5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

LECTURE #0: GENERAL INFORMATION
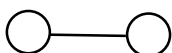
Texts: Bernath   spectra of Atoms and Molecules   ⎫
           Hougen   NBS 115   ⎬ to be handed
           Handouts   ⎭ out
           HLB-RWF   The Spectra and Dynamics of Diatomic Molecules
           WDC   polyatomic vibrations

Assumed background:
Standard QM Models

rigid rotor   rotation $BJ(J + 1)$ $B \propto R^{-2}$

harmonic oscillator   vibration $\omega(v + 1/2)$ $\omega \propto k^{1/2}$

H atom   electronic $-\Re Z^2/n^2$ Z_{eff}, $n^* = n - \mu$

H$_2^{\ddagger}$ LCAO-MO's   MO diagram   bond order
                                                           HOMO, LUMO

Matrix Notation – This is major obstacle to those without 5.73.
                    Schrödinger (ψ) $\leftrightarrow$ Heisenberg (matrix) pictures
                    Read Bernath 2.1-2, 3.1-2, **4.1** $\widehat{\mathbf{H}}$
                    or Handouts
                    or Merzbacher, "Q.M." pages 294-324 (2nd edition)

                                        ⎧ nondegenerate
Perturbation theory (time independent) ⎨ [quasidegenerate (Van Vleck)]
                                        ⎩ degenerate

      Bernath 4.1 $\leftarrow$ more handouts

OUTLINE

1.   ATOMS   "Electronic Structure"
           orbitals→configurations→L–S–J terms
           parametrized in terms of 1e⁻ ($\varepsilon_{n\ell}$, $\zeta_{n\ell}$) and 2e⁻ (F^k, G^k) parameters
           periodicity recovered from $\mathbf{H}^{eff}$ model in terms of ε, ζ, F^k, G^k

2.   DIATOMIC MOLECULES   examples of all tricks in molecular structure theory
           Born-Oppenheimer → potential energy curve V(R)
           rotation
           vibration

$$V(R) = \sum \; a_n \left(\frac{R - R_e}{R_e} \right)^n$$

           Nonrigid, anharmonic, vibrating rotor

$$E_{vJ} = \sum \; Y_{\ell m} \, (v + 1/2)^{\ell} \, [J(J+1)]^m$$

           perturbation theory $\{a_n\} \leftarrow \{Y_{\ell m}\}$
           RKR[WKB]   V(R) ← E_{vJ}
           non-$^1\Sigma$ states (Multiplets, Hund's cases)

3. $\mathbf{H}^{eff}$ MODELS FOR DIATOMICS   FIT MODELS
           derived from infinite $\widehat{\mathbf{H}}$ by Van Vleck Transformation
                1st order effects: "perturbations" (pattern destroyed)
                2nd order effects: centrifugal distortion, Λ-doubling
           fitting of eigenvalues of $\widehat{\mathbf{H}}^{eff}$ to E_{vJ} by adjusting model parameters.

4.   TRANSITION INTENSITIES FOR DIATOMICS
           Limiting Hund's cases → Hönl-London linestrength factors
           General cases $\begin{bmatrix} \text{eigenvectors of } \mathbf{H}^{eff} \\ \text{interference effects} \end{bmatrix}$

5.   ELECTRONIC STRUCTURE **MODELS**: Approximate factorizations of Electronic
                Schrödinger Equation
           Quantum Chemists can calculate anything from 1st principles.
           We want more than a number. We want to know a story, to know why, to know
                how to transfer insight from one molecule to another or one property to
                another.

           $\mathbf{H}_2^+$ LCAO-MO

            Atom in Molecule $\begin{bmatrix} \text{Long Range theory (atoms-in-molecule)} \\ \text{Ligand field theory (atomic-ions-in-molecule)} \end{bmatrix}$

           Molecular Ion in Molecule   Rydberg States   Quantum Defect Theory
           Qualitative MO Theory - Shapes of polyatomic molecules (Walsh)

6.   POLYATOMIC MOLECULES

   Rotation   Symmetric and Asymmetric Tops   A, B, C, rotational constants
                                                            and quantum numbers J_{K_a, K_C}

   Vibration   Normal Modes
                     Wilson's F & G Matrix Methods
                     Point & CNPI Group Theory

   Perturbations   Anharmonic   (Fermi)
                     Local$\leftrightarrow$Normal
                     Rotational   (Coriolis)
                     Polyads
                     IVR

   Electronic Transitions
                     Case Studies
                     Vibronic Coupling

7.   SPECIAL TOPICS AND TECHNIQUES — <u>SUGGESTIONS</u>?
                     Anything you want from <u>The Spectra and Dynamics of Diatomic Molecules</u>
                     (especially Chapter 9)

Structure   Spectrum

balls and springs   line spectrum
motion   transitions between eigenstates
                                             eigenstates are stationary, no motion
How do we get structure and dynamics from eigenstates?

2 approaches — working toward each other.

Q.M. Models — Simplify exact $\widehat{\mathbf{H}} = \widehat{\mathbf{H}}° + \widehat{\mathbf{H}}'$

* what kind of patterns are likely to appear in spectrum?

   symmetry - good QN, especially angular momentum

   approximate separation of coordinates $\widehat{\mathbf{H}}(a, b) = \hat{h}°(a) + \hat{h}°(b) + \hat{h}'(a \sim b)$

* good guesses of model parameters

* internal consistency constraints

         Born-Oppenheimer
         rotation—vibration—electronic
         nearly isolated subunits
   relationships between observables, states, molecules
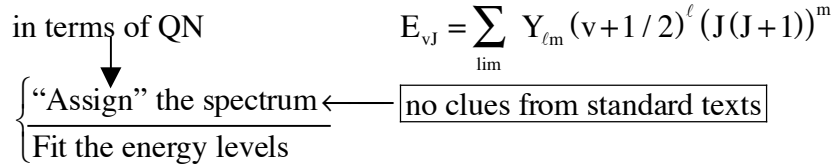 $\longrightarrow$ TRICKS

CRUDE Pattern Recognition in Spectrum

* redundancy
* simplest
  algebraic
  patterns

$\left. \begin{matrix} \text{selection rules} \\ \text{intensity patterns} \end{matrix} \right\}$ for transitions

polynomial representations for energy levels

in terms of QN $E_{vJ} = \sum_{lim} Y_{\ell m} (v + 1/2)^{\ell} (J(J+1))^{m}$

$\left\{ \begin{matrix} \text{"Assign" the spectrum} \longleftarrow \boxed{\text{no clues from standard texts}} \\ \underline{\text{Fit the energy levels}} \end{matrix} \right.$

Chaos vs. Assignability?   at high internal excitation.
QM encodes structure and dynamics into spectrum.
Our job is to learn how to crack this code!

Standard approach

Exact $\widehat{\mathbf{H}}\left(\vec{q}_1, \cdots \vec{q}_n ; \vec{Q}_1, \cdots \vec{Q}_n\right) \equiv \widehat{\mathbf{H}}(\mathbf{q}, \mathbf{Q})$

      n e^- N atoms

replace $\boxed{\begin{matrix} \text{differential} \\ \text{operator} \\ \text{Schrödinger} \\ \text{Representation} \end{matrix}}$ by $\boxed{\begin{matrix} \text{infinite matrix} \\ \text{Heisenberg} \\ \text{Representation} \end{matrix}}$
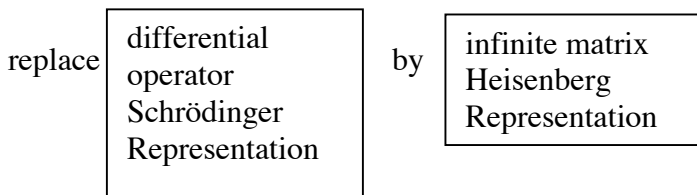
Factor (block diagonalize) this matrix.

     * exactly — good QN $\left[\widehat{\mathbf{H}}, \widehat{\mathbf{A}}\right] = 0$
          blocks still infinite

     * approximately $\widehat{\mathbf{H}} = \widehat{\mathbf{H}}^{\circ} + \widehat{\mathbf{H}}'$
         $\widehat{\mathbf{H}}^{\circ}$ defines complete set of basis functions $\boxed{\begin{matrix} \text{standard models are very useful here} \\ \text{now we can evaluate all matrix elements.} \end{matrix}}$
         always able to write exact ψ as linear combination of basis functions.

   $\widehat{\mathbf{H}}^{\circ}$ is diagonal (i.e. perfectly block diagonalized into |x| submatrices)

         Include effects of infinite $\widehat{\mathbf{H}}'$ by some form of perturbation theory $\left\{ \begin{matrix} \text{nearby perturbers} \\ \text{remote perturbers} \end{matrix} \right.$

$\widehat{\mathbf{H}}^{eff}$ $\left\{ \begin{matrix} \text{How this is done depends on} \\ \\ \quad \text{* region of spectrum (i.e. what is remote?)} \\ \\ \quad \text{* accuracy sought} \\ \\ \quad \text{* whether a phenomenological fit model or an interpretive microscopic model is needed} \end{matrix} \right.$

$$\left\{ \begin{array}{l} \text{Algebraic formulas} \quad \boxed{-\ \text{familiar}} \\ \qquad \text{or} \\ \text{Eigenvalues of } \textbf{computer} \text{ diagonalized matrices} \boxed{\begin{array}{l} -\ \text{more general.} \\ \quad \text{this course} \end{array}} \end{array} \right.$$

Properties other than E are calculable from computer supplied eigenfunctions
     ESPECIALLY TRANSITION PROBABILITIES.

It is a fairly straightforward matter to go from the exact $\widehat{\mathbf{H}}$ to the exact spectrum.

Of course this is not what a spectroscopist does. We attempt to go from spectrum to a determination of all the structural parameters (e.g. force field) that define $\widehat{\mathbf{H}}$.

This is seldom possible!
This is why spectroscopy is still interesting!!!

Diatomic molecules illustrate nearly complete spectrum $\rightarrow \widehat{\mathbf{H}}$ invert-ability.

Polyatomic molecules illustrate the need
for an arsenal of old and new tricks.

pert. theory diatomic molecules	advanced forms of pattern recognition compact generalizations of diatomic tricks

We also ask if there is any insight into new kinds of approximate factorizations of many body systems
BEYOND THE MOLECULAR CONSTANTS.

Why measure something that can be computed *ab initio*? Why measure V(Q) for more than 1 or 2 molecules?

functional groups oxidation states bond E↔bond length barrier systematics