The Potato and its dynamics

by

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Abstract

This is an abstract text.

Acknowledgements

I acknowledge my acknowledgements.

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Introduction

Start your chapter by writing something smart. Then go get coffee.

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Formalism

Given a basis of L single particle functions $|p\rangle$ where

$$\{|p\rangle\}_{p=1}^{L} = \{|i\rangle\}_{i=1}^{N} \cup \{|a\rangle\}_{a=N+1}^{L}. \tag{2.1}$$

Here $i, j, k, \ldots$ represents the N first occupied states of the reference Slater determinant whereas $a, b, c, \ldots$ represent the remaining $M = L - N$ virtual states in the total basis $p, q, r, \ldots$ [1].

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[1]Occupied and virtual states are also known as hole and particle states if we treat the reference Slater determinant as the *Fermi level*

Chapter 3

Hartree-Fock theory

Because its all about that energy, 'bout that energy, 'bout that energy!

Chapter 4

Configuration interaction

A popular post Hartree-Fock method is *configuration interaction*. It consists of expressing the wavefunction as a linear combination of excited Slater determinants in a truncated single-particle and Slater determinant basis.

$$|\Psi_{\text{CI}}\rangle = A_0|\Phi_0\rangle + \sum_{ai} A_i^a|\Phi_i^a\rangle + \frac{1}{4}\sum_{abij} A_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \dots, \qquad (4.1)$$

where we have divided by a factor 4 in the double sum to avoid over counting as both the coefficients and the excited determinants are antisymmetric. By generating all the possible Slater determinants from the L single-particle functions we employ the *full configuration interaction* method. This will give the most accurate value of the energy for the system, but quickly becomes computationally impossible as the FCI space grows in dimensions as $\binom{L}{N}$. [3]

4.1 Time-independent configuration interaction theory

We start with the time-independent Schrödinger equation

$$\hat{H}|\Psi_J\rangle = E_J|\Psi_J\rangle, \qquad (4.2)$$

where $(E_J, |\Psi_J\rangle)$ is an eigenpair for $\hat{H}$. Expanding the CI wavefunction in a Slater determinant basis.

$$|\Psi_J\rangle = \sum_K A_{KJ}|\Phi_K\rangle, \qquad (4.3)$$

where A_{KJ} are the amplitudes for a certain excitation K for a specific energy level J. Inserting Equation 4.3 into Equation 4.2 and left projecting on a state

$|\Phi_I\rangle$ we get

$$\sum_K \langle\Phi_I|\hat{H}|\Phi_K\rangle A_{KJ} = E_J \sum_K \langle\Phi_I|\Phi_K\rangle A_{KJ}. \tag{4.4}$$

We now define the Hamiltonian matrix $H_{IK} = \langle\Phi_I|\hat{H}|\Phi_K\rangle$ and the overlap matrix $S_{IK} = \langle\Phi_I|\Phi_K\rangle$. We can thus formulate the generalized eigenvalue equation

$$\sum_K H_{IK} A_{KJ} = E_J \sum_K S_{IK} A_{KJ} \tag{4.5}$$

$$\implies HA = ESA, \tag{4.6}$$

where $S_{IK} = 1 \iff \langle\Phi_I|\Phi_K\rangle = \delta_{IK}$. We will in this text only care about systems where the Slater determinants are orthonormal. Thus the eigenvalue equation we will solve will be

$$HA = EA, \tag{4.7}$$

which means our job is to construct H_{IJ} and diagonalize the matrix[2]. The elements H_{IJ} are computed by

$$\langle\Phi_I|\hat{H}|\Phi_J\rangle = \sum_{pq}\langle p|\hat{h}|q\rangle\langle\Phi_I|c_p^\dagger c_q|\Phi_J\rangle + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_I|c_p^\dagger c_q^\dagger c_s c_r|\Phi_J\rangle. \tag{4.8}$$

Part II

Appendices

Appendix A

Hartree-Fock

Hartree-Fock appendix.

Appendix B

Reformulating the amplitude equations as matrix products

We will in this appendix show how to formulate the tensor contractions occuring in the coupled cluster equations as matrix products. The reason we wish to do this is to be able to perform these contractions as dot products (or matrix products) as there exists highly optimized code performing these operations, e.g., BLAS[1].

To be able to treat tensors of rank > 2 as matrices we have to create *compound indices* by stacking the dimensions after one another. For instance, by looking at the tensor $g \in \mathbb{C}^{I \times J \times K \times L}$, where we denote a single element by g_{ijkl}. Here g is a tensor of rank 4. By creating compound indices $\tilde{I} = IJ$ and $\tilde{K} = KL$ we can create a new tensor $\tilde{g} = \mathbb{C}^{\tilde{I} \times \tilde{K}}$ of rank 2 (represented as a matrix). Using the indices $\tilde{i} = iJ + j$ and $\tilde{k} = kL + l$ we now construct $\tilde{g}$ in such a way that $\tilde{g}_{\tilde{i}\tilde{k}} = g_{ijkl}$.

It is also possible to create compound indices of more than two indices. For instance; choosing $\tilde{J} = JKL$ and setting $\tilde{j} = jKL + kL + l$ we can construct $\bar{g} = \mathbb{C}^{I \times \tilde{J}}$ where $\bar{g}_{i\tilde{j}} = g_{ijkl}$.

For the sake of brevity and clarity we will in the following avoid renaming the compound indices and their sizes, but we will instead indicate with a comma where we construct new indices.

B.1   Reformulating the CCD equations

B.2   Reformulating the CCSD equations

We use the expressions for the CCSD equations derived by Gauss et al.[1]. We start with the *effective double excitation amplitudes* found at the bottom of table

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[1]BLAS can be found here: http://www.netlib.org/blas/

3 in their article. Note that we rename $\tilde{\tau} \to \xi$ thus reserving the twiddle for intermediate calculations.

$$\tau_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2}P(ij)P(ab)t_i^a t_j^b \tag{B.1}$$

$$\implies \tau_{ab,ij} = t_{ab,ij} + \frac{1}{2}P(ij)P(ab)\left(t_{a,i}t_{b,j}\right)_{ab,ij}, \tag{B.2}$$

$$\xi_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{4}P(ij)P(ab)t_i^a t_j^b \tag{B.3}$$

$$\implies \xi_{ab,ij} = t_{ab,ij} + \frac{1}{4}P(ij)P(ab)\left(t_{a,i}t_{b,j}\right)_{ab,ij}. \tag{B.4}$$

Next we look at the one-body intermediates found at the top of table 3 in the article by Gauss et al.[1]. We use the notation

$$u_{ef}^{am} \equiv \langle am||ef\rangle, \tag{B.5}$$

that is, we treat the matrix elements u as the antisymmetric matrix elements of the two-body operator.

$$F_e^a = f_e^a - \frac{1}{2}f_e^m t_m^a + t_m^f u_{ef}^{am} - \frac{1}{2}\xi_{mn}^{af}u_{ef}^{mn} \tag{B.6}$$

$$\implies F_{a,e} = f_{a,e} - \frac{1}{2}t_{a,m}f_{m,e} + \left(t_{fm}\tilde{u}_{fm,ae}\right)_{a,e} - \frac{1}{2}\xi_{a,fmn}\tilde{u}_{fmn,e}, \tag{B.7}$$

$$F_i^m = f_i^m + \frac{1}{2}f_e^m t_i^e + t_n^e u_{ie}^{mn} + \frac{1}{2}\xi_{in}^{ef}u_{ef}^{mn} \tag{B.8}$$

$$\implies F_{m,i} = f_{m,i} + \frac{1}{2}f_{m,e}t_{e,i} + \left(t_{en}\tilde{u}_{en,mi}\right)_{m,i} + \frac{1}{2}\tilde{u}_{m,nef}\tilde{\xi}_{nef,i}, \tag{B.9}$$

$$F_e^m = f_e^m + t_n^f u_{ef}^{mn} \tag{B.10}$$

$$\implies F_{m,e} = f_{m,e} + \left(t_{fn}\tilde{u}_{fn,me}\right)_{m,e}. \tag{B.11}$$

We now move on to the two-body intermediates found just below the one-body intermediates in table 3 in the article by Gauss et al.[1]. To avoid storing two matrices with M^4 elements we will not create the intermediate W_{ef}^{ab} but rather compute the products in place in the amplitude equations by splitting up the products and do them one-by-one (this will shown in due time). We will therefore still preserve the asymptotical scaling $\mathcal{O}(M^4 N^2)$ but add a constant term at the price of saving memory.

Bibliography

[1] Jürgen Gauss and John F Stanton. "Coupled-cluster calculations of nuclear magnetic resonance chemical shifts". In: *The Journal of chemical physics* 103.9 (1995), pp. 3561–3577.

[2] Jacek Karwowski. *Configuration Interaction*. Jan. 1992, pp. 197–222. ISBN: 0444885129, 9780444885128.

[3] Simen Kvaal. *Lecture notes for FYS-KJM4480 - Quantum mechanics for many-particle systems*. 2017.