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On the quasiclassical calculation of fundamental and overtone intensities

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Various approximations to the transition dipole moment matrix element $\langle n'|M|n\rangle$ are compared with each other and to exact (numerical) values of this overlap integral for different $n\rightarrow n'$ transitions in a Morse potential with a linear dipole moment function. By partitioning the numerical integral into different contributions that involve the classically allowed and forbidden regions of each wave function, we have learned what conditions must be satisfied for validity of the different approximations. In particular, we consider the Landau approximation to the quasiclassical matrix element in which the exact wave function for the upper state is replaced by the Wentzel–Kramers–Brillouin (WKB) wave function in the classically allowed region of that state. We find that the Landau approximation is more accurate than might have been expected because of the compensation of the neglected tunneling contribution by the singular behavior of the WKB wave function in the classically allowed neighborhood of the turning point. Based on this study, we suggest an improved semiclassical approximation for transition dipole matrix elements that involve an arbitrary dipole moment function. This method is applied to the $n'-0$ transition of a Morse oscillator using a linear dipole moment function; it can reproduce the exact values of the transition dipole moment matrix element to better than 5% for $n'=1$ to $n'=15$. Under the condition that the dipole moment function is slowly varying or decreases monotonically with increasing internuclear separation, a simple expression is presented for estimating relative strengths of neighboring high overtone transitions.

I. INTRODUCTION

In calculating intensities of vibrational transitions, the transition dipole matrix element (TDME)

$$M_{n'n}=\langle n'|M|n\rangle \tag{1}$$

must be evaluated. For a harmonic oscillator and a linear dipole moment function, the allowed transitions are known to be subject to the selection rule $n'=n\pm 1$. For an anharmonic oscillator and a nonlinear dipole moment function, all transitions $n\rightarrow n'$ are allowed, but their intensities decrease with increasing $\Delta n=|n'-n|$. The potentials of most diatomic molecules are well approximated by a Morse function, which resembles a harmonic oscillator near the potential minimum. For a Morse potential, the general form of the TDME is known in analytic form for power and exponential dipole moment functions of the vibrational coordinate (e.g., see Ref. 1 and papers cited therein). The practical application of the corresponding formulas is difficult, however, because of the severe cancellation of different terms that enter into the analytical expression.[1] For other potentials, analytical results are not available and therefore either numerical or approximate methods must be used to calculate the TDME.

In this paper, we compare several approximate methods with the exact quantum result for the Morse oscillator and a linear dipole moment function in which we partition the whole integration range into five regions. These regions are illustrated in Fig. 1.

Region 1 extends from minus infinity (the integration was actually carried out from $R=0$, which is practically equivalent to $x=R-R_e=-\infty$) to the left turning point of the upper state $|n'\rangle$; in this region, the classical motion is forbidden for both lower and upper states.

Region 2 extends from the left turning point of the upper state $|n'\rangle$ to the left turning point of the lower state $|n\rangle$; in this region, the classical motion is forbidden for the lower state and allowed for the upper state.

Region 3 extends from the left turning point of the lower state $|n\rangle$ to the right turning point of the same state; in this region, the classical motion is allowed for both states.

Region 4 extends from the right turning point of the lower state $|n\rangle$ to the right turning point of the upper state $|n'\rangle$; in this region, the classical motion is forbidden for the lower state and allowed for the upper state.

Region 5 extends from the right turning point of the upper state $|n'\rangle$ to infinity; in this region, the classical motion is forbidden for both lower and upper states. By evaluating relative contributions to the TDME from the five different regions, we gain insight into the conditions

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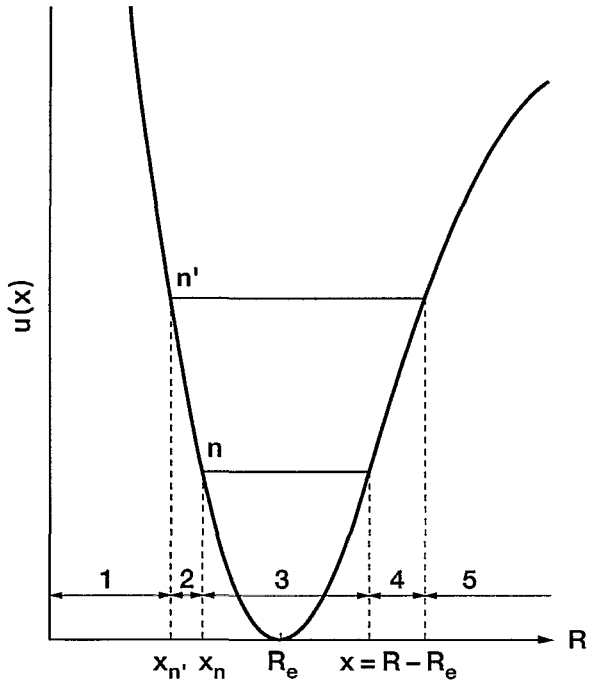

FIG. 1. The five integration regions for a $n \rightarrow n'$ transition.

that define the validity of approximate methods.

The first method, the semiclassical (SC) method, represents one of the possible statements of the correspondence principle[2–5]: if states $|n\rangle$ and $|n'\rangle$ are quasiclassical[6] and not too distant, i.e., if

$$n,n' \gg 1 \tag{2a}$$

and

$$n,n' \gg \Delta n, \tag{2b}$$

then a matrix element $M_{n'n}$ of an operator M is well approximated by the Fourier component of the classical function M at the frequency $\omega_{n'n}=\Delta n \cdot \omega(\bar{n})$. The frequency $\omega(\bar{n})$ characterizes the classical motion of the system along a trajectory specified by the action variable that corresponds to a certain mean "quantum number" $\bar{n}$ that lies between n and n'.

The semiclassical approximation $M(\Delta n,\bar{n})$ to $M_{n'n}$ contains an intrinsic uncertainty $\delta M(\Delta n,\bar{n})$, which is related to the ambiguity of the choice of the trajectory. A rough estimate of $\delta M(\Delta n,\bar{n})$ can be obtained from $M(\Delta n,\bar{n})$ by allowing $\bar{n}$ to vary within its uncertainty range bracketed between n' and n,

$$\delta M(\Delta \mu,\bar{n}) \simeq |M(\Delta n,n')-M(\Delta n,n)|. \tag{3}$$

The semiclassical approximation is valid provided

$$\delta M(\Delta n,\bar{n}) \ll M(\Delta n,\bar{n}). \tag{4}$$

As Δn increases, the value of $M(\Delta n,\bar{n})$ usually decreases, but the ratio $\delta M(\Delta n,\bar{n})/M(\Delta n,\bar{n})$ increases and eventually exceeds unity when Δn approaches $\min(n',n)$.

The second approximate method, which is the Landau method,[2,7] is based on the quasiclassical (QC) approximation and on the assumption that the matrix element $M^L_{n'n}$ is exponentially small with respect to a parameter that contains inverse powers of $\hbar$. The Landau method consists of shifting the integration contour into the complex plane to simplify the integrand that contains the WKB wave function and to solve the integral. Explicitly, conditions (2a) and (2b) are replaced in the Landau method by the conditions

$$n',n \gg 1 \tag{5a}$$

and

$$M^L_{n'n} \text{ is exponentially small.} \tag{5b}$$

Equation (5b) does not restrict how large Δn may be, although it does restrict how small Δn may be. The semiclassical and Landau methods have a common region of applicability in which conditions (2a) and (5a) are satisfied simultaneously.

Since $M(\Delta n,\bar{n})$ is calculated as an integral over a classical trajectory, $M(\Delta n,\bar{n})$ could be expected to provide a good approximation to the portion of the exact TDME that comes from the integration region classically allowed for both quantum states n' and n. Implicit in this statement are the assumptions that the contributions from the classically forbidden regions are negligible and Eq. (4) is satisfied.

We find for our model that the first assumption is incorrect. This result brings up another point concerning the accuracy of the Landau method for calculating quasiclassical matrix elements, which relates to the calculation of dipole matrix elements for overtone transitions.[8–10] Recent results have shown that the Landau method is based on the quasiclassical approximation to the wave functions in regions in which the motion for at least one state is classically allowed.[11] Within this approximation, any contribution from the regions that are classically forbidden for both states are supposed to be negligible. In our study, we found that if the contributions from different regions are calculated on the basis of exact wave functions, the above conclusion is not valid.

This discrepancy raises a general question: why are the quasiclassical results for matrix elements valid far beyond the limits that can be set by inspecting contributions from different regions of the motion? We offer a partial answer to this question below.

On the basis of this study, we suggest an approximation that combines the semiclassical method with the Landau method—the improved semiclassical (ISC) approximation. Although the Landau method describes transitions in which the motion in the lower state is partly classically forbidden, the information needed to implement the ISC formula is purely classical and can be obtained from Fourier analysis of the classical dipole moment at different vibrational energies.

The plan of the paper is as follows: In Sec. II, we set up the model. In Sec. III for transitions with $\Delta n=1$, we compare semiclassical and exact analytical matrix elements for a linear dipole moment function and relate this comparison to our numerical results. In Sec. IV, we consider the

Landau method for transitions with $\Delta n > 1$. Section V describes the ISC approximation for an arbitrary dipole moment function. In Sec. VI, we compare the quasiclassical Landau approximation with the quasiclassical uniform approximation. Section VII summarizes our findings.

II. THE MODEL

We consider the one-dimensional bounded motion of a mass point μ in the field of a Morse potential

$$U(x)=D_e\,[1-\exp(-\alpha x)]^2. \tag{6}$$

The classical trajectory for this problem is known (e.g., see Ref. 12)

$$x(E,t)=\alpha^{-1}\cdot\ln\{1-(E/D_e)^{1/2}\cos[\varphi(t)]\} -\alpha^{-1}\ln(1-E/D). \tag{7}$$

Here, E is the vibrational energy and the phase φ is

$$\varphi(t)=\omega(E)\cdot t=\omega_e\cdot[(D_e-E)/D_e]^{1/2}t, \tag{8}$$

where $\omega(E)$ is the frequency of oscillation at energy E and ω_e is the frequency of harmonic vibrations $\omega_e=\alpha(2D_e/\mu)^{1/2}$; the time $t=0$ corresponds to classical motion starting at the left turning point. The relation between the energy E and the action variable $j=(1/2)\oint p\,dx$ is deduced easily from the differential relation between E and the frequency $\omega(E)$,

$$dE/dj=\omega_e\,[(D_e-E)/D_e]^{1/2}. \tag{9}$$

In this way, we find

$$E(j)=\omega_e\,j(1-j/2J), \tag{10}$$

where J is the maximal action for the bounded motion $J=2D_e/\omega_e$.

The analytic solution of the quantum problem for the Morse potential is also known.[2] The energy levels are obtained from Eq. (10) by the quantization condition

$$j=(n+1/2)\hbar, \tag{11}$$

which yields

$$E_n=\hbar\omega_e(n+1/2)[1-(n+1/2)/2N], \tag{12}$$

where $N=2D_e/\hbar\omega_e$. The integer part of N equals the total number of bound states supported by the Morse potential.

A semiclassical matrix element of a function $M(x)$ is given by the integral

$$M(\Delta n,\bar{n})=(2\pi)^{-1}\int_{-\pi}^{+\pi}M[x(\bar{j},\varphi)]\cdot\cos(\Delta n\varphi)\cdot d\varphi, \tag{13}$$

where $\bar{n}$ and $\bar{j}$ are related through Eq. (11).

In particular, when $M=\alpha x$ (we disregard from now on any additional prefactor), we obtain for $\Delta n>0$ (Ref. 13),

$$M(\Delta n,\bar{n})=-(\Delta n)^{-1}\cdot[(\bar{n}+1/2)/2N]^{\Delta n/2} \times[1-(\bar{n}+1/2)/2N]^{-\Delta n/2}. \tag{14}$$

The quantum mechanical expression for $M_{n'n}$ reads[1] $(n'>n)$

$$M_{n'n}=-(\Delta n)^{-1}\{[1-(n'+1/2)/N]^{1/2} \times[1-(n+1/2)/2N]^{1/2}[1-(n'+n+1)/N]\} \times[\Gamma(n'+1)\Gamma(2N-n')/\Gamma(n+1)\Gamma(2N-n)]^{1/2}, \tag{15}$$

where $\Gamma(k)=(k-1)!$ is the Gamma function. The right side of Eq. (15) differs in the phase factor $(-1)^{\Delta n}$ from expression (9) of Ref. 1, which is caused by a different phase convention in this paper consistent with our choice of zero time.

III. $\Delta n=1$ TRANSITIONS

For $\Delta n=1$ transitions, the semiclassical matrix element (14) simplifies to

$$M(1,\bar{n})=[(\bar{n}+1/2)/2N]^{1/2}[1-(\bar{n}+1/2)/2N]^{-1/2}, \tag{16}$$

whereas the quantum mechanical expression for $M_{n',n'-1}$ is given by Eq. (15) with $n=n'-1$.

To make the ensuing representation simpler, we confine ourselves to transitions between not too highly excited levels, i.e., we assume $N-n\gg 1$. Then the expression in the curly brackets of Eq. (15) simplifies to

$$\{\cdots\}=1+(1/16)(N-n)^{-2}+\cdots \tag{17}$$

and can be replaced safely by unity within the approximation stated. Therefore, we adopt the following expression for the "exact" matrix element of a $\Delta n=1$ transition

$$M_{n',n'-1}=(n'/2N)^{1/2}(1-n'/2N)^{-1/2}, \tag{18}$$

where N has been replaced by its integer value.

The semiclassical expression (16) can be brought into complete agreement with the quantum mechanical expression (18) if $\bar{n}$ is chosen to be the arithmetic mean between the initial quantum number $n'-1$ and the final quantum number n, i.e., $\bar{n}=n'-1/2$. This choice of course does not remove the ambiguity associated with the choice of trajectory because the semiclassical matrix elements for the transitions $n'-1\to n'$ and $n'-1\to n'-2$ are the same, whereas their quantum mechanical counterparts are different.

The relative intrinsic uncertainty in $M(1,\bar{n})$ is

$$\delta M(1,\bar{n})/M(1,\bar{n})=1/2(\bar{n}+1/2), \tag{19}$$

which can now be compared with numerical results.

In our numerical study, we calculated relative contributions $C_k(\Delta n,n')=M^k_{n',n'-\Delta n}/M_{n',n'-\Delta n}$ to the TDME from five regions ($k=1$, 2, 3, 4, and 5) shown in Fig. 1. The contributions were calculated by numerical integration of the corresponding portions of the integral with wave functions for the Morse potential with parameters $\omega_e=3366.95\ \mathrm{cm}^{-1}$ and $D_e=52\,407.4\ \mathrm{cm}^{-1}$, which simulate the C–H stretch oscillations in HCN. For these parameters, the integer value of N is 30. The vibrational wave functions were obtained by numerically solving the Schrö-

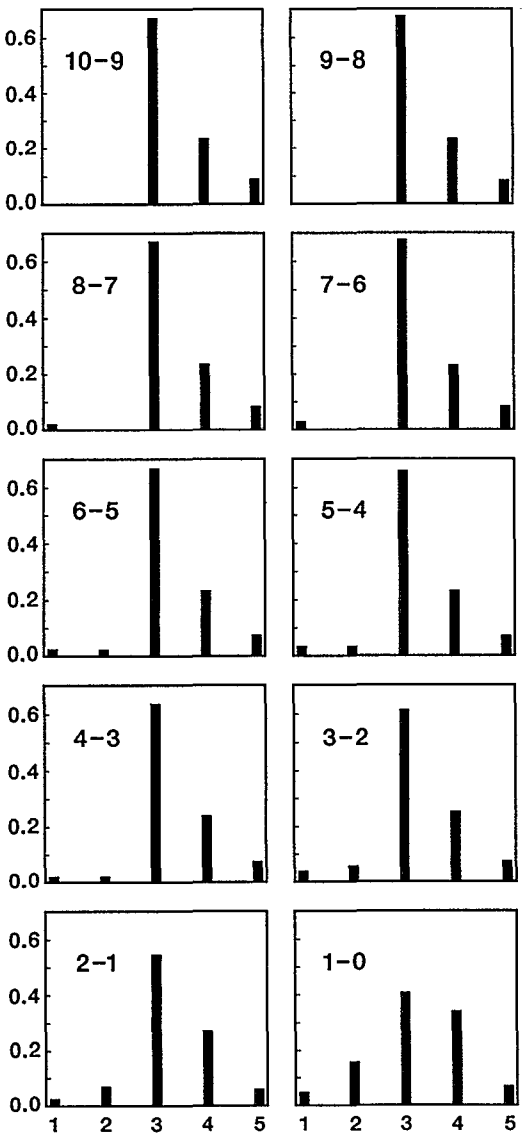

FIG. 2. Contributions of the five different regions for Δn transitions indicated.

dinger equation using the Cooley algorithm.[14,15] The resulting eigenvalue converges within 0.02 cm^{-1} for $n=0$ and within 0.2 cm^{-1} for $n=10$. The wave functions were further tested by orthogonality. The overlap integral for $n \neq n'$ does not exceed 3×10^{-11}. The quantum mechanical matrix elements, as given by Eq. (15), were reproduced accurately. We also tested that the contributions from different regions did not depend on the round-off error in the turning points.

The results of numerical calculations for $\Delta n=1$ are shown in Fig. 2 as bar graphs that represent relative contributions from different regions. For all transitions, the following relation holds true: $C_1 \ll C_2$, $C_5 < C_4 < C_3$.

With an increase in n, the relative contribution from regions 1 and 2 decreases as expected (the motion becomes more classical), while contributions from regions 4 and 5 seem to approach a limiting fraction slightly above 30%. The fully classical region 3 makes the dominant contribution, but this contribution does not exceed 70%. On the basis of Eq. (19), the contribution from regions that are not completely classically allowed would be expected to be about $1/2n'$, which for $n'=10$ amounts to 5%. The appreciable difference between 30% and 5% indicates that the simple picture of the overwhelming contribution to the semiclassical dipole matrix element from the classical allowed region of motion is not valid. Yet the total value of the matrix element is well reproduced by its correspondence principle counterpart, which is based solely on the classical motion.

This paradox can be resolved by noting that regions 2 and 3 for transitions with $\Delta n=1$ cover approximately the range of the first maxima of the wave functions close to the turning points. Since these maxima extend into the classically forbidden region, it is worth noting that the error introduced by the classical description of motion up to the turning point compensates for the unaccounted contribution from the classically forbidden region. This explanation is consistent with the fact that contributions from region 4 are much larger than those from region 2, since the wave function oscillates more slowly close to the right turning point.

TABLE I. Relative deviations of the symmetrized semiclassical TDME and the semiclassical TDME (with $\bar{n}=n'$) from exact quantum TDME for all transitions $n'-\Delta n \to n'$ with $n'=10$, $f^{SSC}(\Delta n,10)$, and $f^{SC}(\Delta n,10)$, respectively.

Δn	$f^{SSC}(\Delta n,10)$	$f^{SC}(\Delta n,10)$	$r(\Delta n,10)$	c/q
1	1.0	1.0	1	c
2	1.001	1.064	2×10^{-1}	c
3	1.006	1.212	5×10^{-2}	c
4	1.017	1.490	1.4×10^{-2}	c
5	1.040	1.996	4×10^{-3}	q
6	1.080	2.954	9×10^{-4}	q
7	1.169	4.932	2×10^{-4}	q
8	1.321	9.580	4×10^{-5}	q
9	1.659	23.025	6.5×10^{-6}	q
10	2.625	78.83	7.4×10^{-7}	q

IV. $\Delta n>1$ TRANSITIONS

As seen from the semiclassical equation (14) and its quantum mechanical counterpart [Eq. (15)], the value of the TDME decreases if n' is fixed and Δn increases. When Δn becomes comparable to n', the ambiguity in $M(\Delta n,\bar{n})$ becomes very large. A semiempirical correction is customarily made to the SC approximation by replacing $\bar{n}$ with

$$\bar{n}=(n+n')/2=n'-\Delta n/2. \tag{20}$$

We call this approximation the symmetrized semiclassical (SSC) approximation. We tested the SC and SSC approximations by calculating the ratios $f^{SSC}(\Delta n,n')=M(\Delta n,n'-\Delta n/2)/M_{n',n'-\Delta n}$ and $f^{SC}(\Delta n,n')=M(\Delta n,n')/M_{n',n'-\Delta n}$. Table I lists the results for all transitions to level $n'=10$ from all smaller $n=n'-\Delta n$. It also gives ratios $r(\Delta n,n')=M_{n',n'-1}/M_{1,0}$ of exact matrix elements.

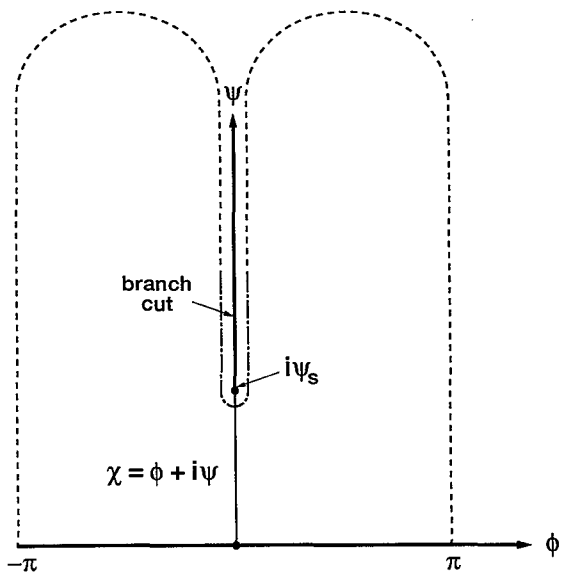

FIG. 3. Initial integration contour $-\pi \leqslant \varphi \ll \pi$ and displaced contour (dashed line) of the integral in Eq. (13). The dash–dot portion of the dashed contour provides the main contribution to the integral when $\Delta n \gg 1$.

Note from this table that the semiclassical approximation with $\bar{n}=n'$ breaks down very soon and that the symmetrized semiclassical approximation with $\bar{n}=n'-\Delta n$ yields an excellent approximation even for $\Delta n/n$ as high as 1/2 and provides reasonable estimates even for larger Δn. The SSC approximation clearly applies beyond the limit expected for its validity. To understand why, we must examine the Landau method for calculating quasiclassical matrix elements.

We illustrate this method within the semiclassical approximation, making use of the fact that both approximations have a common region of applicability [for instance, the SSC approximation yields already very small but approximately correct relative matrix elements for transitions with $3<\Delta n<6$ (see Table I)].

First we note that the integrand in Eq. (13) for large Δn oscillates rapidly along the original integration contour $-\pi<\varphi<\pi$; this behavior implies that the contribution to the integral (however small the total value may be) comes from the whole of region 1. According to the Landau method, we displace the original integration contour into the complex plane $\chi=\varphi+i\psi$ in such a way that the main contribution to the integral could be collected from a small portion of the contour along which the integrand does not oscillate. This contour is shown in Fig. 3 by the dashed line, whose dash–dot part corresponds to the abovementioned portion. Contributions from vertical portions of the contour cancel because of the periodicity of motion, and contributions from the dash–dot portion that goes around the singular point χ_s of the integrand fall off as $\exp(-\Delta n\cdot\psi)$ as ψ runs along the imaginary axis of χ. The singular point χ_s determines how far the contour can be deformed; the lower point of the contour corresponds to the zero of the argument of the logarithm function in Eq. (7), viz.

$$1-(E/D_e)^{1/2}\cos\chi_s=0. \tag{21}$$

A solution to this equation is

$$\chi_s=i\psi_s=i\cdot\operatorname{arccosh}[(D_e/E)^{1/2}]. \tag{22}$$

Note that χ_s is the origin of the branch cut that runs along the ψ axis. Since the integrand decays as $\exp(-\Delta n\psi)$ with ψ increasing, we approximate the argument of the logarithm by a linear function of $\chi-i\psi_s$. The real part of the logarithm is the same on both sides of the branch cut (and therefore does not contribute to the loop integral), but the imaginary part (which is constant) differs in sign on both sides of the cut. Therefore we arrive at the simple expression

$$M(\Delta n,\bar{n})=-\int_{\psi_s}^{\infty}\exp(-\Delta n\psi)\,d\psi$$
$$=-(\Delta n)^{-1}\exp(-\Delta n\cdot\psi_s), \tag{23}$$

where ψ_s is defined in Eq. (22). Transformed to the exponential form, Eq. (23) becomes

$$M(\Delta n,\bar{n})=-(\Delta n)^{-1}\exp\{-(\Delta n/2)[\ln(2N-\bar{n}-1/2)$$
$$-\ln(\bar{n}+1/2)]\} \tag{24}$$

with the help of Eq. (12).

A requirement that $M(\Delta n,\bar{n})$ should be exponentially small becomes equivalent to the condition that the exponent greatly exceeds unity. It can be verified easily that Eq. (23) coincides exactly with Eq. (14), which implies that this result, technically valid only in the limit $\Delta n\gg 1$, is correct for all values of Δn. For a nonlinear dipole moment function, this result will not apply.

In terms of classical motion of the point over the trajectory specified by the "quantum number" $\bar{n}$, Eq. (23) can be interpreted in the following manner: The exponential factor of the matrix element is determined by the imaginary phase $i\cdot\psi_c=\omega(\bar{n})\cdot(i\tau)$ which is related to the imaginary time interval $i\tau$. During the time $i\tau$, the oscillator moves from any point of the classical trajectory (in particular, from the left turning point) to the singular point (which can be called the transition point) $i\psi_s$. The prefactor is determined by the motion of the system close to the transition point. In a sense, the matrix elements for a transition between not too closely lying states ($\Delta n\gg 1$) can be said to depend on the potential function in the classically forbidden region to the left of the left turning point. The above discussion makes clear, however, that the two seemingly contradictory statements (i.e., the contribution comes from the classically allowed region in the original formulation or from the classically forbidden region when calculated along a shifted contour) mean the same. This contradiction is resolved easily by noting that when the integration contour is changed, the analytic continuation of the potential from the classically allowed region into the classically forbidden region is the one actually used, and this continuation is unique.

As Lewerenz and Quack[9] noted, confusion has resulted from the statement that the quasiclassical matrix element depends on the behavior of the potential in the classically forbidden region. From the above discussion, we appreciate that if the potential is an analytic function of x everywhere, this statement applies equally to any part of the potential. If the potential is not analytic in the classically forbidden region, then the statement that the quasiclassical matrix element depends on the behavior of potential in the classically forbidden region is false.

We turn to the quasiclassical Landau method. Contrary to the classical (φ,j) representation in Eq. (13), the Landau method starts with the quasiclassical (x,n) representation and transforms the integration contour from the x axis into the $z=x+iy$ plane. This transformation allows the quasiclassical contributions to the integral from regions 2, 3, and 4 to be taken into account (see Appendix A). Again, if the integral is calculated along the contour passing through the transition point, the exponential part of the matrix element is determined by the difference in imaginary action integrals (divided by $\hbar$) calculated from the turning points to the transition point, and the prefactor is determined by the quasiclassical behavior of the system close to the transition point. An important consequence of this method is that the Landau exponential factor depends on the potential energy function only and not on the exact form of the dipole moment function. Note that in the correspondence principle limit, when $\Delta n \ll n, n'$, the difference in imaginary action integrals becomes the imaginary phase $\Delta n \psi_s$. As long as this form is simple enough, ψ_s is given by Eq. (22) irrespective of the form of the dipole moment. We elaborate on this point more in Sec. V.

The Landau quasiclassical result for the linear dipole function can be extracted from Eq. (15) when the Stirling formula is used for each gamma function. This conclusion follows from the study of quasiclassical matrix elements for the Morse potential.[16] Therefore, the quasiclassical matrix element $M^{\mathrm{QC}}_{n',n}$ within the approximation of Eq. (17) reads

$$M^{\mathrm{QC}}_{n',n} = -(\Delta n)^{-1} \exp[S(n') - S(n)], \tag{25}$$

where

$$S(n) = (n+1/2)\ln(n) + (2N-n-1/2)\ln(2N-n-1). \tag{26}$$

Since the Stirling formula provides an excellent approximation to $\Gamma(k)$ for $k>2$, we expect $M^{\mathrm{QC}}_{n'n}$ to be very close to $M_{n'n}$ for $n>2$. Therefore the question as to why the symmetrized semiclassical result provides a good approximation to the exact result for not too small values of Δn can be addressed in a different form: why does the symmetrized semiclassical result provide a good approximation to the quasiclassical result? In our opinion, the answer to this query is related to the form of the interaction potential.

The main contribution to the semiclassical and quasiclassical matrix elements comes from the classically forbidden region of motion to the left of the left turning points, where the analytic continuation of the Morse potential is very close to the exponential function. On the other hand, the exponential interaction possesses a property that the exponential of the semiclassical matrix element $V_{p,p'}$ (in this case quantum numbers of the continuum states are labeled by asymptotic momenta) can be transformed exactly into the exponential of the quasiclassical matrix element by the substitution $\bar{p}=(p+p')/2$ (see Appendix B). Presumably, this property survives to some extent for other potentials whose analytic continuation exhibits a steep repulsion.

TABLE II. Relative deviations of the symmetrized semiclassical TDME and the semiclassical TDME from exact quantum TDME for $n'-\Delta n \to n'$ transitions to the final states with $n' \leqslant 10$, $f^{\mathrm{SSC}}(4,n')$, and $f^{\mathrm{SC}}(4,n')$, respectively.

n	$f^{\mathrm{SSC}}(4,n)$	$f^{\mathrm{SC}}(4,n)$	$R(4,n)$	c/q
4	1.275	3.435	0.003	q
5	1.118	2.402	0.006	q
6	1.067	1.999	0.011	q
7	1.043	1.783	0.018	c
8	1.030	1.648	0.026	c
9	1.022	1.556	0.036	c
10	1.017	1.49	0.048	c

For a given Δn, the semiclassical approximation progressively worsens as n' decreases. Table II displays values of $f^{\mathrm{SSC}}(\Delta n,n')$ and $f^{\mathrm{SC}}(\Delta n,n')$ together with the ratios $R(\Delta n,n')=M_{n',n'-\Delta n}/M_{1,0}$ for $\Delta n=4$. We see that the symmetrized semiclassical approximation gives a reasonable approximation even for the 6–2 transition, for which the lower state can hardly be described as quasiclassical.

The quasiclassical approximation is expected to fail if the lower state corresponds to a small vibrational quantum number. Medvedev[8,17] and Medvedev and Osherov[18] suggested a method to calculate the TDME from the ground (and low-lying) states into upper states by modifying the Landau method. They used the property of the ground-state wave function to develop the WKB asymptotic behavior in the region that determines the TDME if the dipole moment overlap integral is calculated along a contour displaced into the complex z plane. In contrast to the Landau approach, this method requires changing the normalization constant in front of the tunneling WKB wave function, in contrast to its quasiclassical counterpart. A similar feature was found by Uzer and Child.[19] The results of Medvedev's calculations,[17] given as ratios of the form $f^{\mathrm{MED}}(\Delta n,n') = M^{\mathrm{MED}}_{n'-\Delta n,n'}/M_{n'-\Delta n,n'}$ are compared with $f^{\mathrm{SSC}}(\Delta n,n')$ in Table III for overtone transitions $\Delta n=n'$. Also given are the ratios $R(\Delta n,n')$ for our model potential.

We see that although the f^{SSC} ratio increases with the final quantum number n' of the overtone transition thereby making the agreement with exact results worse, f^{MED} decreases and the agreement becomes better. The reason for this behavior is clear. Increase of f^{SSC} is caused by the breakdown of the semiclassical approximation with increasing Δn; this breakdown reflects the growing intrinsic ambiguity of the TDME within this approach. Decrease of f^{MED} arises from the progressively higher accuracy of the quasiclassical approximation in the region that contributes mostly to the dipole moment overlap integral. We find that

TABLE III. A comparison of the quasiclassical Medvedev calculations $f^{MED}(\Delta,n')$ with the symmetrized semiclassical calculations $f^{SSC}(\Delta n,n')$ for the overtone transitions $0\rightarrow n'$ $(\Delta n=n')$.

n	$f^{SSC}(n,n)$	$f^{MED}(n,n)$	$R(n,n)$	c/q
1	1.0	...	1	c
2	1.061	1.588	9×10^{-2}	c
3	1.13	1.286	1.4×10^{-2}	q
4	1.275	1.196	3×10^{-3}	q
5	1.422	1.555	6.4×10^{-4}	q
6	1.596	1.122	1.7×10^{-4}	q
7	1.799	1.106	5.3×10^{-5}	q
8	2.036	1.091	1.8×10^{-5}	q
9	2.309	1.083	6.5×10^{-6}	q
10	2.625	1.074	2.6×10^{-6}	q

the accuracy of both approximations is comparable for the 0–5 transition, about 50% for this matrix element, and approximately a factor of 2 for the oscillator strength.

We turn to numerical results. In all cases studied for $\Delta n=4$, we found strong cancellation of contributions from regions 2, 3, and 4; absolute values of individual contributions $|C_2|$, $|C_3|$, and $|C_4|$ are much higher than the absolute value of the sum $|C_2+C_3+C_4|$. As for contributions from other regions, we found two different cases—case c (c for almost classical) when $|C_5|\ll|C_1|<|C_2+C_3+C_4|$ and case q (q for strong quantum) when $|C_5|\ll|C_2+C_3+C_4|<C_1$. In case c, cancellation occurs mainly in the region in which the motion is classical at least for one state; in case q, the cancellation is decisively effected by the motion in region 1, which is classically forbidden for both states. The c/q nomenclature for individual transitions is shown in Tables I–III. The c/q characteristic correlates well with the accuracy of the SSC approximation. For the last c states in Tables I–III, the accuracies of the SSC approximation for the TDME are 2%, 4%, and 6%, respectively.

The large contribution of region 1 for q-type transitions with $\Delta n>1$ is caused by the overlap of the first broad oscillation of the upper-state wave function with the tunneling part of the lower-state wave function. The WKB approximation for the upper state fails in this region, giving a diverging wave function when the turning point is approached from the right. Within the Landau method, this wave function is used to calculate the integral from this turning point to the right, thus completely neglecting the contribution from the classically forbidden region of motion.[8] When the integration contour is changed, the same integral can be calculated along a portion of the contour lying in the classically forbidden region.

The manner in which the relative contribution $C_1(\Delta n,n')$ for a transition with large Δn changes with n is instructive. Figure 4 shows the dependence of $C_1(6,n')$ on the upper-state quantum number n' (transitions $n'-6\rightarrow n'$). At the high-n' portion of the graph, C_1 is below unity and it clearly falls off as $\Delta n/n'$ decreases in accord with the correspondence principle. With decreasing n', C_1 increases and becomes larger than unity for the $8\rightarrow14$ transition. This trend is amplified with further decrease in n', ending with a dramatic increase of C_1 for the $0\rightarrow6$ overtone transition. Though the sharp increase of C_1 for small values of the initial quantum number $n'-\Delta n$ can be ascribed to the breakdown of the quasiclassical approximation for the lower state, C_1 clearly may be above unity for states that are certainly quasiclassical and therefore the TDME between these states can be calculated accurately by the Landau method. This result indicates that the incorrect behavior of the WKB wave function to the right from the turning point nearly compensates for the complete neglect of the tunneling contribution from a region adjacent to the turning point from the left. This compensation occurs with remarkable accuracy since the value of the TDME for high Δn is governed by near cancellations of contributions from different regions.

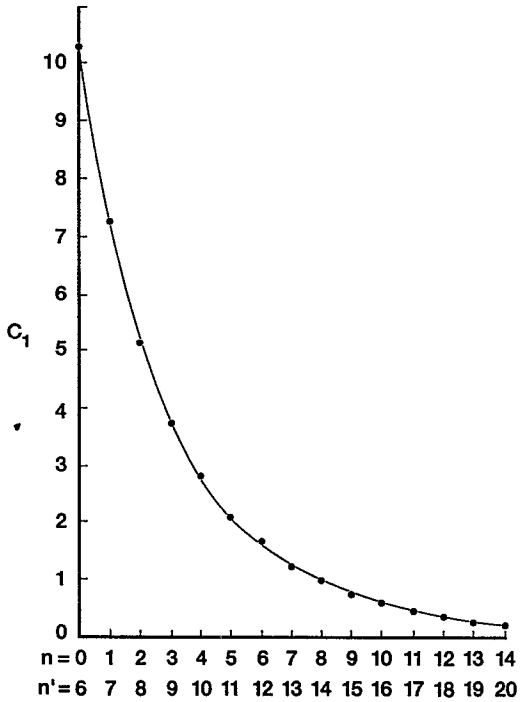

FIG. 4. The relative contributions of region 1 for the $n'-6\rightarrow n'$ transitions indicated.

V. AN IMPROVED SEMICLASSICAL FORMULA FOR THE TRANSITION DIPOLE MATRIX ELEMENT

After examining the conditions of validity of different approaches, we can combine various approximations to develop an improved semiclassical equation for the TDME. This improved equation is based on the following observations:

(i) The semiclassical approximation works well for not too large Δn, but fails for large Δn because the semiclassical exponential cannot reproduce the overlap between distant quantum states.

(ii) When the TDME is small, the Landau method applies for not too low quantum numbers n, and the main dependence of the TDME on Δn is governed by the quasiclassical exponential.

TABLE IV. Ratios $f^{SSC}_{n',0}$ and $f^{ISC}_{n',0}$ for the TDME for linear dipole moment function for a Morse oscillator with $N=30$ for overtone transitions $0\rightarrow n'$.

n'	$f^{SSC}_{n',0}$	$f^{ISC}_{n',0}$
1	1.0	0.978
2	1.061	0.976
3	1.155	0.970
4	1.255	0.969
5	1.422	0.968
6	1.569	0.967
7	1.799	0.967
8	2.038	0.967
9	2.309	0.967
10	2.625	0.966
11	2.989	0.966
12	3.406	0.966
13	3.886	0.986
14	4.436	0.966
15	5.065	0.966

(iii) These approximations have a common region of applicability. Therefore they can be combined in a unified formula, which contains a semiclassical preexponential factor and a quasiclassical exponential factor. Implicit in this approach is the assumption that the preexponential factor depends more weakly on initial and final vibrational quantum numbers than the exponential factor does.

(iv) The quasiclassical exponent [the difference in the action integrals $Q(n')-Q(n)$] can be reconstructed from semiclassical exponent $\Delta n\cdot q(n)$ with the help of the differential relation expressing the correspondence principle limit

$$d[Q(n)]/dn=q(n). \tag{27}$$

For a Morse potential and a linear dipole moment function, the improved semiclassical (ISC) approximation leads to the expression

$$M^{ISC}_{n',n}=-(\Delta n)^{-1}\cdot\exp[Q(n')-Q(n)], \tag{28}$$

where

$$Q(n')-Q(n)=(1/2)\cdot\int_{n+1/2}^{n'+1/2}[\ln(2N-\bar{n})-\ln(\bar{n})]d\bar{n}, \tag{29}$$

from which it follows that (to an arbitrary constant)

$$Q(n)=(1/2)[(2N-n-1/2)\ln(2N-n-1/2)+(n+1/2)\ln(n+1/2)]. \tag{30}$$

Equations (28) and (30) differ from Eqs. (25) and (26) in that they ascribe quantum numbers $n'+1/2$ and $n+1/2$ to the initial and final classical action variables. The use of $n+1/2$ and $n'+1/2$ rather than n and n' is not important for large quantum numbers, but is vital for small quantum numbers. Equations (28)–(30) are tested for a wide range of the overtone transitions $0\rightarrow n'$, including the fundamental transition $0\rightarrow 1$. The results are shown in Table IV, where we compare SSC and ISC approximations in terms of ratios of these TDMEs to exact ones. We see that the ISC approximation nearly reproduces the exact matrix elements for overtone transitions; it is less accurate for transitions with small Δn. This agreement encourages us to believe that the ISC approximation may have many future uses.

Taking into account that N is large ($N\gg 1$), Eqs. (28) and (30) can be rewritten in the following form:

$$M^{ISC}_{n'n}=-(\Delta n)^{-1}m_{n,n+1}\cdot m_{n+1,n+2}\cdot\cdots m_{n'-1,n'}, \tag{31}$$

where

$$m_{k,k+1}=\left[\frac{(k^2-1/4)^{1/4}}{(2N-k)^{1/2}}\right]\cdot\exp\left(k\cdot\ln\frac{km-1/2}{k+1/2}-1\right). \tag{32}$$

If, in addition, k is not too small, $m_{k,k+1}$ can be replaced by a simple expression

$$m_{k,k+1}=[k/(2N-k)]^{1/2}. \tag{33}$$

For k as small as $k=1$, Eq. (33) provides a good approximation to Eq. (32) (better than 5%).

Equation (31) must not be considered simply as yet another approximation to the exact result (15), since, as follows from the Landau method, the product of m values represents the Landau exponential factor, which depends on the oscillator potential and not on the dipole moment function. The factor in front of the product of m values represents the semiclassical prefactor for the transition $0\rightarrow n'$, which in the case of a linear dipole moment does not depend on $\bar{n}$. For a nonlinear dipole moment function, the semiclassical preexponential factor may depend on $\bar{n}$. If this dependence is very weak compared with the dependence on $\bar{n}$ of the exponential, use of a simple symmetrization procedure will suffice to correct the semiclassical preexponential factor.

Note that each factor $m_{k,k+1}$ corresponds to a semiclassical exponent $\exp[-\psi_s(\bar{k})]$ in which $\bar{k}$ is related to the mean classical energy for quantum states k and $k+1$, i.e., $\bar{k}=k+1$. For a given "classical" state k, the exponent $\psi(k+1)$ can be calculated purely classically by running a trajectory, performing the Fourier analysis of the dipole moment for this trajectory, and fitting the classical overtone amplitudes with frequencies $\Delta n\cdot\omega(k+1)$ by an exponential function. This approach contrasts with a standard semiclassical approach in one important step—the semiclassical approach suggests an approximation to the entire product of m values, whereas the improved semiclassical approach suggests an approximation to individual m values.

Equations (31) and (33) suggest the following improved semiclassical equation for the TDME of the Morse oscillator for an arbitrary dipole moment function, provided its semiclassical counterpart is characterized by a preexponential that depends weakly on Δn and n:

$$M^{ISC}_{n',n}=A[\Delta n,(n+n')/2]\cdot m_{n,n+1}\cdot m_{n+1,n+2}\cdots\cdot m_{n'-1,n'}, \tag{34}$$

where the prefactor $A[\Delta n,(n+n')/2]$ is obtained from $A(\Delta n,\bar{n})$ by symmetrization. In turn, $A(\Delta n,\bar{n})$ should be

calculated from Eq. (13) in which $M(x)$ represents an adopted form of the dipole moment function. Usually this function is given as a power series in x, sometimes supplemented with exponential functions of x.

Equation (34) allows a "back-of-the-envelope" calculation of the ratio of successive overtones if the difference in the preexponential factors for transitions $0\rightarrow n'+1$ and $0\rightarrow n'$ is ignored completely. The intensity ratio for such transitions is given by the simple formula

$$\frac{I(0\rightarrow n'+1)}{I(0\rightarrow n')}=(m_{n',n'+1})^2=\frac{n'+1}{2N-(n'+1)}. \tag{35}$$

As an example, we apply Eq. (35) to the high overtone intensities of HBr measured by Carlisle *et al.*[20] We choose HBr because its dipole moment function is one of the best known. We find that Eq. (35) reproduces the ratio of $I(7-0)/I(6-0)$ and $I(8-0)/I(7-0)$ within 50% (we predict a decrease of 0.14 and 0.16, whereas the actual decrease is 0.104 ± 0.005 and 0.105 ± 0.005, respectively). We had hoped that Eq. (35) would have been a better estimate, but this hope ignored the complicated nature of the HBr dipole moment function. Carlisle *et al.* have deduced the form of the dipole moment function from the rotationless dipole moment matrix elements for all $0-n'$ transitions up to $n'=8$. They found that the dipole moment function could be fit only by a power series expansion in x including a term in x^8. We believe this complicated dipole moment function is what reduces the accuracy of Eq. (35). Even so, Eq. (35) was able to provide a very good estimate without any knowledge of the dipole moment function.

We turn to the question as to when the preexponential factor $A(\Delta n,n)$ can be assumed to vary slowly as a function of its arguments. To this end, we consider the semiclassical matrix element $A(\Delta n,n,\lambda)$ of the function $M(x)=\exp(-\lambda\alpha x)$. The matrix elements of the pth power of αx, $A^{(p)}(\Delta n,n)$, or the pth power of x times the exponential, can be generated from $A(\Delta n,n,\lambda')$ by simple differentiation. For instance,

$$A^{(p)}(\Delta n,\bar{n})=p!\cdot(\partial/\partial\lambda)^pA(\Delta n,\bar{n},\lambda)\,|_{\lambda=0}. \tag{36}$$

To calculate the semiclassical matrix element of the exponential function, we substitute into the integral (13) the explicit φ dependence of $\exp(-\lambda\alpha x)$, viz.,

$$M(\varphi,\lambda)=(1-\epsilon)^{\lambda}[1-(\epsilon)^{1/2}\cos\varphi]^{-\lambda}, \tag{37}$$

where $\epsilon=E(n)/D_e$. The integral (13) with $M(\varphi,\lambda)$ from Eq. (37) can be expressed with the help of the formula[13]

$$(2\pi)^{-1}\int_{-\pi}^{+\pi}\frac{\cos(\Delta n\varphi)\cdot d\varphi}{(1-2z\cos\varphi+z^2)^{\lambda}}$$

$$=\frac{z^{\Delta n}\cdot\Gamma(\Delta n+\lambda)}{\Delta n\cdot\Gamma(\lambda)\cdot\Gamma(\Delta n)}-F(\lambda,\Delta n+\lambda,\Delta n+1,z^2), \tag{38}$$

where $F(.,.,.,.)$ is the hypergeometric function and $z=[\bar{n}/(2N-\bar{n})]^{1/2}$.

The formula for the linear dipole moment function (14) follows from Eq. (38) by differentiating both sides of this equation with respect to λ and passing to the limit $\lambda\rightarrow0$. The opposite case $\lambda\rightarrow\infty$ and λz bounded corresponds to the case of the exponential matrix element taken between states of a harmonic oscillator. This case was studied in detail previously by Uzer and Child.[19]

Representing the right side of Eq. (38) as a product of the exponential factor $z^{\Delta n}=\exp(-\Delta n\psi_s)$ and the preexponential factor $A(\Delta n,\bar{n},\lambda)$, we find the explicit expression for the latter. In doing so, we also assume $z^2\ll1$, which, among other uses, allows us to replace the hypergeometric function by unity. Within this approximation, we obtain the following expression for the preexponential factor:

$$A(\Delta n,\bar{n},\lambda)=\Gamma(\Delta n+\lambda)/\Gamma(\lambda)\Gamma(\Delta n+1), \tag{39}$$

which is seen to be independent of $\bar{n}$. If $\Delta n\gg\lambda$, Eq. (39) simplifies to

$$A(\Delta n,\bar{n},\lambda)=(\Delta n)^{\lambda-1}/\Gamma(\lambda). \tag{40}$$

We see that the preexponential factor in Eq. (40) is similar in form to the preexponential factor for transitions between continuum states of the exponential repulsive potential (see Appendix B).

For the particular case of the linear dipole moment function ($\lambda\rightarrow0$) and for exponential functions $\exp(-\alpha x)$ and $\exp(-2\alpha x)$, Eq. (39) gives

$$A^{(1)}(\Delta n)=-1/\Delta n, \tag{41a}$$

$$A(\Delta n,\lambda=1)=1, \tag{41b}$$

and

$$A(\Delta n,\lambda=2)=\Delta n+1. \tag{41c}$$

These preexponential factors coincide, within the approximation stated, with the exact matrix elements [Eqs. (9), (14), and (15) of Ref. 1] provided the Landau exponential is factored out from them. The above form of the dipole moment function corresponds either to a very slow change of $M(x)$ (linear case), or to a smooth decrease of $M(x)$ with increasing x. Therefore we can expect that for this kind of dipole moment function, the ISC approximation will provide a good estimate.

Suppose instead that the dipole moment increases rapidly with x. As an example, consider the functions $\exp(\alpha x)$ and $\exp(2\alpha x)$ ($\lambda=-1$ and -2, respectively). For this form of the dipole moment function, transitions with $\Delta n>1$ and $\Delta n>2$ are completely forbidden, which means, of course, very strong dependence of the preexponential factors on Δn. Though this example is not realistic, it shows that for strongly increasing dipole moments and for dipole moment functions that exhibit nonmonotonic behavior, the ISC approximation will not provide a reliable estimate. As an example of the complicated behavior of dipole moment function, we cite Chackerian and Tipping,[21] who calculated the overtone intensities for CO isotopes. The dipole moment function they used rises steeply from $x=0$, passes through a maximum at $x=0.7R_e$, and then falls off. The calculated successive overtone intensities decrease much faster than predicted by Eq. (35).

VI. A COMPARISON OF THE QUASICLASSICAL LANDAU APPROXIMATION WITH THE QUASICLASSICAL UNIFORM APPROXIMATION

Our study of the TDME for a linear dipole moment function and a Morse oscillator is in some respect similar to an earlier study by Uzer and Child[19] of semiclassical approximations for matrix elements of two different systems. Their case *a* for transitions between continuum states of a system in the field of an exponential repulsive potential (Jackson–Mott model[22]) is relevant to our study, since the value of the matrix element is governed by the motion in the region of the steep (exponential) repulsive wall. Uzer and Child used the uniform semiclassical approximation based on the Airy function to construct the wave functions that exhibit correct asymptotic behavior both in the classically allowed and in the classically forbidden regions. In these regions, far from the turning point, the exact wave functions are well represented by Wentzel–Kramer–Brillouin (WKB) functions (provided the standard conditions for the WKB approximation hold). Uzer and Child compared the quasiclassical matrix element calculated in the stationary phase (STP) approximation I_{STP} with the exact value I_{exact} and found a discrepancy by a factor of $(e^2/4\pi^{1/2}) = 1.0422$. We show in Appendix B that this discrepancy is caused by the failure of the stationary phase approximation (the method of steepest descent).

We note[11] that the analytic continuation of the WKB wave function from the classically allowed region into the classically forbidden region is different from the WKB approximation to the exact wave function in the latter region. Actually, this continuation exhibits an exponential growth that contradicts the expected behavior of the true wave function. This feature arises from the Stokes' phenomenon,[23] which is not properly accounted for with the analytic continuation of the WKB functions. The Landau method is based on WKB wave functions and a specific choice of the integration contour, for which the tunneling contribution from the upper state is completely neglected. Once these two features of the method are recognized, one is free to deform the contour and make the analytic continuation of the WKB functions subject to general rules of the calculus of complex variables (see Appendix A).

Clearly, the uniform approximation is superior to the Landau approximation, but both should give the same result in the limit of exponentially small matrix elements (which is the condition of validity of the Landau approximation). This conclusion is consistent with the results of Uzer and Child[19] that the uniform approximation shows more stationary points than does the Landau approximation. In the Landau limit, however, these extra stationary points are not believed to contribute appreciably to the integral, provided the states are quasiclassical. Also, we should note that the assumption that the dominant contribution to the integral comes from a single stationary phase point, adopted in Uzer and Child,[19] is not necessary for the application of the Landau method. Actually, as we show in Appendix B, the stationary phase approximation completely fails for the linear dipole moment function.

The ability of the Landau method to reproduce the exponentially small matrix elements when the decisive contribution to the integral comes from the almost full cancellation of region 1 with other regions is presumably related to the following two features:

The first concerns the description of the system close to the turning point. The contribution of the first peak of the exact upper-state wave function to the overlap integral, as suggested by the uniform approximation, is roughly proportional to the integral of the Airy function taken over both the classically forbidden and classically allowed regions. The analogous contribution of the WKB wave function, as suggested by the Landau approximation, is proportional to the integral of the asymptotic form of the Airy function taken over the classically allowed region only. It can be verified directly that these two contributions differ by a factor of $(4/3)^{1/2}$, which is only about 15% (see Appendix A).

The second feature is related to the severe cancellation of contributions from different regions. Within the uniform approximation, this cancellation comes naturally as a result of the correct behavior of the wave function in regions that are far and close to the turning point. Within the Landau approximation, this cancellation occurs when the integral is calculated over the classically allowed region using the WKB wave function; equivalently, the same result is obtained when the integration contour is shifted and the integral is evaluated by analytic continuation of the integrand into the classically forbidden region. In accomplishing this analytic continuation, all complications that arise from the Stokes' phenomenon are completely disregarded. It is this feature that makes the Landau approach so relatively simple.

VII. CONCLUSION

By comparing the semiclassical and quasiclassical approximations with exact analytical results and conducting numerical analysis of contributions to the TDME from different regions of the vibrational coordinate, we reach the following conclusions:

(i) For transitions with $\Delta n = 1$ that are well characterized by the correspondence principle for the TDME, the appreciable contribution to the integral comes from regions that are classically allowed for one state and classically forbidden for the other (regions 2 and 4). This conclusion implies that the erroneous description of the behavior close to the turning points in terms of the classical motion in region 3 compensates for contributions from regions 2 and 4, which are neglected in the classical treatment.

(ii) For quasiclassical transitions with $\Delta n > 1$, $(n,n' \gg 1)$ that are well characterized by the symmetrized correspondence principle for the TDME (not too large Δn) or by the Landau method for the TDME (large Δn), the contributions from regions 2 and 4 are very important. Together with the contribution from the classical region 3, they strongly reduce the value of the matrix element because of cancellation. For the former, the contribution from region 1, where motion for both states is classically forbidden, is small. For the latter, this contribution is appreciable and becomes decisive with increasing Δn. This

result again indicates that the WKB description adopted (erroneously) all the way to the turning point from the classically allowed region of the upper state compensates for the tunneling contribution in this state neglected in the Landau treatment.

(iii) For quantum transitions with $\Delta n > 1$ ($0 - \Delta n$ overtones and multiquantum transitions from lower levels), the contribution from region 1, which is classically forbidden for both states, is much larger than the total value of the TDME. The quasiclassical Landau method, as described by Medvedev,[17] is applicable here for large enough Δn when the first oscillation of the wave function of the upper state is in the quasiclassical tunneling region of the wave function of the initial state. With Δn decreasing, the Landau method provides only a rough estimate of the TDME and eventually the symmetrized SC approximation provides higher accuracy. The accuracy of the latter is caused by the fact that the semiclassical approximation does not require the overlap matrix elements to be exponentially small.

After analysis of different approaches, we suggest an improved semiclassical approximation for the TDME of an arbitrary dipole moment function for a Morse oscillator. This approximation, which combines a semiclassical prefactor with the Landau exponential, was tested successfully for the linear dipole moment function. For an arbitrary dipole moment function, the ISC approximation can be used, provided the prefactor depends on Δn and n much more weakly than the Landau exponential does. In this case, a simple formula (35) is presented for the intensity ratio of neighboring high overtones. If the prefactor depends strongly on Δn and n, the TDME ratios are affected substantially by the form of the dipole moment function.

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APPENDIX A: OUTLINE OF THE LANDAU METHOD

In this Appendix, we outline the Landau method in a form that is convenient for passage to the correspondence principle limit. Consider a matrix element $V_{n'n}$ of a function $V(x)$,

$$V_{n'n} = \int V(x)\kappa_{n'}(x)\kappa_n(x)dx. \tag{A1}$$

Assume for simplicity that the motion occurs in the field of a one-dimensional, purely repulsive potential $U(x)$ with left turning points $x_{n'}$ and x_n for each state n' and n; we assume for definiteness that $x_n > x_{n'}$. Let the motion in both states be quasiclassical, i.e., the inverse of the wave vector be small compared to the range of the potential. Far from the turning points, the wave functions $\kappa_{n'}(x)$ and $\kappa_n(x)$ are well approximated by their WKB counterparts $\kappa_{n'}^{QC}(x)$ and $\kappa_n^{QC}(x)$, respectively. Close to the turning points, the QC approximation κ^{QC} to κ fails, but since the singularity is integrable, the integral (A1) for globally quasiclassical conditions can be calculated as

$$V_{n'n}^{QC} = \int V(x)\kappa_{n'}^{QC}(x)\kappa_n^{QC}(x)dx, \tag{A2}$$

although some reservations have been expressed about this possibility.[2] As shown in Fig. 1, the integration domain $-\infty < x < \infty$ is partitioned into three regions. Within these regions, the products of the QC wave functions are (the common normalization factor is omitted here)

(region 3)

$$\kappa_{n'}^{QC}\kappa_n^{QC} = |p_{n'}p_n|^{-1/2}\sin(s_{n'}+\pi/4)\sin(s_n+\pi/4); \tag{A3a}$$

(region 2)

$$\kappa_{n'}^{QC}\kappa_n^{QC} = |p_{n'}p_n|^{-1/2}(1/2)\exp(-\sigma_{n'})\sin(s_n+\pi/4); \tag{A3b}$$

and (region 1)

$$\kappa_{n'}^{QC}\kappa_n^{QC} = |p_{n'}p_n|^{-1/2}(1/4)\exp(-\sigma_{n'}-\sigma_n). \tag{A3c}$$

Here, $s_k = s_k(x) = (1/\hbar)\int_{x_k}^{x} p_k(x)dx$, $\sigma_k(x) = |s_k(x)|$, and p_k is the momentum corresponding to energy E_k.

Assume that the potential $U(x)$ is an analytic function of x across all three regions in the x axis. Each of the functions in Eqs. (A3a)–(A3c) are not analytic continuations of one another, however. The reason is well known—the passage from one region to another requires crossing a Stokes line,[23] which is not smooth. This situation explains why the conventional quasiclassical formulation cannot be used directly to calculate the integral (A2) by the analytic continuation technique. One method is provided by the uniform approximation technique, which ensures a smooth transition between regions via the Airy function.

Landau[7] and Landau and Lifshitz[2] suggested a method to evaluate quasiclassical matrix elements when the value of $V_{n'n}$ is exponentially small. The derivation of this method given below is based on the assumption that the main contribution to the integral (A2) (taken along the real-valued x axis) comes from the classically allowed region 3 and the partly classical region 2. The contribution from the quantal region 1 is neglected and the contribution from the classical region 3 is taken into account approximately by resolving the product of oscillating functions $\kappa_{n'}^{QC}\kappa_{n'}^{QC}$ into slowly and rapidly varying parts and by omitting the latter. Thus we accept the following representation of $\kappa_{n'}^{QC}\kappa_n^{QC}$ in the three regions:

(region 3)

$$(\kappa_{n'}^{QC}\kappa_n^{QC})^L = L_{n'n}(x) = |p_{n'}p_n|^{-1/2}(1/2)\cos(s_{n'}-s_n), \tag{A4a}$$

(region 2)

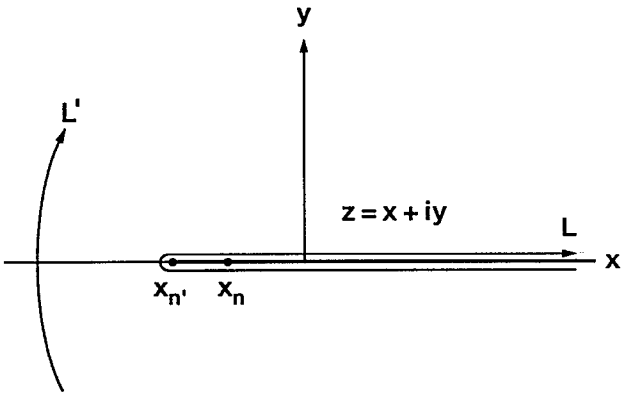

FIG. 5. The integration contours for the Landau method. L is the original contour, L' is a displaced contour, and $x_{n'}$ and x_n are the turning points.

$$(\kappa_{n'}^{QC}\kappa_n^{QC})^L = L_{n'n}(x) = |p_{n'}p_n|^{-1/2}(1/2)\exp(-\sigma_n/\hbar)\sin(s_{n'}+\pi/4), \tag{A4b}$$

and (region 1)

$$(\kappa_n^{QC}\kappa_n^{QC})^L = 0. \tag{A4c}$$

We can obtain the same result by changing the integration contour in such a way that portions (A4a) and (A4b) can be regarded as a single analytic function on this contour, and the contribution from region 1 can be omitted altogether. The analytic function $L_{n'n}(z)$ is of the form

$$L_{n'n}(z) = [p_{n'}(z)p_n(z)]^{-1/2}(1/4)\exp[s_{n'}(z) - s_n(z)], \tag{A5}$$

with $s_k(z) = (1/\hbar)\int_{x_k}^{z} p_k(z)dz$ and $p_k(z) = (2\mu)^{1/2}[E_k - U(z)]^{1/2}$.

The above functions are defined on the complex z plane with branch cuts running from the turning points $x_{n'}$ and x_n to the right. The integration contour L circumvents this cut starting and ending at $+\infty$ (see Fig. 5).

It is easily verified that the sum of contributions from two parts of the contour adjacent to opposite sides of the cut will give expression (A4a) in region 3 and expression (A4b) in region 2, provided that all additional phases that originate from p_k upon passing by the turning points are carefully taken into account.

The analytic continuation of Eq. (A5) into region 1 reads

$$L_{n'n}(x) = |p_{n'}p_n|^{-1/2}(1/4)\exp(\sigma_{n'}/\hbar - \sigma_m/\hbar), \tag{A6}$$

which differs substantially from Eqs. (A3c) and (A4c). The only restrictions for the contour displacements are related to the branch cuts and singular points of the potential $U(x)$ and interaction $V(x)$. *No Stokes lines* remain, which is the main advantage of the Landau method.

In this way, we arrive at the following expression for the Landau–Lifshitz matrix element of a function $V(x)$:

$$V_{n'n}^L = \int_L V(z)L_{n'n}(z)dz, \tag{A7}$$

where L is the contour shown in Fig. 5 or its equivalent. An "equivalent" contour may be quite different in shape from the original. Only a small portion of it usually is important, since the value of the integral under near-adiabatic conditions is determined by integrand singularities that are the closest to the real axis of z. Yet another form of the integral is of interest—V^L can be represented as a real part of an integral taken over the real axis from any point in region 1 to infinity $V^{LL} = V^+ + V^-$ (see Ref. 2, Sec. 52).

The correspondence principle limit follows from the Landau formula when the energies of the initial and final states are so close that two turning points are allowed to coalesce into one $x_{n'}$, $x_n \to x_{\bar{n}}$ and the difference in the action integrals in region 3 is replaced by its first-order term in $E_{n'} - E_n$. The change of the x variable into the t variable via a mean trajectory $x(t) = x(\bar{n},t)$ transforms the loop contour over the x axis into the whole of the t axis. The final result is a familiar expression

$$V_{n'n}^{SC} = \int_{-\infty}^{+\infty} V[x_{\bar{n}}(t)]\exp[i\Delta n\omega(\bar{n})t]dt. \tag{A8}$$

Next we turn our attention to the integral (A1) and analyze a contribution from the first maxima of the upper state wave function, assuming that the rest of the integrand varies slowly over the range of this maxima. We compare two approximations to the upper-state wave function: (i) the Airy function in the classically forbidden and classically allowed regions; and (ii) the Airy function's asymptotic form in the classically allowed region.

Because the prefactors and scales are immaterial for a relative comparison, we compare two integrals

$$I(\text{Airy}) = \int_{-\infty}^{+\infty} \text{Ai}(-x)dx \tag{A9a}$$

and

$$I_{\text{As}}(\text{Airy}) = \int_0^{+\infty} \text{As}[\text{Ai}(-x)]dx, \tag{A9b}$$

where the Airy function $\text{Ai}(-x)$ and its asymptotic form $\text{As}[\text{Ai}(-x)]$ in the classically allowed region are

$$\text{Ai}(x) = (\pi)^{-1}\int_0^{\infty} \cos(s^3/3 + sx)ds \tag{A10a}$$

and

$$\text{As}[\text{Ai}(-x)] = (\pi)^{1/2}\cdot(x)^{1/4}\sin[(2/3)x^{3/2} + \pi/4], \quad x > 0. \tag{A10b}$$

Calculation of the integrals (A9a) is facilitated by noting that $(2\pi)^{-1}\int_{-\infty}^{+\infty}\exp(isx)dx = \delta(s)$, and the substitution $(2/3)x^{3/2} = y^2$ brings the integral (A9b) to a sum of standard integrals $\int_0^{\infty}\sin(y^2)dy = \int_0^{\infty}\cos(y^2)dy = (\pi/2)^{1/2}/2$. The final results are

$$I(\text{Airy}) = 1 \tag{A11a}$$

and

$$I_{\text{As}}(\text{Airy}) = (4/3)^{1/2}. \tag{A11b}$$

APPENDIX B: SEMICLASSICAL MATRIX ELEMENT OF THE EXPONENTIAL FUNCTION FOR THE EXPONENTIAL REPULSIVE INTERACTION AND THE MORSE POTENTIAL

We consider the Fourier component at frequency ω of the function $V(x)=\exp(-\gamma x)$ for the motion of a particle in the field of an exponentially repulsive potential $U(x)=\exp(-\beta x)$ when this matrix element is exponentially small. With $\gamma=\beta$, this problem is encountered in the semiclassical version of the Jackson–Mott model,[22] which is equivalent to the Landau–Teller model.[24]

We use the result of this calculation for three purposes: (i) to show that the exponent does not depend on γ; (ii) to demonstrate the efficiency of the symmetrization procedure in approximating the quasiclassical (Landau) exponential; and (iii) to study the accuracy of the steepest descent approximation.

The classical trajectory for this problem is very simple (e.g., see Ref. 12) and the time dependence of $V[x(t)]$ (up to a constant factor that is not of interest here and that is chosen for convenience to be $\beta\bar{v}/2$) is

$$V[x(t)]=(\beta\bar{v}/2)\cosh^{\lambda}(\beta\bar{v}t/2), \tag{B1}$$

where $\bar{v}$ is the mean asymptotic velocity (at $x\to\infty$) and $\lambda=2\gamma/\beta$. The integral

$$I=\int(\beta\bar{v}/2)\cosh^{-\lambda}(\beta\bar{v}t/2)\exp(i\omega t)dt$$

$$=\int\cosh^{-\lambda}(\tau)\exp(i\xi\tau)d\tau, \tag{B2}$$

where $\xi=2\omega/\beta\bar{v}$ is calculated by displacing the contour into the upper half-plane and letting it go around the singular point (similar to the dash–dot portion of the contour shown in Fig. 2). The singular point τ_s corresponds to zero of the denominator, viz.,

$$\tau_s=i\pi/2. \tag{B3}$$

Taking advantage of the rapid falloff of the exponential along this integration path, we approximate $\cosh^{-\lambda}(\tau)$ by its leading term $(\tau-\tau_s)^{-\lambda}$ and use one of the representations of the gamma function. In this way we get

$$I(\xi,\lambda)=2\pi\xi^{\lambda-1}\exp(-\pi\xi/2)/\Gamma(\lambda). \tag{B4}$$

This formula provides the asymptotic limit (for $\xi\gg1$) to the integral (B2).

From Eq. (B4), we find the following:

(i) The exponent $\pi\xi/2$ does not depend on γ and therefore on the form of the potential. This conclusion is true until the higher terms in the expansion of $\cosh^{-\lambda}(\tau)$ about τ_s begin to affect the integral. The relative importance of the second term in the power expansion of $\cosh^{-\lambda}(\tau)$ about τ_s over the integration range $1/\xi$ is λ/ξ^2, and therefore the form of the potential does not manifest itself in the exponent provided

$$\lambda\ll\xi^2. \tag{B5}$$

(ii) The symmetrization procedure applied to the semiclassical exponent is meant to bring it into an approximate correspondence with the quasiclassical exponent. For our semiclassical model, the exponent is

$$\epsilon^{\mathrm{SC}}=\pi(E-E')/\hbar\beta\bar{v}, \tag{B6}$$

where $(E-E')/\hbar$ is substituted for ω (E and E' are the initial and final kinetic energies). The symmetrization between initial and final states implies a substitution $\bar{v}=(v+v')/2$. In this way, we obtain the symmetrized semiclassical exponent ϵ^{SSC},

$$\epsilon^{\mathrm{SSC}}=\pi\mu[v^2-(v')^2]/\beta(v+v')=(\pi/\beta)(p'-p), \tag{B7}$$

where p and p' are the initial and final asymptotic momenta, respectively. Reference to Medvedev,[17] Uzer and Child[19] or Landau and Lifschitz[2] reveals that the right side of Eq. (B7) represents exactly the quasiclassical exponents ϵ^{QC}. Thus for this model, the symmetrization procedure brings the semiclassical exponent into complete agreement with its quasiclassical counterpart.

(iii) We next discuss the accuracy of the STP approximation for calculating the integral (B2). The STP point τ_{STP} is found from the requirement that the first derivative of the exponent of the integrand $\exp[i\xi\tau-\lambda\ln(\cosh\tau)]$ vanishes. Making use of the condition $\xi\gg1$, we find

$$\tau_{\mathrm{STP}}=i\pi/2-i\lambda/\xi. \tag{B8}$$

The Gaussian approximation to the integrand about τ_{STP} is

$$\exp(i\xi\tau)\cosh^{-\lambda}\tau=\exp(-\pi\xi/2+\lambda)\cdot(\xi/\lambda)^{\lambda}\times\exp[-\xi^2\cdot(\Delta\tau)^2/2\lambda], \tag{B9}$$

where $\Delta\tau=\tau=\tau_{\mathrm{STP}}$. Integrating Eq. (B7) over $\Delta\tau$ along a horizontal straight line [this horizontal line in t representation corresponds to a vertical line in the z representation (see Appendix A)], we obtain

$$I_{\mathrm{STP}}(\xi,\lambda)=2\pi\lambda\cdot\xi^{\lambda-1}\cdot\exp(-\pi\xi/2)/\mathrm{St}(\lambda+1), \tag{B10}$$

where $\mathrm{St}(\lambda+1)$ is the Stirling approximation to gamma function

$$\mathrm{St}(\lambda+1)=\lambda^{\lambda}\cdot\exp(-\lambda)\cdot(2\pi\lambda)^{1/2}. \tag{B11}$$

Comparing Eq. (B4) to Eq. (B9), we find

$$I_{\mathrm{STP}}(\xi,\lambda)/I(\xi,\lambda)=\Gamma(\lambda+1)/\mathrm{St}(\lambda+1). \tag{B12}$$

Note that as the steepness of interaction increases, the ratio $I_{\mathrm{STP}}(\xi,\lambda)/I(\xi,\lambda)$ tends quickly to unity. For $\lambda=2$, the result of Uzer and Child[19] and Nikitin and Ovchinnikova[16] is recovered $I_{\mathrm{STP}}(\xi,2)/I(\xi,2)=1.042$. As λ decreases, the STP approximation becomes worse and breaks down completely for a linear interaction $\lambda\to0$. [Of course, Eq. (B4) gives a correct result in the limit $\lambda\to0$.] The STP approximation fails for a simple reason. For the STP approximation to be applicable, the range of the stationary phase region $\Delta\tau_{\mathrm{STP}}$ (the width of the Gaussian peak) must be small compared with the distance between τ_{STP} and any other singular point, in our case τ_s,

$$\Delta\tau_{\mathrm{STP}}=(2\lambda)^{1/2}/\xi<|\tau_s-\tau_{\mathrm{STP}}|=\lambda/\xi. \tag{B13}$$

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