COUPLED-CLUSTER AND DENSITY FUNCTIONAL THEORY

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Outline

Coupled-cluster theory

The starting point for all non-relativistic treatments of the many-body system is the Schrödinger equation,

$$\widehat{H}|\Psi\rangle = E|\Psi\rangle\,,$$

where

$$\widehat{H} = \widehat{H}_0 + \widehat{V} = \widehat{T} + \widehat{U} + \widehat{V}$$
$$= \sum_{i=1}^{N}\widehat{t}_i + \sum_{i=1}^{N}\widehat{u}_i + \sum_{i<j}^{N}\widehat{v}_{ij} + \sum_{i<j<k}^{N}\widehat{v}_{ijk} + ...$$

$\widehat{T}$ - Kinetic energy, one-body operator
$\widehat{U}$ - External potential, one-body operator
$\widehat{V}$ - Particle interaction, in general a n-body operator

- The *N*-particle Schrödinger equation can in genereal not be solved analytically
  ⇒ Numerical methods

- The coupled-cluster method is today probably the most powerful *ab initio* method to obtain ground state eigenvalues and eigenstates

Coupled-cluster theory

Given an arbitrary set of orthogonal single-particle functions

$$\{\phi_\alpha\}_{\alpha=1}^{\infty}$$

that span the one-particle Hilbert space $\mathcal{H}_1$, the exact wavefunction of an interacting many-fermion systems reads,

$$|\Psi\rangle = \sum_{i=1}^{\infty} C_i |\Phi_i\rangle,$$

where

$$\Phi_i(\mathbf{R}) = \langle \mathbf{R} | \Phi_i \rangle = \frac{1}{\sqrt{N!}} \sum_p (-1)^p \widehat{P} \phi_\alpha(\mathbf{r}_1) \phi_\beta(\mathbf{r}_2) \phi_\gamma(\mathbf{r}_3)..\phi_\delta(\mathbf{r}_N),$$

and

$$\sum_{i=1}^{\infty} |C_i|^2 = 1.$$

- In principle, no other restrictions on the single-particle functions besides completeness and orthogonality,

$$\mathcal{H}_1 = span\{\phi_\alpha\}_{i=1}^{\infty}$$

- In practice, the choice of basis functions is crucial!

- How to deside the appropriate basis functions? Obviously, we want

$$|\Psi\rangle = \sum_{i=1}^{\infty} C_i |\Phi_i\rangle \approx \sum_{i=1}^{k} C_i |\Phi_i\rangle .$$

- When the interaction $\widehat{V}$ is small, natural choice of N-particle basis functions are the eigenfunctions of the non-interacting system,

$$\widehat{H}_0 |\Phi_i\rangle = E_i^0 |\Phi_i\rangle ,$$

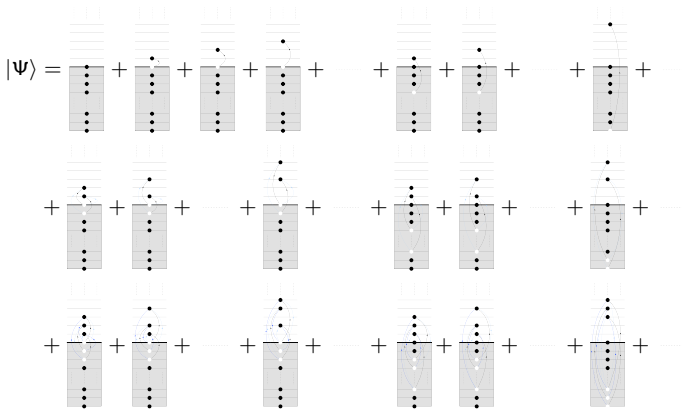such that the single-particle basis functions are given by

$$\widehat{h} |\phi_\alpha\rangle = \epsilon_\alpha |\phi_\alpha\rangle ,$$

where $\widehat{h} = \widehat{t} + \widehat{u}$.

Coupled-cluster theory

The exact wavefunction

- $|\Psi\rangle$ - linear combination of excited states of the non-interacting system
- The correlations in the system are thus represented by excitations in the non-interacting system

Coupled-cluster theory

In the formalism of second quantization, $|\Psi\rangle$ thus reads,

$$|\Psi\rangle = |\Phi_0\rangle + \sum_i^a t_i^a a_a^\dagger a_i |\Phi_0\rangle + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle + \frac{1}{24} \sum_{ijkabc} t_{ijk}^{abc} a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i |\Phi_0\rangle + ..,$$

where $t_{ijk..}^{abc..}$ are the excitation amplitudes. Defining the excitation operators

$$\widehat{T}_1 \equiv \sum_{ia} t_i^a a_a^\dagger a_i$$

$$\widehat{T}_2 \equiv \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

$$\widehat{T}_3 \equiv \frac{1}{24} \sum_{ijkabc} t_{ijk}^{abc} a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i$$

$$\widehat{T}_n \equiv \left(\frac{1}{n!}\right)^2 \sum_{ijk..abc..} t_{ijk..}^{abc..} a_a^\dagger a_b^\dagger a_c^\dagger .... a_k a_j a_i$$

the exact wavefunction reads

$$|\Psi\rangle = \left(1 + \widehat{T}_1 + \widehat{T}_2 + \widehat{T}_3 + ... + \widehat{T}_N\right) |\Phi_0\rangle.$$

Coupled-cluster theory

The coupled-cluster wavefunction - the exponential "ansatz"

- We may also produce, for example, $2p2h$-excitations with $\widehat{T}_1^2$
  $\Rightarrow$ No coupling between single-particle states

- Thus, the exact wavefunction reads

$$|\Psi\rangle = \left(1 + \widehat{T}_1 + \frac{1}{2!}\widehat{T}_1^2 + \widehat{T}_2 + \frac{1}{3!}\widehat{T}_1^3 + \widehat{T}_1\widehat{T}_2 + \widehat{T}_3 + ... + \widehat{T}_N\right)|\Phi_0\rangle$$

- Since all excitation operators commute, all terms above match those from the power series expansion of an exponential function

- We therefore define the coupled-cluster wavefunction as

$$|\Psi_{CC}\rangle = e^{\widehat{T}}|\Phi_0\rangle,$$

where

$$\widehat{T} \equiv \widehat{T}_1 + \widehat{T}_2 + \widehat{T}_3 + ... + \widehat{T}_N.$$

Coupled-cluster theory

The coupled-cluster wavefunction - the exponential "ansatz"

- When $\widehat{T}$ is not truncated and the model space $\mathcal{P}$ is equal to the Hilbert space of N non-interacting fermions,

$$|\Psi\rangle = |\Psi_{CC}\rangle.$$

- In practical calculations, since $dim(\mathcal{H}_N) = /infty$, the model space must be truncated

- Also, choosing a CC scheme, for example CCSD, imply a truncation in $\widehat{T}$

- Therefore, the coupled-cluster wavefunction is called the exponential "ansatz"

- We approximate the exact ground state wavefunction with the coupled-cluster wavefunction,

$$|\Psi\rangle \approx |\Psi_{CC}\rangle,$$

and hope this is a good approximation!

- The unknowns are the excitation amplitudes $t_{ijk..}^{abc..}$ which is determined by the Schrödinger equation

Coupled-cluster theory

The formal coupled-cluster equations are found by substituting the CC function into the Schrödinger equation,

$$\widehat{H} e^{T} |\Phi_0\rangle = E e^{\widehat{T}} |\Phi_0\rangle,$$

and left-multiply with $\langle \Phi_0 | e^{-\widehat{T}}$, yielding the energy equation

$$\left\langle \Phi_0 \left| e^{-\widehat{T}} \widehat{H} e^{\widehat{T}} \right| \Phi_0 \right\rangle = E.$$

The amplitude equations are found by left-multiplying the wanted ampltides $t_{ijk..}^{abc..}$ with $\left\langle \Phi_{ijk..}^{abc..} \right| e^{-\widehat{T}}$, yielding

$$\left\langle \Phi_{ijk..}^{abc..} \left| e^{-\widehat{T}} \widehat{H} e^{\widehat{T}} \right| \Phi_0 \right\rangle = 0.$$

- These equations define the conventional method
- How to solve the CC equations? Normal ordering, Campell-Baker-Hausdorff expansion

Coupled-cluster and density functional theory

- Second quantized from of the hamiltonian (assume 2-body interaction),

$$\widehat{H} = \sum_{pq} \langle p\,|h|\,q \rangle \, a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq\,|v|\,rs \rangle \, a_p^\dagger a_q^\dagger a_s a_r$$

- Wick's theorem,

$$\widehat{A}\widehat{B}\widehat{C}\widehat{D}..\widehat{R}\widehat{X}\widehat{Y}\widehat{Z} = \left\{ \widehat{A}\widehat{B}\widehat{C}\widehat{D}..\widehat{R}\widehat{X}\widehat{Y}\widehat{Z} \right\} + \sum_{[1]} \left\{ \overline{\widehat{A}\widehat{B}}\widehat{C}\widehat{D}..\widehat{R}\widehat{X}\widehat{Y}\widehat{Z} \right\}$$

$$+ ... + \sum_{[\frac{N}{2}]} \left\{ \overline{\widehat{A}\widehat{B}\widehat{C}\widehat{D}}.. \; \overline{\widehat{R}\widehat{X}\widehat{Y}\widehat{Z}} \right\}$$

- Using Wick's theorem, we obtain the following expressions

$$a_p^\dagger a_q = \left\{ a_p^\dagger a_q \right\} + \delta_{pq \subset i}$$

$$a_p^\dagger a_q^\dagger a_s a_r = \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} - \left\{ a_q^\dagger a_r \right\} \delta_{ps \subset i} + \left\{ a_q^\dagger a_s \right\} \delta_{pr \subset i}$$

$$+ \left\{ a_p^\dagger a_r \right\} \delta_{qs \subset i} - \left\{ a_p^\dagger a_s \right\} \delta_{qr \subset i} + \delta_{pr \subset i}\delta_{qs \subset j} - \delta_{ps \subset i}\delta_{qr \subset j},$$

Inserting these expressions into the second quantized form of $\widehat{H}$ yields,

$$
\begin{aligned}
\widehat{H} = & \sum_{pq} \langle p \,|h|\, q \rangle \left\{ a_p^\dagger a_q \right\} + \sum_i \langle i \,|h|\, i \rangle \\
& + \frac{1}{4} \sum_{pqrs} \langle pq \,|v|\, rs \rangle \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} - \frac{1}{4} \sum_{qri} \langle iq \,|v|\, ri \rangle \left\{ a_q^\dagger a_r \right\} + \frac{1}{4} \sum_{qsi} \langle iq \,|v|\, is \rangle \left\{ a_q^\dagger a_s \right\} \\
& + \frac{1}{4} \sum_{pri} \langle pi \,|v|\, ri \rangle \left\{ a_p^\dagger a_r \right\} - \frac{1}{4} \sum_{psi} \langle pi \,|v|\, is \rangle \left\{ a_p^\dagger a_s \right\} + \frac{1}{4} \sum_{ij} \langle ij \,|v|\, ij \rangle - \frac{1}{4} \sum_{ij} \langle ij \,|v|\, ji \rangle \,.
\end{aligned}
$$

Remembering that

$$
\langle pq \,|v|\, rs \rangle = - \langle pr \,|v|\, sr \rangle = - \langle rp \,|v|\, rs \rangle = \langle rp \,|v|\, sr \rangle \,,
$$

we obtain

$$
\begin{aligned}
\widehat{H} = & \sum_{pq} \langle p \,|h|\, q \rangle \left\{ a_p^\dagger a_q \right\} + \sum_{pqi} \langle pi \,|v|\, qi \rangle \left\{ a_p^\dagger a_q \right\} \\
& + \sum_{pqrs} \langle pq \,|v|\, rs \rangle \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} + \sum_i \langle i \,|h|\, i \rangle + \frac{1}{2} \sum_{ij} \langle ij \,|v|\, ij \rangle \,.
\end{aligned}
$$

Coupled-cluster theory

Normal-ordered form of $\widehat{H}$

By defining

$$f_q^p \equiv \langle p\,|h|\,q\rangle + \sum_i \langle pi\,|v|\,qi\rangle$$

$$\widehat{F}_N \equiv \sum_{pq} f_q^p \left\{ a_p^\dagger a_q \right\}$$

$$\widehat{V}_N \equiv \sum_{pqrs} \langle pq\,|v|\,rs\rangle \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\},$$

and observing that

$$\left\langle \Phi_0 \left| \widehat{H} \right| \Phi_0 \right\rangle = \sum_i \langle i\,|h|\,i\rangle + \frac{1}{2} \sum_{ij} \langle ij\,|v|\,ij\rangle,$$

the hamiltonian finally reads

$$\widehat{H} = \widehat{F}_N + \widehat{V}_N + \left\langle \Phi_0 \left| \widehat{H} \right| \Phi_0 \right\rangle$$

$$= \widehat{H}_N + \left\langle \Phi_0 \left| \widehat{H} \right| \Phi_0 \right\rangle.$$

Defining $E_{ref} = \left\langle \Phi_0 \left| \widehat{H} \right| \Phi_0 \right\rangle$, the normal-ordered form of the hamiltonian reads

$$\widehat{H}_N = \widehat{H} - E_{ref}.$$

- The normal-ordered form of the hamiltonian is equal to the hamiltonian itself minus the its reference expectation value

- Thus we consider $\widehat{H}_N$ as a correlation operator

- Substituting $\widehat{H} = \widehat{H}_N + E_{ref}$ into the CC equations yields,

$$\left\langle \Phi_0 \left| e^{-\widehat{T}} \widehat{H}_N e^{\widehat{T}} \right| \Phi_0 \right\rangle = E_{CC}$$
$$\left\langle \Phi_{ijk..}^{abc..} \left| e^{-\widehat{T}} \widehat{H}_N e^{\widehat{T}} \right| \Phi_0 \right\rangle = 0,$$

where we have defined the coupled-cluster energy $E_{CC} = E - E_{ref}$.

Coupled-cluster theory

- The Campbell-Baker-Hausdorff formula allow us to expand the similarity transformed normal-ordered hamiltonian into nested commutators,

$$e^{-\widehat{T}}\widehat{H}_N e^{\widehat{T}} = \widehat{H}_N + \left[\widehat{H}_N, \widehat{T}\right] + \frac{1}{2!}\left[\left[\widehat{H}_N, \widehat{T}\right], \widehat{T}\right] + \frac{1}{3!}\left[\left[\left[\widehat{H}_N, \widehat{T}\right], \widehat{T}\right], \widehat{T}\right] + ...$$

- We limit the discussion to the coupled-cluster singles and doubles (CCSD),

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

- The similarity transformed hamiltonien then reads

$$e^{-\widehat{T}}\widehat{H}_N e^{\widehat{T}} = \widehat{H}_N + \left[\widehat{H}_N, \widehat{T}_1\right] + \left[\widehat{H}_N, \widehat{T}_2\right] + \frac{1}{2!}\left[\left[\widehat{H}_N, \widehat{T}_1\right], \widehat{T}_1\right] + \frac{1}{2!}\left[\left[\widehat{H}_N, \widehat{T}_1\right], \widehat{T}_2\right]$$
$$+ \frac{1}{2!}\left[\left[\widehat{H}_N, \widehat{T}_2\right], \widehat{T}_1\right] + \frac{1}{2!}\left[\left[\widehat{H}_N, \widehat{T}_2\right], \widehat{T}_2\right] + ...$$

- The problem is now reduced to evaluating matrix elements of nested commutators

- One problem, the general Campbell-Baker-Hausdorff expansion is in principle infinite

- However, the sum truncates naturally in the CC context

Programable CCSD equations can be obtained by two different approaches,

- **Algebraic method**
  "The hard way" - Each matrix element of nested commutators are evaluated by using Wick's theorem

- **Diagramatic method**
  "The easy way" - Each matrix element of nested commutators is converted into a diagram, a set of rules transform each diagram into an algebraic expression

Coupled-cluster theory

Algebraic approach - The energy equation

- The energy equation reads

$$E_{CC} = \left\langle \Phi_0 \left| \widehat{H}_N + \left[\widehat{H}_N, \widehat{T}_1\right] + \left[\widehat{H}_N, \widehat{T}_2\right] + \frac{1}{2!}\left[\left[\widehat{H}_N, \widehat{T}_1\right], \widehat{T}_1\right] + ... \right| \Phi_0 \right\rangle$$

- By construction, the reference expectation value of a normal-ordered operator is zero, viz.

$$\left\langle \Phi_0 \left| \widehat{X}_N \right| \Phi_0 \right\rangle = 0$$

- All excitation operators are already normal-ordered, viz.

$$\left\langle \Phi_0 \left| \widehat{T}_i \right| \Phi_0 \right\rangle = 0$$

- In the algebraic approach, each nested commutator between reference states is evaluated using the generalized Wick's theorem,

$$\left\{\widehat{A}\widehat{B}\widehat{C}\widehat{D}..\right\}\left\{\widehat{R}\widehat{X}\widehat{Y}\widehat{Z}..\right\} = \left\{\widehat{A}\widehat{B}\widehat{C}\widehat{D}..\widehat{R}\widehat{X}\widehat{Y}\widehat{Z}\right\} + \sum_{(1)}\left\{\overline{\widehat{A}\widehat{B}\widehat{C}\widehat{D}..\widehat{R}}\widehat{X}\widehat{Y}\widehat{Z}\right\}$$

$$+ \sum_{(2)}\left\{\overline{\overline{\widehat{A}\widehat{B}\widehat{C}\widehat{D}..\widehat{R}}\widehat{X}}\widehat{Y}\widehat{Z}\right\} + ...$$

Coupled-cluster theory

$\Rightarrow$ Only nonzero contributions from fully contracted terms!

(1) $E_{CC} \leftarrow \left\langle \Phi_0 \left| \widehat{H}_N \right| \Phi_0 \right\rangle = 0$

(2) $E_{CC} \leftarrow \left\langle \Phi_0 \left| \left[\widehat{H}_N, \widehat{T}_1 \right] \right| \Phi \right\rangle = \left\langle \Phi \left| \left[\widehat{F}_N, \widehat{T}_1 \right] \right| \Phi \right\rangle + \left\langle \Phi \left| \left[\widehat{V}_N, \widehat{T}_1 \right] \right| \Phi_0 \right\rangle$

The first term,

$$\widehat{F}_1 \widehat{T}_1 = \sum_{pqia} f_q^p t_i^a \left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\}$$

$$\widehat{T}_1 \widehat{F}_1 = \sum_{pqia} f_a^p t_i^a \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\}.$$

The generalized Wick's theorem yields,

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger} a_i \right\} + \left\{ a_p^\dagger a_q \overline{a_a^\dagger a_i} \right\} + \left\{ \overline{\overline{a_p^\dagger a_q a_a^\dagger a_i}} \right\}$$

$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_q a_a^\dagger \right\} \delta_{pi} + \left\{ a_p^\dagger a_i \right\} \delta_{qa} + \delta_{pi} \delta_{qa}$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\}$$

Thus we obtain

$$\left[\widehat{F}_N, T_1\right] = \sum_{qia} f_q^i t_i^a \left\{ a_q a_a^\dagger \right\} + \sum_{pia} f_a^p t_i^a \left\{ a_p^\dagger a_i \right\} + \sum_{ia} f_a^i t_i^a.$$

The second term,

$$\widehat{V}_N \widehat{T}_1 = \frac{1}{4} \sum_{pqrsia} \langle pq |v| rs \rangle t_i^a \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_a^\dagger a_i \right\}$$

$$\widehat{T}_1 \widehat{V}_N = \frac{1}{4} \sum_{pqrsia} \langle pq |v| rs \rangle t_i^a \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\}.$$

Due to Wick's generalized theorem, two normal-ordered stings with different number of creation- and annihilation operators cannot produce fully contracted terms. Thus,

$$E_{CC} \leftarrow \left\langle \Phi_0 \left| \left[\widehat{H}_N, \widehat{T}_1 \right] \right| \Phi \right\rangle = \sum_{ia} f_a^i t_i^a$$

Observation: For a two-body hamiltonian (electron system, coulomb interaction), the energy equation will be on the same form for all schemes (CCSD, CCSDT,...)

(3) $E_{CC} \leftarrow \left\langle \Phi \left| \left[\widehat{H}_N, \widehat{T}_2 \right] \right| \Phi \right\rangle = \left\langle \Phi \left| \left[\widehat{F}_N, \widehat{T}_2 \right] \right| \Phi \right\rangle + \left\langle \Phi \left| \left[\widehat{F}_N, \widehat{T}_2 \right] \right| \Phi \right\rangle$

The first term,

$$\widehat{F}_N \widehat{T}_2 = \frac{1}{4} \sum_{pqijab} f_q^p t_{ij}^{ab} \left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\}$$

$$\widehat{T}_2 \widehat{F}_N = \frac{1}{4} \sum_{pqijab} f_q^p t_{ij}^{ab} \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\} \left\{ a_p^\dagger a_q \right\}.$$

Again, since the number of creation- and annihilation operators are different, no fully contractions are possible, i.e. no nonzero contributions.
The second term,

$$\widehat{V}_N \widehat{T}_2 = \frac{1}{16} \sum_{pqrsijab} t_{ij}^{ab} \left\langle pq \left| v \right| rs \right\rangle \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\}$$

$$\widehat{T}_2 \widehat{V}_N = \frac{1}{16} \sum_{pqrsijab} t_{ij}^{ab} \left\langle pq \left| v \right| rs \right\rangle \left\{ a_a^\dagger a_b^\dagger a_i a_j \right\} \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\}.$$

$$\left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\} = \left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + ...$$

$$= \delta_{pi}\delta_{qj}\delta_{sb}\delta_{ra} - \delta_{pi}\delta_{qj}\delta_{sa}\delta_{rb} - \delta_{pj}\delta_{qi}\delta_{sb}\delta_{ra} + \delta_{pj}\delta_{qi}\delta_{sa}\delta_{rb}$$

$$+ \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + ...$$

$$\left\{ a_a^\dagger a_b^\dagger a_j a_i \right\} \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} = \left\{ a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q^\dagger a_s a_r \right\}$$

$$\left[\widehat{V}_N, \widehat{T}_2 \right] = \frac{1}{16} \sum_{ijab} \left[\langle ij \, |v| \, ab \rangle - \langle ij \, |v| \, ba \rangle - \langle ji \, |v| \, ab \rangle + \langle ji \, |v| \, ba \rangle \right] t_{ij}^{ab} + ...$$

$$= \frac{1}{4} \sum_{ijab} \langle ij \, |v| \, ab \rangle \, t_{ij}^{ab} + ...$$

Thus we obtain the following contribution to the coupled-cluster energy,

$$E_{CC} \leftarrow \left\langle \Phi \left| \left[\widehat{H}_N, \widehat{T}_2 \right] \right| \Phi \right\rangle = \frac{1}{4} \sum_{ijab} \langle ij \left| v \right| ab \rangle \, t_{ij}^{ab}$$

(4) $E_{CC} \leftarrow \frac{1}{2} \left\langle \Phi \left| \left[\left[\widehat{H}_N, \widehat{T}_1 \right], \widehat{T}_1 \right] \right| \Phi \right\rangle$

The first term,

$$\left[\widehat{F}_N, \widehat{T}_1 \right] \widehat{T}_1 = \sum_{qijab} f_q^i t_i^a t_j^b \left\{ a_q a_a^\dagger \right\} \left\{ a_b^\dagger a_j \right\} + \sum_{pijab} f_a^p t_i^a t_j^b \left\{ a_b^\dagger a_i \right\} \left\{ a_b^\dagger a_j \right\} + \sum_{ijab} f_a^i t_i^a t_j^b \left\{ a_b^\dagger a_j \right\}$$

$$\widehat{T}_1 \left[\widehat{F}_N, \widehat{T}_1 \right] = \sum_{qijab} f_q^i t_i^a t_j^b \left\{ a_b^\dagger a_j \right\} \left\{ a_q a_a^\dagger \right\} + \sum_{pijab} f_a^p t_i^a t_j^b \left\{ a_b^\dagger a_j \right\} \left\{ a_p^\dagger a_i \right\} + \sum_{ijab} f_a^i t_i^a t_j^b \left\{ a_b^\dagger a_j \right\}$$

gives no contribution to the energy since only non-zero contractions are between creation (annihilation) operator with quantum number a (i), and an annihilation (creation) operator with quantum number p.

Coupled-cluster theory

The second term,

$$
\left[\widehat{V}_N, \widehat{T}_1\right] \widehat{T}_1 = \frac{1}{4} \sum_{pqrsijab} \langle pq \,|v|\, rs \rangle\, t_i^a t_j^b \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_a^\dagger a_i \right\} \left\{ a_b^\dagger a_j \right\}
$$

$$
+ \frac{1}{4} \sum_{pqrsijab} \langle pq \,|v|\, rs \rangle\, t_i^a t_j^b \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_b^\dagger a_j \right\}
$$

$$
\widehat{T}_1 \left[\widehat{V}_N, \widehat{T}_1\right] = \frac{1}{4} \sum_{pqrsijab} \langle pq \,|v|\, rs \rangle\, t_i^a t_j^b \left\{ a_b^\dagger a_j \right\} \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_a^\dagger a_i \right\}
$$

$$
+ \frac{1}{4} \sum_{pqrsijab} \langle pq \,|v|\, rs \rangle\, t_i^a t_j^b \left\{ a_b^\dagger a_j \right\} \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\}
$$

$$
\frac{1}{2} \left[\left[\widehat{V}_N, \widehat{T}_1\right], \widehat{T}_1\right] = \frac{1}{8} \sum_{pqrsijab} \langle pq \,|v|\, rs \rangle\, t_i^a t_j^b
$$

$$
\times \left(\delta_{pi}\delta_{qj}\delta_{sa}\delta_{rb} - \delta_{pi}\delta_{qj}\delta_{sb}\delta_{ra} - \delta_{pj}\delta_{qi}\delta_{sa}\delta_{rb} + \delta_{pj}\delta_{qi}\delta_{sb}\delta_{ra} \right) + ...
$$

$$
= \frac{1}{8} \sum_{ijab} \left(\langle ij \,|v|\, ba \rangle - \langle ij \,|v|\, ab \rangle - \langle ji \,|v|\, ba \rangle + \langle ji \,|v|\, ab \rangle \right) t_i^a t_j^b + ...
$$

$$
= \frac{1}{2} \sum_{ijab} \langle ij \,|v|\, ab \rangle\, t_i^a t_j^b + ...
$$

Coupled-cluster theory

Algebraic approach - The energy equation

Thus we obtain the following contribution to the coupled-cluster energy,

$$E_{CC} \leftarrow \frac{1}{2} \left\langle \Phi \left| \left[\left[\widehat{V}_N, \widehat{T}_1 \right], \widehat{T}_1 \right] \right| \Phi \right\rangle = \frac{1}{2} \sum_{ijab} \langle ij | v | ab \rangle \, t_i^a t_j^b$$

- An important generalization - Wick's theorem applied to the commutators, the only nonzero terms in the Hausdorff expansion are those in which $\widehat{H}_N$ has at least one contraction with every $\widehat{T}_n$ on its right

- The Hausdorff expansion of the similarity transforem hamiltonian thus reads,

$$e^{-\widehat{T}} \widehat{H} e^{\widehat{T}} = \left(\widehat{H}_N + \widehat{H}_N \widehat{T} + \frac{1}{2!} \widehat{H}_N \widehat{T}^2 + \frac{1}{3!} \widehat{H}_N \widehat{T}^3 + \frac{1}{4!} \widehat{H}_N \widehat{T}^4 + ... \right)_c$$

- We assume an electronic system $\Rightarrow$ 2-body interaction (coulomb)

- The Hausdorff expansion then truncates naturally,

$$e^{-\widehat{T}} \widehat{H} e^{\widehat{T}} = \left(\widehat{H}_N + \widehat{H}_N \widehat{T} + \frac{1}{2} \widehat{H}_N \widehat{T}^2 + \frac{1}{6} \widehat{H}_N \widehat{T}^3 + \frac{1}{24} \widehat{H}_N \widehat{T}^4 \right)_c$$

Coupled-cluster theory

- The CCSD energy equation thus reads,

$$E_{CC} = \left\langle \Phi \left| \left(\widehat{H}_N \widehat{T}_1 + \widehat{H}_N \widehat{T}_2 + \frac{1}{2} \widehat{H}_N \widehat{T}_1^2 \right) \right| \Phi \right\rangle_{fc},$$

  where fc denote that only fully contracted terms give contribution to the energy

- For the electron system, the ground state energy only depends explicitly on t_i^a and t_{ij}^{ab} for all CC schemes (CCSD, CCSDT, CCSDTQ,..)

- However, when including more than singles and doubles, the energy depend implicitly on $t_{ijk..}^{abc..}$ - all ampltides are coupled together

- The final coupled-cluster energy equation reads

$$E_{CC} = \sum_{ia} f_a^i t_i^a + \frac{1}{4} \sum_{ijab} \langle ij \, | v | \, ab \rangle \, t_{ij}^{ab} + \frac{1}{2} \sum_{ijab} \langle ij \, | v | \, ab \rangle \, t_i^a t_j^b$$

Coupled-cluster theory

Algebraic approach - The amplitude equation

- The amplitude equation reads (assume two-body hamiltonian)

$$0 = \left\langle \Phi_{ijk..}^{abc..} \left| e^{-\widehat{T}} \widehat{H}_N e^{\widehat{T}} \right| \Phi_0 \right\rangle$$

$$= \left\langle \Phi_{ijk..}^{abc..} \left| \left(\widehat{H}_N + \widehat{H}_N \widehat{T} + \frac{1}{2} \widehat{H}_N \widehat{T}^2 + \frac{1}{6} \widehat{H}_N \widehat{T}^3 + \frac{1}{24} \widehat{H}_N \widehat{T}^4 \right)_c \right| \Phi_0 \right\rangle$$

- However, since

$$\left\langle \Phi_{ijk..}^{abc..} \middle| \Phi_0 \right\rangle = 0,$$

fully contracted terms DO NOT give contribution

- $\widehat{T}_1$ equation, nonzero contribution from terms with excitation level 1, viz. terms with

$$\left\{ a_a^\dagger a_i \right\}$$

- $\widehat{T}_2$ equation, nonzero contribution from terms with excitation level 2, viz. terms with

$$\left\{ a_a^\dagger a_b^\dagger a_j a_i \right\}$$

Coupled-cluster theory

- The diagramatic approach - far more convenient and practical approach to construct programable equations
- Basic procedure - matrix element is transformed into a diagram, rules determine its corresponding algebraic expression
- Depending on the mathematical context, diagrams can represent wavefunctions, operators and matrix elements

$$= |\Phi\rangle \qquad\qquad = |\Phi_i\rangle$$

$$= |\Phi_i^a\rangle \qquad\qquad = |\Phi^a\rangle$$

Diagramatic method - Wavefunction representation

$$\Big| = \left| \Phi_{ij}^{ab} \right\rangle \qquad\qquad \Big| = \left| \Phi_{ij} \right\rangle$$

$$\Big| = \left| \Phi_{ijk}^{abc} \right\rangle \qquad\qquad \Big| = \left| \Phi^{ab} \right\rangle$$

- Diagrams may represent operators - interested in the diagramatic representation of $\widehat{F}_N$, $\widehat{V}_N$ and $\widehat{T}_n$

$$\widehat{F}_N = \sum_{ab} f_b^a \left\{ a_a^\dagger a_b \right\} + \sum_{ij} f_j^i \left\{ a_i^\dagger a_j \right\} + \sum_{ia} f_a^i \left\{ a_i^\dagger a_a \right\} + \sum_{ai} f_i^a \left\{ a_a^\dagger a_i \right\}$$
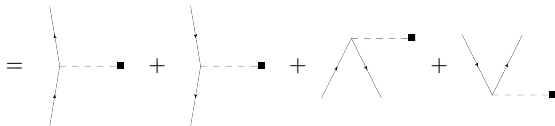
$$\widehat{V}_N =$$
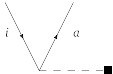
$$\widehat{T}_1 = \sum_{ia} t_i^a \left\{ a_a^\dagger a_i \right\} =$$

$$\widehat{T}_2 = \sum_{ijab} t_{ij}^{ab} \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\} =$$
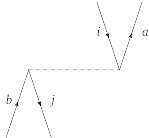
Coupled-cluster theory
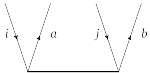
- Diagrams can be interpreted from bottom to top as matrix elements of operators between slater determinants

- Example, fourth fragment of $\widehat{F}_N$ - since $|\Phi_0\rangle$ is represented by emty space, and $\left|\Phi_i^a\right\rangle$ by a pair of directed lines, we may do the following interpretation,

$$\left\langle \Phi_i^a \left| \widehat{F}_N \right| \Phi_0 \right\rangle = $$

- Two other examples, third fragment of $\widehat{V}_N$ and the $2p2h$-excitation operator $\widehat{T}_2$

$$\left\langle \Phi_i^a \left| \widehat{V}_N \right| \Phi_j^b \right\rangle = \qquad\qquad \left\langle \Phi_{ij}^{ab} \left| \widehat{T}_2 \right| \Phi_0 \right\rangle = $$

Coupled-cluster theory

- The coupled-cluster energy equation,

$$E_{CC} = \left\langle \Phi_0 \left| \left(\widehat{H}_N + \widehat{H}_N\widehat{T} + \frac{1}{2!}\widehat{H}_N\widehat{T}^2 + \frac{1}{3!}\widehat{H}_N\widehat{T}^3 + \frac{1}{4!}\widehat{H}_N\widehat{T}^4 + ... \right)_c \right| \Phi_0 \right\rangle$$

- Excitation level - An easy way to determine which diagram that contributes to the energy

- Since $|\Phi_0\rangle$ is represented by emty space, the diagram can not contain directed lines that extend above or below the first or last operator line $\Rightarrow$ Total excitation level 0

- None of the fragments of $\widehat{H}_N$ satisfy this critericon, thus
  $E_{CC} \leftarrow \left\langle \Phi_0 \left| \widehat{H}_N \right| \Phi_0 \right\rangle = 0$

- How should we evaluate the contribution from for example $\left\langle \Phi_0 \left| \widehat{H}_N\widehat{T}_1 \right| \Phi_0 \right\rangle$?

  - Rightmost operator $\widehat{T}_1 \Rightarrow \widehat{T}_1$ interaction line at bottom of the diagram
  - $\widehat{T}_1$ has excitation level +1
  - Total excitaion level must be 0
  - Require those diagrams of $\widehat{H}_N$ with excitaion level -1, and $|\Phi_0\rangle$ at the top
  - Only the third fragment of $\widehat{F}_N$

Coupled-cluster theory

- We then connect the diagrams together (analogous to contractions), yielding

$$\left\langle \Phi_0 \left| \widehat{H}_N \widehat{T}_1 \right| \Phi_0 \right\rangle =$$

- Since $\widehat{H}_N$ has minimum excitation level -2, all excitation operators and products of excitation operators with a larger excitation level than +2 do not contribute

- Therefore,

$$E_{CC} = \left\langle \Phi_0 \left| \left(\widehat{H}_N \widehat{T}_1 + \widehat{H}_N \widehat{T}_2 + \frac{1}{2} \widehat{H}_N \widehat{T}_1^2 \right)_{fc} \right| \Phi_0 \right\rangle$$

- Using same procedure as before, we obtain three diagrams that contribute to the energy,

$$E_{CC} = \qquad + \qquad + \qquad$$

Coupled-cluster and density functional theory

Coupled-cluster theory

- The CCSD amplitude equations

$$0 = \left\langle \Phi_i^a \left| \left(\widehat{H}_N + \widehat{H}_N \widehat{T} + \frac{1}{2!}\widehat{H}_N \widehat{T}^2 + \frac{1}{3!}\widehat{H}_N \widehat{T}^3 + \frac{1}{4!}\widehat{H}_N \widehat{T}^4 + ... \right)_c \right| \Phi_0 \right\rangle$$

$$0 = \left\langle \Phi_{ij}^{ab} \left| \left(\widehat{H}_N + \widehat{H}_N \widehat{T} + \frac{1}{2!}\widehat{H}_N \widehat{T}^2 + \frac{1}{3!}\widehat{H}_N \widehat{T}^3 + \frac{1}{4!}\widehat{H}_N \widehat{T}^4 + ... \right)_c \right| \Phi_0 \right\rangle$$

- Diagrams that contribute to the $\widehat{T}_1$ equation have total excitation level +1

- Diagrams that contribute to the $\widehat{T}_2$ equation have total excitation level +2

- Different fragments of $\widehat{H}_N$ and combinations of excitation operators is then combined to satisfy this critericon

The $\widehat{T}_1$ amplitude equation reads,

Coupled-cluster theory

Diagramatic method - The diagram rules

Diagram rules - Algebraic interpretation of diagrams

- Label all directed lines → Hole lines: *ijk*.., Particle lines: *abc*..
- Operator interaction line contributes with a matrix elememt or amplitude,

$$\widehat{F}_N \rightarrow f_{in}^{out}$$
$$\widehat{V}_N \rightarrow \langle pq\, |v|\, rs \rangle$$
$$\widehat{T}_1 \rightarrow t_i^a$$
$$\widehat{T}_2 \rightarrow t_{ij}^{ab}$$

- Summation over all internal indices
- Sign of diagram determined by the formula $(-1)^{n_h + n_l}$
- For each pair of equivalente lines, a prefactor $\left(\frac{1}{2}\right)$ is included

Coupled-cluster theory

Solving the coupled-cluster equations

- Energy- and amplitude equations - NOT coupled
- $E = E(t_i^a, t_{ij}^{ab})$
- $\widehat{T}_1$ and $\widehat{T}_2 \rightarrow$ non-linear coupled equations
- Must be solved iteratively till self-consistency is obtained

Algorithm

1. Determine modelspace $\mathcal{P}$

2. Calculate the matrix elements f_p^q and $\langle pq \, |v| \, rs \rangle$

3. Initialize $t_i^a = 0$ and $t_{ij}^{ab} = 0$

4. WHILE($|E_{new} - E_{old}| > \epsilon$)
   Calculate new t_i^a and t_{ij}^{ab}
   Calculate new energy E_{new}
   END WHILE

5. $E_0 = E_{new} + E_{ref}$

- DFT in its earliest formulation - description of ground state properties of many-electron systems in terms of electron density
- Why is this possible?
- Implication: Exact grund state density equivalent with exact ground state density

Density Functional Theory

- We consider a many-fermion system with hamiltonian,

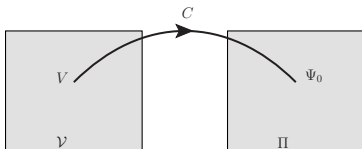$$\widehat{H} = \widehat{T} + \widehat{V} + \widehat{W},$$

  where, for a given system, $\widehat{T}$ and $\widehat{W}$ is specified, $\widehat{V}$ can be varied.

- Define $\mathcal{V}$ as the set of one-particle potentials with the property that the ground state,

$$\left(\widehat{T} + \widehat{V} + \widehat{W} \right) |\Psi_0\rangle = E_0 |\Psi_0\rangle \qquad \widehat{V} \subset \mathcal{V},$$

  is non-degenerate

- Define Π as the set of all these ground state functions

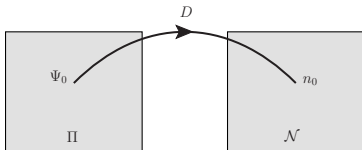- Define the surjective map $C : \mathcal{V} \to \Pi$

- For all ground state wavefunctions $|\Psi_0\rangle \subset \Pi$, we calculate the ground state density,

$$n(\mathbf{r}) = \langle \Psi_0 \, |\widehat{n}(\mathbf{r})| \, \Psi_0 \rangle$$
$$= N \sum_s \int d\mathbf{x}_2 \int d\mathbf{x}_3 ... \int d\mathbf{x}_N \, |\Psi_0(\mathbf{r}s, \mathbf{x}_2, \mathbf{x}_3, .., \mathbf{x}_N)|^2 \,,$$

defining the set $\mathcal{N}$ of ground state densities

- Define the surjective map $D : \Pi \to \mathcal{N}$

Density Functional Theory

Non-degenerate ground state - Basic formalism for non-relativistic systems

- C and D are also injective, viz. one-to-one (proof not shown)
- Hence, $|\Psi_0[n]\rangle$ unique functional of n
- The full inverse map $(CD)^{-1} : n \to V$ is also a unique map
- Properties of system can be totally described by its density $n(\mathbf{r})$!

First statement of Hohenberg-Kohn theorem

The ground state expectation value of *any* observable $\widehat{O}$ is a unique functional of n,

$$\left\langle \Psi_0[n] \left| \widehat{O} \right| \Psi_0[n] \right\rangle = O[n]$$

Density Functional Theory

Second statement of Hohenberg-Kohn theorem

- $\widehat{V}$: External potential $\rightarrow$ unique ground state density $n_0(\mathbf{r})$ and energy E_0

- Define $E_V[n] \equiv \left\langle \Psi[n] \left| \widehat{T} + \widehat{V} + \widehat{W} \right| \Psi[n] \right\rangle$

- Due to the quantum mechanical variational principle,

$$E_0 < E_V[n] \qquad (n \neq n_0)$$
$$E_0 = E_V[n_0]$$

- The exact ground state density (and energy) can be determined by minimizing the energy functional $E_V[n]$ with respect to n,

$$E_0 = \min_{n \subset \mathcal{N}} E_V[n]$$

Density Functional Theory

- The energy functional,

$$E_V [n] = \left\langle \Psi [n] \left| \widehat{T} + \widehat{W} \right| \Psi [n] \right\rangle + \left\langle \Psi [n] \left| \widehat{V} \right| \Psi [n] \right\rangle$$

$$= F_{HK} [n] + \int d^3 r v(\mathbf{r}) n(\mathbf{r})$$

- The Hohenberg-Kohn functional $F_{HK} [n] \equiv \left\langle \Psi [n] \left| \widehat{T} + \widehat{W} \right| \Psi [n] \right\rangle$ is universal in the sense that it does not depend on $\widehat{V}$

- For electronic systems (atoms, quantum dots, molecules,...), $F_{HK} [n]$ is the same

Density Functional Theory

- Basic formalism is easily extended for systems with degenerate ground states
- Define $\mathcal{V}$ as the set of single-particle potentials $\widehat{V}$ that the ground state

$$\left(\widehat{T} + \widehat{V} + \widehat{W}\right)|\Psi_0\rangle = E_0|\Psi_0\rangle \qquad \widehat{V} \subset \mathcal{V},$$

  is degenerate

- Each $\widehat{V} \subset \mathcal{V}$ defines a set of ground state functions

$$\Pi_V = \left\{|\Psi_0\rangle = \sum_{i=1}^{q} c_i \left|\Psi_0^i\right\rangle\right\}$$

- Π_V - continuum of ground states
- $\left|\Psi_0^i\right\rangle$ - not well-defined, chosen to be orthogonal
- Define Π as the union of all subspaces

$$\Pi = \bigcup_{V \subset \mathcal{V}} \Pi_V$$

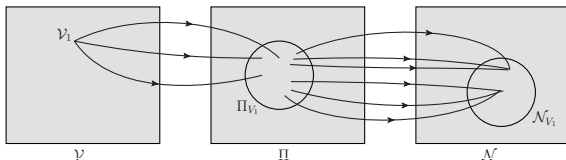- Define $\mathcal{N}_N$ as the set of ground states densities defined by the set of ground sates Π_V,

$$\mathcal{N}_V = \left\{ n(\mathbf{r}) = \langle \Phi_0 | \hat{n}(\mathbf{r}) | \Phi_0 \rangle \, \middle| \, |\Phi_0\rangle \subset \Pi_V \right\}$$

- Define $\mathcal{N}$ as the union of all subspaces

$$\mathcal{N} = \bigcup_{V \subset \mathcal{V}} \mathcal{N}_V$$

- Warning! $|\Psi_0\rangle \neq |\Psi_0[n_0]\rangle$ - not a unique functional of the density

- The variational principle needs a unique functional
  $F_{HK}[n] \equiv \left\langle \Psi[n] \left| \widehat{T} + \widehat{W} \right| \Psi[n] \right\rangle$

- $n \rightarrow V[n]$ unique $+$ constant $\rightarrow$ unique $E_0 +$ constant

- Hence, $F_{HK}[n] \equiv \left\langle \Psi[n] \left| \widehat{T} + \widehat{W} \right| \Psi[n] \right\rangle$ is a unique functional of n

- Variational principle is OK for the degenerate case

Define the hamiltonian of N non-interacting particles

$$\widehat{H}_s = \widehat{T}_s + \widehat{V}_s.$$

According to Hohenberg-Kohn theorem,

$$E_S[n] = \widehat{T}_s[n] + \int d^3 r v_s(\mathbf{r}) n(\mathbf{r})$$

exists, such that

$$E_0^s = \min_{n \subset \mathcal{N}} E_s[n],$$

gives the ground state density n_s of $\widehat{H}_s$.

Density Functional Theory

The Kohn-Sham scheme

- Central assertion in the Kohn-Sham scheme - For any interacting system there exists a local single-particle potential $v_s(\mathbf{r})$ such that the exact ground state density of the interacting system

$$n_0(\mathbf{r}) = n_s(\mathbf{r}),$$

where $n_s(\mathbf{r})$ is the ground state density of the non-interacting system

- Assuming $\widehat{H}_s$ with non-degenerate ground state imply

$$n_0(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

- Obviously, given $v_s(\mathbf{r})$ - system solved

- Thus we are seeking the single-particle potential $v_s(\mathbf{r})$ such that $n_0(\mathbf{r}) = n_s(\mathbf{r})$

Density Functional Theory

- Consider the energy functional,

$$E_V[n] = F_{HK}[n] + \int d^3r v(\mathbf{r}) n(\mathbf{r})$$

$$= T_S[n] + \frac{1}{2} \int \int d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + E_{xc}[n] + \int d^3r v(\mathbf{r}) n(\mathbf{r})$$

$$\Rightarrow E_{xc} = F_{HK}[n] - \frac{1}{2} \int \int d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') - T_s[n]$$

- Explicit form of $F_{HK}[n]$ - unknown
- Hence, $E_{xc}[n]$ is unknown $\Rightarrow$ must be approximated
- What do we need? We need an expression for $v_s(\mathbf{r})$

Density Functional Theory

The Kohn-Sham scheme

We start with the variational principle,

$$
\begin{aligned}
0 = \delta E_V[n] &= E_V[n_0 + \delta n] - E_V[\delta n] \\
&= \delta T_s[n] + \int d^3 r \, \delta n(\mathbf{r}) \left[v(\mathbf{r}) + \int d^3 r' \, w(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}') + v_{xc}([n_0], \mathbf{r}) \right],
\end{aligned}
$$

where

$$
v_{xc}([n_0], \mathbf{r}) = \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{n_0}.
$$

It can be shown through

$$
\widehat{h}_s \left| \phi \right\rangle = \epsilon \left| \phi \right\rangle,
$$

that

$$
\delta T_s[n] = - \int d^3 r \, v_s(\mathbf{r}) \delta n(\mathbf{r}).
$$

Finally we obtain

$$
v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3 r' \, w(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}') + v_{xc}([n_0], \mathbf{r}).
$$

Coupled-cluster and density functional theory

Density Functional Theory

Kohn-Sham scheme for non-degenerate ground states

Kohn-Sham equation,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_s(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_s(\mathbf{r}),$$

where

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3r'\, w(\mathbf{r},\mathbf{r}')n_0(\mathbf{r}') + v_{xc}([n_0],\mathbf{r}).$$

Ground state density given by,

$$n_0(\mathbf{r}) = \sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2.$$

- Wavefunction based methods, like for example *CI* and *CC*, offer a systematic route to the approximate solution of the Schrödinger equation

- In principle - can obtain arbitrary accuracy, CC → *CCSD*, *CCSD*(*T*), *CCSDT*, ...

- However, with increasing system size, ab initio methods like *CI* and *CC* becomes expensive ⇒ Cannot in practice obtain arbitrary accuracy

- DFT - consider a non-interacting model system with ground state density equal to the interacting one

- Problem - The hamiltonian $\widehat{H}_s$ contains an unknown part, must be approximated

- One more problem - No systematic route to determine this contribution ⇒ accuracy is not easily controled

- *Ab initio* methods and DFT - complimentary

- Natural thought: Link *ab initio* with DFT

Linking DFT with ab initio methods

- General hamiltonian (functional of v)

$$\widehat{H}_\lambda[v] = \widehat{T} + \widehat{V} + \lambda\widehat{W},$$

  where the interaction strength is determined by λ

- Remember: Variational principle demand that all trial densities must be pure-state v-representable

- Definition - Ensemble v-representable density

$$n_\gamma(\mathbf{r}) = Tr\left\{\widehat{\gamma}\widehat{n}(\mathbf{r})\right\} = \sum_{i=1}^{q} d_i n_i(\mathbf{r}),$$

  where $n_i(\mathbf{r}) = \langle\Psi_i|\widehat{n}(\mathbf{r})|\Psi_i\rangle$, $\{|\Psi_i\rangle\}_{i=1}^{q}$ are basis set of deg. ground states of $\widehat{H}$ with external potential $\widehat{V}$

- For general coefficients $\Rightarrow n_\gamma(\mathbf{r})$ not a pure-state v-representable

- Possible extension of domain of $F_{HK}[n] \Rightarrow F_L[n]$,

$$F_L[n] = \inf_{\gamma \to n} Tr\left\{\widehat{\gamma}\left(\widehat{T} + \widehat{W}\right)\right\}$$

Coupled-cluster and density functional theory

Linking DFT with ab initio methods

The Lieb formulation

- Standard formulation of variational principle,

$$E_0 = \inf_n E_V[n] = \inf_n \left(F_L[n] + \int d^3 r n(\mathbf{r}) v(\mathbf{r}) \right)$$

- Define $E_\lambda[n]$ as the ground state energy of $\widehat{H}_\lambda[n]$ with Lieb functional $F_\lambda[n]$

- The variational principle can be formulated as

$$E_\lambda[v] = \inf_{\gamma \to N} Tr \left\{ \widehat{H}_\lambda[v] \widehat{\gamma} \right\} \equiv Tr \left\{ \widehat{H}_\lambda[v] \widehat{\gamma}_\lambda^v \right\}$$

- The Lieb functional (showed by Lieb) reads

$$F_\lambda[n] = \inf_{\gamma \to n} Tr \left\{ \widehat{H}_\lambda[0] \widehat{\gamma} \right\} \equiv Tr \left\{ \widehat{H}_\lambda[0] \widehat{\gamma}_\lambda^n \right\}$$

- Lieb established the Legendre transforms between the energy and the universal functional,

$$F_\lambda[n] = \sup_{v \subset \mathcal{V}} \left[E_\lambda[v] - \int d^3 r n(\mathbf{r}) v(\mathbf{r}) \right]$$

$$E_\lambda[v] = \inf_{n \subset \mathcal{N}} \left[F_\lambda[n] + \int d^3 r n(\mathbf{r}) v(\mathbf{r}) \right]$$

- Frenchel inequalities,

$$F_\lambda[n] \geq E_\lambda[v] - \int d^3r\, n(\mathbf{r})v(\mathbf{r})$$

$$E_\lambda[n] \leq F_\lambda[n] + \int d^3r\, n(\mathbf{r})v(\mathbf{r})$$

- Equality may be obtained by maximization with respect to $v(\mathbf{r})$ or minimizing with respect to $n(\mathbf{r})$

Linking DFT with ab initio methods

- Universal Lieb functional $F_\lambda[n]$ and interacting ground state energy $E_\lambda[n]$ may be written as

$$F_\lambda[n] = F_0[n] + \int_0^\lambda \frac{dF_\lambda[n]}{d\lambda} d\lambda$$

$$E_\lambda[v] = E_0[v] + \int_0^\lambda \frac{dE_\lambda[v]}{d\lambda} d\lambda$$

- Hellmann-Feynman theorem yields

$$\frac{dF_\lambda[n]}{d\lambda} = Tr\left\{\widehat{W}\widehat{\gamma}_\lambda^n\right\} = \mathcal{W}_\lambda[n]$$

$$\frac{dE_\lambda[v]}{d\lambda} = Tr\left\{\widehat{W}\widehat{\gamma}_\lambda^v\right\} = \mathcal{W}_\lambda[v]$$

- Inserting explicit expressions for $F_0[n]$ and $E_0[v]$, we obtain

$$F_\lambda[n] = Tr\left\{\widehat{H}_0[0]\widehat{\gamma}_\lambda^n\right\} + \int_0^\lambda \mathcal{W}_\lambda[n] d\lambda$$

$$E_\lambda[v] = Tr\left\{\widehat{H}_0[v]\widehat{\gamma}_\lambda^v\right\} + \int_0^\lambda \mathcal{W}_\lambda[v] d\lambda$$

Coupled-cluster and density functional theory

Linking DFT with ab initio methods

The adiabatic connection

- Defining $\mathcal{W}_{c,\lambda}[n] = \mathcal{W}_{\lambda}[n] - \mathcal{W}_0[n]$ and $\mathcal{W}_{c,\lambda}[v] = \mathcal{W}_{\lambda}[v] - \mathcal{W}_0[v]$, we may write

$$F_{\lambda}[n] = \underbrace{Tr\left\{\widehat{H}_{\lambda}[0]\,\widehat{\gamma}_{\lambda}^n\right\}}_{\text{uncorrelated contribution}} + \underbrace{\int_0^{\lambda}\mathcal{W}_{c,\lambda}[n]\,d\lambda}_{\text{correlation corrections}}$$

$$E_{\lambda}[v] = \underbrace{Tr\left\{\widehat{H}_{\lambda}[v]\,\widehat{\gamma}_{\lambda}^v\right\}}_{\text{uncorrelated contribution}} + \underbrace{\int_0^{\lambda}\mathcal{W}_{c,\lambda}[v]\,d\lambda}_{\text{correlation corrections}}$$

- Standard decomposition of the Lieb functional,

$$F_{\lambda}[n] = T_s[n] + \lambda J[n] + \lambda E_x[n] + E_{c,\lambda}[n]$$

$$T_s[n] = Tr\left\{\widehat{H}_0[0]\,\widehat{\gamma}_0^n\right\} = Tr\left\{\widehat{T}\widehat{\gamma}_0^n\right\}$$

$$J[n] = \int\int n(\mathbf{r}_1)n(\mathbf{r}_2)\frac{1}{r_{12}}\,d\mathbf{r}_1\,d\mathbf{r}_2$$

$$E_x[n] = \mathcal{W}_0[n] - J[n]$$

$$E_{c,\lambda}[n] = \int_0^{\lambda}\mathcal{W}_{c,\lambda}[n]\,d\lambda$$

- Question: How to compute the adiabatic connection integrand $\mathcal{W}_{C,\lambda}$?

- One solution: Extracting the density matrix $\widehat{\gamma}_\lambda^n$ from $E_\lambda[v_\lambda]$ determined by the potential v_λ that maximizes the righthand side of

$$F_\lambda[n] \geq E_\lambda[v] - \int d^3r\, n(\mathbf{r}) v(\mathbf{r})$$

- What do we need? - A method to determine accurately the ground state energy $E_\lambda[v_\lambda]$ for a given λ and for a given modified external potential v_λ

- $\Rightarrow$ AB INITIO METHODS - for example the cupled-cluster method

- We begin by expanding the unknown potential,

$$v_{\lambda,\mathbf{b}} = v_{ext}(\mathbf{r}) + (1-\lambda)v_{ref}(\mathbf{r}) + \sum_i b_i g_i(\mathbf{r}),$$

where $v_{ext}(\mathbf{r})$ is the external potential, $v_{ref}(\mathbf{r})$ is a fixed reference potential, and $g_i(\mathbf{r})$ are gaussion functions

- We next define the functional,

$$\mathcal{F}_{\lambda,\mathbf{b}}[n] = E_\lambda[v_{\lambda,\mathbf{b}}] - \int d\mathbf{r}\, n(\mathbf{r}) v_{\lambda,\mathbf{b}}$$

Linking DFT with ab initio methods

The adiabatic connection

- The universal Lieb functional thus reads

$$F_\lambda [n] = \max_{\mathbf{b}} \mathcal{F}_{\lambda,\mathbf{b}} [n]$$

- Obviously, v_λ given by

$$0 = G_i = \frac{\partial \mathcal{F}_{\lambda,\mathbf{b}} [n]}{\partial b_i} = \int \left[n_{\lambda,\mathbf{b}}(\mathbf{r}) - n(\mathbf{r}) \right] g_i(\mathbf{r}) d\mathbf{r},$$

  where $n_{\lambda,\mathbf{b}}$ is the density corresponding to $E_\lambda \left[v_{\lambda,\mathbf{b}} \right]$

- Possible to set up an iterative procedure based on quasi-Newton maximization of $\mathcal{F}_{\lambda,\mathbf{b}} [n]$

A schematic algorithm

- CC calculation for a relaxed (Lagrangian) density matrix with the full interacting hamiltonian

- Obtain a good approximation of the interacting density - to be used in the first derivative of G_i

- CC code modified to handel general hamiltonians $\widehat{H}_\lambda \left[v_{\lambda,\mathbf{b}} \right]$ to generate $E_\lambda \left[v_{\lambda,\mathbf{b}} \right]$

- Initialization: $\mathbf{b} = 0$, calculate relaxed density matrix calculated, calculate gradient $\mathbf{G}$, the hessian $\mathbf{H}$ is set to $\mathbf{I}$

- WHILE ($\mathcal{F}_{\lambda,\mathbf{b}}$ NOT CONVERGED)
  Calculate $\mathbf{b}_{new} = \mathbf{b}_{old} - \mathbf{H}^{-1}\mathbf{G}$
  Calculate new $\mathbf{H}^{-1}$ and $\mathbf{G}$
  Cacluate $\mathcal{F}_{\lambda,\mathbf{b}}$

- At convergence - correlation contribution $\mathcal{W}_{c,\lambda} \left[n \right]$ calculated from $\mathcal{W}_\lambda = Tr\left\{ \widehat{W}\widehat{\gamma}_\lambda^n \right\}$