Photoexcited Vibrational Dynamics in Vicinity of Surface Crossings

Non-interacting electronic and vibrational (phonon) dynamics in (bio)molecules and solids is characterized by well separated timescales associated with the energies of electronic and vibrational transitions. Interaction between them corresponds to renormalization of their energies and, consequently, dynamics timescales. In such case, separation into slaving and slaved degrees of freedom, i.e. an adiabatic or Born-Oppenheimer approximation significantly simplifies analyzes of the problem.[1] However, there are many examples in polymers, biological complexes and some metal complexes, where the Born-Oppenheimer approximation breaks down. This occurs in the vicinity of electronic adiabatic energy surface crossings (see Fig. 1) where the renormalized electronic and vibrational energies become comparable.[2]

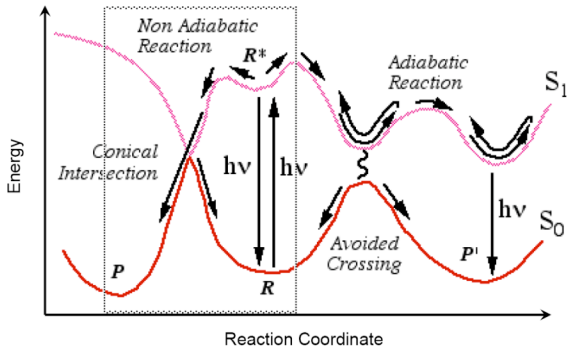

Figure 1 *Examples of surface crossing and photoexcited dynamics.*

If a vibrational wavepacket is photoexcited by ultrafast laser pulses from S_0 to S_1 adiabatic surfaces (Fig. 1) then its dynamics away from the crossing regions can be well described by classical molecular dynamics. However, in the case of avoided level crossing or unavoided one, the so called conical intersection (CI), quantum mechanical effects such as Landau-Zener tunneling or quantum mechanical (semiclassical) scattering become important.[1,2] Such nonadiabatic dynamics is a key to understanding of many effects in photophysics and photochemistry includeing radiativeless energy relaxation, photo-reaction dynamics, e.g. photoisomerizations *etc*.[2]

In our study we focus on two related aspects of photoexcited nonadiabatic dynamics. One is modeling of nonlinear optical response from nonadiabatic degrees of freedom. This should provide a basis for experimental optical probe using sub-picosecond/femtosecond laser pulses. The other aspect is semiclassical description and computer modeling of nonadiabatic dynamics in the vicinity of CI. Below we present our main results obtained in these directions.

Addressing the problem of optical probe/control of nonadiabatic dynamics we have considered a photon-echo response to a train of three phase-locked ultrafast laser pulses, the so called three-pulse echo (3PE), from a coupled electron-phonon system in the regime of strong coupling.[3] This regime can take place in mixed valence metal complexes whose adiabatic potential surfaces form a multiple-well potential in the ground electronic state, and the first excited state surface has avoided type crossing with the ground state one.

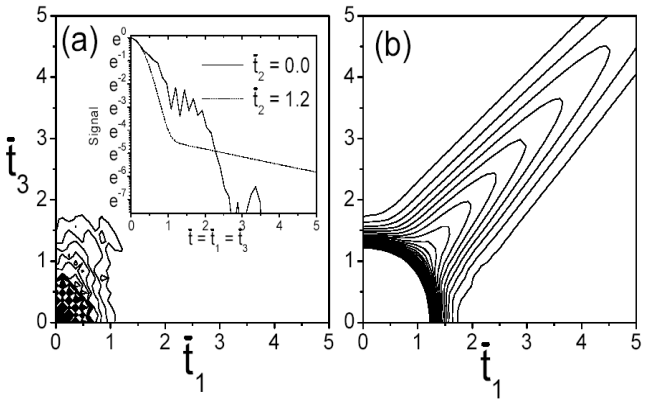

Figure 2 *Contour plot of 3PE signal: (a) populations delay time is smaller than the ground and excited state dephasing times; no echo signal is seen along the diagonal; (b) populations delay time is larger than the ground and excited state dephasing times; echo signal is clearly seen along the diagonal. The inset to (a) shows diagonal slices of (a) and (b).*

A vibrational wavepacket after being excited by the first two pulses (separated by time t_1) passes through the avoided crossing region and scatters between the ground and excited state surfaces. After a number of scattering events, the wavepacket phase can be partially or completely lost. What we found is that the photon echo signal as a function of the delay time between

the second and the third pulses t_2 (the population time) is sensitive to the excited state dephasing, and could be used to probe it as demonstrated in Fig. 2. This effect is counterintuitive, since a 3PE signal appears in the absence of the inhomogeneous broadening only as a result of rephasing of the coherences between the bound vibrational quanta of a single phonon mode.[3] The latter occurs during time t_3 between the third pulse arrival and signal detection event.

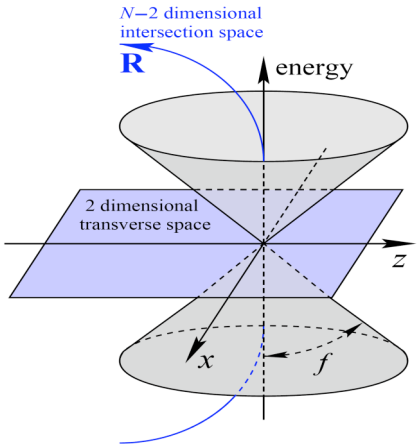

Figure 3 *The potential energy surface in the vicinity of the CI as a function of transverse vibrational coordinates.*

Unavoided surface crossing, i.e. the CI of two electronic surfaces of same symmetry, parameterized by N vibrational coordinates occurs when the dimensionality of the crossing manifold is N-2.[1,2,4] In this case, as illustrated in Fig. 3, it is possible to expand the electronic energy up to the linear terms in two-dimensional transverse coordinate space resulting in a conical type of level crossing. Provided the interaction region between the crossing surfaces is small, the approximation is universal.[2,4]

We have considered ballistic (i.e. constant velocity) scattering regime of vibrational wavepackets in the vicinity of CI, and found that the adopted approximation is controlled by unique dimensionless parameter $g_s \sim \nabla^{1/2}$ as well as the scattering radius r_s scales as $\nabla^{1/2}$.[4] If $g_s << 1$, the ballistic approximation holds. Since $g_s^2 \sim \nabla$, we conclude that the ballistic scattering occurs in the semiclassical regime. In this regime the scattering amplitude can be calculated explicitly, and has similarity with celebrated Landau-Zener formula.[4] Obtained scattering amplitude was compared with the results of direct numerical simulations (Fig. 4), and demonstrated good agreement for the realistic set of parameters.[4] Obtained scattering amplitude could have practical implications for large scale molecular dynamics simulations of (bio)molecular clusters to account for the CI effects.

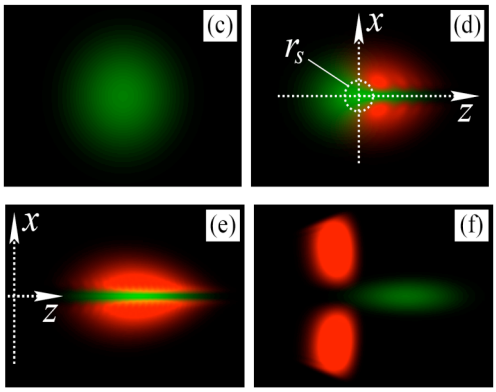

Figure 4 *Numerical simulations of the semiclassical wavepacket scattering on the CI. The wavepacket is propagating in the z-direction (identical in all panels). The origin of the coordinate system indicates the position of the CI. (c) initial wavepacket , (d)-(e) scattering event characterized by the scattering radus r_s; quantum interference fringes are well resolved, (f) scattered to the other surface (green) wavepacket, and two (red) transmitted ones.*

References

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3. A. Piryatinski, S. Tretiak, P. W. Fenimore, A. Saxena, R. L. Martin, and A. R. Bishop "Three-pulse photon-echo spectroscopy as a probe of photoexcited electronic state manifold in coupled electron-phonon systems." Physical Review B, **70**, 161404(R) (2004).
4. A. Piryatinski, M. Stepanov, S. Tretiak, and V. Chernyak "Semiclassical Scattering on Conical Intersections." Physical Review Letters (submitted).

Contact Information: Andrei Piryatinski - Center for Nonlinear Studies and Theoretical Chemistry & Molecular Physics Group T-12, MS-B258 Los Alamos National Laboratory, Los Alamos, NM 87545. Telephone: (505) 665-3639; e-mail: apiryat@lanl.gov