The Concordant Mode Approach for Computing Vibrational Frequencies

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The Concordant Mode Approach (CMA) is a method for computing harmonic vibrational frequencies using lower level of theory normal modes as a basis for higher level of theory force constant computation. CMA0 approximates harmonic frequencies at a high level of theory using lower level of theory normal modes to compute the diagonal force constants at a higher level, utilizing stationary points for each Hessian computed. CMA1 utilizes the same process but with lower level force constants computed atop the higher level geometry to generate the initial Hessian. Utilizing CCSD(T)/cc-pVDZ and B3LYP/6-31G(*2df,p*) starting Hessians for CMA0 on 116 molecules of the G2 test set yields mean deviations of harmonic frequencies from CCSD(T)/cc-pVTZ of -0.03 ± 0.40 cm^{-1} and -0.06 ± 0.62 cm^{-1}, respectively, when removing egregious outliers due to excessive geometric shifts between levels of theory. CMA1 yields mean deviations of -0.04 ± 0.48 cm^{-1} and -0.08 ± 0.46 cm^{-1}, respectively. CMA0 has ZPVE deviations of -0.0015 ± 0.0095 kcal mol^{-1} and -0.0023 ± 0.0077 kcal mol^{-1}, respectively. CMA1 has ZPVE deviations of -0.0008 ± 0.0009 kcal mol^{-1} and -0.0008 ± 0.0010 kcal mol^{-1}, respectively. CMA shows an inherent coordinate dependence.

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