2.1 The Hartree (H) approximation

Electrons are modelled as non-interacting particles with a total wavefunction:

$$\Psi^H(\{\vec{r}_i\}) = \Phi_1(\vec{r}_1) \Phi_2(\vec{r}_2) \cdots \Phi_N(\vec{r}_N)$$

$$\Phi_i(\vec{r}_i)$$: single-particle normalized state

**Total Energy:**

$$E^H = \langle \Psi^H | H | \Psi^H \rangle$$

$$= \sum_i \langle \Phi_i | - \frac{\hbar^2 \nabla^2}{2m} + V_{\text{ion}}(\vec{r}) \Phi_i \rangle$$

$$+ \frac{e^2}{2} \sum_{ij} \langle \Phi_i | \frac{1}{|\vec{r}_i - \vec{r}_j|} | \Phi_j \rangle$$

**Variational calculation of** $$\Phi_i$$ with $$\Psi^H$$ a stationary state (any variation in $$\Psi^H$$ leads to a zero variation in $$E^H$$)

+ Lagrange multipliers

$$\Rightarrow 8 \left[ E^H - \sum_i \epsilon_i \left( \langle \Phi_i | \Phi_i \rangle - 1 \right) \right] = 0$$
\[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\vec{r}) + e^2 \sum_{j} \frac{\phi_j}{|\vec{r} - \vec{r}_j|} \phi_j ] \phi_i(\vec{r}) = \varepsilon \phi_i(\vec{r}) \]

\( V^H(\vec{r}) \) the Hartree potential

- The equation above is the Hartree single-particle equation including only correlations from the Coulomb interactions (no exchange).
- \( V^H(\vec{r}) \) is different for each particle and includes the Coulomb interactions in a mean-field way.

2.2. The Hartree–Fock (HF) method

- Next level of sophistication, at which exchange interactions are included through one Slater determinant for N electrons.
- HF is a properly antisymmetrized version of the Hartree approach.
\[ \psi_{HF}(\vec{r}, \vec{r}_1, \ldots, \vec{r}_N) = \frac{1}{\sqrt{N}} \begin{pmatrix} \phi_1(\vec{r}_1) & \phi_1(\vec{r}_2) & \cdots & \phi_1(\vec{r}_N) \\ \phi_2(\vec{r}_1) & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \phi_2(\vec{r}_N) \\ \phi_N(\vec{r}_1) & \cdots & \cdots & \phi_N(\vec{r}_N) \end{pmatrix} \]

Total energy:
\[ E_{HF} = \langle \psi_{HF} | H | \psi_{HF} \rangle \rightarrow \]
\[ E_{HF} = \sum_i \phi_i \left( -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}}(\vec{r}_i) + V_{\text{e}}(\vec{r}_i) \right) \phi_i(\vec{r}_i) + \frac{e^2}{2} \sum_{ij} \frac{1}{|\vec{r}_i - \vec{r}_j|} \langle \phi_i | \phi_j \rangle \phi_j(\vec{r}_j) \phi_i(\vec{r}_i) - \frac{e^2}{2} \sum_{ij} \frac{1}{|\vec{r}_i - \vec{r}_j|} \langle \phi_i | \phi_j \rangle \phi_j(\vec{r}_j) \phi_i(\vec{r}_i) \]

Again through a variational approach:
\[ \rightarrow \rightarrow \rightarrow \]
\[ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}}(\vec{r}_i) + V_{\text{e}}(\vec{r}_i) \phi_i(\vec{r}_i) - \frac{e^2}{2} \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \langle \phi_j | \phi_i \rangle \phi_i(\vec{r}_i) = \epsilon_i \phi_i(\vec{r}_i) \]

Hartree correlation

exchange term

\[ \uparrow \]
2.3 Post Hartree-Fock schemes

Post HF schemes improve HF by including typically more correlation. This can be done, e.g. by including more than one Slater determinant, account for correlations of electrons with antiparallel spins, include excitations, small perturbations, etc.

Post HF are more accurate than HF, but computationally more demanding:
- Scaling: \( \mathcal{O}(N^{3-N^4}) \)
- post HF \( \mathcal{O}(N^{5-N^10}) \)

Examples:
- Coupled Cluster
- Configuration Interaction
- Møller-Plesset
- Multi-configuration HF
- etc.
Examples: Coupled Cluster (CC)

Includes correction of a given type (single (S), double (D), triple (T) ... excitations) to infinite order.

CC is non-variational, size-consistent, and size-extensive.

The total wavefunction is written as:

\[ |\Psi\rangle = e^\Lambda |\Phi_0\rangle \]

\( \Lambda \) typically Slater determinant from HF

\( \Lambda \) is a cluster or excitation operator, which when acting on \( |\Phi_0\rangle \) produces a linear combination of excited Slater determinants (excitations and unoccupied orbitals taken into account).

\[ \Lambda = \Lambda_1 + \Lambda_2 + \Lambda_3 + \ldots \]

Operator for all single excitations

operator for all double excitations
Using the 2nd quantization formalism:

\[ \hat{\mathcal{Z}}_1 = \sum_a \sum_r t_a \hat{a}_a \hat{a}_r^+ \]

\[ \hat{\mathcal{Z}}_2 = \frac{1}{4} \sum_a \sum_r b_a \hat{\alpha}_a \hat{\alpha}_r^+ \hat{\alpha}_r \hat{\alpha}_r^+ \]

\[ \hat{\alpha}_a^+, \hat{\alpha}_a : \text{occupied orbitals (occ.)} \]

\[ \hat{\alpha}_r, \hat{\alpha}_s : \text{unoccupied orbitals (vir.)} \]

\[ t_a, b_a : \text{elements for certain excitations} \]

\[ \hat{\alpha}_a^+, \hat{\alpha}_a : \text{creation and annihilation operators} \]

\[ \hat{\mathcal{Z}}_1, \hat{\mathcal{Z}}_2, \ldots \text{ convert } \Phi_{\text{occ}} \text{ into a linear combination of single-, double-, \ldots excited Slater determinants.} \]

\[ \text{Solve for } t_a, b_a \ldots \text{ to find } \Phi_{\text{occ}} \]

\[ \text{Use Taylor expansion of certain order:} \]

\[ e^\hat{1} = 1 + \hat{\mathcal{Z}}_1 + \frac{\hat{\mathcal{Z}}_1^2}{2!} + \frac{\hat{\mathcal{Z}}_1^3}{3!} + \ldots \]

\[ = 1 + \hat{\mathcal{Z}}_1 + \frac{\hat{\mathcal{Z}}_1^2}{2!} + \frac{\hat{\mathcal{Z}}_1 \hat{\mathcal{Z}}_2}{2!} + \frac{\hat{\mathcal{Z}}_1^2}{2!} + \ldots \]
According to Brillouin theorem, the $1^{st}$ matrix elements are zero and the $2^{nd}$ ones are

$$E_{cc} = E_0 + \sum_{ab} \sum_{rs} \left( \frac{\alpha}{r_{ab}} + \frac{\tau}{r_{a} + r_{b}} - \frac{\beta}{r_{a} r_{b}} \right) \langle \phi_a \phi_b | \tilde{V} | \phi_r \phi_s \rangle$$

- $\langle \phi_a \phi_b | \tilde{V} | \phi_r \phi_s \rangle$ - closed set of equation for $r_{ab}$

Classification of CC based on the highest number of excitations in $\tilde{V}$:

- **CCSD T**: $\tilde{V} = \tilde{V}_1 + \tilde{V}_2 + \tilde{V}_3$
  - single, double, triple excitations

- **CCSD (CT)**: single, double excitations are fully included, but triple ones as a perturbation.

E.g. $\text{CCSD(T)}$
In practice, series finite as number of orbitals is finite.

- If the highest excitation level is \( n \) in \( \hat{p} \), a Slater det. excited more than \( n \) times may contribute to \( |\Psi\rangle \) due to the non-linearity of the exponential form (e.g. \( n=2 \) "contains" \( \hat{\tau}_1 \hat{\tau}_2 \), \( \hat{\tau}_2 \ldots \))

\[
\hat{H} \exp^\hat{\tau} |\Phi_0\rangle = E_{cc} \exp^\hat{\tau} |\Phi_0\rangle \quad \Rightarrow \\
<\Phi_0 | \hat{H} \exp^\hat{\tau} |\Phi_0\rangle = E_{cc} <\Phi_0 | \exp^\hat{\tau} |\Phi_0\rangle \\
= E_{cc} <\Phi_0 | (1 + \hat{\tau}_1 + \hat{\tau}_2 + \ldots) |\Phi_0\rangle \\
\]

\[
<\Phi_0 | \hat{\tau}_1 |\Phi_0\rangle = 0 \\ E_{cc} = <\Phi_0 | \hat{H} \exp^\hat{\tau} |\Phi_0\rangle
\]

For excitations limited to single and double excited Slater det.

\[
E_{cc} = E_0 + \sum_{\text{occ}} \sum_{\text{vir}} \sum_a \sum_r t_a^r <\Phi_0 | \hat{f}_a^r | \Phi_0^r > \\
+ \sum_{\text{occ}} \sum_{\text{vir}} \sum_{ab} \sum_{\text{vis}} (t_{ab}^s + t_a^s t_b^s - t_{ab}^s t_{ba}^s) <\Phi_0 | \hat{f}_a^r \hat{f}_b^s | \Phi_0^r \Phi_0^s>
\]