Diagrammatic vibrational structure methods for molecules and solids

Matthew Hermes, Murat Keçeli, So Hirata

We have developed new diagrammatic computational methods for anharmonic vibrations of molecules and solids. XVSCF(n) and XVSCF[n] are manifestly size-consistent implementations of the VSCF method designed for molecules, which differ in that the former neglects coupling between anharmonic geometries and frequencies. Both methods omit terms from the VSCF formalism which contribute non-size-consistent quantities to calculated quantities. The resulting equations predict an effectively harmonic vibrational wave function, rendering the basis sets and matrix diagonalization from traditional VSCF unnecessary. The application of Moller-Plesset perturbation theory to the vibrational problem using either XVSCF as a reference is referred to as XVMP2. In lieu of calculating the energies of excited vibrational states, XVMP2 calculates frequencies directly using the Dyson equation for the single-particle vibrational Green's function and a sum of open, connected diagrams. This method enables XVMP2 to predict accurate anharmonic frequencies even for molecules affected by strong anharmonic resonance without a quasi-degenerate implementation.