IX. Molecules

A. Born-Oppenheimer Approximation

- Diatomic molecules
- Fig

- Molecular vs. atomic structure
  - Electrons have less symmetry in molecules
  - Molecule has more degrees of freedom
    - Electronic configurations
    - Rotations about the axes connecting the nuclei
    - Vibrations along the line centers
- Key: The molecular degrees of freedom generally decouple
  - Treat each independently (more or less)
  - Why? The energies have significantly different magnitude
  - $m_e \ll M$
    - Electrons have very small inertia compared to the nuclei
    - Electrons react quickly to changes in the nuclei
    - Electrostatic configurations decouple from the nuclear motions

B. Approximate Energies

- Electrostatic energies
  - Schematic of the electrostatic potential
  - Fig

- ◇ Parameterized by the nuclear separation R
  - ▲ Expect R is on the order of the Bohr radius (i.e. $R_0 \sim a_0$)
  - ▲ Expect energies comparable to energy levels in atom
- ◇ Electrostatic energies

$$E_{el} \sim \frac{e^2}{a_0} = \frac{\hbar^2}{m_e a_0^2} \tag{1}$$

- ◇ Frequencies

$$\hbar\omega_{el} \sim E_{el} \tag{2}$$

  - ▲ $\lambda_{el} \sim 1000\text{Å}$
  - ▲ Ultraviolet or optical transitions

- Vibrational Energies
  - ◇ Displace the nuclei by ΔR from the equilibrium separation R_0
  - ◇ Expect energies similar to the SHO

$$\frac{1}{2} M\omega_{vib}^2 \Delta R^2 \tag{3}$$

  - ◇ If the displacement is comparable to $R_0 \sim a_0$, then we expect energies comparable to the depth of the potential well

$$\frac{1}{2} M\omega_{vib}^2 a_0^2 \sim E_{el} \tag{4}$$

  - ◇ Vibrational energy

$$\hbar\omega_{vib} \sim \left(\frac{m_e}{M}\right)^{\frac{1}{2}} E_{el} \tag{5}$$

    - ▲ For $m_e/M \sim 10^{-3}$ or 10^{-4}, these photons will lie in the near or mid-infrared
    - ▲ For H_2, $\lambda_{vib} \approx 2\mu$

- Rotational Energies
  - ◇ Rotate about axes perpendicular to the line connecting the nuclei
  - ◇ Moment of inertia

$$I \sim Ma_0^2 \tag{6}$$

  - ◇ Angular momentum

$$L \sim I\omega_{rot} \sim Ma_0^2\omega_{rot} \tag{7}$$

  - ◇ Energies
    - ▲ Angular momentum is quantized in units of $\hbar/2$

- ▲ Therefore

$$E_{rot} = \hbar\omega_{rot} \sim \frac{\hbar^2}{Ma_0^2} \sim \frac{m_e}{M}E_{el} \tag{8}$$

- ◇ Frequencies
  - ▲ For $m_e/M \sim 10^{-3} \sim 10^{-4}$, photons will lie in the millimeter range
- Decoupling of Energies

$$E_{rot} : E_{vib} : E_{el} \;\sim\; \left(\frac{m_e}{M}\right) : \left(\frac{m_e}{M}\right)^{\frac{1}{2}} : 1 \tag{9}$$

  - ◇ Hierarchy provides a clean basis for perturbation theory
  - ◇ This is the physics behind the Born-Oppenheimer approx

C. Hamiltonian for a Diatomic Molecule

- Fig (coordinates)

- Ignoring spin-orbit coupling and relativistic corrections
- Separate kinetic energy of the nucleus from the electronic energies

$$H = H_{AB} + H_{el} \tag{10}$$

$$H_{AB} \equiv -\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 \tag{11}$$

$$H_{el} \equiv -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) + V \tag{12}$$

$$V \equiv -\frac{Z_A e^2}{r_{1A}} - \frac{Z_B e^2}{r_{1B}} - \frac{Z_A e^2}{r_{2A}} - \frac{Z_B e^2}{r_{2B}} + \frac{Z_A Z_B e^2}{R} + \frac{e^2}{r_{12}} \tag{13}$$

  - ◇ Note the ∇ operators refer to differentiation with respect to vectors $\vec{r}_A, \vec{r}_B, \ldots$

- ◇ Meanwhile

$$r_{12} \equiv |\vec{r}_1 - \vec{r}_2| \tag{14}$$
$$R \equiv |\vec{r}_A - \vec{r}_B| \tag{15}$$
$$\tag{16}$$

- Schroedinger equation

$$H\Psi_E = i\hbar\frac{\partial\Psi_E}{\partial t} \tag{17}$$

  - ◇ H has no explicit time dependence
  - ◇ Expect energy eigenstates of the form

$$\Psi_E = u(\vec{r}_A, \vec{r}_B, \vec{r}_1, \vec{r}_2)\mathrm{e}^{-iEt/\hbar} \tag{18}$$

  - ◇ Time independent Schroedinger equation

$$H|u\rangle \ = \ E|u\rangle \tag{19}$$

- Born-Oppenheimer Approximation
  - ◇ Note the operator H_{AB} is a factor m_e/M smaller than the kinetic terms in H_{el}
  - ◇ Separate $|u\rangle$ into terms with the electrons and terms with the nuclei

$$|u\rangle = u_{el}(\vec{r}_1, \vec{r}_2, R)u_{AB}(\vec{r}_A, \vec{r}_B) \tag{20}$$

    - ▲ Not entirely separated
    - ▲ u_{el} has dependence on R, the nuclear separation
- Examining the time-independent Schroedinger Equation

$$u_{AB}H_{el}u_{el} + H_{AB}u_{el}u_{AB} = Eu_{el}u_{AB} \tag{21}$$

  - ◇ Expand the second term (Leibnitz's Rule)

$$H_{AB}u_{el}u_{AB} = u_{el}H_{AB}u_{AB} - \frac{\hbar^2}{M_A}\nabla_A u_{el}\cdot\nabla_A u_{AB} \ - \tag{22}$$
$$\frac{\hbar^2}{M_B}\nabla_B u_{el}\cdot\nabla_B u_{AB} \ + \ u_{AB}H_{AB}u_{el} \tag{23}$$

  - ◇ Note (because u_{el} depends only on R)

$$\nabla_A u_{el} = \frac{\vec{R}}{R}\frac{\partial u_{el}}{\partial R} = -\nabla_B u_{el} \tag{24}$$

  - ◇ The middle terms in Equation (23) can be rewritten as

$$\hbar^2\frac{\partial u_{el}}{\partial R}\frac{\vec{R}}{R}\cdot\left(\frac{1}{M_B}\nabla_B - \frac{1}{M_A}\nabla_A\right)u_{AB} \tag{25}$$

- The term in the parenthesis is proportional to $\vec{v}_A - \vec{v}_B$ which should average to zero for a bound molecule
- The last term in Equation (23) can be ignored

$$u_{AB} H_{AB} u_{el} = \frac{m_e}{M} u_{AB} H_{el} u_{el} \tag{26}$$

- Therefore, the second term has been reduced to

$$H_{AB} u_{el} u_{AB} \approx u_{el} H_{AB} u_{AB} \tag{27}$$

- Altogether, our time-independent Schroedinger equation becomes

$$u_{AB} H_{el} u_{el} + u_{el} H_{AB} u_{AB} = E u_{el} u_{AB} \tag{28}$$

  - Rewriting

$$\frac{1}{u_{el}} H_{el} u_{el} = -\frac{1}{u_{AB}} H_{AB} u_{AB} + E \tag{29}$$

  - RHS depends only on $\vec{r}_A$ and $\vec{r}_B$
  - LHS depends only on $\vec{r}_1$ and $\vec{r}_2$ + a parameter dependence on R

- Separation of variables
  - Both sides must equal a constant $E_{el}(R)$

$$H_{el} |u_{el}\rangle = E_{el}(R) |u_{el}\rangle \tag{30}$$

$$H_{AB} |u_{AB}\rangle + E_{el}(R) |u_{AB}\rangle = E |u_{AB}\rangle \tag{31}$$

(32)

  - We have separated the electronic degrees of freedom from the motions of the nuclei {uninteresting}

D. Energies

- Separating translational and internal degrees of freedom
  - Coordinate transformation
  - Center of mass

$$\vec{R}_{CM} \equiv \frac{M_A \vec{r}_A + M_B \vec{r}_B}{M_A + M_B} \tag{33}$$

  - Relative displacement

$$\vec{R} \equiv \vec{r}_A - \vec{r}_B \tag{34}$$

◇ Hamiltonian

$$H_{AB} = -\frac{\hbar^2}{2M}\nabla^2_{CM} - \frac{\hbar^2}{2\mu}\nabla^2_R \tag{35}$$

$$\mu \equiv \frac{M_A M_B}{M_A + M_B} \tag{36}$$

$$M \equiv M_A + M_B \tag{37}$$

◇ Express our state u_{AB} in terms of $\vec{R}$ and $\vec{R}_{CM}$

$$u_{AB} = u_{trans}(\vec{R}_{CM})u_{int}(\vec{R}) \tag{38}$$

▲ u_{trans} describes the translational motions of the nuclei

▲ u_{int} describes the internal motions of the nuclei

- Nuclear equation

$$\frac{1}{u_{trans}}\left(-\frac{\hbar^2}{2M}\nabla^2_{CM}u_{trans}\right) = \frac{1}{u_{int}}\left(\frac{\hbar^2}{2\mu}\nabla^2_R u_{int}\right) - E_{el}(R) + E \tag{39}$$

◇ Examining the equation

▲ LHS depends only on $\vec{R}_{CM}$

▲ RHS depends only on $\vec{R}$

▲ Separation of variables implies each side of Equation (39) must equal a constant E_{trans}

◇ Separation

$$-\frac{\hbar^2}{2M}\nabla^2_{CM}u_{trans} = E_{trans}u_{trans} \tag{40}$$

$$-\frac{\hbar^2}{2\mu}\nabla^2_R u_{int} + E_{el}(R)u_{int} = E_{int}u_{int} \tag{41}$$

$$\text{with } E_{int} = E - E_{trans} \tag{42}$$

◇ We have reduced the motions of the nuclei to translations and internal motions

- Vibrations + Rotations (Internal energies)

$$-\frac{\hbar^2}{2\mu}\nabla^2_R u_{int} + E_{el}(R)u_{el} = E_{int}u_{int} \tag{43}$$

◇ Motions of nuclei A relative to nuclei B are expressed in identical fashion to a single particle with reduced mass μ in a central force field

◇ Hamiltonian is spherically symmetric

▲ Introduce spherical coordinates

$$\nabla^2_R = \frac{1}{R^2}\left[\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{L^2}{\hbar^2}\right] \tag{44}$$

▲ Usual separation of variables

$$u_{int}(\vec{R}) = \frac{1}{R} Z_{vib}(R) Y_{\ell m}(\theta, \phi) \tag{45}$$

◇ Psuedo-spherical harmonics

▲ Usual angular momentum rules

$$L^2 Y_{Jm} = J(J+1)\hbar^2 Y_{Jm} \tag{46}$$

$$L_z Y_{Jm} = m\hbar Y_{Jm} \tag{47}$$

▲ Two angular coordinates correspond (sort of) to the two degrees of freedom for the rotation axes

◇ 'Radial' equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2 Z_{vib}}{dR^2} + E_{el}(R) Z_{vib} = \left[E_{int} - \frac{J(J+1)\hbar^2}{2\mu R^2} \right] Z_{vib} \tag{48}$$

▲ Expresses the motions along the line of centers of the nuclei

◇ Harmonic oscillator approximation

▲ Assume the potential $E_{el}(R)$ has the form we sketched out on page 1

▲ $R = R_0$ corresponds to a minimum in $E_{el}(R)$

▲ Taylor expand around R_0

$$E_{el}(R) = E_{el}(R_0) + \frac{1}{2}\mu\omega_0^2 (R - R_0)^2 + \ldots \tag{49}$$

$$\text{where } \mu\omega_0^2 \equiv E''_{el}(R_0) \tag{50}$$

▲ Change of variables: $x \equiv R - R_0$

▲ Equation (48) to lowest order reduces to the SHO equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2 Z_{vib}}{dx^2} + \frac{1}{2}\mu\omega_0^2 x^2 Z_{vib} = E_{vib} Z_{vib} \tag{51}$$

$$\text{where } E_{vib} \equiv E_{int} - E_{el}(R_0) - \frac{J(J+1)\hbar^2}{2\mu R_0^2} \tag{52}$$

◇ Energies

▲ Define rotation energy

$$E_{rot} \equiv \frac{J(J+1)\hbar^2}{2\mu R_0^2} = J(J+1)B \tag{53}$$

∘ B is the rotational constant of the molecule

∘ B is typically determined experimentally

▲ Vibrational energy

$$E_{vib} = \left(n + \frac{1}{2} \right) \hbar\omega_0 \qquad n = 0, 1, 2, \ldots \tag{54}$$

- ▲ Internal energy is then the sum over 3 terms

$$E_{int} = E_{el}(R_0) + E_{vib} + E_{rot} \tag{55}$$

E. Molecular Structure

- The following is generally (but not entirely) restricted to H_2
- Ground state energy E_0
  - ◇ Estimate E_0 with the Variational Method
    - ▲ For arbitrary wave function Ψ

$$E \equiv \frac{<\Psi|H|\Psi>}{<\Psi|\Psi>} \; > \; E_0 \tag{56}$$

    - ▲ Proof:

$$|\Psi> = \sum_\alpha c_\alpha |u_\alpha> \tag{57}$$

$$E = \frac{\sum_\alpha |c_\alpha|^2 E_\alpha}{\sum_\alpha |c_\alpha|^2} \; > \; E_0 \qquad \text{(Q.E.D.)} \tag{58}$$

  - ◇ Express our wave function in terms of a set of eigenstates $|j>$ (not necessarily orthonormal)

$$|\Psi> = \sum_{j=1}^{n} c_j |j> \tag{59}$$

    - ▲ Our energy is

$$E = \frac{\sum_{i,j=1}^{n} c_i^* H_{ij} c_j}{\sum_{i,j} c_i^* N_{ij} c_j} \tag{60}$$

    - ▲ where $N_{ij} \equiv <i|j>$
    - ▲ Minimizing this energy $\Rightarrow$ require $\partial E / \partial c_k^* = 0$ for each k

$$\sum_{j=1}^{n} (\, H_{kj} - E N_{kj} \,)\, c_j = 0 \quad \text{for } k = 1, 2, \ldots, n \tag{61}$$

    - ▲ Linear algebra solution to these n equations

$$\det (\, H_{kj} - E N_{kj} \,) = 0 \tag{62}$$

- Heilter & London

◇ Hamiltonian (in atomic units where $a_0 = 1 = e^2/a_0$)

$$H_{el} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \tag{63}$$

◇ Let

$$u_{el} = c_1 u(r_{1A})u(r_{2B}) + c_2 u(r_{1B})u(r_{2A}) \tag{64}$$

- ▲ The wave function is two Hydrogen atoms with the electron taken in various combinations
- ▲ This has the correct form for $R \to \infty$
- ▲ $u(r)$ are the ground state wave functions for the Hydrogen atom

◇ Apply the Variational method, e.g. Equation (62)

$$\begin{vmatrix} H_{11} - EN_{11} & H_{12} - EN_{12} \\ H_{21} - EN_{21} & H_{22} - EN_{22} \end{vmatrix} = 0 \tag{65}$$

- ▲ Evaluating H_{ij} and N_{ij}

$$\begin{aligned} N_{11} &= <u(r_{1A})|u(r_{1A})><u(r_{2B})|u(r_{2B})> \\ N_{12} &= <u(r_{1A})|u(r_{1B})><u(r_{2B})|u(r_{2A})> \\ &\vdots \\ H_{11} &= <u(r_{1A})u(r_{2B})|H_{el}|u(r_{1A})u(r_{2B})> \\ &\vdots \end{aligned}$$

- ▲ Evaluate the N terms

$$N_{11} = N_{22} = 1 \tag{66}$$
$$N_{12} = N_{21} = \Theta^2 \tag{67}$$
$$\text{with } \Theta^2 \equiv \frac{1}{\pi}\int d^3x_1 \, \mathrm{e}^{-r_{1A}}\mathrm{e}^{-r_{1B}} \tag{68}$$

- ▲ Evaluate the Hamiltonian terms

$$H_{22} = H_{11} = -1 + \mathcal{C} \tag{69}$$
$$H_{12} = H_{21} = -\Theta^2 + \mathcal{E} \tag{70}$$
$$\mathcal{C} \equiv \frac{1}{\pi^2}\int\int d^3x_1 d^3x_2 \, \mathrm{e}^{-2r_{1A}}\left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R}\right)\mathrm{e}^{-2r_{2B}} \tag{71}$$
$$\mathcal{E} \equiv \frac{1}{\pi^2}\int\int d^3x_1 d^3x_2 \, \mathrm{e}^{-r_{1A}}\mathrm{e}^{-r_{1B}}\left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}\right)\mathrm{e}^{-r_{2A}}\mathrm{e}^{-r_{2B}} \tag{72}$$

  - ○ $\mathcal{C}$ is the Coulomb integral which involves the product of the squares of the wave functions

        - $\mathcal{E}$ is the exchange integral involving the mixed terms;
          i.e. the effect of sharing the electrons
    - Analytic result

$$\Theta = \mathrm{e}^{-R}\left(1 + R + \frac{1}{3}R^2\right) \tag{73}$$

$$\mathcal{C} = \mathrm{e}^{-2R}\left(\frac{1}{R} + \frac{5}{8} - \frac{3}{4}R - \frac{1}{6}R^2\right) \tag{74}$$

$$\mathcal{E} \equiv \text{"too scary for this space"} \tag{75}$$

    - Fig

        - Only $\mathcal{E}$ is significantly negative
        - Therefore, this term is the key to the molecular bond
    - Solving the determinant

$$E_{el}^{\pm} = \frac{H_{11} \pm H_{12}}{1 \pm N_{12}} = -1 + \frac{\mathcal{C} \pm \mathcal{E}}{1 \pm \Theta^2} \tag{76}$$

$$E_{mol}^{\pm} = \frac{\mathcal{C} \pm \mathcal{E}}{1 \pm \Theta^2} \tag{77}$$

        - The -1 is just the energy of the separated individual H atoms
        - The molecular bond is expressed by the 2nd term ($E_{mol}^{\pm}$)
        - Note: Only the 'plus sign' gives a bound state
- Final answer
    - Depth of the potential well at R_0

$$E_{mol}^{+} = -0.125\left(\frac{e^2}{a_0}\right) \tag{78}$$

    - Including the ground state vibrational term ($\frac{1}{2}\hbar\omega_0$)

$$E_{GS} = -0.116\left(\frac{e^2}{a_0}\right) = -3.14 \text{ eV} \tag{79}$$

- ▲ Experiment: -4.476 eV
- ▲ Variational method always gives an upper bound, and generally an amazingly accurate one

- Eigenfunctions
  - ◇ Taking our eigenstate with energy E^{+}_{mol}

$$c_1 = c_2 = \frac{1}{\sqrt{2}} \tag{80}$$

  - ◇ Symmetric spatial wave function
  - ◇ To create an antisymmetric state for our pair of electrons (fermions), couple the spatial wave function with a singlet spin state
  - ◇ Conversely, the unbound state (E^{-}_{mol}) is paired with the triplet spin state
  - ◇ This behavior contrasts with Hund's rules:
    the lower spin state $\Rightarrow$ lower energy
    - ▲ Electrons provide the attractive force here
    - ▲ Farther apart $\Rightarrow$ less 'glue'

F. Excited States

- Spectroscopic Notation
  - ◇ Electronic levels (analogous to $n = 1, 2, 3, \ldots$)
    - ▲ X $\equiv$ Ground state
    - ▲ Bound excited states = B,C,D,...
    - ▲ Unbound excited states = $a, b, c, \ldots$
  - ◇ Orbital angular momentum (Λ)
    - ▲ Atoms: Electronic potential is spherically symmetric $\Rightarrow$ Total angular momentum is conserved
    - ▲ Diatomic molecules: Symmetry about the line of centers $\Rightarrow$ Only the component about the nuclear axis is a constant of the motion
      - ◦ Refer to this component of the angular momentum as Λ
      - ◦ Labels: $\Lambda = 0, 1, 2 \rightarrow \Sigma, \Pi, \Delta$
    - ▲ Other components of the angular momentum precess $\Rightarrow$ the total angular momentum precesses
    - ▲ Fig

- ◇ Electron-spin angular momentum (Σ)
  - ▲ Similar to Λ, the only component which is a constant of the motion (unless $\Lambda = 0$) is the component along the internuclear axis
  - ▲ Refer to this component of S as Σ (to be confused with Σ the $\Lambda = 0$ state as S the $\ell = 0$ state is confused with spin)
  - ▲ Values: $\Sigma = -S, -S+1, \ldots, S-1, S$
- ◇ 'Total' Angular Momentum (Ω)
  - ▲ Sum of the internal components of the spin and orbital angular momentum (i.e. $\Omega = \Lambda + \Sigma$)
  - ▲ <u>Not</u> a vectoral sum
- ◇ Planar Symmetry
  - ▲ If the electronic wave function changes sign under a reflection through any plane connecting the two nuclei $\Rightarrow$ '- state'
  - ▲ Otherwise, '+ state'
- ◇ Center symmetry
  - ▲ If the wave function changes sign when reflected through the center of nuclear charge $\Rightarrow$ 'u state'
  - ▲ Otherwise, 'g state'
- ◇ Nuclear spin
  - ▲ H_2 has two nuclear states: ortho (spin aligned) and para (spin anti-aligned)
  - ▲ ortho has 3× degeneracy over para
- ◇ Fig (Shull & Beckwith)

• Selection Rules for Electric Dipole Transitions

- ◇ Orbital angular momentum

$$\Delta\Lambda = 0, \pm 1 \tag{81}$$

- ◇ Spin

$$\Delta S = 0 \tag{82}$$

- ◇ Plane symmetry

$$+ \to + \quad \text{or} \quad - \to - \tag{83}$$

- ◇ Center symmetry

$$g \to u \quad \text{or} \quad u \to g \tag{84}$$

- ◇ Nuclear

$$\text{ortho} \to \text{para is forbidden}$$

◇ Dipole moment must change!

$$<\phi_f|\vec{d}|\phi_i> \neq 0 \tag{85}$$

- Astrophysical consequences
  (a) $\Delta S = 0$ stabilizes H_2 against photo-dissociation

$$X^1\Sigma_g^+ \; + \gamma \rightarrow b^3\Sigma_u^+ \quad \text{is forbidden} \tag{86}$$

  (b) Photo-dissociation is generally a two-step process

$$\gamma + X^1\Sigma_g^+ \; \rightarrow B^1\Sigma_u^+ \rightarrow (\text{unstable vibrational continuum state}) + \gamma \tag{87}$$

  (c) Change in dipole reduces the likelihood of H_2 formation

$$\mathrm{H}(1s) + \mathrm{H}(1s) \rightarrow X^1\Sigma_g^+ \; + \; \gamma \quad \text{is forbidden} \tag{88}$$

  ◇ This significantly reduces the likelihood of H_2 formation
  ◇ H_2 forms via 3-body collisions or with dust grains as the catalyst

G. Spectroscopy

- Limit the discussion to electric dipole transitions
- Perturbation

$$\begin{aligned} H^{(1)} &= \frac{e}{mc}\vec{A}\cdot\vec{p} \\ &= -\vec{E}\cdot\vec{d} \end{aligned}$$

- Dipole moment
  ◇ $\vec{d}$ is the electronic dipole moment
  ◇ Express it in terms of a nuclear and electric part

$$\vec{d} = \vec{d}_{el} + \vec{d}_{nuc} \tag{89}$$

  ◇ Define positions relative to the center-of-mass

$$\vec{X} = \vec{r} - \vec{R}_{CM} \tag{90}$$

  ◇ Electronic dipole moment becomes

$$\vec{d}_{el} = \sum_{j=1}^{N} \vec{d}_j$$
$$\text{with } \vec{d}_j \equiv -e\vec{X}_j, \;\; \text{the dipole moment of the j-th electron}$$

◇ Nuclear dipole moment

$$\vec{d}_{nuc} = Z_A e\vec{X}_A + Z_B e\vec{X}_B \tag{91}$$

▲ Note: $\vec{X}_A = (M_B/M)\vec{R}$, $\vec{X}_B = -(M_A/M)\vec{R}$

▲ Therefore, $\vec{d}_{nuc}$ vanishes for a homonuclear molecule

• As always, probabilities and transition rate will depend on this matrix element

$$<f|H^{(1)}|i> = -<f|\vec{E}_\omega \cdot (\vec{d}_{el} + \vec{d}_{nuc})|i> \tag{92}$$

◇ $\vec{E}_\omega$ is the Fourier transform of $\vec{E}$: $[\vec{E}_\omega = -i\omega/c\vec{A}(\omega)]$

◇ For molecules, our time-independent energy eigenfunctions have this form

$$|u> = \frac{1}{R} Z_{vib}(R) Y_{Jm}(\theta, \phi) u_{trans} u_{el} \Sigma \tag{93}$$

▲ Σ is the electron-spin wave function

◇ $H^{(1)}$ is independent of the translational state of the molecular u_{trans}

▲ Therefore, $u^i_{trans} = u^f_{trans}$ or the matrix element vanishes

▲ For the following, assume $u^i_{trans} = u^f_{trans} = 1$

(a) Pure rotational spectra

• Assume the initial and final electronic and vibrational states remain the same

• The matrix element reduces to

$$<f|H^{(1)}|i> = \int d\Omega Y_{J'm'} <Z_{vib}|H_D|Z_{vib}> Y_{Jm} \tag{94}$$

◇ where

$$<Z_{vib}|H_D|Z_{vib}> \equiv -\int_0^\infty \vec{E}_\omega \cdot \vec{D}(R, \theta, \phi) |Z_{vib}(R)|^2 dR \tag{95}$$

◇ Integral over separation only!

• Permanent Dipole Moment

◇ $\vec{D}(R, \theta, \phi)$ is the dipole moment $\vec{d}$ after integrating over all electronic coordinates (including spin)

$$\vec{D}(R, \theta, \phi) = \int \vec{d} u_{el}(\vec{X}_1, \vec{X}_2, \ldots, \vec{X}_N; R)\, d^3X_1 d^3X_2 \ldots d^3X_N \tag{96}$$

▲ $\vec{D}$ is referred to as the permanent dipole moment

▲ For the matrix element to not vanish, obviously $\vec{D} \neq 0$

▲ Contrast with atoms where we simply require $\vec{d}$ changes in the transition

$$<f|\vec{d}|i> \neq 0$$

- ◇ H_2
  - ▲ No permanent dipole moment
  - ▲ Rotational transitions are not allowed!
- ◇ Consider the angular dependence of $\vec{D}$
  - ▲ Obviously, $\vec{D}_{nuc} = \vec{d}_{nuc}$ lies along the line-of-centers of the two nuclei
  - ▲ Therefore, $\vec{D}_{nuc}$ only depends on the magnitude of $\vec{R}$
  - ▲ In addition, the reflection symmetry of the electronic distribution implies $\vec{D}_{el}$ (but not $\vec{d}_{el}$) has no component $\perp$ to $\vec{R}$
  - ▲ Therefore $\vec{D}$ has no functional dependence on θ, ϕ

$$\vec{D} \;=\; D(R)\,\frac{\vec{R}}{R} \tag{97}$$

- • Electric-dipole transition
  - ◇ 'Rigid rotator' model → Evaluate $D(R)$ at R_0

$$D(R) \approx D(R_0) \equiv D_0 \tag{98}$$

  - ▲ D_0 is referred to as the reduced dipole moment
  - ▲ Warning: In the literature, D_0 is often written as μ
  - ▲ First (trivial) selection rule: $D_0 \neq 0$
  - ◇ Consider the usual orientations of $\hat{\varepsilon}$
  - ▲ $\hat{\varepsilon} \parallel \hat{z}$

$$\vec{E}_\omega \cdot \vec{D} \propto |E_\omega| D_0 T_k^{(1)} \tag{99}$$

    i. Standard selection rules for the angular terms
    ii. $\Delta J = \pm 1, \Delta m = 0$ (Parity prohibits $\Delta J = 0$)
  - ▲ $\hat{\varepsilon} \perp \hat{z}$: Same story except $\Delta m = \pm 1$
  - ◇ Transition dipole moment
  - ▲ De-excitation probability from $J' = J+1 \to J$
  - ▲ Evaluate by summing over all final m states

$$|D_{J+1,J}|^2 \equiv \sum_m D_0^2 |<Y_{Jm}|T_q^{(1)}|Y_{J+1,m'}>|^2 = \frac{J+1}{2J+3} D_0^2 \tag{100}$$

  - ◇ Rate of spontaneous emission

$$A_{J+1,J} = \frac{4\omega^3}{3\hbar c^3}|\vec{D}_{if}|^2 = \frac{4(J+1)\,\omega^3}{3(2J+3)\hbar c^3} D_0^2 \tag{101}$$

(b) Vibrational-rotational spectra

- • Only the electronic state remains unchanged

- In the SHO approximation, the matrix element is

$$<f|H_d|i> = -|E_\omega| \int d\Omega Y^*_{Jm} <n|D|n'> T^k_q Y_{Jm} \tag{102}$$

- Expand $D(R)$ about R_0

$$D(R) = D_0 + x\left(\frac{dD}{dR}\right)_{R=R_0} + \mathcal{O}(x^2) \tag{103}$$

  ◇ $x \equiv R - R_0$
  ◇ First term corresponds to the pure rotational case (i.e. $n = n'$)
  ◇ Higher order terms account for the vibrational modes
- Identify x as the sum of raising and lowering operators
  ◇ Selection rules: $\Delta n = \pm 1$
  ◇ Additionally:

$$\frac{dD}{dR}|_{R=R_0} \neq 0 \tag{104}$$

- Higher order terms of the $D(R)$ expansion
  ◇ These allow for $\Delta n = \pm 2, \ldots$
  ◇ Each term is down by a factor of

$$\frac{\hbar}{\mu\omega_0 R_0^2} \sim \left(\frac{m_e}{M}\right)^{\frac{1}{2}} \tag{105}$$

- Energies: Expect vibrational transitions to have $\Delta E = \hbar\omega_0$
  ◇ Observationally, larger n levels have smaller spacings because the binding potential is not a pure quadratic well
  ◇ Also, rotational states often change the moment of inertia
- Additional selection rules
  ◇ Expect the same rules on J as for pure rotational transitions (i.e. $\Delta J = \pm 1$)
  ◇ Only true for $\Lambda = 0$ (zero electronic angular moment along $\hat{R}$)
  ◇ If $\Lambda \neq 0$, the parity of the electronic state can change (by flipping the sign of Λ) and $\Delta J = 0$ is allowed
- P and R branches
  ◇ Energies for vibrational and rotational spectra,

$$E_{nJ} = (n + \frac{1}{2})\hbar\omega_0 + J(J+1)B \tag{106}$$

  ◇ Frequencies
    ▲ Transition $n' = n \pm 1$ and $J' = J + 1$ with $J = 0, 1, 2, \ldots$

$$\omega = \omega_0 + 2(J+1)B/\hbar \quad \textbf{R branch} \tag{107}$$

▲ Transition $n' = n \pm 1$ and $J' = J - 1$ with $J = 1, 2, 3, \ldots$

$$\omega = \omega_0 - 2JB/\hbar \quad \textbf{P branch} \tag{108}$$

▲ If $\Lambda = 0 \Rightarrow \Delta J \neq 0$ and there is no line at $\omega = \omega_0$

▲ Fig (FUSE?)

- Corrections to the Energy
  - ◇ True molecular spectra show departures from Equation (107)
  - ◇ Several of our approximations don't hold for real molecules
    - ▲ Centrifugal forces (especially for large J) distort the molecule $\Rightarrow$ Failure of the 'rigid rotator' approx
    - ▲ Expansion of $E_{el}(R)$ beyond the quadratic term implies additional 'overtones' at near-integral multiples of ω_0
  - ◇ Modified vibrational-rotational energy levels

$$E_{nJ} = \left[1 - A(n + \frac{1}{2})\right](n + \frac{1}{2})\hbar\omega_0 \;+\; [\,1 - CJ(J+1)\,]\,J(J+1)B \tag{109}$$

    - ▲ Fractional anharmonicity constant ($A = 0.027$ for H_2)
    - ▲ Fractional centrifugal constant ($C = 7.6 \times 10^{-4}$ for H_2)

(c) Electronic-Vibrational-Rotational Spectra

- "Vibronic" transitions
- Selection rules
  - ◇ Usual rules

$$\begin{aligned}
&\Delta J = 0, \pm 1\\
&\Delta m = 0, \pm 1\\
&\Delta J \neq 0 \text{ if } \Lambda = 0\\
&J = 0 \to 0 \;\text{ is forbidden always}\\
&\Delta\Lambda = 0, \pm 1
\end{aligned}$$

  - ◇ Note, the electronic transitions do not require $D_0 \neq 0$
    - ▲ Therefore H_2 shows UV electronic transitions
- Matrix element

$$\vec{D}_{if} \propto \int dR\; Z^*_{vib,f}(R) Z_{vib,i}(R) \tag{110}$$

  - ◇ This integral has a non-zero value for any Δn value
  - ◇ $\Rightarrow$ vibronic transitions are not limited to $\Delta n = \pm 1$
  - ◇ Qualitatively assess $\vec{D}_{if}$ by considering the wave function of a particle in a potential well

- ▲ For level n, the wave function has $n+1$ maxima between the turning points
- ▲ The Δn transitions with the highest probability correspond to those when the wave functions show coincident maxima
- ▲ The overlap factors are called Frank-Condon factors
- ▲ Figs

- Band and branch structure
  - ◇ For emission spectra, the branches correspond to:
    - ▲ P branch: $\Delta J = +1$
    - ▲ Q branch: $\Delta J = 0$
    - ▲ R branch: $\Delta J = -1$
  - ◇ R(P) branch starts at highest (lowest) frequencies
  - ◇ Differences in the moments of inertia of the final and initial states lead to lines without equal spacing

$$\nu_R = \nu_{el,vib} + h^{-1}\left[2B + (3B - B')J - (B' - B)J^2\right] \quad (B' > B) \tag{111}$$

    - ▲ The J and J^2 terms have opposite sign
    - ▲ For small J, ν_R increases with J until $J = J_{head}$
    - ▲ Then ν_R decreases!
  - ◇ P and Q branches behave differently

$$\nu_Q = \nu_{el,vib} - h^{-1}(B' - B)J(J+1) \tag{112}$$
$$\nu_P = \nu_{el,vib} - h^{-1}\left[(B' + B)J + (B' - B)J^2\right] \tag{113}$$

  - ◇ Figs

- Astrophysics

(a) H_2 has no dipole moment
  - ◇ True of all homonuclear molecules
  - ◇ Rotational transitions are forbidden!
  - ◇ Also $B(H_2) = 87$K $\Rightarrow$ Excitation is very difficult for most astrophysical situations

(b) $^{12}C^{16}O$ – surrogate tracer for molecular clouds
  - ◇ Robust molecule
  - ◇ Most abundant after H_2 and H_2O
  - ◇ Rotational constant $B = 2.77$K
  - ◇ $J = 1 \to 0$ transition occurs at 2.6mm (115GHz)
  - ◇ Small dipole moment
    - ▲ Small spontaneous coefficient

$$A_{10} = 6 \times 10^{-8}\mathrm{s}^{-1} \tag{114}$$

- ▲ Only a minimal number of collisions are needed to populated the excited level
- ▲ $J = 1$ is populated for $n_H \gtrsim 10^3\,\mathrm{cm}^{-3}$

◇ Radio observations with high angular resolution trace the kinematics of molecular clouds

- ▲ Observe typical kinetic temperature of $T_K \approx 10\mathrm{K}$
- ▲ Denser cores may be at 50K

(c) $^{13}C^{16}O$, $^{12}C^{16}O$

◇ Temperature diagnostic (optical thin)