

Summary of work on propensity rules for oscillators

I. EARLIER RESULTS

In a recent paper [J. Chem. Phys. **112**, 4004, 2000], the phase space distribution approach was developed to predict the most preferable outcome of a radiationless transition from the bottom of an upper vibrational potential energy surface of an electronically excited donor state to one of vibrationally excited states on a lower surface of the ground electronic state. This approach to propensity rules for surface jumping gives a general prescription for finding the leakage point of energy-transfer between two Born-Oppenheimer surfaces. By approximating the Wigner function of the acceptor by its classical limit $\delta(E - H_{\text{cl}}(p, q))$, the problem reduces to finding a maximum of the Wigner function of the donor on the accepting surface $H_{\text{cl}}(p, q) = E$ that can be easily solved algebraically.

II. DIRECTIONS OF THE WORK

In the current study, the above results are considered as a starting point for further progress in the area of phase-space formalism and its applications in molecular physics. Firstly, we applied the phase space method for specific molecules that exhibit classically forbidden transitions. Then, we investigated mathematical aspects of application of this approach to multidimensional harmonic and anharmonic oscillator surfaces. In addition, we studied justifications of underlying assumptions of the space-phase method and its relationship with a more traditional quasiclassical Landau method. Below, the three directions of our work are outlined in more details.

III. INTERNAL CONVERSION OF THE BENZENE MOLECULE

The theoretical problem of finding propensity rules for the partition of energy between competing vibrations in a radiationless vibronic relaxation transition is converted by the phase-space method to a simple mathematical problem of finding a maximum of a function under a constraint. The function is the Wigner function of the initial state and the constraint is energy conservation, defining an accepting energy surface in phase space. The initial state is here the ground vibrational state of an excited electronic surface. The final state is a dense quasi-continuum manifold of highly excited vibrational states of the ground electronic state.

Previously, the method was derived for allowed transitions, and applied to a harmonic model system. Now, we have reviewed this phase space method and generalized it to forbidden transitions and to anharmonic force fields. As the first application of this method to a real physical system we have studied within this framework the $S_2^{v=0} \rightarrow S_0$ transition in the benzene molecule.

The absorption spectrum of the $S_0 \rightarrow S_2$ transition is very diffusive due to the non-adiabatic interactions and the quantum yield for the radiative transition is very small in both the fluorescence and phosphorescence paths, yet, the decay rate for the process is extremely fast (140 fs). These phenomena led to the conclusion that the relaxation takes place through internal conversion (IC). It was found previously that the modes that show bands in the spectrum for the IC process belong to the $C - H$ bonds. This gives a clear indication that a significant amount of the electronic energy is transferred in the relaxation process to the $C - H$ modes. In the benzene molecule the most displaced mode is the totally symmetric stretch of the ring. This can be well understood based on the large change of electron density in the region of the backbone of the benzene between the ground and the first and second excited electronic states. From a classical point of view, using the reflection principle, it is easy to show that in the general case, the mode that is the most displaced will be the mode that will receive most of the energy. The experimental results for the benzene

molecule stand as one of the counter examples for this classical behavior.

We showed by simple means of finding a maximum of a 3 dimensional function that in the $S_2^{v=0} \rightarrow S_0$ case, most of the electronic energy released in the IC process converts into vibrational energy of the $C - H$ mode of vibration. We found that in this specific example the partition of the energy between competing modes was not sensitive to the difference between the anharmonic force field and its harmonic approximation, but that the anharmonic terms are expected to strongly enhance the transition rate. From a theoretical perspective it is interesting to note that for a range of parameters which is not physical for this vibronic transition of the benzene molecule, we found that significant differences can arise between the harmonic and anharmonic force fields regarding the order of magnitude of the transition probability, the partition of the energy, and the sensitivity of these results to various parameters such as the magnitude and sign of the displacements of the equilibrium bond lengths of the excited and ground electronic states. The general dependency of these features on different parameters like frequency, displacements, energies and anharmonic force constants is considered from a more mathematical-formal perspective in a separate work devoted to mathematical aspects of the problem.

An interesting problem that could be considered in the future is the “channel three” problem of the benzene $S_1 \rightarrow S_0$ transition, i.e. an extremely fast decrease in the quantum yield for excitations above 3000 cm^{-1} . One of the difficulties in analyzing this phenomena was the identification of the active modes to whom the IC of the molecule occurs. The phase space approach might contribute in finding a simple way to determine which of the many potentially active modes is in fact essential for this process.

IV. MATHEMATICAL ASPECTS OF THE PHASE-SPACE APPROACH

We focus here on mathematical aspects of finding the leakage point for multidimensional harmonic and anharmonic oscillator surfaces. Generally, the Hamiltonian of an acceptor (up to cubic anharmonic terms) is

$$H_F = \frac{1}{2} \sum_{i=1}^N \left(\frac{p_i^2}{m_i} + m_i \omega_i^2 q_i^2 \right) + \frac{1}{6} \sum_{i,j,k=1}^N f_{ijk} q_i q_j q_k + \dots,$$

where p_i and q_i are normal momenta and coordinates, and the Hamiltonian of a donor is

$$H_1 = \frac{1}{2} \sum_{i=1}^N \left(\frac{p_i'^2}{m_i'} + m_i' \omega_i'^2 q_i'^2 \right) + \frac{1}{6} \sum_{i,j,k=1}^N f'_{ijk} q_i' q_j' q_k' + \dots,$$

where $q_i' = \sum_{j=1}^N S_{ij} (q_j' - q_j^{(0)})$.

In harmonic approximation, we give a practical prescription how to determine the leakage point in phase space, (\vec{p}_*, \vec{q}_*) , from the given input parameters of the problem: $\{m_i\}$, $\{\omega_i\}$, $\{m_i'\}$, $\{\omega_i'\}$, $\{S_{ij}\}$, $\{q_i'^{(0)}\}$, and the energy gap E . To describe the jump between the two surfaces, we use a special coordinate system in the phase space which simultaneously diagonalizes quadratic forms for H_F and for logarithm of the Wigner function. In this "transitional" coordinate system, the surface $H_F(\vec{p}, \vec{q}) = E$ is a $2N - 1$ -dimensional sphere, and surfaces of constant Wigner function are ellipsoids with a maximal elongation along the eigenvector corresponding to the smallest eigenvalue of an auxiliary matrix equation. We found that the Frank-Condon phase-space integral is maximal at the point on the sphere $H_F(\vec{p}, \vec{q}) = E$ in the direction of maximum elongation of the ellipsoids, at least for small coordinate displacements $\{q_i'^{(0)}\}$. Coordinates of the leakage point are expressed as rational functions of a useful parameter $\lambda = d \ln \rho / dE$, where ρ is the Wigner function, and this parameter itself is the minimal root of the equation

$$\frac{1}{2} \sum_{i=1}^{2N} \left(\frac{\alpha_i}{\alpha_i - \lambda} \right)^2 x_i^{(0)2} = E,$$

where α_i are eigenvalues of the auxiliary matrix equation and $x_i^{(0)}$ are phase-space coordinates of displacements in the "transitional" coordinate system. We found that coordinates of leakage are smooth functions of the input parameters except the case when some of $x_i^{(0)}$ are zero and when sudden change of sign of some of the leakage coordinate is possible. Asymptotic formulas for small energy gaps, for large energy gaps, and near "reflection approximation" (when the surfaces cross in the classically allowed point $\vec{q}' = 0$) are derived.

Anharmonicity was taken into account by the first order perturbation theory. Anharmonic corrections are expressed as linear combinations of coefficients of cubic anharmonicity, f_{ijk} and f'_{ijk} .

V. ACCURACY OF THE PHASE-SPACE METHOD AND ITS RELATIONSHIP WITH QUASICLASSICAL METHOD

When we use the phase-space approach, we approximate the Wigner function of the acceptor by its classical limit $\delta(E - H_{cl}(p, q))$ (in a more accurate quasiclassical approximation it is Airy function). We studied accuracy of the phase space method on an exactly solvable example of harmonic oscillators and found that accuracy is generally higher when the acceptor potential is steeper.

In the above version of the phase-space approach, the donor state is described fully quantum mechanically, and the acceptor state is described classically. Apart from this approximation, we studied an alternative approximation, when both states are described quasiclassically, as an exponent of the action integral. In this case, it is possible to find the maximum of the integrand by the method of stationary phase. Equations for the stationary phase are easily derived from the formula for a product of two Wigner functions. For one-dimensional potential, we found that one of stationary points (p_*, q_*) has the following properties: $p_* = \text{Re } p_L$, and $q_* = \text{Re } q_L$. Here, p_L, q_L are determined from the equation $H_I(p_L, q_L) = H_F(p_L, q_L) = E$. Note that q_L is complex because potential surfaces don't cross. The point (p_L, q_L) plays a fundamental part in the quasiclassical integral between two wave functions and it is important, for example in theory of pre-dissociation of diatomic molecules. We found that the point (p_*, q_*) plays the same part for the phase-space method as the point (p_L, q_L) for quasiclassical Landau method for Frank-Condon factors, and established a close relationship between two methods. This study is yet unfinished. For example, it remains to be proven that the above stationary point is dominant.

VI. FUTURE WORK

Our preliminary study of the benzene molecule indicates that there are at least four vibrational modes of the acceptor that share around the same probability of radiationless transition. These vibrational modes are C-H stretches. We expect that the equivalence of C-H stretches in respect to a radiationless transition is in fact broken by virtue of anharmonicity of the potential. Currently a study is underway to take into account anharmonicity of both acceptor and donor surfaces that is more consistent than our previous study where we took into account anharmonicity of the donor only.

Benzene molecule is one of the simplest and well studied molecules. We intend to find another candidates for a radiationless transition among, for example, derivatives of benzene and to find the most preferable vibrational modes for excitation using developed technique. It would be especially interesting to consider problems of dissociation too because possible locations of the leakage point in the phase space can be mapped to different channels of dissociation, and so there is an explicit physical manifestation of propensity rules in a choice of a dissociation channel.

In our formal mathematical study, we are going to simplify further the results in order to have an ultimate recipe for a very broad class of potential surfaces (general harmonic oscillators plus cubic anharmonic terms), in a form of a concise formula. In addition, we are going to demonstrate, that for typical molecular systems, there exist still more simple analytical formula for propensity rules because of specific bounds on parameters of molecules. We found previously that the asymptotic formula for large energy gaps is extremely accurate for benzene molecule. This formula is very compact and don't need preliminary solving of an algebraic equation of large degree.

In the study of accuracy of the phase space method and its relation to the quasiclassical method that was discussed in the previous section, most of work remains to be done. We intend to find the leading correction to results found earlier by approximation of the Wigner function of the acceptor by delta-function. It will be done by quasiclassical approximation of

the Wigner function instead of its classical delta-function approximation, with a subsequent expansion of the results in powers of the small parameter $|\vec{\nabla} H_F|^{-1}$ (this parameter is small when the potential is steep). The problem of relationship with the quasiclassical method is especially interesting because the two methods radically differ. Wigner function is considered in a real phase-space, and is almost everywhere positive, at least after smearing, but the quasiclassical wave function is a rapidly oscillating function, and its stationary points lie in a complex plane for non-crossing surfaces. So, the relationship between Landau method for quasiclassical overlap integrals and the phase space method is non-trivial and invites a thorough study.