

Born-Oppenheimer Approximation

Atoms and molecules consist of *heavy* nuclei and *light* electrons. Consider (for simplicity) a diatomic molecule (*e.g.* HCl). Clamp/freeze the nuclei in space, a distance r_0 apart. Under this condition, solve the Schroedinger equation for the stationary *electronic* states. This solution gives us the ground electronic state energy $E_0^{\text{elect}}(r_0)$, the first excited electronic state energy $E_1^{\text{elect}}(r_0)$, etc. Now repeat this procedure for a distance r_1, r_2, \dots “connect the dots” to obtain the potential energy surfaces. Consider being at r_0 with clamped/frozen nuclei, and being in the ground electronic state. Unclamp/unfreeze the nuclei, and suppose r begins to increase and is now $r = r_1$. What is the energy of the electrons (which interact, of course, with the nuclei)? The Born-Oppenheimer, or adiabatic, approximation says that at $r = r_1$, the electrons behave as if the nuclei were always at $r = r_1$ (frozen). In other words, the electrons respond instantaneously (adapt immediately) to changes in r . The electrons “shadow” the nuclei. Since the electrons “track” the nuclei, we only need to figure out how the nuclei behave, and then we will know where the electrons are (in the Born-Oppenheimer picture). E^{elect} *also* includes the potential energy between the (clamped) nuclei. Hence E^{elect} is the potential energy function under which the nuclei move. Whence to find the stationary nuclear states and energies, we should solve

$$\sum_{i=1}^N - \underbrace{\frac{\hbar^2}{2m_i} \nabla_i^2 \psi}_{\text{kinetic energy}} + \underbrace{E^{\text{elect}} \psi}_{\text{potential energy}} = \underbrace{E}_{\text{eigenvalues}} \underbrace{\psi}_{\text{eigenfunctions}} \quad \text{for } N \text{ nuclei} \quad (1)$$

For a diatomic this equation becomes a central force problem. Why? because $E^{\text{elect}} = E^{\text{elect}}(r)$ where $r =$ internuclear separation. The energy E for a central force problem is obtained by solving the *radial* equation after changing to spherical polar coordinates. This looks like (using the reduced mass $1/\mu = 1/M_1 + 1/M_2$)

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \ell(\ell+1)R \right] + E^{\text{elect}}(r)R = ER \quad (2)$$

To proceed, define $F(r) = rR(r)$. Then

$$\frac{dR}{dr} = \frac{d}{dr} \left(\frac{F}{r} \right) = \frac{1}{r} \frac{dF}{dr} - \frac{F}{r^2} \quad (3)$$

and

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = \frac{d}{dr} \left(r \frac{dF}{dr} - F \right) = r \frac{d^2 F}{dr^2} + \frac{dF}{dr} - \frac{dF}{dr} = r \frac{d^2 F}{dr^2} \quad (4)$$

We get

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \left[r \frac{d^2 F}{dr^2} - \ell(\ell+1) \frac{F}{r} \right] + E^{\text{elect}}(r) \frac{F}{r} = E \frac{F}{r} \quad (5)$$

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + E^{\text{elect}}(r) \right] F(r) = EF(r) \quad (6)$$

This energy E is due to *vibrational* and rotational motion. For no rotation (pure vibration) we have $\ell = 0$ to give

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + E^{\text{elect}}(r) \right] F(r) = EF(r) \quad (7)$$

We will now perform a Taylor series expansion of $E^{\text{elect}}(r)$ about its minimum and truncate at 2nd order.

$$E^{\text{elect}}(r) \approx E^{\text{elect}}(r_0) + \frac{1}{2}(r - r_0)^2 \left. \frac{d^2 E^{\text{elect}}}{dr^2} \right|_{r_0} \quad (8)$$

because

$$\left. \frac{dE^{\text{elect}}}{dr} \right|_{r_0} = 0 \quad (9)$$

Let $x = r - r_0$ and

$$\mu\omega_0^2 = \left. \frac{d^2 E^{\text{elect}}}{dr^2} \right|_{r_0} \quad (10)$$

to give

$$[E - E^{\text{elect}}(r_0)] G(x) = \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu\omega_0^2 x^2 \right] G(x) \quad (11)$$

where $G(x) = F(x + r_0)$

This is the harmonic oscillator equation (1d) we solved earlier!

$$E_n = E^{\text{elect}}(r_0) + \hbar\omega_0 \left(n + \frac{1}{2} \right) \quad , \quad n \geq 0 \in \mathbb{Z} \quad (12)$$

Consider now a rigid rotor, namely where $\ell = 0$ but the vibrational motion produces only small displacements: approximate $r = r_0$ in the term

$$\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \quad (13)$$

We are looking to solve

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2} + E^{\text{elect}}(r_0) + \frac{1}{2}(r-r_0)^2 \frac{d^2 E^{\text{elect}}}{dr^2} \Big|_{r_0} \right) F = EF \quad (14)$$

which yields

$$E_{n\ell} = E^{\text{elect}}(r_0) + \hbar\omega_0\left(n + \frac{1}{2}\right) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2} \quad (15)$$

in the rigid rotor harmonic oscillator (RRHO) approximation.

Selection Rules

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. The underlying idea is that, for a molecule to be able to interact with the electromagnetic field and absorb or emit a photon of frequency ω , it must possess, at least transiently, a dipole oscillating at that frequency ω . For emission and absorption spectra (Raman is different) we can say that for *rotational* transitions, there is no spectrum unless the molecule has a permanent dipole moment. That is, the molecule must be polar. A polar molecule appears to possess a fluctuating dipole when rotating but a nonpolar molecule does not.

For *vibrational* transitions, there is no emission/absorption unless the dipole moment of the molecule *changes* during the vibrational motion. The idea is that the molecule can shake the electromagnetic field into oscillation if its dipole changes as it vibrates.

Note 1: The permanent dipole moment of the molecule can be zero as long as it changes during vibration.

Note 2: Some vibrational motions do *not* affect the molecule's dipole moment. Such vibrations are called *inactive* or *dark*.

Now let us specialize to the case of the rigid rotor harmonic oscillator model of a diatomic molecule.

Consider the electric field to be along the z -axis (in the laboratory frame). Transitions between states 1 and 2 occur if

$$(\mu_z)_{12} \equiv \int \psi_2^* \hat{\mu}_z \psi_1 \quad \text{is not zero} \quad (16)$$

where μ_z is the z -component of the molecular dipole moment.

Rigid rotor selection rule is $\Delta\ell = \pm 1$

The rigid rotor wavefunctions are the spherical harmonics $\mathcal{Y}_{\ell m}(\theta, \phi)$ since r is not changing. Transitions between any two states are allowed if

$$(\mu_z)^{\ell, m, \ell', m'} = \int_0^{2\pi} \int_0^\pi \mathcal{Y}_{\ell' m'}^*(\theta, \phi) \mu_z \mathcal{Y}_{\ell m}(\theta, \phi) \sin \theta d\theta d\phi \quad (17)$$

is non-zero. $\mu_z = \mu \cos \theta$, giving

$$(\mu_z)^{\ell, m, \ell', m'} = \mu \int_0^{2\pi} \int_0^\pi \mathcal{Y}_{\ell' m'}^* \mathcal{Y}_{\ell m} \cos \theta \sin \theta d\theta d\phi \quad (18)$$

μ must clearly be non-zero, proving our claim that a molecule must have a permanent dipole moment to have a rotational spectrum.

When is this expression non-zero for $\mu \neq 0$? We need to use the properties of the spherical harmonics. The math is straightforward, and gives

$$m = m' \quad \text{and} \quad \ell' = \ell + 1 \quad \text{or} \quad \ell' = \ell - 1 \quad (19)$$

Another way to express this is $\Delta m = 0, \Delta \ell = \pm 1$

harmonic oscillator selection rule is $\Delta n = \pm 1$

Wavefunctions are

$$\psi_n(x) = (x^n + Ax^{n-2} + Bx^{n-4} + \dots)e^{-\alpha x^2}, \quad n \geq 0 \in \mathcal{Z} \quad (20)$$

For a transition between n and n' we need to look at

$$(\mu_z)_{nn'} = \int_{-\infty}^{\infty} \psi_{n'}^*(x) \mu_z \psi_n(x) dx \quad (21)$$

To proceed, we Taylor expand μ_z about the equilibrium internuclear separation

$$\mu_z = \mu_0 + \left. \frac{d\mu}{dx} \right|_0 x + \dots \quad (22)$$

where $x = 0$ is the equilibrium separation. We truncate at first order, giving

$$(\mu_z)_{nn'} = \mu_0 \int_{-\infty}^{\infty} \psi_{n'}^* \psi_n dx + \left. \frac{d\mu}{dx} \right|_0 \int_{-\infty}^{\infty} \psi_{n'}^* x \psi_n dx \quad (23)$$

The first term is 0 unless $n' = n$ by orthogonality, but $n' = n$ is **not** a transition (no change). Thus, the permanent dipole moment plays no role in vibrational spectroscopy. Note: since real molecules are not harmonic oscillators, we should correct this to read: the permanent dipole moment plays a negligible role in vibrational spectroscopy.

The second term is non-zero for $n' = n + 1$ or $n' = n - 1$, namely if $\Delta n = \pm 1$. This can be proved by using the harmonic oscillator wavefunctions. It is also necessary that $\left. \frac{d\mu}{dx} \right|_0 \neq 0$. This derivative is zero for homonuclear diatomics as well as for certain vibrations of polyatomic molecules (eg. symmetric stretch of CO_2 and CH_4). For polyatomics, the selection rules can be derived from group theory, which we will not cover.

Rigid Rotor Harmonic Oscillator (RRHO) Spectroscopy

The infrared absorption spectrum of HCl can be analyzed to gain information about both rotations and vibrations of the molecule. The absorption lines shown involve transitions from the ground state $n = 0$ to the first excited vibrational state of HCl, $n = 1$. The rotational quantum number must change by $\ell = \pm 1$ during such a vibrational transition according to the RRHO selection rules. This is what we observe experimentally.

The “missing” line in the center would correspond to the $n = 0$ to $n = 1$ transition *without* any change in ℓ . What *is* observed is a closely spaced series of lines going upwards and downwards from the missing pure vibrational line. The splitting of the lines shows the difference in rotational inertia of the two chlorine isotopes ^{35}Cl and ^{37}Cl .

Bond force constant for HCl

Approximate the $n = 0$ to $n = 1$ vibrational transition by the harmonic oscillator model.

$$E_0 = \frac{1}{2}\hbar\omega \quad \text{and} \quad E_1 = \frac{3}{2}\hbar\omega \quad \Rightarrow \quad \Delta E = \hbar\omega \quad (24)$$

and $\omega = \sqrt{k/\mu}$ where $\mu = m_H m_{Cl} / (m_H + m_{Cl})$ is the reduced mass. *But* this is the “missing” line in the infrared absorption spectrum of HCl, so what can we do? We can use the midpoint between the $n = 0, \ell = 1 \rightarrow n = 1, \ell = 0$ and $n = 0, \ell = 0 \rightarrow n = 1, \ell = 1$ transitions. This assumes that the first excited vibrational state does not stretch the bond. We get $k \approx 480 \text{ N/m} = 480 \text{ J/m}^2$.

Bond length of HCl

The rigid rotor energy levels are

$$E_\ell = \frac{\ell(\ell + 1)\hbar^2}{2I} \quad (25)$$

where $I = \mu r^2$ is the moment of inertia.

$$\Delta E_{\ell=1 \rightarrow \ell=0} = \frac{1(2)\hbar^2}{2I} - \frac{0(1)\hbar^2}{2I} = \frac{2\hbar^2}{2I} \quad (26)$$

Twice this is $2\Delta E = 4\hbar^2/(2I)$. This gives $r \approx 0.13 \text{ nm} = 1.3 \text{ \AA}$.

Another way to measure bond lengths is to do pure rotational (microwave) spectroscopy.

From experiment, one can calculate the following information:

cm^{-1}	83.03	103.73	124.3	145.03	165.51	185.86	206.38	226.5
$\ell \rightarrow \ell + 1$	$3 \rightarrow 4$	$4 \rightarrow 5$	$5 \rightarrow 6$	$6 \rightarrow 7$	$7 \rightarrow 8$	$8 \rightarrow 9$	$9 \rightarrow 10$	$10 \rightarrow 11$
r (nm)	0.1288	0.1288	0.1289	0.1289	0.1290	0.1291	0.1292	0.1293