

Optimizing Virtual Spaces for Plane-Wave Hamiltonians: Streamlining Virtual Spaces Through Pairwise Correlation Optimization

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Plane-wave basis sets pose no issues for many-body methods like MCSCF and CASSCF since the number of one-electron orbitals is optimized independently of the basis. High-level quantum chemistry methods such as CI and CC, however, demand a compact basis set due to computational constraints. These methods, rely on second-quantized Hamiltonians derived from many-body electronic Hamiltonians, need to include numerous atomic orbitals for accurate results.

Additionally, accurate chemical behavior prediction requires a virtual space to capture substantial electron-electron correlations. Often, the virtual orbitals in plane-wave Hartree Fock computations are weakly interacting scattering states, capturing a minimal amount correlation energy. Attempts to utilize virtual spaces from one-electron operators have similarly resulted in a low amount of correlation energy captured.

Addressing these challenges, we've developed algorithms to define virtual spaces by optimizing orbitals from compact pairwise CI Hamiltonians, yielding plane-wave derived, correlation-optimized virtual orbitals (COVOs). This novel approach, focusing on select CI problems rather than fitting eigenvalue spectra and band structures, generates virtual spaces with fewer orbitals that capture more correlation than traditional Hartree-Fock and one-electron Hamiltonian methods. Our results align well with full CI/cc-pVTZ and quantum computing methods like VQE and Trotterization for molecules such as H₂ and Be₂ dimers under free boundary conditions, even with a limited number of virtual orbitals.

We also discuss the connection to the OVOS method by Adamowicz and Bartlett and introduce a progression of the COVOs method to periodic systems at the Γ point, factoring in extensive Brillouin integrations. Employing King and Parr's orbital method, we've generalized COVOs for multi-electron systems. The integration of Filon's Integration Strategy for two-electron integrals allows for the generation of CI matrix elements in periodic systems. This method has successfully replicated aperiodic CI results for small molecules within large unit cells under periodic boundary conditions. We aim to apply this approach to CI calculations for minerals like diamond, with up to 18 valence orbitals at the Γ point, and anticipate its utility in various many-body approaches, including CC theory.