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Counterintuitive transitions in multistate curve crossing involving linear potentials

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Abstract. Two problems incorporating a set of horizontal linear potentials crossed by a sloped linear potential are solved analytically and compared with numerical results: (a) the case where boundary conditions are specified at the ends of a finite interval and (b) the case where the sloped linear potential is replaced by a piecewise-linear sloped potential and the boundary conditions are specified at infinity. In the approximation of small gaps between the horizontal potentials, an approach similar to the one used for the degenerate problem (Yurovsky V A and Ben-Reuven A 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 1) is applicable for both problems. The resulting scattering matrix has a form different from the semiclassical result obtained by taking the product of Landau–Zener amplitudes. Counterintuitive transitions involving a pair of successive crossings, in which the second crossing precedes the first one along the direction of motion, are allowed in both models considered here.

1. Introduction

Transitions in multistate curve crossing may be represented intuitively as a sequence of two-state crossings and avoided crossings. In the absence of turning points near the crossings, one would expect that the crossings should occur in the causal ordering of the crossing points along the direction of motion (see the broken arrow in figure 1). It is, however, known from quantum close-coupling calculations that certain *counterintuitive* transitions may also be allowed [1–3], in which the causal arrangement may be broken, letting the second crossing point precede the first one with respect to the direction of motion (see the full arrow in figure 1). Such transitions are forbidden generally in analytical semiclassical theories of multistate curve crossing.

The concept of counterintuitive transitions [1–3] has recently received some attention in the theory of cold-atom collisions, in particular regarding the problem of incomplete optical shielding (or suppression) of loss-inducing collisions (see [2–4] and references therein). Optical shielding of a colliding pair of cold atoms is attained by subjecting an atom to a laser field with the laser frequency shifted to the blue of an asymptotic atomic resonance frequency. The laser field couples the ground molecular state to a repulsive excited molecular state (which correlates asymptotically to the state in which one of the atoms is excited). According to the ordinary (single-crossing) Landau–Zener (LZ) theory [5], the radiative coupling forms a repulsive barrier which diverts and reflects the atoms approaching each other in their ground states. This theory predicts an exponential decrease of the penetration (transmission) probability as the laser power is increased. Experiments indicate, however, that this shielding

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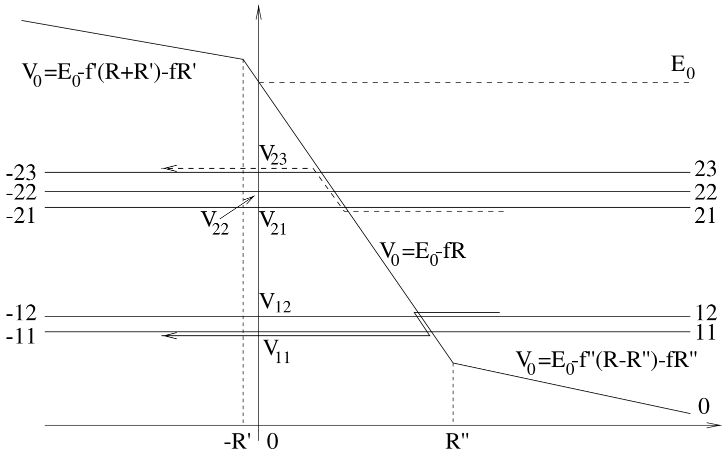

Figure 1. A schematic illustration of the model of a sloped piecewise-linear potential crossing a set of ($n = m = 2$ here) quasi-degenerate groups of horizontal potentials ($d_1 = 2$, $d_2 = 3$ here). Negative numbers denote transmission channels for waves entering from the right. The truncated linear model involves only the finite interval between $-R'$ and R''. Broken and full arrows show intuitive and counterintuitive transitions, respectively.

efficiency saturates at a certain 'hangup' value, at which the transmission probability stays finite.

In some situations the optical shielding effect can be explained by a semiclassical multiple-crossing model, associated with a pair of transitions of the intuitive kind involving partial-wave channels [4]. However, in other situations, in which the former transitions are impeded by various constraints (e.g. centrifugal barriers), it is possible, as demonstrated by close-coupling calculations [2], to attribute the incomplete shielding effect to transitions of the counterintuitive type.

In semiclassical approaches, transition amplitudes in multistate systems are usually constructed from products of single-crossing (or non-crossing) LZ amplitudes [6, 7]. As already stated, counterintuitive transitions are forbidden in such approaches. Even in exactly soluble models, such as the Demkov–Osherov model [8], in which the semiclassical theory provides exact transition amplitudes, counterintuitive transitions are forbidden. This conclusion holds for non-degenerate channel potentials. In a recent publication [1], the Demkov–Osherov model has been extended to the case in which some of the horizontal channel potentials are degenerate. A major observation of that work is that an abrupt change occurs in the transition amplitudes as the gap between two such parallel potentials narrows to zero, making all transitions possible. Also, in this limit, the transition amplitudes are no longer representable as products of single-crossing LZ amplitudes. The range over which the transition occurs seems to diverge on approaching degeneracy.

The Demkov–Osherov model is rather unusual, requiring a set of flat (horizontal) parallel potentials crossing a single linear sloped potential. All potentials are assumed to retain these properties to infinity, disregarding standard boundary conditions used in scattering theory. This peculiar property, combined with the observations on the passage to degeneracy, have led us to inquire whether a modification of the potentials at the far wings, away from the crossing region, may lead to a correction of the Demkov–Osherov results, making the counterintuitive transitions allowable when the potential gap between the flat channels becomes sufficiently small.

We have found that this is indeed the case in the two modified models we have solved. In one model (described in section 2 below), the domain of the model is truncated, confining it to a finite range, with boundary conditions defined at its edges. In the other model (described in section 3), the single-sloped potential is replaced by a piecewise-linear potential (see figure 1), constructed of three connected segments (one finite central segment at the crossing region, and two semi-infinite segments in the wings). We show here, with the help of an analytical perturbation theory, that both models allow for counterintuitive transitions. The probability of these transitions diminishes as the gap between the adjacent horizontal potentials is increased. These results, derived from the analytical theory, are compared with numerical solutions of the associated quantum close-coupling equations in section 4.

2. Truncated linear problem

2.1. Statement of the problem

Consider a sloped linear potential crossing a set of horizontal potentials (figure 1), bunched into some quasi-degenerate groups. (The criteria defining quasi-degeneracy will be specified below.) The case of exact degeneracy may be reduced to the non-degenerate problem in the manner described in [1] and is therefore not considered here.

Let us denote as $|0\rangle$ the (internal) channel state with the sloped potential V_0, and as $|j\nu\rangle$ the channels with horizontal potentials $V_{j\nu}$, where $1 \leqslant j \leqslant m$ denotes a group of quasi-degenerate states and $1 \leqslant \nu \leqslant d_j$ denotes a state within the group. The states are arranged so that $V_{j\nu} < V_{j\nu'}$ for $\nu < \nu'$ and $V_{j\nu} < V_{j'\nu'}$ for $j < j'$ and all ν and ν'. The origin on the external coordinate axis R is chosen as the classical turning point on the sloped potential, so that $V_0 = E_0 - fR$, where E_0 is the total collision energy and f is the repulsive force. The collision energy also determines the highest open channel, with $V_{nd_n} < E_0$ $(n \leqslant m)$. The problem is considered with boundary conditions defined on a finite interval $-R' < R < R''$.

Substitution of the total wavefunction Ψ in the form

$$\Psi = \sum_{j=1}^{m} \sum_{\nu=1}^{d_j} a_{j\nu}(R)|j\nu\rangle + b(R)|0\rangle \tag{2.1}$$

into the Schrödinger equation leads to the set of close-coupling equations for the coefficients $a_{j\nu}(R)$ and $b(R)$,

$$\begin{aligned} &-\frac{1}{2\mu}\frac{\partial^2 a_{j\nu}}{\partial R^2} + V_{j\nu}a_{j\nu} + g_{j\nu}b = E_0 a_{j\nu} \qquad (1 \leqslant j \leqslant m) \\ &-\frac{1}{2\mu}\frac{\partial^2 b}{\partial R^2} - fRb + \sum_{j=1}^{m}\sum_{\nu=1}^{d_j} g_{j\nu}a_{j\nu} = 0. \end{aligned} \tag{2.2}$$

(Atomic units are used here and in what follows.) Here μ is the reduced mass, and the coupling constants $g_{j\nu}$ are assumed to be real and R-independent. Without loss of generality, we can also assume that the horizontal potential channels are not coupled directly onto each other (see [8]).

The solution presented in [1] for the non-degenerate case is applicable to the system discussed here if all the following conditions hold:

$$R', R'' \gg \max\left(\frac{g_{j\nu}^2}{f(E_0 - V_{j\nu})}, \frac{E_0 - V_{j\nu}}{f}, \frac{g_{l\nu'}g_{j\nu}}{|V_{l\nu'} - V_{j\nu}|f}\right) \qquad (l \neq j) \tag{2.3}$$

and

$$R', R'' \gg \frac{g_{j\nu'}g_{j\nu}}{|V_{j\nu'} - V_{j\nu}|f}. \tag{2.4}$$

The scattering matrix (see (5.2) in [1]) may then be rewritten, using the present notation, as

$$
\begin{aligned}
&S_{00}^{\mathrm{lin}} = \exp(-2\Lambda_{10} + 2\mathrm{i}\Lambda') \\
&S_{j\nu,0}^{\mathrm{lin}} = \sqrt{1-\exp(-2\lambda_{j\nu})}\exp(-\Lambda_{j\nu} - \Lambda_{10} + 2\mathrm{i}\Lambda') \\
&S_{-j\nu,0}^{\mathrm{lin}} = -\sqrt{1-\exp(-2\lambda_{j\nu})}\exp(\Lambda_{j\nu} - \Lambda_{10} + \lambda_{j\nu}) \qquad S_{-l\nu',-j\nu}^{\mathrm{lin}} = 0 \\
&S_{l\nu',j\nu}^{\mathrm{lin}} = \sqrt{(1-\exp(-2\lambda_{l\nu'}))(1-\exp(-2\lambda_{j\nu}))}\exp(-\Lambda_{l\nu'} - \Lambda_{j\nu} + 2\mathrm{i}\Lambda') \qquad (2.5) \\
&S_{-l\nu',j\nu}^{\mathrm{lin}} = -\sqrt{(1-\exp(-2\lambda_{l\nu'}))(1-\exp(-2\lambda_{j\nu}))}\exp(\Lambda_{l\nu'} - \Lambda_{j\nu} + \lambda_{l\nu'}) \qquad (V_{l\nu'} > V_{j\nu}) \\
&S_{-j\nu,j\nu}^{\mathrm{lin}} = \exp(-\lambda_{j\nu}) \\
&S_{-l\nu',j\nu}^{\mathrm{lin}} = 0 \qquad (V_{l\nu'} < V_{j\nu}).
\end{aligned}
$$

The remaining scattering matrix elements are obtained by time-reversal symmetry, $S_{k'\nu',k\nu}^{\mathrm{lin}} = S_{k\nu,k'\nu'}^{\mathrm{lin}}$. Here channels $\pm j\nu$ correspond to the system in the state $|j\nu\rangle$ at $R \to \pm\infty$, and

$$
\begin{aligned}
&\lambda_{j\nu} = \pi\frac{\mu g_{j\nu}^2}{p_{j\nu} f} \qquad p_{j\nu} = \sqrt{2\mu(E_0 - V_{j\nu})} \\
&\Lambda_{j\nu} = \sum_{\nu'>\nu}\lambda_{j\nu'} + \sum_{j'=j+1}^{n}\sum_{\nu'=1}^{d_{j'}}\lambda_{j'\nu'} \qquad \Lambda' = \sum_{j=n+1}^{m}\sum_{\nu=1}^{d_j}|\lambda_{j\nu}|.
\end{aligned} \tag{2.6}
$$

The elements of the scattering matrix (2.5) have the form of a product of LZ amplitudes. The counterintuitive transitions are forbidden here, as can be seen from the last equality of (2.5).

The situation changes once condition (2.4) is removed; i.e. if the quasi-degenerate states are close enough, given a certain truncation range. We show here that, under appropriate conditions, one can treat this case by starting from the approach described in [1] for the degenerate problem.

The orthogonal transformation

$$
|j\kappa\rangle' = \sum_{\nu=1}^{d_j} A_{\kappa\nu}^{(j)}|j\nu\rangle \qquad a'_{j\kappa}(R) = \sum_{\nu=1}^{d_j} A_{\kappa\nu}^{(j)} a_{j\nu}(R) \tag{2.7}
$$

performed by the matrix

$$
A_{0\nu}^{(j)} = g_{j\nu}/g_j \qquad g_j = \left(\sum_{\nu=1}^{d_j} g_{j\nu}^2\right)^{1/2} \tag{2.8}
$$

described in [1, 9], leaves only one ($\kappa = 0$) of the new basis states in the jth group coupled to the sloped potential channel. Unlike the strictly degenerate case considered in [1], in the quasi-degenerate case this transformation leads to the non-diagonal potential matrix

$$
V_{\kappa'\kappa}^{(j)} = \sum_{\nu=1}^{d_j} A_{\kappa'\nu}^{(j)} V_{j\nu} A_{\kappa\nu}^{(j)}. \tag{2.9}
$$

The transformed close-coupling coefficients $a'_{j\kappa}(R)$ obey the following equations:

$$
-\frac{1}{2\mu}\frac{\partial^2 a'_{j\kappa}}{\partial R^2} + \sum_{\kappa'=0}^{d_j-1} V_{\kappa\kappa'}^{(j)} a'_{j\kappa'} = E_0 a'_{j\kappa} \qquad (\kappa \neq 0) \tag{2.10}
$$

$$
-\frac{1}{2\mu}\frac{\partial^2 a'_{j0}}{\partial R^2} + \sum_{\kappa=0}^{d_j-1} V_{0\kappa}^{(j)} a'_{j\kappa} + g_j b = E_0 a'_{j0} \tag{2.11}
$$

$$
-\frac{1}{2\mu}\frac{\partial^2 b}{\partial R^2} - fRb + \sum_{j=1}^{m} g_j a'_{j0} = 0. \tag{2.12}
$$

Thus, the non-interacting channels ($\kappa \neq 0$) will be coupled with other channels in this quasi-degenerate group by the non-diagonal elements of the matrix (2.9). In the case of strict degeneracy, $V_{j\nu}$ is ν independent and the matrix (2.9) is then diagonal, as required in [1].

2.2. Perturbation theory

Let us solve equations (2.10)–(2.12) under conditions in which the non-diagonal elements of the potential matrix (2.9) may be considered as a small perturbation. The orthogonality of the matrix $A^{(j)}_{\kappa\nu}$ allows us to evaluate the magnitude of these elements in terms of the characteristic width of the quasi-degenerate group, ΔV_j, defined as

$$\sum_{\kappa,\kappa'=0}^{d_j-1} \left(V^{(j)}_{\kappa\kappa'} - V^{(j)}_{00}\delta_{\kappa\kappa'}\right)^2 = \sum_{\nu=1}^{d_j} \left(V_{j\nu} - V^{(j)}_{00}\right)^2 = d_j \Delta V_j^2. \tag{2.13}$$

Thus, a small ΔV_j means a weak perturbation.

The unperturbed equations are similar to those used in the degenerate case (see [1]). The unperturbed equations (2.10) are uncoupled. Therefore, the curve-crossing problem has the following unit-flux normalized plane-wave solutions:

$$\varphi_{\pm j\kappa} = (\mu/p'_{j\kappa})^{1/2} \exp(\mp \mathrm{i} p'_{j\kappa} R)|j\kappa\rangle' \qquad \kappa \neq 0 \tag{2.14}$$

where the signs $\pm$ denote the location of the source of the incoming wave ($\pm\infty$), and

$$p'_{j\kappa} = \sqrt{2\mu\left(E_0 - V^{(j)}_{\kappa\kappa}\right)}. \tag{2.15}$$

The unperturbed equations (2.11) and (2.12) describe the non-degenerate linear curve-crossing problem considered in [1]. Thus the remaining solutions of the unperturbed problem may be expressed in terms of the fundamental solutions $a_j(R)$ and $b(R)$, introduced in [1]. The solution, containing a unit-flux incoming wave in the state $|0\rangle$, and an outgoing wave containing all other coupled states, has the form

$$\varphi_0 = \mathrm{e}^{-\Lambda_0} \left[b(R)|0\rangle + \sum_{j=1}^{m} a_j(R)|j0\rangle' \right] \tag{2.16}$$

where $a_j(R)$ and $b(R)$ are defined by equations (4.1)–(4.3) in [1], with $p_j = p'_{j0}$ and $s_{\pm l} = 1$ for all l. Here

$$\Lambda_j = \sum_{j'=j+1}^{n} \lambda_{j'} \qquad \lambda_j = \pi \frac{\mu g_j^2}{p'_{j0} f}. \tag{2.17}$$

The solution containing unit-flux incoming waves in the states $|j\kappa\rangle'$ may be constructed using other choices for $s_{\pm l}$†. So, the solutions representing waves incoming from the negative R direction have the form

$$\varphi_{-j0} = (2\sinh\lambda_j)^{-1/2} \exp(-\lambda_j/2 + \Lambda_j - 2\mathrm{i}\Lambda') \Big\{ [b(R, s_{+j} = -1) - b(R)]|0\rangle + \sum_{l=1}^{m} [a_l(R, s_{+j} = -1) - a_l(R)]|l0\rangle' \Big\}. \tag{2.18}$$

The remaining solutions, representing waves incoming from the positive R direction, have the form

$$\varphi_{+j0} = (2\sinh\lambda_j)^{-1/2} \exp(\lambda_j/2 - \Lambda_j) \Big\{ [b(R, s_{-j} = -1) - \mathrm{e}^{-2\lambda_j} b(R)]|0\rangle + \sum_{l=1}^{m} [a_l(R, s_{-j} = -1) - \mathrm{e}^{-2\lambda_j} a_l(R)]|l0\rangle' \Big\}. \tag{2.19}$$

† Values of $s_{\pm l}$ different from 1 will be marked below as additional arguments of a_j and b.

The evaluation of the perturbation matrix elements connecting the unperturbed wavefunctions (2.16)–(2.19) and (2.14) includes an integration over R of the products of the exponential function from (2.14) with $a_j(R)$. (One does not have to evaluate similar integrals with $b(R)$, since the states $|0\rangle$ and $|j\kappa\rangle'$, with $\kappa \neq 0$, are not coupled.) Using the contour-integral representation (3.2) in [1], the integral may be transformed into the following form:

$$\int_{-R'}^{R''} \mathrm{d}R \exp(\pm \mathrm{i} p'_{j\kappa} R)\, a_j(R) = -\mathrm{i} \int_C \mathrm{d}p\, \tilde{a}_j(p) \frac{\exp(\mathrm{i}(p \pm p'_{j\kappa})R'') - \exp(-\mathrm{i}(p \pm p'_{j\kappa})R')}{p \pm p'_{j\kappa}}. \tag{2.20}$$

If conditions (2.3) are satisfied, the asymptotic expansion of the integral may be evaluated in the manner used in [1] for the evaluation of $a_j(R)$. (The integration contour should enclose all the poles $\pm p'_{j\kappa}$ for each j simultaneously.) As a result, the matrix elements are expressible as

$$\begin{aligned}
\langle \varphi_{\pm j\kappa}|V^{(j)}|\varphi_0\rangle &= S_{j0}\xi^{\pm}_{j\kappa}(R'') - S_{-j0}\xi^{\mp *}_{j\kappa}(-R') \\
\langle \varphi_{\pm j\kappa}|V^{(j)}|\varphi_{j'0}\rangle &= \delta_{jj'}\xi^{\mp *}_{j\kappa}(R'') + S_{jj'}\xi^{\pm}_{j\kappa}(R'') - S_{-jj'}\xi^{\mp *}_{j\kappa}(-R') \\
\langle \varphi_{\pm j\kappa}|V^{(j)}|\varphi_{-j'0}\rangle &= -\delta_{jj'}\xi^{\pm}_{j\kappa}(-R') + S_{j-j'}\xi^{\pm}_{j\kappa}(R'').
\end{aligned} \tag{2.21}$$

Here

$$\begin{aligned}
\xi^{+}_{j\kappa}(R) &= -\mathrm{i}(\mu/p'_{j\kappa})^{1/2} V^{(j)}_{\kappa 0} \frac{\alpha_j(R)}{p'_{j0} + p'_{j\kappa}} \exp(\mathrm{i}p'_{j\kappa}R) \\
\xi^{-}_{j\kappa}(R) &= \mathrm{i}(\mu/p'_{j\kappa})^{1/2} V^{(j)}_{\kappa 0} \left[\frac{1}{p'_{j0} + p'_{j\kappa}} + \frac{\pi R}{\lambda_j + \mathrm{i}\pi}\right] \alpha_j(R) \exp(-\mathrm{i}p'_{j\kappa}R)
\end{aligned} \tag{2.22}$$

in which $\alpha_j(R)$ are a set of waves of unit-flux normalization appearing in the asymptotic solution, as defined by (4.9) of [1]. The amplitudes $S_{kk'}$ are the elements of the scattering matrix for the non-degenerate case defined by (5.2) of [1]. They are also obtained from (2.5) by setting $d_j = 1$ for all j and omitting the subscript ν, i.e.

$$S_{kk'} = S^{\mathrm{lin}}_{k1,k'1} \qquad (k, k' \neq 0) \qquad S_{k0} = S^{\mathrm{lin}}_{k1,0} \qquad S_{0k} = S^{\mathrm{lin}}_{0,k1}. \tag{2.23}$$

The perturbation matrix elements between the states (2.14) have the form

$$\begin{aligned}
\langle \varphi_{\sigma' j\kappa'}|V^{(j)}|\varphi_{\sigma j\kappa}\rangle &= \mathrm{i}\mu(p'_{j\kappa}p'_{j\kappa'})^{-1/2} V^{(j)}_{\kappa'\kappa} \\
&\times \frac{\exp(-\mathrm{i}(\sigma p'_{j\kappa} - \sigma' p'_{j\kappa'})R'') - \exp(\mathrm{i}(\sigma p'_{j\kappa} - \sigma' p'_{j\kappa'})R')}{\sigma p'_{j\kappa} - \sigma' p'_{j\kappa'}} \qquad (\sigma, \sigma' = \pm).
\end{aligned} \tag{2.24}$$

The transitions between the unperturbed states are negligible if the matrix elements (2.21) and (2.24) are small compared to a unit. Since $S_{kk'} \leqslant 1$, the matrix elements (2.21) are small if the functions (2.22) are small. This imposes the following restrictions on R' and R'':

$$R', R'' \ll \frac{1}{\Delta V_j}\sqrt{\frac{E_0 - V_{j\nu}}{\mu}} + \frac{g_j^2}{f\Delta V_j} \qquad (j \leqslant m) \tag{2.25}$$

which is the opposite of the condition of applicability (2.4) of the solution for the non-degenerate case. The full conditions of negligibility of the perturbation effect may be written as a restriction on the characteristic width of quasi-degenerate groups

$$\Delta V_j \ll \min\left(4(E_0 - V_{j\nu}),\ \frac{p_j(1 + \lambda_j/\pi)}{\mu R'},\ \frac{p_j(1 + \lambda_j/\pi)}{\mu R''}\right) \tag{2.26}$$

recalling that

$$\frac{p_j(1+\lambda_j/\pi)}{\mu R'} = \frac{1}{R'}\sqrt{\frac{E_0 - V_{j\nu}}{\mu} + \frac{g_j^2}{|V_0(-R') - E_0|}}$$
$$\frac{p_j(1+\lambda_j/\pi)}{\mu R''} = \frac{1}{R''}\sqrt{\frac{E_0 - V_{j\nu}}{\mu} + \frac{g_j^2}{|V_0(R'') - E_0|}}. \qquad (2.27)$$

Thus, if these conditions are obeyed, the transitions in a truncated quasi-degenerate system may be described by using the scattering matrix for the degenerate system; i.e. (5.6) and (5.7) in [1],

$$S_{k'\nu',k\nu} = \frac{g_{|k'|\nu'}g_{|k|\nu}}{g_{|k'|}g_{|k|}}S_{k'k} + \left(\delta_{\nu\nu'} - \frac{g_{|k|\nu'}g_{|k|\nu}}{g_{|k|}^2}\right)\delta_{-kk'} \qquad (2.28)$$

$$S_{k\nu,0} = \frac{g_{|k|\nu}}{g_{|k|}}S_{k0} \qquad S_{0,k\nu} = \frac{g_{|k|\nu}}{g_{|k|}}S_{0k} \qquad (2.29)$$

where $S_{k'k}$ are defined by (2.23) or (5.2) of [1]. The scattering matrix (2.28) cannot be represented in the semiclassical form as a product of LZ amplitudes, and allows for counterintuitive transitions ($k' = -k < 0$, $\nu' < \nu$).

3. Piecewise-linear problem

3.1. Transitions in the external regions

In the previous section it was shown that transitions in the quasi-degenerate system confined to a finite vicinity of the crossing points, defined by the conditions (2.25), may be described by the scattering matrix for the degenerate system, (2.28) and (2.29). However, transitions between the quasi-degenerate states do not stop at the edges of this vicinity. Transitions in the external regions beyond this vicinity ultimately lead to the scattering matrix for the non-degenerate system (2.5). Let us introduce orthogonal matrices $B_{\kappa\nu}^{(k)}$ describing the transitions in the external regions ($R > R''$ for $k > 0$ and $R < -R'$ for $k < 0$) between the asymptotic states $||k|\nu\rangle$ at infinity and the states $||k|\kappa\rangle'$ at the edges of the internal region. These matrices are diagonal with respect to transitions between states of different quasi-degenerate groups since these are fully accomplished within the internal region when the conditions (2.3) are obeyed. Thus, the scattering matrix (2.5) for the quasi-degenerate system in the infinite range can be expressed approximately in the form

$$S_{k'\nu',k\nu}^{\text{lin}} \approx B_{0\nu'}^{(k')}B_{0\nu}^{(k)}S_{k'k} + \sum_{\kappa\neq 0} B_{\kappa\nu'}^{(k')}B_{\kappa\nu}^{(k)}\delta_{-kk'} \qquad (k, k' \neq 0) \qquad (3.1)$$

$$S_{k\nu,0}^{\text{lin}} = S_{0,k\nu}^{\text{lin}} \approx B_{0\nu}^{(k)}S_{k0}. \qquad (3.2)$$

Here use was made of properties (5.3)–(5.5) of [1] concerning the scattering matrix for the degenerate states in the transformed basis.

In the limit of strict degeneracy, where the matrix elements (2.21) and (2.24) vanish, and transitions between the states of the transformed basis cease to exist, $B_{\kappa\nu}^{(k)} = A_{\kappa\nu}^{(|k|)}$, and (3.1) and (3.2) are reduced to (2.28) and (2.29), respectively, defining the scattering matrix in the degenerate case.

The substitution of (2.5) for $S^{\text{lin}}_{k\nu,0}$ and (2.23) for S_{k0} allows us to obtain the following exact expressions for $B^{(k)}_{0\nu}$:

$$B^{(j)}_{0\nu} = \left[\frac{1-\exp(-2\lambda_{j\nu})}{1-\exp(-2\lambda_j)}\right]^{1/2} \exp(\Lambda_j - \Lambda_{j\nu})$$
$$B^{(-j)}_{0\nu} = \left[\frac{1-\exp(-2\lambda_{j\nu})}{1-\exp(-2\lambda_j)}\right]^{1/2} \exp(\Lambda_{j\nu} - \Lambda_j + \lambda_{j\nu} - \lambda_j). \tag{3.3}$$

These expressions also obey (3.1) exactly for $k \neq k'$ when it is independent of $B^{(k)}_{\kappa\nu}$ with $\kappa \neq 0$.

Hereafter, we shall consider only the case in which each quasi-degenerate group consists of two states ($d_j = 2$, $\nu = 1, 2$ and $\kappa = 0, 1$). In this case the remaining elements of $B^{(k)}_{\kappa\nu}$ are defined by the orthogonality of this matrix, resulting in

$$B^{(\pm j)}_{1\nu} = (-1)^{\nu-1}\sigma_\pm B^{(\pm j)}_{03-\nu} \tag{3.4}$$

where $\sigma_\pm$ may be chosen as either +1 or −1.

The matrix $B^{(k)}_{\kappa\nu}$ obtained in this manner obeys the equations (3.1) only approximately. By choosing $\sigma_+ = \sigma_-$, the residuals become smaller than

$$\frac{\lambda_j - \lambda_{j1} - \lambda_{j2}}{\lambda_j} \approx \frac{\Delta V_j}{2\left(E_0 - V^{(j)}_{00}\right)} \tag{3.5}$$

and may be neglected whenever the first criterion in (2.26) is obeyed.

One may expect the inaccuracy of the representation (3.2) and (3.1) to be of the same order as the matrix elements (2.21) and (2.24). However, the inaccuracy is independent of R' and R''. This means that the corresponding errors in the transition amplitudes in the central and external regions cancel each other out in this case of a linear sloped potential. Therefore, the elements $B^{(k)}_{\kappa\nu}$ provide an estimate of the transition amplitudes in the external regions, to the same accuracy as that provided by the scattering matrix of the degenerate case for the transition amplitudes in the central region. The amount of inaccuracy may be estimated by the matrix elements (2.21) and (2.24).

The orthogonality conditions are sufficient to determine the matrix $B^{(\pm j)}_{\kappa\nu}$ for $d_j = 2$ only, since only in a two-dimensional space a given vector (the row $B^{(\pm j)}_{0\nu}$) has only one unit vector orthogonal to it (up to a sign $\sigma_\pm$). The relative signs of $B^{(+j)}_{1\nu}$ and $B^{(-j)}_{1\nu}$ are chosen so as to produce minimal residuals on substitution to (3.1), the absolute signs being insignificant. In the case of a d_j-dimensional space with $d_j > 2$ there are $d_j - 1$ mutually orthogonal vectors which are orthogonal to the given vector (the row $B^{(\pm j)}_{0\nu}$). The matrix $B^{(\pm j)}_{\kappa\nu}$ may also be considered as consisting of d_j mutually orthogonal column vector with fixed components $B^{(\pm j)}_{0\nu}$. These vectors are defined up to a rotation (about the $\kappa = 0$ unit vector), characterized by $d_j - 2$ arbitrary angles, and (3.1) may then define only a relative rotation of $B^{(+j)}_{\kappa\nu}$ and $B^{(-j)}_{\kappa\nu}$.

3.2. Total scattering matrix

As was shown in the previous subsection, the scattering matrix for the quasi-degenerate linear problem may be represented approximately as a product of the scattering matrix for a degenerate problem, describing transitions in a finite vicinity of the crossing points, and the matrices $B^{(k)}_{\kappa\nu}$, describing transitions in the external wings. This fact allows us to consider a piecewise-linear problem (see figure 1), in which the sloped potential consists of three segments of varying slopes ($-f'$ at $R < -R'$, $-f$ at $-R' < R < R''$, and $-f''$ at $R > R''$). If R', R'', and ΔV_j obey the conditions (2.26), we can associate the transitions at $R < -R'$ with the matrix $B^{(-j)}_{\kappa\nu}(f')$, at $-R' < R < R''$ with $S_{kk'}(f)$ and at $R > R''$ with $B^{(j)}_{\kappa\nu}(f'')$. The f arguments refer to the forces with which these matrices should be evaluated. The total scattering matrix can then be written as

$$S^{pl}_{k'\nu',k\nu} \approx B^{(k')}_{0\nu'} B^{(k)}_{0\nu} S_{k'k}(f) + \sum_{\kappa\neq 0} B^{(k')}_{\kappa\nu'} B^{(k)}_{\kappa\nu} \delta_{-kk'} \qquad (k, k' \neq 0)$$
$$S^{pl}_{k\nu,0} \approx B^{(k)}_{0\nu} S_{k0}(f) \qquad S^{pl}_{0,k\nu} \approx B^{(k)}_{0\nu} S_{0k}(f) \tag{3.6}$$

where $B^{(k)}_{\kappa\nu}$ is taken as $B^{(k)}_{\kappa\nu}(f'')$ if $k > 0$ and as $B^{(k)}_{\kappa\nu}(f')$ if $k < 0$. The same sign $\sigma_\pm$ has been chosen for $B^{(-j)}_{\kappa\nu}(f')$ and $B^{(+j)}_{\kappa\nu}(f'')$ in order to maintain continuity at $f' = f$ and $f'' = f$. (The angles describing the arbitrary rotations about the direction of the interacting state if $d_j > 2$, being continuous parameters, may not be determined completely in this manner.) The elements of the scattering matrix (3.6) cannot be represented as a product of LZ amplitudes.

It is interesting to consider in more detail the elements $S^{pl}_{-j\nu',j\nu}$ $(j > 0)$ describing transmission within the same quasi-degenerate group. Substituting (3.3) and (3.4), as well as (2.23), into (3.6) one obtains

$$\begin{aligned} S^{pl}_{-j\nu',j\nu} = {} & [1-\exp(-2\lambda'_j)]^{-1/2}[1-\exp(-2\lambda''_j)]^{-1/2} \\ & \times\Big[\sqrt{(1-\exp(-2\lambda'_{j\nu'}))(1-\exp(-2\lambda''_{j\nu}))}\,\exp(-\lambda_j - \lambda'_{j1}\delta_{\nu'2} - \lambda''_{j2}\delta_{\nu1}) \\ & +(-1)^{\nu-\nu'}\sqrt{(1-\exp(-2\lambda'_{j3-\nu'}))(1-\exp(-2\lambda''_{j3-\nu}))} \\ & \times\exp(-\lambda'_{j1}\delta_{\nu'1} - \lambda''_{j2}\delta_{\nu2})\Big] \end{aligned} \tag{3.7}$$

where $\lambda'_{j\nu}$ and $\lambda''_{j\nu}$ are defined by (2.6) with f replaced by f' or f'', respectively. The counterintuitive transitions then correspond to the matrix elements

$$\begin{aligned} S^{pl}_{-j1,j2} = {} & [1-\exp(-2\lambda'_j)]^{-1/2}[1-\exp(-2\lambda''_j)]^{-1/2} \\ & \times\Big[\sqrt{(1-\exp(-2\lambda'_{j1}))(1-\exp(-2\lambda''_{j2}))}\,\exp(-\lambda_j) \\ & -\sqrt{(1-\exp(-2\lambda'_{j2}))(1-\exp(-2\lambda''_{j1}))}\,\exp(-\lambda'_{j1} - \lambda''_{j2})\Big]. \end{aligned} \tag{3.8}$$

In the limit $f' = f'' = f$ these amplitudes become smaller than (3.5), which serves as a measure of the inaccuracy of this approximation.

Of special interest is the case in which the potential V_0 in one of the external wings is horizontal ($f' = 0$ or $f'' = 0$). In this case the present approach is formally inapplicable, since the finite gap between V_0 and the other potentials does not allow one to neglect the interaction even at infinity and to set the asymptotic boundary conditions with the incoming flux in one channel only. This case may be treated by assuming that the interaction constants $g_{j\nu}$ are gradually turned off towards infinity. This assumption is in agreement with real physical situations. For example, the laser beam inducing the coupling of atomic states has a finite width, which is very large in terms of atomic dimensions.

An adiabatically slow turning on of the interaction makes the system stay in the same adiabatic state. These states are obtained by diagonalization of the potential matrix including the interactions. If the width of the quasi-degenerate group satisfies condition (2.26) with $p_j = 0$, and the potential V_0 is well separated from other potentials (conditions (2.3) being sufficient for this case), the adiabatic states are nothing else but the states $|j\kappa\rangle'$ introduced in (2.7). In the case of $d_j = 2$, the adiabatic energy of the interacting channel state $|j0\rangle'$ and V_0 lie on opposite sides of the adiabatic energy of the non-interacting channel state $|j1\rangle'$. Since the adiabatic potentials do not cross each other, the state $|j0\rangle'$ corresponds adiabatically to $|j2\rangle$ as $R \to \infty$ and to $|j1\rangle$ as $R \to -\infty$. This fact is also known in the theory of 'dark states' (see [10] and references therein). A more detailed analysis yields

$$B^{(+j)}_{\kappa\nu} = 1 - \delta_{\kappa,\nu-1} \qquad B^{(-j)}_{\kappa\nu} = (-1)^{\kappa}\delta_{\kappa,\nu-1} \tag{3.9}$$

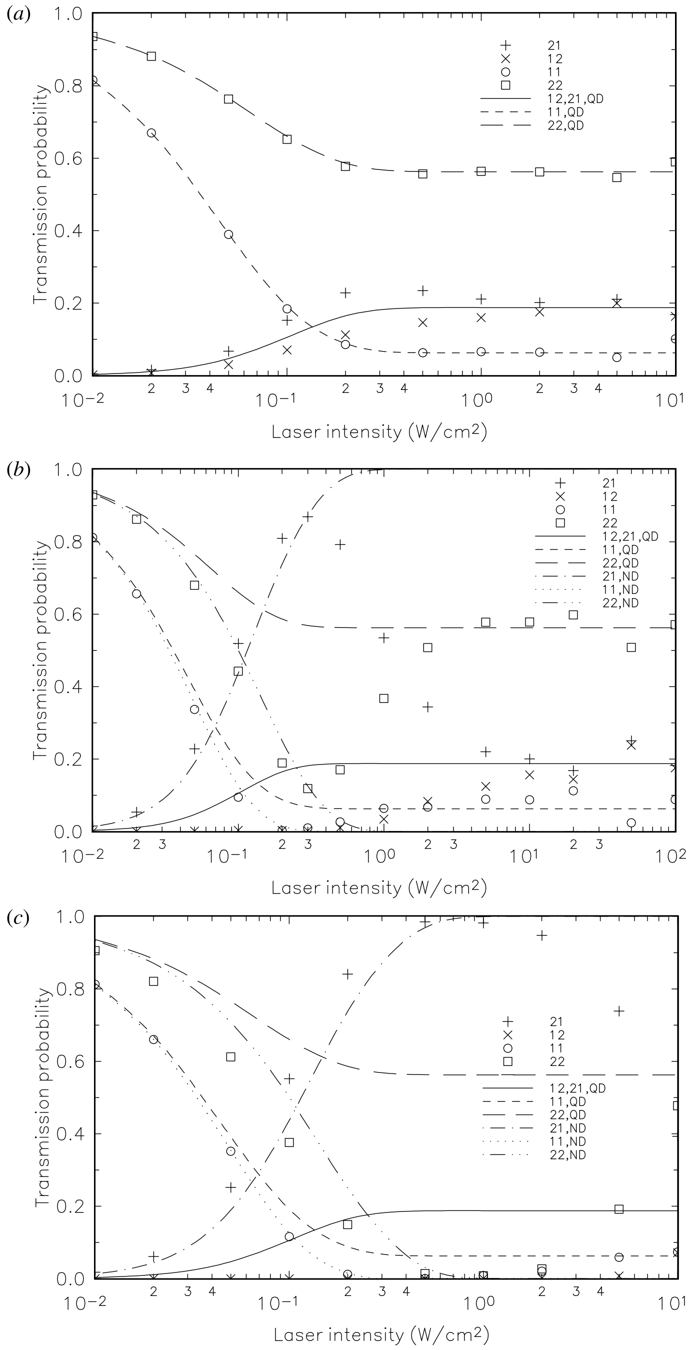

Figure 2. Transmission probability $|S_{-1\nu',1\nu}|^2$ for a truncated linear problem of two horizontal potentials in one quasi-degenerate group. The pairs of numbers assigned to the plots represent $\nu\nu'$. The coupling constants are proportional to the square root of the laser intensity. The curves are obtained using analytical expressions for the quasi-degenerate (QD) and non-degenerate (ND) cases. The points present results of the numerical close-coupling calculations. The values of the gaps between the horizontal potentials $V_{12} - V_{11}$ are (*a*) 6.7×10^{-12}, (*b*) 6.7×10^{-11} and (*c*) 5×10^{-10}.

which coincide with the limiting values of (3.3) and (3.4) as $f' \to 0$ or $f'' \to 0$. Thus, the results of the present theory are applicable to this case as well.

4. Comparison with numerical results

In order to test the approximations used in the present theory, the scattering matrix was evaluated by using the analytical theory provided here, and also calculated numerically, by using the invariant embedding method [11] to solve the associated close-coupling equations, for a specific model. This model involves only two horizontal potentials ($d_1 = 2$) forming one quasi-degenerate group ($n = m = 1$). The parameters of the model were chosen so as to simulate an optical collision of metastable Xe atoms (see [4]). Here $\mu = 66$ AMU (1 AMU $= 1.6605 \times 10^{-27}$ kg), collision energy $E = 10^{-9}$ au (1 au $= 4.3597 \times 10^{-18}$ J) and $f = 2.17 \times 10^{-10}$ au/a_0 ($a_0 = 0.052\,9177$ nm). The coupling constants, which are dependent on the laser intensity I, were taken as $g_{11} = 9.6 \times 10^{-9}$ $[I(\text{W cm}^2)]^{1/2}$ au and $g_{12} = 5.6 \times 10^{-9}$ $[I(\text{W cm}^2)]^{1/2}$ au. The first criterion in (2.3) requires a large value of $R' = R'' = 6 \times 10^3\ a_0$. This value, dictated by the small value of the kinetic energy, is larger than the range one would normally associate with the shielding process simulated by this model.

The results for the truncated linear problem are presented in figure 2, using three different values of the potential gap. The calculations show that for the small gap $V_{12} - V_{11} = 6.7 \times 10^{-12}$ au (figure 2(*a*)), expressions (2.28) and (2.29) for the scattering matrix in the degenerate case are in good agreement with the numerical results. For the large gap $V_{12} - V_{11} = 5 \times 10^{-10}$ au (figure 2(*c*)) the agreement is better with the expressions (2.5) for the scattering matrix in the non-degenerate case. The numerical results for the intermediate gap $V_{12} - V_{11} = 6.7 \times 10^{-11}$ au (figure 2(*b*)) lie between the predictions of the two models. The latter case corresponds to the actual gap between the energies at the crossing points in which the s and d partial-wave potentials of the lower (metastable) state of Xe cross the p partial-wave potential of the excited state. At high intensities, however, the numerical results tend to the predictions of the quasi-degenerate model (as discussed in section 5 below).

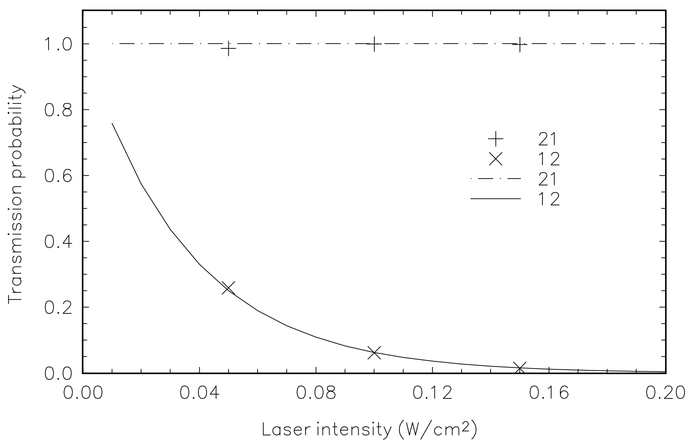

Figure 3. Transmission probabilities $|S_{-1\nu',1\nu}|^2$ for a piecewise-linear model with horizontal wings, showing results of the analytical expressions, in comparison with results of the numerical calculations (represented by points). The pairs of numbers assigned to the plots represent $\nu\nu'$. The value of the gap between the horizontal potentials is $V_{12} - V_{11} = 6.7 \times 10^{-13}$.

The numerical calculations for the piecewise-linear model are somewhat more tedious, as the gap sizes used here require a very wide integration range, reaching near-macroscopic dimensions. We have conducted calculations for the case in which the two wings are flat ($f' = f'' = 0$), keeping all other parameters the same as in the truncated model discussed above. Figure 3 shows two transition elements (the intuitive one above and the counterintuitive one below), demonstrating excellent agreement between the calculations and the analytical results using (3.6) and (3.9).

5. Discussion

We have solved analytically and numerically model problems that are modifications of the Demkov–Osherov model of a sloped linear potential curve crossing a set of horizontal ones. Two types of modifications were considered: (a) truncation, in which the boundary conditions are determined at the ends of a finite interval and (b) modification of the sloped potential into a piecewise-linear form. The modified problems can be treated by using the quasi-degeneracy approximation, which is valid when the criteria (2.3) and (2.26) are obeyed. This approximation means that the results of the degenerate model discussed in [1] should be used. This model allows for counterintuitive transitions. The opposite happens when criteria (2.4) are met. In this case, in which the transition range lies within the range of the finite segment of the sloped potential, the results of the non-degenerate (i.e. the original Demkov–Osherov) model apply, in which case counterintuitive transitions are forbidden. It follows from the present analysis that counterintuitive transitions are generally quite common in situations involving a sloped potential crossing several horizontal ones. In the unmodified problem (dealt with by the Demkov–Osherov model), contributions coming from different parts of the transition region cancel each other out, and lead to the disappearance of the counterintuitive transitions. Such a compensation no longer takes place when the conditions of quasi-degeneracy (2.26) are obeyed.

The criteria (2.26) allow for an interpretation that stems from the viewpoint of the uncertainty principle. Let us denote by $\Delta p_j = \mu \Delta V_j / p_j$ the characteristic difference of momenta in the quasi-degenerate group for a given total energy, and by $t' = \mu R'/p_j$ and $t'' = \mu R''/p_j$ the characteristic times of travelling from R'' to 0 and from 0 to R', respectively. Using this notation, the criteria (2.26) may be written in one of the following forms:

$$\begin{aligned} &\Delta p_j \max(R', R'') \ll \hbar(1 + \lambda_j/\pi) \\ &\Delta V_j \max(t', t'') \ll \hbar(1 + \lambda_j/\pi). \end{aligned} \tag{5.1}$$

The first form means that the momenta in the quasi-degenerate states are indistinguishable at the given coordinate interval. The second one means that the potential energies of the quasi-degenerate states are indistinguishable for the given travelling time. The factor $(1 + \lambda_j/\pi)$ describes a broadening of the uncertainty as the coupling increases. As one may see from figure 2, the higher the intensity becomes, the larger the value of ΔV_j applicable in the quasi-degenerate approximation.

The expansion of the applicability region in the quasi-degenerate model as the coupling constants increase, leads to an interesting property of the transmission amplitudes, that may be interpreted as a stabilization effect. Let us consider, for example, a case in which $g_{j1} = g_{j2} = \cdots = g_{jd_j} = d_j^{-1/2} g_j$. As long as the $g_{j\nu}$ are small, the criteria (2.4) are obeyed, and the system should be considered as a non-degenerate system. The amplitude of elastic transmission in the state $|j\nu\rangle$ is $S_{-j\nu,j\nu} = \exp(-\lambda_{j\nu})$ (see (2.5)). This amplitude decreases exponentially as the coupling constant increases. Upon further increasing $g_{j\nu}$, conditions (2.4) are violated, but conditions (2.26) for the applicability of the quasi-degeneracy approximation are validated. The transmission amplitude $S_{-j\nu,j\nu} = 1-[1-\exp(\lambda_j)]/d_j$ (see equation (2.28)) is close to unity if d_j is large. Moreover, the higher the coupling constants, the more states may be bunched into the quasi-degenerate group, i.e. d_j becomes larger, and the closer to unity this transmission amplitude becomes.

6. Conclusions

We consider here two types of modifications of the exactly soluble Demkov–Osherov model of a sloped linear potential curve crossing a set of horizontal curves.

(a) Truncation of the domain of the model with the boundary conditions specified at the truncation points.
(b) Deformation of the sloped potential into a piecewise-linear shape.

These two modified problems are considered in the quasi-degeneracy approximation. The main results of the present analysis are that the transition amplitudes in both modified models are not to be represented in the semiclassical form of a product of LZ amplitudes, and that both models allow for counterintuitive transitions, which are completely forbidden in semiclassical theories, as well as in the original analytically soluble Demkov–Osherov model.

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