Week 5

Exam and Intro to MO Theory

5.1 First Exam Review

10/17:

- Arrive by 9:25 AM on Wednesday.
- Probably four problems.
  - Won't be doing IRRs for T_d point groups or anything really complicated like that.
- All character tables we need to solve the questions will be provided.
- The questions are independent; if we can't solve problem 1, we'll still be able to take a shot at problem 2.
- Question: Assigning Cartesian coordinates or R_{xyz} to the Mulliken symbols.
  - Example: Assign R_z and $x^2 - y^2$ in D_4.
  - Draw the $d_{x^2-y^2}$ orbital and R_z vector in 3D space.
  - Subject the drawings to each symmetry operation.
    - For E, C_4, C_2, C_2', C_2'', $d_{x^2-y^2}$ gets sent to itself, it's inverse, itself, itself, and it's inverse. Thus, $\Gamma = (1, -1, 1, 1, -1) = B_1$.
    - Likewise, we have for R_z that $\Gamma = (1, 1, 1, -1, -1) = A_2$.
    - $\Gamma_{p_y} = (1, 0, \dots)$. Once you get to $\chi(C_4) = 0$, you know that it must be E. For C_2', $p_x \mapsto 1$ and $p_y \mapsto -1$ or vice versa, so we sum these two to get 0. Since p_x, p_y both have $\chi(C_4) = 0$, they must be degenerate and equal to E.
  - On Wednesday, you don't need to draw out every image, but you need some justification, e.g., "I did a 90° turn."
- Memorize Mulliken symbol rules!
- Question: Problem C on PSet 2.
  - Ignore all of the text about qubits.
  - First step: Figure out what the basis is (it's the outer plane vectors, i.e., the arrows).
  - Point group: D_{4h}.
  - We need to find $\Gamma_{\text{out-of-plane}}$, a reducible representation! We're finding a RR for all of the arrows at once (not projecting one into the others), and then decomposing it into IRRs and hoping that one of them is a_{2u}.
  - We get

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_1$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	−2	0	0	0	−4	2	0

  - We can reduce this down to
$$\Gamma = a_{2u} + b_{2u} + e_g$$
to identify a_{2u}.
  - Similarly, in C_{4v}, we can reduce $\Gamma = (4, 0, 0, 2, 0) = a_1 + b_1 + e$ to identify a_1.

- Review PSets and answers! I keep missing easy things. Really break down a procedure to attack the different types of problems.

- Question: Assign symmetries based off of IR spectra.
  - Example: Vibrational spectroscopy has played a role in supporting the structure of the ion shown below. Raman spectroscopy of the tetramethylammonium salt of this ion shows a single absorption in the region expected for I=O stretching vibrations at 789 cm^{-1}. Is a single Raman band consistent with the proposed trans orientation of the oxygen atoms? Rationalize your answer.
  - Approach: In D_{5h}, create an IRR with the two I=O bond vectors as your basis. Thus,

D_{5h}	E	$2C_5$	$2{C_5}^2$	$5C_2'$	σ_h	$2S_5$	$2{S_5}^3$	$5\sigma_v$
Γ	2	2	2	0	0	0	0	2

  - We have that $\Gamma = a_1' + a_2''$. Since only one of these (a_1') is Raman active, a single Raman band is consistent with this structure.

- Question: Finding vibrational modes.
  - Example: What are the normal modes of *trans*-N_2F_2.
  - Not linear, so we expect $3N - 6 = 6$ normal modes to deal with.
  - We begin doing the Cartesian displacement method.

C_{2h}	E	$C_2(z)$	i	σ_h
Γ_{unm}	4	0	0	4
Γ_{xyz}	3	–	–	1
Γ_{3N}	12	0	0	4

    - Note that we use dashes in two entries of Γ_{xyz} because since there are zeroes above and we are multiplying, it does not matter what these values are (they will end up being zero in the direct product, regardless).
  - We can reduce to $\Gamma_{3N} = 4A_g + 2B_g + 2A_u + 4B_u$. Subtracting out $\Gamma_{\mathrm{rot}} = A_g + 2B_g$ and $\Gamma_{xyz} = A_u + 2B_u$, we end up with $\Gamma_{\mathrm{vib}} = 3A_g + A_u + 2B_u$.
  - Let's go in depth. The spectroscopic activities are:
    - $A_u + 2B_u$ are IR active.
    - $3A_g$ is Raman active.
  - Let's go even more in depth.
    - A_u is the only vibration that has a -1 in σ_h, i.e., it is the only one that vibrates out-of-plane.
    - If $\chi(\sigma_h) = +1$, then the vibration is symmetric with respect to σ_h. This must mean that the molecules are entirely confined to the plane. If $\chi(\sigma_h) = -1$, then we have an out of plane vibration (e.g., F atoms going above and below the plane in equal and opposite amounts — there is a motion that can be inverted). If one F atom goes twice as far, this is probably E (think about what would be required for the projection operator).
    - If you get pictures of normal modes (hint hint!!), you can retroactively get Mulliken symbols by observing the symmetry with respect to the observations.