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Significance of time-reversal symmetry for time-resolved measurements of hydrogenic and other atomic observables*

Gerald Gabrielse†
University of Chicago, Chicago, Illinois 60637
and Argonne National Laboratory, Argonne, Illinois 60439
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Time-resolved measurements of atomic observables are analyzed using a Liouville space formulation and a Hermitian unit tensor base. This approach makes it possible to distinguish cleanly the symmetries of a formation and/or excitation process completed by time $t=0$, a time evolution under experimental control between $t=0$ and $t=t$, and a measurement at $t=t$, even for hydrogenic observables. Each observable is labeled by a time-reversal quantum number, allowing exploration for the first time of the close relationship between time-reversal symmetry and the time evolution of atomic observables. The experimental reconstruction of atomic observables (at $t=0$) from subsequent time-resolved measurements of the anisotropy and polarization of emitted electric dipole photons is discussed. Hydrogenic observables are stressed and the use of strong fields is included, thus generalizing Fano and Macek's approach.

I. INTRODUCTION

Recent measurements of electric dipole radiation from hydrogenic states[1-12] prompted us to extend Fano and Macek's treatment of $E1$ radiation from nonstationary, nonhydrogenic states[13] to include hydrogenic states decaying in the possible presence of strong external fields. The hydrogen problem is much more complicated owing to the large number of $t=0$ observables which determine the subsequent unresolved emission of $E1$ photons. Many source observables are involved in addition to the orientation vector and the alignment tensor of Ref. 13. Frequently, in fact, strong laboratory fields must be used to sort out the large number of source observables. The numerical calculations required by strong fields further complicate the analysis and planning of hydrogen experiments.

We analyze such time-resolved measurements in three stages: A formation and/or excitation process which is completed by $t=0$, the time evolution between $t=0$ and $t=t$ in the possible presence of strong laboratory fields, and a measurements at time t. The clean separation of these three stages is possible because we work in Liouville space,[14] whose vectors represent the operators of the usual Hilbert space of quantum mechanics (such as the density operator and the Hamiltonian). We are able to focus upon the spatial and time-reversal symmetries of each stage (without explicit numerical calculations) because we use a Hermitian unit tensor base. Projections of these unit tensors upon the $t=0$ density operator are the observables which determine the $t=0$ state. Components of a Liouville evolution operator (in this base) describe the time evolution between $t=0$ and $t=t$. Projections of a Hermitian detection operator on the Hermitian base characterize the $t=t$ measurement.

A new feature of our analysis is our use for the first time of time-reversal symmetry to study time evolution. Each of the Hermitian unit tensors defined in Sec. II (building on the work of Fano,[15] Lombardi,[16] and Omont[17]) is labeled by a time-reversal eigenvalue. We use these eigenvalues in Sec. III to classify the form of components of a Liouville space evolution operator. We focus in particular upon the experimental reconstruction of hydrogenic observables at $t=0$ made possible by subsequent time-resolved measurements of the anisotropy and polarization of emitted $E1$ photons. We are, however, able to provide insight into the time evolution of hydrogenic and nonhydrogenic observables alike. In a later paper we shall show that our approach can also be used to analyze the time evolution which occurs during electron-atom collisions.

II. HERMITIAN UNIT TENSOR BASE

A. Definitions

We define the Hermitian unit tensor base using a two-step unitary transformation of irreducible spherical tensors $T^k_q(\alpha F, \beta G)$ in the standard representation[17]:

$$T^k_q(\alpha F, \beta G) = \sum_{MN} (-1)^{G-N} \left| \alpha FM \right\rangle \left\langle \beta GN \right| \left\langle FM, G-N \right| kq \rangle \,. \tag{2.1}$$

Both the state vectors $\left| \alpha FM \right\rangle$ and the spherical tensors are eigenfunctions of the angular-momentum operators $\vec{\mathbf{F}}^2$ and F_z. Omont summarizes the

many equivalent designations of these tensors in the literature.[17]

To emphasize the analogy between unit tensors in Liouville space and unit state vectors we shall frequently employ a bra and ket notation similar to that used by Baranger.[18] The spherical tensors of (2.1) are designated by $|(\alpha F)(\beta G)^\dagger; kq\rangle$; the Hermitian conjugates by $\langle(\alpha F)(\beta G)^\dagger; kq|$. A bra operator joined to a ket operator represents the trace of the product of the two operators. The unit spherical tensors are thus orthonormal in the sense that

$$\langle(\alpha F)(\beta G)^\dagger; kq\,|\,(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^\dagger; \tilde{k}\tilde{q}\rangle = \delta_{kq,\tilde{k}\tilde{q}}\delta_{\alpha F,\tilde{\alpha}\tilde{F}}\delta_{\beta G,\tilde{\beta}\tilde{G}}\,. \tag{2.2}$$

Transformations of vectors in Liouville space are written reminiscent of the transformation of state vectors. Rotations[19] by Euler angles α, β, and γ, for example, are written

$$R(\alpha\beta\gamma)\,|(\alpha F)(\beta G)^\dagger; kq\rangle = \sum_{\tilde{q}} |(\alpha F)(\beta G)^\dagger; k\tilde{q}\rangle\langle k\tilde{q}\,|R(\alpha\beta\gamma)\,|kq\rangle\,, \tag{2.3}$$

using the same rotation matrix elements as for state vectors. These are expressed below in terms of the real Wigner rotation matrices, $d^k_{\tilde{q}q}(\beta)$;

$$\langle k\tilde{q}\,|R(\alpha\beta\gamma)\,|kq\rangle = e^{-i\tilde{q}\alpha}d^k_{\tilde{q}q}(\beta)e^{-iq\gamma}\,. \tag{2.4}$$

Following Fano,[15] we first replace each standard spherical tensor component by a linear combination which is an eigenfunction of $R_y(\pi)$ (rotations of π about $\hat{y}$) rather than an eigenstate of F_z:

$$|(\alpha F)(\beta G)^\dagger; kq\epsilon\rangle = h_{k\epsilon}(q,0)[\epsilon(-1)^{k+q}\,|(\alpha F)(\beta F)^\dagger; kq\rangle + |(\alpha F)(\beta G)^\dagger; k-q\rangle] \tag{2.5}$$

with $q \geq 0$, $\epsilon = \pm 1$,

$$h_{k\epsilon}(a,b) = \left(\frac{\epsilon(-1)^k}{2(1+\delta_{a,b})}\right)^{1/2}, \tag{2.6}$$

and $(-1)^{1/2}$ interpreted as i. These operators differ from those of Fano by a factor of $(-1)^k$ so that

$$R_y(\pi)\,|(\alpha F)(\beta G)^\dagger; kq\epsilon\rangle = \epsilon\,|(\alpha F)(\beta G)^\dagger; kq\epsilon\rangle\,. \tag{2.7}$$

When $q=0$ they vanish unless $\epsilon=(-1)^k$ in which case they reduce to $q=0$ spherical tensors. They are orthonormal in the sense of (2.2) and are Hermitian when $\alpha F=\beta G$, the case considered by Fano. They transform under rotations by the real matrices

$$\langle k\tilde{q}\epsilon\,|R\,|kq\epsilon\rangle = \frac{(-1)^{\tilde{q}+q}}{[(1+\delta_{\tilde{q}0})(1+\delta_{q0})]^{1/2}}[d^k_{\tilde{q}q}(\beta)\cos(\tilde{q}\alpha+q\gamma) + \epsilon(-1)^{k+q}d^k_{\tilde{q}-q}(\beta)\cos(\tilde{q}\alpha-q\gamma)]\,, \tag{2.8}$$

$$\langle k\tilde{q}-\epsilon\,|R\,|kq\epsilon\rangle = \frac{\epsilon(-1)^{k+\tilde{q}+q}}{[(1+\delta_{\tilde{q}0})(1+\delta_{q0})]^{1/2}}[d^k_{\tilde{q}q}(\beta)\sin(\tilde{q}\alpha+q\gamma) + \epsilon(-1)^{k+q}d^k_{\tilde{q}-q}(\beta)\sin(\tilde{q}\alpha-q\gamma)]\,. \tag{2.9}$$

If we further assume that the state vectors $|\alpha FM\rangle$ have definite parity π_α, the tensor components of (2.5) are eigenfunctions of the parity operator P,

$$P\,|(\alpha F)(\beta G)^\dagger; kq\epsilon\rangle = \pi_\alpha\pi_\beta\,|(\alpha F)(\beta G)^\dagger; kq\epsilon\rangle\,. \tag{2.10}$$

Following Omont[17] we further replace each "real standard" component of (2.5) by a linear combination which is Hermitian even when $\alpha F \neq \beta G$,

$$|(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle = h_{kp}(\alpha F,\beta G)[\,|(\alpha F)(\beta G)^\dagger; kq\epsilon\rangle + p(-1)^{G-F+k}\,|(\beta G)(\alpha F)^\dagger; kq\epsilon\rangle]\,, \tag{2.11}$$

using the normalization constant of (2.6). These Hermitian unit tensors undergo the same spatial transformations (2.7)–(2.10) as the real standard components of (2.5). We further take the state vectors $|\alpha FM\rangle$ used to define standard spherical tensors in (2.1) to be real[20] in the sense that the antilinear time-reversal operator K transforms them in the same was as does $R_y(\pi)$. The quantum number p is then the time-reversal eigenvalue with possible values +1 and −1,

$$K\,|(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle = p\,|(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle\,. \tag{2.12}$$

This eigenvalue will play a crucial role in our subsequent analysis of time evolution. When $\alpha F = \beta G$ the Hermitian unit tensors vanish unless $p = (-1)^k$; that is, the time-reversal eigenvalue is determined by the tensor rank. A familiar consequence is the inability of an elementary particle (i.e., $\alpha F=\beta G$) to possess an electric dipole moment (i.e., $p=1$, $k=1$). The Hermitian unit tensors are orthonormal in all quantum numbers providing that the enumeration of states includes $(\alpha F,\beta G)$ or $(\beta G,\alpha F)$, but not both. Care must be taken here since $|(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle$ can differ in sign from $|(\beta G)(\alpha F)^\dagger; kq\epsilon p\rangle$. All summations used in this paper will assume such an enumeration un-

less specifically indicated. The Hermitian unit tensors of (2.11) differ slightly from those defined (but not used) by Omont.[17] Our definition simplifies symmetry relations and interpretations.

B. Density operator

The operators we encounter in the rest of this paper are treated as vectors in Liouville space and expanded in the orthonormal Hermitian base. The density operator is one such vector of particular interest. Its expansion is

$$|\rho\rangle = \sum |(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle\langle(\alpha F)(\beta G)^\dagger; kq\epsilon p|\rho\rangle . \tag{2.13}$$

The summation runs over $k \geq 0$, $0 \leq q \leq k$, $\epsilon = \pm 1$, $p = \pm 1$, and includes all unordered pairs $(\alpha F, \beta G)$ as discussed in the last paragraph. Because $|\rho\rangle$ is Hermitian, the projections of the Hermitian unit tensors upon $|\rho\rangle$ are real. When a standard spherical tensor base is used, this Hermiticity manifests itself instead as a relationship between complex density operator components. Each of our projections on the density operator is thus a real observable, in the sense that each is the average value of a Hermitian operator:

$$\langle(\alpha F)(\beta G)^\dagger; kq\epsilon p|\rho\rangle = \langle T^k_{q\epsilon p}(\alpha F, \beta G)\rangle . \tag{2.14}$$

$T^k_{q\epsilon p}(\alpha F, \beta G)$ is just the more common way of writing $|(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle$. The observables are linear combinations of either real or imaginary parts of the density matrix elements in the Hilbert space of state vectors depending on whether $\epsilon = p$ or $\epsilon = -p$. Specifically,

$$\langle(\alpha F)(\beta G)^\dagger; kq\epsilon p|\rho\rangle = \sum_{MN} (-1)^{G-N} \frac{\epsilon(-1)^{k+q}\langle FM, G-N|kq\rangle + \langle FM, G-N|k-q\rangle}{(1+\delta_{q0})^{1/2}(1+\delta_{\alpha F,\beta G})^{1/2}} \times [(-1)^k p\ \mathrm{Re}\langle\alpha FM|\rho|\beta GN\rangle\delta_{\epsilon p} + \mathrm{Im}\langle\alpha FM|\rho|\beta GN\rangle\delta_{-\epsilon p}] , \tag{2.15}$$

with Re and Im designating real and imaginary parts. We shall show that considering these observables, these particular linear combinations of ordinary density matrix elements, will provide insight into atomic processes in addition to that gained using elements of the usual density matrix or standard spherical tensor components.[21-22]

C. Explicit constructions

In one sense the observables which specify the density operator require no further interpretation. They are identified by their properties which are readily apparent from their quantum numbers. Often, however, it is useful to identify specific observables as average values of tensors made from familiar vectors, such as the position vector, the momentum vector or the angular-momentum vector. The diagonal operators (i.e., $\alpha F = \beta G$) have long been so interpreted. $T^k_{q\epsilon p}(\alpha F, \alpha F)$ is proportional to the component $F^k_{q\epsilon}$ of the tensor made by coupling k angular-momentum vectors, $\vec{F}$. All diagonal observables are therefore average values of angular-momentum tensor components. Fano and Macek,[13] for example, focused particularly upon the diagonal tensors of rank 1 and 2 (the orientation and alignment) because these exhaust the information available in electric dipole radiation from nonhydrogenic states. An alternative identification of diagonal observables using electric and magnetic multipole moments is also very common. Since $p = (-1)^k$ and $\pi = +1$ for non-vanishing diagonal observables, they are included in the two categories indicated in (2.16) and (2.17) and are proportional to electric or magnetic multipoles, respectively.

Hydrogenic observables have recently been calculated and measured which cannot be so easily identified.[4-5,9-10,25] in particular, the observables $\langle(nL)(n\tilde{L})^\dagger; kq\epsilon p|\rho\rangle$ for which $L \neq \tilde{L}$ cannot be identified as average values of orbital angular-momentum tensors. Half of these observables, those classified in (2.16) and (2.17), can still be identified as electric and magnetic multipoles. The remaining two categories, (2.18) and (2.19), are much less familiar and warrant further study;

$$p = 1, \quad \pi = (-1)^k, \quad \text{electric multipoles} \tag{2.16}$$

$$p = -1, \quad \pi = (-1)^{k+1}, \quad \text{magnetic multipoles} \tag{2.17}$$

$$p = -1, \quad \pi = (-1)^k, \tag{2.18}$$

$$p = 1, \quad \pi = (-1)^{k+1} . \tag{2.19}$$

Tensors in category (2.18) can be constructed, for example, by coupling a rank k position tensor to an orbital angular-momentum vector. A rank 1 example is $\vec{r} \times \vec{L}$. Tensors in category (2.19) can be constructed by coupling a rank $k-1$ position tensor to a second rank orbital angular-momentum tensor. Both of these choices must of course be symmetrized to make Hermitian tensors. Of the many other possible choices a useful variation can be obtained by multiplying our suggestions by powers of the position vector magni-

tude. The vector $\vec{r}\times\vec{L}$, for example, could be replaced by $r^{-2}\vec{r}\times\vec{L}$ and identified as the tangential component of the linear-momentum vector. This is an important quantity which has been measured[4,5,9] but not well understood. Use of the linear-momentum vector in this case,[23-24] or of the time derivative $i[H, r^k_{q\epsilon}]$ of position multipoles more generally,[25] obscures the interpretation since the average value of all of these vanish when small, nonessential, non-Coulomb terms in the Hamiltonian are ignored.

Whichever operator components $Q^k_{q\epsilon}$ are used to identify the unit tensors, their projections upon the Hermitian unit tensors can be simply expressed in terms of reduced matrix elements (using the conventions of Ref. 20),

$$\langle(\alpha F)(\beta G)^\dagger; kq\epsilon p\,|\,Q^k_{q\epsilon}\rangle = h^*_{kp}(\alpha F, \beta G)(2k+1)^{-1/2}[\langle\alpha F\,\|Q^k\|\,\beta G\rangle + p(-1)^{G-F+k}\langle\beta G\,\|Q^k\|\,\alpha F\rangle]\,. \tag{2.20}$$

To be directly useful, $Q^k_{q\epsilon}$ must be Hermitian and and have definite time-reversal symmetry. Its reduced matrix elements must thus satisfy conditions (2.21) and (2.22), respectively:

$$\langle\beta G\,\|Q^k\|\,\alpha F\rangle = (-1)^{G-F}\langle\alpha F\,\|Q^k\|\,\beta G\rangle^*, \tag{2.21}$$

$$\langle\beta G\,\|Q^k\|\,\alpha F\rangle = p(-1)^{G-F+k}\langle\alpha F\,\|Q^k\|\,\beta G\rangle\,. \tag{2.22}$$

D. Direct and irreducible products

We conclude our introduction to Hermitian unit tensors by discussing reducing transformations. So far we have expanded the density operator only in terms of irreducible Hermitian unit tensors. The irreducible base is often very useful for describing a time evolution, for example, that of hydrogenic hyperfine states. Sometimes it is desirable, however, to use instead a reducible direct product of irreducible Hermitian unit tensors from the orbital, electronic spin and nuclear spin bases. For example, when hydrogen hyperfine states are produced from spin-unpolarized hydrogen atoms by way of a spin-independent interaction, the reducible base is desirable because only the orbital observables contain dynamical, nonstatistical information. The projections of these direct product operators upon the density operator are also observables (because the Hermitian operators from the separate spaces commute),

$$\langle[(nL)(\tilde{n}\tilde{L})^\dagger; k_L q_L\epsilon_L p_L][S\tilde{S}^\dagger; k_S q_S\epsilon_S p_S][I\tilde{I}^\dagger; k_I q_I\epsilon_I]\,|\,\rho\rangle = \langle T^{k_L}_{q_L\epsilon_L p_L}(nL, \tilde{n}\tilde{L})T^{k_S}_{q_S\epsilon_S p_S}(S, \tilde{S})T^{k_I}_{q_I\epsilon_I p_I}(I, \tilde{I})\rangle\,, \tag{2.23}$$

and they measure the correlations of orbital, electronic spin and nuclear spin operators.

The transformation which reduces the direct product,

$$\langle(\alpha F)(\tilde{\alpha}\tilde{F})^\dagger; kq\epsilon p\,|\,[(nL)(\tilde{n}\tilde{L})^\dagger; k_L q_L\epsilon_L p_L][S\tilde{S}^\dagger; k_S q_S\epsilon_S p_S][I\tilde{I}^\dagger; k_I q_I\epsilon_I p_I]\rangle \tag{2.24}$$

is real and of course preserves the eigenvalues of P, K, and $R_y(\pi)$ so that

$$p = p_L p_S p_I\,, \tag{2.25}$$

$$\epsilon = \epsilon_L\epsilon_S\epsilon_I\,. \tag{2.26}$$

We will use the simple and obvious relationship (2.25) to advantage in our discussion of time evolution. This important result is obscured by using density-matrix elements or standard spherical tensor components instead of Hermitian unit tensors. The transformation coefficient of (2.24) contains dynamical information in the form of overlaps $\langle n\mathrm{LM}_L, \mathrm{SM}_S, \mathrm{IM}_I\,|\,\alpha FM\rangle$ of the direct product states $|n\mathrm{LM}_L, \mathrm{SM}_S, \mathrm{IM}_I\rangle$ upon $|\alpha FM\rangle$, the eigenstates of the total angular momentum and the Hamiltonian. These projections can therefore only be calculated in general by solving the Schrödinger equation numerically. When a geometric coupling scheme such as $[(\mathrm{LS})JI]F$ is dynamically appropriate, the transformation coeffient (2.24) is proportional to Clebsch-Gordan coefficients and a recoupling coefficient.

III. TIME EVOLUTION OF ATOMIC SYSTEMS

A. Formulation

A measurement at time t determines $\langle D\,|\,\rho(t)\rangle$, the projection of the density operator upon a Hermitian detection operator $|D\rangle$, which identifies the particular measurement. Because we are interested in ascertaining the state of the system at some $t=0$ (e.g., the end of a collision) we use an evolution operator $U(t, 0)$ which transforms $|\rho(0)\rangle$ into $|\rho(t)\rangle$,

$$|\rho(t)\rangle = U(t, 0)\,|\rho(0)\rangle\,. \tag{3.1}$$

This Liouville space statement is of course equivalent to the more familiar but less convenient

$$\rho(t) = u(t, 0)\rho(0)u(t, 0)^\dagger, \tag{3.2}$$

where $u(t, 0)$ describes the evolution of state vectors and satisfies Schrödinger's equation. A measurement at t thus determines $\langle D\,|\,U(t, 0)\,|\,\rho(0)\rangle$.

We expand the measured average value in the Hermitian unit tensor base,

$$\langle D|U(t,0)|\rho(0)\rangle=\sum\langle D|(\alpha F)(\beta G)^{\dagger};kq\epsilon p\rangle\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p|U(t,0)|(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle\langle(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}|\rho(0)\rangle\,, \tag{3.3}$$

using the summation convention discussed earlier. A measurement at t is especially useful when its operator D has only a few nonvanishing components, $\langle D|(\alpha F)(\beta G)^{\dagger};kq\epsilon p\rangle$. Control of the environment between $t=0$ and $t=t$ can similarly ensure that only a manageable number of evolution operator components

$$\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p|U(t,0)|(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle$$

will not vanish. We can therefore learn from (3.3) which measurements at t must be made to determine specific observables at $t=0$,

$$\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p|\rho(0)\rangle\,,$$

including those not accessible to $t=0$ measurements alone. Thus, the measureable $t=0$ observables, the time evolution dynamics, and the role of the measurement at t are clearly and simply distinguished (in the spirit of the Fano-Macek approach) and can be discussed separately. Both spatial and time-reversal symmetries are easily studied owing to our use of the Hermitian unit tensor base.

B. The detection operator for electric dipole radiation

The unnormalized detection operator for $E1$ radiation,

$$D=\sum_{f,\hat{\epsilon}}\hat{\epsilon}\cdot\vec{d}\,|f\rangle\langle f|\,\hat{\epsilon}^{*}\cdot\vec{d}\,, \tag{3.4}$$

is so familiar[26] that we will discuss it only enough to reveal its time-reversal properties and facilitate comparison with experiment. The sum is over spectroscopically unresolved atomic final states $|f\rangle$, and over the detected photon polarization $\hat{\epsilon}$ (not to be confused with the quantum number ϵ), $\vec{d}$ is the atomic electric dipole operator and we assume that $\sum|f\rangle\langle f|$ is a scalar. The nonvanishing projections of this detection operator upon the Hermitian unit tensors,

$$\langle D|(\alpha F)(\beta G)^{\dagger};kq\epsilon p\rangle=2(-1)^{F+k+G}[1+\delta_{\alpha F,\beta G}]^{-1/2}S^{k}_{q\epsilon}(\theta,\phi,\hat{\epsilon})\sum_{\alpha_f F_f}\langle\alpha F\|d^{1}\|\alpha_f F_f\rangle\langle\alpha_f F_f\|d^{1}\|\beta G\rangle\begin{Bmatrix}F & k & G\\ 1 & F_f & 1\end{Bmatrix}, \tag{3.5}$$

are of even parity (i.e., $\pi_\alpha=\pi_\beta$), satisfy electric dipole selection rules for transitions from αF and βG to $\alpha_f F_f$, and most important for our purposes satisfy

$$p=(-1)^{k}\,. \tag{3.6}$$

The photon tensors $S^{k}_{q\epsilon}(\theta,\phi)$ depend upon the photon direction given by θ and ϕ and the polarization detected. They are tabulated in Table I for the four easily measured Stokes parameters[27,28] (referred here to the $\hat{\theta}$ axis of a spherical coordinate system with $\hat{r}$ being the propagation direction for the detected photons), since measurement of these exhausts the information carried by photons of a given wave vector. Fano and Macek[13] avoided calculating the electric dipole reduced matrix elements by considering only cases where the sum over $\alpha_f F_f$ reduces to a single term. The reduced matrix elements can then be factored out for all k, q, and ϵ leaving only the $6-j$ symbol and the phase. This shortcut is not always available, particularly for the decay of hydrogenic states.

We have found Table I to be very useful in planning experiments. Notice that eight of the nine distinguishable photon tensors can be determined solely from the ϕ dependence of measured Stokes parameters for photons traveling perpendicular to z (i.e., $\theta=\frac{1}{2}\pi$). When the radiation comes from an even-parity density operator component (such as when radiation from a single multiplet is spectroscopically resolved) and when the radiating state has reflection symmetry in the xz plane, then only the five average values considered by Fano and Macek are nonzero. All of these can be determined from the ϕ dependence of the Stokes parameters. We have used this "ϕ-rotation" technique to study the orientation and alignment produced in fast ions scattered from solid surfaces at grazing angles[29] and that produced in fast ions leaving carbon target foils.[30] The effective photon detection angle ϕ was changed by rotating the reflection symmetry plane about the z axis. No rotation of the optical system was thus required.

C. Time evolution via scalar Hamiltonians

We begin our study of time evolution symmetries by displaying the evolution operator components

TABLE I. The photon tensor components for the Stokes parameters.

	I	M	C	S
S^0_{01}	$-\frac{2}{\sqrt{3}}$	0	0	0
S^1_{0-1}	0	0	0	$\sqrt{2}\cos(\theta)$
S^1_{11}	0	0	0	$\sqrt{2}\sin(\theta)\sin(\phi)$
S^1_{1-1}	0	0	0	$\sqrt{2}\sin(\theta)\cos(\phi)$
S^2_{01}	$-\frac{1}{2\sqrt{6}}[1+3\cos(2\theta)]$	$\frac{1}{2}\frac{3}{\sqrt{2}}[1-\cos(2\theta)$	0	0
S^2_{11}	$-\frac{1}{\sqrt{2}}\sin(2\theta)\cos(\phi)$	$-\frac{1}{\sqrt{2}}\sin(2\theta)\cos(\phi)$	$\sqrt{2}\sin(\theta)\sin(\phi)$	0
S^2_{1-1}	$-\frac{1}{\sqrt{2}}\sin(2\theta)\sin(\phi)$	$-\frac{1}{\sqrt{2}}\sin(2\theta)\sin(\phi)$	$-\sqrt{2}\sin(\theta)\cos(\phi)$	0
S^2_{21}	$-\frac{1}{2\sqrt{2}}[1-\cos(2\theta)]\cos(2\phi)$	$\frac{1}{2\sqrt{2}}[3+\cos(2\theta)]\cos(2\phi)$	$-\sqrt{2}\cos(\theta)\sin(2\phi)$	0
S^2_{2-1}	$-\frac{1}{2\sqrt{2}}[1-\cos(2\theta)]\sin(2\phi)$	$\frac{1}{2\sqrt{2}}[3+\cos(2\theta)]\sin(2\phi)$	$\sqrt{2}\cos(\theta)\cos(2\phi)$	0

for systems developing from $t=0$ to $t=t$ via a scalar Hamiltonian:

$$\langle(\alpha F)(\beta G)^\dagger; kq\epsilon\tilde{p}\,|\,U(t,0)\,|\,(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle = \begin{cases}\cos[\omega(\alpha F)-\omega(\beta G)]t, & \tilde{p}=p\\ \tilde{p}(-1)^k\sin[\omega(\alpha F)-\omega(\beta G)]t, & \tilde{p}=-p\,.\end{cases} \tag{3.7}$$

Components which preserve the time-reversal quantum number oscillate as the cosines of eigenfrequency differences. Components which do not, oscillate as sine functions and thus vanish at $t=0$. In Sec. III F we shall show that an exponential factor,

$$\exp\{-\tfrac{1}{2}[\Gamma(\alpha F)+\Gamma(\beta G)]t\}\,,$$

containing the appropriate decay widths can be multiplied into (3.7) to describe most decaying systems.

Actual measurements could include an integral of (3.7) over time, weighted by the detector's time resolution. It is instructive to consider the case of no detector time resolution at all. We integrate (3.7) with decay widths included to obtain

$$\int_0^\infty \langle(\alpha F)(\beta G)^\dagger; kq\epsilon\tilde{p}\,|\,U(t,0)\,|\,(\alpha F)(\beta G)^\dagger; kq\epsilon p\rangle dt = \{[\omega(\alpha F)-\omega(\beta G)]^2+\tfrac{1}{4}[\Gamma(\alpha F)+\Gamma(\beta G)]^2\}^{-1} \times\begin{cases}\frac{1}{2}[\Gamma(\alpha F)+\Gamma(\beta G)], & \tilde{p}=p\\ (-1)^k\tilde{p}[\omega(\alpha F)-\omega(\beta G)], & \tilde{p}=-p\,.\end{cases} \tag{3.8}$$

The time integration weights the $\tilde{p}=-p$ components over the $\tilde{p}=p$ components by a ratio of a frequency splitting over a decay width. In so far as (3.7) is approximately true for hydrogenic decay within electric fields (Sec. III E) this weighting provides an important constraint upon measurements of the $n=2$ density operator for hydrogen excited by electron impact. The electric dipole moments

$$\langle(2s)(2p)^\dagger; 1q\epsilon 1\,|\,\rho(0)\rangle$$

is much easier to extract from time integrated Lyman α intensity measurements in the presence of a laboratory electric field than are the components

$$\langle(2s)(2p)^\dagger; 1q\epsilon -1\,|\,\rho(0)\rangle\,.$$

Measurements of these components following helium-hydrogen collisions have already been limited by this constraint.[11]

We can immediately apply (3.7)–(3.8) to $E1$ radiation measurements. The detection operator components vanish unless $\tilde{p}=(-1)^k$. Cosine and sine oscillations in $E1$ radiation measurements are therefore associated with $t=0$ observables for which $p=(-1)^k$ and $(-1)^{k+1}$, respectively. This separation of the $t=0$ components with different time-reversal quantum numbers might serve to detect the effect of interactions which violate time-reversal invariance.

To be more concrete, we consider the $E1$ radiation from an $(JI)F$ coupled atom. We assume initially that the atom is unpolarized with respect to nuclear spin at $t=0$ and that final-state hyperfine

structure is not resolved. After the appropriate transformations (Sec. IID) and trace evaluations we find

$$\langle(\alpha J)(\tilde{\alpha}\tilde{J})^\dagger; kq\epsilon(-1)^k \,|\, U(t,0) \,|\, (\alpha J)(\tilde{\alpha}\tilde{J})^\dagger; kq\epsilon p\rangle$$

$$= \sum_{F\tilde{F}} \frac{(2F+1)(2\tilde{F}+1)}{2I+1} \begin{Bmatrix} \tilde{F} & F & k \\ J & \tilde{J} & I \end{Bmatrix}^2 \begin{cases} \cos[\omega(\alpha JIF) - \omega(\tilde{\alpha}\tilde{J}I\tilde{F})]t, & p=(-1)^k \\ \sin[\omega(\alpha JIF) - \omega(\tilde{\alpha}\tilde{J}I\tilde{F})]t, & p=(-1)^{k+1} \end{cases} . \tag{3.9}$$

This sum and the others in this section are restricted only by the requirement that the levels summed over contribute to the spectroscopically unresolved radiation. If the atom is also $(LS)J$ coupled and unpolarized with respect to electron spin at $t=0$, and if final-state fine structure is also not resolved, then,

$$\langle(nL)(\tilde{n}\tilde{L})^\dagger; kq\epsilon(-1)^k \,|\, U(t,0) \,|\, (nL)(\tilde{n}\tilde{L})^\dagger; kq\epsilon p\rangle = \sum_{J\tilde{J},F\tilde{F}} \frac{(2F+1)(2\tilde{F}+1)(2J+1)(2\tilde{J}+1)}{(2I+1)(2S+1)} \begin{Bmatrix} \tilde{F} & F & k \\ J & \tilde{J} & I \end{Bmatrix}^2 \begin{Bmatrix} \tilde{J} & J & k \\ L & \tilde{L} & S \end{Bmatrix}^2$$

$$\times \begin{cases} \cos[\omega(nLSJIF) - \omega(\tilde{n}\tilde{L}S\tilde{J}I\tilde{F})]t, & p=(-1)^k \\ \sin[\omega(nLSJIF) - \omega(\tilde{n}\tilde{L}S\tilde{J}I\tilde{F})]t, & p=(-1)^{k+1} \end{cases} . \tag{3.10}$$

The full reduction coefficients (2.24) must be evaluated when the $t=0$ system is unpolarized with respect to electronic and nuclear spins but fine and hyperfine frequencies can be detected simultaneously (i.e., the atom is not $[(LS)JI]F$ coupled):

$$\langle(nL)(\tilde{n}\tilde{L})^\dagger; kq\epsilon(-1)^k \,|\, U(t,0) \,|\, (nL)(\tilde{n}\tilde{L})^\dagger; kq\epsilon p\rangle$$

$$= \sum_{\alpha F,\tilde{\alpha}\tilde{F}} \langle[(nL)(\tilde{n}\tilde{L})^\dagger; kq\epsilon p][SS^\dagger; 0011][II^\dagger; 0011] \,|\, (\alpha F)(\tilde{\alpha}\tilde{F})^\dagger; kq\epsilon p\rangle^2 \begin{cases} \cos[\omega(\alpha F) - \omega(\tilde{\alpha}\tilde{F})]t, & p=(-1)^k \\ \sin[\omega(\alpha F) - \omega(\tilde{\alpha}\tilde{F})]t, & p=(-1)^{k+1} \end{cases} . \tag{3.11}$$

The three evolution operator components above are generalizations of the "modulation factors" in Eqs. (37), (40), and (44) of Fano and Macek.[13] They considered only nonhydrogenic systems which are diagonal in the dynamically important angular-momentum quantum numbers, $J=\tilde{J}$ for (3.9) and $L=\tilde{L}$ for (3.10) and (3.11). The time-reversal eigenvalue for such diagonal observables is fixed at $p=(-1)^k$ as discussed in Sec. IIA, explaining why Fano and Macek found only cosine oscillations. Sine components of the oscillations have been observed in the decay of hydrogenic states.[4-5,7,9] Our discussion shows that they are detectable because $t=0$ observables with $p=(-1)^{k+1}$ contribute to later $E1$ radiation.

In (3.9)–(3.11) we assume that the $t=0$ state is unpolarized with respect to nuclear and/or electronic spin. Whether or not this is so may be experimentally investigated by measuring the phase of oscillations occurring in $E1$ radiation decay.[31] Each irreducible component of the $t=0$ density operator is associated with sine or cosine oscillations by (3.7) and is linear in a weighted sum of density operator components in the base where L, S, and I are uncoupled (2.23). The reduction transformation (2.24) preserves the time-reversal eigenvalue (2.25). Failure to observe sine oscillations does not therefore indicate that the $t=0$ state is unpolarized with respect to spins, but only the vanishing of the uncoupled density operator components with odd $k_L+k_S+k_I+k$ which otherwise would contribute to the radiation. When $(LS)J$ coupling applies, the time-reversal condition (2.25) separates into two parts:

$$p = p_J(-1)^{k_I}, \tag{3.12}$$

$$p_J = p_L(-1)^{k_S} . \tag{3.13}$$

LS coupling thus simplifies the test of $t=0$ polarization when $\alpha LJ = \tilde{\alpha}\tilde{L}\tilde{J}$ since p_J is then equal to $(-1)^{k_J}$. If no hyperfine sine oscillations are present in this case, then all density operator components which should contribute to the radiation vanish unless k_J+k_I+k is even. Similarly, the lack of fine-structure beats with sine phase indicates that all such $t=0$ components are zero unless k_L+k_S+k is even.

Ellis recently derived the relationship between $t=0$ polarization and the phase of quantum beats for the special case of $E1$ radiation from an LS coupled multiplet.[31] Because he considered only cases for which the time-reversal quantum numbers were determined by rotational quantum numbers and because he assumed an explicit coupling scheme, he was able to base his conclusions upon the properties of a $9-j$ coefficient, without any reference to time reversal.

D. Time evolution in strong laboratory fields—spatial symmetries

In general, many components of the $t=0$ hydrogenic density operator determine the subsequent

unresolved electric dipole radiation. While a much more complete picture of the $t=0$ hydrogenic state is thus potentially possible (as compared to a nonhydrogenic state), the extraction of $t=0$ components is also more difficult. A more complete separation of $t=0$ components is possible when the hydrogenic system evolves from $t=0$ to $t=t$ in the presence of a laboratory field. We consider laboratory fields that are strong compared to the small energy splittings between the hydrogenic levels participating in the unresolved $E1$ radiation (but are weak, of course, compared to the $t<0$ formation and/or excitation process). Although the evolution operator components must often be calculated numerically for strong fields, the residual symmetry of the external fields (manifested as symmetry properties of the evolution operator components) can serve to isolate many desired $t=0$ density operator components, as illustrated below.

We first discuss a use of fields which has already proved very important in the measurement of $n=2$ components of hydrogenic operators. Let $U(V)$ be the evolution operator for a Hamiltonian invariant under parity transformations except for its external field term V. The evolution operator components for the related Hamiltonian PVP^{-1} (the parity transform of V) are simply related to components of $U(V)$,

$$\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p\,|\,U(PVP^{-1})\,|\,(\tilde{\alpha}\tilde{F})\,(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle$$
$$=\pi_{\alpha}\pi_{\beta}\pi_{\tilde{\alpha}}\pi_{\tilde{\beta}}\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p\,|\,U(V)\,|\,(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle\,. \tag{3.14}$$

The evolution operator for even-parity V (V proportional to even rank electric or odd rank magnetic multipoles for example) thus connects only $t=0$ density operator components to detection operator components of the same parity. Only even-parity components of the $t=0$ density operator can therefore be determined by $E1$ radiation measurements when V is parity even.

When V is odd under parity transformations (when V is proportional to odd rank electric or even rank magnetic multipoles, for example), parity condition (3.14) relates evolution operator components for V and $-V$. The sums and differences of average values measured in the presence of these potentials,

$$\langle D\,|\,U(V)\,|\,\rho(0)\rangle\pm\langle D\,|\,U(-V)\,|\,\rho(0)\rangle\,, \tag{3.15}$$

are linear in products of density and detection operator components with the same or opposite parities, respectively. Since the $E1$ radiation detection operator (Sec. III A) has even parity, the sums and differences for $E1$ radiation intensities are proportional to even- and odd-parity components of the $t=0$ density operator, as pointed out by Lombardi, Giroud, and Macek[24] for spatially uniform electric fields and observed earlier by Eck[23] in an explicit two-state calculation of the $E1$ radiation of hydrogen $n=2$ states. The usefulness of this "field reversal" technique has been clearly demonstrated by time-resolved measurements of $E1$ radiation from hydrogen $n=2$ states produced by passing protons through thin carbon targets[4-5,9]; we discuss such measurements in another paper.[9] This technique has also been used to measure hydrogen density operator components for excited atoms produced by H_2 dissociation[6] and by collisions with sodium[6] and helium.[11] Time integrated measurements of Balmer alpha radiation from hydrogen atoms excited by electron impact have also revealed a dependence upon the sign of an electric field.[10] This measurement has been interpreted using sum and difference curves in Ref. 25.

Consider next the relationship between the evolution operator components for V and $R_z(\pi)VR_z(\pi)^{\dagger}$ given by

$$\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p\,|\,U(R_z(\pi)VR_z(\pi)^{\dagger})\,|\,(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle$$
$$=(-1)^{q+\tilde{q}}\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p\,|\,U(V)\,|\,(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle\,. \tag{3.16}$$

Hamiltonians for spatially uniform electric fields parallel to $\hat{z}$ are invariant under $R_z(\pi)$, hence their evolution operator components vanish unless $\tilde{q}+q$ is even. If instead these fields are perpendicular to $\hat{z}$, the sums and differences of average values measured with V and $-V$ will be proportional to detection and density operator components with $(-1)^{q+\tilde{q}}$ equal to 1 and -1, respectively. A spatially uniform electric field which is perpendicular to $\hat{z}$ satisfies parity conditions (3.14) as well as (3.16) and thus

$$\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p\,|\,U(V)\,|\,(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle$$
$$=(-1)^{q+\tilde{q}}\pi_{\alpha}\pi_{\beta}\pi_{\tilde{\alpha}}\pi_{\tilde{\beta}}$$
$$\times\langle(\alpha F)(\beta G)^{\dagger};kq\epsilon p\,|\,U(V)\,|\,(\tilde{\alpha}\tilde{F})(\tilde{\beta}\tilde{G})^{\dagger};\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle\,. \tag{3.17}$$

This phase simplifies to $(-1)^{q}\pi_{\tilde{\alpha}}\pi_{\tilde{\beta}}$ for $E1$ radiation from a state axially symmetric about $\hat{z}$ at $t=0$. Therefore, unpolarized intensity measurements of photons emitted along $\hat{y}$ do not determine odd-parity density operator components. This is why Alguard and Drake's measurement of Lyman-alpha radiation was insensitive to the values of

$$\langle(2s)(2p)^{\dagger};10-11\,|\,\rho(0)\rangle$$

and

$$\langle(2s)\,(2p)^{\dagger};10-1-1\,|\,\rho(0)\rangle\,.$$

E. Time evolution in external fields—time-reversal classification neglecting decay

Time evolution under nonscalar Hamiltonians can be analyzed as in Sec. III C provided that the atomic Hamiltonian is time-reversal invariant and decay is neglected. Suppressing the subspace labels in the Hermitian unit tensors to simplify the expressions we obtain

$$\langle kq\epsilon p\,|\,U\,|\,\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle = \sum_{A\geq B}\frac{2}{1+\delta_{AB}}\,\mathrm{Re}(\langle B\,|\,T^{k}_{q\epsilon p}\,|A\rangle\langle A\,|\,T^{\tilde{k}}_{\tilde{q}\tilde{\epsilon}\tilde{p}}\,|\,B\rangle)\cos(\omega_{AB})t\,, \tag{3.18}$$

$$\langle kq\epsilon p\,|\,U\,|\,\tilde{k}\tilde{q}\tilde{\epsilon}-p\rangle = \sum_{A\geq B}\frac{2}{1+\delta_{AB}}\,\mathrm{Im}(\langle B\,|\,T^{k}_{q\epsilon p}\,|A\rangle\langle A\,|\,T^{\tilde{k}}_{\tilde{q}\tilde{\epsilon}-p}\,|\,B\rangle)\sin(\omega_{AB}t)\,. \tag{3.19}$$

The summation convention $A\geq B$ refers to an arbitrary enumeration of eigenstates of the Hamiltonian, $|A\rangle$ and $|B\rangle$. These states have eigenfrequencies ω_A and ω_B and ω_{AB} denotes $\omega_A-\omega_B$. Re and Im denote real and imaginary parts. Thus instead of the simple sine or cosine components we obtained for time evolution under scalar Hamiltonians in (3.7), we obtain cosine or sine series. We shall show in the next section that (3.18) and (3.19) remain approximately true, even when decay is included, provided the atomic Hamiltonian is time-reversal invariant.

We now relax the assumption that the Hamiltonian H is time-reversal invariant, allowing it to depend upon a magnetic field, for example, but continue to neglect decay. We find that components of the evolution operator $U(H)$ and the evolution operator $U(KHK^{\dagger})$ are related by

$$\langle kq\epsilon p\,|\,U(H)\,|\,\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle = p\tilde{p}\langle\tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\,|\,U(KHK^{\dagger})\,|\,kq\epsilon p\rangle\,. \tag{3.20}$$

The association of $p=\tilde{p}$ with cosine oscillations and $p=-\tilde{p}$ with sine oscillation is no longer true. Consider, for example, the familiar "weak magnetic field." H is time-reversal invariant except for a weak magnetic field term, $V=-g_{\alpha F}BF_z$. The evolution operator has components

$$\langle(\alpha F)(\alpha F)^{\dagger};kq\epsilon p\,|\,U\,|\,(\alpha F)(\alpha F);kq\epsilon p\rangle = e^{-\Gamma_{\alpha F}t}\cos(-g_{\alpha F}Bqt)\,, \tag{3.21}$$

$$\langle(\alpha F)(\alpha F)^{\dagger};kq-\epsilon p\,|\,U\,|\,(\alpha F)(\alpha F);kq\epsilon p\rangle = \epsilon(-1)^{k}e^{-\Gamma_{\alpha F}t}\sin(-g_{\alpha F}Bqt)\,, \tag{3.22}$$

and the decay factor provides no complication for this single level example. These components differ in phase by exactly 90° because $|V\rangle$ is an eigenfunction of $R_y(\pi)$, not because of time-reversal symmetry. The time integrals of (3.21) and (3.22) yield the familiar resonance and dispersion functions used to measure decay widths, g values, and $t=0$ density operator components.[32-34]

F. Decay

Decay processes are not time-reversal invariant. We might expect, therefore, that the time-reversal analysis presented in earlier sections be greatly complicated by the inclusion of decay. By using a Wigner-Weisskopf-type approximation,[35] however, we are able to show that only time evolution via a nonscalar Hamiltonian is significantly complicated by decay. Even for this case the earlier results (Sec. III D) remain approximately true and are useful in analyzing and planning hydrogen experiments.

We analyze the Hamiltonian which governs the time evolution in the form

$$H=H_0+V+H'\,, \tag{3.23}$$

where H_0 is the Hamiltonian of the isolated system (with eigenvalues ω_k and eigenfunctions $|k\rangle$) and V is the potential energy due to an external field. The decay term H' couples the states $|k\rangle$ to other eigenstates of H_0 designated by $|f\rangle$, which are orthogonal to $|k\rangle$. Atomic states which decay by electric dipole radiation are one example. In this case the states $|k\rangle$ are direct products of excited atomic states and the photon vacuum, while the states $|f\rangle$ are the direct products of atomic states and single-photon states.

The time-dependent Schrödinger equation for such a system can be partially solved using a Wigner-Weisskopf[35]-type approximation to eliminate most of the dependence upon the states $|f\rangle$. The remaining coupled equations can be formulated as a time-independent Schrödinger equation with an atomic Hamiltonian $\tilde{H}$ which is not Hermitian:

$$\tilde{H}\,|A\rangle = (\omega_A - i\tfrac{1}{2}\Gamma_A)\,|A\rangle\,, \tag{3.24}$$

with

$$\tilde{H}_{kl}=\omega_k\delta_{kl}-i\tfrac{1}{2}\Gamma^0_{kl}+V_{kl}\,. \tag{3.25}$$

The quasistationary eigenstates $|A\rangle$ of the non-Hermitian Hamiltonian are not orthogonal, develop in time as $\exp(-i\omega_A t-\frac{1}{2}\Gamma_A t)$, and are related to the atomic eigenstates of H_0 by a nonunitary transformation W:

$$|A\rangle=\sum|k\rangle\langle k\,|\,W\,|A\rangle\,,\quad \langle k\,|\,W\,|A\rangle=\langle k\,|A\rangle\,. \tag{3.26}$$

The final states $|f\rangle$ enter into $\tilde{H}$ only within the matrix element Γ^0_{kl} given by

$$\Gamma^0_{kl} = 2\pi \sum_f H'^*_{fk} H'_{fl} . \tag{3.27}$$

The integration over all spatial directions, implicit in the sum over final states in (3.27) causes Γ^0_{kl} to be the matrix element of a scalar operator and hence Γ^0_{kl} vanishes unless the atomic states $|k\rangle$ and $|l\rangle$ have the same rotational symmetry. Most often the matrix Γ^0 is therefore very nearly diagonal, since the states which have the same rotational symmetry are typically widely spaced in energy compared to the strength of their coupling. Γ^0_{ll} is the total decay width for the state $|l\rangle$ as given by Fermi's Golden Rule. If we had taken the states $|k\rangle$ and $|l\rangle$ to be the eigenstates of $H_0 + V$ instead of H_0 alone we would have obtained (3.25) without the V_{kl}. The matrix Γ^0 would not be nearly diagonal with this choice, since the external field reduces the symmetry of the eigenstates of $H_0 + V$, permitting them to be strongly coupled.

When a system develops in time under the influence of a scalar Hamiltonian, (i.e., when $V = 0$), the evolution operator components are very simple. In the absence of closely spaced levels with the same rotational symmetry (i.e., in the absence of off-diagonal elements Γ^0_{kl}), the eigenvectors of the non-Hermitian Hamiltonian $\tilde{H}$, are just the angular-momentum eigenvectors $|\alpha \mathrm{FM}\rangle$. As a result, $|(\alpha F)(\beta G)^\dagger; kq\epsilon\rangle$ is an eigenfunction of $U(t, 0)$ and the nonvanishing components of the evolution operator are given by (3.7) with the appropriate decay factor multiplied in as indicated following (3.7). The Eqs. (3.9)–(3.11) can therefore be similarly modified.

When the system evolves via a nonscalar Hamiltonian ($V \neq 0$), we proceed as in (Sec. III E) except we use the quasistationary states for $|A\rangle$ and $|B\rangle$. Each evolution operator component can still be written as a Fourier series,

$$\langle kq\epsilon p | U(t, 0) | \tilde{k}\tilde{q}\tilde{\epsilon}\tilde{p}\rangle = \sum_{A \geq B} \exp[-\tfrac{1}{2}(\Gamma_A + \Gamma_B)t][C_{AB} \cos(\omega_{AB} t) + S_{AB} \sin(\omega_{AB} t)],$$

$$C_{AB} = \frac{2}{1+\delta_{AB}} \mathrm{Re}(\langle B | W^\dagger T^k_{q\epsilon p} W | A\rangle\langle A | W^{-1} T^{\tilde{k}}_{\tilde{q}\tilde{\epsilon}\tilde{p}} W^{-1\dagger} | B\rangle),$$

$$S_{AB} = \frac{2}{1+\delta_{AB}} \mathrm{Im}(\langle B | W^\dagger T^k_{q\epsilon p} W | A\rangle\langle A | W^{-1} T^{\tilde{k}}_{\tilde{q}\tilde{\epsilon}\tilde{p}} W^{-1\dagger} | B\rangle), \tag{3.28}$$

given here with the subspace labels suppressed. In comparing this expression with the no-decay results of (3.18) and (3.19) [which can be derived from (3.28)] we make the following observations. The non-Hermitian term added to the Hamiltonian in (3.24) is typically small compared to the relevant energy splittings, even in atomic hydrogen. As a result, the transformation W is not unitary at this level and small sine terms are added to the cosine series of (3.18) and small cosine terms are added to (3.19). The small terms are of the order of a decay width over a frequency splitting. We have found Eq. (3.28) and (3.24)–(3.26) to be convenient for numerical calculation of hydrogen evolution operator components when strong fields are present.[9]

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†Present address: Department of Physics, FM-15, University of Washington, Seattle, Washington 98195.

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