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

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

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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.

$$|\Psi_{\text{CI}}\rangle = A_0|\Phi_0\rangle \sum_{ai} A_i^a|\Phi_i^a\rangle + \frac{1}{4}\sum_{abij} A_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \dots, \tag{3.1}$$

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 $\binom{L}{N}$.

Part II

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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 $\mathcal{O}(M^4N^2)$ 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.