Hello hello

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Abstract

Heiie

1 Introduction

2 Theory

2.1 Mathematical framework and notation

Define shortly

$$N, L, R \tag{1}$$

creation and annihilation, anitcommutators, normal order, Hamiltonian, normal order Hamiltonian,

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \tag{2}$$

2.2 Hartree-Fock

a

2.3 Coupled Cluster

The exact solution $|\Psi\rangle$ is approximated by an exponential ansatz $|\Psi_{\mathrm{CC}}\rangle$

$$|\Psi\rangle \approx |\Psi_{\mathrm{CC}}\rangle \equiv e^{\hat{T}} |\Phi_0\rangle . \tag{3}$$

The operators $\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots$ acting on the ground state ansatz $|\Phi_0\rangle$ are the so-called *cluster operators* defined as

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ab\ldots \\ ij\ldots}} t_{ij\ldots}^{ab\ldots} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} \ldots\} \tag{4}$$

where $m \leq N$. The scalars $t_{ij\ldots}^{ab\ldots}$ are unknown expansion coefficients called *amplitudes*, which we need to solve for. All the creation and annihilation operators of Eq. 4 anticommute, giving the restriction that

$$t_{\hat{P}'(ij\ldots)}^{\hat{P}(ab\ldots)} = (-1)^{\sigma(\hat{P})+\sigma(\hat{P}')} t_{ij\ldots}^{ab\ldots}. \tag{5}$$

Here P and P' permutes $\sigma(P)$ and $\sigma(P')$ indices respectively. This is the reason for the prefactor of Eq. 4, since we have $m!$ ways to independently permute particle and hole indices. Instead of having $(L-N)^m N^m$ independent unknowns, we reduce this number by a factor of $(m!)^2$.

2.4 Doubles truncation

Considering N cluster operators in the exponential ansatz of Eq. 3 is not computationally feasible for realistic systems. The common practice is to include one or more $\hat{T}_m$ operators, making a truncation on $|\Psi_{\mathrm{CC}}\rangle$ as well. In the following we will include only the double excitation operator $\hat{T}_2$, know as the CCD approximation. This gives us

$$|\Psi\rangle \approx |\Psi_{\mathrm{CC}}\rangle \approx |\Psi_{\mathrm{CCD}}\rangle \equiv e^{\hat{T}_2} |\Phi_0\rangle , \tag{6}$$

$$\hat{T}_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\}, \tag{7}$$

with the four-fold amplitude permutation symmetry [1],

$$t_{ij}^{ab} = -t_{ij}^{ba} = -t_{ji}^{ab} = t_{ji}^{ba}. \tag{8}$$

Incorporating the CCD approximation in the Schrödinger equation (Eq. 2), we see that

$$\begin{aligned} \hat{H} e^{\hat{T}_2} |\Phi_0\rangle &= E e^{\hat{T}_2} |\Phi_0\rangle , \\ \hat{H}_{\mathrm{N}} e^{\hat{T}_2} |\Phi_0\rangle &= E_{\mathrm{CCD}} e^{\hat{T}_2} |\Phi_0\rangle , \end{aligned} \tag{9}$$

where $E_{\mathrm{CCD}} = E - E_{\mathrm{ref}}$. Expanding both sides and taking the inner product with $\langle\Phi_0|$, we in principle get an equation for the energy. However, this approach is not amenable to practical computer implementation [Bartlett et al., 1984] since the amplitude equation will be coupled with the energy equation. Therefor, we rather apply a similarity transform to Eq. 9 by multiplying by the inverse of $e^{\hat{T}_2}$,

$$\begin{aligned} e^{-\hat{T}_2} \hat{H}_{\mathrm{N}} e^{-\hat{T}_2} |\Phi_0\rangle &= E_{\mathrm{CCD}} |\Phi_0\rangle \\ \langle\Phi_0| \overline{H} |\Phi_0\rangle &= E_{\mathrm{CCD}} \end{aligned} \tag{10}$$

where $\overline{H} = e^{-\hat{T}_2} \hat{H}_{\mathrm{N}} e^{-\hat{T}_2}$. Ask oyvind about $\langle \Phi_{ij}^{ab} |$ equation

[1] For double amplitudes, the index permutation symmetry is equal to that of antisymmetrized two-body matrix elements $\langle pq||rs\rangle$.

3 Method

4 Results

5 Discussion

6 Concluding remarks

References

Rodney J. Bartlett, Clifford E. Dykstra, and Josef Paldus. Coupled-Cluster Methods for Molecular Calculations. In Clifford E. Dykstra, editor, *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, NATO ASI Series, pages 127–159. Springer Netherlands, Dordrecht, 1984. ISBN 978-94-009-6451-8. doi: 10.1007/978-94-009-6451-8_8. URL https://doi.org/10.1007/978-94-009-6451-8_8.