Strong conservation of electron-spin polarization for hydrogenic ions in electric-dipole transitions: Direct transitions

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The aspect of conservation of spin polarization in electric-dipole transitions is addressed for hydrogenic ions in a nonrelativistic time-dependent perturbation theory. The results show that for direct transitions the polarization is highly conserved. The depolarizing influence of the spin-orbit interaction on the initial spin orientation is only of the order of $(\alpha Z)^2$ or less for hydrogenic ions.

I. INTRODUCTION

The availability of highly charged ions of any Z (Ref. 1) is attracting more and more interest in scrutinizing the predictions of relativistic and QED theories. So far, QED claims an unprecedented understanding of the electromagnetic interaction. Indeed, the g factor of the free electron[2] is one of the best known fundamental constants:[3] Radiative corrections account for its value to a precision of several parts in 10^{12}. In this context, some of the challenging questions are: How does the vicinity of a high charge influence the g factor of the electron, and can QED and relativistic theory account for all possible changes?

Answers to these questions could be expected from a $g-2$ experiment on an electron bound to a high charge. Such an experiment must be designed to be as simple as possible in order not to obscure the result by additional interactions. Therefore the hosting charge should be an even-even nucleus. This avoids complications from strong hyperfine structure interactions that can contribute spin-depolarizing features. Inescapable complications arise from the fact that the electron is penetrating the nucleus. Apart from these considerations, however, the essential prerequisite for this type of experiment is that the electron be prepared in the ion in a spin-polarized state. With optical-pumping techniques[4-8] not available in the x-ray range, the only way of obtaining a spin-polarized state is to prepare the electronic spin orientation externally, for instance, before the electron is transferred to the bare ion in a charge-transfer collision.

The following nonrelativistic study explores the suitability of this process with respect to the preparation of a spin-polarized final state in the ion. Its starting point is based on the facts known so far about the process of charge transfer,[9-17] which has been widely investigated for highly to totally stripped projectiles of low velocity and hydrogen atom targets. This is advantageous for our study because hydrogen atoms can be spin-polarized very effectively.[18,19]

In this article we will study only direct electric dipole transitions. In a forthcoming paper we plan to also address the matter for cascading electric-dipole transitions.

II. THEORETICAL METHOD

A. Summary of facts known about charge-transfer collisions

With electron-transfer collisions being the key point for an external preparation of spin polarization, we first compile the essential facts about this process that have been worked out during the past years, both theoretically and experimentally.[9-17] In this field it is common knowledge that electron capture from H atoms by highly charged low-energy ions populates excited states preferentially in a very n-selective way: At most, two principal quantum numbers n are significantly participating.[15] Especially important for our study are the findings about the l and m_l distributions: Due to a postcollision Stark effect by the residual-proton or, equivalently, from a molecular-compound point of view, all possible states are highly mixed in the ion[20,21] and the alignment like (Stark effect) m_l distribution shows a pronounced peak for $m_l = 0$. This has also been confirmed experimentally.[22] With the z axis being chosen to coincide with the velocity vector of the impinging projectile, the predominant population of $m_l = 0$ in a collision between H(1s) and a fully stripped projectile is in agreement with the classical model: The relative angular momentum of the particles is a constant of the motion, and thus can be defined at infinite internuclear separation by the vector product between the impact parameter $\mathbf{b}$ and the initial linear momentum $\mathbf{p}$ of the projectile, $\mathbf{L} = \mathbf{b} \times \mathbf{p}$. $\mathbf{b}$ and $\mathbf{p}$ define the collision plane to which $\mathbf{L}$ is necessarily perpendicular. Since the z axis lies in this plane, $\mathbf{L}$ is also perpendicular to z, hence $m_l = 0$.

For our purposes, however, the possible effects of the collision on the orientation of the spin of the transferred electron are of more concern. To our knowledge, there are no studies that address this problem. With an initially bare ion and $I = 0$, however, we may anticipate that there are only small or even no effects at all since the in-

teraction is purely electrostatic at the small velocities considered. The choice of our initial wave function will therefore be guided by the concept of undisturbed spin transfer and the population of appropriate sublevels $|\alpha l m_l\rangle$.

B. Choice of the initial wave function and its time-evolution under spin-orbit interaction

Following the concept of undisturbed spin transfer we postulate that our initial wave function at $t=0$ be

$$\psi_0 = \sum_{\alpha, l, m_l} B_{\alpha l m_l} |\alpha l m_l s m_s\rangle . \tag{1}$$

This is a pure spin state. The absolute squares of the amplitudes represent the initial population of the (α, l, m_l) manifolds and are proportional to the cross sections: $\sigma_{\alpha l m_l} \sim |B_{\alpha l m_l}|^2$. Alternatively, expression (1) may be transformed to the $|\alpha l s J M_J\rangle$ representation[23]

$$\psi_0 = \sum_{\alpha, l, m_l} \sum_{J, M_J} B_{\alpha l m_l} (-1)^{l-s+M_J} \sqrt{2J+1}$$

$$\times \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix} |\alpha l s J M_J\rangle . \tag{2}$$

This transformation does not change the wave function, Eq. (1), in any way, especially not its main feature, representing a pure spin state.

As soon as the electron starts orbiting about its new host, spin-orbit interaction is present. The operator of the spin-orbit interaction, however, is not diagonal in the set of wave functions $|\alpha l m_l s m_s\rangle$ that make up ψ_0 in Eq. (1), except for the wave functions that represent the largest unidirectional z components of the "stretched" state with $J = l + s$:

$$|\alpha l, +l; s, +s\rangle = |\alpha l s J = l+s, M_J = l+s\rangle$$

or

$$|\alpha l, -l; s, -s\rangle = |\alpha l s J = l+s, M_J = -(l+s)\rangle .$$

For a given spin orientation only one of these states can be realized. All other states will be mixed by spin-orbit interaction. At the same time the electron is exposed to the interaction with the electromagnetic field because it had been captured into an excited state. With no real photons present this interaction is basically provided by the statistic fluctuations of the photon vacuum which are related to the zero point energy of the modes of the electromagnetic field and which eventually trigger the "spontaneous" decay of the state.

Thus we have to investigate the simultaneous effects of spin-orbit coupling and the interaction with the photon vacuum on our wave function as the system evolves with time. We do so by using time-dependent perturbation theory in interaction representation.[24,25] As is well known, the perturbed wave function is expanded into the complete series of eigenfunctions of the unperturbed system which are independent of time in interaction representation. The expansion coefficients are assumed to be time-dependent,

$$\psi_I(\mathbf{r}, t) = \sum_n a_n(t) \psi_n(\mathbf{r}) , \tag{3a}$$

where $\psi_n(\mathbf{r})$ is the nth eigenfunction of the unperturbed Hamiltonian H^0, belonging to the eigenvalue E_n^0,

$$H^0 \psi_n(\mathbf{r}) = E_n^0 \psi_n(\mathbf{r}) , \tag{3b}$$

and where $\psi_I(\mathbf{r}, t)$ is to solve the time-dependent Schrödinger equation

$$H_I' \psi_I(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \psi_I(\mathbf{r}, t) , \tag{4a}$$

with

$$H_I' = e^{iH^0 t/\hbar} H' e^{-iH^0 t/\hbar} \tag{4b}$$

being the perturbation operator in interaction representation.

In our case the set of wave functions $|\alpha l m_l s m_s\rangle$ are the unperturbed eigenfunctions. The time-dependent amplitudes $a_n(t)$ can be determined by solving a system of linear differential equations of first order

$$i\hbar \dot{a}_m(t) = \sum_n a_n(t)\langle m|H'|n\rangle e^{-i\omega_{nm}t} . \tag{5}$$

Here H' stands for one or more small perturbation operators which cause the change of the composition of the wave function as the system evolves with time, and $\omega_{nm} = (1/\hbar)(E_n^0 - E_m^0)$. Since the summation extends over the whole spectrum of eigenvalues, it depends on the properties of H' whether or not there is a diagonal matrix element

$$i\hbar \dot{a}_m(t) = a_m(t)\langle m|H'|m\rangle$$

$$+ \sum_{n \neq m} a_n(t)\langle m|H'|n\rangle e^{-i\omega_{nm}t} . \tag{5a}$$

One of the perturbation operators we have to deal with is the spin-orbit operator of the electron that has been transferred in the charge exchange collision

$$H_1' = H^{so} = g(l \cdot s) . \tag{6}$$

Here g is the coupling strength on which we will elaborate later. The other perturbation operator describes the interaction with the electromagnetic field

$$H_2' = H^r = -\frac{e}{mc} A e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \mathbf{p} . \tag{7a}$$

Here $\boldsymbol{\epsilon}$ is the unit vector of the polarization of the emitted photon, c is the velocity of light, $e = -|e|$ is the electric charge of the electron, m its mass, $\mathbf{p}$ its vector of linear momentum, and $\mathbf{r}$ its position coordinate. $\mathbf{k}$ is the wave vector of the emitted photon and $\mathbf{A} = A\boldsymbol{\epsilon}$ is the amplitude of the transverse vector potential that may be related to the number of photons in the quantized electromagnetic field.[25]

For wavelengths of the emitted light that are much longer than a characteristic ionic diameter a, $ka \ll 1$, the expansion of the exponential in Eq. (7a) can be truncated behind the zeroth-order term. This is the electric-dipole approximation in which the ion cannot tell into which

direction but only with what polarization the photon has been emitted. Additionally we note that the operator of the electron's linear momentum $\mathbf{p}$ is the electron mass m times the time derivative of its position operator $d\mathbf{r}/dt$ and that the latter can be expressed in interaction representation by its commutator with the Hamiltonian H. Thus

$$H_I' = -i\frac{e}{\hbar c}A\boldsymbol{\epsilon}\cdot[H,\mathbf{r}_I] , \tag{7b}$$

where according to Eq. (4b)

$$\mathbf{r}_I = e^{iHt/\hbar}\mathbf{r}e^{-iHt/\hbar} . \tag{7c}$$

The operators Eqs. (6) and (7) have totally different selection rules. The most obvious difference manifests itself in Eq. (7b), where the presence of $\mathbf{r}$ makes H_I' an odd operator which cannot have any diagonal matrix element with wave functions of definite parity. We now may specify the general expression Eq. (5) for the system of linear differential equations

$$i\hbar\dot{a}_m(t) = a_m(t)\langle m|H^{so}|m\rangle$$
$$+ \sum_{n\neq m} a_n(t)\langle m|H^{so}|n\rangle e^{-i\omega_{nm}t}$$
$$+ \sum_{k\neq m} a_k(t)\langle m|H'|k\rangle e^{-i\omega_{km}t} . \tag{8}$$

As far as the simultaneous treatment of both interactions is concerned we note that their coupling strengths are very different as long as only spontaneous radiative

transitions are involved. In this case, due to the statistic character of the vacuum fluctuations, it takes on the average the radiative lifetime until the excited state decays. This time span is very long compared to the period of the orbiting electron. Therefore the spin-orbit interaction has established the appropriate composition of the wave function long before the lifetime elapses. The justification for this concept is given by the ratio of spin-orbit splitting and natural linewidth which usually amounts to many orders of magnitude. In this sense, practically no error is introduced if we do not treat both interactions simultaneously but as though they were "switched on" consecutively.

Hence we start at Eq. (8) and ignore the electromagnetic-interaction term for the time being. This will provide a wave function that is determined by spin-orbit interaction alone, and which we will take for the zeroth-order approximation when treating the influence of the electromagnetic interaction on the system. Because of later reference, this is why H instead of H^0 was tacitly entered into Eqs. (7b) and (7c). For a simultaneous treatment H must be equal to $H^0 + H_r^0$. But for the following consecutive treatment H will be set equal to H^0 in the first step and then in the second step equal to $H^0 + H^{so} + H_r^0$, where H_r^0 is the Hamiltonian of the free electromagnetic field.

The matrix elements of the spin-orbit operator are easily calculated in the $|lm_l sm_s\rangle$ representation by expressing the scalar product in spherical components and making use of the Wigner-Eckart theorem[23]

$$\langle\beta l'm_l'sm_s'|H^{so}|\alpha lm_lsm_s\rangle = \delta_{l'l}\delta_{s's}\tfrac{1}{4}\hbar^2\langle\beta l'|g|\alpha l\rangle(-)^{l+s-m_l'-m_s'}\sqrt{2l(2l+1)(2l+2)}\sqrt{2s(2s+1)(2s+2)}$$

$$\times \sum_q (-1)^q \begin{bmatrix} l & 1 & l \\ -m_l' & q & m_l \end{bmatrix} \begin{bmatrix} s & 1 & s \\ -m_s' & -q & m_s \end{bmatrix} . \tag{9}$$

As is obvious from the properties of the $3j$ symbols,[23] the sum of the z components is a constant: $m_l + m_s = m_l' + m_s'$. According to Eq. (9), the spin-orbit interaction mixes all states α and β within a term series of given l. For the case $s = \frac{1}{2}$, we obtain from the general expression Eq. (9) for the diagonal matrix element

$$H^{so}_{\alpha m,\alpha m} = \langle\alpha lm_l\tfrac{1}{2}m_s|H^{so}|\alpha lm_l\tfrac{1}{2}m_s\rangle$$
$$= \langle\alpha l|g|\alpha l\rangle\hbar^2 m_l m_s . \tag{10}$$

For the same case the nondiagonal matrix elements read

$$H^{so}_{\beta m'\alpha m} = \langle\beta lm_l'\tfrac{1}{2}m_s'|H^{so}|\alpha lm_l\tfrac{1}{2}m_s\rangle$$
$$= \delta_{m_l',m_l\pm 1}\delta_{m_s',m_s\mp 1}\tfrac{1}{2}\langle\beta l|g|\alpha,l\rangle\hbar^2$$
$$\times\sqrt{(l\mp m_l)(l\pm m_l+1)} . \tag{11}$$

Without loss of generality we confine ourselves to the set of wave functions $|\alpha lm_l;\frac{1}{2},+\frac{1}{2}\rangle$ and $|\beta lm_l+1;\frac{1}{2},-\frac{1}{2}\rangle$ which are mixed by spin-orbit interaction. In order to avoid cumbersome strings of indices, we will characterize

these states by αm and $\beta m+1$, respectively. For the radial integrals over the coupling constant the following shorthand notation is introduced:

$$\langle\alpha l|g|\alpha l\rangle = g_{\alpha l}, \quad \langle\beta l|g|\alpha l\rangle = g_{\beta\alpha l} . \tag{12}$$

Later we will need the sum and the difference of the diagonal matrix elements for one principal quantum number α,

$$H^{so}_{\alpha m,\alpha m} - H^{so}_{\alpha m+1,\alpha m+1} = -\tfrac{1}{2}g_{\alpha l}\hbar^2 , \tag{13a}$$

$$H^{so}_{\alpha m,\alpha m} + H^{so}_{\alpha m+1,\alpha m+1} = +\tfrac{1}{2}g_{\alpha l}\hbar^2(2m+1) . \tag{13b}$$

For the special case $s = \frac{1}{2}$ that we are investigating, the system of linear differential equations of first order, as exemplified in expression Eq. (8) with $H'=0$, can be set up now. For any α there are two equations,

$$i\hbar\dot{a}_{\alpha m+1}(t) = a_{\alpha m+1}(t)H^{so}_{\alpha m+1,\alpha m+1} + a_{\alpha m}(t)H^{so}_{\alpha m+1,\alpha m}$$
$$+ \sum_{\beta\neq\alpha} a_{\beta m}(t)H^{so}_{\alpha m+1,\beta m}e^{-i\omega_{\beta\alpha}t} , \tag{14a}$$

$$i\hbar\dot{a}_{\alpha m}(t) = a_{\alpha m}(t)H^{so}_{\alpha m,\alpha m} + a_{\alpha m+1}(t)H^{so}_{\alpha m,\alpha m+1}$$

$$+ \sum_{\beta \neq \alpha} a_{\beta m+1}(t)H^{so}_{\alpha m,\beta m+1}e^{-i\omega_{\beta\alpha}(t)} . \qquad (14b)$$

Before proceeding further, we have to elaborate on the coupling strength g of the spin-orbit interaction. At the moment of capture which is the origin of our time scale, the potential of the capturing ion is deformed very much by the residual donor ion in a way that makes the dependence of g on the space coordinates neither Coulombic nor even central. In a classical picture, the radial motion of the donor comes to a standstill at the moment of electron transfer. Once the electron has been caught by the acceptor, the residual donor ion is being accelerated by electrostatic repulsion thus gradually lifting the deformation it had imposed on the acceptor's potential by its close presence. This makes the coupling strength g in the initial state depend on the internuclear separation and thus on time in an unknown and certainly complicated manner. Due to the mass ratio, however, the residual ion recedes very slowly compared to the speed involved in the motion of the orbing electron. In this concept, we may assume that the dependence of H^{so} on the internuclear separation, which is an implicit dependence on time, may be treated parametrically as it has been done so successfully in the Born-Oppenheimer approximation of the adiabatically adjusted motions of the electrons in a molecule. Hence, with respect to the system of linear differential equations, we can expect H^{so} to be practically time independent. The outcome of our calculation will then include a formal time average of g during the lifetime of the capturing state which is the most affected one at low energies.

Next, let us turn to another approximation that will allow for handling the systems of differential equations, Eqs. (14a) and (14b). As implied by the matrix element Eq. (9), the spin-orbit interaction mixes all states within a given term series. Although we do not know in detail for the case of a noncentral potential what the ratio is for matrix elements of the spin-orbit interaction that are diagonal and nondiagonal with respect to the principal quantum number, respectively, we may assume it to be large. But we do know that these possibly small nondiagonal matrix elements are associated with more or less rapidly oscillating functions in the system of differential equations (14a) and (14b). If we assume $a_{\alpha m}(t)$ and $a_{\alpha m+1}(t)$ to be reasonably smooth functions of t, their course will not be altered significantly by averaging over small consecutive time intervals, the width of which should be very small compared to the lifetime. An appropriate choice for the width of a time increment would be the period of the slowest of the rapid oscillations $T_\alpha = 1/\nu_{\alpha,\alpha+1} = 2\pi/\omega_{\alpha,\alpha+1}$ thereby averaging all oscillation exponentials to zero. This is as if we were looking at the system with too small a time resolution to perceive these rapid oscillations. Instead, we would only realize the coarse time behavior of the amplitudes. In other words, of the total solutions to Eqs. (14a) and (14b), we will only consider the leading lowest frequency components which are directly and only related to the spin-

orbit interaction in the capturing level. Thus, the system of linear differential equations, Eqs. (14a) and (14b), reduces to two equations that hold true for the spin-orbit interaction in an isolated level of principal quantum number α,

$$i\hbar\dot{a}_{\alpha m+1}(t) = a_{\alpha m+1}(t)H^{so}_{\alpha m+1,\alpha m+1} + a_{\alpha m}(t)H^{so}_{\alpha m+1,\alpha m} ,$$
$$(15a)$$

$$i\hbar\dot{a}_{\alpha m}(t) = a_{\alpha m}(t)H^{so}_{\alpha m,\alpha m} + a_{\alpha m+1}(t)H^{so}_{\alpha m,\alpha m+1} . \qquad (15b)$$

These equations describe the balancing between the amplitudes. For both equations to hold simultaneously, we have to transform the two linear differential equations of first order into one linear differential equation of second order. For this purpose we resolve Eq. (15b) with respect to $a_{\alpha m+1}(t)$,

$$a_{\alpha m+1}(t) = \frac{1}{H^{so}_{\alpha m,\alpha m+1}}[i\hbar\dot{a}_{\alpha m}(t) - a_{\alpha m}(t)H^{so}_{\alpha m,\alpha m}] ,$$
$$(15c)$$

and differentiate with respect to t,

$$\dot{a}_{\alpha m+1}(t) = \frac{1}{H^{so}_{\alpha m,\alpha m+1}}[i\hbar\ddot{a}_{\alpha m}(t) - \dot{a}_{\alpha m}(t)H^{so}_{\alpha m,\alpha m}] .$$
$$(15d)$$

Substitution for the respective quantities in Eq. (15a) yields

$$0 = \ddot{a}_{\alpha m}(t) + \frac{i}{\hbar}(H^{so}_{\alpha m,\alpha m} + H^{so}_{\alpha m+1,\alpha m+1})\dot{a}_{\alpha m}(t)$$

$$- \frac{1}{\hbar^2}(H^{so}_{\alpha m,\alpha m}H^{so}_{\alpha m+1,\alpha m+1} - |H^{so}_{\alpha m,\alpha m+1}|^2)a_{\alpha m}(t) .$$
$$(16)$$

Assuming the solution to be proportional to the exponential

$$a_{\alpha m}(t) \sim e^{-i\Omega t} , \qquad (17)$$

we obtain a quadratic equation for the determination of Ω,

$$0 = -\Omega^2 + \frac{1}{\hbar}(H^{so}_{\alpha m,\alpha m} + H^{so}_{\alpha m+1,\alpha m+1})\Omega$$

$$- \frac{1}{\hbar^2}(H^{so}_{\alpha m,\alpha m}H^{so}_{\alpha m+1,\alpha m+1} - |H^{so}_{\alpha m,\alpha m+1}|^2) , \qquad (18a)$$

or with the quadratic extension

$$0 = \left[\Omega - \frac{1}{2\hbar}(H^{so}_{\alpha m,\alpha m} + H^{so}_{\alpha m+1,\alpha m+1})\right]^2$$

$$- \frac{1}{4\hbar^2}[(H^{so}_{\alpha m,\alpha m} - H^{so}_{\alpha m+1,\alpha m+1})^2 + 4|H^{so}_{\alpha m,\alpha m+1}|^2] .$$
$$(18b)$$

Inserting the expressions we had prepared in Eqs. (13a) and (13b) and the nondiagonal matrix element according to Eq. (11), the results are

$$\Omega_{al}^{\pm} = \Omega_{alJ\pm} = \tfrac{1}{2}\overline{g_{al}}\hbar[-\tfrac{1}{2}\pm(l+\tfrac{1}{2})] = \frac{1}{\hbar}\Delta E_{alJ\pm} , \quad (19a)$$

where

$$\Delta E_{alJ+} = \tfrac{1}{2}\overline{g_{al}}\hbar^2 l , \quad (19b)$$

$$\Delta E_{alJ-} = -\tfrac{1}{2}\overline{g_{al}}\hbar^2(l+1) \quad (19c)$$

are the energy shifts of the fine-structure levels associated with $J_+ = l + \tfrac{1}{2}$ and $J_- = l - \tfrac{1}{2}$, respectively, relative to the common center of gravity, and $\overline{g_{al}}$ is an appropriate time average.

The fundamental system of solutions to Eq. (16) is therefore

$$a_{alm;1/2,+1/2}(t) = C_1 e^{-i\Omega_{al}^+ t} + C_2 e^{-i\Omega_{al}^- t} . \quad (20)$$

For determining the second amplitude $a_{am+1;1/2,-1/2}(t)$ we take Eq. (20) and its time derivative to replace the equivalent quantities in Eq. (15c),

$$a_{alm+1;1/2,-1/2}(t)$$
$$= \frac{1}{H_{am,am+1}^{so}}[C_1(\hbar\Omega_{al}^+ - H_{am,am}^{so})e^{-i\Omega_{al}^+ t}$$
$$+ C_2(\hbar\Omega_{al}^- - H_{am,am}^{so})e^{-i\Omega_{al}^- t}] . \quad (21)$$

With the help of Eqs. (10), (11), and (19a) this reduces to

$$a_{alm+1;1/2,-1/2}(t) = C_1 \frac{\sqrt{l-m}}{\sqrt{l+m+1}}e^{-i\Omega_{al}^+ t}$$
$$- C_2 \frac{\sqrt{l+m+1}}{\sqrt{l-m}}e^{-i\Omega_{al}^- t} . \quad (22)$$

In order to satisfy the initial conditions, e.g.,

$$a_{alm;1/2,+1/2}(t=0) = B_{alm} ,$$
$$a_{alm+1;1/2,-1/2}(t=0) = 0 , \quad (23)$$

we set up the following system of linear equations

$$C_1 \frac{\sqrt{l-m}}{\sqrt{l+m+1}} - C_2 \frac{\sqrt{l+m+1}}{\sqrt{l-m}} = 0 , \quad (24a)$$

$$C_1 + C_2 = B_{alm} , \quad (24b)$$

the determinant of which is

$$D = \frac{2l+1}{\sqrt{(l-m)(l+m+1)}} . \quad (25)$$

Then

$$C_1 = \frac{B_{alm}}{D}\frac{\sqrt{l+m+1}}{\sqrt{l-m}} = \frac{B_{alm}}{2l+1}(l+m+1) , \quad (26a)$$

$$C_2 = \frac{B_{alm}}{D}\frac{\sqrt{l-m}}{\sqrt{l+m+1}} = \frac{B_{alm}}{2l+1}(l-m) . \quad (26b)$$

With this solution of the initial value problem the complete amplitudes read

$$a_{alm;1/2,+1/2}(t) = \frac{B_{alm}}{2l+1}[(l+m+1)e^{-i\Omega_{al}^+ t}$$
$$+ (l-m)e^{-i\Omega_{al}^- t}] , \quad (27a)$$

$$a_{alm+1;1/2,-1/2}(t) = \frac{B_{alm}}{2l+1}\sqrt{(l-m)(l+m+1)}$$
$$\times(e^{-i\Omega_{al}^+ t} - e^{-i\Omega_{al}^- t}) . \quad (27b)$$

In our approximation the perturbed wave function of Eq. (3a) with the electromagnetic interaction being switched off is given by

$$\psi_I(t) = \sum_{\alpha,l,m}[a_{alm;1/2,1/2}(t)|alm;\tfrac{1}{2},+\tfrac{1}{2}\rangle + a_{alm+1;1/2,-1/2}(t)|alm+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle] . \quad (28)$$

Substitution of the amplitudes Eqs. (27a) and (27b) and some minor rearrangements let us arrive at

$$\psi_I(t) = \sum_{\alpha,l,m} B_{alm}\left[\frac{\sqrt{l+m+1}}{\sqrt{2l+1}}\left\{\frac{\sqrt{l+m+1}}{\sqrt{2l+1}}|alm;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \frac{\sqrt{l-m}}{\sqrt{2l+1}}|alm+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle\right\}e^{-i\Omega_{al}^+ t}\right.$$

$$\left. \times \frac{\sqrt{l-m}}{\sqrt{2l+1}}\left\{\frac{\sqrt{l-m}}{\sqrt{2l+1}}|alm;\tfrac{1}{2},+\tfrac{1}{2}\rangle - \frac{\sqrt{l+m+1}}{\sqrt{2l+1}}|alm+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle\right\}e^{-i\Omega_{al}^- t}\right] . \quad (29)$$

When we compare the expressions in parentheses with the expressions for the transformation between the representations $|alsJM_J\rangle$ and $|alm_l sm_s\rangle$ (Ref. 23),

$$|alsJM_J\rangle = (-1)^{l-s+M_J}\sqrt{2J+1}\sum_{m_l,m_s}\begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}|alm_l sm_s\rangle , \quad (30)$$

we find

$$|al\tfrac{1}{2}J_+ = l+\tfrac{1}{2}, M_J = m+\tfrac{1}{2}\rangle = \frac{\sqrt{l+m+1}}{\sqrt{2l+1}}|alm;\tfrac{1}{2},+\tfrac{1}{2}\rangle + \frac{\sqrt{l-m}}{\sqrt{2l+1}}|alm+1;\tfrac{1}{2},-\tfrac{1}{2}\rangle , \quad (31a)$$

$$|\alpha l \tfrac{1}{2} J_- = l - \tfrac{1}{2}, \, M_J = m + \tfrac{1}{2}\rangle = -\frac{\sqrt{l-m}}{\sqrt{2l+1}}|\alpha l m \, ; \tfrac{1}{2}, +\tfrac{1}{2}\rangle + \frac{\sqrt{l+m+1}}{\sqrt{2l+1}}|\alpha l m +1 ; \tfrac{1}{2}, -\tfrac{1}{2}\rangle \; . \tag{31b}$$

Thus

$$\psi_I(t) = \sum_{\alpha,l,m} B_{\alpha l m} \left[\frac{\sqrt{l+m+1}}{\sqrt{2l+1}}|\alpha l \tfrac{1}{2} J_+ \, M_J = m + \tfrac{1}{2}\rangle e^{-i\Omega^+_{\alpha l}t} - \frac{\sqrt{l-m}}{\sqrt{2l+1}}|\alpha l \tfrac{1}{2} J_- \, M_J = m + \tfrac{1}{2}\rangle e^{-i\Omega^-_{\alpha l}t} \right] . \tag{32}$$

For $t=0$, expression Eq. (32) must transform into Eq. (1). Since $\psi_I(t=0) = \psi(t=0)$,

$$\psi(t=0) = \sum_{\alpha,l,m} B_{\alpha l m} \left[\frac{\sqrt{l+m+1}}{\sqrt{2l+1}}|\alpha l \tfrac{1}{2} J_+ \, M_J = m + \tfrac{1}{2}\rangle \right.$$

$$\left. - \frac{\sqrt{l-m}}{\sqrt{2l+1}}|\alpha l \tfrac{1}{2} J_- \, M_J = m + \tfrac{1}{2}\rangle \right] ,$$

and indeed, the inverse transformation of Eq. (30) which we had already used in Eq. (2) (Ref. 23),

$$|\alpha l m_l s m_s \rangle = \sum_{J,M_J} (-1)^{l-s+M_J}\sqrt{2J+1}$$

$$\times \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}|\alpha l s J M_J\rangle , \tag{33}$$

yields for the specific initial conditions that we had chosen in Eq. (23)

$$|\alpha l m \, ; \tfrac{1}{2}, +\tfrac{1}{2}\rangle = \frac{\sqrt{l+m+1}}{\sqrt{2l+1}}|\alpha l \tfrac{1}{2} J_+, \, M_J = m + \tfrac{1}{2}\rangle$$

$$- \frac{\sqrt{l-m}}{\sqrt{2l+1}}|\alpha l \tfrac{1}{2} J_-, \, M_J = m - \tfrac{1}{2}\rangle , \tag{34}$$

and thus

$$\psi(t=0) = \psi_0 = \sum_{\alpha,l,m} B_{\alpha l m}|\alpha l m \, ; \tfrac{1}{2}, +\tfrac{1}{2}\rangle . \tag{35}$$

Generalizing according to Eq. (33) and using Schrödinger representation, our wave function Eq. (29) can be written as

$$\psi(t) = \sum_{\alpha,l,m_l} \sum_{J,M_J} B_{\alpha l m_l}(-1)^{l-s+M_J}\sqrt{2J+1}$$

$$\times \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}|\alpha l s J M_J\rangle$$

$$\times e^{-i(E_{\alpha l J}/\hbar)t} , \tag{36}$$

with

$$E_{\alpha l J} = E^0_{\alpha l} + \hbar\Omega_{\alpha l J} \; . \tag{37}$$

Equation (36) shows that with the approximations used the time evolution of our initially pure spin state wave function leads to a superposition of time-dependent wave functions

$$|\alpha l s J M_J\rangle e^{-i(E_{\alpha l J}/\hbar)t}$$

which are true eigenfunctions of the full Hamiltonian, including spin-orbit interaction: With $H = H^0 + H^{so}$ we get in Schrödinger representation

$$H|\alpha l s J M_J\rangle e^{-i(E_{\alpha l J}/\hbar)t} = i\hbar\frac{\partial}{\partial t}|\alpha l s J M_J\rangle e^{-i(E_{\alpha l J}/\hbar)t}$$

$$= (E^0_{\alpha l} + \hbar\Omega_{\alpha l J})|\alpha l s J M_J\rangle$$

$$\times e^{-i(E_{\alpha l J}/\hbar)t} . \tag{38}$$

Thus the system has fully adapted to the additional spin-orbit interaction. This underscores the need of using this kind of wave functions for the system at later times when we have to consider the influence of the electromagnetic interaction.

The presence of the electromagnetic interaction which makes the capturing state a decaying one can be taken into account by attaching the lifetime exponential to the wave function (Ref. 25, p. 168)

$$\psi(t) = \sum_{\alpha,l,m_l} \sum_{J,M_J} B_{\alpha l m_l}(-1)^{l-s+M_J}\sqrt{2J+1}$$

$$\times \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}|\alpha l s J M_J\rangle$$

$$\times e^{-[i(E_{\alpha l J}/\hbar) + \Gamma_{\alpha l J}/2\hbar]t} . \tag{39}$$

Thus, for $t > 0$, the wave function of the initial state turns out to be of the form that we would have intuitively expected from expression Eq. (26). As the state decays, the intensity of the emitted radiation is proportional to the square of the transition matrix element,

$$I \sim |\langle \beta l's J'M_J'|H^r|\psi(t)\rangle|^2$$

$$= \sum_{\alpha,l,m_l} \sum_{J,M_J} |B_{\alpha l m_l}|^2 (2J+1) \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}^2 |\langle \beta l's J'M_J'|H^r|\alpha l s J M_J\rangle|^2 e^{-(\Gamma_{\alpha l J}/\hbar)t}$$

$$+ \sum_{\alpha l m_l \neq \tilde{\alpha}\tilde{l}\tilde{m}_l} \sum_{JM_J \neq \tilde{J}\tilde{M}_J} B_{\alpha l m} B^*_{\tilde{\alpha}\tilde{l}\tilde{m}_l} (-1)^{\tilde{J}+l-2s+M_J+\tilde{M}_J} \sqrt{(2J+1)(2\tilde{J}+1)}$$

$$\times \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix} \begin{bmatrix} \tilde{l} & s & \tilde{J} \\ \tilde{m}_l & m_s & -\tilde{M}_J \end{bmatrix} \langle \beta l's J'M_J'|H^r|\alpha l s J M_J\rangle$$

$$\times \langle \beta l's J'M_J'|H^r|\tilde{\alpha}\tilde{l}s\tilde{J}\,\tilde{M}_J\rangle^* e^{-i\omega_{\alpha l J,\tilde{\alpha}\tilde{l}\tilde{J}}t} e^{-[(\Gamma_{\alpha l J}+\Gamma_{\tilde{\alpha}\tilde{l}\tilde{J}})/2\hbar]t} . \tag{40}$$

The second series of sums with $\alpha \neq \tilde{\alpha}$, $l \neq \tilde{l}$, $m_l \neq \tilde{m}_l$, $J \neq \tilde{J}$, and $M_J \neq \tilde{M}_J$ gives rise to zero field quantum beats[26,27] among states that can decay coherently like fine-structure beats and appropriate l-$\tilde{l}$ beats. Beats of either kind have been observed experimentally after charge exchange.[28,29] This supports the choice of our wave function. [In the context of relation Eq. (40) we may note that whenever the absolute square over sums has to be taken the indices for the complex conjugate will be indicated by an additional tilde ($\sim$).]

C. Direct electric dipole transitions

Once the spin-orbit interaction has determined the character of the wave function, the fine-structure functions $|\alpha l s J M_J\rangle$ are the appropriate zeroth-order wave functions in interaction representation. Using time-dependent perturbation theory in interaction representation, we now calculate the probability amplitude for the final spin-orbit state $|\beta l's J'M_J'\rangle$. This state is generated by the decay of the Schrödinger wave function, Eq. (39), in which, however, the energy exponential has to be skipped in order to hold in interaction representation.

The interaction with the electromagnetic field is described correctly[25] if we take for the unperturbed Hamiltonian of Eq. (3b)

$$H^0 = H^0_{ion} + H^0_r . \tag{41}$$

(There had been objections to an earlier draft of our manuscript regarding the necessity of a treatment that goes beyond our initial semiclassical approximation. The results, however, show that the general statements deduced from the present rigorous theory can—at least qualitatively—also be obtained from the semiclassical approach.) H^0_{ion} and H^0_r are the Hamiltonian operators for the unperturbed ion and the free electromagnetic field, respectively,

$$H^0_{ion}\psi_l = E^0_l \psi_l , \tag{41a}$$

$$H^0_r \Phi_\chi = E^0_r(\chi)\Phi_\chi . \tag{41b}$$

The wave functions Φ_χ of the free electromagnetic field comprise all independent modes λ of the field as represented by the harmonic oscillators with excitation numbers n_λ

$$\Phi_\chi = \phi_{n_1}\phi_{n_2}\cdots\phi_{n_\lambda}\cdots = \prod_\lambda \phi_{n_\lambda} , \tag{42}$$

where the wave function ϕ_{n_λ} of the individual mode λ is the eigenfunction of

$$H^0_\lambda \phi_{n_\lambda} = \hbar\omega_\lambda(n_\lambda + \tfrac{1}{2})\phi_{n_\lambda} \tag{42a}$$

and

$$H^0_r = \sum_\lambda H^0_\lambda . \tag{42b}$$

Hence, χ represents a special set of numbers n_λ $(n_1, n_2, \ldots, n_\lambda, \ldots)$ and the action on Φ_χ of the radiative time-evolution operator consists of generating products of Schrödinger-type functions, as usual,

$$e^{-i(H^0_r/\hbar)t}\Phi_\chi = \exp\left[-i\sum_\lambda \frac{H^0_\lambda}{\hbar}t\right] \prod_\lambda \phi_{n_\lambda}$$

$$= \prod_\lambda e^{-i(H^0_\lambda/\hbar)t}\phi_{n_\lambda}$$

$$= \prod_\lambda \phi_{n_\lambda} e^{-i\omega_\lambda(n_\lambda+1/2)t} . \tag{43}$$

An equivalent relation holds true for the ionic part

$$e^{-i(H^0_{ion}/\hbar)t}\psi_l = \psi_l e^{-i(E^0_l/\hbar)t} . \tag{44}$$

In zeroth order, i.e., without interaction, the compound system is described by

$$H^0\Psi = (H^0_{ion} + H^0_r)\Psi = [E^0_l + E^0_r(\chi)]\psi_l\Phi_\chi . \tag{45}$$

Equation (45) is equivalent to Eq. (3b), whereas the counterpart to Eq. (3a) is

$$\Psi_I(\mathbf{r},t) = \sum_{l,\chi} a_{l\chi}(t)\psi_l(\mathbf{r})\Phi_\chi . \tag{46}$$

Then, according to time-dependent perturbation theory

$$i\hbar\dot{a}_{l'\chi'}(t) = \sum_{l,\chi} a_{l\chi}(t)\langle l'\chi'|H_I'|l\chi\rangle . \tag{47}$$

Using the transformations, Eqs. (4b), (43), and (44), we obtain from Eq. (47)

$$i\hbar\dot{a}_{l'\chi'}(t) = \sum_{l,\chi} a_{l\chi}(t)\left\langle l', \prod_\lambda \phi_{n_\lambda'} \Big| H' \Big| l, \prod_\lambda \phi_{n_\lambda}\right\rangle$$

$$\times e^{-i[\omega_{l,l'}+\omega_\lambda(n_\lambda-n_\lambda')]t} , \qquad (48)$$

where

$$\omega_{l,l'} = \frac{1}{\hbar}(E_l^0 - E_{l'}^0) . \qquad (48a)$$

The next step is to expand the interaction operator Eq. (7a) with respect to the modes of the electromagnetic field

$$H' = -\frac{e}{mc}\sum_\lambda (q_\lambda A_\lambda e^{+i\mathbf{k}_\lambda\cdot\mathbf{r}}\boldsymbol{\epsilon}_\lambda\cdot\mathbf{p} + q_\lambda^* A_\lambda^* e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\boldsymbol{\epsilon}_\lambda^*\cdot\mathbf{p}) .$$

$$(49)$$

The matrix elements of the creation and annihilation operators q_λ^* and q_λ, respectively, are given by[25]

$$\langle\chi'|q_\lambda^*|\chi\rangle = \prod_{\mu\neq\lambda} \delta_{n_\mu',n_\mu}\delta_{n_\lambda',n_\lambda+1}\left[\frac{\hbar}{2\omega_\lambda}(n_\lambda+1)\right]^{1/2} ,$$

$$(50a)$$

$$\langle\chi'|q_\lambda|\chi\rangle = \prod_{\mu\neq\lambda} \delta_{n_\mu',n_\mu}\delta_{n_\lambda',n_\lambda-1}\left[\frac{\hbar}{2\omega_\lambda}n_\lambda\right]^{1/2} . \qquad (50b)$$

In our case only spontaneous transitions matter. Hence, the initial state of the electromagnetic field is the photon vacuum (all $n_\lambda \equiv 0$). In the final state, after the transition, we have one specific photon λ in the radiation field. We take account of this situation by adopting a simpler notation,

$$\chi = (0_1, 0_2, \ldots, 0_\lambda, \ldots) \Longrightarrow 0 ,$$

$$\chi' = (0_1, 0_2, \ldots, 1_\lambda, 0_{\lambda+1}, \ldots) \Longrightarrow 1_\lambda .$$

The matrix elements of Eqs. (50a) and (50b) then simplify to

$$\langle 1_\lambda|q_\lambda^*|0\rangle = \left[\frac{\hbar}{2\omega_\lambda}\right]^{1/2} , \qquad (50c)$$

$$\langle 1_\lambda|q_\lambda|0\rangle = 0 . \qquad (50d)$$

Now, having these tools handy, we incorporate Eq. (49) into the matrix element of Eq. (48) and obtain for the differential equation

$$i\hbar\dot{a}_{l',1_\lambda}(t) = -\frac{eA}{mc}\sum_l a_{l,0}(t)\left[\frac{\hbar}{2\omega_\lambda}\right]^{1/2}$$

$$\times\langle l'|e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\boldsymbol{\epsilon}_\lambda\cdot\mathbf{p}|l\rangle$$

$$\times e^{-i(\omega_{l,l'}-\omega_\lambda)t} . \qquad (51)$$

Here A is being taken to represent a real normalization constant common to all modes, and $\boldsymbol{\epsilon}_\lambda^*$ has been set equal to $\boldsymbol{\epsilon}_\lambda$ without loss of generality. Confining our discussion to the highest-order decay mode, the electric dipole approximation according to Eq. (7b), we approximate the matrix element in Eq. (51) by

$$-\frac{eA}{mc}\langle l'|e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\boldsymbol{\epsilon}_\lambda\cdot\mathbf{p}|l\rangle \simeq i\frac{eA}{c}\omega_{l,l'}\langle l'|\boldsymbol{\epsilon}_\lambda\cdot\mathbf{r}|l\rangle . \qquad (52)$$

Equation (52) provides the frequency dependence of the matrix element which we need to know in a later integration.

The amplitudes of the initial modes of the electromagnetic field are all well defined in the case of spontaneous emission. Hence, we may drop the index 0, and take $a_l(t)$ as referring to the ionic amplitude only. We also know the time evolution of the initial ionic state according to Eq. (39) which in interaction representation reads

$$\psi_I(t) = \sum_k a_k(t)|k\rangle = \sum_{\alpha,l,m_l}\sum_{J,M_J} B_{\alpha l m_l}(-1)^{l-s+M_J}\sqrt{2J+1}\begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}|\alpha l s J M_J\rangle e^{-(\Gamma_{\alpha l J}/2\hbar)t} . \qquad (53)$$

Therefore, with the help of Eqs. (52) and (53), we obtain for the differential equation, Eq. (51),

$$\dot{a}_{\beta l' s J' M_J',1_\lambda}(t) = \frac{eA}{c\sqrt{2\hbar\omega_\lambda}}\sum_{\alpha,l,m_l}\sum_{J,M_J} B_{\alpha l m_l}(-1)^{l-s+M_J}\sqrt{2J+1}\begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}\omega_{\alpha l J,\beta l' J'}$$

$$\times\langle\beta l' s J' M_J'|\boldsymbol{\epsilon}_\lambda\cdot\mathbf{r}|\alpha l s J M_J\rangle e^{-i[\omega_{\alpha l J,\beta l' J'}-\omega_\lambda-i(\Gamma_{\alpha l J}/2\hbar)]t} . \qquad (54)$$

Before the capture of the electron the final state $|\beta l' s J' M_J'\rangle$ was unoccupied, $a_{\beta l' s J' M_J',1_\lambda}(t=0)=0$. Hence, the solution of Eq. (54) which accounts for this initial condition is

$$a_{\beta l' s J' M_J',1_\lambda}(t) = \frac{eA}{c\sqrt{2\hbar\omega_\lambda}}\sum_{\alpha,l,m_l}\sum_{J,M_J} B_{\alpha l m_l}(-1)^{l-s+M_J}\sqrt{2J+1}\begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix}\omega_{\alpha l J,\beta l' J'}$$

$$\times\langle\beta l' s J' M_J'|\boldsymbol{\epsilon}_\lambda\cdot\mathbf{r}|\alpha l s J M_J\rangle\frac{1-e^{-[i(\omega_{\alpha l J,\beta l' J'}-\omega_\lambda)+\Gamma_{\alpha l J}/2\hbar]t}}{i(\omega_{\alpha l J,\beta l' J'}-\omega_\lambda)+\Gamma_{\alpha l J}/2\hbar} . \qquad (55)$$

This is the time dependence of the probability amplitude for the special spontaneous-emission process in which the ion undergoes an electric-dipole transition from a mixed state (superposition of $|\alpha l s J M_J\rangle$ states) into a fine-structure state $|\beta l' s J' M_J'\rangle$ by emitting the special photon λ whose frequency, polarization and direction of propagation are character-

ized by λ. The probability for this process to occur at time t is given by the absolute square of Eq. (55). This expression will contain exponentials with $\omega_{\alpha lJ, \tilde{\alpha} \bar{l} \bar{J}} = \omega_{\alpha lJ, \beta l'J'} - \omega_{\tilde{\alpha} \bar{l} \bar{J}, \beta l'J'}$, the beat frequencies, which we had encountered already in Eq. (40). Thus the specific contribution to the population of the final state as described by the absolute square of Eq. (55) shows the same modulations with time as does the corresponding spontaneous radiation. After a long enough time ($t \to \infty$), the exponentials have faded away due to $\Gamma_{\alpha lJ}$ and $\Gamma_{\tilde{\alpha} \bar{l} \bar{J}}$, and we are left with the asymptotic contribution from this specific decay channel to the final state's population,

$$|a_{\beta l's J' M_J', 1_\lambda}(\infty)|^2$$

$$= \frac{e^2 A^2}{c^2 2\hbar \omega_\lambda} \sum_{\alpha, l, m_l} \sum_{\tilde{\alpha}, \bar{l}, \bar{m}_l} \sum_{J, M_J} \sum_{\bar{J} \bar{M}_J} B_{\alpha l m_l} B^*_{\tilde{\alpha} \bar{l} \bar{m}_l} (-1)^{l + \bar{l} - 2s + M_J + \bar{M}_J}$$

$$\times \sqrt{(2J+1)(2\bar{J}+1)} \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix} \begin{bmatrix} \bar{l} & s & \bar{J} \\ \bar{m}_l & m_s & -\bar{M}_J \end{bmatrix} \omega_{\alpha lJ, \beta l'J'} \omega_{\tilde{\alpha} \bar{l} \bar{J}, \beta l'J'}$$

$$\times \frac{\langle \beta l's J' M_J' | \epsilon_\lambda \cdot \mathbf{r} | \alpha l s J M_J \rangle \langle \beta l's J' M_J' | \epsilon_\lambda \cdot \mathbf{r} | \tilde{\alpha} \bar{l} s \bar{J} \bar{M}_J \rangle^*}{\left[i(\omega_{\alpha lJ, \beta l'J'} - \omega_\lambda) + \dfrac{\Gamma_{\alpha lJ}}{2\hbar} \right] \left[-i(\omega_{\tilde{\alpha} \bar{l} \bar{J}, \beta l'J'} - \omega_\lambda) + \dfrac{\Gamma_{\tilde{\alpha} \bar{l} \bar{J}}}{2\hbar} \right]} . \tag{56a}$$

For $\alpha = \tilde{\alpha}$, $l = \bar{l}$, $m_l = \bar{m}_l$, $J = \bar{J}$, and $M_J = \bar{M}_J$ the familiar Lorentzian is obtained.

The following manipulations take advantage of the fact that Eq. (56a) must be real. To make the manipulations more obvious, we write Eq. (56a) more explicitly,

$$|a_{\beta l's J' M_J', 1_\lambda}(\infty)|^2$$

$$= \frac{e^2 A^2}{c^2 2\hbar \omega_\lambda}$$

$$\times \sum_{\alpha, l, m_l} \sum_{\tilde{\alpha}, \bar{l}, \bar{m}_l} \sum_{J, M_J} \sum_{\bar{J}, \bar{M}_J} (-1)^{l + \bar{l} - 2s + M_J + \bar{M}_J} \sqrt{(2J+1)(2\bar{J}+1)}$$

$$\times \begin{bmatrix} l & s & J \\ m_l & m_s & -M_J \end{bmatrix} \begin{bmatrix} \bar{l} & s & \bar{J} \\ \bar{m}_l & m_s & -\bar{M}_J \end{bmatrix} \omega_{\alpha lJ, \beta l'J'} \omega_{\tilde{\alpha} \bar{l} \bar{J}, \beta l'J'}$$

$$\times [\text{Re}(B_{\alpha l m_l} B^*_{\tilde{\alpha} \bar{l} \bar{m}_l} \langle \beta l's J' M_J' | \epsilon_\lambda \cdot \mathbf{r} | \alpha l s J M_J \rangle \langle \beta l's J' M_J' | \epsilon_\lambda \cdot \mathbf{r} | \tilde{\alpha} \bar{l} s \bar{J} \bar{M}_J \rangle^*)$$

$$+ i \, \text{Im}(B_{\alpha l m_l} B^*_{\tilde{\alpha} \bar{l} \bar{m}_l} \langle \beta l's J' M_J' | \epsilon \cdot \mathbf{r} | \alpha l s J M_J \rangle \langle \beta l's J' M_J' | \epsilon_\lambda \cdot \mathbf{r} | \tilde{\alpha} \bar{l} s \bar{J} \bar{M}_J \rangle^*)]$$

$$\times \frac{\left[\dfrac{\Gamma_{\alpha lJ}}{2\hbar} - i(\omega_{\alpha lJ, \beta l'J'} - \omega_\lambda) \right] \left[\dfrac{\Gamma_{\tilde{\alpha} \bar{l} \bar{J}}}{2\hbar} + i(\omega_{\tilde{\alpha} \bar{l} \bar{J}, \beta l'J'} - \omega_\lambda) \right]}{\left[\left(\dfrac{\Gamma_{\alpha lJ}}{2\hbar} \right)^2 + (\omega_{\alpha lJ, \beta l'J'} - \omega_\lambda)^2 \right] \left[\left(\dfrac{\Gamma_{\tilde{\alpha} \bar{l} \bar{J}}}{2\hbar} \right)^2 + (\omega_{\tilde{\alpha} \bar{l} \bar{J}, \beta l'J'} - \omega_\lambda)^2 \right]} . \tag{56b}$$

Since Eq. (56b) must hold true for any ω_λ, we may investigate the summands of Eq. (56b) individually. For simplifying the notation, we choose the following abbreviations:

$$M = B_{\alpha l m_l} B^*_{\tilde{\alpha} \bar{l} \bar{m}_l} \langle \beta l's J' M_J' | \epsilon_\lambda \cdot \mathbf{r} | \alpha l s J M_J \rangle \langle \beta l's J' M_J' | \epsilon_\lambda \cdot \mathbf{r} | \tilde{\alpha} \bar{l} s \bar{J} \bar{M}_J \rangle^* , \tag{57a}$$

$$\gamma = \frac{\Gamma_{\alpha lJ}}{2\hbar}, \quad \tilde{\gamma} = \frac{\Gamma_{\tilde{\alpha} \bar{l} \bar{J}}}{2\hbar} , \tag{57b}$$

$$\omega_0 = \omega_{\alpha lJ, \beta l'J'}, \quad \tilde{\omega}_0 = \omega_{\tilde{\alpha} \bar{l} \bar{J}, \beta l'J'}, \quad \omega = \omega_\lambda . \tag{57c}$$

With these shorthand notations we treat the relevant part of Eq. (56b) separately,

$$(\text{Re}M + i\,\text{Im}M)\frac{\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)+i\,[\gamma(\tilde{\omega}_0-\omega)-\tilde{\gamma}(\omega_0-\omega)]}{[\gamma^2+(\omega_0-\omega)^2][\tilde{\gamma}^{\,2}+(\tilde{\omega}_0-\omega)^2]}$$

$$=\frac{\text{Re}M\,[\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)]-\text{Im}M\,[\gamma(\tilde{\omega}_0-\omega)-\tilde{\gamma}(\omega_0-\omega)]}{[\gamma^2+(\omega_0-\omega)^2][\tilde{\gamma}^{\,2}+(\tilde{\omega}_0-\omega)^2]}$$

$$+i\frac{\text{Im}M\,[\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)]+\text{Re}M\,[\gamma(\tilde{\omega}_0-\omega)-\tilde{\gamma}(\omega_0-\omega)]}{[\gamma^2+(\omega_0-\omega)^2][\tilde{\gamma}^{\,2}+(\tilde{\omega}_0-\omega)^2]}\ . \tag{58}$$

For this to be real, the imaginary part must vanish. This leads to a necessary relation between the real and imaginary parts of M,

$$-\text{Im}M=\frac{\text{Re}M\,[\gamma(\tilde{\omega}_0-\omega)-\tilde{\gamma}(\omega_0-\omega)]}{\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)}\ . \tag{59}$$

Inserting this relation into Eq. (58) we obtain

$$(\text{Re}M + i\,\text{Im}M)\frac{[\gamma-i(\omega_0-\omega)][\tilde{\gamma}+i(\tilde{\omega}_0-\omega)]}{[\gamma^2+(\omega_0-\omega)^2][\tilde{\gamma}^{\,2}+(\tilde{\omega}_0-\omega)^2]}$$

$$=\frac{\text{Re}M}{[\gamma^2+(\omega_0-\omega)^2][\tilde{\gamma}^{\,2}+(\tilde{\omega}_0-\omega)^2]}\frac{[\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)]^2+[\gamma(\tilde{\omega}_0-\omega)-\tilde{\gamma}(\omega_0-\omega)]^2}{\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)}\ . \tag{60}$$

By regrouping we see that

$$[\gamma^2+(\omega_0-\omega)^2][\tilde{\gamma}^{\,2}+(\tilde{\omega}_0-\omega)^2]=[\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)]^2+[\gamma(\tilde{\omega}_0-\omega)-\tilde{\gamma}(\omega_0-\omega)]^2\ . \tag{61}$$

Whereupon

$$(\text{Re}M + i\,\text{Im}M)\frac{[\gamma-i(\omega_0-\omega)][\tilde{\gamma}+i(\tilde{\omega}_0-\omega)]}{[\gamma^2+(\omega_0-\omega)^2][\tilde{\gamma}^{\,2}+(\tilde{\omega}_0-\omega)]}=\frac{\text{Re}M}{\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)}\ . \tag{62}$$

For convenience in a later integration we rearrange the denominator of Eq. (62),

$$\gamma\tilde{\gamma}+(\omega_0-\omega)(\tilde{\omega}_0-\omega)=\gamma\tilde{\gamma}-\left[\frac{\omega_0-\tilde{\omega}_0}{2}\right]^2+\left[\frac{\omega_0+\tilde{\omega}_0}{2}-\omega\right]^2\ . \tag{63}$$

After these manipulations we return to Eqs. (56a) and (56b) and find

$$|a_{\beta l'sJ'M_J',1_\lambda}(\infty)|^2$$

$$=\frac{e^2A^2}{c^2 2\hbar\omega_\lambda}\sum_{\alpha,l,m_l}\sum_{\tilde{\alpha},\tilde{l},\tilde{m}_l}\sum_{J,M_J}\sum_{\tilde{J},\tilde{M}_J}(-1)^{l+\tilde{l}-2s+M_J+\tilde{M}_J}\sqrt{(2J+1)(2\tilde{J}+1)}$$

$$\times\begin{bmatrix}l & s & J\\ m_l & m_s & -M_J\end{bmatrix}\begin{bmatrix}l & s & \tilde{J}\\ \tilde{m}_l & m_s & -\tilde{M}_J\end{bmatrix}\omega_{\alpha lJ,\beta l'J'}\omega_{\tilde{\alpha}\tilde{l}\tilde{J},\beta l'J'}$$

$$\times\frac{\text{Re}(B_{\alpha lm_l}B^*_{\tilde{\alpha}\tilde{l}\tilde{m}_l}\langle\beta l'sJ'M_J'|\epsilon_\lambda\cdot\mathbf{r}|\alpha lsJM_J\rangle\langle\beta l'sJ'M_J'|\epsilon_\lambda\cdot\mathbf{r}|\tilde{\alpha}\,\tilde{l}\,s\tilde{J}\,\tilde{M}_J\rangle^*)}{\dfrac{\Gamma_{\alpha lJ}\Gamma_{\tilde{\alpha}\tilde{l}\tilde{J}}}{4\hbar^2}-\left[\dfrac{\omega_{\alpha lJ,\beta l'J'}-\omega_{\tilde{\alpha}\tilde{l}\tilde{J},\beta l'J'}}{2}\right]^2+\left[\dfrac{\omega_{\alpha lJ,\beta l'J'}+\omega_{\tilde{\alpha}\tilde{l}\tilde{J},\beta l'J'}}{2}-\omega_\lambda\right]^2}\ . \tag{64}$$

As we have pointed out above, Eqs. (56a), (56b), and (64) describe the probability that, after a sufficiently long time, we find the ion in the final state, $|\beta l'sJ'M_J'\rangle$ and a specific photon λ in the radiation field. Our main interest, however, does not lie in such a specific emission process. Rather, we want to know the asymptotic probability that the ion has definitely made the transition into the specified final state no matter by which photon. We attain this probability by summing over all possible spontaneous-emission processes which include all possible frequencies, polarizations, and directions of the photons. In doing so we must observe that the radiation modes are not evenly distributed over the fre-

quency spectrum but have a density function which depends quadratically on the frequency. Assuming our normalization volume to be sufficiently large, we can take the modes as being continuously spread over the total frequency range. Hence, we can replace the summation over all modes λ by an integration over ω_λ,

$$|a_{\beta l'sJ'M_j'}(\infty)|^2 = \sum_\lambda |a_{\beta l'sJ'M_j',1_\lambda}(\infty)|^2 = 2\int_\Omega \int_0^\infty |a_{\beta l'sJ'M_j',1_\lambda}(\infty)|^2 \frac{\omega_\lambda^2}{(2\pi c)^3} d\omega_\lambda d\Omega .$$ (65)

The factor of 2 accounts for the two orthogonal polarizations per mode.

Using the abbreviations of Eqs. (57a)–(57c), we have to calculate the following integral:

$$\int_0^\infty \frac{\omega\, d\omega}{\gamma\tilde{\gamma} - \left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 + \left[\frac{\omega_0 + \tilde{\omega}_0}{2} - \omega\right]^2}$$

$$= -\frac{1}{2}\int_0^\infty \frac{2\left[\frac{\omega_0 + \tilde{\omega}_0}{2} - \omega\right]d\omega}{\gamma\tilde{\gamma} - \left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 + \left[\frac{\omega_0 + \tilde{\omega}_0}{2} - \omega\right]^2}$$

$$+ \frac{1}{2}\int_0^\infty \frac{(\omega_0 + \tilde{\omega}_0)d\omega}{\gamma\tilde{\gamma} - \left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 + \left[\frac{\omega_0 + \tilde{\omega}_0}{2} - \omega\right]^2} .$$ (66)

The integrand would be a superposition of a Lorentzian and a dispersion curve, both centered at $\frac{1}{2}(\omega_0 + \tilde{\omega}_0)$ with the width $\{\gamma\tilde{\gamma} - [(\omega_0 - \tilde{\omega}_0/2)]^2\}^{1/2}$, provided $\gamma\tilde{\gamma} > [(\omega_0 - \tilde{\omega}_0)/2]^2$. Unless $\omega_0 = \tilde{\omega}_0$, this cannot be true without contradicting our earlier assumption, made in Sec. II B about the ratio of the fine-structure splitting over the lifetime width by which the consecutive treatment of the concurring spin-orbit and radiative interac-

tions had been justified. Therefore we have to investigate the cases $\omega_0 = \tilde{\omega}_0$ and $\omega_0 \neq \tilde{\omega}_0$ separately. For $\omega_0 = \tilde{\omega}_0$, the integrand really is a superposition of a dispersion and a Lorentzian curve centered at ω_0 with a width γ. Since $\gamma <<< \omega_0$, only a negligible error is admitted by extending the lower integration limit to $-\infty$ in order to overcome a logarithmic divergence. Then the dispersion-type integrand is odd with respect to the center frequency ω_0, and the integral vanishes. The integral over the Lorentzian generates an arctan which, at the upper and lower limits, $\pm\infty$, takes on $\pm\pi/2$, respectively. Hence for $\omega_0 = \tilde{\omega}_0$

$$\int_0^\infty \frac{\omega_0\, d\omega}{\gamma^2 + (\omega_0 - \omega)^2} \approx \int_{-\infty}^{+\infty} \frac{\omega_0\, d\omega}{\gamma^2 + (\omega_0 - \omega)^2} = \pi\frac{\omega_0}{\gamma} .$$ (67)

For $\omega_0 \neq \tilde{\omega}_0$, either integrand has two singularities located symmetrically to the left and right of the center of frequency $\frac{1}{2}(\omega_0 + \tilde{\omega}_0)$ at about ω_0 and $\tilde{\omega}_0$, respectively. Far away from these singularities both integrands tend toward zero. Since ω_0 and $\tilde{\omega}_0$ are transition frequencies between different electronic states, they are very high and, hence, far away from zero. Therefore we can extend the lower integration limit to $-\infty$ in this case as well without inflicting any substantial error on our calculation. Then, as in the case before, the integrand of the first integral in Eq. (66) is odd with respect to the center frequency $\frac{1}{2}(\omega_0 + \tilde{\omega}_0)$ over the whole integration range and the integral cannot contribute. The stem function of the second integrand is arctanh which has the asymptotic value ± 1 for $\pm\infty$, respectively. Hence for $\omega_0 \neq \tilde{\omega}_0$

$$\int_0^\infty \frac{\omega_c\, d\omega}{\gamma\tilde{\gamma} - \left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 + \left[\frac{\omega_0 + \tilde{\omega}_0}{2} - \omega\right]^2} \approx \int_{-\infty}^{+\infty} \frac{\omega_c\, d\omega}{\gamma\tilde{\gamma} - \left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 + \left[\frac{\omega_0 + \tilde{\omega}_0}{2} - \omega\right]^2}$$

$$= \frac{\omega_0 + \tilde{\omega}_0}{2\left[\left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 - \gamma\tilde{\gamma}\right]^{1/2}} \text{arctanh} \left[\frac{\frac{\omega_0 + \tilde{\omega}_0}{2} - \omega}{\left[\left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 - \gamma\tilde{\gamma}\right]^{1/2}}\right]\Bigg|_{-\infty}^{+\infty}$$

$$= -\frac{\omega_0 + \tilde{\omega}_0}{\left[\left[\frac{\omega_0 - \tilde{\omega}_0}{2}\right]^2 - \gamma\tilde{\gamma}\right]^{1/2}} .$$ (68)

As imposed by these two cases we have to split the summations with respect to identical and nonidentical sets of summation indexes, when we return to Eqs. (64) and (65),

$$|a_{\beta l's J'M_J'}(\infty)|^2$$

$$= \left|\frac{eA}{c}\right|^2 \frac{1}{\hbar(2c\pi c)^3}$$

$$\times \left[\sum_{\alpha,l,m_l}\sum_{J,M_J}|B_{\alpha l m_2}|^2(-1)^{2(l-s+M_J)}(2J+1)\begin{bmatrix}l & s & J\\m_l & m_s & -M_J\end{bmatrix}^2\right.$$

$$\times \pi\frac{(\omega_{\alpha l J,\beta l'J'})^3}{\Gamma_{\alpha l J}/2\hbar}\int_\Omega|\langle\beta l's J'M_J'|\epsilon\cdot\mathbf{r}|\alpha l s J M_J\rangle|^2 d\Omega$$

$$- \sum_{\alpha,l,m_l}\sum_{\tilde\alpha,\tilde l,\tilde m}\sum_{J,M_J}\sum_{\tilde J,\tilde M_J}(-1)^{l+\tilde l-2s+M_J+\tilde M_J}\sqrt{(2J+1)(2\tilde J+1)}\begin{bmatrix}l & s & J\\m_l & m_s & -M_J\end{bmatrix}$$

$$\times \begin{bmatrix}\tilde l & s & \tilde J\\\tilde m_l & m_s & -\tilde M_J\end{bmatrix}\frac{\omega_{\alpha l J,\beta l'J'}\omega_{\tilde\alpha\tilde l\tilde J,\beta l'J'}(\omega_{\alpha l J,\beta l'J'}+\omega_{\tilde\alpha\tilde l\tilde J,\beta l'J'})}{\left[\left[\dfrac{\omega_{\alpha l J,\beta l'J'}-\omega_{\tilde\alpha\tilde l\tilde J,\beta l'J'}}{2}\right]^2-\dfrac{\Gamma_{\alpha l J}\Gamma_{\tilde\alpha\tilde l\tilde J}}{4\hbar^2}\right]^{1/2}}$$

$$\left.\times\int_\Omega\mathrm{Re}(B_{\alpha l m_l}B^*_{\tilde\alpha\tilde l\tilde m_l}\langle\beta l's J'M_J'|\epsilon\cdot\mathbf{r}|\alpha l s J M_J\rangle\langle\beta l's J'M_J'|\epsilon\cdot\mathbf{r}|\tilde\alpha\tilde l s\tilde J\tilde M_J\rangle^*)d\Omega\right]. \tag{69}$$

The integration over the frequenies has brought us to a point where the computational haze disappears and the target of our study becomes clearly visible: To what extent does the original spin orientation determine the asymptotic population of the final state?

For restoring the original spin orientation, the applicability of Eq. (33) is a necessary condition. As a close look at Eq. (69) shows, Eq. (33) cannot be applied, however, because its use is being blocked by the dependences on J and $\tilde J$ of the frequencies and level widths. These dependences are caused by the spin-orbit interaction in the first place: According to Eq. (37)

$$\omega_{\alpha l J,\beta l'J'}=\omega_{\alpha l,\beta l'}+\Omega_{\alpha l J}-\Omega_{\beta l'J'}$$

$$=\omega_{\alpha l,\beta l'}\left[1+\frac{\Omega_{\alpha l J}-\Omega_{\beta l'J'}}{\omega_{\alpha l,\beta l'}}\right]. \tag{70}$$

The difference of the fine-structure frequency shifts in the initial and final states is much smaller than the transition frequency between the multiplet centers: Using hydrogenic relations for the energy of the multiplet centers and for the fine-structure shifts,[30] the ratio in Eq. (70) can be expressed by

$$\frac{\Omega_{\chi l J}-\Omega_{\lambda l'J'}}{\omega_{\chi l,\lambda l'}}=(\alpha Z)^2F(\chi l J,\lambda l'J'), \tag{71}$$

where α is the fine-structure constant (not to be confused with the hitherto used index α), Z is the atomic number of the ion, and $|F(\chi l J,\lambda l'J')|\leq0.3$ is a lengthy rational expression of the quantum numbers involved. Since the lifetime is practically equal for all members of a multiplet, the frequency over level width rational in Eq. (69)

(first part) can be approximated by

$$\frac{(\omega_{\chi l J,\lambda l'J'})^3}{\Gamma_{\chi l J}/2\hbar}\approx\frac{(\omega_{\chi l,\lambda l'})^3}{\Gamma_{\chi l}/2\hbar}$$

$$\times[1+3(\alpha Z)^2F(\chi l J,\lambda l'J')+\cdots]. \tag{72}$$

Hence, if we neglect the part depending on J in Eq. (72), we introduce an error of the order $(\alpha Z)^2$ or less, but gain the ability to apply Eq. (33) to the first part of Eq. (69). Aiming at the same target, we now investigate the second part of Eq. (69) where the sets of summation indexes must not be identical. Apart from the nominator which can be handled according to Eqs. (70) and (71), we have a denominator which consists of the square root of the difference between the square of half of the difference of transition frequencies into the same final state and the product of lifetime widths of the excited levels involved. When we apply Eq. (70) to the difference of frequencies, we find by observing Eq. (37)

$$\omega_{\alpha l J,\beta l'J'}-\omega_{\tilde\alpha\tilde l\tilde J,\beta l'J'}=\omega_{\alpha l,\tilde\alpha\tilde l}+\Omega_{\alpha l J}-\Omega_{\tilde\alpha\tilde l\tilde J}. \tag{73}$$

The smallest value of this expression is obtained for $\alpha=\tilde\alpha$ and $l=\tilde l$,

$$\omega_{\alpha l J,\beta l'J'}-\omega_{\alpha l\tilde J,\beta l'J'}=\Omega_{\alpha l J}-\Omega_{\alpha l\tilde J}=\Delta_{\alpha l}. \tag{74}$$

$\Delta_{\alpha l}$ is the frequency equivalent of the fine-structure splitting in the state $|\alpha l\rangle$ which, according to Eqs. (19a) and (19b) does not depend on the total angular momentum. One of our basic assumptions justifying the consecutive

treatment of Sec. II B was that $\Delta_{\alpha l}$ be large compared to the lifetime widths. Under these provisions we admit only a minor error when we omit the product of lifetime widths under the root sign. This is even better justifiable in the general case when the difference of transition frequencies is larger due to $\omega_{\alpha l, \bar{\alpha}\bar{l}} \neq 0$ because of αl and $\bar{\alpha}\bar{l}$ not being simultaneously equal. In this case we can expand $1/(\omega_{\alpha l J, \beta l' J'} - \omega_{\bar{\alpha}\bar{l}\bar{J}, \beta l' J'})$ to first order in $(\Omega_{\alpha l J} - \Omega_{\bar{\alpha}\bar{l}\bar{J}})/\omega_{\alpha l, \bar{\alpha}\bar{l}}$,

$$\frac{1}{\omega_{\alpha l J, \beta l' J'} - \omega_{\bar{\alpha}\bar{l}\bar{J}, \beta l' J'}}$$

$$= \frac{1}{\omega_{\alpha l, \bar{\alpha}\bar{l}}} \left[1 - \frac{\Omega_{\alpha l J} - \Omega_{\bar{\alpha}\bar{l}\bar{J}}}{\omega_{\alpha l, \bar{\alpha}\bar{l}}} + \cdots \right] , \quad (75)$$

and apply Eq. (71).

Using Eqs. (70) and (71) the nominator in the frequency expression of the second part of Eq. (69) can be approximated by

$$(\omega_{\chi l J, \lambda l' J'})^2 \omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'} + \omega_{\chi l J, \lambda l' J'} (\omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'})^2$$

$$\approx (\omega_{\chi l, \lambda l'})^2 \omega_{\bar{\chi}\bar{l}, \lambda l'} \{ 1 + (\alpha Z)^2 [2F(\chi l J, \lambda l' J') + F(\bar{\chi}\bar{l}\bar{J}, \lambda l' J')] + \cdots \}$$

$$+ \omega_{\chi l, \lambda l'} (\omega_{\bar{\chi}\bar{l}, \lambda l'})^2 \{ 1 + (\alpha Z)^2 [F(\chi l J, \lambda l' J') + 2F(\bar{\chi}\bar{l}\bar{J}, \lambda l' J')] + \cdots \} . \quad (76)$$

Hence, we obtain the following approximations for the frequency expression in the second part of Eq. (69): for $\chi = \bar{\chi}$ and $l = \bar{l}$

$$\frac{\omega_{\chi l J, \lambda l' J'} \omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'} (\omega_{\chi l J, \lambda l' J'} + \omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'})}{\left[\left[\frac{\omega_{\chi l J, \lambda l' J'} - \omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'}}{2} \right]^2 - \frac{\Gamma_{\chi l J} \Gamma_{\bar{\chi}\bar{l}\bar{J}}}{4\hbar^2} \right]^{1/2}} \approx 4 \frac{(\omega_{\chi l, \lambda l'})^3}{\Delta_{\chi l}} \{ 1 + \tfrac{3}{2}(\alpha Z)^2 [F(\chi l J, \lambda l' J') + F(\chi l \bar{J}, \lambda l' J')] + \cdots \} \quad (77a)$$

and for χ, l and $\bar{\chi}, \bar{l}$ not simultaneously equal

$$\frac{\omega_{\chi l J, \lambda l' J'} \omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'} (\omega_{\chi l J, \lambda l' J'} + \omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'})}{\left[\left[\frac{\omega_{\chi l J, \lambda l' J'} - \omega_{\bar{\chi}\bar{l}\bar{J}, \lambda l' J'}}{2} \right]^2 - \frac{\Gamma_{\chi l J} \Gamma_{\bar{\chi}\bar{l}\bar{J}}}{4\hbar^2} \right]^{1/2}}$$

$$\approx 2 \left[\frac{(\omega_{\chi l, \lambda l'})^2 \omega_{\bar{\chi}\bar{l}, \lambda l'}}{\omega_{\chi l, \bar{\chi}\bar{l}}} \{ 1 + (\alpha Z)^2 [2F(\chi l J, \lambda l' J') + F(\bar{\chi}\bar{l}\bar{J}, \lambda l' J') - F(\chi l J, \bar{\chi}\bar{l}\bar{J})] + \cdots \} \right.$$

$$\left. + \frac{\omega_{\chi l, \lambda l'} (\omega_{\bar{\chi}\bar{l}, \lambda l'})^2}{\omega_{\chi l, \bar{\chi}\bar{l}}} \{ 1 + (\alpha Z)^2 [F(\chi l J, \lambda l' J') + 2F(\bar{\chi}\bar{l}\bar{J}, \lambda l' J') - F(\chi l J, \bar{\chi}\bar{l}\bar{J})] + \cdots \} \right] . \quad (77b)$$

Since the expressions $F(\mu l J, \nu \bar{l}\bar{J})$ can be positive or negative depending on J and $\bar{J}$ with $|F(\mu l J, \nu \bar{l}\bar{J})| \leq 0.3$, a worst case scenario yields an error of $0.9(\alpha Z)^2$ for Eq. (77a) and $1.2(\alpha Z)^2$ for Eq. (77b) if these expressions are neglected.

With these results we are able to answer the rhetoric question made in context with Eq. (69): The original spin orientation determines the asymptotic population of the final state to an extent of $1 - (\alpha Z)^2$ or better. This is to be understood in the following sense: Neglecting the J, $\bar{J}$, and J' dependences of the frequency expression in Eq. (69), we can benefit from the applicability of Eq. (33) at the expense of inflicting an error of $(\alpha Z)^2$ or less on the actual population of the final state. Dividing the total population into a spin-orientation-conserving part

$$|a^c_{\beta l' s J' M'_J}(\infty)|^2$$

and a nonconserving one

$$|a^{nc}_{\beta l' s J' M'_J}(\infty)|^2$$

we have

$$|a_{\beta l' s J' M'_J}(\infty)|^2 = |a^c_{\beta l' s J' M'_J}(\infty)|^2 + |a^{nc}_{\beta l' s J' M'_J}(\infty)|^2 , \quad (78)$$

with

$$|a^c_{\beta l' s J' M'_J}(\infty)|^2 \approx [1 - (\alpha Z)^2] |a_{\beta l' s J' M'_J}(\infty)|^2 . \quad (79)$$

and explicitly, by applying Eq. (33) to Eq. (69),

$$|a^c_{\beta l'sJ'M_J'}(\infty)|^2 = \left[\frac{eA}{c}\right]^2 \frac{2}{\hbar(2\pi c)^3} \left[\sum_{\alpha,l,m_l} |B_{\alpha l m_l}|^2 \pi \frac{(\omega_{\alpha l,\beta l'})^3}{\Gamma_{\alpha l}/\hbar} \int_\Omega |\langle \beta l'sJ'M_J'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\alpha l m_l s m_s\rangle|^2 d\Omega\right.$$

$$- \sum_{\alpha,l,m_{l'},\bar{m}_l} 2\frac{(\omega_{\alpha l,\beta l'})^3}{\Delta_{\alpha l}} \mathrm{Re}\int_\Omega B_{\alpha l m_l} B^*_{\alpha l \bar{m}_l} \langle \beta l'sJ'M_J'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\alpha l m_l s m_s\rangle$$

$$\times \langle \beta l'sJ'M_J'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\alpha l \bar{m}_l s m_s\rangle^* d\Omega$$

$$- \sum_{\alpha,l,m_l} \sum_{\bar{\alpha},\bar{l},\bar{m}_l} \left[\frac{(\omega_{\alpha l,\beta l'})^2 \omega_{\bar{\alpha}\bar{l},\beta l'}}{\omega_{\alpha l,\bar{\alpha}\bar{l}}} + \frac{\omega_{\alpha l,\beta l'}(\omega_{\bar{\alpha}\bar{l},\beta l'})^2}{\omega_{\alpha l,\bar{\alpha}\bar{l}}}\right]$$

$$\times \mathrm{Re}\int_\Omega B_{\alpha l m_l} B^*_{\bar{\alpha}\bar{l}\bar{m}_l} \langle \beta l'sJ'M_J'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\alpha l m_l s m_s\rangle$$

$$\left.\times \langle \beta l'sJ'M_J'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\bar{\alpha}\bar{l}\bar{m}_l s m_s\rangle^* d\Omega\right]. \tag{80}$$

Bearing in mind Eq. (30) to be applied to the wave function $|\beta l'sJ'M_J'\rangle$ of the final state, we realize that only those components in the final state's wave function can emerge from the electric-dipole transition that have the original spin component. This aspect is even more obvious for transitions into pure spin states like $^2S_{1/2}$ where $|\beta 0\frac{1}{2}\frac{1}{2}M_J\rangle = |\beta 00\frac{1}{2}m_s\rangle$, i.e., $M_J = m_s$. In Secs. II C 1 and II C 2 we will take a closer look at these cases.

1. Direct transitions into pure spin states

The form of Eq. (80) makes it particularly simple to calculate transitions between pure spin states. For the time being we must postulate that the wave function of the final pure spin state to be an eigenfunction of the total ionic Hamiltonian which includes spin-orbit interaction. Applying the Wigner-Eckart theorem[23] we will find the matrix elements to be of the following form:

$$\langle \beta l'm_l's m_s'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\alpha l m_l s m_s\rangle = \delta_{m_s'm_s}\sum_q (-1)^q \epsilon_{-q}(-1)^{l'-m_l'}\begin{bmatrix} l' & 1 & l \\ -m_l' & q & m_l \end{bmatrix}\langle \beta l'\|r\|\alpha l\rangle. \tag{81}$$

In the most general case of products of matrix elements as encountered in the last part of Eq. (80) this leads to

$$\int_\Omega \langle \beta l'm_l's m_s'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\alpha l m_l s m_s\rangle \langle \beta l'm_l's m_s'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\bar{\alpha}\bar{l}\bar{m}_l s m_s\rangle^* d\Omega$$

$$= \delta_{m_s'm_s}\sum_{p,q}(-1)^{p+q}\begin{bmatrix} l' & 1 & \bar{l} \\ -m_l' & p & \bar{m}_l \end{bmatrix}\begin{bmatrix} l' & 1 & l \\ -m_l' & q & m_l \end{bmatrix}\langle \beta l'\|r\|\alpha l\rangle\langle \beta l'\|r\|\bar{\alpha}\bar{l}\rangle^* \int_\Omega (\epsilon_{-p})^*\epsilon_{-q}d\Omega$$

$$= \frac{4\pi}{3}\delta_{m_s'm_s}\sum_q \begin{bmatrix} l' & 1 & l \\ -m_l' & q & m_l \end{bmatrix}\begin{bmatrix} l' & 1 & \bar{l} \\ -m_l' & q & \bar{m}_l \end{bmatrix}\langle \beta l'\|r\|\alpha l\rangle\langle \beta l'\|r\|\bar{\alpha}\bar{l}\rangle^* \tag{82}$$

because

$$\int_\Omega (\epsilon_{-p})^*\epsilon_{-q}d\Omega = \frac{4\pi}{3}\delta_{pq}. \tag{83}$$

Substituting expressions like Eq. (82) for the matrix elements in Eq. (80) the conservation of spin orientation is obvious from $\delta_{m_s'm_s}$. The resulting expression becomes more handy if we do not ask for the individual but for the total population in the state $|\beta l'\rangle$. This means summing over m_l' and m_s' and applying one of the orthogonality relations for the $3j$ symbols,[23]

$$\sum_{m_l'm_s'}\int_\Omega \langle \beta l'm_l's m_s'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\alpha l m_l s m_s\rangle \langle \beta l'm_l's m_s'|\boldsymbol{\epsilon}\cdot\mathbf{r}|\bar{\alpha}\bar{l}\bar{m}_l s m_s\rangle^* d\Omega = \frac{4\pi}{3}\delta_{l\bar{l}}\delta_{m_l\bar{m}_l}\frac{\langle \beta l'\|r\|\alpha l\rangle\langle \beta l'\|r\|\bar{\alpha}l\rangle^*}{2l+1}. \tag{84}$$

With the help of Eq. (84) we obtain for the total population

$$\sum_{m_l',m_s'} |a^c_{\beta l'm_l'sm_s'}(\infty)|^2 = \left[\frac{eA}{c}\right]^2 \frac{8\pi}{3\hbar(2\pi c)^3}\left[\sum_{\alpha,l,m_l}\left[\pi\frac{(\omega_{\alpha l,\beta l'})^3}{\Gamma_{\alpha l}/\hbar} - 2\frac{(\omega_{\alpha l,\beta l'})^3}{\Delta_{\alpha l}}\right]|B_{\alpha lm_l}|^2\frac{|\langle\beta l'\|r\|\alpha l\rangle|^2}{2l+1}\right.$$

$$-\sum_{\tilde\alpha\neq\alpha lm_l}\left[\frac{(\omega_{\alpha l,\beta l'})^2\omega_{\tilde\alpha l,\beta l'}}{\omega_{\alpha l,\tilde\alpha l}} + \frac{\omega_{\alpha l,\beta l'}(\omega_{\tilde\alpha l,\beta l'})^2}{\omega_{\alpha l,\tilde\alpha l}}\right]$$

$$\left.\times\mathrm{Re}\left[B_{\alpha lm_l}B^*_{\tilde\alpha lm_l}\frac{\langle\beta l'\|r\|\alpha l\rangle\langle\beta l'\|r\|\tilde\alpha l\rangle^*}{2l+1}\right]\right]. \tag{85}$$

Equation (85) is the most suited relation to calculate the spin population in a final $^2S_{1/2}$ state, bearing in mind that only $m_s'=m_s$ is being population.

2. Direct transitions into fine-structure states

To avoid unnecessary summations and to be able to apply relations deduced in Sec. II C 1 we represent the final fine-structure state by a superposition of spin states according to Eq. (30). Then, we obtain for the matrix element with the help of Eq. (81),

$$\langle\beta l'sJ'M_J'|\boldsymbol\epsilon\cdot\mathbf{r}|\alpha lm_lsm_s\rangle = (-1)^{l'-s+M_J'}\sqrt{2J'+1}\sum_{m_l',q}\begin{bmatrix}l' & s & J' \\ m_l' & m_s & -M_J'\end{bmatrix}(-1)^q\epsilon_{-q}(-1)^{l'-m_l'}$$

$$\times\begin{bmatrix}l' & 1 & l \\ -m_l' & q & m_l\end{bmatrix}\langle\beta l'\|r\|\alpha l\rangle. \tag{86}$$

Using Eq. (83) we calculate for the counterpart of Eq. (82),

$$\int_\Omega\langle\beta l'sJ'M_J'|\boldsymbol\epsilon\cdot\mathbf{r}|\alpha lm_lsm_s\rangle\langle\beta l'sJ'M_J'|\boldsymbol\epsilon\cdot\mathbf{r}|\tilde\alpha\tilde l\tilde m_lsm_s\rangle^*d\Omega$$

$$=\frac{4\pi}{3}(2J'+1)\sum_{m_l',\tilde m_l'}\sum_q\begin{bmatrix}l' & s & J' \\ m_l' & m_s & -M_J'\end{bmatrix}\begin{bmatrix}l' & s & J' \\ \tilde m_l' & m_s & -M_J'\end{bmatrix}\begin{bmatrix}l' & 1 & l \\ -m_l' & q & m_l\end{bmatrix}\begin{bmatrix}l' & 1 & \tilde l \\ -\tilde m_l' & q & \tilde m_l\end{bmatrix}$$

$$\times\langle\beta l'\|r\|\alpha l\rangle\langle\beta l'\|r\|\tilde\alpha\tilde l\rangle^*(-1)^{2l'-m_l'-\tilde m_l'}. \tag{87}$$

Following the same route as before we ask for the total population which we attain by summing over J' and M_J'. This makes possible the application of the second orthogonality relation for the $3j$ symbols[23] to the first pair of $3j$ symbols generating $\delta_{m_l'\tilde m_l'}$. Then, the remaining summation over m_l' and q in the second pair of $3j$ symbols is nothing other than the other orthogonality relation for the $3j$ symbols that we used to arrive at Eq. (84), and hence

$$\sum_{J',M_J'}\int_\Omega\langle\beta l'sJ'M_J'|\boldsymbol\epsilon\cdot\mathbf{r}|\alpha lm_lsm_s\rangle\langle\beta l'sJ'M_J'|\boldsymbol\epsilon\cdot\mathbf{r}|\tilde\alpha\tilde l\tilde m_lsm_s\rangle^*d\Omega = \frac{4\pi}{3}\delta_{l\tilde l}\delta_{m_l\tilde m_l}\frac{\langle\beta l'\|r\|\alpha l\rangle\langle\beta l'\|r\|\tilde\alpha\tilde l\rangle^*}{2l+1}. \tag{88}$$

This is exactly what we had found in Eq. (84) and shows that the part of the total asymptotic population that is conserving the spin orientation is independent of the representation

$$\sum_{J',M_J'}|a^c_{\beta l'sJ'M_J'}(\infty)|^2 = \sum_{m_l',m_s'}|a^c_{\beta l'm_l'sm_s'}(\infty)|^2. \tag{89}$$

This can also be understood as a hint to look beyond individual asymptotic amplitudes. Due to Eq. (89) expression Eq. (85) reflects the asymptotic probability of finding the fine-structure state $|\beta l'sJ'M_J'\rangle$ realized. The fact, however, that the spin orientation is preserved for this part indicates that we must not look at the fine-structure states separately. Rather, we have to view them as a superposition of fine-structure states that results from an unchanged [to order of $1-(\alpha Z)^2$] spin orientation as in Eq.

(2). In setting up this superposition we have to bear in mind that we could only arrive at the equivalence Eq. (89) by absolute squaring. This was possible at the expense of the phase of the amplitudes. So we have to attach unknown phases to the components of the superposition

$$\psi^\infty_{\beta l'}|sm_s\rangle = \frac{1}{N}\sum_{J',M_J'}[|a^c_{\beta l'sJ'M_J'}(\infty)|^2]^{1/2}$$

$$\times e^{i\phi_{\beta l'J'M_J'}}|\beta l'sJ'M_J'\rangle. \tag{90}$$

$1/N$ is the normalization factor where N^2 is given by Eq. (85). The relative phases can be found from orthogonality relations. From Eq. (89) we can directly infer another equivalent representation

$$\psi^{\infty}_{\beta l'}|sm_s\rangle = \frac{1}{N}\sum_{m'_l}[\,|a^{c}_{\beta l'm'_l sm_s}(\infty)|^2]^{1/2}$$

$$\times e^{i\phi_{\beta l'm'_l}}|\beta l'm'_l sm_s\rangle \,. \tag{91}$$

Thus, obviously,

$$\psi^{\infty}_{\beta l'} = \frac{1}{N}\sum_{m'_l}[\,|a^{c}_{\beta l'm'_l sm_s}|^2]^{1/2}e^{i\phi_{\beta l'm'_l}}|\beta l'm'_l\rangle \,. \tag{92}$$

As a result we can state that the initial superposition of pure spin states $|\alpha lm_l sm_s\rangle$ is transformed in direct electric-dipole transitions into a superposition of final pure spin states $|\beta l'm'_l sm_s\rangle$ with the spin orientation conserved to order of $1-(\alpha Z)^2$.

III. CONCLUSION

We have shown that in direct electric-dipole transitions the conservation of spin orientation is violated by spin-orbit interaction only to an extent of the order of $(\alpha Z)^2$.

Even this value, however, is only an upper limit for the following reason: It has been determined by the demand to fully restore the initial pure spin function. The omitted terms, however, depend on J and $\tilde{J}$ and involve matrix elements that contain wave functions with either spin orientation of which only the "wrong" orientation violates the conservation of spin orientation.

From these results we can expect that the initial spin orientation will be largely conserved, even in moderate cascades of not-too-heavy ions. This problem will be dealt with in a forthcoming paper.

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