

Born - Oppenheimer Approximation

When a molecule (such as diatomic) is considered instead of an atom, the problem becomes more complicated and a means of approximation is essentially needed.

Can the vibrational motion be independently treated apart from electronic and rotational motions?

The full Hamiltonian for a molecule which considers the energies of both electrons and nuclei is given by:

$$\hat{H} = T_e + T_n + V_{en}^{(r,R)} + V_{ee}^{(r)} + V_{nn}^{(R)}$$

T : Kinetic energy

V : potential energy

e : electrons

n : nuclei

$\uparrow$
e-n
attraction

$\uparrow$
n-n
repulsion

$\uparrow$
e-e
repulsion

However, electrons move so fast. Thus, the nuclei can be assumed to be fixed when electronic energies are considered:

$$\hat{H}_e = T_e + V_{en} + V_{ee}$$

$$T_n = 0$$

V_{nn} is constant

$$\text{and } \hat{H}_e \Psi_e^{(r,R)} = E_e \Psi_e^{(r,R)}$$

As a result E_e and Ψ_e involve R as a fixed parameter that can be varied to obtain the potential energy curve.

On the other hand, The nuclei see electrons to move very fast that for any position of the nuclei, $\bar{E}_e$ is fixed.

$$\hat{H}_n = T_n + V_{nn} + \bar{E}_e$$

$$\hat{H}_n \Psi_n = \bar{E}_n \Psi_n$$

Since the total wave function can be factorized:

$$\Psi_{\text{tot}} = \Psi_n(R) \Psi_e(r, R)$$

R : internuclear distance

r : electron-nuclear distance

then
$$\bar{E}_{\text{tot}} = \bar{E}_n + \bar{E}_e$$

This means, as a good approximation, we can determine $\bar{E}_e$ and $\bar{E}_n$ separately and then add them to obtain the total energy.

Similarly, since vibrations are about 100 times faster than rotations, we can assume these motions to be separable:

$$\bar{E}_n = \bar{E}_{\text{rot}} + \bar{E}_{\text{vib}}$$

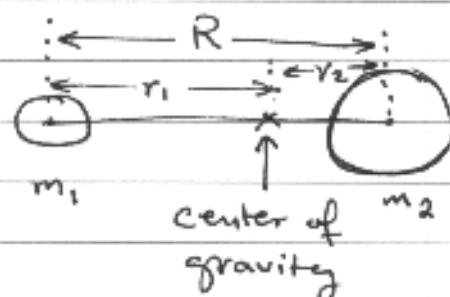
$$\text{as } \Psi_n = \Psi_{\text{rot}} + \Psi_{\text{vib}}$$

A vibration sees no rotation when it occurs.

A rotation cycle has so many vibrations that it sees an average rigid structure.

Molecular Rotations

This is called rigid rotor model, where R distance is fixed.



Moment of inertia, I , about a center of gravity is given by:

$$I = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 + \dots + m_i r_i^2$$

r_i is distance from center of gravity.

Using definition of center of gravity $m_1 r_1 = m_2 r_2$ one can show:

$$r_1 = \frac{m_2}{m_1 + m_2} R \quad ; \quad r_2 = \frac{m_1}{m_1 + m_2} R$$

Substitution gives:

$$I = \frac{m_1 m_2}{m_1 + m_2} R^2 = \underbrace{\mu}_{\text{reduced mass}} R^2$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Schrödinger equation for the diatomic system is given by:

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi$$

$V=0$ for
free rotation

Then,

$$-\frac{\hbar^2}{2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \nabla^2 \Psi = E \Psi$$

$$-\frac{\hbar^2}{2\mu} \nabla^2 \Psi = E \Psi$$

Solution of Schrödinger equation gives:

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad ; \quad J = 0, 1, 2, \dots$$

Rotational QN.

J and l can be used interchangeably to refer to the angular momentum (rotational) quantum numbers.

The angular momentum due to the electron spin is given by: (It is formally called intrinsic angular momentum for the electron)

$$L_s = \sqrt{S(S+1)} \hbar$$

But the electron spin QN can take the value $1/2$ only, i.e. $L_s = \frac{\sqrt{3}}{2} \hbar$

For electron spin space quantization:

$$(L_s)_z = m_s \hbar$$

where $m_s = \pm \frac{1}{2}$ only. (spin-up state & spin-down state)

The resulting fine structure observed in some atomic spectra corresponds to two possibilities for the z -component of the angular momentum.

$$(L_s)_z = \pm \frac{1}{2} \hbar$$

$$\text{As } E_J = \frac{J(J+1) \hbar^2}{2I}$$

we define here the rotational constant, B :

$$B = \frac{\hbar^2}{2I}$$

Then

$$E_J = BJ(J+1)$$

B has energy unit.

$$\text{Also } \bar{E}_J (\text{cm}^{-1}) = \bar{B} J(J+1)$$

where $\bar{B}$ is given in cm^{-1}

This result applies to diatomic molecules as well as linear molecules.

The pure rotational spectra of most diatomic molecules can be observed in the far-ir region.

Selection Rules

$\Delta J = \pm 1$ and molecule must have permanent dipole moment.
 μ must not be zero

for a transition from levels J to $J+1$:

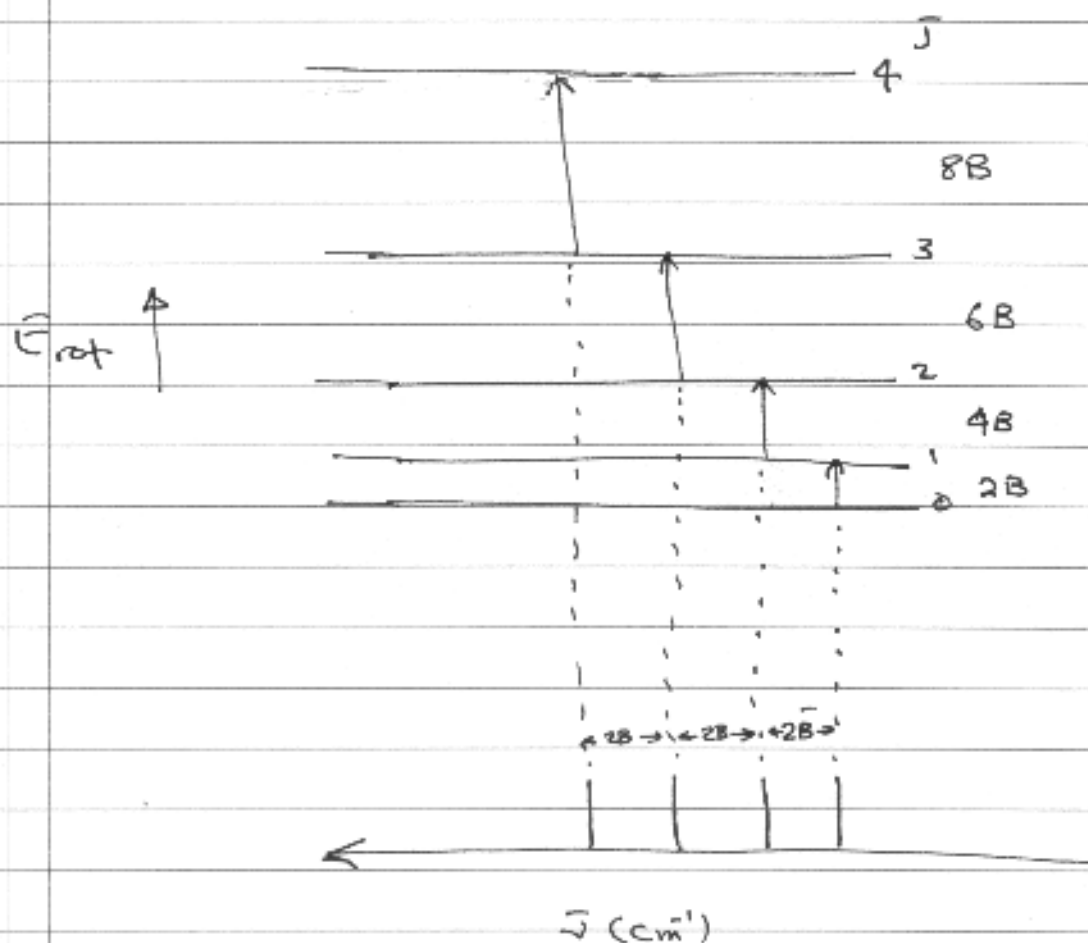
$$\begin{aligned} \Delta \bar{E} &= \bar{E}_{J+1} - \bar{E}_J = \bar{B}(J+1)(J+2) - \bar{B}J(J+1) \\ &= \bar{B}(J^2 + 3J + 2) - \bar{B}(J^2 + J) \\ \Delta \bar{E} &= 2\bar{B}(J+1) \quad ; \quad J = 0, 1, 2, \dots \end{aligned}$$

Transitions take place at:

$$2\bar{B}, 4\bar{B}, 6\bar{B}, 8\bar{B}, \dots$$

for diatomic and linear molecules.

The rotation of a diatomic molecule results in a set of diverging levels as shown below:



$\Delta \nu$ (GHz) for CO

$J'' \rightarrow J'$	$\Delta \nu$ (GHz)
0 $\rightarrow$ 1	115.271
1 $\rightarrow$ 2	115.266
2 $\rightarrow$ 3	115.257
3 $\rightarrow$ 4	115.224