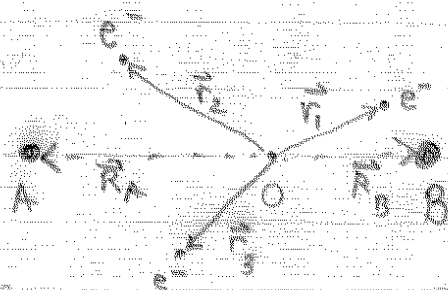


## Physics 531, Lecture 16, Introduction to Molecules

The heart of chemistry is the binding of atoms into molecules. The physical description of the structure of molecules is very complex even for the simplest case, the diatomic (or "dimer"). In this course we will focus on diatomics and only briefly touch on polyatomic molecules.

The basic system: Two nuclei and  $N$ -electrons



We take the origin at the center of mass of the nuclei (with the electrons ignored)

With O fixed, the Hamiltonian (ignoring spins)

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{eN}$$

$$\hat{T}_N = \frac{\vec{p}^2}{2\mu} \left( \frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \right), \quad \hat{T}_e = \sum_i \frac{\vec{p}_i^2}{2m_e}$$

$$\hat{V}_{NN} = \frac{Z_A Z_B e^2}{R}, \quad \hat{V}_{ee} = \sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$\hat{V}_{eN} = - \sum_i \left( \frac{Z_A e^2}{|\vec{r}_i - \vec{R}_A|} + \frac{Z_B e^2}{|\vec{r}_i - \vec{R}_B|} \right)$$

This is a complex many-body problem and hopeless to solve exactly. Moreover, we have a set of disparate particles (nuclei and electrons), so a simple mean-field description won't cut it. We can, however, use the disparity of the masses to make some headway in the analysis due to separation of time scales. The nuclei, being thousands of times heavier than the electrons, are very sluggish compared to the speedy electrons. Thus, to first approximation, the nuclei can be considered as fixed. As the nuclei move, the electrons adjust essentially instantaneously. The electron dynamics are thus "slaved" to the nuclear motion and adiabatically follow. The classical description involves "adiabatic elimination" of the fast variables. The quantum description for molecules is known as the "Born-Oppenheimer approximation" and is the starting point in any description of molecular structure. (More to come)

### Basic Energies and Spectra

Given the separation of time scales we have a separation of energies that characterize the spectrum associated with absorption and emission of molecules.

Recall units:  $1\text{eV} = 8065\text{ cm}^{-1}$ ,  $1\text{ cm}^{-1} \approx 30\text{ GHz}$   
 $1\text{ Hartree} = 219,474\text{ cm}^{-1}$

• Electronic motion:

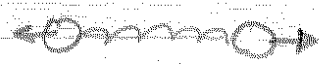
Electron motion confined to distance  $a \sim 1 \text{ \AA}$  (molecular size)

$$\Rightarrow E_e \sim \frac{\hbar^2}{ma^2} \sim \text{few eV} \cong \text{visible} \rightarrow \text{UV}$$

• Nuclear motion:

The nuclei move in the field of the fast electrons. There are two kind of motion

- Vibration



- Rotation

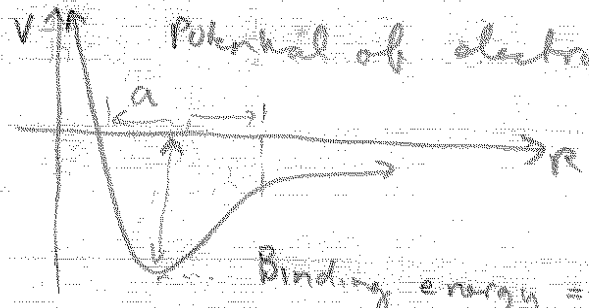


$K$  = nuclear rotation ang. mom.

$I$  = moment of inertia

These energy scales:

- Vibration



Potential of electrons in which nuclei move

$$M \omega_{vib}^2 a^2 = V_{bind} \sim \frac{\hbar^2}{ma^2}$$

$$\Rightarrow \hbar \omega_{vib} \sim \sqrt{\frac{\hbar}{M a^2} \frac{\hbar}{ma^2}} \sim \sqrt{\frac{m}{M}} E_e$$

with  $\frac{m}{M} \sim 10^{-4}$

$$\frac{\hbar \omega_{vib}}{E_e} \sim 10^{-2}$$

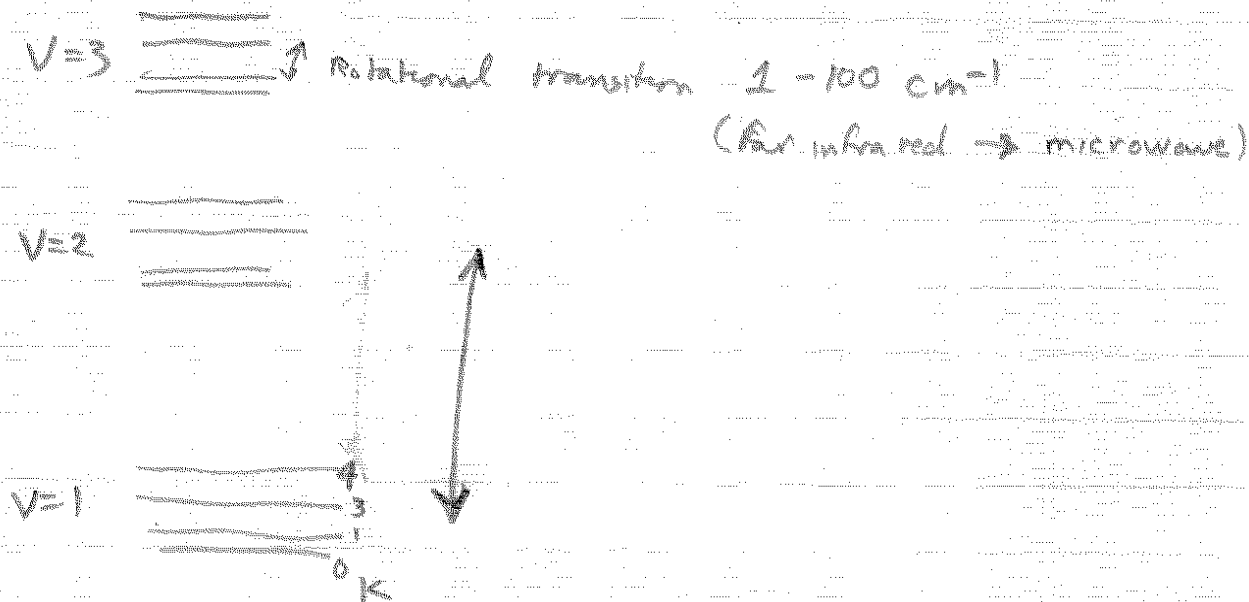
$$\Rightarrow \hbar \omega_{vib} \sim \text{Infrared}$$

- Rotation

$$E_{rot} \sim \frac{K^2}{2I} \cong \frac{\hbar^2}{2(Ma^2)} = \frac{\hbar^2}{Ma^2} = \frac{m}{M} E_e$$

$$\Rightarrow E_{rot} \sim \text{Microwave (for infra-red)}$$

Spectra: For given electronic state  $\Rightarrow$  Rovibrational sequence



### Adiabatic decomposition

To get a quantitative description we proceed as follows.

We define an adiabatic basis of electronic states with the nuclei at some fixed separation  $\vec{R}$ .

These are eigenstates of the Hamiltonian with the nuclear kinetic energy set to zero, and  $\vec{R}$  as a parameter.

$$\underbrace{\left( \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \frac{\sum_i \hbar^2 \vec{e}_i^2}{2m_i} \right)}_{\hat{H}_0} \underbrace{\Phi(\{\vec{e}_i\}, \vec{R})}_{\vec{R} \text{ quantized}} = E_g(\vec{R}) \underbrace{\Phi_g(\{\vec{e}_i\}, \vec{R})}_g$$

Note: the adiabatic energies depend only on  $|\vec{R}| = R$  in the absence of an external field.

For a fixed  $\vec{R}$  these form an orthonormal set

$$\langle \Phi_f(\vec{R}) | \Phi_p(\vec{R}) \rangle = \int d^3r_1 \dots d^3r_n \Phi_f^*(\{\vec{r}_i, \vec{R}\}) \Phi_p(\{\vec{r}_i, \vec{R}\}) = \delta_{fp}$$

Given this completeness, the exact wavefunction for the molecule with a fixed center of mass

$$\Psi(\vec{R}, \{\vec{r}_i\}) = \sum_f \psi_f(\vec{R}) \Phi_f(\{\vec{r}_i, \vec{R}\})$$

Wave function for nuclear motion when electrons in state  $f$  electron wave function parameterised by nuclear distance  $\vec{R}$

The full Schrödinger equation

$$\hat{H}|\Psi\rangle = (\hat{T}_N + \hat{H}_e)|\Psi\rangle = E|\Psi\rangle$$

Now project onto some electronic state  $\langle \Phi_s(\vec{R}) |$

$$\Rightarrow \sum_f \left( \langle \Phi_s(\vec{R}) | \hat{T}_N | \Phi_f(\vec{R}) \rangle \psi_f(\vec{R}) \right) + E_f(\vec{R}) \psi_f(\vec{R}) = E \psi_f(\vec{R})$$

We now make the adiabatic or Born-Oppenheimer approx. The assumption is that  $|\Phi_f(\vec{R})\rangle$  is a very ~~weak~~ slow function of  $\vec{R}$  ( $\vec{R}$  effectively constant to define electronic state)

$$\Rightarrow \langle \Phi_s(\vec{R}) | \hat{T}_N | \Phi_f(\vec{R}) \rangle \approx \delta_{sf} \hat{T}_N$$

(Next Page)

Thus we arrive at an effective Schrödinger equation for the nuclear motion

$$\left( \hat{T}_N + E_g(R) \right) \Psi_g(\vec{R}) = E \Psi_g(\vec{R})$$

The function  $E_g(R)$  is known as the Born-Oppenheimer potential for the nuclei with electrons in state  $|\Phi_g\rangle$ .

$$E_g(R) = \langle \Phi_g(\vec{R}) | \hat{T}_e + \hat{V}_{ee} + V_{eN}(\vec{R}) + V_{ee}(\vec{R}) | \Phi_g(\vec{R}) \rangle$$

The upshot of the B-O approximation is to write

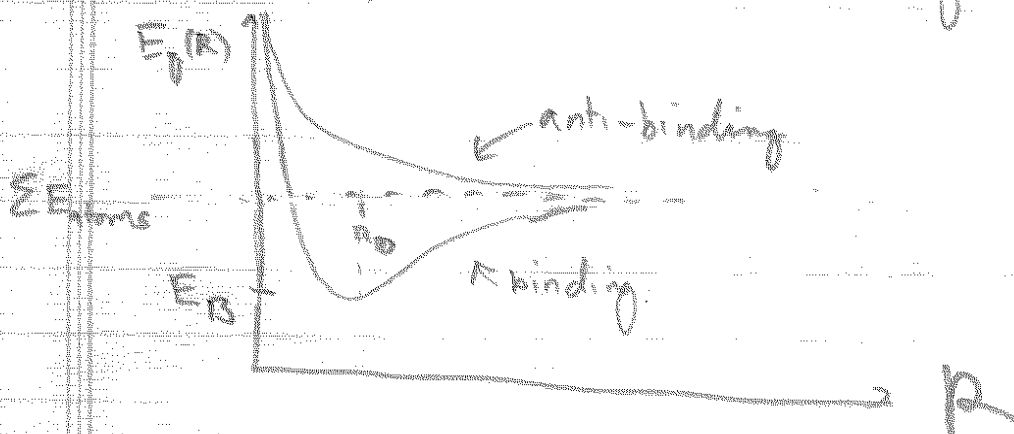
$$\Psi(\{\vec{r}_i, \vec{R}\}) \approx \Psi(\vec{R}) \Phi(\{\vec{r}_i, \vec{R}\})$$

where  $\Phi(\{\vec{r}_i, \vec{R}\})$  is the electronic eigenstate with nuclear motion fixed

Qualitatively  $E_g(R) \rightarrow \infty$  as  $R \rightarrow 0$  since  $\frac{23}{R}$  blows up

$E_g(R) \rightarrow \sum E_{\text{atoms}}$  as  $R \rightarrow \infty$  since cross terms vanish

Two cases, bind vs anti-binding configurations



## Electronic Structure of Diatomic Molecules

The B-O potentials have quantum #'s  $q$  that are determined by symmetries of the electronic Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \left( \frac{Z_1 Z_2 e^2}{R} \right) \leftarrow \text{"constant"}$$

For fixed nuclear axis  $\vec{R}$ , the potential seen by the electrons is not central. The Hamiltonian is not invariant w.r.t. to arbitrary rotations of the electrons about  $x, y, z$ . The internuclear axis defines a special direction. We take this body-fixed axis as  $z$ . Then  $[\hat{L}_z, \hat{H}_e] = 0$ . So we can find simultaneous eigenstates

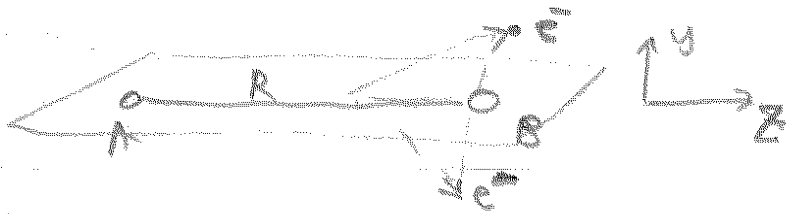
$$\hat{L}_z |\Phi_q\rangle = M_L |\Phi_q\rangle \quad - M_L = 0, \pm 1, \pm 2$$

Since the energy depends only on  $|\Lambda|$  depends only on  $|M_L| \equiv \Lambda \Rightarrow$  Double degeneracy  $\Lambda \neq 0$

Notation: In analogy, we define B-O potential with the Greek equivalent of atom total  $L$  (i.e. S, P, D, F)

$\Lambda$	0	1	2	3
	↓	↓	↓	↓
Code	$\Sigma$	$\Pi$	$\Delta$	$\Phi$

Reflection symmetry  $\hat{R}_y$ ,  $[\hat{R}_y, \hat{H}_e] = 0$



$$y \rightarrow -y$$

Under  $R_y$ :  $\hat{R}_y^\dagger \hat{L}_z \hat{R}_y = -\hat{L}_z$

→ States with  $M_L$  and  $-M_L$  have same energy  
(Wave functions  $e^{\pm iM_L \phi}$ )

Can specify  $\cos \Delta \phi$ ,  $\sin \Delta \phi$  instead  
to uniquely specify  $\pm$  q-number of  $\hat{R}_y$

For  $\Lambda=0$  only one state. Must be  $\pm$  or  
minus to be simultaneous eigenstate of  
 $\hat{H}_e, \hat{L}_z, \hat{R}_y$ , denote  $\Sigma^+$  or  $\Sigma^-$

### Parity

For homonuclear ( $A=B$ ), e.g.  $H_2, O_2$

Origin is center of symmetry  $\Rightarrow \hat{H}_e$  invariant  
under  $\vec{r}_i \rightarrow -\vec{r}_i$ : Parity. Define

g = "gerade" (even)      u = "ungerade" (odd)

e.g.  $\Sigma_g^+$   $\Pi_u$  etc.



Spin:

Total electron spin  $S$ . Effects Pauli principle

Without magnetic spin: Denote B-O potential

$$2S+1 \Lambda$$

e.g.  $1 \Sigma_g^+$

(Singlet  $S=0$   
 $M_L=0$

even parity, + reflection)