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Solution of the Two-State Potential-Curve–Crossing Problem

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A general theory of the two-state curve-crossing problem has been developed, with a complete solution of an accurate model for "close" crossings (including numerical computations for strong coupling). Results clarify the position of the Landau-Zener approximation and its improvements by Nikitin and others, provide a general way of extending these approximations into regions often treated incorrectly (including the high-energy limit), and can be readily adapted to simple, rapid calculations.

This is a brief report of a theoretical analysis of the potential-curve–crossing problem in atomic collisions, with a complete solution of that problem (including computations) for the case of "close crossings." A detailed account of this work will be published in the near future.[1]

The Landau-Zener-Stueckelberg[2] (LZS) approximate solution to the curve-crossing problem has had a long history, and has frequently been successful even in situations where its basic assumptions seem to fail. The need for simple techniques for calculating accurate inelastic transition probabilities associated with curve crossings has led to many attempts to extend and generalize the theory.

Assuming a two-state model for the crossing problem, the coupled second-order Schrödinger equations obtained are commonly replaced with first-order time-dependent equations for the electronic state vector, assuming classical motion for the heavy particles. Recently, we have shown[3] that the same first-order equations result even when the assumption of classical motion is not valid. In particular, using a momentum-space semiclassical approximation we showed[3] that the same equations are valid even when the crossing point is near classical turning points, provided the forces $-dV_{jj}/dR$ in both states have the same sign near the turning points. In this more general semiclassical derivation the invariance of the results with respect to electronic representation choices is essentially preserved. Therefore the coupled first-order "classical trajectory equations" provide a sound basis for accurate treatment of curve crossings.

Remaining assumptions of a curve-crossing theory are then associated with the two-state electronic potentials. The LZS approximation assumes that the diagonal elements $V_{jj}(R)$ are linear near the crossing point and the coupling $V_{12}(R)$ is constant. Bykhovskii, Nikitin, and Ovchinnikova[4] (BNO) have exploited these assumptions consistently and derived a particularly satisfactory form of solution, including analytical formulas useful in various limits, which depends on only two parameters: a reduced collision energy ϵ and a reduced coupling strength β. However, the special assumptions about V_{jj} and V_{12} are a severe limitation, resulting, among other things, in incorrect behavior with increasing energy. We have now generalized the BNO procedure and overcome these difficulties.

For an accurate treatment the motion of the heavy particles, as well as the electronic potentials, must be correctly described. To this end, assuming that the interaction potential V_{12} does

not change its sign during the collision, we define

$$s(\tau)=\hbar^{-1}\int_0^\tau V_{12}(R(\tau'))\,d\tau'; \tag{1}$$

$s(\tau)$ is then a monotonic function of the time τ from the turning point $\tau=0$ to $\tau\to\infty$. In the diabatic representation the classical trajectory equations can then be expressed in terms of s as independent variable:

$$\begin{aligned} i\,dc_1/ds &= c_2\exp[-2i\textstyle\int_0^s t(s')\,ds'],\\ i\,dc_2/ds &= c_1\exp[+2i\textstyle\int_0^s t(s')\,ds'], \end{aligned} \tag{2}$$

where the quantity

$$t\equiv(V_{22}-V_{11})/2V_{12}$$

is expressed as a function of s. *Equations (2) greatly simplify the curve-crossing problem: All effects, both of potential surfaces and heavy-particle motion, are determined by the single function t(s).*

If $|\int_0^\infty V_{12}\,dR|$ is bounded, Eq. (1) maps the semi-infinite time range onto a *finite* range of s ($0\leq s\leq s_\infty$). For a crossing problem, $t(s)$ has a simple structure: At $s=0$ (turning point) $t(0)$ has a finite (negative) value, but $(dt/ds)_0=0$ because $(dR/d\tau)_0=0$. At the crossing point s_x, $t(s_x)=0$ but $(dt/ds)_{s_x}\neq 0$. Finally, $t(s)$ is singular at s_∞ ($\tau\to\infty$), a fact of fundamental importance for the theory.

We define a *close crossing* by the assumption that s_∞ and s_x are sufficiently well separated that the behavior of $t(s)$ near its singularity has no important influence on inelastic scattering; $t(s)$ can then be adequately represented by a few-term Taylor expansion about s_x or $s=0$. In a *distant crossing* the detailed properties of $t(R)$ at very large R must be considered as well as the behavior near R_x. A given crossing may be "distant" for small impact parameters and "close" for large ones, as the turning point approaches the crossing point. Also, since $|\int_0^\infty V_{12}\,dR|$ is bounded, $|s_\infty-s_x|\propto v^{-1}$ for high velocities v, so for any system the effect of the singularity at s_∞ increases with increasing velocity (this is what causes the failure of the LZS formula at high energies[5]). In general, however, a crossing is likely to be "close" when R_x is small.

We treat only the close-crossing case. It is necessary to provide an adequate description of $t(s)$ near $s=0$ and $s=s_x$. Almost all previous theories effectively assume that $t(s)$ is linear, as does the LZS model. However, if s_x is small, it is obvious that (a) the finite size of $t(0)$ and (b) the curvature of $t(s)$ near $s=0$ will have strong effects, and of these the more important is that of curvature in $t(s)$. This curvature is mainly due to acceleration near the classical turning point, but contributions also arise from higher-order variations in the potentials $V_{ij}(R)$. The BNO model[4] is the only curve-crossing theory which adequately treats the effect of acceleration. Their method is equivalent to a quadratic expansion of $t(s)$ about $s=0$.

A simple yet significant improvement can be made on the BNO model using the best quadratic for $t(s)$. Expanding $t(s)$ about s_x, and eliminating s_x via the imposed constraint $(dt/ds)_0=0$, we obtain

$$t(s)=-\epsilon+4s^2/\beta^2, \tag{3}$$

where

$$\epsilon=\epsilon^{\mathrm{BNO}}/(1+2E/DF), \tag{4a}$$

$$\epsilon^{\mathrm{BNO}}=[E(F_1-F_2)/2FV_{12}]_{R_x}; \tag{4b}$$

$$\beta=\beta^{\mathrm{BNO}}/(1+2E/DF)^{1/2}, \tag{4c}$$

$$\beta^{\mathrm{BNO}}=(4V_{12}/\hbar)[MV_{12}/F(F_1-F_2)]_{R_x}^{1/2}; \tag{4d}$$

$$D^{-1}=[(F_1'-F_2')/(F_1-F_2)+3d\ln V_{12}/dR]. \tag{4e}$$

Here M is mass. The F_j are forces $(dV_{jj}/dR)_{R_x}$ with F_j' their derivatives; F and F' are averages of these. The quantities ϵ^{BNO} and β^{BNO} are just the variables ϵ and b defined by BNO—but evaluated at R_x. Using Eq. (3), Eqs. (2) become

$$\begin{aligned} i\,dc_1/ds &= c_2\exp[-i(8s^3/3\beta^2-2\epsilon s)],\\ i\,dc_2/ds &= c_1\exp[+i(8s^3/3\beta^2-2\epsilon s)]. \end{aligned} \tag{5}$$

Equations (5) are identical in form to Eqs. (10) of BNO; the difference between our model and theirs is in the definitions of ϵ and β. BNO's special derivation of Eqs. (5) requires that V_{jj} be strictly linear and V_{12} strictly constant; via the more general derivation of the classical trajectory equations given in Ref. 3 we can relax these restrictions and still recover Eqs. (5). The only resulting change is the E-dependent scaling of ϵ and β given by Eqs. (4a) and (4c). Taking such scaling algorithms into account all the approximate formulas derived by BNO for various limiting conditions on ϵ and β remain valid. We give a summary of these and other formulas in Ref. 1.

Using Eq. (3) for $t(s)$, the classical trajectory equations in the adiabatic (noncrossing) repre-

sentation become

$$d\gamma_a/dt = [2(1+t^2)]^{-1}\gamma_b \times \exp\{-i(\beta/2)\int_{-\epsilon}^{t}[(1+t^2)/(\epsilon+t)]^{1/2}dt\},$$
$$d\gamma_b/dt = -[2(1+t^2)]^{-1}\gamma_a \times \exp\{+i(\beta/2)\int_{-\epsilon}^{t}[(1+t^2)/(\epsilon+t)]^{1/2}dt\}. \quad (6)$$

This representation is less convenient for analytical work because of the complicated integral in the exponent, but it is quite convenient for numerical work for strong β and small ϵ.

We wish to emphasize the necessity of abandoning the linear approximation for $t(s)$ if a valid model for close crossings is to result. This is particularly important in view of the preoccupation with Weber's equation and its asymptotic properties which has dominated past studies of this problem.[2,6-8] In Ref. 1 we show that the reduction to Weber's equation depends upon assuming the effective linearity of $t(s)$. Equations (6) also show quite clearly why this is not a good idea. If $t(s)$ is taken to be linear, Eqs. (6) are modified to a form which is the same except that the integrand in the exponent is replaced by $T_0(1+t^2)^{1/2}$, with $T_0 = \beta/2\sqrt{\epsilon}$. It is evident that if significant coupling occurs near the turning point, the linear approximation is inadequate.

We have computed solutions for a complete grid of parameters (β, ϵ). In Ref. 1 these results are presented in detail and compared with various analytical formulas.

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Linewidth of Tunable Stimulated Raman Scattering

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We report direct measurements of the tunable spin-flip Raman (SFR) laser linewidth, obtained by heterodyning the SFR laser output with the output from a cw gas laser. The measured linewidth for the cw SFR laser operating near 5.3 μm is < 1 kHz and is limited by the spectrum analyzer resolution. The measured linewidth of < 1 kHz is the narrowest known for any tunable source of coherent radiation in the infrared.

A recent report of tunable stimulated Raman scattering[1] from the spin flip of conduction electrons in InSb (i.e., the spin-flip Raman laser) has evoked considerable interest in its use in the investigation of numerous physical phenomena. The tunability of the spin-flip Raman (SFR) laser now covers[1-6] a wavelength range from about 9 to 14.6 μm and from 5.2 to 6.2 μm and has been used in high-resolution infrared spectroscopy,[7] transient infrared spectroscopy,[8] pollution detection,[9] and nonlinear optics.[10] A very important parameter of a tunable laser source is the linewidth of its radiation output. Heretofore, only indirect measurement of the linewidth of the SFR laser was available with a quoted number[7] of ~900 MHz. In this paper we report direct measurements of the SFR laser linewidth by heterodyning the SFR laser output with power output from a cw gas laser. We *measure* a linewidth of $\lesssim$ *1 kHz* for the spin-flip Raman laser pumped at 5.3 μm. The linewidth is limited by spectrum analyzer resolution. The SFR laser linewidth calculated from consideration of the amplitude and phase fluctuations in the laser is ~1 Hz. The contribution of the SFR laser linewidth arising from the fluctuations in the magnetic field which