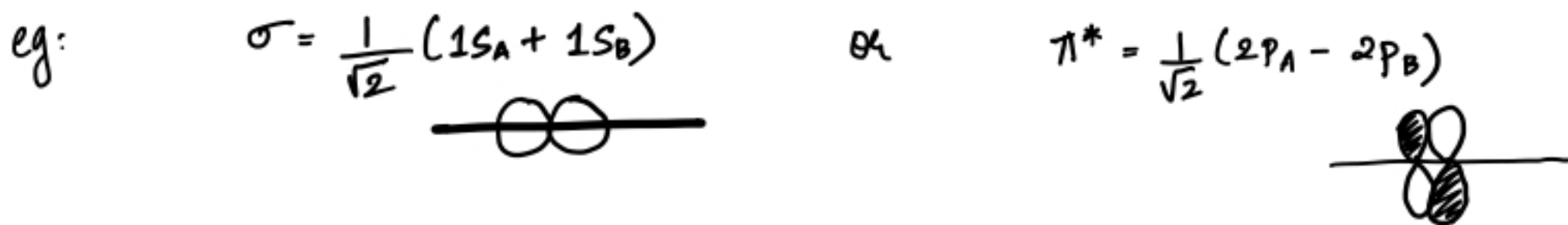


02/18 Last time Building the wavefunction for polyatomic molecules

we want to move from an electron to a multi electron molecule

- 1) For single e^- : atomic functions can be added to make molecular wavefunctions = "orbitals"
- ↳ pretty accurate when the 2 atoms are far apart. Even when they are close, the solution is approximately the one obtained from solving all the math
- } quantum superposition states



- 2) For multiple electrons: 1-electron orbitals are multiplied together to get the complete molecular wavefunction.

$$\Psi_{\text{Hartree}}(x_1, x_2, \dots) = \Psi_1(x_1) \cdot \Psi_2(x_2) \cdot \dots \text{ includes } x, y, z, \text{ spin angle.}$$

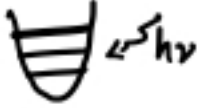
- 3) Postulate 4 requires $\Psi(x_1, x_2, \dots) = -\Psi(x_2, x_1, \dots)$
- ↻
flip 2 e^-

This can be done by permuting all e^- coordinates with a (-) sign for every permutation:

$$\Psi_{\text{Hartree-Fock}}(x_1, x_2, \dots) = \frac{1}{\sqrt{N!}} \left\{ \underbrace{\left(\Psi_1(x_1) \cdot \Psi_2(x_2) \cdot \dots - \Psi_1(x_2) \cdot \Psi_2(x_1) \cdot \dots \right)}_{(1s_A(i) + 1s_B(i))} \right\}$$

→ QM super position states makes solving Schrodinger equation easy (to a very close approximation)

Today: Potential Surfaces of molecules & Spectroscopy

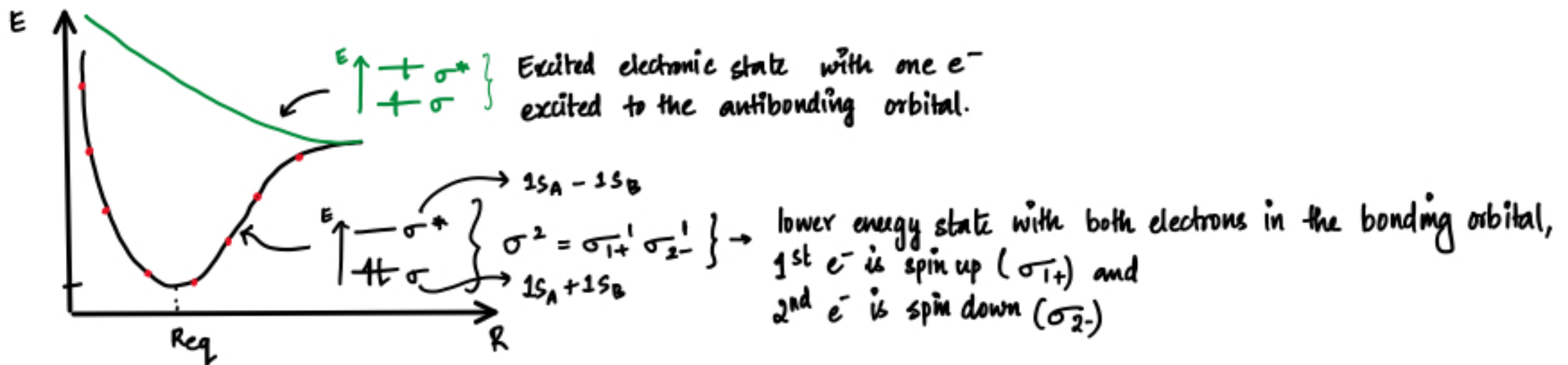
Recall: Harmonic oscillator  $E \sim h\nu$ If we shine light, with energy matching the energy gap, molecules can be excited to higher energy levels

Q: Can we detect alien life from our arm chair?

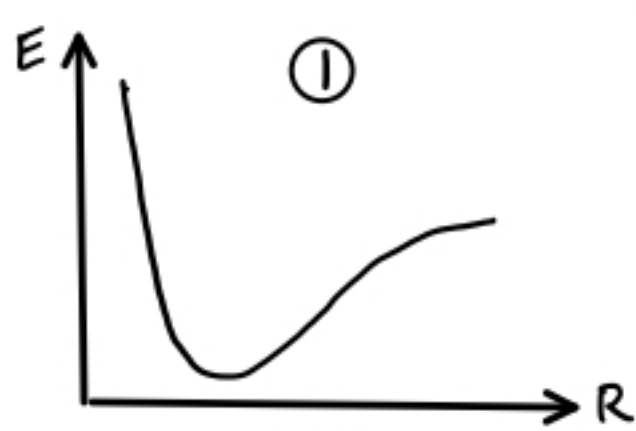
┌ An atmosphere with oxygen & methane ⇒ clue that the planet has some life form that produces enough methane to be detected ┘

Potential Surface = energy as a function of (bond distance, angle, etc)
↳ $E(R)$

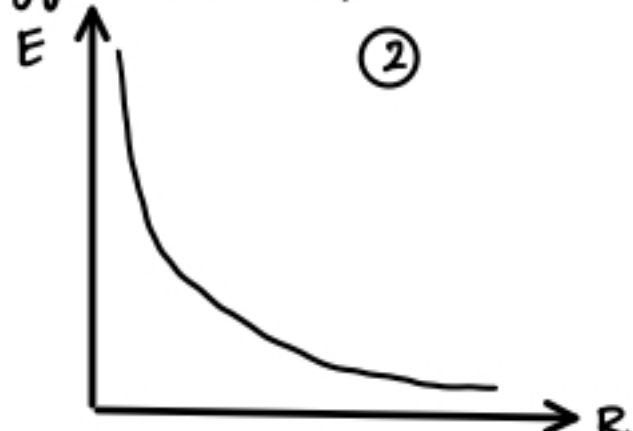
Eg: H_2 molecule:



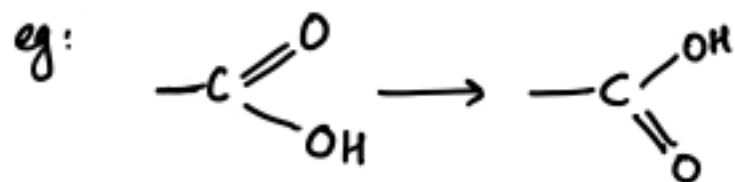
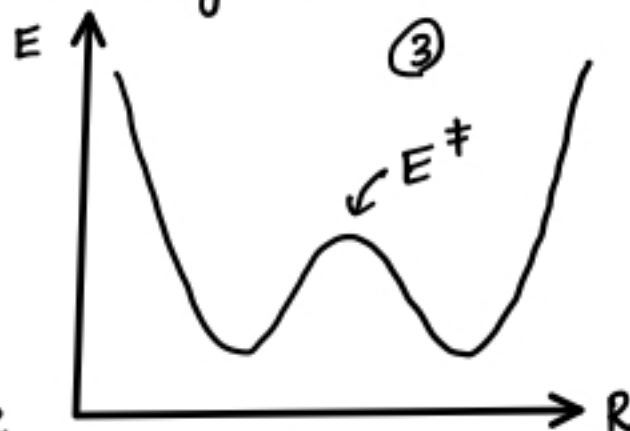
→ Almost all potential energy surfaces fall into three categories:



eg: H_2 bonding



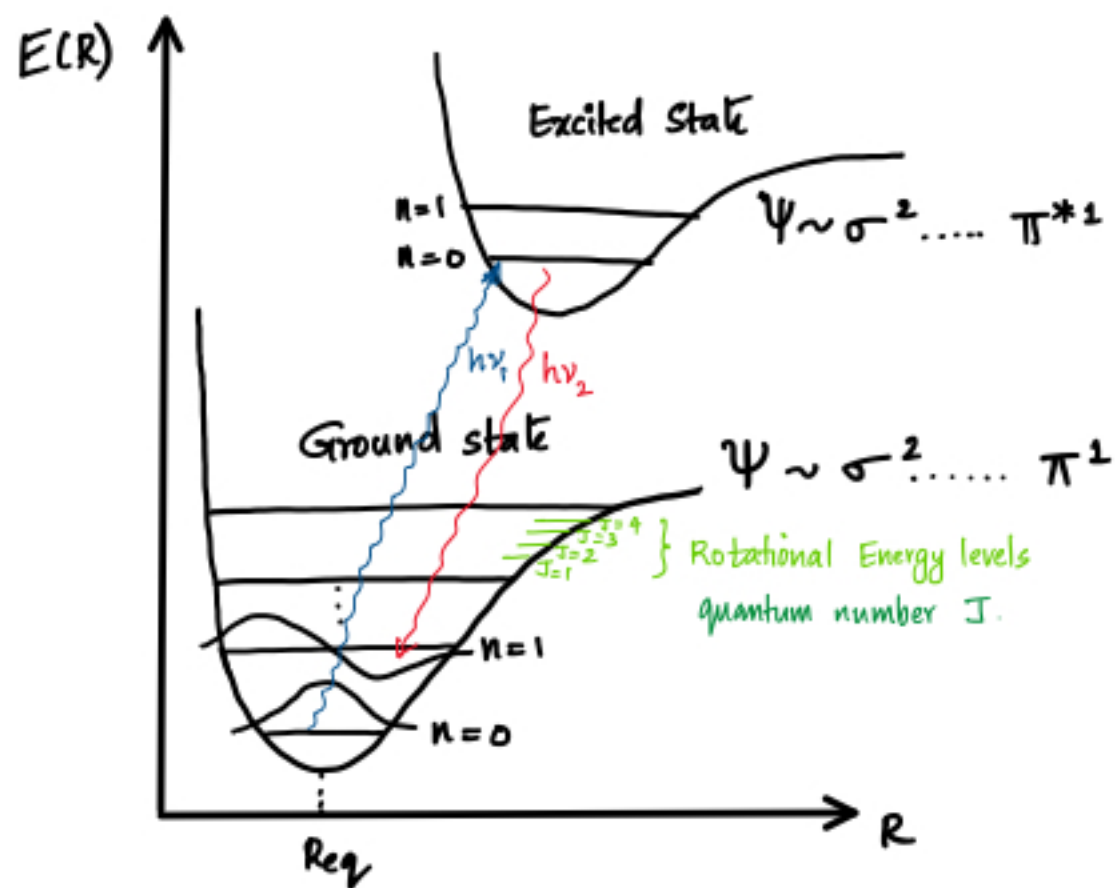
eg: H_2 antibonding



③ is very important and commonly observed in chemistry / chemical reactions. E^\ddagger : Activation barrier

→ Multi electron molecule potential surfaces:

Molecular ground state: molecule is in a particular vibrational energy level, rotational energy level. $\left. \begin{matrix} (n) \\ (J) \end{matrix} \right\}$ But the atoms are close enough so that the electrons are shared between the nuclei

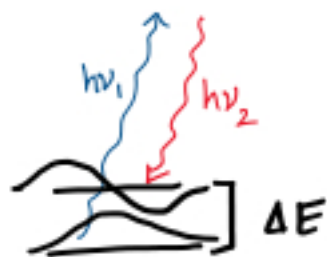


when we excite a molecule, with light of energy $h\nu$, it goes to an excited molecular state, where the excited bond is weaker: here, $\pi \rightarrow \pi^*$. Everything else in the wavefunction Ψ remains the same except for π^1 .

HWK problem:

$$\nu \lambda = c \Rightarrow \lambda = c/\nu$$

When a photon is emitted from an excited molecule, it can go down to a level in the ground state. (↯)



$$\nu_2 < \nu_1$$

$$\Delta E = h(\nu_2 - \nu_1) = h\nu \quad (\lambda = c/\nu)$$

unique for every
molecule

$$\Delta E = \hbar \omega = \hbar \sqrt{\frac{k}{m}}$$