Adiabatic analysis of atomic collisions. II. Properties of velocity-coupled channels*

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The connection between wave functions describing inelastic collisions and a complete set of standing wave functions, expanded in a Born-Oppenheimer-type base, is developed in terms of Jost functions generalized for application to velocity-coupled channels. The Jost functions represent conserved currents which include, in our case, contributions from nuclear motion. Several limiting cases of a recently developed post-adiabatic treatment are examined from the points of view of numerical applications as well as qualitative discussion. The example of a spinning particle traversing a magnetic field of variable direction is worked out.

I. INTRODUCTION

The concept of adiabaticity is helpful for the physical understanding of atomic collision processes as well as a powerful instrument for practical calculation. It derives from the Born-Oppenheimer approximation for diatomic systems, which separates nuclear from electronic motion at smaller collision velocities.

The procedure is, in fact, more general from the point of view that it separates one coordinate (say R) from the set of all others (denoted in the following by ω) even though separability does not hold strictly. So, e.g., this technique has been applied to electron-atom collisions.[1] In e-H and e-He^+ collisions the quasi-separating coordinate R is the mean-square radius of the two electrons, $R=(r_1^2+r_2^2)^{1/2}$, introduced by Fock.[2] The exact two-electron wave function is then represented by a superposition of discrete channel wave functions $\phi_\mu(R;\omega)$ which are eigenfunctions of the Hamiltonian at constant R,

$$\Psi(R;\omega)=\sum_\mu F_\mu(R)\phi_\mu(R;\omega)\,. \tag{1}$$

The adiabatic approximation assumes conservation of channel properties—which become observable only in the limit of large values of R—during all stages of the collision and implies, therefore, slow variation of the channel functions ϕ_μ with respect to R. Exact wave functions are then replaced by adiabatic wave functions,

$$\Psi_\mu^{\mathrm{ad}}(R;\omega)\simeq F_\mu(R)\phi_\mu(R;\omega)\,, \tag{1a}$$

where each $F_\mu(R)$ is now eigenfunction of a *static* potential $U_\mu(R)$.

Following these lines, doubly excited states of He and H^- have been calculated for some lower channels.[1] The position of levels is represented reasonably well; more careful analysis, however, shows that quantum defects become systematically too small for higher excitation. A more drastic breakdown of the hypothesis of adiabaticity has been reported by Lin.[1,3] In the case of e-H he found the elastic phase shift to become rapidly too small with increasing energy, even though all higher channels are well separated in energy from the ground channel under consideration. In the case of He he also reports that channel coupling in the adiabatic frame overestimates experimental transition rates.

This breakdown at still rather small velocities must stem from unrealistic reliance on an energy-independent base. In fact, in the above-mentioned examples no actual or critically avoided crossings occur which could be responsible for such significant deviations. In such more complicated systems as atom-atom collisions similar situations may well occur, but the available numerical material seems insufficient to permit quantitative comparison between experiment and theory.

These circumstances have led Fano and myself recently to outline an extension[4] [hereafter quoted as (I)] of the concept of adiabaticity, which incorporates the collision velocity into an improved Born-Oppenheimer basis. In consequence of quasi- (rather than exact) separability between R and ω, the motion in the ω space induces mock forces in the R space in addition to the static interactions represented by adiabatic potentials $U_\mu(R)$. Post-adiabaticity takes these mock-forces into account and neglects only their variation in R.

An analysis of this mechanical background had been presented by Güttinger[5] in a particularly simple situation. He studied the motion of a spinning particle in a slowly variable magnetic field and showed the spin to precess around an *effective* field consisting of the external and the Coriolis field, provided the Coriolis field itself is considered as constant.

The present paper complements (I) in several respects. (I) dealt with standing wave functions with the implied understanding that a particular superposition of standing waves has to be con-

structed to determine the amplitude for a collisional transition. This construction is familiar in elementary cases, but needs some attention here because (I) replaced the usual formulation by first-order equations with subsidiary wave functions. The language of Jost functions will prove convenient for this purpose; it has also the advantage of splitting a scattering matrix into factors corresponding to ingoing and outgoing stages of a collision. This technique has long been developed in formal scattering theory, but we will have to extend it to velocity-coupled channels in Sec. II.

Section III covers various details of analytical development that were not presented explicitly in Ref. 4. Finally Sec. IV illustrates the post-adiabatic treatment of (I) through its application to the Güttinger-like example of a spin-$\frac{1}{2}$ particle traveling in a magnetic field of variable direction.

II. SCATTERING THEORY

We consider a real Hamiltonian H in the configuration space spanned by $\{R,\omega\}$ so that the coordinate R separates from the set ω. A channel expansion like Eq. (1) leads to the exact set of equations[6]

$$\sum_\nu \{\delta_{\mu\nu}\nabla_R^2 + 2P_{\mu\nu}\nabla_R + Q_{\mu\nu} + 2(E-U_\mu)\delta_{\mu\nu}\}F_\nu(R) = 0, \tag{2}$$

with

$$\begin{aligned} U_\mu(R)\delta_{\mu\nu} &= \int d\omega\, \phi_\mu(R;\omega)^* H_{R=\text{const}}\, \phi_\nu(R;\omega), \\ P_{\mu\nu}(R) &= \int d\omega\, \phi_\mu(R;\omega)^* \nabla_R \phi_\nu(R;\omega) = -P_{\nu\mu}(R), \\ Q_{\mu\nu}(R) &= \int d\omega\, \phi_\mu(R;\omega)^* \nabla_R^2 \phi_\nu(R;\omega) \\ &= \sum_\lambda P_{\mu\lambda}(R)P_{\lambda\nu}(R) + \nabla_R P_{\mu\nu}(R). \end{aligned} \tag{3}$$

We assume, without loss of generality, all $P_{\mu\nu}$ to be real. (They are in fact real if the ω space has a finite volume as in Ref. 1. Complex coupling, being then anti-Hermitian $P_{\mu\nu} = -P^*_{\nu\mu}$, would induce formal but not substantial modifications in some of the following equations.)

Scattering data are usually obtained as elements of the $\underline{S}$ matrix. In the following we represent the $\underline{S}$ matrix as a ratio of two properly defined Jost matrices for two reasons: First, this technique decomposes the process of excitation into two more elementary stages, ingoing and outgoing, respectively. Second, the $\underline{S}$ matrix has singularities in the energy. Familiar singularities are simple poles at bound states and resonances. Jost functions, however, are normally analytic; singularities of the $\underline{S}$ matrix are described by zeros of a denominator. This concept has been developed long ago for single-channel and formal scattering theory[7]; it has been applied also in empirical analysis of scattering data. We extend it here to velocity-coupled multichannel systems.

To this end we rewrite the collision Eq. (2) in matrix notation,

$$(\underline{1}\nabla_R^2 + 2\underline{P}\nabla_R + \underline{Q} + 2\underline{1}E - 2\underline{U})\vec{F}(R) = 0 \tag{4}$$

or, with Eqs. (3), in the equivalent form

$$\{(\underline{1}\nabla_R + \underline{P})^2 + 2(\underline{1}E - \underline{U})\}\vec{F}(R) = 0\,. \tag{4a}$$

A complete set of regular wave functions representing standing waves is denoted by $\underline{F}^{\text{st}}(R) = \{\vec{F}^{\text{st}}_\mu(R)\}$ where the index μ labels channels identified by the behavior near $R=0$,

$$\lim_{R\to 0} R^{-n_\mu} F^{\text{st}}_{\mu\nu}(R) = \delta_{\mu\nu}\,.$$

The characteristic exponents $n_\mu > 0$ result from an investigation of the indicial equation near $R=0$; see, e.g., Fock[2] for the applications of Ref. 1.

These standing wave solutions may be resolved at large values of R into complex-conjugate parts representing out- and in-going waves, respectively,

$$F^{\text{st}}_{\mu\nu}(R) \to \frac{1}{2i}[e^{ik_\nu R}A_{\mu\nu} - e^{-ik_\nu R}A^*_{\mu\nu}]\,. \tag{5}$$

The coefficients $A_{\mu\nu}$ and $A^*_{\mu\nu}$ constitute probability amplitudes to find in- and out-going flux in channel ν at $R=\infty$ with respect to a unit probability concentrated in a *single channel* μ at $R=0$. Physical boundary conditions at $R=\infty$, however, correspond generally to a normalized incoming flux in *a single channel.* Therefore, we construct linear combinations of the standing waves with complex coefficients,

$$F_{\lambda\nu}(R) = \sum_\mu C_{\lambda\mu}F^{\text{st}}_{\mu\nu}(R)\,,$$

with

$$\sum_\mu C_{\lambda\mu}A^*_{\mu\nu} = \delta_{\mu\nu}\,,$$

as one does for simple potential scattering. Equation (5) reads now

$$F_{\lambda\nu}(R) \to \frac{1}{2i}[e^{ik_\nu R}S_{\lambda\nu} - e^{-ik_\nu R}\delta_{\lambda\nu}]\,. \tag{5a}$$

The matrix elements $S_{\lambda\nu} = \sum_\mu C_{\lambda\mu}A_{\mu\nu}$ represent the probability amplitudes for outgoing flux in channel ν with respect to the flux which enters *only* in channel λ with unit strength. This is the $\underline{S}$ matrix to within normalization.

Equation (5a) relates more directly to the experiments; Eq. (5) shows symmetry under time

reversal and involves no matrix division. Moreover, we show now that the coefficients $A_{\mu\nu}$ and $A^*_{\mu\nu}$ can be identified as physically relevant quantities at all stages of the collision and not only in the limit where the colliding system is separated. To this end we define two alternative *complete sets* of solutions identified by in- and out-going wave boundary conditions at $R=\infty$,

$$F^{\pm}_{\mu\nu}(R) \to \delta_{\mu\nu} e^{\pm i k_\nu R};$$

the aggregates of these component functions constitute matrices $\underline{F}^{\pm}$. Equation (5) extends then to all values of R,

$$F^{\mathrm{st}}_{\mu\nu}(R) = \frac{1}{2i}\sum_{\rho}[F^{+}_{\mu\rho}(R)A_{\rho\nu} - F^{-}_{\mu\rho}(R)A^*_{\rho\nu}]. \qquad (6)$$

Note that $\underline{A}$ and $\underline{A}^*$ don't depend on R because three complete sets $\underline{F}^{\mathrm{st}}$, $\underline{F}^{+}$, and $\underline{F}^{-}$, as solutions of a second-order equation, are linearly dependent. Therefore, they are constants of motion rather than mathematical coefficients of an asymptotic expansion. Such constants of motion are conveniently expressed by Wronskians. It is easy to verify that, for each pair of complete solutions $\{\underline{F}_1, \underline{F}_2\}$ of Eq. (4), the quantity

$$\underline{W}(\underline{F}_1, \underline{F}_2) = \tilde{\underline{F}}_1\underline{G}_2 - \tilde{\underline{G}}_1\underline{F}_2$$

with

$$\underline{G}_i(R) = -(\underline{1}\nabla_R + \underline{P})\underline{F}_i(R) \qquad (7)$$

is a constant matrix. In the special case where $\underline{F}_2 = \underline{F}_1^*$, this Wronskian represents a conserved current. Note that Eq. (7) represents this current as the sum of two parts, neither of which is conserved separately. This extended definition of a Wronskian constitutes the extension required to deal with the velocity coupling in Eq. (4).

Jost matrices are now given by

$$\underline{W}(\underline{F}^{\mathrm{st}}(R), \underline{F}^{\pm}(R)) = \underline{J}^{\pm} \qquad (8)$$

and are related to $\underline{A}$ and $\underline{A}^*$ as

$$J^{+}_{\mu\nu} = k_\mu A^*_{\mu\nu}, \quad J^{-}_{\mu\nu} = k_\mu A_{\mu\nu}$$

with wave numbers

$$k_\mu = \{2[E - U_\mu(\infty)]\}^{1/2}.$$

The experimental $\underline{S}$ matrix requires normalization of $\underline{F}^{\pm}(R)$ per unit volume and reads in matrix notation

$$\underline{S}^{\mathrm{expt}} = \underline{k}^{-1/2}\underline{J}^{-}(\underline{J}^{+})^{-1}\underline{k}^{1/2}.$$

Symmetry of $\underline{S}^{\mathrm{expt}}$ is demonstrated by formal evaluation of $\underline{W}(\underline{F}^{\mathrm{st}}(R), \underline{F}^{\mathrm{st}}(R)) = \underline{0}$ and is expressed in terms of Jost functions by

$$\underline{J}^{-}(\underline{J}^{+})^{-1} = \underline{k}(\tilde{\underline{J}}^{+})^{-1}\tilde{\underline{J}}^{-}\underline{k}^{-1}.$$

This conclusion requires $\nabla_R \underline{F}^{\mathrm{st}}(0)$ and $\underline{P}(0)$ to be finite.

Unitarity reads for open channels $\underline{S}^{\mathrm{expt}}(\underline{S}^{\mathrm{expt}})^* = 1$; it follows from $\underline{F}^{+}(R)^* = \underline{F}^{-}(R)$ and holds if the Hamiltonian is real.

III. POST-ADIABATICITY

In Eq. (8) we have seen that the auxiliary functions $\underline{G}$ given in Eq. (7) prove relevant as they generate the conserved current together with the wave function $\underline{F}$ itself in a transparent way. We use them now as a second set of independent variables and replace the Schrödinger equation by a first-order system,

$$\begin{pmatrix} \underline{1}\nabla_R + \underline{P} & \underline{1} \\ -2(\underline{1}E - \underline{U}) & \underline{1}\nabla_R + \underline{P} \end{pmatrix}\begin{pmatrix} \vec{\mathrm{F}} \\ \vec{\mathrm{G}} \end{pmatrix} = 0, \qquad (9)$$

which is now linear also in the coupling $\underline{P}$, in contrast to the original version. Note that the $\underline{Q}$ matrix of Eq. (4) no longer appears. Note also that the minus sign in front of the element $-2(\underline{1}E - \underline{U})$ of Eq. (9) was inadvertently omitted in (I).

The linearity of Eq. (9) suggests now transforming away the coupling $\underline{P}$ by a linear transformation

$$\begin{pmatrix} \vec{\mathrm{F}} \\ \vec{\mathrm{G}} \end{pmatrix} = \begin{pmatrix} \underline{V} & \underline{W} \\ \underline{X} & \underline{Y} \end{pmatrix}\begin{pmatrix} \vec{\mathrm{f}} \\ \vec{\mathrm{g}} \end{pmatrix}. \qquad (10)$$

The transformation matrices $\{\underline{V}, \underline{W}, \underline{X}, \underline{Y}\}$ were determined in (I) firstly by setting

$$\underline{X} = -\underline{P}\underline{V} - 2\underline{W}(\underline{1}E - \underline{U}), \quad \underline{Y} = \underline{V} - \underline{P}\underline{W},$$

and then identifying each column $\{\vec{\mathrm{V}}_\nu, \vec{\mathrm{W}}_\nu\}$ of the matrices $\{\underline{V}, \underline{W}\}$ as an eigenvector of

$$\begin{pmatrix} \underline{U} - \frac{1}{2}\underline{P}^2 - \underline{1}u_\nu & 2(E - u_\nu)\underline{P} \\ -\underline{P} & \underline{U} - \frac{1}{2}\underline{P}^2 - \underline{1}u_\nu \end{pmatrix}\begin{pmatrix} \vec{\mathrm{V}}_\nu \\ \vec{\mathrm{W}}_\nu \end{pmatrix} = 0. \qquad (11)$$

The coefficients $\underline{P}$ and $\underline{U}$ in this equation are functions of R, and so are its eigenvalues $u_\nu(R)$ and eigenvectors $\{\vec{\mathrm{V}}_\nu, \vec{\mathrm{W}}_\nu\}$. The eigenvalues $\{u_\nu(R)\}$ constitute a new set of post-adiabatic channel potentials which replace the initial $\underline{U}(R)$. Note that both u_ν and $\{\vec{\mathrm{V}}_\nu, \vec{\mathrm{W}}_\nu\}$ depend on the energy E as a parameter of Eq. (11).

Substitution of Eqs. (10) and (11) into Eq. (9) provides the equations obeyed by the new radial functions $\{f_\nu(R), g_\nu(R)\}$ in the postadiabatic base, namely,

$$\begin{pmatrix} \underline{1}\nabla_R & \underline{1} \\ -2(\underline{1}E - \underline{u}) & \underline{1}\nabla_R \end{pmatrix}\begin{pmatrix} \vec{f} \\ \vec{g} \end{pmatrix} + \begin{pmatrix} \underline{\Pi}_{11} & \underline{\Pi}_{12} \\ \underline{\Pi}_{21} & \underline{\Pi}_{22} \end{pmatrix}\begin{pmatrix} \vec{f} \\ \vec{g} \end{pmatrix} = 0, \qquad (12)$$

where $\underline{u}$ is diagonal and consists of the eigenvalues u_ν. The matrix $\underline{\Pi}$ is the logarithmic derivative

of the transformation, Eq. (10),

$$\begin{pmatrix} \underline{\Pi}_{11} & \underline{\Pi}_{12} \\ \underline{\Pi}_{21} & \underline{\Pi}_{22} \end{pmatrix} = \begin{pmatrix} \underline{V} & \underline{W} \\ \underline{X} & \underline{Y} \end{pmatrix}^{-1} \begin{pmatrix} \nabla_R \underline{V} & \nabla_R \underline{W} \\ \nabla_R \underline{X} & \nabla_R \underline{Y} \end{pmatrix}.$$

The term of Eq. (12) with the matrix $\underline{\Pi}$ was not given explicitly in the corresponding Eq. (7) of (I).

Let it be recalled that no approximation is involved in the analytic developments up to this point. Even the assumption that the matrix $\underline{U}$ is diagonal, in Eq. (2), is unnecessary. Approximations are involved only at further stages, with the intent of decoupling the equations, and consist of disregarding the $\underline{P}$ matrix in the adiabatic approximation or the $\underline{\Pi}$ matrix in the first post-adiabatic approximation. The smallness of each matrix element $P_{\mu\nu}$ (or, respectively, $\Pi_{\mu\nu}$) is often judged by comparing it with the corresponding separation of potential curves, $|U_\mu - U_\nu|$ (or $|u_\mu - u_\nu|$). This separation may itself become very small at avoided crossings, but we are not concerned in the present paper with the special effects related to crossings. These effects are taken into account by appropriate treatments limited to the channels whose potential curves nearly cross and to the relevant range of R. We shall discuss, instead, several aspects of the first post-adiabatic approximation which are not given in (I) or only sketched very briefly there.

Numerical treatment of Eq. (11) prefers the eigenvalue equation in standard form with the eigenvalue appearing only along the diagonal. This is easily done by multiplying Eq. (11) from the left by

$$\begin{pmatrix} \underline{1} & -2\underline{P} \\ \underline{0} & \underline{1} \end{pmatrix},$$

yielding

$$\begin{pmatrix} \underline{U} + \frac{3}{2}\underline{P}^2 & 2\underline{P}(1E - \underline{U} + \frac{1}{2}\underline{P}^2) \\ -\underline{P} & \underline{U} - \frac{1}{2}\underline{P}^2 \end{pmatrix} \begin{pmatrix} \vec{\mathbb{V}}_\nu \\ \vec{\mathbb{W}}_\nu \end{pmatrix} = u_\nu \begin{pmatrix} \vec{\mathbb{V}}_\nu \\ \vec{\mathbb{W}}_\nu \end{pmatrix}. \tag{13}$$

A basic *property of these eigenvalues* is that their values for the lower channels are depressed with respect to those of the corresponding adiabatic potentials $U_\nu(R)$. This can be seen by eliminating $\vec{\mathbb{W}}_\nu$ in Eq. (11) leading to

$$\left(\underline{U} - \tfrac{1}{2}\underline{P}^2 + 2(E - u_\nu)\underline{P} \frac{1}{\underline{U} - \frac{1}{2}\underline{P}^2 - u_\nu \underline{1}} \underline{P}\right) \vec{\mathbb{V}}_\nu = u_\nu \vec{\mathbb{V}}_\nu \tag{14}$$

and treating terms with $\underline{P}$ perturbatively. In the limit of weak coupling,

$$P_{\mu\nu}^2 \ll |U_\mu - U_\nu|, \tag{15}$$

and not too large kinetic energy $E - u_\nu$ we find

$$u_\nu(R, E) \simeq U_\nu(R) - \tfrac{1}{2}(P^2)_{\nu\nu} + 2(E - U_\nu) \sum_\mu \frac{P_{\nu\mu}^2}{U_\nu - U_\mu}. \tag{16}$$

Note that the term $\mu = \nu$ does not contribute because $P_{\nu\nu} = 0$. For the lowest channels that are open, i.e., with $U_\nu < E$, the contribution to Eq. (16) from all the higher channels, with $U_\mu > U_\nu$, is *negative*, and thus depresses the eigenvalue u_ν with respect to U_ν. This contribution *increases* with increasing values of the energy E and should thus generate a progressive increase of the scattering phase shift.

The *validity of the Born-Oppenheimer* approximation can be investigated by inspection of Eqs. (14) and (16), at least qualitatively. An expansion like Eq. (16) demonstrates clearly that weak coupling in the sense of Eq. (15) is an insufficient criterion because the perturbation is *amplified* by the coefficients $E - U_\nu$. Indeed, the effective channel kinetic energy $\epsilon_\nu = E - u_\nu$ already appears in Eq. (14) as a coefficient of $\underline{P}$. Even for small velocities of the colliding particles at large separation, significant deviations from the adiabatic limit may result if the channels are attractive because the velocity will then increase during the collision.

Transitions between channels do not occur in the first post-adiabatic approximation, as pointed out in (I), at least as long as the channels are discrete and their coupling vanishes sufficiently fast at large separation R. This can be seen from the explicit form of the wave function, which is now given by

$$\Psi_\nu(R, \omega) \simeq \sum_\mu \phi_\mu(R; \omega)[V_{\mu\nu}(R) + W_{\mu\nu}(R)\nabla_R] f_\nu(R), \tag{17}$$

rather than by the simple Eq. (1a). No transition results according to Sec. II, if our eigenvalue problem yields $V_{\mu\nu} \to \delta_{\mu\nu}$, $W_{\mu\nu} \to 0$, and $u_\nu \to U_\mu \delta_{\mu\nu}$ at both $R = 0$ and $R = \infty$. At small values of R the potentials in a collision process diverge and the coupling remains finite. In this region the expansion, Eq. (16), does not hold, but from Eq. (14) we find for $R \to 0$

$$u_\nu(R) \simeq U_\nu(R)\left(1 - 2\sum_\mu \frac{P_{\mu\nu}^2}{U_\mu - U_\nu}\right) \to U_\nu(R),$$

and, therefore, $\underline{V} \to \underline{1}$. The matrix $\underline{W}$ vanishes in this limit of ineffective coupling as seen from Eq. (11), which gives

$$\vec{\mathbb{W}}_\nu \simeq \frac{1}{\underline{U} - u_\nu \underline{1}} \underline{P} \vec{\mathbb{V}}_\nu.$$

At large distances $R \to \infty$, the coupling $\underline{P}$ vanishes. The conclusion that no transition occurs is nevertheless far from obvious. For example, for electron-atom collisions all channels are in fact discrete, but they *accumulate* near an ionization threshold. Our Eqs. (11), (13), and (14) must then be examined carefully. In this case the expansion Eq. (16) need not hold because in the ratios $P_{\mu\nu}^2/(U_\mu - U_\nu)$ the denominator may also vanish at $R \to \infty$. In a more mathematical language, it has to be checked whether the degeneracy of many adiabatic channels at $R \to \infty$ will be removed by channel coupling. We only mention here that this degeneracy will in fact *not* be removed if

$$\lim_{R\to\infty} \frac{P_{\mu\nu}(R)}{U_\mu(R) - U_\nu(R)} = 0 .$$

Note that this criterion depends sensitively on the behavior of $\underline{P}$ and $\underline{U}$ and imposes a restriction far stronger than the Eq. (15) which was derived for nondegenerate channels only.

A *WKB approximation* shares some basic assumptions with our post-adiabatic treatment and serves to illustrate some of its features. The basic assumption, common to the two approaches, concerns the slow variation of channel properties and leads one to disregard the derivative terms $\underline{\Pi}$ in Eq. (12). The remaining parameters in this equation can then be represented as wave numbers

$$\kappa_\nu(R) = \{2[E - u_\nu(R)]\}^{1/2} . \tag{18}$$

The WKB approximate solution of Eq. (12) with $\underline{\Pi} \to 0$,

$$f_\nu^{\pm}(R) \sim \kappa_\nu^{-1/2} \exp\left(\pm i \int^R \kappa_\nu(R')\, dR'\right) ,$$

diverges at the turning points, where κ_ν vanishes. The post-adiabatic treatment must avoid this divergence, because turning points have an essential role in collision problems. The divergence can, however, be avoided while retaining the concept of pairs of solutions $f_\nu^{\pm}$ propagating in opposite directions with the same wave number κ_ν. To this end one transforms Eq. (11), which determines the pair of vectors $\{\vec{V}_\nu, \vec{W}_\nu\}$, by replacing this pair by the pair of complex-conjugate vectors

$$\vec{Z}_\nu^{\pm} = \vec{V}_\nu \pm i\kappa_\nu \vec{W}_\nu . \tag{19}$$

Equation (11) is then seen to split into *separate equations*

$$[(\pm i\kappa_\nu \underline{1} + \underline{P})^2 - 2(E\underline{1} - \underline{U})]\vec{Z}_\nu^{\pm} = 0 \tag{20}$$

with the *common eigenvalue* κ_ν in place of u_ν. This equation holds regardless of the occurrence of a branch point of κ_ν at the turning points, when introduced through our post-adiabatic approach via Eq. (11), in contrast to the divergence that would have been met by deriving it directly from Eq. (4) by a WKB approximation.

The *residual coupling* of channels represented by the $\underline{\Pi}$ matrices in Eq. (12) remains to be discussed. Assuming again slow variation of parameters, one might attempt to eliminate also this coupling disregarding its derivatives—i.e., second derivatives of the initial coupling $\underline{P}$—in a *second* step of post-adiabatic approximation. It is quite doubtful whether this iteration procedure would converge, nor has a convergence criterion been formulated. Anyhow, we can anticipate some features of a further post-adiabatic transformation by inspection of Eq. (12).

To this end we again transform as in (I), substitute

$$\begin{pmatrix} \vec{f} \\ \vec{g} \end{pmatrix} = \begin{pmatrix} \underline{V}^{(2)} & \underline{W}^{(2)} \\ \underline{X}^{(2)} & \underline{Y}^{(2)} \end{pmatrix} \begin{pmatrix} \vec{f}^{(2)} \\ \vec{g}^{(2)} \end{pmatrix} = \underline{\mathcal{U}}^{(2)} \begin{pmatrix} \vec{f}^{(2)} \\ \vec{g}^{(2)} \end{pmatrix}$$

and require

$$\nabla_R \vec{f}^{(2)} = -\vec{g}^{(2)} + O(\nabla_R \underline{\mathcal{U}}^{(2)})$$

$$\nabla_R \vec{g}^{(2)} = 2(\underline{1}E - \underline{u}^{(2)})\vec{f}^{(2)} + O(\nabla_R \underline{\mathcal{U}}^{(2)}) .$$

After elimination of $\underline{X}^{(2)}$ and $\underline{Y}^{(2)}$ we find, in analogy to Eq. (20), for the combinations

$$\vec{Z}_\nu^{(2)\pm} = \vec{V}_\nu^{(2)} \pm i\kappa_\nu^{(2)} \vec{W}_\nu^{(2)} ,$$

$$\left\{(\pm i\underline{1}\kappa_\nu^{(2)} + \underline{\Pi}_{22}) \frac{1}{\underline{1} + \underline{\Pi}_{12}} (\pm i\underline{1}\kappa_\nu^{(2)} + \underline{\Pi}_{11}) - 2(\underline{1}E - \underline{u} + \tfrac{1}{2}\underline{\Pi}_{21})\right\} \vec{Z}_\nu^{(2)\pm} = 0 . \tag{21}$$

Here the diagonal matrix $\underline{u}$ consists of the post-adiabatic potentials. The next-order potentials $u_\nu^{(2)}$ are expressed in terms of wave numbers $\kappa_\nu^{(2)} = [2(E - u_\nu^{(2)})]^{1/2}$.

A first remark is that the coupling represented by $\underline{\Pi}$ in the post-adiabatic Eq. (12) has far lower symmetry than the initial coupling $\underline{P}$ in the adiabatic Eq. (9), which occurred only and identically in the two diagonal blocks. This lowered symmetry distinguishes Eq. (21) from Eq. (20) and leads to two consequences: (a) Whereas the first post-adiabatic transformation replaced the initial adiabatic potentials $\{U_n(R)\}$ by an *equal* number of $\{u_\nu(R;E)\}$ owing to the degeneracy in Eq. (20), elimination of the couplings $\underline{\Pi}$ now doubles the number of potential curves $\{u_\nu^{(2)}\}$. (b) This doubling replaces each u_ν by a *pair of complex conjugate* second-post-adiabatic potentials $\{u_\nu^{(2)}, u_\nu^{(2)*}\}$. This may be seen by inspection of Eqs. (21). If κ_ν is one eigenvalue with eigenvector $\vec{Z}_\nu^{+}$, $-\kappa_\nu$ is also an eigenvalue with eigenvector $\vec{Z}_\nu^{-}$. In addition, however, $\pm\kappa_\nu^*$ are also eigenvalues with eigenvectors $(\vec{Z}_\nu^{\mp})^*$. We note that $(\vec{Z}_\nu^{\pm})^* = \vec{Z}_\nu^{\mp}$ *no longer* holds, even if the channels are open. A complex

potential implies attenuation of propagation in one channel and its transfer to the others. One fourfold set of channel wave numbers might conceivably pertain to in- and out-going wave propagation, each mode accompanied with excitation or deexcitation with respect to first-post-adiabatic channels, but no clear interpretation can be offered at this time.

IV. ILLUSTRATIVE EXAMPLE

We consider a spin-$\frac{1}{2}$ particle with gyromagnetic ratio γ moving parallel to the y axis in a magnetic field $\vec{B}$ which is constant in strength, perpendicular to the y axis and rotates slowly in the x-z plane as a function of y,

$$\vec{B} = B(\cos_2\varphi, 0, -\sin^2\varphi),$$

with $\varphi = \varphi(y)$ and $\varphi'' \ll (\varphi')^2$. This arrangement is similar to Güttinger's.[5] Our field, however, varies in space rather than in time, whereby the problem relates more directly to our time-independent collision theory. The Schrödinger equation in the adiabatic (rotating) frame, in which $\vec{B}$ is constant and the magnetic energy diagonal, reads in exact analogy to our Eq. (4)

$$\left[\frac{1}{2}\left(\frac{d}{dy} + i\varphi'\sigma_y\right)^2 + E - \gamma B\sigma_z\right]F = 0 . \qquad (22)$$

The corresponding form of Eq. (13) can then be solved analytically and yields post-adiabatic channels labeled by spin quantum numbers $\nu = \pm\frac{1}{2}$, whose parameters read in dimensionless units

$$u_\nu(y) = 2\nu(\gamma^2B^2 + 2E\varphi'^2)^{1/2} - \tfrac{1}{2}\varphi'^2 , \qquad (23)$$

$$V_{m\nu}(y) = \delta_{m\nu}\cos\theta_\nu ,$$
$$W_{m\nu}(y) = (1-\delta_{m\nu})(-1)^{1/2-\nu}\sin\theta_\nu , \qquad (24)$$

with

$$\tan\theta_\nu = \frac{\varphi'}{(\gamma^2B^2 + 2E\varphi'^2)^{1/2} + \gamma B - 2\nu\varphi'^2} \qquad 25)$$

Note that, in our two-channel system, channel mixing stems only from $\underline{W}$ because $\underline{P}^2$ is diagonal ($\underline{P} = i\varphi'\sigma_y$). Note also that the eigenvalues, Eq. (23), are no longer proportional to $\nu = \pm\frac{1}{2}$ owing to their linear and quadratic dependence on the Coriolis force. The effective field $B_{\text{eff}} = u_\nu/\nu$ depends itself on the magnetic quantum number ν; the rotation angles in Eq. (25) also depend on ν for the same reason. The wave functions now have the form

$$F_\nu(y) = \sum_m |m\rangle\left(V_{m\nu}(y) + W_{m\nu}(y)\frac{d}{dy}\right)f_\nu(y) . \qquad (26)$$

In this particular example a WKB approximation for the $f_\nu(y)$ is acceptable as no turning point occurs for $E > u_\nu(y)$. Equation (26) would then simplify to

$$F_\nu^\pm \simeq |\nu\rangle f_\nu^{\text{WKB}} ,$$

with

$$|\nu\rangle = \sum_m |m\rangle(V_{m\nu} \pm i\kappa_\nu W_{m\nu}) \qquad (27)$$

and

$$\kappa_\nu = [2(E - u_\nu)]^{1/2} .$$

The post-adiabatic spin states $|\nu\rangle$, defined by Eq. (27), differ for in- and out-going waves ($\pm$) as inversion of the direction of wave propagation inverts the sign of the mock interaction $\kappa_\nu\varphi'\sigma_y$.

For any value of the energy E both terms $\underline{V}$ and $\underline{W}$ contribute to Eq. (27). In the special case of very large energy ($E \to \infty$), we find from Eqs. (24) and (25) the limits $V_{m\nu} \to \delta_{m\nu}$ and $\kappa_\nu W_{m\nu} \to (1-\delta_{m\nu})(-1)^{1/2-\nu}$.

The potentials u_ν in Eq. (23) differ from their adiabatic limits $\pm\gamma B$ by being (a) shifted by $\frac{1}{2}\varphi'^2$ and (b) separated by $u_{1/2} - u_{-1/2} > \gamma B$. The shift is due to the quadratic term $\underline{P}^2$ of Eq. (4a), the energy-dependent increase of level separation stems from the cross term $\underline{P}d/dy$. Equation (23) shows clearly that the lower channel is depressed, $u_{-1/2}(y) < -\gamma B$. Finally, our example demonstrates that a perturbative treatment of adiabatic channel coupling would have rather limited applicability. In fact, an expansion of the square root in Eq. (23) would converge reasonably fast only if

$$2\varphi'^2E \ll (\gamma B)^2 . \qquad (28)$$

An estimation of convergence based on the simple comparison of matrix elements appearing in the Schrödinger equation, $\varphi'^2 \ll 2\gamma B$, leads in general to a wrong conclusion because it disregards the coefficient E in Eq. (28).

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