Quantum mechanics for many-particle systems

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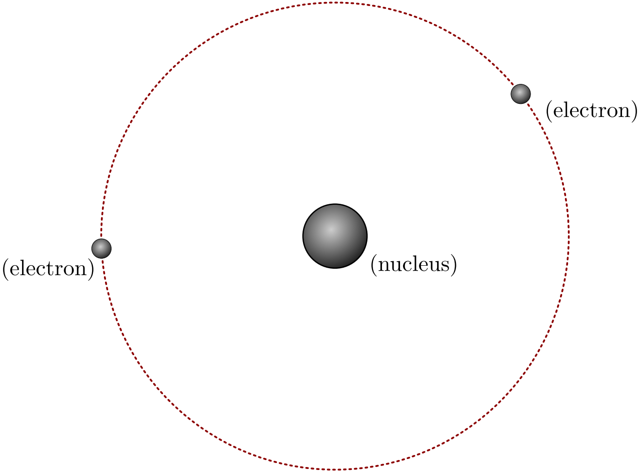

$$\hat{H} = \sum_i t(x_i) - \sum_i k\frac{Ze^2}{r_i} + \frac{ke^2}{r_{ij}}$$

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$$\Psi(x_1, x_2) = \psi_1(x_1)\psi_2(x_2).$$

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$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\big(\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)\big).$$

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For a N-particle system, we have the Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(r_1) & \psi_1(r_2) & \dots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \dots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \dots & \psi_N(r_N) \end{pmatrix} = \sqrt{N!}\mathcal{A}\phi_H.$$

The Hartree–Fock Method

Variational Principle

$$\langle \Psi | \hat{H} | \Psi \rangle \geq E_0.$$

A method is called *variational* if we can be sure the approximate solutions never undershoot the true ground state.

$$\begin{aligned}
\langle \Psi | \hat{H} | \Psi \rangle &= \sum_{ij} \langle \Psi | \phi_i \rangle \langle \phi_i | \hat{H} | \phi_j \rangle \langle \phi_j | \Psi \rangle \\
&= \sum_i |C_i|^2 E_i \geq \sum_i |C_i|^2 E_0 \\
&\geq E_0
\end{aligned}$$

Define the energy of a general SD as a functional

$$E[\Phi] = \sum_{p=1}^{N} \langle p|\hat{h}_0|p\rangle + \frac{1}{2}\sum_{p=1}^{N}\sum_{q=1}^{N} \langle pq||pq\rangle.$$

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Expand the single-particle states into a new (general) basis

$$\sum_{p=1}^{N}\sum_{\alpha\beta} C^*_{p\alpha} C_{p\beta}\langle\alpha|\hat{h}_0|\beta\rangle + \frac{1}{2}\sum_{pq}^{N}\sum_{\alpha\beta\gamma\delta} C^*_{p\alpha} C^*_{q\beta} C_{p\gamma} C_{q\delta}\langle\alpha\beta||\gamma\delta\rangle.$$

Minimize $E[\Phi]$ with respect $C_{p\alpha}$, constraint to

$$\sum_{\alpha} C^{*}_{a\alpha} C_{a\alpha} - \delta_{a\alpha} = 0 \quad \forall \quad a.$$

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Can now use the method of Lagrange multipliers

$$E = E - \sum_{a} \epsilon_a \left(\sum_{\alpha} C^*_{a\alpha} C_{a\alpha} - \delta_{a\alpha} \right).$$

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To find the minimum, we look for a stationary point

$$\delta E = 0.$$

The minimization results in the Hartree–Fock equations

$$\sum_{\gamma}\left(\langle\alpha|\hat{h}_0|\gamma\rangle+\sum_{p=1}^{N}\sum_{\beta\delta}C^*_{p\beta}C_{p\delta}\langle\alpha\beta||\gamma\delta\rangle\right)C_{k\gamma}=\epsilon_k C_{k\alpha}\ \forall\ k,\alpha.$$

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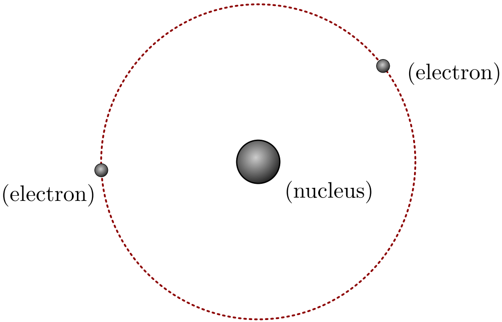
$$h^{\mathrm{HF}} C_k = \epsilon_k C_k,$$

The Hartree–Fock method is exactly equivalent to the self-consistent field method



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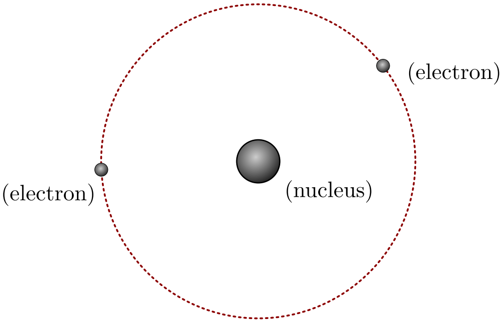
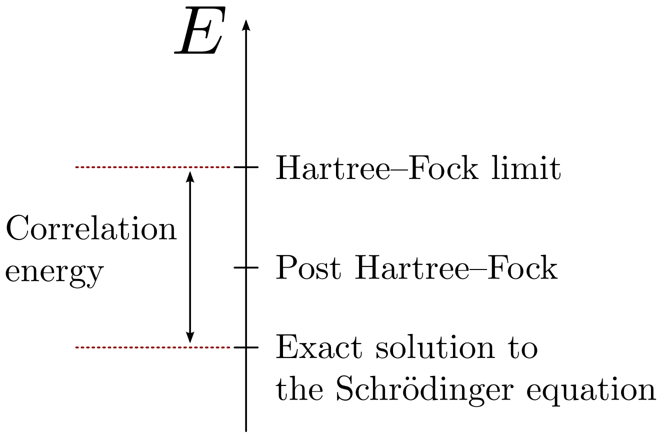


$$\hat{F}\phi_i = \epsilon_i \phi_i$$


E
Hartree–Fock limit
Correlation energy
Post Hartree–Fock
Exact solution to the Schrödinger equation

Configuration Interaction

$$\Psi = \Phi_{\mathrm{HF}} + \chi_{\mathrm{corr}}$$

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The set $\{\Phi_i\}_{i=0}^{N}$ is an orthonormal basis

$$H_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle.$$

$$HC = EC.$$

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The computational cost of CI grows exponentially with the size of the system. It is also not extensive, meaning the energy of a calculation scales erroneously with the system size.

Many-Body Perturbation Theory

We now decompose the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}, \qquad \hat{H}_0 \Phi_0 = E_0 \Phi_0.$$

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We expand the solution as a power series

$$\Psi = \Phi_0 + \chi = \Phi_0 + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \lambda^3\Psi^{(3)} + \dots.$$

$$E = E_0 + \Delta E = E_0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \dots.$$

Insert the power series into the Schrödinger equation

$$(\hat{H} - E)\Psi = 0.$$

$$\left(\hat{H}_0 + \lambda\hat{V} - E_0 - \lambda E^{(1)} - \dots\right)\left(\Phi_0 + \lambda\Psi^{(1)} + \dots\right).$$

We can now comparte terms order by order

$$\begin{aligned}
\text{(zeroth order) } (\hat{H}_0 - E_0)\Psi^{(0)} &= 0 \\
\text{(first order) } (\hat{H}_0 - E_0)\Psi^{(1)} &= (E^{(1)} - \hat{V})\Psi^{(0)} \\
\text{(second order) } (\hat{H}_0 - E_0)\Psi^{(2)} &= (E^{(1)} - \hat{V})\Psi^{(1)} + E^{(2)}\Psi^{(0)} \\
&\vdots
\end{aligned}$$

We now turn to Rayleigh-Schrödinger perturbation theory

$$\Psi = \sum_{m=0}^{\infty} \left[\hat{R}_0 (\hat{V} - \Delta E) \right]^m \Phi_0,$$

$$\Delta E = \sum_{m=0}^{\infty} \langle \Phi_0 | \hat{V} \left[\hat{R}_0 (\hat{V} - \Delta E) \right]^m | \Phi_0 \rangle.$$

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$$

$$
\begin{aligned}
E^{(1)} &= \langle \Phi | \hat{V} | \Phi \rangle, \\
E^{(2)} &= \langle \Phi | \hat{V} \hat{R}_0 \hat{V} | \Phi \rangle, \\
E^{(3)} &= \langle \Phi | \hat{V} \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 \hat{V} | \Phi \rangle, \\
E^{(4)} &= \langle \Phi | \hat{V} \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 \hat{V} | \Phi \rangle - E^{(2)} \langle \Phi | \hat{V} \hat{R}_0^2 \hat{V} | \Phi \rangle
\end{aligned}
$$

$$E^{(1)} = \langle\Phi|\hat{V}|\Phi\rangle,$$
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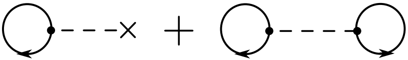
Diagrams are often very useful in finding the different contributions

First order: $E^{(1)} = \langle \Phi | \hat{V} | \Phi \rangle$



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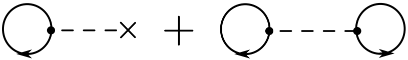

$E^{(1)} = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle$

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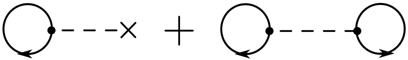

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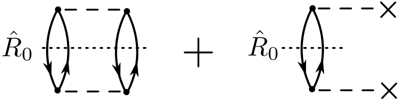

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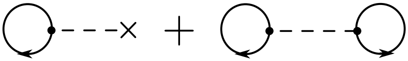

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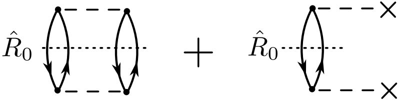
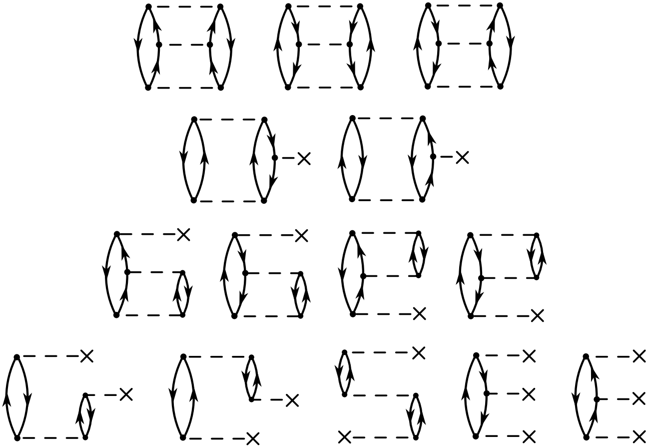
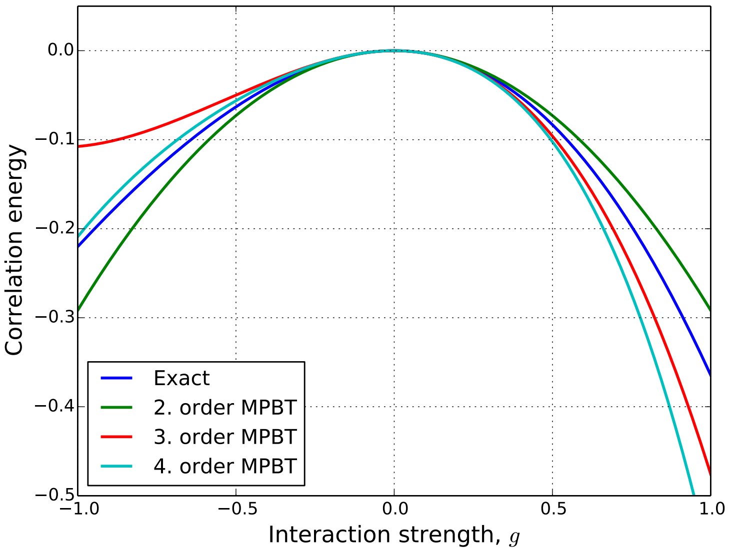


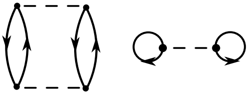
$$E^{(2)} = \frac{1}{4} \sum_{abij} \frac{\langle ab || ij \rangle \langle ij || ab \rangle}{\epsilon_{ij}^{ab}} + \sum_{ai} \frac{\langle a | \hat{f} | i \rangle \langle i | \hat{f} | a \rangle}{\epsilon_i^a}.$$

Third order: $E^{(3)} = \langle\Phi|\hat{V}\hat{R}_0\hat{W}\hat{R}_0\hat{V}|\Phi\rangle$




Exact
2. order MPBT
3. order MPBT
4. order MPBT
Correlation energy
Interaction strength, g
0.0
−0.1
−0.2
−0.3
−0.4
−0.5
−1.0
−0.5
0.0
0.5
1.0

Goldstones linked diagram theorem



Coupled Cluster

Coupled Cluster is based on the exponential ansatz

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The cluster operator is defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N.$$

$$\hat{T}_1 = \sum_{ai} t_i^a \{\hat{a}^\dagger \hat{i}\}$$

$$\hat{T}_2 = \sum_{abij} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\}$$

We limit the infinite series by truncating the cluster operator

$$\hat{T}_{\mathrm{CCD}} = \hat{T}_2, \qquad \hat{T}_{\mathrm{CCSD}} = \hat{T}_1 + \hat{T}_2.$$

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The normal-product Schroödinger equation

$$(\hat{H}_{\mathrm{N}} - \Delta E)e^{\hat{T}}\Phi_0 = 0.$$

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$$(\mathcal{H} - \Delta E)\Phi_0 = 0.$$

$$\begin{aligned} \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle &= \Delta E, \quad && \text{(energy equation)} \\ \langle \Phi_{ij\dots}^{ab\dots} | \mathcal{H} | \Phi_0 \rangle &= 0. && \text{(amplitude equation)} \end{aligned}$$

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Using Campbell-Baker-Hausdorff expansion, we rewrite

$$\mathcal{H} = \hat{H}_{\mathrm{N}} + [\hat{H}_{\mathrm{N}}, \hat{T}] + \frac{1}{2!}[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}] + \frac{1}{3!}\left[[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}], \hat{T}\right] + \ldots$$

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&= \left(\hat{H}_{\mathrm{N}} e^{\hat{T}}\right)_{\mathrm{C}}
\end{aligned}$$

These are the CC equations

$$\langle\Phi_0|\hat{H}_{\mathrm{N}} e^{\hat{T}}|\Phi_0\rangle_{\mathrm{C}} = \Delta E, \quad \text{(energy equation)}$$

$$\langle\Phi_{ij\ldots}^{ab\ldots}|\hat{H}_{\mathrm{N}} e^{\hat{T}}|\Phi_0\rangle_{\mathrm{C}} = 0. \quad \text{(amplitude equation)}$$

Example: Equation for the energy for CCSD

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$

$$\langle \Phi_0 | \hat{H}_{\mathrm{N}} \big(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \dots \big) | \Phi_0 \rangle_{\mathrm{C}} = \Delta E$$

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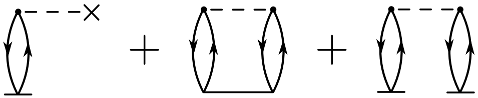

$$\Delta E = \sum_{ai} f_{ai} t_i^a + \frac{1}{2} \sum_{abij} \langle ab || ij \rangle t_i^a t_j^b + \frac{1}{4} \sum_{abij} \langle ab || ij \rangle t_{ij}^{ab}.$$

The Hartree–Fock method finds the lowest-energy single SD for the system. It can be found either from a mathematical minimization problem, or from a self-consistent field approach.

A single SD is often too simple, and so HF does not account for the **electron correlation energy**. Is therefore a good starting point, but rarely sufficient.

The method is both **variational** and **extensive**.

Configuration interaction is the simplest post Hartree-Fock method, both conceptually and computationally—it does however scale poorly with the system size.

FCI always gives the exact result, but is rarely possible.

Truncated CI is **variational**, but **not extensive**.

Many-body perturbation theory results taking a power-expansion of the perturbed wave-function and energy. We the compare the corrections order-by-order.

It is **extensive** in every order, but **not variational**. There is also no guaranteee of convergence.

Coupled cluster is based on the exponential ansatz. It can be seen as taking certain contributions from MBPT and summing them to infinite order (Shavitt and Bartlett). Alternatively as CI with added complexities (Szabo).

It is **extensive**, but **not variational**.

Just as for CI, CC has to be truncated, but for CCD and CCSD we usually have better results than for CID and CISD.

	Variational	Extensive
HF	✓	✓
FCI	✓	✓
CI	✓	✗
MBPT	✗	✓
CC	✗	✓