Week 5

Exam and Intro to MO Theory

5.1 First Exam Review

- 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 $789\,\text{cm}^{-1}$. 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	$2C_5$	$2C_5{}^2$	$5C_2'$	σ_h	$2S_5$	$2S_5{}^3$	$5\sigma_v$
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 $\Gamma_{\text{rot}} = A_g + 2B_g$ and $\Gamma_{xyz} = A_u + 2B_u$, we end up with $\Gamma_{\text{vib}} = 3A_g + A_u + 2B_u$.

  - 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 $\chi(\sigma_h) = -1$, 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.

5.2   Midterm Thoughts

10/26:

- Generating a RR based on a basis set tells us the symmetry of something (vibrations, stretches, orbitals, ...). Projecting out an IRR on a basis gives us a specific example of something (an actual molecular orbital, vibrational mode, ...).

- Determining the depolarization ratio. Determine which Mulliken symbols are the *most* symmetric, i.e., symmetric to the most elements. For example, A_2 is more symmetric than B_2 because it is antisymmetric to 1 element instead of 2 elements.

5.3   MO Theory: Fundamental Concepts and Diatomics

10/28:

- The name of the game for the second half of the course is *electronic* spectroscopy.

  - The first half was *vibrational* spectroscopy.

- **Molecular orbital theory**: A theory of orbitals that posits that they are in general spread over the entirety of the molecule, so considerations of molecular symmetry properties are useful in this theory. *Also known as* **MO theory**.

- **Linear combination of atomic orbitals**: An approximation employed to reduce the notion of an MO to a practical form. *Also known as* **LCAO**.

  - Each MO is written as a linear combination of atomic orbitals on the various atoms.
  - The fact that this is an *approximation* is very important to note.
  - We use a simple basis set (e.g., the atomic orbitals) and let our molecular orbital be a linear combination of them.
  - For H_2 for example, our LCAO is $\Psi = c_1\phi_1 + c_2\phi_2$, where ϕ_1 denotes the atomic orbital on H_1 and ϕ_2 denotes the atomic orbital on H_2.

- We obtain an expression for the energy E by applying the Hamiltonian $\hat{H}$ on our guess function (use the LCAO) and integrating over all space.

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{H} \Psi \, d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi \, d\tau} = \frac{\int_{-\infty}^{\infty} (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2)\, d\tau}{\int_{-\infty}^{\infty} (c_1\phi_1 + c_2\phi_2)\, d\tau}$$

  - Denote the numerator in the rightmost term above by N and the corresponding denominator by D.
  - Then

$$N = c_1^2 \underbrace{\int \phi_1 \hat{H} \phi_1 \, d\tau}_{H_{11}} + c_1 c_2 \underbrace{\int \phi_1 \hat{H} \phi_2 \, d\tau}_{H_{12}} + c_2 c_1 \underbrace{\int \phi_2 \hat{H} \phi_1 \, d\tau}_{H_{21}} + c_2^2 \underbrace{\int \phi_2 \hat{H} \phi_2 \, d\tau}_{H_{22}}$$

    - H_{11} is the energy of the electron in orbital 1.
    - H_{12} and H_{21} are the **resonance integrals**.
    - H_{22} is the energy of the electron in orbital 2.
  - It follows that

$$N = c_1^2 H_{11} + c_1 c_2 H_{12} + c_2 c_1 H_{21} + c_2^2 H_{22}$$

  - Additionally,

$$D = c_1^2 \underbrace{\int \phi_1 \phi_1 \, d\tau}_{1} + c_1 c_2 \underbrace{\int \phi_1 \phi_2 \, d\tau}_{S} + c_2 c_1 \underbrace{\int \phi_2 \phi_1 \, d\tau}_{S} + c_2^2 \underbrace{\int \phi_2 \phi_2 \, d\tau}_{1}$$

    - The left- and rightmost integrals above evaluate to 1 because the AOs are normalized.

■ The middle two integrals above are the **overlap integral**.

− It follows that

$$D = c_1^2 + 2c_1c_2S + c_2^2$$

− Using our above results and the **secular determinant** (which we will not cover in this course since the focus is not on quantum mechanics), we find that

$$E = \frac{H \pm H_{12}}{1 \pm S}$$

• **Resonance integral**: An integral describing the strength of the bonding interaction due to the overlap of AOs in the MO.

• **Overlap integral**: An integral that measures the effectiveness of the overlap.

− Dependent on the type of bond. In particular, it is dependent on two factors.
1. Spatial overlap ($\sigma > \pi > \delta$ bonds).
2. Energy overlap (based on **Valence Orbital Ionization Energies** [given in electron volts]).
■ As a first approximation, oribtals separated by greater than 1 Rydberg ($R_H = 13.6\,\text{eV}$) do *not* overlap significantly[1].

• **Valence Orbital Ionization Energy**: Exactly like it sounds. *Also known as* **VOIE**.

• This result leads to H_2's MOs. Ignoring overlap (i.e., taking $S = 0$) we have the following orbital diagram.
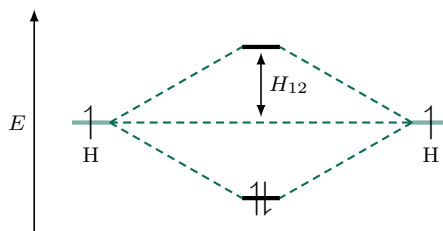

Figure 5.1: H_2 MO diagram.

• **Bond order**: The following quantity. *Denoted by* **B.O.**. *Given by*

$$\text{B.O.} = \frac{\#\text{ electrons in bonding orbitals} - \#\text{ electrons in antibonding orbitals}}{2}$$
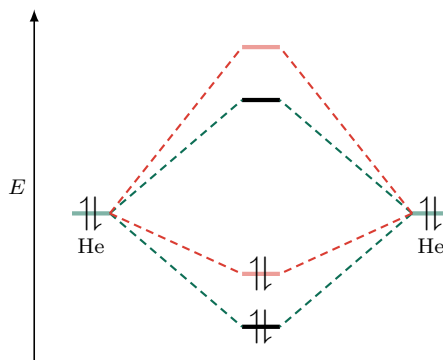
− For H_2, B.O. $= 1$.

• Now we do He_2.

Figure 5.2: He_2 MO diagram.

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[1]This is related to Talapin's arbitrary $10\,\text{eV}$!

- Here, we get

$$E_+ = \frac{H + H_{12}}{1 + S} \qquad\qquad E_- = \frac{H - H_{12}}{1 - S}$$

- The bond order is zero.
- No consideration of S leads to the green diagram.
- If we assume $S \neq 0$, then we get the red diagram. Note that the antibonding is more destabilized than the bonding is stabilized. This is key!

- Investigation of the diatomics of the 2nd row main group elements.

  - The dividing line between N_2 and O_2: O_2 and heavier have the "normal" filling order, while N_2 and below have significant mixing.
  - When mixing is significant, σ, σ^* for the 2s orbitals both go down in energy, i.e., become more bonding; σ, σ^* for the 2p orbitals both go up in energy, i.e., become more antibonding.

- Fundamentals when generating molecular orbitals.

  1. When generating molecular orbitals, starting with a given number of atomic orbitals, we must generate the same number of molecular orbitals.
  2. Molecular orbitals must have the same symmetries as the atomic orbitals of which they are composed.
  3. Molecular orbitals should be within 1 Rydberg to mix.

- Strategy for MOs of heterodiatomics:

  1. Determine VOIEs.
  2. Determine symmetry equivalence.
  3. Draw correlations.
  4. Look for potential s-p-d mixing.
  5. Fill electrons, determine BO.

- HF example.

  - See Figure III.10 and the associated discussion from Labalme (2022).
  - No consideration of point groups necessary.
  - We know we can only mix in σ interactions (i.e., s with $2p_z$), not π interactions with p_x or p_y.

- Review QMech notes and come up with questions!