Coupled-Cluster teori

Fra Schrodingers ligning til dataprogram

Total bølgefunksjon:

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle \tag{1}$$

hvor Φ er referansebølgefunksjonen.

Introduksjon

Slaterdeterminanten

Slaterdeterminanten for N partikler på Diracform

$$|\Phi\rangle = |\phi_i(x_1)\phi_j(x_2)\cdots\phi_o(x_N)\rangle \tag{2}$$

Orbitalfunksjoner

$$f_i(x_m) = \sum_a t_i^a \phi_a(x_m), \quad f_{ij}(x_m, x_n) = \sum_{a>b} t_{ij}^{ab}\phi_a(x_m)\phi_b(x_n) \tag{3}$$

Introduksjon

Forbedret bølgefunksjon

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

Introduksjon

Orbitaloperatorer

$$\hat{t}_i \equiv \sum_a t_i^a c_a^\dagger c_i, \quad \hat{t}_{ij} \equiv \sum_{a>b} t_{ij}^{ab} c_a^\dagger c_b^\dagger c_j c_i \tag{4}$$

Som gir en total bølgefunksjon på

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

Introduksjon

Totale clusteroperatorer

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

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

som gir

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

Introduksjon

Forenklet bølgerfunksjon

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

$$|\Psi\rangle = e^{\hat{T}_1 + \hat{T}_2}|\Phi\rangle \equiv e^{\hat{T}}|\Phi\rangle \tag{5}$$

hvor

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \sum_{n=4}^{\infty} \frac{\hat{T}^n}{n!} \tag{6}$$

Ulinkede CC ligninger

...

Energiligning

$$\langle \Phi | \hat{H} e^{\hat{T}} | \Phi \rangle = E \tag{7}$$

Amplitudeligning

$$\langle \Phi_X | \hat{H} e^{\hat{T}} | \Phi \rangle = 0. \tag{8}$$

Linkede CC ligninger

...

$$\langle\Phi|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi\rangle = E \tag{9}$$

$$\langle\Phi_X|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi\rangle = 0 \tag{10}$$

Å regne med de linkede CC ligningene

Hausdorffs ekspansjon

$$
\begin{aligned}
e^{-\hat{T}}\hat{H}e^{\hat{T}} &= \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2!}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{3!}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \cdots \\
&= \hat{H} + \{\hat{H}\hat{T}\}_c + \frac{1}{2}\{\{\hat{H}\hat{T}\}_c\hat{T}\}_c + \ldots
\end{aligned}
$$

Hamiltonianoperatoren

...

Hamiltonoperatoren

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

med

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

Vi vårt tilfelle får

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

Motivasjon

Matriseelementene i energiligningen

$$\langle\Phi|\hat{H}_N|\Phi\rangle = 0$$

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

$$\langle\Phi|\{\hat{V}_N\hat{T}_1\}_c|\Phi\rangle = 0$$

$$\langle\Phi|\{\hat{F}_N\hat{T}_2\}_c|\Phi\rangle = 0$$

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

$$\frac{1}{2}\langle\Phi|\{\hat{F}_N\hat{T}_1^2\}_c|\Phi\rangle = 0$$

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

Motivasjon

Matriseelementene i amplitudeligningen

Nå har vi altså i prinsippet funnet et uttrykk for energien E som en funksjon av amplitudene når vi antar at f_q^p og W_{ab}^{ij} er gitt. For å finne amplitudene, må vi først finne matriseelementene i amplitudeligningen. I motsetning til for energiligningen, skriver jeg bare opp de leddene som gir full kontraksjon og som dermed bidrar (ettersom vi får veldig mange ledd):

$$\langle \Phi_i^a | \hat{F}_N | \Phi \rangle =$$

Motivasjon

...

Motivasjon

...

Motivasjon

...

Motivasjon

...