Quantum Rotational Coherences in Complex Media

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Rotational wavepackets are superpositions of angular momentum eigenstates generated in general via sequential, Rabi-type cycles in moderately-intense laser fields. The fascinating spatial and temporal properties of such wavepackets follow directly from the phase relations among their rotational components. These include sharp alignment, whose quality could not be obtained via other alignment techniques, and, in the short pulse case, a rotational revival structure that mirrors the underlying rotational eigenvalue spectrum. The highly nonlinear nature of rotational spectra, along with the coherence properties of the excitation laser pulse, make for a unique revival structure, fundamentally different from vibrational and electronic revival patterns.

In the limit of small isolated molecules, rotational coherences, with the ensuing nonadiabatic alignment, have evolved during the past 2 decades into an active field of theoretical and experimental research with a rich variety of applications. In the present talk we extend these concepts to complex systems. First we consider the case of asymmetric top molecules, where alignment overcomes the mechanisms that render the rotations chaotic in the classical limit. Next we focus on dissipative media, and illustrate the application of rotational coherence as a probe of the decohering properties of the environment. We extend alignment to control the torsional motions of polyatomic molecules, and apply torsional control to manipulate charge transfer events. Turning to interfaces, we introduce a route to guided molecular assembly, wherein laser alignment is extended to induce long-range orientational order in molecular layers. Combining rotational coherence with recent research on nanoplasmonics and on conductance via molecular junctions, we develop an approach to coherent control of transport in the nanoscale. Finally, we explore the case of dense molecular ensembles, where alignment generalizes into a collective phenomenon that gives rise to formation of molecular assembly with long range translational and orientational order.