Unified semiclassical theory for the two-state system: An analytical solution for general nonadiabatic tunneling

Chaoyuan Zhu and Sheng Hsien Lin

Citation: The Journal of Chemical Physics **125**, 044104 (2006); doi: 10.1063/1.2227399
View online: http://dx.doi.org/10.1063/1.2227399
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/125/4?ver=pdfcov
Published by the AIP Publishing

Unified semiclassical theory for the two-state system: An analytical solution for general nonadiabatic tunneling

Chaoyuan Zhu[a)]
Department of Applied Chemistry, National Chiao-Tung University, Hsinchu 300, Taiwan;
Institute of Molecular Science, National Chiao-Tung University, Hsinchu 300, Taiwan;
and Center for Interdisciplinary Molecular Science, National Chiao-Tung University, Hsinchu 300, Taiwan

Sheng Hsien Lin
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan
and Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

(Received 26 May 2006; accepted 21 June 2006; published online 26 July 2006)

Unified semiclasical solution for general nonadiabatic tunneling between two adiabatic potential energy surfaces is established by employing unified semiclassical solution for pure nonadiabatic transition [C. Zhu, J. Chem. Phys. **105**, 4159 (1996)] with the certain symmetry transformation. This symmetry comes from a detailed analysis of the reduced scattering matrix for Landau-Zener type of crossing as a special case of nonadiabatic transition and nonadiabatic tunneling. Traditional classification of crossing and noncrossing types of nonadiabatic transition can be quantitatively defined by the rotation angle of adiabatic-to-diabatic transformation, and this rotational angle enters the analytical solution for general nonadiabatic tunneling. The certain two-state exponential potential models are employed for numerical tests, and the calculations from the present general nonadiabatic tunneling formula are demonstrated in very good agreement with the results from exact quantum mechanical calculations. The present general nonadiabatic tunneling formula can be incorporated with various mixed quantum-classical methods for modeling electronically nonadiabatic processes in photochemistry. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2227399]

I. INTRODUCTION

A fully quantum mechanical solution for many-body Schrödinger equation is generally investigated by two approaches. One of them is to reformulate the Schrödinger equation into a formally solvable equation first and then to do various approximations. The other is to start from the certain classical and/or semiclassical approximation first and then to bring all neglecting quantum effects back to this approximation. The time-dependent density function theory (TDDFT) represents the former case in which solving electronic and nuclear motions simultaneously has been proposed[1] and the demonstration for the simple system has been achieved.[2] The Born-Oppenheimer approximation represents the latter case in which electronic and nuclear motions are treated separately first, and then the nonadiabatic transitions are treated by various semiclassical approximations. The quantum-classical mean field or semiclassical Ehrefect (SE) method,[3,4] the trajectory surface hopping (TSH) method,[5] semiclasssical initial value representation (IVR) method,[6] the multiconfiguration time-dependent Hartree (MCTDH) method,[7] and analytical semiclassical solution (ASS) method[8,9] all deal with the nonadiabatic transitions with some different schemes. Among the various approximated methods, various combinations of the different methods can improve accuracy for simulating nonadiabatic molecular dynamics. For instance, the method of decay of mixing with coherent switching that combines SE with TSH methods has been demonstrated to be more accurate than both SE and TSH.[10] The method of combining TSH with DTDFT has been shown to be more accurate than the method of combining SE with DTDFT.[11] The method of combining ASS with TSH has brought nonadiababtic tunneling back to TSH and showed a significant contribution to the charge transfer reaction even for high collision energy.[12] An advantage of the ASS method for the nonadiabatic dynamics is that the analytical formula can be flexibly and accurately incorporated into all the other methods for the molecular dynamical simulation based on the Born-Oppenheimer approximation. The analytical semiclassical solution can provide intermediate nonadiabatic dynamic information that is very useful to interpret the experimental results. The analytical semiclassical solution bridges a visible semiclassical formula to connect nonadiabatic dynamics through two or more adiabatic potential energy surfaces and provides a quantitative description for nonadiabatic transition as well as nonadiabatic tunneling.

Nonadiabatic transitions can be classified into two categories from semiclassical point of views; one is classically allowed transition that is pure nonadiabatic transition, as shown in region $E>E_0$ of Fig. 1 and the other is classically forbidden transition that is nonadiabatic transition accompanied with tunneling (it is also called as nonadiabatic tunneling), as shown in region $E<E_0$ of Fig. 1. The coordinate R in Fig. 1 represents the certain curved one-dimensional space

a)Electronic mail: cyzhu@mail.nctu.edu.tw

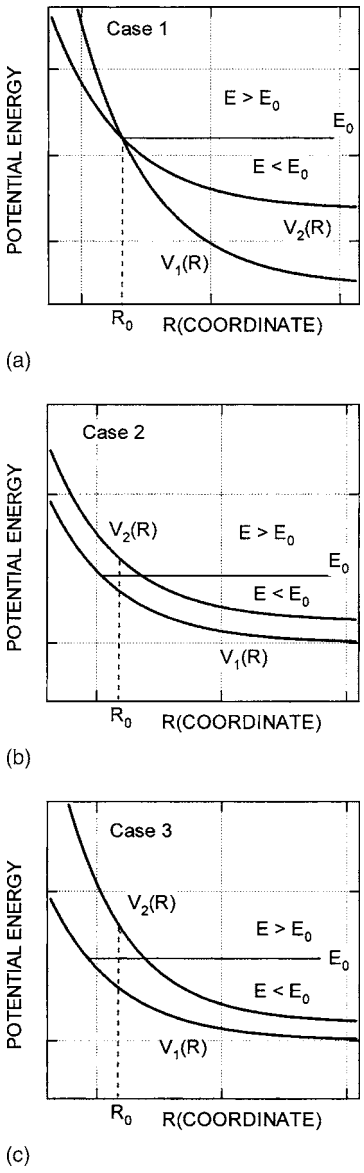

FIG. 1. $E>E_0$ corresponds to pure nonadiabatic transition zone and $E<E_0$ corresponds to nonadiabatic tunneling zone. (a) Landau-Zener type of the crossing at R_0, where $d\ (R_0)\gg 2$. (b) Rosen-Zener-Demkov type of the noncrossing at R_0, where $d\ (R_0)\approx 2$. (c) Far-apart type of noncrossing at R_0, where $d\ (R_0)\sim 1$.

along which nonadiabatic transition and tunneling take place. Figure 1(a) shows Landau-Zener type of crossing, where analytical formulas for pure nonadiabatic transition were initially found by Landau,[13] Zener,[14] and Stückelberg,[15] and analytical formulas for nonadiabatic tunneling were studied by Barany,[16] Nikitin,[4] and Child.[17] Zhu and Nakamura[8] applied exact semiclassical method based on the Stokes constant and established the most sophisticated analytical formulas for both nonadiabatic transition and tunneling. Figure 1(b) shows Rosen-Zener-Demkov type of noncrossing, and analytical formulas for pure nonadiabatic transition were studied by Rosen and Zener,[18] Demkov,[19] and Osherov and Voronin.[20] Figure 1(c) shows far-apart type of noncrossing, where analytical formula for pure nonadiabatic transition was studied by Nikitin and Umanskii.[21] However, in both Rosen-Zener-Demkov and far-apart noncrossing types there are no analytical formulas for nonadiabatic tunneling. This is the motivation of the present study. Three types of crossing and noncrossing nonadiabatic transitions in Fig. 1 were unified into a single analytical formula[9] in which the type of nonadiabatic transition can be quantitatively described by the rotation angle of adiabatic-to-diabatic transformation [see Eq. (1) below]. However, this unified semiclassical formula can only deal with pure nonadiabatic transition. In this work, we will develop unified semiclassical formula in terms of the rotation angle for general nonadiabatic tunneling including three types in Fig. 1. Unified semiclassical formula for pure nonadiabatic transition was expressed in terms of the following quantity:[9]

$$d = d(R_0) = 1 + \tan^2[2\theta(R_0)], \tag{1}$$

where R_0 is the real part of the complex crossing point between two adiabatic potential energy surfaces and $\theta(R)$ is the rotation angle which defines a transformation between adiabatic and diabatic representations,

$$\tan[2\theta(R)] = \frac{2V_{12}(R)}{V_2(R) - V_1(R)}, \tag{2}$$

where $V_1(R)$ and $V_2(R)$ are diabatic potential energy surfaces in Fig. 1 and $V_{12}(R)$ is diabatic coupling.

Section II explores symmetry relation of the reduced scattering matrix between pure nonadiabatic transition and nonadiabatic tunneling in Landau-Zener type of crossing. This symmetry relation is extended to general nonadiabatic transition and tunneling in Sec. III where analytical semiclassical solution for general nonadiabatic tunneling is newly developed. Section IV demonstrates numerical examples in which the present general nonadiabatic tunneling formula well reproduces exact quantum nonadiabatic tunneling probability. Section V presents conclusions.

II. SYMMETRY PROPERTY BETWEEN PURE NONADIABATIC TRANSITION AND NONADIABATIC TUNNELING IN LANDAU-ZENER CASE

The ordinary tunneling through the potential energy barrier can be described by the Wentzle-Kramers-Brillouin (WKB) semiclassical formula with phase integral between two classical turning points. As collision energy rises above potential energy barrier, two real classical turning points become two complex turning points and the phase integral through two complex turning points can be still utilized for calculating barrier top reflection probability. Even in multidimensional tunneling case, the instanton theory can run classical trajectory on the upside-down potential energy surface around the potential barrier zone.[22] Such symmetry connection in ordinary tunneling should also exist in nonadiabatic tunneling case.

Nonadiabatic tunneling differs from ordinary tunneling. The nonadiabatic tunneling is generally through two adiabatic potential energy surfaces along the path in the direction of nonadiabatic coupling vector, while the ordinary tunneling is usually through a single adiabatic potential energy surface from the reactant to product region along the minimum potential energy path. The nonadiabatic tunneling through two

coupled adiabatic potential energy surfaces is in general related to the four complex turning points described by the semiclassical method associated with Stokes phenomenon.[23] Within two-state linear curve crossing model, there are symmetry relations among these four complex turning points and their geometry structures in complex plane were well analyzed in Ref. 23. We start with the fundamental differential equation for determining the reduced scattering matrix in Eq. (2.1) of Ref. 24,

$$\frac{d^2B(t)}{dt^2} + q(t)B(t) = 0, \tag{3}$$

where

$$q(t) = \tfrac{1}{4} - ia^2t + \tfrac{1}{4}(a^2t^2 - b^2)^2, \tag{4}$$

in which the unitless parameter a^2 represents an effective nonadiabatic coupling constant and the b^2 represents an effective collision energy [roughly speaking, $b^2>0$ corresponds to pure nonadiabatic transition, i.e., $E>E_0$ in Fig. 1(a), while $b^2<0$ corresponds to nonadiabatic tunneling, i.e., $E<E_0$ in Fig. 1(a)]. The reduced scattering matrix can be expressed in terms of a single Stokes constant U_1 that is a function of two parameters a^2 and b^2 (or σ and δ),

$$S^R(U_1(a^2,b^2)) = S^R(U_1(\sigma,\delta)), \tag{5}$$

where the two sets of parameters are connected by the following relations in the case of pure nonadiabatic transition under condition $b^2 \gg 1$:[24]

$$\sigma = \frac{2a^2x_0^3}{3} + \delta\ln\left(\frac{x_0^2}{\delta^2}\right) - \delta, \tag{6}$$

$$\delta = \frac{1}{8\sqrt{a^2b^2}}, \tag{7}$$

and

$$x_0^2 = \frac{b^2}{a^2}. \tag{8}$$

In order to find good semiclassical approximation for the Stokes constant U_1 in Eq. (5), for pure nonadiabatic transition ($b^2 \gg 1$) we derived it from the connection matrix that connects asymptotic wave functions between $B(\infty)$ and $B(-\infty)$ in Eq. (3), and for nonadiabatic tunneling ($b^2 \ll -1$) we derived it from the connection matrix between $B(i\infty)$ and $B(-i\infty)$ in Eq. (3). This suggests that we can make transformation $t=it'$, and then Eq. (3) becomes

$$\frac{d^2B(t')}{dt'^2} + q_1(t')B(t') = 0, \tag{9}$$

where

$$\begin{aligned} q_1(t') &= -\tfrac{1}{4} - a^2t' - \tfrac{1}{4}(a^2t'^2 - (-b^2))^2 \\ &= -\tfrac{1}{4} - i[-ia^2]t' + \tfrac{1}{4}([-ia^2]t'^2 - [-i|b^2|])^2. \end{aligned} \tag{10}$$

It should be noted that the Stokes constant for nonadiabatic tunneling is in the region $b^2 \ll -1$ with the connection matrix equivalently for Eq. (9) at $t' = \pm\infty$. Comparing Eq. (10) with Eq. (4), an essential difference is only in the sign of the first term of 1/4 (this effect is negligible under condition $|b^2| \gg 1$). Thus, we can write the reduced scattering matrix for nonadiabatic tunneling from Eq. (5) as

$$S^R(b^2 \ll -1) \approx S^R(U_1(-ia^2,-i|b^2|)) = S^R(U_1(-i\sigma,-i\delta)), \tag{11}$$

in which Eqs. (6)–(8) are employed for the last equality. In the nonadiabatic tunneling case, notations of σ and δ are just interchanged [see Eqs. (5.4), (5.5), (5.15), and (5.16) of Ref. 24]. This means that the following replacement:

$$\delta \to -i\sigma \text{ and } \sigma \to -i\delta, \tag{12}$$

can be applied to the following expression of Stokes constant for pure nonadiabatic transition:[24]

$$U_1(\sigma,\delta) = \sqrt{\frac{1}{p} - 1}\exp(i\psi), \tag{13}$$

where

$$p = e^{-2\delta} \tag{14}$$

and

$$\psi = \sigma - \frac{\delta}{\pi} + \frac{\delta}{\pi}\ln\left(\frac{\delta}{\pi}\right) - \arg\Gamma\left(i\frac{\delta}{\pi}\right) - \frac{\pi}{4}. \tag{15}$$

Under the replacement of Eq. (12), we can easily show that the phase part in Eq. (15) turns out to be

$$\begin{aligned} \exp(i\psi) \to \exp\left[\delta - \frac{\sigma}{\pi} + \frac{\sigma}{\pi}\ln\left(\frac{\sigma}{\pi}\right) - i\frac{\sigma}{2} - i\frac{\pi}{4}\right] \\ \times \frac{\pi}{i\Gamma(\sigma/\pi)\sqrt{\sigma\sin\sigma}}, \end{aligned} \tag{16}$$

and that the amplitude part in Eq. (14) turns to be

$$\sqrt{\frac{1}{p} - 1} \to \sqrt{e^{-i2\sigma} - 1} = \sqrt{-2ie^{-i\sigma}\sin\sigma}. \tag{17}$$

Finally, Eq. (13) turns out to be

$$U_1 = U_0\exp(-i\sigma), \tag{18}$$

where

$$U_0 = \exp\left(\delta - \frac{\sigma}{\pi} + \frac{\sigma}{\pi}\ln\left(\frac{\sigma}{\pi}\right)\right)\frac{\sqrt{2}\pi}{\sqrt{\sigma}\Gamma(\sigma/\pi)}. \tag{19}$$

Equations (18) and (19) exactly coincide with the expression of the Stokes constant for nonadiabatic tunneling that can be directly derived from Eq. (3), as it should be the case from general analysis of symmetry relation discussed above.

The two-state linear curve crossing model can be generalized to treat general two-state curve crossing problems by computing parameters σ and δ in the expression of Stokes constant for both pure nonadiabatic transition and nonadiabatic tunneling from the following complex integral:

$$\sigma + i\delta = \int_{T_-}^{R^*} K_-(R)dR - \int_{T_+}^{R^*} K_+(R)dR, \tag{20}$$

where $T_-(T_+)$ is a classical turning point on the lower (upper) adiabatic potential energy surface, R^* is the complex cross-

ing point between two surfaces, and the explicit expressions of $K_{\pm}(R)$ in Eq. (20) is given by

$$K_{\pm}(R) = \sqrt{2\mu(E - W_{\pm}(R))}/\hbar, \tag{21}$$

which is basically the classical wave number on the upper and lower adiabatic potential energy surfaces, respectively. Two adiabatic potential energy surfaces in Eq. (21) can be expressed in terms of diabatic potential and coupling energy surfaces,

$$W_{\pm}(R) = [V_1(R) + V_2(R)]/2 \pm \sqrt{[V_1(R) - V_2(R)]^2 + 4V_{12}(R)}/2. \tag{22}$$

Finally, the overall nonadiabatic transition probability for both pure nonadiabatic transition and nonadiabatic tunneling can be expressed in terms of the Stokes constant U_1,[8,24]

$$P_{12} = \left[\frac{2 \text{ Im } U_1}{|U_1|^2 + 1}\right]^2. \tag{23}$$

Before going to the next section, we comment on the symmetry relation of the reduced scattering matrix derived from Eqs. (4) and (10). This symmetry is approximated symmetry and it is good only under the condition $|b^2| \gg 1$. Since $b^2 \gg 1$ corresponds to very high collision energy and $b^2 \ll -1$ corresponds to very low collision energy, this means that the symmetry is for the region in which pure nonadiabatic transition and deep nonadiabatic tunneling can be well separated from each other. As the collision energy is close to E_0 in Fig. 1(a) where $|b^2| < 1$, nonadiabatic transition and tunneling are well mixed from the semiclassical method point of view. Nevertheless, in practice, Stokes constant for nonadiabatic tunneling in Eq. (18) derived from the condition $b^2 \ll -1$ still works at $b^2 < -1$. A more sophisticated Stokes constant [see Eqs. (28) and (29) below] derived from $b^2 < -1$ still works at $b^2 < 0$. All numerical calculations with detailed analysis are discussed in Ref. 24.

III. ANALYTICAL SEMICLASSICAL SOLUTION FOR GENERAL NONADIABATIC TUNNELING

Exact quantum simulation requires all the values of R along the certain nonadiabatic transition path in Fig. 1, while the semiclassical method based on the complex phase integral[24–26] indicates that nonadiabatic transitions occur locally around the complex crossing points between the two adiabatic potential energy surfaces. This is similar to the tunneling on a single adiabatic potential energy surface, where the tunneling occurs around the classical turning points. The complex crossing points for nonadiabatic tunneling are sort of extension of such classical turning points to the complex plane. Detailed analysis of those complex crossing points associated with the Stokes phenomenon can lead to the semiclassical solution for nonadiabatic transition and tunneling probability. This was done for two-state Landau-Zener type of crossing for both pure nonadiabatic transition and nonadiabatic tunneling. However, for general two-state system with $1 < d(R) < \infty$ in Eq. (1) the analytical formula is found only for pure nonadiabatic transition case.[9] We would like to reformulate the reduced scattering matrix for general two-state system in terms of Stokes constants U_1 $[\sigma, \delta, d(R_0)]$, in which there is one more parameter $d(R_0)$ compared to Landau-Zener type of crossing [actually $d(R_0) = \infty$ for Landau-Zener case]. For all three cases of $E > E_0$ in Fig. 1 we define the expression of Stokes constant in Eq. (13) with the following expressions for p and ψ:[9]

$$p = \frac{\sinh[(d-1)\delta]}{\sinh(d\delta)} e^{-\delta} \tag{24}$$

and

$$\psi = \sigma + \arg\Gamma\left[i(d-1)\frac{\delta}{\pi}\right] - \arg\Gamma\left(i\frac{\delta}{\pi}\right) - (d-1)\frac{\delta}{\pi}\ln(d-1) - (d-2)\frac{\delta}{\pi}\left(\ln\left(\frac{\delta}{\pi}\right) - 1\right). \tag{25}$$

It should be noted that the overall nonadiabatic transition probability is still given by Eq. (23), and parameters σ and δ are also evaluated from Eq. (20). The most important quantity d in Eqs. (24) and (25) is defined by Eq. (1) which represents a type of nonadiabatic transition. If $d \to \infty$, Eqs. (24) and (25) turn to be Eqs. (14) and (15) in the Landau-Zener case, respectively.

In order to derive the expression of the Stokes constant for general nonadiabatic tunneling case, we assume that the reduced scattering matrix has the same symmetry relation as it has in Sec. II of Landau-Zener case, namely, we can employ replacement of Eq. (12) to Eqs. (24) and (25). After some tedious derivation, we finally find the Stokes constant for general nonadiabatic tunneling case,

$$U_1 = U_0 \exp[-i\sigma], \tag{26}$$

where

$$U_0 = \frac{\Gamma[(d-1)\sigma/\pi]}{\Gamma(\sigma/\pi)}\sqrt{d-1}\exp\left[\delta - (d-1)\frac{\sigma}{\pi}\ln(d-1) - (d-2)\frac{\sigma}{\pi}\left(\ln\left(\frac{\sigma}{\pi}\right) - 1\right)\right]. \tag{27}$$

It is easy to confirm that Eq. (27) becomes Eq. (19) at $d \to \infty$. The Stokes constant in Eq. (19) for the Landau-Zener case includes contribution only from dominant part of the semiclassical phase integral. By adding contribution from the subdominant part of the semiclassical phase integral, Zhu-Nakamura finally found the most sophisticated formula for nonadiabatic tunneling,[24]

$$\text{Re } U_1 = \cos\sigma[U_0 - \sin^2\sigma/U_0], \tag{28}$$

$$\text{Im } U_1 = -\sin\sigma\sqrt{U_0^2 - \sin^2\sigma\cos^2\sigma/U_0^2 + \cos(2\sigma)}, \tag{29}$$

where U_0 is defined in Eq. (19) for the Landau-Zener case. We can directly generalize Eqs. (28) and (29) to general nonadiabatic tunneling case by replacing U_0 with Eq. (27).

IV. NUMERICAL COMPARISONS

In order to demonstrate and test the newly developed unified semiclassical nonadiabatic tunneling formula in Eq. (27) with Eqs. (28) and (29), without losing generality, we

present numerical calculation with the two-state exponential potential model given in the diabatic representation by the following potential energy surfaces:

$$V_{11}(x) = 1.1 \exp(-a_1 x) - 0.12, \tag{30}$$

$$V_{22}(x) = \exp(-a_2 x), \tag{31}$$

with the diabatic coupling function

$$V_{21}(x) = V_0 \exp(-1.5x), \tag{32}$$

in which a_1, a_2, and V_0 are to be selected to determine a type of nonadiabatic transition like the crossing or noncrossing case in which a quantitative description of nonadiabatic type is given by Eq. (1). All calculations are carried out in a.u. (the reduced mass of system is 1000 a.u.). Exact results shown in Fig. 2 are calculated from a quantal close-coupling method. Two semiclassical results of nonadiabatic tunneling probability are calculated from Eq. (23) with expressions of Stokes constant given by Eqs. (28) and (29), but the Zhu-Nakamura (ZN) formula uses Eq. (19) and the present new semiclassical formula employs Eq. (27) for U_0. Table I summarizes three cases with d=7.76, 2.28, and 1.21. Case 1 is the Landau-Zener case in Fig. 1(a) with large d so that both the ZN and the present semiclassical formulas work well for overall nonadiabatic tunneling probability, as shown in Fig. 2(a). As d gets smaller in case 2 that corresponds to two nearly parallel diabatic potential energy surfaces around nonadiabatic transition zone which is similar to the Rosen-Zener-Demkov case in Fig. 1(b), the ZN formula starts to deviate from the exact calculation and gets worse as collision energy becomes close to E_0 (see Table I), as shown in Fig. 2(b). Case 3 is the most dramatic case because d=1.21 that is close to unity, as shown in Fig. 1(c), for far-apart noncrossing case, the ZN formula shows very bad results in Fig. 2(c), while the present new formula still works very well. This can be well understood from the fact that there is no nonadiabatic tunneling if d=1. It is easy to check that the present new formula shows this correct limit. As d goes to unity, U_0 in Eq. (27) turns to be infinity and thus the nonadiabatic tunneling probability in Eq. (23) turns to be zero, while the ZN formula completely fails because the ZN formula is a special case of the new formula with $d=\infty$. The quantity d in Eq. (1) can be considered as an effective nonadiabatic coupling strength, and it gets weaker as d gets smaller. Although the crossing type of nonadiabatic transition is generally more localized than the noncrossing type, an essential mechanism of nonadiabatic transition is the same that is governed by the complex crossing points between two adiabatic potential energy surfaces. Those complex crossings will be all localized in the certain region of complex plane. This is the reason why we can develop the present unified semiclassical formula based on an extension of the symmetry relation in Sec. II that is held in Landau-Zener type of crossing.

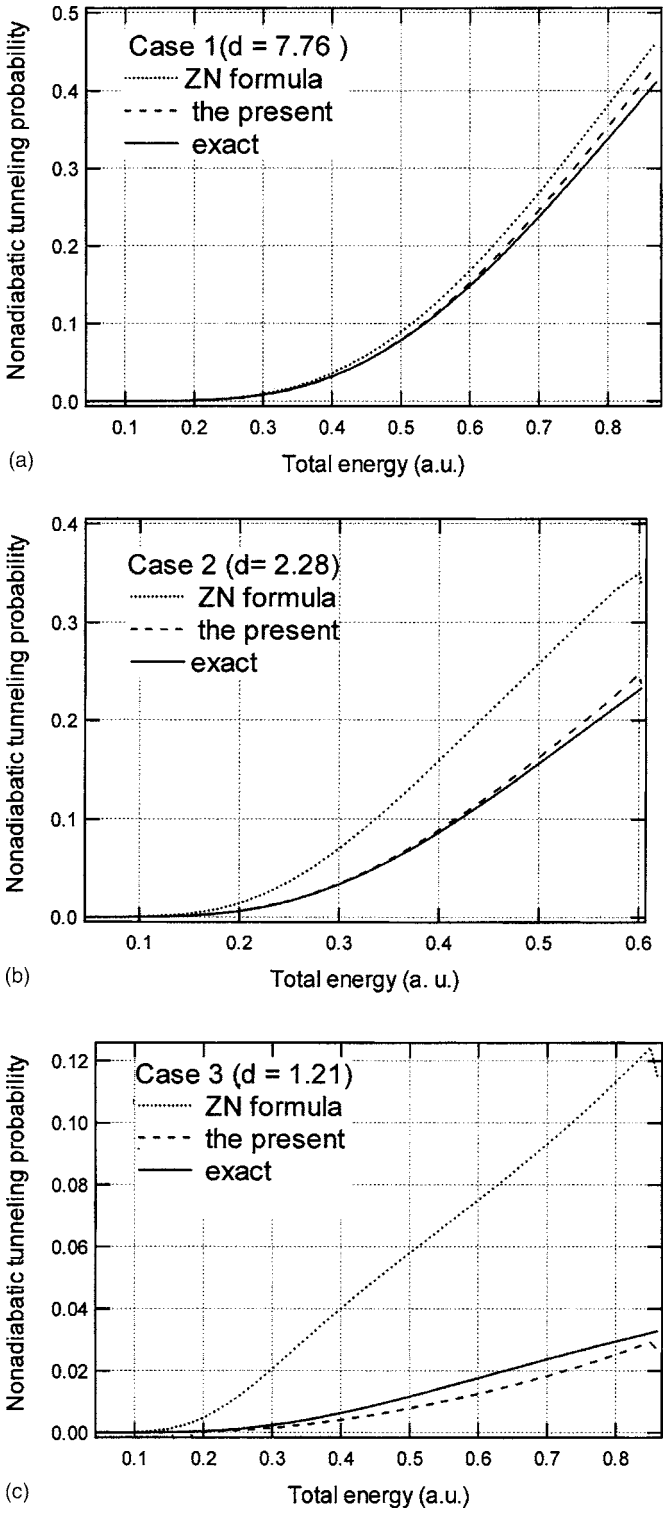

FIG. 2. Nonadiabatic tunneling probability against total energy $E<E_0$ shown in Fig. 1 for three crossing and noncrossing types. (a) Case 1 corresponds to Fig. 1(a) (note the real crossing point at R=−0.127 differs from the real part of complex crossing point at R_0=0.0383). (b) Case 2 corresponds to Fig. 1(b). (c) Case 3 corresponds to Fig. 1(c).

V. CONCLUSIONS

Unified semiclassical formula for general nonadiabatic tunneling with Stokes constant in Eqs. (27)–(29) is developed, combining the formula for pure nonadiabatic transition with Stokes constant in Eqs. (13)–(15) we have finally completed unified semiclassical formula for both classically allowed and forbidden nonadiabatic transition. Application of the unified semiclassical theory to photochemical processes associated with various types of conical intersections will be studied in the near future. The conical intersections in real

TABLE I. Three selected cases. R^* is the complex crossing point between two adiabatic potential energy surfaces. $E_0=(W_+(R_0)+W_-(R_0))/2$, where R_0 is the real part of the complex crossing. d is computed from Eq. (1).

	a_1	a_2	V_0	R^*	E_0	d
Case 1	1.95	2.0	0.035	(0.0383,0.3125)	0.91	7.76
Case 2	1.8	2.0	0.02	(0.24,0.3125)	0.61	2.28
Case 3	1.8	2.0	0.005	(0.064,0.3125)	0.87	1.21

photochemistry can form very complicated structures around the nonadiabatic transition zone,[27] in which the type of nonadiabatic transition can be any value of $1<d<\infty$. Even in the case that the low-lying electronically excited states may not be energetically accessible, the nonadiabatic tunneling can still contribute to the overall reaction. By applying analytical semiclassical formula derived here, we do not have to calculate large region of the configuration space of electronically excited states and we only need to calculate the small region near nonadiabatic tunneling zone. The present calculations with the certain model potential energy surfaces have shown very good agreement between the present nonadiabatic semiclassical formula and exactly quantum mechanical method. It should be noted that the present analytical nonadiabatic tunneling formula would work well for general two-state problems, and the model here is very general in the sense that it covers various configuration structure near the nonadiabatic tunneling zone. It is an advantage that analytical semiclassical solution grasps an essential feature of nonadiabatic transition and nonadiabatic tunneling. A general application of the present semiclassical solutions to multidimensional nonadiabatic dynamics requires the certain manipulation of one-dimensional reduction. A natural one-dimensional reduction takes place in the direction of the nonadiabatic coupling vector. For instance, incorporating with the trajectory surface hopping method[5,12] to deal with nonadiabatic reaction, we can compute nonadiabatic transition and tunneling probability along the hopping direction that is curved one-dimensional potential energy surface profiles. The present sophisticated semiclassical analytical solution will be a powerful analytical tool for dealing with nonadiabatic tunneling induced by various conical intersections in photochemistry.

ACKNOWLEDGMENTS

One of the authors (C.Z.) would like to thank Professor S. H. Lin for providing summer visiting support at the IAMS, Taipei in 2005. This work was supported by the National Science Council of Taiwan of the Republic of China under Grant No. 95-2113-M-009-013 and by National Chaio-Tung University.

[1] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984); M. A. L. Marques and E. K. U. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).
[2] T. Kreibich and E. K. U. Gross, Phys. Rev. Lett. **86**, 2984 (2001).
[3] G. D. Billing, Chem. Phys. **81**, 754 (1975); Int. Rev. Phys. Chem. **13**, 309 (1994).
[4] E. E. Niktin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Clarendon, Oxford, 1974).
[5] P. Pechukas, Phys. Rev. **181**, 174 (1969); J. C. Tully and R. K. Preston, J. Chem. Phys. **55**, 562 (1971); **93**, 1061 (1990).
[6] M. Thoss, W. H. Miller, and G. Stock, J. Chem. Phys. **112**, 10282 (2000); X. Sun, H. Wang, and W. H. Miller, *ibid.* **109**, 7064 (1998); X. Sun and W. H. Miller, *ibid.* **106**, 6346 (1997).
[7] H.-D. Meyer, U. Manthe, and L. S. Cederbaum, Chem. Phys. Lett. **165**, 73 (1990); A. Raab, G. A. Worth, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **110**, 936 (1999); G. A. Worth, H.-D. Meyer, and L. S. Cederbaum, *ibid.* **105**, 4412 (1996).
[8] C. Zhu and H. Nakamura, J. Chem. Phys. **101**, 10630 (1994); **102**, 7448 (1995).
[9] C. Zhu, J. Chem. Phys. **105**, 4159 (1996); J. Phys. A **29**, 1293 (1996); J. Chin. Chem. Soc. (Taipei) **50**, 777 (2003).
[10] C. Zhu, A. W. Jasper, and D. G. Truhlar, J. Chem. Phys. **120**, 5543 (2004); J. Chem. Theory Comput. **1**, 527 (2005); M. D. Hack and D. G. Truhlar, J. Chem. Phys. **114**, 9305 (2001).
[11] C. F. Craig, W. R. Duncan, and O. V. Prezhdo, Phys. Rev. Lett. **95**, 163001 (2005).
[12] C. Zhu, H. Kamisaka, and H. Nakamura, J. Chem. Phys. **115**, 11036 (2001); **116**, 3234 (2002).
[13] D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932).
[14] C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[15] C. G. Stückelberg, Helv. Phys. Acta **5**, 369 (1932).
[16] A. Bárány, Report No. 25 (Institute of Theoretical Physics, Uppsala University, Sweden, 1979).
[17] M. S. Child, *Molecular Collision Theory* (Academic, London, 1974).
[18] N. Rosen and C. Zener, Phys. Rev. **40**, 502 (1932).
[19] Yu. N. Demkov, Sov. Phys. JETP **18**, 941 (1962).
[20] V. I. Osherov and A. I. Voronin, Phys. Rev. A **49**, 265 (1994).
[21] E. E. Niktin and S. Ya. Umanskii, *Theory of Slow Atomic Collisions* (Springer, Berlin, 1984).
[22] V. A. Benderskii, V. I. Goldanskii, and D. E. Makarov, Phys. Rep. **233**, 195 (1993).
[23] C. Zhu, H. Nakamura, N. Re, and V. Aquilanti, J. Chem. Phys. **97**, 1892 (1992).
[24] C. Zhu and H. Nakamura, J. Chem. Phys. **97**, 8497 (1992).
[25] M. S. Child, *Semiclassical Mechanics with Molecular Applications* (Oxford University Press, New York, 1991).
[26] J. Heading, *An Introduction to Phase-Integral Methods* (Methuen, London, 1962).
[27] See excellent book, *Conical Intersections in Electronic Structure, Dynamics and Spectroscopy*, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004).