Chapter. 10  
Molecules and Solids

Outline:
- 10.1 Molecular Bonding and Spectra
- 10.2 Stimulated Emission and Lasers
- 10.3 Structural Properties of Solids
- 10.4 Thermal and Magnetic Properties of Solids
- 10.5 Superconductivity
- 10.6 Applications of Superconductivity

In Chapter 7 & 8, we learned about the properties of individual atoms. This chapter builds on that knowledge to find out what happens when those atoms join together to form molecules & solids.

10.1: Molecular Bonding and Spectra
- The Coulomb force is the only one to bind atoms.
- The combination of attractive and repulsive forces creates a stable molecular structure.
- Force is related to potential energy $F = -\frac{dV}{dr}$, where $r$ is the distance separation.

It is useful to look at molecular binding using potential energy $V$.
- Negative slope ($dV/dr < 0$) with repulsive force
- Positive slope ($dV/dr > 0$) with attractive force

Molecular Bonding and Spectra
- An approximation of the potential of one atom in the vicinity of another atom is
  $$V = \frac{A}{r^n} - \frac{B}{r^m}$$

  where $A$ and $B$ are positive constants.
- Because of the complicated shielding effects of the various electron shells, $n$ and $m$ are not equal to 1.

Eq. 10.1: $V$ produced a potential well that provides a stable equilibrium for total energy $E < 0$. The shape of the curve depends on the parameters $A$, $B$, $n$, and $m$.

Also $n > m$ (in the Fig.)
**Molecular Bonding and Spectra**

- Vibrations are excited thermally, so the exact level of $E$ depends on temperature.
- Once a pair of atoms is joined, then:
- One would have to supply enough energy to raise the total energy of the system to zero in order to separate the molecule into two neutral atoms.
- The PE curves have minimum value, & corresponding value of $r$ is an *equilibrium separation*.
- The amount of energy to separate the two atoms completely is the *binding energy* which is roughly equal to the depth of the potential well.

**Molecular Bonds**

**Ionic bonds:**
- The simplest bonding mechanisms; occurs when 2 atoms are easily ionized.
- *e.g.*: Sodium $(1s^22s^22p^63s^1)$ readily gives up its 3s electron to become $Na^+$, while chlorine $(1s^22s^22p^63s^23p^5)$ readily gains an electron to become $Cl^-$. That forms the NaCl molecule.

**Covalent bonds:**
- The atoms are not as easily ionized.
- *e.g.*: Diatomic molecules $(H_2, N_2, O_2)$ formed by the combination of two identical atoms tend to be covalent. These are referred to as homopolar molecules.
- Larger molecules (like organic molecules) are formed with covalent bonds.

**Van der Waals bond:**
- A relatively Weak bond found mostly in liquids and solids at low temperature
- *e.g.*: In graphite, the van der Waals bond holds together adjacent sheets of carbon atoms. As a result, one layer of atoms slides over the next layer with little friction. The graphite in a pencil slides easily over paper.

**Hydrogen bond:**
- Holds many organic molecules together: *e.g.* water.

**Metallic bond:**
- Free valence electrons may be shared by a number of atoms.

**Rotational States**

**Molecular spectroscopy:**
- We can learn about molecules by studying how molecules absorb, emit, and scatter electromagnetic radiation.
- From the equipartition theorem, the $N_2$ molecule may be thought of as two N atoms held together with a massless, rigid rod (rigid rotator model).
- In a purely rotational system, the kinetic energy is expressed in terms of the angular momentum $L$ and rotational inertia $I$.

$$E_{rot} = \frac{L^2}{2I}$$
Rotational States

- \( L \) is quantized (see section 7.3).
- The energy levels of a simple rotational state are
  \[ E_{\text{rot}} = \frac{\hbar^2 \ell (\ell + 1)}{2I} \]
- \( E_{\text{rot}} \) varies only as a function of the quantum number \( \ell \).

Vibrational States

- In addition to rotation, there is also the possibility that a vibrational energy mode will be excited.
- There will be no thermal excitation of this mode in a diatomic gas at ordinary temperature.
- However, it is possible to stimulate vibrations in molecules using electromagnetic radiation.

Vibrational States

- The energy levels are those of a quantum-mechanical oscillator (6.6)
  \[ E_{\text{vibr}} = (n + \frac{1}{2}) \hbar \omega \]
- The frequency of a two-particle oscillator is
  \[ \omega = \sqrt{\frac{\kappa}{\mu}} \]
  where the reduced mass: \( \mu = m_1 m_2 / (m_1 + m_2) \) & the spring constant: \( \kappa \).
- If it is a purely ionic bond, we can compute \( \kappa \) by assuming that the force holding the masses together is Coulomb.
  \[ \kappa = \frac{dF}{dr} \approx \frac{d}{dr} \left( \frac{e^2}{4\pi\varepsilon_0 r^2} \right) = \frac{e^2}{2\pi\varepsilon_0 r^3} \]
  and
  \[ \omega \approx \sqrt{\frac{e^2}{2\pi\varepsilon_0 \mu r^3}} \]
  If we use \( r \sim 10^{-10} \text{ m}, k \sim 460 \text{ N/m}, \omega \sim 2 \times 10^{14} \text{ s}^{-1}, \)
  \( E_{\text{vibr}} \sim 0.2 \text{ eV for the } n = 1 \text{ vibrational level of } \text{N}_2 \)

Vibration and Rotation Combined

- It is possible to excite the rotational and vibrational modes simultaneously.
- Total energy of simple vibration-rotation system:
  \[ E = E_{\text{rot}} + E_{\text{vibr}} = \frac{\hbar^2 \ell (\ell + 1)}{2I} + \frac{(n + \frac{1}{2}) \hbar \omega}{2} \]
- Vibrational energies are spaced at regular intervals.
  - emission features due to vibrational transitions appear at regular intervals: \( \frac{1}{2} \hbar \omega, \frac{3}{2} \hbar \omega, \text{ etc.} \)
- Consider, for example, a transition from \( \ell + 1 \) to \( \ell \):
  - Photon will have an energy
    \[ E_{\text{ph}} = \frac{\hbar^2}{2I} \left[ (\ell + 1)(\ell + 2) - \ell (\ell + 1) \right] \]
    \[ = \frac{\hbar^2}{2I} \left[ \ell^2 + 3\ell + 2 - \ell^2 - \ell \right] = \frac{\hbar^2}{I} (\ell + 1) \]
Vibration and Rotation Combined

- Now we see an emission-spectrum spacing that varies with \( l \)
  > The higher the starting energy level, the greater the photon energy for a transition with \( \Delta l = -1 \)

- Vibrational energies are typically greater than rotational energies. This energy difference results in the band spectrum.

Typical section of the emission spectrum of a diatomic molecule. Equally spaced groups of lines correspond to the equal spacings between vibrational levels. The structure within each group is due to transitions between rotational levels.