Chem 279 Final Presentation

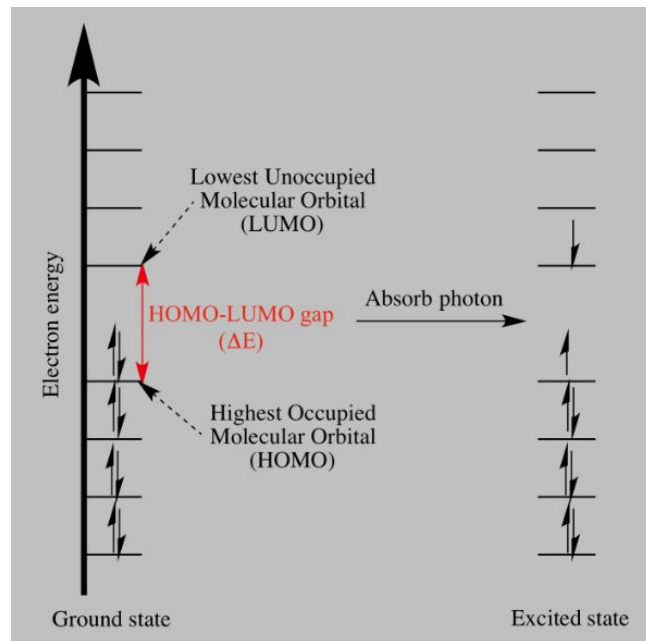Ariel Espinoza and Shree Patel

Overview

1. Introduction to Band Gap and Molecular Dipole
2. Refresher on CNDO/2
3. Extension to Energy Gap
4. Extension to Molecular Dipole
5. Results, Interpretations, and Next Steps

Band Gap and Molecular Dipole

Energy Gap

- Energy difference between where electrons normally reside and where they are free to move
- HOMO (Highest Occupied Molecular Orbital)
  - Represents where the most weakly held electrons are.
  - Electrons in the HOMO are the first to participate in reactions (e.g. oxidation, nucleophilic).
  - A higher HOMO energy indicates electrons are easier to remove which means molecule is more reactive as an electron donor.

"Illustrated Glossary of Organic Chemistry." Illustrated Glossary of Organic Chemistry - HOMO-Lumo Gap, UCLA, www.chem.ucla.edu/~harding/IGOC/H/homo_lumo_gap.html. Accessed 7 Dec. 2025.
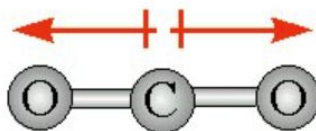
Energy Gap Continued

- LUMO (Lowest Unoccupied Molecular Orbital)
  - Represents the lowest available orbital electrons can jump into.
  - Determines how easily a molecule can accept electrons (reduction, electrophilic).
  - A lower LUMO energy indicates easier to add electrons which means better electron acceptor.
- Band Gap = LUMO − HOMO
  - Small Band Gap: Electrons can be excited easily → molecule is chemically reactive
  - Large Band Gap: Requires high energy to excite electrons → chemically inert
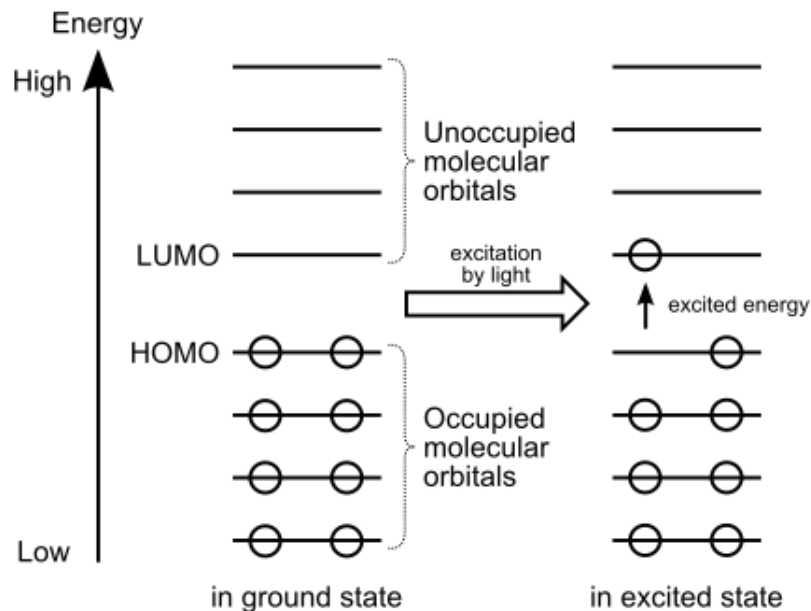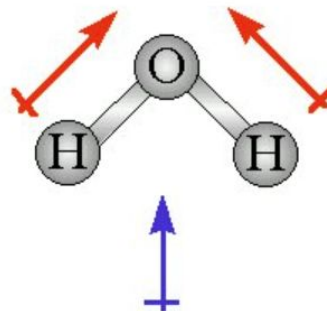
Molecular Dipole

- Separation of positive and negative charge in a molecule, creating a net polarity
  - Arises from polar bonds (unequal electron sharing) that don't completely cancel out due to molecule's asymmetrical shape
- Dipole-dipole interactions influence properties like solubility, boiling and melting point, and viscosity
  - Polar molecules are loosely attracted to each other because of slightly positive and negative regions

"Bond Polarity and Dipole Moments." Chemistry, asoefkersaachemistry.weebly.com/bond-polarity-and-dipole-moments.html. Accessed 7 Dec. 2025.

Refresher on CNDO/2

CNDO (Complete Neglect of Differential Overlap)

- What is CNDO/2?
  - Semi-empirical quantum chemistry method for approximating molecular electronic structure
  - Treats only valence electrons, reducing the basis size and computational effort
  - Uses STO 3G basis functions and parameterized atomic integrals
  - Produces a simplified Fock matrix that still captures essential bonding and charge distribution trends

CNDO/2 Fock Matrix Equations

1. Diagonal Fock Elements

$$F_{\mu\mu} = -\left(\frac{I_A + A_A}{2}\right) + (P_A - Z_A^*)\,\gamma_{AA} - \left(P_{\mu\mu}^\sigma - \frac{1}{2}\right)\gamma_{AA} + \sum_{C \neq A}(P_C - Z_C^*)\,\gamma_{AC}$$

2. Off-Diagonal Fock Elements

$$F_{\mu\nu} = \frac{1}{2}(\beta_A + \beta_B)\,S_{\mu\nu} - P_{\mu\nu}^\sigma\,\gamma_{AB} \qquad (\mu \in A,\ \nu \in B,\ A \neq B)$$

3. Two-Center Coulomb Interaction

$$\gamma_{AB} = \iint \frac{\phi_A(\mathbf{r}_1)^2\,\phi_B(\mathbf{r}_2)^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1\,d\mathbf{r}_2$$

Extension to Energy Gap

How We Computed Observables

- After SCF convergence, we diagonalize the final alpha and beta Fock matrices to get molecular orbital MO energies and coefficients.
- This produces two sets of MO energies because we use unrestricted Hartree Fock (alpha and beta spins treated separately).
- We sort the MO energies from lowest to highest.
- We determine which orbitals are occupied using the electron counts:
  - Fill the lowest num_alpha alpha-spin orbitals.
  - Fill the lowest num_beta beta-spin orbitals.
- The occupied orbitals are used to build the electron density matrix used in the SCF cycle.
- The eigenvectors give the shape of each MO; the eigenvalues are the MO energy levels.

Determining HOMO, LUMO, and the Energy Gap

- HOMO = the last filled orbital in the **sorted** list.
- LUMO = the next unfilled orbital after the HOMO.
  - HOMO alpha/beta = orbital index (num_alpha/beta − 1)
  - LUMO alpha/beta = orbital index (num_alpha/beta)
- Overall HOMO = the larger of HOMO alpha and HOMO beta energies.
- Overall LUMO = the smaller of LUMO alpha and LUMO beta energies.
- Energy Gap = Change in Energy
  - This gap indicates how easily an electron can be promoted to an excited state.

Molecular Systems We Tested On

H$_2$

HF

Water

HO
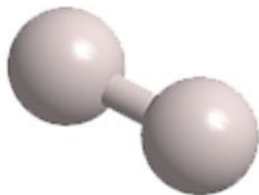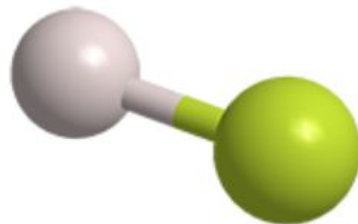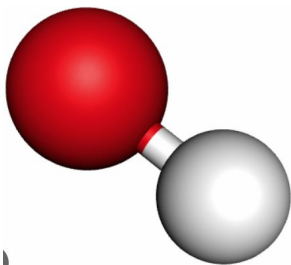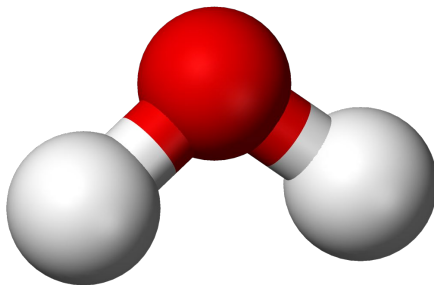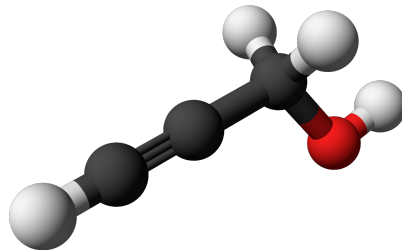
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Results

Molecule	Our HOMO (eV)	Our LUMO (eV)	Our Gap (eV)	Expected Gap (eV)
H2	-20.87	6.52	27.39	~15
H2O	-18.51	15.19	33.70	~12
HF	-21.26	8.99	30.25	~16
HO	-18.87	3.37	22.24	~11
Propynol	86.23	91.33	5.10	~5-10

Interpretation and Discussion

- HOMO–LUMO gap is still a good proxy for qualitative behavior
- Even when not numerically correct:
  - Small HF gap → molecule is more reactive, easier to excite
  - Large HF gap → more stable, harder to excite
- HF overestimates the gap, but the trend/motifs across molecules is preserved.
- HF gives qualitatively correct trends
  - Even though HF overestimates the numerical gap, it still gets the ordering right:
  - Conjugated molecules → smaller gaps
  - Radicals → intermediate gaps
  - Closed shell molecules → large gaps

Extension to Molecular Dipole

Basics of Dipole Calculation

- Molecular dipole is a vector that sums up all the individual bond dipoles
- Need to calculate positive and negative contribution to the dipole
- To perform this calculation, we need:
  - AO dipole integrals – x, y, z components of $\langle \mu | \hat{r} | v \rangle$ for every AO pair – product center of each basis-function pair and the contracted STO-3G normalization factors
  - Final MO coefficients in orthonormal representation – MOs must be S-orthonormalized before building a reliable density since CNDO/2 uses non-orthonormalized AO's
  - Final AO density matrix – distribution of electric charge —"negative" part of the dipole
  - CNDO-consistent nuclear charges – Z^* for consistency with valence-only electronic model – "positive" part
  - A way to combine the electronic and nuclear terms
  - Conversion to Debye units

Sahu, Sridhar, and Alok Shukla. "Fortran 90 Implementation of the Hartree-Fock Approach within the CNDO/2 and Indo Models." *arXiv.Org*, 19 Dec. 2008, arxiv.org/abs/0812.3690.

Translating Theory to Implementation

1. Build AO Dipole Integrals
   a. Evaluated and assembled D_x, D_y, D_z into full AO dipole matrices
2. Prepare SCF Quantities
   a. S-orthonormalized final MOs to ensure $\mathbf{C^T S C = I}$
   b. Constructed final AO density matrix from occupied orthonormalized MOs.
3. Electronic Dipole
   a. Contracted density with AO dipole matrices: $\boldsymbol{\mu}\textbf{elec=Tr(PD}_k\textbf{) for k=x,y,z}$
4. Nuclear Dipole (CNDO Effective Charges)
   a. Used CNDO effective valence charges Z_A^*
   b. Computed nuclear component: $\boldsymbol{\mu}\textbf{nuc=}\sum_A \mathbf{Z}_A^* \mathbf{R}_A$
5. Total Dipole + Units
   a. Combined components: $\boldsymbol{\mu}\textbf{total=}\boldsymbol{\mu}\textbf{nuc}-\boldsymbol{\mu}\textbf{elec}$
   b. Converted from a.u. to Debye

Sahu, Sridhar, and Alok Shukla. "Fortran 90 Implementation of the Hartree-Fock Approach within the CNDO/2 and Indo Models." *arXiv.Org*, 19 Dec. 2008, arxiv.org/abs/0812.3690.

Calculation Results

Molecule	Our Dipole (Debye)	Literature Dipole (Debye)	Approximate Error	Comments
H2	0	0	0 %	exactly zero dipole by symmetry
H2O	1.15	1.85	18 %	Trend is correct
HF	1.62	1.83	10.2 %	Semi empirical HF tends to give slightly smaller dipoles
HO	1.47	1.66	10.24 %	order of magnitude error as HF - makes sense
Propynol	141.16	~2	Way off	Breakdown of the model for large complex molecules

Interpretation and Discussion

- CNDO/2 captures correct polarity trends, but slightly underestimates magnitudes.
- Why results are reasonable for small systems:
  - Geometry is compact, minimizing origin effects.
  - Polarization is limited so CNDO/2's approximations remain stable.
  - Electron distribution is simple and dominated by a single bond dipole (O–H, H–F).
  - For water, our model is close showing that i can handle small bent polar molecules reasonably well despite approximation.

- Propynol dipole model breakdown.
  - Geometry is long and nearly linear, giving a very large "lever arm" for charge separation.
  - CNDO/2 significantly over-polarizes extended π systems and strongly electronegative atoms (O).
  - Minimal basis set cannot describe electron delocalization properly this forces electrons toward one end.
  - Dipole moment becomes highly origin dependent when the molecule spans a large coordinate range.
  - **Semi empirical parameters were built for small, compact molecules, not long chain alcohols with complex bonds.**

Thank you