Post-HF methods

- HF only has mean-field limit and only one determinant
- Correlation important for relative energy differences, driving chemistry
    - Reaction energies
    - Barrier heights
- Correlation: "How does having a single electron here impact all other electrons?"
    - Often understood as expansion in excitations
- Different approaches
    - Full Configuration Interaction (FCI)
    - Perturbative: Moller-Plesset (MPn)
    - Truncated: Coupled Cluster (e.g. CCSD)
    - Multi-reference Methods

$$\Psi_{\mathrm{FCI}} = c_0 \psi + \sum_a^{\mathrm{occ}} \sum_r^{\mathrm{virt}} c_a^r \psi_a^r + \sum_{a<b}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{virt}} c_{ab}^{rs} \psi_{ab}^{rs} + \sum_{a<b<c}^{\mathrm{occ}} \sum_{r<s<t}^{\mathrm{virt}} c_{abc}^{rst} \psi_{abc}^{rst} + \dots$$

- Expansion in excited determinants of the HF solution
- Find coefficients c* by minimizing energy subject to normalization
- Exact iff all orders are included and we have a complete basis set, otherwise upper limit
    - Unoccupied orbitals need to be represented well
- Inefficient: number of determinants quickly becomes too large
- Split into two regimes:
    - "Dynamic/weak correlation": c_0 dominates, i.e. HF is a good approximation
    - "Static/strong correlation": otherwise, requires multi-reference methods
- Yields energies, new wave function, variational

$$\psi \equiv \Psi_{\mathrm{HF}}$$

$$\Psi_{\mathrm{CISD}} = c_0 \psi + \sum_a^{\mathrm{occ}} \sum_r^{\mathrm{virt}} c_a^r \psi_a^r + \sum_{a<b}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{virt}} c_{ab}^{rs} \psi_{ab}^{rs}$$

- Finite truncation after first orders
  - Here "Configuration Interaction Singles Doubles"
- No size consistency
  - E(A+B at infinite separation) != E(A) + E(B)
- Yields energies, new wave functions, variational

$$E_{\mathrm{MP2,c}} = -\frac{1}{4} \sum_{a<b}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{virt}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

- Include correlation as perturbation up to order n
  - Zeroth order is Hartree-Fock
- Does not necessarily converge (or behave well)
- Comparably simple method, common for weak correlation
- Higher orders possible, yet much more expensive and not quite better
- Yields energies, no new wave functions, not variational, size-consistent

$$\Psi_{\mathrm{CCSD}} = \exp(\hat{T}_1 + \hat{T}_2)\Psi_{\mathrm{HF}}$$

$$\hat{T}_1 = \sum_a^{\mathrm{occ}} \sum_r^{\mathrm{vir}} t_a^r \hat{a}_r^\dagger \hat{a}_a$$

$$\hat{T}_2 = \frac{1}{4} \sum_{ab}^{\mathrm{occ}} \sum_{rs}^{\mathrm{vir}} t_{ab}^{rs} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_a \hat{a}_b$$

- T_1 are all single excitations, T_2 all double, …
- Taylor expansion of exp yields combinations and relation between amplitudes t and FCI coefficients c
- Rearrange all terms from FCI, formally equivalent if all excitations would be included
- Common variants: CCSD (singles doubles), CCSD(T) (singles doubles with perturbative triples)
- Methods beyond CCSD(T) are rare
- CCSD(T) is often called the "gold standard" for weak correlation
- Yields energies, new wave function, not variational, size consistent

Depends on number of basis functions n (ignoring screening & implementation tricks for now)

DFT	$O(n^3)$
HF	$O(n^4)$
MP2	$O(n^5)$
MP3	$O(n^6)$
MP4	$O(n^7)$
CCSD	$O(n^6)$
CCSD(T)	$O(n^7)$
CCSDT	$O(n^8)$
CCSDTQ	$O(n^{10})$
FCI	$O(n!)$