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Most probable path in phase space for a radiationless transition in a molecule

Alexey V Sergeev and Bilha Segev

Department of Chemistry, Ben-Gurion University of the Negev, POB 653,
Beer-Sheva 84105, Israel

E-mail: bsegev@bgumail.bgu.ac.il

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Abstract

We study a radiationless transition in a polyatomic molecule when the electronic energy of an excited electronic state is transferred to the vibrational degrees of freedom of the nuclei, and when some nuclear coordinates change abruptly. This jump between the donor energy surface and the acceptor one gives the initial conditions for the subsequent dynamics on the acceptor surface, and the partition of energy between competing accepting modes. In the Wigner representation, the physical problem of recognizing the accepting modes for a radiationless vibronic relaxation reduces to the mathematical problem of finding the maximum of a function of many variables under a constraint. The function is the initial Wigner function of the nuclei and the constraint is energy conservation. In a harmonic approximation for the potential surfaces, the problem is equivalent to finding the distance from a given point to a multidimensional ellipsoid. This geometrical problem is solved in closed form. For nonharmonic potentials, the optimization problem is solved perturbatively.

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1. Introduction

Molecules are made of heavy particles, the nuclei, and light particles, the electrons. In the Born–Oppenheimer approximation, one uses this separation of scales in mass, and hence in velocities, to obtain electronic terms. Each electronic term corresponds to some wavefunction of the electrons: S_0 is the ground electronic state, S_1 and S_2 the first and second singlet excited states, respectively, etc. For a given electronic term, the nuclei move on a potential surface created by the electrostatic repulsion between them and the attractive force of the chemical bonds that the electrons create. As long as a molecule stays in the same electronic state, the motion of the nuclei can be analysed by propagating wave packets or by a semiclassical solution for the Schrödinger equation or a classical solution of the equation of motion with

a given potential. What happens to the nuclei during an electronic transition, say a radiative one, in which a photon is emitted or absorbed, or in a radiationless (forbidden) transition? Usually, nothing happens. Since the nuclei are so heavy and the electronic transition is so fast, the initial conditions for the motion of the nuclei on the accepting potential surface are then given by the position and velocity of the nuclei on the donor potential surface. This is called a vertical transition. Sometimes, however, a vertical transition cannot take place, for example when it violates energy conservation. In this case, the nuclei must ‘jump’ during the electronic transition. The jump can be a change in the position or momentum of one or many nuclei on the fast time scale of the electronic transition. Predicting this jump for each molecule and transition is a difficult problem and an old one in molecular physics and photochemistry. We have developed a simple method to predict this jump. In a number of cases our results indicate that the dimension of the problem reduces considerably: if only one nucleus moves out of, say, 14 in a given molecule, we need not consider the other 13 nuclei with the same careful detailed analysis when calculating and studying properties of the transition. Usually one form of motion of the nuclei, which is called the accepting mode (and need not be a normal mode), does all the ‘jumping’, whereas the rest of the degrees of freedom undergo a practically vertical transition. The theory of surface jumping, as we call this process, was developed in [1], where it was also applied to a simple model. Recently, we have applied it to a 30-dimensional model of the benzene molecule.

The mechanism of surface jumping is important for applications in molecular physics and photochemistry [2, 3]. The subject of this paper, however, is not the application of this mechanism to specific molecules but the general mathematical problem one faces when analysing these jumps. Here we aim at a rigorous formulation of the problem and its general formal solution. The physical system is presented in section 2, and the mathematical formulation of the problem is given in section 3. The complete solution in the harmonic approximation, examples of simple cases and corrections due to anharmonicity are, respectively, studied in sections 4, 5 and 6. Section 7 gives the conclusions.

2. The physical system

Let us consider a molecule described by a potential $V(\mathbf{R}, \mathbf{r})$, where \mathbf{R} and \mathbf{r} are coordinates of the nuclei and electrons, respectively. In the adiabatic approximation, the quantum states of the molecule are determined in two steps. First, the Schrödinger equation is solved with respect to the coordinates of the electrons for an arbitrary frozen configuration of the nuclei described by coordinates \mathbf{R} that are treated as parameters of the Schrödinger equation. The result is an eigenfunction $\varphi_n(\mathbf{r}; \mathbf{R})$ and an eigenvalue $U_n(\mathbf{R})$, where n is a set of electronic quantum numbers. The second step is to solve the Schrödinger equation with respect to the coordinates of the nuclei, \mathbf{R} , in an effective potential $U_n(\mathbf{R})$ (which was found in the first step), and to find eigenfunctions $\chi_{N,n}(\mathbf{R})$ and eigenvalues $E_{N,n}$, where N is a set of vibrational and rotational quantum numbers of the nuclear motion (in this equation, n are parameters because the potential $U_n(\mathbf{R})$ depends on n). The result of the adiabatic approximation is wavefunctions of the form

$$\Psi_{N,n}(\mathbf{R}, \mathbf{r}) = \chi_{N,n}(\mathbf{R})\varphi_n(\mathbf{r}; \mathbf{R}) \quad (1)$$

and the corresponding energies $E_{N,n}$. Even when the adiabatic approximation does not apply, one can use these wavefunctions as a basis set.

We study the following problem. Let some initial state $\Psi_{(N_1, n_1)}$ of a molecule have quantum numbers (N_1, n_1) . Now, suppose that there exist several possible final states with

another set of electronic quantum numbers n_F and different sets of nuclear quantum numbers N_F , e.g.

$$(N_F^{(1)}, n_F), (N_F^{(2)}, n_F), (N_F^{(3)}, n_F), \dots \quad (2)$$

Since the state $\Psi_{(N_I, n_I)}$ is actually a mixed quantum state due to small nonadiabatic effects, in the process of its evolution in time there is a nonzero probability of finding the molecule in one of the states (2) even if it was initially prepared in the state (N_I, n_I) . According to the theory of radiationless transitions [4], this probability is maximal for states having the same energy as the initial state (N_I, n_I) , and is proportional to the density of final states multiplied by the square of the Franck–Condon integral—an overlap integral between the nuclear components of the wavefunctions,

$$\int \chi_{N_I, n_I}(\mathbf{R}) \chi_{N_F, n_F}(\mathbf{R}) d\mathbf{R} \quad (3)$$

where here and in the following all integrals are from $-\infty$ to $+\infty$.

The purpose of this study is to develop a method of choosing a state (N_F^*, n_F) or a superposition of such states among all possible final states (2) satisfying the energy conservation condition

$$E(N_F^*, n_F) = E(N_I, n_I) \quad (4)$$

for which the square of the integral (3) reaches its maximum. This state is the most preferable accepting mode for a radiationless transition.

The idea of our approach is to use the Wigner transformations of the wavefunctions. The Wigner transform of a given wavefunction $\psi(\mathbf{R})$ is defined as

$$\rho(\mathbf{R}, \mathbf{P}) = \left(\frac{1}{2\pi}\right)^N \int d\boldsymbol{\eta} e^{-i\mathbf{P}\cdot\boldsymbol{\eta}} \psi^*(\mathbf{R} + \boldsymbol{\eta}/2) \psi(\mathbf{R} - \boldsymbol{\eta}/2) \quad (5)$$

where N is the number of independent coordinates. Here and henceforth we use units where $\hbar = 1$. In the Wigner representation, a squared overlap integral can be rewritten as an integral over phase space coordinates,

$$\left| \int \psi_1^* \psi_2 d\mathbf{R} \right|^2 = (2\pi)^N \int \int d\mathbf{R} d\mathbf{P} \rho_1 \rho_2 \quad (6)$$

where $\rho_1 = \rho_1(\mathbf{R}, \mathbf{P})$ and $\rho_2 = \rho_2(\mathbf{R}, \mathbf{P})$ are Wigner transforms of the functions $\psi_1 = \psi_1(\mathbf{R})$ and $\psi_2 = \psi_2(\mathbf{R})$, respectively.

The total rate of transition from a state (N_I, n_I) to a manifold of states (N_F, n_F) with a definite n_F and all possible N_F is proportional to a sum

$$\sum_{E(N_F, n_F)=E} \left(\int \chi_{N_I, n_I}(\mathbf{R}) \chi_{N_F, n_F}(\mathbf{R}) d\mathbf{R} \right)^2 \quad (7)$$

where both the Franck–Condon factor and the density of final states are included in the expression, $E = E(N_I, n_I)$, and $\chi_{N_I, n_I}(\mathbf{R})$ is assumed to be real. In terms of Wigner functions, (7) is proportional to

$$(2\pi)^N \int \int d\mathbf{R} d\mathbf{P} \rho_{N_I, n_I} \sum_{E(N_F, n_F)=E} \rho_{N_F, n_F} \quad (8)$$

where $\rho_{N, n} = \rho_{N, n}(\mathbf{R}, \mathbf{P})$. Here we study the expression in (8), which is to be integrated. We are especially interested in finding a maximum of this integrand. The importance of the point of maximum of the phase space integrand was stressed in [1], where the phase space derivation

of propensity rules for energy transfer processes between Born–Oppenheimer surfaces was presented.

We use the following approximation for the second factor in the integrand of (8):

$$(2\pi)^N \sum_{E(N_F, n_F)=E} \rho_{N_F, n_F}(\mathbf{R}, \mathbf{P}) = \delta(H_F(\mathbf{R}, \mathbf{P}) - E) \quad (9)$$

which is equivalent to replacing this function by the zero-order classical term of its semiclassical expansion in powers of \hbar^2 [5, 6]. The approximation (9) reduces the integral (8) to

$$\int_{H_F(\mathbf{R}, \mathbf{P})=E} |\nabla H_F|^{-1} \rho_{N_1, n_1}(\mathbf{R}, \mathbf{P}) d\mathbf{R} d\mathbf{P} \quad (10)$$

where $|\nabla H_F| = [(\nabla_{\mathbf{R}} H_F)^2 + (\nabla_{\mathbf{P}} H_F)^2]^{1/2}$ is the gradient of the function H_F in phase space. The rest of the paper is devoted to finding a maximum of the Wigner function $\rho_{N_1, n_1}(\mathbf{R}, \mathbf{P})$ on an equipotential surface defined through the equation $H_F(\mathbf{R}, \mathbf{P}) = E$ for both harmonic and anharmonic potentials. In doing so we set the ground for the future analysis of radiationless transitions of specific large polyatomic molecules. In addition, we formulate and prove some general yet simple rules of thumb for predicting the accepting mode of a given radiationless transition.

3. Formulation of the problem

The Hamiltonian of the acceptor is approximated by a harmonic oscillator plus third-order anharmonic terms,

$$H_F = \frac{1}{2} \sum_{i=1}^N (p_i^2 + \omega_i^2 q_i^2) + \frac{1}{6} \sum_{i,j,k=1}^N v_{ijk} q_i q_j q_k \quad (11)$$

where p_i and q_i are mass-weighted normal momenta and coordinates, $q_i = R_i \sqrt{m_i}$ and $p_i = P_i / \sqrt{m_i}$. Similarly, the Hamiltonian of the donor surface is

$$H_I = \frac{1}{2} \sum_{i=1}^N (p_i'^2 + \omega_i'^2 q_i'^2) + \frac{1}{6} \sum_{i,j,k=1}^N v'_{ijk} q_i' q_j' q_k'. \quad (12)$$

The mass-weighted normal coordinates $p_i' = P_i' / \sqrt{m_i'}$ and $q_i' = R_i' \sqrt{m_i'}$ are generally some linear combinations of p_i and q_i ,

$$\mathbf{q}' = \mathbf{S}(\mathbf{q} - \mathbf{q}^{(0)}) \quad \mathbf{p}' = \mathbf{S}\mathbf{p} \quad (13)$$

where \mathbf{S} is an orthogonal $N \times N$ matrix ($\mathbf{S}^T = \mathbf{S}^{-1}$) and the vector $\mathbf{q}^{(0)}$ corresponds to the change of the equilibrium structure of the molecule relative to the donor state. An element $S_{ij} \neq \delta_{ij}$ only when the i th and j th normal coordinates have the same symmetry (so called Duschinsky rotation). The same matrix transforms both \mathbf{q} and \mathbf{p} since the transformation preserves the commutation relations $[q_i', p_j'] = [q_i, p_j] = i\hbar\delta_{ij}$ and since the Hamiltonians (11) and (12) have the same kinetic energy term, $\sum_{i=1}^N p_i'^2 = \sum_{i=1}^N p_i^2$.

We restrict ourselves to the ground state in the donor potential,

$$\chi_{N_1, n_1}(\mathbf{q}) = C \exp\left(-\frac{1}{2} \sum_{i=1}^N \omega_i' q_i'^2\right) + \chi_1 \quad (14)$$

where C is a normalization factor, and χ_1 is the first anharmonic correction (a linear function of the coefficients v_{ijk}) derived in section 6. The Wigner transform of $\chi_{N_1, n_1}(\mathbf{q})$ is $C' \exp(-2W)$, where C' is a constant prefactor,

$$W = \frac{1}{2} \sum_{i=1}^N \frac{1}{\omega'_i} (p_i'^2 + \omega_i'^2 q_i'^2) + W_1 \quad (15)$$

and W_1 is the first anharmonic correction derived in section 6.

The jumping between the donor and acceptor states occurs at a point of minimum W subject to a constraint $H_F = E$. There are several approaches to solving a problem of constrained minimum [7]. One could use a method of direct substitution by eliminating one of the variables from the function W . This method is not symmetrical with respect to the treatment of the variables $\{x_i\}$ ($i = 1, 2, \dots, M$, $M = 2N$) that are arguments of the functions W and H , i.e. $\{q_i, p_i\}$ for $i = 1, 2, \dots, N$ (later, these collective variables will be redefined). To avoid distinction between the variables, we use a method of Lagrange multiplier by introducing an undetermined constant λ and forming a function $F(\mathbf{x}, \lambda) = W(\mathbf{x}) - \lambda H(\mathbf{x})$. This function is to be made stationary with respect to all variables $\{x_i\}$, so that

$$\frac{\partial F}{\partial x_i}(\mathbf{x}^*, \lambda^*) = 0 \quad (16)$$

for $i = 1, 2, \dots, M$, and the constant λ^* is to be selected so that

$$H(\mathbf{x}^*) = E. \quad (17)$$

Conditions (16) and (17) provide a system of $M + 1$ equations for $M + 1$ unknowns, $x_1^*, x_2^*, \dots, x_M^*$, and λ^* which can be briefly summarized as

$$\nabla W = \lambda \nabla H \quad H = E. \quad (18)$$

The Lagrange multiplier λ has a concrete physical meaning. Since

$$\frac{d}{dE} W(\mathbf{x}^*) = \sum_{i=1}^M \frac{\partial W}{\partial x_i}(\mathbf{x}^*) \frac{dx_i^*}{dE} = \lambda^* \sum_{i=1}^M \frac{\partial H}{\partial x_i}(\mathbf{x}^*) \frac{dx_i^*}{dE} = \lambda^* \frac{d}{dE} H(\mathbf{x}^*) = \lambda^* \quad (19)$$

the parameter λ^* is the sensitivity of the minimum value of W to the energy gap.

After finding all the stationary points \mathbf{x}^* , it is necessary to determine for each point whether it is a minimum of the function W under restriction (17), a saddle point or a maximum, and which of all the local minima gives the smallest value for W . The global minimum found in this way is a true solution of the optimization problem, see figure 1.

In order to efficiently find this jumping point, it is convenient to use variables x_i with which both H_F and W assume a particularly simple form:

$$H_F = \frac{1}{2} \sum_{i=1}^M x_i^2 + H_1 = E \quad (20)$$

$$W = \frac{1}{2} \sum_{i=1}^M \alpha_i (x_i - X_i)^2 + W_1 \quad (21)$$

where H_1 and W_1 are anharmonic corrections.

The transformation from q_i and p_i ($i = 1, 2, \dots, N$) to x_i ($i = 1, 2, \dots, M = 2N$) is performed in the following way. In normal coordinates of the acceptor, and after defining

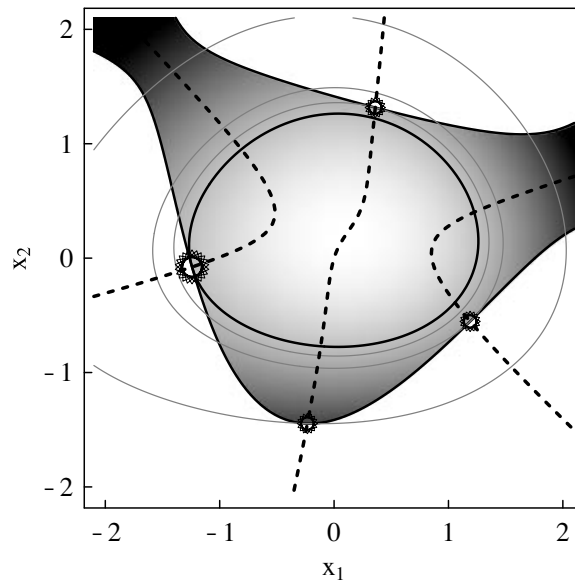


Figure 1. Finding the minimum of the function W under the energy constraint $H = E$. For this example, $W(x_1, x_2) = 0.4(x_1 - 0.1)^2 + 0.6(x_2 - 0.2)^2 + 0.05[(x_1 - 0.1)^3 + (x_1 - 0.1)^2(x_2 - 0.2) + (x_1 - 0.1)(x_2 - 0.2)^2 - (x_2 - 0.2)^3]$, $H(x_1, x_2) = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 + 0.1[-x_1^3 - 3x_1^2x_2 + 2x_1x_2^2 + 1]$ and $E = 1$. Dashed lines represent stationary points of the function $F = W - \lambda H$, equation (16). Energy-constraint points satisfying equation (17) lie on the border of the dark area, $H < E$ (the darker the colour, the greater is the function W). Ellipses represent curves of constant W . Stationary points of the function W under the energy constraint are marked by circles. A point with the smallest W marked by a large circle is the solution of the problem: $x_1^* = -1.24$, $x_2^* = -0.08$, $W^* = 0.62$.

$\tilde{q}_i \equiv \omega_i q_i$, equations (11) and (15) read

$$H_F = \frac{1}{2} \sum_{i=1}^N (p_i^2 + \tilde{q}_i^2) + H_1 \tag{22}$$

$$W = \frac{1}{2} \sum_{i,j=1}^N (W_{ij}^{(q)} (\tilde{q}_i - \tilde{q}_i^{(0)}) (\tilde{q}_j - \tilde{q}_j^{(0)}) + W_{ij}^{(p)} p_i p_j) + W_1 \tag{23}$$

where

$$W_{ij}^{(p)} \equiv \sum_{k=1}^N \frac{1}{\omega_k} S_{ki} S_{kj} \quad W_{ij}^{(q)} \equiv \sum_{k=1}^N \frac{\omega'_k}{\omega_i \omega_j} S_{ki} S_{kj}. \tag{24}$$

Defining $\tilde{x}_i = \tilde{q}_i$, $\tilde{x}_i^{(0)} = \tilde{q}_i^{(0)}$ and $W_{ij} = W_{ij}^{(q)}$ for $i, j = 1, 2, \dots, N$; $\tilde{x}_i = p_i \tilde{x}_i^{(0)} = 0$ and $W_{ij} = W_{ij}^{(p)}$ for $i, j = N + 1, N + 2, \dots, 2N$; and $W_{ij} = 0$ otherwise, we get

$$H_F = \frac{1}{2} \sum_{i=1}^M \tilde{x}_i^2 + H_1 \quad W = \frac{1}{2} \sum_{i,j=1}^M (W_{ij} (\tilde{x}_i - \tilde{x}_i^{(0)}) (\tilde{x}_j - \tilde{x}_j^{(0)})) + W_1.$$

It is now straightforward to obtain equations (20) and (21) by diagonalizing the matrix \mathbf{W} with the elements W_{ij} . Namely, construct a unitary matrix \mathbf{U} so that $\mathbf{U}^{-1} \mathbf{W} \mathbf{U}$ is a diagonal matrix with diagonal matrix elements α_i ($i = 1, 2, \dots, M$). The new coordinates x_i ($i = 1, 2, \dots, M = 2N$) are then given by $\mathbf{x} \equiv \mathbf{U}^{-1} \tilde{\mathbf{x}}$ and $\mathbf{X} \equiv \mathbf{U}^{-1} \tilde{\mathbf{x}}^{(0)}$.

Note that the new coordinates do not maintain their relations as conjugate coordinates and momenta. Note also, that this transformation could be performed starting from any coordinate system (not necessarily normal coordinates of the acceptor).

4. Harmonic approximation

In this section we solve the problem of finding the accepting modes for a radiationless transition in the harmonic approximation. Results of the harmonic approximation are later used as the zero-order terms in a perturbative approach to the anharmonicities.

4.1. Finding the minimum of W

We are looking for a minimum of W , where

$$W = \frac{1}{2} \sum_{i=1}^M \alpha_i (x_i - X_i)^2 \quad (25)$$

subject to the constraint

$$H_F = \frac{1}{2} \sum_{i=1}^M x_i^2 = E. \quad (26)$$

The parameters characterizing the transition are the energy gap E , the normalized displacements $\{X_i\}$ between the acceptor and donor potential surfaces and the parameters $\{\alpha_i\}$. These parameters define the minimization problem that determines the jumping point \mathbf{x}^* characterizing the nature of the transition.

It is interesting to note that in another coordinate system, $y_i = \alpha_i^{1/2}(x_i - X_i)$, the problem has a simple geometrical interpretation: finding the minimum of $W = \frac{1}{2} \sum y_i^2$ under the constraint $H_F = E$ is equivalent to finding the point on the ellipsoid $\sum (\alpha_i^{-1/2} y_i + X_i)^2 = E$ of the closest approach to the origin, i.e. the distance from this ellipsoid to the origin. Let us implement the method of the previous section for the quadratic functions given by formulae (25) and (26).

The equations for the stationary point, (16),

$$\alpha_i(x_i^* - X_i) - \lambda^* x_i^* = 0 \quad (27)$$

are solved explicitly,

$$x_i^* = \frac{\alpha_i}{\alpha_i - \lambda^*} X_i \quad (28)$$

for $i = 1, \dots, M$ if $\lambda^* \neq \alpha_i$. By substituting (28) into (26), we get an equation for λ^* ,

$$h(\lambda^*) = E \quad (29)$$

where the function $h(\lambda)$ is the Hamiltonian H expressed through λ ,

$$h(\lambda) = \frac{1}{2} \sum_{i=1}^M \left(\frac{\alpha_i}{\alpha_i - \lambda} \right)^2 X_i^2. \quad (30)$$

By substituting (28) into (25), the value of the function W at its stationary point is expressed as a function of λ ,

$$W^* = w(\lambda^*) \quad (31)$$

where

$$w(\lambda) = \frac{1}{2} \sum_{i=1}^M \alpha_i \left(\frac{\lambda}{\alpha_i - \lambda} \right)^2 X_i^2. \tag{32}$$

Since equation (29) reduces to a polynomial equation of degree $2M$, it has at most $2M$ real roots each of which corresponds to some stationary point \mathbf{x}^* given by (28). Let λ_1 and λ_2 be two different roots of equation (29), i.e. $h(\lambda_1) = h(\lambda_2) = E$. In order to select the smallest of the corresponding values of W , $w(\lambda_1)$ and $w(\lambda_2)$, we note that

$$w(\lambda_2) - w(\lambda_1) = \frac{1}{2}(\lambda_1 + \lambda_2)[h(\lambda_2) - h(\lambda_1)] + \frac{1}{4}(\lambda_2 - \lambda_1)^3 \sum_{i=1}^M \left[\frac{\alpha_i X_i}{(\alpha_i - \lambda_1)(\alpha_i - \lambda_2)} \right]^2. \tag{33}$$

The validity of identity (33) can be easily checked by substituting expressions (30) and (32) for the functions h and w . Since $h(\lambda_2) - h(\lambda_1) = 0$ and the sum over i is positive, $w(\lambda_2) - w(\lambda_1)$ has the same sign as $\lambda_2 - \lambda_1$. Thus for harmonic potentials, the smaller the root λ^* , the smaller is the function W .

For convenience, we re-enumerate henceforth the variables (α_i, X_i, x_i) ($i = 1, 2, \dots, M$) so that $\alpha_1 = \alpha_2 = \dots = \alpha_L = \alpha_{\min}$ and $\alpha_j > \alpha_{\min}$ for $j > L$, where α_{\min} is the minimal number among α_i ($i = 1, 2, \dots, M$), and L is the number of entries of α_{\min} in the set $\{\alpha_i\}$ ($i = 1, 2, \dots, M$). When λ increases from $-\infty$ to α_{\min} , the function $h(\lambda)$ monotonically increases from 0 to

$$E_1 = \frac{1}{2} \sum_{i>L} \left(\frac{\alpha_i}{\alpha_i - \alpha_{\min}} \right)^2 X_i^2 \tag{34}$$

if $X_1 = X_2 = \dots = X_L = 0$, otherwise it increases from 0 to $E_1 = \infty$.

There are two possible cases. In the first case, when $X_1 = X_2 = \dots = X_L = 0$ and $E > E_1$, the minimal root of (17) is $\lambda^* = \alpha_{\min}$, x_j^* for $j > L$ are expressed through λ^* by (28), and from (26) we get a set of possible $(x_1^*, x_2^*, \dots, x_L^*)$. In the second case, when $E \leq E_1$, there is a unique root λ^* of equation (29) in the interval $(-\infty, \alpha_{\min})$, the coordinates of this minimum are expressed through λ^* by (28), and the minimum of W is given by (31).

4.2. Results

Let us summarize the solution in the harmonic approximation. Given an initial Wigner function and an accepting Hamiltonian, applying a harmonic approximation and a change of variables, re-enumerating the variables so that $\alpha_1 = \alpha_2 = \dots = \alpha_L$ equal the smallest of all α_i , and explicitly solving equations (25) and (26), we get the jumping point for the radiationless transition. There are two cases:

Case I. In this case (when $X_1 = X_2 = \dots = X_L = 0$ and $E > E_1$), there exist several points of minimum with the same value of W . If $L = 1$, then two jumping points differ in the sign of the first coordinate

$$x_1^* = \pm [2(E - E_1)]^{1/2}. \tag{35}$$

For $i \neq 1$ the coordinates are

$$x_i^* = \frac{\alpha_i}{\alpha_i - \alpha_{\min}} X_i. \tag{36}$$

If $L > 1$, then $(x_1^*, x_2^*, \dots, x_L^*)$ fill an $(L - 1)$ -dimensional sphere of radius $[2(E - E_1)]^{1/2}$,

$$\frac{1}{2} (x_1^2 + x_2^2 + \dots + x_L^2) = E - E_1 \tag{37}$$

which follows from equation (26). The rest of the coordinates, for $i > L$, are defined unambiguously by equation (36).

The minimum of W is

$$W^* = \alpha_{\min} E - \frac{\alpha_{\min}}{2} \sum_{i>L} \frac{\alpha_i X_i^2}{\alpha_i - \alpha_{\min}}. \tag{38}$$

Below, for example in equation (49), we assume that $L = 1$, or that $\alpha_i > \alpha_1$ for $i = 2, 3, \dots, M$.

Case II. This case applies when at least one of X_i with $i \leq L$ is nonzero, or when $X_1 = X_2 = \dots = X_L = 0$ and $E \leq E_1$. The coordinates at the jumping point are given by equation (28):

$$x_i^* = \frac{\alpha_i}{\alpha_i - \lambda_*} X_i \tag{39}$$

where $\lambda_* \leq \alpha_{\min}$ is the unique root of

$$\frac{1}{2} \sum_i \left(\frac{\alpha_i}{\alpha_i - \lambda} \right)^2 X_i^2 = E. \tag{40}$$

4.3. Discussion

In a radiative vertical transition, only displaced modes are excited. The initial conditions for dynamics on the accepting potential energy surface, which we call the jumping point, are then given by

$$x_i^* = X_i. \tag{41}$$

The energy that goes into vibration and the value of the logarithm of the Wigner function at the jumping point are then given, respectively, by

$$E_0 = \frac{1}{2} \sum_{i=1}^M \alpha_i^2 X_i^2 \quad W_0 = \frac{1}{2} \sum_{i=1}^M \alpha_i X_i^2. \tag{42}$$

Energy is conserved because the photon takes the rest of the energy

$$E_{\text{photon}} = E - E_0 \tag{43}$$

where E is the energy gap between the minima of the donor and accepting surfaces.

In a radiationless transition, there is no photon. The released electronic energy must become vibrational energy. The two cases I and II differ in how this energy is distributed between the different vibrations.

In case I, despite the fact that $X_1 = 0$, i.e. there is no displacement along the x_1 direction in phase space (be it a coordinate or momentum), x_1 is an accepting mode for this transition *because the initial phase space quasidistribution comes closest to the final energy hypersurface in this direction*. We shall refer to x_1 as the major accepting mode. This mode, which absorbs the excess energy $E - E_1$, plays the same role as electromagnetic field modes during a radiative transition, when an emitting photon accepts the excess energy relative to the vertical transition.

In contrast, case II does not look essentially different from a vertical transition. Namely, only displaced modes are involved in the transition, and the jump for each coordinate involved is proportional to the displacement of this mode. No momentum jumps exist, since the Hamiltonians are never displaced along a momentum phase space coordinate. The smaller the $|\lambda_*|$, the closest is the transition to a vertical one, as $\alpha_i/(\alpha_i - \lambda_*)$ is closer to 1. Physically a small $|\lambda_*|$ corresponds to the special case when $H_F(\mathbf{X}) = E$.

4.4. Dependence on the energy gap

In case I the dependence on the energy gap is trivial. All the phase space coordinates at the jumping point but one do not depend on the energy gap, but only on their respective displacements and the relative difference of the parameters α_i between each of them and the major accepting mode. x_1^* , the jumping coordinate of the major accepting mode, grows with the energy gap. The larger the energy gap, the more important is this accepting mode.

In order to consider the properties of the jumping point as a function of the energy gap E in case II, for both limits of small and large E , equation (40) is rewritten here in a simplified form

$$\sum_{i=1}^M \left(\frac{\beta_i}{\alpha_i - \lambda} \right)^2 = 1 \quad (44)$$

where $\beta_i = \alpha_i |X_i| (2E)^{-1/2}$.

For a small energy gap, equation (44) has two real roots $\lambda = \pm (\sum \beta_i^2)^{1/2}$. The solution corresponding to the minimal (negative) root asymptotically behaves as

$$\lambda^* = -(E_0/E)^{1/2} \quad (45)$$

$$x_i^* = \alpha_i X_i (E/E_0)^{1/2} \quad (46)$$

$$W^* = W_0 - 2(EE_0)^{1/2}. \quad (47)$$

In the limit of a large energy gap, when $\beta_i \rightarrow 0$, equation (44) has $2M$ roots $\lambda = \alpha_i \pm \beta_i$ ($i = 1, 2, \dots, M$). The minimal root corresponding to the minimum of W is $\lambda^* = \alpha_1 - \beta_1$. It is clear that $X_1 = 0$ belongs to case I for sufficiently large E . A perturbative solution, with $\varepsilon = \text{sign} X_1 (2E)^{-1/2}$ as a small parameter, shows that for $X_1 \neq 0$ as well, although λ^* depends on the energy, this dependence approaches zero for a large enough energy gap, for which

$$x_1^* \approx \sqrt{2E} \text{sign}(X_1) \quad (48)$$

$$x_{i \neq 1}^* = \frac{\alpha_i}{\alpha_i - \alpha_1} X_i - \frac{\alpha_i \alpha_1}{(\alpha_i - \alpha_1)^2} \frac{|X_1| X_i}{\sqrt{2E}} + O(\varepsilon^2). \quad (49)$$

Here, again, in the limit of a large energy gap x_1 is the major accepting mode regardless of it being displaced or not. If the displacement $X_1 = 0$ there are two jumping points with opposite signs, whereas if $X_1 \neq 0$ the sign of the jump is determined by the sign of the displacement.

5. Simple cases

In the previous section a complete solution in the harmonic approximation was derived. For any given radiationless transition, the accepting mode(s) can be found by applying this procedure. To gain some intuition, here we apply it to some simple examples. We separately check the influence of the frequencies, Duschinsky rotations and the displacements on the results. We also check the predictive power of the results on the energy distribution between the modes, for example, where this energy distribution is well defined.

5.1. Frequencies

In the simplest case, when the normal coordinates of the initial and final states are the same ($\mathbf{q} = \mathbf{q}'$, $\mathbf{p} = \mathbf{p}'$) and $m_i = m'_i$, the set of variables $\{x_1, x_2, \dots, x_M\}$ consists of $\sqrt{m_i} \omega_i R_i$ and

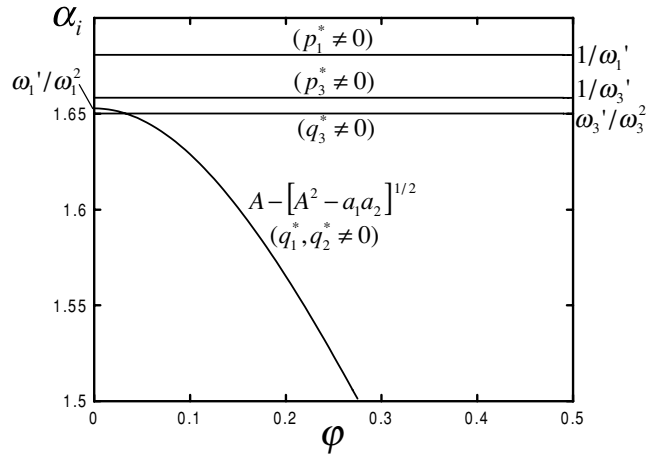


Figure 2. The dependence of the smallest four eigenvalues α_i , $i = 1, 2, 3, 4$, on the rotation angle φ for the example in section 5.2. The rest of the eigenvalues $\{1/\omega'_2, A + [A^2 - a_1 a_2]^{1/2}\}$ are larger than 3. The smallest eigenvalue α_{\min} determines the minimum of W ($W_{\min} = \alpha_{\min} E$).

$1/\sqrt{m_i} P_i$, and the set $\{\alpha_1, \alpha_2, \dots, \alpha_M\}$ consists of ω'_i/ω_i^2 and $1/\omega'_i$ sorted in ascending order. Since $E_1 = 0$, this system belongs to case I considered in the previous section, with $x_1^* = \pm\sqrt{2E}$ and $x_2^* = x_3^* = \dots = x_M^* = 0$. There is only one accepting mode. In terms of normal mode coordinates, it means that if the minimum number in the set $\{\omega'_i/\omega_i^2, 1/\omega'_i\}$ is $\alpha_1 = \omega'_{i_0}/\omega_{i_0}^2$, then the launching point for the transition is at $R_{i_0} = \pm(2E/m_{i_0})^{1/2}/\omega_{i_0}$ and the other coordinates and momenta are zero. If $\alpha_1 = 1/\omega'_{i_0}$, then $P_{i_0} = \pm(2Em_{i_0})^{1/2}$ and the other coordinates and momenta are zero.

5.2. Duschinsky rotation

Now, suppose that $q_0 = 0$ and $m_i = m'_i = m$, $N = 2$ and the matrix S is a unitary matrix of general form

$$S = \begin{pmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{pmatrix}$$

where φ is a rotation angle. Then, $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4\}$ consists of the following four numbers: $\{A \pm [A^2 - a_1 a_2]^{1/2}, 1/\omega'_1, 1/\omega'_2\}$, where $A = \frac{1}{2}(a_1 + a_2) \cos^2 \varphi + \frac{1}{2}(b_1 + b_2) \sin^2 \varphi$, $a_1 = \omega'_1/\omega_1^2$, $a_2 = \omega'_2/\omega_2^2$, $b_1 = \omega'_2/\omega_1^2$, $b_2 = \omega'_1/\omega_2^2$. If $\varphi = 0$, then it is $\{a_1, a_2, 1/\omega'_1, 1/\omega'_2\}$. If $\varphi = \pi/2$, then it is $\{b_1, b_2, 1/\omega'_1, 1/\omega'_2\}$.

The next example is numerical. It demonstrates that a Duschinsky rotation can influence the jumping point and the value of the Wigner function at that point. Suppose that $q_0 = 0$ and $m_i = m'_i = m$, $N = 3$,

$$S = \begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\omega_1 = 0.6$, $\omega_2 = 0.3$, $\omega_3 = 0.603$, $\omega'_1 = 0.595$, $\omega'_2 = 0.298$, $\omega'_3 = 0.6$ (ω'_i are taken slightly smaller than ω_i as usually happens in molecules). The dependence of $\{\alpha_i\}$ on φ is shown in figure 2. The jumping point for $\varphi > 0.033$ differs from that at $\varphi = 0$. Here, since α_i are independent of the energy, and because of the fact that $dW_{\min}/dE = \alpha_{\min}$, $W_{\min} = \alpha_{\min} E$ and the value of the Wigner function is proportional to $\exp(-2\alpha_{\min} E)$.

5.3. Displacements

Consider a simple case with nonzero displacement, with $N = 2$, $m_i = m'_i$, and $q_0 = (Q, 0)$, i.e. $q'_1 = q_1 - Q$, $q'_2 = q_2$. We define

$$\lambda_* = \frac{\omega'_1}{\omega_1^2} \left[1 - \left(\frac{m_1 \omega_1^2 Q^2}{2E} \right)^{1/2} \right] \quad (50)$$

$$\sigma = \min \left(\lambda_*, \frac{\omega'_1}{\omega_1^2}, \frac{\omega'_2}{\omega_2^2}, \frac{1}{\omega'_1}, \frac{1}{\omega'_2} \right). \quad (51)$$

There are four subcases. (1) If $\sigma = 1/\omega'_1$ or $\sigma = \lambda_*$, there is only one nonzero jumping coordinate

$$q_1^* = Q / (1 - \lambda_* \omega_1^2 / \omega'_1). \quad (52)$$

Otherwise, there are two nonzero jumping coordinates q_1^* and (2) q_2^* if $\sigma = \omega'_2 / \omega_2^2$, (3) p_1^* if $\sigma = 1/\omega'_1$, (4) p_2^* if $\sigma = 1/\omega'_2$.

The larger the displacement and smaller the energy gap, the smaller is λ_* , and q_1 becomes the only accepting mode. In contrast, in the limit of a very large energy gap, the displacement no longer plays a role in the minimization problem predicting the jump. In this limit, the frequencies alone determine the jump as in the previous case of zero displacement.

5.4. Predictive power of the jumping point

The latter case with additional simplifications $m_1 = m_2 = 1$ and $\omega_1 = \omega_2 = 1$ was considered in [1]. This paper has plots of the initial wavefunction

$$\Psi_I(q_1, q_2) = \psi_0(q_1 - Q) \psi_0(q_2) \quad (53)$$

versus the final wavefunction

$$\Psi_F(q_1, q_2) = \sum_{j=0}^n C_j \psi_j(q_1) \psi_{n-j}(q_2) \quad (54)$$

where $\psi_i(q)$ is a harmonic oscillator wavefunction, $E = n + 1$, and C_j is an overlap integral between the ground state Ψ_I and the excited wavefunction $\psi_j(q_1) \psi_{n-j}(q_2)$.

It was demonstrated that the pattern of the final wavefunction depends on the position of the phase space jump. Here, we reconsider six numerical examples from the paper [1] by a *quantitative* comparison with the phase space results. We calculate partial energies of excitations along two different modes,

$$E_1 = P_E^{-1} \sum_{j=0}^n C_j^2 \left(j + \frac{1}{2} \right) \quad E_2 = P_E^{-1} \sum_{j=0}^n C_j^2 \left(n - j + \frac{1}{2} \right) \quad (55)$$

where $P_E = \sum_{j=0}^n C_j^2$ is the total probability of a transition to $E_F = E$. E_1 and E_2 are well defined physical observables because the two-dimensional harmonic oscillator considered here is separable along q_1 and q_2 . They can be calculated exactly and compared to their phase space counterparts

Table 1. Accuracy of the prediction, by the phase space method, of the partition of energy between different modes for the model of two coupled harmonic oscillator, $H_I = \frac{1}{2}(\omega_1'^2 p_1^2 + \omega_2'^2 p_2^2 + (q_1 - Q)^2 + q_2^2)$, $H_F = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2)$, for examples studied earlier in [1]. The percentage of energy going to the first mode is given by equation (57).

Label	Parameters			R_1 (%)				
	ω_1'	ω_2'	Q	$n = 2$	$n = 6$	$n = 12$	$n = 20$	$n = 30$
a	0.02	0.18	0	60.4	74.0	82.5	91.6	94.5
				83.3 ^a	92.9 ^a	96.2 ^a	97.6 ^a	98.4 ^a
b	10	2.2	0	71.8	87.8	93.8	96.3	97.5
				83.3 ^a	92.9 ^a	96.2 ^a	97.6 ^a	98.4 ^a
c	0.45	0.01	0	25.3	10.4	5.4	3.3	2.2
				16.7 ^a	7.1 ^a	3.8 ^a	2.4 ^a	1.6 ^a
d	2	18	0	24.8	10.1	5.2	3.2	2.2
				16.7 ^a	7.1 ^a	3.8 ^a	2.4 ^a	1.6 ^a
e	2	0.1	3	82.6	82.0	44.9	27.2	18.3
				83.3 ^a	78.4 ^a	42.2 ^a	26.1 ^a	17.7 ^a
f	2	10	3	82.6	82.0	44.9	27.2	18.3
				83.3 ^a	78.4 ^a	42.2 ^a	26.1 ^a	17.7 ^a

^a The phase space result R_1^* .

$$E_1^* = \frac{1}{2}(p_1^{*2} + q_1^{*2}) + \frac{1}{2} \quad E_2^* = \frac{1}{2}(p_2^{*2} + q_2^{*2}) + \frac{1}{2} \quad (56)$$

where q_1^* , p_1^* , q_2^* , p_2^* are the phase space coordinates of the jump

$$E = E_1^* + E_2^* = n + 1.$$

Note that the classical energies in equation (56) are corrected by incorporating the quantum energy of zero vibrations, $1/2$. Without the zero vibrational energy, we found that the results are less satisfactory.

We compare the percentage of energy going into the first mode, exact versus phase space result

$$R_1 = E_1/E \quad R_1^* = E_1^*/E. \quad (57)$$

Table 1 shows that R_1 and R_1^* agree within 6% for all examples with $N \geq 20$. The examples are chosen in pairs (a, b), (c, d) and (e, f) to demonstrate that very different initial states can give similar results for R_1 and R_1^* .

We have also compared the exact wavefunctions with the trajectory of a classical particle moving in the potential H_F with the initial conditions of the phase space coordinates of the jump: at the position (q_1^*, q_2^*) , with momentum (p_1^*, p_2^*) . The results are depicted in figure 3. The agreement is remarkable.

6. Anharmonicity

In this section we study the effect of anharmonicities on the jump. We consider anharmonic potential surfaces for the donor's and acceptor's Hamiltonians, focusing here on Hamiltonians of harmonic oscillators perturbed by cubic anharmonic terms as in equations (11) and (12). Generalization to any polynomial anharmonicity is straightforward.

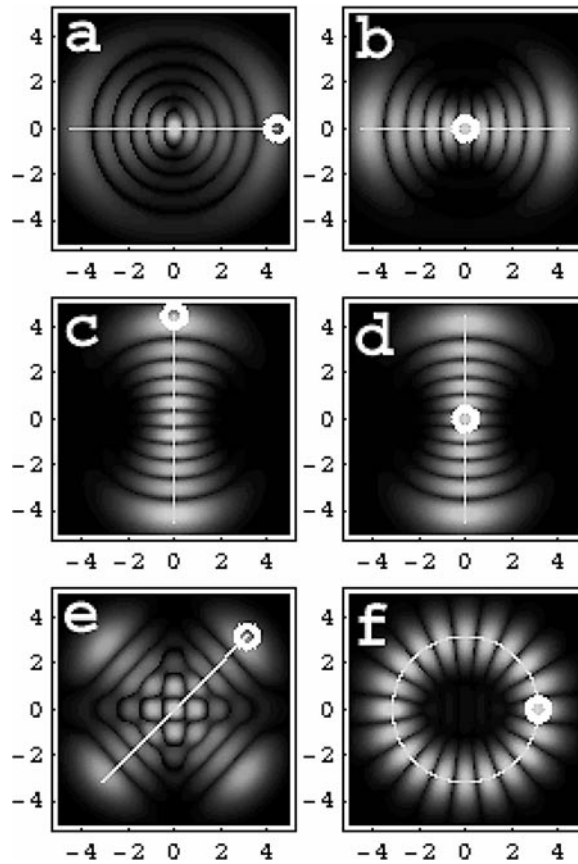


Figure 3. Density plot of the final wavefunction. The white dot marks the jumping point (q_1^*, q_2^*) that with (p_1^*, p_2^*) defines the initial conditions for the classical trajectory shown by a light line or an ellipse. Here, $n = 10$. The parameters ω'_1, ω'_2 and Q are listed in table 1. In example (e), we show only one of two symmetric jumping points of equal significance.

6.1. The ground-state Wigner function for an anharmonic oscillator

The Hamiltonian of the donor, equation (12), is rewritten in this section as

$$\begin{aligned}
 H(\mathbf{q}, \mathbf{p}) &= \frac{1}{2} \sum_{i=1}^N p_i^2 + V(\mathbf{q}) \\
 V(\mathbf{q}) &= \frac{1}{2} \sum_{i=1}^N \omega_i^2 q_i^2 + \xi V_1(\mathbf{q}) \quad V_1(\mathbf{q}) = \frac{1}{6} \sum_{i,j,k=1}^N v_{ijk} q_i q_j q_k
 \end{aligned}
 \tag{58}$$

where we omit the primes, although we have in mind the excited donor surface which is marked by primed variables in the previous and subsequent sections. We omit the subscript ‘1’ in H_1 and V_1 too. In (58), we introduce a dummy expansion parameter $\xi = 1$.

Rewriting the Schrödinger equation for the ground state wavefunction $\Psi(\mathbf{q})$ in terms of the function $S(\mathbf{q}) \equiv -\ln \Psi(\mathbf{q})$ [8] gives

$$-\frac{1}{2} \sum_{i=1}^N \left(\frac{\partial S}{\partial q_i} \right)^2 + \frac{1}{2} \sum_{i=1}^N \frac{\partial^2 S}{\partial q_i^2} + V(\mathbf{q}) - E = 0.
 \tag{59}$$

Without the second sum, equation (59) reduces to the Hamilton–Jacobi equation for the action of a classical particle moving in the potential $E - V(\mathbf{q})$. In such a quasiclassical limit, a perturbation theory for $S(\mathbf{q})$ is easily developed [9]. The more general quantum case which is considered here is still solvable analytically, but the corrections obtained have more monomial terms.

The function $S(\mathbf{q})$ and the energy E are expanded in powers of ξ ,

$$S(\mathbf{q}) = S_0(\mathbf{q}) + \xi S_1(\mathbf{q}) + O(\xi^2) \tag{60}$$

$$E = E_0 + \xi E_1 + O(\xi^2) \tag{61}$$

where the zero-order terms are

$$S_0(\mathbf{q}) = \frac{1}{2} \sum_{i=1}^N \omega_i q_i^2 + \text{const} \qquad E_0 = \frac{1}{2} \sum_{i=1}^N \omega_i \tag{62}$$

and the constant in $S_0(\mathbf{q})$ is responsible for the normalization of the wavefunction.

Let us find the first-order anharmonic corrections. To first order in ξ , equation (59) reduces to a linear equation with respect to the number E_1 and the function $S_1(\mathbf{q})$

$$-\sum_{i=1}^N \frac{\partial S_0}{\partial q_i} \frac{\partial S_1}{\partial q_i} + \frac{1}{2} \sum_{i=1}^N \frac{\partial^2 S_1}{\partial q_i^2} + V_1(\mathbf{q}) - E_1 = 0. \tag{63}$$

Let us suppose that $S_1(\mathbf{q})$ is a polynomial, then, as soon as the inhomogeneous part of equation (63), $V_1(\mathbf{q}) - E_1$, becomes a third-degree polynomial, it may be shown that the solution is at most a third-degree polynomial too,

$$S_1(\mathbf{q}) = \sum_{i=1}^N A_i q_i + \frac{1}{2} \sum_{i,j} B_{ij} q_i q_j + \frac{1}{6} \sum_{i,j,k=1}^N C_{ijk} q_i q_j q_k. \tag{64}$$

We substitute (64) and (58) in equation (63) and solve to obtain

$$E_1 = 0 \qquad A_i = \frac{1}{2\omega_i} \sum_{j=1}^N \frac{v_{ijj}}{\omega_i + 2\omega_j} \qquad B_{ij} = 0 \qquad C_{ijk} = \frac{v_{ijk}}{\omega_i + \omega_j + \omega_k}. \tag{65}$$

Having calculated S_1 , we would like to calculate the logarithm of the Wigner function expanded in powers of ξ :

$$\rho(\mathbf{q}, \mathbf{p}) = C' \exp(-2W(\mathbf{q}, \mathbf{p})) \qquad W(\mathbf{q}, \mathbf{p}) = W_0(\mathbf{q}, \mathbf{p}) + \xi W_1(\mathbf{q}, \mathbf{p}) + O(\xi^2) \tag{66}$$

where

$$W_0(\mathbf{q}, \mathbf{p}) = \frac{1}{2} \sum_{i=1}^N \left(\frac{p_i^2}{\omega_i} + \omega_i q_i^2 \right) \tag{67}$$

$W_1(\mathbf{q}, \mathbf{p})$ is the first anharmonic correction to be determined here. Substituting the perturbed wavefunction

$$\Psi(\mathbf{q}) = [1 - \xi S_1(\mathbf{q})] \exp(-S_0(\mathbf{q})) + O(\xi^2) \tag{68}$$

in the definition of the Wigner function, we get

$$\rho(\mathbf{q}, \mathbf{p}) \approx \left(\frac{1}{2\pi} \right)^N \int d\boldsymbol{\eta} e^{-i\mathbf{p}\cdot\boldsymbol{\eta}} [1 - \xi S_1(\mathbf{q} + \boldsymbol{\eta}/2) - \xi S_1(\mathbf{q} - \boldsymbol{\eta}/2)] \times \exp[-S_0(\mathbf{q} + \boldsymbol{\eta}/2) - S_0(\mathbf{q} - \boldsymbol{\eta}/2)] \tag{69}$$

and, using equation (65)

$$W_1(q, p) = \sum_{i,j} \frac{v_{ijj}}{2\omega_i\omega_j} q_i + \sum_{i,j,k} \frac{v_{ijk}}{\omega_i + \omega_j + \omega_k} \left(\frac{q_i q_j q_k}{3} - \frac{q_i p_j p_k}{\omega_j \omega_k} \right). \tag{70}$$

The complete expression for $W = W_0 + \xi W_1$ is obtained by substituting (70) in equation (15) and changing variables as in section 3 above:

$$W = \frac{1}{2} \sum_i \alpha_i (x_i - X_i)^2 + \xi \sum_i \gamma_i (x_i - X_i) + \frac{\xi}{6} \sum_{ijk} w_{ijk} (x_i - X_i)(x_j - X_j)(x_k - X_k) \tag{71}$$

where x_i are variables collecting coordinates and momenta, and X_i are displacements. We eliminate linear terms in equation (71) by including them into effective displacements $\tilde{X}_i = X_i + \xi \gamma / \alpha$:

$$W = \frac{1}{2} \sum_i \alpha_i \bar{x}_i^2 + \frac{\xi}{6} \sum_{ijk} w_{ijk} \bar{x}_i \bar{x}_j \bar{x}_k + O(\xi^2) \tag{72}$$

where $\bar{x}_i = x_i - \tilde{X}_i$. When $v_{ijj} = 0$, $\tilde{X}_i = X_i$.

6.2. Anharmonic effects on the jump

There are two effects of anharmonicities on the minimization problem that we solve using equations (18). First, the initial Wigner function is shifted, redefining the effective displacement between the two potential surfaces as \tilde{X}_i instead of X_i . Second, third-order terms are added to the harmonic terms in both W and H . We treat these third-order terms by perturbation theory, for the functions $H = H^{(0)} + H^{(1)}\xi$, $W = W^{(0)} + W^{(1)}\xi$, where

$$H^{(0)} = \frac{1}{2} \sum_i x_i^2 \quad H^{(1)} = \frac{1}{6} \sum_{i,j,k} h_{ijk} x_i x_j x_k \tag{73}$$

$$W^{(0)} = \frac{1}{2} \sum_i \alpha_i \bar{x}_i^2 \quad W^{(1)} = \frac{1}{6} \sum_{i,j,k} w_{ijk} \bar{x}_i \bar{x}_j \bar{x}_k. \tag{74}$$

$\alpha_i, x_i, \bar{x}_i, w_{ijk}$ have been defined above and h_{ijk} are linear combinations of v_{ijk} .

Equation (18) is equivalent to

$$\alpha_i \bar{x}_i + \frac{\xi}{2} \sum_{j,k} w_{ijk} \bar{x}_j \bar{x}_k = \lambda \left(x_i + \frac{\xi}{2} \sum_{j,k} h_{ijk} x_j x_k \right) \tag{75}$$

$$\frac{1}{2} \sum_i x_i^2 + \frac{\xi}{6} \sum_{i,j,k} h_{ijk} x_i x_j x_k = E. \tag{76}$$

The unknown variables x_i ($i = 1, \dots, M$) and the Lagrange multiplier λ are searched for in the form

$$x_i = x_i^{(0)} + x_i^{(1)}\xi + o(\xi) \tag{77}$$

$$\lambda = \lambda^{(0)} + \lambda^{(1)}\xi + o(\xi). \tag{78}$$

In the zero-order approximation ($\xi = 0$), equations (75) and (76) are

$$\alpha_i \bar{x}_i^{(0)} = \lambda^{(0)} x_i^{(0)} \quad \frac{1}{2} \sum_i x_i^{(0)2} = E$$

where $\bar{x}_i^{(0)} = x_i^{(0)} - \tilde{X}_i$. In the first order in ξ , equations (75) and (76) are

$$\alpha_i x_i^{(1)} + \frac{1}{2} \sum_{j,k} w_{ijk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} = \lambda^{(0)} \left(x_i^{(1)} + \frac{1}{2} \sum_{j,k} h_{ijk} x_j^{(0)} x_k^{(0)} \right) + \lambda^{(1)} x_i^{(0)} \quad (79)$$

$$\sum_i x_i^{(0)} x_i^{(1)} + \frac{1}{6} \sum_{i,j,k} h_{ijk} x_i^{(0)} x_j^{(0)} x_k^{(0)} = 0. \quad (80)$$

Let us find the first correction to the harmonic approximation for the two cases discussed above using these formulae.

Case (1). The unperturbed coordinates are given in this case by equations (35) and (36) whereas the unperturbed Lagrange multiplier is $\lambda^{(0)} = \alpha_1$. It then follows from (79), for $i = 1$, that

$$\lambda^{(1)} = \frac{1}{2x_1^{(0)}} \sum_{j,k} \left(\omega_{1jk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} - \alpha_1 h_{1jk} x_j^{(0)} x_k^{(0)} \right) \quad (81)$$

and from (79), for $i \neq 1$, that

$$x_i^{(1)} = \frac{1}{\alpha_i - \alpha_1} \left[\frac{1}{2} \sum_{j,k} \left(\alpha_1 h_{ijk} x_j^{(0)} x_k^{(0)} - w_{ijk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} \right) + \lambda^{(1)} x_i^{(0)} \right] \quad i \neq 1. \quad (82)$$

Finally, the remaining unknown variable $x_1^{(1)}$ can be found by substituting (82) into (80),

$$x_1^{(1)} = -\frac{1}{x_1^{(0)}} \left[\sum_{i \neq 1} x_i^{(0)} x_i^{(1)} + \frac{1}{6} \sum_{i,j,k} h_{ijk} x_i^{(0)} x_j^{(0)} x_k^{(0)} \right]. \quad (83)$$

In zero order (harmonic approximation), there are two points of minimum differing by a sign of x_1 with the same W_{\min} given by (38). In the first-order approximation, W_{\min} is given by (86), and it is no longer the same for the two points, corresponding to different signs in equation (35). So, the true minimum is the one for which (86) is smaller.

Case (2). In this case the unperturbed coordinates and Lagrange multiplier are given by equations (28) and (40). It follows from (79) that

$$x_i^{(1)} = \frac{1}{\alpha_i - \lambda^{(0)}} \left[\frac{1}{2} \sum_{j,k} \left(\lambda^{(0)} h_{ijk} x_j^{(0)} x_k^{(0)} - w_{ijk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} \right) + \lambda^{(1)} x_i^{(0)} \right]. \quad (84)$$

Inserting (84) into (80), we find

$$\lambda^{(1)} = \frac{1}{6} \left(\sum_i \frac{x_i^{(0)2}}{\alpha_i - \lambda^{(0)}} \right)^{-1} \sum_{i,j,k} \frac{x_i^{(0)}}{\alpha_i - \lambda^{(0)}} \left[3w_{ijk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} - (2\lambda^{(0)} + \alpha_i) h_{ijk} x_j^{(0)} x_k^{(0)} \right]. \quad (85)$$

In this case, we first determine $\lambda^{(1)}$ by equation (85), and then $x_i^{(1)}$ by substituting $\lambda^{(1)}$ into equation (84).

W in both cases. In both cases expanding the minimum value of the constrained function W into a power series $W_{\min} = W_{\min}^{(0)} + W_{\min}^{(1)} \xi + O(\xi^2)$, we find that $W_{\min}^{(0)}$ is given by equation (31), and

$$W_{\min}^{(1)} = \sum_i \alpha_i \bar{x}_i^{(0)} x_i^{(1)} + \frac{1}{6} \sum_{i,j,k} w_{ijk} \bar{x}_i^{(0)} \bar{x}_j^{(0)} \bar{x}_k^{(0)}. \quad (86)$$

6.3. Anharmonic potentials with no effective displacements

As a simple example, consider the case of no effective displacements and Duschinsky rotation, with $\bar{x}_i = x_i$, $x_i^{(0)} = 0$ for all $i \neq 1$ and $x_1^{(0)} = \pm\sqrt{2E}$. The unperturbed Lagrange multiplier is $\lambda^{(0)} = \alpha_1$. It then follows that

$$\lambda^{(1)} = \frac{1}{2}x_1^{(0)}(w_{111} - \alpha_1 h_{111}) \quad (87)$$

$$x_{i \neq 1}^{(1)} = -\frac{1}{2} \frac{x_1^{(0)2}}{\alpha_i - \alpha_1} (w_{i11} - \alpha_1 h_{i11}) \quad (88)$$

$$x_1^{(1)} = -\frac{1}{6}x_1^{(0)2}h_{111}. \quad (89)$$

$$W_{\min}^{(1)} = \frac{1}{6}x_1^{(0)3}(w_{111} - \alpha_1 h_{111}). \quad (90)$$

For $\xi \neq 0$ the two minima $W_{\min}^{(0)} + \xi W_{\min}^{(1)}$ corresponding to two different signs of $x_1^{(0)}$ are not the same, the global minimum is reached when $x_1^{(0)}$ has the opposite sign to $\xi(w_{111} - \alpha_1 h_{111})$.

6.4. A numerical example

Figure 4 shows typical behaviour of the minimum with a change in the anharmonicity. Evolution of the jumping point, or the location of the minimum, is shown in figure 5. For $\xi < 0.1$, the first-order perturbation theory gives good results, but for larger ξ it breaks both because of the presence of nonlinear terms and an abrupt change of position of the global minimum.

6.5. Discussion

The following observations can be made: when anharmonicities are small enough to allow for a perturbative treatment, their influence on the jumping point grows with increasing energy gap, linearly with energy, and increases for degrees of freedom i for which $\alpha_i \approx \alpha_1$. There is a compensating effect of the anharmonicities on the two surfaces: their effects occur with opposite signs. Finally, we note that not all anharmonic potentials could be treated perturbatively, and that for completely general potential surfaces, an analytic treatment becomes impossible. In these cases a numerical approach is needed.

7. Summary and conclusions

Intramolecular energy transfer is an important part of many chemical processes. Very often, energy transfer processes in molecules involve degrees of freedom with a separation of timescales, for example electronic and vibrational–rotational motion. Sometimes, the electrons transfer much energy to the vibrations and rotations in a sudden process. This exchange is usually followed by further intramolecular vibrational energy transfer. The nuclei have to make a leap in coordinate or momentum to reach the other Born–Oppenheimer surface in such nonvertical transitions, and the direction of the jump from one surface to another can be very specific.

A procedure for recognizing the jumping points in phase space in the noncrossing regime was introduced in [1, 10]. Here we have presented a closed-form complete solution for finding the jumping point for any transition between harmonic potentials and a perturbative treatment of the nonharmonic effects.

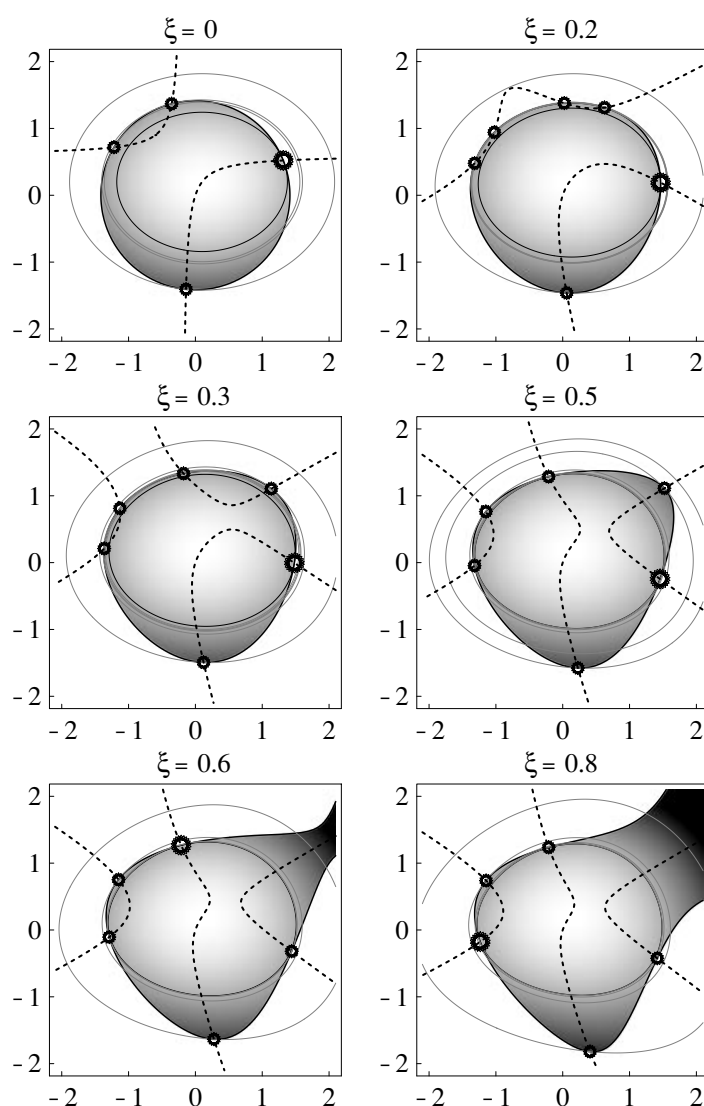


Figure 4. Evolution of the minimum of the function W under the energy constraint $H = E$ with strengthening of the anharmonicity. In W and H , we introduced an overall coupling parameter ξ : $W(x_1, x_2) = 0.4(x_1 - 0.1)^2 + 0.6(x_2 - 0.2)^2 + 0.05\xi[2(x_1 - 0.1)^2(x_2 - 0.2) - 2(x_1 - 0.1)(x_2 - 0.2)^2 + (x_2 - 0.2)^3]$, $H(x_1, x_2) = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 + 0.1\xi[-x_1^3 - 3x_1^2x_2 - 3x_1x_2^2 + x_2^3]$, $E = 1$. The upper left corner refers to the harmonic approximation ($\xi = 0$). The position of the global minimum marked by the largest circle is a discontinuous function of the anharmonicity since between $\xi = 0.52$ and $\xi = 0.53$ as well as between $\xi = 0.75$ and $\xi = 0.76$, the global minimum swaps with one of the secondary local minima. This example shows that for strong anharmonicities, the dependence $x^*(\xi)$ cannot be approximated by an analytic function.

The ingredients needed to predict the quantum jump are the classical Hamiltonian for the nuclei at the final (accepting) electronic state and the Wigner function of the initial state $\exp -2W$. In a special coordinate system, described in detail in section 3, both assume the

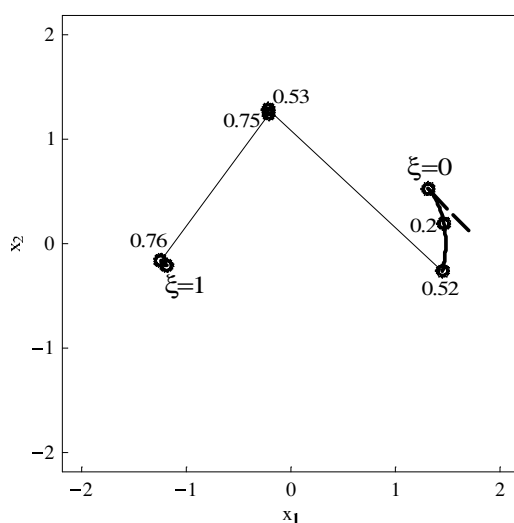


Figure 5. The location of the minimum x^* as a function of the strength of the anharmonicity ξ (solid line). Here, W , H and E are the same as in figure 4. The discontinuity is the result of competition for the global minimum between several local minima, see figure 4. The dashed line is the result of the first-order perturbation theory (section 6). After the first discontinuity occurs at $\xi = 0.53$, this linear approximation completely fails. There are appreciable errors of this approximation even at $\xi > 0.2$ due to the presence of quadratic terms.

particularly simple form of equations (20) and (21). In the harmonic approximation, equations (25) and (26) replace equations (20) and (21) allowing for a closed form, exact solution.

In the harmonic approximation, the parameters characterizing the transition are the energy gap E , the normalized displacements $\{X_i\}$ between the acceptor and donor potential surfaces and the parameters $\{\alpha_i\}$. For a small energy gap, the transition is almost vertical and the accepting modes are the displaced ones. For a large energy gap, the major accepting mode is the one with the smallest α , in general, some mixed coordinate and momentum for which the initial distribution comes closest to the final energy surface.

The richness of possible phenomena and excitations comes about from the transformation of coordinates from the mathematically accessible ones to the physical coordinates of the atoms in the molecule. Some simple examples have been presented.

The harmonic case is completely solved here. Future applications to harmonic models of specific molecules is now a straightforward procedure. When nonharmonic potential surfaces are known, it is possible to use the harmonic model and perturbatively correct the anharmonicities, only if the anharmonicities are small. More complicated surfaces require a numerical approach.

The predictive power of the jumping point for energy distribution between different accepting modes has also been demonstrated. Predictions for the physical features of the radiationless transition based on location of the jumping points deserve further study.

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