Calculation of Transition Probabilities Using the Landau-Zener Model

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The Landau-Zener formula is discussed in connection with numerical calculations of the nonadiabatic transition probability in atomic collisions. The present treatment in the case of weak interaction leads to an additional constant phase $\frac{1}{4}\pi$ beyond the semiclassical one and, in contrast to the conclusions of Olson and Smith, gives good agreement with their close-coupled and distorted-wave numerical results.

The interpretation of many inelastic-differential-scattering experiments in atomic-collision spectroscopy requires an understanding of oscillatory structure in the observed cross section. The inelastic scattering often arises through transitions at a pseudocrossing of two adiabatic-potential-energy curves at some value of the internuclear separation $R = R_c$. The oscillatory structure then arises from the quantum-mechanical interference of waves scattered by the two potentials in the region $R < R_c$. The observed oscillations contain a great deal of information about the potentials and the interactions in the pseudocrossing region.[1,2] Part of the theoretical problem here is the proper calculation of the differential cross section in the threshold region of the oscillations as a function of angular momentum l, a region corresponding to the smallest scattering angles for which the oscillations appear.[3-5]

In the understanding of the collision in terms of well-known model problems involving nonadiabatic coupling, the potential matrix is ordinarily piecewise approximated by certain simple functions, a procedure that resolves specific nonadiabatic problems more or less accurately. Those errors that arise because of differences between the "exact" and model potentials should ordinarily be evaluated through the accurate solution of both the true and model problems. However, the direct comparison of approximate model solutions with the results of numerical calculations for realistic potentials has in the past been susceptible to two kinds of uncertainties; the first is associated with the modeling of interactions, while the second arises through approximations made during the solution of model problems. For the case of a practical theory that is thought to be useful for reconstructing potentials, one hopes that uncertainties of the second type will be fewer in number than those of the first type.

A recent calculation by Olson and Smith makes possible the kind of comparison discussed above.[1] By using a potential matrix describing the pseudocrossing of terms for the He^+-Ne system,

$$He^+ + Ne(2p^6) \rightarrow He^+ + Ne(2p^5 3s) \quad ,$$

they calculated the transition probability P_{12} as a function of angular momentum for an energy of 70.9 eV. A compairson of close-coupling (CC) and distorted-wave (DW) calculations verified the usefulnes of first-order perturbation theory, even for values of l near the threshold value $l_x = 322$. The quantity P_{12} was also calculated using the Landau-Zener (LZ) expression,

$$P_{LZ}(l) = 4\sin^2[\Delta\phi(l) + \gamma(l)]e^{-2\pi\delta_l}(1 - e^{-2\pi\delta_l}) \quad , \quad (1)$$

where δ_l is the usual LZ parameter determining the nonadiabatic-transition amplitude in the pseudocrossing region, $\Delta\phi(l)$ is the difference of action integrals for adiabatic terms as taken from the turning point to the pseudocrossing point, and $\gamma(l)$ is an additional phase that depends on δ_l. The quantity δ_l is equal to $a^2/\hbar|\Delta F|v_l$, where a is an off-diagonal interaction matrix element considered constant in Eq. (1), ΔF is the difference in slopes of terms, v_l is the radial velocity, and all quantities are evaluated at $R = R_c$. It is well known that (1) is valid far away from the turning point where $\Delta\phi(l) \gg 1$.[6]

Olson and Smith found that the extrema of the oscillations in their DW and LZ results for $P_{12}(l)$ coincided when the assumption is made that

$$\gamma(l) = \tfrac{1}{4}\pi \exp[-\Delta\phi(l)/20] \quad , \quad (2)$$

where $\gamma(l)$ and $\Delta\phi(l)$ are in radians. On the other hand, an analytical expression for $\gamma(l)$ valid except near threshold has been derived by Kotova[7] and independently by Child,[8]

$$\gamma(l) = \tfrac{1}{4}\pi + \delta_l \ln\delta_l - \delta_l - \arg\Gamma(1 + i\delta_l) \quad . \quad (3)$$

In the limit of a weak interaction $\delta_l \ll 1$, we thus have $\gamma(l) = \frac{1}{4}\pi$, just the value contained in the Landau formula obtained as a result of pertubation theory[9]

$$P_L(l) = 8\pi\delta_l \sin^2[\Delta\phi(l) + \tfrac{1}{4}\pi] \quad . \quad (4)$$

In the vicinity of threshold, however, the condition $\Delta\phi(l) \gg 1$ is violated, and Eq. (1) must be replace by another one deduced from a numerical integration of the equations for nonadiabatic coupling. Such a treatment for the case of linear potentials

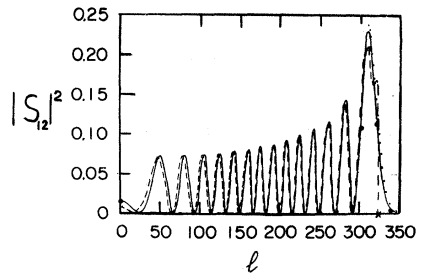

FIG. 1. Transition probability $|S_{12}|^2$ as a function of angular momentum l: solid line: DW result (Ref. 1); closed circles: CC result (Ref. 1); dashed lines: our LZ result; dotted line: Airy solution; crosses: threshold $l_X = 322$.

was carried through by Delos,[10] who obtained all the S-matrix elements for the LZ model without any restrictions on the value of $\Delta\phi$. An extension of the theory beyond the framework of the linear model may be accomplished while still using Eq. (1), provided that the asymptotic value of $|S_{12}|^2$ as given by (1) for $\Delta\phi \gg 1$ is reached before the linear approximation for the diabatic potentials in the crossing region breaks down.[11] If this is not the situation, then in general the LZ model [i.e., Eq. (1)] will not be able to describe the variation of $P(l)$ for all l.

The obvious discrepancy between expressions (2) and (3) stimulated a recalculation of the LZ probability (1) using the potentials of Ref. 1. The evaluation of the action integrals was accomplished numerically using a Simpson-quadrature routine and was verified using a Gaussian-quadrature routine with identical results. It has been found that the present LZ result with $\gamma(l) = \frac{1}{4}\pi$ is very close to the DW and CC results for $l \leq 308$, i.e., away from threshold (see Fig. 1). In the figure two maxima can be seen in the LZ solution close to threshold. The first at $l = 308$ is due to the oscillating factor in Eq. (1) and practically coincides with the CC result. The second at $l = 321.6$ is due to the maximum in the envelope of (1) and is artificial as being too close to $l_x = 322$. Our LZ result with $\gamma(l) = \frac{1}{4}\pi$ is in agreement with DW and CC but not with the LZ results of Olson and Smith.[1] We cannot provide a reasonable explanation for this. It thus appears that the LZ theory with the appropriate phase factor (3) is useful for calculating differential-inelastic-scattering cross sections, whenever the point of closest approach R_0 is not close to R_c.

In the vicinity of threshold ($R_0 \approx R_c$) and in the tunneling region ($R_0 > R_c$) the LZ theory is not applicable. Here, however, a pertubation-theory solution in terms of Airy functions is available for the case of weak interaction.[9] So the Airy-function approximation was used to calculate $P(l)$ starting with the last maximum and continuing to the nonclassical region for $l > l_x$. We observe again a good agreement between the CC result and the approach based on the linear model. The discrepancy between the LZ result and the Airy-function approximation at the last maximum is due to the fact that LZ formula (1) takes into account the back coupling (through weak) of the states.

Summarizing, we believe that the LZ formula with the phase $\gamma(l)$ given by (3) will be good approximation to any pesudocrossing situation though the actual comparison of the model calculations with CC results for not very small δ_l will be instructive.

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