Structure of Diatomic Molecules

I. Born-Openerheimer Approximation: Separability of electronic and nuclear motion for $M_i \gg m_e$

For any diatomic molecule, the non-relativistic Hamiltonian excluding spin is

$$H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{1}{2} \sum_{i,j} \frac{\nabla_i^2}{M_i} + \sum_{i>j} \frac{k e^2}{r_{ij}}$$

$$+ \frac{k Z_A Z_B e^2}{R_{AB}} - \sum_i \frac{k Z_i e^2}{r_i}$$

For $M_i \gg m$, approximate solution as

$$\psi = \Psi_e (r_i, \vec{R}) \chi (\vec{R})$$

The most drastic form of the B-O approx is the frozen nucleus approximation:

(i) Solve for electronic motion with frozen nuclei --- at internuclear separation $R_{AB} = R$.

$$\psi_e (r_i, R, \theta_i, \phi_i) = E_e (R) \psi_e (r_i, \theta_i, \phi_i)$$

Then we have an approximate electronic wave function and energy for every value of $R$.

(ii) Solve for the slower nuclear motion, using $E_e (R)$ as an effective potential in which the nuclei move:

$$\psi_e (r_i, R, \theta_i, \phi_i) \chi = E \chi$$

(If $L \neq 0$, this must be refined to incorporate projection of $\vec{L}$ along $\vec{R}_{AB}$)

In (iv), $E = E_e + E_{\text{vib}} + E_{\text{rot}}$

large \text{ \smaller \smaller}
Size of neglected terms is \( O(\frac{m}{M}) \), so this is usually good to about 2-3 decimal places.

II. \( H_2^+ \) --- the Simplest Molecule

A. Bonding and Antibonding Orbitals in the \( H_2^+ \) ground state electronic wave function

We will find an approximate solution using hydrogenic wave functions in a simple variational calculation, looking only at the radial part for now. This is the simplest possible molecular orbital calculation using a linear combination of atomic orbitals ("MO - LCAO"). Actually, in the B-C approximation, an exact solution is possible, but it's not very interesting.

For a fixed \( R \), the electronic Hamiltonian is

\[
H_e = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ke^2}{r_A} - \frac{Ke^2}{r_B} + \frac{Ke^2}{R} \tag{5}
\]

\[

\]

Write the wave function as an arbitrary sum of two \( H(1s) \) orbitals (one could do better, but it's a start!):

\[
\Psi_e = C_A \Phi_A + C_B \Phi_B \tag{6}
\]

Because the nuclei are identical, it's very reasonable to assume that the two orbitals \( \Phi_A \) and \( \Phi_B \) should be of the same type (both 1s, or both 2p, or whatever).

Now, minimize \( \bar{E}_e = \frac{\langle \Psi_e | H_e | \Psi_e \rangle}{\langle \Psi_e | \Psi_e \rangle} \) \( \tag{7} \)
It is convenient to define some parameters,

\[ S = \text{overlap integral} \equiv \langle \Phi_A | \Phi_B \rangle \]

\[ H_{AA} = H_{BB} = \text{Coulomb integral} \equiv \langle \Phi_A | H_e | \Phi_A \rangle \]

or \[ \langle \Phi_B | H_e | \Phi_B \rangle \]

\[ H_{AB} = H_{BA} = \text{resonance (or "exchange") integral}, \]

\[ \equiv \langle \Phi_A | H_e | \Phi_B \rangle = \langle \Phi_B | H_e | \Phi_A \rangle \]

In this notation, Eq. 7 becomes,

\[ E_e (c_A^2 + c_B^2 + 2c_A c_B S) = c_A^2 H_{AA} + c_B^2 H_{BB} + 2 c_A c_B H_{AB} \]

Now set \[ \frac{\partial E_e}{\partial c_A} = \frac{\partial E_e}{\partial c_B} = 0 \] to give a pair of linear equations whose compatibility condition is the secular equation,

\[ \begin{vmatrix}
    H_{AA} - E_e & H_{AB} - E_e S \\
    H_{BA} - E_e S & H_{BB} - E_e
\end{vmatrix} = 0 \]

Eigenvalues:

\[ E_1 = \frac{H_{AA} + H_{AB}}{1 + S} \]

\[ E_2 = \frac{H_{AA} - H_{AB}}{1 - S} \]

Eigenfunctions:

\[ \Psi_1 = \frac{\Phi_A + \Phi_B}{\sqrt{2(1+S)}} \equiv 1\sigma^+ \]

\[ \Psi_2 = \frac{\Phi_A - \Phi_B}{\sqrt{2(1-S)}} \equiv 1\sigma^- \]
The Coulomb integral $H_{AA}$ has two parts:

\[ \Phi_A^2 \left\langle \text{Cross-sections for } \Phi \text{ along } R_{ab} \right\rangle \]

\[ V(R) \left\langle \text{energy of } H_{1s} \right\rangle \]

(There are corresponding pictures for $\Phi_B$, of course.)

The exchange term is a little different. For the $\Phi_{AB}$ part,

\[ \Phi_A^2 \Phi_B^2 \]

\[ \text{Overlap of } \Phi_A, \Phi_B, \text{and } V_{AB} \]

\[ \text{Exchange integral corresponds to exchange of } e^- \text{ from } V_A \text{ to } V_B. \]

Using $H$ atom wave functions, the energies $E$, and $E_e$ can be worked out explicitly:

\[ \Phi_A = (1s)_A = \frac{1}{\sqrt{\pi}} \ e^{-r_A} \]

\[ \Phi_B = \frac{1}{\sqrt{\pi}} \ e^{-r_B} \]

\[ E_e = E(H_{\text{atom}}, 1s) - \frac{1}{15} \ \frac{e^2}{a_0} \left( \frac{1}{p} - e^{-2p} (1 + p) + e^{-p} (1 + p) \right) \]

\[ \text{where } p = \frac{R}{a_0} \]

\[ D_e = \text{dissociation energy rel. to bottom of potential well} \]

\[ E_e (\text{Ry}) \]

\[ 1 \sigma^+ \]

\[ 1 \sigma_2^+ \]

\[ \text{exact solution lies lower, } D_e = 2.79 \text{ eV} \]

\[ \text{rather than 1.76 eV} \]
The 10\textsuperscript{g} ground state is a bonding orbital. The purely repulsive 10\textsuperscript{u\ast} is antibonding.

\[ |10\textsuperscript{g}\rangle \quad |10\textsuperscript{u\ast}\rangle \]

In this simple calculation, the bond energy $D_e$ is off by about 50%. Allowing the effective $Z$ to be varied improves things considerably, but a bigger and more flexible basis set is needed for really accurate results. For more complex molecules, proceed in some way using Slater determinants.

B. Vibration and Rotation for $H_2^+$ (much here is generalizable)

We now need to go back to Eq. 4, and solve for the nuclear motion in the potential formed by the electronic energy. The idea is that the electronic motion is much faster, so we reconfigures itself at each $R$ as the nuclei slowly move. Thus $E_e (R)$ is treated as an effective potential, and we can write 4 as:

\[ \left( -\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V(R) \right) \chi = E \chi \]
Switch to the center of mass with \( \mu = M_1M_2 / (M_1 + M_2) \) and ignore motion of center of mass. Then,

\[
\left( -\frac{\hbar^2}{2\mu} \nabla^2 + V(R) \right) \chi = E\chi
\]

(Here we have assumed the electronic angular momentum is zero, by the way; otherwise it needs to be included as well.) In spherical coordinates, writing

\[
\chi = \psi_{\text{rot}}(\Theta, \Phi) \psi_{\nu}(R),
\]

we find

\[
R^2 \left( \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) \psi_{\nu} + \frac{2\mu R^2}{\hbar^2} (E - V(R)) \psi_{\nu} = \hbar^2 J(J+1) \psi_{\nu}
\]

and

\[
-\frac{\hbar^2}{2\mu} \left( R^4 \sin^2 \theta \left( \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi_{\text{rot}} = E_{\text{rot}} \psi_{\text{rot}}
\]

\[
= -\frac{J^2}{\hbar^2 R^2}
\]

In general numerical methods are needed, but simple results apply for the lower rotational and vibrational levels, where the internuclear excursions are small.

Here we approximate \( R = R_e \) (fixed) for rotation, and \( V(R) \approx -D_e + \frac{1}{2} K (R - R_e)^2 \) for vibration.

**Rigid rotator:** For \( R = R_e \), we have

\[
\frac{J^2}{2M R_e^2} \psi_{\text{rot}} = E_{\text{rot}} \psi_{\text{rot}}
\]

So that

\[
J^2 \psi_{\text{rot}} = \hbar^2 J(J+1) \psi_{\text{rot}} = 2M R_e^2 \psi_{\text{rot}} E_{\text{rot}}
\]

and

\[
E_{\text{rot}} = \frac{\hbar^2}{2M R_e^2} J(J+1) = BJ(J+1)
\]

\( B \equiv \) "rotational constant"; \( J = 0, 1, 2, ... \)
Eq. (17) is just the quantized version of the classical rotational energy:

with \( I = m R_e^2 \), \( \text{E}_\text{rot} = \frac{h^2 J (J+1)}{2I} \)

\( \text{E}_\text{rot} = \text{eigenvalue of} \ \frac{J^2}{2I} \) \( \tag{18} \)

**Variation of \( B \) with \( v \) and \( J \):**

In an actual molecule, even \( H_2^+ \), we cannot ignore the non-rigid character of what's rotating. There are two principal effects:

a) Dependence of \( B \) on vibration and anharmonicity

Looking at (16), we see that the Hamiltonian depends on \( R \). In the limit that \( \text{E}_\text{vib} \gg \text{E}_\text{rot} \), we can account for this by replacing

\[ B_v = \frac{\hbar^2}{2 \mu R_e^2} \quad \text{with} \quad B_v = \frac{\hbar^2}{2 \mu} \langle v | \frac{1}{R^2} | v \rangle \] \( \tag{19} \)

Because \( B \) now depends weakly on vibration, we approximate

\[ B_v = B_e - \alpha_e (v + \frac{1}{2}) + \gamma_e (v + \frac{1}{2})^2 + \ldots \] \( \tag{20} \)

Even for a pure harmonic oscillator, \( \alpha_e \neq 0 \), but it mainly reflects anharmonicity of \( V(R) \).

**Typical values:**

For \( H_2^+ \), \( B_e = 30.2 \), \( \alpha_e = 1.65 \). For some other cases,

\[ \begin{array}{ccc}
H_2 & \times & ^1\Sigma_g^+ \\
B_e (\text{cm}^{-1}) & 60.853 & 3.062 \\
\alpha_e (\text{cm}^{-1}) & 7.5\% \\
K_2 & \times & ^1\Sigma_g^+ \\
B_e (\text{cm}^{-1}) & 0.0567 & 0.000165 \\
\alpha_e (\text{cm}^{-1}) & 0.4\% \\
N_2 & \times & ^1\Sigma_g^+ \\
B_e (\text{cm}^{-1}) & 1.9982 & 0.01732 \\
\alpha_e (\text{cm}^{-1}) & 1.3\% \\
NO & \times & ^2\Pi \\
\begin{align*}
B_e (\text{cm}^{-1}) & (1.67195, 1.72016) \\
\alpha_e (\text{cm}^{-1}) & (0.0182, 0.0171) \\
\end{align*} \\
\end{array} \]

Each level has two \( \Delta \)-doubling components, of opposite parity.
b) **Centrifugal distortion** - variation of $B$ with $J$.

The axis $R_{ab}$ is a rotating reference frame, so a force $F$ acts to increase $R_e$. As a result, we write, for a given vibrational level $\nu$, using (20) to define $B_\nu$:

$$E_{rot} = B_\nu J(J+1) - D_\nu \left( J(J+1) \right)^2 + H_\nu \left( J(J+1) \right)^3 + \cdots$$

and in turn, when accuracy is high and perturbations are minor, we can even expand

$$D_\nu = D_e - \beta_e \left( \nu + \frac{1}{2} \right)$$

For empirical fitting of spectra, the expansions (20) and (21) are often generalized into high-order expansions in "Dunham coefficients."

Typical values:

- $H_2^+$: $D_e \approx 0.018 \text{ cm}^{-1}$
- $H_2$: $D_e = 0.0471$
- $K_2$: $D_e = 8.63 \times 10^{-8}$
- $N_2$: $D_e = 5.8 \times 10^{-6}$
- $NO$: $D_e \approx 5 \times 10^{-6}$

*All in ground $X$ state, effects of $\beta_e$ too small to see, relevant to other shifts.*

**Vibrational energy levels of $H_2^+$ (or other diatomics)**

We return to Eq. (15), which follows from the $B$-O approximation in its frozen-nucleus limit.

Rewrite it as,

$$-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) \psi_\nu + \left( V(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} \right) \psi_\nu = E \psi_\nu$$

Centrifugal potential due to rotation.

To lowest order, we can make a harmonic oscillator approximation,

$$V(R) \approx -D_e + \frac{1}{2} k (R-R_e)^2 \quad V_{centrip} \approx 0.$$ We then have $E = E_e + E_{rot} + \frac{1}{2} \hbar \nu \left( \nu + \frac{1}{2} \right)$.

**Vibrational constants**

$$\nu_0 = \sqrt{\frac{K_e}{M}}$$

Vibrational quantum $\nu = 0, 1, 2, \ldots$
Because the effects of anharmonicity are usually obvious, it is again conventional to expand in a power series,

\[
E_{\text{vib}} = \hbar \omega e (\nu + \frac{1}{2}) - \hbar \omega e (\nu + \frac{1}{2})^2 + \ldots
\]

Typical values (for ground \( \nu \) states)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \omega e (\text{cm}^{-1}) )</th>
<th>( \omega e \mathrm{x} e (\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2^+ )</td>
<td>2321.</td>
<td>66.2</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>4401.2</td>
<td>121.3</td>
</tr>
<tr>
<td>( \text{K}_2 )</td>
<td>92.021</td>
<td>0.2829</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>159.124</td>
<td>0.725</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>1904.2</td>
<td>14.1</td>
</tr>
</tbody>
</table>

So typically, \( \omega e \) is \( \sim 1000 \times B \), but note that this is mass dependent -- classically, \( B \propto \sqrt{m} \), while \( \omega e \propto \sqrt{m} \).

III. Molecular Orbitals for Diatomic Molecules

Just as we can use single-electron configurations to understand the overall structure of electronic states in multi-electron atoms, we can use single-electron molecular orbitals (MO's) to do the same for molecules. The most common choice for assigning electronic configurations is the linear combination of atomic orbitals, MO-LCAO. It is primarily intended for covalent bonding, and is a poor basis set for highly ionic species such as HCl.

Start with atomic orbitals (AO) 1s, 2s, 2p, etc. These are sometimes designated by their orientation,

\[
\begin{align*}
&\downarrow \quad \uparrow \quad \downarrow \\
&\text{P}_z \quad \text{P}_x \quad \text{P}_y
\end{align*}
\]

They are then combined to form the molecular orbitals.
When we form an MO, such as \( \phi_1 s = (1s_a + 1s_b) \sqrt{2} \), we still use the atomic quantum numbers \( n, l, \) and \( m_s \). We also introduce two new quantum numbers.

1) \( \lambda = |m_e| \), useful for all MO's, the projection of \( \vec{p} \) on the internuclear axis \( \vec{R}_{AB} \). For each \( \lambda \), when symmetry permits, there are two nearly degenerate sublevels with \( m_e = \pm \lambda \).

2) \( g \) (gerade) \quad \{ \\
\( u \) (ungerade)
\}
For homonuclear molecules only \((A=B)\).
This is the eigenvalue of the symmetry operator \( \vec{i} = \) inversion of coordinates about midpoint.
\((+) = g \quad (-) = u \).

**Nomenclature for MO's:**

\[ 2p \Pi_g^* \quad * \text{for antibonding orbital} \]
\[ 2p \Pi_u^* \quad u \text{ or } g \text{ for homonuclear molecule} \]

\[
\begin{array}{c|c|c}
\text{for } \phi_0 & \text{name} & \text{like } s, p, d, f \\
\hline
0 & \sigma & (\text{for } l) \\
1 & \Pi & \\
2 & \sigma & \\
3 & \Pi & \\
\end{array}
\]

This particular orbital looks like,

\[
\left[ (2p_x)_A - (2p_x)_B \right] / \sqrt{2} = 2p \Pi_g^* \quad \text{(also written as } \Pi_u^* \text{)}
\]

The following three pages show how molecules can be built up from MO's, just as atoms are described using the shell model. The MO's are filled more or less in the order shown on the top chart on p. M11, with some deviations. For \( N_2 \) \((p, M12)\), two N atoms, \( 1s^2 2s^2 2p^3 \), form the configuration,

\[
(1s\sigma_g)^2 (1s\sigma_u^*)^2 (2s\sigma_g)^2 (2s\sigma_u^*)^2 (2p\sigma_g)^2 (2p\pi_g)^4
\]
Molecular Orbitals and the Building-up Principle


Table 13.1. Possible electronic states in molecules. The atomic orbitals (AO) are combined into molecular orbitals (MO). Their spatial extent is indicated schematically, along with their multiplicities and spins

<table>
<thead>
<tr>
<th>AO</th>
<th>MO</th>
<th>nlλ</th>
<th>Multiplicity orbital spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p</td>
<td>2pα*</td>
<td>∞∞</td>
<td>1 2</td>
</tr>
<tr>
<td></td>
<td>2pπ*</td>
<td>∞∞</td>
<td>2 2</td>
</tr>
<tr>
<td></td>
<td>2pπu</td>
<td>∞∞</td>
<td>2 2</td>
</tr>
<tr>
<td></td>
<td>2pδg</td>
<td>∞∞</td>
<td>1 2</td>
</tr>
<tr>
<td>2s</td>
<td>2sαg</td>
<td>∞∞</td>
<td>1 2</td>
</tr>
<tr>
<td></td>
<td>2sαu</td>
<td>∞∞</td>
<td>1 2</td>
</tr>
<tr>
<td>1s</td>
<td>1sαu</td>
<td>∞∞</td>
<td>1 2</td>
</tr>
<tr>
<td></td>
<td>1sσg</td>
<td>∞∞</td>
<td>1 2</td>
</tr>
</tbody>
</table>

Note: Order is reversed for Li₂ to N₂.

Fig. 13.2. An energy level diagram of the molecular orbitals of the H₂ molecule. The linear combinations of the two s electrons 1s_A and 1s_B yield a bonding orbital σ and an antibonding orbital σ*.

Fig. 13.3. Upper part: In the H₂ molecule, the two electrons can both occupy the lowest, bonding orbital. Lower part: In the He₂ molecule, two electrons are in a bonding orbital and two in an antibonding orbital. The state is not bound, and a stable He₂ molecule does not exist in its ground state.
Molecular Orbitals for Many-Electron Molecules


Fig. 13.4. Left-hand part: The molecular orbitals of \( \text{N}_2 \), showing their origins from atomic orbitals and their electron occupations in the ground state, following the molecular orbital scheme. The energy ordering of the molecular orbitals derived from the \( 2p \) atomic orbitals can be found from experiment and from detailed calculations including the electron-electron interactions. In a simple first-order picture, one would expect that the splittings \( 2p_\sigma/2p_\sigma^* \) and \( 2p_\pi/2p_\pi^* \) would be located symmetrically with respect to the original position, i.e. with respect to the atomic orbitals, as in Table 13.1. Right-hand part: The same scheme for the \( \text{O}_2 \) molecule.

Fig. 13.5. Ordering of the molecular orbitals in a homonuclear diatomic system. At the left, the term symbols in the combined-nucleus atom are shown; on the right are those for the separated atoms, and in the centre, for the molecule. The connection between the left and the right sides of the diagram is in reality not linear; the lines were assumed here for simplicity, but the true variation of the term energies with \( R \) must be calculated. The positions of some molecules in the diagram are indicated. After Herzberg.

<table>
<thead>
<tr>
<th>MOLECULAR ORBITAL</th>
<th>1σ&lt;sub&gt;g&lt;/sub&gt;</th>
<th>2σ&lt;sub&gt;g&lt;/sub&gt;</th>
<th>3σ&lt;sub&gt;g&lt;/sub&gt;</th>
<th>1π&lt;sub&gt;g&lt;/sub&gt;</th>
<th>2π&lt;sub&gt;π&lt;sup&gt;*&lt;/sup&gt;&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt; 1Σ&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He&lt;sub&gt;2&lt;/sub&gt; 1Σ&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image3" alt="Image" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt; 1Σ&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be&lt;sub&gt;2&lt;/sub&gt; 1Σ&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image7" alt="Image" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt; 3Σ&lt;sup&gt;−&lt;/sup&gt;</td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt; 1Σ&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
<td><img src="image15" alt="Image" /></td>
<td><img src="image16" alt="Image" /></td>
<td><img src="image17" alt="Image" /></td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt; 1Σ&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image18" alt="Image" /></td>
<td><img src="image19" alt="Image" /></td>
<td><img src="image20" alt="Image" /></td>
<td><img src="image21" alt="Image" /></td>
<td><img src="image22" alt="Image" /></td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt; 3Σ&lt;sup&gt;−&lt;/sup&gt;</td>
<td><img src="image23" alt="Image" /></td>
<td><img src="image24" alt="Image" /></td>
<td><img src="image25" alt="Image" /></td>
<td><img src="image26" alt="Image" /></td>
<td><img src="image27" alt="Image" /></td>
</tr>
<tr>
<td>F&lt;sub&gt;2&lt;/sub&gt; 1Σ&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image28" alt="Image" /></td>
<td><img src="image29" alt="Image" /></td>
<td><img src="image30" alt="Image" /></td>
<td><img src="image31" alt="Image" /></td>
<td><img src="image32" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 3.12
Electron density contour maps of 1σ<sub>g</sub> through 3σ<sub>g</sub> molecular orbitals, for H<sub>2</sub> through F<sub>2</sub>. These are based on highly accurate calculations done by Dr. A. C. Wahl at the Argonne National Laboratory. [Reproduced with permission.]
Rotational and Vibrational Spectra for Diatomics

A. Pure rotational transitions (microwave or far-IR)

For a fixed electronic state and $\nu$, we have

$J = 0, 1, 2, \ldots$  
(Note: for states with $\Delta \not= 0$ or $\Omega \not= 0$,
the lowest levels will not exist.)

Which transitions are allowed? There is no induced
electronic dipole moment, so we need matrix elements of

$H_{E1} = \vec{M} \cdot \vec{E}$  
(for rot., vib. transitions)

permanent dipole moment,
$= 0$ for homonuclear molecules

Heteronuclear molecules only. Homonuclear
molecules have no pure rotational or vibration-
rotation spectra, with the following exceptions:

1) Weak $E2$ transitions
2) For electronic states with $S \not= 0$, weak $M1$ transitions
3) Raman-type transitions (two-photon) with $J \rightarrow J'$

The selection rules are easy for a pure rigid
rotator in a $\Sigma$ state, where $\Delta = \Omega = 0$:

Rate $\propto | < J M | \vec{M} \cdot \vec{E} | J' M' > |^2$  

$= \sum_{J_m} R_{J_m}^J \rightarrow R_{J_m}$, i.e., oriented along $R_{ab}$

$\Rightarrow \Delta M = 0, \pm 1$  
and  $\Delta J = \pm 1$ (parity forbids $\Delta J = 0$)

Actually, $\Delta J = \pm 1$ remains a rather good selection
rule even when the above assumptions are relaxed.

Spectrum: for $J' \leftrightarrow J$, $J' = J \pm 1$

$E_{rot} (J') - E_{rot} (J) \approx B (J+1)(J+2) - B(J)(J+4) = 2B(J+1)$

$\uparrow$

Series of evenly spaced lines,
shifted slightly due to $D_B$
An actual spectrum is shown on p. M16. The line strengths are modified by the distribution of initial states in thermal equilibrium,

\[ P(J) \propto (2J+1) e^{-E/kT} \]

peaks near \( J = 7 \)

for CO at 300K

B. Vibration-rotation spectra, \( \Delta V \neq 0 \).

Again, \( E1 \) transitions exist for heteronuclears only, for which we have,

\[ \text{Rate} \propto \left| \langle \nu J M | \hat{\mu}(R) \cdot \hat{E} | \nu' J' M' \rangle \right|^2 \]

It's the variation of \( \mu \) with \( R \) that makes vibrational transitions possible.

Expanding \( \mu = \mu_{\text{static}} + \frac{\partial \mu}{\partial R} (R - R_0) + \cdots \)

\[ \text{Rate} \propto \left( \mu_{\text{static}} \langle \nu | \mu | \nu' \rangle + \frac{\partial \mu}{\partial R} \int x_{\text{vib}}^* (R - R_0) x_{\nu' \text{vib}} dR + \cdots \right)^2 \]

\[ = \sigma_{\nu \nu'} \]

(where only the \( \nu \) dependence is shown)

For a harmonic oscillator, \( x_{\nu \text{vib}} \) is a Hermite polynomial, and it turns out that

\[ \langle \nu | \mu | \nu' \rangle \propto (\sqrt{\nu+1} \sigma_{\nu \nu+1} + \sqrt{\nu} \sigma_{\nu \nu-1}) \]

So in vibrational absorption, the strongest transition is the "fundamental," \( \Delta V = 1 \), and the others are "overtones."

Each vibrational "band" also has rotational structure with \( \Delta J = +1, -1 \), as shown on the next page:
Figure 6.14. Pure rotational emission of hot HF molecules. The spectrum also contains weaker lines due to H₂O and LiF molecules.

Fig. 10.7. A band in the rotational-vibrational spectrum of the HBr molecule, showing the term scheme and the transitions. The origin of the band is denoted by ν₀. A Q branch is not allowed here.