

CHEM 30100 (Advanced Inorganic Chemistry I) Notes

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Week 1

A Rigorous Definition of Symmetry

1.1 Symmetry: Symmetry Elements and Operations

9/28:

- Dr. Anna Wuttig (AH-nuh WUH-tig).
 - Teaches exclusively on the blackboard.
 - Will record lectures, however; if there is a technical error, she will upload last year's lecture.
- Syllabus.
 - PSets graded on completion, not accuracy.
 - Two exams: One on the first half of the course; one on the second half of the course.
 - Cumulativeness: You'll need to understand the first half to do the second half, but there won't be questions specifically targeted to first-half material.
 - No final.
 - Participation. Showing up to class and working in groups.
- Chris, Dan, Amy, Matt, Jintong, Yibin, Ben, Sara, Ryan, Joe, Owen, Isabella, Pierce are the people.
 - People come from a diversity of chemistry subfields (physical, inorganic, organic, materials, biological).
- Every day will have a handout that we will write on (in pencil).
- Study the learning objectives!
- (Local) symmetry of a molecule helps us predict and describe bonding, spectroscopic properties, and reactivity.
 - We describe symmetry with group theory.
- **Symmetry operation:** An operation which moves a molecule into a new orientation equivalent to its original one (geometrically indistinguishable).
 - Symmetry operations that can be applied to an object always form a **group**.
- **Symmetry element:** A point, line, or plane about which a symmetry operation is applied.
- Symmetry operations.
 1. Identity operation (E): Do nothing; null operation.
 2. Reflection through a plane (σ): Subdivided into...

- σ_d : dihedral mirror planes, which contain the principle C_n axis and bisect the angles formed between adjacent C_2 axes;
 - σ_h : horizontal mirror planes, in which the mirror plane is perpendicular to the principal C_n axis;
 - σ_v : vertical mirror planes, which contain the C_n axis and are not dihedral mirror planes.
3. Rotation about an axis (C_n): A clockwise^[1] rotation about the C_n axis.
4. Improper rotation (S_n): A two-step symmetry operation consisting of a C_n followed by a σ that is perpendicular to C_n (i.e., σ_h).
5. Inversion (i): Take any point with coordinates (x, y, z) to $(-x, -y, -z)$.

- To describe the operations, we'll introduce **stereographic projections**.



(a) Rotations.

(b) Improper rotations.

Table 1.1: Symbols for stereographic projections.

- We have a working area (the plane of the page is the xy -plane). It is useful to draw quadrants.
- We describe a general point which experiences our symmetry operation.
 - When the point reflects through the working area, we denote the image with an “X” instead of a circle.
 - We need a gear symbol in the middle for rotations and improper rotations (see Table 1.1).
 - Must stereographic projections be drawn one at a time because it seems that the squares should not be in a reflection?
 - No — the symbols are to help us and should be included somewhere, but there are no hard-and-fast rules.
- Stereographic projections for each of the five elementary symmetry operations.

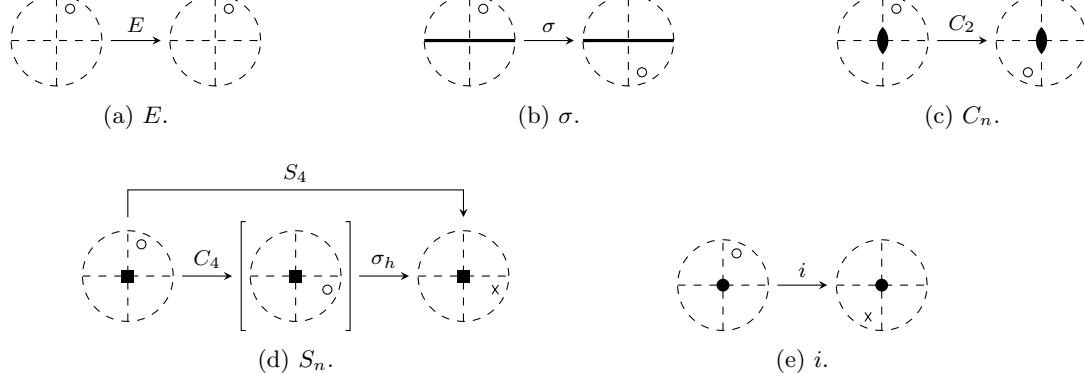


Figure 1.1: Stereographic projections of the elementary symmetry operations.

- Principal C_n axis: The C_n axis for which n is the highest.
 - In a stereographic projection, the C_n axis is the one that is perpendicular to the working area (goes in/out of the page).

¹Really?

- Example: Give the symmetry elements of NH_3 .
 - C_3 axis, 3 σ_v mirror planes (denoted σ_v , σ'_v , and σ''_v).
 - The symmetry operations are E , C_3 , C_3^2 , σ_v , σ'_v , and σ''_v . These operations form the C_{3v} point group.
- Direct products of symmetry operations: $YX = Z$ means “operation X is carried out first and then operation Y ,” giving the same net effect as would the carrying out of the single operation Z .
 - If $YX = XY = Z$, then the two operations Y and X commute.
- What is the direct product of C_2 and σ_h ?
 - $\sigma_h C_2 = S_2 = i$. They do commute.
- Do C_4 and $\sigma_{x,z}$ commute? Take the plane of this page as xy .
 - They do not (determine by drawing out both sets of stereographic projections).
- Don’t get careless, Steven. This is easy, but it’s also easy to make easy mistakes.
- New symmetry operations *of your group* are generated by taking the direct product of two.

1.2 Point Groups

9/30:

- The symmetry operations that apply to a given molecule collectively possess the properties of a mathematical **group**.
- **Group:** A set of symmetry operations that satisfy the following conditions.
 - *Closure:* All binary products must be in the group, i.e., the product of any two operators must also be a member of the group.
 - *Identity:* Must contain an identity, i.e., E must be part of the group.
 - *Inverse:* All elements must have an inverse in the group, and they must commute with their inverse.
 - *Associativity:* The associative law $(A \cdot B) \cdot C = A \cdot (B \cdot C)$ must hold.
- **Abelian** (group): A group in which all direct products commute.
 - Not all groups are Abelian.
- Question: Do C_3 and σ_v form a group?
 - No: No identity (for example).
 - Wuttig draws out a stereographic projection for $C_3 \cdot \sigma_v$ and overlays the first and last picture, showing that $C_3 \cdot \sigma_v$ is a reflection over a new mirror plane σ'_v .
 - C_3 and σ_v do **generate** the set of operations $E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v$, which collectively form the **point group C_{3v}** .
- To prove something on a pset or exam, it’s probably a good idea to do it in terms of stereographic projections!
- **Point group:** A group such that at least one point in space is invariant to all operations in the group.
- **Group order:** The number of symmetry operations in the group. *Denoted by h .*
- Table activity: Finding E , principal C_n , σ , $C_2 \perp C_n$, C_n position relative to σ (collinear or perpendicular), and i for various point groups.

- These properties are the ones that distinguish each point group from every other point group.
- Notes on the pedagogy: Animations and/or tangible models should be used to discuss this stuff. PowerPoint slides are definitely the way to go — far more tangible tools; blackboard should be a supplement. It is key to be careful what you say (*element* and *operation* must be consistently used). Dr. Wuttig is skipping a lot of key points (like naming point groups).
- Developing a flow chart that distinguishes between D_{nh} , D_{nd} , D_n , C_{nh} , C_{nv} , C_n , and S_n .

Week 2

Introduction to Representation Theory

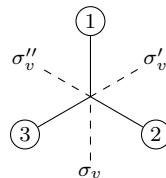
2.1 Matrix Representations of Symmetry Operations

- 10/3:
- Tools for identifying symmetry elements.
 - Chem 3D (visualization).
 - Otterbein University symmetry gallery (examples of molecules that satisfy all of the point groups).
 - Gives examples of molecules that satisfy the high-symmetry point groups.
 - $C_{\infty v}$: CO.
 - $D_{\infty h}$: CO₂.
 - T_d : CH₄.
 - T_h : [Co(NO₂)₆]³⁺.
 - T_h is T_d with σ_h symmetry.
 - O_h : [Co(NH₃)₆]³⁺
 - I_h : N/a.
 - 120 symmetry elements in total; we will not be asked to identify all of these!
 - K_h : N/a.
 - Symmetry of the sphere.
 - T, O, I are subgroups of T_h, O_h, I_h , respectively, and only have proper (not improper) rotations. These are very rare point groups. An example of a molecule in the T point group is [Ca(THF)₆]²⁺.
 - Learn T, O, I from Otterbein University example and ask questions!
 - Low symmetry: C_1, C_i, C_s .
 - The mirror plane in a C_s molecule is denoted by σ (no subscript).
 - **Vector**: A series of numbers which we write in a row or a column.
 - **Matrix**: Any rectangular array of numbers set between two brackets.
 - Basics of matrix multiplication: $A \cdot \vec{x} = \vec{y}$ given in terms of matrix multiplication, e.g., if A is $n \times m$ and $\vec{x} \in \mathbb{R}^m$, then

$$y_i = \sum_{j=1}^m a_{ij} x_j$$

for $i = 1, \dots, n$.

- Matrix representations:
 - E : What matrix A satisfies $A \cdot \vec{x} = \vec{x}$ for all \vec{x} ? The 3×3 matrix I does.
 - i : What matrix A satisfies $A \cdot \vec{x} = -\vec{x}$ for all \vec{x} ? The 3×3 matrix $-I$ does.
 - σ_{xy} : What matrix A flips the sign of the z -coordinate of \vec{x} ? The 3×3 matrix $\text{diag}(1, 1, -1)$ does.
 - C_2 : What matrix A flips the sign of the x, y -coordinates of \vec{x} ? The 3×3 matrix $\text{diag}(-1, -1, 1)$ does.
 - C_3 : Consider a C_{3v} molecule.

Figure 2.1: C_3 matrix representation setup.

Instead of describing a rotation in \mathbb{R}^3 using radians, we can think of a rotation as a permutation of the numbered atoms. So in this example,

$$\underbrace{\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}}_{C_3} \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 2 \\ 3 \\ 1 \end{bmatrix}$$

- We will only be asked for matrix representations of very simple things, e.g., these or 90° or 180° turns.
 - The above matrices form a mathematical group, which obeys the same multiplication table as the operations.
 - For example,
- $$\underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{C_2} \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}}_{\sigma_h} = \underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}}_{i}$$
- The matrix representations given above are not the “simplest” way of describing these symmetry operations.
 - The simplest way is using the **character**.
 - We find the character using a **similarity transformation** to take our matrix representations to block-diagonalized forms and then compute the characters of the blocks from there.
 - Recall that analogous blocks multiply in a block-diagonal matrix.
 - **Character** (of a symmetry operation): The trace (sum of the diagonal elements) of the matrix representation of that operation. *Denoted by χ .*
 - **Similarity transformation** (matrix): The matrix which, when conjugated with a matrix representation of a symmetry operation, yields the block-diagonalized form of that matrix. *Denoted by R .*
 - We don’t need to know how to compute these.

- Similarity transformation example: The C_3 matrix representation given above is not block diagonal, but there exists a matrix R (that we don't have to know how to find) such that

$$RC_3R^{-1} = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array} \right]$$

- The characters of the blocks of the above matrix are 1 and -1 , respectively. The character of the overall matrix is still 0.

2.2 Characters and Irreducible Representations

10/5:

- The PSet has been posted — remember that its graded for completion.
 - Answer key will be posted the day it's due.
 - Submit via email or give her a printed copy/write it out on blank paper (preferred).
- Review: NH_3 is in the C_{3v} point group.
- Denote the bond vectors of NH_3 by d_1, d_2, d_3 . Let's use them as a basis of the representation Γ . Also label the hydrogen atoms 1-3.

Symmetry element	Matrix	Character
E	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix}$	3
C_3	$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_2 \\ H_3 \\ H_1 \end{bmatrix}$	0
C_3^2	$\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_3 \\ H_1 \\ H_2 \end{bmatrix}$	0
σ_v (along d_1)	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_1 \\ H_3 \\ H_2 \end{bmatrix}$	1
σ'_v (along d_2)	$\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_3 \\ H_2 \\ H_1 \end{bmatrix}$	1
σ_v (along d_1)	$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_2 \\ H_1 \\ H_3 \end{bmatrix}$	1

Table 2.1: NH_3 symmetry operations, matrices, and characters.

- Draw out each symmetry operation, its effect on each H atom, and the matrix representation of each. What is the character for each matrix representation? See the above table.
- The characters for each matrix divide the symmetry operations into three classes (the identity, rotation, and reflection classes).

- If we use the Cartesian axes as our basis, we get the following transformation matrices.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_a = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_b = \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_c = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- All of these are block-diagonal, so there must be some similarity transformation that gets us from the matrices in Table 2.1 to these matrices.
- Notice that the character is preserved under similarity transformation.
- The matrix representations in \vec{e} have blocks, which we can call the 2D block and the 1D block.
- Building a character table with different representations.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_e	3	0	1
Γ_{2D}	2	-1	0
Γ_{1D}	1	1	1

Table 2.2: Some representations of C_{3v} .

- Γ_e is the representation corresponding to the full 3×3 matrices.
- Γ_{2D} is the representation corresponding to the 2D blocks.
- Γ_{1D} is the representation corresponding to the 1D blocks.
- The latter two are called the irreducible representations; the first one is called a reducible representations. In fact,

$$\Gamma_e = \Gamma_{2D} + \Gamma_{1D}$$

- Every point group has a specific number of irreducible representations (IRRs); are Γ_{2D}, Γ_{1D} it?

- No — we will use the rules to find the others.

- IRRs have 4 rules.

1. The number of IRRs: The number of non-equivalent IRRs is equal to the number of classes in the group.
2. Dimensionality of IRRs: The sum of the squares of the dimensions ℓ of IRRs in a class is equal to the order of the group.

$$\sum_i \ell_i^2 = \sum_i \chi_i^2(\text{class}) = h$$

3. Characters of IRRs: The sum of the squares of the characters under any IRR equals the order of the group.

$$\sum_R g(R) \chi_i^2(R) = h$$

4. Orthogonality rule: The sum of the products of characters under any two irreducible representations is equal to zero.

$$\sum_R g(R) \chi_i(R) \chi_j(R) = 0$$

- Examples of the rules in C_{3v} .
 - Rule 1: C_{3v} has three classes, so it must have three more IRR than listed in Table 2.2.
 - Rule 2: We must have that

$$1^2 + 2^2 + \ell_3^2 = 6$$
 - Rule 3: For Γ_{2D} , for example,

$$(1)(2)^2 + 2(-1)^2 + 3(0)^2 = 6$$
 - Rule 4: With Γ_{1D}, Γ_{2D} , for example,

$$(1)(1)(2) + (2)(1)(-1) + (3)(1)(0) = 0$$
- Finding the last representation of C_{3v} .
 - General procedure: Apply rule 1, then 2, then 4. Check with 3.
 - For example, we can find that the last $\Gamma = (1, 1, -1)$.

2.3 Character Tables and Mulliken Symbols

10/7:

- The algebraic rules discussed last lecture are sufficient to derive a character table. They are summarized in the following procedure.
 1. Determine the number of classes in order to find the number of irreducible representations.
 2. All groups have a totally symmetric irreducible representation.
 3. Determine the dimensionality of the irreducible representations.
 4. Apply the orthogonality rule.
 5. Verify using the sum of squares of characters rule.
- Example: Deriving the C_{3v} character table using the above strategy.

C_{3v}	E	$2C_3$	$3\sigma_v$	linear	quadratic
A_1	1	1	1	z	z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Table 2.3: C_{3v} character table.

- There are three classes; hence, we will have $\Gamma_1, \Gamma_2, \Gamma_3$.
 - See below for an explanation of their labels.
- Let $\Gamma_1 = (1, 1, 1)$ be the totally symmetric irreducible representation.
- If we want the sum of the squares of the dimensionalities to be natural numbers which add to $h = 6$, then we must choose $\ell_2 = 1$ and $\ell_3 = 2$.
- Applying the orthogonality rule, we can find the remaining four values in the table (those in the lower-right block) by inspection.
 - We may, indeed, confirm using the sum of the squares rule.
 - Also see below for an explanation of the Cartesian coordinates on the right-hand side.
- It will be beneficial to have a standard method for naming our irreducible representations.

- **Mulliken symbol:** The designation of an irreducible representation assigned according to the following procedure. *Given by*
 1. All 1D representations are A or B . 2D is E . 3D is T .
 2. Distinguishing A and B .
 - (a) $\chi(C_n) = +1 \implies A$.
 - (b) $\chi(C_n) = -1 \implies B$.
 3. Numerical subscripts: For groups that contain a secondary C_2 axis (or in its absence, σ_v).
 - (a) $\chi(C_2 \text{ or } \sigma_v) = +1 \implies$ Subscript 1.
 - (b) $\chi(C_2 \text{ or } \sigma_v) = -1 \implies$ Subscript 2.
 4. Alphabetical subscripts: For groups that contain i .
 - (a) $\chi(i) = +1 \implies$ Subscript g .
 - (b) $\chi(i) = -1 \implies$ Subscript u .
 5. Prime subscripts: For groups that contain σ_h .
 - (a) $\chi(\sigma_h) = +1 \implies$ Superscript '
 - (b) $\chi(\sigma_h) = -1 \implies$ Superscript ''.
- **Symmetric (IRR wrt. a symmetry operation):** An IRR for which the character of the symmetry operation in question is $+1$.
- **Unsymmetric (IRR wrt. a symmetry operation):** An IRR for which the character of the symmetry operation in question is -1 . *Also known as antisymmetric.*
- Based on the above rules, we can conclude that for C_{3v} , $\Gamma_1 = A_1$, $\Gamma_2 = A_2$, and $\Gamma_3 = E$.
- The last two elements we need to construct the C_{3v} character table are the Cartesian coordinates. These are easy to derive for z -axis elements and groups that contain x - and y -axis rotations (e.g., C_2, C_4). If n is odd, these latter ones will be given to you.
 - There are two types of linear bases to consider: x, y, z and R_x, R_y, R_z . The former corresponds to p orbitals. The latter corresponds to rotations about one of the Cartesian axes.
 - There is one type of quadratic base to consider: $z^2, x^2 - y^2, xy, xz, yz$. These correspond to d orbitals.
 - Wuttig draws out the effect of each symmetry operation in C_{3v} on p_z, d_{z^2} , and R_z . She concludes for the first two that they are totally symmetric with respect to the operations; hence, they are A_1 . She also concludes with respect to the last one that it is symmetric to the identity and to rotation, but unsymmetric to reflection about the z -axis; hence, it is A_2 .
 - The others are filled in toward us.
- Summary: Anatomy of a character table.
 1. Point group.
 2. Irreducible representations, as denoted by Mulliken symbols.
 3. Classes of symmetry operations.
 4. Characters of irreducible representations.
 5. Linear basis: Axes and rotations (basis functions for the irreducible representations).
 - (a) p orbitals: Denoted as z, x, y .
 - (b) Rotations around z, x, y : Denoted as R_z, R_x, R_y .
 6. Quadratic basis (basis functions for the irreducible representations).
 - (a) d orbitals: Denoted as $z^2, x^2 - y^2, xy, xz, yz$.

- Example: Filling in the C_{2v} character table.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Table 2.4: C_{2v} character table.

- Special case where the two σ have different characters: With respect to determining which of the bottom two representations is B_1 and which is B_2 , we must pick a σ_v to use as a reference and stick with it.

Week 3

Applications of Representation Theory

3.1 Reducible Representations and Direct Products

10/10:

- PSet is due at the beginning of next class. Email or submit in paper. Show your work!
- Since molecules have more than one point, we need to work with the characters of reducible representations. In particular, when applying group theory to chemical problems, we need to find the IRRs whose sum is the reducible representation.
- **Reduction formula:** The formula which takes a Γ_{red} and decomposes it into a sum of Γ_{IRRs} . *Given by*
$$n(\Gamma_A) = \frac{1}{h} \sum_i g(R) \chi_{\text{IRR}}(R) \chi_{\text{RR}}(R)$$
 - $n(\Gamma_A)$ is the number of times the IRR A occurs in Γ_{red} .
 - h is the order of the group.
 - $g(R)$ is the order of the class under the symmetry operation R .
 - $\chi_{\text{IRR}}(R)$ is the character of the IRR under the symmetry operation R .
 - $\chi_{\text{RR}}(R)$ is the character of the reducible representation under the symmetry operation R .
- Recall $\Gamma_{\text{red}} = (3, 0, 1)$ in C_{3v} from Lecture 2.2.
 - The number of times each IRR appears is, according to the reduction formula:
$$n(A_1) = \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot -1 \cdot 0 + 3 \cdot -1 \cdot 1) = 1$$
$$n(A_2) = \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot -1 \cdot 0 + 3 \cdot -1 \cdot 1) = 0$$
$$n(E) = \frac{1}{6}(1 \cdot 2 \cdot 3 + 2 \cdot -1 \cdot 0 + 3 \cdot 0 \cdot 1) = 1$$

- Simple cases (like this and the next one) we can often do by inspection.
- Example: $\Gamma_{\text{RR}} = (6, 0, 0)$.
 - Decompose it into $A_1 + A_2 + 2E$.
- **Direct product** (of two representations): The (reducible or irreducible) representation obtained by multiplying the characters of the two representations which correspond under each operation. *Denoted by $M \times N$, where M, N are Mulliken symbols.*

- Examples:
 - $A_1 \times E = E$.
 - $A_2 \times E = E$.
 - $E \times E = A_1 + A_2 + E$.
 - $A_2 \times A_2 = A_1$.
- We now dive into how to use the symmetry properties of a collection of orbitals to determine the states that arise by populating them with electrons. To do this for a given basis set of valence atomic orbitals, we need to ask what set of IRRs they fall into.
- Procedure.
 1. Generate the characters of this representation by examining the trace of the relevant transform matrices.
 - +1 on the diagonal if a particular basis function is left unchanged during the symmetry operation.
 - 0 on the diagonal if the basis function is transformed to another function.
 - -1 on the diagonal if the function is converted into minus itself.
 - Indeed, only basis set elements that do not move contribute to the trace (i.e., character) of the representation.
 2. Check that the dimension is greater than the largest dimension permissible in the point group. If so, we need to reduce to IRRs. This is an important step to construct SALCs.
- Example: Consider the set of H_{1s} orbitals of NH_3 as the representation.
 - $\Gamma_{3H_{1s}} = (3, 0, 1)$ since all 3 orbitals stay under E , all orbitals move under $2C_3$, and 1 orbital stays under $3\sigma_v$.
 - Decompose into $A_1 + E$.
 - Therefore, the $1s$ orbital of H within C_{3v} of NH_3 transforms in $a_1 + e$ symmetry.
 - Note that we use lowercase Mulliken symbols for atomic/molecular orbitals and vibrational modes and uppercase Mulliken symbols for electronic states.
 - This $a_1 + e$ symmetry for the H_{1s} group orbitals implies that there are 3 SALC orbitals: 1 of a_1 symmetry and 2 of e symmetry.
- Example: H_2O .
 - $\Gamma = (2, 0, 0, 2) = A_1 + B_2$.

3.2 Projection Operations and SALCs

- 10/12:
- PSet 2 is posted and due 10/21.
 - Go over questions on the HW in the review classes prior to exams.
 - **Symmetry-Adapted Linear Combination:** An orthonormal linear combination of one or more sets of orthonormal functions (which are either atomic orbitals or internal coordinates of a molecule) taken in such a way that the combinations form bases for irreducible representations of the symmetry group of the molecule. *Also known as SALC.*
 - Last time, we investigated the SALCs of NH_3 . We found them by decomposing a reducible representation of the H_{1s} basis set to its irreducible representations and naming them via the character table.

- Goal: What do the SALCs of NH_3 look like?
 - We know that we need 3 SALCs, 1 of a_1 symmetry and 2 of e symmetry.
 - To achieve the goal, we apply the **projection operator** to each irreducible representation.
- **Projection operator** (on an IRR): The operator defined as follows, which acts on IRRs. *Denoted by \hat{P} . Given by*

$$\hat{P}(\Gamma_i) = \frac{\ell_i}{h} \sum_R \chi_i(R) \hat{R}$$
 - ℓ_i is the dimension(ality) of the IRR.
 - Γ_i is the IRR.
 - \hat{R} is the symmetry operation to be applied to the basis.
 - $\chi_i(R)$ is the character of the given symmetry operation for Γ_i .
 - In other words, we need to evaluate what happens to the H_{1s} orbitals under each symmetry operation.
- It follows that we need the character table to evaluate what happens to the H_{1s} orbitals for each symmetry operation.
 - Note that for the projection operator, we do *not* do this by class (i.e., we do need to apply *every single* symmetry operation)^[1].
 - Focus on one orbital in particular, and see to which orbital each symmetry operation takes it.
- NH_3 example.
 - We have

$$E : x_1 \mapsto x_1 \quad C_3 : x_1 \mapsto x_2 \quad C_3^2 : x_1 \mapsto x_3 \quad \sigma_v : x_1 \mapsto x_1 \quad \sigma'_v : x_1 \mapsto x_3 \quad \sigma''_v : x_1 \mapsto x_2$$

- We can do the same for where x_2, x_3 go.
- It follows that

$$\hat{P}(A_1)_{x_1} = 1x_1 + 1x_2 + 1x_3 + 1x_1 + 1x_3 + 1x_2 = 2(x_1 + x_2 + x_3) \approx x_1 + x_2 + x_3$$

- This implies that under the totally symmetric representation, all orbitals are the same, as we might expect. Note that the constant factor of 2 does not affect the functional form and therefore does not affect the symmetry properties.
- We don't carry through ℓ_i/h because it's a constant??
- Note that

$$\hat{P}(A_1)_{x_2} = \hat{P}(A_1)_{x_3} = \hat{P}(A_1)_{x_1}$$

- As another example,

$$\hat{P}(E)_{x_1} = 2x_1 - x_2 - x_3 + 0x_1 + 0x_3 + 0x_2 = 2x_1 - x_2 - x_3$$

- Similarly,

$$\begin{aligned}\hat{P}(E)_{x_2} &= 2x_2 - x_3 - x_1 \\ \hat{P}(E)_{x_3} &= 2x_3 - x_1 - x_2\end{aligned}$$

- Note that all of these functions must be orthonormal.
- We have three functions, but we only need 2 in e ! Thus, we employ the orthonormal rule to figure it out.

¹Notice that the order of the class is not present in the projection operator!

- We have that the first and second, and first and third are not orthogonal:

$$(\Psi_{E,x_1}, \Psi_{E,x_2}) = (2)(-1) + (2)(-1) + (-1)(-1) = 3 \neq 0$$

$$(\Psi_{E,x_1}, \Psi_{E,x_3}) = (2)(-1) + (-1)(-1) + (-1)(2) = 3 \neq 0$$

- What we can do is take a linear combination of 2 and 3 so that it's orthogonal to 1.

- Let's try

$$\Psi_{E,\text{new}} = \Psi_{E,x_2} - \Psi_{E,x_3} = 3x_2 - 3x_3 \approx x_2 - x_3$$

- Indeed,

$$(\Psi_{E,x_1}, \Psi_{E,\text{new}}) = (2)(0) + (-1)(1) + (-1)(-1) = 0$$

as desired.

- Note that adding does not get us something orthogonal.

- Normalize the SALCs.

- At this point, we have that

$$\Psi_{A_1 \text{ SALC}} = x_1 + x_2 + x_3 \quad \Psi_E \text{ SALC} = 2x_1 - x_2 - x_3 \quad \Psi_E \text{ SALC} = x_2 - x_3$$

- Normalization means adjusting the normalization constant N such that

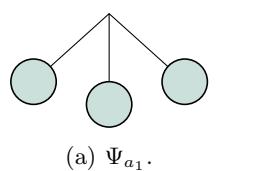
$$\int [N(x_1 + x_2 + x_3)]^2 = 1$$

- More simply, we multiply each of the above by 1 over the square root of the sum of the squares of the extant coefficients. So

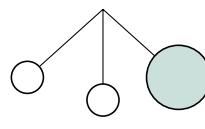
$$\begin{aligned} \Psi_{A_1 \text{ SALC}} &= \frac{1}{\sqrt{1^2 + 1^2 + 1^2}}(x_1 + x_2 + x_3) & \Psi_E \text{ SALC} &= \frac{1}{\sqrt{2^2 + (-1)^2 + (-1)^2}}(2x_1 - x_2 - x_3) \\ &= \frac{1}{\sqrt{3}}(x_1 + x_2 + x_3) & &= \frac{1}{\sqrt{6}}(2x_1 - x_2 - x_3) \end{aligned}$$

$$\begin{aligned} \Psi_E \text{ SALC} &= \frac{1}{\sqrt{0^2 + 1^2 + (-1)^2}}(x_2 - x_3) \\ &= \frac{1}{\sqrt{2}}(x_2 - x_3) \end{aligned}$$

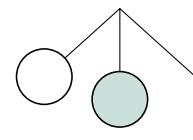
- Lastly, we can draw the orbitals.



(a) Ψ_{a_1} .



(b) Ψ_{e_a} .



(c) Ψ_{e_b} .

Figure 3.1: NH₃ SALCs.

3.3 Vibrational Modes and Symmetry

10/14:

- Purposes of the basis set → RRs → IRRs → SALCs workflow.

1. Helps us understand the symmetry properties of molecular vibrations (we are going to look at this first).
2. Helps us understand MO diagrams (we will look at this after Exam 1).

- Symmetry properties of molecular vibrations: Any vibrational motion of a molecule can be decomposed in a combination of normal modes, and all normal modes form the basis of an irreducible representation of the point group of the molecule.
- How many normal modes do we have for a given molecule?
 - N atoms.
 - $3N$ degrees of freedom.
 - 3 translations.
 - 3 rotations (2 for linear molecules).
 - $3N - 6$ (resp. $3N - 5$) vibrations (i.e., normal modes).
- How to determine normal modes.
 1. Determine the point group.
 2. Consider the motion of atoms independently.
 3. Use the Cartesian displacement method, reduce $\Gamma_{\text{Cartesian}}$ to IRRs, and compare with the character table to determine which can be accounted for by translation (x, y, z) and rotation (R_x, R_y, R_z).
 4. Use the stretching and/or bending vectors as basis sets and use \hat{P} to determine what the normal modes look like.
- Example: H_2O .
 1. C_{2v} .
 2. 3 degrees of freedom for each atom (atom i can move in the x_i, y_i, z_i direction for $i = 1, 2, 3$).
 3. Multiple steps:
 - (a) Find $\Gamma_{\text{unmoved}} = (3, 1, 1, 3)$.
 - (b) Find Γ_{xyz} : From the relevant character table, $\Gamma_{xyz} = A_1 + B_1 + B_2 = (3, -1, 1, 1)$.
 - (c) Find $\Gamma_{\text{Cartesian}} = \Gamma_{\text{unmoved}} \times \Gamma_{xyz} = (9, -1, 1, 3)$.
 - (d) Apply the reduction formula: $\Gamma_{\text{Cartesian}} = 3A_1 + A_2 + 2B_1 + 3B_2$.
 - (e) Notice that A_1 corresponds to the z -translation, A_2 corresponds to the z -rotation, B_1 corresponds to the x -translation and y -rotation, and B_2 corresponds to the y -translation and x -rotation. If we want to determine the vibrational modes of symmetry, we need to subtract out the modes corresponding to translations and rotations of the full molecule. Thus,

$$\Gamma_{\text{vibs}} = 3A_1 + A_2 + 2B_1 + 3B_2 - (A_1 + A_2 + 2B_1 + 2B_2) = 2A_1 + B_2$$

4. Multiple steps:
 - (a) Stretching IRR(s): Label the bond vectors r_1, r_2 . Find their representation.

$$\Gamma_1 = (2, 0, 0, 2) = A_1 + B_2$$
 - Since Γ_1 decomposes into two IRRs, this basis set accounts for 2/3 of the normal vibrational modes.
 - To get the last, we'll need another basis set, but we'll do that later.
 - (b) Stretching SALC(s): Apply the projection operator to these normal modes.

$$\begin{aligned}\hat{P}(A_1)_{r_1} &= 2(r_1 + r_2) \approx r_1 + r_2 \\ \hat{P}(B_2)_{r_1} &= 2(r_1 - r_2) \approx r_1 - r_2\end{aligned}$$

- (c) Bending IRR(s): Label the bending basis (angle between r_1, r_2) $\Delta\theta$. Find its representation.

$$\Gamma_2 = (1, 1, 1, 1) = A_1$$

- (d) Bending SALC(s): Apply the projection operator to this normal mode.

$$\hat{P}(A_1)_{\Delta\theta} = 4\Delta\theta \approx \Delta\theta$$

- (e) Visualize the normal modes: $r_1 + r_2$ corresponds to a symmetric stretch ν_s , $r_1 - r_2$ corresponds to an asymmetric stretch ν_a , and $\Delta\theta$ corresponds to a bend δ .

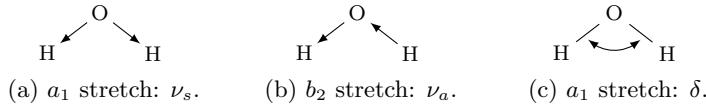


Figure 3.2: H_2O vibrational modes.

- (f) Quantum mechanically calculate the stretching frequencies: For H_2O , $\nu_s = 3657 \text{ cm}^{-1}$, $\nu_a = 3756 \text{ cm}^{-1}$, and $\delta = 1595 \text{ cm}^{-1}$.

- Example: PH_3 stretching modes.

- C_{3v} .
- $\Gamma_\nu = (3, 0, 1) = a_1 + e$.
- Projecting:

$$\hat{P}(A_1)_{r_1} \approx r_1 + r_2 + r_3 \quad \hat{P}(E)_{r_1} \approx 2r_1 - r_2 - r_3 \quad \hat{P}(E)_{r_2-r_3} \approx r_2 - r_3$$

- Drawing:

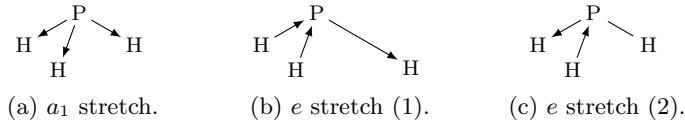


Figure 3.3: PH_3 vibrational modes.

- Note that we don't need Γ_{3N} to derive Γ_ν ! We would only need it for Γ_δ , unless Wuttig gives us a bending basis with which to work.
- Some observation on orthogonal projections.

- Suppose we want to derive $3r_2 - 3r_3$. Since \hat{P} is a linear operator, we can equally well take the difference $\hat{P}(E)_{r_2} - \hat{P}(E)_{r_3}$ and project out $r_2 - r_3$ via $\hat{P}_{r_2-r_3}$ to start.
- Moreover, I suspect that the projection operator is unitary (i.e., maps orthogonal vectors to orthogonal vectors). At least in this case, notice that r_1 and $r_2 - r_3$ are very much orthogonal (see Figure 3.4), just like their projections.

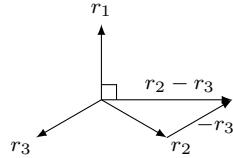


Figure 3.4: Orthogonal stretching basis.

Week 4

Spectroscopy

4.1 IR Selection Rules and Stretching Mode Analysis

10/17:

- Fill out the Google Form to indicate topics we want Wuttig to cover during the review session.
- The most common experiments we do to determine normal modes are IR and Raman experiments.
 - Vibration modes can be IR and/or Raman active.
 - IR spectroscopy probes direct absorption of IR light to excite vibrational modes.
 - We will first determine the IR selection rules.
- IR selection rules:
 - We want $\Delta v = \pm 1$.
 - The transition moment integral is for transitions $v \rightarrow v'$; it is written as

$$M_{vv'} = \int_{-\infty}^{\infty} \Psi^*(v') \mu \Psi(v) dx$$

where μ is the electric dipole moment and $[M_{vv'}]^2$ is the probability of the transition.

- If μ were a constant, then

$$M_{vv'} = \mu \int_{-\infty}^{\infty} \Psi^*(v') \Psi(v) dx = 0$$

since $\Psi^*(v')$ and $\Psi^*(v)$ are orthogonal functions.

- Therefore, μ cannot be a constant; it needs to be a function of x and needs to change during the vibration for the transition to be allowed.
- A more general form of $[M_{vv'}]^2$ is

$$[M_{vv'}]^2 = \int_{\text{all space}} \Psi^*(v') \hat{\mu} \Psi(v) d\tau$$

- In order for the above integral to not evaluate to zero, the direct product of the excited state wave function, transition dipole moment, and ground state wave function must contain the totally symmetric IRR. Symbolically,

$$\Gamma_{\text{IRR}}(\Psi(v')) \times \Gamma_{\text{IRR}}(\hat{\mu}) \times \Gamma_{\text{IRR}}(\Psi(v))$$

decomposes into a sum of IRRs including A_1 .

- Bottom line: A vibration will be IR active if it causes a change in the electric dipole moment of a molecule. A fundamental mode will be IR active if the normal mode which is excited belongs to the same representation as any one or several of the Cartesian coordinates.
- What modes are IR active for water?
 - Recall that the vibrational modes for H_2O are a_1 corresponding to ν_a , b_2 corresponding to ν_{as} , and a_1 corresponding to δ .
 - Looking at the character table, we notice that both a_1, b_2 transform as a linear function (z, y , respectively), so all modes are IR active.
 - More specifically, let's look at b_2 . If b_2 transforms as a linear function, it is true that it is IR active. Here's why: If b_2 transforms as a linear function, then it will be a component of $\hat{\mu}$. In this case, when we take the direct product $\Gamma_{v'} \times \hat{\mu}$, one term we will evaluate is $b_2 \times b_2$. But by the second of the three important theorems, the direct product of any representation times itself will contain the totally symmetric irreducible representation, which is required for IR visibility as per the third of the three important theorems.
 - Show by direct product analysis that these IR modes are allowed.
 - The first transition (ν_a) goes from $a_1 \rightarrow a_1$ (the ground state is relaxed, hence a_1 , and the excited state is Γ_{vibs} for ν_a , which is a_1). It follows that

$$\Psi^*(v')\hat{\mu}\Psi(v) \sim [1]a_1 \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix} a_1 = \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix}$$

Since the result of our calculation contains the totally symmetric representation (in its first entry), we know that ν_a is allowed.

- The asymmetric stretch has ground a_1 and excited state b_2 . $\hat{\mu}$ is the same as before.

$$\Psi^*(v')\hat{\mu}\Psi(v) \sim b_2 \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix} a_1 = \begin{pmatrix} b_2 \\ a_2 \\ a_1 \end{pmatrix}$$

Since it still contains the all-symmetric wavefunction, it's allowed.

- Example:

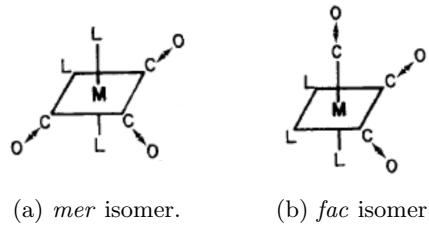


Figure 4.1: Isomers of an octahedral $\text{ML}_3(\text{CO})_3$ complex.

1. Determine the number, symmetries, and IR activities of the carbonyl stretching modes for the two isomers of an octahedral $\text{ML}_3(\text{CO})_3$ complex.
 - Since we are asked to determine the *carbonyl stretching* modes, we choose as our basis set the three vectors which run parallel to the CO bonds in both cases.
 - The point group of the *mer* isomer is C_{2v} ; the point group of the *fac* isomer is C_{3v} .
 - With this information, the rest of the question is fairly straightforward.

¹~ denotes “transforms as.”

2. The IR spectrum of the compound $\text{Mo}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_3$ exhibits bands at 1993, 1919 and 1890 cm^{-1} . The IR spectrum of compound $\text{Cr}(\text{CO})_3(\text{CHCH}_3)_3$ exhibits bands at 1942 and 1860 cm^{-1} . Based on your answer from part (1), how would you assign the *fac* vs. *mer* structure of these two complexes?
- From part (1), determine which structure gave rise to three nondegenerate stretching modes, and which gave rise to two.
 - This example shows that we can determine the stretching modes for just some functional groups.
 - Be careful with what the basis set is!
 - Example: Structures for OsO_4N .
 - This molecule has four reasonable structures, having symmetry C_{2v} , C_{3v} , C_{4v} , and C_s . It is a great example! Especially when paired with preceding molecules using some subset of these character tables.

4.2 Raman Selection Rules and Normal Mode Analysis

10/19:

- PSet 2 is due at the beginning of class on Friday.
- Raman and IR are complementary, and together they can distinguish geometric possibilities of an unknown molecule.
- **Raman spectroscopy:** A type of spectroscopy which probes inelastic scattering of light where the loss in energy corresponds to a vibrational frequency (**Stokes shift**).
 - In Raman, you go to **virtual energy states**.
 - **Virtual energy state:** The coupling of a photon with a high energy state.
 - **Rayleigh scattering:** The amount of energy put in is the amount of energy you get out. *Also known as elastic scattering.*
 - Doesn't give us a change, so we filter this out.
 - **Stokes Raman scattering:** The photon out has less energy than the photon in; some energy was scattered.
 - We excite from the ground state to a virtual energy state, and then fall back down but not all the way to the ground state, i.e., the electron remains in an excited state even after emitting its photon.
 - **Anti-Stokes Raman scattering:** The photon out has more energy than the photon in; we start at a higher energy state and then fall back to ground.
 - We excite from an excited state to a virtual energy state, and the fall back down all the way to the ground state.
- A vibrational mode will be Raman active if the polarizability of the molecule changes during the vibration. A fundamental transition will be Raman active (i.e., will give rise to a Raman shift) if the normal mode involved belongs to the same representation as one or more of the components of the polarizability tensor of the molecule.
- Transition probability in Raman:

$$M_w^2 = \left[\int_{-\infty}^{\infty} \Psi_v^* \hat{a} \Phi_v d\tau \right]^2$$

- Polarizability describes the shape of the electron cloud and can be described by a tensor.

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

- The matrix above is the polarizability tensor, and the right vector above describes the electric field.
- Three α values are redundant: The matrix above is symmetric, so

$$\alpha_{xz} = \alpha_{zx} \quad \alpha_{yz} = \alpha_{zy} \quad \alpha_{yx} = \alpha_{xy}$$

- Thus, $\hat{\alpha}$ has six different components.
- If you do the math, you learn that the transition is allowed if the symmetric IRR is in the direct product and the normal mode is a quadratic function.

- Recall: Linear for IR, quadratic for Raman.
- Example: The nine modes of vibration, two pairs of which are degenerate, are derived below for XeF_4 . Show that the b_{1g} fundamental transition is allowed for Raman but forbidden for infrared.

$$\Gamma_{\text{vibs}} = a_{1g} + b_{1g} + b_{2g} + a_{2g} + a_{2u} + b_{2u} + 2e_u$$

- Checking the D_{4h} character table, we see that the two linear representations are a_{2u} and e_u . Thus,

$$\Psi_{v'}^* \hat{\mu} \Psi_v \sim b_{1g} \begin{pmatrix} a_{2u} \\ e_u \end{pmatrix} a_{1g} = \begin{pmatrix} b_{2u} \\ e_u \end{pmatrix}$$

Thus, since a_{1g} doesn't appear, the IR transition is not allowed.

- Checking the D_{4h} character table, we see that the four quadratic representations are a_{1g} , b_{1g} , b_{2g} , and e_g . Thus,

$$\Psi_{v'}^* \hat{\mu} \Psi_v \sim b_{1g} \begin{pmatrix} a_{1g} \\ b_{1g} \\ b_{2g} \\ e_g \end{pmatrix} a_{1g} = \begin{pmatrix} b_{1g} \\ a_{1g} \\ a_{2g} \\ e_g \end{pmatrix}$$

Thus, since a_{1g} appears, the Raman transition is allowed.

- **Fundamental transition:** A transition starting from the ground state.
 - Ψ_v is always the totally symmetric IRR for a fundamental transition.
 - The wording “ b_{1g} fundamental transition” in the previous example means “the transition form a_{1g} to b_{1g} .”
 - Essentially, we’re not dealing with overtones, not starting from an excited state, no coupling, nothing fancy.
 - We will briefly talk about overtones later.
- Example: Determine the symmetries and activities of the normal modes of vibration for the cyclopropenyl cation. Use all atoms ($N = 6$), i.e., use the Cartesian displacement method.
 - Point group: D_{3h} .
 - $\Gamma_{xyz} = (3, 0, -1, 1, -2, 1)$.
 - $\Gamma_{\text{unmoved}} = (6, 0, 2, 6, 0, 2)$.
 - $\Gamma_{3N} = (18, 0, -2, 6, 0, 2) = 2A'_1 + 2A'_2 + 4E' + 2A'_2 + 2E'$.
 - $\Gamma_{\text{vibs}} = 2A'_1 + A'_2 + 3E' + A''_2 + E''$.

- Operators:

$$\hat{\mu} = \begin{pmatrix} e' \\ e''_2 \end{pmatrix} \quad \hat{\alpha} = \begin{pmatrix} a'_1 \\ e' \\ e'' \end{pmatrix}$$

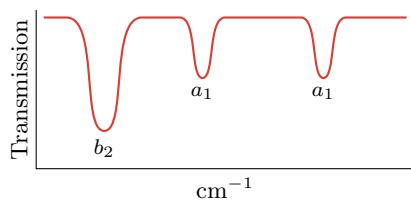
– a'_1 is Raman active, e' is both, a''_2 is IR active, and e'' is both.

- You only need uppercase Mulliken symbols for character tables and Tanabe-Sugano diagrams.
- **Rule of mutual exclusion:** No normal modes can be both infrared and Raman active in a molecule that possesses a center of symmetry.
- Question: Spectrum analysis. What symmetry element must be present?
 - Observation: Lack of coincidental IR and Raman peaks in the spectra of benzene.
 - Thus, no linear bases or quadratic bases overlap. The linear must all be -1 and the quadratic must all be 1 .
 - Thus, an inversion i is present.

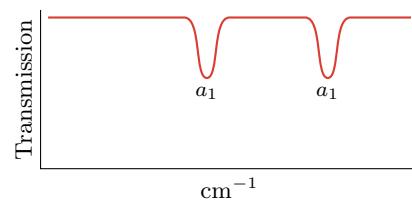
4.3 Special Spectroscopic Bands

10/21:

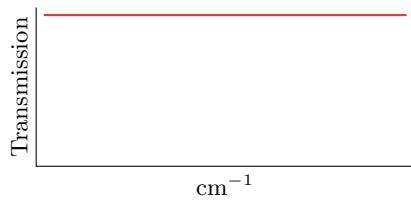
- Calculators that aren't connected to the internet are permitted. Arrive by 9:25. Think of it as a quiz more than an exam — there's only so much you can do in 50 minutes.
- **Polarization:** When electric fields are restricted to a specific direction by filtration.
- Recall H_2O and its vibrational modes ν_1, ν_2, ν_3 , which are symmetric stretch, bending, and asymmetric stretch, respectively. Consider the *hypothetical* case where we can “hold” water molecules such that they are oriented on the Cartesian plane.



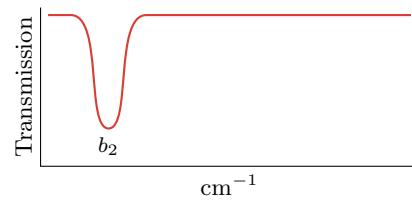
(a) Unpolarized.



(b) z -polarized.



(c) x -polarized.



(d) y -polarized.

Figure 4.2: Polarized IR spectra of H_2O .

- The unpolarized IR spectrum would be the result of what we predicted last time.
- The z -polarized spectrum: ν_1, ν_2 are a_1 and hence transform with the same symmetry as z . You filter out the b_2 for a z -polarized spectrum.

- y -polarized gives you just b_2 .
- x -polarized gives you nothing.
- Linear functions give you the right answer, but you can also rationalize from the vectors.
 - For example, drawing out the vectors for ν_1 in H_2O , you see that the major dipole moment is in the z -direction. Same for ν_2 . However, for ν_3 , the major dipole moment is in the y -direction.
 - What we're polarizing here is the incoming IR radiation. If all molecules were held with the correct orientation and then we shot z -polarized light at them, only vibrations in the z direction would get excited (x, y are equally and oppositely cancelled).
- Polarization is most commonly used in Raman spectroscopy.
- Experimental setup.

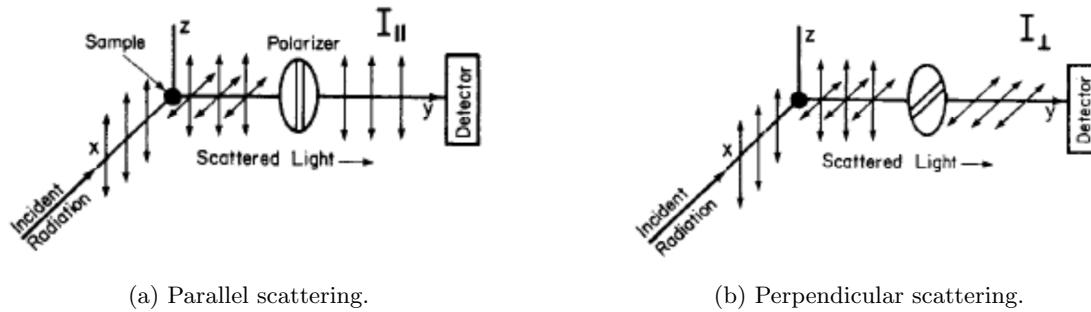


Figure 4.3: Raman polarization setup.

- We place the sample solution at the origin of our coordinate system, shoot xz -polarized light down one axis, and measure the polarization of the emitted radiation down a perpendicular axis.
- From this setup, we can determine the extent to which the molecules that absorb plane-polarized light emit light in the same plane or in a perpendicular plane.
- **Depolarization ratio:** The following quantity, where I_{\perp} is the intensity of the scattered light polarized in the plane perpendicular to the incident light and I_{\parallel} is the intensity of the scattered light in the same plane as the incident light. *Denoted by ρ . Given by*

$$\rho = \frac{I_{\perp}}{I_{\parallel}}$$

- Depolarized (unpolarized) bands will exhibit $\rho \approx 3/4$. In contrast, polarized bands will exhibit ρ values between 0 and 3/4.
 - Polarized bands appear from vibrations that are totally symmetric.
 - The more highly symmetric the molecule, the closer ρ is to zero (polarization is high).
- Example: For each IR transition of the cyclopropenyl cation, determine the direction of the adsorption. Determine which Raman active fundamentals of the compound are polarized or depolarized.
 - IR: The polarization of the e' adsorption is (x, y) and the direction of polarization of a''_2 is z .
 - What does the degenerate polarization of e' mean?? Does it mean that either x - or y -polarized light will excite this transition?
 - Raman: a'_1 is your most polarized Raman active mode. e' and e'' are polarized but not as much.
- Most IR spectra show more bands than we predict for fundamentals. These are **overtones, combination bands, and hot bands**.

- **Overtone:** A band that occurs when a mode is excited beyond $v = 1$ by a single photon. *picture*
 - Example: If our three normal modes are $\Psi_1(0)\Psi_2(0)\Psi_3(0)$ and we excite one of them such that it goes to a third state $\Psi_1(0)\Psi_2(3)\Psi_3(0)$. This is the **second overtone** of the normal mode ν_2 . We are taking $v = 0$ to $v = 3$ here.
 - The energy of this transition would be approximately 3 times the fundamental $v_0 \rightarrow v_1$.
- **Combination band:** A band that occurs when more than one vibration is excited by one photon. *Also known as combo band.*
 - Example:

$$\Psi_1(0)\Psi_2(0)\Psi_3(0) \rightarrow \Psi_1(1)\Psi_2(1)\Psi_3(0)$$
 - Example:

$$\Psi_1(0)\Psi_2(0)\Psi_3(0) \rightarrow \Psi_1(2)\Psi_2(0)\Psi_3(1)$$
 - I.e., you can throw in overtones, too.
 - What this means for the energy: Energy of the combination band transition is the sum of the energies of the individual transitions.
 - Energy for example 1: $v_1 + v_2$.
 - Energy for example 2: $2v_1 + v_3$.
- **Hot band:** A band that occurs when an already excited vibration is further excited.
 - Example:

$$\Psi_1(0)\Psi_2(1)\Psi_3(0) \rightarrow \Psi_1(0)\Psi_2(2)\Psi_3(0)$$
 - The probability of this event depends on the temperature because it relies on the thermal population of an already excited state.
 - The population increases as a function of temperature.
 - Thermal population of the initial state is low, but it increases with temperature and hence is called a *hot* band.
- The selection rules for predicting whether an overtone, combo band, or hot band is possible use the same direct product math.
 - We won't cover this in depth, though.
- **Fermi resonance:** The mixing of two states, which can have two effects:
 1. The overtone can gain intensity from the nearby fundamental of the same symmetry.
 2. Both energy levels are shifted away from each other.
- Predicting when Fermi resonance occurs is hard; it is done only after ruling out the possibility of an overtone, combo band, or hot band as accounting for your data.
- Example: CO₂.
 - Since there are four normal modes, you might predict four IR bands.
 - The δ_d bending modes have $E = 667\text{ cm}^{-1}$. You'd predict their first overtone to have $E = 1334\text{ cm}^{-1}$. However, this mode has a similar symmetry to the symmetric stretch ν_s at $E = 1337\text{ cm}^{-1}$. Thus, they will mix via Fermi resonance, producing two really strong bands at 1388 cm^{-1} and 1286 cm^{-1} .
 - According to Wuttig, it is purely a coincidence that energies in this example are similar; states don't only mix when their energies are similar.

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, its inverse, itself, itself, and its 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	$2C_5$	$2C_5^2$	$5C'_2$	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*-N₂F₂.
- 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_{unn}	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,

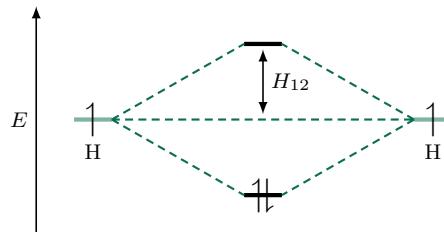
$$D = c_1^2 \underbrace{\int \phi_1 \phi_1 d\tau}_{1} + c_1 c_2 \underbrace{\int \phi_1 \phi_2 d\tau}_{S} + c_2 c_1 \underbrace{\int \phi_2 \phi_1 d\tau}_{S} + c_2^2 \underbrace{\int \phi_2 \phi_2 d\tau}_{1}$$

- 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

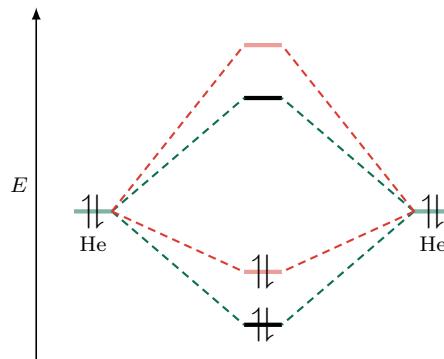
$$E = \frac{H \pm H_{12}}{1 \pm S}$$
- **Resonance integral:** An integral describing the strength of the bonding interaction due to the overlap of AOs in the MO.
- **Overlap integral:** An integral that measures the effectiveness of the overlap.
 - Dependent on the type of bond. In particular, it is 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, orbitals 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.

¹This is related to Talapin's arbitrary 10 eV!

- Here, we get

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

- 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 2pz), not π interactions with px or py.
- Review QMech notes and come up with questions!

Week 6

Complex MO Diagrams

6.1 MO Theory: LCAOs and Group Orbitals

10/31:

- Last time: Building MO diagrams by qualitatively identifying a basis of atomic orbitals (e.g., 1s for H, 2s and 2p for F) and intuitively determining an axis to about which they transform within the linear point group $C_{\infty v}$.
- Today: Making this process more formal, as is necessary for more complex, polyatomic molecules.
- For polyatomic molecules, we need to determine how the basis atomic orbitals transform. This will allow us to approximate molecular orbitals with linear combinations of them (the AOs) that transform with the same symmetry.
 - To do this, we need to understand how to group together valence atomic orbitals, i.e., how to construct **group orbitals**.
- **Group orbital:** An MO of a complex molecule.
- Strategy for building group orbitals and creating the relevant MO diagram.
 1. Determine the point group of the molecule. If it is a linear molecule, substituting a simpler point group that still retains the symmetry of the orbitals (ignoring the signs) makes the process easier by eliminating infinite-fold rotation axes.
 - We will substitute the 2-fold **subgroup** of the relevant point group in these cases.
 - In particular, substitute D_{2h} for $D_{\infty h}$ and C_{2v} for $C_{\infty v}$.
 2. Assign xyz coordinates.
 3. Construct reducible representations for the valence orbitals on the peripheral atoms.
 4. Reduce each representation to its IRRs (i.e., find the symmetry of the group orbitals). Group orbitals are the combinations of atomic orbitals that match the symmetry of the IRRs.
 5. Identify the atomic orbitals on the central atom with the same symmetries (IRRs) as those found in step 4.
 6. Combine the atomic orbitals with matching symmetry and similar energy. The total number of MOs must be equal to the number of atomic orbitals used from all the atoms.
 - Energy scaling of MOs $\sigma < \pi < \text{lone pairs} < \pi^* < \sigma^*$. More nodes equals higher in energy.
 7. Label MOs.
 - σ implies a SALC with infinite-fold rotational symmetry about the bond axis; π implies a SALC with 2-fold rotational symmetry about the bond axis.
 - No superscript implies a bonding interaction; superscript * implies an antibonding interaction.

- Subscript *g* implies symmetrical with respect to inversion; subscript *u* implies asymmetrical with respect to inversion.

8. Fill in the electrons.

- Example: CO₂.

1. $D_{\infty h} \rightarrow D_{2h}$.

D_{2h}	E	C ₂ (z)	C ₂ (y)	C ₂ (x)	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	linear functions, rotations	quadratic functions	cubic functions
A _g	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2, y^2, z^2	-
B _{1g}	+1	+1	-1	-1	+1	+1	-1	-1	R _z	xy	-
B _{2g}	+1	-1	+1	-1	+1	-1	+1	-1	R _y	xz	-
B _{3g}	+1	-1	-1	+1	+1	-1	-1	+1	R _x	yz	-
A _u	+1	+1	+1	+1	-1	-1	-1	-1	-	-	xyz
B _{1u}	+1	+1	-1	-1	-1	-1	+1	+1	z	-	z^3, y^2z, x^2z
B _{2u}	+1	-1	+1	-1	-1	+1	-1	+1	y	-	yz^2, y^3, x^2y
B _{3u}	+1	-1	-1	+1	-1	+1	+1	-1	x	-	xz^2, xy^2, x^3

Table 6.1: D_{2h} character table.

2. xyz coordinates are chosen as per Figure 6.1.

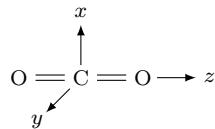


Figure 6.1: CO₂ xyz coordinates.

3. The two oxygen atoms are peripheral; their valence orbitals are $2s$, $2p_x$, $2p_y$, and $2p_z$. Thus, we have from the D_{2h} character table and Figure 6.1 that

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{O(2s)}$	2	2	0	0	0	0	2	2
$\Gamma_{O(2p_z)}$	2	2	0	0	0	0	2	2
$\Gamma_{O(2p_x)}$	2	-2	0	0	0	0	2	-2
$\Gamma_{O(2p_y)}$	2	-2	0	0	0	0	-2	2

Table 6.2: Representations for the valence orbitals of CO₂.

- We get 0 characters for $\Gamma_{O(2p_z)}$ because the individual orbitals move, even though the “overall basis” inverts.

4. As follows.

$$\Gamma_{O(2s)} = \Gamma_{O(2p_z)} = a_g + b_{1u}$$

$$\Gamma_{O(2p_x)} = b_{3u} + b_{2g}$$

$$\Gamma_{O(2p_y)} = b_{2u} + b_{3g}$$

5. Carbon AOs: From the D_{2h} character table,

$$\text{C}(2s) = a_g$$

$$\text{C}(2p_z) = b_{1u}$$

$$\text{C}(2p_x) = b_{3u}$$

$$\text{C}(2p_y) = b_{2u}$$

6. We can now construct the following MO diagram.

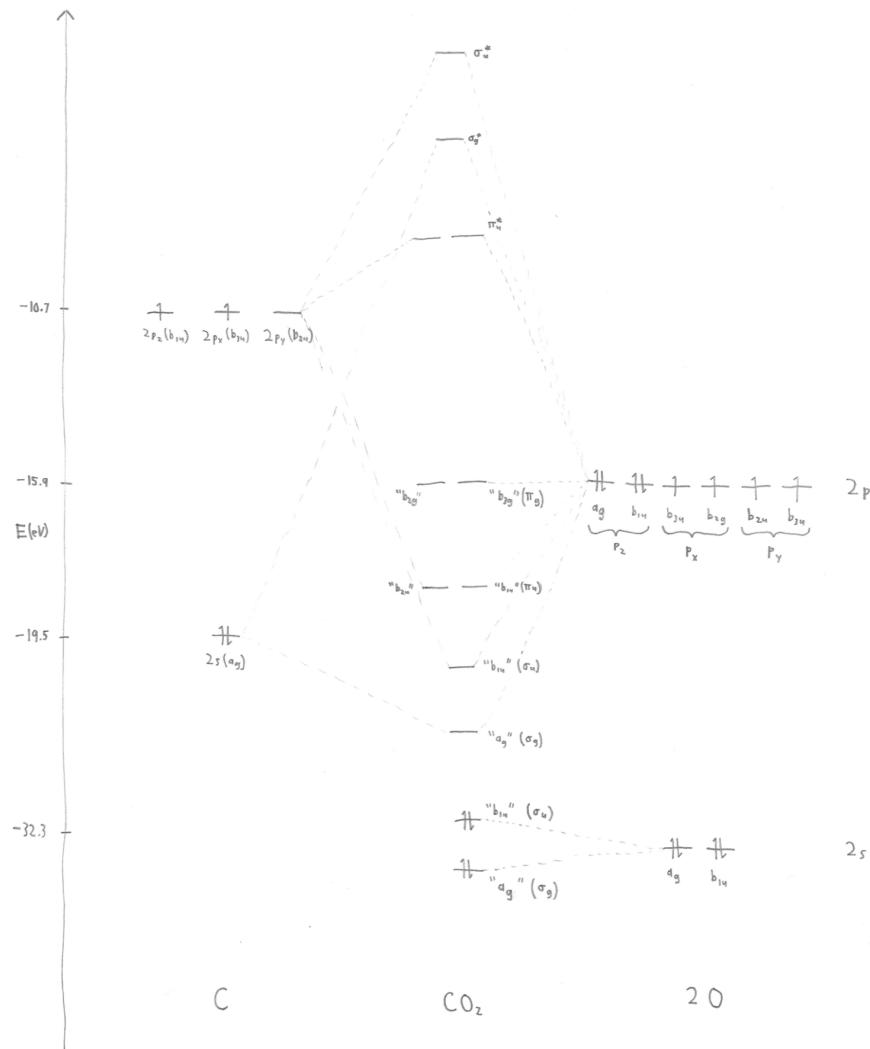
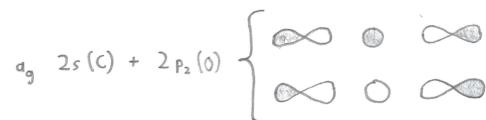


Figure 6.2: CO_2 MO diagram.

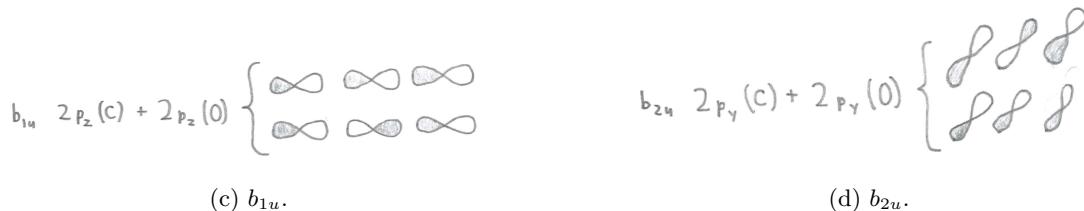
Moreover, a selection of key SALCs may be visualized as follows.



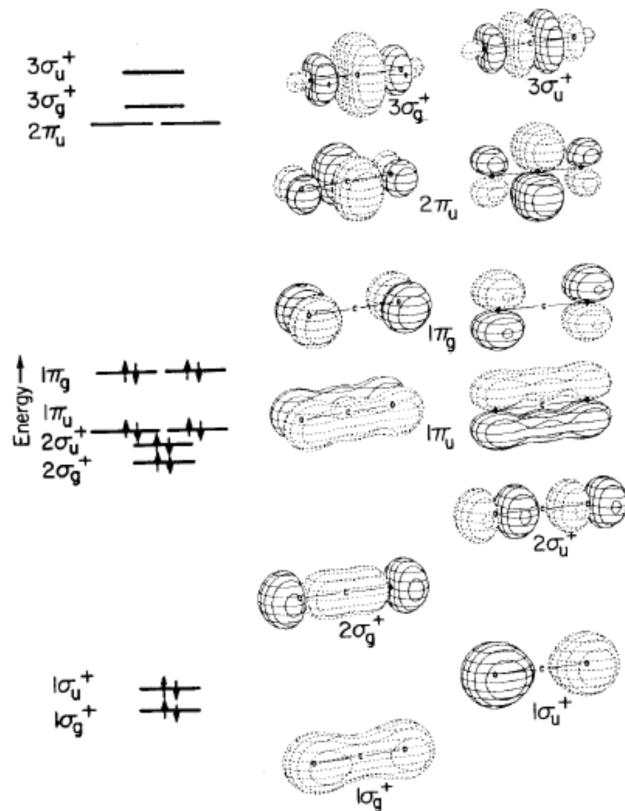
(a) $\text{O}(2s)$.



(b) a_g .

Figure 6.3: Selected CO₂ SALCs.

- From the 1 Rydberg rule, oxygen 2s orbitals will not significantly overlap with carbon 2s or 2p orbitals.
 - However, we still know that the bonding orbital is slightly lower in energy than the antibonding orbital by counting nodes
 - A bit of mixing also occurs, though (see the discussion surrounding Figure 6.4).
 - We have so many oxygen electrons since we have *two* oxygens and we are considering their *group* orbitals.
 - We can draw SALCs intuitively by combining orbitals in a bonding or antibonding fashion, or rigorously using the projection operator.
 - *Redraw & add electrons later!*
7. Done (see Figure 6.2).
 8. Done (see Figure 6.2).
- Differences between the CO₂ MOs derived from first principles (Figure 6.2) and the MOs calculated by a computer's quantum mechanics program (Figure 6.4).

Figure 6.4: Quantum-mechanically calculated MOs for CO₂.

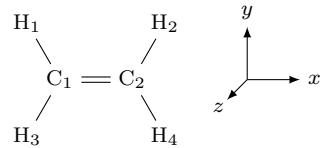
- In the calculated version, $1\sigma_g$ does not have a node at the carbon atom. This differs from the corresponding SALC we derived from first principles. Thus, in reality, we have some mixing between $1\sigma_g$ and $2\sigma_g$. It follows that we can describe the orbital a bit better as O(2s) lone pairs plus CO σ bonds.
- Takeaway: The MOs we get from first principles do not take into account all of the interactions that the computer can.
- Note that in Figure 6.4, the electron density at each contour surface is 0.0675 electrons/ \AA^3 for one-electron wave functions. This value was chosen merely for satisfactory visual display of the orbitals.

6.2 Group Orbitals for Nonlinear Molecules

11/2:

- Last time: Making MOs for combinations that have two linear “outer atoms” like CO_2 .
- Today: Making MOs for cases in which we can’t just add and subtract two valence orbitals to visualize the group orbitals.
- Strategy: Make group orbitals for “central atoms” and “peripheral atoms” and combine.
- Example: MO diagram for ethylene.

 1. Point group: D_{2h} .
 2. xyz coordinates (and numbering for the projection operator).

Figure 6.5: C_2H_4 xyz coordinates.

3. Representations.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\text{H}(1s)}$	4	0	0	0	0	4	0	0
$\Gamma_{\text{C}(2s)}$	2	0	0	2	0	2	2	0
$\Gamma_{\text{C}(2p_x)}$	2	0	0	2	0	2	2	0
$\Gamma_{\text{C}(2p_y)}$	2	0	0	-2	0	2	-2	0
$\Gamma_{\text{C}(2p_z)}$	2	0	0	-2	0	-2	2	0

Table 6.3: Representations for the valence orbitals of C_2H_4 .

4. Reductions.

$$\begin{aligned}\Gamma_{\text{H}(1s)} &= a_g + b_{1g} + b_{2u} + b_{3u} \\ \Gamma_{\text{C}(2s)} &= a_g + b_{3u} \\ \Gamma_{\text{C}(2p_x)} &= a_g + b_{3u} \\ \Gamma_{\text{C}(2p_y)} &= b_{1g} + b_{2u} \\ \Gamma_{\text{C}(2p_z)} &= b_{2g} + b_{1u}\end{aligned}$$

- Let’s get a handle on what some of these orbitals look like using the projection operator.

- Let's see how H_1 and $C_{2p_y(1)}$ transform.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
H_1	H_1	H_4	H_2	H_3	H_4	H_1	H_3	H_2
$C_{2p_y(1)}$	$C_{2p_y(1)}$	$-C_{2p_y(2)}$	$C_{2p_y(2)}$	$-C_{2p_y(1)}$	$-C_{2p_y(2)}$	$C_{2p_y(1)}$	$-C_{2p_y(1)}$	$C_{2p_y(2)}$

Table 6.4: How selected C_2H_4 orbitals transform under the D_{2h} symmetry operations operators.

- We will visualize how these transform under b_{2u} . For H_1 , we get

$$\begin{aligned}\hat{P}(H_{1s})_{b_{2u}} &= H_1 - H_4 + H_2 - H_3 - H_4 + H_1 - H_3 + H_2 \\ &= 2H_1 - 2H_4 + 2H_2 - 2H_3 \\ &\approx H_1 - H_4 + H_2 - H_3\end{aligned}$$

and for $C_{2p_y(1)}$, we get

$$\begin{aligned}\hat{P}(C_{2p_y(1)})_{b_{2u}} &= C_{2p_y(1)} + C_{2p_y(2)} + C_{2p_y(2)} + C_{2p_y(1)} + C_{2p_y(2)} + C_{2p_y(1)} + C_{2p_y(1)} + C_{2p_y(2)} \\ &= 4(C_{2p_y(1)} + C_{2p_y(2)}) \\ &\approx C_{2p_y(1)} + C_{2p_y(2)}\end{aligned}$$

- Thus, individually, these group orbitals may be visualized as follows.

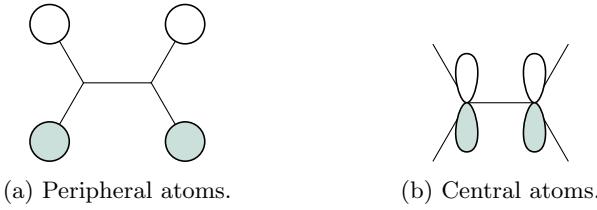


Figure 6.6: C_2H_4 b_{2u} SALCs.

- Now we take two orthogonal linear combinations of the two to get our MOs.

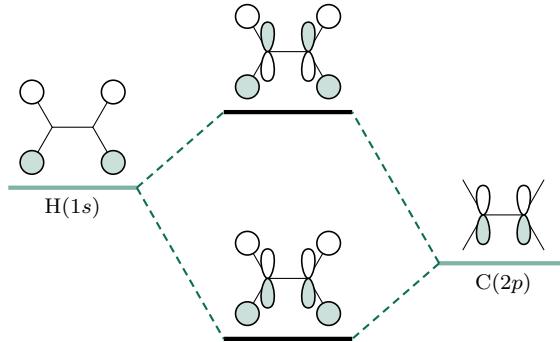
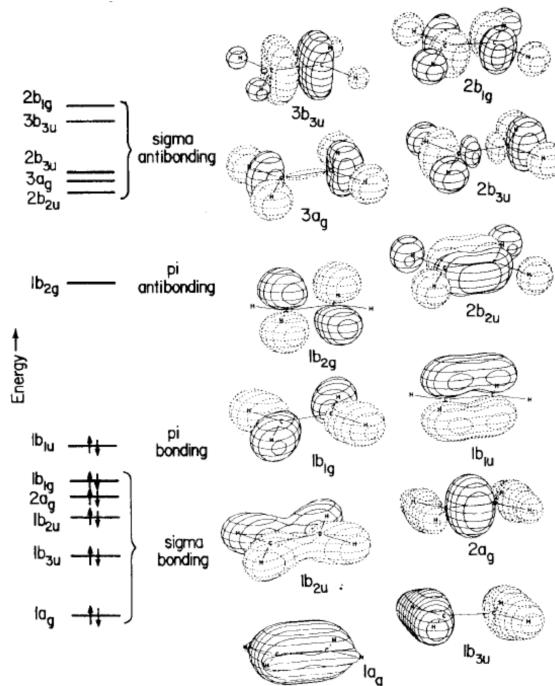


Figure 6.7: C_2H_4 b_{2u} MOs.

- Note that we label the MOs by comparing to the computed orbitals in Figure 6.8.

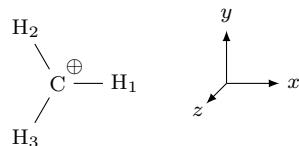
Figure 6.8: Quantum-mechanically calculated MOs for C_2H_4 .

- What about how we make MOs for group orbitals that transform with e symmetry?
 - Example: Methyl cation.
1. Point group: D_{3h} .

\mathbf{D}_{3h}	E	2C_3 (z)	$3\text{C}'_2$	σ_h (xy)	2S_3	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
A'1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	$x(x^2-3y^2)$
A'2	+1	+1	-1	+1	+1	-1	R_z	-	$y(3x^2-y^2)$
E'	+2	-1	0	+2	-1	0	(x, y)	(x^2-y^2, xy)	$(xz^2, yz^2) [x(x^2+y^2), y(x^2+y^2)]$
A''1	+1	+1	+1	-1	-1	-1	-	-	-
A''2	+1	+1	-1	-1	-1	+1	z	-	$z^3, z(x^2+y^2)$
E''	+2	-1	0	-2	+1	0	(R_x, R_y)	(xz, yz)	$[\text{xyz}, z(x^2-y^2)]$

Table 6.5: D_{3h} character table.

2. xyz coordinates.

Figure 6.9: CH_3^+ xyz coordinates.

3. Representations.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{H(1s)}$	3	0	1	3	0	1
$\Gamma_{C(2s)}$	1	1	1	1	1	1
$\Gamma_{C(2p_x, 2p_y)}$	2	-1	0	2	-1	0
$\Gamma_{C(2p_z)}$	1	1	-1	-1	-1	1

Table 6.6: Representations for the valence orbitals of CH_3^+ .

4. Reductions.

$$\begin{aligned}\Gamma_{H(1s)} &= a'_1 + e' \\ \Gamma_{C(2s)} &= a'_1 \\ \Gamma_{C(2p_x, 2p_y)} &= e' \\ \Gamma_{C(2p_z)} &= a''_2\end{aligned}$$

- The projection operator is only necessary for what group orbitals look like.

- How hydrogen orbitals transforms.

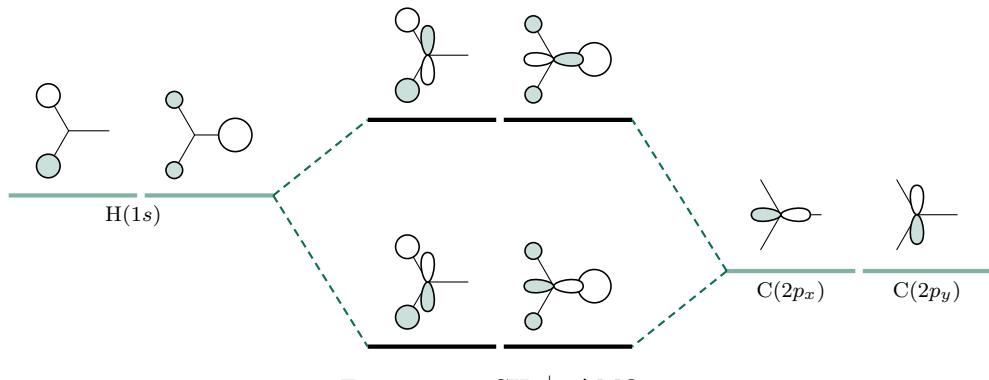
D_{3h}	E	C_3	C_3^2	C_2	C_2'	C_2''	σ_h	S_3	S_3^{-1}	σ_v	σ'_v	σ''_v
H ₁	H ₁	H ₂	H ₃	H ₁	H ₃	H ₂	H ₁	H ₂	H ₃	H ₁	H ₂	H ₃
H ₂	H ₂	H ₃	H ₁	H ₂	H ₁	H ₃	H ₂	H ₃	H ₁	H ₂	H ₃	H ₁
H ₃	H ₃	H ₁	H ₂	H ₃	H ₂	H ₁	H ₃	H ₁	H ₂	H ₃	H ₁	H ₂

Table 6.7: How selected CH_3^+ orbitals transform under the D_{3h} symmetry operations operators.

- Transformations under e' .

$$\begin{aligned}\hat{P}(H_1)_{e'} &\approx 2H_1 - H_2 - H_3 \\ \hat{P}(H_2)_{e'} &\approx 2H_2 - H_3 - H_1 \\ \hat{P}(H_3)_{e'} &\approx 2H_3 - H_1 - H_2\end{aligned}$$

- We take the first and subtract the second two to get $H_2 - H_3$ as our second orthogonal orbital.
- To draw MOs, we either pair C_{2p_x} with $2H_1 - H_2 - H_3$ and C_{2p_y} with $H_2 - H_3$ or vice versa.

Figure 6.10: CH_3^+ e' MOs.

- Note that the two bonding and the two antibonding MOs here are pairwise degenerate.

- Should we label the MOs via PES as in CHEM 201?
 - Yes.
- Finding energies from SALCs?

6.3 Photoelectron Spectroscopy and MO Diagrams of Coordination Complexes

11/4:

- The problem set is deceptively hard; get started early!
- Today: Experimental verification of molecular orbitals.
- **Photoelectron spectroscopy:** A widely used technique that allows us to obtain information about the energies of the electrons in orbitals.
- Key equation.

$$\text{BE} = h\nu - \text{KE}$$
 - BE is the binding energy of the expelled electron.
 - $h\nu$ is the incident photon energy.
 - KE is the kinetic energy of the expelled electron.
- Fine structure in PES comes from the interaction of the electronic levels with the vibrational levels. This yields multiple peaks for a single given electronic transition.
- Example: How many peaks in the PES should we expect for each occupied MO of ethylene? Label each peak with the relevant valence molecular orbitals for ethylene.

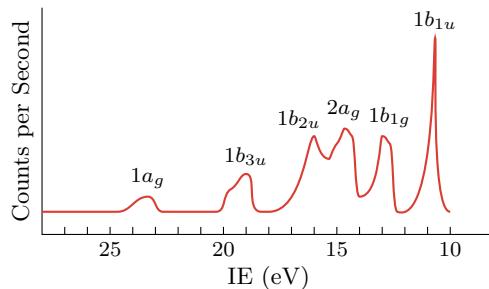


Figure 6.11: Photoelectron spectrum of C_2H_4 .

- 1 peak for each occupied MO.
- Highest IE corresponds to the most core orbital. Decreases in energy as we get to higher energy orbitals.
- When Wuttig says in the homework that she wants us to draw a qualitative photoelectron spectrum, this is what she means.
- We now translate the principals of MO diagrams we've developed to understand bonding and structure in coordination complexes. We abbreviate the metal as M and the ligand as L.
- Basis sets are denoted by ϕ .
- Basis sets.
 - M: $(n+1)p$, $(n+1)s$, and nd .

- L: $\sigma \rightarrow \sigma$ interactions, $\pi \rightarrow \pi$ interactions, and $\pi^* \rightarrow \pi^*$ interactions.
 - Today: The $\sigma \rightarrow \sigma$ case only.
 - A few general rules for M-L bonding (these are essentially a rephrasing of those we have developed for the MOs of the organic species we have discussed this far).
 1. M-L atomic orbital mixing is proportional to the overlap of the M and L orbitals.
 - (a) But only orbitals of correct symmetry can mix.
 - (b) σ interactions typically give rise to larger interaction energies than π interactions which, in turn, typically give rise to larger interaction energies than δ interactions. This is because we have more directional bonding as we move from $\sigma \rightarrow \pi \rightarrow \delta$.
 2. M-L atomic orbital mixing is inversely proportional to energy difference of mixing orbitals.
 3. The order of the E_L and E_M energy levels almost always is the following.
- $$\sigma(L) < \pi(L) < nd < (n+1)s < (n+1)p$$
- (a) Energy ordering origin: Metal/main group VOIEs and ligand electronic spectra.
 - Impact of VOIE as you move later in the periodic table.
 - Metals.
 - More covalency with L.
 - Less d-s-p mixing.
 - Common ligands.
 - More mixing with lone pairs compared to bonding orbitals.
 - Conclusions from examining VOIEs.
 1. The s orbitals are generally too low in energy to participate in bonding.
 2. The filled p orbitals are the frontier orbitals, and they have VOIEs that place them below metal orbitals.
 3. For ligands, since the frontier orbitals comprise s and p orbitals, filled ligand orbitals have energies E that are stabilized relative to metal orbitals.
 - Symmetry.
 - We will now build the σ -only MO diagram for the important ML_6 octahedral case.
 1. Point group: O_h .

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Table 6.8: Character table for the O_h point group.

2. A coordinate system is not particularly necessary here since the molecule is symmetric along every Cartesian axis.
3. Reducible representation for the σ orbitals.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_σ	6	0	0	2	2	0	0	0	4	2

Table 6.9: Representation for the σ orbitals of ML_6 .

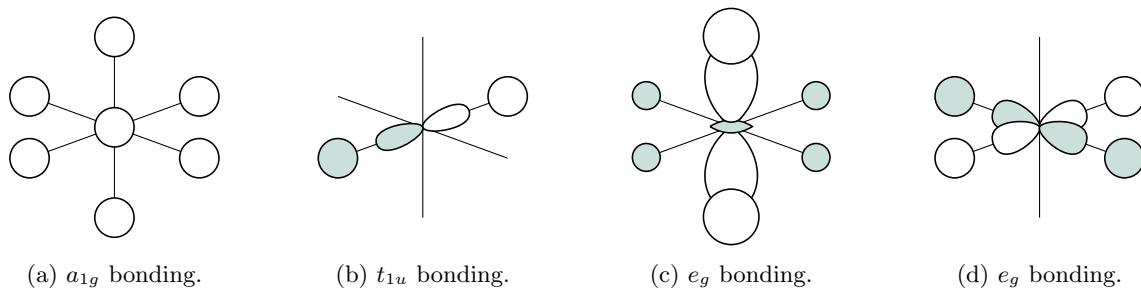
4. Reduction.

$$\Gamma_\sigma = a_{1g} + e_g + t_{1u}$$

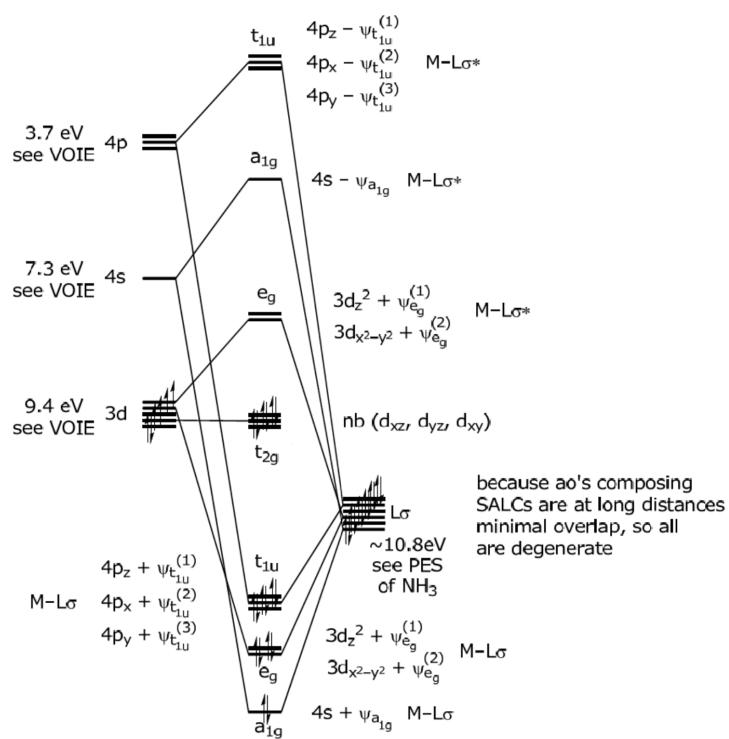
5. Symmetries of the metal atomic orbitals (from Table 6.8).

$$s \sim a_{1g} \quad p_x, p_y, p_z \sim t_{1u} \quad d_{z^2}, d_{x^2-y^2} \sim e_g \quad d_{xz}, d_{yz}, d_{xy} \sim t_{2g}$$

6. What the SALCs end up looking like.

Figure 6.12: ML_6 SALCs.

- Note that the t_{2g} set will end up being nonbonding.
- Wuttig did not explicitly compute these; she took a shortcut of guessing their shape inspired by the symmetry of the central orbital and assured us that the guess is what you get from the projection operator.
- Doing the SALC for the d_{z^2} e_g set gives you twice the electron density for the z -axis regions as for the xy -plane regions.
- 7. Now we can make sense of the full σ -only MO diagram (see Figure 6.13).
 - In particular, we want to be able to determine what all of the MOs on the diagram look like.
- π -donating ligands.
 - Typical π -donating ligands include halides (X^-), amides ($CONH_2$), sulfides (S^{2-}), and oxides (O^{2-}).
 - Pictures of σ - and π -donation (see Figure VI.4 of Labalme (2022)).
- π -accepting ligands.
 - Typical π -accepting ligands include CO , NO^+ , CN^- , CNR , and PPh_3 .
 - Pictures of σ -donation and π acceptance (see Figure VI.4 of Labalme (2022)).

Figure 6.13: ML₆ MO diagram.

Week 7

Bonding in Coordination Complexes

7.1 Coordination Complexes: π Bonding and all- σ Distortions

11/7:

- Video lecture Wed and Fri; watch by Mon and have questions.
- Last time: MO diagram for an ML_6 coordination complex whose ligands only engage in σ interactions.
- Today: The case where the ligands also have π orbitals.
- As per usual, we follow the procedure from Lecture 6.1.
 1. Point group: O_h .
 2. Assigning coordinate axes is a bit more complicated here, but the following will work.

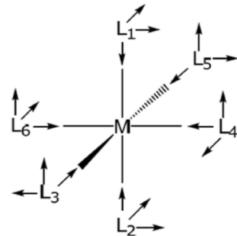


Figure 7.1: ML_6 π xyz coordinates.

- We have two orthogonal $p\pi$ bonds.
- The arrows indicate the directional phase of the p orbitals.
- 3. Let's create a representation for the 12 p orbitals capable of π bonding.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_{12\pi}$	12	0	0	0	-4	0	0	0	0	0

Table 7.1: Representation for the $p\pi$ ligand orbitals of ML_6 .

4. Reducing, we get

$$\Gamma_{12\pi} = T_{1g} + T_{1u} + T_{2g} + T_{2u}$$

5. From Table 6.8, the atomic orbitals of the metal transform as

$$s \sim a_{1g} \quad p_x, p_y, p_z \sim t_{1u} \quad d_{z^2}, d_{x^2-y^2} \sim e_g \quad d_{xz}, d_{yz}, d_{xy} \sim t_{2g}$$

- Thus, the metal p and d_{xz}, d_{yz}, d_{xy} orbitals interact with the ligand π SALCS.

6. Once again, we can “guess” the SALCs based on experience.

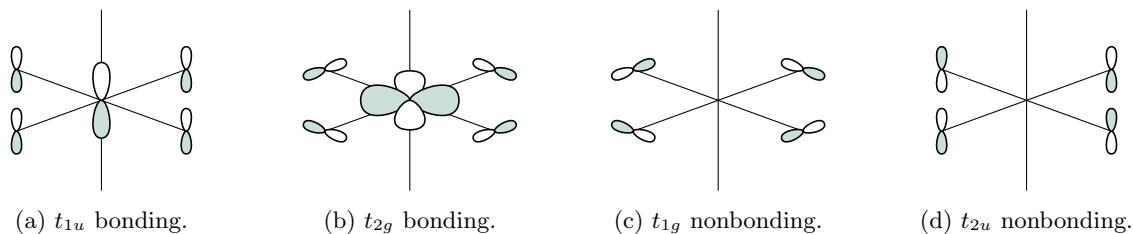


Figure 7.2: $\text{ML}_6 \pi$ SALCs.

- In addition to these, there are two more (oriented along the other orthogonal coordinate axes) for each IRR.
- 7. We can now make sense of the MO diagram.

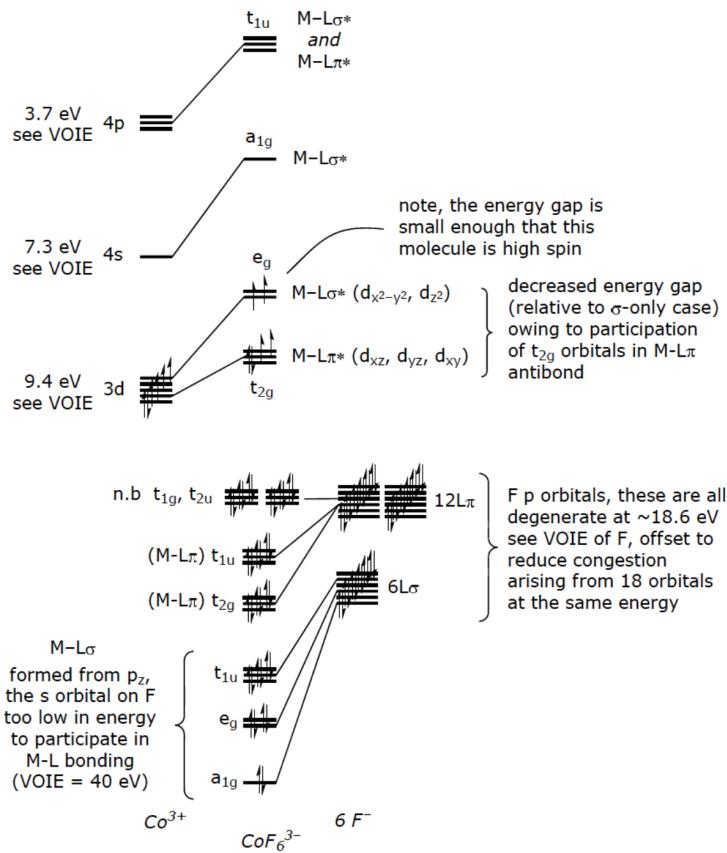


Figure 7.3: $\text{ML}_6 \pi$ MO diagram.

- Wuttig compares this MO diagram to the all- σ case (Figure 6.13).
 - The $\text{M-L}\sigma$ and $\text{M-L}\sigma^*$ distortions stay the same; we now just have *additional* $\text{M-L}\pi$ and $\text{M-L}\pi^*$ distortions to consider.
 - π -donating ligands, such as the fluoride ligands causing the interactions in Figure 7.3, *raise* the t_{2g} set in energy; they contribute *antibonding* interactions.
 - Note that the $\text{L}\pi$ orbitals sit above the $\text{L}\sigma$ orbitals.
- Wuttig probably expects us to be familiar with the $\text{M-L}\pi^*$ notation.

- It seems that now we're done. But wait: We have made an assumption that is not necessarily justified in every case.
 - We have treated the ligand as a point particle with atomic orbitals that mirror the metal center (i.e., your typical s , p , etc. orbitals).
 - This is justified in the case of fluoride (as in Figure 7.3). But what about a ligand such as carbon monoxide? CO certainly has molecular orbitals more complicated than the atomic orbitals of either carbon or oxygen alone, so is it still valid to treat it as a point particle with "atomic" orbitals?
 - In fact, it is not, and we will now see how to treat that case.
 - As with fluoride, the frontier orbitals of CO will be the ones that interact with the metal center.
 - To draw SALCs of the interactions of these MOs with the metal center, we need to know what *they* look like first. Fortunately, we have encountered the SALCs for heteronuclear diatomics before, and we can simply use these as our basis set to draw the overall SALCs.

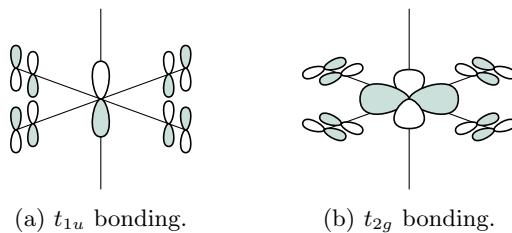
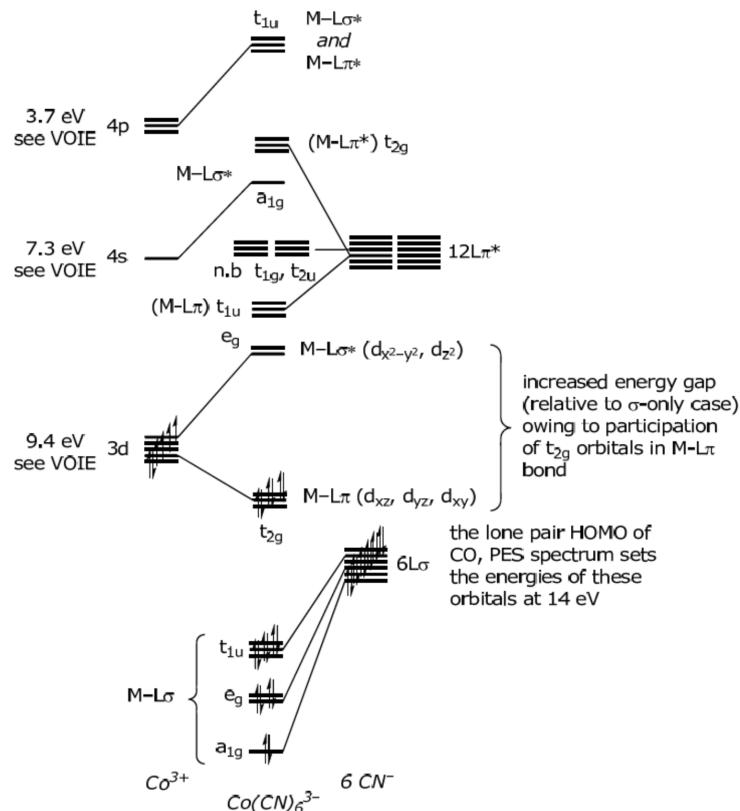


Figure 7.4: $M(CO)_6$ π -bonding SALCs.

- Wuttig draws the Figure 7.4a interactions in-plane, too, though??
 - Wuttig also doesn't draw the nonbonding ones, but they still exist??
 - To reiterate, the π^* orbitals of CO will participate in t_{1u} and t_{2g} bonding interactions, and t_{1g} and t_{2u} nonbonding interactions just like the p orbitals of F; it is *strictly* and *solely* the basis set that we're changing.
 - An additional complication arises from the fact that the frontier orbitals of CO are fundamentally different than those of F.
 - In particular, the frontier orbitals of F are filled π -donating atomic orbitals, while CO has a filled σ -donating frontier orbital (HOMO) and an unfilled π^* -accepting frontier orbital (LUMO).
 - Thus, we need to consider the new *energetics* of these orbitals as well.
 - For a π -donating ligand such as monoatomic fluoride, the σ and π orbitals are degenerate.
 - This is because all 18 ligand orbitals come from the $2p$ *atomic* orbitals of fluorine.
 - However...
 - Are the σ and π orbitals of the π -accepting ligands degenerate in energy?
 - They are not.
 - This is because we are considering the interactions of nondegenerate ligand *molecular* orbitals with the metal center.
 - Evidence: We can inspect the photoelectron spectrum of our ligand (e.g., for CO, we observe distinct peaks corresponding to its σ -donating and π^* -accepting orbitals).
 - Note that ligands such as CO still have filled π MOs; it's just that these lie so low in energy that they don't interact with the metal center.

- The consequence of this is that the π ligand orbitals of a π -accepting ligand lie significantly higher in energy.
 - In fact, they lie higher in energy than a metal's d orbitals, meaning that the metal t_{2g} set is now M-L π bonding instead of antibonding and hence lower in energy, leading to a greater d orbital splitting.
- All of this can be summarized by the MO diagram for a ML_6 complex with π -accepting ligands.

Figure 7.5: ML_6 π -accepting MO diagram.

- Distortions from σ interactions.
- Consider a ML_6 complex with σ -only interactions, as discussed last class.
 - Goal: Predict Jahn-Teller distortions from first principles.
 - Two possible distortions: A tetragonal compression or a Jahn-Teller elongation.
 - See Figure VI.10 of Labalme (2022).
 - Are both of these distortions not “Jahn-Teller” effects??
 - Either distortion changes the point group from O_h to D_{4h} .
- We now seek to build an MO diagram for the t_{2g} and e_g set of each distortion.
 - To begin, we determine the symmetries are the d orbitals in the two point groups (see Table 7.2).
 - Since the t_{2g} set is nonbonding in a σ -only complex, their energy doesn't change much, so the distorted t_{2g} set is basically still degenerate. However, we do have to draw the b_{2g} MO slightly higher (or lower, but we choose higher) since it has a different symmetry.

	O_h	D_{4h}
$d_{x^2-y^2}$	e_g	b_{1g}
d_{z^2}	e_g	a_{1g}
d_{xy}	t_{2g}	b_{2g}
d_{yz}	t_{2g}	e_g
d_{xz}	t_{2g}	e_g

Table 7.2: d -orbital symmetries in O_h vs. D_{4h} .

- The e_g orbitals definitively split, going in different directions as the axial ligands compress or expand. In particular, compressing the axial ligands drives d_{z^2} up (and $d_{x^2-y^2}$ down), and vice versa for expanding the axial ligands.
- Note that the original e_g set is M-L σ^* , which is why compression drives up energy (more mixing between regions of opposite phases is not energetically favorable).

7.2 Descent in Symmetry

11/9:

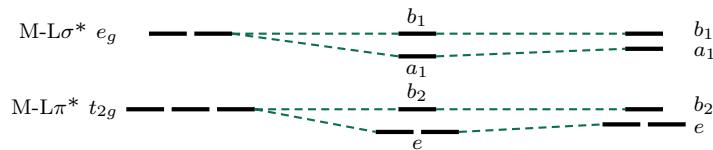
- Goal: Consequences of distortion and descent in symmetry on the MOs of coordination complexes.
- **Homoleptic:** A coordination complex, the ligands of which are all identical.
- **Heteroleptic:** A coordination complex containing at least two distinct ligands.
- Most interesting chemistry occurs for heteroleptics, so we should consider their MOs, too.
- But how do we construct such molecular orbitals? Use a Descent in Symmetry Analysis.
 - Similar to the Jahn-Teller distortion and tetragonal compression discussed in Lecture 16, but now we're taking this a step further by fully removing ligands. We then investigate the effects of this on orbital energetics.
- How do the symmetries of the d orbitals compare from $\text{Co}(\text{CN})_6$ to the hypothetical “chopped off $\text{Co}(\text{CN})_5$ complex,” i.e., C_{4v} fragment?
 - We rip a cyano group off of the axial position and will substitute a bromo group later.
 - Changing from O_h to C_{4v} involves a change in the symmetries of the orbitals, as follows.

	O_h	C_{4v}
$d_{x^2-y^2}$	e_g	b_1
d_{z^2}	e_g	a_1
d_{xz}	t_{2g}	e
d_{yz}	t_{2g}	e
d_{xy}	t_{2g}	b_2

Table 7.3: d -orbital symmetries in O_h vs. C_{4v} .

- Taking a π -acceptor off of the z -axis won't affect $d_{x^2-y^2}$; we just change the label from $e_g \mapsto b_1$.
- Since d_{z^2} now has a less productive σ -bonding interaction, the M-L σ^* d_{z^2} orbital decreases in energy (and changes to a_1).
- As with $d_{x^2-y^2}$, d_{xy} doesn't change except in symmetry.
- Analogously to d_{z^2} , d_{xz} and d_{yz} now increase in energy because we lose the stabilizing effect of the π^* ligand acceptance.

- Now what happens when we add Br^- back in?
 - Br^- is a π -donor!
 - Quantitatively, we need to find the symmetry of the Br^- atomic orbitals and mix them with the MOs of the fragment.
 - Since p_z has a_1 symmetry, it can interact with the d_{z^2} orbital of Co. Thus, it will be M-L σ^* with respect to the metal, and M-L σ with respect to the Br^- .
 - p_x, p_y have e symmetry. Thus, they can interact with d_{xz}, d_{yz} of the metal via M-L π^* interactions, raising the e set higher.
- Key point: Bonding character is mixed in heteroleptics because MOs have multiple parentage. Let's build the MO for the target complex now.
 - The a_1 and e sets of the $\text{Co}(\text{CN})_5$ fragment are both raised in energy.
 - We see multiple parentage in the e set, for instance, where we have M-L π interactions with cyano ligands and M-L π^* interactions with the bromo ligand.
 - Cyano ligands act as stabilizing π -acceptors on d_{xz}, d_{yz} .
 - Bromo ligands act as destabilizing π -donors on d_{xz}, d_{yz} .
 - We fill in 6 d electrons for $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ because such a structure implies Co^{3+} , which has 6 d electrons.
- Example: NbCl_5O .

Figure 7.6: NbCl_5O d orbitals derivation.

- Remove a π -donor; add back another π -donor.
- Thus, we drop the e and a_1 sets, and then raise them back up (but not all the way to degeneracy).
- The M-L σ^* notation denotes molecular orbital **parentage**!
- Further descents in symmetry: Two ligands gone means D_{4h} ; three ligands gone means C_{2v} .

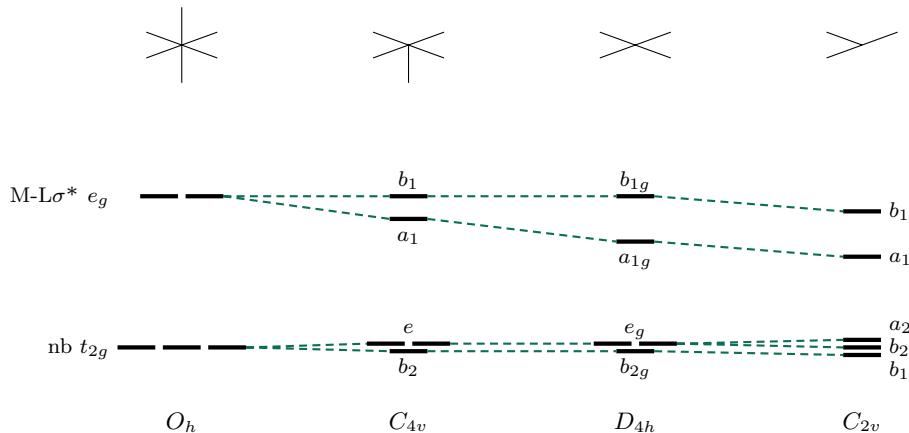


Figure 7.7: Full descent in symmetry.

- Wuttig considers the σ -only case here.
- D_{4h} : Another z σ -donor gone lowers $a_1 \rightarrow a_{1g}$ further.
- C_{2v} : Fewer z donors means lower a_1 . Fewer xy -donors means lower b_1 . The nonbonding t_{2g} set is still unchanged.

7.3 Metal-Metal Bonding

11/11:

- Picking up from last time with Walsh diagrams; we'll get to metal-metal bonding later.
- Last time, we talked about descents in symmetry from one particular point group to another destination point group.
- Today: What about intermediate geometries that don't quite fit any particular point group?
 - We use **Walsh diagrams** to treat these cases.
- **Walsh diagram:** A plot of orbital energy vs. a measure of distortion, often the angle θ between some bonds.
- Let's look at an example of a Walsh diagram. We'll break down how and when to build one, and what information we can glean from one.
- Consider a square pyramidal C_{4v} complex.

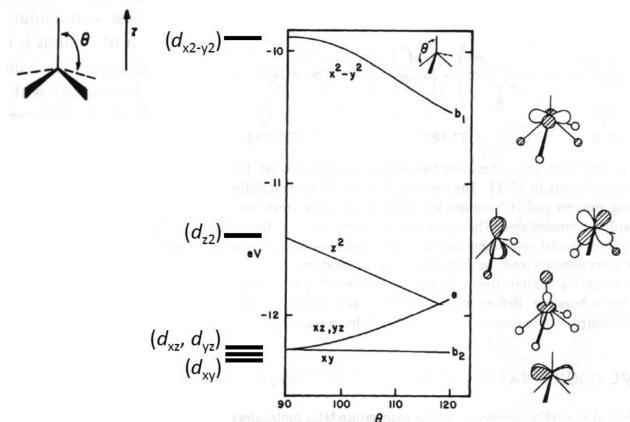
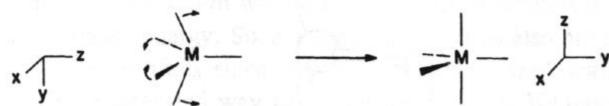


Figure 7.8: Walsh diagram for the distortion of a C_{4v} coordination complex.

- As we increase the angle between the axial ligand and each equatorial ligand, we remain in the C_{4v} point group, but we have changes among orbital energy, too.
- Derive one side, then the other side, and then draw a line connecting the two analogous orbitals.
- A benefit of Walsh diagrams: They allow us to predict the distortion as a function of electron count.
- Continuing with the C_{4v} example in Figure 7.8...
 - For d^0-d^2 , steric pressures imply a distorted pyramid; electronic stability isn't significant.
 - For d^3-d^6 , however, we can expect a flat pyramid since the orbitals that are now being filled (d_{xz}, d_{yz} of e symmetry) are destabilized in the distorted geometry. In fact, the more electrons we add, the stronger the preference for flat.
 - For d^7-d^8 , the equilibrium shifts back toward distortion ($x^2 - y^2$ gets stabilized by distortion).
 - For d^9-d^{10} , the distortion grows even more rapidly (z^2 also gets stabilized by distortion).

- What happens when the principal rotation axis is not preserved as a function of descending symmetry?
- Consider the case where we go from distorted C_{4v} to trigonal bipyramidal (D_{3h}).

Figure 7.9: Distortion from C_{4v} to D_{3h} .

- In a nutshell, we must derive d -orbital manifolds in both point groups and connect them just like before, but we now have the additional challenge of orbital labels changing. Let's begin.
- Note that not only does the point group change here, but we are forced to reorient the axes if we want to keep the z -axis as the principal axis.
- Once again, we assume σ -only interactions.
- Determine what axis maps to what other axis: $x \mapsto x$, $z \mapsto y$, and $y \mapsto z$.
 - Note that we don't send $y \mapsto -z$ because we are only interested in direction (mapping *axes* to *axes*), not intra-basis orientation.
- Drawing a Walsh diagram for the case we've been discussing.

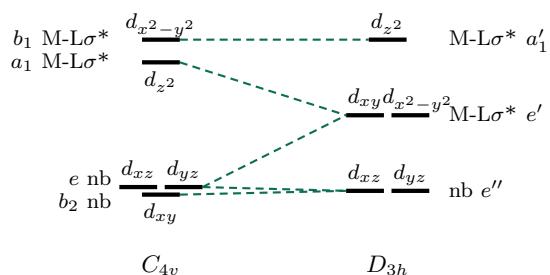


Figure 7.10: Walsh diagram when the principal axis is not preserved.

- Start with the C_{4v} d -orbital manifold on the left and the D_{3h} d -orbital manifold on the right.
- Be cognizant of the fact that we have to relabel orbitals because we relabeled axes! Indeed, $d_{xy} \mapsto d_{xz}$, $d_{yz} \mapsto d_{yz}$, and $d_{xz} \mapsto d_{xy}$.
 - Thus, what we call the d_{xz} orbital on the right (for example) is literally the d_{xy} orbital on the left.
- Wuttig rationalizes the D_{3h} splitting using the ligand SALCs and their symmetries.
 - For the D_{3h} molecule, the ligand SALCS transform as

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{L-\sigma}$	5	2	1	3	0	3

Table 7.4: Representations for the L σ orbitals of a D_{3h} complex.

i.e.,

$$\Gamma_{L-\sigma} = 2a'_1 + e' + a''_2$$

- The a''_2 SALCs are nonbonding, but e' and a'_1 both have M-L σ^* interactions.
- How did Wuttig determine which of $d_{x^2-y^2}$ and d_{z^2} went to which product orbitals??

- Connect like orbitals with lines.
- Using MO theory to predict if complexes containing NO as a ligand prefer bent or linear NO.

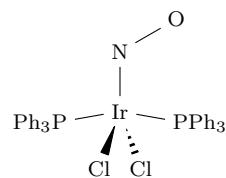
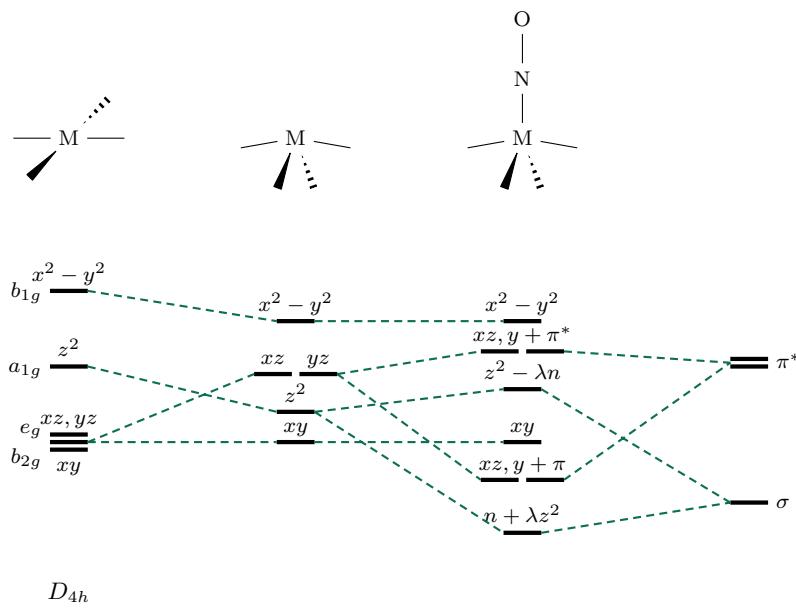


Figure 7.11: An NO complex.

- Strategy.
 1. Pyramidalize D_{4h} : Derive the MO diagram for just the $\text{Ir}(\text{PPh}_3)_2\text{Cl}_2$ ligands, assuming all ligands are the same.
 2. Combine with NO orbitals.
 3. Bend NO.
- Completing the example in Figure 7.11.

Figure 7.12: $\text{Ir}(\text{PPh}_3)_2\text{Cl}_2(\text{NO})$ MOs.

- Generalize all ligands to a generic π -donor (like Cl^-).
- Pyramidalize the molecular fragment to the D_{4h} molecular geometry.
- Give the d -orbital splitting for this point group.
- Bend the molecule and change the orbital energies accordingly: Loss of planar antibonding interactions lowers $d_{x^2-y^2}$ and d_{z^2} , loss of σ_h increases d_{xz}, d_{yz} , no change in symmetry about the principal axis means that d_{xy} is unaffected.
- These orbitals can be mixed with the linear NO frontier orbitals (a high-lying π^* one and a low-lying σ one) to generate an initial MO diagram.
- We can use a Walsh diagram to describe the distortion in the MO diagram in Figure 7.12 as we bend the NO ligand.

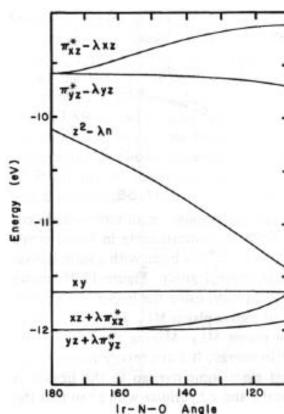
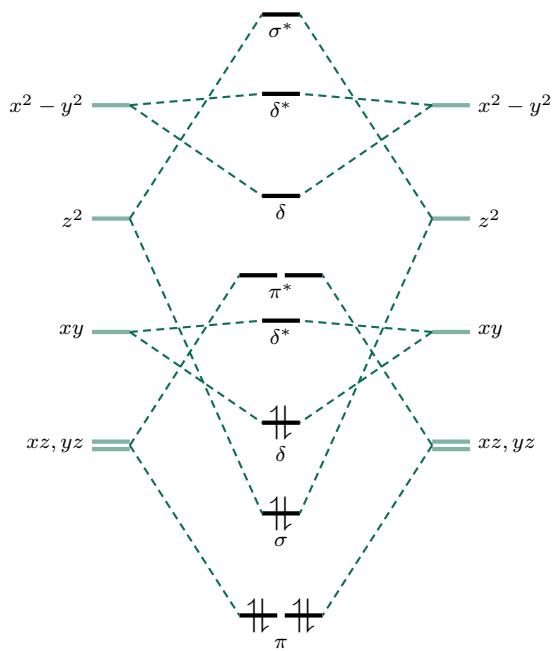


Figure 7.13: Walsh diagram for varying Ir-N-O bond angles.

- Do d^6 , d^7 , and d^8 prefer linear or bent geometries?
 - d^6 prefers linear since those orbitals lie lower in energy.
 - d^7 prefers bent for the same reason (we now have an electron in the drastically changing $z^2 - \lambda n$).
 - d^8 prefers an intermediate angle, even though we would expect fully bent based on the Walsh diagram.
- We now move to metal-metal bonding.
- Metal-metal bonding involves δ bonds.
 - Different types of $d-d$ molecular orbitals are shown (see Figure III.8 of Labalme (2022)).
- Seminal work of Al Cotton, a giant of inorganic chemistry: One of the first quadruple-bonded complexes, $[\text{Re}_2\text{Cl}_8]^{2-}$.
- Investigating the bond-order for the Re-Re bond.

Figure 7.14: $[\text{Re}_2\text{Cl}_8]^{2-}$ MOs.

- Denote the Re–Re axis as the z -axis.
 - We form two C_{4v} ReCl_4 fragments. Their d -orbital splitting (we only care about the d -orbitals of the metal centers since we're trying to investigate the Re–Re bond) mirrors that in Figure 7.6.
 - Note that since the d_{xy}, d_{xz}, d_{yz} orbitals are M–L π^* , they are less antibonding than in the octahedral case because we no longer have the π^* contribution from the orbitals along the z -axis??
 - We then mix their identical orbitals.
 - Filling in the d -electrons on the two Re^{3+} species, we see that B.O. = 4.
- $\sigma > \pi > \delta$ in terms of bond strength and MO splitting.

Week 8

Transition Metal Electronic Structure

8.1 Crystal Field Theory and Ligand Field Theory

11/14:

- Questions from the video lectures.
- For descent in symmetry questions, how do we qualitatively describe orbital energy? Do the Mulliken symbols matter?
 - Rationalize based on the molecular orbital parentage.
 - a_1 may or may not be more stable than a_{1g} , for example.
 - We need to visualize the orbitals and see if we're ripping something off from the axial or equatorial positions, for example, because that matters.
 - The labels are just there to make sure that our molecular orbital assignments are correct within the point group. It's mainly a bookkeeping thing. It also helps us create further MOs based on symmetry, though.
 - The Mulliken symbol alone doesn't convey any information about energetics.
- Walsh diagram structure.
 - Curved vs. straight lines is irrelevant; we just need to know whether the energy increases or decreases qualitatively under a procedural change in the molecule.
 - All we need to be able to do is derive the initial and final state and know what maps to what.
- How do you determine straight vs. curved line?
 - No way to do this from first principles; you need a combination of DFT and experiment.
- Comparing orbital energies.
 - If we're deriving from a new set of orbitals (as in the FeBz example), we need SALCs.
 - In an exam setting, though, we won't encounter brand new orbitals.
- We now start in on today's lecture topic.
- **CFT** and **LFT** are frameworks that help us estimate orbital energies.
 - They are quantitative methods for evaluating d -orbital splitting.
- **Crystal field theory:** A method in which one estimates ligands as point charges (which is not great, but ok) and the metal as a cation C. *Also known as CFT.*
 - Established by physicists at the same time as the birth of inorganic chemistry, before chemists came on the scene.

- Ligands are structure-less and orbital-less (think like a physicist; no structure, just charge).
 - Group theory tells us that a d -orbital in an O_h environment has t_{2g} or e_g symmetry regardless of how much structure is present.
 - Even though the transition metal C is positive, the electrons in the d -orbitals are negative, so we get the following visualization.
 - Visualization: In the free ion, you have five degenerate d -orbitals. You then first approximate a negatively charged spherical field around the point charge, which causes the d -orbitals to go-up in energy. Lastly, we split the t_{2g} and e_g set in an O_h field. Essentially, Wuttig redraws Figure VI.11 of Labalme (2022).
- **Crystal field splitting parameter:** The difference in energy between the e_g and t_{2g} set. Denoted by Δ_0 , $10Dq$. Also known as **field strength, field splitting**.
 - $10Dq$ nomenclature will return when we derive Tanabe-Sugano diagrams from scratch.
 - This is a *quantitative* term for the field splitting, different from every other aspect of the course this far (all of which have been qualitative).
 - This is phenomenological parameter that is determined from experiment and cannot be calculated from first principles.
 - The typical experiment is something like UV-Vis spectroscopy.
 - The terms field strength and field splitting are basically synonymous. However, we can also think of “field strength [as] the quantitative number associated with the field splitting.”
 - Main takeaway of CFT: The origin of something called field splitting, and the origin of quantitatively understanding d -orbital energetics.
 - We now move on from CFT to LFT.
 - **Ligand field theory:** The same as CFT; we just put the bonds back in.
 - It's not just point charges any more; there are actual bonds created by overlapping the metal d -orbitals (which we had also previously assumed to exist) with the ligand orbitals (which we are only adding in now).
 - Thus, free d electrons have adjustable interelectronic repulsion parameters. These are important in free ion terms.
 - Field splitting.
 - Origins of ligand field splitting: Molecular symmetry and group theory, as discussed since the beginning of the course.
 - Extent of ligand field splitting: We will talk about this now.
 - Manifestations of ligand field splitting: The colors of TM complexes, reactivity, magnetism, life (bioinorganic chemistry), and many more.
 - There are four main things to consider when determining the magnitude of the field strength.
 1. σ and π effects.
 - We talked a bit about this when we derived the ML_6 MO diagrams from scratch with and without π orbitals.
 - Recall the discussion regarding Figures 6.13, 7.3, and 7.5.
 - We want to compare a π -donor, to a σ -only ligand, to a π -acceptor.
 - In every case, the e_g set will be comprised of $M-L\sigma^*$ orbitals.
 - However, the t_{2g} set will decrease in energy from $M-L\pi^*$ to nb to $M-L\pi$, respectively.
 - It follows that Δ_0 increases as we go from π -donors, to σ -only donors, to π -acceptors.

- People made this observation by looking at a series of homoleptic O_h complexes, specifically the **spectrochemical series**.
- 2. Oxidation state.
 - As oxidation state increases (the metal ion becomes more positive), ligand field splitting increases, too.
 - This is because orbital overlap increases as ligands are pulled in and hence the amount of ligand field splitting increases, too.
 - Mathematically, increasing the oxidation state increases the overlap integral S .
 - Alternatively, we can think of this as more electropositive transition metals drawing more electrons toward them.
 - Wuttig illustrates this point with example Δ_o values for compounds that are alike in every way except for the oxidation state. For instance,

$$\begin{aligned}\Delta_o(\text{Cr}(\text{H}_2\text{O})_6^{2+}) &= 14\,100 \text{ cm}^{-1} \\ \Delta_o(\text{Cr}(\text{H}_2\text{O})_6^{3+}) &= 17\,000 \text{ cm}^{-1}\end{aligned}$$

- 3. Row of the TM on the periodic table.

- The first row has a lower field strength than the second row, which has a similar field strength to the third row.
- This is because the radial extension of second and third row metals is much higher, leading to better overlap (higher S), and thus higher splitting of bonding/anti-bonding orbitals.
- Example: In the following d^6 complexes, we can observe a drastic increase in Δ_o between the first- and second-row TM and a smaller increase in Δ_o between the second- and third-row TM.

$$\begin{aligned}\Delta_o(\text{Co}(\text{NH}_3)_6^{3+}) &= 22\,870 \text{ cm}^{-1} \\ \Delta_o(\text{Rh}(\text{NH}_3)_6^{3+}) &= 34\,100 \text{ cm}^{-1} \\ \Delta_o(\text{Ir}(\text{NH}_3)_6^{3+}) &= 41\,200 \text{ cm}^{-1}\end{aligned}$$

- 4. Geometry.

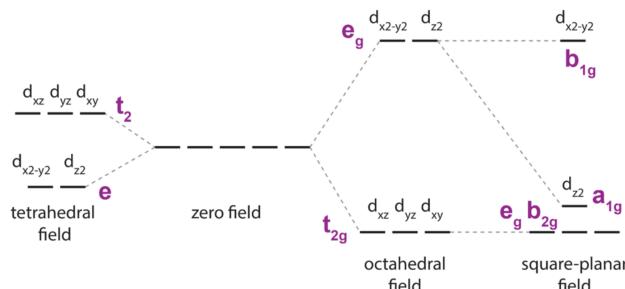
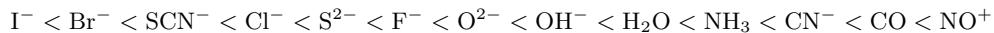


Figure 8.1: Geometry affects field strength.

- The number of ligands around the metal, as well as whether or not certain ligands are on-axis, affects the number of interactions and hence the splitting.
- In a T_d field for example, there are far fewer on-axis repulsive interactions compared to O_h .
- **Spectrochemical series:** A measure of the orbital overlap, electronegativity, and VOLE considerations that determine how big the ligand field splitting is.
 - Some ligands engender higher splitting energies than others, and we can measure this via the electronic transitions of (light absorbed/emitted by) homoleptic complexes.



————— π-donor ————— σ-only ————— π-acceptor —————

Figure 8.2: The spectrochemical series.

- The spectrochemical series was initially just a qualitative observation; it was later explained by MO theory.
- Example: Rationalize the following energy trends

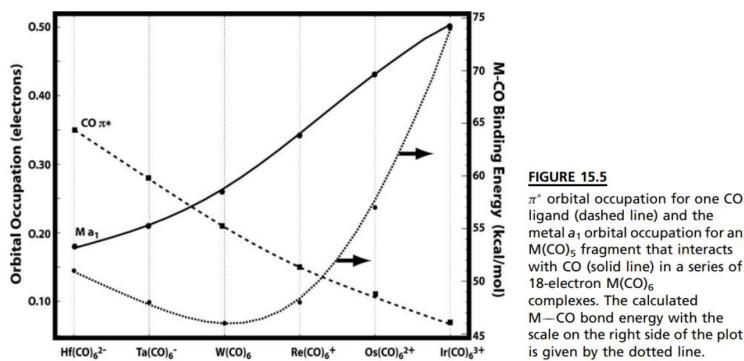


Figure 8.3: Energy trends across a row.

- Trends: The M–CO binding energy increases left to right. The orbital occupation of the $\text{CO}(\pi^*)$ decreases left to right. Regardless, the orbital occupation of the $M(a_1)$ (primarily of d_{z^2} parentage) increases left to right.
- The analytical procedure is as follows.
 - Investigate the ligand: CO is a π -acceptor; thus, the d_{z^2} orbital is of $M-\text{L}\sigma^*$ parentage. Recall from the PES of CO that its LUMO (π^* symmetry) lies higher in energy than the d atomic orbitals, which are sandwiched between that and the HOMO (σ symmetry).
 - Investigate the metal center: All molecules are third-row d^6 transition metals.
 - Investigate what changes: The charge (e.g., Ir^{3+} vs. Hf^{2-}) and the electronegativity of the metal center (decreases left to right; does she mean the amount of negative charge?? Seems like she's been using electronegativity and electropositivity potentially wrong a few times??).
 - On the left side, the metal d orbitals are high in energy, so they are close to the high-lying $\text{CO}(\pi^*)$ orbitals in energy, so they donate a lot of electron density to $\text{CO}(\pi^*)$. On the right side, the opposite is true.
 - Additionally, there is a smaller gap between d_{z^2} and $\text{CO}(\sigma)$ on the right side.
- **Electronic spectroscopy:** Electron absorption spectra are broad — occur much more rapidly than molecular vibrations, i.e., we see a snapshot of the molecule in various rotational vibrational states.
- We're done learning about trends and onto quantifying stuff. To understand how to quantify things better, we need to understand the origins of electronic spectra.
- Thus, we'll discuss some basic properties of UV-Vis spectra in relation to the Franck-Condon principle.
- In the first half of the course, we focused on vibration. Now we're looking at electronic excitations and, in particular, electronic excitation wells.

- Franck-Condon Principle.

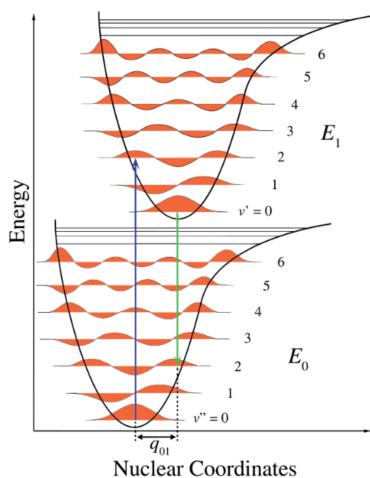


Figure 8.4: Franck-Condon Principle potential wells.

- E_0 is our ground electronic state.
- E_1 is the first electronic excited state.
- All of the little levels in between are the vibrational energy levels (overtones, etc.) that we discussed in the beginning.
- We now assume that an electronic transition is much faster than a vibrational transition, and hence occurs virtually without a change in nuclear coordinates. We just do a vertical jump from one well to the other, without moving nuclear coordinates along a vibration (“electronic transitions are ‘vertical’ with respect to the nuclear coordinate axis”).
- The Franck-Condon principle arises from the Born-Oppenheimer approximation.
- **Born-Oppenheimer approximation:** We can separate the electronic and vibrational wave functions of a given molecule.
- Terms next time.

8.2 Electronic Spectroscopy II

11/16:

- No in-person lecture on Friday; a video will be posted. Watch before Monday’s lecture (last lecture of the class). Wednesday is the review session, Friday is the second exam, no final.
- Last problem set has been posted; due the review session day. Submit virtually (as a PDF).
- Goal: Understand and derive term symbols in the context of electron configuration. Free ions \rightarrow weak field \rightarrow strong field. It’s important to understand where these things come from because that allows us to use the tools in the literature in a more informed fashion.
- Terms allow us to predict the energy of the electronic transition. But where do they come from? How do they vary for ground and excited states?
- **Term:** Energy level of a spectrum.
- Free ion term: d -orbital manifold in the absence of any other geometry. We have 5 d orbitals and, suppose, a d^2 system. We can fill electrons however we want as long as we satisfy the Pauli exclusion principle. But different fillings have different energies. *picture*

- Multi-electron transition metal ions have multiple energy levels even when *d*-orbital degeneracy is not lifted by a ligand field.
- **Configuration:** The assignment of a given set of electrons to a certain set of orbitals.
 - Applies to *d* orbital setups that are *not* free ion, i.e., degeneracy has been lifted.
 - Each configuration gives rise to a number of energy levels and the number of energy levels have to have an even number of terms.
- Example:
 - 2 electrons in *d* orbitals. (t_{2g}^2) , for instance, implies that we have 2 electrons in 2 t_{2g} orbitals.
 - 4 electrons in *d* orbitals. t_{2g}^4 , for instance, implies that all electrons are in the t_{2g} set. $(t_{2g}^2)(t_{2g}^2)$, for instance, implies that electrons are in different orbitals; this describes an excited state.
- Energy ordering of the terms.
 - To construct suitable energy level diagrams for various states in a transition metal ion, we consider the last three terms (IER – interelectronic repulsion, SOC – spin-orbit coupling, and LFI – ligand field interaction).
 - The interaction between these three terms determines whether we're in a weak or strong field.
 - Case 1: IER > LFI > SOC gives rise to the weak field approximation (ligand field induces only a small perturbation of the energy levels).
 - Case 2: LFI > IER > SOC gives rise to the strong field approximation (implies more low spin configurations).
- We've now started understanding the underlying principles that change the energy ordering.
- Consider only weak field approximation. We first approximate the weakest field possible: Where there is no field. World's most boring electronic structure, but helps us understand how to build correlation diagrams. Let's determine the number of microstates or the ways we can put a single electron into *d* orbitals.
 - d^1 case: No effects from other electrons, yet there are still numerous microstates.
 - A *d* orbital can be described by $\ell = 2$ (the angular momentum quantum number), $m_\ell \in \{-2, -1, 0, 1, 2\}$ (the magnetic quantum number; takes integer values that span $-\ell$ to ℓ), and $m_s = \pm 1/2$ (the spin quantum number).
 - Thus, there are 5 degenerate *d* orbitals (one for each m_ℓ ; these labels can be thought of as alternatives to $z^2, x^2 - y^2, \dots$).
 - The one electron can occupy any *d* orbital and take spin $\pm 1/2$ for 10 total degenerate sets of microstates.
 - We can designate the collection of microstates with a term symbol.
- **Term symbol:** An abbreviation describing a selection of microstates.
- How do I know that I need to get 10 microstates?
 - The number ℓ^q of microstates for a given configuration, where ℓ is the angular momentum quantum number and q is the number of electrons, can be calculated for a number of equivalent electrons. The formula is
$$n = \frac{(4\ell + 2)!}{q!(4\ell + 2 - q)!}^{[1]}$$

¹Wuttig puts $4\ell - 2$ in the denominator.

- If we do this for $\ell = 2$, $q = 1$, we get

$$n = \frac{10!}{9!} = 10$$

- How do I know what the term symbol is?
 - Term symbols have the form $^{2S+1}L_J$.
 - $M_L = \sum m_\ell$ for a given microstate.
 - $M_S = \sum m_s$ for a given microstate.
 - S , the spin multiplicity, is the total spin angular momentum (values $0, 1/2, 1, 3/2, 2, 5/2$) or the maximum M_S value.
 - L , the total orbital angular momentum, is the maximum M_L value.
 - J , the L-S/Russell-Saunders/spin-orbit coupling, is only relevant for multielectron systems where the presence of an electron in the same shell diminishes the coupling of another. J is the total angular momentum. $J = L + S, L + S - 1, L + S - 2, \dots, L - S - 1, L - S$ ^[2].
- Example: Term symbol for d^1 .
 - We must have $S = 1/2$ (the smallest possible value of S , and the only one achievable by one electron) and $L = 2$ (degenerate set of orbitals that span -2 to 2). Thus, 2D .
 - No spin-orbit coupling to worry about because there's only one electron in the system (coupling inherently requires two or more electrons).
- Multielectron atom procedure.
 1. Determine the total number of microstates (m_ℓ, m_s values).
 2. Determine the possible values of $M_L = \sum m_\ell$ and $M_S = \sum m_s$.
 3. Construct a Pauli-allowed chart of microstates.
 4. Group microstates into terms.
 5. Assign ground state term symbol.
- Let's tackle d^2 .
 - By the formula, there are 45 microstates.
 - Goes through the microstate table and rectangles (we won't be asked to derive this, though).
 - The maximum value of L is 4. This means the two electrons are in the same orbital, so we have $S = 0$. Thus, we get 1G for our term symbol. We now slash off all microstates for which $L = 4$ and $S = 0$, i.e., microstates for which $M_L = 0, \pm 1, \pm 2, \pm 3, \pm 4$ and $M_S = 0$.
 - Next up is $L = 3$ for maximum possible L . Maximum possible S in this case is 1. Thus, we slash off all states for which $M_L = 0, \pm 1, \pm 2, \pm 3$ and $M_S = 0, \pm 1$ except the ones we've already counted^[3]. Now that we have $L = 3$, the electrons can be in different orbitals, so $S = 1$.
 - My big question: What do the microstates that we group together into one term symbol have in common??
- Takeaway: We have multiple term symbols/energy levels for free ion states.
- For d^2 , we show in handout that we have 5 terms:

 1S 3P 1D 3F 1G

- But how do we order the energy? Use Hund's rules:

²This is probably wrong, too; should iterate down to $|L - S|$.

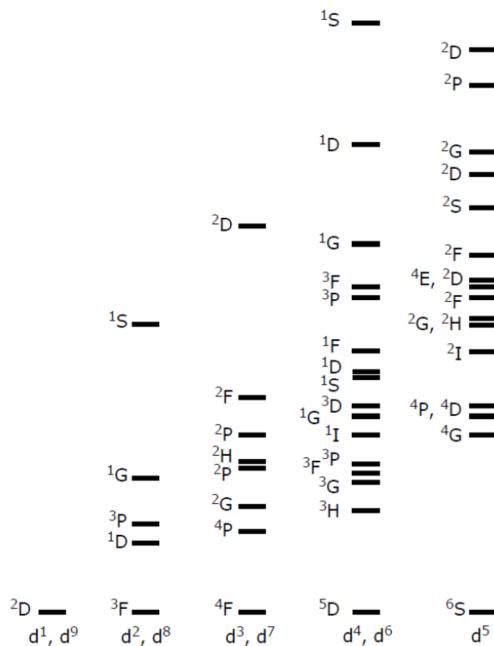
³Note that since there are $7 = 2L + 1$ possible M_L values and $3 = 2S + 1$ possible M_S values, we will have $7 \cdot 3 = 21$ microstates of this type. This is where Talapin's $(2L + 1)(2S + 1)$ formula comes from!

1. Maximize the spin multiplicity (i.e., terms with higher multiplicity will have lower energy).
 2. Maximize the total angular momentum (i.e., terms with higher L will have lower energy).
- Thus, the energy ordering is $^3F, ^3P, ^1G, ^1D, ^1S$.
 - Electron hole formalism: d^n and d^{10-n} have equivalent weak field energy orderings.
 - Will be asked about in our homework.

8.3 Electronic Spectroscopy III and TS Diagrams

11/18:

- Goals:
 - Building Tanabe-Sugano diagrams from scratch.
 - More about term symbols (deriving and ordering them; ground states v. excited states).
- Last time: We derived the term symbols and ordering for d^1, d^9 and d^2, d^8 . These term symbols have different energies; these must be spectroscopically determined.

Figure 8.5: d -orbital weak field splittings.

- The weak field energy orderings are shown without spin-orbit coupling (the J term).
- But recall that S-O coupling can exist.
- Example: 3F S-O coupling for d^2 .
 - 3F means $L = 3$ and $S = 1$.
 - We can split it into $(L + S) - (L - S) + 1 = 2S + 1 = 3$ terms^[4], namely those with $L + S = 4$, $L + S - 1 = 3$, and $L - S = 2$. Thus, we get 3F_4 as the highest energy of these terms, 3F_3 in the middle, and 3F_2 at the bottom.

⁴This is the spin multiplicity, as expected.

- Additional energy ordering rule: If the free ion term is less than half-filled, the lowest J has the lowest energy; if the free ion term is more than half-filled, the highest J has the lowest energy!
- We now start to include a ligand field.
- Splitting of energy levels can be described by the character table.
- Example: Consider the 1D term in the free ion for d^2 in an O_h field.
 - In a similar fashion to the d orbitals in an O_h field, the D states arising from groups of electrons have the same 5-fold degeneracy, so splitting will be the same.
 - Thus, we split 1D into 1E_g and $^1T_{2g}$.
 - Notice that the spin multiplicity is conserved under splitting. This is because the chemical environment does not directly interact with spin, so all the states into which a particular term is split have the same spin multiplicity as the parent term.
- Example: Consider the 3F term in the free ion for d^2 in an O_h field (without S-O coupling).
 - f orbitals transform as the cubic functions, i.e., as a_{2u}, t_{1u}, t_{2u} (see Table 6.8).
 - However, since this is a d^n configuration and all d orbitals have a center of symmetry, we change the u to a g .
 - Thus, the splitting is $^3A_{2g}$, $^3T_{1g}$, and $^3T_{2g}$.
- We can now undertake the full construction of energy level diagrams.
- Continue with the d^2 example.
 - At this point, we know how to get the weak field energy ordering and split each free ion term into its relative weak field splitting. This latter splitting gives the **weak free ion**.
 - Thus, we can now derive the left (weak field) side of the correlation diagram for d^2 in an O_h environment.
- **Weak free ion:** The interaction with the O_h chemical environment by assuming that the electron in the d -orbital manifold is repulsed by the negative charge around it.
 - This is essentially CFT.
- Next task: Strong field terms.
 - Given a large splitting of d^2 in O_h , the following configurations are possible: $t_{2g}^2, t_{2g}e_g, e_g^2$.
 - The latter two are excited states.
 - These are analogous to the initial term symbols, in that these states only exist in an infinitely strong ligand field.
 - As the ligand field weakens...
 1. The electrons will feel each other's presence and start to couple.
 2. The symmetry properties of these states can be determined by taking the direct products of the representation of a single electron.
 - Example:

$$\begin{aligned}t_{2g}^2 &= t_{2g} \times t_{2g} = A_{1g} + E_g + T_{1g} + T_{2g} \\t_{2g} \times e_g &= T_{1g} + T_{2g} \\e_g \times e_g &= A_{1g} + A_{2g} + E_g\end{aligned}$$

- Remember that both explicit computation and a direct product table can lead to the right answer in computations such as these.

- Full correlation diagram.

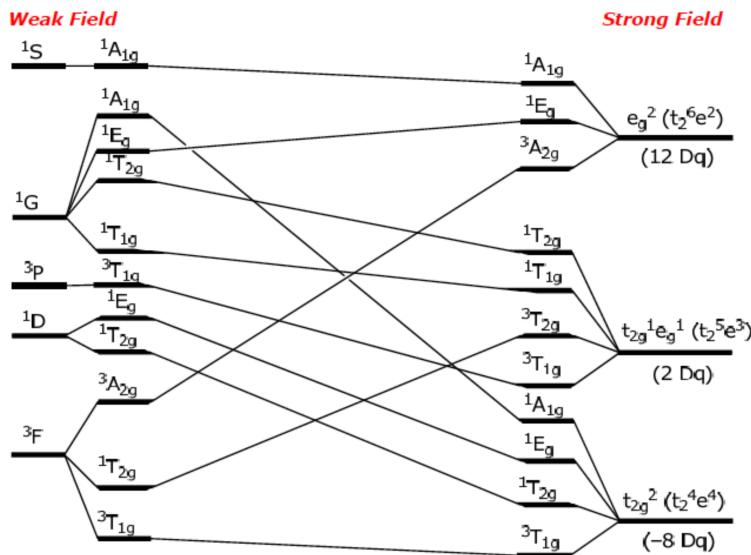


Figure 8.6: Correlation diagram for a d^2 configuration.

- Axioms:
 1. There must exist a 1-to-1 correspondence between the states at the 2 extremes of the abscissa.
 2. As the strength of the interaction changes, states of the same spin degeneracy do not cross.
- The multiplicities of the strong field splitting terms are difficult to determine using the principles of *this* course. Determined by descent in symmetry to reveal population and split degenerate states. Beyond the scope of this course. The multiplicities will always be given to us.
- This concludes the construction of correlation diagrams.
- **Tanabe-Sugano diagrams:** Correlation diagrams that are useful in interpretation of electronic spectra of coordination compounds.
 - Answer the question of the precise scaling of the energies of these states with the ligand field strength.
 - Dreamt up by two physicists in 1954.
- Example: d^1 case (simplest; e.g., Ti^{3+} in an O_h field).

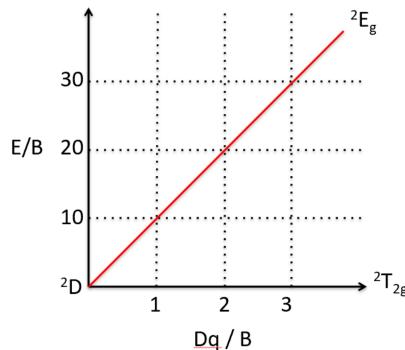


Figure 8.7: Tanabe-Sugano diagram for a d^1 configuration.

- We have one free ion term 2D .
- Our strong field terms are $^2T_{2g}$ and 2E_g (possible one electron configurations are t_{2g}^{-1}, e_g^{-1}).
 - 2E_g is the excited state in the octahedron.
 - $^2T_{2g}$ is the lowest energy on the horizontal, so the vertical distance between the x -axis and the sloping line is a measure of the energy of the excited state above the ground state (and hence is directly proportional to Δ_o).
- E describes the energy of the optical transition.
- B is the **Racah parameter**.
- Interpretation, a d^1 TM complex (such as a Ti^{3+} complex) should have one absorption.
- **Racah parameter:** A measure of the repulsion between terms of the same multiplicity. *Denoted by B . Given by*
$$B = \frac{e^2}{r_{ij}}$$

 - Directly correlated to the degree of electron repulsion (see its definition).
 - Originally defined as a purely free ion parameter, but does change upon coordination (**nephelauxetic effect**).
 - Important trends:
 - Complexes have smaller B than free ions.
 - More covalent M–L bonds implies lower B .

- Example (continued): Does the spectrum for $Ti(OH_2)_6^{3+}$ reflect our intuition that there should only be one absorption?

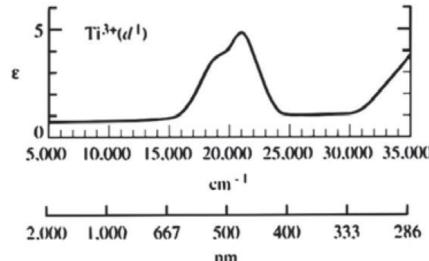


Figure 8.8: Spectrum for $Ti(OH_2)_6^{3+}$.

- The spectrum for the titanium complex does (mostly) reflect this intuition.
- There is a slight shoulder (pH dependent) due to deprotonation of an aqua group resulting in some $Ti(OH_2)_5(OH)^{2+}$ in solution.
- The **molar extinction coefficient** ϵ is very low ($\epsilon \approx 4 M^{-1} cm^{-1}$).
 - The transition is weak because it is Laporte forbidden ($g \rightarrow g$).
 - Selection rules will be covered in greater detail on Monday.
- **Electron hole formalism:** A d^{10-n} configuration will behave in the same way, at all points along the abscissa of the energy level diagram, as the corresponding d^n configuration except that all energies of the interaction with the environment will have the opposite sign.
 - n holes in a d shell can be treated like n positrons. n positrons interact with each other the same way as electrons with each other, but with the environment, they will behave as attractive forces because these positive entities are now interacting with a negative ligand field.

- An application of the electron hole formalism.
 - The TS diagram in Figure 8.7 also treats the d^9 case!
- Example: Does the spectrum for $\text{Cu}(\text{OH}_2)_6^{2+}$ reflect our intuition that there should only be one absorption?

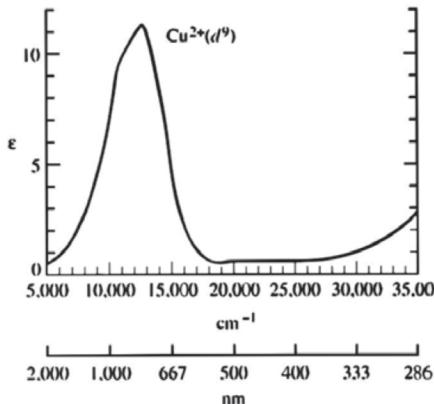


Figure 8.9: Spectrum for $\text{Cu}(\text{OH}_2)_6^{2+}$.

- Mostly yes, and we have the same shoulder again.
- This shoulder can also come from a Jahn-Teller distortion, yielding transitions from the the bottom two d orbitals to the top one. (Why isn't there a transition from the third from the bottom to the top??)
- Note that J-T is not seen in d^1 because the t_{2g} set is primarily nonbonding for the σ -only aquo ligands.
 - Review J-T distortion!!
 - Similarly small ε . Owing to Laporte forbiddenness again.
 - Note that since we're in the hole formalism, the TS diagram labels need to be switched since the hole is moving up.
 - Overall same TS diagram as Figure 8.7, but the ${}^2T_{2g}$ and 2E_g labels are flipped.
- Example: d^2 case (increasingly complex).

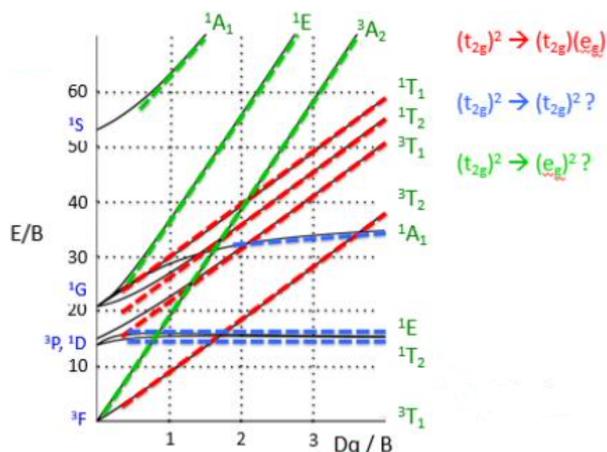


Figure 8.10: Tanabe-Sugano diagram for a d^2 configuration.

- Once again, free ion terms on the left and strong field terms on the right.
 - Note that sometimes, g labels are left out (see the strong field terms).
- Red lines: $t_{2g}^2 \rightarrow t_{2g}e_g$ transitions.
- Blue lines: $t_{2g}^2 \rightarrow t_{2g}^2$ transitions (e.g., spin flip).
- Green lines: $t_{2g}^2 \rightarrow e_g^2$ transitions (two photon transitions have a low probability).
- Curvature: Caused by mixing of states of the same symmetry.
- Spin-allowed transitions include ${}^3T_1 \rightarrow {}^3T_2$ and ${}^3T_1 \rightarrow {}^3T_1$ (both red-line transitions). These should be particularly noticeable.
- Example (continued): Assigning transitions to peaks in a V^{3+} (d^2) complex's spectrum.

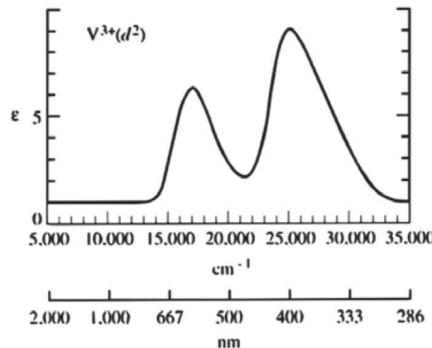


Figure 8.11: Spectrum for a V^{3+} (d^2) complex.

- We assign the lower energy transition (${}^3T_1 \rightarrow {}^3T_2$) to the peak at a lower wavenumber, and the higher energy transition (${}^3T_1 \rightarrow {}^3T_1$) to the peak at the higher wavenumber.
- Example (continued): Estimating B and Dq .

- Take the ratio of the two transitions' wavenumbers in Figure 8.11.

$$\frac{25\,600\,\text{cm}^{-1}}{17\,200\,\text{cm}^{-1}} = 1.49$$

- Looking at the d^2 TS diagram (Figure 8.10), we can see that if we draw a vertical line at $Dq/B = 2.8$, then $E/B = 25.9$ for the lower transition and $E/B = 38.7$ for the higher transition. These energy values also have a ratio of about 1.49^[5].
- Use the equations $E/B_1 = 25.9 = 17200/B_1$ and $E/B_2 = 38.7 = 25600/B_2$ to solve for two values of B that we can average to get a decent estimate for B . Indeed,

$$B_1 = \frac{17\,200\,\text{cm}^{-1}}{25.9} = 664\,\text{cm}^{-1} \quad B_2 = \frac{25\,600\,\text{cm}^{-1}}{38.7} = 661\,\text{cm}^{-1}$$

so

$$B = \frac{664\,\text{cm}^{-1} + 661\,\text{cm}^{-1}}{2} = 663\,\text{cm}^{-1}$$

- We can take this one step further now and estimate the crystal field splitting parameter Dq :

$$\begin{aligned} \frac{Dq}{B} &= 2.8 \\ Dq &= 2.8 \cdot 663\,\text{cm}^{-1} \\ &= 1860\,\text{cm}^{-1} \end{aligned}$$

⁵We can see that moving to the left would increase the ratio, diverging to $+\infty$, and moving to the right would decrease the ratio, converging to 1. Thus, 1.49 is the sweet spot. Note that given linear equations for these two essentially parallel lines, we could also explicitly calculate the sweet spot.

- Some d -electron counts have high- and low-spin cases.

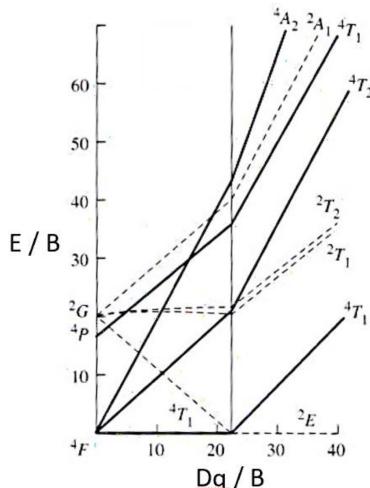


Figure 8.12: Tanabe-Sugano diagram for a d^7 configuration.

- As the field gets stronger, we will eventually have a sharp transition from high spin to low spin.
 - Essentially two different TS diagrams on the two sides of the divide.
- The HS-LS transition is directly proportional to $10Dq = e^2/r_{ij}$.
- In the HS case, we have a negatively sloped line representing a transition from the e_g set to the t_{2g} set that technically forms an excited state since the complex is high spin.

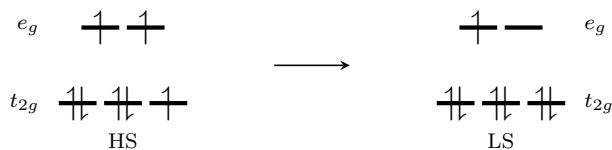


Figure 8.13: Explaining the negatively sloped transition.

- In particular, the transition requires energy because it involves spin pairing, which is costly in a weak field.
- All of the lines on the TS diagram informs us of possible transitions. But are they probable?
 - We've started to make some loose conclusions about what is allowed: Transitions between terms of the same spin multiplicity are spin-allowed, two-photon transitions have low probability, $g \rightarrow g$ transitions have low probability.
 - We will discuss these selection rules next time!
 - The probability of a transition is correlated to its intensity and directly proportional to oscillator strength.
 - We will discuss some applications of high-probability transitions, e.g., photovoltaic cells.
- Conclude the class on Wednesday with a review of bonding and electronic spectroscopy.

Week 9

Selection Rules and Exam

9.1 Electronic Spectroscopy: Selection Rules

11/28:

- Last in-class assessment on Friday. Same rules and format as last time.
- Review session this Wednesday; submit questions via the GForm. Submit Wuttig questions by the end of the day today. If there are no questions, Wuttig will treat the class as office hours.
- Last time: Electronic spectroscopy. We outlined how to rationalize, assign, and determine B and Δ_o values for experimental electronic transitions for octahedral complexes.
- Today: We will derive the basis for the selection rules.
- **Selection rules:** All of the lines on the TS diagrams inform us of possible transitions. But are they probable?
- When deriving these, something we want to consider is oscillator strength. This is given by

$$\int_0^\infty \varepsilon(\nu) d\nu \propto \langle \Psi_{\text{gs}} | M | \Psi_{\text{es}} \rangle^2$$

- This is the integral under the spectrum of your compound.
- Conclusion: The oscillator strength is directly proportional to the transition moment integral.
- The ground state and excited state have electronic, spin, and vibrational contributions.
- We now dissect M .
 - By the B-O approximation, we can separate out the total wave function into the electronic contribution and the vibrational contribution because we assume the time-scale of the electronic and vibrational transitions are distinct.

$$\Psi = \Psi_e \Psi_v$$

- Rationale for separating electronic and vibrational motion: Experimental observation of vertical electronic transitions (see Figure 8.4) means that electrons move before the nuclear coordinate can significantly change.

- Thus, we can dissect

$$\hat{M} = \langle \Psi_{\text{esv}} | \Psi_{\text{gsv}} \rangle \langle \Psi_{\text{ese}} | \hat{\mu} | \Psi_{\text{gse}} \rangle \langle \Psi_{\text{ess}} | \Psi_{\text{gss}} \rangle$$

where we write v for vibrational, e for electronic, and s for spin.

- $\hat{\mu}$ is the electronic polarization operator. It transforms as xyz , meaning that it has u (ungerade) symmetry as a linear operator, similar to the p -orbitals.

- We now dissect the components of \hat{M} further.

- Spin.
 - The spin contribution is nonzero iff $\Delta s = 0$ (i.e., no change in spin). This justifies the **spin selection rule**.
- **Spin selection rule:** We *must* have the same spin state in the ground and excited states.
- Vibration.
 - Typically, an electronic excitation will produce a vibrationally hot excited state (recall hot bands).
 - Is the hot excited state the result of relaxation after electronic excitation, or will there be a hot excited state?
 - We go to a hot vibrational excited state.
 - For example, in going from $E = 0$ to $E = 1$, we will often go from $v = 0$ to $v = 2$ or something (see Figure 8.4 again).
 - This can relax some selection rules and make transitions more probable.
- Electronic.
 - The component is nonzero iff the direct product contains a_{1g} (i.e., is even over all space).
- Electronic component in the context of *d-d* transitions.
 - For a *d-d* transition, $\hat{\mu}$ is *u* but the *d* orbitals are *g* (they are symmetric with respect to inversion). Taking the direct product yields *u* symmetry.

$$g_{\text{es}} \times u \times g_{\text{gs}} = u$$
 - It follows that the *d-d* transitions are forbidden (this is the **Laporte selection rule**).
 - Even though these transitions are formally Laporte forbidden, coupling with the hot bands in the vibrational state makes these become allowed.
 - Wuttig will not go through all the math.
 - Note: Coupling of g_{es} with u_{vib} can relax the rule!
- **Laporte selection rule:** *d-d* transitions are allowed iff the overall direct product has gerade symmetry. *Also known as orbital selection rule.*
- Rank the following compounds in terms of oscillation strength.

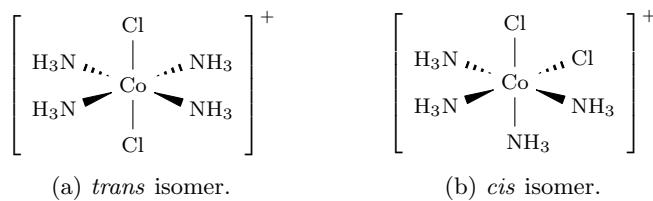


Figure 9.1: Oscillation strength comparison.

- Comparing the compounds: Same *d*-electron count, same ligand composition. Thus perhaps it really is something to do with the ligand field?
- The *trans* isomer is more symmetric than the *cis* isomer (D_{4h} vs. C_{2v}).
- If we have a more symmetric field, we'll have a lower oscillation strength, and vice versa for the less symmetric field. This is because the less symmetric field is more *u*-like, leading to greater vibrational coupling.

- LMCT and MLCT.
- One way to relax the Laporte selection rule is to couple with vibrationally hot excited states. Another way is to have the transition occur from another part of the molecule.
- LMCT transitions.

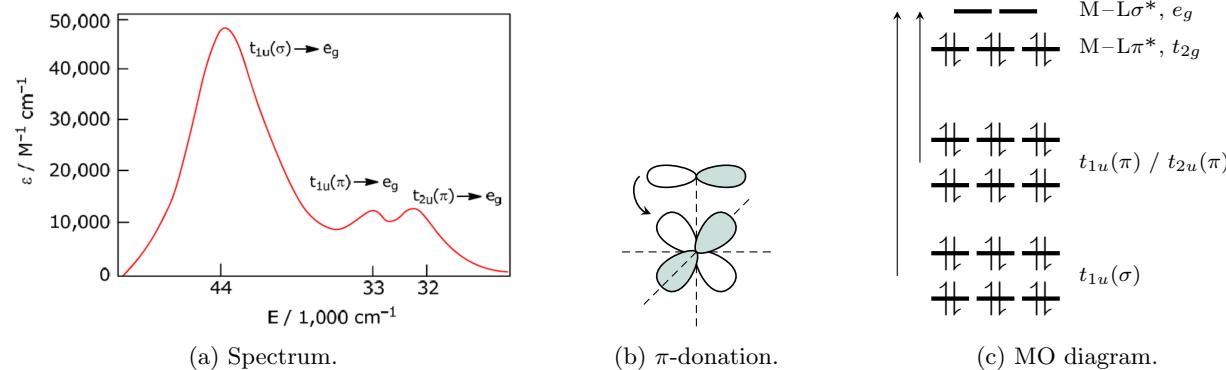


Figure 9.2: LMCT dynamics.

- Figure 9.2a depicts the spectrum for $[\text{PtBr}_6]^{2-}$.
- All ligands are π -donating.
- If we think about the MO parentage (ligand p -orbital and metal d -orbital), we can have a charge transfer from the ligand to the metal because of the MO diagram (see Figure 9.2b; Wuttig appears to draw it as antibonding?? Reversed p -orbital sign??).
- All of the orbitals below the frontier t_{2g} M-L π^* set are completely occupied, and what we're observing is the transition from those lower-lying orbitals, up, as illustrated in Figure 9.2c.
 - Notice that the transitions in this MO diagram exactly mirror those in the spectrum in Figure 9.2a.
 - Possible inconsistency??: Figure 9.2a is consistent with Figure 9.2c, but according to Figure 7.3, $t_{2u}(\pi)$ should be degenerate with $t_{1g}(\pi)$, not $t_{1u}(\pi)$. Overall actually, the orbitals don't look entirely consistent. What modifications are we making?
- LMCT is Laporte allowed because the ligand p orbital (ground state) is ungerade and the metal d orbital (excited state) is gerade. Mathematically,

$$g_{\text{es}} \times u \times u_{\text{gs}} = g$$

- Molar extinction coefficients are *very* high (tens of thousands vs. single-digit d - d transitions).
- Question: Rank the energy of the LMCT transitions among $[\text{OsBr}_6]^{2-}$, $[\text{OsCl}_6]^{2-}$, and $[\text{OsI}_6]^{2-}$.
 - Largest electronegativity (chloride) leads to the largest LMCT transition; smallest leads to smallest (iodide).
 - This is because larger electronegativity leads to lower bonding orbitals and thus a higher energy jump up to the frontier orbitals.
- MLCT transitions.
 - Figure 9.3a depicts the spectrum for $[\text{Cr}(\text{CO})_6]^{3+}$.
 - All ligands are π -accepting
 - Once again, we get very large extinction coefficients, so we must be relaxing the Laporte selection rule.

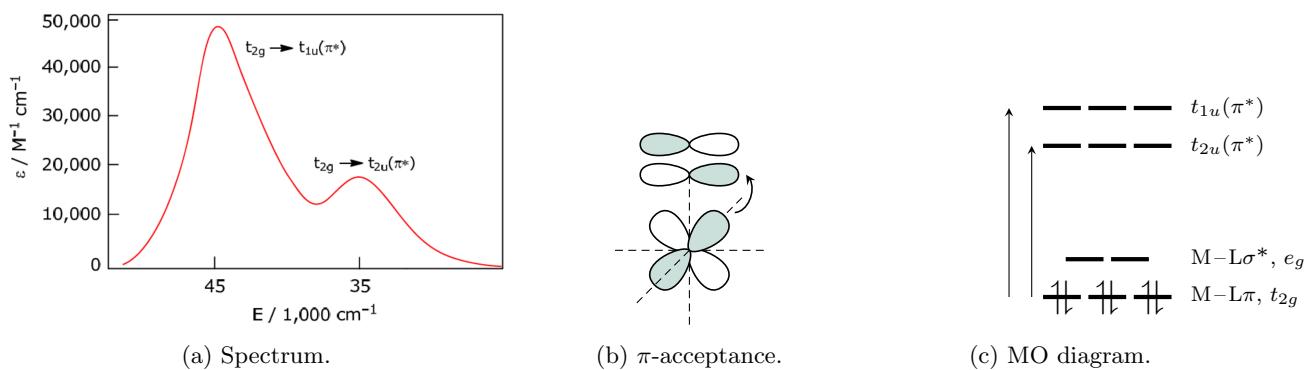


Figure 9.3: MLCT dynamics.

- Laporte allowed due to transitions occurring from gerade ground states to ungerade excited states.
 - We excite electrons from the metal to the ligand in the MO diagram, resulting in two transitions in both the diagram (Figure 9.3c) and the spectrum (Figure 9.3a).
- Technological applications of MLCT.
 - The transitions are so allowed that we get a lot of applications.
- The Grätzel Cell (by Michael Grätzel at EPFL). You can't store energy, but you can take light and generate an electric current.

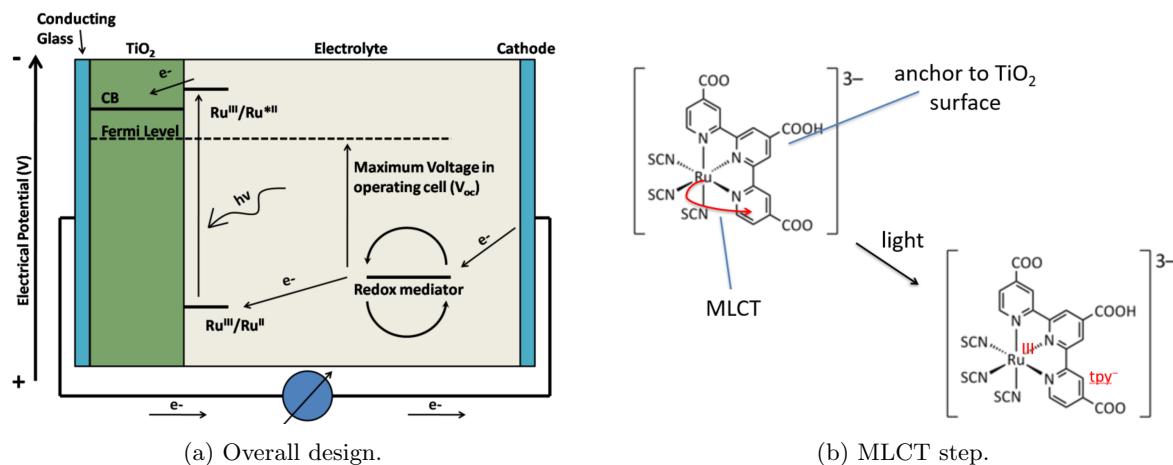


Figure 9.4: Grätzel Cell mechanism.

- A bit like artificial photosynthesis. We can't generate fuel like in a fuel cell, but we can generate current.
- Uses a $\text{Ru}(\text{SCN})_3\text{L}$ complex. Experimentally, this molecule has a very deep MLCT charge transfer band, allowing it to absorb into the red and IR spectrum (needed for direct sunlight to electricity conversion).
- The compound is anchored onto a TiO_2 (semiconducting) surface. The band gap is about 3 eV. The **conduction band** (LUMO for an extended solid) is poised at a level such that when you photoexcite Ru^{II} , oxidizing via MLCT $\text{Ru}^{\text{II}} \longrightarrow \text{Ru}^{\text{III}}$ and reducing the tpy ligand, you get an electron in an orbital (on tpy^-) that is higher than the TiO_2 conduction band.

- Thus, you can dump the electron into TiO_2 .
- TiO_2 is connected to a conducting glass (usually fluorine-doped tin oxide) from which you can harvest the electron and use it for electricity.
- An additional redox mediator is used in solution to harvest electrons at a cathode and regenerate Ru^{2+} ; this is essential in order to be able to do the same thing again (think salt bridge). The mediator goes from



- The lifetimes aren't that great.
- Selling point is that it is made out of very cheap materials, and is efficient because it makes use of very highly allowed MLCTs.

- Photoredox catalysis.

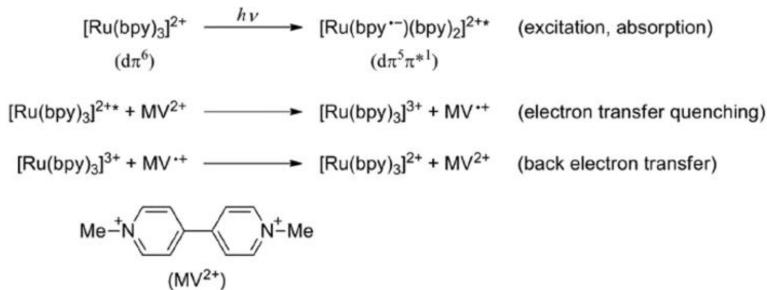
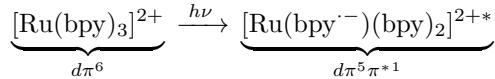
(a) $[\text{Ru}(\text{bpy})_3]^{2+}$ light absorption.(b) Discovery mechanism: Quenching with MV^{2+} .

Figure 9.5: Photoredox catalysis.

- Organic chemists have usurped it for catalysis, but it all came from inorganic chemistry.
- Whitten and Meyer established that $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes have charge transfer processes, that the excited electron can reduce various organic compounds, and that the hole left behind can be refilled.



- Discovered this by quenching the reaction with methyl viologen (MV^{2+}).
- The seminal papers are the **Meyer papers**.
- We improve photoredox catalysis further by thinking about the relative energy levels between where the d electrons are coming from and where they're going.
- To this end, people have put in tons of CF_3 groups to make a more powerful reductant.

- **Meyer papers:** The two papers Bock et al. (1974) and Thompson et al. (2013).

References

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