Hello hello

Håkon Kvernmoen

May 14, 2023

Abstract

Heiie

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

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

The simplest ground state ansatz

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

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

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

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

$$\hat{H} = \hat{H}_{\mathrm{N}} + E_{\mathrm{ref}} = \hat{F}_{\mathrm{N}} + \hat{V}_{\mathrm{N}} + E_{\mathrm{ref}}$$

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

$$\hat{F}_{\mathrm{N}} = \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\}, \tag{3}$$
$$\hat{V}_{\mathrm{N}} = \frac{1}{4} \sum_{pqrs} u_{rs}^{pq} \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\} \tag{4}$$

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].

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \tag{5}$$

2.2 Hartree-Fock

The Hartree-Fock method is one of the cheapest and most commonly applicated 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 $\alpha, \beta \ldots$, 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

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

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

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

$$h^{\mathrm{HF}}_{\alpha\beta} = h_{\alpha\beta} + \sum_{\gamma\delta} \rho_{\gamma\delta} u^{\alpha\gamma}_{\beta\delta}, \qquad \rho_{\gamma\delta} = \sum_i C^*_{\gamma i} C_{\delta i} \tag{7}$$

having the coefficients as eigenvectors and the Lagrange multipliers as eigenvalues

$$\sum_{\beta} h^{\mathrm{HF}}_{\alpha\beta} C_{i\beta} = \epsilon_i C_{i\alpha}. \tag{8}$$

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 $|\Psi_{\mathrm{CC}}\rangle$

$$|\Psi\rangle \approx |\Psi_{\mathrm{CC}}\rangle \equiv e^{\hat{T}} |\Phi_0\rangle . \tag{9}$$

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

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ab\ldots \\ ij\ldots}} t^{ab\ldots}_{ij\ldots} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} \ldots\} \tag{10}$$

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

[1] Note that this is over occupied states

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

$$t^{\hat{P}(ab\ldots)}_{\hat{P}'(ij\ldots)} = (-1)^{\sigma(\hat{P}) + \sigma(\hat{P}')} t^{ab\ldots}_{ij\ldots}. \tag{11}$$

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 $|\Psi_{\mathrm{CC}}\rangle$ as well. In the following we will include only the double excitation operator $\hat{T}_2$, know as the CCD approximation. This gives us

$$|\Psi\rangle \approx |\Psi_{\mathrm{CC}}\rangle \approx |\Psi_{\mathrm{CCD}}\rangle \equiv e^{\hat{T}_2} |\Phi_0\rangle , \tag{12}$$

$$\hat{T}_2 = \frac{1}{4} \sum_{abij} t^{ab}_{ij} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\}, \tag{13}$$

with the four-fold amplitude permutation symmetry [2],

$$t^{ab}_{ij} = -t^{ba}_{ij} = -t^{ab}_{ji} = t^{ba}_{ji}. \tag{14}$$

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

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

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. 15 by multiplying by the inverse of $e^{\hat{T}_2}$,

$$\begin{aligned} e^{-\hat{T}_2} \hat{H}_{\mathrm{N}} e^{-\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\mathrm{CCD}} |\Phi_0\rangle \\ \overline{H} |\Phi_0\rangle &= \Delta E_{\mathrm{CCD}} |\Phi_0\rangle \end{aligned} \tag{16}$$

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^{ab}_{ij}. Considering $\langle \Phi_0 |$ we get

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

$$\langle \Phi_0 | \overline{H} | \Phi_0 \rangle = \Delta E_{\text{CCD}}, \tag{17}$$

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

$$\left\langle \Phi_{ij\dots}^{ab\cdots} \right| \overline{H} | \Phi_0 \rangle , \tag{18}$$

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

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

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 $\hat{H}_{\text{N}}$. Therefor having eight creation and annihilation operators in two $\hat{T}_2$, four of them can be contracted with the four from $\hat{H}_{\text{N}}$, while the other four with the operators from $\left\langle \Phi_{ij}^{ab} \right|$. This gives the CCD amplitude equation calculated from

$$\left\langle \Phi_{ij}^{ab} \right| \overline{H} | \Phi_0 \rangle = 0 \tag{19}$$

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

3.1 Quantum Mechanical System

3.1.1 Helium and Beryllium

The initial testing during development of the CCD and RCCD implementations was performed using Hydrogen wave functions. As a choice of basis sets, these functions are 'physically motivated' in the sense of being solutions to the one body electron case. The well-know relevant quantum numbers determining the form of the spatial wave functions are n as the principal quantum number, with l and m as orbital angular momentum and projection respectively. Due to the spherically symmetric potential, the wave function ψ_{nlm} can be separated in a radial function $R_{nl}(r)$ and a spherical harmonic Y_l^m,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi). \tag{20}$$

The radial part $R_{nl}(r)$ has the form

$$R_{nl}(r) = A_{nl} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l \left[L_{n-l-1}^{2l+1}(2r/na_0)\right]$$

$$A_{nl} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}$$

With L as the associated Laguerre polynomials and a_0 the Bohr radius. For $l > 0$ the Coulomb interaction integral of Eq. 20 can not be easily evaluated due to Y_l^m having a non-trivial θ and ϕ dependence. Therefor for simplicity we only consider s orbital ($l = 0$ states), when calculating $\langle pq | \hat{v} | rs \rangle$. This is briefly sketched in Sec. A. The one-body term h_{pq} are diagonal with

$$h_{nm} = -\frac{Z}{2n^2} \delta_{nm} \tag{21}$$

3.1.2 Two-Dimensional Harmonic Oscillator

3.1.3 Doubly Magic Nuclei

Define

$$R \tag{22}$$

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.

L. Ferialdi and L. Diósi. General Wick's Theorem for bosonic and fermionic operators. *Physical Review A*, 104(5):052209, November 2021. ISSN 2469-9926, 2469-9934. doi: 10.1103/PhysRevA.104.052209. URL http://arxiv.org/abs/2110.02920. arXiv:2110.02920 [hep-th, physics:math-ph, physics:quant-ph].

Luca Guido Molinari. Notes on Wick's theorem in many-body theory, October 2017. URL http://arxiv.org/abs/1710.09248. arXiv:1710.09248 [cond-mat, physics:math-ph].

A Hydrogen Coulomb integrals