Journal of Statistical Physics, Vol. 48, Nos. 5/6, 1987

Star-Unitary Transformations As a Tool in Single-Atom Pulse Spectroscopy

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Received May 17, 1987

Star-unitary transformations, of the type developed by I. Prigogine and his group, are used to study the pulse excitation and subsequent decay of a single atom coupled to the electromagnetic field. A systematic perturbation scheme is proposed for atomic properties, valid without limitation of time scale or strength of pulse irradiation, provided that the total duration of the pulses is shorter than the radiative lifetimes. In the absence of irradiation, Bloch-like rate equations are obtained as an exact result (in the "thermodynamic limit" of a large box enclosing the field).

KEY WORDS: Irreversibility; star-unitary transformations; pulse spectroscopy; decay of excited states; optical Bloch equations.

1. INTRODUCTION

As a tribute to our very dear friend and colleague Prof. I. Prigogine, we present here a progress report on work we have undertaken to apply the ideas on irreversible N-body dynamics developed by him and his group (see, e.g., Refs. 1–3) to simple problems of direct experimental interest in single-atom pulse spectroscopy. We share the enthusiasm expressed by Rosenfeld (see Ref. 4, pp. 563–564) for the power and usefulness of these ideas, and we feel that the extensive investigation of issues of principle on very simple models has generated a theoretical tool that should now be confronted with actual experiments.

Atomic spectroscopy combines many favorable features for such a comparison. Even a single fixed atom shows the essential irreversible process of spontaneous emission. The corresponding Hamiltonian is par-

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0022-4715/87/0900-1321$05.00/0

ticularly simple and has been studied in detail. Clean measurements can be made on the electromagnetic field at a large distance from the atom, by recording the time of each successive photoelectric event. A variety of time-dependent properties of the field are accessible by correlating these detection times among themselves, and by shining additional "reference" radiation on the photodetectors. Pulse techniques enable one to perform transient experiments in which time itself is the variable of interest on a scale that ranges continuously from much shorter to much larger than the characteristic time of spontaneous emission. In the overall theoretical description of such experiments, irreversibility manifests itself at least in two places: in spontaneous emission by the atom and also in the measurement process (photoelectric detection in the present case). We shall not discuss this latter problem here, however.

The model we shall use in the present paper has already been discussed in detail in a previous publication[5] in which we also examined some of its short-time properties. In brief, the time-independent Hamiltonian describes a fixed, bound atom interacting with the electromagnetic field and the initial condition describes the atom in the dressed ground state of the coupled atom–field system together with an approaching pulse of coherent radiation that will hit the atom later on. This model is summarized in Section 2, using a superoperator presentation convenient for our present purpose.

In Section 3 we briefly recall the main features of the nonunitary Λ transformation, showing in some detail how the standard procedures can be adapted to our somewhat unconventional model.

Finally, in Section 4 we derive a hierarchy of equations of motion for variants of the reduced density operator for the atom and a finite number of field modes. In the absence of irradiation (i.e., before *and* after irradiation), the equation of motion for the atom alone is in closed form and displays the expected decay of population from higher to lower lying eigenstates of the atomic Hamiltonian together with damped oscillations of the off-diagonal matrix elements at the Lamb-shifted Bohr frequencies of the atom. We emphasize the fact that these typically irreversible rate equations have been obtained as an "exact" result, with no approximation besides the "thermodynamic limit" of large volume of the "box" enclosing the field that is inherent in the Λ transformation used throughout. The situation is less simple during the periods of irradiation, because the whole hierarchy of equations has to be dealt with. However, we show how a systematic perturbation scheme can be developed for pulse spectroscopy, with no limitation on time scale or intensity of irradiation, provided that the total duration of the pulses is shorter than the radiative lifetimes.

In conclusion, we have shown on a simple example that the star-

unitary transformations developed by I. Prigogine and his group do provide a tool for predicting the behavior of Hamiltonian systems of experimental interest. The results obtained so far are "exact" confirmations of rate equations derived already using a combination of quantum mechanics, neglect of "small" terms, and heuristic arguments. We hope that new and unexpected predictions will be made, perhaps for experiments involving multiple photoelectric detection.

2. DESCRIPTION OF THE MODEL

2.1. Notation

We have found desirable to keep the convenience and clarity of the "ket" and "bra" notation used, e.g., in Ref. 6 when going over to the presentation of quantum mechanics in terms of operators and superoperators required for our present purpose.[3] To each operator A we associate a superket $|A\rangle$, which is an element of a linear vector space. The association is linear. To each superket $|A\rangle$, we associate a superbra $\langle A|$ using the trace metric $\langle A|B\rangle = \mathrm{Tr}\{A^\dagger B\}$. This association is antilinear. A superoperator $\mathscr{K}$ associates a superket $|B\rangle = \mathscr{K}|A\rangle$ to any superket $|A\rangle$. This association is linear. In many cases the relevant operators will be of the type $A = |b\rangle\langle c|$, where $|b\rangle$ and $\langle c|$ are conventional kets and bras, and we shall use the notation $|A\rangle = |(|b\rangle\langle c|)\rangle = |b, c\rangle$ and $\langle A| = \langle b, c|$. No ambiguity results from using the same typography for kets and superkets, because ket labels and operators are always distinct objects. Unit operators will be denoted by 1 and unit superoperators by **1**.

Whenever useful, we shall explicitly indicate the relevant state space for the various quantum objects (kets, operators, etc.) using a subscript A for the bare atom, F for the free field, S for the atom-field system, and k for the single mode k of the field (the operators $a_k^\dagger$ and a_k will be tacitly extended to the whole field space whenever necessary).

2.2. Liouvillian and Sketch of Initial Condition

The model, which is presented in detail in Ref. 5, consists of a time-independent Liouvillian (or Hamiltonian) and a dynamical initial condition. The Hamiltonian operator H_S describes a bare and bound atom at a fixed position in space, the complete electromagnetic field, and an atom–

[3] For a different presentation of the superoperator formalism, see, e.g., Refs. 1 and 7.

field coupling λV_S, which we shall assume to be linear in the field for simplicity:

$$H_S = H_{0A} \otimes 1_F + 1_A \otimes H_{0F} + \lambda V_S \tag{2.1}$$

$$H_{0A} = \sum_i \hbar\omega_i \, |i\rangle\langle i| \tag{2.2}$$

$$H_{0F} = \sum_k \hbar\omega_k a_k^\dagger a_k \tag{2.3}$$

$$\lambda V_S = \lambda \sum_k \sum_i \sum_j \{v_{i,jk} \, |i\rangle\langle j| \, a_k + v_{ik,j} \, |i\rangle\langle j| \, a_k^\dagger\} \tag{2.4}$$

where λ is introduced for further use as a perturbation parameter, i labels the eigenstates of the bare atom Hamiltonian, and $i = 1$ denotes the ground state (assumed to be nondegenerate); a_k and $a_k^\dagger$ are the usual boson annihilation and creation operators, and the Hermiticity of V implies that $v_{i,jk} = (v_{jk,i})^{\text{c.c.}}$.

The Liouvillian superoperator L_S is given by

$$L_S = [H_S, \cdot] = H_S \times 1_S - 1_S \times H_S \tag{2.5}$$

where the superoperator $A \times B$ is constructed from the operators A and B by requiring that, for any operator C, $(A \times B) \, |C\rangle = |ACB\rangle$. The Liouvillian will be written as

$$L_S = L_{0S} + \lambda \, \delta L_S \tag{2.6}$$

where

$$L_{0S} = L_{0A} \otimes \mathbf{1}_F + \mathbf{1}_A \otimes L_{0F} \tag{2.7}$$

$$L_{0A} = H_{0A} \times 1_A - 1_A \times H_{0A} \tag{2.8}$$

$$L_{0F} = H_{0F} \times 1_F - 1_F \times H_{0F} \tag{2.9}$$

$$\lambda \, \delta L_S = \lambda V_S \times 1_S - 1_S \times \lambda V_S \tag{2.10}$$

The initial condition, which will be discussed at the end of Section 2.4 is a consistent quantum mechanical description of the naive idea in which the atom and the field in its vicinity are in the exact ground state of the coupled atom–field problem, whereas the distant field contains a (perhaps large) quasiclassical excitation which will interact with the atom later. In the absence of the atom, the quasiclassical state of the field is completely specified by the classical (i.e., quantum averaged) fields $\alpha \mathbf{E}_{\text{cl}}(\mathbf{r}, t)$ and $\alpha \mathbf{B}_{\text{cl}}(\mathbf{r}, t)$, or by the set of coherent state parameters $\alpha\alpha_k(t)$ for all field modes k. The (real) parameter α has been introduced here for further use in

perturbation expansions. When the classical field is known [and symbolized by $\alpha f_{\rm cl}(t)$], the corresponding quasiclassical state of the field can be written as

$$|\alpha f_{\rm cl}(t)\rangle_F = M_F(\alpha f_{\rm cl}(t))\,|0\rangle_F \tag{2.11}$$

where the unitary "displacement operator" $M_F(\alpha f_{\rm cl}(t))$ is given by

$$M_F(\alpha f_{\rm cl}(t)) = \prod_k \exp[\alpha\alpha_k(t)\,a_k^\dagger - \alpha\alpha_k{}^{\rm c.c.}(t)\,a_k] \tag{2.12}$$

and $|0\rangle_F$ is the ground state of the bare field. We shall use the short-hand notation $M_F(t)$ for $M_F(\alpha f_{\rm cl}(t))$, and denote by

$$\mathcal{M}_F(t) = \mathcal{M}_F(\alpha f_{\rm cl}(t)) = M_F(\alpha f_{\rm cl}(t)) \times M_F^\dagger(\alpha f_{\rm cl}(t)) \tag{2.13}$$

the unitary superoperator constructed from $M_F(t)$ and $M_F^\dagger(t)$. The quasiclassical state of the free field (2.11) can be described by the density operator

$$\rho_F(t) = |\alpha f_{\rm cl}(t)\rangle_{\rm FF}\,\langle\alpha f_{\rm cl}(t)| = M_F(\alpha f_{\rm cl}(t))\,|0\rangle_{\rm FF}\,\langle 0|\,M_F^\dagger(\alpha f_{\rm cl}(t)) \tag{2.14}$$

Hence, by the density superket

$$|\rho_F(t)\rangle = \mathcal{M}_F(\alpha f_{\rm cl}(t))\,|\rho_{0F}\rangle \tag{2.15}$$

where $\rho_{0F} = |0\rangle_{\rm FF}\,\langle 0|$ describes the ground state of the free field.

Useful properties of $\mathcal{M}_F(t)$ are

$$\mathcal{M}_F^\dagger(\alpha f_{\rm cl}(t)) = \mathcal{M}_F^{-1}(\alpha f_{\rm cl}(t)) = \mathcal{M}_F(-\alpha f_{\rm cl}(t)) \tag{2.16}$$

$$\mathcal{M}_F(f_{\rm cl,1}(t))\,\mathcal{M}_F(f_{\rm cl,2}(t)) = \mathcal{M}_F(f_{\rm cl,1}(t) + f_{\rm cl,2}(t)) \tag{2.17}$$

$$\frac{\partial}{\partial t}\,\mathcal{M}_F(f_{\rm cl}(t)) = (1/i\hbar)[\mathcal{M}_F(f_{\rm cl}(t)),\, L_{0F}] \tag{2.18}$$

Finally, the $\mathcal{M}_F(\alpha f_{\rm cl}(t))$ superoperator is extended to the atom–field problem as

$$\mathcal{M}_S(\alpha f_{\rm cl}(t)) = \mathbf{1}_A \otimes \mathcal{M}_F(\alpha f_{\rm cl}(t)) \tag{2.19}$$

2.3. Disentangling the Quasiclassical Field Excitation from the Rest of the Problem

With the initial condition sketched above, and a weak atom–field coupling, we anticipate that the field will remain for a long time *close* to

the quasiclassical state (2.14), even during and after the overlap between pulse and atom; hence, the system will be *close* to a density superket of the type

$$|\rho_A(t) \otimes M_F(t)\, \rho_{0F} M_F^\dagger(t)\rangle = \mathscr{M}_S(t)\, |\rho_A(t) \otimes \rho_{0F}\rangle$$

This suggests using the unitary transformation $\mathscr{M}_S^\dagger(t) = \mathscr{M}_S^{-1}(t)$ to "remove" the coherent field excitation from the density superket in an attempt to simplify the dynamical problem. For this purpose, we define "bar"-transformed versions of the quantum objects as

$$\begin{aligned} |\bar{A}_S(t)\rangle &= \mathscr{M}_S^\dagger(t)\, |A_S(t)\rangle = |M_S^\dagger(t)\, A_S(t)\, M_S(t)\rangle \\ \langle \bar{B}_S(t)| &= \langle B_S(t)|\, \mathscr{M}_S(t) \end{aligned} \tag{2.20}$$

for any superket $|\bar{A}_S(t)\rangle$ and superbra $\langle \bar{B}_S(t)|$, and

$$\bar{\mathscr{K}}_S(t) = \mathscr{M}_S^\dagger(t)\, \mathscr{K}_S(t)\, \mathscr{M}_S(t) \tag{2.21}$$

for any superoperator $\mathscr{K}_S(t)$ involving the single time t.

If the density superket $|\rho_S(t)\rangle$ evolves according to the usual von Neumann equation of motion

$$(\partial/\partial t)\, |\rho_S(t)\rangle = (1/i\hbar)\, L_S\, |\rho_S(t)\rangle \tag{2.22}$$

with the Liouvillian superoperator (2.6), then the corresponding bar-transformed density superket $|\bar{\rho}_S(t)\rangle$ evolves according to

$$(\partial/\partial t)\, |\bar{\rho}_S(t)\rangle = (1/i\hbar)[L_S + \lambda(\overline{\delta L}_S(t) - \delta L_S)]\, |\bar{\rho}_S(t)\rangle \tag{2.23}$$

When only the terms linear in the field are retained in the atom–field coupling [see (2.4)], the term $\lambda(\overline{\delta L}_S(t) - \delta L_S)$ appearing in (2.23) takes the very simple form of a superoperator proportional to the magnitude α of the quasiclassical field excitation, acting nontrivially in the atomic state space only:

$$\lambda(\overline{\delta L}_S(t) - \delta L_S) = \lambda\alpha \mathscr{W}_A(t) \otimes \mathbf{1}_F \tag{2.24}$$

and a similar situation prevails in the traditional presentation of quantum mechanics:

$$\lambda(\bar{V}_S(t) - V_S) = \lambda\alpha W_A(t) \otimes 1_F \tag{2.25}$$

with

$$\mathscr{W}_A(t) = W_A(t) \times 1_A - 1_A \times W_A(t) \tag{2.26}$$

The superoperator $\mathscr{W}_A(t)$ is exactly the perturbing Liouvillian that would be used to describe the atom–field coupling in semiclassical models in which the atom is described quantum mechanically and the field classically. Combining (2.6), (2.23), and (2.24), we can rewrite the equation of motion for $|\bar{\rho}_S(t)\rangle$ under the form

$$(\partial/\partial t)\,|\bar{\rho}_S(t)\rangle = (1/i\hbar)[L_{0S} + \lambda\alpha\mathscr{W}_A(t)\otimes \mathbf{1}_F + \lambda\delta L_S]\,|\bar{\rho}_S(t)\rangle \quad (2.27)$$

Note that the transformations leading to (2.27) are *exact* and that the rhs of this equation of motion still contains the complete atom–field coupling $\lambda\delta L_S$ in addition to the semiclassical, time-dependent term (2.24).

2.4. Realistic Initial Conditions

Whenever the unperturbed classical field $\alpha f_{\mathrm{cl}}(\mathbf{r}, t)$ is exactly zero in the region of space occupied by the atom, the semiclassical term (2.24) is also exactly zero. This will be the case for all times t_i during the initial idle period of our model; hence, the equation of motion for $|\bar{\rho}_S(t_i)\rangle$ is

$$(\partial/\partial t_i)\,|\bar{\rho}_S(t_i)\rangle = (1/i\hbar)\,L_S\,|\bar{\rho}_S(t_i)\rangle \quad (2.28)$$

When the initial idle period is also one of rest (apart for the free propagation of the quasiclassical excitation of the field) then, *during this period*, $|\bar{\rho}_S(t_i)\rangle = |\bar{\rho}_{\mathrm{init}\,S}\rangle$ is time-independent and one can show that the quantum average energy is given by

$$\langle H_S\rangle = \langle H_S|\,\rho_S(t_i)\rangle = \langle \bar{H}_S|\,\bar{\rho}_{\mathrm{init}\,S}\rangle = \langle H_S|\,\bar{\rho}_{\mathrm{init}\,S}\rangle + \alpha^2 \sum_k \hbar\omega_k\,|\alpha_k|^2 \quad (2.29)$$

where the last term in the rhs of (2.29) is the energy of the unperturbed quasiclassical excitation of the field. For a given $\alpha f_{\mathrm{cl}}(t)$, the time-independent solution of (2.28) with the lowest possible quantum average energy is provided by the ground state $|G\rangle_S$ of the Hamiltonian H_S:

$$|\bar{\rho}_{\mathrm{init}\,S}\rangle = |\rho_{\mathrm{GS}}\rangle = |(|G\rangle_{SS}\langle G|)\rangle \quad (2.30)$$

We can now undo the bar transformation and obtain

$$|\rho_S(t_i)\rangle = \mathscr{M}_S(t_i)\,|\rho_{\mathrm{GS}}\rangle \quad (2.31)$$

This is a dynamical initial situation which is an *exact* solution of the von Neumann equation of motion during the whole initial idle period,

describing an atom in its dressed ground state and an approaching quasi-classical excitation of the field. This is the initial condition that will be used in the present paper.

2.5. The Energy Superoperator $\mathscr{H}$

Besides the Liouvillian (2.5), we shall make extensive use of a second superoperator similarly constructed from the Hamiltonian H_S: the "energy superoperator" $\mathscr{H}_S$, which is defined as

$$\mathscr{H}_S = \tfrac{1}{2}(H_S \times 1_S + 1_S \times H_S) \tag{2.32}$$

and has the following properties:

(a) It is Hermitian, $\mathscr{H}_S = \mathscr{H}_S^\dagger$.

(b) $\mathscr{H}_S |1_S\rangle = |H_S\rangle$ and $\langle 1_S| \mathscr{H}_S = \langle H_S|$; hence, $\langle H_S\rangle = \langle H_S|\rho_S\rangle = \langle 1_S| \mathscr{H}_S |\rho_S\rangle$, which explains the name "energy superoperator."

(c) $(\mathscr{H}_S)^n |1_S\rangle = |(H_S)^n\rangle$ for any positive integer n.

(d) It commutes with the Liouvillian, $[\mathscr{H}_S, L_S] = 0$.

(e) The lowest eigenvalue of $\mathscr{H}_S$ is the same as the lowest eigenvalue of the Hamiltonian H_S, and the corresponding "eigensuperket" is $|\rho_{GS}\rangle$ (after suitable normalization, assuming a nondegenerate eigenstate for H_S).

It is worth noting that the properties (a)–(e) above would *not* specify $\mathscr{H}_S$ completely, and that superoperators satisfying properties (a)–(d) above may have eigenvalues lower than the ground state of the Hamiltonian.

2.6. Standard Perturbative Approach for Short Times, Weak Coupling λ, and Arbitrary Excitation Strength λα

The equation of motion (2.27), together with the initial condition (2.30), can be solved for time intervals much shorter than the radiative lifetimes by ordinary perturbative techniques in which λ is used as a small expansion parameter, whereas $\lambda\alpha$ is treated as a finite quantity (by suitably letting α tend to infinity when λ tends to zero). At zeroth order in λ (denoted by a superscript zero in parentheses), the initial condition is factorized between atom and field quantum spaces, $|\bar{\rho}_{\text{init } S}\rangle^{(0)} = |(|1\rangle_{AA}\langle 1|)\rangle_A \otimes |\rho_{0F}\rangle$, and this property persists for all times,

$$|\bar{\rho}_S(t)\rangle^{(0)} = |\sigma_A(t)\rangle^{(0)} \otimes |\rho_{0F}\rangle \tag{2.33}$$

with the reduced atom density superket $|\sigma_A(t)\rangle^{(0)}$ obeying the usual

equation of motion of the semiclassical model (Bloch equations without relaxation):

$$(\partial/\partial t)\,|\sigma_A(t)\rangle^{(0)} = (1/i\hbar)[L_{0A} + \lambda\alpha \mathscr{W}_A(t)]\,|\sigma_A(t)\rangle^{(0)} \tag{2.34}$$

As discussed at length in Ref. 5, great care must be taken in such a perturbative scheme when the average value of an observable (denoted K_S here)

$$\langle K_S\rangle(t) = \langle K_S|\,\rho_S(t)\rangle = \langle \bar{K}_S|\,\bar{\rho}_S(t)\rangle \tag{2.35}$$

is expanded as a power series in λ, because the bar transformation of the observable may introduce factors α that behave as λ^{-1}. For instance, the evaluation of the average value of the contribution $1_A \otimes H_{0F}$ to the Hamiltonian (2.1) to order zero in λ requires the evaluation of $|\bar{\rho}_S(t)\rangle$ up to order one in λ.

At order one in λ, the resulting description of the coupled atom–field system closely resembles the usual "Maxwell–Bloch" scheme of quantum optics.

However, an attempt to understand the radiative effects also over long times, entirely from first principles, by pursuing such a perturbative scheme systematically to higher orders in λ would lead (at best) into forbidding complications. In the next sections, we briefly show on a few examples how the star-unitary transformations introduced by I. Prigogine and his coworkers provide an effective tool for the discussion of such effects over any time scale.

To conclude this presentation of our model, we stress that the conventional picture of the field as a collection of "particles" (photons) is most inadequate in the present case of a short quasiclassical pulse of radiation. Even for a single mode of the field, the correlations between eigenstates of the field Hamiltonian are the main feature of quasiclassical states (see, e.g., Ref. 9, p. 284). In the present case of a field pulse, the localization of the disturbance in a comparatively small region of space is furthermore also the result of large systematic correlations involving *all* the field modes. If one treats the pulse excitation of the atom in the limit of small λ and small $\lambda\alpha$ (Born approximation, keeping only terms up to order λ^2 in the formal solution of the equation of motion), the disturbance of the atom appears as directly related to these *correlations* in the field state, and not to the occupation probability of the various eigenstates of the free field Hamiltonian.

3. DISENTANGLING EXCITATION AND RELAXATION THROUGH STAR-UNITARY TRANSFORMATIONS

In the present section, we briefly recall the scheme involving star-unitary transformations (referring the reader to the literature for details;

see, e.g., Refs. 1–3, 7, and 8) and show how we have used it for the model described in the previous section. The approach will still be a perturbative one, with the strength λ of the atom–field coupling treated as a small expansion parameter, keeping the excitation strength $\lambda\alpha$ constant and finite. However, time intervals (after the onset of the excitation) will no longer be required to be short. The new feature is the "thermodynamic limit," i.e., the limit of a very large system, which is used from the very beginning in the definition and construction of the transformation Λ. In the present model, only the size of the "box" enclosing the field tends to infinity, whereas the atom remains unique and the quasiclassical field always causes the same excitation.

3.1. Definition of Suitable Transformations $\Lambda(L)$

For any superoperator $K(L)$ depending upon the Liouvillian L, the star-transform is defined as

$$K^*(L) = [K(-L)]^\dagger \tag{3.1}$$

The essential property of the transformation $\Lambda(L)$ that we shall use is its star-unitarity:

$$\Lambda(L)\,\Lambda^*(L) = \Lambda^*(L)\,\Lambda(L) = \mathbf{1} \tag{3.2}$$

Transformed versions of superkets, superbras, and superoperators will be denoted by a superscript p:

$$\Lambda^*\,|A\rangle = |A\rangle^{\mathrm{p}}, \qquad \langle B|\,\Lambda = {}^{\mathrm{p}}\langle B|, \qquad \Lambda^*\mathscr{K}\Lambda = {}^{\mathrm{p}}\mathscr{K} \tag{3.3}$$

Combining (3.2) and (3.3), we have

$$\langle B|\,\mathscr{K}\,|A\rangle = {}^{\mathrm{p}}\langle B|\,{}^{\mathrm{p}}\mathscr{K}\,|A\rangle^{\mathrm{p}} \tag{3.4}$$

It is worth noting that, in general, $\Lambda(L)$ is *not* unitary, hence ${}^{\mathrm{p}}\langle A|$ is *not* the superbra corresponding to $|A\rangle^{\mathrm{p}}$.

The p-transformed version of the equation of motion (2.27) can be written as[4]

$$(\partial/\partial t)\,|\bar{\rho}_S(t)\rangle^{\mathrm{p}} = (1/i\hbar)[{}^{\mathrm{p}}L_S + \lambda\alpha\,{}^{\mathrm{p}}\mathscr{W}_S(t)]\,|\bar{\rho}_S(t)\rangle^{\mathrm{p}} \tag{3.5}$$

where

$$|\bar{\rho}_S(t)\rangle^{\mathrm{p}} = \Lambda^*\,|\bar{\rho}_S(t)\rangle = \Lambda^*\mathscr{M}^\dagger(t)\,|\rho_S(t)\rangle \tag{3.6}$$

[4] The superoperator ${}^{\mathrm{p}}L_S$ is denoted Φ in most papers on this topic.

Further properties of $\Lambda(L)$ are as follows:

(a) Λ and Λ^* are adjoint symmetric: if $A = A^\dagger$, $|A\rangle^{\mathrm{P}} = \Lambda^* |A\rangle = |B\rangle$, and ${}^{\mathrm{P}}\langle A| = \langle A| \Lambda = \langle C|$, then $B = B^\dagger$ and $C = C^\dagger$.

(b) When $\lambda \to 0$, then $\Lambda(L) \to \mathbf{1}$ and $\Lambda^*(L) \to \mathbf{1}$.

(c) If we denote by $|a, b\rangle = |(|a\rangle\langle b|)\rangle$ the elements of a superbasis constructed with the eigenstates $|a\rangle$ of the unperturbed Hamiltonian $H_{0S} = H_{0A} \otimes 1_F + 1_A \otimes H_{0F}$, such that $H_{0S} |a\rangle = \hbar\omega_a |a\rangle$, then

$$\begin{aligned} {}^{\mathrm{P}}\langle 1 | a, b\rangle &= \langle 1| \Lambda |a, b\rangle = \delta_{a,b}\, {}^{\mathrm{P}}\langle 1 | a, a\rangle \\ \langle a, b | 1\rangle^{\mathrm{P}} &= \langle a, b| \Lambda^* |1\rangle = \delta_{a,b} \langle a, a | 1\rangle^{\mathrm{P}} \end{aligned} \tag{3.7}$$

$$\langle a, b|\, {}^{\mathrm{P}}\mathscr{H} |c, d\rangle = \langle a, b| \Lambda^* \mathscr{H} \Lambda |c, d\rangle = \delta_{a,c}\delta_{b,d} \langle a, b|\, {}^{\mathrm{P}}\mathscr{H} |a, b\rangle \tag{3.8}$$

The main tool for constructing useful transformations with the above properties is provided by the relation

$$\Pi^{(\nu)} = \Lambda P^{(\nu)} \Lambda^* \tag{3.9}$$

valid for all eigenvalues $\hbar\nu = \hbar\omega_a - \hbar\omega_b$ of the unperturbed Liouvillian L_{0S}, where the $\Pi^{(\nu)}$ and $P^{(\nu)}$ are two complete sets of orthogonal superprojectors (which are identical in the limit $\lambda \to 0$). The set $P^{(\nu)}$ is defined by

$$P^{(\nu)} = -(1/2\pi i) \int_{(\nu)} dz \sum_{a,b,c,d} |a, b\rangle\langle a, b|\, 1/(z - L_0)\, |c, d\rangle\langle c, d| \tag{3.10}$$

where the symbol (ν) means that the integration has to be performed on a clockwise contour surrounding the singularity at $z = \hbar\nu$ only. This leads to

$$\begin{aligned} P^{(\nu)} &= \mathrm{Res}_{z=\hbar\nu} \sum_{a,b,c,d} |a, b\rangle\langle a, b|\, 1/(z - L_0)\, |c, d\rangle\langle c, d| \\ &= \sum_{a,b;(\omega_a - \omega_b = \nu)} |a, b\rangle\langle a, b| \end{aligned} \tag{3.11}$$

where the last summation is only over the pairs a, b for which $\omega_a - \omega_b = \nu$. In the case of a discrete system, the λ-dependent superprojectors $\Pi^{(\nu)}$ can easily be defined by replacing L_0 by L and the unperturbed energy differences by the exact energy differences in the above expression for $P^{(\nu)}$. Such an expression can be written as a Taylor expansion in λ, which, in turn, is the starting point for the extension to systems where the thermodynamic limit leads to a continuous spectrum, hence to problems of analytical

continuation. In all that follows, the superprojectors $\Pi^{(\nu)}$ will be defined only in the framework of perturbation expansions,[5] i.e., as

$$\Pi^{(\nu)} = \mathrm{Res}_{z=\hbar\nu+i\varepsilon'} \sum_{a,b,c,d} |a,b\rangle\langle a,b|\, 1/(z-L_0) \times \sum_{n=0}^{\infty} [\delta L/(z-L_0)]^n\, |c,d\rangle\langle c,d| \tag{3.12}$$

where ε' means, with $\varepsilon > 0$, that, when computing the residue, z has to be replaced by $(\hbar\nu + i\varepsilon)$ in certain propagators and by $(\hbar\nu - i\varepsilon)$ in the others, according to a well-defined rule (see, e.g., Refs. 3 and 12). The well-defined character of this rule requires the definition of the degree of correlation of superstates $|a,b\rangle$ and a theorem in dynamics of correlations. We refer to the literature for more details and only want to point out here that, whereas the vacuum of correlation is usually defined as the set of superstates $|a,a\rangle$ corresponding to the eigenvalue $\nu = 0$ of L_0, in the problem considered here one must add to this set all the superstates $|a,b\rangle$ corresponding to the Bohr frequencies of the bare atom,[13] $\nu_{ij} = (\omega_i - \omega_j)$. When this is done, an n-correlated state $|a,b\rangle$ is such that n different boson frequencies appear in $(\omega_a - \omega_b)$.

With $A^{(\nu)}$, $C^{(\nu)}$, $D^{(\nu)}$, and $\chi^{(\nu)}$ defined by

$$A^{(\nu)} = P^{(\nu)}\Pi^{(\nu)}P^{(\nu)} \tag{3.13}$$

$$C^{(\nu)}A^{(\nu)} = (\mathbf{1} - P^{(\nu)})\,\Pi^{(\nu)}P^{(\nu)} \tag{3.14}$$

$$A^{(\nu)}D^{(\nu)} = P^{(\nu)}\Pi^{(\nu)}(\mathbf{1} - P^{(\nu)}) \tag{3.15}$$

$$\chi^{(\nu)} = P^{(\nu)}\Lambda P^{(\nu)}, \qquad \chi^{*(\nu)} = P^{(\nu)}\Lambda^* P^{(\nu)} \tag{3.16}$$

relation (3.9) leads to a class of star-unitary transformations such that

$$(\mathbf{1} - P^{(\nu)})\,\Lambda P^{(\nu)} = C^{(\nu)}\chi^{(\nu)} \tag{3.17}$$

$$P^{(\nu)}\Lambda^*(\mathbf{1} - P^{(\nu)}) = \chi^{*(\nu)}D^{(\nu)} \tag{3.18}$$

with the following condition on $\chi^{(\nu)}$ and $\chi^{*(\nu)}$:

$$\chi^{(\nu)}\chi^{*(\nu)} = A^{(\nu)} \tag{3.19}$$

Note that this condition only provides a link between $\chi^{(\nu)}$ and $\chi^{*(\nu)}$. For this class of star-unitary transformations, the supplementary requirements (3.7) and (3.8) lead to conditions on the $\chi^{(\nu)}$ that are still not sufficient to

[5] Nonperturbative constructions of $\Pi^{(\nu)}$ have been found in some extremely simple cases (see Ref. 3, especially Appendix F, and Refs. 10 and 11).

determine these superoperators completely. This problem will be discussed at length in further publications. We point out here that some useful properties can nevertheless be established.

First of all, it is possible[14] to show that the real quantities

$$\hbar\Gamma_a = i\langle a, a|^{\mathrm{P}} L_S |a, a\rangle \tag{3.20}$$

$$\hbar\Omega_a = \langle a, a|^{\mathrm{P}} \mathscr{H}_S |a, a\rangle \tag{3.21}$$

are identical for *all* star-unitary transformations satisfying (3.7)–(3.9). Moreover, with the short-hand notation i for $i\{0_k\}$, at least up to order λ^4 (at arbitrary order in λ for two-level systems and for a three-level system within the RWA), one can show that $\hbar\Omega_i$ and Γ_i are identical with the Lamb-shifted energy $\hbar\bar{\Omega}_i$ and inverse lifetime $\bar{\Gamma}_i$ obtained in the Green's function formalism (see, e.g., Ref. 15, Chapter 8). More precisely, if $\eta_i^+(z)$ denotes the analytical continuation from above of the function $\eta_i(z) = [\langle i|\, 1/(z-H)\, |i\rangle]^{-1}$, then $\hbar(\bar{\Omega}_i - i\bar{\Gamma}_i/2)$ is the root of the equation $\eta_i^+(z) = 0$ that is identical to $\hbar\omega_i$ when $\lambda = 0$.

3.2. Equation of Motion for Transformed Quantities

The above results are still "static" results (time is not involved). To discuss *dynamical* aspects, it appears interesting to consider, rather than the global evolution of $|\bar{\rho}_S(t)\rangle^{\mathrm{P}}$, the evolution of its various projections $P^{(\nu)}|\bar{\rho}_S(t)\rangle^{\mathrm{P}}$. It can be shown that (3.5) leads to

$$(\partial/\partial t)[P^{(\nu)}|\bar{\rho}_S(t)\rangle^{\mathrm{P}}] = (1/i\hbar)\,\lambda\alpha \sum_{\nu'} [P^{(\nu)\,\mathrm{P}}\mathscr{W}_S(t)\, P^{(\nu')}][P^{(\nu')}|\bar{\rho}_S(t)\rangle^{\mathrm{P}}]$$
$$+ (1/i\hbar)[P^{(\nu)\,\mathrm{P}}L_S P^{(\nu)}][P^{(\nu)}|\bar{\rho}_S(t)\rangle^{\mathrm{P}}] \tag{3.22}$$

The fact that the second term in the rhs involves only $P^{(\nu)}|\bar{\rho}_S(t)\rangle^{\mathrm{P}}$, in contrast with the first one, which involves all the projections $P^{(\nu')}|\bar{\rho}_S(t)\rangle^{\mathrm{P}}$, is a consequence of (3.9), the commutation relation $[\Pi^{(\nu)}, L] = 0$, and the orthogonality property $P^{(\nu)}P^{(\nu')} = \delta_{\nu,\nu'}P^{(\nu)}$.

For all times τ for which the unperturbed field excitation does not overlap the atom (this includes the initial idle period), only the second term (in ${}^{\mathrm{P}}L_S$) in the rhs of (3.22) is different from zero and (3.22) takes the simple form

$$(\partial/\partial\tau)[P^{(\nu)}|\bar{\rho}_S(\tau)\rangle^{\mathrm{P}}] = (1/i\hbar)[P^{(\nu)\,\mathrm{P}}L_S P^{(\nu)}][P^{(\nu)}|\bar{\rho}_S(\tau)\rangle^{\mathrm{P}}] \tag{3.23}$$

of separated equations of motion for each projection $[P^{(\nu)}|\bar{\rho}_S(\tau)\rangle^{\mathrm{P}}]$. In contrast, during the excitation period (i.e., during the overlap of the unperturbed field excitation with the atom), the term in ${}^{\mathrm{P}}\mathscr{W}_S(t)$ in (3.22) mixes all

the "subdynamics" (see the summation over all v'). With the choice of transformations made in the present paper, this mixing is an essential feature of the excitation period.

In his work on the evolution of a system under the action of an external time-dependent force, Coveney[16] obtained the same kind of result: the action of the external field mixes the various subdynamics; in contrast with his work, we shall not attempt to look for transformations that would restore this decomposition.

To go further, we mention that, as a consequence of the diagonality condition (3.8) for ${}^{\mathrm{p}}\mathscr{H}$ and of the commutativity of $\mathscr{H}$ and L, we can show that

$$\langle a, a|^{\mathrm{p}} L_S |b, b\rangle \propto \delta(\Omega_a - \Omega_b) \qquad \text{for} \quad a \neq b \tag{3.24}$$

For times τ such that there is no overlap between the unperturbed field excitation and the atom, this means that the evolution is governed by Pauli-like equations,

$$(\partial/\partial\tau)\langle a, a|\bar{\rho}_S(\tau)\rangle^{\mathrm{p}} = (1/i\hbar)\sum_b \langle a, a|^{\mathrm{p}} L_S |b, b\rangle\langle b, b|\bar{\rho}_S(\tau)\rangle^{\mathrm{p}} \tag{3.25}$$

More specifically, at lowest nonvanishing order in λ, we have, e.g., for $a \neq b$,

$$(1/i\hbar)\langle a, a|^{\mathrm{p}} L_S |b, b\rangle^{(0)} = \gamma_{a,b} = \lambda^2 |\langle a| V_S |b\rangle|^2 (2\pi/\hbar^2)\,\delta(\omega_a - \omega_b) \tag{3.26}$$

and

$$(1/i\hbar)\langle a, a|^{\mathrm{p}} L_S |a, a\rangle^{(0)} = -\gamma_a = -\sum_{b\,(\neq a)} \gamma_{a,b} \tag{3.27}$$

where the above relations define the rates $\gamma_{a,b}$ and γ_a.

If we restrict ourselves to interactions that do not introduce level crossings (i.e., such that $\Omega_a < \Omega_b$ if $\omega_a < \omega_b$) and use the short-hand notation $\{0_k\}$ to denote the ground state of the free field (all n_k equal to zero), then (3.24) and the fact that $\gamma_{1\{0_k\}} = 0$ imply that

$$\langle a, a|^{\mathrm{p}} L_S |1\{0_k\}, 1\{0_k\}\rangle = 0 \qquad \text{for all} \quad a \tag{3.28}$$

As a consequence, for $\tau = t_i$ in the initial idle period, the relations

$$\begin{aligned} {}^{\mathrm{p}}\langle 1|1\{0_k\}, 1\{0_k\}\rangle\langle 1\{0_k\}, 1\{0_k\}|\bar{\rho}_S(t_i)\rangle^{\mathrm{p}} &= 1 \\ \langle a, b|\bar{\rho}_S(t_i)\rangle^{\mathrm{p}} &= 0 \qquad \text{for all} \quad \langle a, b| \neq \langle 1\{0_k\}, 1\{0_k\}| \end{aligned} \tag{3.29}$$

imply that the p-transformed superket

$$|\bar{\rho}_S(t_i)\rangle^{\mathrm{p}} = |1\{0_k\}, 1\{0_k\}\rangle({}^{\mathrm{p}}\langle 1|1\{0_k\}, 1\{0_k\}\rangle)^{-1} \tag{3.30}$$

is a stationary solution of (3.23) to all orders in λ, with the proper normalization for describing the state of a physical system:

$$1 = \langle 1 \,|\, \rho_S(t) \rangle = \langle 1 \,|\, \bar{\rho}_S(t) \rangle = {}^{\mathrm{p}}\langle 1 \,|\, \bar{\rho}_S(t) \rangle^{\mathrm{p}} \tag{3.31}$$

Combining (3.6), (3.7), the limit property $\Lambda \to \mathbf{1}$ when $\lambda \to 0$, and the remark leading to (2.33), it is obvious that, *at order zero in* λ, the expressions (3.30) and (2.31) describe exactly the same state of the coupled atom–field system. The question, however, arises of this equivalence at *arbitrary order in* λ. If there is only one "stable" situation for a given approaching pulse of radiation, the answer must be yes, if the whole scheme is consistent. Using the general properties that define the Λ transformation, we have been able to prove that the p-bar transform of (2.31) is indeed (3.30) up to order λ^2, and we have many indications that the proof will extend to higher orders.

4. REDUCING TO SMALL SUBSPACES AFTER THE Λ AND $\mathscr{M}$ TRANSFORMATIONS

As usual in statistical physics, reducing to small subspaces is a powerful tool in the present context when the relevant observables act nontrivially only in such subspaces and the hierarchy of equations of motion for the corresponding reduced distribution functions (more exactly "reduced density superkets") can be truncated in the framework of a systematic perturbation scheme.

4.1. Reduced Density Superkets

The subspaces used here explicitly are the subspace of the bare atom (denoted A) and the subspace of the bare atom and the single mode k of the field (denoted Ak). Other interesting subspaces would involve the bare atom and a finite list of field modes, or field modes only. In all cases, the reduction takes place by the superspace version of "taking a partial trace over the subspace that is eliminated in the reduction," Using a notation for eigenstates of the unperturbed Hamiltonian in which i and j label the eigenstates of the bare atom, n_k stands for an eigenvalue of $a_k^\dagger a_k$ and $\{\cdot\}$ denotes the set of all field modes, the relevant reduced density superkets can be defined by the following expressions for their components:

$${}_A\langle i, j \,|\, \sigma_A(t) \rangle_A = \sum_{\{n_k\}} {}_S\langle i\{n_k\}, j\{n_k\} \,|\, \bar{\rho}_S(t) \rangle_S^{\mathrm{p}} \tag{4.1}$$

$${}_{Ak}\langle in_k, jn'_k \,|\, \sigma_{Ak}(t) \rangle_{Ak}$$

$$= \sum_{\{n_{k'}\}(k' \neq k)} {}_S\langle in_k\{n_{k'}\}, jn'_k\{n_{k'}\} \,|\, \bar{\rho}_S(t) \rangle_S^{\mathrm{p}} \tag{4.2}$$

In the case of the initial condition of our model [using version (3.30) of this dynamical state], the atom reduced density superket takes the very simple form

$$|\sigma_A\rangle_A = |(|1\rangle_{AA}\langle 1|)\rangle_A \, ({}^{\mathrm{p}}_{S}\langle 1\,|\,1\{0_k\}, 1\{0_k\}\rangle_S)^{-1} \tag{4.3}$$

and all reduced density superkets involving one or more field modes are exactly zero.

The asymptotic behavior of various objects for large volumes $\mathcal{V}$ accessible to the field is an important property in the present scheme in which the transformation Λ itself is also defined in the limit of large $\mathcal{V}$. The fact that the initial condition (3.30) involves the ground state of the field, together with the dependence in $\mathcal{V}^{-1/2}$ of the matrix elements of the atom–field coupling Liouvillian δL_S, imply, with $n = \sum_k n_k$ and $n' = \sum_k n'_k$, that

$${}_S\langle i\{n_k\}, j\{n'_k\}\,|\,\bar{\rho}_S(t)\rangle^{\mathrm{p}}_S = O(\mathcal{V}^{-(n+n')/2}) \tag{4.4}$$

Using a notation in which n_k is not written when it is equal to zero and k itself is written when $n_k = 1$, we can express a first consequence of (4.4) as

$$\begin{aligned} {}_A\langle i, j\,|\,\sigma_A(t)\rangle_A = {}_S\langle i, j\,|\,\bar{\rho}_S(t)\rangle^{\mathrm{p}}_S + \sum_{r\,(r\geqslant 1)} (1/r!) \\ \times \sum_{k_1\cdots k_r} \langle ik_1\cdots k_t, jk_1\cdots k_r\,|\,\bar{\rho}_S(t)\rangle^{\mathrm{p}}_S + O(\mathcal{V}^{-1}) \end{aligned} \tag{4.5}$$

4.2. Evolution of $|\sigma_A(\tau)\rangle$ without Irradiation

A second consequence is that, *for all times τ for which the unperturbed field excitation does not overlap the atom*, and in the limit of large volume $\mathcal{V}$, the reduced density superket [in the sense of (4.1) and (4.2)] for a subsystem involving the atom and a finite number of field modes has an equation of evolution that involves only the reduced density superket itself and more strongly reduced density superkets for subsystems involving the atom and some of these field modes. In other words, there is no hierarchy of equations, hence no need to truncate it, in this regime. In the particularly simple case of the atom reduced density superket, the equation of motion can be written as the following closed system of differential equations for the components of $|\sigma_A(\tau)\rangle_A$ (assuming for simplicity that all Bohr frequencies of the atom are different): a set of coupled equations for the "diagonal" (i, i) elements,

$$(\partial/\partial t)\ {}_A\langle i, i|\sigma_A(\tau)\rangle_A$$
$$= (1/i\hbar)\ {}_S\langle i, i|\ {}^{\mathrm{P}}L_S\ |i, i\rangle_S\ {}_A\langle i, i|\sigma_A(\tau)\rangle_A$$
$$+ (1/i\hbar) \sum_{r(r\geqslant 1)} \sum_{k_1\cdots k_r} \sum_{j(\omega_j > \omega_i)}$$
$$\times\ {}_S\langle ik_1\cdots k_r, ik_1\cdots k_r|\ {}^{\mathrm{P}}L_S\ |j, j\rangle_S\ {}_A\langle j, j|\sigma_A(\tau)\rangle_A \qquad (4.6)$$

and separated equations for each "nondiagonal" ($i \neq j$) element,

$$(\partial/\partial\tau)\ {}_A\langle i, j|\sigma_A(\tau)\rangle_A = (1/i\hbar)\ {}_S\langle i, j|\ {}^{\mathrm{P}}L_S\ |i, j\rangle_S\ {}_A\langle i, j|\sigma_A(\tau)\rangle_A \qquad (4.7)$$

Equation (3.28) implies that $\langle 1, 1|\ {}^{\mathrm{P}}L_S\ |1, 1\rangle = 0$; hence, only the second term remains in the rhs of (4.6) for the ground state $i = 1$, while, due to Eq. (3.24), only the first term in the rhs of (4.6) remains for the highest excited state.

Some useful properties of the matrix elements appearing in the above equations are

$$(1/i\hbar)\ {}_S\langle i, i|\ {}^{\mathrm{P}}L_S\ |i, i\rangle_S$$
$$= -\lambda^2\gamma_i = -(2\pi/\hbar^2)\,\lambda^2 \sum_k \sum_{j(\omega_j < \omega_i)} |v_{i,jk}|^2\,\delta(\omega_i - \omega_j - \omega_k) + O(\lambda^4) \qquad (4.8)$$

$$(1/i\hbar) \sum_{j(\omega_j > \omega_i)}\ {}_S\langle ik_1\cdots k_r, ik_1\cdots k_r|\ {}^{\mathrm{P}}L_S\ |j, j\rangle_S = O(\lambda^{2r}) \qquad (4.9)$$

$$(1/i\hbar)\ {}_S\langle ik, ik|\ {}^{\mathrm{P}}L_S\ |j, j\rangle_S$$
$$= \lambda^2\gamma_{ik,j} = (2\pi/\hbar^2)\,\lambda^2\,|v_{ik,j}|^2\,\delta(\omega_i + \omega_k - \omega_j) + O(\lambda^4) \qquad (4.10)$$

$$(1/i\hbar)\ {}_S\langle i, j|\ {}^{\mathrm{P}}L_S\ |i, j\rangle_S$$
$$= -i(\omega_i + \lambda^2\,\delta\Omega_i - \omega_j - \lambda^2\,\delta\Omega_j) - \lambda^2[(\gamma_i + \gamma_j)/2] + O(\lambda^4) \qquad (4.11)$$

The set of equations (4.6)–(4.7) has the exact structure of the expected Bloch equations with relaxation (in the absence of irradiation), describing the systematic flow from high- to low-lying eigenstates of H_{0A}, and the independent behavior of each nondiagonal component ${}_A\langle i, j|\sigma_A(\tau)\rangle_A$ with its oscillation at the Lamb-shifted Bohr frequency and its decay.

It is worth noting that the present derivation of the "irreversible" equations of motion (4.6)–(4.7) only uses the thermodynamic limit (i.e., volume $\mathcal{V} \to \infty$), which is inherent in the Λ-transformation scheme, and the initial condition (3.30). No assumptions about short or long time intervals were involved, no "small terms" were neglected during the derivation, and limited expansions in powers of the small strength λ of the atom–field coupling were used only in the final evaluation of the constants appearing in the equations.

4.3. Evolution of $|\sigma_A(t)\rangle$ during a Short Pulse of Irradiation

With the choice of transformations and reductions made in the present paper, the evolution during the overlap of the unperturbed field excitation with the atom is much less simple and one is faced with the usual hierarchy of equations involving reduced density superkets for subspaces with increasing number of field modes. We now indicate how this hierarchy can be truncated by a perturbation scheme in which the duration of the excitation period (i.e., of the overlap) and the irradiation strength $\lambda\alpha$ are treated as finite constants, whereas the strength λ of the atom–field coupling (when it is *not* multiplied by α) is used as a small parameter in power series expansions.

Using the formal iterative solution of the evolution equation and the initial condition (3.30), we see that the introduction of r bosons requires the use of the superoperator $\lambda\,\delta L_S$ (either in Λ, Λ^*, or ${}^{\mathrm{p}}L_S$) *at least* r times; hence, we have

$$ {}_S\langle ik_1 \cdots k_r, jk'_1 \cdots k'_{r'} | \bar{\rho}_S(t)\rangle_S^{\mathrm{p}} \propto \lambda^{r+r'} \tag{4.12} $$

and similar relations for the elements of the reduced density superkets for subspaces involving field modes. As a result of this, the limitation of series expansions in powers of λ to the first few terms is equivalent to a corresponding truncation of the hierarchy. Note that the present discussion of orders of magnitude in λ holds only because we consider the duration of excitation as a constant, so that the relevant "small" values of λ correspond to "large" values of the radiative lifetimes (which are of order λ^{-2}), much larger than the duration of excitation. If the durations of interest were of the order of the radiative lifetimes or longer, a different perturbation scheme would be required.

At order zero in λ, the presence of a nonzero term $\lambda\alpha\,{}^{\mathrm{p}}\mathscr{W}_S(t)$ in the equation of motion (3.5) for $|\bar{\rho}_S(t)\rangle^{\mathrm{p}}$ manifests itself in the equations of motion (4.6)–(4.7) for $|\sigma_A(t)\rangle$ as an additional contribution to the rhs of the form (for $i=j$ as well as $i\neq j$)

$$ \lambda\alpha(1/i\hbar)\left\{\sum_{i_1} G_{i,i_1}(t)\;{}_A\langle i_1, j|\sigma_A(t)\rangle_A - \sum_{j_1} G_{j_1,j}(t)\;{}_A\langle i, j_1|\sigma_A(t)\rangle_A\right\} \tag{4.13} $$

where the irradiation is completely described by the complex functions of time

$$ G_{i_1,j_1}(t) = [G_{j_1,i_1}(t)]^{\mathrm{c.c.}} = \sum_k \{\alpha_k(t)\, v_{i_1,j_1 k} + \alpha_k^{\mathrm{c.c.}}(t)\, v_{i_1 k,j_1}\} \tag{4.14} $$

At this very primitive level of discussion, the equations and results corre-

spond to the usual semiclassical approximation (2.34) and the hierarchical structure does not show up yet.

At order one in the series expansion of ${}^{\mathrm{p}}\mathscr{W}_S(t)$ in powers of λ, a further contribution has to be added to the rhs of (4.6)–(4.7), of the form (for $i=j$ as well as $i\neq j$, and in the limit $i\varepsilon\to 0$, $\varepsilon>0$)

$$\begin{aligned}\lambda(\lambda\alpha)(1/i\hbar)\sum_k \Big\{ &\sum_{i_1}\big[N_{i,i_1k}(t,i\varepsilon)\ {}_{Ak}\langle i_1k,j|\sigma_{Ak}(t)\rangle_{Ak} \\ &+ N_{i_1,ik}(t,i\varepsilon)^{\text{c.c.}}\ {}_{Ak}\langle i_1,jk|\sigma_{Ak}(t)\rangle_{Ak}\big] \\ &-\sum_{j_1}\big[N_{j_1,jk}(t,i\varepsilon)\ {}_{Ak}\langle ik,j_1|\sigma_{Ak}(t)\rangle_{Ak} \\ &+ N_{j,j_1k}(t,i\varepsilon)^{\text{c.c.}}\ {}_{Ak}\langle i,j_1k|\sigma_{Ak}(t)\rangle_{Ak}\big]\Big\}\end{aligned} \tag{4.15}$$

where the complex functions $N_{i_1,j_1k}(t,i\varepsilon)$ are given by

$$\begin{aligned}N_{i_1,j_1k}(t,i\varepsilon)=\sum_m \{&v_{i_1,mk}G_{m,j_1}(t)[1/(\omega_{i_1}-\omega_m-\omega_k+i\varepsilon)] \\ &+ G_{i_1m}(t)\,v_{m,j_1k}[1/(\omega_{j_1}+\omega_k-\omega_m-i\varepsilon)]\}\end{aligned} \tag{4.16}$$

and the analog of (4.5) is

$$\begin{aligned}{}_{Ak}\langle i_1k,j_1|\sigma_{Ak}(t)\rangle_{Ak} = {}_S\langle i_1k,j_1|\bar\rho_S(t)\rangle_S^{\mathrm{p}} + \sum_{r(r\geqslant 1)}(1/r!) \\ \times\sum_{k_1\cdots k_r}{}_S\langle i_1kk_1\cdots k_r,j_1k_1\cdots k_r|\bar\rho_S(t)\rangle_S^{\mathrm{p}}\end{aligned} \tag{4.17}$$

Eq. (4.12) shows that (4.17) is $O(\lambda)$, hence (4.15) is $O(\lambda^2)$. If the contribution (4.15) to the r.h.s. of (4.6)–(4.7) is kept, the consistency of the whole perturbation scheme implies that *all* the other contributions of the same order in λ must also be included, namely contributions arising from ${}^{\mathrm{p}}\mathscr{W}_S(t)$ at order λ^2 and contributions in λ^2 arising from the terms which are already present in the absence of irradiation. However, such corrections do not lead to an extension of the hierarchy and will not be discussed here any further.

In the typical fashion of hierarchical structures, (4.15) has to be supplemented with information about reduced density superkets for subspaces involving the atom and one field mode. We recall that these are all exactly zero in the initial condition. After some calculations, the following equation of motion is obtained:

$$
\begin{aligned}
&(\partial/\partial t)\ {}_{Ak}\langle ik, j|\sigma_{Ak}(t)\rangle_{Ak} \\
&\quad = [(\partial/\partial t)\ {}_{Ak}\langle j, ik|\sigma_{Ak}(t)\rangle_{Ak}]^{\text{c.c.}} \\
&\quad = \lambda\alpha(1/i\hbar)\left\{\sum_{i_1} G_{i,i_1}(t)\ {}_{Ak}\langle i_1 k, j|\sigma_{Ak}(t)\rangle_{Ak}\right. \\
&\qquad \left. - \sum_{j_1} G_{j_1,j}(t)\ {}_{Ak}\langle ik, j_1|\sigma_{Ak}(t)\rangle_{Ak}\right\} \\
&\qquad + \lambda(\lambda\alpha)(1/i\hbar)\sum_{i_1}[N_{i_1,ik}(t,-i\varepsilon)]^{\text{c.c.}}\ {}_{A}\langle i_1, j|\sigma_{A}(t)\rangle_{A} + O(\lambda^3) \qquad (4.18)
\end{aligned}
$$

in which the contributions of order λ^3 contain reduced density superkets for subspaces involving the atom and two field modes, hence extending the hierarchy when terms of order higher than λ^2 are required for the description of the effect of the pulse.

When the techniques indicated here are used to express the relevant reduced density superkets immediately after a short pulse of irradiation in terms of the same superkets immediately before the pulse as a power series in λ, two quite distinct "small parameters" appear: the strength λ of the atom–field coupling and the combination $\lambda^2\,\Delta t$, which is proportional to the ratio of the duration Δt of the pulse to the radiative lifetime [which is $O(\lambda^{-2})$]. Combining the results outlined in this subsection and in the previous subsection, we can make clean and systematic predictions about the reduced density superkets of the type $|\sigma_A(t)\rangle$, $|\sigma_{Ak}(t)\rangle$,..., for experiments involving a small number of short pulses with *arbitrary* separations between the pulses. For this, the time intervals with and without irradiation are treated separately and the approximate reduced density superkets evaluated at the end of each time interval are used as an initial condition for the next time interval. Great care has to be taken to ensure the overall consistency of such a scheme in which different types of approximations are used in successive time intervals. The resulting density superkets are much needed intermediates for the calculation of the "few-field modes" reduced density superkets, which, in turn, are needed to make predictions of the same quality about the directly observable photoelectric detection of light.

4.2. Observables and Average Values

In the traditional presentation of quantum mechanics, one is led to associate superkets of the type

$$
{}_{S}\langle Q_S| = {}_{A}\langle q_A| \otimes {}_{F}\langle 1_F| \qquad (4.19)
$$

where Q_S and q_A are Hermitian operators, with "observables" involving the atom only. For instance, ${}_{A}\langle q_A| = {}_{A}\langle(|i\rangle_A\ {}_A\langle i|)|$ for the population of

the eigenstate $|i\rangle_A$ of H_{0A} and ${}_A\langle q_A| = {}_A\langle(|i\rangle_A\,{}_A\langle j|)|$ for the "correlation" between eigenstates $|i\rangle_A$ and $|j\rangle_A$. Under these conditions, the evaluation of the average value

$$\langle Q_S\rangle(t) = {}_S\langle Q_S|\rho_S(t)\rangle_S = {}_S\langle q_A \otimes 1_F|\rho_S(t)\rangle_S = {}_A\langle q_A|\rho_A(t)\rangle_A \tag{4.20}$$

of such observables only requires the knowledge of the atom reduced density superket

$$|\rho_A(t)\rangle_A = \sum_{i,j}\sum_{\{n_k\}} |i,j\rangle_A\,{}_S\langle i\{n_k\}, j\{n_k\}|\rho_S(t)\rangle_S \tag{4.21}$$

The presence of radiation has no direct influence on the average values of such observables and, for instance, either ${}_S\langle Q_S|$ or $|\rho_S(t)\rangle_S$ or both can be replaced by their bar-transform (2.20) in (4.20).

However, the object of actual interest is usually not the simplified fiction of a "bare atom," but rather the complex structure resulting from the permanent interaction of this bare atom with the electromagnetic field. Both objects coincide only in the limit $\lambda \to 0$, so that average values of the type (4.20) do not provide the expected simple and satisfactory tool for discussing radiative effects in atomic physics.

In the presentation of quantum mechanics outlined in this section, and for situations in which the field is very close to the quasiclassical state (2.15), the reduced density superket $|\sigma_A(t)\rangle_A$ given by (4.1) offers a description of the dynamical behavior of the atom that incorporates the radiative effects in a particularly simple way. This leads to the tempting conjecture that average properties of "dressed atoms" would be given by expressions of the type

$$\langle B_S\rangle(t) = {}_A\langle b_A|\sigma_A(t)\rangle_A \tag{4.22}$$

in which, for instance, ${}_A\langle b_A|$ would be proportional to ${}_A\langle(|i\rangle_A\,{}_A\langle i|)|$ for the population of the dressed atomic state i, and proportional to ${}_A\langle(|i\rangle_A\,{}_A\langle j|)|$ for the "correlation" between dressed states i and j. Using the definition (4.1) of $|\sigma_A(t)\rangle_A$ and relation (3.4), we see that (4.22) can hold if the superbra ${}_S\langle B_S|$ is such that its p-bar transformed version has the form

$${}^{\mathrm{p}}_{S}\langle \bar{B}_S| = {}_A\langle b_A| \otimes {}_F\langle 1_F| \tag{4.23}$$

because this implies that

$$\begin{aligned}\langle B_S\rangle(t) &= {}_S\langle B_S|\rho_S(t)\rangle_S = {}^{\mathrm{p}}_{S}\langle \bar{B}_S|\bar{\rho}_S(t)\rangle^{\mathrm{p}}_{S}\\ &= ({}_A\langle b_A| \otimes {}_F\langle 1_F|)\,|\bar{\rho}_S(t)\rangle^{\mathrm{p}}_{S}\\ &= \sum_{i,j} {}_A\langle b_A|i,j\rangle_A \sum_{\{n_k\}} ({}_A\langle i,j| \otimes {}_F\langle\{n_k\},\{n_k\}|)\,|\bar{\rho}_S(t)\rangle^{\mathrm{p}}_{S}\\ &= {}_A\langle b_A|\sigma_A(\tau)\rangle_A\end{aligned} \tag{4.24}$$

In the limit $\lambda \to 0$, the conditions (4.19) and (4.23) are equivalent and the reduced superkets defined by (4.1) and (4.21) are equal. When λ differs from zero, one must keep in mind that the definition of $|\sigma_A(t)\rangle_A$ involves the *nonunitary* transformation A, with the consequence that $|\sigma_A(t)\rangle_A$ does not have all the usual properties of a conventional density superket. For instance, the example of (4.3) clearly shows that ${}_A\langle 1_A|\sigma_A(t)\rangle_A$ is different from 1 in general; hence, the diagonal matrix elements of the Hermitian operator $\sigma_A(t)$ cannot be directly interpreted as occupation probabilities. In spite of these difficulties, we have indications that, for real atoms, the conjecture (4.22) will provide more satisfactory predictions than the rough, "bare atom" method (4.19). However, a number of consistency checks should still be performed before taking (4.22) seriously or even more sophisticated versions of it [involving, for instance, the replacement of $|\sigma_A(t)\rangle_A$ by a properly normalized variant and a suitable association of superbras ${}_A\langle b_A|$ with "observable" properties in order to mitigate some of the difficulties]. Whatever the result of these checks, the average values of "observables involving one real atom only" (i.e., not the field) will presumably remain of heuristic interest because these average values cannot be measured *directly* (i.e., independently of the field). Our view is that clear comparisons between predictions and observations should use measurements of properties of the field performed at large distances from the atom. In such cases, we expect that reduced density superkets of the type $|\sigma_A(t)\rangle_A$ will play a role only as intermediates in the calculations of the field properties. We plan to investigate this idea in detail and we hope to report on it later.

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