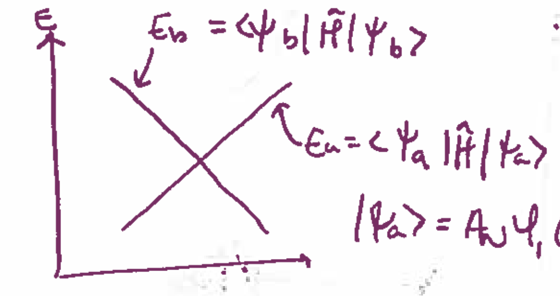
Final lecture

Chemical rxn: $\Psi = \sum c_i(R)\Psi_i$, c_i are continuous fn.



$$\begin{matrix} E_a & \langle\Psi_a|\hat{H}|\Psi_b\rangle \\ \langle\Psi_b|\hat{H}|\Psi_a\rangle & E_b \end{matrix}$$

$|\Psi_a\rangle = A_N \varphi_1(1)\ldots\varphi_N(N)$ diagonalize $\Rightarrow E_1, E_2$
Ψ_1, Ψ_2

Using spectroscopy to measure properties of their molecular surfaces

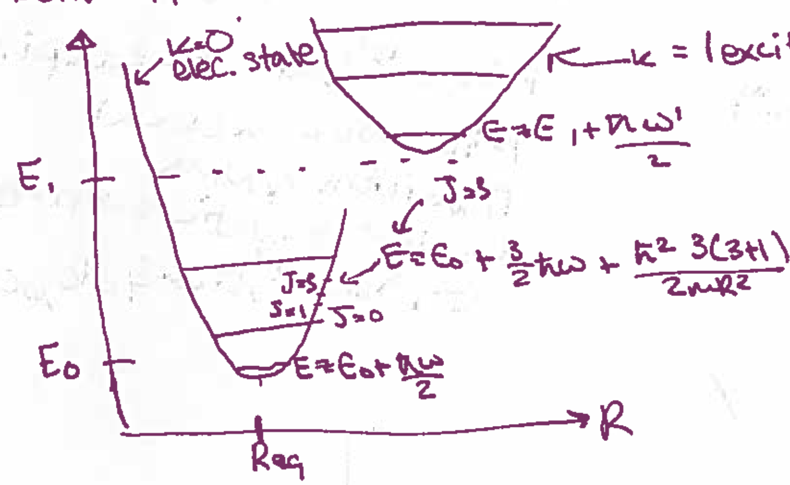
$E_{total} \approx E_{electronic} + E_{vibrational} + E_{rotational} + E_{spin} \ldots$

$E_k \quad + \sum \hbar\omega_i(n_i + 1/2) + \frac{\hat{L}^2}{2\mu R^2} - \mu M_s \cdot B_z$ ← external field

$\Psi_{total} \approx \Psi_k(\vec{r}_i) \cdot X_{vib}(R_n) \cdot Y_{lm}(\theta,\varphi) \cdot |I\tfrac{1}{2}\rangle$

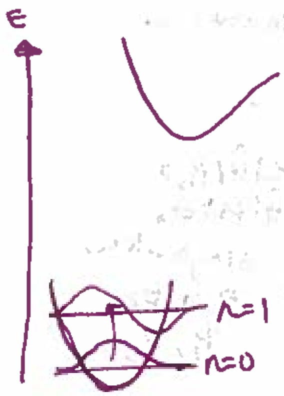
$A_N\, \varphi_1(1)\ldots\varphi_N(N)$ $\quad X_1(R_1)\ldots X_N(R_N)$ $\quad P_{lm}(\theta)\cdot e^{im\varphi}$

Born-Oppenheimer = solve for Ψ

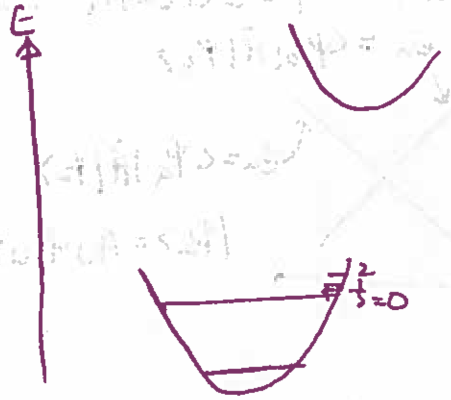


Different spectroscopies

UV-vis
$E \sim 20{,}000\ cm^{-1}$, 200 kJ/mol



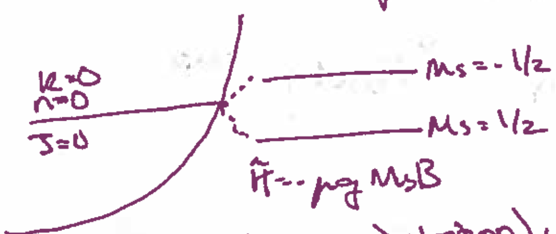
IR
(vibrational)
$E \sim 2000\ cm^{-1}$, 20 kJ/mole



$E \sim 20\ cm^{-1}$, 200 J/mol

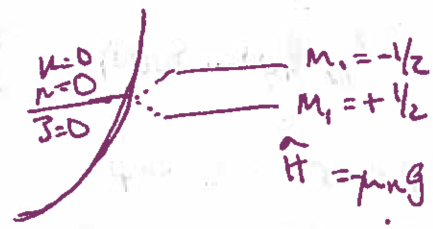
Spectroscopy on smaller scales than rotational

If you put the molecule in a magnetic field B, the electron and nuclear spin energies will split depending on whether the spin is aligned with the magnetic field or not



$\hat{H} = -\mu_B g M_S B$

If $S \neq 0$ (unpaired electron) we can do EPR spectroscopy ("Electron Paramagnetic Resonance")
$E \sim 2\ cm^{-1}$, 20 J/mole



$\hat{H} = -\mu_n g M_I B$

Protons ^{13}C, also have a spin $I = 1/2$, so we can look at transitions by NMR (nuclear magnetic resonance)
$E \sim .02\ cm^{-1}$, 0.2 kJ/mole, 60 MH