MOLECULES

BONDS

- Ionic: closed shell (+) or open shell (-)
- Covalent: both open shells neutral ("share" e)
- Other (skip): van der Waals (He-He)…Hydrogen bonds (in DNA, proteins, etc)

ENERGY LEVELS

- electronic
- vibrational
- rotational
Ionic Bonds - NaCl

• First approximation. Both atoms are ions (no electron sharing) and bond due to EM force between two charged bodies

\[ \text{Na}^+ \iff \text{bond} \implies \text{Cl}^- \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Valence</th>
<th>Ionization</th>
<th>( \sim \text{eff}Z )</th>
<th>Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>3s</td>
<td>5.1 eV</td>
<td>1.8</td>
<td>0.17 nm</td>
</tr>
<tr>
<td>Cl</td>
<td>3s^23p^5</td>
<td>13 eV</td>
<td>2.9</td>
<td>0.07 nm</td>
</tr>
<tr>
<td>Ar</td>
<td>3s^23p^6</td>
<td>16 eV</td>
<td>3.3</td>
<td>0.07 nm</td>
</tr>
</tbody>
</table>

\[
E = \frac{-13.6 \ Z_{\text{eff}}^2}{n^2}
\]

• Ar more tightly bound than Cl. But Cl\(^-\) “looks” like Ar and more tightly bound then neutral Cl Has effective Z \( \sim 3 \)

\[
E(\text{Cl}^-) = E(\text{Cl}^0) - 3.8eV
\]

\[
\text{need} : (5.1 - 3.8)eV \quad \text{Na} + \text{Cl} \rightarrow \text{Na}^+ + \text{Cl}^-
\]
Atomic Properties

Atomic Radii

0.1 nm

Ionization Energy (first electron)

10 eV

TABLE 8.3 IONIZATION ENERGIES (IN eV) OF NEUTRAL ATOMS OF SOME ELEMENTS

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>13.60</td>
</tr>
<tr>
<td>He</td>
<td>24.59</td>
</tr>
<tr>
<td>Li</td>
<td>5.39</td>
</tr>
<tr>
<td>Be</td>
<td>9.32</td>
</tr>
<tr>
<td>Ne</td>
<td>21.56</td>
</tr>
<tr>
<td>Na</td>
<td>5.14</td>
</tr>
<tr>
<td>Ar</td>
<td>15.76</td>
</tr>
<tr>
<td>K</td>
<td>4.34</td>
</tr>
<tr>
<td>Cu</td>
<td>7.72</td>
</tr>
<tr>
<td>Kr</td>
<td>14.00</td>
</tr>
<tr>
<td>Rb</td>
<td>4.18</td>
</tr>
<tr>
<td>Au</td>
<td>9.22</td>
</tr>
</tbody>
</table>
NaCl potential vs R

Pauli repulsion at small R

→ shielding of nuclei becomes incomplete

→ electrons’ wave functions overlap and electrons forced to higher states (2p → 3s)
Ionic Bonds - KCl

• another example. What is the energy required to dissociate a KCl molecule into K atom and Cl atom given

• Ionization energy K = 4.34 eV
• electron affinity Cl = 3.82 eV
• separation distance R = 2.79 angstroms
• attractive EM potential for 2.79 Å = -5.16 eV

→ takes 5.16 eV to separate K+ and Cl- ions to infinity

→ takes 3.82 eV to pull electron from Cl- to form neutral Cl

→ gain 4.34 eV when K+ captures electron and forms neutral K

5.16 + 3.82 - 4.34 = 4.64 eV = energy required
Ionic vs Covalent

• As R >> 0.05 (size of 2p orbit), there is little overlap in the electron wave function between the Na and Cl ions \( \rightarrow \) mostly ionic bond “94% ionic and 6% covalent” (DH makes up numbers).

• look at HF\(_1\) molecule
  \( \text{H} \) ionization energy = 13.6 eV
  \( \text{F} \) electron affinity = 3.4 eV
  \( \rightarrow \) need 10.2 eV in electrostatic energy

\[
R = \frac{-e^2}{4\pi\varepsilon_0 U} = -\frac{1.4eV\text{nm}}{10.2eV} = .14\text{nm}
\]

• as the size of filled 2p in \( \text{F} \) is about 0.05 nm and the nominal 1s in an \( \text{H} \) atom is 0.05 nm, the electrons are attached to both atoms \( \rightarrow \) covalent bond “10% ionic and 90% covalent” (DH made up numbers).

• the nuclei will start to not be shielded from each other \( \rightarrow \) some ++ repulsion
Covalent Bonds - Diatomic Molecules

- assume all valence electrons are shared
- often S=0 lowest energy but not always (Oxygen is S=1)
- if both atoms are the same then $|\psi|^2$ same if switch atom(1) and atom(2) --- electron densities around each atom are the same (even sort of holds if different atoms like CO)

$$H(1s) \quad \text{--- very far apart ---}> \quad H(1s)$$
$$\text{close together} \quad H(“1s”)H(“1s”)$$

- electron wavefunctions overlap - “shared”

- two energy levels (S=0,1) which have

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

<table>
<thead>
<tr>
<th>E</th>
<th>bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=\infty</td>
<td>1s*1s</td>
</tr>
<tr>
<td>(atoms)</td>
<td>Vib and rot</td>
</tr>
</tbody>
</table>
Covalent Bonds - Hydrogen

- even if only 1 electron, bond is covalent
- look first at ionized diatomic H $H_2^+$
- have repulsive potential between 2 protons depends on $R = p-p$ separation (about 0.11 nm)

\[ V_{pp} = \frac{e^2}{4\pi \varepsilon_0 R} \]

- but then have attractive energy $V_e$ for the electron. It will depend on $R$ (and one calculates $R_0$ by looking at the minimum of $V_e + V_{pp}$)
Covalent Bonds - Hydrogen

- guess at a 3D solution for the wave function. Must not depend on 1 vs 2 for two atoms. Only one electron and 1,2 are locations of two protons

\[ |\psi(1,2)|^2 = |\psi(2,1)|^2 \quad (1,2 \text{ spatial}) \]

- at large separation just two H atoms

\[
\psi_{1S}(H) = \pm e^{-r/a_0} \quad \Rightarrow \\
\psi(1,2) \approx A(e^{-|\vec{r} - \vec{r}_1|/a_0} \pm e^{-|\vec{r} - \vec{r}_2|/a_0})
\]

- two possibilities: symmetric and antisymmetric when the separation becomes small

![Graphs showing wave function behavior](image)
Covalent Bonds - Hydrogen+

- symmetric wave function has lower energy
- less curvature. 1 “node” vs 2 “nodes” (compare to particle in a box)
- also greater shielding of protons from each other as higher probability for the electron to be between the two protons (antisymmetric goes to 0 at midpoint)
- can extrapolate to R=0 --- symmetric becomes a 1S state of He and antisymmetric (with wavefunction=0 at origin) becomes a 2P state

\[ total \ E = V_{pp} + E_e \]

- determine this as a function of R internuclear separation. Find there is a minimum for symmetric but not for antisymmetric \(\rightarrow\) “covalent” bond
Covalent Bonds - Hydrogen+

E- → stable point at u = 16 eV
Binding energy = (16 - 12.6)eV = 3 eV

\[ E_\pm = \text{symmetric} \]

\[ R = 0 \text{ → just } H - 13.6 \text{ eV} \]
\[ n = 0 \text{ → } \text{He}^+ - 54.4 \text{ eV} \]

\[ E_- = \text{anti-symmetric} \]

\[ R = 0 \text{ → just } H - 13.6 \text{ eV} \]
\[ n = 0 \text{ → He but with } -54.4/4 = \psi(0) = 0 \Rightarrow 2P \text{ eV} - 13.6 \text{ eV} \]
Energy Levels

- for given electronic states (1s, 3p, etc S=0, S=1) determine effective V(R) and see if a minimum (bound state) exists
- as NOT V(r) potential, Sch. Eq. Not separable into (THETA, PHI) parts
- $L^2$ not eigenfunction, L not good eigenvalue
- but often phi symmetry $\Rightarrow L_z$ m “good”
- will then have H.O. vibrations around minimum

\[
\begin{align*}
V & \quad R = \text{nuclear separation} \\
\end{align*}
\]
Neutral Hydrogen Molecule

\[ H_2^+ + 2.7\text{eV} \rightarrow H + H^+ \]
\[ H_2 + 4.7\text{eV} \rightarrow H + H \]

- more tightly bound with 2 electrons. Have:
- additional shielding of protons (lower E)
- e-e repulsion (higher E)
- end up: R=0.07 nm (compared to about 0.09 nm with single electron)
- the “size” of a H atom is about 0.05 nm and so the 1s wavefunctions of the 2 atoms are overlapping and need to use Fermi-Dirac statistics \( \rightarrow \) Pauli exclusion and a totally antisymmetric wavefunction

\[ \psi(e_1, e_2) = \psi_{\text{space}} \ast \psi_{\text{spin}} = -\psi(e_2, e_1) \Rightarrow \]
\[ \text{if } S = 1 \Rightarrow \psi_{\text{spin}} \text{sym}, \psi_{\text{space}} \text{antisym} \]
\[ \text{if } S = 0 \Rightarrow \psi_{\text{spin}} \text{antisym}, \psi_{\text{space}} \text{sym} \]
Neutral Hydrogen Molecule

- the antisymmetric space has $\psi=0$ when $r_1 = r_2$
- gives: lower electron probability between protons
- less shielding $\rightarrow$ higher energy
- in this case (and in most cases) have covalent bond when electrons are paired with “antiparallel” spin $S=0$

\[
E = E_{e1} + E_{e2} + V_{pp}
\]

\[
S=1
\]

\[
R_{pp}
\]

\[
S=0
\]
Covalent Bonds

• #bonds = #unpaired electrons
  O : 2      H₂O      N : 3     NH₃
  C : 2      CH₂ (2s²2p²) or C : 4     CH₄ (2s¹2p³)
• can numerically determine wave functions. Lots of approximations; often use elliptical coordinates
• can cover in physical chemistry. Now there is a cottage industry providing calculations for often complicated molecules. Often need some guiding by hand. Use exp(-r²) for electrons instead of exp(-r) as faster to calculate

\[ \rho \]
\[ p \]

equal
electron
probability
contours
Molecular Bonding

- computer code can now calculate many molecular bonds. A common one is called GAUSS
- to save time usually set up "by hand" configurations.

Figure 50. Theoretical calculations involving solvated histidine. Both the distance from the Na⁺ to the oxygen of the acetone and the stabilization energies are reported.

Figure 25. The structure of acetone. On the left, acetone is shown as a simple drawing. The figure on the right is the acetone molecule as optimized by Gaussian 03.
Covalent 2p Bonding

- bonding in N₂ and O₂ (and sort of in molecules with C and other atoms) depend on 2p orbital shapes
- 3 different 3p wave functions. Along “x” “y” and “z” directions. (If have 2s2p³ then along 4 legs of tetrahedron)
- For covalent bonds with identical atoms, symmetry requires that both atoms have the same electron distributions. So |ψ|² will have xx,yy,zz combinations only.
- Let x be the axis of the molecule and y,z be perpendicular. y,z give same energy eigenvalues and so can have mixing → φ symmetry
Covalent 2p Bonding

• just based on symmetry between the 2 atoms electron distributions, can sketch out the bond and antibonding wave functions. If electrons are between nuclei $\rightarrow$ lower energy

\[
\begin{array}{ccc}
\text{BOND} & \text{YY,ZZ} & \text{ANTIBOND} \\
N & N & N \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{BOND} & \text{XX} & \text{ANTIBOND} \\
N & N & N \\
\end{array}
\]

\[
\begin{array}{ccc}
p & N & N \\
N & N & N \\
\end{array}
\]
Covalent 2p Bonding

• give energy levels which are then filled
• energy ordering changes between O and N as different electron distributions
• usually think of covalent bonds as $S=0$ but have $S=1$ for $O_2$

\[
\begin{align*}
N_2 & \quad O_2 \\
\text{x------} & \quad \text{2P anti} & \quad \text{-------x} \\
\text{y------} & \quad \text{z------} & \quad \text{y------} & \quad \text{z------} \\
\text{x------} & \quad \text{2P bond} & \quad \text{y------} & \quad \text{z------} \\
\text{y------} & \quad \text{z------} & \quad \text{x------} & \quad \text{2S antibond} & \quad \text{2S bond} \\
\text{p} & \quad \text{2S antibond} & \quad \text{2S bond} \\
\text{1S} & \quad \text{1S}
\end{align*}
\]
MOLECULAR ENERGY LEVELS

• Have Schrod. Eq. For H₂ (same ideas for more complicated). For proton and electron 1,2

\[- \frac{\hbar^2}{2m} \left[ \nabla^2_{p1} + \nabla^2_{p2} + \nabla^2_{e1} + \nabla^2_{e2} \right] \psi + \left[ V_{pp} + V_{ee} + V_{e1p1} + V_{e2p2} + V_{e1p2} + V_{e2p1} \right] \psi = E \psi \]

• real solution: numeric. But “solve” by separating

\[ \psi = \psi_{\text{electronic}} \psi_{\text{rotational}} \psi_{\text{vibrational}} \]

• these are fairly independent. e.g. electronic sets potential well vs distance between protons \( \rightarrow \) vibrational modes (which don’t really change separation by much). Rotational also set by distance

\[ \Delta E_e \approx \text{visible, UV} \]
\[ \Delta E_{rot}, \Delta E_{\text{vib}} \approx \text{microwave, IR} \]
Rotations

- Go to center-of-mass frame for two atoms

\[ M_1 \leftrightarrow R_0 \quad \Rightarrow M_2 \]
\[ M_1 \leftrightarrow R_1 \quad \Rightarrow c.m. \leftrightarrow R_2 \quad \Rightarrow M_2 \]

\[ E_{rot} = \frac{1}{2} \mu \omega^2 R_0^2 = \frac{1}{2} \frac{L^2}{I} = \frac{1}{2} \mu \nu^2 \]

with \[ \mu = \frac{m_1 m_2}{m_1 + m_2} \quad I = \mu R_0^2 \]

- Write down Schrod. Eq. For rotational energy

\[ H_{rot} \psi_{rot} = \frac{L^2}{2I} \psi_{rot} = E_{rot} \psi_{rot} \quad (V = 0) \]

- Spherically symmetric in cm frame. Rotationally confined to sphere \( r = R_0 \) (E&R Ch 7 20-26)

\[ \psi_{rot} = Y_{rm}(\theta, \phi) = \text{spherical harmonics} \]

\[ \langle L^2 \rangle = r(r + 1)\hbar^2 \quad r = \text{integer} \]

\[ \langle L_z \rangle = m\hbar \quad -r < m < r \quad \text{integer} \]
Rotations

• As know angular momentum eigenvalues

\[ E_{\text{rot}} = \frac{\langle L^2 \rangle}{2I} = \frac{r(r+1)\hbar^2}{2I} \Rightarrow \text{spacing} \]

\[ \Delta E = E_r - E_{r-1} = \frac{\hbar^2}{2I} \left[ r(r + 1) - (r - 1)r \right] = \frac{\hbar^2}{I} \]

• use NaCl as example. \( R_0 = 0.24 \text{ nm} \)

\[ \mu = \frac{23 \times 35}{23 + 35} = 13.9 \]

\[ \frac{\hbar^2}{I} = \frac{(\hbar c)^2}{\mu c^2 R_0^2} = \]

\[ \frac{(197eV \times fm)^2}{13.9 \times 931MeV \times (.24 fm)^2} = .0005eV \]

• \( kT = 0.025 \text{ eV} \) for \( T=300 \). Easy to be in an “excited” state and relative amount is another way to measure temperature
Ex. 12-2 and Prob 12-5a

\[
\text{find } \frac{n_r}{n_0} = \frac{\text{# in level } r}{\text{# in level } 0} \quad \text{# states } = 2r + 1
\]

\[
E = \frac{\hbar^2}{2I} r(r + 1)
\]

\[
\frac{\text{# quantum states } r}{\text{# quantum states } 0} e^{-E_r/kt} = \frac{\text{# quantum states } r}{\text{# quantum states } 0} e^{-E_0/kt} \approx (2r + 1)e^{-r(r+1)\hbar^2/2Ikt}
\]

• 12-5a which level is most highly populated?

\[
\frac{\partial n_r}{\partial r} = \left[ 2 - \frac{\hbar^2}{2Ikt} (2r + 1)^2 \right] e^{-E/kt} = 0
\]

\[
r_{\text{prob}} = \left( \frac{IkT}{\hbar^2} \right)^{0.5} - 0.5
\]

\[
\approx \sqrt{0.025/0.0005} - 0.5 \approx 7
\]

NaCl at T=300
Absorption/Emission-Rotation

• occurs if molecule has an electric dipole moment (if not will have electronic-vibrational-rotational)
• can partially calculate using 470 EM. QM mechanics selection rules similar to atoms dr=+-1 (can have dr=+-2 in higher order)

\[ E = r(r + 1) \frac{\hbar^2}{2I} \]

<table>
<thead>
<tr>
<th>r</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 (above v/e)</td>
</tr>
<tr>
<td>1</td>
<td>( E_R )</td>
</tr>
<tr>
<td>2</td>
<td>( 3E_R )</td>
</tr>
<tr>
<td>3</td>
<td>( 6E_R )</td>
</tr>
</tbody>
</table>

\[ v = \frac{\Delta E}{h} \approx \frac{.004eV}{4.1 \times 10^{-13} eV/sec} \]

\[ \approx 10^{10} \text{Hz} \]

• equally spaced absorption energies
• but if large angular momentum (large r), not symmetric and R separation increases, I increases, energy spacing changes
Absorption/Emission-Rotation

• Different isotopes have different mass, different moments of inertia $I \rightarrow$ energy shift

$$\text{Cl}^{35} \text{ vs } \text{Cl}^{37} \quad \mu = 13.9 \Rightarrow 14.2 \quad 2\%$$

• different excited states (both electronic and vibrational) will have different separation between the molecules. So different $I$ and different $dE$ and photon energy

• spectrum has broad, ~continuous spectrum with absorption peaks superimposed

$E_\gamma$

P461 - Molecules 25
Spectrum and Molecular Properties

- can use measured spectrum to determine molecular properties
- CO molecule. Measure energy spacing of absorbed photons

\[ r = 0 \rightarrow r = 1 \quad \nu = 1.5 \times 10^{11} \, \text{Hz} \]

\[ \frac{\hbar^2}{I} = h \nu \quad \mu = \frac{12 \times 16}{12 + 16} = 6.9 \quad I = \mu R_0^2 \]

\[ \Rightarrow R_0 = \sqrt{\frac{\hbar}{2\pi \nu \mu}} = 1.1 \times 10^{-10} \, m \]

- measures average separation between the C + 0 atoms
Molecular Vibrations

- minimum in separation distance can be approximated as a parabola
- PHYS460 gave QM solutions to Schrod. Eq. For harmonic oscillator
- let \( v = \) vibrational quantum number = 0, 1, 2...

\[
E_{vib} = \left( v + \frac{1}{2} \right) \hbar \nu_0 \quad \nu_0 = \frac{1}{2\pi} \sqrt{\frac{C}{\mu}}
\]

\[
C = \frac{\partial^2 E_{tot}}{\partial R^2} \bigg|_{R=R_0} = \text{curvature of parabola}
\]

\[
NaCl : h \nu_0 \approx 0.04eV \quad HCl : h \nu_0 \approx 0.4eV
\]
Molecular Vibrations

• Ex. 12-3. Knowing the force constant in HCl, find the photon energy (in reality use measured photon energy to understand the shape of $E_{\text{total}}$)

\[
\text{force const} \tan t = 470nt / m = 2900eV / fm^2
\]

\[
\mu = \frac{m_H m_{\text{Cl}}}{m_H + m_{\text{Cl}}} = \frac{35}{36} m_H = 913MeV / c^2
\]

\[
E_\gamma = h \nu_0 = \frac{h}{2\pi} \sqrt{\frac{C}{\mu}} = \hbar c \sqrt{\frac{C}{\mu c^2}} = 197MeVf \sqrt{\frac{2900eV / fm^2}{913MeV}} = 0.35eV
\]
Rotational-Vibrational Energy Levels

• The # of rotational levels only fixed by the top of the finite energy well $\rightarrow$ different vibrational levels can overlap

$$E_{v-r} = \left( v + \frac{1}{2} \right) \hbar \sqrt{\frac{C}{\mu}} + \frac{\hbar^2 r(r + 1)}{2 \mu a^2}$$

• often just called rotational-vibrational band

• spacing (between vibrational levels and rotational levels) will vary as move to the top of the well. The electron distribution changes and so average separation changes. Well non-symmetric

• at room $T$, most molecules in lowest vib. State

$$\frac{n_1}{n_0} = \frac{\# \text{ states} 1}{\# \text{ states} 2} e^{-h v_0 / kT} = \frac{1}{1} e^{-35/0.025} \approx 10^{-7}$$

• well is finite $\rightarrow$ limited number of vibrational states ($\sim 40$ for some before dissociation)
Molecular Spectra

Molecular Spectra complicated. Can't try to really understand (Intensity)

Figure 12-10. Top: Energy-level diagram and transitions leading to the formation of an electronic band. Unlike Figure 12-7, the band spectrum indicated not only back on itself, giving a to a band head at the right end of the spectrum. Again note that the transition of quency ν₂ is missing. Bottom: Bands of the CN and C₂ molecules in a carbon arc in air. (From Herzberg, *Spectra of Diatomic Molecules*, 1950. D. Van Nostrand Co., Inc., New York).
“Electronic” Energy Levels

• Electrons can be in higher energy states (equivalent to 2p → 3s, 3d etc)

• can still have a molecular bond as long as a minimum in the $E_{\text{total}}$ vs $R$ distribution

• the potential well tends to be shallow

  > fewer vibrational modes

  > different vibrational and rotational energy spacing as different moment of inertia (spacing) and “spring” constant
Absorption and Emission Spectrum

- Will depend on the electric dipole moment (edm)
- If edm=0 (in symmetric molecules) mostly need to have electronic transition for non-zero matrix element and therefore transition in UV
- If asymmetric (CO, etc) then have non-zero edm. Can have pure rotational (microwave) and vibrational-rotational (IR) transitions
- Obtain selection rules from perturbation theory

\[
\left| \left\langle \text{final} \left| \mathbf{V}_{\text{pert}} \right| \text{initial} \right\rangle \right|^2 \neq 0
\]

- Similar wavefunctions and so same H.O. and angular momentum selection rules as in 460:
  \[ \text{rotational} \implies \Delta r = \pm 1 \]
  \[ \text{vibrational} \implies \Delta v = 0, \pm 1 \]
- If change in electronic state, the vib. and rot. wave functions in the two states are often very different and “breaks” the selection rules
Electronic Transitions

- Use Frank-Conden and Heitler-London principles
- compare initial and final state wavefunctions. Want them to be “similar” and overlap in space
- rotational and vibrational selection rules can be broken
- matrix element. Need to work out integrals

\[ v_{fi} = \int \psi_f^* \psi_{\text{pert}} \psi_i d\text{Volume} \]

Green overlaps
orange doesn’t
Photon Scattering

• Both light passing through a gas and a technique

\[ \gamma_{in} \quad M_b \quad \sim M_a \quad \gamma_{out} \]

• If photon is at a resonant frequency. Then \( M_b \) is an excited state and the outgoing photon energy depends on the details of the energy levels.

• If photon not at a resonance, \( M_b \) is virtual. But electric-dipole selection rules hold at each vertex

\[ \Delta r = \pm 1 \quad each \ vertex \Rightarrow for \ both \]
\[ \Delta r = 0 \quad \Delta \nu = 0 \quad (Rayleigh) \ or \]
\[ \Delta r = \pm 2 \quad \Delta \nu = 0, \pm 1 \quad (Raman) \]
Molecular Symmetry Effects

• Identical nuclei O₂, H₂ etc

\[ |\psi(1,2)|^2 = |\psi(2,1)|^2 \]

\[ \text{spin}_N = 0,1,..(Boson) \Rightarrow \psi_M = \text{symmetric} \]

\[ \text{spin}_N = \frac{1}{2}, \frac{3}{2}..(Fermion) \Rightarrow \psi_M = \text{antisymmetric} \]

• different components of molecular wavefunction

\[ \psi_M = \psi_{\text{electronic}} \psi_{\text{vibrational}} \psi_{\text{rotational}} \psi_{\text{nucleus}} \]

\[ \psi_{\text{elec}} = \text{symmetric} \Rightarrow e-e \text{ covalent bond} \]

\[ \psi_{\text{vib}} = \text{symmetric} \Rightarrow R_0 = |x_1 - x_2| \]

\[ \psi_{\text{rot}} = (-1)^r = \text{Parity} \]

• the symmetry of the nuclear part of the wavefunction will depend on the nuclear spin combination (same as in atoms)
Molecular Symmetry Effects

- Fermionic Nuclei \( \text{H}_2 \): total wavefunction must be antisymmetric. So rotational\(^*\)nuclear = “odd”
- combine nuclear spin
  \[ \vec{S}_N = \vec{S}_{N1} + \vec{S}_{N2} \quad \text{both} \quad S = \frac{1}{2} \]
  \[ S_N = 1(\text{triplet}) \psi_N = \text{symmetric} \equiv \text{ortho} \]
  \[ \Rightarrow \psi_{\text{rotation}} = \text{antisymmetric} = \text{odd} \]
  \[ S_N = 0(\text{sin glet}) \psi_N = \text{antisymmetric} \equiv \text{para} \]
  \[ \Rightarrow \psi_{\text{rotation}} = \text{symmetric} = \text{even} \]

- ortho=\text{symmetric nuclear spin} \quad \text{para}=\text{antisymmetric}
- A given molecule is either ortho or para. It stays that way for a long time since very weak internuclear forces which might flip the spin. Raman scattering preserves this as \( \Delta r=2 \) \( \Rightarrow \) look at spectral lines and count number of odd vs even transitions \( \Rightarrow \) gives nuclear spin
Molecular Symmetry Effects

• observed transitions

Fermionic nuclei
- \( r=5 \)
- \( r=4 \)
- \( r=3 \)
- \( r=2 \)
- \( r=1 \)
- \( r=0 \)

Bosonic nuclei

ortho para para ortho

• ortho=symmetric nuclear spin para=antisymmetric

• look at spectral lines and count number of odd vs even transitions \( \rightarrow \) gives nuclear spin. Each transition unique energy

\[
E_r = \frac{\hbar^2}{2I} r(r + 1)
\]

\[
\Delta E = E_{r+2} - E_r = \frac{\hbar^2}{2I} (4r + 6)
\]
Ortho vs Para in Diatomic Molecules

- Assume 2 identical nuclei each with $S=i$
- $(2i+1)\times(2i+1)$ total states
- $2i+1$ - both $m$ are the same $\rightarrow$ symmetric
  have $(2i+1)(2i+1)-(2i+1) = 2i(2i+1)$ remaining
  states: half symmetric and half antisymmetric
- total # symmetric $= (2i+1)+i(2i+1) = (2i+1)(i+1)$
  total # antisymmetric $= i(2i+1)$

\[
\frac{\text{# ortho}}{\text{# para}} = \frac{\text{# sym}}{\text{# antisym}} = \frac{i+1}{i}
\]

- Example: 2 spin 1/2 nuclei

\[
\begin{align*}
|S = 1, S_z = 1\rangle &= |S_{z1} = \frac{1}{2}, S_{z2} = \frac{1}{2}\rangle \\
|1,0\rangle &= \frac{1}{\sqrt{2}} \left(|\frac{1}{2}, -\frac{1}{2}\rangle + | -\frac{1}{2}, \frac{1}{2}\rangle\right) \\
|0,0\rangle &= \frac{1}{\sqrt{2}} \left(|\frac{1}{2}, -\frac{1}{2}\rangle - | -\frac{1}{2}, \frac{1}{2}\rangle\right) \\
|1,-1\rangle &= \left|\frac{1}{2}, -\frac{1}{2}\right\rangle
\end{align*}
\]

\[
\frac{\frac{1}{2}+1}{\frac{1}{2}} = 3
\]
Molecular Symmetry Effects

• Bosonic Nuclei $O_2$, $N_2$ etc. have totally symmetric wavefunction

• nuclear-rotational: sym-sym or antisym-antisym

\[
O_2 : S_{Ni} = 0 \implies S_N = 0 = \text{symmetric}
\]
\[
\implies \text{only } \psi_{\text{rotation}} = \text{symmetric} = \text{even}
\]
\[
N_2 : S_{Ni} = 1 \implies S_N = 2, 0 = \text{symmetric}
\]
\[
\implies \psi_{\text{rotation}} = \text{symmetric} = \text{even}
\]
\[
\quad \text{or } S_N = 1 = \text{antisymmetric}
\]
\[
\implies \psi_{\text{rotation}} = \text{antisymmetric} = \text{odd}
\]

• $O(16)$-$O(16)$ or $C(12)$-$C(12)$ molecules can only have $r=$ even states. $C(13)$ discovered by seeing “forbidden” $(1 \rightarrow 3)$ transitions in Raman scattering

• $N(14)$-$N(14)$ even $r$ transitions $(0 \rightarrow 2$, etc) most intense

\[ = \text{odd} \quad \frac{i}{i+1} = \frac{1}{1+1}
\]
\[ = \text{even} \quad \frac{i}{i+1} = \frac{1}{1+1}
\]