

Quasiclassical Approximation for Rotational and Vibrational Transition Probabilities in Gas-Surface Scattering

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Abstract. Quasiclassical approximation for probabilities of rotational and vibrational transitions initiated by molecular-surface interactions is studied. Only inelastic processes in the molecule itself is considered (molecule-surface energy exchange is out of the present consideration). The necessity of usage for initial and final rotational wave functions the Legendre polynomials instead of previously proposed plain rotator ones is shown.

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INTRODUCTION

Direct Monte-Carlo simulation of molecular gas flow near the solid surface requires both the data on inelastic cross-sections for bulk processes [1] and the data on molecule-surface inelastic scattering probabilities. Classical models for these probabilities are limited in their practical use, while quantum mechanics approaches are too complicated for obtaining the approximations for a wide range of energies and large number of open channels [2] typical for gas-dynamic problems. Therefore the most promising approach for getting approximations for gas-surface interaction characteristics is the quasiclassical one. One of the versions of the uniform quasiclassical approximation for molecule-molecule collisions was developed in [3, 4]. Expressions obtained there for inelastic transition probabilities were used for DSMC computations in [1]. A corresponding approach for molecule-surface scattering was formulated in [5]. Here we represent similar approximations for rotational and vibrational transitions initiated by molecular-surface interactions. We restrict ourselves to inelastic processes in a molecules themselves initiated by their collision with the surface, and do not consider molecule-surface energy exchange. Surface is treated as a rigid flat plane. This leads to the total molecule energy conservation during the collision. The main difference from the previous results consists in the usage of more accurate approximation for asymptotic rotational wave functions. The new choice of these functions leads to essential change of the inelastic probability values.

THE UNIFORM QUASICLASSICAL REPRESENTATION

In the framework of a quasiclassical approximation a relative to surface molecular motion is described in the phase space (\vec{p}, \vec{r}) , with $\vec{r} = (X, Y, z) = (\vec{R}, z)$, z being the normal distance to the surface, while X and Y are orthogonal co-ordinates in the surface plane (with X directed along one of the crystal principal axes if surface structure is taken into consideration). Rotational and vibrational molecular motion is described using action-angle variables $(\vec{I}, \vec{\varphi})$ [3] with $\vec{\varphi}$ being the vector of angular variables ($0 \leq \varphi_i \leq 2\pi$) and \vec{I} that of conjugated canonical action variables connected with the quantum numbers vector \vec{n} through the quantization rule: $I_{nq} = \hbar(n_q + 1/2)$ for vibration degrees of freedom, and $I_j = \hbar\sqrt{j(j+1)}$, $I_{m_j} = \hbar m_j$ for rotation ones (only

diatomic or linear molecules are considered here for simplicity). To simplify the notation we shall sometimes denote $P = (\vec{p}, \vec{I})$ and $Q = (\vec{r}, \vec{\varphi})$. The Hamiltonian function of the corresponding classical problem can be written in the form

$$H = p^2/2\mu + H_0(\vec{I}) + V(\vec{r}, \vec{I}, \vec{\varphi}) = H_f + V, \quad (1)$$

where μ is the molecule mass, $H_0(\vec{I})$ is the Hamiltonian function of its internal motion, H_f is the Hamiltonian function of its free motion and V is the molecule-surface interaction potential. Since coordinate \vec{r} increase infinitely when $t \rightarrow \pm\infty$ while $\vec{\varphi}$ changes periodically it is much more convenient to formulate the correspondent classical trajectory problem in terms of new variables: $P' = P$, $Q' = Q - \partial H_f / \partial P \cdot t$.

Using canonical transformation one obtains the equations of motion (apostrophes are omitted)

$$dP/dt = -\nabla_Q V(Q + \partial H_f / \partial P t, P), \quad dQ/dt = \nabla_P V(Q + \partial H_f / \partial P t, P). \quad (2)$$

The correspondent boundary conditions are used in a form $P(-\infty) = P_i$, $Q(0) = Q_0$, $P(\infty) = P_f$, defining the “in-” and “out-going” brunches of the trajectory.

The quasiclassical representation for the molecule – plane surface scattering Γ -profiles with the former internal degrees of freedom excitation in the introduced variables can be written in the form

$$\langle P_f | \Gamma | P_i \rangle = \int \frac{d\vec{\varphi}_0}{(2\pi)^m} \exp[i\vec{\varphi}_0 \cdot (\vec{N}_i - \vec{N}_f) - iS(\vec{\varphi}_0)/\hbar], \quad S(\vec{\varphi}_0) = \int_{-\infty}^{\infty} V(z(t), \vec{\varphi}_0 + \vec{\omega}t, \vec{P}) dt \quad (3)$$

Here \vec{N} is a complete vector of the molecular quantum numbers, $\vec{\omega} = \partial H / \partial \vec{I}$ is a correspondent frequency vector, and m is a dimension of the space of internal degrees of freedom. Interacting potential V is assumed to have strong dependence on z -co-ordinate while the dependence on internal co-ordinates is considered as a perturbation: $V(z, \vec{\varphi}, \vec{I}) = V_0(z) + (a_r V_r + a_a V_a) \cdot v(\vec{\varphi}, \vec{I})$, where the elastic part of the potential V_0 is represented as a sum of repulsive V_r and attractive V_a parts: $V_0(z) = V_r(z) + V_a(z)$. For $V_0(z)$ the Born-Maier approximation:

$$A \exp(-\lambda z) \quad (V_{BMa}(z) \equiv 0), \text{ or Morse one: } D \left[\exp\left(-2 \frac{z-R_0}{d}\right) - 2 \exp\left(-\frac{z-R_0}{d}\right) \right] \equiv V_{Mr} + V_{Ma} \text{ is used.}$$

For both cases one-dimensional equations of motion can be solved exactly. According to generalized eikonal approximation approach [3] the trajectory is separated on in- and out-going parts with correspondent boundary conditions ($P(\mp\infty) = P_{i,f}$). In the framework of perturbation theory this compounded trajectory is used for action increment calculation determining the exponent in the expression for T -amplitude.

The term $v(\vec{\varphi}, \vec{I})$ is responsible for rotational-vibrational transitions and is represented as an expansion over Q_q series and into Fourier series over $P_l(\cos \chi)$. Here Q_q are terms proportional to the deviations of the Cartesian atomic co-ordinates in the molecule from their equilibrium values $r_q - r_{eq}$, $P_l(\cos \chi)$ are Legendre polynomials, $\cos \chi = \sqrt{1 - m_j^2 / j^2} \cos \varphi_j$, j is the quantum number that corresponds to the molecule angular momentum, m_j is the quantum number that corresponds to its z -axis projection, and φ_j is the correspondent angle variable. A transition from Cartesian co-ordinates to the action-angle ones is achieved by transformation $Q_q = \sqrt{\varepsilon_{nq}} \cos \varphi_q$, $\varepsilon_{nq} = E_{nq} / \hbar \omega_{eq}$, where E_{nq} is the energy of the q -th vibrational mode while ω_{eq} is correspondent harmonic vibration frequency.

For vibrational frequency the inharmonic approximation $\omega_{nq} = \omega_{eq} (1 - x_{eq} (n_q + 1/2))$ is used as a rule. For diatomic spectrum the quasiclassical approximation based on rotating Morse oscillator model that takes into account rotational-vibrational coupling was suggested in [6]. More exact approximation for vibration-rotation spectrum for

diatomics can be achieved by the use of Tietz-Wei potential model [7] $V_{TW} = D_e \left[\frac{1 - e^{-\beta(r-r_e)}}{1 - \xi e^{-\beta(r-r_e)}} \right]^2$, $\beta = (1 - \xi)/d$, since this model contains three fit parameters [8, 9]. For purely vibrational motion one has

$$E_{nq} = \hbar \omega_{eq} (n_q + 1/2) \frac{(1 - x_e (1 - \xi)(n_q + 1/2))(1 + \xi x_{eq} (1 - \xi)(n_q + 1/2))(1 + \xi x_{eq} (n_q + 1/2))}{(1 + 2\xi x_{eq} (n_q + 1/2))^2}, \quad \omega_{nq} = \frac{\partial E_{nq}}{\partial I_{nq}}.$$

Finally, we will use the molecule-surface interaction potential in a following form:

$$V(z, \vec{\varphi}, \vec{I}) = V_0(z) + \left[V_r \sum_{q=1}^{N_V} a_{VTrq} Q_q + V_a \sum_{q=1}^{N_V} a_{VTaq} Q_q + V_r \sum_{\substack{p=1, q=1 \\ p \neq q}}^{N_V} a_{VVrpq} Q_p Q_q + V_a \sum_{\substack{p=1, q=1 \\ p \neq q}}^{N_V} a_{VVapq} Q_p Q_q + \right. \\ \left. + (V_r a_{RT_r} + V_a a_{RTa}) P_l(\cos \chi(\varphi_j)) + V_r \sum_{q=1}^{N_V} a_{VRRq} Q_p Q_q P_l(\cos \chi(\varphi_j)) + V_a \sum_{q=1}^{N_V} a_{V Raq} Q_p Q_q P_l(\cos \chi(\varphi_j)) \right] \quad (4)$$

Here N_V is the number of vibrational degrees of freedom, coefficients a with different subscripts are potential fitting parameters (anisotropy parameters) responsible for VT , VVT , RT , and VRT transitions respectively. Subscript $l = 1$ is for asymmetric molecules and $l = 2$ is for symmetric ones. Coefficients with subscripts r and a are responsible for contributions from repulsive and attractive parts of the potential respectively.

For this potential model one can write the action increment S from (3) in an additive form

$$S = S_0 + S_{VT} + S_{VV} + S_{RT} + S_{VR}, \quad (5)$$

with terms determined by correspondent items in potential (4). The S_0 term determines the amplitudes phase and therefore is not essential in our case. Others can be written in the form

$$S_{VT} = \hbar \sum_q F_{VTq} \cos(\varphi_{nq}), \quad S_{VV} = \hbar \sum_{\substack{p, q \\ p \neq q}} F_{VVpq} \cos(\varphi_{npq}), \quad \varphi_{npq} = \varphi_{np} - \varphi_{nq} \\ S_{RT} = \hbar F_{RT} \cos(\varphi_j), \quad S_{VR} = \hbar \sum_q F_{VRq} \cos(\varphi_{njq}), \quad \varphi_{njq} = \varphi_{nq} - \varphi_j. \quad (6)$$

For F -factors calculated with Morse model for elastic part of the potential one has

$$F_{VTq} = F_{VTqi} + F_{VTqf}, \quad (7) \\ F_{VTqk} = \varepsilon_{VTqk}^{1/2} \frac{\pi d}{4 \hbar \text{sh} \frac{\pi \omega_{nqk} \mu d}{p_{zk}}} \left[a_{VTrq} \omega_{nqk} \mu d \text{ch} \frac{\omega_{nqk} \mu d (\pi - \arctg(\sqrt{p_{zk}^2 / (2 \mu D)}))}{p_{zk}} - \right]$$

$$-\left(2a_{VTaq} - a_{VTrq}\right)\sqrt{2\mu D} \operatorname{sh} \frac{\omega_{nqk} \mu d \left(\pi - \arctg\left(\sqrt{p_{zk}^2/(2\mu D)}\right)\right)}{p_{zk}} \Bigg], \quad (8)$$

$$F_{VVpqk}^- = \varepsilon_{VVpqk}^{1/2} \frac{\pi d}{4\hbar \operatorname{sh} \frac{\pi \omega_{npqk}^- \mu d}{p_{zk}}} \left[a_{VVrpq} \omega_{npqk}^- \mu d \operatorname{ch} \frac{\omega_{npqk}^- \mu d \left(\pi - \arctg\left(\sqrt{p_{zk}^2/(2\mu D)}\right)\right)}{p_{zk}} - \right. \\ \left. - \left(2a_{Vvapq} - a_{Vvrpq}\right)\sqrt{2\mu D} \operatorname{sh} \frac{\omega_{npqk}^- \mu d \left(\pi - \arctg\left(\sqrt{p_{zk}^2/(2\mu D)}\right)\right)}{p_{zk}} \right], \quad (9)$$

$$F_{RTk}^{(l)} = \frac{\pi d(l+1)}{8l\hbar \operatorname{sh} \frac{\pi \omega_{jk} \mu d}{p_{zk}}} \left(1 - \frac{m_{jk}^2}{j_k^2}\right)^{1/2} \left[a_{RT r} \omega_{jk} \mu d \operatorname{ch} \frac{l \omega_{jk} \mu d \left(\pi - \arctg\left(\sqrt{p_{zk}^2/(2\mu D)}\right)\right)}{p_{zk}} - \right. \\ \left. - \left(2a_{RTa} - a_{RT r}\right)\sqrt{2\mu D} \operatorname{sh} \frac{l \omega_{jk} \mu d \left(\pi - \arctg\left(\sqrt{p_{zk}^2/(2\mu D)}\right)\right)}{p_{zk}} \right] \equiv \bar{F}_{RTk}^{(l)} \left(1 - \frac{m_{jk}^2}{j_k^2}\right)^{1/2}, \quad (10)$$

$$F_{VRqk}^{(l)-} = \frac{\pi d(l+1)}{16l\hbar \operatorname{sh} \frac{\pi \omega_{njqk}^{(l)-} \mu d}{p_{zk}}} \left(1 - \frac{m_{jk}^2}{j_k^2}\right)^{1/2} \left[a_{VRrq} \omega_{njqk}^{(l)-} \mu d \operatorname{ch} \frac{\omega_{njqk}^{(l)-} \mu d \left(\pi - \arctg\left(\sqrt{p_{zk}^2/(2\mu D)}\right)\right)}{p_{zk}} - \right. \\ \left. - \left(2a_{VRaq} - a_{VRrq}\right)\sqrt{2\mu D} \operatorname{sh} \frac{\omega_{njqk}^{(l)-} \mu d \left(\pi - \arctg\left(\sqrt{p_{zk}^2/(2\mu D)}\right)\right)}{p_{zk}} \right] \equiv \bar{F}_{VRqk}^{(l)-} \left(1 - \frac{m_{jk}^2}{j_k^2}\right)^{1/2}, \quad (11)$$

where $\omega_{npk}^- = |\omega_{nqk} - \omega_{npk}|$ and $\omega_{njqk}^{(l)-} = |\omega_{nqk} - l\omega_{jk}|$, $k = i, f$, $\omega_j = \partial H_0 / \partial I_j$.

F -factor for instance for RT excitation in the case of Born-Maier elastic potential has the form

$$F_{RTk}^{(l)} = a_{RT r} \frac{\pi(l+1)\mu\omega_{jk}}{4l\lambda^2 \hbar \operatorname{sh} \frac{\pi \omega_{nqk} \mu d}{p_{zk}}} \left(1 - \frac{m_{jk}^2}{j_k^2}\right)^{1/2} = \bar{F}_{RTk}^{(l)} \left(1 - \frac{m_{jk}^2}{j_k^2}\right)^{1/2}. \quad (12)$$

TRANSITION PROBABILITIES

Each term in (5) determines correspondent Γ -profile squared modulus of which determines in turn the probability of the correspondent process: $P_p = |\Gamma_p|^2$. Quasiclassical representation (3) for the Γ -profile with action increment S in the form (5), (6) give rise to the partial Γ -profiles for different transitions each of whom reduces to Bessel function approximation that leads to the following expressions for probabilities:

$$P_{VTq} = J_{|\Delta n_q|}^2(F_{VTq}), \quad \Delta n_q = n_{qf} - n_{qi}, \quad (13)$$

$$P_{VVPq} = J_{\kappa_{n pq}^-}^2(F_{VVPq}^-), \quad \kappa_{n pq}^- = |\Delta n_p - \Delta n_q|/2, \quad (14)$$

$$P_{RT} = \frac{2\tilde{j}+1}{2j_i+1} \frac{\Gamma(1/2)\Gamma(|\Delta j|+1)/2}{2\Gamma(|\Delta j|/2+1)} J_{|\Delta j|/l}^2(\bar{F}_{RT}^{(l)}), \quad \Delta j = j_f - j_i, \quad \tilde{j} = \min\{j_i, j_f\}, \quad (15)$$

$$P_{VRq} = \frac{2\tilde{j}+1}{2j_i+1} \frac{\Gamma(1/2)\Gamma(|\Delta j|+1)/2}{2\Gamma(|\Delta j|/2+1)} J_{|\kappa_{njq}^-}^2(\bar{F}_{VRq}^{(l)}), \quad \kappa_{njq}^- = |\Delta n_q - \Delta j/l|/2, \quad (16)$$

Since the z -projections of the angular momentum are not fixed the averaging over initial quantum numbers m_{ji} and summation over final ones m_{jf} is done. During fulfilling this operation the summation is replaced by integration and it is accounted that integration over $\varphi_{m_j 0}$ give rise to Kronecker's symbol $\delta_{m_{ji}, m_{jf}}$ multiplier in the expressions for both RT - and VR -transition probabilities.

In general for all intermodal processes (VVT and VRT) the correspondent probability contains one more multiplier that is $J_{\kappa_p^+}^2(F_p^+)$ where F_p^+ are calculated with $\omega_{qp}^+ = (\omega_q + \omega_p)$ instead of ω_{qp}^- . It is assumed however that the correspondent adiabatic parameters $\Lambda_{zk}^+ = \pi\omega^+ \mu d / p_{zk}$ are large for all these processes, so that the F^+ -factors are small enough ($F^+ \ll 1$). In this case Bessel function degenerates giving rise to Kronecker's symbol. For VVT transitions it is $\delta_{\kappa_{n pq}^+, 0}$, that leads to so called adiabatic propensity rule [10]: $\Delta n_p = -\Delta n_q$. For VRT transitions this rule leads to the relationship $\Delta n = -\Delta j/l$. These expressions are also interpreted as generalized isoquantum transition conditions [10].

RECALCULATION RULES

Special attention should be paid on the fact that at the presence of rotational degrees of freedom in the representation (3) the wave functions of plain rotator (plane waves in action-angle space) are used for initial and final states that are the Fourier harmonics. For more correct description the Legendre polynomials $P_j(\cos \vartheta)$ should be used as the asymptotic wave functions. In this case it is more convenient to calculate only excitation probabilities from the ground state and recalculate the whole transition probability matrix using these excitation probabilities and Vigner's coefficients [11, 12]. This approach is based on the relationship

$$P_{j_f}(\cos \vartheta) P_{j_i}(\cos \vartheta) = \sum_{j_s=0}^{\infty} (j_f j_i j_s) P_{j_s}(\cos \vartheta) \quad \text{where} \quad (j_f j_i j_s) = \begin{pmatrix} j_f & j_i & j_s \\ 0 & 0 & 0 \end{pmatrix}^2 \quad \text{are squared Vigner's}$$

coefficients. Then instead of cylindrical Bessel approximation (15) for RT transition probability one obtains the spherical Bessel approximation:

$$P_{RT} = \sum_{j_s} (j_f j_i j_s) \frac{\Gamma(1/2)\Gamma((j_f+1)/2)}{2\Gamma(j_f/2+1)} j_{j_s}^2(\bar{F}_{RT}^{(l)}), \quad (17)$$

with $j_n(F) = \frac{1}{2} \sqrt{2\pi/F} J_{n+1/2}(F)$ and $(j_f - j_i)/l$ being integer. If $F_{RT}^{(l)}$ is a function of initial and final states (as for (7) and (10)) expression (17) is called generalized recalculation rule [12], otherwise (as for instance for sudden perturbation approximation) it is called ordinary recalculation rule [12].

RESULTS AND CONCLUSIONS

The HD + Pt(111) colliding system was studied with Morse potential parameters taken from [13] $D = 57.75$ meV, $d = 1.058$ Å, and anisotropy parameters $a_{RT_r} = 0.16$ and $a_{RT_a} = 0$. Collisions normal to the surface were considered. Excitation probabilities for different transitions as a function of the initial energy E_i for the range $100 \div 1000$ meV are presented on Fig. 1.a-e. Transition probabilities calculated using cylindrical Bessel approximation exceed the correspondent values obtained in the framework of spherical Bessel approximation by an order of magnitude. This means that the use of the plain rotator approximation for asymptotical wave functions leads to essential errors in rotational transition probabilities evaluation.

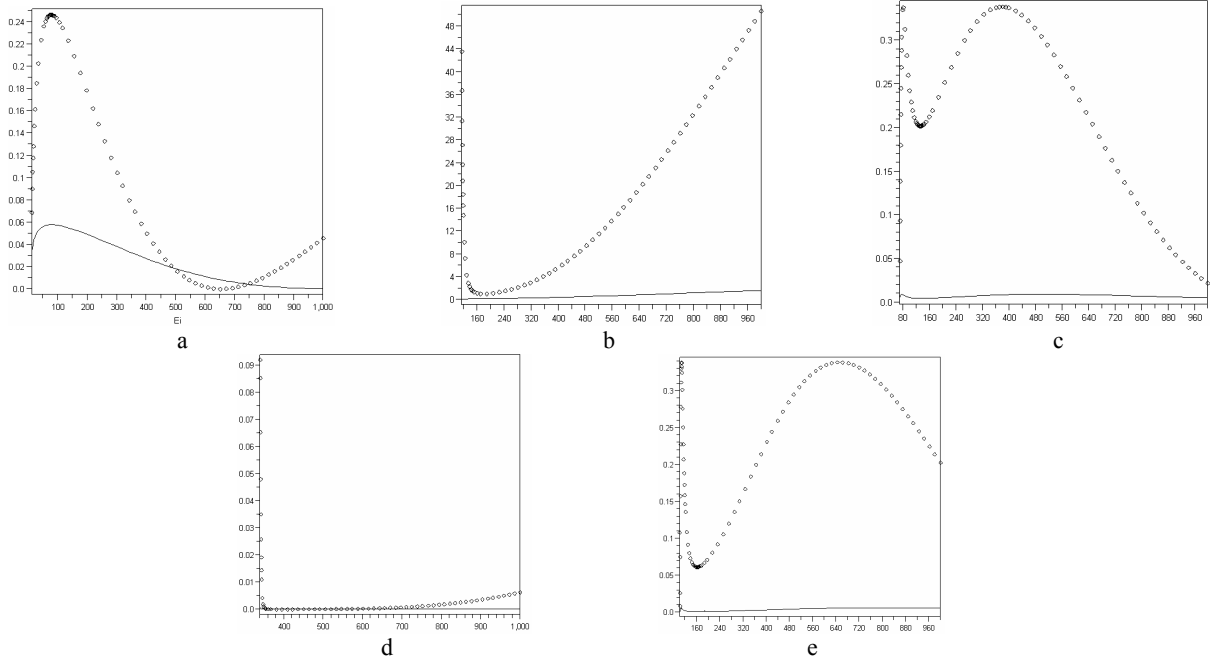


FIGURE 1. Transition probabilities as a function of the initial energy E_i (meV) for $0 \rightarrow 1$ (a), $0 \rightarrow 4$ (b), $5 \rightarrow 6$ (c), $5 \rightarrow 9$ (d), $(8 \rightarrow 9)$ (e) transitions; line – spherical Bessel approximation, dots – cylindrical Bessel approximation.

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