Hello hello

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May 11, 2023

Abstract

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1 Introduction

2 Theory

2.1 Mathematical framework and notation

In the following we will use the occupation representation, making use of creation $a_p^\dagger$ and annihilation a_p operators. As a shorthand, we will write $\hat{p}^\dagger \equiv a_p^\dagger$ and $\hat{p} \equiv a_p$ when no confusion can be made. N represents the number of occupied states while L the total number of states in our calculations. The indicies $p, q, \ldots$ are reserved for the L general states, the N occupied states are indexed by $i, j, \ldots$, while the $L-N$ unoccupied (virtual) states by $a, b, \ldots$ indicies.

Since we are treating fermionic systems, the canonical anticommutation relations are used

$$\{\hat{p}^\dagger, \hat{q}^\dagger\} = \{\hat{p}, \hat{q}\} = 0 \qquad \{\hat{p}^\dagger, \hat{q}\} = \delta_{pq}.$$

One and two body matrix elements are calculated using a computational basis, with explicit expressions for one body Hamiltonians $h(\boldsymbol{x})$ and two body interaction $v(\boldsymbol{x}, \boldsymbol{x}')$ here presented in position space

$$\langle p| \hat{h} |q\rangle = \int \mathrm{d}\boldsymbol{x}\, \psi_p^*(x)\hat{h}(\boldsymbol{x})\psi_q(x)$$
$$\langle pq| \hat{v} |rs\rangle = \int \mathrm{d}\boldsymbol{x}\, \mathrm{d}\boldsymbol{x}'\, \psi_p^*(\boldsymbol{x})\psi_q^*(\boldsymbol{x}')\hat{v}(\boldsymbol{x}, \boldsymbol{x}')\psi_r(\boldsymbol{x})\psi_s(\boldsymbol{x}')$$

with ψ_p being a single particle wave function, often chosen to be the eigenfunction of $\hat{h}$. Note that p also contain the spin quantum number, meaning that $\mathrm{d}\boldsymbol{x}$ implicitly contains a spin component. If $\hat{h}$ or $\hat{v}$ is spin *independent*, this simply reduces to Kronecker deltas for the spin component. It is often convenient to use antisymmetrized matrix elements, defined as

$$\langle pq||rs\rangle = \langle pq| \hat{v} |rs\rangle - \langle pq| \hat{v} |sr\rangle$$

The shorthands $h_{pq} \equiv \langle p| \hat{h} |q\rangle$, $v_{rs}^{pq} \equiv \langle pq| \hat{v} |rs\rangle$ and $u_{rs}^{pq} \equiv \langle pq||rs\rangle$ will often be used. Using this formulation, a general two-body operator can be constructed

$$\hat{H} = \sum_{pq} h_{pq}\hat{p}^\dagger\hat{q} + \frac{1}{4}\sum_{pqrs} u_{rs}^{pq}\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}$$

normal order, Hamiltonian, normal order Hamiltonian,

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

2.2 Hartree-Fock

2.3 Coupled Cluster

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

$$|\Psi\rangle \approx |\Psi_{\mathrm{CC}}\rangle \equiv e^{\hat{T}} |\Phi_0\rangle . \tag{2}$$

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

$$\hat{T}_m = \frac{1}{(m!)^2}\sum_{\substack{ab\ldots \\ ij\ldots}} t_{ij\ldots}^{ab\ldots}\{\hat{a}^\dagger\hat{i}\hat{b}^\dagger\hat{j}\ldots\} \tag{3}$$

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. 3 anticommute, giving the restriction that

$$t_{\hat{P}'(ij\ldots)}^{\hat{P}(ab\ldots)} = (-1)^{\sigma(\hat{P})+\sigma(\hat{P}')} t_{ij\ldots}^{ab\ldots}. \tag{4}$$

Here P and P' permutes $\sigma(P)$ and $\sigma(P')$ indices respectively. This is the reason for the prefactor of Eq. 3, 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. 2 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

$$|\Psi\rangle \approx |\Psi_{\mathrm{CC}}\rangle \approx |\Psi_{\mathrm{CCD}}\rangle \equiv e^{\hat{T}_2} |\Phi_0\rangle \,, \tag{5}$$

$$\hat{T}_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\}, \tag{6}$$

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

$$t_{ij}^{ab} = -t_{ij}^{ba} = -t_{ji}^{ab} = t_{ji}^{ba}. \tag{7}$$

Incorporating the CCD approximation in the Schrödinger equation (Eq. 1), we see that

$$\begin{aligned} \hat{H} e^{\hat{T}_2} |\Phi_0\rangle &= E e^{\hat{T}_2} |\Phi_0\rangle \,, \\ \hat{H}_{\mathrm{N}} e^{\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\mathrm{CCD}} e^{\hat{T}_2} |\Phi_0\rangle \,, \end{aligned} \tag{8}$$

where $\Delta E_{\mathrm{CCD}} = E - E_{\mathrm{ref}}$. 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. 8 by multiplying by the inverse of $e^{\hat{T}_2}$,

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

where $\overline{H} = e^{-\hat{T}_2} \hat{H}_{\mathrm{N}} e^{-\hat{T}_2}$ is the similarity transformed Hamiltonian. Using this reformulated eigenvalue problem, we can perform the inner product with different states to calculate both ΔE_{CCD} and t_{ij}^{ab}. Considering $\langle\Phi_0|$ we get

$$\langle\Phi_0| \overline{H} |\Phi_0\rangle = \Delta E_{\mathrm{CCD}}, \tag{10}$$

named the *energy equation*. Considering excited states, we arrive at the *amplitude equations*

$$\left\langle \Phi_{ij\ldots}^{ab\ldots} \right| \overline{H} |\Phi_0\rangle \,, \tag{11}$$

used for finding the unknown amplitudes t_{ij}^{ab}. To find explicit expressions for Eq. 10 and Eq. 11, we expand $\overline{H}$ using the Hausdorff expansion

$$\overline{H} = \hat{H}_{\mathrm{N}} + \left[\hat{H}_{\mathrm{N}}, \hat{T}_2\right] + \frac{1}{2!}\left[\left[\hat{H}_{\mathrm{N}}, \hat{T}_2\right], \hat{T}_2\right] + \ldots$$

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

3 Method

Define

$$R \tag{12}$$

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.