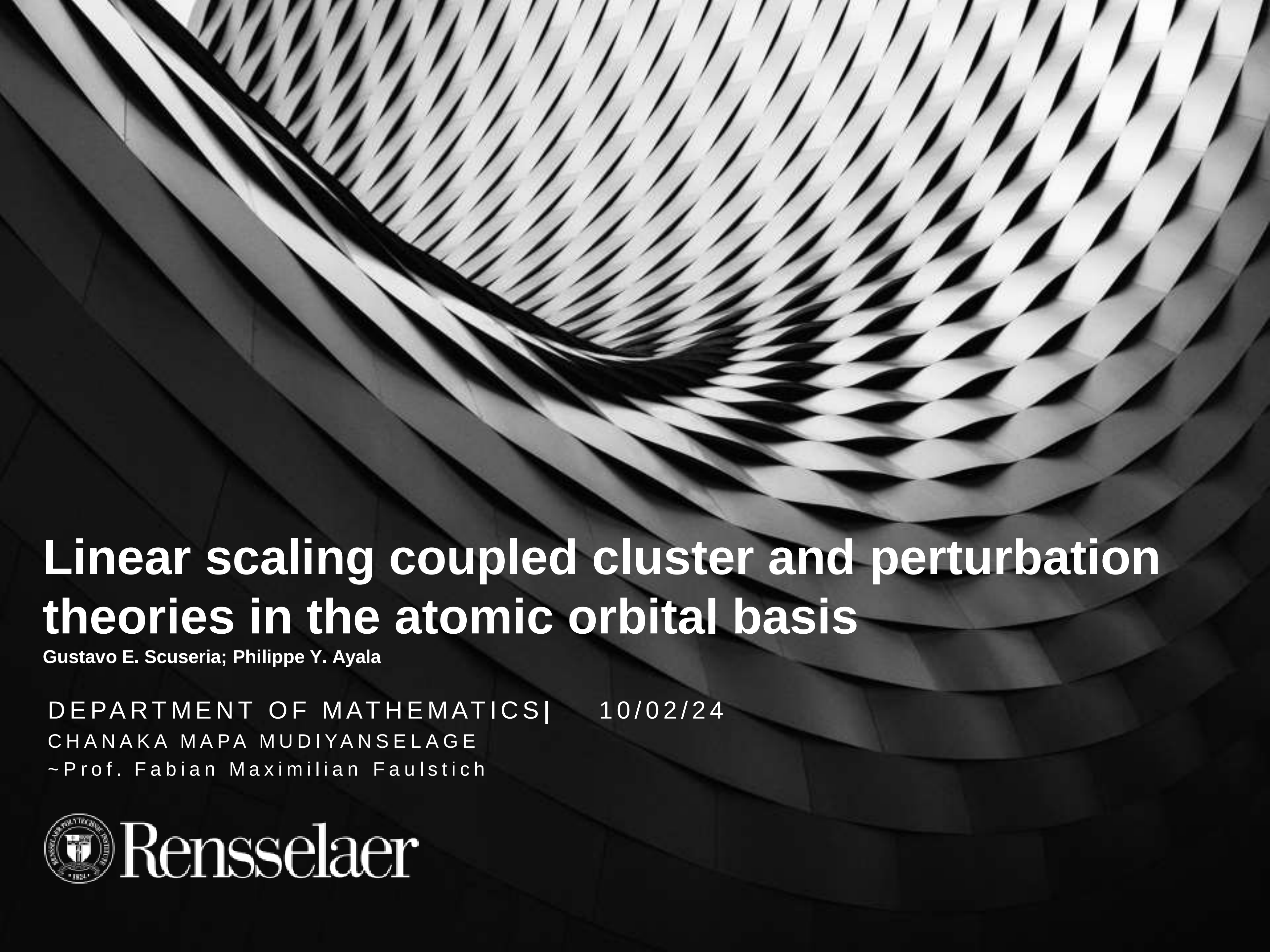

Linear scaling coupled cluster and perturbation theories in the atomic orbital basis

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Key details

- **Objective**: Reformulate the coupled cluster (CC) and perturbation theories in the atomic orbital (AO) basis to achieve **linear scaling** in computational cost.
- **Motivation**: Traditional methods scale **exponentially** with system size, limiting their use for large molecules.
- **Main Contribution**: Development of an AO-based CC algorithm that leverages the **decay properties** of integrals and excitation amplitudes to reduce the computational cost.

Abstract

- **Reformulation of CC Equations**: The coupled cluster (CC) equations are reformulated in the atomic orbital (AO) basis.
- **Linear Scaling Algorithm**: This reformulation results in a linear scaling algorithm, advantageous for handling large molecules.
- **Screening Process**: A screening process is used to neglect certain excitation amplitudes, maintaining target energy accuracy while optimizing performance.
- **Comparable Performance for Small Molecules**: Despite using the AO basis, this method performs comparably to traditional molecular orbital (MO) approaches for smaller molecules.

Abstract

- **Efficiency for Large Molecules**: For larger molecules, the decay properties of integrals and excitation amplitudes lead to linear scaling, overcoming the exponential scaling challenge of traditional high-level MO quantum chemistry calculations.
- **Benchmark Validation**: Benchmark calculations demonstrate the method’s efficiency and

Introduction

- **Linear Scaling Methods**:
- **MP2 Calculations**:
- **Extension to Coupled-Cluster Theory**:
- **Comparison to Localized MO Approaches**:
- **Quantum Locality and Mathematical Bounds**:

Theory

A. Coupled cluster theory in the atomic orbital basis
B. Comparison with alternative formulations
C. Computational cost and scaling prefactor considerations
D. The atomic orbital MP2 equations
E. Asymptotic behavior and screening of AO amplitudes

A. Coupled cluster theory in the atomic orbital basis

We will start from…

$$E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \omega_{ab}^{ij} t_{ij}^{ab}$$ - (a)

,where

$$\omega_{ab}^{ij} = 2\, v_{ab}^{ij} - v_{ba}^{ij}$$

$$v_{ab}^{ij} = \int i(1) j(2) \frac{1}{r_{12}} a(1) b(2) dr_1\, dr_2$$ - (b)

Indices i, j, k, l are occupied MOs and a, b, c, d are virtual Mos.

A. Coupled cluster theory in the atomic orbital basis

MO basis are obtained by transformation from the atomic orbital ~AO! Basis

$$V^{ij}_{ab} = c_{\mu i} c_{\nu j} c_{\lambda a} c_{\sigma b} V^{\mu\nu}_{\lambda\sigma} \qquad \text{-(c)}$$

The c coefficients determine the linear combination of AOs that constitute the MOs and provide a transformation from a nonorthogonal ~AO! to an orthogonal representation ~MO!

In the HF case, the c coefficients are simply the eigenvectors of the Fock matrix f and;

$$\bar{c}_{\mu i} = S^{\alpha}_{\mu} c_{\alpha i}$$

$$c_{\mu p} \bar{c}_{\mu q} = c_{\mu p} S^{\alpha}_{\mu} c_{\alpha q} = \delta_{pq}$$

where S is the overlap matrix between AO basis functions.

A. Coupled cluster theory in the atomic orbital basis

We also need for later use the AO one-particle density matrix (P) of the reference state, its complementary projector (Q), and related projectors:

$$P_\mu^\nu = c_{\mu i} c_{\nu i},$$

$$Q_\mu^\nu = c_{\mu a} c_{\nu a},$$

$$\overline{P}_\mu^\nu = S_\mu^\alpha P_\alpha^\nu = \overline{c}_{\mu i} c_{\nu i},$$

$$\overline{Q}_\sigma^\lambda = S_\alpha^\lambda Q_\sigma^\alpha = \overline{c}_{\lambda a} c_{\sigma a}.$$

P and Q are idempotent and orthogonal through the overlap matrix

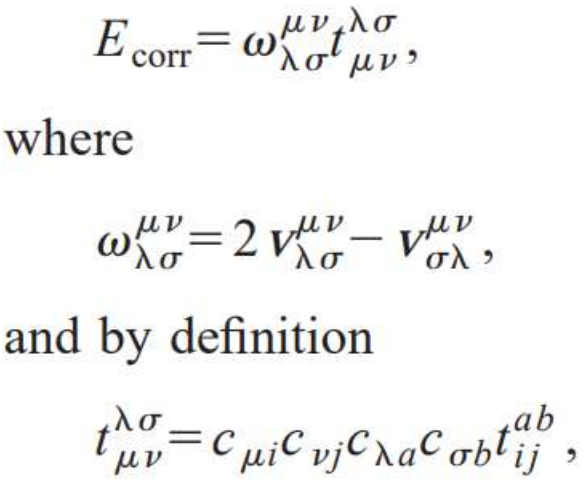
$$PSP = P,\quad QSQ = Q,\quad PSQ = 0,\quad P + Q = S^{-1},$$

whereas $\overline{P}$ and $\overline{Q}$ are not symmetric and satisfy

$$\overline{PP} = \overline{P},\quad \overline{QQ} = \overline{Q},\quad \overline{PQ} = 0,\quad \overline{P} + \overline{Q} = \hat{I}.$$

A. Coupled cluster theory in the atomic orbital basis

In order to write the correlation energy in the AO basis, one can simply replace equation ~(c) in equation ~(a) and use ~(b) to obtain



$$E_{\text{corr}} = \omega^{\mu\nu}_{\lambda\sigma} t^{\lambda\sigma}_{\mu\nu},$$

where

$$\omega^{\mu\nu}_{\lambda\sigma} = 2\, v^{\mu\nu}_{\lambda\sigma} - v^{\mu\nu}_{\sigma\lambda},$$

and by definition

$$t^{\lambda\sigma}_{\mu\nu} = c_{\mu i} c_{\nu j} c_{\lambda a} c_{\sigma b} t^{ab}_{ij},$$

-(d)

A. Coupled cluster theory in the atomic orbital basis

The MO t_{ijab} amplitudes can be recovered from the $t_{\mu\nu\lambda\sigma}$ amplitudes using the inverse transformation

$$t_{ij}^{ab} = \overline{c}_{\mu i}\overline{c}_{\nu j}\overline{c}_{\lambda a}\overline{c}_{\sigma b}t_{\mu\nu}^{\lambda\sigma} \qquad \text{-(e)}$$

The most convenient AO representation for large molecules is the one given by

$$E_{\mathrm{corr}} = \Pi_{\lambda\sigma}^{\mu\nu}\theta_{\mu\nu}^{\lambda\sigma} = \pi_{\lambda\sigma}^{\mu\nu}\Theta_{\mu\nu}^{\lambda\sigma},$$

where

$$\Pi_{\lambda\sigma}^{\mu\nu} = 2\,\pi_{\lambda\sigma}^{\mu\nu} - \pi_{\sigma\lambda}^{\mu\nu},$$

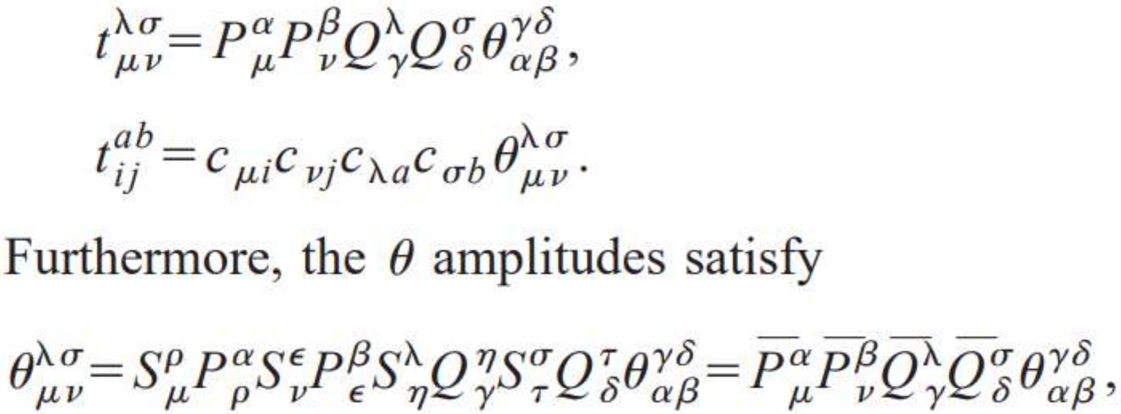
$$\Theta_{\mu\nu}^{\lambda\sigma} = 2\,\theta_{\mu\nu}^{\lambda\sigma} - \theta_{\mu\nu}^{\sigma\lambda}$$

And $$\theta_{\mu\nu}^{\lambda\sigma} = S_{\mu}^{\alpha}S_{\nu}^{\beta}S_{\gamma}^{\lambda}S_{\delta}^{\sigma}t_{\alpha\beta}^{\gamma\delta} = \overline{c}_{\mu i}\overline{c}_{\nu j}\overline{c}_{\lambda a}\overline{c}_{\sigma b}t_{ij}^{ab}, \qquad \text{-(f)}$$

$$\pi_{\lambda\sigma}^{\mu\nu} = P_{\alpha}^{\mu}P_{\beta}^{\nu}v_{\gamma\delta}^{\alpha\beta}Q_{\lambda}^{\gamma}Q_{\sigma}^{\delta}$$

A. Coupled cluster theory in the atomic orbital basis

Note also that because of the symmetry of the t_{ijab} amplitudes, $\theta_{\mu\nu\lambda\sigma} = \theta_{\nu\mu\sigma\lambda}$. Of course, all sets of excitation amplitudes are connected; besides ~(d), ~(e), and ~(f), we also have



$$t^{\lambda\sigma}_{\mu\nu} = P^{\alpha}_{\mu} P^{\beta}_{\nu} Q^{\lambda}_{\gamma} Q^{\sigma}_{\delta} \theta^{\gamma\delta}_{\alpha\beta},$$

$$t^{ab}_{ij} = c_{\mu i} c_{\nu j} c_{\lambda a} c_{\sigma b} \theta^{\lambda\sigma}_{\mu\nu}.$$

Furthermore, the θ amplitudes satisfy

$$\theta^{\lambda\sigma}_{\mu\nu} = S^{\rho}_{\mu} P^{\alpha}_{\rho} S^{\epsilon}_{\nu} P^{\beta}_{\epsilon} S^{\lambda}_{\eta} Q^{\eta}_{\gamma} S^{\sigma}_{\tau} Q^{\tau}_{\delta} \theta^{\gamma\delta}_{\alpha\beta} = \overline{P}^{\alpha}_{\mu} \overline{P}^{\beta}_{\nu} \overline{Q}^{\lambda}_{\gamma} \overline{Q}^{\sigma}_{\delta} \theta^{\gamma\delta}_{\alpha\beta},$$

A. Coupled cluster theory in the atomic orbital basis

We next write the CC equations in the AO basis by transformation from the MO basis. For the closed-shell case, the t_{ijab} amplitudes satisfy

$$Z_{ij}^{ab} = v_{ij}^{ab} + v_{ij}^{kl} t_{kl}^{ab} + v_{cd}^{ab} t_{ij}^{cd} + v_{cd}^{kl} t_{ij}^{cd} t_{kl}^{ab} + \Omega_{ij}^{ab} [g_c^a t_{ij}^{cb} - g_i^k t_{kj}^{ab}$$

$$+ j_{ic}^{ak} (2 t_{kj}^{cb} - t_{kj}^{bc}) - k_{ic}^{ka} t_{kj}^{cb} - k_{ic}^{kb} t_{kj}^{ac}] = 0$$

Note that in this equation i, j,a, and b are ‘‘external’’ ~i.e., uncontracted! indices.

- Contraction, external, internal indices???
- What is Ω ???

A. Coupled cluster theory in the atomic orbital basis

The intermediates in above equation are

$$g_i^k = f_i^k + \omega_{cd}^{kl} t_{il}^{cd} \, ,$$

$$g_c^a = f_c^a - \omega_{cd}^{kl} t_{kl}^{ad} \, ,$$

$$j_{ic}^{ak} = v_{ic}^{ak} - \tfrac{1}{2} v_{cd}^{kl} t_{il}^{da} + \tfrac{1}{2} \omega_{cd}^{kl} t_{il}^{ad} \, ,$$

$$k_{ic}^{ka} = v_{ic}^{ka} - \tfrac{1}{2} v_{dc}^{kl} t_{il}^{da} \, ,$$

where f is the Fock matrix.

A. Coupled cluster theory in the atomic orbital basis

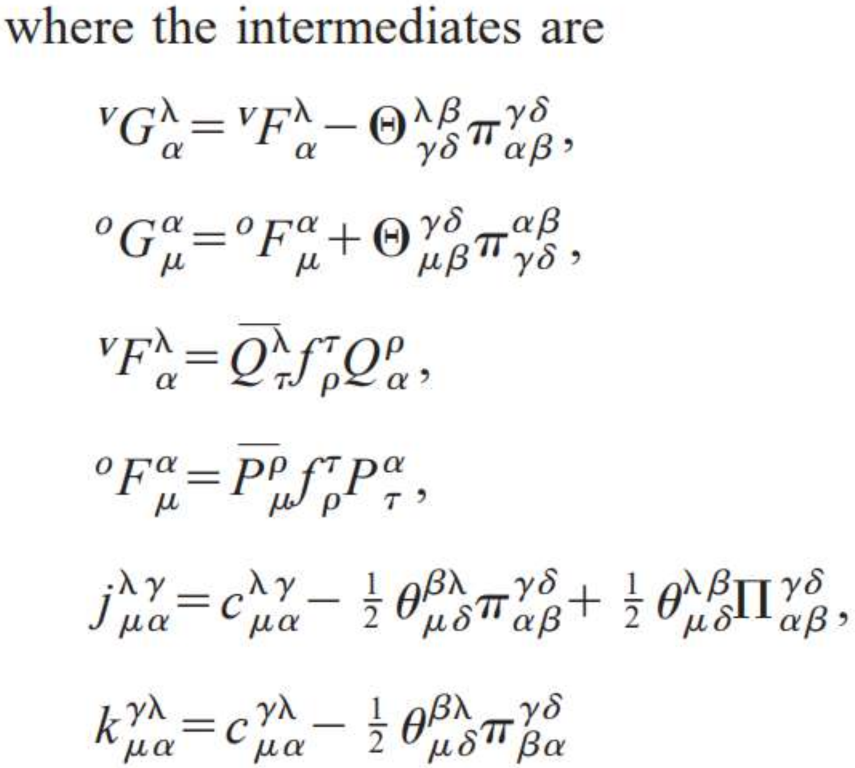
We present below the CC equations in the AO basis for $\theta_{\mu\nu\lambda\sigma}$ amplitudes. The algebraic manipulations to derive these equations are simple. First, we contract Z_{ijab} with c coefficients and overlap matrices to yield an AO doubles equation:

$$Z^{\lambda\sigma}_{\mu\nu} = \bar{c}_{\mu i} \bar{c}_{\nu j} \bar{c}_{\lambda a} \bar{c}_{\sigma b} Z^{ab}_{ij} = 0$$

The resulting equation for the $\theta_{\mu\nu\lambda\sigma}$ amplitudes is

$$\begin{aligned}
&d^{\lambda\sigma}_{\mu\nu} + a^{\alpha\beta}_{\mu\nu}\theta^{\lambda\sigma}_{\alpha\beta} + \theta^{\alpha\beta}_{\mu\nu} b^{\lambda\sigma}_{\alpha\beta} + \theta^{\alpha\beta}_{\mu\nu}\pi^{\gamma\delta}_{\alpha\beta}\theta^{\lambda\sigma}_{\gamma\delta}, \\
&\quad + \Omega^{\lambda\sigma}_{\mu\nu}[{}^{v}G^{\lambda}_{\alpha}\theta^{\alpha\sigma}_{\mu\nu} - {}^{o}G^{\alpha}_{\mu}\theta^{\lambda\sigma}_{\alpha\nu} + j^{\lambda\gamma}_{\mu\alpha}\Theta^{\alpha\sigma}_{\gamma\nu} - k^{\gamma\lambda}_{\mu\alpha}\theta^{\alpha\sigma}_{\gamma\nu} \\
&\quad - k^{\gamma\sigma}_{\mu\alpha}\theta^{\lambda\alpha}_{\gamma\nu}] = 0,
\end{aligned}$$

A. Coupled cluster theory in the atomic orbital basis



where the intermediates are

$$^{v}G_{\alpha}^{\lambda} = {}^{v}F_{\alpha}^{\lambda} - \Theta_{\gamma\delta}^{\lambda\beta}\pi_{\alpha\beta}^{\gamma\delta},$$

$$^{o}G_{\mu}^{\alpha} = {}^{o}F_{\mu}^{\alpha} + \Theta_{\mu\beta}^{\gamma\delta}\pi_{\gamma\delta}^{\alpha\beta},$$

$$^{v}F_{\alpha}^{\lambda} = \overline{Q}_{\tau}^{\lambda} f_{\rho}^{\tau} Q_{\alpha}^{\rho},$$

$$^{o}F_{\mu}^{\alpha} = \overline{P}_{\mu}^{\rho} f_{\rho}^{\tau} P_{\tau}^{\alpha},$$

$$j_{\mu\alpha}^{\lambda\gamma} = c_{\mu\alpha}^{\lambda\gamma} - \tfrac{1}{2}\theta_{\mu\delta}^{\beta\lambda}\pi_{\alpha\beta}^{\gamma\delta} + \tfrac{1}{2}\theta_{\mu\delta}^{\lambda\beta}\Pi_{\alpha\beta}^{\gamma\delta},$$

$$k_{\mu\alpha}^{\gamma\lambda} = c_{\mu\alpha}^{\gamma\lambda} - \tfrac{1}{2}\theta_{\mu\delta}^{\beta\lambda}\pi_{\beta\alpha}^{\gamma\delta}$$

A. Coupled cluster theory in the atomic orbital basis

and fours sets of transformed AO two-electron integrals are needed

$$a^{\alpha\beta}_{\mu\nu} = \overline{P}^{\rho}_{\mu}\overline{P}^{\epsilon}_{\nu} v^{\eta\tau}_{\rho\epsilon} P^{\alpha}_{\eta} P^{\beta}_{\tau},$$

$$b^{\lambda\sigma}_{\alpha\beta} = Q^{\rho}_{\alpha} Q^{\epsilon}_{\beta} v^{\eta\tau}_{\rho\epsilon} \overline{Q}^{\lambda}_{\eta} \overline{Q}^{\sigma}_{\tau},$$

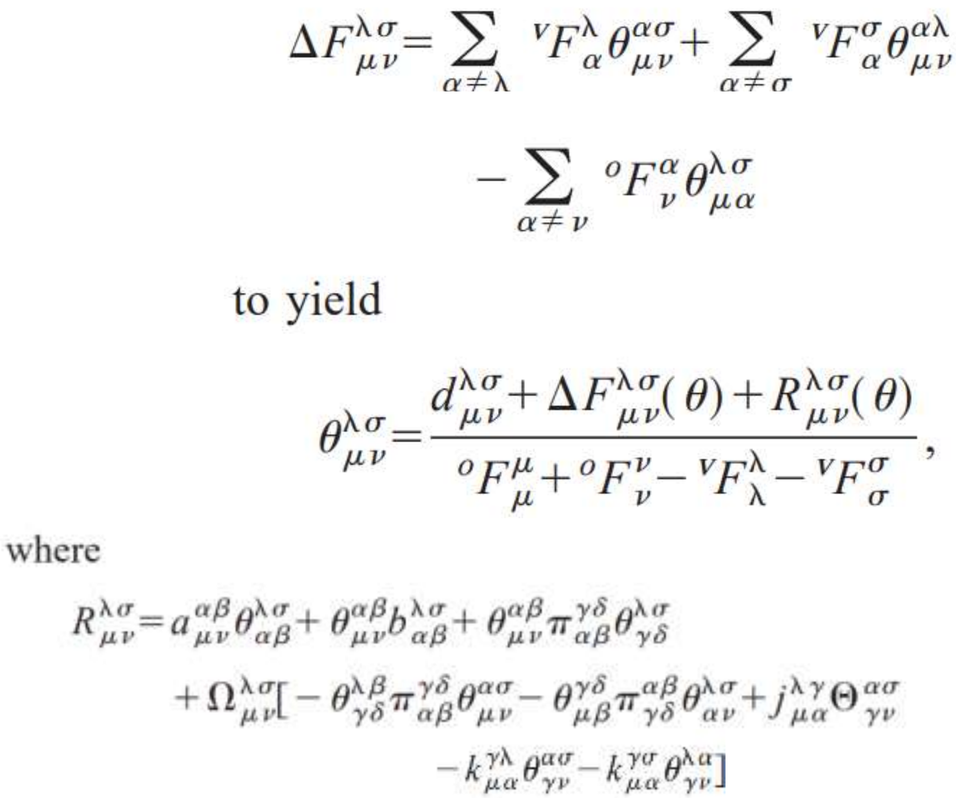
$$c^{\gamma\lambda}_{\mu\alpha} = \overline{P}^{\rho}_{\mu} Q^{\epsilon}_{\alpha} v^{\eta\tau}_{\rho\epsilon} P^{\gamma}_{\eta} \overline{Q}^{\lambda}_{\tau},$$

$$d^{\lambda\sigma}_{\mu\nu} = \overline{P}^{\rho}_{\mu}\overline{P}^{\epsilon}_{\nu} v^{\eta\tau}_{\rho\epsilon} \overline{Q}^{\lambda}_{\eta} \overline{Q}^{\sigma}_{\tau}.$$

Note that $d_{\mu\nu\lambda\sigma}$ is related to $\pi_{\mu\nu\lambda\sigma}$ through overlap matrices.

A. Coupled cluster theory in the atomic orbital basis

The doubles equation in the AO basis can be solved iteratively after partitioning it in a manner similar to the MO case. In the four terms involving products of the Fock matrix, we simply separate the term containing $\theta_{\mu\nu\lambda\sigma}$ and define



$$\Delta F^{\lambda\sigma}_{\mu\nu} = \sum_{\alpha\neq\lambda} {}^{v}F^{\lambda}_{\alpha}\theta^{\alpha\sigma}_{\mu\nu} + \sum_{\alpha\neq\sigma} {}^{v}F^{\sigma}_{\alpha}\theta^{\alpha\lambda}_{\mu\nu} - \sum_{\alpha\neq\mu} {}^{o}F^{\alpha}_{\mu}\theta^{\lambda\sigma}_{\alpha\nu}$$

$$- \sum_{\alpha\neq\nu} {}^{o}F^{\alpha}_{\nu}\theta^{\lambda\sigma}_{\mu\alpha}$$

to yield

$$\theta^{\lambda\sigma}_{\mu\nu} = \frac{d^{\lambda\sigma}_{\mu\nu} + \Delta F^{\lambda\sigma}_{\mu\nu}(\theta) + R^{\lambda\sigma}_{\mu\nu}(\theta)}{{}^{o}F^{\mu}_{\mu} + {}^{o}F^{\nu}_{\nu} - {}^{v}F^{\lambda}_{\lambda} - {}^{v}F^{\sigma}_{\sigma}},$$

where

$$\begin{aligned} R^{\lambda\sigma}_{\mu\nu} = {} & a^{\alpha\beta}_{\mu\nu}\theta^{\lambda\sigma}_{\alpha\beta} + \theta^{\alpha\beta}_{\mu\nu}b^{\lambda\sigma}_{\alpha\beta} + \theta^{\alpha\beta}_{\mu\nu}\pi^{\gamma\delta}_{\alpha\beta}\theta^{\lambda\sigma}_{\gamma\delta} \\ & + \Omega^{\lambda\sigma}_{\mu\nu}[-\theta^{\lambda\beta}_{\gamma\delta}\pi^{\gamma\delta}_{\alpha\beta}\theta^{\alpha\sigma}_{\mu\nu} - \theta^{\gamma\delta}_{\mu\beta}\pi^{\alpha\beta}_{\gamma\delta}\theta^{\lambda\sigma}_{\alpha\nu} + j^{\lambda\gamma}_{\mu\alpha}\Theta^{\alpha\sigma}_{\gamma\nu} \\ & - k^{\gamma\lambda}_{\mu\alpha}\theta^{\alpha\sigma}_{\gamma\nu} - k^{\gamma\sigma}_{\mu\alpha}\theta^{\lambda\alpha}_{\gamma\nu}] \end{aligned}$$

B. Coupled cluster theory in the atomic orbital basis

- **Introduction**: Before diving further into the AO approach, it’s important to consider alternative methods developed by other researchers. These alternatives revolve around local and localized correlation techniques.
- **Key Alternatives**:
    - **MO-Based with Localized Orbitals**
    - **Mixed AO–MO Methods**

B. Coupled cluster theory in the atomic orbital basis

Alternative 1: Localized Molecular Orbitals (MO)

- **Concept**: Localize both **occupied** and **virtual** molecular orbitals (MOs) to reduce computational cost.
    - This is done by rotating the CC equations using unitary matrices that **localize the orbitals**.

- **Invariance of CC**: The CC theory is invariant to localization as long as occupied and virtual orbitals aren't mixed, so **localized and delocalized orbitals give the same energy**.

B. Coupled cluster theory in the atomic orbital basis

Methods to Achieve Localization

- **Approaches to Localize MOs**:
  - **Pseudodiagonalization**: This can help avoid diagonalizing large Hamiltonians in big systems but may not always work.
  - Example: For **diamond-like systems**, it has been challenging to localize orbitals via pseudodiagonalization.
- **Conclusion**: While feasible, **MO localization** comes with practical difficulties, especially in large systems.

Alternative 2: Mixed AO–MO Approaches

- **Concept**: Another approach is to **localize only the occupied orbitals** and retain the virtual orbitals in the AO basis.
  - This combines the benefits of **localized MOs** for occupied states with **atomic orbitals (AOs)** for the virtual space.

B. Coupled cluster theory in the atomic orbital basis

Localized MO Method: Benefits and Challenges

- **Benefit**: Localizing MOs allows for **neglecting excitations** between spatially distant orbitals, which makes negligible contributions to correlation energy.
- **Challenge**:
  - Localization depends on successful **localization procedures**.
  - For large molecules, localizing MOs becomes **computationally expensive**.
  - **Virtual orbitals** are harder to localize than occupied ones.
  - Errors from neglecting orbitals are hard to control.

B. Coupled cluster theory in the atomic orbital basis

Full AO Approach vs Mixed AO–MO

- **AO-Based Method**:
  - The proposed **full AO approach** does not rely on any molecular orbitals, making it unique.
  - All information about the system is contained in **PPP and QQQ** matrices, which project the **occupied and virtual spaces** in the AO basis.
- **Comparison**:
  - **Mixed AO–MO**: Still relies on some form of molecular orbitals for the occupied space.
  - **Full AO**: No MOs required, simplifying the process further.

Key Advantage of Full AO Approach

- **Scalability**: The AO approach achieves **O(N^2) scaling**, which can reduce to **O(N)** for large systems.
  - This makes the AO method highly efficient, even for large molecular systems.
- **Conclusion**: Even in small systems, the AO method is competitive with MO-based methods while avoiding the complexity of localization procedures.

C. Computational cost and scaling prefactor considerations

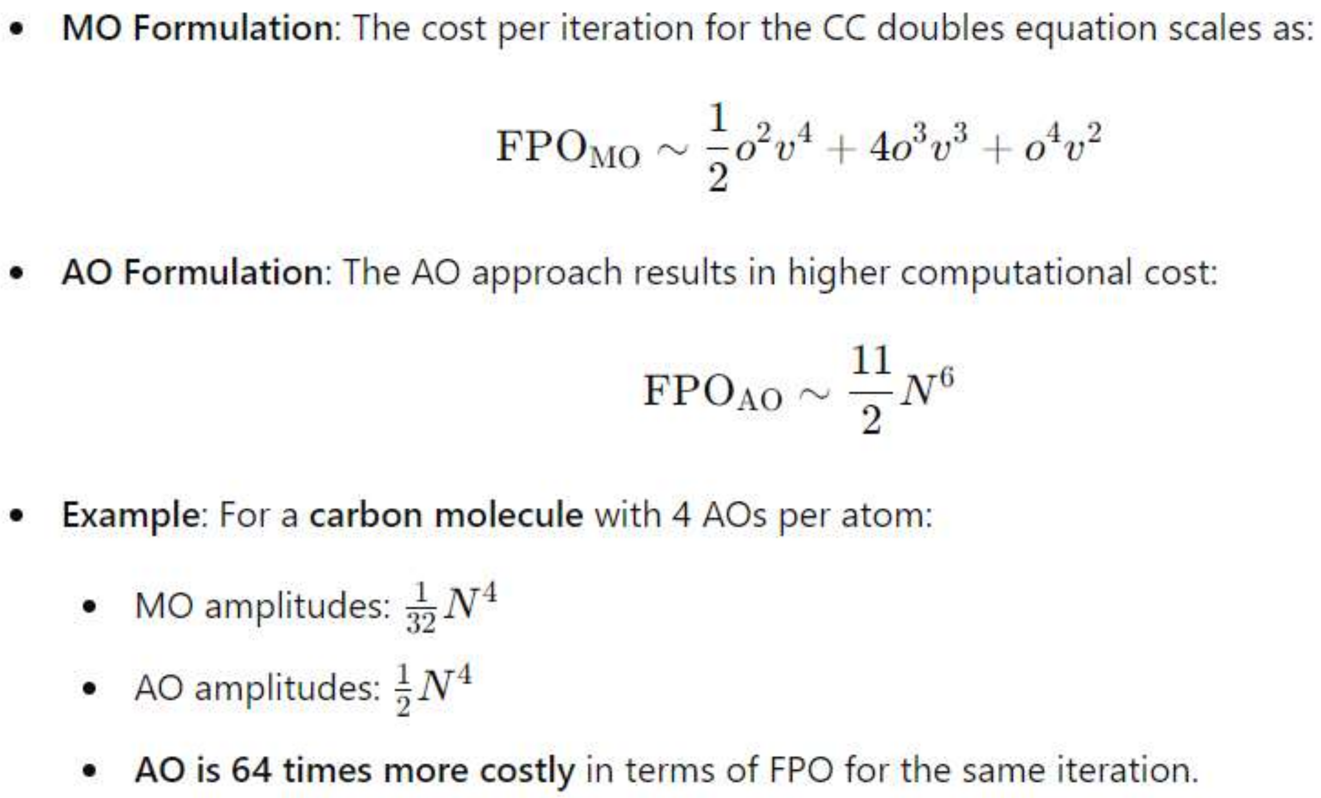
Computational Cost and Scaling: MO vs AO Basis

- **Key Variables**:
  - **o**: Number of occupied molecular orbitals.
  - **v**: Number of virtual orbitals.
  - **N:** Number of atomic orbitals (AOs), with N=o+v

  Number of Amplitudes:
  - **MO Basis**: The number of **t** amplitudes (MO) is ½ o^2*v^2+ov
  - **AO Basis**: The number of θ amplitudes (AO) is ½ N^2(N+1).
- **Implication**: The AO formulation requires **many more amplitudes** compared to MO:
  - For large systems, the number of AO-based θ amplitudes can be **16 times larger** than the MO-based **t** amplitudes.

C. Computational cost and scaling prefactor considerations

Floating Point Operations (FPO) per Iteration



- **MO Formulation**: The cost per iteration for the CC doubles equation scales as:

$$\mathrm{FPO}_{\mathrm{MO}} \sim \frac{1}{2}o^2v^4 + 4o^3v^3 + o^4v^2$$

- **AO Formulation**: The AO approach results in higher computational cost:

$$\mathrm{FPO}_{\mathrm{AO}} \sim \frac{11}{2}N^6$$

- **Example**: For a **carbon molecule** with 4 AOs per atom:
    - MO amplitudes: $\frac{1}{32}N^4$
    - AO amplitudes: $\frac{1}{2}N^4$
    - **AO is 64 times more costly** in terms of FPO for the same iteration.

C. Computational cost and scaling prefactor considerations

Asymptotic Advantage of AO in Large Systems

- **Scaling Consideration**:
  - **MO Methods**: Favorable for **small molecules** due to fewer amplitudes and lower FPO cost.
  - **AO Methods**: Become favorable as **molecular size grows**.
- **Screening in AO**:
  - AO amplitudes decay rapidly with **distance** between atomic orbitals, allowing efficient **screening** of negligible contributions.
  - Screening drastically reduces the number of **significant variables**, yielding **O(N)** scaling for large systems.
- **Conclusion**: The **crossover** point (where AO becomes more efficient than MO) occurs at **modest molecular sizes**, making AO advantageous for large systems.

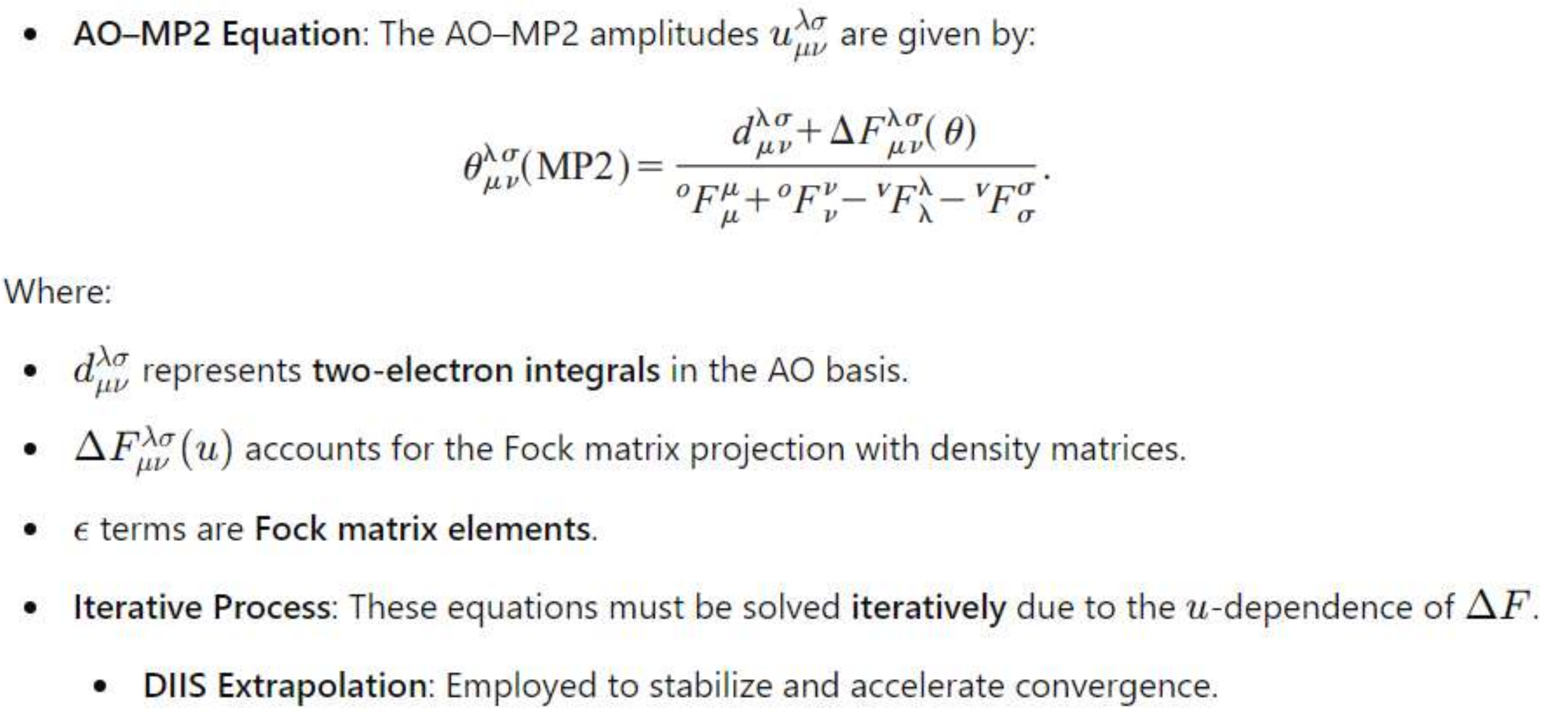
C. Computational cost and scaling prefactor considerations

For a detailed analysis of the FPO cost for solving the CC equations, you are referred to Refs. 35 and 36.

- 35.5G. E. Scuseria, C. L. Janssen, and H. F. Schaefer, J. Chem. Phys. 89, 7382 ~1988!.
- 36.G. E. Scuseria and H. F. Schaefer, J. Chem. Phys. 90, 3700 ~1989!

D. The atomic orbital MP2 equations

Atomic Orbital MP2 Equations



- **AO–MP2 Equation**: The AO–MP2 amplitudes $u_{\mu\nu}^{\lambda\sigma}$ are given by:

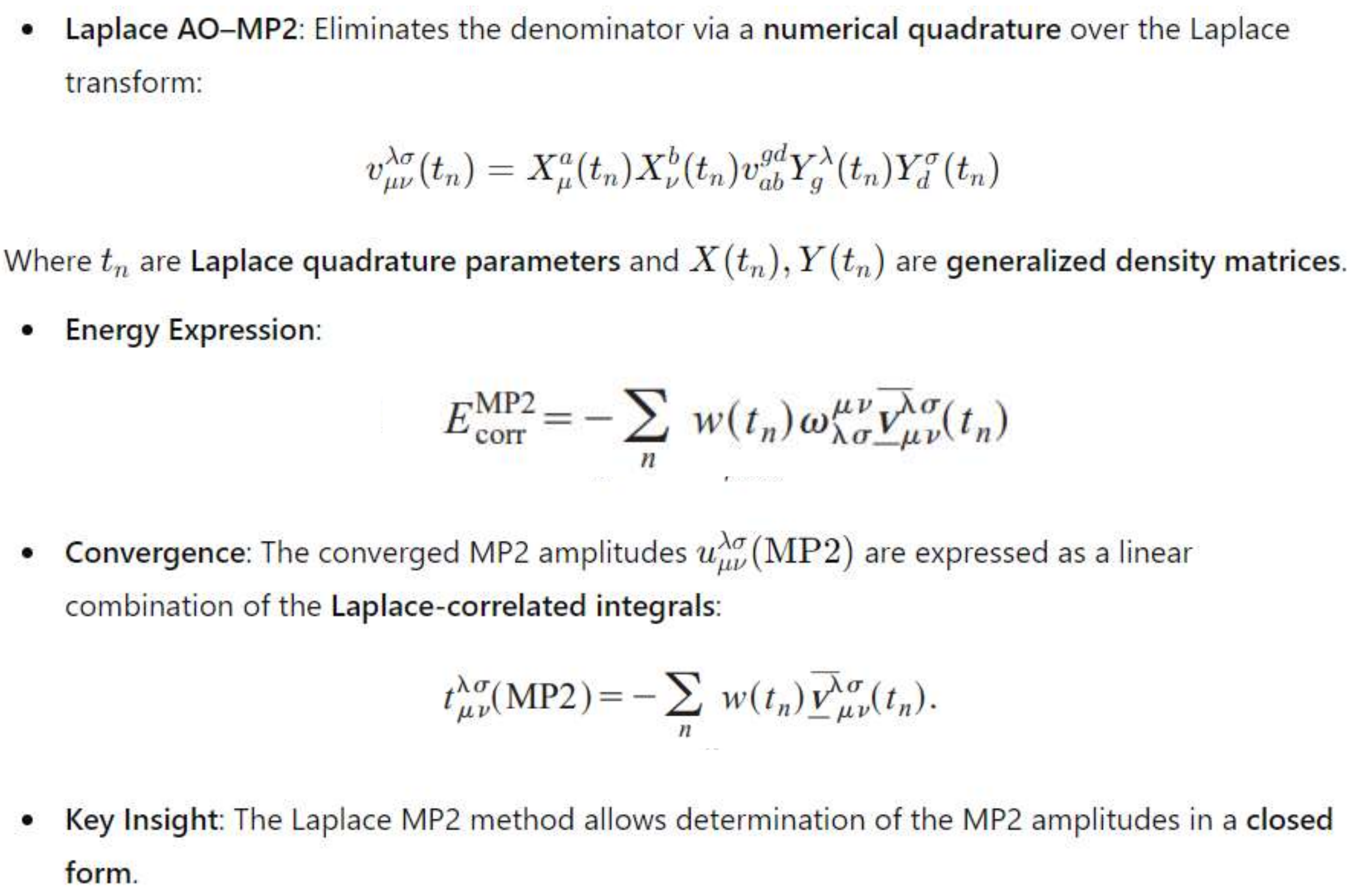
$$\theta_{\mu\nu}^{\lambda\sigma}(\mathrm{MP2}) = \frac{d_{\mu\nu}^{\lambda\sigma} + \Delta F_{\mu\nu}^{\lambda\sigma}(\theta)}{{}^{o}F_{\mu}^{\mu} + {}^{o}F_{\nu}^{\nu} - {}^{v}F_{\lambda}^{\lambda} - {}^{v}F_{\sigma}^{\sigma}}.$$

Where:

- $d_{\mu\nu}^{\lambda\sigma}$ represents **two-electron integrals** in the AO basis.
- $\Delta F_{\mu\nu}^{\lambda\sigma}(u)$ accounts for the Fock matrix projection with density matrices.
- ϵ terms are **Fock matrix elements**.
- **Iterative Process**: These equations must be solved **iteratively** due to the u-dependence of ΔF.
  - **DIIS Extrapolation**: Employed to stabilize and accelerate convergence.

D. The atomic orbital MP2 equations

Comparison with Laplace AO–MP2 Method



- **Laplace AO–MP2**: Eliminates the denominator via a **numerical quadrature** over the Laplace transform:

$$v^{\lambda\sigma}_{\mu\nu}(t_n) = X^{a}_{\mu}(t_n)X^{b}_{\nu}(t_n)v^{gd}_{ab}Y^{\lambda}_{g}(t_n)Y^{\sigma}_{d}(t_n)$$

Where t_n are **Laplace quadrature parameters** and $X(t_n), Y(t_n)$ are **generalized density matrices**.

- **Energy Expression**:

$$E^{\text{MP2}}_{\text{corr}} = -\sum_{n} w(t_n)\,\omega^{\mu\nu}_{\lambda\sigma}\underline{\overline{v}}^{\lambda\sigma}_{\mu\nu}(t_n)$$

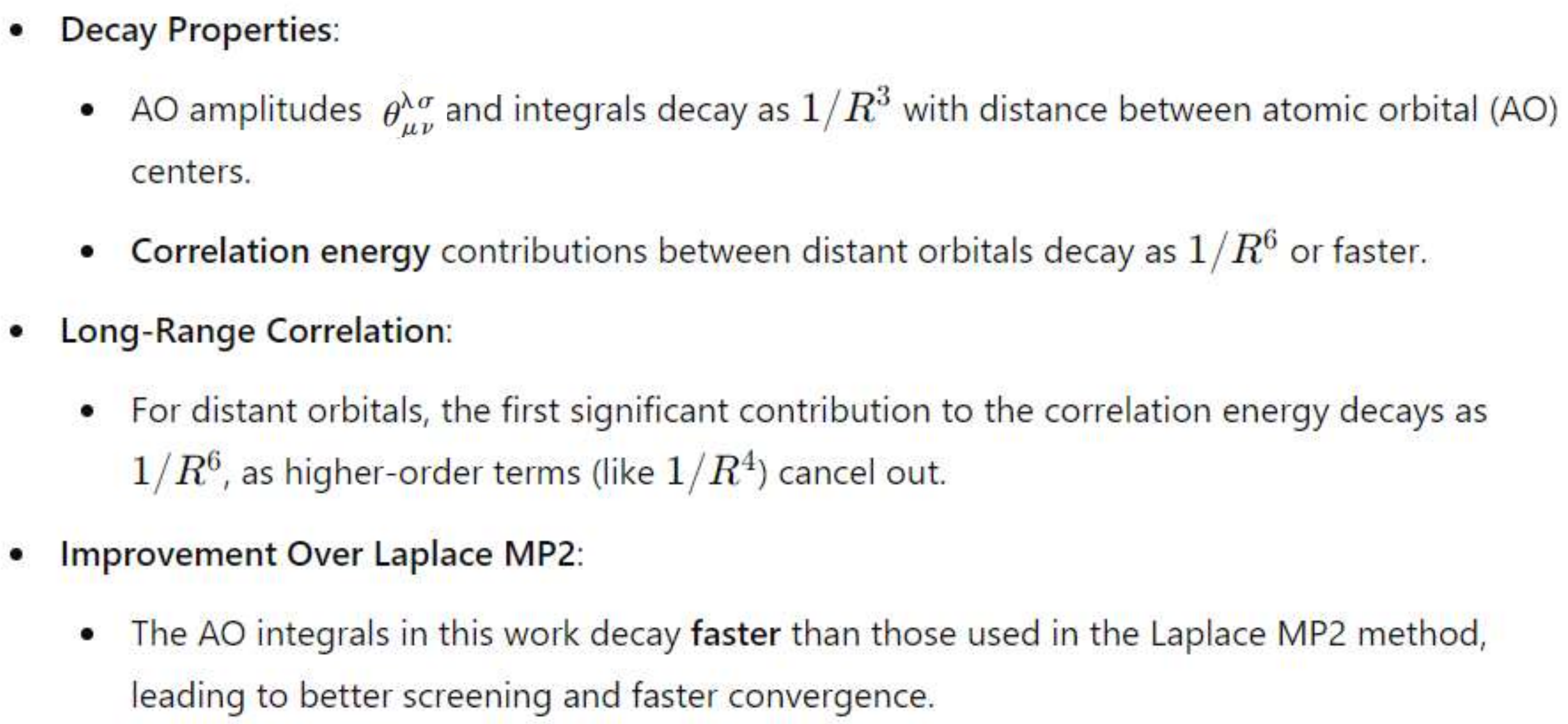
- **Convergence**: The converged MP2 amplitudes $u^{\lambda\sigma}_{\mu\nu}(\text{MP2})$ are expressed as a linear combination of the **Laplace-correlated integrals**:

$$t^{\lambda\sigma}_{\mu\nu}(\text{MP2}) = -\sum_{n} w(t_n)\underline{\overline{v}}^{\lambda\sigma}_{\mu\nu}(t_n).$$

- **Key Insight**: The Laplace MP2 method allows determination of the MP2 amplitudes in a **closed form**.

E. Asymptotic behavior and screening of AO amplitudes

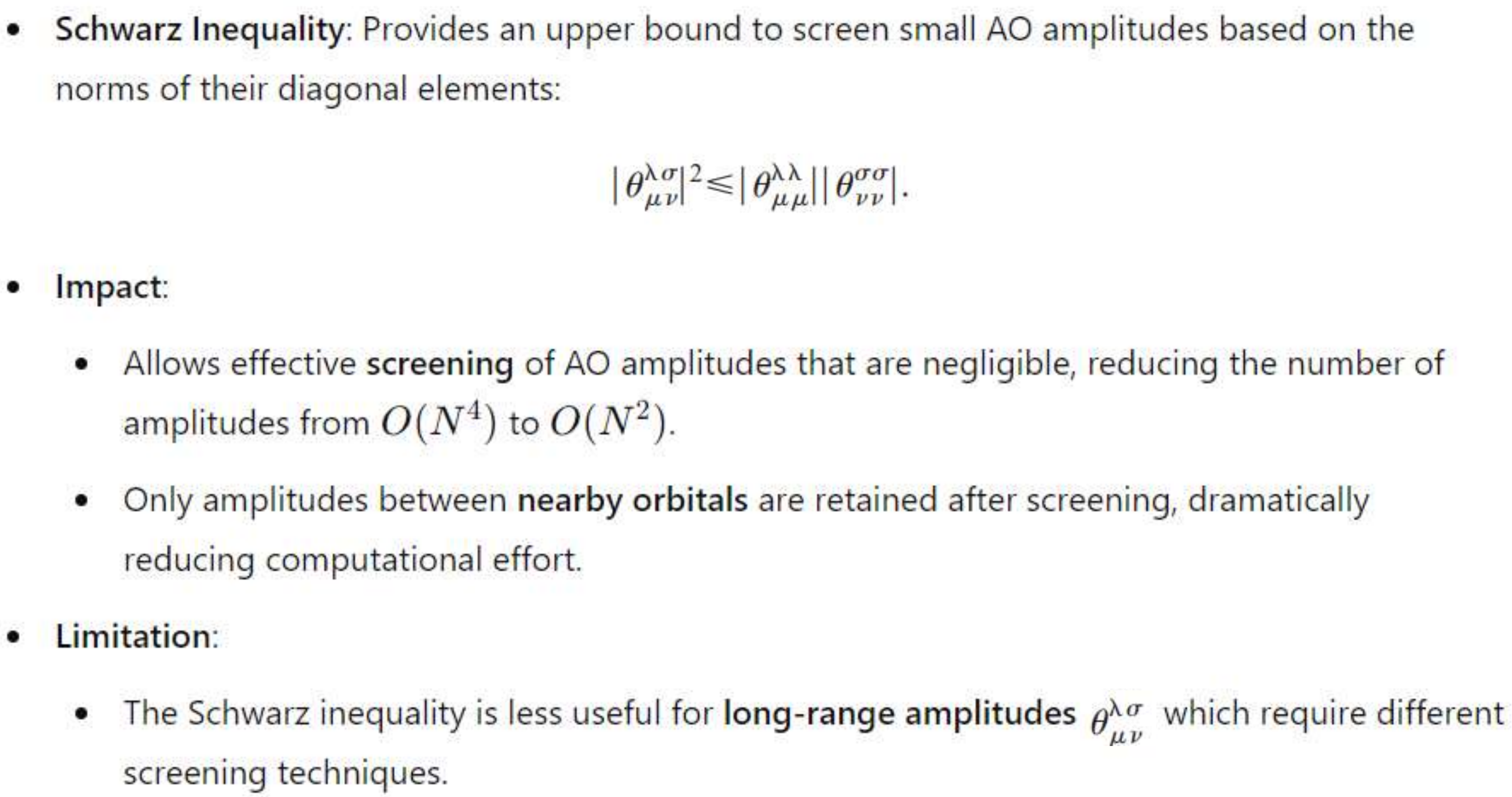
Asymptotic Behavior of AO Amplitudes



- **Decay Properties**:
    - AO amplitudes $\theta_{\mu\nu}^{\lambda\sigma}$ and integrals decay as $1/R^3$ with distance between atomic orbital (AO) centers.
    - **Correlation energy** contributions between distant orbitals decay as $1/R^6$ or faster.
- **Long-Range Correlation**:
    - For distant orbitals, the first significant contribution to the correlation energy decays as $1/R^6$, as higher-order terms (like $1/R^4$) cancel out.
- **Improvement Over Laplace MP2**:
    - The AO integrals in this work decay **faster** than those used in the Laplace MP2 method, leading to better screening and faster convergence.

E. Asymptotic behavior and screening of AO amplitudes

Screening of AO Amplitudes Using Schwarz Inequality



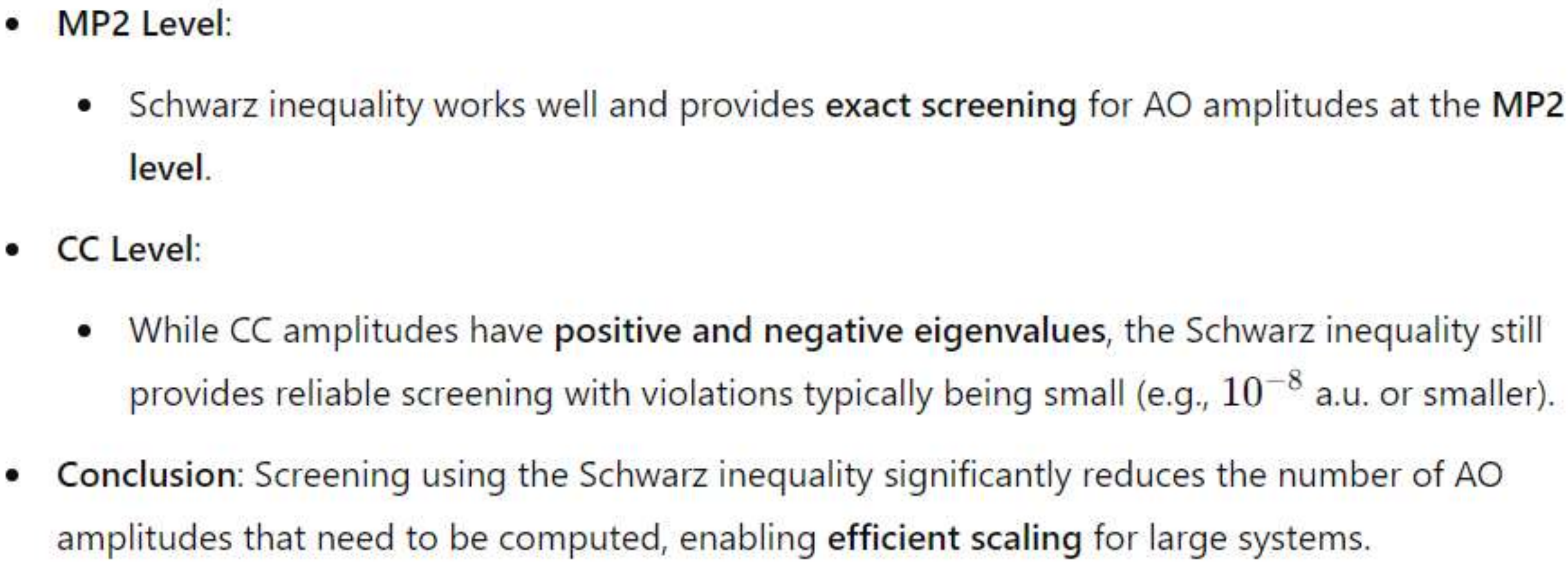
- **Schwarz Inequality**: Provides an upper bound to screen small AO amplitudes based on the norms of their diagonal elements:

$$|\theta_{\mu\nu}^{\lambda\sigma}|^2 \leqslant |\theta_{\mu\mu}^{\lambda\lambda}||\theta_{\nu\nu}^{\sigma\sigma}|.$$

- **Impact**:
  - Allows effective **screening** of AO amplitudes that are negligible, reducing the number of amplitudes from $O(N^4)$ to $O(N^2)$.
  - Only amplitudes between **nearby orbitals** are retained after screening, dramatically reducing computational effort.
- **Limitation**:
  - The Schwarz inequality is less useful for **long-range amplitudes** $\theta_{\mu\nu}^{\lambda\sigma}$ which require different screening techniques.

E. Asymptotic behavior and screening of AO amplitudes

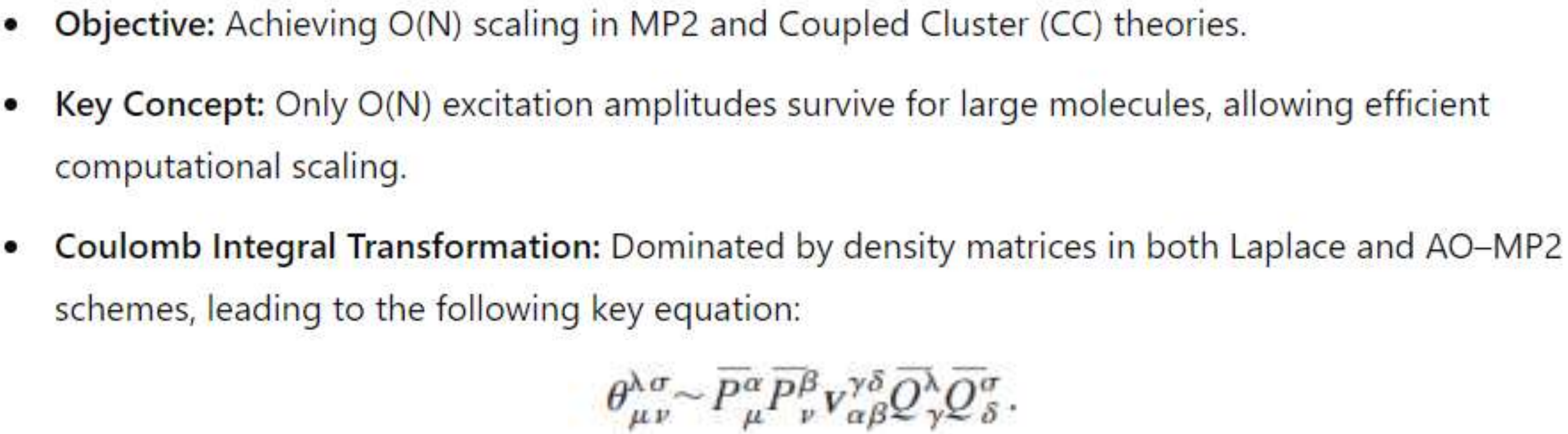
Practical Application of Screening in AO Methods



- **MP2 Level**:
  - Schwarz inequality works well and provides **exact screening** for AO amplitudes at the **MP2 level**.
- **CC Level**:
  - While CC amplitudes have **positive and negative eigenvalues**, the Schwarz inequality still provides reliable screening with violations typically being small (e.g., 10^{-8} a.u. or smaller).
- **Conclusion**: Screening using the Schwarz inequality significantly reduces the number of AO amplitudes that need to be computed, enabling **efficient scaling** for large systems.

F. Linear scaling perturbation and coupled cluster theories

Introduction to Linear Scaling in MP2 and CC Theories

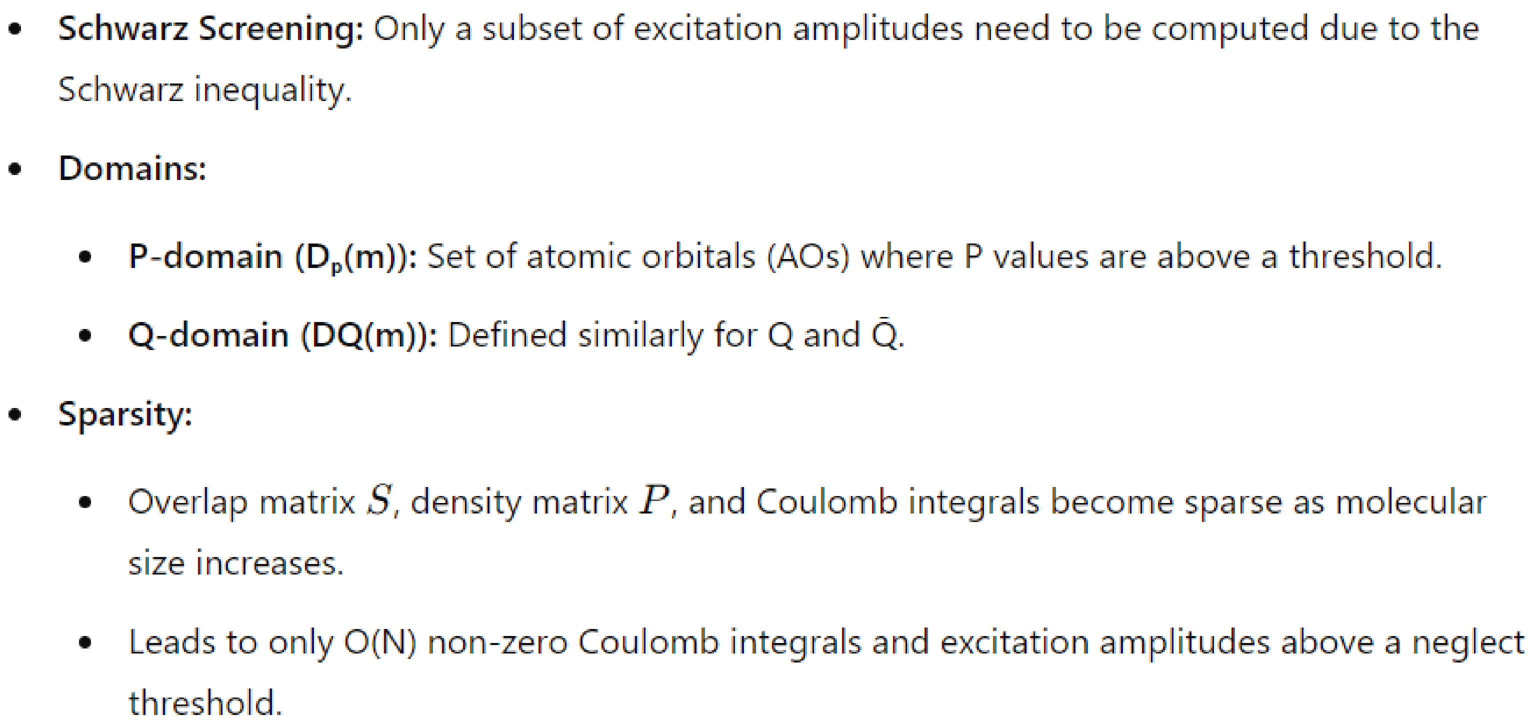


- **Objective:** Achieving O(N) scaling in MP2 and Coupled Cluster (CC) theories.
- **Key Concept:** Only O(N) excitation amplitudes survive for large molecules, allowing efficient computational scaling.
- **Coulomb Integral Transformation:** Dominated by density matrices in both Laplace and AO–MP2 schemes, leading to the following key equation:

$$\theta_{\mu\nu}^{\lambda\sigma} \sim \overline{P}_{\mu}^{\alpha}\overline{P}_{\nu}^{\beta} v_{\alpha\beta}^{\gamma\delta}\overline{Q}_{\gamma}^{\lambda}\overline{Q}_{\delta}^{\sigma}.$$

F. Linear scaling perturbation and coupled cluster theories

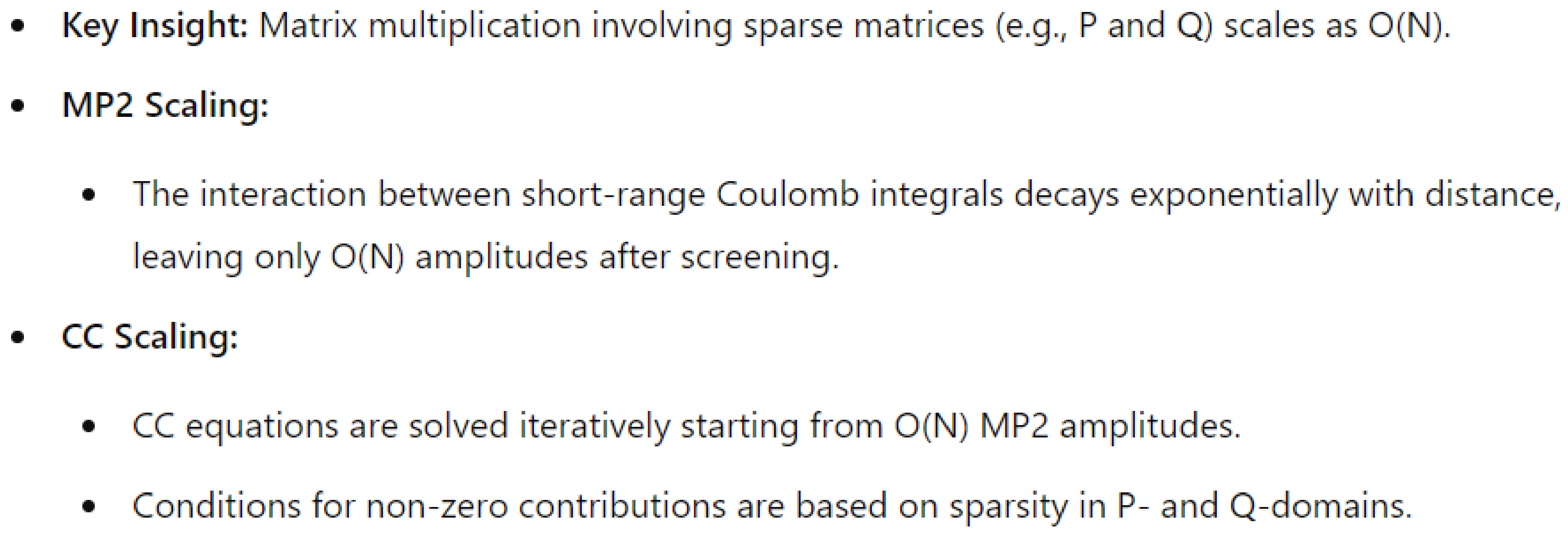
Schwarz Screening and Sparsit



- **Schwarz Screening:** Only a subset of excitation amplitudes need to be computed due to the Schwarz inequality.
- **Domains:**
  - **P-domain ($D_p(m)$):** Set of atomic orbitals (AOs) where P values are above a threshold.
  - **Q-domain (DQ(m)):** Defined similarly for Q and $\bar{Q}$.
- **Sparsity:**
  - Overlap matrix S, density matrix P, and Coulomb integrals become sparse as molecular size increases.
  - Leads to only O(N) non-zero Coulomb integrals and excitation amplitudes above a neglect threshold.

F. Linear scaling perturbation and coupled cluster theories

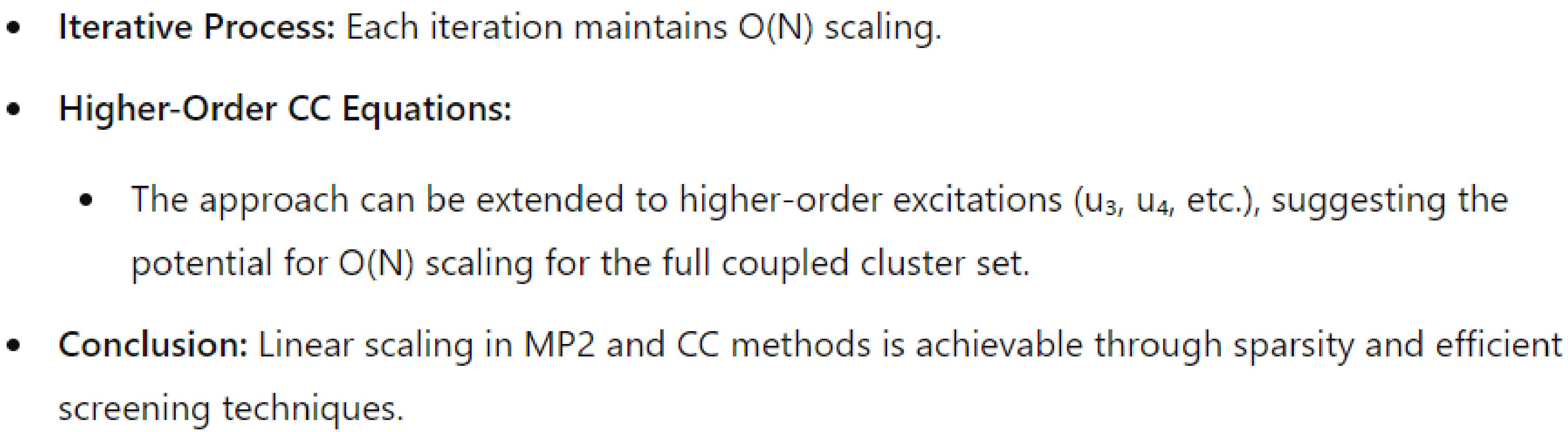
Proof of O(N) Scaling for MP2 and CC



- **Key Insight:** Matrix multiplication involving sparse matrices (e.g., P and Q) scales as O(N).
- **MP2 Scaling:**
  - The interaction between short-range Coulomb integrals decays exponentially with distance, leaving only O(N) amplitudes after screening.
- **CC Scaling:**
  - CC equations are solved iteratively starting from O(N) MP2 amplitudes.
  - Conditions for non-zero contributions are based on sparsity in P- and Q-domains.

F. Linear scaling perturbation and coupled cluster theories

Extending to Higher Order CC Equations



- **Iterative Process:** Each iteration maintains O(N) scaling.
- **Higher-Order CC Equations:**
    - The approach can be extended to higher-order excitations (u_3, u_4, etc.), suggesting the potential for O(N) scaling for the full coupled cluster set.
- **Conclusion:** Linear scaling in MP2 and CC methods is achievable through sparsity and efficient screening techniques.

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Thank you!