

A Perturbation Theory Approach for the Diagonalization of “Strongly Correlated” Matrices

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Since the advent of modern quantum chemistry, the diagonalization of extremely large matrices has been inextricably linked to solving the Schrodinger equation. Due to scaling issues, several iterative techniques have been proposed to target the lowest or highest roots of a matrix via the Rayleigh-Ritz (variational) principle. In this regard, the Davidson diagonalization strategy has found ubiquitous use across many quantum chemistry software packages as - for the vast majority of standard chemistry problems - it exhibits attractive convergence properties assuming a reasonable starting guess vector and a diagonally-dominant matrix. However, in situations where either of these conditions are not met, the convergence of the Davidson technique can be poor.

In this work, we introduce a novel approach for the diagonalization of non-diagonally dominant matrices based on Brillouin-Wigner Perturbation Theory (BW-PT). This technique is characterized by redefining the zeroth order Hamiltonian after low order iteration. It is shown that the power in this approach originates from the inherent flexibility associated with the BW-PT resolvent operator, which can be optimized according to the structure of the matrix being studied. These broad conclusions are based on a benchmark of a non-diagonally dominant Hermitian matrix; notably, the water dimer Configuration Interaction Singles (CIS) built from a Natural Localized Molecular Orbital (NLMO) reference. By comparing against standard single-vector Davidson, we show this approach to be a competitive technique suitable for any matrix describing physical processes with strong couplings across matrix elements.