

Ariel Espinoza and Shree Patel

Chem 279

15 December 2025

# Chem 279 Final Project Report: Band Gap and Molecular Dipole

# Abstract

This project extends the semi-empirical Complete Neglect of Differential Overlap (CNDO/2) method, expanding upon an existing Self-Consistent Field (SCF) computational framework, to investigate molecular dipole moments and HOMO–LUMO energy gaps. Key results from the dipole moment calculations are as follows: for  $\text{H}_2$ , the calculated dipole moment is 0.00 D; for HF, it is 1.62 D; for  $\text{H}_2\text{O}$ , it is 1.16 D; for HO, it is 1.47 D; for  $\text{CH}_4$ , it's 0.00 D; and for propynol, it's 141.16 D. The calculated HOMO–LUMO energy gaps are:  $\text{H}_2$ , 27.39 eV; HF, 30.25 eV;  $\text{H}_2\text{O}$ , 33.70 eV; HO, 22.24 eV;  $\text{CH}_4$ , 14.13 eV; and propynol, 5.10 eV. These computed properties provide insight into how electron density is spatially and energetically distributed within the tested molecules, and highlight both the strengths and limitations of the CNDO/2 method, which are discussed later in this paper.

# Background

## Objectives and Summary of This Work

Our primary objective is to establish a clear relationship between the calculated CNDO/2 electron density and observable molecular characteristics.

The focus of this work is on the calculation of the band gap,  $E_{\text{LUMO-HOMO}}$  and the molecular dipole moment  $\mu$ . The band gap offers insights into reactivity, bonding behavior, and excitability of molecules, while the molecular dipole provides insight into the spatial distribution of electronic charge within a molecule, which manifests into properties like polarity, boiling, and solubility. To validate our extended CNDO/2 implementation, dipole moments were computed for a series of small molecules, including:

- Diatomics: Hydrogen ( $\text{H}_2$ ), Hydrogen Fluoride (HF), and Hydroxyl (OH)
- Small Polyatomics: Water ( $\text{H}_2\text{O}$ ) and Methane ( $\text{CH}_4$ )
- Larger System: Propynol ( $\text{C}_3\text{H}_4\text{O}$ )

In a further exploration of the electronic structure, we also investigated the energy band gap. This was approximated by the energy difference between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) obtained from the converged Fock matrix. The  $E_{\text{LUMO-HOMO}}$  gap serves as a proxy for the excitation energy and provides information on the distribution of electrons in energy space.

It is important to note that our CNDO/2 extension code, being a semi-empirical method that relies on significant approximations (like the neglect of differential overlap) and parameterized inputs, may differ from highly accurate experimental and *ab initio* data.

## Chemical Significance and Motivation

The electronic structure of a molecule dictates its chemical behavior. The HOMO represents the energy level where the most weakly held electrons reside. These are the electrons most readily available to participate in chemical reactions, such as oxidation or nucleophilic attacks. Consequently, a higher HOMO energy suggests that electrons are easier to remove, making the molecule a better electron donor and thus more chemically reactive (Szabo and Ostlund).

The LUMO represents the lowest energy orbital available for an incoming electron to occupy. This orbital determines how easily a molecule can accept electrons, making it crucial in reduction or electrophilic reactions. A lower LUMO energy signifies that electrons are easier to add, which means the molecule acts as a better electron acceptor ((Szabo and Ostlund). The energy difference between these two frontier orbitals is defined as the Band Gap ( $E_{\text{LUMO-HOMO}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ ). A small Band Gap indicates that electrons can be excited easily, leading to a chemically reactive molecule, whereas a large Band Gap requires high energy to promote an electron, resulting in a more chemically inert substance.

Beyond energy levels, the molecular dipole moment provides critical insight into the spatial distribution of charge. This property quantifies the net polarity that arises from the separation of positive and negative charge within a molecule. It originates from individual polar bonds, where electrons are unequally shared between atoms, that do not geometrically cancel out due to an asymmetrical molecular shape. The resulting charge separation generates dipole-dipole interactions between adjacent molecules. These weak attractions influence bulk physical properties such as solubility, boiling point, melting point, and viscosity, as polar molecules are loosely drawn to one another by their slightly positive and negative regions.

Our motivation in pursuing this work is understanding how physical, observable properties are broken down into mathematical approximations in the computational space, bridging both non-physical and physical systems to reach the same understanding.

## Methodology

### Implementation of CNDO/2 with SCF

Prior to the calculation of molecular properties, the system must be built in the virtual environment, which was accomplished with a semi-empirical approximation of the Hartree-Fock (HF) method, the CNDO/2 method with SCF. As this work served as the basis for our calculations and was conducted in a prior assignment, details surrounding the implementation are included in the appendix.

### Extension of CNDO2 to Calculate Band Gap

The extension of the CNDO2 framework to compute the HOMO - LUMO energy gap required no modification of the underlying SCF procedure. Instead, the band gap was obtained as a post SCF analysis using the converged Fock matrices and molecular orbital occupations.

#### *Function #1: Fock Matrix Diagonalization*

After SCF convergence, the final  $\alpha$  and  $\beta$  Fock matrices are diagonalized using a symmetric eigenvalue solver. This produces:

1. A vector of molecular orbital (MO) energies
2. A matrix of corresponding MO coefficients

The resulting eigenvalues represent the energies of the molecular orbitals, while the eigenvectors describe the AO composition of each MO.

#### *Function: #2 Orbital Sorting and Occupation Assignment*

The MO energies are sorted in ascending order for both  $\alpha$  and  $\beta$  spin channels. Orbital occupation is then assigned based on the number of  $\alpha$  and  $\beta$  electrons specified in the input:

1. The lowest num\_alpha orbitals are occupied in the  $\alpha$  channel

2. The lowest num\_beta orbitals are occupied in the  $\beta$  channel

This procedure identifies the highest occupied molecular orbital and the lowest unoccupied molecular orbital for each spin channel.

#### *Function #3 : HOMO - LUMO Gap Evaluation*

The band gap is computed as the difference between the lowest unoccupied and highest occupied orbital energies:

- HOMO energy =  $\max(E_{\text{HOMO}}^{\alpha}, E_{\text{HOMO}}^{\beta})$
- LUMO energy =  $\min(E_{\text{LUMO}}^{\alpha}, E_{\text{LUMO}}^{\beta})$

The gap provides a simple estimate of the molecule's electronic excitation threshold and is reported in electron volts.

### **Extension of CNDO/2 to Calculate Molecular Dipole**

The calculation of molecular dipole moments required additional functionality beyond the standard CNDO/2 SCF procedure. In particular, atomic orbital (AO) dipole integrals were computed and contracted with the converged electronic density matrix.

#### *Data Structures for Dipole Calculation*

This struct stores the three AO dipole integral matrices:

1. Dx: x-component dipole integrals, 2. Dy: y-component dipole integrals, 3. Dz: z-component

These matrices are used to compute the electronic contribution to the molecular dipole.

#### *Function #1: build\_dipole\_integrals*

This function constructs the AO dipole integrals for all AO pairs using Gaussian basis functions. For each pair of contracted atomic orbitals:

- Primitive Gaussian overlaps are evaluated
- Obara Saika relations are used to compute first-order moment integrals
- Contributions are contracted using STO-3G coefficients and normalization constants

The resulting dipole integrals are stored in the Dx, Dy, and Dz matrices.

#### *Function #2: Molecular Orbital Orthonormalization*

Because the AO basis is non orthogonal, the converged molecular orbital coefficient matrices are orthonormalized with respect to the overlap matrix S. This ensures that the density matrix constructed from the occupied orbitals is consistent with the AO metric.

#### *Function #3: Density Matrix Reconstruction*

New  $\alpha$  and  $\beta$  density matrices are constructed from the orthonormalized molecular orbitals:

- Each occupied orbital contributes an outer product to the density matrix

- The total density matrix is obtained as the sum of  $\alpha$  and  $\beta$  densities

This step ensures that the electronic density used in the dipole calculation reflects the final converged wavefunction.

#### *Function #4: Electronic Dipole Evaluation*

The electronic dipole moment is computed by contracting the total density matrix with the AO dipole integral matrices:

$$1. \mu_{\text{elec},x} = \text{Tr}(P \cdot D_x), 2. \mu_{\text{elec},y} = \text{Tr}(P \cdot D_y), 3. \mu_{\text{elec},z} = \text{Tr}(P \cdot D_z)$$

This yields the electronic contribution to the molecular dipole in atomic units.

#### *Function #5: Nuclear Dipole Evaluation*

The nuclear dipole moment is computed as a classical point charge contribution using the effective CNDO2 nuclear charges and atomic coordinates:

$$\mu_{\text{nuc}} = \sum_A Z^*_A R_A$$

#### *Function #5: Total Dipole Moment*

The total molecular dipole moment is obtained by subtracting the electronic contribution from the nuclear contribution. The final dipole magnitude is converted from atomic units for final reporting.

This implementation combines CNDO 2 with SCF iteration, minimal STO 3G basis functions, and post SCF analysis to compute molecular orbital energies, HOMO LUMO gaps, and dipole moments. While computationally inexpensive, the approach captures key qualitative trends in molecular electronic structure and serves as a useful framework for exploring the strengths and limitations of semi-empirical methods.

## Results and Discussion

### Computed Dipole Moments

Table 1 summarizes the dipole moments obtained from the CNDO/2 SCF calculations for the molecules studied in this work. Symmetry considerations are correctly captured for nonpolar molecules such as  $H_2$  and  $CH_4$ , both of which yield zero dipole moments in agreement with experimental observations (National Institute of Standards and Technology, CCCBDB). For small polar molecules such as HF,  $H_2O$ , and HO, the calculated dipole moments follow the correct qualitative trends, with HF exhibiting the strongest polarity. While the absolute values deviate from experiment, this behavior is expected. HF methods are known to overestimate charge separation and exaggerate dipole moments due to the neglect of electron correlation effects (Szabo and Ostlund; Dewar and Thiel).

However, the dipole moment computed for propynol is unphysically large. This behavior reflects a known limitation of CNDO/2 and HF semi empirical methods when applied to larger, extended molecules. In these systems, electron delocalization and screening effects are poorly represented, leading to exaggerated charge separation and over polarization (Dewar and Thiel). As a result, the propynol dipole moment should be interpreted as an illustration of model breakdown rather than a quantitative prediction.

Molecule	Dipole Moment (Debye)	Literature Value (Debye)
H <sub>2</sub>	0.00	0.00
HF	1.62	1.83
H <sub>2</sub> O	1.16	1.85
HO	1.47	1.66
CH <sub>4</sub>	0.00	0.00
Propynol	141.16	1.7

**Table 1.** Dipole Moments (National Institute of Standards and Technology, CCCBDB & NIST Chemistry WebBook)

## HOMO LUMO Energy Gaps

The HOMO LUMO energy gaps were computed from the converged  $\alpha$  and  $\beta$  Fock matrices by identifying the highest occupied and lowest unoccupied molecular orbitals based on the total electron count. As expected for closed shell systems,  $\alpha$  and  $\beta$  orbital energies are identical.

The results show that CNDO2 significantly overestimates absolute HOMO LUMO gaps compared to experimental optical gaps, a well known characteristic of HF based methods. The relative trends across molecules are physically meaningful. Small, stable molecules such as H<sub>2</sub>, HF, and H<sub>2</sub>O exhibit large gaps, indicating low chemical reactivity, while the conjugated system propynol displays a much smaller gap, consistent with increased electronic delocalization and reactivity. This behavior is fairly common and known for HF methods, which neglect electron correlation and yield overly stabilized occupied orbitals and excessively high virtual orbital energies (Jain, Chelikowsky, and Louie; Szabo and Ostlund).

The HO radical exhibits an intermediate gap, reflecting its open shell nature and enhanced chemical reactivity compared to closed-shell molecules.

Molecule	HOMO LUMO Gap (eV)	Literature Trend and Value (eV) <i>Experimental gaps vary by definition and measurement</i>
H <sub>2</sub>	27.39	Very Large, ~15.4
HF	30.25	Large, ~16
H <sub>2</sub> O	33.70	Large, ~12.6

HO	22.24	Medium, ~11.3
CH <sub>4</sub>	14.13	Small - Med, ~12.6
Propynol	5.10	Small, ~10

**Table 2.** HOMO LUMO Energy Gaps (NIST Chemistry WebBook)

The CNDO/2 method successfully captures qualitative chemical trends in both dipole moments and electronic energy gaps for small molecules, validating its usefulness as a low cost educational and exploratory electronic structure method. However, the results also clearly demonstrate its limitations for larger and more complex systems, where exaggerated polarization and minimal basis set constraints lead to unphysical predictions. These findings highlight the importance of method selection when modeling extended or conjugated molecules. Experimental reference trends for ionization energies and electron affinities were taken from the NIST Chemistry WebBook.

Overall, the results demonstrate that while CNDO/2 does not provide quantitatively accurate electronic properties, it reliably captures qualitative trends in molecular polarity and electronic structure. Molecules with high symmetry such as H<sub>2</sub> and CH<sub>4</sub> correctly exhibit zero dipole moments, while polar bonds and electronegativity differences lead to nonzero dipoles in HF, H<sub>2</sub>O, and HO. Similarly, larger HOMO LUMO gaps are observed for small, closed shell molecules, indicating greater electronic stability, whereas reduced gaps in larger or more conjugated systems signal increased reactivity. These trends align with chemical intuition and underscore the pedagogical value of CNDO2 as a kind of “light weight” method for exploring electronic structure, despite its known limitations for quantitative predictions.

## Conclusions

In this project, we successfully extended the existing CNDO2 SCF framework to compute molecular orbital energies, HOMO LUMO energy gaps, and molecular dipole moments for a range of small molecules. The implementation correctly captured qualitative electronic structure trends, including zero dipole moments for highly symmetric molecules and increasing polarity for heteronuclear systems. While the absolute band gaps and dipole magnitudes were often overestimated, these deviations are consistent with known limitations of HF semi empirical methods. Overall, this work demonstrates that CNDO 2 provides a computationally efficient and conceptually valuable approach for exploring molecular electronic structure, while clearly illustrating the need for more sophisticated methods when quantitative accuracy is required.

## Future Work

Future work could include and focus on improving the accuracy of the calculated molecular properties. This can be done by incorporating geometry optimization into the computational pipeline. Rather than relying on the fixed XYZ files, the nuclear positions could be iteratively adjusted to minimize the total energy, thus allowing the molecules to relax to lower energy states before computing both the dipole moments and the band gaps. Implementing these additions could significantly improve the physical reliability of the results, especially for larger molecules.

# Appendix

## Implementation of CNDO/2 with SCF

### *Data Structures and Molecule Setup*

To keep the code organized and set up molecules in a systematic manner, we utilized custom structs to hold key molecular information. The structs used for the CNDO/2 method are as follows:

- AtomParam: This struct stores the CNDO/2 semi-empirical parameters for each element (H, C, N, O, F). The map `cndo_parameters` associates an element symbol with its AtomParam values and is used when building both the core Hamiltonian and the Fock matrix.
- Primitive: The code uses contracted Gaussian functions (STO-3G) to approximate Slater-type orbitals. Two maps, `sto3g_s` and `sto3g_p`, store the three Gaussian primitives and their contraction coefficients for s and p orbitals, respectively, for each element.
- Basis\_components: Each Basis\_components instance represents one contracted atomic orbital (AO): an s-type AO ( $l = m = n = 0$ ) or one of the p-type AOs (e.g.,  $l = 1, m = n = 0$ ). The vectors hold the three Gaussian primitives and related coefficients for that AO.

The following global containers were also referenced multiple times throughout the code to ensure continuity in values used in calculation:

- `std::vector<std::string> element_symbols`: chemical symbol for each atom.
- `std::vector<arma::vec> atom_positions`: nuclear coordinates (x, y, z) for each atom.
- `std::vector<int> ao_to_atom`: maps each AO index  $\mu$  to the atom index  $A$  on which it is centered. This is crucial for building the core Hamiltonian and Fock matrices in a way that respects the CNDO/2 approximation (which works at the level of atoms rather than individual AO pairs).

### *Function #1: read\_xyz*

The function `read_xyz` reads an XYZ-style input file, where each line provides an atomic number and Cartesian coordinates. It:

- Reads the number of atoms.
- For each atom:
  - Converts the atomic number (1, 6, 7, 8, 9) to the corresponding element symbol ("H", "C", "N", "O", "F").
  - Stores the symbol in `element_symbols`.
  - Stores the position vector in `atom_positions`.
  - Exits with an error if an unsupported element is encountered.

#### *Function #2: build\_ao\_to\_atom*

CNDO/2 treats hydrogen as having a single valence s orbital and second-row atoms (C, N, O, F) as having one s and three p orbitals. `build_ao_to_atom`:

- Iterates over atoms.
- Assigns:
  - 1 AO for H atoms.
  - 4 AOs (1 s + 3 p) for heavier atoms.
  - Fills `ao_to_atom` so that each AO index  $\mu$  can be traced back to its parent atom A.

This mapping is later used to accumulate on-atom densities and to look up the correct AtomParam values for each AO.

#### *Function #3: build\_basis*

This function builds the full list of contracted atomic orbitals for the molecule:

- For each atom in `element_symbols` and `atom_positions`:
  - If the atom is hydrogen:
    - Create a single s-type `Basis_components` centered at the atomic position.
    - Fill its exponents and coeffs from `sto3g_s["H"]`.
  - For heavier atoms:
    - Create one s-type AO, with exponents and coefficients from `sto3g_s[element]`.
    - Create three p-type AOs with  $(l,m,n) = (1,0,0), (0,1,0), (0,0,1)$ , with exponents and coefficients from `sto3g_p[element]`.
  - Return the vector of `Basis_components`, which defines the molecular basis.

#### *Function #4: normalize\_basis*

Each primitive Gaussian in a contracted AO must be normalized. `normalize_basis`:

- Loops over each `Basis_components` object.
- For each primitive (index k), computes the overlap of that primitive with itself using `calc_overlap`.
- Sets the normalization factor as  $N_k = 1/\sqrt{S_{kk}}$  and stores it in `norm_coeff`.

The normalized primitives are then used in the construction of the overlap matrix and in the  $\gamma$  integrals.

## *Overlap Matrix and Integral Utilities*

Three small helper lambdas (factorial, double factorial, binomial) implement standard combinatorial functions needed for Gaussian integrals:

- factorial – standard factorial  $n!$
- two\_factorial – double factorial  $n!!$
- binomial – binomial coefficient  $(nk)$

They are used inside the overlap integral implementation to evaluate the polynomial prefactors of Gaussian products.

### *Function #5: calc\_overlap*

calc\_overlap computes the overlap integral between two primitive Gaussians with given centers, exponents, and angular momentum powers  $(l,m,n)$ . Internally, it:

- Computes the Gaussian product center (“reduced position”) along each axis.
- Evaluates the exponential separation term for each axis.
- Performs the double sums over indices  $i$  and  $j$  with binomial coefficients and double factorials, enforcing the parity condition  $(i+j)$
- Multiplies the contributions along x, y, and z to obtain the full 3D overlap integral.

This low-level integral is reused for both normalization and construction of the AO overlap matrix.

### *Function #6: build\_S*

build\_S constructs the AO overlap matrix  $S_{\mu\nu}$ :

- Loops over all pairs of contracted AOs  $(\mu, \nu)$ .
- For each pair, double-loops over the three primitives in each contraction ( $k$  in  $\mu$ ,  $l$  in  $\nu$ ).
  - For each primitive pair:
  - Calls calc\_overlap with the appropriate centers, exponents, and angular momenta.
  - Multiplies by the contraction coefficients and normalization factors:
    - $S_{\mu\nu} += d_{\mu k} d_{\nu l} N_{\mu k} N_{\nu l} S_{kl}$

$$S_{\mu\nu} += d_{\mu k} d_{\nu l} N_{\mu k} N_{\nu l} S_{kl}$$

- Returns the full overlap matrix as an arma::mat.

In the main program, small elements (below 1e-10) are set to zero for numerical cleanliness before further use.

## *CNDO/2 $\gamma$ Integrals and Auxiliary Functions*

The CNDO/2 method replaces full four center electron repulsion integrals with a simplified set of effective Coulomb interactions  $\gamma_{AB}$  between atoms A and B. In this code,  $\gamma_{AB}$  is computed from STO-3G-like s-type basis functions.

- calculate\_sigma: Computes the combined exponent parameter (add equation) used in the CNDO/2  $\gamma$  integral.
- calculate\_V\_squared: Equation 9.
- calculate\_T: Forms the dimensionless quantity, Equation 10.
- calculate\_UA: Computes Equation 11.
- calculate\_primitive\_nonzero: Evaluates the primitive contribution for non-zero inter-atomic separation, using Equation 12.
- calculate\_primitive\_zero: Provides a finite limit for the  $RAB \rightarrow 0$  when  $RAB$  is not equal to 0 (Equation 13) or  $RAB \rightarrow 0$  case to avoid division by zero, using Equation 14.

### *Function #7: calculate\_gamma*

calculate\_gamma computes the effective Coulomb interaction  $\gamma_{AB}$  between atoms A and B:

- Retrieves the nuclear positions  $RA$  and  $RB$ , and the contracted s-type basis sets from sto3g\_s.
- Computes the inter-atomic distance  $RAB$  and its square.
- Performs a four-fold sum over s-type primitives on atom A ( $k, k'$ ) and atom B ( $l, l'$ ):
  - Builds normalization factors for each primitive.
  - Evaluates  $\sigma_A, \sigma_B, U_A, U_B, V^2$ , and  $T$ .
  - Uses either calculate\_primitive\_nonzero or calculate\_primitive\_zero depending on whether  $RAB$  is effectively zero.
  - Accumulates the primitive contributions weighted by the product of contraction and normalization coefficients.
- Converts the result from Hartree to eV by multiplying with AU\_back\_EV.

The resulting  $\gamma_{AB}$  values are stored in a matrix gamma\_matrix(A,B) and reused when building both the core Hamiltonian and the Fock matrices.

## *Core Hamiltonian and Fock Matrix Construction*

### *Function #8: make\_core\_hamiltonian*

The core Hamiltonian  $H_{\mu\nu}^{\text{core}}$  contains the one-electron terms and the purely nuclear contributions in the CNDO/2 approximation.

- Precompute on-site  $\gamma_{AA}$

- For each atom A, compute  $\gamma_{AA}[A] = \text{calculate\_gamma}(A, A)$ .
- Diagonal elements ( $\mu = v$ )
  - Determine the parent atom A of AO  $\mu$  using `ao_to_atom[mu]`.
  - Retrieve the element symbol and corresponding AtomParam.
  - Determine whether the AO is s- or p-type from  $l+m+n$  and choose the appropriate orbital parameter:
    - s orbital: `Ip_plus_Ap_over_2`
    - p orbital: `Ip_plus_Ap_p_over_2`
  - Form the diagonal term using CNDO/2 expressions:
    - Start with  $-1/2(I_p + A_p)$  (stored as `-half_IplusA`)
    - Subtract self-interaction and interactions with other nuclei using  $\gamma_{AA}$  and  $\gamma_{AC}$  and the effective charges  $Z^*$
    - Store the result in `core_ham(mu, mu)`.
- Off-diagonal elements ( $\mu \neq v$ )
  - For AO  $\mu$  on atom A and AO  $v$  on atom B:
    - Retrieve  $\beta_A$  and  $\beta_B$  from `cndo_parameters`.
    - Use the CNDO/2 formula for resonance terms:  $H_{\mu\nu}^{\text{core}} = 1/2(\beta_A + \beta_B)S_{\mu\nu}$ 
      - Implemented as  $\text{core\_ham}(\mu, \nu) = 0.5 * (\beta_A + \beta_B) * \text{overlap\_matrix}(\mu, \nu)$ .

The resulting `core_ham` matrix is used both during SCF and in the final energy evaluation.

#### *Function #9: build\_fock*

- On-atom electron populations
  - For each atom A, sum the diagonal elements of the total density matrix `total_density` over all AOs centered on A to obtain  $PAA$ . This is stored in `pAA[A]`.
- Diagonal elements ( $\mu = v$ )
  - For AO  $\mu$  on atom A:
    - Look up the appropriate orbital parameter (s vs p) from AtomParam.
    - Use the precomputed on-atom population `pAA[A]`, the effective charge  $Z^*$ , and `calculate_gamma(A, A)` to form on-site Coulomb and exchange contributions.
    - Add contributions from all other atoms C via  $(p_{AA}[C] - Z_C^*)\gamma_{AC}$

- Subtract a spin-dependent term proportional to the diagonal of the spin density matrix, implementing the CNDO/2 exchange contribution
- Off-diagonal elements ( $\mu \neq \nu$ )
  - For AO  $\mu$  on atom A and AO  $\nu$  on atom B:
    - Compute a resonance term using the average of  $\beta_A$  and  $\beta_B$  and the overlap  $S_{\mu\nu}$ .
    - Add a Coulomb term proportional to  $-P^{\text{spin}}_{\mu\nu}\gamma_{AB}$ , where  $\text{spin\_density}(\mu, \nu)$  is the appropriate spin density ( $\alpha$  or  $\beta$ ).

This function is called separately with (Ptot, Palpha, ...) and (Ptot, Pbeta, ...) to build Falpha and Fbeta.

## *SCF Procedure*

The SCF cycle iteratively refines the density matrices until the Fock matrix and the density are consistent.

1. Initialization
  - a. Build the basis: `basis_functions = build_basis()`
  - b. Normalize primitives: `normalize_basis(basis_functions)`
  - c. Construct overlap: `overlap_matrix = build_S(basis_functions)`
  - d. Build AO–atom map: `build_ao_to_atom(element_symbols)`
  - e. Initialize density matrices to zero
  - f. Build an initial Fock for each spin using `build_fock`.
2. Iterative loop
  - a. The SCF loop runs until either convergence is achieved or a maximum iteration count (`max_iterations = 100`) is reached
  - b. Build Fock matrices
  - c. Conduct diagonalization for each spin. The eigenvalues (orbital energies) are sorted and the corresponding eigenvectors (MO coefficients) are reordered accordingly.
  - d. Update density with new density matrices are built by occupying the lowest-energy molecular orbitals. The total density is  $P_{\text{tot\_new}} = P_{\text{alpha\_new}} + P_{\text{beta\_new}}$ .
3. Convergence check
  - a. The maximum absolute change in the density matrices is computed
  - b. If  $\text{convergence\_value} < \text{convergence\_threshold}$  (set to  $10^{-6}$ ), the SCF is considered converged.
  - c. If not converged, set  $P_{\text{alpha}} = P_{\text{alpha\_new}}$   $P_{\text{beta}} = P_{\text{beta\_new}}$ ;  $P_{\text{tot}} = P_{\text{tot\_new}}$ ; and repeat.

#### 4. Final diagonalization

- a. After convergence, final Fock matrices are built and diagonalized once more to obtain the converged molecular orbital energies and coefficients for  $\alpha$  and  $\beta$  spins (final\_Ea, final\_Eb, final\_Ca, final\_Cb).

#### *CNDO/2 Energy Evaluation*

Once the SCF converges, then the final energy is calculated as the sum of the electronic energy calculated with the converged density matrices and Fock matrices and the nuclear energy using effective nuclear charge and interatomic distances.

## Equations ( in Latex for Readability below)

### Hartree–Fock and SCF

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (1)$$

$$P_{\mu\nu}^{\alpha} = \sum_{i \in \text{occ } \alpha} C_{\mu i}^{\alpha} C_{\nu i}^{\alpha} \quad (2)$$

$$P_{\mu\nu}^{\beta} = \sum_{i \in \text{occ } \beta} C_{\mu i}^{\beta} C_{\nu i}^{\beta} \quad (3)$$

$$P_{\mu\nu} = P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta} \quad (4)$$

### CNDO2 Fock Matrix

$$F_{\mu\mu} = -\left(\frac{I_A + A_A}{2}\right) + (P_{AA} - Z_A)\gamma_{AA} - \left(P_{\mu\mu}^{\text{spin}} - \frac{1}{2}\right)\gamma_{AA} + \sum_{C \neq A} (P_{CC} - Z_C)\gamma_{AC} \quad (5)$$

$$F_{\mu\nu} = \frac{1}{2}(\beta_A + \beta_B)S_{\mu\nu} - P_{\mu\nu}^{\text{spin}}\gamma_{AB}, \quad \mu \neq \nu \quad (6)$$

### Overlap Integrals

$$S_{\mu\nu} = \int g_{\mu}(\mathbf{r})g_{\nu}(\mathbf{r}) d\mathbf{r} \quad (7)$$

$$S_{\mu\nu} = \sum_{k,l} c_{\mu k} c_{\nu l} N_{\mu k} N_{\nu l} S_{kl} \quad (8)$$

### CNDO2 $\gamma$ gamma Integrals

$$\sigma = \frac{1}{\alpha_k + \alpha_{k'}} \quad (9)$$

$$V^2 = \frac{1}{\sigma_A + \sigma_B} \quad (10)$$

$$T = V^2 R_{AB}^2 \quad (11)$$

$$U_A = (\pi\sigma_A)^{3/2} \quad (12)$$

$$\gamma_{AB}^{\text{prim}} = U_A U_B \frac{\text{erf}(\sqrt{T})}{R_{AB}} \quad (13)$$

$$\gamma_{AA}^{\text{prim}} = U_A U_B \frac{2\sqrt{V^2}}{\sqrt{\pi}} \quad (14)$$

## HOMO LUMO Energy Gap

$$\Delta E_{\text{gap}} = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \quad (15)$$

$$\varepsilon_{\text{HOMO}} = \max(\varepsilon_{\text{HOMO}}^{\alpha}, \varepsilon_{\text{HOMO}}^{\beta}) \quad (16)$$

$$\varepsilon_{\text{LUMO}} = \min(\varepsilon_{\text{LUMO}}^{\alpha}, \varepsilon_{\text{LUMO}}^{\beta}) \quad (17)$$

## Molecular Dipole Moment

$$\boldsymbol{\mu}_{\text{elec}} = \text{Tr}(\mathbf{PD}) \quad (18)$$

$$\mu_x = \sum_{\mu\nu} P_{\mu\nu} D_{\mu\nu}^x \quad (19)$$

$$\boldsymbol{\mu}_{\text{nuc}} = \sum_A Z_A^* \mathbf{R}_A \quad (20)$$

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{\text{nuc}} - \boldsymbol{\mu}_{\text{elec}} \quad (21)$$

$$|\boldsymbol{\mu}| = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (22)$$

## Contributions

- Ariel
  - Mid-Progress Slides (~60%)
  - Final Presentation (~40%)
  - Written Report (~50%)
  - Band Gap Implementation (100%)
- Shree
  - Mid-Progress Slides (~40%)
  - Final Presentation (~60%)
  - Written Report (~50%)
  - Molecular Dipole Implementation (100%)

## Works Cited:

- Amusia, M. Ya., et al. *Atomic Photoeffect*. Springer, 2004.
- Dewar, Michael J. S., and Walter Thiel. "Ground States of Molecules. 38. The MNDO Method. Approximations and Parameters." *Journal of the American Chemical Society*, vol. 99, no. 15, 1977, pp. 4899–4907, <https://doi.org/10.1021/ja00457a004>
- Jain, Mayank, James R. Chelikowsky, and Steven G. Louie. "Reliability of Hybrid Functionals in Predicting Band Gaps." *Physical Review Letters*, vol. 107, no. 21, 2011, article 216806, <https://doi.org/10.1103/PhysRevLett.107.216806>
- National Institute of Standards and Technology. *Computational Chemistry Comparison and Benchmark Database (CCCBDB)*, <https://cccbdb.nist.gov/>. Accessed 2025
- National Institute of Standards and Technology. NIST Chemistry WebBook, <https://webbook.nist.gov/chemistry>, Accessed 2025.
- Szabo, Attila, and Neil S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications, 1996.
- .