ity results). We demonstrate this in Fig. 2. The value of $D_e$ (LiH) and the RKR curve of LiH are now generally accepted as reliable. Therefore, we use in Fig. 2 the RPC of LiH for comparison with the RPCs of KH for various values of $D_e$ (KH). A very slight crossing appears for the nominal value $D_e$ (KH) = 14 776 cm$^{-1}$ which, however, still could be due to slight errors in the constants or in the RKR calculation. The value $D_e$ (KH) = 14 726 cm$^{-1}$ is evidently too small, since a significant crossing of the two RPCs appears. The value $D_e$ (KH) = 14 826 cm$^{-1}$ does not lead to confluence of the two curves, however, could still seem to be acceptable. So, at any rate, the true value of $D_e$ (KH) should lie between 14 776 and 14 826 cm$^{-1}$. The old value (15 000 cm$^{-1}$) evidently is too high and may be safely discarded (cf. Ref. 1).

High accuracy in the analysis of the spectra and in the calculation of the potentials is, of course, a necessary condition for this application of the RPC method.

6. No significant changes for the graphical picture result from a new evaluation of the data of Ref. 7 in the Ph.D. thesis of Yat-Chen (The University of Iowa, 1986).
8. Since both, the RKR and the RPC methods, are approximations, we take such estimates with the necessary portion of sceptical reserve. Therefore, in Fig. 2 we use a rather large interval ± 50 cm$^{-1}$ for comparison. Note the unnatural curvature of the KH curves in Fig. 2 which might indicate a very slight error in the last point of the KH potential (or the LiH potential).

**COMMENTS**

**Comment on "Probability oscillations in single pass curve crossings: Semiclassical predictions of nonmonotonic dependence on crossing velocity"**

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In a recent paper1 Nesbitt and Hynes (NH) discussed the fact that the electronically nonadiabatic transition probability for a typical two-state curve crossing situation can show oscillations as a function of translational energy even when the particle's trajectory makes only a "single pass" through the transition (i.e., avoided crossing) region. They emphasize that these oscillations are not of the usual "in-out" St"uckelberg type, which result from multiple passes through the transition region (e.g., for radial motion inward and then outward during a collision) and which are semiclassical interferences between different trajectories that contribute to the transition (i.e., that "hop" from one curve to the other at different times).

The point of this Comment is to note that the oscillations discussed by NH can in fact be understood to arise from semiclassical interference between trajectories that hop from one curve to the other at different times. This happens because there are actually two relevant transition regions for the functional forms of the potential curves considered by NH.

To see this, recall the generalized St"uckelberg model for nonadiabatic transitions as described by Miller and George.2-3 Transitions occur at the complex times when the adiabatic curves intersect, i.e., at the roots of the equation

$$0 = \Delta W(x(t)) = \{(V_{22}(x(t)) - V_{11}(x(t)))^2 + 4V_{12}(x(t))^2\}^{1/2},$$

(1)

where $W_1$ and $W_2$ are the two adiabatic potential curves, $\Delta W = W_2 - W_1$, and $V_{ij}(x)$ is the diabatic potential matrix. Like NH, a constant velocity trajectory $x(t) = x_0 + ut$ is assumed for the discussion.

In the usual Landau--Zener situation one has $V_{22}(x) - V_{11}(x) = V_0(x - x_0)$, $V_{12}(x) = constant$, and there is then only one complex crossing point [i.e., root to Eq. (1)],

$$t_{0} = \frac{2V_{12}}{u\Delta V_0}$$

(2)

(plus its complex conjugate). For the functional forms used by NH, however, there will be more than one. This is illustrated most simply by taking the diabatic potential as $\Delta V(x) = \frac{1}{2}V_0(x - x_0)^2$, $V_{12}(x) = constant$, which is the essential character of the physical example treated in NH's Sec. V. This gives complex crossing times.

\[ t_{\pm} = \pm \sqrt{2V_{12}/\Delta V_0^2/v} + i\sqrt{2V_{12}/\Delta V_{0u}^2/v} \]  
\text{(plus complex conjugates). Since these two complex crossing times are equidistant from the real t axis, they give rise to equal transition probabilities, so that the interference between a trajectory which makes the transition at } t_- \text{ and one that makes it at } t_+ \text{ will be prominent (even completely destructive for some velocities). For other potential functions considered by NH there are more than two complex crossing points, but even for these cases there are two that are equally closest to the real axis and thus dominate the contribution.}

More specifically, the nonadiabatic transition amplitude \( S_{2,1} \), given by the generalized Stückelberg model\(^2,3\) is

\[
S_{2,1} = \sum_k \exp \left[ -\frac{i}{\hbar} \int_{t_i}^{t_f} dt W_1(x(t)) -\frac{i}{\hbar} \int_{t_i}^{t_f} dt W_2(x(t)) \right],
\]

where \( t_i (t_f) \) is the initial (final) time, \( t_k \) is a complex crossing time [i.e., root to Eq. (1)], and the sum is over all such values; one typically keeps only the terms which yield the largest probabilities. [Equation (4) is a "primitive" semiclassical expression; if the real phase difference between the terms is too small for this to be valid—cf. coalescing points of stationary phase—then one must resort to a uniform semiclassical formula.] For the case of two complex crossing points, as in the examples considered by NH, the nonadiabatic transition probability is

\[
|S_{2,1}|^2 = p_1 + p_2 + 2\sqrt{p_1 p_2} \cos(\Delta \phi),
\]

where

\[
\rho_k = \exp \left[ -\frac{2}{\hbar} \text{Im} \int_{t_i}^{t_f} dt \Delta W(x(t)) \right],
\]

\[
\Delta \phi = \frac{1}{\hbar} \int_{t_i}^{t_f} dt \Delta W(x(t))
\]

For the case \( p_1 = p_2 = p \), this becomes \( |S_{2,1}|^2 = 4p \cos^2(\Delta \phi/2) \); the uniform WKB expression which corresponds to this primitive expression is

\[
|S_{2,1}|^2 = 4p(1 + p)\cos^2(\Delta \phi/2)/\left[1 + 4p(1 + p)\cos^2(\Delta \phi/2)\right].
\]

It is not difficult to show that the interference structure in Eqs. (5) and (6) accounts for that seen by NH.

Finally, it is useful to note that the generalized Stückelberg model\(^2,3\) can be derived by precisely the WKB approximation used by NH. More specifically, by an appropriate transformation one eliminates the first derivative term in NH's Eq. (2.8) to obtain a standard Schrödinger-like equation to which the WKB approximation can be applied,

\[
\frac{d^2}{dt^2} + (k(t))^2 f(t) = 0,
\]

where (upon neglecting some terms, as NH do) \( k(t) = \Delta W(x(t))/2\hbar \). Since \( k(t) \neq 0 \) for all real \( t \), Eq. (7) is analogous to the "over-barrier" WKB problem for the 1D Schrödinger equation, and the nonadiabatic transition probability is the reflection probability for this over-barrier problem. For the situation discussed above, where there are two complex crossing times, one is dealing with a double barrier case.

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ERRATA

Erratum: Germanium \( L_{2,3}M_{4s}M_{4s}M_{4s} \) and \( L_{2,3}M_{2s}M_{4s} \) Auger spectra of volatile germanium compounds [J. Chem. Phys. 84, 4797 (1986)]

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An earlier paper on the \( L_{2,3}M_{4s}M_{4s} \) Auger spectra of volatile germanium compounds\(^1\) was inadvertently overlooked in the course of our study.\(^2\) Results for some Auger energies of four compounds GeH\(_4\), GeF\(_4\), GeCl\(_4\), and Ge(CH\(_3\))\(_4\) can be compared. Our values for the \( L_{2}M_{4s}M_{4s} \) components of GeH\(_4\) (except for \( ^3P \)) are in good agreement with these previous results. The \( ^3P \) and \( ^1D \) components of the \( L_{2}M_{4s}M_{4s} \) spectrum,\(^1\) which were not resolved in our work, were extracted by curve fitting procedures yielding peaks at \(+0.8 \pm 1.6 \text{ eV}\) relative to the \(^1G_{4s}\) positions, values which are in reasonable agreement with theory. The intensity of the \( ^3P \) component was however too high relative to the \( ^1D \) component. Relative intensities were not discussed in the earlier work.\(^1\) In the case of the \( L_{2}M_{4s}M_{4s} \) spectrum of GeH\(_4\), their curve fitting yielded components which were assigned to \( ^3P \) and \( ^1D \) at \(+1.4 \pm 3.4 \text{ eV}\) relative to \(^1G\). Since the predictions for spin-orbit splittings are the same for \( L_{2} \) and \( L_{3} \) spectra at the level of theory employed these as-