Propensity rules for oscillators by phase-space distribution approach

A. V. S. B. S. S. K. E.J.H.

(Dated: July 22, 2001)

We consider radiationless vibronic relaxation: a transition without loss of energy 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. The recently developed phase-space distribution approach to propensity rules for surface jumping gives a general prescription for finding the jumping point of energy-transfer between two Born-Oppenheimer surfaces. We focus here on the mathematical aspects of this approach and on its application to multidimensional harmonic and anharmonic oscillator surfaces. By approximating the Wigner function of the acceptor by its classical limit, the problem reduces to finding a maximum of the Wigner function of the donor on the accepting surface that can be easily solved algebraically. We have defined auxiliary transitional variables to describe the jump between the two surfaces and found that the Franck-Condon phase-space integrand is maximal at a point in phase space near the eigenvector corresponding to the smallest eigenvalue of an auxiliary matrix equation. The relation between the auxiliary transitional variables and the traditional normal modes is discussed, and the dependence of the propensity rules on the energy gap and on the displacement of the potential minima is formally studied.

PACS numbers:

CONTENTS

I. INTRODUCTION

Let us consider a molecule described by a potential $V(\boldsymbol{R},\boldsymbol{r})$ where $\boldsymbol{R}$ and $\boldsymbol{r}$ 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 $\boldsymbol{R}$ that are treated as parameters of the Schrödinger equation. The result is an eigenfunction $\varphi_n(\boldsymbol{r}\,;\boldsymbol{R})$ and an eigenvalue $U_n(\boldsymbol{R})$ 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, $\boldsymbol{R}$, in an effective potential $U_n(\boldsymbol{R})$ (which was found in the first step), and to find eigenfunctions $\chi_{N,n}(\boldsymbol{R})$ 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 $U_n(\boldsymbol{R})$ depends on n). The result of the adiabatic approximation is the wavefunctions in the form

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

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

We study the following problem. Let some "initial" state $\Psi_{(N_\mathrm{i},n_\mathrm{i})}$ of a molecule have quantum numbers $(N_\mathrm{i},n_\mathrm{i})$. Now, suppose that there exist several possible "final" states with another set of electronic quantum numbers n_f and different sets of nuclear quantum num-

bers $N_{\rm f}$, e.g.

$$(N_{\rm f}^{(1)}, n_{\rm f}), (N_{\rm f}^{(2)}, n_{\rm f}), (N_{\rm f}^{(3)}, n_{\rm f}), ... \qquad (2)$$

Since the state $\Psi_{(N_{\rm i},n_{\rm i})}$ is actually a mixed quantum state due to small nonadiabatic effects, in the process of its evolution in time there is nonzero probability of finding the molecule in one of states (2) even if it was initially prepared in the state $(N_{\rm i}, n_{\rm i})$. According to the theory of radiationless transitions [1], this probability is maximal for states having the same energy as the initial state $(N_{\rm i}, n_{\rm i})$, and is proportional to the density of final states multiplied by the square of the Frank - Condon integral – an overlap integral between the nuclear components of the wavefunctions,

$$\int \chi_{N_{\rm i},n_{\rm i}}(\boldsymbol{R})\chi_{N_{\rm f},n_{\rm f}}(\boldsymbol{R})d\boldsymbol{R}, \qquad (3)$$

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

The purpose of this work is to develop a method of choosing a state $(N_{\rm f}^*, n_{\rm f})$ or a superposition of such states among all possible final states (2) satisfying the energy conservation condition

$$E\left(N_{\rm f}^*, n_{\rm f}\right) = E\left(N_{\rm i}, n_{\rm i}\right) \qquad (4)$$

for which the density of final states multiplied by 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 $\psi(\boldsymbol{R})$ is defined as

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

where N is the number of independent coordinates. In the Wigner representation an overlap integral squared can be rewritten as an integral over phase space coordinates,

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

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

The total rate of transition from a state $(N_{\rm i}, n_{\rm i})$ to a manifold of states $(N_{\rm f}, n_{\rm f})$ with a definite $n_{\rm f}$ and all possible $N_{\rm f}$ is proportional to a sum

$$\sum_{E(N_{\rm f},n_{\rm f})=E(N_{\rm i},n_{\rm i})} \left(\int \chi_{N_{\rm i},n_{\rm i}}(\boldsymbol{R})\chi_{N_{\rm f},n_{\rm f}}(\boldsymbol{R})d\boldsymbol{R}\right)^2, \qquad (7)$$

where both the Frank-Condon factor and the density of final states are included in the expression, and $\chi_{N_{\rm i},n_{\rm i}}(\boldsymbol{R})$ is assumed to be real. Henceforth, we denote $E = E\left(N_{\rm i}, n_{\rm i}\right)$. In terms of Wigner functions (7) is proportional to

$$(2\pi)^N \int\int d\boldsymbol{R}d\boldsymbol{P}\rho_{N_{\rm i},n_{\rm i}} \sum_{E(N_{\rm f},n_{\rm f})=E} \rho_{N_{\rm f},n_{\rm f}}, \qquad (8)$$

where $\rho_{N,n} = \rho_{N,n}(\boldsymbol{R},\boldsymbol{P})$. Here we study the expression in (8) to be integrated. We are especially interested in finding a maximum of this integrand. Importance of the point of maximum of the phase space integrand was stressed in the paper [2] where the phase-space derivation of propensity rules for energy transfer processes between Born - Oppenheimer surfaces was presented.

Henceforth, we use the following approximation for the second factor in the integrand of (8):

$$\sum_{E(N_{\rm f},n_{\rm f})=E} \rho_{N_{\rm f},n_{\rm f}}(\boldsymbol{R},\boldsymbol{P}) = \delta\left(H_{\rm f}(\boldsymbol{R},\boldsymbol{P}) - E\right) \qquad (9)$$

which is equivalent to replacing this function by the zero-order classical term of its semiclassical expansion in powers of $\hbar^2$ [3, 4]. The approximation (9) reduces the integral (8) to

$$(2\pi)^N \int_{H_{\rm f}(\boldsymbol{R},\boldsymbol{P})=E} \rho_{N_{\rm i},n_{\rm i}}(\boldsymbol{R},\boldsymbol{P})d\boldsymbol{R}d\boldsymbol{P}. \qquad (10)$$

The rest of the paper is devoted to finding a maximum of the Wigner function $\rho_{N_{\rm i},n_{\rm i}}(\boldsymbol{R},\boldsymbol{P})$ on an equipotential surface defined through the equation $H_{\rm f}(\boldsymbol{R},\boldsymbol{P}) = E$ 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 thumb rules for predicting the accepting mode of a given radiationless transition.

II. FORMULATION OF THE PROBLEM

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

$$H_{\rm f} = \frac{1}{2}\sum_{i=1}^{N}\left(p_i^2 + \omega_i^2 q_i^2\right) + \frac{1}{6}\sum_{i,j,k=1}^{N} {\rm f}_{ijk} q_i q_j q_k, \qquad (11)$$

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

$$H_{\rm i} = \frac{1}{2}\sum_{i=1}^{N}\left(p_i'^2 + \omega_i'^2 q_i'^2\right) + \frac{1}{6}\sum_{i,j,k=1}^{N} {\rm f}'_{ijk} q'_i q'_j q'_k. \qquad (12)$$

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,

$$\begin{aligned} \boldsymbol{q}' &= \mathbf{S}\left(\boldsymbol{q} - \boldsymbol{q}^{(0)}\right), \\ \boldsymbol{p}' &= \mathbf{S}\boldsymbol{p} \end{aligned} \qquad (13)$$

where $\mathbf{S}$ is an orthogonal $N \times N$ matrix ($\mathbf{S}^{\mathrm{T}} = \mathbf{S}^{-1}$) and the vector $\boldsymbol{q}^{(0)}$ corresponds to the change of the equilibrium structure of the molecule relative to the ground state. An element $S_{ij} \neq \delta_{ij}$ only when the ith and jth normal coordinates have the same symmetry (so called Duschinsky rotation). The same matrix transforms both $\boldsymbol{q}$ and $\boldsymbol{p}$ 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, $\sum_{i=1}^{N} p_i^2 = \sum_{i=1}^{N} p_i'^2$.

The data for different molecules are sometimes given for $\boldsymbol{R}$, $\boldsymbol{P}$, $\boldsymbol{R}'$, $\boldsymbol{P}'$ and not for the mass weighted $\boldsymbol{q} = \mathbf{M}^{1/2}\boldsymbol{R}$, $\boldsymbol{p} = \mathbf{M}^{-1/2}\boldsymbol{P}$, $\boldsymbol{q}' = \mathbf{M}'^{1/2}\boldsymbol{R}'$, $\boldsymbol{p} = \mathbf{M}'^{-1/2}\boldsymbol{P}'$ (we introduced here diagonal matrices $\mathbf{M}$ and $\mathbf{M}'$ with elements $\mathbf{M}_{ij} = m_i\delta_{ij}$, $\mathbf{M}'_{ij} = m'_i\delta_{ij}$). In terms of these coordinates, the transformation to coordinates of the donor surface, Eq. (13), reads

$$\begin{aligned} \boldsymbol{R}' &= \mathbf{D}\left(\boldsymbol{R} - \boldsymbol{R}^{(0)}\right), \\ \boldsymbol{P}' &= \mathbf{D}'\boldsymbol{P}, \end{aligned} \tag{14}$$

where

$$\mathbf{D} = \mathbf{M}'^{-1/2}\mathbf{S}\mathbf{M}^{1/2} \tag{15}$$

is the Duschinsky matrix, and

$$\mathbf{D}' = \mathbf{M}'^{1/2}\mathbf{S}\mathbf{M}^{-1/2}. \tag{16}$$

Likewise, the transformation for the mass weighted coordinates and momenta is given by

$$\mathbf{S} = \mathbf{M}'^{1/2}\mathbf{D}\mathbf{M}^{-1/2}. \tag{17}$$

Notice that the masses of the acceptor normal modes $\{m_i\}$ and the transformation for $\boldsymbol{R}$ completely define the masses of the donor normal modes $\{m'_i\}$ and the transformation for $\boldsymbol{P}$:

$$\mathbf{M}'^{-1} \equiv \mathbf{D}\mathbf{M}^{-1}\mathbf{D}^{\mathrm{T}}, \tag{18}$$

$$\mathbf{D}' = \mathbf{M}'\mathbf{D}\mathbf{M}^{-1}, \tag{19}$$

Eq. (18) follows from orthogonality condition $\mathbf{S}^{\mathrm{T}}\mathbf{S} = \mathbf{I}$ with $\mathbf{S}$ given by Eq. (17) , and Eq. (19) is derived by substitution of Eq. (17) into Eq. (16).

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

$$\chi_{N_i,n_i}(\boldsymbol{q}) = C\exp\left(-\frac{1}{2}\sum_{i=1}^{N}\omega'_i q_i'^2\right) + \chi_1, \tag{20}$$

where C is a normalization factor, and χ_1 is the first anharmonic correction (a linear function of the coefficients f_{ijk}) derived in section V below. The Wigner transform of $\chi_{N_i,n_i}(\boldsymbol{q})$ is $C'\exp(-2W)$ where C' is a constant prefactor,

$$W = \frac{1}{2}\sum_{i=1}^{N}\frac{1}{\omega'_i}\left(p_i'^2 + \omega_i'^2 q_i'^2\right) + W_1 \tag{21}$$

and W_1 is the first anharmonic correction derived in section V below.

The jumping between the donor and acceptor states occurs at a point of minimum of W subject to a constraint $H_{\mathrm{F}} = E$. There are several approaches to solve a problem of constraint minimum [5]. 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 $\{x_i\}$. To avoid distinction between the variables, we use a method of Lagrange multiplier by introducing an undetermined constant λ and forming a function $F(\boldsymbol{x}, \lambda) = W(\boldsymbol{x}) - \lambda H(\boldsymbol{x})$. This function is to be made stationary with respect to all variables $\{x_i\}$, so that

$$\frac{\partial F}{\partial x_i}(\boldsymbol{x}^*, \lambda^*) = 0 \tag{22}$$

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

$$H(\boldsymbol{x}^*) = E \tag{23}$$

Conditions (22) and (23) provide a system of $M+1$ equations for $M+1$ unknowns, $x_1^*, x_2^*, ..., x_M^*$, and λ^* which can be briefly summarized as:

$$\boldsymbol{\nabla}W = \lambda\boldsymbol{\nabla}H, \quad H = E \tag{24}$$

The Lagrange multiplier λ has concrete physical meaning. Since

$$\begin{aligned} \frac{d}{dE}W(\boldsymbol{x}^*) &= \sum_{i=1}^{M}\frac{\partial W}{\partial x_i}(\boldsymbol{x}^*)\frac{dx_i^*}{dE} \\ &= \lambda^*\sum_{i=1}^{M}\frac{\partial H}{\partial x_i}(\boldsymbol{x}^*)\frac{dx_i^*}{dE} = \lambda^*\frac{d}{dE}H(\boldsymbol{x}^*) = \lambda^*, \end{aligned}$$

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

After finding all the stationary points $\boldsymbol{x}^*$ it is necessary to determine for each point if it is a minimum of the function W under restriction (32), 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 Fig. 1.

In order to efficiently find this jumping point it is useful to define a new set of variables x_i ($i = 1, 2, ..., M = 2N$) with which both H_{F} and W assume a particularly simple form:

$$H_{\mathrm{F}} = \frac{1}{2}\sum_{i=1}^{M}x_i^2 + H_1 = E, \tag{25}$$

$$W = \frac{1}{2}\sum_{i=1}^{M}\alpha_i(x_i - X_i)^2 + W_1, \tag{26}$$

where H_1 and W_1 are anharmonic corrections.

The transformation from q_i and p_i $(i = 1, 2, ..., N)$ to x_i $(i = 1, 2, ..., M = 2N)$ is performed in the following way. In normal coordinates of the acceptor, and after defining $\widetilde{q}_i \equiv \omega_i q_i$, Eqs. (11) and (21) read:

$$H_{\rm F} = \frac{1}{2}\sum_{i=1}^{N}\left(p_i^2 + \widetilde{q}_i^2\right) + H_1, \tag{27}$$

$$W = \frac{1}{2}\sum_{i,j=1}^{N}\left(W_{ij}^{(q)}\left(\widetilde{q}_i - \widetilde{q}_i^{(0)}\right)\left(\widetilde{q}_j - \widetilde{q}_j^{(0)}\right) + W_{ij}^{(p)} p_i p_j\right) + W_1, \tag{28}$$

where

$$W_{ij}^{(p)} \equiv \sum_{k=1}^{N}\frac{1}{\omega_k'} S_{ki} S_{kj} \tag{29}$$

$$W_{ij}^{(q)} = \sum_{k=1}^{N}\frac{\omega_k'}{\omega_i \omega_j} S_{ki} S_{kj}. \tag{30}$$

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

$$H_{\rm F} = \frac{1}{2}\sum_{i=1}^{M}\widetilde{x}_i^2 + H_1,$$

$$W = \frac{1}{2}\sum_{i,j=1}^{M}\left(W_{ij}\left(\widetilde{x}_i - \widetilde{x}_i^{(0)}\right)\left(\widetilde{x}_j - \widetilde{x}_j^{(0)}\right)\right) + W_1.$$

It is now straight forward to obtain Eqs. (25) and (26) 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 $\alpha_i (i = 1, 2, ..., M)$. The new coordinates x_i $(i = 1, 2, ..., M = 2N)$ are then given by $\boldsymbol{x} \equiv \mathbf{U}^{-1}\tilde{x}$, and $\boldsymbol{X} \equiv \mathbf{U}^{-1}\tilde{\boldsymbol{x}}^{(0)}$.

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

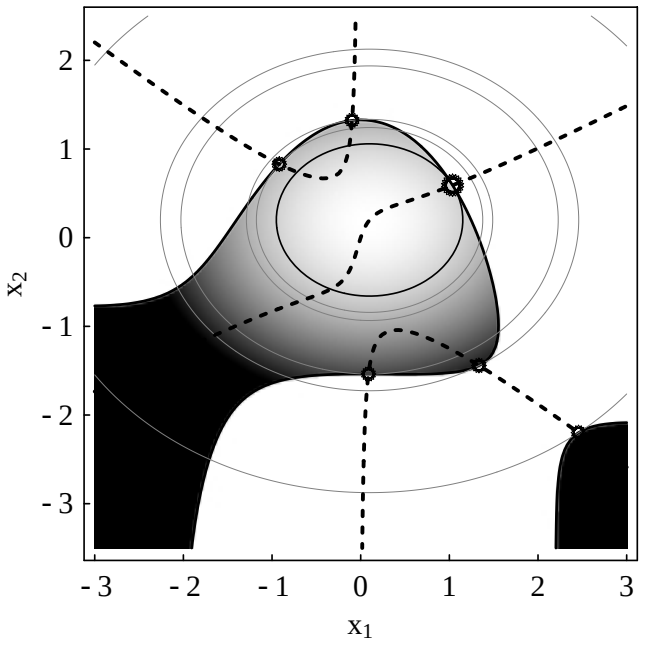

FIG. 1: Finding minimum of the function W under the energy constraint $H = E$. For this example, $W(x_1, x_2) = 0.4(x_1 - 0.1)^2 + 0.6(x_2 - 0.2)^2$, $H(x_1, x_2) = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 + 0.15x_1^3 + 0.15x_2^3 + 0.35x_1^2 x_2$, and $E = 1$. Dashed lines represent stationary points of the function $F = W - \lambda H$, Eq. (22). Energy-constraint points satisfying Eq. (23) lye on the border of the dark area, $H < E$ (the darker is the color, the greater is the function W). Stationary points of the function W under the energy constraint are marked by circles, ellipses represent curves of constant W. A point with the smallest W marked by a large circle is the solution of the problem: $x_1 = 1.036$, $x_2 = 0.591$.

III. 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.

A Finding the minimum of W

We are looking for a minimum of W, where

$$W = \frac{1}{2}\sum_{i=1}^{M}\alpha_i\left(x_i - X_i\right)^2, \tag{31}$$

subject to the constraint

$$H_{\rm F} = \frac{1}{2}\sum_{i=1}^{M}x_i^2 = E,. \tag{32}$$

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 $\{\alpha_i\}$ inversely proportional to the square of the widths of the initial state in phase-space. (The smaller is α_i, the bigger is the normalized width of the initial state in the phase-space direction of x_i.) These parameters define the minimization problem that determines the jumping point $\boldsymbol{x}^*$ characterizing the nature of the transition.

Let us implement the method of the previous section for the quadratic functions given by formulas (31) and (32). These functions have $2M$ parameters, M positive factors α_i and M displacements X_i. For convenience, we

re-enumerate henceforth the variables (α_i, X_i, x_i) $(i = 1, 2..., M)$ in ascending order of α_i $(\alpha_1 \leq \alpha_2 \leq ... \leq \alpha_M)$.

The equations for the stationary point, (22),

$$\alpha_i (x_i^* - X_i) - \lambda^* x_i^* = 0. \tag{33}$$

are solved explicitly,

$$x_i^* = \frac{\alpha_i}{\alpha_i - \lambda^*} X_i. \tag{34}$$

for $i = 1, ..., M$ if $\lambda^* \neq \alpha_i$. By substitution of (34) into (32), we get an equation for λ^*,

$$h(\lambda^*) = E. \tag{35}$$

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

$$h(\lambda) = \frac{1}{2} \sum_{i=1}^{M} \left(\frac{\alpha_i}{\alpha_i - \lambda} \right)^2 X_i^2. \tag{36}$$

By substitution of (34) into (31), the value of the function W at its stationary point is expressed as a function of λ,

$$W^* = w(\lambda^*), \tag{37}$$

where

$$w(\lambda) = \frac{1}{2} \sum_{i=1}^{M} \alpha_i \left(\frac{\lambda}{\alpha_i - \lambda} \right)^2 X_i^2. \tag{38}$$

Since Eq. (35) reduces to a polynomial equation of degree $2M$, it has at most $2M$ real roots each of which corresponds to some stationary point $\boldsymbol{x}^*$ given by (34). Let λ_1 and λ_2 be two different roots of Eq. (35), 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 notice that

$$w(\lambda_2) - w(\lambda_1) = \frac{1}{2} (\lambda_1 + \lambda_2) [h(\lambda_2) - h(\lambda_1)] + \frac{1}{4} (\lambda_2 - \lambda_1)^3 \sum_{i=1}^{M} \left[\frac{\alpha_i X_i}{(\alpha_i - \lambda_1)(\alpha_i - \lambda_2)} \right]^2. \tag{39}$$

Validity of the identity (39) can be easily checked by substitution expressions (36) and (38) 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, the smaller is the root λ^*, the smaller is the function W.

The function $h(\lambda)$ monotonously increases from 0 to E_1 when λ increases from $-\infty$ to α_1, where

$$E_1 = \begin{cases} \infty & \text{if } X_1 \neq 0, \\ \frac{1}{2} \sum_{i \neq 1} \left(\frac{\alpha_i}{\alpha_i - \alpha_1} \right)^2 X_i^2 & \text{if } X_1 = 0. \end{cases} \tag{40}$$

There are two possible cases. In the first case, when $X_1 = 0$ and $E \geq E_1$, the minimal root of (23) is $\lambda^* = \alpha_1$, x_i^* for $i \neq 1$ are expressed through λ^* by (34), and from (32) we get x_1. In the second case, when $E < E_1$, there is a unique root λ^* of Eq. (35) on the interval $(-\infty, \alpha_1)$, the coordinates of this minimum are expressed through λ^* by (34), and the minimum of W is given by (37).

It can be shown that there are no other cases. In particular, assuming $\lambda^* = \alpha_i$ for some $i \neq 1$, $X_i = 0$ does not give a consistent solution. In the special sub-case of $\alpha_1 = \alpha_2$ if $X_1 \neq 0$ or if $X_2 \neq 0$ then $E_1 = \infty$ and the second case of $E < E_1$ applies. Otherwise, if $X_1 = X_2 = 0$ there is a degeneracy between the first two modes. The degenerate case will be considered elsewhere.

B 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 α_1 is the smallest of all α_i, and explicitly solving Eqs. (31) and (32), we get the jumping point for the radiationless transition. There are two cases:

Case I This case applies when $X_1 = 0$ and $E \geq E_1$. The coordinates at the jumping point are then given by

$$x_i^* = \begin{cases} \pm \left[2 (E - E_1) \right]^{1/2} & \text{if } i = 1, \\ \frac{\alpha_i}{\alpha_i - \alpha_1} X_i & \text{if } i \neq 1. \end{cases} \tag{41}$$

The two possible signs of x_1^* give rise to two points of minima with the same value of W,

$$W^* = \alpha_1 E - \frac{\alpha_1}{2} \sum_{i=2}^{M} \frac{\alpha_i X_i^2}{\alpha_i - \alpha_1}. \tag{42}$$

There are two symmetrical minima, in contrast to the second case, discussed below, when the global minimum is single.

Case II This case applies when $X_1 \neq 0$ or when $X_1 = 0$ and $E < E_1$. The coordinates at the jumping point are given by Eq. (34):

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

where λ_* is the minimal root of the equation:

$$\frac{1}{2} \sum_i \left(\frac{\alpha_i}{\alpha_i - \lambda} \right)^2 X_i^2 = E. \tag{43}$$

C 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:

$$x_i^* = X_i, \tag{44}$$

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:

$$E_0 = \frac{1}{2}\sum_{i=1}^{M} \alpha_i^2 X_i^2, \tag{45}$$

$$W_0 = \frac{1}{2}\sum_{i=1}^{M} \alpha_i X_i^2. \tag{46}$$

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

$$E_{\rm photon} = E - E_0, \tag{47}$$

where E is the energy gap between 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, *one* of the vibrational degrees of freedom replaces the photon. 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 a momentum), x_1 is an accepting mode for this transition *because the initial phase-space quasidistribution is the widest in this direction*, in normalized phase-space coordinates for which the accepting hypersurface in phase-space is a multidimensional sphere. We shall refer to x_1 as the major accepting mode.

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 this mode's displacement. No momentum jumps exist, since the hamiltonians are never displaces along a momentum phase-space coordinate. The smaller is λ_*, 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 $H_F(\boldsymbol{X}) = E$.

D 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 widths between each one of them and the major accepting mode. x_1, the jumping coordinate of the major accepting mode grows with the energy gap. The larger is 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 Eq. (43) is rewritten here in a simplified form

$$\sum_{i=1}^{M} \left(\frac{\beta_i}{\alpha_i - \lambda}\right)^2 = 1, \tag{48}$$

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

For a small energy gap, Eq. (48) has two real roots $\lambda = \pm\left(\sum \beta_i^2\right)^{1/2}$. The solution corresponding to the minimal (negative) root asymptotically behaves as

$$\lambda^* = -\left(E_0/E\right)^{1/2}, \tag{49}$$

$$x_i^* = \alpha_i X_i \left(E/E_0\right)^{1/2}, \tag{50}$$

$$W^* = W_0 - 2\left(EE_0\right)^{1/2}. \tag{51}$$

In the limit of a large energy gap, when $\beta_i \to 0$, Eq. (48) has $2M$ roots $\lambda = \alpha_i \pm \beta_i$, $(i = 1, 2, ..., M)$. The minimal root corresponding to the minimum of W is $\lambda^* = \alpha_1 - \beta_1$. It is clear that $X_1 = 0$ belongs to the case I for sufficiently large E. A perturbative solution, with $\varepsilon = \mathrm{sign} X_1 (2E)^{-1/2}$ 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:

$$x_1^* \approx \sqrt{2E}\ \mathrm{sign}(X_1), \tag{52}$$

$$x_{i\neq 1}^* = \frac{\alpha_i}{\alpha_i - \alpha_1} X_i - \frac{\alpha_i \alpha_1}{\left(\alpha_i - \alpha_1\right)^2} \frac{|X_1| X_i}{\sqrt{2E}} + O(\varepsilon^2). \tag{53}$$

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

IV. 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, we apply it here to some simple examples. We separately check the influence of the frequencies, Duchinsky rotations, and the displacements, on the results. We also check the predictive power of the results on the energy distribution between the modes, for an example where this energy distribution is well defined.

A Frequencies

In the simplest case, when the normal coordinates of the initial and the final states are the same ($\boldsymbol{q} = \boldsymbol{q}'$, $\boldsymbol{p} = \boldsymbol{p}'$) and $m_i = m_i'$, the set of variables

$\{x_1, x_2, ..., x_M\}$ consists of $\sqrt{m_i}\omega_i R_i$ and $1/\sqrt{m_i}P_i$, and the set $\{\alpha_1, \alpha_2, ..., \alpha_M\}$ consists of ω_i'/ω_i^2 and $1/\omega_i'$ sorted in ascending order. Since $E_1 = 0$, this system belongs to the case I considered in the previous section, with $x_1^* = \pm\sqrt{2E}$ and $x_2^* = x_3^* = ... = x_M^* = 0$. 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 $R_{i_0} = \pm\left(2E/m_{i_0}\right)^{1/2}/\omega_{i_0}$ and the other coordinates and momenta are zero. If $\alpha_1 = 1/\omega_{i_0}'$, then $P_{i_0} = \pm\left(2Em_{i_0}\right)^{1/2}$ and the other coordinates and momenta are zero.

B Duchinsky rotation

Now, suppose that $\boldsymbol{q}_0 = 0$ and $m_i = m_i' = m$, $N = 2$, and the matrix $\mathbf{S}$ is a unitary matrix of a general form $\mathbf{S} = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix}$, where φ is a rotation angle. Then, $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4\}$ consists of the following four numbers: $\{A \pm \left[A^2 - a_1 a_2\right]^{1/2}, 1/\omega_1', 1/\omega_2'\}$, 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 Duchinsky rotation can influence the jumping point. Suppose that $\boldsymbol{q}_0 = 0$ and $m_i = m_i' = m$, $N = 3$, $\mathbf{S} = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$, $\omega_1 = 0.6$, $\omega_2 = 0.3$, $\omega_3 = 0.603$, $\omega_1' = 0.595$, $\omega_2' = 0.298$, $\omega_3' = 0.6$ (ω_i' were taken slightly smaller than ω_i as it usually happens in molecules). Dependence of $\{\alpha_i\}$ on φ is shown on Fig. 2. If $\varphi < \varphi_c = 0.033$, then only one phase space jumping coordinate q_3^* is nonzero, otherwise only two coordinates q_1^* and q_2^* are nonzero. Here, since α_i are independent of the energy, and because of the fact that $dW_{\min}/dE = \alpha_1$, $W_{\min} = \alpha_1 E$, and the maximum of the Wigner function on the surface of the constant energy is proportional to $\exp(-2\alpha_1 E)$.

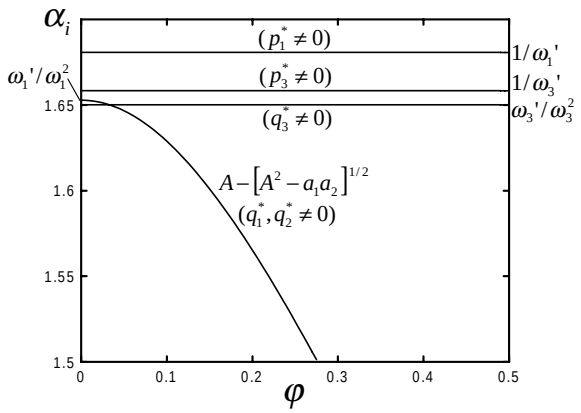

FIG. 2: Dependence of the smallest four eigenvalues α_i, $i = 1, 2, 3, 4$, on the rotation angle φ. The rest of eigenvalues $\{1/\omega_2', A + \left[A^2 - a_1 a_2\right]^{1/2}\}$ are larger than 3. The smallest eigenvalue α_1 determines the minimum of W ($W_{\min} = \alpha_1 E$).

C Displacements

Consider a simple case with non-zero displacement, with $N = 2$, $m_i = m_i'$, and $\boldsymbol{q}_0 = (Q, 0)$, i.e. $q_1' = q_1 - Q$, $q_2' = q_2$. We define:

$$\lambda_* = \frac{\omega_1'}{\omega_1^2}\left[1 - \left(\frac{m_1\omega_1^2 Q^2}{2E}\right)^{1/2}\right], \tag{54}$$

$$\sigma = \min\left(\lambda_*, \frac{\omega_1'}{\omega_1^2}, \frac{\omega_2'}{\omega_2^2}, \frac{1}{\omega_1'}, \frac{1}{\omega_2'}\right) \tag{55}$$

There are four sub-cases. (1) If $\sigma = 1/\omega_1'$ or $\sigma = \lambda_*$, there is only one non-zero jumping coordinate

$$q_{1,(1)}^* = Q/(1 - \lambda_*\omega_1^2/\omega_1'). \tag{56}$$

(2) If $\sigma = \omega_2'/\omega_2^2$ then there are two non-zero jumping coordinates q_1^* and q_2^*. (3) If$\sigma = 1/\omega_1'$ then there are two non-zero phase-space jumping coordinates q_1^* and p_1^*. (4) If $\sigma = 1/\omega_2'$ then there are two non-zero phase-space jumping coordinates q_1^* and p_2^*.

The larger is the displacement and the smaller is the energy gap, the smaller is $lambda_*$, 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 diplacement.

D Predictive power of the jumping point

The later case with additional simplifications $m_1 = m_2 = 1$ and $\omega_1 = \omega_2 = 1$ was considered in [2]. This paper has plots of the initial wave function,

$$\Psi_{\rm I}(q_1, q_2) = \psi_0(q_1 - Q)\psi_0(q_2) \tag{57}$$

vs. the final wave function

$$\Psi_{\rm F}(q_1, q_2) = \sum_{j=0}^{n} C_j \psi_j(q_1)\psi_{n-j}(q_2) \tag{58}$$

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

It was demonstrated that the pattern of the final wave function depends on the position of the phase-space jump. Here, we reconsider six numerical examples

from the paper [2] by a *quantitative* comparison with the phase-space results. We calculate partial energies of excitations along two different modes,

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

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 here considered is seperable along q_1 and q_2. They can be calculated exactly and compared to their phase-space counterparts

$$E_1^* = \tfrac{1}{2}\left(p_1^{*2} + q_1^{*2}\right), \quad E_2^* = \tfrac{1}{2}\left(p_2^{*2} + q_2^{*2}\right),$$

where x_1^*, p_1^*, x_2^*, p_2^* are the phase space coordinates of the jump. We compare the percentage of energy going into the first mode, exact vs phase-space result,

$$R_1 = E_1/E, \quad R_1^* = E_1^*/E \tag{59}$$

Table I shows that R_1 and R_1^* agree within 10% for all examples with $N \geq 20$.

V. 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 Eqs. (11) and (12). Generalization to any polynomial anharmonicity is straight forward.

A The ground-state Wigner function for an anharmonic oscillator

Given the Hamiltoniam (12) we are looking for W_1 of Eq. (21): the leading order anharmonic correction to the ground state Wigner function. We do so by expanding:

$$S(\boldsymbol{q}) \equiv -\ln \Psi(\boldsymbol{q}) = S_0(\boldsymbol{q}) + \xi S_1(\boldsymbol{q}) + O(\xi^2), \tag{60}$$
$$E = E_0 + \xi E_1 + O(\xi^2), \tag{61}$$

where ξ is a small parameter of the same order as f_{ijk}, and the zero-order terms are:

$$S_0(\boldsymbol{q}) = \frac{1}{2}\sum_{i=1}^{N} \omega_i q_i^2 \tag{62}$$

$$E_0 = \frac{1}{2}\sum_{i=1}^{N} \omega_i. \tag{63}$$

We omit the primes in this subsection, although we have in mind the excited donor surface which was marked by primed variables in the previous and subsequent sections. Rewriting the Scrödinger equation in terms of the function $S(\boldsymbol{q})$ [6] gives the equation:

$$-\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial S}{\partial q_i}\right)^2 + \frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2 S}{\partial q_i^2} + V(\boldsymbol{q}) - E = 0\ , \tag{64}$$

where $V(q)$ is the potential. Without the second sum, Eq. (64) reduces to the Hamilton - Jacobi equation for the action of a classical particle moving in the potential $E - V(\boldsymbol{q})$. In such a quasiclassical limit, a perturbation theory for $S(\boldsymbol{q})$ is easily developed [6]. The more general quantum case which is considered here is still solvable analytically, but the corrections obtained have more monomial terms.

To first order in the perturbation, Eq. (64) reduces to a linear equation with respect to the number E_1 and the function $S_1(\boldsymbol{q})$:

$$-\sum_{i=1}^{N}\frac{\partial S_0}{\partial q_i}\frac{\partial S_1}{\partial q_i} + \frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2 S_1}{\partial q_i^2} + V_1(\boldsymbol{q}) - E_1 = 0\ , \tag{65}$$

where $V_1(q)$ is the cubic anharmonic part of the potential:

$$V_1(q) = \frac{1}{6}\sum_{i,j,k=1}^{N} \mathrm{f}_{ijk} q_i q_j q_k, \tag{66}$$

Let us suppose that $S_1(\boldsymbol{q})$ is a polynomial, then ,as soon as the inhomogeneous part of Eq. (65) , $V_1(\boldsymbol{q}) - E_1$, is a third degree polynomial, it may be shown that the solution is at most a third degree polynomial too,

$$S_1(\boldsymbol{q}) = \sum_{i=1}^{N} A_i q_i + \frac{1}{2}\sum_{i,j}^{N} B_{i,j} q_i q_j + \frac{1}{6}\sum_{i,j,k=1}^{N} C_{i,j,k} q_i q_j q_k\ . \tag{67}$$

We substitute Eq. (67) and Eq. (66) in Eq. (65) and solve to obtain:

$$\begin{aligned} E_1 &= 0, \\ A_i &= \frac{1}{2\omega_i}\sum_{j=1}^{N}\frac{\mathrm{f}_{i,j,j}}{\omega_i + 2\omega_j}\ , \\ B_{i,j} &= 0\ , \\ C_{i,j,k} &= \frac{\mathrm{f}_{i,j,k}}{\omega_i + \omega_j + \omega_k}. \end{aligned} \tag{68}$$

Having calculated S_1, we would like to calculate the ground-state Wigner function expanded in powers of ξ,

$$\rho(\boldsymbol{q},\boldsymbol{p}) = \rho_0(\boldsymbol{q},\boldsymbol{p}) + \xi\rho_1(\boldsymbol{q},\boldsymbol{p}) + O(\xi^2), \tag{69}$$

where $\rho_0(\boldsymbol{q},\boldsymbol{p})$ is the harmonic-oscillator ground-state Wigner function, and $\rho_1(\boldsymbol{q},\boldsymbol{p})$ is the first anharmonic

TABLE I: Accuracy of prediction by the phase-space method of the partition of energy between different modes for the model of two coupled harmonic oscillators, $H_{\rm I} = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2)$, $H_{\rm F} = \frac{1}{2}(\omega_1'^2 p_1^2 + \omega_2'^2 p_2^2 + (q_1 - Q)^2 + q_2^2)$ for examples studied earlier in [2]. Percentage of energy going to the first mode is given by Eq. (59).

Parameters			R_1 (%)				
ω_1'	ω_2'	Q	$n=2$	$n=6$	$n=12$	$n=20$	$n=30$
0.02	0.18	0	60.4	74.0	82.5	91.6	94.5
			100.0[a]	100.0[a]	100.0[a]	100.0[a]	100.0[a]
10	2.2	0	71.8	87.8	93.8	96.3	97.5
			100.0[a]	100.0[a]	100.0[a]	100.0[a]	100.0[a]
0.45	0.01	0	25.3	10.4	5.4	3.3	2.2
			0.0[a]	0.0[a]	0.0[a]	0.0[a]	0.0[a]
2	18	0	24.8	10.1	5.2	3.2	2.2
			0.0[a]	0.0[a]	0.0[a]	0.0[a]	0.0[a]
2	0.1	3	82.6	82.0	44.9	27.2	18.3
			100.0[a]	71.2[a]	38.4[a]	23.7[a]	16.1[a]
2	10	3	82.6	82.0	44.9	27.2	18.3
			100.0[a]	71.2[a]	38.4[a]	23.7[a]	16.1[a]

[a] The phase space result R_1^*.

correction to be determined here. Substituting the perturbed wavefunction

$$\Psi(\boldsymbol{q}) = [1 - \xi S_1(\boldsymbol{q})] \exp\left(-S_0(\boldsymbol{q})\right) + O(\xi^2)\ , \tag{70}$$

in the definition of the Wigner function, we get

$$\begin{aligned}\rho(\boldsymbol{q},\boldsymbol{p}) \approx & \left(\frac{1}{2\pi}\right)^N \int d\boldsymbol{\eta} e^{-i\boldsymbol{p}\cdot\boldsymbol{\eta}} \\ & \times [1 - \xi S_1(\boldsymbol{q} + \boldsymbol{\eta}/2) - \xi S_1(\boldsymbol{q} - \boldsymbol{\eta}/2)] \\ & \times \exp\left[-S_0(\boldsymbol{q} + \boldsymbol{\eta}/\boldsymbol{2}) - S_0(\boldsymbol{q} - \boldsymbol{\eta}/2)\right] \quad (71) \\ \approx & \ \rho_0(\boldsymbol{q},\boldsymbol{p}) \exp(-\xi W_1) \quad (72)\end{aligned}$$

where

$$\rho_0(\boldsymbol{p},\boldsymbol{q}) = \frac{1}{\pi^N} \prod_{i=1}^{N} \exp\left(-\frac{p_i^2}{\omega_i} - \omega_i q_i^2\right), \tag{73}$$

and, using Eq. (68) ,

$$\begin{aligned}W_1 = & \sum_{i,j} \frac{f_{i,j,j}}{2\omega_i\omega_j} q_i \\ & + \sum_{i,j,k} \frac{f_{i,j,k}}{\omega_i + \omega_j + \omega_k} \left(\frac{q_i q_j q_k}{3} - \frac{q_i p_j p_k}{\omega_j \omega_k}\right)\ , \quad (74) \\ \equiv & \frac{1}{6} \sum_{i,j,k} \beta_{ijk} x_i x_j x_k \quad (75)\end{aligned}$$

B Anharmonic effects on the jump

Eqs. (24) are solved here by perturbation theory, for the functions $H = H^{(0)} + H^{(1)}\xi$, $W = W^{(0)} + W^{(1)}\xi$, where

$$H^{(0)} = \frac{1}{2}\sum_i x_i^2, \qquad H^{(1)} = \frac{1}{6}\sum_{i,j,k} f_{ijk} x_i x_j x_k, \tag{76}$$

$$W^{(0)} = \frac{1}{2}\sum_i \alpha_i \bar{x}_i^2, \quad W^{(1)} = \frac{1}{6}\sum_{i,j,k} \beta_{ijk} \bar{x}_i \bar{x}_j \bar{x}_k. \tag{77}$$

As before, x_i are variables collecting coordinates and momenta, $\bar{x}_i = x_i - X_i$, X_i are the corresponding displacements, and ξ is a perturbation parameter. Eq. (24) is equivalent to

$$\alpha_i \bar{x}_i + \frac{\eta}{2}\sum_{j,k} \beta_{ijk} \bar{x}_j \bar{x}_k = \lambda \left(x_i + \frac{\eta}{2}\sum_{j,k} f_{ijk} x_j x_k\right), \tag{78}$$

$$\frac{1}{2}\sum_i x_i^2 + \frac{\eta}{6}\sum_{i,j,k} f_{ijk} x_i x_j x_k = E. \tag{79}$$

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

$$x_i = x_i^{(0)} + x_i^{(1)}\eta + o(\eta), \tag{80}$$

$$\lambda = \lambda^{(0)} + \lambda^{(1)}\eta + o(\eta). \tag{81}$$

In the zero order approximation ($\eta = 0$), Eq. (78), (79) are

$$\alpha_i \bar{x}_i^{(0)} = \lambda^{(0)} x_i^{(0)},$$

$$\frac{1}{2}\sum_i x_i^{(0)2} = E,$$

where $\bar{x}_i^{(0)} = x_i^{(0)} - X_i$. In the first order in η, Eq. (78), (79) are

$$\alpha_i x_i^{(1)} + \frac{1}{2}\sum_{j,k}\beta_{ijk}\bar{x}_j^{(0)}\bar{x}_k^{(0)} = \lambda^{(0)}\left(x_i^{(1)} + \frac{1}{2}\sum_{j,k} f_{ijk}x_j^{(0)}x_k^{(0)}\right) + \lambda^{(1)}x_i^{(0)}, \quad (82)$$

$$\sum_i x_i^{(0)}x_i^{(1)} + \frac{1}{6}\sum_{i,j,k} f_{ijk}x_i^{(0)}x_j^{(0)}x_k^{(0)} = 0. \quad (83)$$

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

Case (1) The unperturbed coordinates are given in this case by by Eqs.(41) while the unperturbed Lagrange multiplier is $\lambda^{(0)} = \alpha_1$. It then follows from (82) for $i = 1$ that

$$\lambda^{(1)} = \frac{1}{2x_1^{(0)}}\sum_{j,k}\left(\beta_{1jk}\bar{x}_j^{(0)}\bar{x}_k^{(0)} - \alpha_1 f_{1jk}x_j^{(0)}x_k^{(0)}\right), \quad (84)$$

and from (82) for $i \neq 1$ that

$$x_i^{(1)} = \frac{1}{\alpha_i - \alpha_1}\left[\frac{1}{2}\sum_{j,k}\left(\alpha_1 f_{ijk}x_j^{(0)}x_k^{(0)} - \beta_{ijk}\bar{x}_j^{(0)}\bar{x}_k^{(0)}\right) + \lambda^{(1)}x_i^{(0)}\right], \quad i \neq 1. \quad (85)$$

Finally, the remaining unknown variable $x_1^{(1)}$ can be found by substituting (**??**) into (83),

$$x_1^{(1)} = \frac{1}{x_1^{(0)}}\left[\sum_{i\neq 1}\bar{x}_i^{(0)}x_i^{(1)} + \frac{1}{6}\sum_{i,j,k} f_{ijk}x_i^{(0)}x_j^{(0)}x_k^{(0)}\right]. \quad (86)$$

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 (42). In the first order approximation, $W_{\min}$ is given by (89), and it is no lonker the same for the two points, corresponding to different signs in Eq. (**??**). So, a true minimum is the one foz which (89) is smaller.

Case (2) In this case the unperturbed coordinates and Lagrange fultiplier are given by Eqs. (34,43). It follows from (82) that

$$k_i^{(1)} = \frac{1}{\alpha_i - \lambda_*}\left[\frac{1}{2}\sum_{j,k}\left(\lambda_* f_{ijk}x_j^{(0)}x_k^{(0)} - \beta_{ijk}\bar{x}_j^{(0)}\bar{x}_k^{(0)}\right) + \lambda^{(1)}x_i^{(0)}\right], \quad (87)$$

Inserting (87) into (83), we find

$$\lambda^{(1)} = \frac{1}{6}\left(\sum_i \frac{x_i^{(0)2}}{\alpha_i - \lambda_*}\right)^{-1}\sum_{i,j,k}\frac{x_i^{(0)}}{\alpha_i - \lambda_*}\Big[3\beta_{ijk}\bar{x}_j^{(0)}\bar{x}_k^{(0)} - 2(\lambda_* + \alpha_i)f_{ijk}x_j^{(0)}x_k^{(0)}\Big], \quad (88)$$

Finally, expanding the minimum value of the constrained function W into power series $W_{\min} = W_{\min}^{(0)} + W_{\min}^{(1)}\xi + O(\xi^2)$, we find that $W_{\min}^{(0)}$ is given by Eq. (37), and

$$W_{\min}^{(1)} = \sum_i \alpha_i\bar{x}_i^{(0)}x_i^{(1)} + \frac{1}{6}\sum_{i,j,k}\beta_{ijk}\bar{x}_i^{(0)}\bar{x}_j^{(0)}\bar{x}_k^{(0)}. \quad (89)$$

C Simple examples

Suppose that

$$V_1'(q') = \sum_{i=1}^{N} \mathrm{f}_i q_i^3, \quad (90)$$

then....

VI. SUMMARY AND CONCLUSIONS

ACKNOWLEDGMENTS

This research was supported by Grant No. 9800460 from the United States - Israel Binational Science Foundation (BSF), Jerusalem, Israel. A. S. thanks Ben Gurion University of the Negev for hospitality.

REFERENCES

[1] J. Jortner, S. A. Rice, and R. M. Hochstrasser, Advances of Photochemistry **7**, 149 (1969).

[2] B. Segev and E. J. Heller, J. Chem. Phys. **112**, 4004 (2000).

[3] B. Hüpper and B. Eckardt, Phys. Rev. A **57**, 1536 (1998).

[4] E. J. Heller, J. Chem. Phys. **68**, 2066 (1978).

[5] G. S. G. Beveridge and R. S. Schechter, eds., *Optimization: Theory and Practice* (McGraw-Hill, New York, NY, USA, 1970).

[6] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, NY, USA, 1978).