Choices in Vibrational Perturbation Theory Resonance Diagnosis and Treatment

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We present our black-box algorithm for resonance diagnosis and treatment of divergences encountered in vibrational perturbation theory (VPT). Previous black box diagnosis algorithms of divergent denominators encountered in VPT relied on numerical cutoffs of the size of Van Vleck matrix elements relative to KS-DFT data over a small amount of careful experimental data. We improve upon such work by considering CCSD(T) data as the basis for determining resonances, consider resonance diagnosis methods other than the size of the Van Vleck matrix element size, and use a large amount of experimental data from the HITRAN database. Our resonance diagnosis code, Melkor, is used in conjunction with the CFOUR software and with post-processing of the Gaussian software. We compute the accuracy of broadened IR signals relative to CCSD(T) computation within the new black-box algorithms for resonance treatment. We observe some challenges in a lack of permutational invariance in some of the more newly suggested resonance treatment algorithms, and attempt to remedy this problem. Lastly, we also investigate a choice in the variational diagonalization of the resonant states, owing to a degree of freedom in defining what states are “connected.”