1 Finding the total integral

The purpose of this study is to find the probability of transition from the ground state of a donor described by a wave function $\psi_{\rm I}(\boldsymbol{q})$ to some excited state of an acceptor of a given energy E described by a wave function ψ_n where n is a set of quantum numbers of the excited state. This probability is expressed through the overlap integral between two wavefunctions as

$$I(E) = D_{\rm F}(E)\left[\int d\boldsymbol{q}\psi_{\rm I}(\boldsymbol{q})\psi_n(\boldsymbol{q})\right]^2, \tag{1}$$

where $D_{\rm F}(E)$ is the density of states on the acceptor surface.

We use phase space approach. Wigner functions are

$$\rho_{\rm I}(\boldsymbol{q},\boldsymbol{p}) = \frac{1}{(\pi\hbar)^N}\int d\boldsymbol{\eta}\psi_{\rm I}(\boldsymbol{q}+\boldsymbol{\eta})\psi_{\rm I}(\boldsymbol{q}-\boldsymbol{\eta})\exp(-2i\boldsymbol{p}\boldsymbol{\eta}/\hbar), \tag{2}$$

$$\rho_n(\boldsymbol{q},\boldsymbol{p}) = \frac{1}{(\pi\hbar)^N}\int d\boldsymbol{\eta}\psi_n(\boldsymbol{q}+\boldsymbol{\eta})\psi_n(\boldsymbol{q}-\boldsymbol{\eta})\exp(-2i\boldsymbol{p}\boldsymbol{\eta}/\hbar). \tag{3}$$

The transition probability is expressed through an integral over the phase space as

$$I(E) = \int d\boldsymbol{q}d\boldsymbol{p}\rho_{\rm I}(\boldsymbol{q},\boldsymbol{p})\sigma_E(\boldsymbol{q},\boldsymbol{p}), \tag{4}$$

where $\sigma_E(\boldsymbol{q},\boldsymbol{p}) = 2\pi\hbar D_{\rm F}(E)\rho_n(\boldsymbol{q},\boldsymbol{p})$.

Notice that $I(E)$ is a probability distribution over the energy since

$$\int I(E)dE \approx 1. \tag{5}$$

which follows from completeness of the basis set $\{\psi_n(\boldsymbol{q})\}$ (disregarding continuous spectrum):

$$1 = \sum_n <\psi_{\rm I}|\psi_n>^2 = \frac{dE_n}{dn}\sum_n I(E_n) \approx \frac{dE}{dn}\int I\left(E(n)\right)dn = \int I(E)dE, \tag{6}$$

where functions $I(E)$ and $E(n)$ are defined as some interpolations of $I(E_n)$ and E_n on continuous range of arguments (the above proof is given for one-dimensional case, but it can be generalized to any dimensions).

1.1 Classical limit for the acceptor state

In the limit of $\hbar \to 0$

$$\sigma_E(\boldsymbol{q},\boldsymbol{p}) = \delta(H(\boldsymbol{q},\boldsymbol{p}) - E), \tag{7}$$

and $\rho_{\rm I}(\boldsymbol{q},\boldsymbol{p})$ tends to δ-function in the phase space centered at the point of minimum, $(\boldsymbol{q}_{\rm min},\boldsymbol{p}_{\rm min})$, of $H_{\rm I}(\boldsymbol{q},\boldsymbol{p})$. This classical limit corresponds to a particle resting at the point of minimum of the potential $V_{\rm I}(\boldsymbol{q})$.

Since in the classical limit the functions $\rho_{\rm I}(\boldsymbol{q},\boldsymbol{p})$ and $\sigma_E(\boldsymbol{q},\boldsymbol{p})$ don't overlap, the integral (4) is zero except one special case when $E = H_{\rm I}(\boldsymbol{q}_{\rm min},\boldsymbol{p}_{\rm min})$, i.e.

$$I(E) \to I_{0,0}(E) = \delta\left(H_{\rm I}(\boldsymbol{q}_{\rm min},\boldsymbol{p}_{\rm min}) - E\right). \tag{8}$$

In (8), lower zero indexes refer to the classical limit both for the initial and for the final state Wigner functions. Alternatively, we introduce the approximation

$$I_{\infty,0}(E) = \int d\boldsymbol{q}d\boldsymbol{p}\rho_{\rm I}(\boldsymbol{q},\boldsymbol{p})\delta(H(\boldsymbol{q},\boldsymbol{p}) - E) \tag{9}$$

by replacing in Eq. (4) the Wigner function of the final state by its classical limit, and leaving the Wigner function of the initial state unchanged. The approximation (9) is useful if the Wigner function of the donor is known explicitly. The examples are a harmonic oscillator,

$$H_{\rm I}(\boldsymbol{q},\boldsymbol{p}) = \frac{1}{2}\sum_{i=1}^{N}(p_i^2 + \omega_i^2 q_i^2), \tag{10}$$

with the Wigner function

$$\rho_{\rm I}(\boldsymbol{q},\boldsymbol{p}) = \frac{1}{(\pi\hbar)^N}\exp\left(\tfrac{1}{\hbar}\sum_{i=1}^{N}(\omega_i^{-1}p_i^2 + \omega_i q_i^2)\right), \tag{11}$$

and the Morse oscillator,

$$H_{\rm I}(q,p) = \frac{1}{2}p^2 + \frac{1}{2\beta^2}\left[1 - \exp(-\beta q)\right]^2,\ \beta = \left(\hbar(j+\tfrac{1}{2})\right)^{-1/2}, \tag{12}$$

with the Wigner function [1]

$$\rho_{\rm I}(q,p) = \frac{2}{\pi\hbar\Gamma(2j)}\xi^{2j}K_{-2ip/(\beta\hbar)}(\xi),\ \xi = (2j+1)\exp(-\beta q). \tag{13}$$

Notice that both $I_{\infty,0}(E)$ and the cruder approximation $I_{0,0}(E)$ share the normalization property (6).

In this section, we use quasiclassical approximation for the initial wave function,

$$\psi_{\rm I} = \exp\left(-\tfrac{1}{\hbar}(S_0 + S_1\hbar + \dots)\right). \tag{14}$$

In Eq. (14), S_0 is the function satisfying the equation

$$H_{\rm I}(\boldsymbol{q}, i\boldsymbol{\nabla}S_0) = E. \tag{15}$$

Since momenta enter $H(\boldsymbol{q},\boldsymbol{p})$ quadratically, and the potential $V(\boldsymbol{q},\boldsymbol{p})$ enters $H(\boldsymbol{q},\boldsymbol{p})$ linearly, then Eq. (15) is Hamilton - Jacobi, or eikonal equation in the upturned potential $-V(\boldsymbol{q},\boldsymbol{p})$. It may be shown that

$$S_0 = \tfrac{1}{2}\sum_{i=1}^{N}\omega_i Q_i^2 + \mathrm{cubicandhigherorderterms}, \tag{16}$$

where Q_i are normal mode coordinates and $\omega_i = \frac{\partial^2}{\partial Q_i^2} V$ are frequencies in the potential $V(\boldsymbol{q}, \boldsymbol{p})$. Recurrence relations for calculation of cubic and higher order terms in Eq. (16) are given in [2].

Substituting Eq. (14) into Eq. (2) and estimating the integral by Laplace's method we obtain

$$\rho_{\mathrm{I}}(\boldsymbol{q}, \boldsymbol{p}) = (\pi\hbar)^{-N} C(\boldsymbol{q}, \boldsymbol{p}) \exp\left(-\tfrac{2}{\hbar} W(\boldsymbol{q}, \boldsymbol{p})\right), \tag{17}$$

where $W(\boldsymbol{q}, \boldsymbol{p})$ is the minimum or the stationary point of the function $\eta \mapsto \frac{1}{2}\left[S_0(\boldsymbol{q}+\boldsymbol{\eta}) + S_0(\boldsymbol{q}-\boldsymbol{\eta})\right] - i\boldsymbol{\eta}\boldsymbol{p}$. In a particular case of a harmonic oscillator,

$$W(\boldsymbol{q}, \boldsymbol{p}) = \tfrac{1}{2} \sum_{i=1}^{N} \left(\omega_i q_i^2 + \omega_i^{-1} p_i^2\right) \tag{18}$$

and $C(\boldsymbol{q}, \boldsymbol{p}) = 1$ in agreement with the exact formula (11).

The function (17) is changing rapidly in scale $\sim \hbar$ so that for small $\hbar$ only a vicinity of one point where $H(\boldsymbol{q}, \boldsymbol{p}) = E$ and where $\rho_{\mathrm{I}}(\boldsymbol{q}, \boldsymbol{p})$ is maximal contributes to the integral (9). We assume that $W(\boldsymbol{q}, \boldsymbol{p})$ has a minimum $(\boldsymbol{q}^*, \boldsymbol{p}^*)$ under a constraint $H(\boldsymbol{q}, \boldsymbol{p}) = E$ at which point $\boldsymbol{\nabla} W = \lambda \boldsymbol{\nabla} H$. We use a coordinate system in the phase space with the first axis along $\boldsymbol{\nabla} H$ and 2-nd, 3-rd, ..., $2N$-th axes perpendicular to $\boldsymbol{\nabla} H$ and with an origin at the point $(\boldsymbol{q}^*, \boldsymbol{p}^*)$. We expand H and W in Taylor series around $(\boldsymbol{q}^*, \boldsymbol{p}^*)$ in this basis set,

$$H = H^* + H_1 x_1 + \frac{1}{2} \sum_{i,j=1}^{2N} H_{ij} x_i x_j + \dots, \tag{19}$$

$$W = W^* + W_1 x_1 + \frac{1}{2} \sum_{i,j=1}^{2N} W_{ij} x_i x_j + \dots, \tag{20}$$

where

$$H^* = H(\boldsymbol{q}^*, \boldsymbol{p}^*) = E,\ W^* = W(\boldsymbol{q}^*, \boldsymbol{p}^*),$$
$$H_1 = \partial H/\partial x_1 = \boldsymbol{\nabla} H,\ W_1 = \partial W/\partial x_1 = \lambda H_1 = \pm|\boldsymbol{\nabla} W|,$$
$$H_{ij} = \partial^2 H/\partial x_i \partial x_j,\ W_{ij} = \partial^2 W/\partial x_i \partial x_j,$$

and all derivatives are estimated at the point $(\boldsymbol{q}^*, \boldsymbol{p}^*)$.

After integration over x_1 in Eq. (9) we arrive to the integral in $2N-1$ variables,

$$I_{\infty,0}(E) = (\pi\hbar)^{-N} \exp\left(-\tfrac{2}{\hbar} W^*\right) \int G(x_2, x_3, \dots, x_{2N}) dx_2 dx_3 \dots dx_{2N}, \tag{21}$$

where

$$G(x_2, x_3, \dots, x_{2N}) = \textstyle\int dx_1 f(x_1) \delta\left(g(x_1)\right) = f(x_1^{(0)})/g'(x_1^{(0)}), \tag{22}$$

$$f(x_1) = \rho_{\mathrm{I}},\ g(x_1) = H - H^*, \tag{23}$$

and $x_1^{(0)}$ is a root of the function $g(x_1)$ that goes to zero as $x_2, x_3, \dots, x_{2N} \to 0$. Eq. (22) follows from a general formula

$$\int dx_1 f(x_1)\delta\left(g(x_1)\right) = \sum_i f(x_1^{(i)})/\left|g'(x_1^{(i)})\right|, \tag{24}$$

with summation over all the roots $x_1^{(i)}$ of the function $g(x_1)$. Here, we consider small $x_2, x_3, \dots, x_{2N} \to 0$, and only one root $x_1^{(0)} \approx 0$ with $g'(x_1^{(0)}) \approx |\boldsymbol{\nabla} H| > 0$.

Using Eq. (19) and (20) after algebraic manipulations we obtain

$$x_1^{(0)} = -\tfrac{1}{2H_1}\textstyle\sum_{i,j=2}^{2N} H_{ij}x_ix_j + \dots, \tag{25}$$

$$f(x_1^{(0)}) = C\exp\left(-\tfrac{1}{\hbar}\textstyle\sum_{i,j=2}^{2N}(W_{ij} - \tfrac{W_1}{H_1}H_{ij})x_ix_j + \dots\right), \tag{26}$$

$$g'(x_1^{(0)}) = H_1 + \textstyle\sum_{i=2}^{2N} H_{1i}x_i + \tfrac{1}{2}\sum_{i,j=2}^{2N}\left(H_{1ij} - \tfrac{H_{11}}{H_1}H_{ij}\right)x_ix_j + \dots. \tag{27}$$

We leave in Eq. (26) and (27) only leading terms of the expansions, and arrive to the integral

$$I_{1,0}(E) = \frac{C}{H_1(\pi\hbar)^N}\exp\left(-\tfrac{2}{\hbar}W^*\right)\int dx_2dx_3\dots dx_{2N}\left[\exp\left(-\tfrac{1}{\hbar}\sum_{i,j=2}^{2N}F_{ij}x_ix_j\right)\right], \tag{28}$$

where $F_{ij} = W_{ij} - \lambda H_{ij}$ $(i,j = 2,3,\dots,2N)$, $\lambda = W_1/H_1$. The integral (28) is a Gaussian integral, and can be estimated as

$$I_{1,0}(E) = CH_1^{-1}\exp\left(-\tfrac{2}{\hbar}W^*\right)(\pi\hbar\mathrm{Det}F)^{-1/2}. \tag{29}$$

Notice that in Eq. (28) and (29) we replaced $I_{\infty,0}$ by $I_{1,0}$ since we use the quasiclassical approximation (17). In similar way we could consider a refined approximation

$$\rho_{\mathrm{I}}(\boldsymbol{q},\boldsymbol{p}) = (\pi\hbar)^{-N}\exp\left(-\tfrac{2}{\hbar}\left[W_0(\boldsymbol{q},\boldsymbol{p}) + W_1(\boldsymbol{q},\boldsymbol{p})\hbar + W_2(\boldsymbol{q},\boldsymbol{p})\hbar^2\right]\right), \tag{30}$$

and after a lengthier expansions arrive to a more accurate approximation for the overlap integral,

$$I_{2,0}(E) = (\pi\hbar)^{-1/2}\exp\left(-\tfrac{2}{\hbar}(c_0 + c_1\hbar + c_2\hbar^2)\right), \tag{31}$$

where $c_0 = W(\boldsymbol{q}^*,\boldsymbol{p}^*)$, and c_1, c_2 are expressed through partial derivatives of the functions C, W_0, and W_1 at the point $(\boldsymbol{q}^*,\boldsymbol{p}^*)$, see Appendix, where derivations are done in case of two dimensions.

1.2 Quasiclassical limit for the acceptor state

The quasiclassical expansion of the Wigner function of the donor state is organized as a power series in $\mu = \hbar^2$ [3],

$$\sigma_E(\boldsymbol{q},\boldsymbol{p}) = \sigma_E^{(0)}(\boldsymbol{q},\boldsymbol{p}) + \sigma_E^{(1)}(\boldsymbol{q},\boldsymbol{p})\mu + \sigma_E^{(2)}(\boldsymbol{q},\boldsymbol{p})\mu^2 + \dots, \tag{32}$$

where

$$\sigma_E^{(0)}(\boldsymbol{q},\boldsymbol{p}) = \delta(E - H(\boldsymbol{q},\boldsymbol{p})), \tag{33}$$

$$\sigma_E^{(1)}(\boldsymbol{q},\boldsymbol{p}) = -f_2\delta''(E - H(\boldsymbol{q},\boldsymbol{p})) + f_3\delta'''(E - H(\boldsymbol{q},\boldsymbol{p})), \tag{34}$$

and according to [4]

$$f_2 = \tfrac{1}{8}\sum_{i=1}^{N} V''_{ii}/m_i, \tag{35}$$

$$f_3 = \tfrac{1}{24}\sum_{i=1}^{N}(V'_i)^2/m_i + \tfrac{1}{24}\sum_{i,k=1}^{N} V''_{ik}p_ip_k/(m_im_k). \tag{36}$$

Alternatively, the expansion (34) is asymptotically equivalent up to terms $\sim \hbar^2$ to the Airy function representation [4]

$$\sigma_E(\boldsymbol{q},\boldsymbol{p}) = \exp\left[-(H-E)f_2/3f_3 - 2\hbar^2 f_2^3/27f_3^2\right] \times\alpha\mathrm{Ai}\left[\alpha(H - E + \hbar^2 f_2^2/f_3)\right], \tag{37}$$

with

$$\alpha = \left(3\hbar^2 f_3\right)^{-1/3}. \tag{38}$$

Approximation of the acceptor Wigner function by Airy function (37) and the classical approximation of the donor Wigner function by δ-function leads to the following approximation for the overlap integral:

$$I_{0,1}(E) = \exp\left[-(H_{\min}-E)f_2/3f_3 - 2\hbar^2 f_2^3/27f_3^2\right] \times\alpha\mathrm{Ai}\left[\alpha(H_{\min} - E + \hbar^2 f_2^2/3(?)f_3)\right], \tag{39}$$

where $H_{\min} = (\boldsymbol{q}_{\min},\boldsymbol{p}_{\min})$, and f_2 and f_3 in (39) are evaluated at the point $(\boldsymbol{q}_{\min},\boldsymbol{p}_{\min})$. Notice that (39) satisfies the normalization condition (6).

Finally, we determine the approximation $I_{1,1}$ by truncating both expansions, Eq. (31) and (32) to the first two terms. We use here the following formulas

$$\int dx_1 f(x_1)f_2(x_1)\delta''(g(x_1)) = h^3 f_2 f'' + \dots, \tag{40}$$

$$\int dx_1 f(x_1)f_3(x_1)\delta'''(g(x_1)) = -h^4 f_3 f''' - \left(3h^4 f'_3 + 6h^2 h' f_3\right) f'' + \dots, \tag{41}$$

where functions f and g are defined as in Eq. (23), $h = 1/g'$, differentiation is over x_1, and functions with unspecified arguments are evaluated at the root $x_1^{(0)}$ of the function $g(x_1)$. In Eq. (40) and (41) only terms of orders $\sim 1/\hbar^3$ and $\sim 1/\hbar^2$ are displayed, terms containing $f' \sim 1/\hbar$ and $f \sim 1$ are of subdominant orders, and are replaced by dots.

The approximation $I_{1,1}$ is the sum of $I_{1,0}$, Eq. (29), and an additional term

$$\delta I = \hbar^2 \int \sigma_E^{(1)}(\boldsymbol{q},\boldsymbol{p})\rho_{\mathrm{I}}(\boldsymbol{q},\boldsymbol{p}) =$$
$$\hbar^2 \int d\boldsymbol{q}d\boldsymbol{p}\left[-f_2\delta''\left(E - H(\boldsymbol{q},\boldsymbol{p})\right) + f_3\delta'''\left(E - H(\boldsymbol{q},\boldsymbol{p})\right)\right]\rho_{\mathrm{I}}(\boldsymbol{q},\boldsymbol{p}). \tag{42}$$

Disregarding in (42) terms that go to zero as $\hbar \to 0$, it can be evaluated using (40) and (41) as

$$\delta I =$$
$$-4\frac{W^2}{H_1^3}f_2G_2\rho_{\mathrm{I}} - 8\hbar^{-1}\frac{W^3}{H_1^4}f_3G_3\rho_{\mathrm{I}} - 4W^2(3H_1^{-4}f_3'G_2 - 6H_1^{-4}H''f_3G_2)\rho_{\mathrm{I}} =$$
$$a_2G_2\rho_{\mathrm{I}} + \hbar^{-1}a_3G_3\rho_{\mathrm{I}}. \tag{43}$$

In Eq. (43), all functions are evaluated at the "leakage" point $(\boldsymbol{q}_*, \boldsymbol{p}_*)$, derivatives are taken in direction of $\boldsymbol{\nabla}H$, for example $f_3' = (\boldsymbol{\nabla}f_3, \boldsymbol{\nabla}H)/H_1$, $H_1 = |\boldsymbol{\nabla}H|$, and G_2, G_3 are Gaussian integrals similar to (21) that appear as a result of expansion of the functions f'', f''' over variables $x_2, x_3, ..., x_{2N}$ with subsequent integration over these variables, and will be derived later. In a similar fashion, $I_{1,0}$ can be rewritten as

$$I_{1,0} = G_0H_1^{-1}\rho_{\mathrm{I}} = a_0G_0\rho_{\mathrm{I}}, \tag{44}$$

where $a_0 = H_1^{-1}$. Combining Eq. (43) and (44), we finally have

$$I_{1,0} = (a_0G_0 + a_2G_2 + \hbar^{-1}a_3G_3)\rho_{\mathrm{I}} \approx$$
$$(a_0G_0 + a_2G_2)(\pi\hbar)^{-N}C\exp\left(\tfrac{1}{\hbar}\left(-2W + \frac{a_3G_3}{a_0G_0}\right)\right). \tag{45}$$

We found finally that $\frac{a_3G_3}{a_0G_0} = -8\lambda^3 f_3\frac{G_3}{G_0}$ is the correction to the exponent, and a_2G_2 is the correction to the Gaussian factor to a less accurate approximation (29).

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