Reprinted from THE PHYSICAL REVIEW, Vol. 179, No. 5, 1253–1261, 25 March 1969
Printed in U. S. A.

Radiative Effects in Semiclassical Theory*

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(Received 22 November 1968)

Unquantized field calculations are extended to include the effect of an atom's field acting back upon the atom. It is shown that, in the absence of an applied field, semiclassical theory predicts that an atom will decay spontaneously from an excited state with a characteristic time equal to the reciprocal of the Einstein A coefficient for the transition. The theory also predicts that the frequency of the light radiated during a transition will have a small time dependence. The corresponding frequency shifts are compared with the Lamb shift in hydrogen. The derived equations are used to study the response of a many-level atom to an applied, monochromatic field. In the case of a three-level system, it is predicted that optical nutations are not just limited to the resonant transition, but are also present in the fluorescence involving the other level.

INTRODUCTION

CALCULATIONS with an unquantized electromagnetic field have proved adequate to explain such quantum-electronic phenomena as photon echoes,[1] self-induced transparency,[2] and optical nutation.[3] It is argued that a quantized field is not necessary for the understanding of these effects because strong fields consisting of large numbers of quanta are involved. The present paper investigates the consequences of retaining a classical field in treating the problem of an atom interacting with weak electromagnetic radiation. It is shown that the phenomenon of the spontaneous decay of an atom can be obtained semiclassically, provided one includes the effects upon the atom of fields created by the atomic currents. These currents are assumed to be equal to the probability current of the atomic electrons multiplied by the electronic charge e. This assumption couples the Maxwell and Schrödinger equations, and this paper is devoted to the solution and interpretation of this set of simultaneous, nonlinear differential equations.

Even though it is generally believed that a full quantum-electrodynamic treatment is necessary in order to obtain all radiative effects correctly, many calculations involving the interaction of radiation and matter were first done without quantizing the electromagnetic field. Thus in the case of the photoelectric effect,[4] the scattering of radiation from a free electron (Klein-Nishina formula),[5] stimulated emission and absorption of radiation by an atom,[6] and vacuum polarization,[7] the correct predictions were first obtained by semiclassical methods.

On the other hand, quantum electrodynamics has been applied to a much wider range of phenomena with great success, in the sense that there is as yet no clear-cut evidence for any discrepancy between its predictions and experiment. However, in spite of the labors of two generations of theorists in improving the formulation of the theory and developing more powerful methods of calculation, present quantum electrodynamics contains many mathematical and logical difficulties. In almost every calculation one encounters divergent and/or ambiguous integrals, which must be disposed of by various devices. Thus, the infinite zero-point energy is simply subtracted arbitrarily, some divergent expressions are set equal to zero on grounds of relativistic invariance, others on grounds of gauge invariance, and the order of some divergences is reduced by the *ad hoc* device of regulators. The remaining divergences are not really removed, but only concealed from view, by the devices of mass and charge renormalization.

In some cases it is not yet clear whether the difficulty is due to a defect in the formulation of the theory, or whether it arises merely from inadequacies in our methods of calculation (i.e., perturbation expansions in powers of e^2 may not "exist" in the analytical sense). However, in some particularly simple cases [such as the vacuum expectation value of the current operator, $\langle J_\mu(x)\rangle$, which is a violently divergent expression set equal to zero on grounds of Lorentz invariance], no real "calculation" is involved. Another difficulty that cannot be attributed to inadequate methods of calculation is the infinite vacuum fluctuations, and consequent infinite zero-point energy, of the electromagnetic field. Indeed, at first glance it seems remarkable that *any* finite results or reproducible effects could emerge from

* Work supported in part by the Joint Services Electronics Program under Contract No. DA-28-043 AMC-00099(E).

† This paper is based on a thesis submitted to Washington University in partial fulfillment of the requirements for the Ph.D. degree.

[1] N. A. Kurnit, I. D. Abella, and S. R. Hartmann, Phys. Rev. Letters **13**, 567 (1964).

[2] S. L. McCall and E. L. Hahn, Phys. Rev. Letters **18**, 908 (1967).

[3] G. B. Hocker and C. L. Tang, Phys. Rev. Letters **21**, 591 (1968).

[4] G. Wentzel, Z. Physik **41**, 828 (1927).

[5] O. Klein and Y. Nishina, Z. Physik **52**, 853 (1929).

[6] O. Klein, Z. Physik **41**, 407 (1927).

[7] E. A. Uehling, Phys. Rev. **48**, 55 (1935).

a theory based on point interactions to a field with infinite random fluctuations.

Therefore, even though we have now learned how to manipulate the divergences of quantum electrodynamics with enough art to extract meaningful finite results, it seems undeniable that there are fundamental defects in the basic formulation of the present theory; a correctly formulated theory should not require additional *ad hoc* devices in order to obtain physical predictions. Theorists are in quite general agreement that some very deep modifications will be required in quantum electrodynamics before we have the elusive "future correct theory" of radiation phenomena. In what specific way, then, should the present theory be changed? To this question we have as yet no answers, and few suggestions.

Now semiclasscial calculations are conspicuously free from many of the divergence problems of quantum electrodynamics; the classical electromagnetic field due to a finite and continuous current distribution is everywhere finite and well behaved. As the list of successful semiclassical calculations grows, the question arises whether the necessary modification of quantum electrodynamics may lie in the direction of the semiclassical approach. Any such change would, of course, impy a revision of the physical ideas underlying the present theory and would probably be as radical as the change which took place in the interpretation of the Dirac equation in the transition from the original one-electron Dirac theory to the hole theory.

For these reasons it is of interest to extend the list of semiclassical calculations as far as possible. To date, it is generally thought that the phenomena of blackbody radiation, spontaneous emission, and the Lamb shift actually require the quantizing of the electromagnetic field. It is the purpose of this paper to examine the possibilities of a semiclassical theory of the last two, closely related, effects.

In a previous paper[8] it was shown that, in the dipole approximation, the expectation of the dipole moment $\langle\mu\rangle$ and the expectation of the energy $\langle\mathcal{H}\rangle$ of a two-level atom evolve according to

$$\frac{d^2}{dt^2}\langle\mu\rangle+\Omega^2\langle\mu\rangle=-\left(\frac{2\mu}{\hbar}\right)^2\langle\mathcal{H}\rangle E(t)\,,$$

$$d\langle\mathcal{H}\rangle/dt=E(t)d\langle\mu\rangle/dt\,,$$

where $E(t)$ is the electric field in the vicinity of the atom. If the expectation of the dipole moment is interpreted as an actual dipole moment, its oscillation will create electromagnetic fields and cause energy to be radiated away from the atom.

In order to understand how the effects of spontaneous decay and frequency shifts come about in semiclassical theory, consider the following intuitive argument. It is shown in this paper that the radiation field which reacts upon the atom consists of two components, one in phase with the atomic currents and the other 90° out of phase [see Eq. (9)]. For a two-level atom in the dipole approximation, this corresponds to assuming an electric field of the form

$$E(t)=-K\frac{d^2}{dt^2}\langle\mu\rangle+\frac{2}{3c^3}\frac{d^3}{dt^3}\langle\mu\rangle\,,$$

where the constant K depends upon the detailed structure of the atom and hence cannot be derived rigorously in the dipole limit. The second term, $(2/3c^3)(d^3/dt^3)\langle\mu\rangle$, is the classical radiation reaction field[9] and is independent of the structural details of the atom.

The field $E(t)$ is weak compared with $\hbar\Omega/\mu$, so that

$$\frac{d^2}{dt^2}\langle\mu\rangle\approx-\Omega^2\langle\mu\rangle\,,$$

and the field acting back upon the atom may be approximated by

$$E(t)=\Omega^2K\langle\mu\rangle-\frac{2}{3}\frac{\Omega^2}{c^3}\frac{d}{dt}\langle\mu\rangle\,.$$

Substituting this into the equation of motion of the dipole moment, one obtains

$$\frac{d^2}{dt^2}\langle\mu\rangle-\frac{8}{3}\frac{\mu^2\Omega^2}{\hbar^2c^3}\langle\mathcal{H}\rangle\frac{d\langle\mu\rangle}{dt}+\Omega^2\left(1+\frac{4\mu^2}{\hbar^2}\langle\mathcal{H}\rangle K\right)\langle\mu\rangle=0\,.$$

This equation resembles that of a damped harmonic oscillator with a damping coefficient $(-8/3)(\mu^2\Omega^2/\hbar^2c^3)\times\langle\mathcal{H}\rangle$ and a shifted frequency $\Omega[1+(4\mu^2/\hbar^2)\langle\mathcal{H}\rangle K]^{1/2}$. If the atom is excited, $\langle\mathcal{H}\rangle$ is greater than zero and the dipole moment grows spontaneously until $\langle\mathcal{H}\rangle$ becomes negative, at which time the dipole moment begins its decay to zero. In this way a dipole's field reacting upon the dipole can give rise to spontaneous decay and frequency shifts.

DERIVATION OF BASIC EQUATIONS

Consider a nonrelativistic, spinless atom which is described by the Hamiltonian

$$\mathcal{H}=\mathcal{H}_0-V\,, \tag{1}$$

where $\mathcal{H}_0$ is the Hamiltonian of the atomic system in the absence of electromagnetic fields, and V is the interaction term arising from the presence of fields. To be specific, set

$$\mathcal{H}_0=\mathbf{p}^2/2m-e^2/r\,, \tag{2a}$$

$$V=(e/mc)\mathbf{A}(\mathbf{x},t)\cdot\mathbf{p}\,. \tag{2b}$$

The diamagnetic term $(e^2/2mc^2)\mathbf{A}^2(\mathbf{x},t)$ in V has been

[8] E. T. Jaynes and F. W. Cummings, Proc. IEEE **51**, 89 (1963).

[9] L. D. Landau and E. M. Lifshitz, *The Classical Theory of Fields* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962), 2nd ed., Eq. (75.4).

neglected because the fields treated in this paper are weak. [The magnitude of the vector potential $\mathbf{A}(\mathbf{x},t)$ will be of the order of $e\alpha^2(mc/\hbar)$.]

Any state of the atomic system may be expressed as

$$\Psi(\mathbf{x},t)=\sum_j a_j(t)\psi_j(\mathbf{x}), \tag{3}$$

where $\psi_j(\mathbf{x})$ are eigenfunctions of $\mathcal{H}_0$, i.e.,

$$\mathcal{H}_0\psi_j(\mathbf{x})=E_j\psi_j(\mathbf{x}).$$

The continuum states are not included in Eq. (3) because they are not significantly excited by radiation of the optical frequencies treated here.

It is assumed that an atom in the state $\Psi(\mathbf{x},t)$ contains charge currents which are given by

$$\mathbf{J}(\mathbf{x},t)=(e/m)\,\mathrm{Re}[\Psi^*(\mathbf{x},t)\mathbf{p}\Psi(\mathbf{x},t)]. \tag{4}$$

Again a higher-order term, $(e^2/mc)[\mathbf{A}(\mathbf{x},t)|\Psi(\mathbf{x},t)|^2]$, has been neglected because of the smallness of $\mathbf{A}(\mathbf{x},t)$. Substituting Eq. (3) in Eq. (4), one obtains

$$\mathbf{J}(\mathbf{x},t)=\frac{e\hbar}{2mi}\sum_{\alpha,\beta}[\sigma_{\beta\alpha}\psi_\alpha^*\nabla\psi_\beta-\sigma_{\alpha\beta}\psi_\alpha\nabla\psi_\beta^*], \tag{5}$$

where the density matrix elements in the Schrödinger picture, $\sigma_{\beta\alpha}(t)$, are defined by

$$\sigma_{\beta\alpha}(t)\equiv a_\beta(t)a_\alpha^*(t), \tag{6}$$

and evolve according to

$$i\hbar\dot{\sigma}_{lm}=\sum_j[\mathcal{H}_{lj}\sigma_{jm}-\sigma_{lj}\mathcal{H}_{jm}]. \tag{7}$$

The atomic currents create a transverse[10] vector potential which may be written in the Coulomb gauge as

$$\mathbf{A}(\mathbf{x},t)=\frac{1}{c}\int\frac{\mathbf{J}_t(\mathbf{x}',t-|\mathbf{x}-\mathbf{x}'|/c)}{|\mathbf{x}-\mathbf{x}'|}d^3x'+\mathbf{A}_0(\mathbf{x},t), \tag{8}$$

where $\mathbf{J}_t(\mathbf{x},t)$ is the transverse component of the current density, and the vector potential $\mathbf{A}_0(\mathbf{x},t)$ represents an externally applied field. In the calculations to follow, both the source point $\mathbf{x}'$, and the observation point $\mathbf{x}$ are contained within the atom so that the retardation $(|\mathbf{x}-\mathbf{x}'|)/c$ is small compared with the period of oscillation of $\mathbf{J}_t(\mathbf{x},t)$, and Eq. (8) can be rewritten as

$$\mathbf{A}(\mathbf{x},t)=\frac{1}{c}\int\frac{\mathbf{J}_t(\mathbf{x}',t)}{|\mathbf{x}-\mathbf{x}'|}d^3x'-\frac{1}{c^2}\frac{d}{dt}\int\mathbf{J}_t(\mathbf{x}',t)d^3x'+\mathbf{A}_0(\mathbf{x},t) \tag{9}$$

in the vicinity of the atom. The expression of Eq. (5) may be used in Eq. (9) with the aid of the following identities:

$$\frac{1}{|\mathbf{x}-\mathbf{x}'|}=\frac{1}{2\pi^2}\int_0^\infty dk\int d\Omega\, e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}, \tag{10a}$$

$$\int\mathbf{J}_t(\mathbf{x}',t)e^{-i\mathbf{k}\cdot\mathbf{x}'}d^3x'=-\frac{\mathbf{k}}{|\mathbf{k}|}\times\left[\frac{\mathbf{k}}{|\mathbf{k}|}\times\int\mathbf{J}(\mathbf{x}',t)e^{-i\mathbf{k}\cdot\mathbf{x}'}d^3x'\right], \tag{10b}$$

$$\int\mathbf{J}_t(\mathbf{x}',t)d^3x'=\frac{2}{3}\int\mathbf{J}(\mathbf{x}',t)d^3x', \tag{10c}$$

where the integral $\int d\Omega$ is over solid angle in $\mathbf{k}$ space. One obtains

$$\mathbf{A}(\mathbf{x},t)=\sum_{\alpha,\beta}\sigma_{\beta\alpha}(t)\left(\frac{-i}{2\pi^2}\frac{e\hbar}{mc}\int_0^\infty dk\int d\Omega(\alpha|e^{-i\mathbf{k}\cdot\mathbf{x}}\nabla|\beta)_1e^{i\mathbf{k}\cdot\mathbf{x}}+\frac{2}{3}\frac{\Omega_{\alpha\beta}^2}{c^2}\mathbf{u}_{\alpha\beta}\right)+\mathbf{A}_0(\mathbf{x},t) \tag{11}$$

for the field which acts upon the atomic currents. The definition

$$(\alpha|e^{-i\mathbf{k}\cdot\mathbf{x}}\nabla|\beta)_1\equiv-\frac{\mathbf{k}}{|\mathbf{k}|}\times\left(\frac{\mathbf{k}}{|\mathbf{k}|}\times(\alpha|e^{-i\mathbf{k}\cdot\mathbf{x}}\nabla|\beta)\right)$$

has been made.

The applied field will be assumed to be that of a monochromatic plane wave of the form

$$\mathbf{A}_0(\mathbf{x},t)=\frac{c\mathbf{E}_0}{\omega}\cos(\omega t-\mathbf{k}\cdot\mathbf{x}), \tag{12}$$

where ω is an optical frequency. Since at optical frequencies the phase of $\mathbf{A}_0(\mathbf{x},t)$ does not vary significantly over the volume of the atom, the dipole approximation is valid and the vector potential may be evaluated at the center of the atom, i.e.,

$$\mathbf{A}_0(0,t)=\frac{c\mathbf{E}_0}{\omega}\cos\omega t \tag{13}$$

may be used in Eq. (11).

Equations (11), (2b), and (1) may be used in Eq. (7) and, if the nonresonant terms are neglected (the details of this calculation appear in Appendix A), one obtains

$$\dot{\sigma}_{lm}=-i[\Omega_{lm}-\sum_j(\Gamma_{lj}-\Gamma_{jm})\sigma_{jj}(t)]\sigma_{lm}-[\sum_j\tfrac{1}{2}(A_{lj}+A_{mj})\sigma_{jj}(t)]\sigma_{lm}-\frac{\mathbf{A}_0(0,t)}{\hbar c}\cdot\sum_j[\Omega_{lj}\mathbf{u}_{lj}\sigma_{jm}-\sigma_{lj}\Omega_{jm}\mathbf{u}_{jm}]. \tag{14}$$

[10] It is assumed that the atomic electrons do not see their longitudinal self-fields.

FIG. 1. Energy-level diagram for a two-level atom.

In Eq. (14), the definition

$$\Gamma_{lj}\equiv\frac{1}{2\pi^2}\frac{e^2\hbar}{m^2c^2}\int_0^\infty dk\int d\Omega(l|\,e^{i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\nabla}\,|j)_\perp\cdot(j|\,e^{-i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\nabla}\,|l)_\perp=\Gamma_{jl}\quad(15)$$

has been made, and the Einstein A coefficients A_{lj} are defined according to

$$A_{lj}\equiv\tfrac{4}{3}(\boldsymbol{\mu}_{lj}\cdot\boldsymbol{\mu}_{jl}/\hbar c^3)\Omega_{lj}^3=-A_{jl}.\quad(16)$$

The electric dipole moment matrix element $\boldsymbol{\mu}_{lj}$ and the transition frequencies Ω_{lj} are defined, respectively, as

$$\boldsymbol{\mu}_{lj}\equiv\int\psi_l^*(\mathbf{x})e\mathbf{x}\psi_j(\mathbf{x})d^3x,\quad(17a)$$

$$\hbar\Omega_{lj}\equiv E_l-E_j.\quad(17b)$$

It is seen from Eq. (14) that the off-diagonal density matrix elements oscillate at frequencies $\Omega_{lm}+\delta\Omega_{lm}(t)$, where the time-dependent frequency shifts $\delta\Omega_{lm}(t)$ are given by

$$\delta\Omega_{lm}(t)=-\sum_j(\Gamma_{lj}-\Gamma_{jm})\sigma_{jj}(t).\quad(18)$$

Now the expectation of the dipole moment of the atom is defined by

$$\langle\boldsymbol{\mu}\rangle\equiv\int\Psi^*(\mathbf{x},t)e\mathbf{x}\Psi(\mathbf{x},t)d^3x$$

and, using Eq. (3), one can write

$$\langle\boldsymbol{\mu}\rangle=\sum_{\alpha,\beta}\boldsymbol{\mu}_{\alpha\beta}\sigma_{\beta\alpha}(t).$$

Thus the off-diagonal matrix elements are directly related to the expectation of the dipole moment. Since semiclassical theory assumes that the expectation of the dipole moment is responsible for radiation by the atom, Eq. (18) is a prediction of a frequency shift in the radiation emitted or absorbed by an atom. Such a frequency shift is a new phenomenon which has not appeared in other semiclassical calculations.

If a hydrogen atom were prepared in its ground state, σ_{1s1s} would be equal to unity and all other σ_{jj} would be zero. The quantity Γ_{1s1s} is identically zero, so in this case Eq. (18) predicts that the hydrogen atom would respond resonantly to an applied field whose frequency is given by

$$\omega=\Omega_{2p1s}-\Gamma_{1s2p}.$$

This $1s$-$2p$ frequency shift Γ_{1s2p} is calculated in Appendix B to be 0.285 cm^{-1}. Herzberg[11] has determined the $1s$-$2p$ Lamb shift in deuterium by measuring the $1s$-$2p$ absorption line. The reported value is 0.262 ± 0.038 cm^{-1}. The comparison of other semiclassical frequency shifts with the corresponding Lamb-shift values is given in Table I. The values of Γ_{lm} reported in the table have been corrected for the effect of vacuum polarization. The vacuum-polarization calculation, as first done by Uehling,[7] uses an unquantized electromagnetic field and therefore can be fitted into the framework of this paper.

TABLE I. Comparison of the semiclassical frequency shifts with the experimentally measured and the quantum-electrodynamically calculated Lamb shift. Both the semiclassical and the quantum-electrodynamic calculations include the corrections for vacuum polarization.

ns-mp	$\Gamma_{nm}/2\pi$	$\delta\omega_{\text{expt}}$	$\delta\omega_{\text{QED}}$
$1s$-$2p$	0.278 cm^{-1}	0.262 ± 0.038 cm^{-1} [a]	0.2726 cm^{-1}
$2s$-$2p$	657.20 MHz	1057.77 ± 0.10 MHz [b]	1057.19 MHz
$3s$-$3p$	0.0027 cm^{-1}	$0.0083_{-0.003}^{+0.002}$ cm^{-1} [c]	0.0105 cm^{-1}

[a] G. Herzberg (Ref. 11).
[b] S. Triebwasser, E. S. Dayhoff, and W. E. Lamb, Phys. Rev. **89**, 98 (1953).
[c] G. W. Series, Proc. Roy. Soc. (London) **A208**, 277 (1951).

The agreement between the $1s$-$2p$ quantum-electrodynamic Lamb shift and the corresponding semiclassical frequency shift is surprisingly good when it is recalled that the semiclassical calculation corresponds to a two-level, spinless, nonrelativistic hydrogen atom. The other semiclassical frequency shifts agree in sign and order of magnitude with their quantum-electrodynamic counterparts.

SPONTANEOUS DECAY

Equation (14) predicts that,[12] in the absence of an applied field, the diagonal matrix elements will decay according to

$$\dot\sigma_{ll}=-\sum_j A_{lj}\sigma_{jj}\sigma_{ll}.\quad(19)$$

In the case of a two-level system (see Fig. 1), these equations become

$$\dot\sigma_{22}=-A_{21}\sigma_{22}\sigma_{11},$$
$$\dot\sigma_{11}=A_{21}\sigma_{22}\sigma_{11}.$$

Adding these equations, one sees that probability is conserved, i.e.,

$$\sigma_{11}+\sigma_{22}=1.$$

This constant of motion allows one to integrate the equations and obtain

$$\sigma_{22}=1/(e^{A_{21}(t-t_0)}+1),\quad(20a)$$

$$\sigma_{11}=1/(e^{-A_{21}(t-t_0)}+1).\quad(20b)$$

[11] G. Herzberg, Proc. Roy. Soc. (London) **A234**, 516 (1956).
[12] In the following sections, the atomic eigenfunctions $\psi_l(\mathbf{x})$ will be chosen to be real. This step is not necessary, but it does result in considerable simplification of the equations.

The constant of integration t_0 is determined by the initial state of the atom. From this solution it follows that the expectation of the energy evolves in time according to

$$\langle \mathcal{H}_0 \rangle = \tfrac{1}{2}\hbar\Omega_{21}(\sigma_{22}-\sigma_{11}) = -\tfrac{1}{2}\hbar\Omega_{21}\tanh[\tfrac{1}{2}A_{21}(t-t_0)]. \quad (21)$$

According to Eq. (14), when $\mathbf{A}_0(0,t)$ is zero, the off-diagonal matrix element satisfies

$$\dot{\sigma}_{21} = -i\{\Omega_{21}-\Gamma_{12}\tanh[\tfrac{1}{2}A_{21}(t-t_0)]\}\sigma_{21} - \{\tfrac{1}{2}A_{21}\tanh[\tfrac{1}{2}A_{21}(t-t_0)]\}\sigma_{21}.$$

Integrating this, it is seen that the expectation of the dipole moment varies according to

$$\langle \boldsymbol{\mu} \rangle \equiv \boldsymbol{\mu}_{12}(\sigma_{12}+\sigma_{21}) = \boldsymbol{\mu}_{12}\,\mathrm{sech}[\tfrac{1}{2}A_{21}(t-t_0)] \times \cos[\Omega_{21}t+\theta(t)], \quad (22)$$

where $\theta(t)$ is defined by

$$\theta(t) \equiv \theta_0 - (2\Gamma_{12}/A_{21})\ln\{\cosh[\tfrac{1}{2}A_{21}(t-t_0)]\}$$

and corresponds to a time-dependent frequency shift given by

$$\delta\Omega_{21}(t) = d\theta/dt = -\Gamma_{12}\tanh[\tfrac{1}{2}A_{21}(t-t_0)]. \quad (23)$$

Graphs of the expectation of the energy and the envelope of the dipole moment are shown in Fig. 2.

It should be noted that Eq. (20a) predicts a nonexponential decay for an atom in its excited state. This corresponds to a fundamental difference between semiclassical theory and quantum electrodynamics. In semiclassical theory it is assumed that the expectation of the dipole moment of the atom is responsible for radiation, and hence an excited atom radiates slowly until its dipole moment grows to an appreciable magnitude (see Fig. 2). In quantum electrodynamics, the probability that a given atom radiates is largest im-

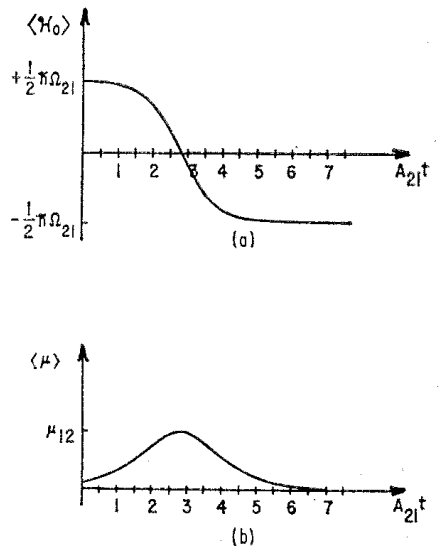

FIG. 2. (a) Decay of the expectation of the energy of the two-level atom in absence of applied fields. Time is in units of A_{21}^{-1}, where A_{21} is the Einstein A coefficient for the atom. (b) Evolution of the envelope of the expectation of the dipole moment for the two-level atom.

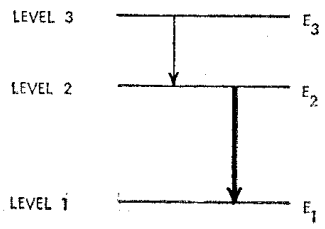

FIG. 3. Energy-level diagram for a three-level system. Transitions are allowed between adjacent levels.

mediately after the atom is excited. The semiclassical decay does go asymptotically into an exponential decay as $t-t_0$ becomes large.

In the case of a three-level system with transitions allowed between adjacent levels (see Fig. 3), Eq. (19) becomes

$$\dot{\sigma}_{33} = -A_{32}\sigma_{33}\sigma_{22}, \quad (24a)$$

$$\dot{\sigma}_{22} = A_{32}\sigma_{33}\sigma_{22} - A_{21}\sigma_{22}\sigma_{11}, \quad (24b)$$

$$\dot{\sigma}_{11} = A_{21}\sigma_{22}\sigma_{11}. \quad (24c)$$

Addition of these equations shows that they are consistent with conservation of probability, i.e.,

$$\sigma_{11}+\sigma_{22}+\sigma_{11} = 1. \quad (25)$$

Dividing Eq. (24a) by Eq. (24c), it follows that

$$\dot{\sigma}_{33}/A_{32}\sigma_{33} = -\dot{\sigma}_{11}/A_{21}\sigma_{11}$$

or

$$[\sigma_{33}(t)]^{A_{21}/A_{32}}[\sigma_{11}(t)] = \alpha_0, \quad (26)$$

where α_0 is a constant of integration. The constant of motion of Eq. (26) is of a new type, not found in conventional theory. It has the effect of preventing the system from completely decaying to its ground state. Thus Eq. (26) predicts that the third level should be "conditionally metastable"; i.e., in the absence of external perturbations it can retain a nonzero amplitude indefinitely. In such a state, however, the slightest perturbation will cause the decay to resume.

The constants of motion given in Eqs. (25) and (26) are sufficient to allow integration of the equations, and one obtains

$$\int \frac{d\sigma_{33}}{\sigma_{33}(1-\alpha_0\sigma_{33}^{-r}-\sigma_{33})} = -A_{32}t+\text{const}, \quad (27a)$$

$$\int \frac{d\sigma_{11}}{\sigma_{11}(1-\alpha_0^{1/r}\sigma_{11}^{-1/r}-\sigma_{11})} = A_{21}t+\text{const}, \quad (27b)$$

$$\sigma_{22} = 1-\sigma_{11}-\sigma_{33}, \quad (27c)$$

where the parameter r is defined according to

$$r \equiv A_{21}/A_{32}.$$

Equations (27a) and (27b) have been integrated for the case $r=1$, that is, when the two Einstein A coefficients are equal. It follows from this solution that the expectation of the energy of the atom, which is given by

$$\langle \mathcal{H}_0 \rangle = E_1\sigma_{11}(t)+E_2\sigma_{22}(t)+E_3\sigma_{33}(t),$$

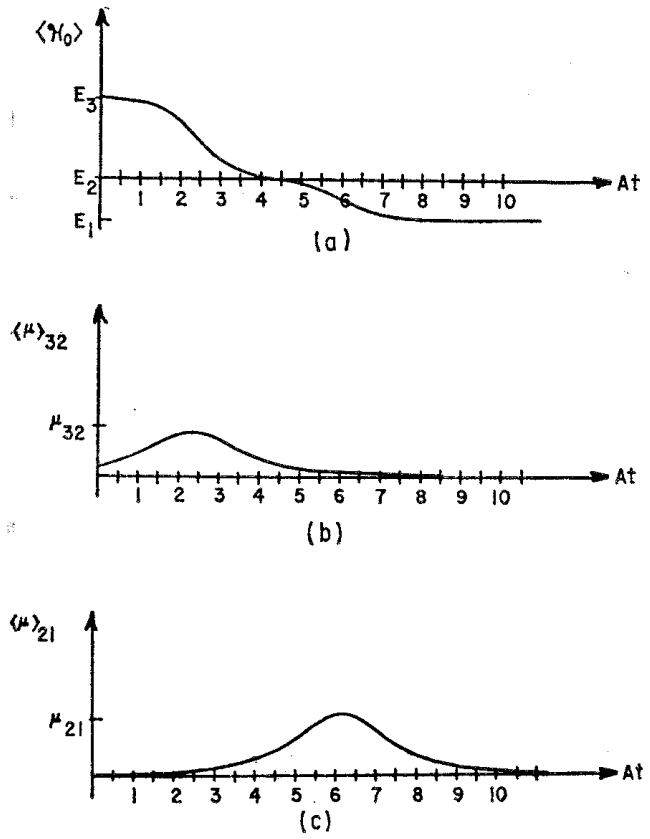

FIG. 4. (a) Decay of the expectation of the energy of a three-level system. The Einstein A coefficients A_{21} and A_{32} are chosen to be equal. Time is in units of A^{-1}, where $A \equiv A_{21} = A_{32}$. (b) Component of the envelope of the expectation of the dipole moment which oscillates at Ω_{32}. (c) Component of the envelope of the expectation of the dipole moment which oscillates at Ω_{21}.

evolves in time according to

$$\langle \mathcal{H}_0 \rangle = \tfrac{1}{2}(E_1+E_3) - (\tfrac{1}{4}-\alpha_0)^{1/2}\hbar\{\Omega_{32}\tanh[(\tfrac{1}{4}-\alpha_0)^{1/2} \times A(t-t_3)] + \Omega_{21}\tanh[(\tfrac{1}{4}-\alpha_0)^{1/2}A(t-t_1)]\},$$

where A is the Einstein A coefficient for the system. Further calculation reveals that the expectation of the dipole moment consists of two components, one oscillating at the frequency Ω_{32} and the other at the frequency Ω_{21}. Both components are modulated by hyperbolic secant envelopes. Graphs of the energy and the two components of the dipole moment are shown in Fig. 4.

The solutions of Eqs. (24) have been studied on an analog computer[13] in the case where $A_{21} \neq A_{32}$. Typical solutions are illustrated in Figs. 5 and 6. Figure 5 shows the cascading of the atom's energy down to the ground state, each transition of the atom being accompanied by the appearance of a dipole moment which oscillates at the transition frequency. Figure 6 illustrates the case in which the second level is short lived compared to the third ($A_{21} \gg A_{32}$). It is seen that the 3-2 dipole moment starts out looking somewhat like a hyperbolic secant, but then the fast 2-1 transition occurs and causes the truncation of the 3-2 dipole moment. Physically this "quenching" of the 3-2 dipole moment results in a broadening of the corresponding spectral line which would be qualitatively similar to the lifetime broadening which was first predicted quantum-electrodynamically by Weisskopf and Wigner.[14]

[13] These computations were supported by the Washington University computing facilities through National Science Foundation Grant No. G-22296.

INCLUSION OF AN APPLIED FIELD

Now consider the basic Eq. (14), including the applied field given by Eq. (13). When the applied field is tuned in frequency so that it is in near resonance with a pair of levels a and b, i.e., $\omega \approx \Omega_{ab}$, Eq. (14), as shown in Appendix A, becomes

$$\dot{\sigma}_{lm} = -i[\Omega_{lm} - \sum_j (\Gamma_{lj}-\Gamma_{jm})\sigma_{jj}(t)]\sigma_{lm} - \tfrac{1}{2}\sum_j (A_{lj}+A_{mj})\sigma_{jj}\sigma_{lm} + \tfrac{1}{2}\epsilon_{ba}\sigma_{am}e^{i\omega t}\delta_{l,b} - \tfrac{1}{2}\epsilon_{ab}\sigma_{bm}e^{-i\omega t}\delta_{l,a} - \tfrac{1}{2}\epsilon_{ba}\sigma_{lb}e^{i\omega t}\delta_{m,a} + \tfrac{1}{2}\epsilon_{ab}\sigma_{la}e^{-i\omega t}\delta_{m,b} \quad (28)$$

when only resonant terms are kept. The definition

$$\epsilon_{lm} \equiv \frac{|\Omega_{lm}|}{\omega}\frac{\mathbf{u}_{lm}\cdot\mathbf{E}_0}{\hbar}$$

has been made.

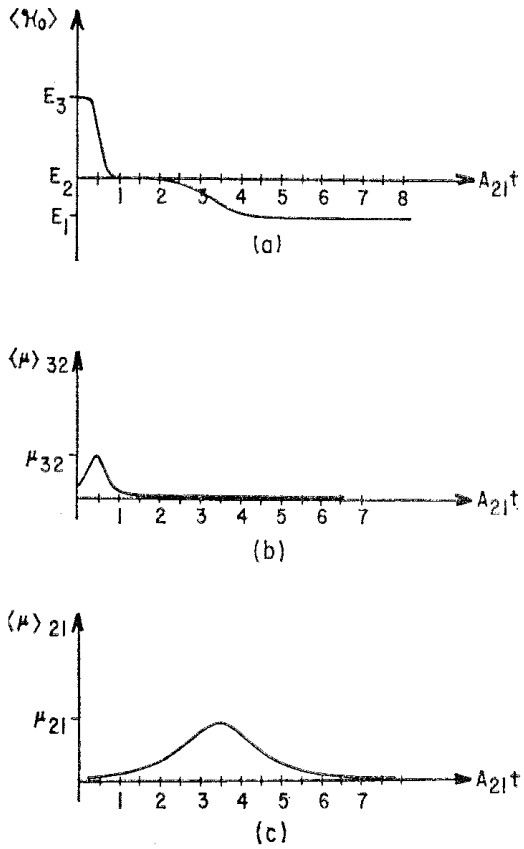

FIG. 5. (a) Cascading of the expectation of the energy of a three-level atom with $A_{32} = 4A_{21}$. Time is measured in units of A_{21}^{-1}. (b) Envelope of the expectation of the component of the dipole moment which oscillates at Ω_{32}. (c) Envelope of the expectation of the component of the dipole moment that oscillates at Ω_{21}.

[14] V. Weisskopf and E. Wigner, Z. Physik **63**, 73 (1930).

The following change of variables[15]

$$\tfrac{1}{2}(x-iy)e^{-i\omega t}\equiv\sigma_{ab}, \tag{29a}$$

$$z\equiv\sigma_{aa}-\sigma_{bb}, \tag{29b}$$

can be used along with the definitions

$$\epsilon_2+i\epsilon_1\equiv\epsilon_{ab},$$
$$\Delta\equiv\Omega_{ab}-\omega.$$

It follows from Eq. (28) that the variables x, y, and z evolve according to

$$\dot{x}=\epsilon_2 z-(\Delta-\sum_j(\Gamma_{aj}-\Gamma_{bj})\sigma_{jj})y - \sum_j \tfrac{1}{2}(A_{aj}+A_{bj})\sigma_{jj}x, \tag{30a}$$

$$\dot{y}=(\Delta-\sum_j(\Gamma_{aj}-\Gamma_{bj})\sigma_{jj})x-\epsilon_1 z - \sum_j \tfrac{1}{2}(A_{aj}+A_{bj})\sigma_{jj}y, \tag{30b}$$

$$\dot{z}=\epsilon_1 y-\epsilon_2 x-\sum_j(A_{aj}\sigma_{aa}-A_{bj}\sigma_{bb})\sigma_{jj}, \tag{30c}$$

and when l is not equal to a or b,

$$\dot{\sigma}_{ll}=-\sum_j A_{lj}\sigma_{jj}\sigma_{ll}. \tag{30d}$$

The variables x, y, and z satisfy the relation

$$x^2+y^2+z^2=(1-\sum_{j\neq a,b}\sigma_{jj}(t))^2;$$

therefore a solution of Eqs. (30) is confined to the surface of a sphere whose time-dependent radius is

$$R_{ab}\equiv 1-\sum_{j\neq a,b}\sigma_{jj}(t).$$

The component of the dipole moment which oscillates at the frequency $\omega\approx\Omega_{ab}$ is given by

$$\mu_{ab}(\sigma_{ab}+\sigma_{ba})=\mu_{ab}(x\cos\omega t-y\sin\omega t).$$

Thus $\mu_{ab}x(t)$ should be interpreted as the component of the dipole moment which oscillates in phase with the applied vector potential [see Eq. (13)], and $-\mu_{ab}y(t)$ as the component which is 90° behind.

For the case of a two-level system, Eqs. (30) may be written, respectively, as

$$\dot{x}=\epsilon z-[\Delta+\Gamma_{12}z]y+\tfrac{1}{2}A_{21}xz, \tag{31a}$$

$$\dot{y}=[\Delta+\Gamma_{12}z]x+\tfrac{1}{2}A_{21}yz, \tag{31b}$$

$$\dot{z}=-\epsilon x-\tfrac{1}{2}A_{21}(1-z^2). \tag{31c}$$

As indicated above, the wave functions have been chosen real so that ϵ_1 is zero and ϵ_2 is written as ϵ. A detailed study of the solutions of these nonlinear differential equations will be the subject of a future publication.[16] A salient feature of these equations is the existence of the "critical field." In the case of exact resonance $\Delta=0$, there are two distinct types of solutions of Eqs. (31), depending upon whether the applied field strength E_0 is greater or less than the critical field E_c. For applied field strengths less than that of the critical field, the system point attains a stationary point on the unit sphere. Physically this corresponds to the atom's dipole moment maintaining a constant phase relation with respect to the applied field and scattering light coherently. For applied fields greater than this critical field, the solutions are oscillatory; the system point moves in an orbit on the sphere. Physically this corresponds to the atom's absorbing and emitting radiation with no constant phase relation maintained between the applied field and the dipole moment. The critical field strength is given by

$$E_c=(\hbar/\mu)[(\tfrac{1}{2}A_{21})^2+\Gamma_{12}^2]^{1/2}.$$

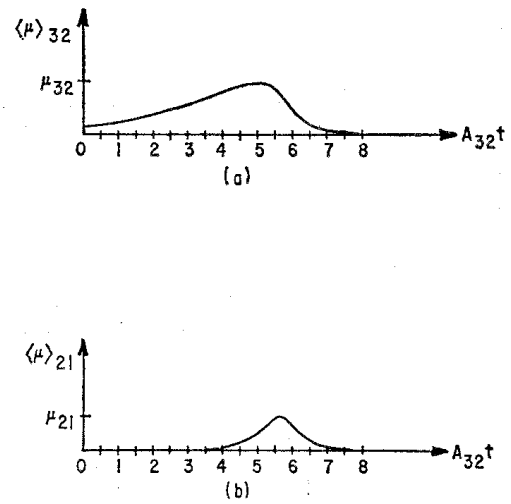

FIG. 6. (a) Envelope of the 3-2 dipole moment is shown in order to illustrate dipole moment quenching. Truncation of the 3-2 dipole moment is caused by the fast 2-1 transition. Time is in units of A_{32}^{-1}, where $A_{21}=10A_{32}$. (b) Envelope of the 2-1 dipole moment.

It is seen from Table I that the frequency shifts Γ_{lm} decrease rapidly with increasing quantum number. It is of interest, therefore, to seek solutions of Eqs. (30) when the Γ_{lm}'s are neglected. These solutions would be expected to give a fair description of alkali atoms such as sodium and potassium.

If one neglects the Γ_{lm}'s and applies the field nearly in resonance with the upper two levels, Eqs. (30) become

$$\dot{x}=\epsilon z-\Delta y+\tfrac{1}{2}(A_{32}z-A_{21}\sigma_{11})x, \tag{32a}$$

$$\dot{y}=\Delta x+\tfrac{1}{2}(A_{32}z-A_{21}\sigma_{11})y, \tag{32b}$$

$$\dot{z}=-\epsilon x-\tfrac{1}{2}A_{32}[(1-\sigma_{11})^2-z^2] + \tfrac{1}{2}A_{21}\sigma_{11}(1-\sigma_{11}-z), \tag{32c}$$

$$\dot{\sigma}_{11}=\tfrac{1}{2}A_{21}\sigma_{11}(1-\sigma_{11}-z). \tag{32d}$$

An analytic solution of these equations has been found in the case of exact resonance $\Delta=0$, and when the

[15] R. Feynman, F. Vernon, and R. Hellwarth, J. Appl. Phys. 28, 49 (1957).

[16] C. Stroud (private communication).

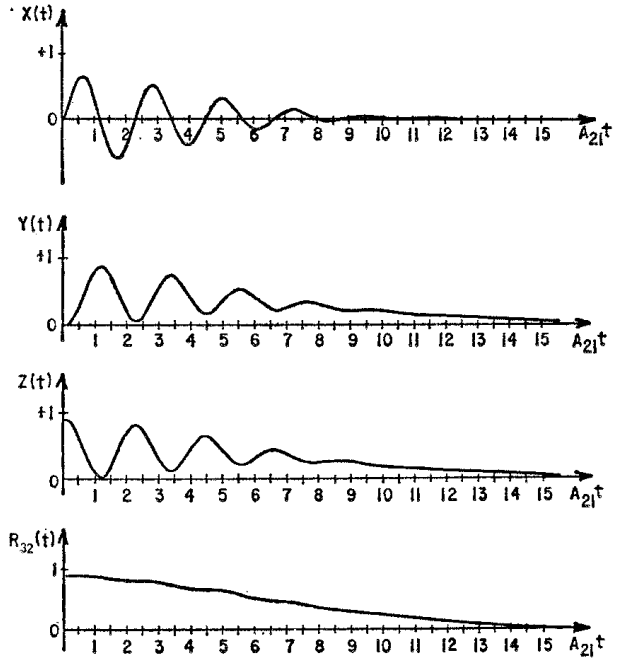

FIG. 7. Response of a three-level atom to a field applied at frequency $\omega=\Omega_{32}-A_{21}$ and with a strength of $\epsilon=A_{21}$. Time is in units of A_{21}^{-1}.

applied field is very strong so that $\epsilon\gg A_{21}$ and A_{32}. The derivation of Eq. (28) outlined in Appendix A tacitly contains the assumption that $\Omega\gg\epsilon$, where Ω represents the smallest optical frequency of the atom. Therefore, the solution given below will be valid within the range

$$A_{21},A_{32}\ll\epsilon\ll\Omega_{32},\Omega_{21}.$$

In this range the variables y, σ_{11}, and

$$X\equiv(x+iz)e^{i\epsilon t}$$

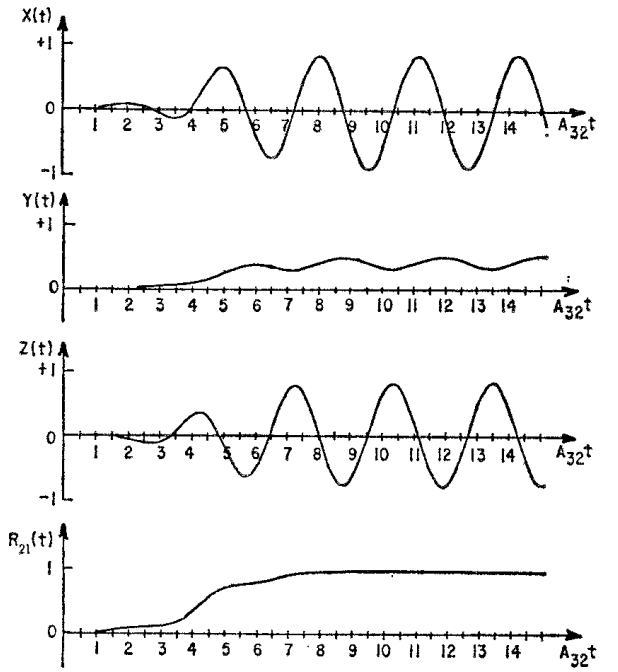

FIG. 8. Response of a three-level atom to a field applied with $\omega=\Omega_{21}-A_{32}$ and of strength $\epsilon=2A_{32}$. Time is in units of A_{32}^{-1}.

are slowly varying when compared with $e^{i\epsilon t}$, and the result of neglecting the rapidly oscillating terms is the solution

$$x(t)=\frac{2B\cos(\epsilon t+\theta_0)}{e^{\frac{1}{2}A_{21}(t-t_0)}+1}, \tag{33a}$$

$$y(t)=\frac{2y(t_0)}{e^{\frac{1}{2}A_{21}(t-t_0)}+1}, \tag{33b}$$

$$z(t)=\frac{-2B\sin(\epsilon t+\theta_0)}{e^{\frac{1}{2}A_{21}(t-t_0)}+1}, \tag{33c}$$

where B, θ_0, and t_0 are constants determined by the initial conditions. Geometrically, this solution corresponds to a system point rotating at angular rate ϵ about the y axis, while the radius of the sphere decreases slowly according to

$$R_{32}(t)=(e^{\frac{1}{2}A_{21}(t-t_0)}+1)^{-1}.$$

Further calculation shows that Eqs. (33a) and (33b) are components of a dipole moment given by

$$\begin{aligned}\langle\mathfrak{u}\rangle=&\,2\mathfrak{u}_{32}/[e^{\frac{1}{2}A_{21}(t-t_0)}+1]\\&\times[B\cos(\epsilon t+\theta_0)\cos\Omega_{32}t-y(t_0)\sin\Omega_{32}t]\\&+\mathfrak{u}_{21}\operatorname{sech}[\tfrac{1}{4}A_{21}(t-t_0)][C_1\cos(\tfrac{1}{2}\epsilon t+\theta_1)\cos\Omega_{21}t\\&-C_2\cos(\tfrac{1}{2}\epsilon t+\theta_2)\sin\Omega_{21}t],\end{aligned}$$

where C_1, C_2, θ_1, and θ_2 are constants. It can be seen that the component dipole moment oscillating at frequency Ω_{32} is amplitude modulated at frequency ϵ, while the component oscillating at Ω_{21} is amplitude modulated at frequency $\frac{1}{2}\epsilon$. A comparison of the 2-1 component of the dipole moment with Eq. (22) shows that the application of the saturating field to the 3-2 transition causes a narrowing of the 2-1 fluorescence by a factor of $\frac{1}{2}$.

More complete solutions of Eqs. (32) have been computed on an analog computer. Figure 7 shows the response of a three-level system in the case where $\omega\approx\Omega_{32}$, and Fig. 8 shows the response of the same system to a field with $\omega\approx\Omega_{21}$.

APPENDIX A

The density matrix elements in the interaction picture are defined according to

$$\rho_{lm}(t)\equiv\sigma_{lm}(t)e^{i\Omega_{lm}t}, \tag{A1}$$

and will be used to identify the rapidly oscillating terms. Substituting Eq. (11) into Eq. (7), one obtains

$$\begin{aligned}\dot\rho_{lm}=-\sum_{\alpha,\beta}\sum_j&[(\tfrac{1}{2}A_{lj}{}^{\beta\alpha}-i\Gamma_{lj}{}^{\beta\alpha})\rho_{\beta\alpha}\rho_{jm}e^{i(\Omega_{lj}+\Omega_{\alpha\beta})t}\\&-\rho_{lj}\rho_{\beta\alpha}(\tfrac{1}{2}A_{jm}{}^{\beta\alpha}-i\Gamma_{jm}{}^{\beta\alpha})e^{i(\Omega_{jm}+\Omega_{\alpha\beta})t}]\\&-\frac{\vec{A}_0(0,t)}{\hbar c}\cdot\sum_j[\Omega_{lj}\mathfrak{u}_{lj}\rho_{jm}e^{i\Omega_{lj}t}-\rho_{lj}\Omega_{jm}\mathfrak{u}_{jm}e^{i\Omega_{jm}t}],\end{aligned} \tag{A2}$$

where the definitions

$$A_{lj}{}^{\beta\alpha}\equiv\frac{4}{3}\frac{\mathfrak{u}_{\alpha\beta}\cdot\mathfrak{u}_{lj}}{\hbar c^3}\Omega_{\alpha\beta}{}^2\Omega_{lj} \tag{A3}$$

and

$$\Gamma_{lj}{}^{\beta\alpha}\equiv-\frac{1}{2\pi^2}\frac{e^2\hbar}{m^2c^2}\int_0^\infty dk\int d\Omega(\alpha|e^{-i\mathbf{k}\cdot\mathbf{x}}\nabla|\beta)_\perp \cdot(l|e^{i\mathbf{k}\cdot\mathbf{x}}\nabla|j)_\perp \tag{A4}$$

has been made.

The terms on the right-hand side of Eq. (A2) will be rapidly oscillating unless the argument of the exponential is zero. For example, in order for the term containing $\exp[i(\Omega_{lj}+\Omega_{\alpha\beta})t]$ to contribute significantly to ρ_{lm}, it is necessary that $\alpha=j$ and $\beta=l$. The sums over α and β can be eliminated by repeated use of this argument, and with the observation that

$$\rho_{lj}\rho_{jm}=\rho_{lm}\rho_{jj},$$

Eq. (A2) leads to Eq. (14).[17]

The applied field term in Eq. (A2) may be wrtten as

$$-\frac{\mathbf{E}_0}{\hbar\omega}\cdot\sum_j[\Omega_{lj}\mathfrak{u}_{lj}\rho_{jm}e^{i\Omega_{lj}t}\tfrac{1}{2}(e^{i\omega t}+e^{-i\omega t}) -\rho_{lj}\Omega_{jm}\mathfrak{u}_{jm}e^{i\Omega_{jm}t}\tfrac{1}{2}(e^{i\omega t}+e^{-i\omega t})] \tag{A5}$$

when Eq. (13) is used for $\mathbf{A}_0(0,t)$. Under the assumption that $\omega\approx\Omega_{ab}$, it is easy to pick out the resonant terms of the form $\exp[\pm i(\Omega_{ab}-\omega)t]$ in Eq. (A5). The nonresonant terms in Eq. (A5) will be neglected. The result, when substituted into Eq. (A2) and rewritten in the Schrödinger picture, is given by Eq. (28).

APPENDIX B

According to Eq. (18) and definition (15), the frequency shift in the $1s$-$2p$ absorption line of hydrogen would be

$$\delta\Omega_{2p_01s}=\frac{1}{2\pi^2}\frac{e^2\hbar}{m^2c^2}\int_0^\infty dk\int d\Omega(2p_0|e^{i\mathbf{k}\cdot\mathbf{x}}\nabla|1s)_\perp \cdot(1s|e^{-i\mathbf{k}\cdot\mathbf{x}}\nabla|2p_0)_\perp. \tag{B1}$$

Using

$$\psi_{1s}(\mathbf{x})=1/(\pi a^3)^{1/2}e^{-r/a},$$
$$\psi_{2p_0}(\mathbf{x})=1/(32\pi a^3)^{1/2}(z/a)e^{-r/2a},$$

it follows that

$$(2p_0|e^{i\mathbf{k}\cdot\mathbf{x}}\nabla|1s)_\perp\equiv-\frac{\mathbf{k}}{|\mathbf{k}|}\times\left[\frac{\mathbf{k}}{|\mathbf{k}|}\times(2p_0|e^{i\mathbf{k}\cdot\mathbf{x}}\nabla|1s)\right] =\frac{\sqrt{2}}{a^5}\frac{(\mathbf{k}/|\mathbf{k}|)\times[(\mathbf{k}/|\mathbf{k}|)\times\hat{e}_3]}{[k^2+(3/2a)^2]^2}$$

and

$$(1s|e^{-i\mathbf{k}\cdot\mathbf{x}}\nabla|2p_0)_\perp=-(2p_0|e^{i\mathbf{k}\cdot\mathbf{x}}\nabla|1s)_\perp,$$

and Eq. (B1) becomes

$$\delta\Omega_{2p_01s}=-\frac{1}{2\pi^2}\frac{e^2\hbar}{m^2c^2}\frac{2}{a^{10}}\int_0^\infty\frac{dk}{[k^2+(3/2a)^2]^4} \times\int\left[\frac{\mathbf{k}}{|\mathbf{k}|}\times\left(\frac{\mathbf{k}}{|\mathbf{k}|}\times\hat{e}_3\right)\right]^2d\Omega, \tag{B2}$$

where the vector $\hat{e}_3$ is a unit vector along the k_3 axis. Integrating Eq. (B2) gives

$$\delta\Omega_{2p_01s}=-\frac{5\times2^5}{3^8}\frac{e^2\hbar}{m^2c^2}\frac{1}{a^3}=-\frac{160}{6561}\alpha^4\left(\frac{mc^2}{\hbar}\right).$$

It should be noted that for fields stronger than the critical field (50 V/cm in hydrogen), Eq. (18) predicts that $\delta\Omega_{2p_01s}$ should vary with the applied field strength. The fields involved in Herzberg's experiment were much less than this.

[17] Caution must be exercised in the case where there are more than one set of α, β such that $\Omega_{\alpha\beta}=\Omega_{jl}$. For example, the first four levels of a spinless hydrogen atom ($1s$, $2p\pm1$, $2p_0$) exhibit a frequency degeneracy $\Omega_{2p_{\pm1}1s}=\Omega_{2p_01s}$. In cases such as this, however, $A_{lj}{}^{\beta\alpha}$ and $\Gamma_{lj}{}^{\beta\alpha}$ are zero unless $\alpha=j$ and $\beta=l$, so that this system is also described by Eq. (14).