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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 H_2, the calculated dipole moment is 0.00 D; for HF, it is 1.62 D; for H_2O, it is 1.16 D; for HO, it is 1.47 D; for CH_4, it's 0.00 D; and for propynol, it's 141.16 D. The calculated HOMO–LUMO energy gaps are: H_2, 27.39 eV; HF, 30.25 eV; H_2O, 33.70 eV; HO, 22.24 eV; 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, $E_{LUMO-HOMO}$ and the molecular dipole moment μ. 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 (H_2), Hydrogen Fluoride (HF), and Hydroxyl (OH)

- Small Polyatomics: Water (H_2O) and Methane (CH_4)

- Larger System: Propynol (C_3H_4O)

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 $E_{LUMO-HOMO}$ 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 ($E_{LUMO-HOMO} = E_{LUMO} - E_{HOMO}$). 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 α and β 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 α and β spin channels. Orbital occupation is then assigned based on the number of α and β electrons specified in the input:

1. The lowest num_alpha orbitals are occupied in the α channel

2. The lowest num_beta orbitals are occupied in the β 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_HOMO^α, E_HOMO^β)

- LUMO energy = min(E_LUMO^α, E_LUMO^β)

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 α and β 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 α and β 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. $\mu\_elec,x = Tr(P \cdot Dx)$, 2. $\mu\_elec,y = Tr(P \cdot Dy)$, 3. $\mu\_elec,z = Tr(P \cdot Dz)$

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:

$\mu\_nuc = \Sigma\_A Z^*\_A R\_A$

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	Diple Moment (Debye)	Literature Value (Debye)
H2	0.00	0.00
HF	1.62	1.83
H2O	1.16	1.85
HO	1.47	1.66
CH4	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 α and β Fock matrices by identifying the highest occupied and lowest unoccupied molecular orbitals based on the total electron count. As expected for closed shell systems, α and β 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_2, HF, and H_2O 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) *Experimental gaps vary by definition and measurement*
H2	27.39	Very Large, ~15.4
HF	30.25	Large, ~16
H2O	33.70	Large, ~12.6

HO	22.24	Medium, ~11.3
CH4	14.13	Med. - Large, ~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_2 and CH_4 correctly exhibit zero dipole moments, while polar bonds and electronegativity differences lead to nonzero dipoles in HF, H_2O, 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 μ 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 μ 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 γ 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 (μ, ν).

- For each pair, double-loops over the three primitives in each contraction (k in μ, l in ν).

    - For each primitive pair:

    - Calls calc_overlap with the appropriate centers, exponents, and angular momenta.

    - Multiplies by the contraction coefficients and normalization factors:

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

    - 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 γ Integrals and Auxiliary Functions

The CNDO/2 method replaces full four center electron repulsion integrals with a simplified set of effective Coulomb interactions γ_AB between atoms A and B. In this code, γ_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 γ 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→0 when RAB is not equal to 0 (Equation 13) or RAB→0 case to avoid division by zero, using Equation 14.

Function #7: calculate_gamma

calculate_gamma computes the effective Coulomb interaction γ_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 σ_A, σ_B, U_A, U_B, V², 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 γ_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 $H_{\mu v}^{core}$ contains the one-electron terms and the purely nuclear contributions in the CNDO/2 approximation.

- Precompute on-site γ_AA

- ○ For each atom A, compute gamma_AA[A] = calculate_gamma(A, A).

- Diagonal elements ($\mu = \nu$)

  - ○ Determine the parent atom A of AO μ 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 γ_AA and γ_AC and the effective charges Z*

    - ■ Store the result in core_ham(mu, mu).

- Off-diagonal elements ($\mu \neq \nu$)

  - ○ For AO μ on atom A and AO ν on atom B:

    - ■ Retrieve β_A and β_B from cndo_parameters.

    - ■ Use the CNDO/2 formula for resonance terms: $H_{\mu\nu}^{core}=1/2(\beta_A+\beta_B)S_{\mu\nu}$

      - ● Implemented as core_ham(mu, nu) = 0.5 * (beta_A + beta_B) * 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 ($\mu = \nu$)

  - ○ For AO μ 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 μ on atom A and AO ν on atom B:

    ■ Compute a resonance term using the average of β_A and β_B and the overlap S_$\mu\nu$.

    ■ Add a Coulomb term proportional to $-P^{spin}_{\mu\nu}\gamma_{AB}$, where spin_density(mu,nu) is the appropriate spin density (α or β).

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 Ptot_new = Palpha_new + Pbeta_new.

3. Convergence check

   a. The maximum absolute change in the density matrices is computed

   b. If convergence_value < convergence_threshold (set to 10^{-6}), the SCF is considered converged.

   c. If not converged, set Palpha = Palpha_new Pbeta = Pbeta_new; Ptot = Ptot_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 α and β 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

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{1}$$

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

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

$$P_{\mu\nu} = P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta} \tag{4}$$

CNDO2 Fock Matrix

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

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

Overlap Integrals

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

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

CNDO2 γgamma Integrals

$$\sigma = \frac{1}{\alpha_k + \alpha_{k'}} \tag{9}$$

$$V^2 = \frac{1}{\sigma_A + \sigma_B} \tag{10}$$

$$T = V^2 R_{AB}^2 \tag{11}$$

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

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

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

HOMO LUMO Energy Gap

$$\Delta E_{\text{gap}} = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \tag{15}$$

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

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

Molecular Dipole Moment

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

$$\mu_x = \sum_{\mu\nu} P_{\mu\nu} D^x_{\mu\nu} \tag{19}$$

$$\boldsymbol{\mu}_{\text{nuc}} = \sum_A Z^{\star}_A \mathbf{R}_A \tag{20}$$

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{\text{nuc}} - \boldsymbol{\mu}_{\text{elec}} \tag{21}$$

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

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%)

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