

Topic III

Introduction to Structure and Bonding

III.1 Module 11: Quantum chemistry 101

- 1/27:
- We will have a normal class on Friday and hold review sessions at different times where we can ask questions.
 - Suggested readings: Nocera Lecture 6, Nocera Lecture 7, MIT OCW quantum mechanics^[1].
 - In chemistry, most problems are solved with the time-independent Schrödinger equation $\hat{H}\Psi = E\Psi$.
 - Ψ is the wavefunction; it contains information on movement of the electron and its position.
 - $|\Psi(x, y, z)|^2 \propto P(x, y, z)$.
 - E is an eigenvalue of \hat{H} .
 - If we are working with the time-dependent Schrödinger equation, we have another variable besides x, y, z , namely t . This allows us to calculate the probability that an electron is in a certain position at a given time.
 - The Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$ describes the total energy.
 - \hat{T} is the kinetic energy operator. $\hat{T} = \frac{\hat{p}^2}{2m}$, where $\hat{p}_x = -i\hbar \frac{d}{dx}$ is the momentum operator.
 - \hat{V} is the potential energy operator. It typically describes the Coulombic attraction between the nucleus and the electron, which is approximately $\frac{1}{r}$ where r is the distance from the nucleus to the electron.

- For a free electron in one dimension, the Schrödinger equation reduces to

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi$$
$$\frac{d^2\Psi}{dx^2} = -\frac{2mE}{\hbar^2} \Psi$$

- Dirac's bra-ket notation $\langle\Psi|A|\Psi\rangle \equiv \int_V \Psi^* \hat{A} \Psi \, dx \, dy \, dz$.
 - The **bra vector** (the first term inside the brackets) and **ket vector** (the last term inside the brackets) correspond to complex conjugates of the wave function.

¹Many chemistry courses go too deep into the math and physics of quantum mechanics, which obfuscates the chemistry and confuses us in Dr. Talapin's opinion.

- **LCAO method:** A way of finding the wavefunction of a molecule; of solving the Schrödinger equation after applying simplifications. Short for linear combination of atomic wavefunctions, i.e., the atomic orbitals ϕ .

$$\Psi = \sum_i c_i \phi_i$$

- Each c_i is a coefficient, and the atomic orbitals form the basis set.
- Basically, we think of the wave function of a molecule as a linear combination of its atomic orbitals.
- ϕ is normalized, thus $\int \phi_i^2 d\tau = 1$ where $d\tau = \partial x \partial y \partial z$.
- Continuing, we can calculate the expected value of \hat{H} :

$$E = \frac{\int \Psi \hat{H} \Psi d\tau}{\int \Psi^2 d\tau}$$

- Shortcomings: Does not count for electron correlation and a few other things.
- Electronic structure of H_2 molecule.
 - H_2 's structure is H–H.
 - $\Psi = a\phi_1 + b\phi_2$, where $\phi_{1,2}$ are two atomic hydrogen $1s$ orbitals.
 - The electron density function is: $\phi^2 = a^2\phi_1^2 + b^2\phi_2^2 + 2ab\phi_1\phi_2$.
 - By symmetry of H–H molecule, $a = \pm b$.
 - Symmetry of the coefficients should reflect symmetry of the atoms.
 - Hydrogen atoms are indistinguishable, so since the electron can't identify which atom it corresponds to, the math shouldn't either.
 - If $S = \int \phi_1 \phi_2 d\tau$ or $\langle \phi_1 | \phi_2 \rangle$ is the overlap integral between two hydrogen $1s$ orbitals, we have bonding and antibonding orbitals:

$$\Psi_b = \frac{1}{\sqrt{2(1+s)}}(\phi_1 + \phi_2) \qquad \Psi_a = \frac{1}{\sqrt{2(1-s)}}(\phi_1 - \phi_2)$$

- The first orbital is σ_g bonding.
 - The second orbital is σ_u^* antibonding.
 - Introducing the normalizing requirement gives us the above coefficients.
- In the Hückel theory:

$$\alpha = \langle \phi_1 | \hat{H}_{\text{eff}} | \phi_1 \rangle = \langle \phi_2 | \hat{H}_{\text{eff}} | \phi_2 \rangle \qquad \beta = \langle \phi_1 | \hat{H}_{\text{eff}} | \phi_2 \rangle$$

- If we calculate the expectation integrals, we will arrive at the above.
 - \hat{H}_{eff} is some effective Hamiltonian.
 - The α integral is the **Coulomb integral**.
 - The β integral is the **interaction integral**.
- In the **Hückel approximation** (the simplest approximation of quantum mechanics), we define integrals as parameters that we can extract from empirical data:
 - $H_{ii} = \alpha$.
 - $H_{ij} = 0$ for ϕ_i not adjacent to ϕ_j .
 - $H_{ij} = \beta$ for ϕ_i adjacent to ϕ_j .
 - $S_{ii} = 1$.
 - $S_{ij} = 0$.

- Expectation values for energy are

$$E_{a,b} = \frac{\langle \Psi_{a,b} | \hat{H}_{\text{eff}} | \Psi_{a,b} \rangle}{\langle \Psi_{a,b} | \Psi_{a,b} \rangle}$$

so

$$E_a = \frac{\alpha - \beta}{1 - s} \qquad E_b = \frac{\alpha + \beta}{1 + s}$$

- Note that $\beta < 0$ for atomic s -orbitals and $\beta > 0$ for p -orbitals for σ -bonds.
- Also, in the Hückel one-electron model, the integrals α and β remain unsolved.
- Note: As always, the bonding orbitals are less stabilized than the antibonding orbitals are destabilized.
 - This is a consequence of overlap, e.g., for a dimer, the $1 \pm S$ term in $E_{+/-} = \frac{\alpha \pm \beta}{1 \pm S}$.
 - This is why He_2 does not exist.
- **Overlap integral:** An integral proportional to the degree of spatial overlap between two orbitals. It is the product of wave functions centered on different lattice sites. Varies from 0 (no overlap) to 1 (perfect overlap). *Also known as S .*
- **Coulomb integral:** An integral giving the kinetic and potential energy of an electron in an atomic orbital experiencing interactions with all the other electrons and all the positive nuclei. *Also known as α .*
- **Interaction integral** (on two orbitals 1,2): An integral giving the energy of an electron in the region of space where orbitals 1 and 2 overlap. The value is finite for orbitals on adjacent atoms, and assumed to be zero otherwise. *Also known as β_{12} , resonance integral, exchange integral.*
- Symmetry and quantum mechanics:
 - Say we have $\hat{H}\Psi = E\Psi$ where \hat{H} is the Hamiltonian and R is a symmetry operator (e.g., C_2 or σ_v).
 - Note that the Hamiltonian commutes with the symmetry operator: $R\hat{H} = \hat{H}R$.
 - Since a symmetry operation does not change the energy of a molecule (it just moves it), $\hat{H}R\Psi_i = E_i R\Psi_i$.
 - It follows that R does not change the form of the wave function, i.e., $R\Psi_i = \pm 1\Psi_i$. This reflects the fact that R cannot change the probability $P[e(x, y, z)] = |\Psi(x, y, z)|^2$ of finding an electron somewhere.
 - Thus, the eigenfunctions of the Schrödinger equation generate a representation of the group.
 - Non-degenerate wave functions are A or B type.
 - Double-degenerate wave functions are E type.
 - Triple-degenerate wave functions are T type.
- Back to the LCAO method:

$$E_i = \frac{\int \Psi_i^* H \Psi_i dV}{\int \Psi_i^* \Psi_i dV} \qquad \Psi_i = \sum_j c_j \phi_j$$

- If we have a sizeable molecule with a couple dozen atoms, every molecular orbital (wave function) will be the sum of a couple dozen atomic orbitals.
- This generates a set of i linear homogenous equations, numbering in the hundreds or thousands that need to be solved.
- This is clearly too computationally expensive, so we need a trick.

- An example where symmetry arguments help a lot:
 - If f is odd ($f(x) = -f(-x)$), then we know that $\int_{-\infty}^{\infty} f(x) dx = 0$.
- Group theory allows us to generalize this method to broader symmetry operations.
- Three important theorems:
 1. The characters of the representation of a direct product are equal to the products of the characters of the representations based on the individual sets of functions.
 - For example, in the T_d point group, $T_1 = (3, 0, -1, 1, -1)$, and $T_2 = (3, 0, -1, -1, 1)$. By the theorem, $T_1 \times T_2 = (9, 0, 1, -1, -1)$.
 2. A representation of a direct product, $\Gamma_c = \Gamma_a \times \Gamma_b$, will contain the totally symmetric representation only if the irreducible representations of a and b contain at least one common irreducible representation.
 - Continuing with the above example, $T_1 \times T_2$ can be decomposed into $A_2 + E + T_1 + T_2$. Thus, by this theorem, if we take the product $\Gamma_c = E \times T_1 \times T_2$, the representation will contain the totally symmetric representation A_1 (since $\Gamma_b = E$ and $\Gamma_a = T_1 \times T_2$ both contain E). Indeed, $E \times T_1 \times T_2 = (18, 0, 2, 0, 0)$.
 3. The value of any integral relating to a molecule $\int_V \Psi d\tau$ will be zero unless the integrand is invariant under all operations of the symmetry point group to which the molecule belongs. That is Γ_Ψ must contain the totally symmetric irreducible representation.
 - This example will concern the D_{4d} point group. We want to evaluate the integral $\int_V \Psi_a \mu_z \Psi_b d\tau$ where $\Gamma_{\Psi_a} = A_1$, $\Gamma_{\mu_z} = B_2$, and $\Gamma_{\Psi_b} = E_1$.
 - By Theorem 1, we can easily determine the representation $\Psi_a \times \mu_z$. We can then decompose it.
 - Noting that it does not contain the E_1 irreducible representation (the only representation in Ψ_b), we can learn from Theorem 2 that $\Psi_a \mu_z \Psi_b$ does not contain the A_1 irreducible representation.
 - Therefore, by Theorem 3, $\int_V \Psi d\tau = \int_V \Psi_a \mu_z \Psi_b d\tau = 0$.
- We use these three theorems to tell us what integrals will be zero in a much less computationally intensive fashion. We can then evaluate the remaining nonzero integrals.
- We can take direct products by hand, but there are also tables of direct products of irreducible representations.

III.2 Module 12: IR and Raman active vibrations (part 2)

- **Fermi's golden rule:** The rate of an optical transition from a single initial state to a final state is given by the transition rate for a single state.

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} E_0^2 |\langle f | H' | i \rangle|^2 \delta(E_f - E_i - h\nu)$$

- By state, we typically mean energy level.
- The transition rate is the probability of a transition happening.
- If it's an optical transition, conservation of energy implies that the energy difference between the initial and final state will equal the energy of the photon that the molecule absorbs or emits.
- E_0^2 is the light intensity.
- $h\nu$ is the photon energy.
- $\langle f | H' | i \rangle = \int \Psi_f^* H' \Psi_i d\tau$ is the square of the matrix element (the strength of the coupling between the states).

- $\delta(E_f - E_i - h\nu)$ is the resonance condition (energy conservation).
- In the dipole approximation, $H' = -e\vec{r} \cdot \vec{E}$.
- This is derived with time-dependent perturbation theory.
 - The matrix element $M = \langle f|H'|i\rangle = \int \Psi_f^*(\vec{r})H'\Psi_i(\vec{r}) d^3\vec{r}$.
 - Perturbation: $H' = -\vec{p}_e \cdot \vec{E}_{\text{photon}}$. Dipole moment: $\vec{p}_e = -e\vec{r}$. Light wave: $\vec{E}_{\text{photon}}(r) = \vec{E}_0 e^{\pm i\vec{k} \cdot \vec{r}}$, $H'(\vec{r}) = e\vec{E}_0 \cdot \vec{r} e^{\pm i\vec{k} \cdot \vec{r}}$.
 - This implies that in one dimension, $|M| \propto \int \Psi_f^*(\vec{r})x\Psi_i(\vec{r}) d^3\vec{r}$.
 - We include other variables in higher dimensions.
- For IR absorption, the intensity I satisfies $I \propto \int \Psi_{\text{e.s.}} \hat{\mu}_e \Psi_{\text{g.s.}} d\tau$.
 - $\Psi_{\text{e.s.}}$ is the excited state wavefunction, $\Psi_{\text{g.s.}}$ is the ground state wavefunction, and $\hat{\mu}_e$ is the dipole operator.
 - We now apply the three theorems:
 - It is always true in vibration spectroscopy that $\Gamma_{\text{g.s.}} = A_1$. This is because in the ground state, the molecule is completely relaxed (nothing is perturbed).
 - Thus, we can already reduce to $\Gamma_{\text{e.s.}} \cdot \Gamma_{\mu} \cdot \Gamma_{\text{g.s.}} = \Gamma_{\text{e.s.}} \cdot \Gamma_{\mu} \cdot 1$.
 - Now Γ_{μ} transforms as x, y, z unit vectors. In D_{3h} , this implies that $\Gamma_{\mu} = E' + A_2''$.
 - Therefore, $I \propto \Gamma_{\text{vibs}} \cdot (E' + A_2'')$.
 - For PF_5 , since $\Gamma_{\text{vibs}} = 2A_1' + 3E' + 2A_2'' + E''$ has E' and A_2'' in common with Γ_{μ} , only $3E'$ and $2A_2''$ are IR active.
 - Additionally, with elements in common, $\Gamma_{\text{vibs}} \cdot \Gamma_{\mu}$ will contain A_1 by Theorem 2, and thus, the integrals $\int \Psi_{\text{e.s.}} x \Psi_{\text{g.s.}} d\tau$, $\int \Psi_{\text{e.s.}} y \Psi_{\text{g.s.}} d\tau$, and $\int \Psi_{\text{e.s.}} z \Psi_{\text{g.s.}} d\tau$ are all nonzero. Some linear combination of them will be proportional to I .
- The exam will include material from today's class, but not Friday's class.
- PSets 1 and 2 will cover all material on the exam?