An Extension of the Concordant Mode Approach (CMA)

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The determination and assignment of molecular vibrational modes has been a cornerstone of solving many problems in theoretical chemistry. The computational determination of vibrational modes depends on the second derivative of the nuclear coordinate potential energy. The unfavorable $9N^2$-33N + 31 scaling (where N = the number of atoms in a non-linear polyatomic molecule) becomes unfeasible for popular *ab initio* methods such as CCSD(T) for systems with greater than 10 heavy atoms. The Concordant Mode Approach (CMA) by Lahm et al. has proven to be a very powerful method for approximating the exact Hessian by using the normal coordinates computed at a lower level of theory as the basis for computing the normal modes at the higher level of theory. By necessitating that only the diagonal force constants need be computed in the higher level of theory, the method scales linearly as 6N – 11. We present a powerful extension of the CMA methodology which includes the means to eliminate errors due to geometric shifts (CMA1), and the ability to selectively predict and compute off-diagonal force constants to eliminate normal mode coupling (CMA0/1 + off-diagonals). Preliminary results within the G2 test set were computed for CMA0 and CMA1 modes with error > 2.5 cm^{-1}. The normal coordinate basis used to target the exact CCSD(T)/cc-pVTZ vibrational modes was computed using CCSD(T)/cc-pVDZ and B3LYP/6-31G(2df,p). By selectively including off-diagonal force constants, the average error in the CMA0 results was reduced from 3.28 cm^{-1} to 0.36 cm^{-1}, and 3.94 cm^{-1} to 0.54 cm^{-1} for the (T)/DZ and DFT lower level of theory, respectively. Likewise, the CMA1 average error was reduced from 3.10 cm^{-1} to 0.50 cm^{-1} and 3.66 cm^{-1} to 0.73 cm^{-1} for the (T)/DZ and DFT lower levels of theory, respectively. These preliminary results show the powerful CMA methodology is convergent to the exact normal modes.