Coupled-Cluser teori

Even Marius Nordhagen

Universitetet i Oslo

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Eksponensialansats

Den tidsuavhengige Schrödingerligningen er gitt ved

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{1}$$

som kan løses eksakt med Coupled-Cluster teori.
Bølgefunksjonen i Coupled-Cluster teori er som følger

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle \tag{2}$$

hvor Φ er referansebølgefunksjonen.

Bakgrunn

Slaterdeterminant

Slaterdeterminanten for N partikler på Diracform konstruert med Hartree-Fock er gitt ved

$$|\Phi\rangle = |\phi_i(x_1)\phi_j(x_2)\cdots\phi_o(x_N)\rangle \tag{3}$$

Orbitalfunksjoner

$$f_i(x_m) = \sum_a t_i^a \phi_a(x_m), \quad f_{ij}(x_m, x_n) = \sum_{a>b} t_{ij}^{ab} \phi_a(x_m)\phi_b(x_n) \tag{4}$$

Bakgrunn

Forbedret bølgefunksjon

$$
\begin{aligned}
\Psi = {} & |\phi_i\phi_j\phi_k\phi_l\rangle + |f_i\phi_j\phi_k\phi_l\rangle + |\phi_i f_j\phi_k\phi_l\rangle + |\phi_i\phi_j f_k\phi_l\rangle + |\phi_i\phi_j\phi_k f_l\rangle \\
& + |f_i f_j\phi_k\phi_l\rangle + |f_i\phi_j f_k\phi_l\rangle + |f_i\phi_j\phi_k f_l\rangle + |\phi_i f_j f_k\phi_l\rangle + |\phi_i f_j\phi_k f_l\rangle \\
& + |\phi_i\phi_j f_k f_l\rangle + |f_i f_j f_k\phi_l\rangle + |f_i f_j\phi_k f_l\rangle + |f_i\phi_j f_k f_l\rangle + |\phi_i f_j f_k f_l\rangle \\
& + |f_{ij}\phi_k\phi_l\rangle - |f_{ik}\phi_j\phi_l\rangle + |f_{il}\phi_j\phi_k\rangle + |\phi_i f_{jk}\phi_l\rangle - |\phi_i f_{jl}\phi_k\rangle \\
& + |\phi_i\phi_j f_{kl}\rangle + |f_{ij} f_{kl}\rangle - |f_{ik} f_{jl}\rangle + |f_{il} f_{jk}\rangle + |f_i f_j f_k f_l\rangle \\
& + |f_{ij} f_k\phi_l\rangle + |f_{ij}\phi_k f_l\rangle + |f_{ij} f_k f_l\rangle - |f_{ik} f_j\phi_l\rangle - |f_{ik}\phi_j f_l\rangle - |f_{ik} f_j f_l\rangle \\
& + |f_{il} f_j\phi_k\rangle + |f_{il}\phi_j f_k\rangle + |f_{il} f_j f_k\rangle + |f_i f_{jk}\phi_l\rangle + |\phi_i f_{jk} f_l\rangle + |f_i f_{jk} f_l\rangle \\
& - |f_i f_{jl}\phi_k\rangle - |\phi_i f_{jl} f_k\rangle - |f_i f_{jl} f_k\rangle + |f_i\phi_j f_{kl}\rangle + |\phi_i f_j f_{kl}\rangle + |f_i f_j f_{kl}\rangle
\end{aligned}
$$

Bakgrunn

Orbitaloperatorer

$$\hat{t}_i \equiv \sum_a t_i^a c_a^\dagger c_i, \quad \hat{t}_{ij} \equiv \sum_{a>b} t_{ij}^{ab} c_a^\dagger c_b^\dagger c_j c_i \tag{5}$$

Som gir en total bølgefunksjon på

$$\begin{aligned} |\Psi\rangle = \Bigg(1 &+ \sum_i \hat{t}_i + \frac{1}{2}\sum_{ij} \hat{t}_i \hat{t}_j + \frac{1}{6}\sum_{ijk} \hat{t}_i \hat{t}_j \hat{t}_k \\ &+ \frac{1}{2}\sum_{ij} \hat{t}_{ij} + \frac{1}{8}\sum_{ijkl} \hat{t}_{ij}\hat{t}_{kl} + \frac{1}{24}\sum_{ijkl} \hat{t}_i \hat{t}_j \hat{t}_k \hat{t}_l \\ &+ \frac{1}{2}\sum_{ijk} \hat{t}_{ij}\hat{t}_k + \frac{1}{4}\sum_{ijkl} \hat{t}_{ij}\hat{t}_k \hat{t}_l \Bigg)|\Phi\rangle \end{aligned} \tag{6}$$

Bakgrunn

Totale clusteroperatorer

$$\hat{T}_1 = \sum_i \hat{t}_i = \sum_{ia} t_i^a c_a^\dagger c_i \tag{7}$$

$$\hat{T}_2 = \frac{1}{2} \sum_{ij} \hat{t}_{ij} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} c_a^\dagger c_b^\dagger c_j c_i \tag{8}$$

som gir

$$|\Psi\rangle = \left(1 + \hat{T}_1 + \frac{1}{2!}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \frac{1}{4!}\hat{T}_1^4 + \hat{T}_2\hat{T}_1 + \frac{1}{2!}\hat{T}_2\hat{T}_1^2\right)|\Phi\rangle \tag{9}$$

Bakgrunn

Forenklet bølgerfunksjon

Vi definerer $\hat{T} \equiv \hat{T}_1 + \hat{T}_2$:

$$|\Psi\rangle = e^{\hat{T}_1 + \hat{T}_2}|\Phi\rangle \equiv e^{\hat{T}}|\Phi\rangle \tag{10}$$

$$\hat{H}e^{\hat{T}}|\Phi\rangle = Ee^{\hat{T}}|\Phi\rangle \tag{11}$$

hvor

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \sum_{n=4}^{\infty} \frac{\hat{T}^n}{n!} \tag{12}$$

Coupled Cluster ligningene

Ulinkede

$$\langle \Phi | \hat{H} e^{\hat{T}} | \Phi \rangle = E \quad (13)$$

$$\langle \Phi_X | \hat{H} e^{\hat{T}} | \Phi \rangle = 0 \quad (14)$$

Linkede

$$\langle \Phi | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle = E \quad (15)$$

$$\langle \Phi_X | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle = 0 \quad (16)$$

Hausdorffs ekspansjon

Utvikling av $e^{-\hat{T}}\hat{H}e^{\hat{T}}$ (Hausdorffekspansjon):

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \cdots$$

Det kan vises at dette er ekvivalent med

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + \{\hat{H}\hat{T}\}_c + \frac{1}{2}\{\{\hat{H}\hat{T}\}_c\hat{T}\}_c + \frac{1}{6}\{\{\{\hat{H}\hat{T}\}_c\hat{T}\}_c\hat{T}\}_c + \ldots$$

Hamiltonianoperatoren

Den normalordnede elektroniske Hamiltonoperatoren er gitt ved

$$\hat{H}_N = \hat{H} - E_{ref} = \hat{F}_N + \hat{V}_N \tag{17}$$

med

$$\hat{F}_N = \sum_{pq} f_q^p \{c_p^\dagger c_q\}, \quad \hat{V}_N = \frac{1}{4} \sum_{pqrs} W_{rs}^{pq} \{c_p^\dagger c_q^\dagger c_s c_r\}$$

For vårt tilfelle får vi

$$\begin{aligned} e^{-\hat{T}} \hat{H}_N e^{\hat{T}} &= \hat{H}_N + \{\hat{F}_N \hat{T}_1\}_c + \{\hat{V}_N \hat{T}_1\}_c + \{\hat{F}_N \hat{T}_2\}_c \\ &+ \{\hat{V}_N \hat{T}_2\}_c + \{\hat{F}_N \hat{T}_1^2\}_c + \{\hat{V}_N \hat{T}_1^2\}_c \end{aligned} \tag{18}$$

Et uttrykk for energien

$$E_{CCSD} - E_{ref} = \langle \Phi | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi \rangle \tag{19}$$

De leddene som bidrar er

$$\langle \Phi | \{ \hat{F}_N \hat{T}_1 \}_c | \Phi \rangle = \sum_{ia} f_a^i t_i^a$$

$$\langle \Phi | \{ \hat{V}_N \hat{T}_2 \}_c | \Phi \rangle = \frac{1}{4} \sum_{aibj} W_{ab}^{ij} t_{ij}^{ab}$$

$$\frac{1}{2} \langle \Phi | \{ \hat{V}_N \hat{T}_1^2 \}_c | \Phi \rangle = \frac{1}{2} \sum_{aibj} W_{ab}^{ij} t_i^a t_j^b$$

Energiligningen skrevet ut

$$E = \sum_{ia} f_a^i t_i^a + \frac{1}{4} \sum_{aibj} W_{ab}^{ij} t_{ij}^{ab} + \frac{1}{2} \sum_{aibj} W_{ab}^{ij} t_i^a t_j^b \tag{20}$$

Finne amplitudene

Matriseelementene for amplitudeligningene (CCSD)

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle = \langle \Phi | (c_i^\dagger c_a) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle = 0 \qquad (21)$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle = \langle \Phi | (c_i^\dagger c_j^\dagger c_b c_a) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle = 0 \qquad (22)$$

Finne amplitudene ved iterasjon

$$F_i^a t_i^a + G_i^a(t) = 0 \quad \Rightarrow \quad t_i^{a(k+1)} = -(F_i^a)^{-1} G_i^a(t^{(k)})$$

$$F_{ij}^{ab} t_{ij}^{ab} + G_{ij}^{ab}(t) = 0 \quad \Rightarrow \quad t_{ij}^{ab(k+1)} = -(F_{ij}^{ab})^{-1} G_{ij}^{ab}(t^{(k)})$$

$$t_i^{a(0)} = \cdots$$

$$t_{ij}^{ab(0)} = \cdots$$