

Full Configuration Interaction and the Slater-Condon Rules

Henry Mull

CCQC Summer Program 2022

6-22-22

Hartree-Fock isn't cutting it anymore

Hartree-Fock theory often gives qualitatively incorrect results

- N₂ ionization potentials
- CO dipole moment

We need



$$E_{corr} = E_{exact} - E_{HF}$$
$$E_{corr} < 0$$

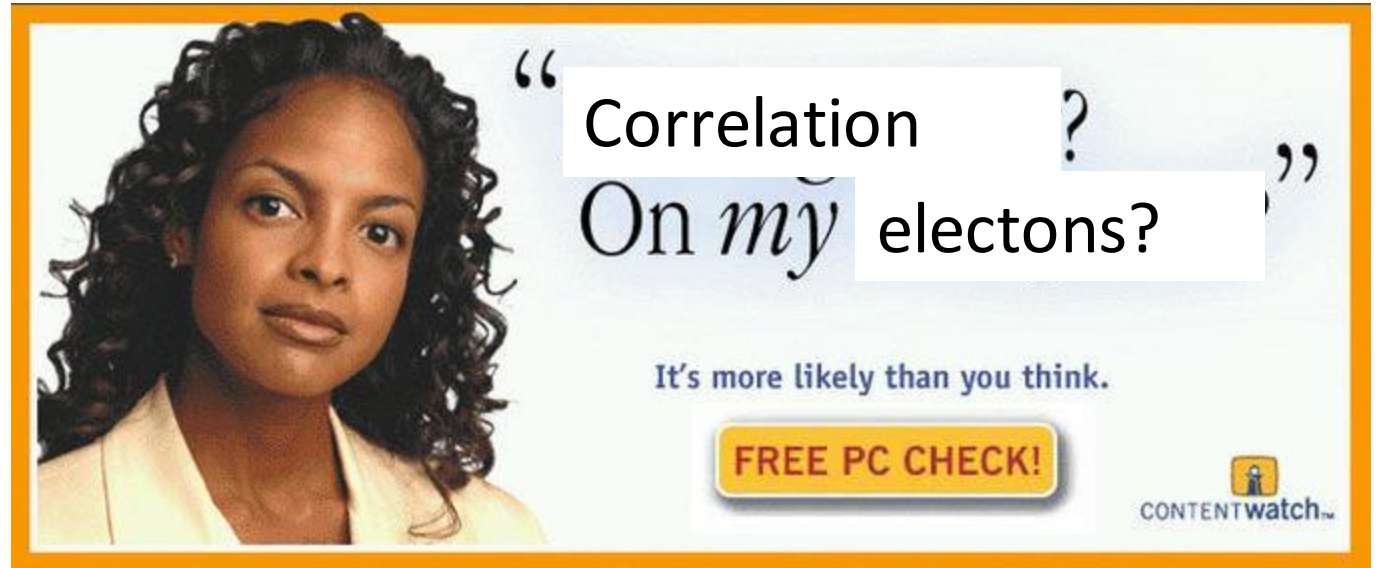
Electron Correlation

Dynamic correlation

- HF electron-electron interaction is averaged
- Electron positions are interdependent

Static correlation

- A single Slater Determinant sometimes isn't enough
- HF is single reference



Configuration Interaction (CI) to the rescue

Diagonalize N-electron Hamiltonian in a basis of N-electron Slater determinants



Take all possible Slater determinants using a given basis set, and let them interact with each other

(Kinda like Hartree-Fock)

Conceptually the simplest, but computationally the most difficult
“True” energy within the limit of finite basis set

The CI Wave Function

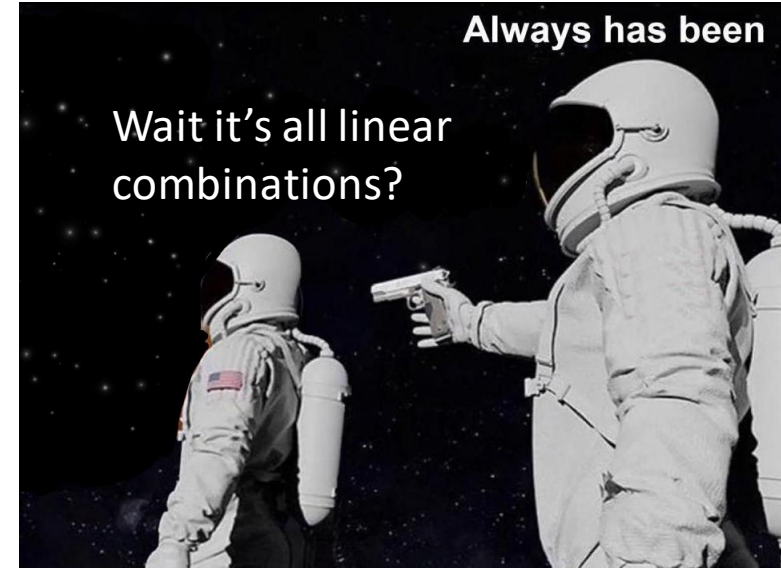
Linear combination of Slater Determinants

$$|\Psi\rangle = \sum_i c_i |\phi_i\rangle \quad |\phi_i\rangle = \sum_{i,j} c_{ij} |\chi_{ij}\rangle$$

Introduce reference wave function and excitations

$$|\Psi\rangle = c_0 |\phi_0\rangle + \sum_{ia} c_i^a |\phi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab} |\phi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc} |\phi_{ijk}^{abc}\rangle + \dots$$

$$|\Psi\rangle = c_0 |\phi_0\rangle + \left(\frac{1}{1!}\right)^2 \sum_{ia} c_i^a |\phi_i^a\rangle + \left(\frac{1}{2!}\right)^2 \sum_{\substack{ij \\ ab}} c_{ij}^{ab} |\phi_{ij}^{ab}\rangle + \left(\frac{1}{3!}\right)^2 \sum_{\substack{ijk \\ abc}} c_{ijk}^{abc} |\phi_{ijk}^{abc}\rangle + \dots$$



The CI Wave Function

$\binom{m}{n}$ possible Slater determinants

- STO-3G Water has 14 spin orbitals, 10 electrons
- 1001 possible determinants

Intermediate Normalization

$$\langle \Psi | \phi_0 \rangle = c_0 = 1$$



The CI Energy

It can be shown (Second Quantization) that the CI correlation energy expression is:

$$E_{corr} = \frac{1}{4} \sum_{\substack{i < j \\ a < b}} \langle ij || ab \rangle c_{ij}^{ab}$$

However, you can't only use double excitations, all CI coefficients are interdependent.

The CI Hamiltonian

$$\begin{array}{c}
 \langle \Phi | \\
 \langle \Phi_m^e | \\
 \langle \Phi_{mn}^{ef} | \\
 \langle \Phi_{mno}^{efg} | \\
 \langle \Phi_{mnop}^{efgh} | \\
 \vdots
 \end{array}
 \begin{pmatrix}
 |\Phi\rangle & |\Phi_i^a\rangle & |\Phi_{ij}^{ab}\rangle & |\Phi_{ijk}^{abc}\rangle & |\Phi_{ijkl}^{abcd}\rangle & \dots \\
 \langle \Phi | H_c | \Phi \rangle & \mathbf{0} & \langle \Phi | H_c | \Phi_{ij}^{ab} \rangle & \mathbf{0} & \mathbf{0} & \dots \\
 \langle \Phi_m^e | H_c | \Phi_i^a \rangle & \langle \Phi_m^e | H_c | \Phi_{ij}^{ab} \rangle & \langle \Phi_m^e | H_c | \Phi_{ijk}^{abc} \rangle & \mathbf{0} & \mathbf{0} & \dots \\
 \langle \Phi_{mn}^{ef} | H_c | \Phi_{ij}^{ab} \rangle & \langle \Phi_{mn}^{ef} | H_c | \Phi_{ijk}^{abc} \rangle & \langle \Phi_{mn}^{ef} | H_c | \Phi_{ijkl}^{abcd} \rangle & \dots & \dots & \dots \\
 \langle \Phi_{mno}^{efg} | H_c | \Phi_{ijkl}^{abcd} \rangle & \dots & \dots & \dots & \dots & \dots \\
 \langle \Phi_{mnop}^{efgh} | H_c | \Phi_{ijkl}^{abcd} \rangle & \dots & \dots & \dots & \dots & \dots \\
 \vdots & \ddots & \ddots & \ddots & \ddots & \ddots
 \end{pmatrix}$$

Hamiltonian elements determined by Slater-Condon Rules

Slater-Condon Rules

A set of rules which give the expectation values of the Hamiltonian between two Slater determinants (i.e. the matrix elements of the CI Hamiltonian)

Only 4 cases to consider

1. Same determinant
2. Singly excited determinant
3. Doubly excited determinant
4. Triply excited and above determinants

Slater-Condon Rules

~~Rule 1: We do not talk about the Slater-Condon Rules~~

Rule 1: Same Determinant (Hartree-Fock)

$$\langle \phi | \hat{H} | \phi \rangle = \sum_i^N \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^N \langle ij || ij \rangle$$

Slater-Condon Rules

Rule 2: Singly Excited Determinant

$$\langle \phi | \hat{H} | \phi_i^a \rangle = \langle i | \hat{h} | a \rangle + \sum_j^N \langle ij || aj \rangle$$

Rule 3: Double Excited Determinant

$$\langle \phi | \hat{H} | \phi_{ij}^{ab} \rangle = \langle ij || ab \rangle$$

Rule 4: Triply Excited and Above Determinants

$$\langle \phi | \hat{H} | \phi_{ijk...}^{abc...} \rangle = 0$$

Truncated CI

Full CI (FCI) for most systems would not finish before we die

To make CI computationally feasible, we truncate the CI expansion (i.e. we ignore the really hard parts)

e.g. CISD (Singles and Doubles)

$$|\Psi\rangle = |\phi_0\rangle + \left(\frac{1}{1!}\right)^2 \sum_{ia} c_i^a |\phi_i^a\rangle + \left(\frac{1}{2!}\right)^2 \sum_{ij} \sum_{ab} c_{ij}^{ab} |\phi_{ij}^{ab}\rangle$$

Truncated CI

Requires use of energy expression

$$E_{corr} = \frac{1}{4} \sum_{\substack{i < j \\ a < b}} \langle ij || ab \rangle c_{ij}^{ab}$$

No longer size consistent (Alex lecture)



Further Reading

Chem8950 Github: https://github.com/CCQC/chem-8950/blob/master/2020/lecture_notes/4_CI.pdf

Modern Quantum Chemistry, Szabo and Ostlund

Probably any QM textbook