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The conical intersection effects and adiabatic single-surface approximations on scattering processes: A time-dependent wave packet approach

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Using a quasi-Jahn-Teller model and an extended version of the approximate Born-Oppenheimer (BO) single surface equations, Baer, Charutz, Kosloff, and Baer [J. Chem. Phys. **105**, 9141 (1996)] have performed time-independent scattering calculations to study a direct effect on the symmetry of the nuclear wave function due to conical intersections between BO potential energy surfaces. In this article, we have addressed the same problem using the same model by introducing either a vector potential in the nuclear Hamiltonian or by incorporating a phase factor in the nuclear wave function. The scattering calculations have been carried out by using a time-dependent wave packet approach.

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I. INTRODUCTION

Initially, the Born Oppenheimer (BO) adiabatic separation of electronic and nuclear motion was introduced by ignoring the parametric dependence of the adiabatic electronic wave function on the nuclear coordinates with the assumption that the effects of nuclear motion can be included in a perturbative manner. But, this scenario suffered from some complication due to the presence of conical intersections¹⁻⁹ which has been demonstrated by Herzberg and Longuet-Higgins.¹⁰⁻¹³ In general, when BO potential energy surfaces of a molecular system are degenerate, the nonadiabatic coupling terms become infinitely large in a region of space configuration. Usually, if the nonadiabatic coupling terms are singular at an isolated point, these cases are known as conical intersections between BO potential energy surfaces and this can affect symmetry properties of the system.

For systems with three identical atoms, the Jahn-Teller (JT) effect is the most well known phenomena^{1,13-17} and well studied in bound systems¹⁸⁻²⁰ whereas the effect of singularities on scattering processes has also been addressed recently by extending the Jahn-Teller model.²¹ Using a simple two-dimensional quasi-JT model, the effect of symmetry on transition probabilities, i.e., nonreactive and reactive probabilities, calculations were performed using approximate extended version of the BO equations. Equations which can be derived from the Schrödinger equation if the energy of the system is sufficiently low compared to the upper surface in space configuration. These extended BO equations are different from the ordinary BO approximations and it has been shown that numerical calculations using ordinary BO equations on the quasi-JT model could not follow the proper symmetry of the system whereas the extended BO equations responded with relevant symmetry and consequently, offered correct transition probabilities. Finally, a two surface calculation on a quasi-JT model confirmed the validity of the extended BO equations. It has also been dem-

onstrated that nonadiabatic coupling terms can be strong enough in the degenerate region of the electronic states to produce numerical instability,²² but one can move from the adiabatic to the diabatic representation to eliminate these terms.²²⁻²⁴ This change of representation is basically performed by an orthogonal transformation where the transformation angle,^{23,24} α , is explicitly used to represent the two surface system. Though this adiabatic-diabatic angle, α , can be a complicated function of the spatial coordinates,²² it is in the case of a quasi-JT model a very simple function of the coordinates, i.e., $\phi/2$, where ϕ is the polar coordinate.^{18,19}

The motivation of the generalized BO treatment came in order to avoid double valuedness of the total wave function. Contrary to the above procedure, there are also two other proposed ways of generalization. Mead and Truhlar²⁵ generalized the BO equations by introducing a vector potential into the nuclear Schrödinger equation to ensure a single valued and continuous total wave function. In this approach, the wave function is multiplied by a complex phase factor and the nuclear Schrödinger equation consequently acquires a vector potential. When the nuclear coordinates travel through a close path around the conical intersection, the vector potential can introduce the required sign change and make the total wave function single valued. In an another approach, Kuppermann *et al.* and others²⁶ ensured the required sign change by multiplying the total wave function with a phase factor. Using accurate quantum scattering calculations, Kuppermann and co-workers have identified this effect for the first time in chemical reactions (H_3 and its isotopic variants) and the theoretically calculated differential and state-resolved cross sections agreed well with experimental data at different energies. As the conical intersection of the ground and the excited states of the H_3 system occurs at the symmetric triangular configuration in hyperspherical coordinates, it is possible to incorporate the effect into the basis functions directly such that the nuclear Schrödinger equation does not need a vector potential. Though this is a reasonably good approximation for isotopic variants of X_3 in hyperspherical

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coordinates, for general situation and complicated molecules (where the point of the conical intersection does not coincide with a special symmetry of coordinate system) the introduction of a vector potential to get extended BO equations will be the obvious choice. As this effective nuclear Schrödinger equation due to the vector potential is similar to those differential equations which can mimic a charged particle moving in the presence of a magnetic solenoid, this phenomenon is called “molecular Aharonov-Bohm effect”²⁷ and it is a special case of Berry’s phase.²⁸

The general form of vector potential in hyperspherical coordinates for the A+B₂ reactive system even when the position of the conical intersection could be arbitrary, has been formulated and the influence of the vector potential on the differential and state-resolved cross sections for the D+H₂ system has been studied by quasiclassical trajectory (QCT) calculations.²⁹ The relative shift of the rotational distribution and the change of differential cross sections in presence of vector potential are qualitatively the same as indicated by Kuppermann and Wu. We have also performed semiclassical calculations³⁰ either by including a vector potential in the nuclear Hamiltonian or by incorporating a phase factor into the basis set for the D+H₂ system where once again the same shift of the rotational distribution was shown.

In this article, we intend to extend the ordinary BO equations introducing a vector potential within the JT model to get the correct transition probabilities and to formulate a modified vector potential due to the shift of the point of conical intersection from the origin of the coordinate system. In both the cases, we have compared the transition probabilities with the corresponding two surface calculations. Finally, we have also incorporated the phase directly into the basis set in the case where the position of the conical intersection is shifted from the origin of the coordinate system.³¹ Obviously, as we have mentioned the inclusion of the phase in the basis set with a shift of the conical intersection from the origin is an approximate scheme, it will therefore be interesting to see how well it works in the present problem.

II. THEORETICAL APPROACH

In this article, we will study a two-coordinate quasi-“JT scattering” model²¹ where the nuclear kinetic energy operator in cartesian coordinates can be written as,

$$T_n(R, r) = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial R^2} \right] \quad (1)$$

and in terms of polar coordinates,

$$T_n(q, \phi) = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial q^2} + \frac{1}{q} \frac{\partial}{\partial q} + \frac{1}{q^2} \frac{\partial^2}{\partial \phi^2} \right]. \quad (2)$$

R and r are defined in the intervals, $-\infty \leq R \leq \infty$ and $-\infty \leq r \leq \infty$ and these are related to q and ϕ in the following way,

$$r = q \sin \phi, \quad R = q \cos \phi \quad \text{and} \quad \phi = \arctan\left(\frac{r}{R}\right).$$

TABLE I. Potential energy parameters used in all calculations.

m	0.58 amu
A	3.0 eV
D	5.0 eV
σ	0.30 Å
σ_1	0.75 Å
ω_0	$39.14 \times 10^{13} \text{ s}^{-1}$
ω_1	$7.83 \times 10^{13} \text{ s}^{-1}$

Again, the two adiabatic potential energy surfaces which we will use in the present calculations, are called a reactive double slit model (RDSM)²¹ where the first surface is the lower and the second the upper surface, respectively,

$$u_1(R, r) = \frac{1}{2} m [\omega_0 - \tilde{\omega}_1(R)]^2 r^2 + A f(R, r) + g(R),$$

$$u_2(R, r) = \frac{1}{2} m \omega_0^2 r^2 - (D - A) f(R, r) + D, \quad (3)$$

with,

$$\tilde{\omega}_1(R) = \omega_1 \exp\left[-\left(\frac{R}{\sigma}\right)^2\right],$$

$$f(R, r) = \exp\left[-\left(\frac{R^2 + r^2}{\sigma^2}\right)\right], \quad g(R) = 0.$$

The parameters used in the above expressions for the potential energy surfaces and the calculations are given in Table I.

As we have mentioned earlier, in case of a conical intersection between two adjacent adiabatic electronic surfaces, the ordinary BO equations for single surface calculations need to be modified to get the correct transition probabilities either by including a vector potential in the nuclear Hamiltonian or by incorporation an extra phase in the basis set directly. The effective nuclear kinetic energy operator due to the vector potential can be formulated by multiplying the adiabatic eigenfunction of the system, $\psi(R, r)$ with $\exp[1/2 \arctan(r/R)]$, and operating with $T_n(R, r)$, as defined in Eq. (1), on the product function and after little algebraic simplification, one can obtain the following effective kinetic energy operator [see Eqs. (41)–(43) of Ref. 21],

$$T'_n(R, r) = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial R^2} + \left(\frac{R}{r^2 + R^2} \right) i \frac{\partial}{\partial r} - \left(\frac{r}{r^2 + R^2} \right) i \frac{\partial}{\partial R} - \frac{1}{4(r^2 + R^2)} \right]. \quad (4)$$

Similarly, the expression for effective kinetic energy operator in polar coordinates will be,

$$T'_n(q, \phi) = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial q^2} + \frac{1}{q} \frac{\partial}{\partial q} + \frac{1}{q^2} \frac{\partial^2}{\partial \phi^2} - i \frac{1}{q^2} \frac{\partial}{\partial \phi} - \frac{1}{4q^2} \right]. \quad (5)$$

If the position of the conical intersection is shifted from the origin of the coordinate system to (r_0, R_0) , the relation between Cartesian and polar coordinates for the present system can be given as,

$r \pm r_0 = q \sin \phi$, $R \pm R_0 = q \cos \phi$ and $\phi = \arctan(r \pm r_0 / R \pm R_0)$. Consequently, the effective nuclear kinetic energy operator will be,³²

$$T_n''(R, r) = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial R^2} + \left(\frac{R \pm R_0}{(r \pm r_0)^2 + (R \pm R_0)^2} \right) i \frac{\partial}{\partial r} - \left(\frac{(r \pm r_0)}{(r \pm r_0)^2 + (R \pm R_0)^2} \right) i \frac{\partial}{\partial R} - \left(\frac{1}{4[(r \pm r_0)^2 + (R \pm R_0)^2]} \right) \right], \quad (6)$$

in Cartesian coordinates and in polar coordinate the expression in Eq. (5) will remain unchanged due to shifted conical intersection from the origin, but in both cases, r and R in u_1 and u_2 will be replaced by $r' = r \pm r_0$ and $R' = R \pm R_0$. Note that the formulation is general, i.e., no matter whether r_0 or R_0 is changed the effect of shifting the origin will appear according to the corresponding two surface results.

The ordinary BO equations in the adiabatic representation can also be used for single surface calculations and the geometrical phase effect incorporated by a phase change in ϕ . The correct phase treatment of the ϕ coordinate can be obtained using a special technique when the kinetic energy operators are evaluated. More specifically the geometrical phase effect can be introduced by modifying the fast Fourier transformation (FFT)³³ procedure. The wave function $\psi(q, \phi)$ is multiplied with $\exp(i\phi/2)$, then after doing forward FFT the coefficients are multiplied with slightly different frequencies ($k + \frac{1}{2}$) instead of k only and finally completing the backward FFT, the wave function is multiplied with $\exp(-i\phi/2)$ and the same procedure needs to be repeated in each time step of propagation.

The transition probabilities obtained due to the above two modified treatments of single surface calculations need to be compared with those transition probabilities obtained by two surface calculations which proves the validity of these former treatments. The two surface calculations in the diabatic representation is rather straightforward with the following Hamiltonian matrix,

$$\mathbf{H} = \mathbf{T} + \mathbf{W} = T_n \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}, \quad (7)$$

where the diabatic potential matrix elements,

$$\begin{aligned} W_{11} &= \frac{1}{2} [u_1 + u_2 + (u_1 - u_2) \cos \phi], \\ W_{22} &= \frac{1}{2} [u_1 - u_2 + (u_1 - u_2) \cos \phi], \\ W_{12} = W_{21} &= \frac{1}{2} (u_1 - u_2) \sin \phi, \end{aligned} \quad (8)$$

are obtained by the following orthogonal transformation,

$$\mathbf{W} = \mathbf{T}^* \mathbf{U} \mathbf{T} \quad (9)$$

$$\text{with } \mathbf{T} = \begin{pmatrix} \cos \phi/2 & -\sin \phi/2 \\ \sin \phi/2 & \cos \phi/2 \end{pmatrix} \text{ and } \mathbf{U} = \begin{pmatrix} u_1 & 0 \\ 0 & u_2 \end{pmatrix}.$$

III. INITIALIZATION, PROPAGATION, AND PROJECTION

Single surface calculations with vector potential in the adiabatic representation and two surface calculations in the diabatic representation with or without shifting the conical intersection from the origin are performed in Cartesian coordinates. As in the asymptotic region the two coordinates of the model represent a translational and a vibrational mode, respectively, the initial wave function for the ground state can be represented as,

$$\Psi_{ad}(R, r, t_0) = \psi_{GWP}^{k_0}(R, t_0) \Phi_v(r, t_0), \quad (10)$$

where $\psi_{GWP}^{k_0}(R, t_0)$ is a Gaussian wave packet and $\Phi_v(r, t_0)$ a harmonic oscillator wave function.

We have mentioned earlier that the two surface calculations will be carried out in diabatic representation. One can get the initial diabatic wave function matrix for the two surface calculations using the above adiabatic initial wave function by the following orthogonal transformation,

$$\begin{pmatrix} \Psi_{di}^1(R, r, t_0) \\ \Psi_{di}^2(R, r, t_0) \end{pmatrix} = \begin{pmatrix} \cos \phi/2 & \sin \phi/2 \\ -\sin \phi/2 & \cos \phi/2 \end{pmatrix} \begin{pmatrix} \Psi_{ad}(R, r, t_0) \\ 0 \end{pmatrix}. \quad (11)$$

Single surface calculations with proper phase treatment in the adiabatic representation with shifted conical intersection has been performed in polar coordinates. For this calculation, the initial adiabatic wave function $\Psi_{ad}(q, \phi, t_0)$ is obtained by mapping $\Psi_{ad}(R, r, t_0)$ into polar space using the relations, $r \pm r_0 = q \sin \phi$ and $R \pm R_0 = q \cos \phi$. At this point, it is necessary to mention that in all the above cases the initial wave function is localized at the positive end of the R coordinate where the negative and positive ends of the R coordinate are considered as reactive and nonreactive channels.

The kinetic energy operator evaluation and then, the propagation of the R, r or q, ϕ degrees of freedom have been performed by a fast Fourier transformation (FFT)³³ method followed by Lanczos reduction technique.³⁴ A negative imaginary potential,^{26(e)}

$$V_{Im}(R) = -\frac{iV_{Im}^{max}}{\cosh^2[(R_{max}^\pm - R)/\beta]}, \quad (12)$$

has been used to remove the wave packet from the grid before it is reflected from the negative and positive ends of the R grid boundary. The parameters used in the above expression and other data are given in Table II.

The transition probability at a particular total energy (E_n) from vibrational level i to f may be expressed as the ratio between the corresponding outgoing and incoming quantities,³⁵

TABLE II. Parameters used in absorbing potential and data for initialization, propagation and projection.

Initialization:			
R_{min}	-6.0 Å	R_{max}	6.0 Å
r_{min}	-1.5 Å	r_{max}	1.5 Å
r_0	0.0 Å	R_0	-0.5 Å
$N_R \times N_r$	512 × 128		
q_{min}	0.0 Å	q_{max}	7.5 Å
ϕ_{min}	$-\pi$	ϕ_{max}	π
$N_q \times N_\phi$	512 × 512		
k_0	21.5 Å^{-1}		
Absorbing potential:			
V_{im}^{max}	1.38 eV		
β	0.25 Å		
R_{max}^-	-4.5	R_{max}^+	4.5
Propagation:			
Δt (10^{-16} s)	1.0		
Magnitude of the five last Lanczos vectors	10^{-20}		
Projection:			
R_0^-	-3.5 Å	R_0^+	3.5 Å

$$P_{i \rightarrow f}^\pm(E_n) = \frac{\int_{-\infty}^{\infty} \xi_{k_{f,n}}^\pm(t) dt}{\int_{k_{min,i,n}}^{k_{max,i,n}} |\eta(k_{i,n})|^2 dk_{i,n}}, \quad (13)$$

where (+) and (-) sign in the above expression indicate nonreactive and reactive transition probabilities. If we propagate the system from the initial vibrational state, i , and are interested in projecting at a particular energy, E_n , and final vibrational state, f , the following equation can dictate the distribution of energy between the two modes (R, r),

$$\frac{\hbar^2 k_{i,n}^2}{2m} + \hbar \omega_0 \left(i + \frac{1}{2} \right) = E_n = \frac{\hbar^2 k_{f,n}^2}{2m} + \hbar \omega_0 \left(f + \frac{1}{2} \right). \quad (14)$$

One can get the explicit expressions for $\xi_{k_{f,n}}^+$ and $\xi_{k_{f,n}}^-$ as defined in Eq. (13) considering the following outgoing fluxes in nonreactive and reactive channels,

$$\xi_f^+(t) = Re \left\{ \psi_f^*(R_0^+, t) \times (-i\hbar/m) \times \left(\frac{\partial \psi_f(R, t)}{\partial R} \right)_{R_0^+} \right\} \quad (15)$$

and

$$\xi_f^-(t) = Re \left\{ \psi_f^*(R_0^-, t) \times (i\hbar/m) \times \left(\frac{\partial \psi_f(R, t)}{\partial R} \right)_{R_0^-} \right\}, \quad (16)$$

where

$$\psi_f(R, t) = \int_{-\infty}^{\infty} \Psi_{ad}^*(R, r, t) \Phi_f(r) dr. \quad (17)$$

The discrete fourier expansion of $\psi_f(R, t)$ can be written as,

$$\begin{aligned} \psi_f(R, t) &= \sum_{n=-\frac{N_R}{2}+1}^{\frac{N_R}{2}} C_n(t) \exp \left[2i\pi(n-1) \left(\frac{R-R_{min}}{R_{max}-R_{min}} \right) \right] \\ &= \sum_n C_n(t) \exp \left[\frac{2i\pi(n-1)(i-1)}{N_R} \right], \end{aligned} \quad (18)$$

where,

$$R = R_{min} + (i-1) \left(\frac{R_{max}-R_{min}}{N_R} \right)$$

and N_R is total number of grid points in R space. Substituting equation (18) in (15) and (16), one can easily arrive to,

$$\begin{aligned} \xi_f^+(t) &= Re \left\{ \psi_f^*(R_0^+, t) \sum_{n=0}^{\frac{N_R}{2}} \left\{ \left(\frac{2\pi\hbar(n-1)}{m(R_{max}-R_{min})} \right) \right. \right. \\ &\quad \times \exp \left[\frac{2i\pi(n-1)(i_0^+-1)}{N_R} \right] C_n(t) \left. \right\} \end{aligned} \quad (19)$$

and

$$\begin{aligned} \xi_f^-(t) &= Re \left\{ \psi_f^*(R_0^-, t) \sum_{n=-\frac{N_R}{2}+1}^{-1} \left\{ \left(\frac{2\pi\hbar(n-1)}{m(R_{max}-R_{min})} \right) \right. \right. \\ &\quad \times \exp \left[\frac{2i\pi(n-1)(i_0^--1)}{N_R} \right] C_n(t) \left. \right\}, \end{aligned} \quad (20)$$

where

$$i_0^\pm = \left\lceil \frac{R_0^\pm - R_{min}}{R_{max} - R_{min}} \right\rceil + 1.$$

It is important to note that in $\xi_f^+(t)$ only positive and in $\xi_f^-(t)$ only negative values of n have been considered. It has been numerically verified that negative components of n in $\xi_f^+(t)$ and positive components of n in $\xi_f^-(t)$ have actually negligible contribution. This is a consequence of being in the asymptotic region, where only outgoing components are present in the wave function.

We are now in a position to write from Eq. (19) and (20),

$$\xi_f^+(t) = \sum_{n=0}^{\frac{N_R}{2}} \xi_{k_{f,n}}^+, \quad (21)$$

and

$$\xi_f^-(t) = \sum_{n=-\frac{N_R}{2}+1}^{-1} \xi_{k_{f,n}}^-, \quad (22)$$

respectively.

The denominator in Eq. (13) can be interpreted as an average value over the momentum distribution from the initial wave packet, i.e.,

TABLE III. (a) Nonreactive state-to-state transition probabilities when calculations are performed keeping the position of conical intersection at the origin of the coordinates.

E (eV)	0→0	0→1	0→2	0→3	0→4	0→5	0→6	0→7	0→8	0→9
1.0	0.2599 ^a	0.0000	0.6065	0.0000						
	0.2537 ^b	0.0007	0.6066	0.0016						
	0.2518 ^c	0.0000	0.6106	0.0000						
1.5	0.3662	0.0000	0.2474	0.0000	0.1732	0.0000				
	0.3664	0.0001	0.2453	0.0006	0.1702	0.0012				
	0.3600	0.0000	0.2535	0.0000	0.1677	0.0000				
2.0	0.2762	0.0000	0.1223	0.0000	0.0706	0.0000	0.0304	0.0000		
	0.2772	0.0001	0.1236	0.0002	0.0670	0.0007	0.0408	0.0017		
	0.2804	0.0000	0.1407	0.0000	0.0880	0.0000	0.0402	0.0000		
2.5	0.2109	0.0000	0.1119	0.0000	0.0241	0.0000	0.0159	0.0000	0.0423	0.0000
	0.2078	0.0001	0.1144	0.0003	0.0235	0.0009	0.0231	0.0012	0.0428	0.0005
	0.1838	0.0000	0.1292	0.0000	0.0715	0.0000	0.0404	0.0000	0.0504	0.0000

^aTwo surface calculation.^bSingle surface calculation with vector potential.^cSingle surface calculation without vector potential.

From flux conservation we estimate the error bars to be less than 5%.

$$\eta(k_{i,n}) = \frac{1}{2\pi} \int_0^\infty \psi_{GWP}^{k_0}(R, t_0) \exp(ik_{i,n}R) dR, \quad (23)$$

and the limits ($k_{min,i,n}$, $k_{max,i,n}$) of the integral in the denominator of Eq. (13) over the variable $k_{i,n}$ can be obtained if we consider the wave number interval of the corresponding final f channel,

$$k_{min,f,n} = k_{f,n} - \frac{\pi}{R_{max} - R_{min}}, k_{max,f,n} = k_{f,n} + \frac{\pi}{R_{max} - R_{min}}, \quad (24)$$

and these are related to the initial wave number intervals by the following equations,

$$\frac{\hbar^2}{2m} (k_{min,i,n})^2 + \hbar\omega_0 \left(i + \frac{1}{2} \right) = \frac{\hbar^2}{2m} (k_{min,f,n})^2 + \hbar\omega_0 \left(f + \frac{1}{2} \right),$$

$$\frac{\hbar^2}{2m} (k_{max,i,n})^2 + \hbar\omega_0 \left(i + \frac{1}{2} \right) = \frac{\hbar^2}{2m} (k_{max,f,n})^2 + \hbar\omega_0 \left(f + \frac{1}{2} \right). \quad (25)$$

We have used the above analysis scheme for all single surface and two surface calculations. Thus, when the wave function is represented in polar coordinates, we have mapped the wave function, $\Psi_{ad}(q, \phi, t)$ to $\Psi_{ad}(R, r, t)$ in each time step to use in Eq. (17) and as the two surface calculations are performed in the diabatic representation, the wave function matrix is back transformed to the adiabatic representation in each time step as,

$$\begin{pmatrix} \Psi_{ad}^1(R, r, t) \\ \Psi_{ad}^2(R, r, t) \end{pmatrix} = \begin{pmatrix} \cos \phi/2 & -\sin \phi/2 \\ \sin \phi/2 & \cos \phi/2 \end{pmatrix} \begin{pmatrix} \Psi_{di}^1(R, r, t) \\ \Psi_{di}^2(R, r, t) \end{pmatrix} \quad (26)$$

and used in Eq. (17) for analysis.

For all cases we have propagated, the system is started in initial vibrational state, $i=0$, with total average energy 1.75 eV and projected at four selected energies, 1.0, 1.5, 2.0, and 2.5 eV, respectively.

IV. RESULTS AND DISCUSSION

We will first present vibrational state-to-state transition probabilities on the ground adiabatic surface obtained by two surface calculations and then compare with those transition probabilities obtained by single surface calculations with or without including the vector potential in the nuclear Hamiltonian. In these calculations, the position of conical intersection coincides with the origin of the coordinates. Next, shifting the position of conical intersection from the origin of the coordinates, two surface results and modified single surface results obtained either by introducing a vector potential in the nuclear Hamiltonian or by incorporating a phase factor in the basis set, will also be presented.

At this point, it is important to note that as the potential energy surfaces are even in the vibrational coordinate (r), the same parity, i.e., even \rightarrow even and odd \rightarrow odd transitions should be allowed for both nonreactive and reactive cases but due to the conical intersection, the situation for the reactive case differ from the above expectation, i.e., odd \rightarrow even and even \rightarrow odd transitions have appeared.

In Table III(a), we have presented various nonreactive state-to-state transition probabilities for four selected energies (1.0, 1.5, 2.0, and 2.5 eV.) where all calculations are done keeping the point of conical intersection at the origin of the coordinates. The first row of this table indicates the results due to two surface calculations where only even \rightarrow even and odd \rightarrow odd transitions appear as allowed. These results are well reproduced for all energies by single surface

TABLE III. (b) Reactive state-to-state transition probabilities when calculations are performed keeping the position of conical intersection at the origin of the coordinates.

E (eV)	0 \rightarrow 0	0 \rightarrow 1	0 \rightarrow 2	0 \rightarrow 3	0 \rightarrow 4	0 \rightarrow 5	0 \rightarrow 6	0 \rightarrow 7	0 \rightarrow 8	0 \rightarrow 9
1.0	0.0000	0.0033	0.0000	0.0220						
	0.0001	0.0101	0.0008	0.0345						
	0.0094	0.0000	0.0361	0.0000						
1.5	0.0000	0.1000	0.0000	0.0342	0.0000	0.0764				
	0.0001	0.1046	0.0001	0.0370	0.0004	0.0582				
	0.0719	0.0000	0.0664	0.0000	0.0827	0.0000				
2.0	0.0000	0.1323	0.0000	0.0535	0.0000	0.0266	0.0000	0.2395		
	0.0002	0.1323	0.0000	0.0583	0.0001	0.0267	0.0007	0.2383		
	0.1331	0.0000	0.0208	0.0000	0.0300	0.0000	0.1963	0.0000		
2.5	0.0000	0.0987	0.0000	0.0858	0.0000	0.0901	0.0000	0.0248	0.0000	0.2529
	0.0001	0.0983	0.0001	0.0903	0.0005	0.0870	0.0010	0.0297	0.0007	0.2492
	0.2116	0.0000	0.0382	0.0000	0.0121	0.0000	0.1783	0.0000	0.1119	0.0000

calculations with a vector potential as shown in the second row of Table III(a). The results in the third row of the same table are from single surface calculations without the vector potential. They have less agreement with corresponding transition probabilities predicted in the previous rows.

In Table III(b), various reactive state-to-state transition probabilities are presented for the same four selected energies where again we should mention that calculations are performed considering the point of conical intersection and the origin of the coordinate system to coincide. Similarly, the numbers of the first row of this table are from two surface calculations but only odd \rightarrow even and even \rightarrow odd transitions are allowed. Single surface results including a vector potential not only give the correct parity for the transitions but also the agreement between the first and the second row numbers is very good for all energies. The third row of Table III(b) indicates the numbers from a single surface calculation without a vector potential. We notice that the parity as well as the actual numbers are wrong. Calculations with the

simple phase factor approach mentioned above have not been performed for this case since the results will be identical to those obtained by including the vector potential. Finally, in Tables IV(a) and (b), we have given various nonreactive and reactive state-to-state transition probabilities for the above mentioned four selected energies where the position of the conical intersection is shifted from the origin of the coordinates. The first row of both tables represent results from two surface calculations where in the nonreactive case the same parity and in the reactive case different parity transitions appear as allowed transitions. Numbers shown in the second row of both tables came from single surface calculations with a vector potential and the results not only follow the parity (same parity for the nonreactive case and different parity for the reactive case) but also agree well for all energies with the numbers shown in the first row of Tables IV(a) and (b). Results from single surface calculations incorporating a phase factor into the basis set are shown in the third row of Table IV(a) and (b) for nonreactive and reactive

TABLE IV. (a) Nonreactive state-to-state transition probabilities when calculations are performed by shifting the position of conical intersection from the origin of the coordinates.

E (eV)	0 \rightarrow 0	0 \rightarrow 1	0 \rightarrow 2	0 \rightarrow 3	0 \rightarrow 4	0 \rightarrow 5	0 \rightarrow 6	0 \rightarrow 7	0 \rightarrow 8	0 \rightarrow 9
1.0	0.3978 ^a	0.0000	0.6394	0.0000						
	0.4077 ^b	0.0005	0.6390	0.0034						
	0.3902 ^c	0.0005	0.6156	0.0017						
1.5	0.3331	0.0000	0.2122	0.0000	0.1373	0.0000				
	0.3331	0.0001	0.2134	0.0004	0.1291	0.0013				
	0.3392	0.0001	0.2465	0.0001	0.0922	0.0009				
2.0	0.3108	0.0000	0.1269	0.0000	0.0362	0.0000	0.0372	0.0000		
	0.3114	0.0001	0.1296	0.0002	0.0351	0.0005	0.0453	0.0015		
	0.2700	0.0001	0.1257	0.0001	0.0458	0.0000	0.0590	0.0012		
2.5	0.2784	0.0000	0.0930	0.0000	0.0475	0.0000	0.0235	0.0000	0.0285	0.0000
	0.2720	0.0001	0.0976	0.0004	0.0467	0.0005	0.0339	0.0014	0.0266	0.0017
	0.2511	0.0000	0.1036	0.0001	0.0998	0.0004	0.0252	0.0003	0.0567	0.0023

^aTwo surface calculation.

^bSingle surface calculation with vector potential.

^cSingle surface calculation with phase factor approximation.

TABLE IV. (b) Reactive state-to-state transition probabilities when calculations are performed by shifting the position of conical intersection from the origin of the coordinates.

E (eV)	0 \rightarrow 0	0 \rightarrow 1	0 \rightarrow 2	0 \rightarrow 3	0 \rightarrow 4	0 \rightarrow 5	0 \rightarrow 6	0 \rightarrow 7	0 \rightarrow 8	0 \rightarrow 9
1.0	0.0000	0.0119	0.0000	0.0090						
	0.0001	0.0113	0.0004	0.0060						
	0.0003	0.0363	0.0004	0.0271						
1.5	0.0000	0.1043	0.0000	0.0334	0.0000	0.0571				
	0.0000	0.1084	0.0001	0.0346	0.0002	0.0592				
	0.0001	0.1390	0.0000	0.0183	0.0001	0.0050				
2.0	0.0000	0.1281	0.0000	0.0561	0.0000	0.0365	0.0000	0.2443		
	0.0001	0.1286	0.0002	0.0604	0.0001	0.0319	0.0001	0.2609		
	0.0000	0.1040	0.0001	0.0853	0.0004	0.0526	0.0002	0.2185		
2.5	0.0000	0.0869	0.0000	0.0909	0.0000	0.0788	0.0000	0.0211	0.0000	0.2525
	0.0002	0.0864	0.0002	0.0981	0.0007	0.0750	0.0002	0.0342	0.0018	0.2387
	0.0000	0.0711	0.0002	0.0877	0.0006	0.0932	0.0009	0.0479	0.0019	0.2611

cases, respectively. This way of accounting for the phase effect is approximate as earlier mentioned. Though these numbers appear with proper parity, they have less agreement for all energies with the numbers presented in the first and second rows of Tables IV(a) and (b).

V. CONCLUSION

In this article, using a time-dependent wave packet approach, we have studied the extended “JT” model to see the symmetry effects on the scattering processes. To do this, we have first performed two surface numerical calculations, which are considered to be the exact ones as they can follow interference effect due to the conical intersection. Calculations with or without shifting the position of the conical intersection from the origin of the coordinates have been performed. Next, we have seen that the ordinary BO approximation have failed to treat the symmetry effect and finally, modified single surface calculations either by including a vector potential into the nuclear Hamiltonian or by incorporating a phase factor in the basis set, can reproduce the two surface results for different situations. Though the transition probabilities calculated by Baer, Charutz, Kosloff, and Baer [J. Chem. Phys. **105**, 9141 (1996)] using same model are qualitatively the same as the present numbers, small quantitative differences are present, particularly, at higher energies. We believe that some of these deviations could be due to the projection technique described in Sec. III, where the information from the time dependent wave function is used to obtain energy resolved probabilities. However, we emphasize that the same technique has been used with excellent results in previous work.³⁵ Since the same methodology has been used in all the calculations - the differences between them are due to the dynamic effects of the potential, the vector potential or the phase changes in the wave function. We may therefore conclude that if the energy is below the conical intersection - then the effect of it is well described by simply adding a vector potential to the Hamiltonian. Also the simple phase change in the angle ϕ - which when increased by 2π makes the system encircle the intersection, appears to work well - even if the intersection is

shifted away from the origin. However, this conclusion is based on a single calculation with a shift of -0.5 Å in the R coordinate.

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