetries: rotations around axes, reflections on planes, and combination of these operations among themselves and with translations that are not lattice vectors.

**SPACE GROUP:** The complete set of rigid body motions that take crystal into itself

\[ S = \vec{t} + R(\hat{u}, \theta) \]
5 Bravais Lattices in 2D

Inversion Symmetry is obeyed by all lattices:

Invariance under \( \vec{r} \rightarrow -\vec{r} \)

2D lattices are not mathematical fiction—they naturally appear as surfaces and interfaces of real crystals.
A collection of points in which the neighborhood of each point is the same as the neighborhood of every other point under some translation is called a Bravais lattice.

The primitive unit cell is the parallel piped (in 3D) formed by the primitive lattice vectors which are defined as those lattice vectors that produce the primitive cell with the smallest volume \( \Omega_p = \vec{a} \times (\vec{b} \cdot \vec{c}) \).

There are many different primitive unit cells—common features: Each cell has the same volume and contains only one site of Bravais lattice (Wigner-Seitz cell → single site sits in the center of the cell which is invariant under all symmetry operation that leave the crystal invariant).

Non-primitive unit cell: Lattice region (which can contain several sites and usually has the same Point Group symmetry as the lattice itself) which produces the full crystal upon repetition.
Primitive Vectors are not Unique

Hexagonal

\[
\vec{a}_1 = (a, 0)
\]

\[
\vec{a}_2 = \left( \frac{a}{2}, \frac{a \sqrt{3}}{2} \right)
\]

\[
\vec{a}_1 = \left( -\frac{a}{2}, \frac{a \sqrt{3}}{2} \right)
\]

\[
\vec{a}_2 = \left( \frac{a}{2}, \frac{a \sqrt{3}}{2} \right)
\]

\[n_1 \vec{a}_1 + n_2 \vec{a}_2 = 0 \iff n_1 = n_2 = 0\]
Primitive Cells are Not Unique

- **Tiling of the plane**: Cells are free to have rather peculiar shapes, as long as they fit together properly.

- Primitive unit cells put end to end fill the crystal.

- Since they contain only a single particle, the volume $\Omega_{PUC}$ of the primitive cell is exactly the inverse of the density of the crystal.
Most of lattices occurring in nature are not Bravais lattices, but are lattices with a basis constructed by beginning with a Bravais lattice and putting at each lattice site an identical assembly of particles rather than a single rotationally invariant particle.

The dotted line is a glide line the lattice is invariant when translated vertically by $a/2$ and reflected about this line, but it is not invariant under either operation separately!

Start with hexagonal 2D lattice (A) and replace single point in the center with a pair of points (B).
Non-Primitive (Elementary) Unit Cell: Minimal volume of the crystal (containing several particles) which has the same point group symmetry as the crystal itself and which produces the full crystal upon repetition.

\[ \vec{r}_n = \vec{R}_n + \vec{r}_i \]
\[ \vec{r}_i = x_i \vec{a}_1 + y_i \vec{a}_2 + z_i \vec{a}_3 \]
\[ x_i, y_i, z_i \in (0,1), i = 1, 2, \ldots, k \]

Pay attention to 45° rotation around axis passing through the yellow atom.
To account for more complex structures like molecular solids, salts, etc., one also allows each lattice point to have structure in the form of a basis. A good example of this in 2D is the CuO₂ planes which characterize the cuprate high-temperature superconductors.

The basis is composed of two oxygens and one copper atom laid down on a simple square lattice with the Cu atom centered on the lattice points.
"Lattice with a Basis": Centered Rectangular

The centered lattice is special since it may also be considered as a lattice composed of a two-component basis, and a rectangular unit cell.
Once we decorate lattice with a basis, its symmetries will change.
Adding a basis does not automatically destroy the rotational and reflection symmetries of the original lattice.

Decoration of a triangular lattice with chiral molecules will preserve its rotational symmetries, but will destroy reflection symmetries of the original lattice.
Two lattices are the same if one can be transformed *continuously* into the other without changing any symmetry operations along the way.

Two lattices are equivalent if their space groups $S$ and $S'$ are the same up to linear change of coordinate systems (i.e., there exist a single matrix $O$ representing the change of coordinate system):

$$O R O^{-1} + O^{-1} \vec{t} = R' + \vec{t'}$$
The various planar patterns can be classified by the transformation groups that leave them invariant, their symmetry groups. A mathematical analysis of these groups shows that there are exactly 17 different plane symmetry groups:

http://www.clarku.edu/~djoyce/wallpaper/seventeen.htm
14 Bravais Lattices and 7 Crystal Systems in 3D

- **Cubic**: \(a=b=c\) \(\alpha=\beta=\gamma=90^\circ\)
- **Tetragonal**: \(a=b\neq c\) \(\alpha=\beta=\gamma=90^\circ\)
- **Orthorhombic**: \(a\neq b\neq c\) \(\alpha=\beta=\gamma=90^\circ\)
- **Monoclinic**: \(a\neq b\neq c\) \(\alpha=\gamma=90^\circ\) \(\beta\neq 90^\circ\)
- **Triclinic**: \(a\neq b\neq c\) \(\alpha\neq \beta\neq \gamma\neq 90^\circ\)
- **Hexagonal**: \(a=b\neq c\) \(\alpha=\beta=90^\circ\) \(\gamma=120^\circ\)
- **Rhombohedral**: \(a=b=c\) \(\alpha=\beta=\gamma\neq 90^\circ\)

**Simple**

**Base-Centered**

**Body-Centered**

**Face-Centered**

\[ \Omega_{PUC} = \frac{\Omega_C}{2} \]

\[ \Omega_{PUC} = \frac{\Omega_C}{2} \]

\[ \Omega_{PUC} = \frac{\Omega_C}{4} \]
Symmetry transformations form GROUPS.

Group \((S, \circ)\) is defined as a set \(\{E, A, B, C \ldots\}\) which is closed under a binary operation \(\circ: S \times S \rightarrow S\) \((A \circ B \in S)\) and satisfies the following axioms:

- the binary operation is associative \((A \circ B) \circ C = A \circ (B \circ C)\)
- There exists an identity \(E \circ A = A \circ E = A\)
- For each \(A \in S\) there exist an inverse element \(A^{-1} \in S\) such that: \(A \circ A^{-1} = A^{-1} \circ A = E\)

Space Group elements: translations \(\{E|\vec{R}_n\}\in T\), inversions, reflections, rotations, improper rotations (inversion and reflection) \(\{U|0\}\in P\), and \(\{U\vec{t}\}\in S\)

The binary operation \(\circ\) is composition of SG elements \(\{U|\vec{t}\}\vec{r} = U\vec{r} + \vec{t} \in S\)

\[\{U_1|\vec{t}_1\} \circ \{U_2|\vec{t}_2\} \vec{r} = \{U_1|\vec{t}_1\}(U_2\vec{r} + \vec{t}_2) = U_1U_2\vec{r} + U_1\vec{t}_2 + \vec{t}_1 \Rightarrow \{U_1U_2|U_1\vec{t}_2 + \vec{t}_1\} \in S\]

\[\{U|\vec{t}\}^{-1} = \{U^{-1}|-U^{-1}\vec{t}\} \in S\]

\[\{E|0\} \in S\]
Quantum Mechanical Description of Symmetry: Group Representation Theory

- **Wigner 1926**: Symmetry operations \( \langle \Psi | \hat{U}^\dagger \hat{U} | \Phi \rangle = \langle \Psi | \Phi \rangle \) in Hilbert spaces (or, more properly, space of rays) are represented by unitary or antiunitary (time-reversal \( t \rightarrow -t, p \rightarrow -p, L \rightarrow -L, B \rightarrow -B, \Psi \rightarrow \Psi^* \)) operators.
- In the Hilbert space of (coordinate) wave functions:

\[
\hat{U}_{\{U|\vec{r}\}} \Psi(\vec{r}) = \Psi(\{U|\vec{t}\}^{-1} \vec{r})
\]

- **Group Representation**: Group of Unitary Operators \( \hat{U}_{\{U|\vec{r}\}} \) is isomorphic to the space group:

\[
\hat{U}_{\{U_1|\vec{r}_1\}} \hat{U}_{\{U_2|\vec{r}_2\}} \Psi(\vec{r}) = \hat{U}_{\{U_1|\vec{r}_1\} \circ \{U_2|\vec{r}_2\}} \Psi(\vec{r})
\]

- The representation is reducible if there exist a non-trivial subspace of the Hilbert space which is invariant for all \( \hat{U}_{\{U|\vec{r}\}} \) and irreducible if such subspace does not exist.
The point group is not enough to determine the lattice: Different lattices can be invariant under precisely the same set of point symmetry operations.

For example, if we choose any lattice point as the origin then both rectangular and centered rectangular 2D lattices can be reflected about the x or y axis, and each is invariant under a 180° rotations!
**Schönflies Notation:**

→ $C_m$ ("cyclic") when there is a single axis of rotation and number $m$ indicates the $m$-fold symmetry around the axis.

→ $D$ ("dyhedral") when there are two-fold axes at the right angles to another axis.

→ $T$ ("tetrahedral") when there are four sets of rotation axes of three fold-symmetry as in tetrahedron.

→ $O$ ("octahedral") when there is a four-fold rotation axis combined with perpendicular two-fold rotation axis, as in octahedron.

**International Tables of Crystallography:**

→ Example: 6m is mirror plane containing a sixfold axis, 6/m is a mirror plane perpendicular to a sixfold axis.
32 Point Groups in 3D

- **Stereogram**: Two-dimensional projections of a point (that does not belong to any special axis or plane of symmetry) on the surface of a sphere and its images generated by acting on the sphere with various symmetry operations of the point group. Pick a point on a sphere.
230 Space Groups: Symmorphic vs. Non-Symmorphics

- The space group always has only translations as its subgroup
  \[ T = \{ E, \vec{R}_n \} < S \]

- In general, it cannot be formed from these subgroups because of the glide planes (translation + reflection) and screw axes (translation + rotation).

- In general, Point Group leaves the Bravais lattice invariant but not the crystal itself (recall that the crystal is defined as the Bravais lattice and the atomic basis in each unit cell).

  - 157 Non-Symmorphic Groups: include glide planes and screw axes.
  - 73 Symmorphic Groups: \( P < S, S = P \land T \)
  - 1651 Magnetic (Shubnikov or Color) Groups: for the lattices whose points are decorated with quantum-mechanical spin-\( \frac{1}{2} \).
Classical Consequences of Symmetry

- Sharp peaks in X-ray diffraction pattern are exclusively result of lattice symmetries (the intensity of the peaks depends on details).

- Order parameter has to have the same symmetry as the lattice itself → **Ferroelectrics** have dipole moment (rule out any symmetry group that has perpendicular mirror plane or rotoinversion axis because dipole changes sign under these operations): $C_n$, $C_{nv}$, $C_{1h}$

- **Piezoelectric**, such as quartz, do not have dipole moment but acquire one upon mechanical deformation in some direction:

\[
e_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} \right) \Rightarrow P_\gamma = \sum_{\alpha\beta} B_{\alpha\beta\gamma} e_{\alpha\beta}
\]

\[
\vec{r} \rightarrow -\vec{r} \Rightarrow e_{\alpha\beta} = e_{\alpha\beta}, \quad \vec{P} = -\vec{P}, \quad B_{\alpha\beta\gamma} = -B_{\alpha\beta\gamma}
\]

Such crystals cannot be **centrosymmetric** (excludes point groups $D_{nh}$ and $S_2$) which rules out possibility of (large) effect in a huge number of compounds.
If a Hamiltonian $\hat{H}$ is invariant under certain symmetry operations, then we may choose to classify the energy eigenstates as states of the symmetry operation and $\hat{H}$ will not connect states of different symmetry.

$$\hat{U}\hat{H}\hat{U}^\dagger = \hat{H} \implies [\hat{H}, \hat{U}] = 0$$

$$\hat{U}|u_j\rangle = u_j|u_j\rangle \implies \hat{I} = \sum_j |u_j\rangle \langle u_j|$$

$$\sum_k \langle u_i|\hat{U}|u_k\rangle \langle u_k|\hat{H}|u_j\rangle = \sum_k \langle u_i|\hat{H}|u_k\rangle \langle u_k|\hat{U}|u_j\rangle \equiv 0$$

$$\iff$$

$$\left(\langle u_i|\hat{U}|u_i\rangle - \langle u_j|\hat{U}|u_j\rangle\right)\langle u_i|\hat{H}|u_j\rangle = 0 \iff (u_i - u_j)\langle u_i|\hat{H}|u_j\rangle = 0$$
Quantum Consequences of Symmetry: Band Structure and Selection Rules

Effective single-particle Hamiltonian of a solid commutes with the representations of space group operations:

\[
[\hat{H}, U_{\{U|\vec{f}\}}] = 0 \Rightarrow U_{\{U|\vec{f}\}}[\hat{H}\Psi^n_k(\vec{r})] = U_{\{U|\vec{f}\}}[\epsilon_n(\vec{k})\Psi^n_k(\vec{r})]
\]

\[
\hat{H}[\hat{U}_{\{U|\vec{f}\}}\Psi^n_k(\vec{r})] = \epsilon_n(\vec{k})[\hat{U}_{\{U|\vec{f}\}}\Psi^n_k(\vec{r})]
\]

One can further reduce complexity from solving Schrödinger equation in a unit cell (secured by translational symmetry) to finding band dispersion and Bloch eigenstates only in a portion of the BZ.

\[
\{U|\vec{f}\} \in S \Rightarrow \begin{cases} 
\epsilon_n(U\vec{k}) = \epsilon_n(\vec{k}) \\
\Psi^n_{U\vec{k}}(\vec{r}) = \hat{U}_{\{U|\vec{f}\}}\Psi^n_k(\vec{r}) = \Psi^n_k(U^{-1}\vec{r} - U^{-1}\vec{f})
\end{cases}
\]

Selection rules (Wigner-Eckert theorem)

\[
\langle\Psi_1|\hat{O}|\Psi_2\rangle \neq 0 \iff \Gamma_{\Psi_2} \otimes \Gamma_o = \Gamma_{\Psi_1} \oplus \ldots
\]
Irreducible Part of the Brillouin Zone

Table 3.2. Group multiplication table for symmetries of the 2D square lattice.

<table>
<thead>
<tr>
<th>E:</th>
<th>(x, y) → (x, y)</th>
<th>E</th>
<th>C_y</th>
<th>C_4</th>
<th>C_2</th>
<th>C_4^3</th>
<th>σ_x</th>
<th>σ_y</th>
<th>σ_1</th>
<th>σ_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_4:</td>
<td>(x, y) → (−y, x)</td>
<td>C_4</td>
<td>C_2</td>
<td>C_4</td>
<td>E</td>
<td>σ_1</td>
<td>σ_3</td>
<td>σ_y</td>
<td>σ_x</td>
<td>σ_1</td>
</tr>
<tr>
<td>C_2:</td>
<td>(x, y) → (−x, −y)</td>
<td>C_2</td>
<td>C_4</td>
<td>E</td>
<td>C_2</td>
<td>σ_y</td>
<td>σ_x</td>
<td>σ_1</td>
<td>σ_y</td>
<td>σ_x</td>
</tr>
<tr>
<td>C_4^3:</td>
<td>(x, y) → (y, −x)</td>
<td>C_4^3</td>
<td>E</td>
<td>C_4</td>
<td>C_2</td>
<td>σ_2</td>
<td>σ_1</td>
<td>σ_y</td>
<td>σ_x</td>
<td>σ_1</td>
</tr>
<tr>
<td>σ_x:</td>
<td>(x, y) → (x, −y)</td>
<td>σ_x</td>
<td>σ_3</td>
<td>σ_y</td>
<td>σ_1</td>
<td>E</td>
<td>C_2</td>
<td>C_4^3</td>
<td>C_4</td>
<td></td>
</tr>
<tr>
<td>σ_y:</td>
<td>(x, y) → (−x, y)</td>
<td>σ_y</td>
<td>σ_1</td>
<td>σ_x</td>
<td>σ_3</td>
<td>C_2</td>
<td>E</td>
<td>C_4</td>
<td>C_4^3</td>
<td></td>
</tr>
<tr>
<td>σ_1:</td>
<td>(x, y) → (y, x)</td>
<td>σ_1</td>
<td>σ_3</td>
<td>σ_y</td>
<td>σ_x</td>
<td>C_4</td>
<td>C_4^3</td>
<td>E</td>
<td>C_2</td>
<td></td>
</tr>
<tr>
<td>σ_3:</td>
<td>(x, y) → (−y, −x)</td>
<td>σ_3</td>
<td>σ_y</td>
<td>σ_1</td>
<td>σ_x</td>
<td>C_4^3</td>
<td>E</td>
<td>C_4</td>
<td>C_2</td>
<td></td>
</tr>
</tbody>
</table>

1. \( \Gamma = (0, 0) \), which has the full symmetry of the point group;
2. \( M = (1, 1)(\pi/a) \), which also has the full symmetry of the point group;
3. \( X = (1, 0)(\pi/a) \), which has the symmetries \( E, C_2, \sigma_x, \sigma_y \);
4. \( \Delta = (k, 0)(\pi/a), 0 < k < 1 \), which has the symmetries \( E, \sigma_x \);
5. \( \Sigma = (k, k)(\pi/a), 0 < k < 1 \), which has the symmetries \( E, \sigma_1 \);
6. \( Z = (1, k)(\pi/a), 0 < k < 1 \), which has the symmetries \( E, \sigma_y \).
Solids are composed of elements with multiple orbitals that produce multiple bonds. Now imagine what happens if we have several orbitals on each site (s,p,d, etc.), as we reduce the separation between the orbitals and increase their overlap, these bonds increase in width and may eventually overlap, forming bands.

Valance orbitals, which generally have a greater spatial extent, will overlap more so their bands will broaden more.

Eventually we will stop gaining energy from bringing the atoms closer together, due to overlap of the cores ⇒ Once we have reached the optimal point we fill the states 2 particles per, until we run out of electrons.

Electronic correlations $n^\uparrow n^\downarrow$ complicate this simple picture of band formation since they strive to keep the orbitals from being multiply occupied.
### Band Developments and Filling

<table>
<thead>
<tr>
<th>quantum numbers $nl$</th>
<th>elemental solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>H, He</td>
</tr>
<tr>
<td>2s</td>
<td>Li, Be</td>
</tr>
<tr>
<td>2p</td>
<td>B→Ne</td>
</tr>
<tr>
<td>3s</td>
<td>Na, Mg</td>
</tr>
<tr>
<td>3p</td>
<td>Al→Ar</td>
</tr>
<tr>
<td>4s</td>
<td>K, Ca</td>
</tr>
<tr>
<td>3d</td>
<td>transition metals Sc→Zn</td>
</tr>
<tr>
<td>4p</td>
<td>Ga→Kr</td>
</tr>
<tr>
<td>5s</td>
<td>Rb, Sr</td>
</tr>
<tr>
<td>4d</td>
<td>transition metals Y→Cd</td>
</tr>
<tr>
<td>5p</td>
<td>In-Xe</td>
</tr>
<tr>
<td>6s</td>
<td>Cs, Ba</td>
</tr>
<tr>
<td>4f</td>
<td>Rare Earths (Lanthanides) Ce→Lu</td>
</tr>
<tr>
<td>5d</td>
<td>Transition metals La→Hg</td>
</tr>
<tr>
<td>6p</td>
<td>Tl→Rn</td>
</tr>
</tbody>
</table>
For large $n$, the orbitals do not fill up simply as a function of $n$ as we would expect from a simple Hydrogenic model with

$$E_n = -\frac{m e^4}{2 \hbar^2 n^2} Z^2$$

Level crossings due to atomic screening. The potential felt by states with large $l$ are screened since they cannot access the nucleus. Thus, orbitals of different principle quantum numbers can be close in energy. For example, in elemental Ce ($4f^{15}d^16s^2$) both the $5d$ and $4f$ orbitals may be considered to be in the valence shell, and form metallic bands. However, the $5d$ orbitals are much larger and of higher symmetry than the $4f$ ones. Thus, electrons tend to hybridize (move on or off) with the $5d$ orbitals more effectively. The Coulomb repulsion between electrons on the same $4f$ orbital will be strong, so these electrons on these orbitals tend to form magnetic moments.
Chemical Bonds in Solids: Wan der Waals

- **Wan der Waals bonding:** formed by atoms that do not have valence electrons available for sharing (the noble elements and crystals or organic molecules) - “fluctuating dipole” (zero-point motion) of van der Waals interaction is due to slight polarization of the electronic wave function in one atom due to the surrounding atoms.

- **Lowering of zero-point energy by dipole-dipole interaction:**

\[
\Delta E \approx \frac{\hbar \omega_0}{4} \left( \frac{2e^2}{m \omega_0^2 R^3} \right)^2 \hbar \rightarrow 0 \rightarrow 0
\]
Chemical Bonds in Solids: Covalent

- **Covalent Bonding**: formed when electrons in well defined directional orbitals, which can be thought as linear combinations of the original atomic orbitals, have strong overlap with similar orbitals in neighboring atoms (solids produced in this way are semiconductors or insulators).
Chemical Bonds in Solids: Ionic

Ionic Bonding: Formed when two different type of atoms are combined, one that prefers to lose some of its valence electrons and become positive ion, and one that prefers to grab electrons from other atoms and become a negative ion. Bonding then occurs by Coulomb attraction between the ions. Combinations of such elements are I-VII, II-VI, and III-V. In the first case bonding is purely ionic, in the other two there is a degree of covalent bonding present.

The energy per molecule of a crystal of sodium chloride is \((7.9-5.1+3.6)\, \text{eV}=6.4\, \text{eV}\) lower than the energy of the separated neutral atoms. The cohesive energy with respect to separated ions is \(7.9\, \text{eV}\) per molecular unit. All values on the figure are experimental.

\[
\Phi = N_{\text{pairs}} \left( -\frac{e}{4\pi\varepsilon_0 r} \sum_{i\neq j} \frac{\pm 1}{p_{ij}} + \frac{B}{r^n} \sum_{i\neq j} \frac{1}{p^m_{ij}} \right)
\]

Madelung constant (\(A=1.748\) for NaCl)

Coulomb

Repulsion between electron clouds
Ionic and covalent bondings are two limiting cases, of which, only the later can exist in solids composed of a single type of atom. In majority of cases the bonding is of an intermediate nature representing a mixture of the two extremes.
**Metallic Bonding**: formed when electrons are shared by all atoms in the solid producing a uniform “sea” of negative charge.

In metallic Ni (FCC, $3d^84s^2$), the $4s$- and $3d$-orbitals are almost degenerate and thus, both participate in the bonding. However, the $4s$-orbitals are so large compared to the $3d$-orbitals that they encompass many other lattice sites, forming non-directional bonds. In addition, they hybridize weakly with the $d$-orbitals (the different symmetries of the orbitals cause their overlap to almost cancel) which in turn hybridize weakly with each other. Thus, whereas the $s$-orbitals form a broad metallic band, the $d$-orbitals form a narrow one.
Metallic Bonds Involve Many Neighbors

In contrast to covalent bonding, electronic wave functions in metals are very extended compared to the separation between atoms.

Fig. 1.9. The amplitude of the $3d_{zz}$-wavefunction and the $4s$-wavefunction of Ni [1.4]. The half-distances to the first, second and third nearest neighbors ($r_1$, $r_2$ and $r_3$) are shown for comparison.
Hydrogen Bonding: formed when H is present and bounded to two other atoms (organic molecules, DNA, and water, ice); this is a special bond due to its lack of core electrons (bare proton left after sharing 1s electron), its light mass (must use quantum mechanics for, e.g., zero-point proton motion) and high ionization energy.
The type of bond that forms between two orbitals is dictated largely by the amount that these orbitals overlap relative to their separation $a$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Overlap</th>
<th>Lattice</th>
<th>constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>very small ($&lt; a$)</td>
<td>closest unfrustrated packing</td>
<td>dissimilar</td>
</tr>
<tr>
<td>Covalent</td>
<td>small ($\sim a$)</td>
<td>determined by the structure of the orbitals</td>
<td>similar</td>
</tr>
<tr>
<td>Metallic</td>
<td>very large ($\gg a$)</td>
<td>closest packed</td>
<td>unfilled valence orbitals</td>
</tr>
</tbody>
</table>
Origin of Chemical Bonding: Virial Theorem in Quantum Mechanics

**Born-Oppenheimer Approximation:**

\[
\hat{H}(\vec{r}_1^{\text{nucl}}, \ldots \vec{r}_N^{\text{nucl}}) \left| \Psi(\vec{r}_1^{\text{nucl}}, \ldots \vec{r}_N^{\text{nucl}}) \right\rangle = E(\vec{r}_1^{\text{nucl}}, \ldots \vec{r}_N^{\text{nucl}}) \left| \Psi(\vec{r}_1^{\text{nucl}}, \ldots \vec{r}_N^{\text{nucl}}) \right\rangle
\]

\[
T_{\text{electron}} + V = \sum_{i=1}^{Q} \left( \frac{P_i^{\text{electron}}}{2m} \right)^2 + V_{ee} + V_{en}(\vec{r}_1^{\text{nucl}}, \ldots \vec{r}_N^{\text{nucl}}) + V_{nn}(\vec{r}_1^{\text{nucl}}, \ldots \vec{r}_N^{\text{nucl}})
\]

**Virial Theorem:**

\[
\langle T_{\text{electron}} \rangle = -E - \sum_{k=1}^{N} \vec{r}_k^{\text{nucl}} \cdot \nabla_k E
\]

\[
\langle V \rangle = 2E + \sum_{k=1}^{N} \vec{r}_k^{\text{nucl}} \cdot \nabla_k E
\]

**Stability:**

\[
E_0 < E_\infty, \left[ \nabla_k E(\vec{r}_1^{\text{nucl}}, \ldots \vec{r}_N^{\text{nucl}}) \right]_0 = 0
\]

\[
\langle T_{\text{electron}} \rangle_0 - \langle T_{\text{electron}} \rangle_\infty = -(E_0 - E_\infty) > 0
\]

\[
\langle V \rangle_0 - \langle V \rangle_\infty = 2(E_0 - E_\infty) < 0
\]

⇔ \{ \langle T_{\text{electron}} \rangle, \langle V_{nn} \rangle \} are increasing

\{ \langle V_{ee} \rangle, \langle V_{en} \rangle \} are decreasing

PHYS 624: Crystalline Solids: Symmetry and Bonding
Many elements adopt multiple crystal structures between 0 K and their melting temperature.

Plutonium has particularly elaborate phase diagram:

<table>
<thead>
<tr>
<th>Transformation Temp, C</th>
<th>Phase</th>
<th>Structure (atoms per unit cell)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>α</td>
<td>monoclinic (16)</td>
<td>19.8</td>
</tr>
<tr>
<td>185</td>
<td>β</td>
<td>fc monoclinic (34)</td>
<td>17.8</td>
</tr>
<tr>
<td>310</td>
<td>γ</td>
<td>fc orthorhombic (8)</td>
<td>17.1</td>
</tr>
<tr>
<td>450</td>
<td>δ</td>
<td>fcc (4)</td>
<td>15.9</td>
</tr>
<tr>
<td>475</td>
<td>δ'</td>
<td>fc tetragonal (2)</td>
<td>16.0</td>
</tr>
<tr>
<td>640</td>
<td>ε</td>
<td>bcc (2)</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Crystalline Phases of Carbon: Diamond
Chemistry of Diamond: \( \text{sp}^3 \) hybridization, covalent bonds, and all that

\[
C : 1s^2 2s^2 2p^2
\]

\[
\phi^A_B = \frac{1}{2} \left( s^A_B + p^A_B \mp p^A_B \mp p^A_B \right)
\]

\[
\phi^B_A = \frac{1}{2} \left( s^A_B \pm p^A_B \pm p^A_B \pm p^A_B \right)
\]

\[
\phi^A_B = \frac{1}{2} \left( s^A_B \pm p^A_B \pm p^A_B \mp p^A_B \right)
\]

\[
\phi^B_A = \frac{1}{2} \left( s^A_B \pm p^A_B \mp p^A_B \pm p^A_B \right)
\]

\[
\Psi_{i}^{\text{bonding}} = \frac{1}{2} \left( \phi_i^A + \phi_i^B \right), \quad \Psi_{i}^{\text{antibonding}} = \frac{1}{2} \left( \phi_i^A - \phi_i^B \right)
\]
In the crystal, the bonding and antibonding states acquire dispersion $\varepsilon_n^b(k)$ which leads to the formation of the valence and conduction energy bands with a gap $\varepsilon_{\text{gap}}$ between the two manifolds of states.
Crystalline Phases of Carbon: Graphite

PHYS 624: Crystalline Solids: Symmetry and Bonding
Selecting a Unit Cell in Hexagonal Lattice of Graphene

**2D Lattice**

- **Unit Cells**
  - Atom 1: \((2/3, 1/3)\)
  - Atom 2: \((1/3, 2/3)\)

*Fractional Atomic \((xy)\) Coordinates*

*(As a fraction of unit cell dimension)*

*i.e. true dimensions are \(ax\) and \(by\)*
Chemistry of Graphite: $sp^2$ hybridization, covalent bonds, and all that

\[ \phi_{1,2,3,4}^{A,B} = \frac{1}{\sqrt{3}} S^{A,B} \pm \frac{2}{\sqrt{3}} p_{x,y}^{A,B} \]

\[ \phi_{2,3}^{A,B} = \frac{1}{\sqrt{6}} S^{A,B} \pm \frac{1}{\sqrt{6}} p_{x,y}^{A,B} \]

\[ \phi_{3,4}^{A,B} = \frac{1}{\sqrt{6}} S^{A,B} \pm \frac{1}{\sqrt{6}} p_{x,y}^{A,B} \]

\[ \phi_4^{A,B} = p_z^{A,B} \]

\[ \psi_{i}^{b(onding)} = \frac{1}{2} (\phi_i^A + \phi_i^B) \]

\[ \psi_{i}^{a(ntibonding)} = \frac{1}{2} (\phi_i^A - \phi_i^B) \]
Crystalline Phases of Carbon: Carbon Nanotubes

Zigzag nanotubes correspond to \((n, 0)\) or \((0, m)\) and have a chiral angle of 0°, armchair nanotubes have \((n, n)\) and a chiral angle of 30°, while chiral nanotubes have general \((n, m)\) values and a chiral angle of between 0° and 30°. According to the theory, nanotubes can either be metallic (green circles) or semiconducting (blue circles).
Fullerenes are the only form of molecular carbon known. The stability of fullerenes come from the giant delocalized electron system which, in the case of the $C_{60}$, contains 12 pentagonal and 20 hexagonal rings, but no pentagonal faces will share a side (an effect known as isolated pentagon rule).
A Copper (**Cu**) atom is surrounded by six Oxygen (**O**) atoms which form an octahedron; the Cu-O atoms are bonded by strong covalent bonds.

The empty space between Cu-O octahedra can accommodate atoms which are easily ionized, to produce mixed covalent ionic structure.

The crystallographic structure of high-temperature superconductors (HTSC) comprises two basic functional elements: (i) layered quasi-two dimensional \(CuO_2\)-lattice planes and (ii) inter-planar regions, mostly containing metallic spacer atoms in a certain concentration ratio (e.g. \(La_{1-x}Sr_x\)). The essential role of these spacer regions is to provide the \(CuO_2\) planes with a suitable amount of mobile charge carriers. At a favourable charge carrier concentration, and for sufficiently low temperatures, the planes enter a superconducting state with highly unusual properties.
Complex Solids: Perovskites $\text{ABO}_3$

- $\text{CaTiO}_3$, $\text{PbTiO}_3$, $\text{BaTiO}_3$, $\text{PbZrO}_3$ can behave as Piezoelectrics or Ferroelectrics.

- The $p_x$, $p_y$, $p_z$ orbitals of the three O atoms and the $d_x$, $d_{3z^2-r^2}$ orbitals of the B atom participate in the formation of covalent bonds in the octahedron.

- **Complexity:** Strong covalent bond between B-O as well as ionic character of the bond between B-O units and the A atoms (A atoms provide the necessary number of electrons to satisfy all covalent bonds).