Chemical Bonding

Molecule | Separate Atoms
---|---

\[ U_{\text{Mol}} = +V_{++} + V_{--} - 4 \cdot V_{+-} \]
\[ U_{\text{At}} = -2 \cdot V_{+-} \]
\[ \Delta U = +V_{++} + V_{--} - 2 \cdot V_{+-} \]

A delicate balance between Coulomb attraction and repulsion results in two positive and two negative energy terms in \( \Delta U = U_{\text{Mol}} - U_{\text{At}} \).

The energy is reduced if both electrons share the space between the ions: \( V_{+-} > V_{++}, V_{--} \)

In a nutshell, the **Coulomb attraction** between a valence electron and **more than one ion** holds a molecule or solid together. The way these charges are distributed determines the type of bonding.

**Types of Bonds**

1) **Covalent** (C, organics, Si, semiconductors)
2) **Ionic** (NaCl, oxides, insulators)
3) **Metallic** (Al)
4) **Hydrogen** (Ice, protein folding, DNA base pairing)
5) **Molecular** (Bond between molecules)

1) **Covalent Bond**: Shared electron pair between the two positive ions

\( \text{H}_2^+ \): 1 electron, \( \psi(r) \) symmetric / antisymmetric with respect to \( r \leftrightarrow r \).

\( \text{H}_2 \): 2 electrons, \( \psi(r_1,r_2) \) antisymmetric with respect to \( 1 \leftrightarrow 2 \).

Start with the 1s wave functions of the two individual H atoms, \( \psi_\alpha \) and \( \psi_\beta \):
It is difficult to display the two-electron wave function in the six-dimensional $r_1, r_2$ space. Nevertheless, the symmetric spatial wave function

$$\psi_S(r_1, r_2) = \left[ \psi_\alpha(r_1) \cdot \psi_\beta(r_2) + \psi_\alpha(r_2) \cdot \psi_\beta(r_1) \right] / \sqrt{2}$$

leads to an increased electron density between the positive ions, as for $\text{H}_2^+$. The overall antisymmetry forces the spin wave function to be antisymmetric:

$$\chi^\Lambda(1,2) = \left[ \uparrow_1 \downarrow_2 - \uparrow_2 \downarrow_1 \right] / \sqrt{2} = (\uparrow \downarrow - \downarrow \uparrow)$$

$\Rightarrow$ Pairing of electrons with opposite spin
**Solids:** Covalent sp$^3$ bonding in tetrahedral semiconductors (Diamond, Si, Ge)

C atom: 1s$^2$ 2s$^2$ 2p$^2$  
Diamond: 1s$^2$ 2s$^1$ 2p$^3$

The promotion $2s \rightarrow 2p$ in diamond costs energy ($\approx 4$eV), but that is more than made up by the energy reduction due to covalent bonding. The resulting sp$^3$ orbitals point towards four neighbor atoms at the corners of a tetrahedron:

```
  s + three p → four sp$^3$
  (l=0)       (l=1)
```

The covalent bond is highly directional. That leads to specific broken bond orbitals at surfaces:

```
+---------------------+---------------------+
|                     |                     |
|                      | surface             |
| 1 up, 3 down         |                     |
| (111) surface        |                     |
|                     |                     |
| Orthogonal scissors  |                     |
| (100) surface        |                     |
```

2) **Ionic Bond:** Coulomb attraction between ions of opposite charge

**Molecules AB:**

Covalent wave function $\psi_{AB}$

Ionic wave function $\psi_{A^+B^-}$

A linear combination of covalent and ionic wave functions is chosen to minimize the average energy $<\psi|H|\psi>$:

$$\psi = A \cdot \psi_{AB} + B \cdot \psi_{A^+B^-} \quad A^2 + B^2 = 1$$
Variational Principle:
The wave function $\psi_0$ of the ground state can be approximated by a set of trial wave functions $\psi$. The function that produces the lowest energy $<\psi|H|\psi>$ is the most accurate.

Explanation: The exact solution $\psi_0$ for the ground state has the lowest energy eigenvalue $E_0 = <\psi_0|H|\psi_0>$. All other $\psi$ contain admixtures of $\psi_n$ with higher energy eigenvalues $E_n$. They raise the average energy.

Energy Balance:

1. $\text{Na}^0 + U_I = \text{Na}^+ + e^- \quad \text{Ionization Energy} \quad U_I \approx +5 \text{ eV}$
2. $\text{Cl}^0 - U_A = \text{Cl}^- + e^- \quad \text{Electron Affinity} \quad U_A \approx +4 \text{ eV}$
3. $\text{Na}^+ + \text{Cl}^- = \text{Na}^+\text{Cl}^- - U_C \quad \text{Coulomb Energy} \quad U_C \approx -6 \text{ eV} \quad (-9 \text{ eV solid})$

Sum: $\text{Na}^0 + \text{Cl}^0 = \text{Na}^+\text{Cl}^- + U_B \quad \text{Binding Energy} \quad U_B \approx +5 \text{ eV} \quad (8 \text{ eV solid})$

$U_B = -U_I + U_A - U_C$

Signs: It costs energy to form positive ions, whereas energy is released by forming negative ions and by the Coulomb attraction between positive and negative ions. $U_I$ and $U_A$ are defined asymmetrically such that they become positive.

Coulomb Energy:

For a molecule with the charges $q_1,q_2$:

$$U_C = \frac{q_1 q_2}{r} \quad < 0 \quad q_i = \pm n \cdot e \cdot \text{ionicity} \quad r = \text{bond length} \quad \text{factor} \quad 1/4\pi\varepsilon_0 \text{ in SI units}$$

In a solid, the Coulomb energy of an ion with all the other ions can be summed up into a similar formula where the charge $q_2$ is replaced by an effective charge $A \cdot q_2$:

$$U_C = \sum_i \frac{q_1 q_i}{r_i} = A \frac{q_1 q_2}{r} \quad < 0 \quad \text{Madelung constant} \quad A \approx 1.7$$

The series becomes convergent by taking partial sums over neutral shells of atoms (compensation of repulsive and attractive terms).
Electronegativity: The ability of an atom to bind electrons

The goal: Find a simple number for each element that tells us the type of bonding.

\[ \chi = 0.184 \cdot (U_I + U_A) \]

\( U_I = \) ionization energy, \( U_A = \) electron affinity

\( \Delta \chi \) large \( \Rightarrow \) Ionic bond

\( \Delta \chi \) small \( \Rightarrow \) Covalent bond (\( \chi \) large / medium)

Metallic bond (\( \chi \) small)

Extremes: F (\( \chi = 4.0 \)), Cs (\( \chi = 0.9 \))  
Middle: C (\( \chi = 2.5 \)), Si (\( \chi = 1.8 \))

3) **Metallic Bond:** Loosely-bound electrons roaming in the averaged ion potential

Isotropic \( \Rightarrow \) Maximum number of neighbors. Examples: Alkali metals, aluminum.

The key parameter is the **electron density**.

![Diagram of metallic bond](image)

- Vacuum level: \( E_V \)
- Work function: \( \Phi \)
- Fermi level: \( E_F \)
- Inner potential: \( V_0 \)

- Jellium model = particle in a box
- Muffin tin potential
- Equivalent single-electron pseudopotential

\( E \)
4) **Hydrogen Bond**: Shared proton attracted by two negative ions

\[ |\psi|^2 \]

Often asymmetric, with a covalent bond on one side

Examples: Water and ice, base pairs in DNA, protein folding.
Analog to the covalent bond, where an electron shares the attraction of two protons (roles of electron and proton reversed).

5) **Molecular (Van der Waals) Bond**: Attraction of oscillating dipoles

Bonds between saturated molecules, attraction to a surface (atomic force microscopy).

A temporary electric dipole is created on atom i by zero point oscillations of the electrons at their optical resonance frequency (\(\hbar \omega_0\) in the ultraviolet).
This dipole creates an electric field \(\mathbf{E}\) at the neighbor atom j. There is attraction since opposite charges are closer to each other than equal charges. \(1/r^6\) power law.

Dipole field:
\[ \mathbf{E} \sim 1/r_{ij}^3 \]

Induced dipole moment \(\mu\) on atom j:
\[ \mu \sim \mathbf{E} \sim 1/r_{ij}^3 \]

Energy of the induced dipole in the electric field:
\[ U_C \sim -\mu \mathbf{E} \sim -1/r_{ij}^6 \]
Bonding and Structure

**Ionic AB**: CsCl → NaCl → Zincblende (decreasing metal/halogen radius)  **AB₂**: CaF₂

Surfaces: **Charge neutrality** avoids the diverging Coulomb energy of a charge sheet: NaCl(100), CaF₂(111)

**Covalent AA**: Diamond  **AB**: Zincblende (cubic), Wurtzite (hexagonal).

Surfaces: Intricate structures attempt to minimize the density of broken bonds by surface rearrangement = reconstruction with n×m surface unit cells. Typical examples are adatoms on the (111) surface and dimers on the (100) surface.

**Metallic**: Isotropic bonding favors a close-packed structure with many neighbors.

- face centered cubic (fcc) = ababc stacking, hexagonal close packed (hcp) = abab.
- body centered cubic (bcc). Densest surface lattices: fcc(111), hcp(0001), bcc(110).

**Crystal Structures**

A crystal is invariant under translation by a lattice vector. The crystal lattice is a set of mathematical points defined by: \( \mathbf{r} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \) \( n_1, n_2, n_3 \) integer.

The vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) define the unit cell. Additional lattice points inside the unit cell are called basis.

\[
\text{Crystal Structure} = \text{Lattice} + \text{Basis}
\]

**Reciprocal space** = Fourier transform of real space = Diffraction pattern = \( k \)-space

The reciprocal lattice is defined by the vectors:

\[ \mathbf{G} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*, \quad h, k, l \text{ integer (Miller indices)}, \quad \mathbf{a}^* = 2\pi \mathbf{b} \times \mathbf{c} / \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) \ldots \]

\( \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^* \) define the unit cell in reciprocal space = Brillouin zone.

(h k l) defines a set of lattice planes that produce a diffraction peak (Bragg reflection and Laue spots, see 448 quantum notes, p. 5)

For cubic crystals, the direction [h k l] (vector) is perpendicular to the plane (h k l).

For surfaces, the term \( n \times m \) refers to the size of the surface unit cell in units of the truncated bulk structure (for example Si(111)7×7, the most stable silicon surface).
The reciprocal lattice of fcc is bcc and vice versa.

**Crystal Symmetries:**

1) Translation $\Rightarrow$ Bravais Lattices (14 in 3D, 5 in 2D; fcc, bcc, etc.)
2) Point Operations $\Rightarrow$ Point Groups (32 in 3D, 10 in 2D; rotation, mirror)
1) + 2) $\Rightarrow$ Space Groups (230 in 3D, 17 in 2D; crystal structures)

**Liquid Crystals**

Translational order is partially lost, but orientational order remains.

<table>
<thead>
<tr>
<th>Liquid Crystal Type</th>
<th>Translational Order</th>
<th>Orientational Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nematic</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Smectic A,C</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hexatic</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Columnar</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2-dim. Crystal</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

**Quasicrystals**

These are crystals in higher dimensions that are projected onto three-dimensional space at an angle with irrational slope. Translation and rotation invariance are lost. However, local rotation symmetry remains, for example 5- and 10-fold which is not compatible with translational invariance. The diffraction spots in $\mathbf{k}$-space remain sharp ("quasiperiodicity"), but there is no minimum spacing between them.

http://www.geom.umn.edu/apps/quasitiler/about.html
http://www.cmp.caltech.edu/~lifshitz/quasicrystals.html