

HIGH-ORDER VIBRATIONAL RESONANCES OF CARBONYL SULFIDE REVEALED BY THE RESUMMATION TECHNIQUE

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The high-order Rayleigh-Schrödinger perturbation theory (RSPT), being a classical quantum-mechanical technique for solving many problems with a known analytic solution for the zero-order approximation, is rarely used in the context of molecular vibrations since such RSPT series usually diverge. This divergence is caused by resonance couplings that mix vibrational states and produce abnormally small denominators in RSPT corrections.

However, divergent series still contain information about coupled vibrational states that can be properly extracted and described in terms of specially designed multi-valued functions, called approximants. Among them the quartic Padé-Hermite approximant (PHA) is one of the most efficient:

$$P(\lambda) + Q(\lambda)E(\lambda) + R(\lambda)E^2(\lambda) + S(\lambda)E^3(\lambda) + T(\lambda)E^4(\lambda) = 0.$$

The resummation procedure transforms a large portion (up to $\approx 200^{\text{th}}$ order) of corrections of a divergent vibrational RSPT series into PHA with algebraic coefficients via solving a linear system of equations or in an incremental way.¹

As a result, one of several PHA values accurately reproduces the exact variational solution of the same problem, while the others usually coincide with nearby resonant energy levels. It is very interesting that singularities of the RSPT/PHA solutions can be described in terms of the complex-valued perturbation parameter $\bar{\lambda} = \Re(\bar{\lambda}) + \Im(\bar{\lambda})$, while the resonant states can be characterized by coinciding complex singularities with the condition $|\bar{\lambda}| \leq 1$.²

This RSPT resummation technique was applied to vibrational states of the series of OCS isotopologues. The Watson Hamiltonians were calculated using the *ab initio* equilibrium geometry and quartic/sextic PES at CCSD(T)/cc-pV(Q+d)Z level. The analysis of the resulting PHA approximants revealed most of experimentally observed high-order resonances including those which break down the known polyad formula $P = 2v_1 + v_2 + 4v_3$.

¹[doi:10.1016/j.cpc.2004.02.002](https://doi.org/10.1016/j.cpc.2004.02.002), T. M. Feil, H. H. H. Homeier, *Comput. Phys. Commun.*, **158**, 124–135 (2004).

²[doi:10.1021/jp211400w](https://doi.org/10.1021/jp211400w), X. Chang, E. O. Dobrolyubov, S. V. Krasnoshchekov, *Phys. Chem. Chem. Phys.*, **24**, 6655–6675 (2022).