

DIAGRAMMATIC VIBRATIONAL COUPLED-CLUSTER

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A diagrammatic vibrational coupled-cluster method for calculation of zero-point energies and an equation-of-motion coupled-cluster method for calculation of anharmonic vibrational frequencies are developed. The methods, which we refer to as XVCC and EOM-XVCC respectively, rely on the size-extensive vibrational self-consistent field (XVSCF) method for reference wave functions. The methods retain the efficiency advantages of XVSCF making them suitable for applications to large molecules and solids, while they are numerically shown to accurately predict zero-point energies and frequencies of small molecules as well. In particular, EOM-XVCC is shown to perform well for modes which undergo Fermi resonance where traditional perturbative methods fail. Rules for the systematic generation and interpretation of the XVCC and EOM-XVCC diagrams to any order are presented.