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Semiclassical picture of depolarizing collisions: Application to collisional studies using laser spectroscopy

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An extension of the Jeffreys-Wentzel-Kramers-Brillouin approximation to inelastic processes is used to obtain the scattering amplitude which describes the collisionally induced depolarization of magnetic substate coherences. It is found that the scattering amplitudes contain contributions from two overlapping regions. For large interatomic separations, the different Zeeman sublevels are shifted and mixed by collisions, but follow a common collision trajectory. For small interatomic separations, it is possible to find adiabatic eigenstates which follow distinct collision trajectories. The theory is used to investigate the nature of the depolarizing collision kernels and rates which enter into the analysis of laser spectroscopy experiments.

I. INTRODUCTION

Laser saturation spectroscopy experiments are beginning to provide an important probe of collisional processes occurring in low pressure gases.[1] The elimination of the broad Doppler background encountered in standard spectroscopy permits a more sensitive measure of the manner in which collisions perturb the energy levels and alter the velocity of atoms.

A particularly interesting process that may be studied in such experiments is the way in which collisions perturb *superposition* states in atoms that have been created by an atom-field interaction. Since the various internal states comprising the superposition state are generally shifted and scattered *differently* in a collision, one is led to a somewhat complicated description of the entire scattering process for the superposition state, especially if collisions can also couple the superposition levels. Formal theories[2,3] have been developed to describe the scattering and time evolution of atomic superposition states via a quantum-mechanical transport equation, but little progress has been made in obtaining solutions or physical interpretations of the results. It is the purpose of this paper to provide a simplification of the transport equation and some additional physical insight into the scattering process. Methods of semiclassical scattering theory are used to achieve these goals.

The specific problem we choose to study involves the scattering of atoms prepared in a linear superposition of magnetic substates of a level characterized by internal-angular-momentum quantum number j. The way in which collisions couple, shift, and scatter the various magnetic substates is investigated. Coherent superpositions of magnetic substates (magnetic moments, Zeeman coherences) are conveniently created and probed using the "three-level" system of Fig. 1. The 1-2 transition is excited with a nearly monochromatic laser beam and the 2-3 transition is probed with another colinear laser beam. Level 2 (shown for $j=1$) is $(2j+1)$ fold degenerate; Zeeman coherences within level 2 may be produced and detected using a proper choice of the laser beam polarizations. Owing to the Doppler effect, the excitation-detection scheme excites or probes only those atoms having a specific velocity component along the laser beam direction. Thus, any collision-induced modification of the Zeeman coherences for atoms having a specific longitudinal velocity can be monitored in such a system. The Zeeman coherences tend to be destroyed by inseparable contributions from collisional effects on the internal (shifting and mixing of magnetic sublevels) and external (state-dependent scattering for the different magnetic sublevels) atomic degrees of freedom. In such experiments, the collisional relaxation is determined by the number of collisions per lifetime of the level under con-

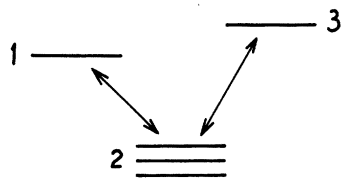

FIG. 1. "Three-level" scheme for depolarizing collision studies. Levels 1 and 3 are nondegenerate. Level 2 has three substates which, though separately indicated in the figure, are assumed to be energy degenerate.

sideration and the specific interatomic potential.

It should be noted that collisional depolarization studies are not new. Optical pumping techniques have been used to investigate depolarizing collisions between optically oriented excited state atoms and ground-state perturbers.[4] However the general nature of such optical pumping work (broadband sources, total cross-section measurements) does not lead to results that are overly sensitive to velocity-changing effects. Recent laser saturation experiments[5] based on schemes similar to that shown in Fig. 1 provide a more sensitive measure of such effects.

In attempting to analyze the scattering process for an atom in a linear superposition of magnetic substates one is naturally led to examine the applicability of the classical pictures shown in Fig. 2. The first drawing represents the single-trajectory limit. The dependence of the deflection on internal state is negligible so that the internal and the translational motions are decoupled. The second scheme depicts the situation where a diagonal representation has been found. Then each sublevel obeys the rules of elastic scattering along a substate-labeled trajectory. When none of these extreme situations holds, is a classical picture still possible? Answering this question would help to complete the blanks in the third drawing of Fig. 2. It should be noticed that the existence of a classical picture is questionable since depolarizing collisions imply a coupling between the internal motion, which is highly quantumlike due to the smallness of the electronic angular momentum, and the translational motion which can be quasiclassical.[6] We shall discuss applicability of the various limits and approximations in terms of standard treatments of collision problems.

In Sec. II various methods available for treating inelastic scattering, when the de Broglie wavelength of the colliding particle is much smaller than the characteristic dimension of the interaction region, are reviewed. In Sec. III exact equations for the scattering amplitudes are obtained

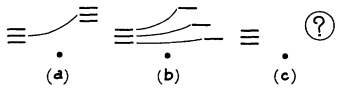

FIG. 2. Schematic representation of atomic trajectories during a depolarizing collision. In (a) an atom in a superposition state is scattered along a trajectory common to the three substates which are mixed by the collision. In (b) a distinct trajectory is associated with each substate and no transition between substates is induced by the collision. In (c) the single-trajectory approximation is not valid and transitions are induced between substates: What trajectory does the atom follow?

and those expressions are evaluated in the various semiclassical limits discussed in Sec. II. In Sec. IV we return to the problem encountered in laser spectroscopy and examine the semiclassical limit of the transport equation for atomic multipoles of a degenerate level. A summary is given in Sec. V.

II. APPROXIMATIONS IN INELASTIC SCATTERING THEORY

A few years ago, the development of research in the fields of collisional rotational and vibrational excitation of molecules,[7,8] and of electronic excitation and charge transfer in atoms[9] stimulated efforts for obtaining a semiclassical description of inelastic collisions,[10-16] which should be, by far, more tractable than a purely quantum approach. Since certain procedures in these theories are similar to those encountered in obtaining semiclassical limits of elastic scattering, it is useful to recall that two semiclassical approximation schemes[17] may be used to calculate the elastic scattering amplitude,

$$f(\theta)=\frac{1}{2iK}\sum_l (2l+1)(e^{2i\eta_l}-1)P_l(\cos\theta) \qquad (1)$$

(where K is the magnitude of the atomic wave vector and η_l is the phase shift of the l-labeled partial wave).

(i) The first method is the semiclassical phase shift approximation, which is valid when the de Broglie wavelength λ is much smaller than the distance of closest approach r_c. In this form of the JWKB approximation, each η_l is calculated along a classical path which is characterized by the initial velocity and the impact parameter $(l+\frac{1}{2})/K$. Although the η_l are calculated along classical trajectories, the classical correspondence between scattering angle θ and impact parameter is lost in Eq. (1) since a large range of l values contribute to scattering at angle θ.

(ii) The second method, valid under the more stringent condition $\sqrt{\lambda} \ll \sqrt{r_c}$, is the classical trajectory limit. The condition $\sqrt{\lambda} \ll \sqrt{r_c}$ permits one to retain in Eq. (1) only those l values such that the impact parameter $(l+\frac{1}{2})/K$ corresponds to classical scattering at angle θ.

A number of papers have explored the conditions for generalizing the JWKB approximation to inelastic processes[13-15] using an approach which was initiated by Kemble.[18] They have concluded that such an extension is possible only when the atomic translational motion is nearly independent of the internal states. In the case when the additional condition $\sqrt{\lambda} \ll \sqrt{r_c}$ is fulfilled, the JWKB

extension is thus possible only when atoms follow the same common spatial trajectory in any of the coupled internal states as in Fig. 1(a). A completely different approach has been developed under the name of classical S-matrix theory by Miller and Marcus.[10,11] They treat the internal degrees of freedom quasiclassically, retaining only the interference properties of quantum mechanics, since they calculate scattering amplitudes. In these papers there is no apparent condition of common trajectory. A special mention must be made to the work of Pechukas[16] which bypasses the common trajectory condition at the expense of complications with a noncausal interaction.

In light of these general methods let us examine the depolarizing collision problem. A ground-state spinless particle, the perturber, collides with an atom having internal angular momentum $\vec{j}$. The magnitude of $\vec{j}$ is on the order of a few $\hbar$ and is supposed to be much smaller than that of the translational angular momentum. Since the collision is assumed to result only in a change of direction of $\vec{j}$, the other numbers which characterize the internal state of the active atom are implicit. The effective interatomic potential is a function of the internuclear distance $\vec{r}$ and of the angle $(\vec{r},\vec{j})$.

A classical S-matrix method[10,11] seems very tempting for solving the problem formulated in this manner. With this approach, for given initial and final values for the variables describing the system (internal and interparticle angular momenta, energy), one calculates S-matrix elements classically along the trajectory connecting these initial- and final-state values. A phase $\varphi_c = \int \vec{p}\cdot d\vec{r}/\hbar$ evaluated along each trajectory enables one to account for any quantum interference effect arising from contribution of several trajectories to a given S-matrix element. The classical S matrix has the advantage of eliminating the discussion about common trajectory for the various magnetic substates since it is only the initial- and final-state variables that determine the scattering process. However, the solution of the problem in the frame of classical mechanics is rather difficult: the couple of colliding particles in the center-of-mass system has 8 degrees of freedom and after taking account of the conservation of $|\vec{j}|$, of the total angular momentum J, of total energy E, one is left with three differential equations, two of which are coupled. In general these equations must be solved numerically.

If instead, we adopt a quantum-mechanical formulation of the problem, certain simplifications are possible. Since the interatomic potential depends only on the quantum variable $\vec{r}$ and on the operator $\hat{\vec{j}}\cdot\hat{\vec{r}}$, one immediately notes that, if the "instantaneous" axis of quantization is taken along $\vec{r}$, then the Hamiltonian is a function of $\vec{r}$ and $\hat{j}_z$ and commutes with $\hat{j}_z$ (recall that $[\hat{\vec{r}},\hat{\vec{j}}]=0$ since $\vec{r}$ is the interatomic separation and $\hat{\vec{j}}$ acts in the active-atom subspace). Thus using this basis, known as the helicity representation after Jacob and Wick,[19] one concludes that the various magnetic sublevels in this representation are coupled only by the rotation of the internuclear axis during a collision. Two limiting cases may be envisioned:

(i) If the various instantaneous magnetic substates experience approximatively the same collisional interaction (the explicit condition is prescribed in the next section), then the notion of a common classical trajectory may be valid. The coupling between magnetic substates induced by the rotation of the internuclear axis can be significant in this case since the "instantaneous" eigenfrequencies differ by less than the inverse duration of a collision (i.e., the helicity representation is *not* an adiabatic one in this limit). The coupling and scattering of the levels can be calculated using a semiclassical phase-shift approach. One expects that the limit of nearly equal collisional interaction for the different substates is achieved for collisions with large impact parameters.

(ii) In the other extreme, one can imagine that the helicity representation is an adiabatic one. The various magnetic sublevels experience significantly different collisional interactions and are scattered independently according to the equations of classical scattering theory. Normally, one requires small internuclear separations to achieve this adiabatic limit.[20]

It is the classical trajectory limit of these two extreme situations which is illustrated in Figs. 2(a) and 2(b). One might expect that the range of validity of the semiclassical picture could be extended by combining these two approximations. For example, in a given collision, limits (i) and (ii) could be used for large and small internuclear separations, respectively. The precise conditions of validity of these different situations are examined in the next section.

III. CALCULATION OF THE SCATTERING AMPLITUDE

The calculation is performed using the helicity representation which has been defined in the preceding section. During a collision, the z component of the internal angular momentum changes from an initial value $\hbar M$ relative to a quantization axis directed *opposite* to the initial velocity (i.e., in the direction of the interparticle separation

$\vec{r}$) to a final value $\hbar M'$ relative to a quantization axis which is taken along the final direction $\theta\varphi$. The scattering amplitude takes the closed form[17]

$$f^{\rm hel}_{MM'}(\theta,\varphi)=\frac{(-1)^{M-M'}}{2iK}\sum_J(2J+1)(S^J_{MM'}-\delta_{MM'})\times\mathfrak{D}^{J*}_{MM'}(\varphi,\theta,0), \tag{2}$$

where $S^J_{MM'}$ is an S-matrix element and $\mathfrak{D}^J_{MM'}(\varphi,\theta,0)$ is the rotation matrix of rank J. The internal angular momentum $\vec{j}$ and the relative orbital angular momentum $\vec{l}$ have been coupled into the total angular momentum $\vec{J}$ and the summation is over all allowed values of $\vec{J}=\vec{l}+\vec{j}$. The S-matrix elements can be obtained in terms of the asymptotic form of the radial wave functions $\psi^{JJ}_M(r)$ as (see Appendix A)[21]

$$\lim_{r\to\infty}\psi^{JJ}_M(r)=-\frac{2J+1}{2iK}(-1)^{M'-M+j+J}\times[\delta_{-M'M}e^{-iKr}-(-1)^{j+J}S^J_{M'M}e^{iKr}]. \tag{3}$$

This boundary condition selects appropriate solutions of the radial equation

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}-\frac{\hbar^2K^2}{2\mu}+\langle M|V|M\rangle\right)\psi^{JJ}_M(r)=-\sum_{M'\neq M}\langle M|V|M'\rangle\psi^{JJ}_{M'}(r), \tag{4}$$

which is derived from the Schrödinger equation (see Appendix A). In this equation, μ is the reduced mass, and

$$\langle M|V|M'\rangle=\left(V_M(r)+\frac{J(J+1)}{2\mu r^2}\hbar^2\right)\delta_{MM'}-\frac{\hbar^2}{2\mu r^2}[\lambda_+(J,M)\lambda_+(j,M)\delta_{MM'-1}-\lambda_-(j,M)\lambda_-(J,M)\delta_{MM'+1}],$$

where $V_M(r)$ is the interatomic potential in substate M and

$$\lambda_\pm(J,M')=[J(J+1)-M'(M'\pm1)]^{1/2}.$$

In the absence of coupling between the channels, Eq. (4) reduces to

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}-\frac{\hbar^2K^2}{2\mu}+V_M(r)+\frac{J(J+1)}{2\mu r^2}\hbar^2\right)\psi^{JJ}_M(r)=0. \tag{5}$$

The general solution of this equation in the JWKB approximation is a linear combination of functions $e^{\pm iQ_{JM}}/\mathcal{P}^{1/2}_{JM}$ where

$$\mathcal{P}_{JM}=\left(\hbar^2K^2-\frac{J(J+1)}{r^2}\hbar^2-2\mu V_M(r)\right)^{1/2},\qquad Q_{JM}=\int_{r_1}^{r}\frac{\mathcal{P}_{JM}(r')}{\hbar}dr'. \tag{6}$$

This suggests that one tries solutions to Eq. (4) of the form

$$\psi^{Jj}_M(r)=b^+_{JM}(r)\frac{e^{iQ_{JM}}}{\mathcal{P}^{1/2}_{JM}}+b^-_{JM}(r)\frac{e^{-iQ_{JM}}}{\mathcal{P}^{1/2}_{JM}}. \tag{7}$$

The standard theory of second-order differential equations states that, in addition to the boundary conditions, a supplementary condition is needed to determine $b^\pm_{JM}(r)$.[14] We have chosen the following condition:

$$b^{+\prime}_{JM}e^{iQ_{JM}}+b^{-\prime}_{JM}e^{-iQ_{JM}}-\frac{1}{2}\frac{\mathcal{P}'_{JM}}{\mathcal{P}_{JM}}(b^+_{JM}e^{iQ_{JM}}+b^-_{JM}e^{-iQ_{JM}})=0, \tag{8}$$

which transforms Eq. (4) into the set of first-order differential equations

$$b^{\pm\prime}_{JM}(r)=\frac{\mathcal{P}'_{JM}}{2\mathcal{P}_{JM}}b^\mp_{JM}e^{\mp2iQ_{JM}}\pm\frac{\hbar X^+_{JM}}{2i(\mathcal{P}_{JM}\mathcal{P}_{JM+1})^{1/2}}(b^+_{JM+1}e^{i(Q_{JM+1}\mp Q_{JM})}+b^-_{JM+1}e^{-i(Q_{JM+1}\pm Q_{JM})})\pm\frac{\hbar X^-_{JM}}{2i(\mathcal{P}_{JM}\mathcal{P}_{JM-1})^{1/2}}(b^+_{JM-1}e^{i(Q_{JM-1}\mp Q_{JM})}+b^-_{JM-1}e^{-i(Q_{JM-1}\pm Q_{JM})}), \tag{9}$$

where

$$X^\pm_{JM}=\lambda_\pm(J,M)\lambda_\pm(j,M)/r^2 \tag{10}$$

and a prime indicates d/dr. Except within a distance of a few χ from the turning points where $\mathcal{P}_{JM}$ is close to zero, these "exact" equations may be simplified by using the conditions that we have imposed at the beginning. From $\chi\ll r_c$, it follows that $\mathcal{P}'_{JM}\ll\mathcal{P}^2_{JM}/\hbar$ and since $j\ll J$, it follows that $\hbar X_{JM}/2(\mathcal{P}_{JM}\mathcal{P}_{JM\pm1})^{1/2}\ll\mathcal{P}_{JM}/\hbar$. Using these two inequalities one may neglect the terms having rapidly varying phase factors in Eq. (9) and obtain

$$b^{\pm\prime}_{JM}=\sum_{M'}A^\pm_{MM'}b^\pm_{JM'}, \tag{11}$$

where

$$A^\pm_{MM'}=\pm\frac{\hbar}{2i(\mathcal{P}_{JM}\mathcal{P}_{JM'})^{1/2}}(X^+_{JM}\delta_{M'M+1}+X^-_{JM}\delta_{M'M-1})e^{\pm i(Q_{JM'}-Q_{JM})}.$$

Thus, the inward wave (represented by b^-_{JM}) is decoupled from the outward wave (represented by b^+_{JM}). This is the essence of the semiclassical ap-

proximation and can be considered as an expression of microscopic causality. However, the semiclassical approximation requires, in addition, that a connection can be made between inward and outward waves at the classical turning point. This is accomplished provided one of the two following conditions is fulfilled[14]:

(i) $|\mathcal{P}_{JM}-\mathcal{P}_{JM\pm1}|\ll\mathcal{P}_{JM}+\mathcal{P}_{JM\pm1}$. This condition permits one to define a turning point, which is common to all the channels. When in addition $\sqrt{K}\ll\sqrt{r_c}$, a common trajectory is available.

(ii) $|\mathcal{P}_{JM}-\mathcal{P}_{JM\pm1}|\gg X^{\pm}_{JM}\hbar^2/2(\mathcal{P}_{JM}\mathcal{P}_{JM\pm1})^{1/2}$. In this case the $A_{MM'}$ in Eq. (11) are very rapidly varying functions of r. Thus the substates are not significantly mixed by collisions and the $b^{\pm}_{JM}$ are approximately constant. This decoupling corresponds to the adiabatic approximation.

These explicit requirements for a semiclassical description, correspond, as expected, to the limiting situations that we have evoked in the previous section. In terms of the potential difference between the internal states, the above conditions are, respectively, transformed into

$$|V_M(r)-V_{M\pm1}(r)|\ll(\mathcal{P}_{JM}+\mathcal{P}_{JM\pm1})^2/2\mu=E_1\,, \tag{12a}$$

$$|V_M(r)-V_{M\pm1}(r)|\gg X^{\pm}_{JM}\frac{\hbar^2}{4\mu}\frac{\mathcal{P}_{JM}+\mathcal{P}_{JM\pm1}}{(\mathcal{P}_{JM}\mathcal{P}_{JM\pm1})^{1/2}}=E_2\,. \tag{12b}$$

Condition (12a) requires that the difference between the scattering potentials for different magnetic substates be small enough to allow for a "single-trajectory" approach to the problem while condition (12b) requires that the potentials *differ* enough so that the collision is adiabatic with regard to the helicity eigenstates. Except in the vicinity of a classical turning point, E_1 is of the order of thermal energy and is much larger than E_2 which is of the order of $\hbar^2K/\mu r$. Therefore, throughout the classically accessible region, at least one of the inequalities (12) is satisfied by any potential difference. This guarantees the general validity of a semiclassical description of depolarizing collisions.

As an illustration, we consider a simple potential such that $|V_M(r)-V_{M\pm1}(r)|$ is a monotonic, decreasing function of r. Thus if r_0 is a distance such that $E_2\ll|V_M(r_0)-V_{M\pm1}(r_0)|\ll E_1$, the conditions (12a) and (12b) are fulfilled, respectively, when $r>r_0$ and $r<r_0$. This situation is represented in Fig. 3 which exhibits the overlap of the adiabatic and single-trajectory regions. In this situation one may transform Eq. (11) in order to examine the classical motion character of the problem. We define a set of classical trajectories using a time parameter t. The radial coordinate $r_{JM}(t)$ satisfies the equations

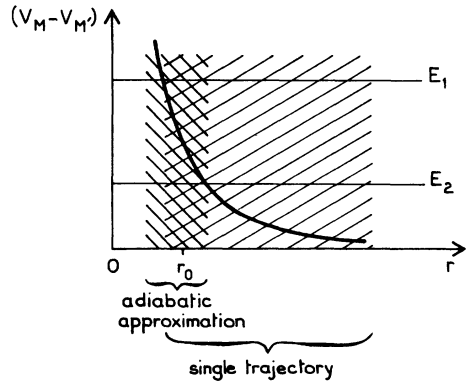

FIG. 3. The spatial domains for adiabatic and single-trajectory approximations are represented in the case of continuously decreasing $|V_M(r)-V_{M'}(r)|$. At r_0 both approximations are valid.

$$\frac{dr_{JM}}{dt}=\begin{cases}-v_{JM}(r_{JM}(t)) & \text{when } t<0\,,\\ v_{JM}(r_{JM}(t)) & \text{when } t>0\,,\end{cases} \tag{13}$$
$$r_{JM}(0)=r^{(TP)}_{JM}\,,$$

where the radial speed $v_{JM}(r)$ is

$$v_{JM}(r)=\begin{cases}\mathcal{P}_{JM}(r)/\mu & \text{when } r<r_0\,,\\ v_J(r)=\langle\mathcal{P}_{JM'}(r)\rangle_{M'}/\mu & \text{when } r>r_0\,,\end{cases} \tag{14}$$

and $r^{(TP)}_{JM}$ is the coordinate of the classical turning point in channel M, with angular momentum $\vec{J}$.

Two different situations may be examined in the limits that $r^{(TP)}_{JM}$ is larger or smaller than r_0.

$r^{(TP)}_{JM}<r_0$. The incident particle first reaches the radius r_0 at a time t^-_J which is M independent assuming a common trajectory $r_J(t)$ for $-\infty<t<t^-_J$ (since this interval corresponds to $r>r_0$). In Eq. (11) we replace $b^-_{JM}(r)$ by $c_{JM}(t)$ defined by

$$c_{JM}(t)=b^-_{JM}(r_J(t))\,,\quad t<t^-_J \tag{15}$$

and find that $c_{JM}(t)$ obeys the differential equation

$$\frac{d}{dt}c_{JM}(t)=\sum_{M'}B^J_{MM'}(t)c_{JM'}(t)\,,\quad t<t^-_J \tag{16}$$

where

$$B^J_{MM'}(t)=\frac{\hbar}{2i\mu}[X^+_{JM}(r_J(t))\delta_{M'M+1}+X^-_{JM}(r_J(t))\delta_{M'M-1}]$$
$$\times\exp\frac{i}{\hbar}\int_{t^-_J}^{t}[V_M(r_J(t'))-V_{M'}(r_J(t'))]\,dt'\,,\quad t<t^-_J\,. \tag{17}$$

In arriving at Eqs. (16) and (17), we set $(\mathcal{P}_{JM}\mathcal{P}_{JM'})^{1/2}\simeq(\mathcal{P}_{JM}+\mathcal{P}_{JM'})/2\simeq\mu v_J(r)$ and evaluate the phase difference $(i/\hbar)\int_{r_0}^{r}(\mathcal{P}_{JM}-\mathcal{P}_{JM'})dr'$ to first order in $V_M-V_{M'}$.

In the region $r<r_0$, the $b^{\pm}_{JM}(r)$ are constant owing

to the adiabatic nature of the collision for $r<r_0$. There is a classical trajectory r_{JM} which may be associated with each helicity state and a corresponding classical turning point $r_{JM}^{(TP)}$. The JWKB connection formulas are used at the turning point to relate $b_{JM}^{\pm}(r)$ and one finds

$$ib_{JM}^{+}(r_{JM}^{(TP)})e^{iQ_{JM}(r_{JM}^{(TP)})}=b_{JM}^{-}(r_{JM}^{(TP)})e^{-iQ_{JM}(r_{JM}^{(TP)})}. \quad (18a)$$

Since the $b_{JM}^{\pm}(r)$ are constant for $r<r_0$, Eq. (18a) may be written

$$ib_{JM}^{+}(r_0)=b_{JM}^{-}(r_0)e^{-2iQ_{JM}(r_{JM}^{(TP)})}. \quad (18b)$$

Connection with the time-dependent $c_{JM}(t)$ amplitudes is achieved by associating

$$c_{JM}(t)=\begin{cases} b_{JM}^{-}(r_{JM}(t)), & t<\dfrac{t_J^{-}+t_{JM}^{+}}{2} \quad (19a)\\ ib_{JM}^{+}(r_{JM}(t)), & t>\dfrac{t_J^{-}+t_{JM}^{+}}{2} \quad (19b)\end{cases}$$

where t_{JM}^{+} is the M-dependent time at which a classical particle moving along the r_{JM} trajectory would exit the $r<r_0$ region. Using Eqs. (19), (18), and (6) we find

$$c_{JM}(t_{JM}^{+})=c_{JM}(t_J^{-})\exp\left(-\frac{i}{\hbar}\int_{t_J^{-}}^{t_{JM}^{+}}\frac{\mathcal{P}_{JM}^2(r_{JM}(\tau))d\tau}{\mu}\right). \quad (20)$$

Finally, for times $t>t_{JM}^{+}$, we are again in the $r>r_0$ zone. Each r_{JM} trajectory created for $r<r_0$ now continues into the $r>r_0$ region without further splitting. *Thus, each trajectory can be labeled by its M value in the $r<r_0$ region.* For $t>t_{JM}^{+}$ (i.e., $r>r_0$) there is again coupling of the $b_{JM}^{+}(r)$ along each trajectory. Defining

$$c_{JM}^{M'}(t)=ib_{JM}^{+}(r_{JM'}(t)), \quad t>t_{JM}^{+} \quad (21)$$

where $r_{JM'}(t)$ is the extension of the trajectory associated with $M=M'$ in the $r<r_0$ region, one finds that $c_{JM}^{M'}$ obeys equations analogous to (16) and (17). The final value for $b_{JM}^{+}(\infty)$ is given by a sum over all trajectories, i.e.,

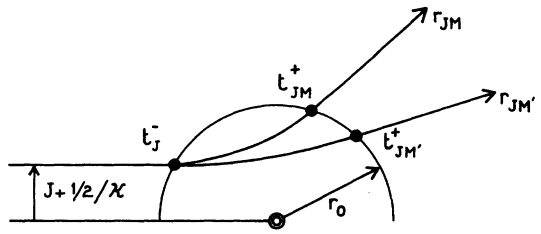

FIG. 4. An atom in a superposition state enters the interaction region with an impact parameter $(J+\frac{1}{2})/K$. From time t_J^{-} to t_{JM}^{+} or $t_{JM'}^{+}$ no transition occurs between substates and their respective trajectories may part from each other. After t_{JM}^{+} or $t_{JM'}^{+}$ a single trajectory starts from the point reached at t_{JM}^{+} or $t_{JM'}^{+}$.

$$ib_{JM}^{+}(\infty)=i\sum_{M'}b_{JM}^{+}(r_{JM'}(\infty))=\sum_{M'}c_{JM}^{M'}(\infty). \quad (22)$$

This equation can be put into a more transparent form if time evolution operators are introduced such that

$$c_{JM}(t)=\sum_{M''}U_{M''M}^{J}(t',t)c_{JM''}(t'), \quad t<t_J^{-} \quad (23a)$$

$$c_{JM}^{M'}(t)=\sum_{M''}U_{M''M}^{JM'}(t',t)c_{JM''}(t'), \quad t>t_{JM'}^{+}. \quad (23b)$$

One can combine Eqs. (22), (23), and (20) to obtain

$$ib_{JM}^{+}(\infty)=\sum_{M''M'}U_{M'M}^{JM'}(t_{JM'}^{+},\infty)\times\exp\left(\frac{i}{\hbar\mu}\int_{t_J^{-}}^{t_{JM'}^{+}}\mathcal{P}_{JM'}^2(r_{JM'}(\tau))d\tau\right)\times U_{M''M'}^{J}(-\infty,t_J^{-})b_{JM''}^{-}(-\infty). \quad (24)$$

Equation (24) may be given a simple physical interpretation (see Fig. 4). In order to calculate the contribution of the Jth partial wave to the scattering amplitude, one starts a collision at $t=-\infty$ with $b_{JM''}^{-}(-\infty)$. For $-\infty<t<t_J^{-}$, collisions mix all states along an average common trajectory and this mixing is represented by $U_{M''M'}^{J}(-\infty,t_J^{-})$. For $t_J^{-}<t<t_{JM}^{+}$, the adiabatic states are not mixed by the collisions and one evaluates elastic scattering phase shifts along each trajectory. Finally, the states are again mixed along each of the final trajectories as represented by $U_{M'M}^{JM'}(t_{JM'}^{+},\infty)$ (recall that the superscript M' labels the trajectory in the *adiabatic* region). The time-evolution operators describe the mixing and shifting of atomic substates as the atoms move along classical trajectories. The spatial coordinates have been changed from quantum-mechanical variables into time-dependent parameters. However, there subsists in Eq. (24) an exponential phase factor which attests to the quantum-mechanical character of the translational motion in the region where $r<r_0$.

To get expressions for the time-evolution operators, one may use Eqs. (23), (16), and (17) to obtain

$$\frac{d}{dt}U_{M'M}^{J}(t',t)=\sum_{M''}B_{MM''}^{J}(t)U_{M'M''}^{J}(t',t), \quad t<t_J^{-} \quad (25a)$$

$$\frac{d}{dt}U_{M'M}^{JM'}(t_{JM'}^{+},t)=\sum_{M''}B_{MM''}^{JM'}(t)U_{M'M''}^{JM'}(t_{JM'}^{+},t), \quad t>t_{JM'}^{+} \quad (25b)$$

subject to

$$U_{M'M}^{J}(t,t)=\delta_{MM'}, \quad U_{M'M''}^{JM'}(t_{JM'}^{+},t_{JM'}^{+})=\delta_{M'M''}, \quad (25c)$$

where $B^J_{MM'}$ is given by Eq. (17) and $B^{JM'}_{M''M}(t)$ is also given by Eq. (17) with $r_J(t)$ replaced by $r_{JM'}(t)$ (recall that $r_{JM''}$ indicates the trajectory associated with the M'' helicity state in the *adiabatic* region).

An expression for S-matrix elements is obtained by substituting Eq. (24) into Eq. (7) and making a comparison with Eq. (3). One finds[21]

$$S^J_{-M'M} = (-1)^j \sum_{M''} U^J_{M'M''}(-\infty, t_J^-) U^{JM''}_{M''M}(t^+_{JM''}, \infty) \times \exp(i\Delta^{JM''}_{M'M} + 2i\eta_{JM''}) , \quad (26)$$

where

$$\eta_{JM''} = \lim_{r\to\infty} \int_{r^{(TP)}_{JM''}}^{r} \frac{\mathcal{P}_{JM''}(r')}{\hbar} dr' - Kr + (J+\tfrac{1}{2})\frac{\pi}{2} \quad (27a)$$

and

$$\Delta^{JM''}_{M'M} = \frac{1}{\hbar}\int_{-\infty}^{t_J^-} [V_{M''}(r_J(\tau)) - V_M(r_J(\tau))]d\tau + \frac{1}{\hbar}\int_{t^+_{JM''}}^{\infty} [V_{M''}(r_{JM''}(\tau)) - V_M(r_{JM''}(\tau))]d\tau , \quad (27b)$$

$r^{(TP)}_{JM} > r_0$. In this case the time interval $[t_J^-, t^+_{JM}]$, during which the trajectories part from one another, collapses, so that t_J^- and t^+_{JM} may be set to 0 in Eq. (22) which reduces to

$$S^J_{-M'M} = (-1)^j U^J_{M'M}(-\infty, \infty)\exp(i\eta_{JM'} + i\eta_{JM}) , \quad (28)$$

where

$$U^J_{M'M}(-\infty, \infty) = \sum_{M''} U^J_{M'M''}(-\infty, 0) U^J_{M''M}(0, \infty) .$$

This region corresponds to weak (large impact parameter) collisions.

This is the farthest point which can be reached in the direction of a semiclassical picture under the approximation $\lambda\!\!\!^{-} \ll r_c$. As has already been noted in Sec. II, the classical trajectories which have been hitherto considered may not be regarded as actual paths since deflection in direction $\theta\varphi$, which is described by the scattering amplitude [Eq. (2)] involves contribution from all the impact parameters $(J+\frac{1}{2})/K$.

The final step of the semiclassical approximation is possible provided $\sqrt{\lambda\!\!\!^{-}} \ll \sqrt{r_c}$. It consists in using the stationary-phase method to calculate the scattering amplitude [Eq. (2)]. This calculation is performed in Appendix B. In the simplest case, that of a purely repulsive interaction, one obtains

$$f^{\text{hel}}_{-M'M}(\theta,\varphi) = \frac{(-1)^j}{K(\sin\theta)^{1/2}} \sum_{M''} (J_{\theta M''})^{1/2} U^{J_{\theta M''}M''M'}_{M'M''}(-\infty, t_J^-) U^{J_{\theta M''}M''M}_{M''M}(t^+_{JM''}, \infty)\exp(i\Delta^{J_{\theta M''}M''M'}_{M'M} + 2i\eta_{J_{\theta M''}M''}) \times \left(\frac{\partial\theta}{\partial J_{\theta M''}}\right)^{1/2} \exp\left(-\frac{i\pi}{2} - i(M'+M)\frac{\pi}{2} - iJ_{\theta M''}\theta\right)\exp(-iM\varphi) , \quad (29)$$

where $J_{\theta M''}$ is the angular momentum giving rise to scattering at $\theta\varphi$ for an atom following trajectory M'' in the adiabatic region. This result is valid provided that $\sqrt{\lambda\!\!\!^{-}} \ll \sqrt{r_0}$ and $J_{\theta M}\theta \gg 1$. The former condition allows one to use a stationary-phase method, and the latter condition implies that validity of Eq. (29) breaks down in the small-angle diffractive region.

As in elastic scattering, the major contribution in the sum over J comes from specific values of J, linking these values and the scattering direction $(\theta\varphi)$. However, Eq. (24) differs from the usual elastic scattering amplitude in the fact that for a given deflection direction $\theta\varphi$, a distinct impact parameter $(J_{\theta M''}+\frac{1}{2})/K$ is associated with each intermediate internal substate M''. For more general forms of the interaction potential, a rainbow angle may be defined and when θ is smaller than it, several values of J are generally involved in the scattering amplitude for given θ and M''.

Throughout this section mention has been made of classical trajectories. However, this notion is actually meaningful, only when collisional effects on observables are considered. Then scattering cross sections instead of scattering amplitudes are involved. The aim of the next section is to discuss the classical trajectory picture of depolarizing collisions on the observables which are accessible in laser spectroscopy.

IV. DEPOLARIZING COLLISIONS IN LASER SPECTROSCOPY

In a gas cell, the quantum-mechanical state of atoms within a small domain of position-velocity space around $(\vec{r},\vec{v})$ is most conveniently described by the density-matrix elements $\rho_{\alpha\alpha'}(\vec{r},\vec{v})$ where α and α' label internal states. We shall limit the discussion to the case where α and α' belong to the same j level since we are interested in studying the effect of depolarizing collisions. The general transport equation which determines the collisional evolution of density-matrix elements of "active atoms" immersed in a perturber bath is given by[2]

$$\frac{d}{dt}\rho^j_{\alpha\beta}\Big|_{\text{coll}} = -\sum_{\alpha'\beta'}\Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v})\rho^j_{\alpha'\beta'}(\vec{r},\vec{v},t) + \sum_{\alpha'\beta'}\int d^3v' W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}',\vec{v})\rho^j_{\alpha'\beta'}(\vec{r},\vec{v}',t), \tag{30a}$$

where

$$\Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v}) = N\int d^3v_b W_b(\vec{v}_b)\left(\frac{2\pi\hbar}{i\mu}[f_{\alpha\alpha'}(\vec{v}_r,\vec{v}_r)\delta_{\beta\beta'} - f_{\beta\beta'}(\vec{v}_r,\vec{v}_r)\delta_{\alpha\alpha'}]\right) \tag{30b}$$

and

$$W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}',\vec{v}) = N\int d^3v_r \int d^3v_{r'}\,\delta(\vec{v}'-\vec{v}-\vec{\Upsilon})W_b(\vec{v}-\vec{v}_r'+\vec{\Upsilon})\delta(v_r - v_r')v_r^{-1}f_{\alpha'\alpha}(\vec{v}_r',\vec{v}_r)f^*_{\beta'\beta}(\vec{v}_r',\vec{v}_r), \tag{30c}$$

where $\vec{v}_r$ is the relative velocity between active atom and perturber, $W_b(\vec{v}_b)$ is the perturber equilibrium velocity distribution, $\vec{\Upsilon} = (\mu/m)(\vec{v}_r' - \vec{v}_r)$, N is the perturber density, and $f_{\alpha'\alpha}(\vec{v}_r',\vec{v}_r)$ is the $\alpha',\vec{v}_r' \leftarrow \alpha,\vec{v}_r$ inelastic scattering amplitude. In our case the internal state is labeled by the magnetic number m and the relevant scattering amplitudes are $f_{mm'}(\vec{v}_r',\vec{v}_r,\hat{A})$ where m and m' are taken along a fixed quantization axis $\hat{A}$. This scattering amplitude may be expressed as a function of the scattering amplitude in the helicity representation by

$$f_{mm'}(\vec{v}_r',\vec{v}_r,\hat{A}) = \sum_{MM'}\mathfrak{D}^{J*}_{mM}(\mathfrak{R}')\mathfrak{D}^{J}_{m'M'}(\mathfrak{R})f^{\text{hel}}_{MM'}(\vec{v}_r',\vec{v}_r), \tag{31}$$

where $\mathfrak{R} = (\varphi_{v_r}, \theta_{v_r}, 0)$ and $\mathfrak{R}' = (\varphi_{v_r'}, \theta_{v_r'}, 0)$ and φ and θ are polar angles with respect to $\hat{A}$.

In traditional optical pumping experiments in which depolarizing collisions are studied,[4] neither the vapor excitation nor the signal detection is velocity selective. In these experiments, the broadband excitation creates density-matrix elements $\rho^j_{mm'}(\vec{r},\vec{v},t)$ in a state of given j and the intensity of radiation emitted (or absorbed) from these mm' substates in a given direction and with a specific polarization is monitored. With broadband excitation and detection, the signal is a function of velocity-averaged density-matrix elements

$$\rho^j_{mm'}(\vec{r},t) = \int d^3v\,\rho^j_{mm'}(\vec{r},\vec{v},t)$$

and provides some measure of the effects of depolarizing collisions in level j. Integrating Eq. (30a) over velocity we find

$$\frac{d}{dt}\rho^j_{mm'}(\vec{r},t)\Big|_{\text{coll}} = -\sum_{m''m'''}\int d\vec{v}\,\gamma^{m''m'''}_{mm'}(\vec{v})\rho^j_{m''m'''}(\vec{r},\vec{v},t), \tag{32a}$$

where

$$\gamma^{m''m'''}_{mm'} = \Gamma^{m''m'''}_{mm'}(\vec{v}) - \int d^3v' W^{m''m'''}_{mm'}(\vec{v},\vec{v}'). \tag{32b}$$

Equation (32a) does not decouple γ and ρ; however, an approximation that is often made[22] is to neglect the $\vec{v}$ dependence of the γ's. In effect, one replaces $\gamma^{m''m'''}_{mm'}(\vec{v})$ by

$$\gamma^{m''m'''}_{mm'} = \int d^3v W(\vec{v})\gamma^{m''m'''}_{mm'}(\vec{v}), \tag{33}$$

where $W(\vec{v})$ is the active atom velocity distribution. A good approximation to Eq. (32a) is then

$$\frac{d}{dt}\rho^j_{mm'}(\vec{r},t)\Big|_{\text{coll}} = -\sum_{m''m'''}\gamma^{m''m'''}_{mm'}\rho^j_{m''m'''}(\vec{r},t). \tag{34}$$

The $\gamma^{m''m'''}_{mm'}$ describe the (velocity-averaged) coupling between magnetic sublevels and, as such, reflect the nature of the collisional interaction. Thus the structure of the $\gamma^{m''m'''}_{mm'}$ can provide some insight into the collisional process. By combining Eqs. (33), (32b), (30b), and (30c) and performing some of the integrations, one may obtain[2]

$$\gamma^{m''m'''}_{mm'} = N\int d^3v_r W_r(\vec{v}_r)v_r\left(\frac{2\pi}{iK}[f_{m''m}(\vec{v}_r,\vec{v}_r)\delta_{m'm''} - f^*_{m'''m'}(\vec{v}_r,\vec{v}_r)\delta_{mm''}] - \int d\Omega_{v_r}, f_{m''m}(\vec{v}_r',\vec{v}_r)f^*_{m'''m'}(\vec{v}_r',\vec{v}_r)\right). \tag{35}$$

This expression can be written in terms of S-matrix elements if Eqs. (31) and (2) are used for the scattering amplitudes. The resulting equation can be simplified by using the relation $\mathfrak{D}^J_{MM'}(\theta,\varphi,0) = \sum_{M''}\mathfrak{D}^J_{MM''}(\mathfrak{R})\mathfrak{D}^{J*}_{M'M''}(\mathfrak{R}')$ and other elementary properties of the $\mathfrak{D}$ matrices. The integrals over $d\Omega_{v_r}$ and $d\Omega_{v_r'}$ can be carried out and, after some cancellation of terms, one is left with

$$\gamma_{mm'}^{m''m'''}=\frac{4\pi^2N}{K^2}\sum(-1)^q(2J+1)(2J'+1)(2f+1)\begin{pmatrix}j & j & f\\ m & -m' & q\end{pmatrix}\begin{pmatrix}j & j & f\\ m'' & -m''' & q\end{pmatrix}\begin{pmatrix}j & j & f\\ M & -M' & q\end{pmatrix}\begin{pmatrix}J & J' & f\\ M'' & -M''' & q\end{pmatrix}$$
$$\times\begin{pmatrix}J & J' & f\\ M'' & -M''' & q\end{pmatrix}\int dv_r W_r(v_r)v_r^3(\delta_{MM'}\delta_{M'M'''}-S_{M''M}^{J}S_{M'''M'}^{J'*}), \tag{36}$$

where the sum is over all repeated indices (except j). Equation (36) contains the selection rule $m-m''=m'-m'''$ which may also be obtained from symmetry considerations. One can verify that $\sum_m\gamma_{mm}^{m''m'''}=0$, reflecting the conservation of probability $\sum_m d\rho_{mm}(\vec{r},t)/dt\,|_{\text{coll}}=0$.

Using Eq. (26), one can write the dynamical factor appearing in Eq. (36) as

$$\delta_{M'''M'}\delta_{M''M}-S_{M'''M'}^{J'*}S_{M''M}^{J}=\delta_{M'''M'}\delta_{M''M}-\sum_{nn'}U_{-M'''n'}^{J*}(-\infty,t_J^-)U_{-M''n}^{J}(-\infty,t_J^-)U_{n'M'}^{Jn'*}(t_{Jn'}^+,+\infty)$$
$$\times U_{nM}^{Jn}(t_{Jn}^+,+\infty)\exp[-i(\Delta_{-M'''M'}^{Jn'}-\Delta_{-M''M}^{Jn})]\exp[-2i(\eta_{Jn'}-\eta_{Jn})]. \tag{37}$$

In writing Eq. (37) we have implicitly used the selection rule $|J-J'|\leq j$ which is imposed by the $3-j$ symbols appearing in Eq. (36). Since $J\gg j$, differences between J and J' can be neglected in all but phase factors. In the previous section it has been shown that the quantum-mechanical aspect of the translational motion is concentrated in the factors $\exp[-2i(\eta_{J'n'}-\eta_{Jn})]$. The other factors describe the evolution of internal substates along classical paths $r_{Jn}(t)$. Let $\hbar J_0$ be the angular momentum for which $r_{JM}^{(TP)}=r_0$. In Eq. (36), the sum over J may be regarded as a sum over the impact parameter $(J+\frac{1}{2})/K$, in analogy with the classical mechanics calculation. In the region where $J>J_0$ [or $r_0<r_{JM}^{(TP)}$] a common motion approximation is valid. Since $|J-J'|\ll J$, the phase difference in Eq. (37) can be expanded under the form

$$\eta_{J'n'}-\eta_{Jn}=\eta_{Jn'}-\eta_{Jn}+(J'-J)\frac{\partial\eta_{Jn'}}{\partial J}, \tag{38}$$

where $2\partial\eta_{Jn'}/\partial J$ can be identified as the classical deflection angle θ_J (see Appendix B). Then, following Eq. (28) one reduces Eq. (37) to

$$\delta_{M'''M'}\delta_{M''M}-S_{M'''M'}^{J'*}S_{M''M}^{J}=\delta_{M'''M'}\delta_{M''M}-U_{-M'''M'}^{J*}(-\infty,+\infty)U_{-M''M}^{J}(-\infty,+\infty)$$
$$\times\exp\frac{i}{\hbar}\int_0^\infty[V_{-M'''}(r_J(t))+V_{M'}(r_J(t))-V_{-M''}(r_J(t))-V_M(r_J(t))]dt\exp[-i(J'-J)\theta_J], \tag{39}$$

where $(\eta_{Jn}-\eta_{Jn'})$ have been expanded to lowest order in the potentials. This expression describes the substate mixing along a single trajectory $r_J(t)$.

When $J<J_0$ [or $r_0>r_{JM}^{(TP)}$], it may be verified that $|\eta_{Jn}-\eta_{J'n'}|\gg1$ and that the factor $\exp[-2i(\eta_{J'n'}-\eta_{Jn})]$ averages to zero by summation over J and J' for $|n|\neq|n'|$. A classical trajectory r_{Jn} may still be assigned to elements of the density matrix which are diagonal (in the helicity representation) on entering the region $r<r_0$ but the classical picture fails for nondiagonal elements. In other words at $r=r_0$ the magnetic substate populations ρ_{JnJn} are scattered along separate trajectories r_{Jn} but the coherence between substates is lost owing to trajectory separation. After the departure from the region $r<r_0$, substate mixing starts again along each separate trajectory. In some sense the images given in Figs. 2(a) and 2(b) are valid when the interatomic distance r is, respectively, larger or smaller than r_0. To work out this semiclassical picture, the only needed condition on the de Broglie wavelength has been

$\lambda\ll r_c$. This condition is not sufficient to regard the atoms as wave packets of dimension much smaller than the interaction distance. Thus, in analogy with JWKB calculations of scattering amplitudes, the classical trajectories that we have mentioned are not really followed by the atoms. A specific evaluation of $\gamma_{mm'}^{m''m'''}$ will be given in a future work.

Velocity selective laser spectroscopy

In velocity selective laser spectroscopy, the relevant quantity which describes collisional effects is the collision kernel $W_{mm'}^{m''m'''}(\vec{v}',\vec{v})$. Calculation of this kernel from Eqs. (30c) and (31) requires the knowledge of products of differential scattering amplitudes of the form

$$f_{M'''M'}^{*\text{hel}}(\vec{v}_r',\vec{v}_r)f_{M''M}^{\text{hel}}(\vec{v}_r',\vec{v}_r).$$

The stringent condition $\sqrt{\lambda}\ll\sqrt{r_c}$ is needed to obtain a semiclassical approximation of this quantity. We consider still the simple case of purely repulsive interaction for which a semiclassical

scattering amplitude has been calculated (Eq. 29). Since Eq. (29) is valid only if $J_{\theta M}\theta \gg 1$, a supplementary assumption is needed to take into account small-angle scattering. We suppose that the width of $\rho_{mm'}(\vec{r},\vec{v},t)$ in velocity space is much larger than the velocity change which corresponds to the deflection angle defined by $J_{\theta M}\theta = 1$. Thus, the collisional transport equation may be written

$$\left.\frac{d\rho_{mm'}}{dt}\right|_{\text{coll}} = \sum_{m''m'''} -\Gamma_{mm'}^{m''m'''}(\vec{v})\rho_{m''m'''}(\vec{r},\vec{v},t) + \sum_{m''m'''} \rho_{m''m'''}(\vec{r},\vec{v},t)\int d^3v' W_{mm'<}^{m''m'''}(\vec{v}',\vec{v}) + \sum_{m''m'''}\int d^3v' W_{mm'>}^{m''m'''}(\vec{v}',\vec{v})\rho_{m''m'''}(\vec{r},\vec{v}',t), \tag{40}$$

where $W_{mm'>}^{m''m'''}(\vec{v}',\vec{v})$ describes collisions which are such that $J_{\theta M}\theta > 1$ and $W_{mm'<}^{m''m'''}(\vec{v}',\vec{v})$ describes the remaining very small-angle collisions. The first two terms may be calculated in the same way as $\gamma_{mm'}^{m''m'''}$.

The semiclassical approximation of scattering amplitudes is needed to determine $W_{mm'>}^{m''m'''}(\vec{v}',\vec{v})$.

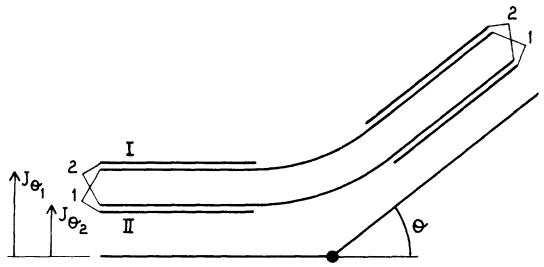

FIG. 5. The scattering of two-substate atoms at angle θ results from the contribution of two trajectories: the one which enters the $r < r_0$ region in substate 1 at impact parameter $(J_{\theta_1} + \frac{1}{2})K$ (I) and the one which enters the $r < r_0$ region in substate 2 at impact parameter $(J_{\theta_2} + \frac{1}{2})/K$ (II). Along each trajectory mixing between substates occurs for $r < r_0$. The trajectories of substate 2 in I and substate 1 in II would lead to scattering at an angle *other than* θ and are, therefore, not continued into the $r < r_0$ region.

As above, two collision regions may be distinguished depending on whether $J_{\theta M}$ is larger or smaller than J_0. When $J_{\theta M} > J_0$, a single trajectory is available and one obtains

$$f_{M'''M'}^{*\text{hel}}(\theta,\varphi) f_{M''M}^{\text{hel}}(\theta,\varphi) = \frac{J_\theta}{K^2\pi\sin\theta\left|\frac{d\theta}{dJ_\theta}\right|} U_{-M'''M'}^{J_\theta}(-\infty,+\infty)^* U_{-M''M}^{J_\theta}(-\infty,+\infty) \times \exp\frac{i\mu}{\hbar}\int_0^\infty dt[V_{-M'''}(r_{J_\theta}(t)) - V_{-M''}(r_{J_\theta}(t)) + V_{M'}(r_{J_\theta}(t)) - V_M(r_{J_\theta}(t))] \times \exp\left(-i(M''' - M'' + M - M')\frac{\pi}{2}\right) \tag{41}$$

for use in Eqs. (30c) and (31). This result contains the product of a semiclassical elastic differential scattering cross section by a factor which accounts for the MM' transitions along this trajectory.

When $J_{\theta M} > J_0$, distinct trajectories corresponding to distinct substates may contribute to scattering at $\theta\varphi$ and

$$f_{M'''M'}^{*\text{hel}}(\theta,\varphi) f_{M''M}^{\text{hel}}(\theta,\varphi) = \frac{1}{K^2\pi\sin\theta}\sum_{nn'}(J_{\theta n}J_{\theta n'})^{1/2} U_{-M'''n}^{J_{\theta n}}(-\infty,t_J^-)^* U_{-M''n'}^{J_{\theta n'}}(-\infty,t_J^-) U_{nM'}^{J_{\theta n}}(t_{Jn}^+,\infty)^* U_{n'M}^{J_{\theta n'}}(t_{Jn'}^+,\infty) \times \exp[-i(\Delta_{-M'''M'}^{J_{\theta n}n} - \Delta_{-M''M}^{J_{\theta n'}n'})]\exp\left(-i(M''' - M' - M'' + M)\frac{\pi}{2} + i(M' - M)\varphi\right) \times \left(\frac{\partial\theta}{\partial J_{\theta n}}\frac{\partial\theta}{\partial J_{\theta n'}}\right)^{-1/2}\exp[2i(\eta_{J_{\theta n'}n'} - \eta_{J_{\theta n}n}) + i(J_{\theta n} - J_{\theta n'})\theta]. \tag{42}$$

The last factor in Eq. (42) represents interference effects between diverging trajectories. Its angular dependence is given by

$$\frac{d}{d\theta}[2(\eta_{J_{\theta n'}n'} - \eta_{J_{\theta n}n}) - (J_{\theta n'} - J_{\theta n})\theta] = J_{\theta n} - J_{\theta n'}. \tag{43}$$

This angular dependence leads to oscillations of $W_{mm'>}^{m''m'''}(\vec{v}',\vec{v})$ as a function of $\vec{v}$ and $\vec{v}'$. In $\int W_{mm'>}^{m''m'''}(\vec{v}',\vec{v})\rho_{m''m'''}(\vec{v}')d^3v'$, the integral over v' averages to zero for terms with $|n| \neq |n'|$ *provided* $(\mu/m)u\,|J_{\theta n} - J_{\theta n'}|^{-1}$ is much smaller than the width of $\rho_{mm'}(\vec{v})$ in velocity space, where u is the active-atom mean speed.

The net effect of scattering in direction $\theta\varphi$ for a two-level system in this limit is shown in Fig. 5. The angular momenta $J_{\theta i}(i = 1, 2)$ correspond to scattering of an atom in state i through the

angle $\theta\varphi$. For $r > r_0$ the substates are mixed by the collisional interaction along each of the two trajectories I and II. For $r < r_0$ the two states in each of trajectories I and II are split by the collisional interaction, but only *one* trajectory in each leads to scattering at $(\theta\varphi)$. Finally, the states in a given trajectory are again mixed for $r > r_0$. The internal final state is a combination of internal states which have experienced the history shown in Fig. 5. When the above conditions are not fulfilled, no simple picture can be given. It should be noticed that the phase factor in Eq. (42) cannot be clearly separated into a "spatial phase shift" which would represent interference effects between diverging trajectories, and an "internal phase shift" which results from internal substate mixing and which is present along a common classical trajectory.

Thus, the methods used to calculate $\gamma_{mm'}^{m''m'''}$ and $W_{mm'}^{m''m'''}(\vec{v}', \vec{v})$ are perfectly consistent with the JWKB and classical trajectory approximations, respectively, that are used to calculate total and differential scattering cross sections. Assuming $\lambda \ll r_c$, the result for $\gamma_{mm'}^{m''m'''}$ can be interpreted in terms of a large number of partial waves giving rise to scattering at angle $\theta\varphi$ with *no* classical correspondence between impact parameter and scattering angle; however, the relevant phase shifts and substate coupling *are* calculated along classical trajectories (just as the η_l are calculated along classical trajectories in the JWKB evaluation of collision cross sections). Under the more stringent condition $\sqrt{\lambda} \ll \sqrt{r_c}$, the derived expression for the kernel $W_{mm'}^{m''m'''}(\vec{v}', \vec{v})$ can be interpreted as arising from collisions having the appropriate impact parameter to give rise to classical scattering at $\theta\varphi$. There may be a number of such impact parameters reflecting the different interaction potentials for the various magnetic substates.

We have not attempted to give an interpretation to $W_{mm'}^{m''m'''}(\vec{v}', \vec{v})$ under the less restrictive semiclassical condition $\lambda \ll r_c$; in this limit the large number of partial waves contributing to each scattering amplitude leads to a very complicated expression when bilinear products of the scattering amplitudes are taken to form the collision kernel. Only when *total* cross sections, such as those represented by $\gamma_{mm'}^{m''m'''}$, are evaluated does one regain a result with a simple physical interpretation.

V. SUMMARY

In view of understanding the signal formation in laser spectroscopic experiments when depolarizing collisions are present, we have developed a semiclassical theory of these collisions. First we have shown that single-trajectory approximation and adiabatic approximation can be combined to obtain a generally valid expression for the semiclassical phase shifts (provided $\chi \ll r_c$). An explicit calculation of this phase shift has been outlined in the simple case of a continuously decreasing difference of the substate dependent interatomic potentials. The conditions of validity for using a semiclassical scattering amplitude have been examined and the case of a purely repulsive interaction has been treated in some detail. Using semiclassical approximations to the scattering amplitudes, we investigated the nature of the depolarization collision kernels and rates which enter into laser spectroscopic experiments. For these two quantities a picture of the scattering, in terms of classical trajectories, has been given. In a forthcoming paper, expressions that we have obtained will be used in a numerical calculation of the corresponding signal profiles which could be observed in laser spectroscopic experiments.

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APPENDIX A: DERIVATION OF THE RADIAL EQUATION[17]

A convenient set of commuting observables in the center-of-mass frame consists of the Hamiltonian H, j^2, and the total angular-momentum operators J^2, J_z, where J_z is taken along a laboratory fixed axis of quantization Oz. The corresponding eigenfunctions are $\Psi^{Jj M_J}(\vec{r}, \vec{\rho})$ where M_J is an eigenvalue of J_z and $\vec{\rho}$ denotes the ensemble of electronic coordinates of the colliding atoms. The total Hamiltonian H is

$$H = H_0(\vec{\rho}) + \frac{P^2}{2\mu} + V(\vec{r}, \vec{\rho}),$$

where $H_0(\vec{\rho})$ is the internal Hamiltonian, $V(\vec{r}, \vec{\rho})$ is the interatomic potential, and

$$P^2 = -\hbar^2 \frac{\partial^2}{\partial r^2} + \frac{(J^2 + j^2 - 2\vec{J}\cdot\vec{j})}{r^2}\hbar^2 .$$

The Hamiltonian, without internuclear motion, is

$$H_0 = H_0(\vec{\rho}) + \frac{j^2\hbar^2}{2\mu r^2} + V(\vec{r}, \vec{\rho}).$$

Its eigenfunctions are $\varphi_{M'}^{j}(r, \vec{\rho})$ where M' is the simultaneous eigenvalue of $J_{z'}$ and $j_{z'}$ along the

rotating axis of quantization $\vec{r}$. The expansion of $\Psi^{JjM}(\vec{r},\vec{\rho})$ in terms of $\varphi^{j}_{M}(r,\vec{\rho})$, and the wave function $\psi^{Jj}_{M'}(r)$ describing the scattering is[17]

$$\Psi^{JjM_J}(\vec{r},\vec{\rho})=\frac{1}{r}\sum_{M'}\mathfrak{D}^{J*}_{M_J M'}(\mathfrak{R})\psi^{Jj}_{M'}(r)\varphi^{j}_{M'}(r,\vec{\rho}),$$

where $\mathfrak{R}$ is the rotation which brings $\vec{r}$ along Oz. We substitute this expression into the Schrödinger equation

$$\frac{\hbar^2K^2}{2\mu}\Psi^{JjM_J}(\vec{r},\vec{\rho})=H\Psi^{JjM_J}(\vec{r},\vec{\rho}),$$

where K is the magnitude of the relative motion wave vector. Projection on $\varphi^{j*}_{M}(r,\vec{\rho})$ leads to the radial equation

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}-\frac{\hbar^2}{2\mu}\bar{\pi}\frac{d}{dr}-\frac{\hbar^2K^2}{2\mu}+\langle M|V|M\rangle\right)\psi^{Jj}_{M}(r)$$

$$=-\sum_{M'\neq M}\langle M|V|M'\rangle\psi^{Jj}_{M'}(r),$$

where

$$\bar{\pi}=\int d\vec{\rho}\,\varphi^{j*}_{M}(r,\vec{\rho})\frac{\partial}{\partial r}\varphi^{j}_{M}(r,\vec{\rho}),$$

$$\langle M|V|M'\rangle=\left(V_M(r)+\frac{J(J+1)-2M^2+j(j+1)}{2\mu r^2}\hbar^2\right)\delta_{MM'}$$

$$-\frac{\hbar^2}{2\mu r^2}[\lambda_+(J,M)\lambda_+(j,M)\delta_{MM'-1}$$

$$+\lambda_-(j,M)\lambda_-(J,M)\delta_{MM'+1}],$$

$\lambda_\pm(J,M')=[J(J+1)-M'(M'\pm1)]^{1/2}$, and $V_M(r)$ is the value of the interatomic potential in substate M. In the diagonal term, the contributions which contain $\bar{\pi}$ and $j(j+1)-2M^2$ may be neglected as they are of the order of λ/r_c.

The boundary-value condition which is necessary to select the appropriate solution of the radial equation is determined by the asymptotic form of a scattered plane wave which is

$$\Psi\to e^{i\vec{K}\cdot\vec{r}}\bar{\varphi}^{j}_{M}(\vec{\rho})+\sum_{M'}\frac{e^{iKr}}{r}f^{\mathrm{hel}}_{MM'}(\theta,\varphi)\varphi^{j}_{M'}(\infty,\vec{\rho}),$$

where $\bar{\varphi}^{j}_{M}(\vec{\rho})$ is the electronic wave function assuming that the quantization axis is along $\vec{K}$, and $f^{\mathrm{hel}}_{MM'}(\theta,\varphi)$ is the scattering amplitude in the helicity representation. The connection between $\bar{\varphi}^{j}_{M}(\vec{\rho})$ and $\varphi^{j}_{M'}(\infty,\vec{\rho})$ is

$$\bar{\varphi}^{j}_{M}(\vec{\rho})=\sum_{M'}\mathfrak{D}^{j*}_{MM'}(\mathfrak{R})\varphi^{j}_{M'}(\infty,\vec{\rho}).$$

Expansion of the plane-wave function in terms of spherical harmonics leads to

$$e^{i\vec{K}\vec{r}}\bar{\varphi}^{j}_{M}(\vec{\rho})\to\frac{1}{2iKr}\sum_{\substack{lM'\\J}}(2l+1)(2J+1)(e^{iKr}-(-1)^{l}e^{-iKr})$$

$$\times\begin{pmatrix}l & j & J\\ 0 & M & -M\end{pmatrix}\begin{pmatrix}l & j & J\\ 0 & M' & -M'\end{pmatrix}$$

$$\times\mathfrak{D}^{J}_{-M-M'}(\mathfrak{R})\varphi^{j}_{M'}(\infty,\vec{\rho}).$$

Summing over l and using Eq. (2) one finally obtains

$$\Psi\to\frac{1}{2iKr}\sum_{JM'}(2J+1)[-(-1)^{J+j}\delta_{M',-M}e^{-iKr}+S^{J}_{MM'}e^{iKr}]$$

$$\times(-1)^{M-M'}\mathfrak{D}^{J*}_{MM'}(\mathfrak{R})\varphi^{j}_{M'}(\infty,\vec{\rho}).$$

Since $\Psi=\sum_{JM'}\Psi^{JjM'}(\vec{r},\vec{\rho})$, we see that the asymptotic form of the radial wave function is[21]

$$\lim_{r\to\infty}\psi^{Jj}_{M'}(r)=-\frac{2J+1}{2iK}(-1)^{M-M'+j+J}$$

$$\times[\delta_{-MM'}e^{-iKr}-(-1)^{j+J}S^{J}_{MM'}e^{iKr}].$$

APPENDIX B: STATIONARY-PHASE CALCULATION

The needed approximation for $\mathfrak{D}_{MM'}(\varphi,\theta,0)$ for large J values is given by Brussaard and Tolhoek,[23]

$$\mathfrak{D}^{J}_{MM'}(0,\theta,0)=\left(\frac{\pi}{2}\sin\theta k(\theta)\right)^{-1/2}\sin\left(\frac{\pi}{4}+M\pi+W^{J}_{MM'}(\theta)\right),\tag{B1}$$

where

$$k(\theta)=[J^2-(M^2+M'^2-2MM'\cos\theta)/\sin^2\theta]^{1/2}\tag{B2}$$

and

$$W^{J}_{MM'}(\theta)=J\cos^{-1}[(J^2\cos\theta-MM')/(J^2-M^2)^{1/2}(J^2-M'^2)^{1/2}]$$

$$-M\cos^{-1}[(M\cos\theta-M')/\sin\theta(J^2-M^2)^{1/2}]-M'\cos^{-1}[(M'\cos\theta-M)/\sin\theta(J^2-M'^2)^{1/2}].\tag{B3}$$

This approximation is valid provided $W^J_{MM'}(\theta) \gg 1$. This expression is substituted into Eq. (2). The sum of the term involving $\delta_{MM'}$ vanishes[17] and one is left with

$$f^{\rm hel}_{MM'}(\theta,\varphi) = \frac{(-1)^{M-M'}}{2iK} \sum_J (2J+1) S^J_{MM'} \mathfrak{D}^{J\,*}_{MM'}(\varphi,\theta,0), \tag{B4}$$

where $S^J_{MM'}$ is to be given by Eq. (26). The quantities $U^{JM'}_{MM'}(t,t')$ and $\exp(i\Delta^{JM''}_{M'M})$, appearing in Eq. (26) are slowly varying functions of J with respect to $\exp(2i\eta_{JM''})$. Thus, they can be taken out of the sum over J and evaluated at a point of maximum contribution to the sum. One may use the stationary-phase method to calculate

$$\int dJ \exp[2i\eta_{JM''} \pm iW^J_{MM'}(\theta)]. \tag{B5}$$

The stationary-phase condition is $d/dJ[2\eta_{JM''} \pm W^J_{MM'}(\theta)] = 0$ which leads to

$$2\frac{d\eta_{JM''}}{dJ} = \pm\cos^{-1}\left(\frac{J^2\cos\theta - MM'}{(J^2-M^2)^{1/2}(J^2-M'^2)^{1/2}}\right) \tag{B6}$$

or, when $M \ll J$,

$$2\frac{d\eta_{JM''}}{dJ} = \pm\theta + O\left(\frac{M^2}{J^2}, \frac{MM'}{J^2}, \frac{M'^2}{J^2}\right). \tag{B7}$$

The classical deflection angle Θ is defined by

$$\Theta = 2\frac{d\eta_{JM''}}{dJ}, \tag{B8}$$

where $d\eta_{JM''}/dJ$ satisfies Eq. (B7) to first order in M'/J. A set of angular momenta $J_{\Theta M''}$ may satisfy Eq. (B8). We restrict now our calculation to the single case of a purely repulsive potential. Then $\theta = \Theta$ and the semiclassical scattering amplitude may be evaluated from Eqs. (B4), (22), and (B1) using the method of stationary phase. One obtains

$$f^{\rm hel}_{-M'M}(\theta,\varphi) = \frac{1}{K(\sin\theta)^{1/2}} \sum_{M''} (J_{\Theta M''})^{1/2} \left(\frac{\partial\theta}{\partial J_{\Theta M''}}\right)^{-1/2} U^{J_{\Theta M''}}_{M'M''}(-\infty, t_J^-) U^{J_{\Theta M''}}_{M''M}(t^+_{JM''}, \infty) \exp(i\Delta^{J_{\Theta M''}M''M}_{M'M} + 2i\eta_{J_{\Theta M''}M''})$$
$$\times \exp\left(-i\frac{\pi}{2} - i(M'+M)\frac{\pi}{2} - iJ_{\Theta M'},\theta\right)\exp(-iM\varphi). \tag{B9}$$

This expression is bound to the validity of the stationary-phase approximation which requires that

$$\left|\frac{\partial^2\theta}{\partial J^2}\left(\frac{\partial\theta}{\partial J}\right)^{-3/2}\right| \ll 1. \tag{B10}$$

This condition generally reduces to $\sqrt{\chi} \ll \sqrt{r_c}$. One has to also take account of the condition of validity of the approximation used for $\mathfrak{D}^J_{MM'}(0,\theta,0)$. To first order in M/J the approximation demands that

$$|J_{M''\theta}\sin\theta| \gg 1. \tag{B11}$$

The points of stationary phase for channels M and M' are well separated provided that

$$|J_{M\theta} - J_{M'\theta}| \gg (\partial\theta/\partial J)^{-1/2}. \tag{B12}$$

The fulfillment of this condition implies that the wave packets in channels M and M' do not overlap. When condition (B12) is not fulfilled the distinct wave packets coalesce into a single one, but Eq. (B9) is still valid, since Eq. (B8) still has a single solution for a given value of M''.

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[21]We insist upon the fact that in $S^J_{M'M}$, M' is taken along $\vec{K}$ while M is measured along $\vec{r}$. Thus, in the absence of any collisional interaction, looking in the forward direction one observes a final momentum M along $\vec{r}$, which is equal to the initial momentum M' along direction $\vec{K}$. This implies that $S^J_{MM'}$ is diagonal in M. On the other hand, in the adiabatic approximation, as the internal momentum is linked to the internuclear axis, a final momentum M corresponds to the same momentum along the initial internuclear axis, i.e., to the opposite value $-M$ along direction $\vec{K}$. Thus $S^J_{MM'}$ is proportional to $\delta_{-MM'}$.
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