Imaging of nodal planes of vibrational wavefunctions and nonadiabatic coupling

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A natural origin for dynamic change of molecules is nonadiabaticity in the form of coupling between bound and continuum states. Triatomic molecules show distinct signatures of such coupling in the decay into three fragment atoms. If the three atoms appear in their electronic ground state, the total molecular energy is converted entirely into kinetic energy of the fragments. Thus the fragment atoms preserve memory of the internal molecular momentum distribution in a correlation between the linear momentum vectors of the three separating atoms, the nonadiabatic coupling operator acting as link between the two worlds, molecule and separated atoms.
This situation occurs for bound excited electronic states of H_3 and D_3. Their decay has been studied since the seminal work on three-particle momentum correlation by Müller and Cosby in 1999 [1]. Numerous experiments have extended the original study. To date no intuitive quantitative explanation for the rich structural complexity observed in the momentum vector correlation maps (MVCs, also called Dalitz-plots [2]) has been found. Recently simulations of MVCs for H_3 and D_3 by quantum chemists [3, 4, 5] specifically considered the short lived $2sA'_1$ Rydberg initial state. They combined the quantum description of the bound Rydberg state and its nonadiabatic transition operator with classical trajectories or wavepacket propagation on the two Jahn-Teller-split ground state surfaces.
In this contribution a symmetry-based model is presented which explains dominant features, such as nodal structures, in the MVCs for selected experimental $2sA'_1$ Rydberg initial states [6]. The starting point of the approach is a spatial representation of the vibrational wavefunction and coupling operator, which is converted into momentum representation - as appropriate for comparison with the Dalitz plot. The equivalence of the symmetry based map and experimental observations leads to the conclusion that experimental imaging of 3-particle coincident momentum maps provides a direct view of the product space of vibrational wavefunction and nonadiabatic coupling operator.

References:

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