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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 [6]

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

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 [3].

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

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

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

where $C_{\alpha i}$ are the basis coefficients. These are the objects used for the parameter search in configuration space. We are however not free to choose an arbitrary transformation, since we require the Hartree-Fock states to be orthogonal $\langle i|j\rangle = \delta_{ij}$. We formulate this constraint as a function of the coefficients C

$$\begin{aligned} \mathcal{G}(C) &= \sum_{ij} \epsilon_{ij} (\delta_{ij} - \langle i|j\rangle) \\ &= \sum_{ij} \sum_{\alpha\beta} \epsilon_{ij} (\delta_{ij} - C_{\alpha i}^* C_{\beta j} \langle \alpha|\beta\rangle) = 0 \end{aligned}$$

Where ϵ_{ij} as the Lagrange multipliers. The goal is minimizing

$$\begin{aligned} \mathcal{E}(C) &= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \sum_{\alpha\beta} C_{\alpha i}^* C_{\beta i} h_{\alpha\beta} \\ &+ \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{\alpha i}^* C_{\beta j}^* C_{\gamma i} C_{\delta j} u_{\gamma\delta}^{\alpha\beta} \end{aligned}$$

and thus the relevant Lagrangian then becomes

$$\mathcal{L}(C) = \mathcal{E}(C) + \mathcal{G}(C).$$

The equation to solve are then found by considering a stationary point of the Lagrangian $\delta\mathcal{L} = 0$ wrt. the coefficients C . Performing this minimization, we achieve an eigenvalue problem with the matrix

$$h_{\alpha\beta}^{\text{HF}} = h_{\alpha\beta} + \sum_{\gamma\delta} \rho_{\gamma\delta} u_{\beta\delta}^{\alpha\gamma}, \quad \rho_{\gamma\delta} = \sum_i C_{\gamma i}^* C_{\delta i} \quad (6)$$

having the coefficients as eigenvectors and the Lagrange multipliers as eigenvalues

$$\sum_{\beta} h_{\alpha\beta}^{\text{HF}} C_{i\beta} = \epsilon_i C_{i\alpha}. \quad (7)$$

Where the Lagrange multipliers are diagonal since by their Hermiticity we can perform a unitary transformation to a basis where they are diagonal $\epsilon = U\epsilon'U^\dagger$.

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.

¹Note that this is over occupied states

2.3 Coupled Cluster

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

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \equiv e^{\hat{T}} |\Phi_0\rangle. \quad (8)$$

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

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ab\dots \\ ij\dots}} t_{ij\dots}^{ab\dots} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \dots\} \quad (9)$$

where $m \leq N$. The scalars $t_{ij\dots}^{ab\dots}$ are unknown expansion coefficients called *amplitudes*, which we need to solve for. All the creation and annihilation operators of Eq. 9 anticommute, giving the restriction that

$$t_{\hat{P}'(ij\dots)}^{\hat{P}(ab\dots)} = (-1)^{\sigma(\hat{P}) + \sigma(\hat{P}')} t_{ij\dots}^{ab\dots}. \quad (10)$$

Here P and P' permutes $\sigma(P)$ and $\sigma(P')$ indices respectively. This is the reason for the prefactor of Eq. 9, 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. 8 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

$$|\Psi\rangle \approx |\Psi_{\text{CC}}\rangle \approx |\Psi_{\text{CCD}}\rangle \equiv e^{\hat{T}_2} |\Phi_0\rangle, \quad (11)$$

$$\hat{T}_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}\}, \quad (12)$$

with the four-fold amplitude permutation symmetry²,

$$t_{ij}^{ab} = -t_{ij}^{ba} = -t_{ji}^{ab} = t_{ji}^{ba}. \quad (13)$$

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

$$\begin{aligned} \hat{H} e^{\hat{T}_2} |\Phi_0\rangle &= E e^{\hat{T}_2} |\Phi_0\rangle, \\ \hat{H}_N e^{\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} e^{\hat{T}_2} |\Phi_0\rangle, \end{aligned} \quad (14)$$

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

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

not amenable to practical computer implementation [2] since the amplitude equation will be coupled with the energy equation. Therefor, we rather apply a similarity transform to Eq. 14 by multiplying by the inverse of $e^{\hat{T}_2}$,

$$\begin{aligned} e^{-\hat{T}_2} \hat{H}_N e^{-\hat{T}_2} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \\ \bar{H} |\Phi_0\rangle &= \Delta E_{\text{CCD}} |\Phi_0\rangle \end{aligned} \quad (15)$$

where $\bar{H} = e^{-\hat{T}_2} \hat{H}_N e^{-\hat{T}_2}$ 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

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = \Delta E_{\text{CCD}}, \quad (16)$$

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

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle, \quad (17)$$

used for finding the unknown amplitudes t_{ij}^{ab} . To find explicit expressions for Eq. 16 and Eq. 17, we expand \bar{H} using the Hausdorff expansion

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

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

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0 \quad (18)$$

To make practical use of Eq. 16 and Eq. 18

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 ,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi). \quad (19)$$

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

$$\begin{aligned} R_{nl}(r) &= A_{nl} e^{-r/na_0} \left(\frac{2r}{na_0} \right)^l [L_{n-l-1}^{2l+1}(2r/na_0)] \\ A_{nl} &= \sqrt{\left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \end{aligned}$$

With L as the associated Laguerre polynomials and a_0 the Bohr radius. For $l > 0$ the Coulomb interaction integral of Eq. 19 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

$$h_{nm} = -\frac{Z}{2n^2} \delta_{nm} \quad (20)$$

We will be interested in calculating the ground state energy for Helium and Beryllium, with two and four electrons respectively. In addition to Hartree-Fock and CCD calculations, a comparison to configuration interaction using singles (CIS) will be performed for both Helium and Beryllium. The results will also be benchmarked against the famous work done by Egil A. Hylleraas [4].

3.1.2 Two-Dimensional Harmonic Oscillator

To test the HF and CCD implementations on larger basis sets, the two-dimensional harmonic oscillator was chosen. N electrons are confined in a potential characterized by the oscillation frequency ω , with a repulsive Coulomb term

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \omega^2 r_i^2 \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (21)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The natural single particle basis for this problem is the solutions to the non-interactive harmonic oscillator case. Characterized by two quantum numbers n_x and n_y , the position space wave function in Cartesian coordinates are expressed as

$$\psi_{n_x n_y}(x, y) = A_{n_x n_y} H_{n_x}(\sqrt{\omega}x) H_{n_y}(\sqrt{\omega}y) e^{-\omega(x^2+y^2)/2}$$

$$A_{n_x n_y} = \sqrt{\frac{\omega}{\pi 2^{(n_x+n_y)} n_x! n_y!}}$$

The one-body Hamiltonian is diagonal, with the well known energies

$$E_{n_x, n_y} = \hbar\omega(n_x + n_y + 1) \quad (22)$$

for two dimensions. For the Coulomb integral from Eq. 21 a more nuanced consideration is in order. The simplest approach is to solve the Coulomb integrals numerically, however even though we just work in two dimensions, the integral will be two-dimensional with a quite complex integrand. For larger basis sets where $L \sim 100$, this approach can not be performed without any clever performance tricks. Luckily this problem has been solved analytically spherical coordinates [1], giving a much cheaper way to incorporate the Coulomb integrals. The implementation co-authored by Ø. Schøyen has been used ³.

We will consider closed shell systems, that is the particle number N will always correspond to all sets of (n_x, n_y) which gives the same single particle energy from Eq. 22 and every energy below this. These shell closures are tabulated in Tab. 1.

R	(n_x, n_y)	d	N
1	(0, 0)	2	2
2	(1, 0) ₁	4	6
3	(2, 0) ₁ , (1, 1)	6	12
4	(3, 0) ₁ , (2, 1) ₁	8	20
5	(4, 0) ₁ , (3, 1) ₁ , (2, 2)	10	30
6	(5, 0) ₁ , (4, 1) ₁ , (3, 2) ₁	12	42
7	(6, 0) ₁ , (5, 1) ₁ , (4, 2) ₁ , (3, 3)	14	56
8	(7, 0) ₁ , (6, 1) ₁ , (5, 2) ₁ , (4, 3) ₁	16	72
9	(8, 0) ₁ , (7, 1) ₁ , (6, 2) ₁ , (5, 3) ₁ , (4, 4)	18	90

Table 1: Showing shell closure for first 9 shells. Degeneracy follows $d = 2R$ with energy per particle $R\hbar\omega$. The subscript 1 means the set on n can be permuted once, $(x, y)_1 = (x, y), (y, x)$.

The interactive $N = 2$ case for $\omega = 1$ has been solved analytically, giving a ground state energy of 3 a.u.[8]. In addition, [7] have tabulated multiple ω frequencies with up to $N = 20$ electrons, calculated for a variety of CC truncation and schemes.

³Implementation is present at <https://github.com/HyQD/quantum-systems/tree/master>

3.1.3 Doubly Magic Nuclei

Define

$$R \quad (23)$$

4 Results

4.1 Helium and Beryllium

The closed shell Helium and Beryllium calculations are presented in Tab. 2, with relative errors compared to FCI in Tab. 3. For both HF add CCD in both restricted and unrestricted schemes, no problems of convergence was encountered. Adding a mixing parameter $p > 0$ for CCD only resulted in slower convergence.

Atom	E_{ref}	CI	FCI	HF	RHF
He	-2.7500	-2.8385	-2.9037	-2.8311	-2.8311
Be	-13.7160	-14.3621	-14.6674	-14.5083	-14.5083

Atom	CCD	RCCD	CCD(HF)	RCCD(HF)
He	-2.7516	-2.7516	-2.8391	-2.8391
Be	-13.7195	-13.7195	-14.5129	-14.5129

Table 2: Ground state energies for Helium and Beryllium in a.u. Calculations done with configuration interaction with both singles and no constraints (full), in addition to HF and CCD in both restricted and unrestricted schemes.

Atom	E_{ref}	CI	HF	RHF
He	5.29	2.25	2.50	2.50
Be	6.49	2.08	1.09	1.09

Atom	CCD	RCCD	CCD(HF)	RCCD(HF)
He	5.24	5.24	2.22	2.22
Be	6.46	6.46	1.05	1.05

Table 3: Relative error in % for Helium and Beryllium from Tab. 2, using the FCI results as the exact energies.

4.2 Harmonic Oscillator

5 Discussion

6 Concluding remarks

References

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A Hydrogen Coulomb integrals

Considering states without orbital angular momentum, we remove the dependence on the two quantum numbers l and m , giving

$$\begin{aligned}\psi_{nlm}(r, \theta, \phi) &\longrightarrow \psi_n(r, \theta, \phi) \\ &= \sqrt{\left(\frac{4}{n^5}\right)} e^{-r/n} L_{n-1}^1(2r/n) Y_0^0.\end{aligned}$$

Where we work in distances of the Bohr radius $r/a_0 \longrightarrow r$. Since the Coulomb integral is over two $\mathbf{r}_1, \mathbf{r}_2 \in \mathbb{R}^3$ spaces, we align \mathbf{r}_1 along the y -axis and perform the \mathbf{r}_2 integral first. In spherical coordinates, the Coulomb interaction then becomes

$$\hat{v}(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{Z}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} \quad (\text{A.1})$$

With these preparations, the integrals can be solved for all p, q, r, s combinations. The integrals were solved using SymPy [5]