Chapter. 10
Molecules and Solids

Outline:
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10.3 Structural Properties of Solids
10.4 Thermal and Magnetic Properties of Solids
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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

An approximation of the potential of one atom in the vicinity of another atom is

\[
V = \frac{A}{r^n} - \frac{B}{r^m}
\]

The sum of attractive & repulsive potentials

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.

Molecular 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).
  \[
  L = \sqrt{\ell(\ell + 1)} \hbar
  \]
- 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.

  Assume that the 2 atoms are point masses connected by a massless spring with simple harmonic motion:

**Vibration and Rotation Combined**

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

Typically, in any molecular spectrum, the positions and intensities of the observed bands are ruled by quantum mechanics. Note that two features in particular:

1) The relative intensities of the bands are due to different transition probabilities. The probabilities of transitions from an initial state (e.g. $n=5$) to each possible final state ($n=4, 3, \ldots$) are not necessarily the same.

2) Some transitions are forbidden by the selection rule that requires $\Delta l = \pm 1$.

Absorption spectra:

- When electromagnetic radiation is incident upon a collection of a particular kind of molecule (e.g. in a closed gas cell), molecules can absorb photons and make transitions to a higher vibrational state only if the rotational state changes by $\Delta l = \pm 1$.

$\Delta E$ increases linearly with $l$ as in eq. (10.8), one expects to see absorption band at regular intervals of energy.

In the absorption spectrum of HCl, the spacing between the peaks can be used to compute the rotational inertia $I$. (Prob.15a)

The missing peak in the center corresponds to the forbidden $\Delta l = 0$ transition.

The central frequency:

$$ f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} $$
Vibration and Rotation Combined

Physicists & chemists have developed sophisticated equipment and data reduction methods to study molecular spectra. One of the most popular methods is ...

Fourier transform infrared (FTIR) spectroscopy:
- In Fourier analysis, a spectrum can be decomposed into an infinite series of sine and cosine functions.
- Random and instrumental noise can be reduced in order to produce a “clean” spectrum.

Raman scattering:
- It is not necessary that an incoming photon’s energy precisely match the transition energy ΔE.
- If a photon’s energy greater than ΔE is absorbed by a molecule, the excess energy may be released in the form of a scattered photon of lower energy; this process is known as Raman scattering.
- The angular momentum selection rule becomes Δℓ = ±2.

Consider a transition from ℓ to ℓ + 2, the rotational part of the transition E:
\[ \Delta E_{rot} = \frac{\hbar^2}{2I} [(\ell + 2)(\ell + 3) - \ell(\ell + 1)] \]
\[ = \frac{\hbar^2}{1} [2\ell + 3] \]

Let hf be the Raman-scattered energy of an incoming photon and hf’ is the energy of the scattered photon. The frequency of the scattered photon can be found in terms of the relevant rotational variables:
\[ hf' = hf - \Delta E_{rot} = hf - \frac{\hbar^2}{1} [2\ell + 3] \]
\[ f' = f - \frac{\hbar}{2\pi I} [2\ell + 3] \]

Raman spectroscopy can be a useful tool in determining rotational properties of molecules. It’s also used to study the vibrational properties of liquids and solids.

10.2: Stimulated Emission and Lasers

Spontaneous emission:
- A molecule in an excited state will decay to a lower energy state and emit a photon, without any stimulus from the outside.

Because the process is probabilistic (QM), the best we can do is calculate the probability that a spontaneous transition will occur; i.e. mean lifetime of an excited state.

If a spectral line has a width ΔE, then Heisenberg’s uncertainty principle gives a lower-bound estimate of the lifetime: \( \Delta t = \frac{\hbar}{2 \Delta E} \).