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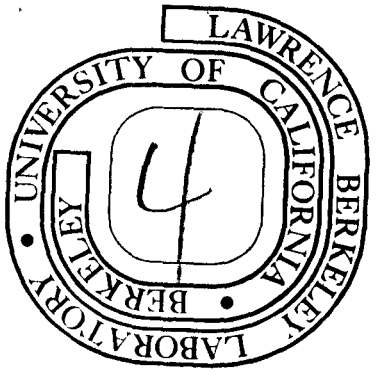

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RESONANCE EFFECTS IN THE SEMICLASSICAL THEORY OF ELECTRONICALLY NON-ADIABATIC COLLISION PROCESSES*

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Abstract

Significant advances in the theory of electronically non-adiabatic collision processes have been made in recent years by the advent of models that treat all the "heavy particle" degrees of freedom--i.e., translation, vibration, and rotation--by classical mechanics; only electronic degrees of freedom are treated quantum mechanically. The "surface hopping" model of Tully and Preston and the generalized Stuckelberg model of Miller and George are examples of this type of approach. There have, however, been questions as to whether or not such models are capable of describing resonance effects in electronic-vibrational energy transfer, e.g., $A^* + BC(v=0) \rightarrow A + BC(v=1)$, with $\Delta E_A \simeq \hbar\omega_{BC}$. This paper shows that these resonance effects are the result of interference of amplitudes for different classical trajectories that contribute to the transition. The Miller-George model, which incorporates interference and tunneling within the framework of classical S-matrix theory, thus describes resonance behavior, while the Tully-Preston model, which adds probabilities (rather than amplitudes) for the various trajectories, does not.

I. Introduction

As one better understands the dynamics of molecular collision processes that occur on one potential energy surface (i.e., within one adiabatic electronic state), greater attention is being directed to extending theoretical models to deal with non-adiabatic phenomena, i.e., those that involve transitions from one potential energy surface to another.[1] Since atoms and molecules are "heavy particles", their dynamics is often well approximated by classical mechanics, and the utility of classical trajectory methods for treating inelastic and reactive molecular collisions on a single potential energy surface is well-known.[2] One thus wishes to extend such methods as far as possible to deal with electronically nonadiabatic collisions.

A major contribution to accomplishing this was Tully and Preston's[3] "surface hopping" model, which they successfully applied to the $H^+ + H_2$ collision system. The important feature introduced by the Tully-Preston approach is that all heavy particle degrees of freedom--translation and vibration (and rotation, too, but it will be ignored for purposes of discussion)--are treated classically, as classical trajectories moving on a potential energy surface. Only electronic degrees of freedom are described quantum mechanically, i.e., as states; each adiabatic electronic state is a different potential energy surface. Most other approaches[4] have treated electronic and vibrational degrees of freedom quantum mechanically, while translation is treated classically; i.e., one considers translational trajectories on "vibronic" potential energy curves. The fundamental shortcoming of this latter approach is that the coupling between translation and vibration cannot be treated correctly (because vibration is quantum mechanical

and translation is classical). For molecular collisions it appears that in general it is more realistic to treat the coupling between translation and vibration consistently, even if classically.

Somewhat later Miller and George[5] presented a more general semiclassical theory which, while still utilizing the full classical trajectories of the heavy particle motion, incorporated quantum mechanical interference and tunneling effects. Miller-George theory, which combined an approximation of Stuckelberg[6] with an idea introduced by Pechukas,[7] was shown[8] to include a number of disparant models in a unified framework. It was seen, for example, that the model does not even require that the two potential energy surfaces have an "avoided intersection". In its most primitive (and most easily applicable) limit that the surfaces do have a well-defined avoided intersection and that semiclassical interference effects are discarded, the Miller-George approach reduces essentially to that of Tully and Preston.

In addition to including quantum mechanical interference and tunneling effects, the Miller-George model has the desirable feature of not requiring a somewhat ill-defined "hop" from one potential energy surface to another; the transition between surfaces is continuous, and uniquely determined by the classical mechanics on the adiabatic potential energy surfaces. Furthermore, the probability of the transition is also determined consistently by the classical dynamics on the potential energy surfaces (as a classical action integral). In the Tully-Preston approach, on the other hand, the transition probability is determined separately by solving the two-state time-dependent Schrödinger equation, and this precludes a proper coupling of the nuclear dynamics and the electronic transition.

The question has recently arisen,[9] however, as to whether or not the Tully-Preston or Miller-George models are capable of describing resonant transitions correctly, and the purpose of this paper is to explore this question. The particular application for which the question arose is electronic-vibrational energy transfer, e.g.,

$$Br^* + HC\ell(v=0) \rightarrow Br + HC\ell(v=1) \quad , \qquad (1)$$

where Br^* is the $^2P_{\frac{1}{2}}$ state. ΔE_{Br}, the excitation energy of the bromine atom, is close to $\hbar\omega$, the vibrational separation in $HC\ell$. The net energy which must come from, or go into translation is thus small and the cross section for the process is "anomalously" large. Such resonance effects are well-known, and it is also well-known that they are well described by the time-dependent Schrödinger equation if the internal states in question are treated quantum mechanically, i.e., if electronic and vibrational degrees of freedom are treated quantum mechanically. As discussed above, however, the key feature that makes the Tully-Preston and Miller-George approaches useful is that all heavy particle degrees of freedom are treated classically, i.e., via classical trajectories. It is thus important to find out if resonance behavior can be described by models of this type.

The main conclusion of the paper is that this resonance behavior results from interference of amplitudes for the different classical trajectories that contribute to the transition. Since Miller-George theory incorporates interference and tunneling effects within the framework of "classical S-matrix" theory,[8] it describes the resonance features; the Tully-Preston approach, on the other hand, adds probabilities (rather than probability amplitudes) for the different trajectories, and thus cannot. Section II shows more explicitly how this comes about by considering a simple model.

II. Resonant Transitions; A Simple Example

The example chosen is the simplest one which illustrates the resonance effects of interest; it is an ultra-simplified model of vibrational-electronic energy transfer. Let i and j (= 1 or 2) denote two diabatic electronic states, and $H_{ij}(R,r)$ the 2 x 2 electronic Hamiltonian matrix. R and r are the translational and vibrational coordinates, respectively; rotation is ignored, i.e., the model is that of a collinear A + BC collision. The two adiabatic potential energy surfaces, $W_1(R,r)$ and $W_2(R,r)$, are

$$W_i = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}[\Delta H^2 + 4H_{12}^2]^{\frac{1}{2}} \quad , \tag{2.1}$$

where i = 1 and 2 correspond to - and +, respectively, and $\Delta H = H_{22}-H_{11}$.

The model is simplified further by assuming

$$\Delta H = 0 \quad , \tag{2.2a}$$

and by linearizing H_{12} in the vibrational displacement,

$$H_{12}(R,r) \simeq H_{12}(R,r_0) + \frac{\partial H_{12}(R,r_0)}{\partial r_0}(r-r_0) \quad , \tag{2.2b}$$

where r_0 is the equilibrium position of r. R and r are functions of time which, in a rigorous version of the model, are determined by classical motion on the adiabatic potential energy surface, but which here are taken to be unperturbed classical motion,

$$R(t) = R_0 + vt \tag{2.3a}$$

$$r(t) - r_0 = \sqrt{\frac{2n+1}{m\omega}} \cos(\omega t) \quad , \tag{2.3b}$$

where the vibrational motion is that of a harmonic oscillator. The oscillatory time-dependence of r(t) is the key feature of the resonance effect, so to make the model simple enough for an analytic solution the time dependence of R(t) is neglected. With Eq. (2.3), the potential model thus assumes the form

$$\Delta H = 0 \tag{2.4a}$$

$$H_{12}(t) \equiv H_{12}(R(t),r(t))$$

$$= \frac{\Delta\varepsilon}{2} - \lambda \cos(\omega t) \quad , \tag{2.4b}$$

where $\Delta\varepsilon$ and λ are time independent,

$$\Delta\varepsilon = 2\, H_{12}(R_0,r_0) \tag{2.5a}$$

$$\lambda = -\sqrt{\frac{2n+1}{m\omega}}\ \frac{\partial H_{12}(R_0,r_0)}{\partial r_0} \quad ; \tag{2.5b}$$

$\Delta\varepsilon$ is the electronic energy defect.

For this simple model [Eq. (2.4)] consider first the Tully-Preston approach with the entire time interval taken as the "transition region". With R(t) and r(t) given as above, the $1 \to 2$ electronic transition is determined quantum mechanically, and in order to carry this out analytically perturbation theory is used; the result will thus be valid only to lowest order in the coupling parameter λ. $S_{2,1}$, the amplitude of the transition, is given in first-order time-dependent perturbation theory by

$$S_{2,1} = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt\ e^{-i\Delta\varepsilon t/\hbar}\ H_{12}(t) \quad , \tag{2.6}$$

and with $H_{12}(t)$ from Eq. (2.4b) this becomes

$$S_{2,1} = -\frac{i}{\hbar}\int_{-\infty}^{\infty} dt\, e^{-\frac{i\Delta\varepsilon}{\hbar}t}\,[\frac{\Delta\varepsilon}{2} - \lambda\cos(\omega t)]$$

$$= -\frac{i}{2\hbar}\int_{-\infty}^{\infty} dt\, e^{-\frac{i\Delta\varepsilon}{\hbar}t}\,[\Delta\varepsilon - \lambda e^{i\omega t} - \lambda e^{-i\omega t}] \quad .$$

The time integral is seen to involve integral representations of the Dirac delta function,

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{ixt} \quad ,$$

so if $\Delta\varepsilon > 0$, the transition amplitude is

$$S_{2,1} = \frac{i\pi\lambda}{\Delta\varepsilon}\,\delta(\frac{\Delta\varepsilon}{\hbar\omega} - 1) \quad . \tag{2.7}$$

This model thus shows the resonance effect--i.e., a large transition probability if $\Delta\varepsilon = \hbar\omega$--to the extreme. For more realistic models the delta function is broadened and made finite because $H_{12}(t) \neq 0$ for only a finite time interval (rather than the infinite time interval as above).

Consider now the Miller-George approach. From Eqs. (2.1) and (2.4) one sees that the adiabatic potential difference $\Delta W(t) = W_2(t) - W_1(t)$ is

$$\Delta W(t) = 2\,H_{12}(t)$$

$$= \Delta\varepsilon - 2\lambda\cos(\omega t) \quad . \tag{2.8}$$

A transition between potential energy surfaces 1 and 2 is possible whenever $\Delta W(t)$ has a complex crossing point, and this is often identified by the real times at which $\Delta W(t)$ has a relative minimum. As shown in Figure 1a, $\Delta W(t)$ from Eq. (2.8) has minima at $t = 2\pi n/\omega$, where n is any integer. The complex crossing times, i.e., the roots of the equation

$$\Delta W(t) = 0 \quad ,$$

are seen to be simply related to the times when $\Delta W(t)$ has minima:

$$t_n = \frac{2n\pi}{\omega} + \frac{i}{\omega} \cosh^{-1} \left(\frac{\Delta\varepsilon}{2\lambda}\right) \quad . \tag{2.9}$$

The amplitude $S_{2,1}$ is the superposition of amplitudes for all the possible crossing times, i.e., for all the possible trajectories that can lead to the $1 \rightarrow 2$ transition:

$$S_{2,1} = \sum_{n=-\infty}^{\infty} S_n \quad , \tag{2.10}$$

where S_n is the amplitude for the $1 \rightarrow 2$ transition to take place at the complex time t_n. (Since $S_{2,1}$ is being calculated only to lowest order in λ--to compare with Eq. (2.7)--it is not necessary to take re-crossings into account.) S_n is given in Miller-George theory by[5,8]

$$S_n = \exp\left(\frac{i}{\hbar} \varepsilon_2 t_f\right) \exp\left(-\frac{i}{\hbar} \int_{t_n}^{t_f} dt\, W_2 - \frac{i}{\hbar} \int_{t_i}^{t_n} dt\, W_1\right) \exp\left(-\frac{i}{\hbar} \varepsilon_1 t_i\right) \tag{2.11a}$$

$$= e^{i\alpha} \exp\left[\frac{i}{\hbar} \int_0^{t_n} dt\, \Delta W(t)\right] \tag{2.11b}$$

where $t_i \to -\infty$ and $t_f \to +\infty$ are the initial and final times. α is a constant phase independent of the index n. The interpretation of Eq. (2.11a), apart from the unperturbed phase factors $e^{i\varepsilon_2 t_f/\hbar}$ and $e^{-i\varepsilon_1 t_1/\hbar}$, is that the particle moves on potential surface W_1 from t_i to t_n, crosses to W_2 as t_n (where $W_1 = W_2$), and then moves on W_2 from t_n to t_f. The relevant action integral in Eq. (2.11b) is easily evaluated

$$\int_0^{t_n} dt\ \Delta W(t) = \int_0^{t_n} dt\ [\Delta\varepsilon - 2\lambda\cos(\omega t)]$$

$$= \Delta\varepsilon t_n - \frac{2\lambda}{\omega}\sin(\omega t_n)$$

$$= \frac{\Delta\varepsilon 2n\pi}{\omega} + \frac{i\Delta\varepsilon}{\omega}\left[\cosh^{-1}\left(\frac{\Delta\varepsilon}{2\lambda}\right) - \sqrt{1 - \frac{4\lambda^2}{\Delta\varepsilon^2}}\right] . \quad (2.12)$$

To lowest order in λ,

$$\cosh^{-1}\left(\frac{\Delta\varepsilon}{2\lambda}\right) - \sqrt{1 - \frac{4\lambda^2}{\Delta\varepsilon^2}} = \ell n\left(\frac{\Delta\varepsilon}{e\lambda}\right) + O(\lambda^2) \quad , \quad (2.13)$$

so that the net amplitude is

$$S_{2,1} = \sum_{n=-\infty}^{\infty} e^{\frac{i\Delta\varepsilon}{\hbar\omega} 2n\pi} \exp\left[-\frac{\Delta\varepsilon}{\hbar\omega}\ell n\left(\frac{\Delta\varepsilon}{e\lambda}\right)\right] \quad , \quad (2.14)$$

where the constant phase factor has been discarded. The Poisson sum formula[11] implies that

$$\sum_{n=-\infty}^{\infty} e^{\frac{i\Delta\varepsilon}{\hbar\omega} 2n\pi} = \sum_{\ell=-\infty}^{\infty} \delta\left(\frac{\Delta\varepsilon}{\hbar\omega} - \ell\right) \quad , \quad (2.15)$$

and since $\Delta\varepsilon > 0$ it is then easy to show that Eq. (2.14) becomes

$$S_{2,1} = \sum_{\ell=1}^{\infty} \delta(\frac{\Delta\varepsilon}{\hbar\omega} - \ell) \ (\frac{e\lambda}{\Delta\varepsilon})^{\ell} \quad . \tag{2.16}$$

To compare this to the result of quantum mechanical time-dependent perturbation theory, Eq. (2.7), one needs only the term of Eq. (2.16) that is lowest order in λ, the ℓ=1 term,

$$S_{2,1} \simeq \frac{\lambda e}{\Delta\varepsilon} \ \delta(\frac{\Delta\varepsilon}{\hbar\omega} - 1) \quad , \tag{2.17}$$

which is the same (apart from constant phase factors) as Eq. (2.7) except that the multiplicative constant $e \simeq 2.72$ appears rather than $\pi \simeq 3.14$. The terms $\ell > 1$ describe multiple vibrational resonances, $\Delta\varepsilon = \ell\hbar\omega$; i.e.,

$$A^* + BC(v=0) \rightarrow A + BC(v=\ell) \quad .$$

The important feature this calculation demonstrates is that the resonance effect is correctly described by the Miller-George model. It comes from the interference of amplitudes that correspond to the different times at which the transition can occur. In the perturbative limit it has the same form as the result given by quantum mechanical time-dependent perturbation theory, although it does make an error ($\sim$ 13%) in the multiplicative numerical factor.

In actual application there will not be an infinite number of terms in the sum over integers n in Eq. (2.15). (Nor will the different terms have precisely the same phase factors). Figure 1b shows the behavior of

$\Delta W(t)$ that might be expected for a more realistic model; here there would be only a finite number of avoided crossings with significant transition probabilities. A finite and broadened resonance function would thus replace the delta function.

It is important to note that the Tully-Preston model obtains the resonance behavior only if the entire time interval is taken as the "transition region" during which the time-dependent Schrödinger equation is used to determine the transition probability associated with the transition region. During this transition time interval, however, the classical path must be assumed, rather than determined by the classical equations of motion. (In the Tully-Preston model the trajectory is determined by classical mechanics between the various transition regions.) Thus if the entire time interval is the transition region, the classical path must be assumed for the entire time interval, and the model thus looses its greatest charm, namely that of allowing the classical path to be determined dynamically rather than having to assume it a priori. If each avoided crossing--i.e., each minimum of $\Delta W(t)$--is treated as a separate crossing region, as it should be for the model to be consistent, then the Tully-Preston model misses the resonance effect completely since it would add the probabilities (rather than probability amplitudes) related to the different avoided crossings.

III. Concluding Remarks

The essential point in realizing that Miller-George theory describes resonance behavior in electronic-vibrational energy transfer is that $\Delta W(t) = \Delta W(R(t),r(t))$ is in general an oscillatory function of t because r(t) is. $\Delta W(t)$ will thus have a number of "avoided crossings" (i.e., minima), and the superposition of the amplitudes for the various possible trajectories that change from surface 1 to surface 2 interfere and can cause resonance effects. How sharp the resonance structure is depends on how many amplitudes have comparable transition probabilities. The model discussed in Section II, although grossly oversimplified in order to make a simple analytic solution possible, illustrates the way resonance effects appear.

Since the Tully-Preston model does not include this kind of interference behavior, why has it been as successful as it has, e.g., for the $H^+ + H_2$ system? Here, too, there are usually several different trajectories that contribute to a given process, and the proper thing to do is to superpose amplitudes for these different trajectories, rather than add probabilities. For non-resonance processes, however, the different trajectories leading to a given transition are essentially uncorrelated with each other, and averages over impact parameter, rotational degeneracy, etc., quench the interference effects. For a nearly resonant process, on the other hand, the different avoided crossings are highly correlated with each other, i.e., the phases of the amplitudes for the different trajectories differ from each other in a regular manner. Since these phase relations are approximately independent of impact parameter,

etc., the interference between these various amplitudes is less likely to be quenched by averages over unobserved collision parameters.

Miller-George theory is difficult to apply in its fully rigorous form, but there are several ways[12] of simplifying it to a level that makes it comparable in applicability to the Tully-Preston model, but which still retain interference information. One would expect this to be a usefully accurate description of resonance behavior in non-adiabatic collision phenomena.

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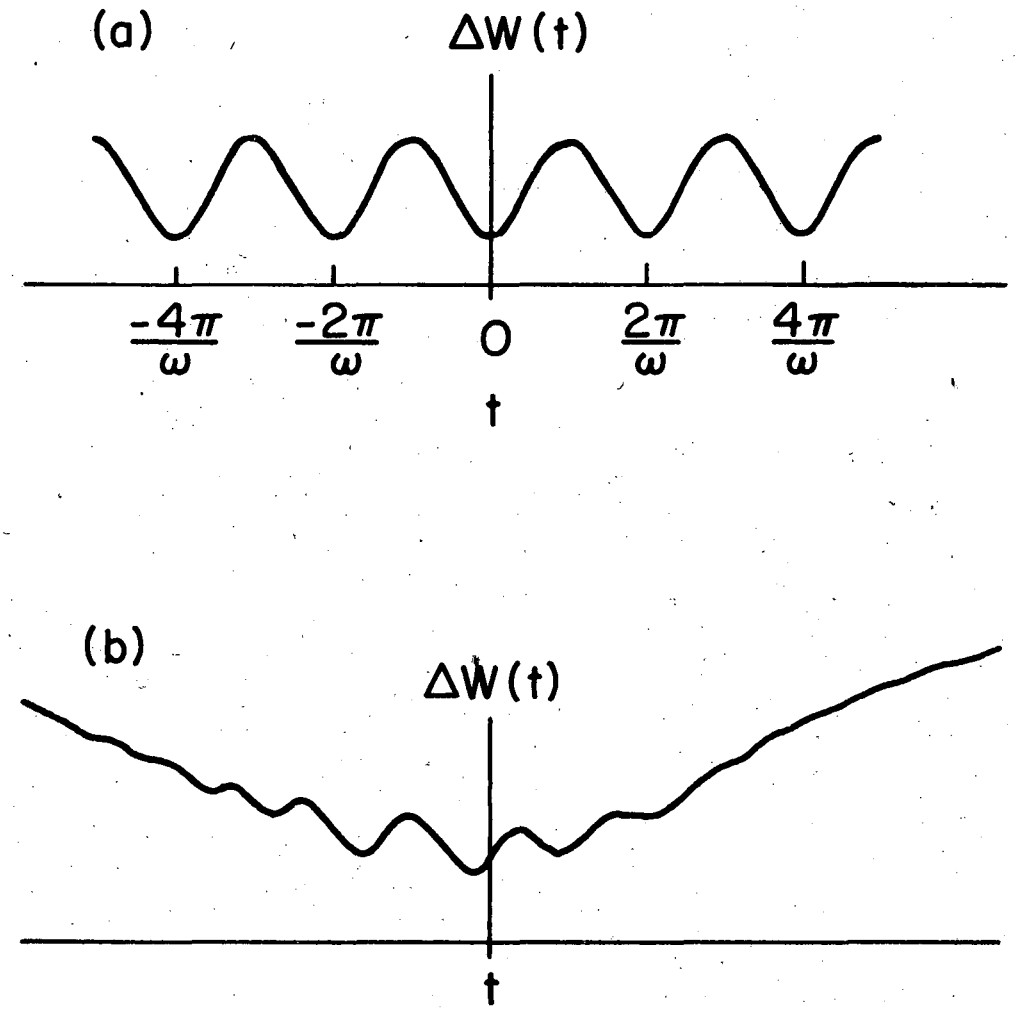
Figure Caption

(a) The adiabatic potential difference $\Delta W(t)$ as a function of time for the model given by Eq. (2.8).

(b) The adiabatic potential difference as a function of time for a more realistic model.



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