

Hello hello

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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 indices p, q, \dots are reserved for the L general states, the N occupied states are indexed by i, j, \dots , while the $L - N$ unoccupied (virtual) states by a, b, \dots indices.

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

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

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

$$\langle p | \hat{h} | q \rangle = \int d\mathbf{x} \psi_p^*(\mathbf{x}) \hat{h}(\mathbf{x}) \psi_q(\mathbf{x})$$

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

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 $d\mathbf{x}$ 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

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

The simplest ground state ansatz

$$|\Phi_0\rangle = \hat{i}^\dagger \hat{j}^\dagger \dots |0\rangle,$$

can be evaluated to calculate the simplest energy estimate using Wicks Theorem [Molinari, 2017]

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{ij} u_{ij}^{ij} \equiv E_{\text{ref}}, \quad (2)$$

named the *reference energy*. Commonly wicks theorem is applied to Eq. 1 to pick out the Eq. 2 contribution, defining the *normal ordered* Hamiltonian

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

where \hat{F}_N and \hat{V}_N is the normal ordered *Fock operator* and two body interaction respectively.

$$\hat{F}_N = \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\}, \quad (3)$$

$$\hat{V}_N = \frac{1}{4} \sum_{pqrs} u_{rs}^{pq} \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\} \quad (4)$$

The operators inside the curly brackets denotes *normal ordering*. In constructing the Fock operator, the matrix elements f_{pq} are given as

$$f_{pq} = h_{pq} + \sum_i u_{qi}^{pi}$$

One major reason for doing this is the applicability of the *Generalized Wicks Theorem*, such that we only need to consider contractions between different normal ordered strings [Ferialdi and Diósi, 2021].

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (5)$$

2.2 Hartree-Fock

The Hartree-Fock method is one of the cheapest and most commonly applied many-body methods. Using the reference energy equation Eq. 2, we perform a basis change to the Hartree-Fock basis, based on minimizing the ansatz expectation value. Using Greek letters to index the computational basis $\alpha, \beta \dots$, going over all states L we can change to the Hartree-Fock basis using

$$|p\rangle = \sum_{\alpha} C_{\alpha p} |\alpha\rangle$$

where $C_{\alpha p}$ are the basis coefficients. Assuming the

We are however not free to choose an arbitrary transformation, since we re

$$\mathcal{L} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \sum_i \epsilon_{i\alpha} (\delta_{ij} - \langle i | j \rangle) \quad (6)$$

$$\delta \mathcal{L} = 0$$

Performing this minimization, we achieve an eigenvalue problem with the matrix

$$h_{\alpha\beta}^{\text{HF}} = h_{\alpha\beta} + \sum_{\gamma\delta} \rho_{\gamma\delta} u_{\beta\delta}^{\alpha\gamma}, \quad \rho_{\gamma\delta} = \sum_i C_{\gamma i}^* C_{\delta i} \quad (7)$$

having the coefficients as eigenvectors and the Lagrange multipliers as eigenvalues

$$\sum_{\beta} h_{\alpha\beta}^{\text{HF}} C_{i\beta} = \epsilon_i C_{i\alpha}. \quad (8)$$

method? This is solved iteratively, starting with $C_{ii} = 1$ ¹, repeatedly diagonalizing C . As a stopping criteria, the sum of Lagrange multipliers per occupied states between iterations is used.

2.3 Coupled Cluster

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

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \equiv e^{\hat{T}} |\Phi_0\rangle. \quad (9)$$

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

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ab\dots \\ ij\dots}} t_{ij\dots}^{ab\dots} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \dots\} \quad (10)$$

where $m \leq N$. The scalars $t_{ij\dots}^{ab\dots}$ are unknown expansion coefficients called *amplitudes*, which we need to solve for.

¹Note that this is over occupied states

All the creation and annihilation operators of Eq. 10 anticommute, giving the restriction that

$$t_{\hat{P}'(ij\dots)}^{\hat{P}(ab\dots)} = (-1)^{\sigma(\hat{P}) + \sigma(\hat{P}')} t_{ij\dots}^{ab\dots}. \quad (11)$$

Here P and P' permutes $\sigma(P)$ and $\sigma(P')$ indices respectively. This is the reason for the prefactor of Eq. 10, 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. 9 is not computationally feasible for realistic systems. The common practice is to include one or more \hat{T}_m operators, making a truncation on $|\Psi_{\text{CC}}\rangle$ as well. In the following we will include only the double excitation operator \hat{T}_2 , know as the CCD approximation. This gives us

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \approx |\Psi_{\text{CCD}}\rangle \equiv e^{\hat{T}_2} |\Phi_0\rangle, \quad (12)$$

$$\hat{T}_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}\}, \quad (13)$$

with the four-fold amplitude permutation symmetry²,

$$t_{ij}^{ab} = -t_{ij}^{ba} = -t_{ji}^{ab} = t_{ji}^{ba}. \quad (14)$$

Incorporating the CCD approximation in the Schrödinger equation (Eq. 5), we see that

$$\begin{aligned} \hat{H} e^{\hat{T}_2} |\Phi_0\rangle &= E e^{\hat{T}_2} |\Phi_0\rangle, \\ \hat{H}_{\text{N}} e^{\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} e^{\hat{T}_2} |\Phi_0\rangle, \end{aligned} \quad (15)$$

where $\Delta E_{\text{CCD}} = E - E_{\text{ref}}$. 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. Therefore, we rather apply a similarity transform to Eq. 15 by multiplying by the inverse of $e^{\hat{T}_2}$,

$$\begin{aligned} e^{-\hat{T}_2} \hat{H}_{\text{N}} e^{-\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \\ \bar{H} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \end{aligned} \quad (16)$$

where $\bar{H} = e^{-\hat{T}_2} \hat{H}_{\text{N}} e^{-\hat{T}_2}$ 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

²For double amplitudes, the index permutation symmetry is equal to that of antisymmetrized two-body matrix elements $\langle pq || rs \rangle$.

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = \Delta E_{\text{CCD}}, \quad (17)$$

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

$$\langle \Phi_{ij\dots}^{ab\dots} | \bar{H} | \Phi_0 \rangle, \quad (18)$$

used for finding the unknown amplitudes t_{ij}^{ab} . To find explicit expressions for Eq. 17 and Eq. 18, we expand \bar{H} using the Hausdorff expansion

$$\bar{H} = \hat{H}_N + \left[\hat{H}_N, \hat{T}_2 \right] + \frac{1}{2!} \left[\left[\hat{H}_N, \hat{T}_2 \right], \hat{T}_2 \right].$$

The truncation at the two-fold commutator comes from the fact that we have a two-body interaction. When evaluated with a doubly excited state, at least one creation or annihilation operator from each of the cluster operators has to be contracted with \hat{H}_N . Therefor having eight creation and annihilation operators in two \hat{T}_2 , four of them can be contracted with the four from \hat{H}_N , while the other four with the operators from $\langle \Phi_{ij}^{ab} |$. This gives the CCD amplitude equation calculated from

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0 \quad (19)$$

To make practical use of Eq. 17 and Eq. 19

2.5 Spin restriction

Both the HF and CCD frameworks presented here treats matrix elements including spin. If the Hamiltonian is spin-independent, both storing and summation over matrix elements can be significantly reduced. Separating relevant quantum numbers and spin, explicitly $p = (P, \sigma_P)$ with P as relevant numbers and σ_P as spin, we see that a general matrix element

$$\langle pq | \hat{v} | rs \rangle = \langle PQ | \hat{v} | RS \rangle \delta_{\sigma_P \sigma_R} \delta_{\sigma_Q \sigma_S},$$

only gives non-zero contributions when both the spins of p, r and q, s align. This reduces 16 equal (or vanishing) elements to a single element, improving both storage and computation time. To make use of this however, we must explicitly expand matrix elements and perform spin summations.

3 Method

Define

$$R \quad (20)$$

4 Results

5 Discussion

6 Concluding remarks

References

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