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Improving Spectral Interpretation with Learned Vibrational Coordinates

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Spectral assignment of rovibrational spectra links observed features to labeled energy levels, enabling interpretation through effective Hamiltonians. This labeling relies on identifying coordinates that approximately separate the Hamiltonian into subsystems. For example, in the harmonic approximation, normal coordinates decouple the vibrational Hamiltonian into $3N - 6$ independent modes. However, when anharmonicity is included the assignment becomes less direct, as energy levels no longer correspond directly to individual mode excitations. In general, assigning quantum numbers becomes increasingly difficult as the complexity of the computational model grows. This challenge is especially pronounced for delocalized vibrational states, such as those found in hydrogen-bound systems, where calculating accurate spectra requires advanced models. In such cases, the wavefunctions often show strong mode coupling, reflecting a suboptimal choice of coordinates that do not decouple the vibrational motions.

We introduce normalizing-flow vibrational coordinates, a new class of coordinates that can be tailored to a specific system and basis set [1]. Analogous to how spherical coordinates naturally simplify the hydrogen atom problem by embedding physical insight into the coordinate system, normalizing-flow coordinates offload complexity from the basis functions into the coordinates (Figure). This shift improves basis set convergence, interpretability, and spectral assignment.

[1] Y. Saleh, Á. Fernández Corral, E. Vogt, A. Iske, J. Küpper, A. Yachmenev, JCTC, 2025, 21(10), 5221-5229

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