Photoexcited Vibrational Dynamics in Vicinity of Conical Intersections

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Noninteracting electronic and vibrational dynamics in (bio)molecules and solids is characterized by well separated timescales associated with the energies of electronic and vibrational transitions. Switching on interaction between these degrees of freedom leads to renormalization of their energies and, consequently, dynamics timescales. Provided the electronic surfaces in a molecule are still sufficiently separated, photophysical and spectroscopic processes can be well described within *adiabatic*, i.e., the Born-Oppenheimer approximation. In such a case, separation into slaving and slaved degrees of freedom significantly simplifies analyses of the problem[1]. For instance, molecular dynamics (MD) simulations reduce to propagation of classical nuclei trajectories on the excited electronic state potential surface (Fig. 1), while the forces can be computed separately using first principle quantum chemical methods or model approaches.

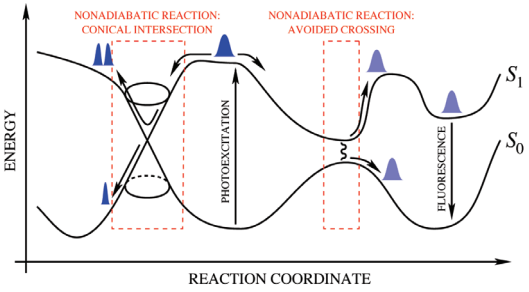


Fig. 1.
Examples of surface crossing and photo-excited dynamics.

The Born-Oppenheimer approximation breaks down in the vicinity of surface crossings resulting in the need for *nonadiabatic* quantum mechanical MD, which is computationally expensive and often intractable. A variety of ultrafast photoreactions in biological molecules occur in the vicinity of the surface crossings. Among them rhodopsin photoisomerization, radiativeless excited state energy relaxation in fluorescent proteins and DNA base pairs. Importance of these processes for extending our fundamental knowledge in photochemistry of biological objects, as well as rich potential for developing biological and chemical sensor suitable for medical applications, motivates extensive study of nonadiabatic dynamics in macromolecules [2].

There are two important cases of the electronic energy crossings illustrated in Fig. 1. Provided the electronic states coupled to N vibrational degrees of freedom have identical symmetry, and intersect. If the dimensionality of the intersections manifold is $N–1$ then any small interaction lifts the degeneracy corresponding to the so-called avoided crossing[1, 2]. Tunneling through the avoided crossing gap is well described by the celebrated Landau-Zener formula valid in the semiclassical regime.

The other, much more complicated case of true surface crossing occurs when the dimensionality of the crossing manifold becomes $N–2$. As illustrated in Fig. 2, it is possible to expand the electronic energy in the vicinity of the surface crossing up to the linear terms in two-dimensional transverse coordinate space. As a result, the electronic surface becomes a double cone giving rise to the

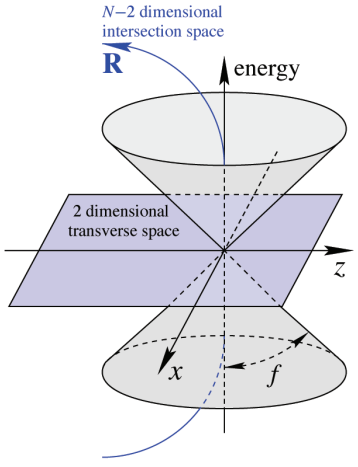
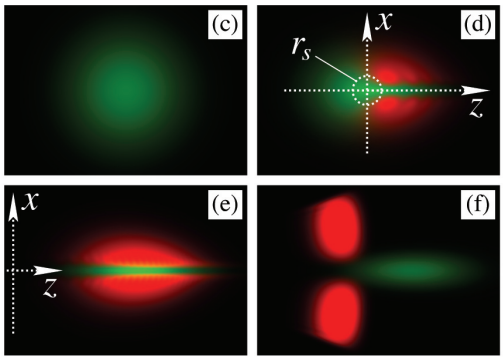


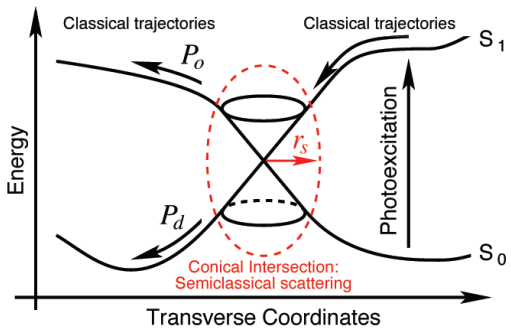
Fig. 2.
The potential energy surface in the vicinity of the CI as a function of transverse vibrational coordinates.

name of conical intersection (CI) for a true crossing case. The point where the cones touch each other represent N–2 degeneracy space. Provided the interaction region between the surfaces is small, the CI approximation becomes universal [2, 3]. However, no small interaction can lift the degeneracy at the crossing space, and as a result, cannot remove singularity which significantly complicates MD.



To address the problem of MD in the vicinity of CI, we have developed a wavepacket scattering matrix approach [3]. The theory is based on the scattering matrix expansion controlled by unique dimensionless parameter g_s. The scaling of $g_s \sim \hbar^{1/2}$ suggests that the scattering takes place in the semiclassical regime when $g_s << 1$. We have also found that the scattering radius r_s, also scales as $\hbar^{1/2}$, and that the wavepacket passes through this small vicinity of CI with negligible changes in its velocity, i.e., in the ballistic regime. Calculated zero order scattering amplitude has simple analytical expressions resembling celebrated Landau-Zener result. To verify our analytical results, obtained scattering amplitude was compared with the results of direct numerical simulations (Fig. 3), and demonstrated good agreement for the realistic set of parameters.

Obtained analytical expressions could have several practical implications for large-scale MD simulations as we illustrate in Fig. 4. In the adiabatic regions, a classical treatment of the vibrational degrees of freedom is satisfactory. Therefore, photoexcited dynamics away from CIs can be modeled by running an ensemble of classical trajectories. If some trajectories approach the explicitly defined scattering region r_s around a CI, the dynamics becomes nonadiabatic and should be treated quantum mechanically. According to our theory, instead of numerically demanding quantum calculations, we propose propagating an ensemble of classical trajectories through r_s using our analytical expressions with input parameters from classical MD data. This approach is widely adopted for the case of fast passages through an avoided crossing where the Landau-Zener theory works. Since our results are similar in spirit to the latter theory, their generalization to far more complicated cases of CIs should be efficient and universal.



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[2] *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, W. Domcke, D.R. Yarkony, and H. Koppel, Eds. (World Scientific, New Jersey, 2004).
[3] A. Piryatinski, et al., "Semiclassical Scattering on Conical Intersections," *Phys. Rev. Lett.* **95**, 223001 (2005).

Fig. 3. ***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.***

Fig. 4. ***Proposed scheme for large-scale quantum mechanicanics/molecular mechanics photoexcited molecular dynamics incorporating analytical expressions for the CI transition P_O and scattering P_d probabilities entering the semiclassical scattering matrix.***