Spin-Exchange Scattering in Uniform Magnetic Fields*†

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The role of a uniform magnetic field in the collision of two one-electron atoms is analyzed using previously developed density-matrix techniques. During the collision, all magnetic-moment interactions are small compared to the usual singlet and triplet potentials, and the only effect of the magnetic field is to alter the asymptotic states. This effect may be described in terms of the unitary transformation which diagonalizes the Breit–Rabi Hamiltonian. The properties of this transformation are given in detail for electronic spin $\frac{1}{2}$ and arbitrary nuclear spin. In addition to presenting a general formulation for this scattering problem, explicit formulas are given for spin exchange in the scattering of polarized beams from unpolarized targets.

I. INTRODUCTION

IN theoretical treatments of spin-exchange scattering, it is customary to ignore effects of the external magnetic fields used in experiments.[1] Because all magnetic-moment interactions are negligible during such collisions, the only effect of the field is to change the character of the asymptotic states. The scattering in the presence of an external magnetic field must therefore be related by a suitable unitary transformation to that which occurs in the absence of the field. It is the purpose of this paper to exploit this simple idea to obtain an improved theory of spin exchange.[2] The starting point will be the general theory already developed by one of the present authors, which was formulated independently of the particular properties of the initial and final states of the collision.[3]

In Sec. II we show how the unitary transformation which diagonalizes the Breit-Rabi Hamiltonian for a single paramagnetic atom plays a role in the collision of two such atoms. The details of this transformation for the case of electronic spin $\frac{1}{2}$ and arbitrary nuclear spin are then given in Sec. III in a form suitable for this problem. Finally, explicit cross-section formulas are obtained in Sec. IV for the case of the scattering of a polarized beam of atoms from an unpolarized target.

II. FORMULATION OF THE SCATTERING PROBLEM

The interaction of two paramagnetic atoms may be written as

$$H=H_A(1)+H_A(2)+V(1\,2), \tag{2.1}$$

where $H_A(1)$ and $H_A(2)$ describe the free systems and V describes their interaction. We consider collisions in which V causes transitions between eigenstates of $H_A(1)+H_A(2)$. The main difference between this and earlier treatments[4–6] is that the free Hamiltonians now include the interaction energy associated with a uniform external magnetic field, i.e.,

$$H_A=K+H_{\mathrm{BR}}, \tag{2.2}$$

where K is the kinetic energy and H_{BR} is the Breit–Rabi Hamiltonian for an atom

$$H_{\mathrm{BR}}=a+bJ_3+cI_3+A\mathbf{J}\cdot\mathbf{I}. \tag{2.3}$$

Here a is the energy of the atom in the absence of the hyperfine and Zeeman interactions, $\mathbf{J}$ and $\mathbf{I}$ are electronic and nuclear spins, $b=-g_J\mu_0\mathcal{H}$ and $c=-g_I\mu_0\mathcal{H}$, with g_J and g_I electronic and nuclear gyromagnetic ratios, μ_0 the Bohr magneton, $\mathcal{H}$ the external magnetic field, and A the hyperfine coupling proportional to g_Jg_I. The interaction V is, on the other hand, the same as used heretofore,

$$V=\sum_S V_S(r_{12})\,P_S, \tag{2.4}$$

where P_S is the projection operator for states of total electronic spin S, r_{12} is the interatomic separation, and $V_S(r_{12})$ is the static potential defined in Born-Oppenheimer approximation.

The problem as stated above neglects all dynamic spin-spin interactions between the two atomic systems, and also neglects the modification of the Breit–Rabi Hamiltonian which occurs when the atoms approach one another and become distorted. The justification for these approximations is the observation that the potential V_S induced by the Coulomb interactions are much larger than the neglected interactions over extended regions of space.[7] It should be pointed out, moreover, that the neglect of these effects, and the resulting assumption that V has the form (2.4), does not represent an essential change in the previous formulations of the scattering theory for two para-

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[1] B. Bederson and K. Rubin (private communication).

[2] A related discussion of this problem has been given for electrons scattered from alkali atoms by K. Rubin, in *Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965*, edited by L. Kerwin and W. Fite (Science Bookcrafters, Hastings-on-Hudson, New York, 1965).

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[6] A. Dalgarno, Proc. Phys. Soc. (London) **A262**, 132 (1961).

[7] It is very difficult to make a quantitative estimate of such effects, but some recent work of one of the present authors is helpful in this connection: James F. Walker, New York University Technical Report N67-2, 1967 (unpublished).

magnetic atoms. The main change here is rather the extension to the case $b\neq 0$, $c\neq 0$ in (2.3).

For sufficiently large r_{12}, $H_A(1)+H_A(2)$ dominates V, and the change $\Delta H_A=bJ_3+cI_3$ induced by the magnetic field affects the character of the initial and final states. Indeed, this is the only change, since $H_{\rm BR}(1)+H_{\rm BR}(2)$ is, according to (2.3), independent of r_{12}. Furthermore, it will be shown in the following that, because of the simple form assumed for V in (2.4), it is possible to take into account this alteration in asymptotic states without recalculating any scattering amplitudes, simply by introducing a suitable unitary transformation.

We now develop the role of the unitary transformation connecting the different sets of asymptotic states for this type of scattering problem. The Hamiltonian (2.1) is written as

$$H=H_0+H_1+V, \tag{2.5}$$

$$H_0=K(1)+K(2), \tag{2.6}$$

$$H_1=H_{\rm BR}(1)+H_{\rm BR}(2). \tag{2.7}$$

We observe that $[H_1, H_0]=0$ and that $[H_1, V_S]=0$, the latter being essential to the theory, as discussed above. The scattering is described by the basic relation

$$\rho_{\rm sc}=\mathcal{G}\rho_{\rm in}\mathcal{G}^\dagger, \tag{2.8}$$

regardless of whether $H_1=0$ or not. In this relation $\rho_{\rm in}$ is the density matrix for the initial states (before collision), $\rho_{\rm sc}$ is the density matrix for the final states (after collision), and $\mathcal{G}$ is a scattering operator which depends on H_0, V, and to some extent on H_1. It is in the limit that the H_1 dependence of $\mathcal{G}$ is negligible, that a recalculation of $\mathcal{G}$ is unnecessary. If both atomic systems have spin $\frac{1}{2}$, for example, then

$$\mathcal{G}=F_d+F_x\mathfrak{o}(1)\cdot\mathfrak{o}(2), \tag{2.9}$$

where the $\mathfrak{o}$'s are Pauli operators, and F_d and F_x are related to the familiar singlet- and triplet-scattering amplitudes f_0 and f_1 by the relations

$$F_d=\tfrac{1}{4}f_0+\tfrac{3}{4}f_1, \tag{2.10a}$$

$$F_x=-\tfrac{1}{4}f_0+\tfrac{1}{4}f_1. \tag{2.10b}$$

As we will see in the following, these amplitudes f_S may be obtained by solving the Schrödinger equation with Hamiltonian $K(1)+K(2)+V_S(r_{12})$, i.e., without H_1.

We apply these ideas to the problem of expressing the cross section for a transition between states ψ_μ and $\psi_{\mu'}$ of the Hamiltonian H_0+H_1. The notation used here is that $|\phi_\mu\rangle$ and $|\psi_\mu\rangle$ are corresponding eigenstates of H_0 and H_0+H_1, respectively, i.e.,

$$H_0\,|\,\phi_\mu\rangle=\epsilon_0(\mu)\,|\,\phi_\mu\rangle, \tag{2.11}$$

$$(H_0+H_1)\,|\,\psi_\mu\rangle=\epsilon(\mu)\,|\,\psi_\mu\rangle, \tag{2.12}$$

where

$$\epsilon(\mu)=\epsilon_0(\mu)+\Delta_\mu, \tag{2.13a}$$

$$\Delta_\mu=\langle\psi_\mu\,|\,H_1\,|\,\psi_\mu\rangle. \tag{2.13b}$$

The transformation between these states is unitary:

$$U\,|\,\phi_\mu(\epsilon_0(\mu))\rangle=|\,\psi_\mu(\epsilon(\mu))\rangle, \tag{2.14}$$

$$U^\dagger U=UU^\dagger=I. \tag{2.15}$$

Note that although the unitary transformation changes the energy of the state, it leaves the kinetic energy unchanged, i.e.,

$$\langle\phi_\mu\,|\,\mathrm{H}_0\,|\,\phi_\mu\rangle=\langle\psi_\mu\,|\,H_0\,|\,\psi_\mu\rangle. \tag{2.16}$$

The cross section for the transition $\psi_\mu\to\psi_{\mu'}$ is[3]

$$\sigma(\mu\to\mu')=\mathrm{Tr}[P(\psi_{\mu'}(\epsilon))\mathcal{G}P(\psi_\mu(\epsilon))\mathcal{G}^\dagger]. \tag{2.17}$$

$P(\psi_\mu)$ is the projection operator

$$P(\psi_\mu)=|\,\psi_\mu\rangle\langle\psi_\mu\,|. \tag{2.18}$$

This projection operator is related by (2.14) to the corresponding projection operator in the $H_1=0$ basis,

$$P(\phi_\mu)=|\,\phi_\mu\rangle\langle\phi_\mu\,|, \tag{2.19}$$

by the relation

$$P(\psi_\mu(\epsilon))=UP(\phi_\mu(\epsilon-\Delta_\mu))U^\dagger. \tag{2.20}$$

This implies that (2.17) may be written

$$\sigma(\mu\to\mu')=\mathrm{Tr}[P(\phi_{\mu'}(\epsilon-\Delta_{\mu'}))\mathcal{G}'P(\phi_\mu(\epsilon-\Delta_\mu))\mathcal{G}'^\dagger], \tag{2.21}$$

where

$$\mathcal{G}'=U^\dagger\mathcal{G}U. \tag{2.22}$$

In other words, the scattering in the presence of the Hamiltonian H_1 may be considered to occur as if H_1 did not exist, but with a suitably modified scattering-amplitude operator, i.e., Eq. (2.22). This statement should be modified slightly by the observation that the energy of the final state $\phi_{\mu'}$ in the process described in Eq. (2.21) is different from the energy of the initial state ϕ_μ when $\Delta_\mu\neq\Delta_{\mu'}$. This is simply a reflection of the fact that the channels ψ_μ and $\psi_{\mu'}$ may have different kinetic energies even though their total energies are equal. Although the energy-nonconserving process (2.21) is not physically realizable, it differs very little from the actual energy-conserving scattering. This is because the energies Δ_μ are extremely small compared to the energies involved in the scattering process, and probably small compared to the energy resolution of the experiments. It is with this in mind that we say the original process is equivalent to scattering in the absence of H_1 with amplitude $\mathcal{G}'$. We can state the result (2.21) in more general terms by rewriting (2.8) as

$$\rho_{\rm sc}'=\mathcal{G}'\rho'_{\rm in}\mathcal{G}'^\dagger, \tag{2.23}$$

where

$$\rho_{\rm in}'=U^\dagger\rho_{\rm in}U, \tag{2.24a}$$

$$\rho_{\rm sc}'=U^\dagger\rho_{\rm sc}U. \tag{2.24b}$$

Because of the energy-shifting nature of U, the various spin states in the new density matrices $\rho_{\rm in}'$ and $\rho_{\rm sc}'$ will have energies which differ from one another by

small amounts. These effects may be neglected by the same reasoning as above. Therefore, in this more general case, the scattering in the presence of H_1 may still be considered to occur in the absence of H_1 with amplitude $\mathcal{G}'$ given by (2.22), and with the same distribution over μ of states $|\phi_\mu\rangle$ as exist for $|\psi_\mu\rangle$ in the original problem, i.e.,

$$\langle\phi_\mu|\rho_{\text{in}}'|\phi_{\mu'}\rangle\equiv\langle\psi_\mu|\rho_{\text{in}}|\psi_{\mu'}\rangle. \tag{2.25}$$

The same can be said for the scattered density matrix ρ_{sc}. Therefore, the result of performing an experiment with H_1 present and scattering amplitude $\mathcal{G}$ is a distribution of states $|\psi_\mu\rangle$, which is the same distribution one would obtain for the states $|\phi_\mu\rangle$ for an experiment with H_1 absent, and scattering amplitude $\mathcal{G}'$ given by (2.22).

In the presence of strong magnetic fields, the transformation U goes into the identity transformation. Therefore, the above theory relates the scattering at intermediate fields to that for strong fields.

It is also possible to diagonalize the zero-field form of H_1 simply by vector addition, which transforms the states $|IM_I, JM_J\rangle$ into states of definite F, M where

$$\mathbf{F}=\mathbf{I}+\mathbf{J}, \tag{2.26a}$$

$$M=M_I+M_J. \tag{2.26b}$$

Denoting this unitary transformation by

$$U_0\equiv U(\mathcal{H}=0), \tag{2.27}$$

the intermediate-field problem is related to the zero-field problem by the unitary transformation

$$\mathfrak{U}=UU_0{}^\dagger, \tag{2.28}$$

since

$$|\psi_\mu(\mathcal{H})\rangle=UU_0{}^\dagger|\psi_\mu(0)\rangle. \tag{2.29}$$

In order to apply this formalism to the collision of paramagnetic atoms, we have to first obtain the unitary transformation U associated with the basis change (2.14); this will be done in Sec. III. Next we must evaluate $\mathcal{G}'$ and then investigate the consequences of either (2.21) or (2.23); this will be done in Sec. IV. The determination of $\mathcal{G}'$ is especially simple; from (2.9) we find that

$$\mathcal{G}'=F_d+F_x\mathfrak{d}(1)'\cdot\mathfrak{d}(2)', \tag{2.30}$$

where

$$\mathfrak{d}(1)'=U(1)^\dagger\mathfrak{d}(1)U(1), \tag{2.31a}$$

$$\mathfrak{d}(2)'=U^\dagger(2)\mathfrak{d}(2)U(2), \tag{2.31b}$$

and

$$U=U(1)\otimes U(2). \tag{2.32}$$

The relation (2.32) is implied by the additivity property of H_0 and H_1. The fact, that F_d and F_x for the actual scattering amplitude $\mathcal{G}$ are the same as for $\mathcal{G}'$, is a result of the neglect of spin-dependent interactions—implied, as previously stated, by the choice (2.4) for V. It must be qualified by a statement similar to that made following (2.22), to the effect that energy shifts of the order of Δ_μ are negligible for the processes considered.

III. UNITARY TRANSFORMATION FOR THE BREIT-RABI HAMILTONIAN FOR $J=\frac{1}{2}$

In this section we discuss the unitary transformation which diagonalizes the Breit–Rabi Hamiltonian for the case $J=\frac{1}{2}$ and comment briefly on the situation for $J>\frac{1}{2}$. Breit and Rabi[8] obtained the eigenvalues of (2.3) in 1931; the expansion coefficients for the eigenvectors in terms of the uncoupled-spins basis were given by Torrey in 1938.[9] Our main objective here is to reformulate their results in a form suitable for application to the scattering problem discussed in the previous section.

The basis for uncoupled spins $\mathbf{J}$ and $\mathbf{I}$ is labeled by the eigenvalues M_J and M_I. Because $[H_{\text{BR}}, J_3+I_3]=0$, $M=M_J+M_I$ is a good quantum number, and H_{BR} is reducible into a direct sum

$$H=\sum_M h_{\text{BR}}(M), \tag{3.1}$$

where M ranges from $-(I+\frac{1}{2})$ to $+(I+\frac{1}{2})$. For $|M|=I+\frac{1}{2}$, h_{BR} is one dimensional and already diagonal; for $|M|\leq I-\frac{1}{2}$, h_{BR} is two dimensional:

$$h_{\text{BR}}(M)=\begin{pmatrix}\alpha(M) & \gamma(M)\\ \gamma(M) & \beta(M)\end{pmatrix}, \tag{3.2}$$

with

$$\alpha=a+\tfrac{1}{2}b+(M-\tfrac{1}{2})c+\tfrac{1}{2}(M-\tfrac{1}{2})A, \tag{3.3a}$$

$$\beta=a-\tfrac{1}{2}b+(M+\tfrac{1}{2})c-\tfrac{1}{2}(M+\tfrac{1}{2})A, \tag{3.3b}$$

$$\gamma=\tfrac{1}{2}A[(I+\tfrac{1}{2})^2-M^2]^{1/2}. \tag{3.3c}$$

Any 2×2 matrix can be expanded in terms of the identity matrix and standard Pauli matrices $\mathfrak{d}_P=(\sigma_P{}^{(1)}, \sigma_P{}^{(2)}, \sigma_P{}^{(3)})$. Therefore, h_{BR} may be written as

$$h_{\text{BR}}=[TI+p(\sigma_P{}^{(1)}\sin s+\sigma_P{}^{(3)}\cos s)], \tag{3.4}$$

where

$$T\equiv\tfrac{1}{2}(\alpha+\beta)=a-\tfrac{1}{4}A+Mc, \tag{3.5a}$$

$$p=(A/|A|)[(\alpha-\beta)^2/4+\gamma^2]^{1/2}$$
$$=\tfrac{1}{2}(I+\tfrac{1}{2})A[1+2Mx/(I+\tfrac{1}{2})+x^2]^{1/2}, \tag{3.5b}$$

$$x\equiv(b-c)A/(I+\tfrac{1}{2}), \tag{3.6}$$

$$\tan s=\gamma/\tfrac{1}{2}(\alpha-\beta)=[(I+\tfrac{1}{2})^2-M^2]^{1/2}/[M+x(I+\tfrac{1}{2})]. \tag{3.7a}$$

$$\tan s=\sin s_0/(\cos s_0+x), \tag{3.7b}$$

$$\cos s_0\equiv M/(I+\tfrac{1}{2}), \qquad 0\leq s_0\leq\pi. \tag{3.7c}$$

The subscript P has been introduced in order to distinguish $\mathfrak{d}_P$ from the Pauli operator for the electronic spin in this case ($J=\frac{1}{2}$), $\mathfrak{d}=2\mathbf{J}$. It may be noted, in this connection, that $\mathfrak{d}$ has matrix elements between states of different $M=M_J+M_I$, whereas $\mathfrak{d}_P$ in (3.4) does not. The subscript zero in (3.7) indicates the

[8] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).
[9] H. C. Torrey, Phys. Rev. **53**, 384 (1938).

case $\mathcal{H}=0$. The parameters T, p, and s appearing in (3.4) are determined by the physical parameters M, $\mathcal{H}$, and A, which have all been suppressed above.

From (3.4) we see that $h_{\rm BR}$ may be diagonalized by a particular rotation of the coordinate axis in the three-dimensional space associated with the components $\sigma_P^{(1)}$, $\sigma_P^{(2)}$, $\sigma_P^{(3)}$; this is a rotation about the 2 axis through an angle s:

$$\sigma_P'^{(3)}=\sigma_P^{(3)}\cos s+\sigma_P^{(1)}\sin s, \tag{3.8a}$$

$$\sigma_P'^{(1)}=-\sigma_P^{(3)}\sin s+\sigma_P^{(1)}\cos s, \tag{3.8b}$$

$$\sigma_P'^{(2)}=\sigma_P^{(2)}. \tag{3.8c}$$

The eigenvalues of $h_{\rm BR}$ are obviously $T\pm p$, and this yields the famous Breit–Rabi formula when (3.5) is used for T and p. More important here is the corresponding unitary transformation[10]

$$u(s)=\begin{pmatrix}\cos\frac{1}{2}s & -\sin\frac{1}{2}s\\ \sin\frac{1}{2}s & \cos\frac{1}{2}s\end{pmatrix}, \tag{3.9}$$

with the property $u^\dagger\sigma_P'^{(3)}u=\sigma_P^{(3)}$. Of course, $u(s)$ is the Wigner rotation matrix $d^{1/2}(s)=D^{1/2}(0,s,0)$ for spin-$\frac{1}{2}$.[11] To diagonalize the complete Breit–Rabi Hamiltonian (3.1), the direct product must be used:

$$U(\mathcal{H})=\prod_M u(M,\mathcal{H}). \tag{3.10}$$

For $|M|=I+\frac{1}{2}$, u is the one-dimensional identity; for $|M|\leq I-\frac{1}{2}$, u is given by (3.9), which describes the rotation of a pseudospin about the 2 axis through the angle $s(M,\mathcal{H})$. A physical interpretation may be given to the angle s by calculation of the expectation value of the real-spin vector in an eigenstate of $h_{\rm BR}(M)$:

$$\langle\mathfrak{s}\rangle=\pm\cos s(M,\mathcal{H})\hat{e}_3, \tag{3.11}$$

where the $\pm$ sign refers to the two eigenvalues in the Breit–Rabi formula.

In the particular case $\mathcal{H}=0$, the unitary transformation (3.10) must reduce to that familiar from the vector addition of two angular momenta. Indeed, the phases in (3.9) have been selected to be in accord with the Clebsch-Gordan coefficients of Ref. 11. The pseudospin rotation angles appropriate to zero field $s_0(M)\equiv s(M,0)$ are given by (3.7c), and are independent of the hyperfine-coupling parameter A. As discussed in Sec. II, the unitary transformation from "weak" fields ($A\neq 0$, $\mathcal{H}=0$) to arbitrary fields ($A\neq 0$, $\mathcal{H}\neq 0$) is $U(\mathcal{H})U^\dagger(0)$. Applying the results of this section, this transformation may be written

$$U(\mathcal{H})U^\dagger(0)=\prod_M u(s(M,\mathcal{H})-s(M,0)), \tag{3.12}$$

in the notation of (3.9).

[10] The rows and columns of u will be labeled by the integers $\nu,\nu'=\pm 1$: $u_{\nu\nu'}$, in such a way that u_{11} is the upper left element in (3.9).

[11] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 71.

It would probably not prove fruitful to attempt to extend this simple description of the unitary transformation to electronic spin $J>\frac{1}{2}$. For the case $J=\frac{1}{2}$ one depends essentially on the connection between the three-dimensional rotation group and the two-dimensional unitary group, i.e., on the equivalence of (3.8) and (3.9). For $J>\frac{1}{2}$ this correspondence no longer holds, and it becomes necessary to diagonalize matrices with dimension as large as $(2J+1)$. More generally, $h_{\rm BR}(M)$ is a matrix of order $g(M)$, where

$$\begin{aligned} g(M)&=2J+1 && \text{for } |M|\leq I-J\\ &=2J+1-[|M|-(I-J)] && \text{for } |M|>I-J\end{aligned} \tag{3.13}$$

for $I\geq J$. For $|M|=I+J-1$ one may still follow the spin-$\frac{1}{2}$ approach, since $g=2$ in this case for arbitrary J and I.

IV. CROSS SECTIONS FOR SPIN EXCHANGE

The cross section for any collision between paramagnetic atoms may now be calculated since the unitary transformation required to obtain the scattering-amplitude operator $\mathcal{G}'$ of (2.30) is available in (3.10). In particular, the transformed Pauli spin operators (2.31) are given by

$$\langle\nu'M'|\sigma_3'|\nu M\rangle=\delta_{M'M}\sum_{\nu''}u^\dagger(M)_{\nu'\nu''}\nu''u(M)_{\nu''\nu}, \tag{4.1a}$$

and

$$\langle\nu'M'|(\sigma_1'+i\sigma_2')/\sqrt{2}|\nu M\rangle =\sqrt{2}\delta_{M',M+1}\sum_{\nu''}u^\dagger(M+1)_{\nu',\nu''+2}u(M)_{\nu'',\nu}, \tag{4.1b}$$

where $u(M)_{\nu\nu'}$ is the matrix given in (3.9) for $\nu,\nu'=\pm 1$, and zero otherwise. The representation used in (4.1) and throughout the remainder of this section is that appropriate to two uncoupled spins, i.e., $|\nu M\rangle$ is the eigenfunction of J_3 and I_3 with eigenvalues $\frac{1}{2}\nu$ and $M-\frac{1}{2}\nu$, respectively.[12]

[12] The quantum numbers ν and M may still be used when the spins interact according to the Breit–Rabi Hamiltonian because the eigenvalues of (2.3) are continuous functions of the parameters A and $\mathcal{H}$. Although M retains its meaning as the eigenvalue of J_3+I_3, ν will generally distinguish the two signs of the radical in the Breit–Rabi formula, i.e.,

$$E_{\rm BR}(M)=T(M)+\nu p(M), \qquad (\nu=\pm 1,\ |M|\neq I+\tfrac{1}{2})$$

in the notation of (3.5). Therefore we may define a state $|\nu,M;\mathcal{H}\rangle$ for arbitrary $\mathcal{H}$, which (a) for $\mathcal{H}=0$, is an eigenfunction of $\mathbf{F}^2$ with eigenvalue given by

$$\begin{aligned} F&=I+\tfrac{1}{2}\nu, && |M|\neq I+\tfrac{1}{2}\\ &=I+\tfrac{1}{2}, && |M|=I+\tfrac{1}{2};\end{aligned}$$

(b) for $\mathcal{H}=\infty$, J_3 and I_3 are separately diagonal and $\nu=\pm 2M_J$ for $x\to\pm\infty$, i.e.,

$$\begin{aligned} |\nu,M;\mathcal{H}\rangle&\to|\nu,M\rangle, && x\to+\infty\\ &\to|-\nu,M\rangle, && x\to-\infty.\end{aligned}$$

The connection with the notation of Sec. II is that μ, for example, in (2.21), has been explicitly written as $\nu(1)$, $M(1)$, $\nu(2)$, $M(2)$.

As an illustration of this theory we consider a situation similar to that studied in Ref. 3, in which polarized atomic beams are scattered from unpolarized target atoms. For simplicity the atoms will be assumed not to be identical. Upon averaging over the initial and summing over the final target states, (2.21) becomes an equation relating the (transformed) initial and final density matrices for only the incident atoms:

$$\rho_{\rm sc}'(1) = |F_d|^2\rho_{\rm in}'(1) + |F_x|^2 \sum_{i=1}^{3} \sigma_i'(1)\rho_{\rm in}'(1)\sigma_i'(1). \tag{4.2}$$

Equivalently, the cross section for the transition $\nu M \to \nu' M'$ for the incident beam is

$$\sigma(\nu M, \nu' M') = \delta_{\nu'\nu}\delta_{M'M}|F_d|^2 + \Delta(\nu M, \nu' M')|F_x|^2, \tag{4.3}$$

where[13]

$$\Delta(\nu M, \nu' M') \equiv \sum_i {\rm Tr}[\sigma_i' P(\nu M)\sigma_i' P(\nu' M')], \tag{4.4}$$

and $P(\nu M)$ is a projection operator for the uncoupled basis. By evaluating the trace in this basis and introducing the spherical components[14] $\sigma_m'(m=1, 0, -1)$, (4.4) becomes

$$\Delta(\nu M, \nu' M') = \sum_{m=-1}^{1} |\langle \nu' M'|\sigma_m'|\nu M\rangle|^2. \tag{4.5}$$

All that remains before obtaining the final form for $\sigma(\nu M, \nu' M')$ is to substitute (4.1) into (4.5). We will omit these calculational details and only give the final result. Taking advantage of the symmetry property apparent from (4.5),

$$\Delta(\nu M, \nu' M') = \Delta(\nu' M', \nu M), \tag{4.6}$$

$$\sigma(\nu M, \nu' M') = [|F_d|^2 + \cos^2 s(M)|F_x|^2]\delta_{\nu\nu'}\delta_{MM'} + \Gamma(\nu, M; \nu', M')|F_x|^2, \tag{4.7}$$

where the dependence of s on $\mathcal{C}$ and A has been suppressed and Γ, which has no diagonal elements, is given in terms of simple trigonometric functions:

$$\Gamma(1, I+\tfrac{1}{2}; 1, I-\tfrac{1}{2}) = 2\sin^2[\tfrac{1}{2}s(I-\tfrac{1}{2})], \tag{4.8a}$$

$$\Gamma(1, I+\tfrac{1}{2}, -1, I-\tfrac{1}{2}) = 2\cos^2[\tfrac{1}{2}s(I-\tfrac{1}{2})], \tag{4.8b}$$

$$\Gamma(-1, -I-\tfrac{1}{2}; 1, -I+\tfrac{1}{2}) = 2\cos^2[\tfrac{1}{2}s(-I+\tfrac{1}{2})], \tag{4.9a}$$

$$\Gamma(-1, -I-\tfrac{1}{2}; -1, -I+\tfrac{1}{2}) = 2\sin^2[\tfrac{1}{2}s(-I+\tfrac{1}{2})], \tag{4.9b}$$

for either $|M|$ or $|M'| = I+\tfrac{1}{2}$, and

$$\Gamma(1M; -1M) = \sin^2 s(M), \tag{4.10}$$

$$\Gamma(1, M+1; 1, M) = 2\cos^2[\tfrac{1}{2}s(M+1)]\sin^2[\tfrac{1}{2}s(M)], \tag{4.11a}$$

$$\Gamma(-1, M+1; -1, M) = 2\sin^2[\tfrac{1}{2}s(M+1)]\cos^2[\tfrac{1}{2}s(M)], \tag{4.11b}$$

$$\Gamma(1, M+1; -1, M) = 2\cos^2[\tfrac{1}{2}s(M+1)]\cos^2[\tfrac{1}{2}s(M)], \tag{4.11c}$$

$$\Gamma(-1, M+1; 1, M) = 2\sin^2[\tfrac{1}{2}s(M+1)]\sin^2[\tfrac{1}{2}s(M)] \tag{4.11d}$$

for $|M| < |M'| \leq I-\tfrac{1}{2}$.

It is not difficult to verify that (4.7) reduces in the appropriate way to the previously given strong- and weak-field limits.[3] For strong fields $x=\pm\infty$, $\nu=\pm 2M_J$, and $s=0, \pi$. Then (4.7) reduces to

$$\sigma_\infty(M_J M_I, M_J' M_I') = (|F_d|^2 + |F_x|^2)\delta_{M_J M_J'}\delta_{M_I M_I'} + 2\delta_{M_I, M_I'}(\delta_{M_J', M_J-1} + \delta_{M_J', M_J+1})|F_x|^2, \tag{4.12}$$

where $\sigma_\infty(M_J M_I, M_J' M_I')$ is $\sigma(\pm\nu M, \pm\nu' M')$ for $\mathcal{C}=\infty$, $x=\pm\infty$. For weak fields, $|M| \neq I+\tfrac{1}{2}$, $F=I+\tfrac{1}{2}\nu$ and $s=s_0$; using (3.7c) for s_0 we can easily demonstrate that (4.7) is equivalent to

$$\sigma_0(FM, F'M') = \delta_{FF'}\delta_{MM'}|F_d|^2 + (I+\tfrac{1}{2})^{-1}[(F+\tfrac{1}{2})(F'+\tfrac{1}{2}) + \tfrac{1}{3}(-)^{F-F'+1}I(I+1)] \times (FM, F'-M'|1\,M-M')^2|F_x|^2, \tag{4.13}$$

where $\sigma_0(FM, F'M')$ is $\sigma(\nu M, \nu' M')$ for $\mathcal{C}=0$. Finally, the coefficient $\Delta(\nu M, \nu' M')$ of (4.3) satisfies the sum rule

$$[2(2I+1)]^{-1}\sum_{\nu M}\sum_{\nu' M'}\Delta(\nu M; \nu' M) = 3. \tag{4.14}$$

This implies that the cross section for completely unpolarized scattering (unpolarized incident beam as well as unpolarized target) is independent of all spin couplings:

$$\sigma = [2(2I+1)]^{-1}\sum_{\nu M}\sum_{\nu' M'}\sigma(\nu M, \nu' M') = |F_d|^2 + 3|F_x|^2. \tag{4.15}$$

In conclusion, we see from (4.7) that the measurement of spin-exchange cross sections in the presence of a magnetic field can not yield any additional information over that available from measurements in either weak or strong fields. Thus, if one scatters polarized beams from unpolarized targets, only $|F_d|$ and $|F_x|$ can be determined. The presence of the magnetic field does not afford an opportunity to obtain the relative

[13] Equations (4.2) and (4.3) above are the analogs of Eqs. (2.14) and (2.13) of Ref. 3. No detailed derivation of these equations is given here because the general development of Sec. II of Ref. 3 applies.

[14] M. E. Rose, Ref. 11, p. 71.

phase of F_d and F_x, for example, simply because the colliding systems have negligible interaction with the field *during* the scattering process.[15] On the other hand, the dependence on magnetic field of various cross sections, such as (4.7), can be used by experimentalists to check the consistency of measured cross sections and the assumptions of the present theory. By varying $\mathcal{H}$, the relative importance of the spin-exchange process [as compared with the $\delta_{\nu\nu'}\delta_{MM'}$ term in (4.7)] can also be changed.

[15] The "complete" determination of the scattering amplitudes at a particular angle requires measuring the scattering of polarized beams by polarized targets, since the unpolarized scattering (4.15) gives $|F_d|^2+3|F_x|^2$ and the depolarization (or spin exchange) of a polarized beam by an unpolarized target is proportional to $|F_x|^2$. For example, the scattering amplitude in the triplet spin state is, according to (2.10), $f_1=F_d+F_x$, and thus contains the interference between F_d and F_x.

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Large-Z Expansion Theory for the Ground State of a One-Electron Ion Perturbed by r^N†

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Large-Z (nuclear charge) expansion theory is applied to the nonrelativistic ground state of a one-electron ion which is perturbed by a repulsive central field potential which goes as the Nth power of the radial distance of the electron from the nucleus where N is an integer ($N=-1; N\geqq 1$). The energy-expansion parameters for these problems are determined self-consistently within the asymptotic method itself. General recursive relations for the wave-function expansion coefficients in the basic asymptotic expansion and the stretched solution are obtained. For the case of $N=1$, the wave function and the energy expansion are obtained explicitly through third order. For $N=-1$, the basic asymptotic solution is the exact solution. For r large, a few terms of the conventional large-Z perturbation-theory expansion for the $N=-1$ case give an inaccurate representation for the exact wave function. The relative error associated with first-order perturbation-theory expectation-value results is shown to increase as the operator probes the outer part of the atom to a greater extent.

I. DISCUSSION OF THE PROBLEM

In a previous paper[1] (I), the large-Z asymptotic method (Z is the nuclear charge) was applied to the many-electron atom or ion. It was pointed out that differences exist between conventional perturbation theory[2–4] and the asymptotic method. It was also suggested that the energy-expansion parameters, which were considered in I as input quantities determined either by perturbation-variation theory or from experimental data, should be determined self-consistently within the asymptotic method itself. In order to clarify some of the above ideas and to see how the asymptotic method works for a simpler more transparent problem, we have applied it to the nonrelativistic ground state of a one-electron ion of large Z which is perturbed by a repulsive central field potential which goes as s^N (s is the distance in Bohr radii of the electron from the nucleus; N is any positive integer or -1).

The Schrödinger equation for an S state of a one-electron ion with a nucleus of charge Z which is perturbed by a repulsive central field potential of the form λs^N with N an integer and λ the coupling constant, can be written in dimensionless form,

$$-\tfrac{1}{2}(d^2\psi/ds^2)-s^{-1}(d\psi/ds)-(Z/s)\psi+\lambda s^N\psi=E\psi, \quad (1)$$

where E is the energy of the system in atomic units (approximately 27.2 eV). In the limit $\lambda\to 0$, $\psi\to e^{-Zs}$, and $E\to-\frac{1}{2}Z^2$ for the ground state. In the conventional large-Z perturbation theory, we make a transformation of variables $\xi=Zs$ and Eq. (1) becomes for $\Psi(\xi)$

$$-\frac{1}{2}\frac{d^2\Psi}{d\xi^2}-\frac{1}{\xi}\frac{d\Psi}{d\xi}-\frac{\Psi}{\xi}+\left(\frac{\lambda}{Z^{N+2}}\right)\xi^N\Psi=\frac{E}{Z^2}\Psi. \quad (2)$$

Thus from the ξ form of the equation, it is observed that the natural perturbation-theory parameter for a perturbation s^N is $\epsilon=\lambda/Z^{N+2}$. Therefore we look for

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