Generator Coordinate Method for Electronic Structure

Amir Ayati[1], Stijn De Baerdemacker[1] and Hugh Burton[2]

[1]Department of Chemistry, University of New Brunswick, NB, Email: aayati@unb.ca
[2]Department of Chemistry, University of Oxford, UK

We are developing a novel quantum many-body method built on a straightforward representation of the quantum correlations between the electron-spin degrees of freedom of the molecule. The generator Coordinate Method (GCM) constructs a linear superposition of many different product wave functions and is, in a sense, a generalization of the LCAO method in molecular physics for the case of continuously labeled basis functions. The general idea is to identify an observable from a broken symmetry in the system and construct a manifold of simple mean-field quantum states with the observable as a constraint. It is well known that the HF mean-field description of molecular dissociation phenomena improves whenever the spin symmetry is explicitly broken. This points directly to the use of the spin variable as a crucial observable in the GCM framework.

In contrast to the HF solution, the artificial spin-symmetry breaking is ultimately restored in the GCM thanks to the use of a no-CI approach, which also reintroduces missing quantum correlations between the spin degrees of freedom. It is an alternative view on the Holomorphic Hartree-Fock theory by Hugh Burton and Alex Thom [1] in which a non-orthogonal Configuration Interaction (no-CI) is constructed from a basis set consisting of the restricted and unrestricted HF solution. The GCM is conceptually much simpler than HHF as it constructs a basis set from a constrained HF approach, rather than by the holomorphization of HHF.

The method was applied on a simple system with 2 electrons, described by the Hubbard dimer (eq.1). Spin-constrained UHF calculations were applied to this system and the resulting states with values of S were obtained. The minimum energy is found around S=0, whereas a non-zero S solution is preferred once the Coulson-Fisher point is crossed. This is consistent with the idea of a symmetry breaking. In the case of Hubbard dimer, the spectrum for n=2 and n=3 calculations are given if fig.1 with n being the dimension of our no-CI calculation. The n=3 results coincide with the full CI calculations.
In the next stage of the project, typical strongly correlated benchmark systems will be targeted to assess the strengths, weaknesses and opportunities of the proposed method. Afterwards, it will be interesting to apply the method using Generalized HF instead of UHF, since UHF will not be able to describe fully polarized spin states for N particle systems (S=0.5N). Another idea for this method could be adding the spin constraint on spin projection (Sz) in addition to the total spin, especially in case of GHF since Sz symmetry will break if generalized calculations were applied.

$$H = -t \sum_{\sigma=\downarrow,\uparrow} [a^{\dagger}_{L\sigma} a_{R\sigma} + a^{\dagger}_{R\sigma} a_{L\sigma}] + U[n_{L\uparrow} n_{L\downarrow} + n_{R\uparrow} n_{R\downarrow}]$$

Equation 1): The Hamiltonian of the Hubbard dimer. L and R denote the left and right site of the model, U and t are the typical on-site repulsion and hopping parameters, respectively.

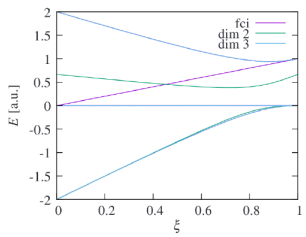

Figure 1): GCM calculations for 2-site Hubbard with an equidistant grid in S.

References:

[1] Burton, Hugh GA, Mark Gross, and Alex JW Thom. "Holomorphic Hartree–Fock Theory: The Nature of Two-Electron Problems." *Journal of chemical theory and computation* 14.2 (2018): 607-618.