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Influence of relaxation phenomena in the unified description of resonant and nonresonant radiative transitions

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A comprehensive quantum-mechanical description of resonant and nonresonant radiative transitions in complex electronic systems is developed, using a density-matrix approach. Specific applications are made to the unified treatment of radiative and dielectronic recombination of electrons with many-electron ions in high-temperature plasmas and to the unified treatment of transverse bound-bound and free-bound radiative transitions of energetic electrons channeled in crystal lattices. Both time-independent (resolvent-operator) and time-dependent (equation-of-motion) formulations of the density-matrix approach are presented. Liouville-space projection-operator techniques, which have been developed in the nonequilibrium quantum-statistical-mechanics description of relaxation phenomena, are employed. Self-consistent treatments are achieved for the excited-level populations and the spectral-line shapes. Applications are discussed for the broadening of atomic spectral lines by autoionization processes, radiative transitions, charged-particle collisions, and the action of the plasma electric microfields, and also for electron-channeling-radiation broadening by electron-electron, electron-photon, and electron-phonon interactions in a crystal lattice. The unified treatment of resonant and nonresonant radiative transitions is accomplished by means of a partition of the "relevant" Liouville space into separate subspaces corresponding to discrete resonance and nonresonant continuum states of the electronic system of interest. Although only single-photon processes are considered and only lowest-order quantum-electrodynamical perturbation theory is explicitly evaluated for the electron interaction with the radiation field, the general resolvent-operator and propagator formulations that are presented in this investigation can be applied to the descrption of multiphoton processes and, with the adoption of a suitable renormalization program, to the incorporation of radiative corrections to the transition probabilities.

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I. INTRODUCTION

We investigate radiative transitions in an electronic system that is simultaneously interacting with a much larger system, through a multitude of collisional and radiative processes. Our primary interests are directed at two specific problems. The first involves photorecombination of electrons with many-electron ions in a high-temperature plasma. The analysis of dielectronic recombination satellite lines in the x-ray emission spectra has become one of the most widely used methods for determining the basic physical properties of high-temperature plasmas [1], such as the electron temperature, the electron density, and the state of ionization. Our central objective in this application is the incorporation of relaxation phenomena, within the framework of the unified treatments of radiative and dielectronic recombination, which have been reported by Alber, Cooper, and Rau [2], by Jacobs, Cooper, and Haan [3], and by Haan and Jacobs [4]. Specifically, we wish to further incorporate a description of the Stark broadening, resulting from the charged-particle collisions and the action of the plasma electric microfields, which would be on an equal footing with the treatment of the natural broadening, due to the autoionization and spontaneous radiative decay processes. The second problem is concerned with a unified treatment of transverse bound-bound and free-bound radiative transitions of energetic electrons channeled along an axis or plane of symmetry in a crystal lattice. We are motivated by the need to incorporate into the relativistic quantum-mechanical treatments of these transitions, by Sáenz, Überall, and Nagl [5] and by Sáenz, Nagl, and Überall [6], a self-consistent description of the level-population and line-broadening mechanisms, which are associated with electron-electron, electron-photon, and electron-phonon interactions in a crystal lattice. We shall give particular emphasis to the close analogy between these two problems, both of which involve resonant and nonresonant radiative transitions.

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A. Relaxation phenomena

The influence of relaxation phenomena on radiative transitions of the microscopic electronic subsystem of interest can be most generally investigated by employing the methods and techniques of nonequilibrium quantum-statistical mechanics [7]. A particularly convenient representation for the systematic description of relaxation phenomena in interacting quantum-mechanical systems is provided by the density-matrix approach [8], in conjunction with the Liouville-space projection-operator and resolvent-operator (or equation-of-motion) formalisms [9,10]. In the Liouville-space representation, in which tetradic states (occurring in the representation of density operators) play the role of Hilbert-space state vectors, one can introduce analogs of the familiar Lippmann-Schwinger scattering-theory equations [11] which involve tetradic resolvent or Green's operators [12]. The self-energy corrections (giving rise to line broadening), which occur in the expression for the perturbed Liouville-space resolvent operator, are defined as projections of a Liouville-space relaxation operator onto the restricted subspace of degrees of freedom pertaining to the microscopic electronic subsystem of interest, together with the relevant modes of the quantized radiation field. It has been emphasized by Girardeau [13] that the application of Liouville-space resolvent-operator methods is not restricted by the common assumption that the initial state of the interacting matter and radiation-field system must correspond to a thermodynamic equilibrium ensemble. Consequently, these methods can be employed to investigate the dynamical evolution of interacting many-body systems that are initially in nonequilibrium states.

B. Radiative transitions involving autoionizing resonances in many-electron atoms

The radiation emitted or absorbed in collisions between electrons and many-electron ions has been traditionally classified in terms of free-free, free-bound, bound-free, and bound-bound transitions [14]. The free-bound radiative emission process is usually described as involving predominantly either direct (nonresonant) radiative recombination, which is the inverse of the ordinary (bound-free) photoionization process, or two-step (resonant) dielectronic recombination [15], which consists of a radiationless electron capture (accompanied by excitation of the initial ion to form a doubly excited autoionizing state) followed by a spontaneous, radiatively stabilizing transition to a singly excited bound final state. It has been pointed out, however, by Alber, Cooper, and Rau [2] and by Jacobs, Cooper, and Haan [3] that the traditional treatment of radiative and dielectronic recombination as two distinct, noninterfering processes is not strictly permissible within the framework of a rigorous quantum-mechanical collision theory, according to which the probability for a given free-bound radiative transition must be expressed as the square of the sum of the nonresonant and resonant transition amplitudes. The total cross section for the entire electron-ion photorecombination process is consequently obtained as the sum of the cross sections associated with the direct radiative recombination and the two-step dielectronic-recombination process, together with an additional contribution representing the interference between the transition amplitudes corresponding to radiative and dielectronic recombination.

In previous investigations [2–4], a unified description of radiative and dielectronic recombination has been developed which also includes an additional interference phenomenon, arising from a nonperturbative treatment of the electromagnetic coupling between the unperturbed autoionization and spontaneous-radiative-decay continua [16–18]. In particular, the work of Jacobs, Cooper, and Haan [3] has provided a generalization of the scattering or S-matrix theory analysis of Alber, Cooper, and Rau [2] to explicitly take into account degenerate magnetic sublevels of the atomic system and multiple angular-momentum contributions in the partial-wave expansion for the electron-continuum eigenstate. This analysis has been further generalized by Haan and Jacobs [4] for application to photorecombination processes involving multiple electron continua and/or multiple photon continua. This generalization has been accomplished by taking full advantage of the projection-operator and resolvent-operator techniques that were originally introduced in the theory of nuclear reactions by Feshbach [19] and also utilized in the description of decay processes from virtual or prepared states [11,20]. The result of the unified description is an expression for the transition operator T describing the entire electron-ion photorecombination process which separates naturally into the sum of a nonresonant transition or direct radiative-recombination amplitude, which is represented by a vertex (or level-shift) operator, and a resonant transition or dielectronic-recombination amplitude, which involves both the vertex operator and the projection of the resolvent operator onto the subspace of the discrete autoionizing states.

The self-consistent incorporation of relaxation phenomena becomes a necessity in the realistic treatment of the spectral-line shapes associated with the dielectronic-recombination satellite transitions in high-density plasmas [21], for which collisional processes can substantially alter the spectral predictions of the conventional low-density theory of dielectronic recombination. In the absence of relaxation processes, the unified description developed previously leads to a precise expression for the total electron-ion photorecombination cross section, which naturally separates into a resonant, a nonresonant, and an interference contribution. The resonant term represents a modified dielectronic-recombination cross section, which can be reexpressed in the familiar Breit-Wigner [22] form by introducing effective autoionization and spontaneous radiative-decay rates that incorporate the interference between the autoionization and radiative-decay continua. Alternatively, the combined transition probability for the entire electron-ion photorecombination process may be represented in terms of a modified Fano-type [23] autoionization line-profile function, which is further shifted and broadened as a result of the electromagnetic coupling between the unperturbed autoionization and radiative-decay continua [2,24]. The incorporation of relaxation phenomena is expected to lead to spectral distributions which are further modified from these simple line-profile theories, due to the interactions of the radiating electronic subsystem with the multitude of perturbing charged particles and radiation-field modes.

C. Radiative transitions of many-electron ions in plasmas

The broadening of atomic spectral lines by plasmas has been extensively investigated using the modern quantum-mechanical approaches developed by Baranger [25], by Kolb and Griem [26], and by Smith, Cooper, and Vidal [27]. These approaches were developed primarily for the treatment of bound-bound atomic radiative transitions in a plasma environment, with particular emphasis on the need to take into account the shifting and broadening of numerous overlapping components by the combined effects of the charged-particle collisions and the distribution of plasma electric microfields [28]. These approaches to the treatment of spectral line broadening area based on an evaluation of the autocorrelation function of the electric dipole moment operator for the radiating electronic system [29]. The collisional broadening of spectral lines in neutral gases has been investigated by Fano [10], using an alternative procedure that is based on the concepts and methods of the Liouville-space scattering theory. The central quantity in this procedure is the frequency-dependent Liouville-space relaxation operator that was introduced by Zwanzig [9]. Smith and Hooper [30] have developed a relaxation theory of spectral-line broadening by plasmas, which is closely derived from the procedure adopted by Fano [10]. The advantage of the Liouville-space relaxation-operator approach is its direct applicability to other line-broadening mechanisms, in addition to those associated with collisions, such as autoionization processes and radiative transitions.

The Liouville-space projection-operator and resolvent-operator methods, which were developed by Zwanzig [9] and Fano [10] and refined by Ben-Reuven and Rabin [31], have been applied by Jacobs and Davis [32] to investigate the spectral-line broadening by autoionization processes, spontaneous and stimulated radiative transitions, and electron collisions. From an evaluation of the Liouville-space expression for the spontaneous electric dipole radiative emission rate, Jacobs and Davis [32] obtained a general line-shape formula. This formula has the same form as the overlapping line-shape formula first derived by Baranger [25] and independently obtained by Kolb and Griem [26]. The general line-shape formula of Jacobs and Davis is, however, applicable to other broadening mechanisms, in addition to those resulting from a plasma environment. The lowest-order nonvanishing perturbation-theory contributions to the diagonal tetradic matrix elements of the Liouville-space relaxation operator were explicitly evaluated, and it was demonstrated that the total line width (occurring in the isolated-line and impact approximations) can be expressed as the sum of the rates produced by the individual autoionization, radiative, and inelastic electron-collisional transitions from the initial and final states comprising the spectral line, together with a term involving the square of the difference between the elastic electron-scattering amplitudes. A similar result has been obtained for ordinary bound-bound radiative transitions by Baranger [29]. The primary objective of the present investigation is the development of a more comprehensive theory, in which higher-order perturbation theory contributions and interferences between amplitudes for line and continuum radiative processes can be systematically and self-consistently taken into account.

D. Radiative transitions of atomic systems in the presence of intense electromagnetic fields

In highly charged ions, the natural spectral-line broadening due to spontaneous radiative decay can be comparable with the collisional and Stark broadening, except in very high-density plasmas. The availability of high-intensity laser sources, covering an ever-increasing portion of the electromagnetic spectrum, offers numerous opportunities to observe the effects of intense radiation fields on spectral-line shapes. Illustrations of the complexity of high-intensity radiation-field phenomena include the observed persistence of substantial resonant multiphoton ionization in spite of the existence of appreciable dynamic Stark shifts [33], the ubiquitous phenomenon of above-threshold ionization, where the outgoing electrons absorb many quanta from the laser field, and the observed production of very high (≥ 30) harmonics of the laser field [34]. A nonperturbative (dressed-atom) treatment for an atomic system in the presence of an intense, coherent (classical) radiation field has been developed by, e.g., Cohen-Tannoudji and Reynaud [35]. The dressed-atom treatment of the dynamic Stark effect may be viewed as being analogous to the quasistatic approximation for the action of the plasma ions on a radiating atomic system, which involves the determination of the eigenstates of the radiating system in the presence of a static electric field [28]. Both treatments obviously involve classical or external-field representations rather than the quantization of the applied fields. The shapes of spectral lines in the presence of weak collisions and intense radiation fields have been investigated by Lambropoulos [36], using the Liouville-space projection-operator and resolvent-operator approaches [9,10]. Although the line-shape formulas were evaluated by Lambropoulos only in the isolated-line and lowest-order perturbation-theory approximations, the treatment of several line-broadening mechanisms on an equal footing has provided a foundation for a further extension to include the broadening by autoionization [32]. The effect of collisions on autoionization has also been treated by using a model in which the action of the collisions is described by introducing a fluctuating, stochastic electric field [37].

When the Liouville-space relaxation operator is investigated beyond the approximation of lowest-order perturbation theory, the widths of spectral lines can no longer be expressed simply as the sums of the rates that each individual broadening mechanism would produce if acting alone. This is physically a consequence of the fact that the different collisional and radiative mechanisms, which are capable of causing transitions between the quantum states of the radiating electronic system, are acting simultaneously and not independently. By considering the equation of motion for the projection of the density operator onto the "relevant" subspace of the radiating electronic system, Ballagh and Cooper [38] have investigated the modifications to the population-rate equations (governing the diagonal elements of the density matrix) which result from correlations between collisional and radiative processes. This investigation was based on the time-dependent density-operator approach developed by Burnett, Cooper, Ballagh, and Smith [39], who were particularly concerned with the establishment of precise criteria for the validity of the Markov short-memory-time approximations in the treatment of radiation damping and for the validity of the binary-collision approximation in the description of the collisional redistribution of scattered laser radiation. They obtained general formulas which reduce to the impact (Markovian) and quasistatic (non-Markovian) approximation in the appropriate limits. They gave particular emphasis to the fact that the existence of correlation phenomena prevents the density operator, for the combined interacting matter plus radiation-field system, from being expressible, at an arbitrary time, in the factorized form involving the direct product of density operators separately defined within the subspaces of the radiating system, the perturbing particles, and the radiation field. The time-dependent density-operator approach is necessary for the correct treatment of time-resolved spectra in short-pulsed laser fields and also for the precise incorporation of kinetic-theory phenomena, such as the Doppler shifts and broadening.

The projection-operator and resolvent-operator techniques have also been employed in investigations of laser-induced autoionization, which may be viewed as the inverse process corresponding to stimulated dielectronic recombination, and in descriptions of multiphoton autoionization, where discrete autoionizing resonances can occur as the final states and the intermediate states, in both resonant and nonresonant multiphoton transitions. Lambropoulos and Zoller [40] have presented both equation-of-motion and resolvent-operator formulations in their investigation of radiative transitions involving discrete autoionizing states in strong fields, for which the induced radiative transition rates become comparable with the autoionization and spontaneous radiative emission rates. They have demonstrated that such strong fields can cause significant distortions of the spectral profiles for photoelectron ejection and photon emission. When two or more autoionizing states are strongly coupled by the atom-field interaction, the spectral-line shapes can be appreciably altered by dynamic Stark shifts and Rabi oscillations. The subject of multiphoton autoionization has been reviewed by Lambropoulos and Zoller [41], and they have pointed out the prominent role that can be played by intermediate autoionizing states in multiple-electron ionization processes and the accessibility in multiphoton transitions of final autoionizing states, particularly with high angular momenta, which cannot be excited in ordinary single-photon absorption processes. Intermediate autoionizing states can also play an important role in such nonlinear optical phenomena as harmonic generation, and the photoexcitation of radiative transitions between autoionizing states has been investigated as a mechanism for the generation of amplified spontaneous emission at photon wavelengths approaching the x-ray region [42–44].

In recent investigations of laser-induced autoionization, the spectral profiles describing photoelectron ejection and spontaneous radiative emission have been shown to be strongly altered by the effects of various relaxation processes. Agarwal, Haan, Burnett, and Cooper [45] and Agarwal, Haan, and Cooper [46] have employed a time-dependent density-operator (or master-equation) approach, in conjunction with a sequential diagonalization of the total atom plus radiation-field Hamiltonian, to investigate the modification of the Fano line-shape function [23] resulting from the influence of spontaneous radiative decay. Using a resolvent-operator approach, in combination with a simultaneous diagonalization of the total Hamiltonian within a restricted subspace of discrete atomic states together with electron and photon continua, Haan and Agarwal [47] have investigated the effects of spontaneous radiative emission and recombination on the steady-state photoelectron and photoemission spectra. In an extension of this investigation, Haan and Agarwal [48] have adopted a projection-operator approach. In a series of papers by Agarwal, Ravi, and Cooper [49], the time-dependent density-operator approach has been employed to treat the effects of strong fields on processes involving autoionization phenomena. The influence of collisional dephasing processes on the spectral profiles following laser-induced autoionization has been investigated by Deng [50], using Liouville-space projection-operator and resolvent-operator techniques. A central objective of the present investigation is the systematic and self-consistent incorporation of field effects and relaxation phenomena, together with the interference between line and continuum radiation processes.

E. Radiative transitions of energetic electrons in crystal lattices

The radiative transitions of energetic electrons traversing a crystal lattice are in several respects analogous to the radiative transitions of atomic systems in a plasma. As in the case of the atomic field, the fundamental influence of the crystal field is the modification of the energy-momentum conservation relationships, which allows the single-photon radiative transition. One may view a crystal lattice as a limiting case of a strongly coupled plasma, for which the electrostatic-interaction energies of the charged particles greatly exceed their mean kinetic energies. In the case of a periodic crystal potential, an essential new phenomenon is the possibility of coherent interactions that involve a large number of atomic centers. These coherent interactions can be described by the use of Bloch-type wave functions to represent the eigenstates of an electron in the periodic crystal field. The many-body electrostatic, electron-phonon, and radiative interactions, which cannot be described by the use of a static, local crystal field, can be treated as relaxation phenomena, by employing the Liouville-space projection-operator and resolvent-operator techniques that we are developing for application to the nonequilibrium quantum-statistical-mechanics description of radiation processes involving many-electron ions in a high-temperature plasma.

In a manner analogous to the description of atomic radiation processes, the radiative interactions of energetic electrons in a crystal lattice may be classified in terms of free-free, free-bound, and bound-bound transitions. This classification can be accomplished by introducing a separation of the longitudinal and transverse motions of the incident electrons, relative to an axis or plane of crystal symmetry. This separation is motivated by the existence of axial or planar channels, in which charged particles can become bound by the transverse electrostatic potential. In most cases of interest, the direction of the incident electrons is nearly coincident with a symmetry direction and the distribution of population among the various bound and continuum states of the transverse potential is sensitively dependent on the angle of incidence. The bound states have been frequently referred to as "quasibound" or "transversely bound" states, in order to indicate that they are unbound with respect to the longitudinal direction. The radiation emitted during transitions between free or continuum states of the transverse potential corresponds to the coherent bremsstrahlung process, which was first described by Überall [51], without consideration of transverse binding effects. Because of the longitudinal periodicity of the crystal lattice, coherent bremsstrahlung exhibits spectral and polarization characteristics that are quite distinct from those of ordinary bremsstrahlung from electrons in the field of a single atomic center, as described by the Bethe-Heitler theory [52]. The radiation emitted during transitions between transversely bound states was first described by Kumakhov [53] and has been referred to as "channeling radiation." The intermediate case of free-bound transitions, which is analogous to electron-ion photorecombination, has been treated within the context of channeling radiation by Sáenz, Nagl, and Überall [6].

For energetic electrons traversing a crystal lattice, it is now recognized that the free-free, free-bound, and bound-bound transitions can occur simultaneously at a given electron energy and incident direction, although a particular transition may be predominant in a specific photon frequency region and for special ranges of the incident electron energy and angle with respect to the symmetry direction. Physically, the simultaneous occurrence of these transitions is a consequence of the fact that the propagating electrons always experience both the transverse periodic potential, which gives rise to channeling radiation, and the longitudinal periodic potential, which is responsible for coherent bremsstrahlung. Anderson *et al.* [54] have pointed out that coherent bremsstrahlung, which is associated with the free-free transitions, and channeling radiation, which involves the bound-bound transitions, can be considered as two different aspects of the same fundamental radiation process. The distinction between them has been established by the traditional description, which is based on the separation of the longitudinal and transverse motions of the incident electrons with respect to the symmetry direction. Kurizki and McIver [55] have emphasized that the equivalence between the two radiation phenomena arises naturally from a description that is based on the three-dimensional Bloch representation for the eigenstates of the electron in the crystal field. Consequently, the total intensity of the spontaneously emitted radiation, at a given photon frequency, is most rigorously given by the sum of the contributions from the free-free, free-bound, and bound-bound transitions, together with terms involving the interference among all three types of transition amplitudes.

The bound states of the transverse crystal potential may be treated as discrete resonances that are embedded in the continuous spectrum of eigenstates of the full three-dimensional potential. Accordingly, the free-bound and bound-bound transitions in the electron channeling radiation process may be regarded as nonresonant and resonant radiative transitions, respectively, in close analogy with the direct radiative and dielectronic recombination of many-electron ions. In addition to the radiative transitions among the various eigenstates of the transverse crystal potential, an analog of the autoionization process can occur as a result of the many-body interactions that cannot be described by the static, local crystal field. The multitude of nonradiative (electron-electron and electron-phonon) and radiative (electron-photon) interactions, which can cause transitions among the Bloch-type eigenstates of the crystal potential, must be systematically and self-consistently taken into account in the determination of the spectral-line widths and shifts [56], together with the population distributions of the transversely bound resonance states. Because the population distributions or level occupations can undergo a continuous evolution during the penetration of the incident electron beam into the crystal, it is necessary to employ a kinetic-theory description [57] in order to treat the transport process. A kinetic-theory description is also necessary for a detailed investigation of the concept of producing stimulated emission in the x-ray region based on electron channeling radiation [58] and for a complete analysis of channeling-radiation observations that are made for the purpose of determining the crystal potential experienced by the channeled electrons [59].

F. Organization of this paper

In this paper, we present a general density-matrix formalism that will be applied in future communications to derive explicit expressions for the probabilities or rates of specific radiative transitions in various electronic systems, which are simultaneously interacting with a multitude of perturbing particles and radiation-field modes. For example, the spectral distribution for single-photon emission (or absorption) is proportional to the rate for the emission (or absorption) of a photon with a specific frequency and polarization. In Sec. II we introduce the density-matrix description and the Liouville-space operator formalism. Particular emphasis is given to the definition of the transition probabilities for quantum-mechanical systems that are interacting with other, much larger, quantum-mechanical systems. The effects of the collisional and radiative relaxation processes are incorporated by introducing the Zwanzig projection-operator approach, in which the complete Liouville space is partitioned into a reduced ("relevant") subspace, corresponding to the uncorrelated electronic subsystem and the relevant modes of the quantized radiation field, and an orthogonal subspace, in which the electronic-subsystem and radiation-field states are dynamically correlated with the "bath" degrees of freedom. The function of the Zwanzig projection operator is to perform an average over the bath degrees of freedom, which leads to reduced Liouville-space operators that are defined on the subspace of the "relevant" degrees of freedom. The time-independent formulation is developed in terms of the relevant projection of the Liouville-space transition operator, which is defined in terms of the relevant projections of the resolvent operator and the interaction operator by means of a tetradic Lippmann-Schwinger equation, while the time-dependent formulation is based on the equation of motion for the relevant part of either the density operator or the Liouville-space time-evolution operator. In Sec. III the Liouville-space projection-operator formalism is adapted to the unified description of resonant and nonresonant radiative transitions of an electronic subsystem in the presence of collisional and radiative relaxation processes. The goal has been to provide a generalization of the ordinary Hilbert-space projection-operator and scattering-operator approach developed by Haan and Jacobs [4], which was motivated primarily for application to the unified treatment of radiative and dielectronic recombination. In order to accomplish this generalization, it has been necessary to introduce a partition of the relevant Liouville space into separate subspaces corresponding to discrete resonance and nonresonant continuum states of the electronic subsystem of interest. We emphasize that this decomposition is introduced into the expression for the reduced relevant Liouville-space transition operator or time-evolution operator only after the average over the bath degrees of freedom has been carried out. At any given time, but not over a long time interval, it is possible to make a distinction between the bath electrons (i.e., the perturbing electrons) and the electrons that are associated with the relevant resonance process. We also point out that this partition is complicated by the occurrence of mixed, nonstationary unperturbed states or coherences, which must be taken into account in order to provide a complete set of intermediate states in the relevant Liouville space. The time-independent formulation of the generalized unified scattering-theory description is presented in terms of a rearrangement of the tetradic Lippmann-Schwinger relationship for the reduced, relevant Liouville-space transition operator, which provides a natural separation of the total relevant transition amplitude into a direct nonresonant continuum part and a discrete resonant contribution. An analogous rearrangement is introduced in the time-dependent scattering-theory formulation, which leads to separate equations of motion for the discrete resonant and nonresonant continuum parts of either the reduced density operator or the reduced Liouville-space time-evolution operator. We point out that, as an alternative to the Liouville-space scattering-theory approach, which is appropriate for the description of a single resonance (e.g., autoionizing or radiationless capture) population event, one may adopt a relaxation-theory approach, in which the discrete resonance states are treated as the initial states in the radiative transitions of interest and the steady-state or time-dependent populations and coherences of these states are determined by means of a separate set of kinetic-theory equations. Ignoring coherent or long-time laser interactions, the time that is relevant in the determination of the spectral distribution for photon emission is sufficiently short that only a single resonance population event is important. A substantial effort has been devoted to providing a general procedure for deriving explicit expressions for the various (electron and photon) continuum projections of the reduced, relevant Liouville-space continuum resolvent operator. These projections are required in our general procedure for evaluating the desired tetradic matrix elements of the reduced, relevant Liouville-space transition operator. Finally, our conclusions are presented in Sec. IV together with a discussion of the applications which will be treated in future communications.

II. DENSITY-MATRIX DESCRIPTION

We wish to investigate radiative transitions of an electronic system which is simultaneously interacting with the fields of a large number of perturbing particles and photon modes. It will be convenient to introduce a partition of the total Hamiltonian H, for the entire interacting matter and radiation-field system, as follows:

$$H = H^0 + V \ , \tag{1}$$

where

$$H^0 = H^M + H^R = H^S + H^P + H^R \tag{2}$$

and

$$V = V^M + V^{MR} = V^{SP} + V^{SR} + V^{PR} \ . \tag{3}$$

The total unperturbed Hamiltonian H^0 is the sum of the unperturbed matter Hamiltonian H^M and the free radiation-field Hamiltonian H^R. The unperturbed matter Hamiltonian H^M may be expressed as the sum of a Hamiltonian H^S representing the isolated electronic subsystem and a Hamiltonian H^P for the system of perturbing particles. It is often convenient to include in H^S that portion of the interaction V^{SP}, between the electronic subsystem and the perturbing particles, which can be represented by a static local potential. Examples of such local fields include the quasistatic ion-generated electric microfield acting on a many-electron ion in a high-temperature plasma and the static electric field acting on an energetic electron in a crystal lattice. It is sometimes customary to include in H^S the monopole interaction between atomic ions which does not depend on the state of the electronic subsystem (i.e., the Coulombic interaction which gives rise to classical hyperbolic trajectories). It is often advantageous to include in H^S the contribution from the interaction V^{SR}, between the electronic subsystem and the radiation field, which corresponds to a radiation field that is static in the "rotating-wave" approximation; this procedure may be followed by the introduction of dressed-atom states, accounting for the presence of a strong laser field. Since we shall be primarily concerned with transitions induced by the interaction V^{SR}, we will neglect the interaction V^{PR} of the perturbers with the radiation field. We point out that the interference between perturber radiation and atomic spectral-line radiation has been considered by Burgess [60] and V^{PR} plays an essential role in the "collisionally induced" radiation processes studied by Alber and Cooper [61]. The interaction V^{PR} is also important in the description of resonance broadening, where the transfer of excitation between identical atomic systems can take place.

The interaction V^{SP} may also be redefined to include the portion of H^S which is responsible for atomic autoionization, in order that autoionization may be treated on an equal footing with radiative decay. In the treatment of autoionization, and the inverse radiationless electron-capture process which occurs in the two-step dielectronic recombination process, it appears appropriate to consider the continuum electron as a part of the atomic subsystem. However, one should be concerned with the problem of distinguishing the "captured" or "ejected" electron from the multitude of "perturber" electrons.

We shall assume that the eigenvalue problem

$$H^0|a\rangle=\hbar\omega_a|a\rangle \ , \tag{4}$$

corresponding to the unperturbed Hamiltonian H^0, can be solved to provide a complete basis set of zeroth-order states $|a\rangle$, including bound states, discrete (autoionizing) resonances, and nonresonant continuum states. Since the zeroth-order Hamiltonian H^0 has been taken as the sum, given by Eq. (2), of the unperturbed Hamiltonians for the isolated subsystems, the unperturbed eigenstates $|a\rangle$ can be expressed as direct products of the eigenstates $|\alpha\rangle$ of the many-electron ion or crystal-field electron, the eigenstates $|p\rangle$ representing the subsystem of perturbing particles (possibly including perturber-perturber interactions), and the eigenstates $|n\rangle$ specifying the occupation numbers of all modes of the quantized radiation field. We emphasize that the symbols $|\alpha\rangle$, $|p\rangle$, and $|n\rangle$ are, in general, abbreviations for many-body states of the respective subsystems. The electronic-subsystem states $|\alpha\rangle$ may be single-electron ionic states or states of a single crystal-field electron; but many-particle atomic states of the Fano type may also be used. The Fano-type states are obtained from a diagonalization of the Hamiltonian H^S, including the electron-electron interaction part of V^{SP} which is responsible for autoionization, within a subspace of discrete resonance and single-electron nonresonant continuum basis states [46]. The eigenstates $|p\rangle$ of the perturbing particles are most easily determined when their mutual interactions, which are included in H^P, are either neglected or treated according to a procedure leading to shielded quasiparticles. For the treatment of multiphoton processes, it may be necessary to take into account photon-photon correlations. By adopting a second-quantization description for the charged particles, as well as for the electromagnetic radiation field, one may employ a quantum-field-theory approach to treat all interactions included in V on an equal footing.

A general density operator ρ_i for a state $|i\rangle$ of the unperturbed Hamiltonian H^0 can be represented by the direct product

$$\rho_i=\rho^S\otimes\rho^P\otimes\rho^R \ , \tag{5}$$

where ρ^S, ρ^P, and ρ^R denote the density operators for the isolated electronic subsystem, the perturbing particles, and the electromagnetic radiation field, respectively. Assuming this separable form for the initial-state density operator, describing the combined interacting system, implies the neglect of initial correlations among the separate subsystems, as discussed by Burnett, Cooper, Ballagh, and Smith [39]. In the relaxation-theory approach to the description of the interactions included in V, the uncorrelated, direct-product representation is adopted for the initial-state density operator $\rho_i(t)$ at the time $t_0=0$. In the scattering-theory approach, it is more natural to assume the separable form as the initial condition at $t_0\rightarrow-\infty$. In either approach, the correlation effects are allowed to be built up during the evolution of the system to the "time of interest."

The individual initial-state density operators ρ^S, ρ^P, and ρ^R will be assumed to be represented by diagonal matrices in the respective basis sets $\{|\alpha\rangle\}$, $\{|p\rangle\}$, and $\{|n\rangle\}$. For example, the density operator ρ^S, for the many-electron ion or the energetic electron in a crystal field, may be represented by means of the expansion

$$\rho^S=\sum_{\alpha}\rho^S_\alpha|\alpha\rangle\langle\alpha| \ , \tag{6}$$

in terms of the complete basis set $\{|\alpha\rangle\}$, consisting of bound, discrete resonance, and nonresonant continuum eigenstates of H^S. It should be emphasized that the individual density operators ρ^S, ρ^P, and ρ^R, representing the isolated subsystems, will not be required to correspond to the distributions of a thermodynamic equilibrium ensemble.

A. Liouville-space operator formalism

In order to investigate the transitions between the unperturbed eigenstates of H^0 which are induced by the interactions included in V, it is necessary to study the time evolution of the density operator $\rho(t)$ for the entire interacting matter and radiation-field system. We wish to emphasize that the density operator $\rho(t)$, at an arbitrary time t, cannot be assumed to be expressible in the separable, direct-product form given for the initial-state density operator ρ_i in Eq. (5). Physically, this departure from the separable form is a consequence of the fact that the radiative transitions of the electronic subsystem of interest are occurring simultaneously with, and are therefore correlated with, the multitude of collisional and radiative interactions that are responsible for the relaxation phenomena. For the description of a particular measurement process, such as one involving only the detection of spontaneously emitted photons in a particular frequency range, it is ultimately necessary to introduce a reduced description involving a projection of the full density operator onto a restricted subspace corresponding to the relevant degrees of freedom.

The time evolution of the density operator $\rho(t)$ is described by the quantum Liouville equation of motion [7]

$$\frac{\partial\rho(t)}{\partial t}=-\frac{i}{\hbar}[H,\rho(t)]=-i\bar{L}\rho(t)\ , \tag{7}$$

which defines the Liouville-space operator $\bar{L}$, associated with the Hamiltonian H, in terms of the usual Hilbert-space commutator $[H,\rho(t)]$. Sometimes the factor of $-i$ is included in the definition of $\bar{L}$ [39]. The Liouville-space operators, which we will distinguish from the ordinary Hilbert-space operators by using the overbar, are often referred to as superoperators. They operate in a space in which the ordinary Hilbert-space linear operators, such as $\rho(t)$, play the role of vectors. Moreover, the complete set of linear operators acting on ordinary Hilbert space forms a basis set for Liouville space. An element $|a\rangle\langle b|$ of this complete basis set may be denoted, using the Liouville-space Dirac notation, by $|a,b\rangle\rangle$. An arbitrary density operator ρ can then be expanded in the form

$$\rho=|\rho\rangle\rangle=\sum_{a,b}|a\rangle\langle a|\rho|b\rangle\langle b|=\sum_{a,b}|a,b\rangle\rangle\langle a|\rho|b\rangle\ . \tag{8}$$

The complex inner product of two Liouville-space vectors ρ_1 and ρ_2 can be defined as the ordinary Hilbert-space trace

$$\langle\langle\rho_1|\rho_2\rangle\rangle=\mathrm{tr}(\rho_1^\dagger\rho_2)\ , \tag{9}$$

where $\rho_1^\dagger$ denotes the Hermitian conjugate of ρ_1. The orthogonality condition on the Liouville-space basis states $|a,b\rangle\rangle$ can be expressed as

$$\begin{aligned}\langle\langle a,b|c,d\rangle\rangle&=\mathrm{tr}(|b\rangle\langle a||c\rangle\langle d|)\\&=\langle d|b\rangle\langle a|c\rangle=\delta(d,b)\delta(a,c)\ .\end{aligned} \tag{10}$$

It follows that $\langle\langle a,b|\rho\rangle\rangle=\langle a|\rho|b\rangle$ and

$$\rho=\sum_{a,b}|a,b\rangle\rangle\langle\langle a,b|\rho\rangle\rangle=\bar{I}\rho\ , \tag{11}$$

which defines the Liouville-space identity operator $\bar{I}$.

The Liouville-space operator $\bar{L}$ can be represented, in terms of the basis states $|a,b\rangle\rangle$, in the form

$$\bar{L}=\sum_{a,b}\sum_{c,d}|a,b\rangle\rangle\langle\langle a,b|\bar{L}|c,d\rangle\rangle\langle\langle c,d|\ . \tag{12}$$

Since four indices are required in its matrix representation, the operator $\bar{L}$ is also referred to as a tetradic operator. From the definition of $\bar{L}$, it follows that the tetradic matrix elements of the Liouville-space operator $\bar{L}$ associated with the Hamiltonian H are given by

$$\langle\langle a,b|\bar{L}|c,d\rangle\rangle=\frac{1}{\hbar}[\langle a|H|c\rangle\delta(d,b)-\delta(a,c)\langle d|H|b\rangle]\ . \tag{13}$$

It can be seen that the eigenvalues of $\bar{L}$ will correspond to energy differences divided by $\hbar$. The Liouville-space Dirac notation, which was introduced in the theory of spectral-line shapes by Baranger [25], is most advantageous for Liouville-space operators which can be expressed in the direct-product form, as in Eq. (13).

If the Hamiltonian H is independent of time and conservative, the density operator $\rho(t)$, which solves Eq. (7), can be formally related to the density operator $\rho(t_0)$, at the initial time t_0, by means of the ordinary Hilbert-space time-evolution operator

$$U(t,t_0)=\exp\left[\left(\frac{-i}{\hbar}\right)H(t-t_0)\right]\ , \tag{14}$$

in the following manner:

$$\rho(t)=U(t,t_0)\rho(t_0)[U(t,t_0)]^\dagger\equiv\bar{g}(t,t_0)\rho(t_0)\ . \tag{15}$$

The Liouville-space time-evolution operator $\bar{g}(t,t_0)$ is, accordingly, expressible in the form

$$\bar{g}(t,t_0)=\exp[-i\bar{L}(t-t_0)]\ . \tag{16}$$

We will also be concerned with problems where the Hamiltonian is dependent on time. In this case Eq. (16) must be replaced by a more general relationship. Although the notation $\bar{U}(t,t_0)$ is sometimes employed for $\bar{g}(t,t_0)$, we will ultimately introduce a reduced density-operator description in which the corresponding time-evolution operator, which takes into account collisional and radiative damping phenomena, will no loner be unitary.

The Liouville-space equivalent of the Feynman-Dyson perturbation-theory expansion can be most conveniently formulated by introducing the transformation to the interaction picture. The transformation from the Schrödinger picture, in which the density operator $\rho(t)$ is defined, to the interaction picture, in which all operators will be designated by means of the superscript I, can be accomplished in the following manner:

$$\begin{aligned}\rho^I(t)&=\exp\left[\left(\frac{i}{\hbar}\right)H^0t\right]\rho(t)\exp\left[-\left(\frac{i}{\hbar}\right)H^0t\right]\\&=\exp(i\bar{L}^0t)\rho(t)\ ,\end{aligned} \tag{17}$$

where $\bar{L}^0$ denotes the Liouville-space operator corresponding to the unperturbed Hamiltonian H^0. The time evolution of the density operator $\rho^I(t)$, in the interaction picture, is then described by the equation of motion

$$\frac{\partial\rho^I(t)}{\partial t}=-\left(\frac{i}{\hbar}\right)[V^I(t),\rho^I(t)]=-i\bar{V}^I(t)\rho^I(t)\ , \tag{18}$$

where $\bar{V}^I(t)$ is the Liouville-space operator

$$\bar{V}^I(t)=\exp(i\bar{L}^0t)\bar{V}(t)\exp(-i\bar{L}^0t)\ , \tag{19}$$

which is obtained by the transformation of the Liouville-space perturbation operator $\bar{V}(t)$ to the interaction picture. It should be noted that the Liouville equation of motion for the density operator differs in the sign of the right-hand side when compared with the equation of motion for a quantum-mechanical operator in the Heisenberg representation.

If the interaction $\bar{V}^I$ is independent of time, then Eq. (18) has the simple formal solution

$$\rho^I(t)=\bar{g}^I(t,t_0)\rho^I(t_0)=\exp[-i\bar{V}^I(t-t_0)]\rho^I(t_0) \tag{20}$$

together with the initial condition

$$\rho^I(t_0)=\rho(t_0) \ . \tag{21}$$

The Liouville-space time-evolution operator $\bar{g}^I(t,t_0)$, in the interaction picture, is not necessarily unitary after a reduced density-operator description has been introduced in which $\bar{V}^I$ becomes complex, due to the inclusion of collisional and radiative damping phenomena. We will investigate the equation of motion for the density operator, in the presence of time-dependent interactions, by introducing the time-ordering operator and utilizing the integral equation for the propagator $\bar{g}^I(t,t_0)$ corresponding to the time-dependent perturbations, as described by Burnett, Cooper, Ballagh, and Smith [39].

B. Transition probabilities for interacting systems

In order to define a transition probability for a quantum-mechanical system that is interacting with other quantum-mechanical systems, it is convenient to introduce a projection operator P_f, which specifies the final state f of the combined interacting system, corresponding to a specific measurement process involving the subsystem of interest. The projection operator pertaining to the subsystem of interest may be converted into the projection operator P_f, which is defined in the space of the composite system, simply by forming the direct product with the unit operator I_B corresponding to the remaining systems, which will be treated as a very large, but not necessarily thermal, bath. For example, the detection of a single spontaneously emitted photon with momentum $\hbar\mathbf{k}$ and helicity λ can be described by using the final-state projection operator

$$P_f=\sum_{\beta}|\beta\rangle\langle\beta|\otimes I_B\otimes|1,\hbar\mathbf{k},\lambda\rangle\langle 1,\hbar\mathbf{k},\lambda| \ , \tag{22}$$

where the summation over β includes the complete spectrum of bound, discrete resonance, and nonresonant continuum eigenstates of the electronic subsystem under investigation and the unit operator I_B is defined in the very large subspace of degrees of freedom pertaining to the perturbing particles and all additional modes of the quantized radiation field. The ket $|1,\hbar\mathbf{k},\lambda\rangle$ denotes the occupation-number or Fock-space eigenstate corresponding to a single photon in the observed mode of the quantized electromagnetic field. The density operator formalism for composite systems has been presented by Fano [8].

The probability per unit time for the transition $i\to f$ in the combined interacting system can be defined as [31,61]

$$\begin{aligned} A(i\to f)&=\lim_{t\to\infty}\frac{d}{dt}\mathrm{Tr}[P_f\rho(t)] \\ &=\lim_{t\to\infty}\frac{d}{dt}\mathrm{Tr}[P_f\bar{g}(t,t_0)\rho_i(t_0)] \ , \end{aligned} \tag{23}$$

where in the second equation we have substituted for $\rho(t)$ using Eq. (15). Using the inner product definition given by Eq. (9), the transition rate (pertaining to the combined system) can be written as the Liouville-space inner product

$$A(i\to f)=\lim_{t\to\infty}\frac{d}{dt}\langle\langle P_f|\bar{g}(t,t_0)|\rho_i(t_0)\rangle\rangle \ . \tag{24}$$

Alternatively, $A(i\to f)$ may be expressed in the Liouville-space interaction picture, using the first part of Eq. (20). After introducing the explicit form given by Eq. (22) for the projection operator P_f, which describes the detection of a single photon, Eq. (24) can be reduced to an expression involving the trace over all quantum states except those specifying the detected mode of the quantized radiation field. The result of performing this restricted trace can be represented in terms of the diagonal matrix element $\langle 1|\rho^D|1\rangle$ of a single-photon-detection density operator ρ^D, which is defined by taking the restricted trace of the composite-system final-state density operator $\rho(t)$.

For very short time-scale interactions, which cannot be described by a transition probability per unit time, it is necessary to investigate the detailed time variation of the final-state projection of the solution to the equation of motion for the composite-system density operator $\rho(t)$, i.e., the $t\to\infty$ limit cannot be taken in Eq. (24).

C. Tetradic scattering operators

1. *Time-independent formulation*

The time-independent tetradic scattering-operator formalism has been presented by Fano [10] and by Ben-Reuven and Mukamel [12]. To evaluate the asymptotic time limit in Eq. (24), defining the transition rate for the combined system, one uses the relationship

$$\lim_{t\to\infty}\left\{\frac{d}{dt}\left[\lim_{t_0\to-\infty}\bar{g}(t,t_0)\right]\right\}=-i\lim_{\varepsilon\downarrow 0}\bar{T}(+i\varepsilon) \ , \tag{25}$$

where $\bar{T}(z)$ is the Liouville-space analog of the ordinary Hilbert-space transition operator [11]. The tetradic representations of the Lippmann-Schwinger equations can be expressed in the forms

$$\bar{T}(z)=\bar{V}+\bar{V}\bar{G}^0(z)\bar{T}(z)$$

and

$$\bar{T}(z)=\bar{V}+\bar{V}\bar{G}(z)\bar{V} \ , \tag{26}$$

where the tetradic resolvent or Green's operators are defined by

$$\bar{G}^0(z)=(z-\bar{L}^0)^{-1}$$

and

$$\bar{G}(z)=(z-\bar{L})^{-1} \ . \tag{27}$$

The usual scattering-theory boundary condition is incorporated by taking the limit as $\varepsilon\downarrow 0$ of the complex variable $z=+i\varepsilon$, giving rise to on-the-energy-shell matrix elements of $\bar{T}(z)$. In the treatment of processes involving nonstationary (e.g., decaying) states, the $\varepsilon\downarrow 0$ limit may not be appropriate (i.e., the $t \to \infty$ limit may not be what is desired). In the reduced density-operator description, one may need to consider a system which is excited at t_0 and observed at t. The treatment of this process would necessarily involve off-the-energy-shell matrix elements of the tetradic transition operator $\bar{T}(z)$. We will employ the scattering-theory approach in order to define the probability per unit time for a particular radiative transition or set of transitions contributing to the spectral feature of interest. Since the initial-state density operator $\rho_i(t_0)$ occurs in the definition of the transition rate that is given by Eq. (24), this density operator must be either known from the initial conditions or determined by means of a separate kinetic-theory description, accounting for an entire sequence of collisional and radiative relaxation processes. An extension of the present investigation would be required for the treatment of a nondiagonal initial-state density operator, because we have assumed that this density operator is diagonal in the unperturbed basis set.

The Liouville-space time-evolution operator $\bar{g}(t,t_0)$ can be formally related to the resolvent operator $\bar{G}(z)$ by means of the transformation

$$\bar{g}(t,t_0)=\lim_{\varepsilon\to 0}\frac{1}{2\pi i}\oint dz\,\exp[-iz(t-t_0)]\bar{G}(z+i\varepsilon)\ , \qquad (28)$$

which has the form of a Fourier or Laplace transform for $t_0 \to -\infty$ or $t_0=0$, respectively, with the application of the appropriate contour integration.

Assuming that the usual scattering-theory boundary condition is appropriate, the cross section for the scattering process can be defined by [12]

$$\sigma(i\to f)=-i\lim_{\varepsilon\to 0}\frac{1}{F_i}\langle\langle P_f|\bar{T}(+i\varepsilon)|\rho_i\rangle\rangle\ , \qquad (29)$$

where F_i denotes the flux of incident particles or photons in the channel corresponding to the initial state that is represented by ρ_i. The treatment in terms of a single scattering event can be employed for the short times that are important in the determination of the spectral distribution produced by the radiative transitions of interest, because only for a short time can one distinguish between the perturber electrons and the electron that is involved in the (autoionizing) resonance process.

We will apply equations from scattering theory for the interaction $\bar{V}$ arising from the partition

$$\bar{L}=\bar{L}^0+\bar{V} \qquad (30)$$

of the Liouville-space operator $\bar{L}$, for the entire interacting matter and radiation-field system, into an unperturbed part $\bar{L}^0$ and a perturbation $\bar{V}$. This procedure is only valid for a system satisfying the steady-state conditions

$$\bar{L}^0\rho_i=\bar{L}^0\rho_f=0\ . \qquad (31)$$

These conditions will be satisfied if the initial-state density operator ρ_i and the final-state projection operator P_f correspond to stationary states of $\bar{L}^0$. Decaying states are not stationary, but one can introduce a steady-state condition under certain excitations, e.g., by an external field, but then $\bar{L}^0$ is not Hermitian. It should be pointed out that it is possible to define suitable eigenstates even for a non-Hermitian Liouville-space operator, but in general these states are not orthogonal (and consequently it is necessary to construct orthogonal basis sets, e.g., as described by Baranger [25]).

The Liouville-space formalism, as developed in terms of the tetradic scattering operators, provides a suitable framework for the incorporation of relaxation phenomena arising from the interactions between the electronic subsystem of interest and the much larger bath system. When account is taken of the appropriate boundary condition on ε and any off-the-energy-shell matrix elements of $\bar{T}(+i\varepsilon)$ which may be required, the Liouville-space scattering theory can be applied to the description of radiative transitions occurring in the presence of relaxation processes. The application of the Liouville-space scattering theory is greatly facilitated by assuming that the initial-state density operator ρ_i is not only expressible in the separable direct-product form, but is also represented by a diagonal matrix in the basis of unperturbed $\bar{L}^0$ eigenstates (which may include states in a classical static or radiation field).

2. *Time-dependent formulation*

The time-evolution operator appropriate for the description of time-dependent interactions can be formally expressed, in the Liouville-space interaction picture, in the form

$$\bar{g}^I(t,t_0)=\mathcal{T}\exp\left|-i\int_{t_0}^{t}dt'\bar{V}^I(t)\right|\ , \qquad (32)$$

where $\mathcal{T}$ denotes the time-ordering operator. The Liouville-space time-evolution operator or propagator $\bar{g}^I(t,t_0)$ satisfies the equation of motion

$$\frac{\partial}{\partial t}\bar{g}^I(t,t_0)=-i\bar{V}^I(t)\bar{g}^I(t,t_0) \qquad (33)$$

together with the initial condition

$$\bar{g}^I(t_0,t_0)=\bar{I}\ . \qquad (34)$$

The integral equation employed by Burnett, Cooper, Ballagh, and Smith [39] can be derived by expressing the Liouville-space interaction $\bar{V}^I(t)$ as the sum

$$\bar{V}^I(t)=\bar{V}_0^I+\bar{V}_T^I(t) \qquad (35)$$

of a time-independent (or quasistatic) contribution $\bar{V}_0^I$ and a time-dependent part $\bar{V}_T^I(t)$. After applying a standard operator identity, the integral equation for $\bar{g}^I(t,t_0)$ can be presented in the form

$$\bar{g}^I(t,t_0)=\bar{g}_0^I(t,t_0)+\int_{t_0}^{t}dt'\bar{g}_0^I(t,t')\bar{V}_T^I(t')\bar{g}^I(t',t_0)\ , \qquad (36)$$

where $\bar{g}_0^I(t,t_0)$ is the Liouville-space time-evolution operator corresponding to the time-independent interaction $\bar{V}_0^I$ and is obtained simply by replacing $\bar{V}^I$ with $\bar{V}_0^I$ in Eq. (20). It should be emphasized that the propagator identity expressed by Eq. (36) is valid for any arbitrary decomposition of the interaction $\bar{V}^I(t)$, provided that a suitable result for $\bar{g}_0^I(t,t_0)$ is employed. In particular, when using a reduced density-operator description, some damping processes can be included in $\bar{g}_0^I(t,t_0)$, as well as some time-dependent interactions.

D. Zwanzig projection-operator approach to the treatment of relaxation phenomena

1. Time-independent formulation

The evaluation of the radiative transition probability per unit time can be simplified substantially by introducing a partition of the complete Liouville space into a reduced (relevant) subspace, corresponding to the uncorrelated electronic subsystem and the radiation-field modes that are relevant to the photon detection process, and a complementary orthogonal subspace, in which these electronic-subsystem and radiation-field states are dynamically correlated with the multitude of bath degrees of freedom. Following Zwanzig [9], we denote by $\bar{P}$ the projection operator onto the relevant Liouville subspace, of the "free" states corresponding to the relevant degrees of freedom, and we denote by $\bar{Q}=\bar{1}-\bar{P}$ the projection operator onto the Liouville subspace of the dynamically correlated states. The Zwanzig projection operators play a role analogous to that of the ordinary Hilbert-space projection operators introduced by Feshbach [19] in the theory of nuclear reactions. Assuming that we are dealing with the full time-independent Hamiltonian and that we have not previously introduced a reduced density-operator description, we will demonstrate that the Liouville-space transition operator, within the subspace of the projection operator $\bar{P}$, can be expressed by means of a tetradic Lippmann-Schwinger-type equation that explicitly involves only the relevant Liouville-space interaction of the detected-photon modes with the uncorrelated electronic subsystem of interest. The multitude of interactions with the perturbing particles and remaining modes of the radiation field, which will be referred to as the "irrelevant" interactions, are thereby incorporated by the introduction of a Liouville-space self-energy operator in the formal expression for the relevant ($\bar{P}$-space) projection of the Liouville-space resolvent operator. More specifically, the Liouville-space projection operator $\bar{P}$ formally represents an average over the bath degrees of freedom, corresponding to the multitude of perturbing particles and remaining radiation-field modes.

To illustrate the Zwanzig projection-operator approach, we first treat as the relevant part of the Liouville-space interaction the projection

$$\bar{V}^r=\bar{P}\bar{V}_{\mathbf{k}\lambda}^{SR}\bar{P} \ , \tag{37}$$

where $\bar{V}_{\mathbf{k}\lambda}^{SR}$ denotes the interaction of the electronic subsystem with the set $\{\mathbf{k}\lambda\}$ of radiation-field modes that are involved in the photon detection process. Later we shall treat this interaction on an equal footing with the interaction that is responsible for atomic autoionization. This will be accomplished by means of the inclusion of the relevant part of the electron-electron interaction in $\bar{V}^r$ together with the partition of the relevant Liouville space into resonant and nonresonant subspaces. The remaining interactions are included in the irrelevant contribution

$$\bar{V}^{\text{ir}}=\bar{V}-\bar{V}^r=\bar{P}\bar{V}^B\bar{P}+\bar{P}\bar{V}\bar{Q}+\bar{Q}\bar{V}\bar{P}+\bar{Q}\bar{V}\bar{Q} \ , \tag{38}$$

where $\bar{V}^B$ denotes the Liouville-space bath interactions, involving the multitude of perturbing particles and remaining photon modes. In the scattering-theory treatment of the autoionization and the electron-capture processes that are associated with the radiative transition of interest, the captured or ejected electron can be considered not as a perturber but as a part of the electronic subsystem of interest. This procedure is expected to be valid for the short times that are relevant for the determination of the radiative transition rate. In the treatment of radiative decay, the relevant modes of the quantized radiation field should be considered separately from those included in the bath degrees of freedom. Since the number of bath particles and radiation-field modes is very large, no significant counting errors nor deviations in the perturber energy distributions are expected to occur in connection with approximations in these treatments.

We now employ the mathematical structure of the ordinary Hilbert-space projection-operator approach presented by Haan and Jacobs [4], which provides a unified treatment of radiative and dielectronic recombination. In Sec. III, we shall introduce a Liouville-space version of this approach. The Lippmann-Schwinger equation for the Liouville-space transition operator $\bar{T}(z)$, in the form given by the second part of Eq. (26), is first rewritten in the alternative, but equivalent, form

$$\bar{T}(z)=\bar{R}(z)+\bar{R}(z)\bar{G}^r(z)\bar{R}(z) \ , \tag{39}$$

where

$$\bar{R}(z)=\bar{V}+\bar{V}\bar{Q}(z-\bar{Q}\bar{L}\bar{Q})^{-1}\bar{Q}\bar{V} \tag{40}$$

and

$$\bar{G}^r(z)=\bar{P}\bar{G}\bar{P}=\bar{P}[z-\bar{P}\bar{L}^0\bar{P}-\bar{P}\bar{R}(z)\bar{P}]^{-1}\bar{P} \ . \tag{41}$$

The operator $\bar{R}(z)$ is the relaxation operator introduced by Fano [10] and utilized by Ben-Reuven and Rabin [31]. It is the Liouville-space analog of the level-shift operator introduced by Goldberger and Watson [11], which has also been referred to as the vertex operator. The relationship between the Liouville-space transition operator $\bar{T}(z)$ and the Liouville-space relaxation operator $\bar{R}(z)$ is analogous to the connection between the self-energy and the proper self-energy operators in quantum field theory. Ben-Reuven and Mukamel [12] have emphasized that the operators $\bar{T}(z)$ and $\bar{R}(z)$ are interchangeable only to lowest order in the expansion in powers of the interaction $\bar{V}$, which corresponds to an expansion in powers of the density of the perturbing particles and in powers of the intensity of the radiation field. Beyond the lowest-order approximation, it is necessary to make a distinction between the scattering and relaxation processes.

In order to obtain a useful expression for the projected Liouville-space transition operator $\bar{P}\ \bar{T}(z)\bar{P}$, which describes the radiative transition of interest, it is convenient to write

$$\bar{P}\bar{R}(z)\bar{P}=\bar{V}^r+\bar{\Sigma}(z) \ , \tag{42}$$

where $\overline{\Sigma}(z)$ is the Liouville-space proper self-energy operator that represents the effects of the collisional and radiative relaxation processes. Following the wave-operator approach employed by Ben-Reuven and Rabin [31], we also define the tetradic Møller wave operators by

$$\begin{aligned} \overline{M}^{\rm ir}_{(+)}(z) &= \overline{1}+[z-\overline{P}\overline{L}^0\overline{P}-\overline{\Sigma}(z)]^{-1}\overline{\Sigma}(z) \ , \\ \overline{M}^{\rm ir}_{(-)}(z) &= \overline{1}+\overline{\Sigma}(z)[z-\overline{P}\overline{L}^0\overline{P}-\overline{\Sigma}(z)]^{-1} \ , \end{aligned} \tag{43}$$

which describe the rearrangement of the eigenstates of $\overline{L}^0$ as a result of the irrelevant interactions incorporated into $\overline{\Sigma}(z)$.

We utilize the following Liouville-space analogs of the ordinary Hilbert-space scattering theory relationships:

$$\begin{aligned} \overline{1}+\overline{G}^r(z)[\overline{V}^r+\overline{\Sigma}(z)] &= [\overline{1}+\overline{G}^r(z)\overline{V}^r]\overline{M}^{\rm ir}_{(+)}(z) \ , \\ \overline{1}+[\overline{V}^r+\overline{\Sigma}(z)]\overline{G}^r(z) &= \overline{M}^{\rm ir}_{(-)}(z)[\overline{V}^r\overline{G}^r(z)+\overline{1}] \ . \end{aligned} \tag{44}$$

The required projection of $\overline{T}(z)$ can now be expressed in the form

$$\overline{P}\overline{T}(z)\overline{P}=[\overline{M}^{\rm ir}_{(-)}(z)\overline{T}^r(z)+\overline{\Sigma}(z)]\overline{M}^{\rm ir}_{(+)}(z) \ , \tag{45}$$

where $\overline{T}^r(z)$ is the relevant Liouville-space transition operator defined by

$$\overline{T}^r(z)=\overline{V}^r+\overline{V}^r\overline{G}^r(z)\overline{V}^r \ . \tag{46}$$

The relevant Liouville-space transition operator $\overline{T}^r(z)$ is expressed, by means of Eq. (46), explicitly in terms of the relevant part of the Liouville-space interaction $\overline{V}^r$, while the collisional and radiative relaxation effects are incorporated by means of the Liouville-space self-energy operator $\overline{\Sigma}(z)$ in the expression for the relevant Liouville-space resolvent operator $\overline{G}^r(z)$. Equations (45) and (46) have been obtained by Ben-Reuven and Rabin [31], and we have adopted their notation. Equations (40) and (41) are the Liouville-space analogs of the results obtained by Mower [20] for the ordinary Hilbert-space resolvent operator. Equation (46) expresses the relevant Liouville-space transition operator $\overline{T}^r(z)$ as a sum of a resonant part and a nonresonant part, with respect to the collisional and radiative relaxation processes. In order to provide a description of autoionization resonance processes in the presence of relaxation phenomena, we shall modify this approach by including the interaction responsible for autoionization as a part of the relevant interaction and by introducing a partition of the relevant Liouville space into orthogonal parts, corresponding to the discrete autoionizing states and the nonresonant continuum states representing the final states in the autoionization and radiative stabilization processes.

The expression for $\overline{P}\overline{T}(z)\overline{P}$ can be significantly simplified by imposing suitable conditions on the initial-state density operator $|\rho_i\rangle\rangle$ and on the final-state projection operator $|P_f\rangle\rangle$, which are treated as state vectors in the Liouville-space representation. If we now invoke the assumptions that the initial-state $|\rho_i\rangle\rangle$ is confined to the subspace spanned by the projection operator $\overline{P}$ and is expressible in the uncorrelated direct-product form given by Eq. (5), it immediately follows that [31]

$$\overline{\Sigma}(z)|\rho_i\rangle\rangle=0 \tag{47}$$

and that

$$\overline{M}^{\rm ir}_{(+)}(z)|\rho_i\rangle\rangle=|\rho_i\rangle\rangle \ . \tag{48}$$

Equation (47) reflects the exclusion of the relevant interaction $\overline{V}^r$ from the definition of the Liouville-space self-energy operator $\overline{\Sigma}(z)$. Similarly, after making the assumptions that the final-state $|P_f\rangle\rangle$ is confined to the $\overline{P}$ subspace and is expressible in the direct-product form given by Eq. (22), we arrive at the conditions [31]

$$\langle\langle P_f|\overline{\Sigma}(z)=0 \ , \tag{49}$$

$$\langle\langle P_f|\overline{M}^{\rm ir}_{(-)}(z)=\langle\langle P_f| \ . \tag{50}$$

Consequently, we may omit from Eq. (45) the operators $\overline{M}^{\rm ir}_{(+)}(z)$ and $\overline{M}^{\rm ir}_{(-)}(z)$, as well as the additional $\overline{\Sigma}(z)$ contribution, which describes transitions between the initial and final states due solely to the irrelevant interactions. The final result is that the radiative transition of the electronic subsystem of interest, in the presence of relaxation processes, is completely described by substituting $\overline{T}^r(z)$ in place of $\overline{T}$ in Eq. (29) and in related expressions.

The requirements expressed by Eqs. (47)–(50) can be satisfied by adopting the definition introduced by Zwanzig [9] for the Liouville-space projection operator $\overline{P}$. Using the Liouville-space Dirac notation, the definition for $\overline{P}$ given by Zwanzig can be expressed in the form

$$\overline{P}=|\rho_B\rangle\rangle\langle\langle I_B| \ , \tag{51}$$

where ρ_B denotes the component of the factorized density operator ρ_i, for the initial state of the uncorrelated composite system, which represents the bath degrees of freedom, and I_B denotes the unit operator in the Liouville subspace of these degrees of freedom. In general, $\overline{P}$ corresponds to a many-body operator. In order to obtain explicit expressions for the desired projections of the Liouville-space resolvent and self-energy operators, it will be necessary to introduce approximations, such as the binary-collision approximation in the treatment of the "perturber-electron" collisions [39]. The effect of the Zwanzig projection operator $\overline{P}$ on the arbitrary tetradic operator $\overline{A}$ can be expressed in the form

$$\langle\langle \overline{P}\overline{A}|\rho_i\rangle\rangle=\langle\langle {\rm Tr}_B(\overline{A}\rho_B)|\rho_i\rangle\rangle \ . \tag{52}$$

The result of the trace operation is an average over the bath degrees of freedom This average yields a reduced tetradic operator, which is defined on the Liouville subspace spanned by the relevant degrees of freedom. The most general state vectors in the (relevant) Liouville subspace of the projection operator $\overline{P}$ may be denoted by $|\alpha\beta,mn\rangle\rangle$, where $|\alpha\beta\rangle\rangle$ represents the operator $|\alpha\rangle\langle\beta|$ in the ordinary Hilbert space of eigenstates of the electronic-subsystem Hamiltonian H^S and $|mn\rangle\rangle$ similarly represents the operator $|m\rangle\langle n|$ in the Fock space of occupation-number states for the relevant modes of the quantized electromagnetic field. In contrast to the unperturbed basis used here, the actual eigenstates of the reduced $\overline{P}$-space Liouville operator that allows for relaxation processes are states of a non-Hermitian operator and are therefore not members of an orthogonal basis set.

We are now in a position to present expressions for the steady-state radiative transition rates in terms of the tetradic matrix elements of the reduced, relevant Liouville-space transition operator $\bar{T}^r(z)$. For illustration, we consider the spontaneous single-photon emission process of an electronic subsystem, which is simultaneously interacting with a bath of perturbing particles and quantized radiation-field modes. The relevant components ρ_i^r and P_f^r of the initial-state density operator ρ_i and the final-state projection operator P_f can be, respectively, represented in the forms

$$\rho_i^r=\sum_\alpha \rho_\alpha |\alpha\alpha,00\rangle\rangle \ , \tag{53}$$

$$P_f^r=\sum_\beta |\beta\beta,11\rangle\rangle \ , \tag{54}$$

which involve expansions in terms of the unperturbed eigenstates for the electronic subsystem and the detected mode of the radiation field. The single-photon spontaneous emission rate, which is defined by Eqs. (24) and (25), can now be evaluated as follows:

$$\begin{aligned} A(i\to f) &= -i\lim_{\varepsilon\to 0}\langle\langle P_f|\bar{P}\bar{T}(+i\varepsilon)\bar{P}|\rho_i\rangle\rangle \\ &= -i\lim_{\varepsilon\to 0}\langle\langle P_f^r|\bar{T}^r(+i\varepsilon)|\rho_i^r\rangle\rangle \\ &= -i\lim_{\varepsilon\to 0}\sum_{\alpha,\beta}\rho_\alpha\langle\langle\beta\beta,11|\bar{T}^r(+i\varepsilon)|\alpha\alpha,00\rangle\rangle \ . \end{aligned} \tag{55}$$

The summations over α and β in general involve the complete set of bound, discrete resonance, and nonresonant continuum eigenstates of the isolated electronic subsystem. In practice, it is necessary to restrict these summations to include only the finite subsets of the states $\{\alpha\}$ and $\{\beta\}$, which are expected to provide the dominant contributions to the radiative transition rate in the spectral region of interest. In the scattering-theory approach to the unified description of resonant and nonresonant radiative transitions, the initial states $\{\alpha\}$ will be taken as the single-electron-continuum states, e.g., the states of the incident-electron initial-ion system in the photorecombination process. The scattering-theory approach corresponds to the treatment of a single resonance (autoionizing) population event rather than a sequence of collisional and radiative population events. We shall also introduce an alternative relaxation-theory approach, in which the initial states $\{\alpha\}$ will be taken as the discrete resonance states, e.g., the intermediate autoionization states in the dielectronic recombination mechanism. In this approach, it will be necessary to introduce a separate set of kinetic-theory equations for the determination of the population distribution (possibly including the coherences) of the initial, discrete resonance states of the electronic subsystem. In the relaxation-theory approach, one may take into account an entire sequence of collisional and radiative population processes. Finally, special care must be taken to employ appropriate generalizations of Eqs. (53) and (54) for cases where nonorthogonal basis states are involved, such as may be encountered in the use of "complex or decaying dressed" states in the presence of a classical laser field [62].

2. *Time-dependent formulation*

The time-dependent treatment of radiative transitions of the electronic subsystem is based on the equation of motion for the reduced relevant part of the density operator, which is defined as the projection of the full density operator, for the entire interacting matter and radiation-field system, onto the Liouville subspace of the relevant degrees of freedom. We will present a derivation of a Liouville-type equation of motion for the relevant part of the density operator, which will explicitly involve only the relevant Liouville-space interaction. The irrelevant interactions will be incorporated by means of a Liouville-space self-energy operator, which plays the role of a kernel in a time integral appearing in the equation of motion for the relevant density operator. In order to obtain a closed equation for the relevant part of the density operator, which has been referred to as the generalized master equation [7,63], it will be necessary to invoke the assumption that the density operator, for the entire interacting matter and radiation-field system, can be expressed in the uncorrelated factorized form at some initial time t_0. This assumption is expected to be valid, provided that the system has a finite correlation time and that t_0 is "sufficiently far in the past."

We now introduce the Zwanzig tetradic projection operators $\bar{P}$ and $\bar{Q}$, so that we can investigate the projections of the equation of motion for the density operator onto the orthogonal Liouville subspaces corresponding to the relevant and irrelevant degrees of freedom, respectively. Our time-dependent formulation will be based on the form of the equation of motion given by Eq. (18), which is expressed in the Liouville-space interaction picture. The Liouville-space perturbation operator $\bar{V}^I(t)$, which is defined in the interaction picture by means of Eq. (19), will include on an equal footing all collisional and radiative interactions of the electronic subsystem of interest, without regard for the possible time independence of some of these interactions. The general analysis that we will present is closely related to the equation-of-motion formulation of Burnett, Cooper, Ballagh, and Smith [39], except for two essential differences. First they carry out two sequential projections. The first projection corresponds to an average over the radiation-field modes, while the second projection involves an average over the states of the perturbing particles. Second they employ the equation of motion in the Schrödinger picture to treat the radiative interactions, while they adopt the interaction picture to describe the collisional perturbations. In their investigation, the phenomenon of particular interest is the time-dependent interactions of the electronic subsystem with the perturbing particles and an external (classical) laser-radiation field.

The two orthogonal projection of Eq. (18) may be written in the forms

$$\frac{\partial}{\partial t}[\bar{P}\rho^I(t)]=-i\bar{P}\bar{V}^I(t)\bar{P}\rho^I(t)-i\bar{P}\bar{V}^I(t)\bar{Q}\rho^I(t) \tag{56}$$

and

$$\frac{\partial}{\partial t}[\bar{Q}\rho^I(t)] = -i\bar{Q}\bar{V}^I(t)\bar{P}\rho^I(t) - i\bar{Q}\bar{V}^I(t)\bar{Q}\rho^I(t) \ . \tag{57}$$

We now employ a Liouville-space propagator identity of the type given by Eq. (36). This propagator identity may be written as

$$\bar{g}^I(t,t_0) = \bar{g}^I_Q(t,t_0) - i\int_{t_0}^{t} dt' \bar{g}^I_Q(t,t')\bar{Q}\bar{V}^I(t')\bar{P}\bar{g}^I(t',t_0) \ , \tag{58}$$

where the full Liouville-space propagator in the interaction picture $\bar{g}^I(t,t_0)$ is defined by Eq. (20) and the Liouville-space propagator $\bar{g}^I_Q(t,t_0)$ corresponding to the irrelevant part of the interaction $\bar{Q}\bar{V}^I(t)\bar{Q}$ may be formally expressed, in terms of the time-ordering operator $\mathcal{T}$, in the form

$$\bar{g}^I_Q(t,t_0) = \mathcal{T}\exp\left[-i\int_{t_0}^{t} dt' \bar{Q}\bar{V}^I(t')\bar{Q}\right] \ . \tag{59}$$

The Liouville-space propagator identity given by Eq. (58) allows the introduction of a formal solution to Eq. (57), which may be written as

$$\begin{aligned}\bar{Q}\rho^I(t) = {} & \bar{Q}\bar{g}^I_Q(t,t_0)\bar{Q}\rho^I(t_0) \\ & - i\int_{t_0}^{t} dt' [\bar{Q}\bar{g}^I_Q(t,t')\bar{Q}\bar{V}^I(t')\bar{P}\rho^I(t')] \ .\end{aligned} \tag{60}$$

After substituting the formal solution for $\bar{Q}\rho^I(t)$ given by Eq. (60) into Eq. (56), we obtain an exact equation for the reduced relevant part of the density operator $\bar{P}\rho^I(t)$ in the form

$$\begin{aligned}\frac{\partial}{\partial t}[\bar{P}\rho^I(t)] = {} & -i\bar{P}\bar{V}^I(t)\bar{P}\rho^I(t) - i\left[\int_{t_0}^{t} dt' \bar{P}\bar{\Sigma}^I(t,t')\bar{P}\rho^I(t')\right] \\ & - i\bar{P}\bar{V}^I(t)\bar{Q}\bar{g}^I_Q(t,t_0)\bar{Q}\rho^I(t_0) \ ,\end{aligned} \tag{61}$$

where the Liouville-space self-energy operator kernel is defined by

$$\bar{\Sigma}^I(t,t') = -i\bar{P}\bar{V}^I(t)\bar{Q}\bar{g}^I_Q(t,t')\bar{Q}\bar{V}^I(t')\bar{P} \ . \tag{62}$$

Equation (61) cannot be regarded as a closed equation for the reduced relevant part of the density operator $\bar{P}\rho^I(t)$ because of the presence of the last term, which involves the correlated part of the density operator $\bar{Q}\rho^I(t_0)$ evaluated at the initial time t_0. If we are interested in times t such that $t - t_0$ is long compared to a "correlation time," we may invoke the assumption that the initial correlations decay away and can be neglected. This assumption is most simply expressed by the condition

$$\bar{Q}\rho^I(t_0) = 0 \ . \tag{63}$$

This condition implies that the full density operator $\rho^I(t_0)$ at the initial time t_0, which is related to the density operator $\rho(t_0)$ defined in the Schrödinger picture by means of Eq. (17), can be expressed in the uncorrelated direct-product form. The closed form equation for $\bar{P}\rho^I(t)$, which is obtained by omitting the last term in Eq. (61), has been referred to as the generalized master equation [7,63]. The generalized master equation provides a quantum kinetic-theory foundation for the determination of the population distribution of the states of the electronic subsystem together with the statistical distribution for the relevant modes of the quantized radiation field, in the presence of the multitude of collisional and radiative interactions that are incorporated in the Liouville-space self-energy operator kernel. The generalized master equation also allows for the investigation of the effects of the coherences. In some circumstances, the time of interest $t - t_0$ is short. Then the initial correlations, which are represented by the last term in Eq. (61), cannot be neglected. In this case, the last term in Eq. (61) must be directly evaluated, as described by Burnett and Cooper [64].

In order to establish the relationship between the time-dependent and time-independent Liouville space projection-operator formulations, we first rewrite the generalized master equation, which is obtained from Eq. (61) after omitting the initial-correlation term, in the alternative and more abstract form

$$\begin{aligned}\frac{\partial}{\partial t}[\bar{P}\bar{g}^I(t,t_0)\bar{P}] = {} & -i\bar{P}\bar{V}^I(t)\bar{P}\bar{g}^I(t,t_0)\bar{P} \\ & - i\int_{t_0}^{t} dt' \bar{P}\bar{\Sigma}^I(t,t')\bar{P}\bar{g}^I(t',t_0)\bar{P} \ ,\end{aligned} \tag{64}$$

which follows directly from using the definition of the full Liouville-space propagator $\bar{g}^I(t,t_0)$ in the interaction picture, given by the first part of Eq. (20). A major complication that is encountered in the treatment of Eq. (64) is that the Liouville-space projection operators are many-body operators. In the binary-collision approximation for the perturbing particles, Burnett, Cooper, Ballagh, and Smith [39] have shown how Eq. (64) can be reduced to a relationship involving two-body operators. The connection with the time-independent formulation can now be obtained by assuming that the Liouville-space perturbation operator $\bar{V}$ is independent of time. However, the binary-collision approximation is often introduced by invoking the fact that the interaction $\bar{V}^I(t)$ is localized in time. After introducing the Laplace-transform version of the general contour-integral relationship given by Eq. (28), which corresponds to the initial condition $t_0 = 0$, it follows from the application of standard transform techniques that

$$\bar{P}\bar{G}^I(z)\bar{P} = [z - \bar{P}\bar{V}\bar{P} - \bar{P}\bar{\Sigma}(z)\bar{P}]^{-1} \ , \tag{65}$$

where $\bar{P}\bar{G}^I(z)\bar{P}$ and $\bar{P}\bar{\Sigma}(z)\bar{P}$ denote the transforms corresponding to the Liouville-space operators $\bar{P}\bar{g}^I(t,t_0)\bar{P}$ and $\bar{P}\bar{\Sigma}^I(t,t_0)\bar{P}$, respectively. The relationship expressed by Eq. (65) is equivalent to that given by Eq. (41) for the relevant part of the Liouville-space resolvent operator $\bar{P}\bar{G}(z)\bar{P}$, which is associated with the Liouville-space propagator defined in the alternative Schrödinger picture, by means of Eq. (28). This equivalence follows from Eq. (17), which implies that

$$\bar{g}^I(t,t_0) = \exp[i\bar{L}^0(t - t_0)]\bar{g}(t,t_0) \ . \tag{66}$$

Note that the unnecessary superscript I has been omitted from the time-independent Liouville-space operators $\bar{V}$ and $\bar{\Sigma}(z)$ in Eq. (65).

The widely used, but not necessarily widely valid, Markov approximation can be introduced by assuming that the Liouville-space self-energy or memory kernel can be simplified into the form [65]

$$\bar{\Sigma}^I(t,t') = \lim_{z\to+i0} \bar{\Sigma}(z)\delta(t-t') \ , \qquad (67)$$

which corresponds to an infinitesimally short memory time. This approximation allows the equation of motion for the relevant part of the density operator to be expressed entirely in terms of the reduced effective Liouville-space interaction $\bar{P}\bar{V}^I(t)\bar{P}+\bar{\Sigma}(+i0)$. Since $\bar{\Sigma}(z)$ is composed of both real and imaginary parts, corresponding to the line shift and width operators, respectively, the reduced density-operator description is necessarily based on a non-Hermitian interaction, for which the corresponding Liouville-space time-evolution operator or propagator, in the reduced (relevant) space, cannot be assumed to be unitary. Burnett, Cooper, Ballagh, and Smith [39] employ the Markov approximation to simplify the master equation accounting for the radiation-damping processes, but they do not restrict their subsequent average over the states of the perturbing particles by the assumption of short-memory-time collisional interactions. However, they introduce the binary-collision approximation, in order to reduce the Liouville-space projection operators to two-body operators.

Instead of the transition probability per unit time which is introduced in the time-independent formulation, the time-dependent transition probability defined by

$$C(i\to f) = \langle\langle P_f^I(t)|\bar{P}\bar{g}^I(t,t_0)\bar{P}|\rho_i^I(t_0)\rangle\rangle \qquad (68)$$

provides a basis for the description of radiative transitions in the time-dependent formulation. For the spontaneous single-photon emission process of the electronic subsystem, which is simultaneously interacting with the perturbing particles and radiation-field modes, the time-dependent transition probability associated with Eq. (55) can be expressed in the form

$$C(i\to f) = \sum_{\alpha,\beta} \rho_\alpha \langle\langle \beta\beta,11|\bar{g}^r(t,t_0)|\alpha\alpha,00\rangle\rangle \ , \qquad (69)$$

where $\bar{g}^r(t,t_0)$ denotes the reduced relevant part of the Liouville-space interaction-picture propagator, whose asymptotic time derivative gives the relevant transition operator $\bar{T}^r(z)$. The Liouville-space propagator $\bar{g}^r(t,t_0)$ represents the quantity that has been denoted by $\bar{P}\bar{g}^I(t,t_0)\bar{P}$, and in the master-equation approximation this projected propagator is governed by Eq. (64). The Liouville-space state vectors in Eq. (69) are understood to be defined in the Liouville-space interaction picture. As indicated by Alber and Cooper [61], the spontaneous emission spectrum may be described by introducing the transition rate

$$A(i\to f) = \frac{d}{dt}C(i\to f) \ , \qquad (70)$$

for which we do not necessarily take the limit $t\to\infty$ employed in the definition of the steady-state transition rate given by Eq. (24). For electric dipole transitions, this definition for the spontaneous emission spectrum can be reduced to the standard form involving the dipole autocorrelation function. It should be noted that, while the transition probability defined by Eq. (68) may in perturbation theory diverge, the transition rate expressed by Eq. (70) is well defined.

III. UNIFIED TREATMENT OF RESONANT AND NONRESONANT RADIATIVE TRANSITIONS

In this section, the Liouville-space projection-operator formalism that was presented in the preceding section is adapted to the unified treatment of resonant and nonresonant radiative transitions of an electronic subsystem that is simultaneously interacting with a multitude of perturbing particles and modes of the quantized radiation field. Our objective has been to provide a generalization of the ordinary Hilbert-space projection-operator approach presented by Haan and Jacobs [4], which was formulated for application to the unified treatment of radiative and dielectronic recombination, in the absence of interactions with the bath degrees of freedom. In the ordinary Hilbert-space projection-operator approach, allowance was made for decay only by autoionization processes and spontaneous radiative transitions. The desired generalization may be accomplished by treating the collisional and radiative interactions, which are included in the Liouville-space self-energy operator $\bar{\Sigma}(z)$, on an equal footing with the autoionization and spontaneous radiation processes that are described by the relevant Liouville-space interaction $\bar{V}^r$. Although our primary interests in the present investigation are directed to the unified descriptions of radiative and dielectronic recombination of many-electron ions and of free-bound and bound-bound transitions in electron channeling radiation, our general formalism is expected to be applicable to the investigation of a diverse class of radiative transitions in complex electronic systems.

A. Projection-operator formalism

The initial states $[\alpha]$, occurring in the expressions for the single-photon spontaneous emission rate which were presented in the preceding section, will now be taken as the single-electron continuum states, e.g., the states of the incident-electron initial-ion system in the photorecombination process. It should be emphasized that additional contributions to the photon emission rate at the frequency of interest may be produced by transitions from other types of initial states, e.g., by excitation of the discrete resonance states from the bound states of the combined electron-ion system. After the average over the multitude of perturber particles and radiation-field modes has been carried out, by means of the Liouville-space projection operator $\bar{P}$ in the formal expressions for the reduced Liouville-space transition operator or time-evolution operator, the tetradic operators occurring in these formal expressions will be defined entirely on the relevant Liouville space, corresponding to the subspace of the uncorrelated states of the electronic subsystem together with the relevant photon modes. We now introduce a partition of the reduced, relevant Liouville space in the following manner:

$$\bar{P}=\bar{P}(\bar{P}_a+\bar{P}_c)\bar{P}=\bar{P}(\bar{P}_a+\bar{P}_\varepsilon+\bar{P}_\omega)\bar{P} \ . \tag{71}$$

It is understood that the average over the bath degrees of freedom, which is the result of the action of the Zwanzig projection operator $\bar{P}$, has been carried out before the partition of the relevant Liouville space into resonant and nonresonant subspaces, as indicated formally by Eq. (71). Specifically, the average over the bath degrees of freedom is included in the definition of the Liouville-space self-energy operator $\bar{\Sigma}(z)$. This average leaves the self-energy operator, and all other Liouville-space operators occurring in the subsequent analysis, defined solely within the subspace of the relevant degrees of freedom. Consequently, the states corresponding to the bath degrees of freedom may be omitted in the specification of the three relevant Liouville-space projection operators $\bar{P}_a$, $\bar{P}_\varepsilon$, and $\bar{P}_\omega$. The operator $\bar{P}_a$ projects onto the Liouville subspace of the discrete resonance states that are composed of the ordinary Hilbert-space states $|\alpha\rangle$, while the operator $\bar{P}_c$ projects onto the Liouville subspace of the nonresonant continuum states. As indicated, the continuum projection operator $\bar{P}_c$ may be further decomposed as a sum of an electron-continuum projection operator $\bar{P}_\varepsilon$ and a photon-continuum projection operator $\bar{P}_\omega$. The Liouville-space electron-continuum states are composed of the ordinary Hilbert-space states $|\mu\varepsilon\rangle$, where μ denotes the bound state of the residual ion and ε is the energy of the continuum electron. The Liouville-space photon-continuum states are formed from the ordinary Hilbert-space direct-product states $|\beta,1\rangle$, which correspond to the electronic subsystem in the bound eigenstate $|\beta\rangle$ and a single photon with energy $\hbar\omega$.

It will be necessary to adopt the following definitions for the three relevant Liouville-space projection operators $\bar{P}_a$, $\bar{P}_\varepsilon$, and $\bar{P}_\omega$:

$$\begin{aligned}\bar{P}_a=&\sum_\alpha\sum_{\alpha'}|\alpha\alpha',00\rangle\rangle\langle\langle\alpha\alpha',00|+\sum_\alpha\sum_\beta\int d\hbar\omega|\alpha\beta,01\rangle\rangle\langle\langle\alpha\beta,01|+\sum_\alpha\sum_\beta\int d\hbar\omega|\beta\alpha,10\rangle\rangle\langle\langle\beta\alpha,10|\\&+\sum_\alpha\sum_\mu\int d\varepsilon|\alpha,\mu\varepsilon;00\rangle\rangle\langle\langle\alpha,\mu\varepsilon;00|+\sum_\alpha\sum_\mu\int d\varepsilon|\mu\varepsilon,\alpha;00\rangle\rangle\langle\langle\mu\varepsilon,\alpha;00| \ ,\end{aligned}\tag{72}$$

$$\bar{P}_\varepsilon=\sum_\mu\sum_{\mu'}\int d\varepsilon\int d\varepsilon'|\mu\varepsilon,\mu'\varepsilon';00\rangle\rangle\langle\langle\mu\varepsilon,\mu'\varepsilon';00| \ , \tag{73}$$

$$\begin{aligned}\bar{P}_\omega=&\sum_\beta\sum_{\beta'}\int d\hbar\omega\int d\hbar\omega'|\beta\beta',11'\rangle\rangle\langle\langle\beta\beta',11'|\\&+\sum_\mu\sum_\beta\int d\varepsilon\int d\hbar\omega|\mu\varepsilon,\beta;01\rangle\rangle\langle\langle\mu\varepsilon,\beta;01|+\sum_\mu\sum_\beta\int d\varepsilon\int d\hbar\omega|\beta,\mu\varepsilon;10\rangle\rangle\langle\langle\beta,\mu\varepsilon;10| \ .\end{aligned}\tag{74}$$

The component of the projection operator $\bar{P}_\varepsilon$ corresponding to the Liouville-space states $|\mu\varepsilon,\mu\varepsilon;00\rangle\rangle$ and the component of the projection operators $\bar{P}_a$ corresponding to the Liouville-space states $|\alpha\alpha,00\rangle\rangle$, which are stationary states of the unperturbed relevant Liouville-space operator $\bar{P}\bar{L}^0\bar{P}$, are the Liouville-space analogs of the ordinary Hilbert-space projection operators P and Q, respectively, which were introduced by Feshbach [19]. The component of the projection operator $\bar{P}_\omega$ representing the stationary Liouville-space states $|\beta\beta,11\rangle\rangle$ is the Liouville-space analog of the ordinary Hilbert-space projection operator R used by Gau and Hahn [66] and by LaGattuta [67]. The partition of the reduced, relevant Liouville space which we have introduced is appropriate only for the description of the specific single-photon transition, which is associated with a single resonant one-electron population event. While the initial and final states (in the sense of scattering states) in the radiative transition of interest will be assumed to correspond to stationary states of the unperturbed relevant Liouville-space operator $\bar{P}\bar{L}^0\bar{P}$, the inclusion of the nonstationary mixed states or coherences in the definitions given above will be required in order to provide a complete set of intermediate states in the relevant Liouville subspace. We shall assume that the relevant Liouville-space projection operators $\bar{P}_a$, $\bar{P}_c$, $\bar{P}_\varepsilon$, and $\bar{P}_\omega$ satisfy commutation, completeness, and orthogonality relationships that are analogous to those for the ordinary Hilbert-space projection operators Q, C, P, and R [4].

In the application to radiative and dielectric recombination of many-electron ions in plasmas, $\bar{P}_a$ will represent the projection operator onto the Liouville subspace of the discrete autoionizing resonance states, $\bar{P}_\varepsilon$ will correspond to the projection operator onto the Liouville subspace of the nonresonant single-electron-continuum states (consisting of an incident- or ejected-electron state and a residual-ion state), which may be the initial state in a radiationless capture process or the result of an autoionization process, and $\bar{P}_\omega$ will be the projection operator onto the Liouville subspace of the single-photon-continuum states (composed of an emitted photon state and a bound state of the recombined ion), which may be produced by a spontaneous radiatively stabilizing transition. The mixed resonance-electron and resonance-photon coherence states must be included in the general definition of $\bar{P}_a$, as indicated in Eq. (72), while the mixed electron-photon coherence states must be taken into account in the general definition of $\bar{P}_\omega$, which is given by Eq. (74). The relevant Liouville-space interaction denoted by $\bar{V}^r$ may have nonvanishing tetradic matrix elements coupling the discrete autoionizing states with the electron- and photon-continuum states and also coupling electron-continuum states with photon-continuum states. The complete basis sets for the three orthogonal relevant Liouville subspaces are provided by the appropriate eigenstates of the relevant zeroth-order Liouvillian $\bar{P}\bar{L}^0\bar{P}$. If autoionization is incorporated by means of the alternative representation in terms of diagonalized Fano-type continuum states of the electron-ion system, the relevant Liouville-space projection operators $\bar{P}_a$ and $\bar{P}_\varepsilon$ must be combined and $\bar{V}^r$ will be given by Eq. (37) alone, without the inclusion of the interaction responsible for autoionization. An ordinary Hilbert-space analysis utilizing these diagonalized Fano-type continuum states has been presented by Lambropoulos and Zoller [40,41]. The electrons, which can undergo radiationless capture or be produced by autoionization, constitute only a very small fraction of the ensemble of free electrons (since their energies are severely restricted). Moreover, the ejected electrons are rapidly "rethermalized." Consequently, these relevant electrons may be treated as being effectively independent from the multitude of perturber electrons whose effects are incorporated by means of the Zwanzig projection operator $\bar{P}$. The effective independence of these two sets of free electrons can be expressed, in the binary-collision approximation, in terms of products of single-body projection operators. Analogous considerations pertain in the treatment of the relevant photon mode and the multitude of remaining quantized radiation-field modes.

In the application to channeling radiation from energetic electrons in crystal lattices, the transversely bound states may be treated as discrete resonances and represented by means of the relevant Liouville-space projection operator $\bar{P}_a$. The projection operator $\bar{P}_\varepsilon$ can be used to represent the relevant Liouville subspace of the nonresonant single-electron-continuum states, corresponding to the free states that may be the initial and final states in the coherent bremsstrahlung process. The operator $\bar{P}_\omega$ can be used to project onto the relevant Liouville subspace of the single-photon-continuum states, which can be the result of the electron channeling radiation process (involving the emission of a photon in a transition between two bound states of an electron in the transverse crystal potential). As in the case of electron-ion photorecombination, additional contributions to the photon emission rate at the frequency of interest may be produced by transitions from other types of initial states, other than the free-electron crystal-field states. In particular, it is necessary to take into account the direct excitation of the transversely bound states from the free-electron states outside of the crystal lattice. The bound-free radiationless transition of the channeled electron, which can be induced by the longitudinal component of the local crystal potential, may be considered as an analog of the atomic autoionization process, within the context of the relevant Liouville-space projection-operator description. It should be noted, however, that nonlocal interactions, such as those involving the interactions with other electrons and with phonons (lattice vibrations), are known to be primarily responsible for the dechanneling process, which we describe in terms of a bound-free radiationless transition that is induced within the relevant Liouville subspace by the longitudinal component of the local crystal potential. The complete description of the dechanneling process will be provided by the systematic incorporation of relaxation phenomena. This will be accomplished by means of the inclusion of the multitude of collisional and radiative interactions in the Liouville-space self-energy operator $\bar{\Sigma}(z)$.

1. *Time-independent formulation*

The unified treatment of resonant and nonresonant radiative transitions can be provided by introducing an alternative expression for the reduced, relevant Liouville-space transition operator $\bar{T}^r(z)$, which is defined by Eq. (46). In order to derive this alternative expression for $\bar{T}^r(z)$, it is first necessary to obtain useful expressions for the various projections of the relevant Liouville-space resolvent operator $\bar{G}^r(z)$. Following the procedure employed by Haan and Jacobs [4] for the ordinary Hilbert-space resolvent operator $G(z)=(z-H^0-V)^{-1}$, with the use of Eq. (42) the definition given for $\bar{G}^r(z)$ by Eq. (41) may be rewritten in the equivalent form

$$(z-\bar{P}\bar{L}^0\bar{P})\bar{G}^r(z)=\bar{P}+[\bar{V}^r+\bar{\Sigma}(z)]\bar{G}^r(z)\ . \tag{75}$$

We emphasize that the Liouville-space operators in this equation can be considered as being defined on the reduced, relevant subspace referring to the electronic subsystem and the detected photon modes. The average over the many-body bath degrees of freedom has lead to the introduction of the Liouville-space self-energy operator $\bar{\Sigma}(z)$. After introducing the partition of the relevant Liouville space into resonant and nonresonant subspaces, which is formally indicated by Eq. (71), and forming the various orthogonal projections of Eq. (75), we obtain the following expressions for the required projections of $\bar{G}^r(z)$:

$$\bar{P}_a\bar{G}^r(z)\bar{P}_a=\bar{P}_a\{\bar{P}_a[z-\bar{L}^0-\bar{\Lambda}(z)]\bar{P}_a\}^{-1}\ , \tag{76}$$

$$\bar{P}_c\bar{G}^r(z)\bar{P}_a=\bar{P}_c\bar{\Phi}(z)\bar{P}_c[\bar{V}^r+\bar{\Sigma}(z)]\bar{P}_a\bar{G}^r(z)\bar{P}_a\ , \tag{77}$$

$$\bar{P}_a\bar{G}^r(z)\bar{P}_c=\bar{P}_a\bar{G}^r(z)\bar{P}_a[\bar{V}^r+\bar{\Sigma}(z)]\bar{P}_c\bar{\Phi}(z)\bar{P}_c\ , \tag{78}$$

$$\bar{P}_c\bar{G}^r(z)\bar{P}_c=\bar{P}_c\bar{\Phi}(z)\bar{P}_c\{\bar{1}+[\bar{V}^r+\bar{\Sigma}(z)]\bar{P}_a\bar{G}^r(z)\bar{P}_c\}\ . \tag{79}$$

The continuum-space resolvent operator $\bar{\Phi}(z)$ and the line-shift or vertex operator $\bar{\Lambda}(z)$ are defined by

$$\bar{\Phi}(z)=\bar{P}_c\{\bar{P}_c[z-\bar{L}^0-\bar{V}^r-\bar{\Sigma}(z)]\bar{P}_c\}^{-1}\ , \tag{80}$$

$$\bar{\Lambda}(z)=\bar{V}^r+\bar{\Sigma}(z)+[\bar{V}^r+\bar{\Sigma}(z)]\bar{P}_c\bar{\Phi}(z)\bar{P}_c[\bar{V}^r+\bar{\Sigma}(z)]\ . \tag{81}$$

The line-shift operator $\bar{\Lambda}(z)$ has the same structure as the relaxation operator $\bar{R}(z)$, which is defined by Eq. (40). According to Eq. (76), the line-shift operator $\bar{\Lambda}(z)$ provides self-energy corrections to $\bar{P}_a\bar{G}^r(z)\bar{P}_a$, which corresponds to the resolvent operator within the Liouville subspace of the discrete resonance states and resonance-state coherences. The relevant interactions included in $\bar{V}^r$ give rise to the spontaneous transitions from the discrete resonance states to the relevant electron- and photon-continuum states, while the collisional and radiative perturbations incorporated into $\bar{\Sigma}(z)$ account for the interactions of the electronic subsystem in the discrete resonance states with the bath corresponding to the multitude of perturbing particles and remaining radiation-field modes. From the structure of Eqs. (40) and (81), it is clear that the total widths of the discrete resonance levels cannot be expressed simply as the sums of the rates of the individual line-broadening mechanisms acting independently, except in the lowest-order perturbation-theory approximation with respect to the combined effective Liouville-space interaction $\bar{V}^r+\bar{\Sigma}(z)$ in Eq. (81) and with respect to the irrelevant interaction in Eq. (40).

The reduced, relevant Liouville-space transition operator $\bar{T}^r(z)$, which is defined explicitly in terms of the relevant interaction $\bar{V}^r$ by means of Eq. (46), can be expressed, in terms of the combined effective Liouville-space interaction $\bar{V}^r+\bar{\Sigma}(z)$, in the alternative form

$$\bar{T}^r(z)=\bar{V}^r+\bar{\Sigma}(z)+[\bar{V}^r+\bar{\Sigma}(z)]\bar{G}^r(z)[\bar{V}^r+\bar{\Sigma}(z)]\ . \qquad (82)$$

The equivalence between the alternative form given by Eq. (82) and the original definition expressed by Eq. (46) can be demonstrated simply by invoking the assumptions expressed by Eqs. (47) and (49). These assumptions imply that the Liouville-space self-energy operator $\bar{\Sigma}(z)$ can be added or omitted without altering the double-space matrix elements that involve the initial or the final states in the radiative transition of interest because these states are assumed to be stationary states of the unperturbed Liouville-space operators $\bar{P}\bar{L}^0\bar{P}$. It is also clear that the mixed nonstationary states or coherences, which are included in the general definitions of the relevant Liouville-space projection operators, are introduced only to satisfy the completeness requirements for the intermediate states and do not directly contribute to tetradic matrix elements involving the initial and final states. The alternative form given by Eq. (82) allows us to directly employ Eqs. (76)–(79), together with the partition of the relevant Liouville space into resonant and nonresonant subspaces, to obtain the rearrangement

$$\bar{T}^r(z)=\bar{\Lambda}(z)+\bar{\Lambda}(z)\bar{P}_a\bar{G}^r(z)\bar{P}_a\bar{\Lambda}(z)\ , \qquad (83)$$

which is analogous to the rearrangement presented by Haan and Jacobs [4] for the ordinary Hilbert-space transition operator describing the electron-ion photorecombination process in the absence of relaxation phenomena, due to a multitude of collisional and radiative interactions.

The unified treatment of resonant and nonresonant radiative transitions can be developed by means of an analysis of the appropriate projection of the reduced, relevant Liouville-space transition operator $\bar{T}^r(z)$. For example, when the electronic subsystem of interest evolves from a single-electron-continuum state (in the Liouville subspace of the projection operator $\bar{P}_\varepsilon$) into a single-photon-continuum state (in the Liouville subspace of the projection operator $\bar{P}_\omega$), the appropriate projection of Eq. (83) is given by

$$\bar{P}_\omega\bar{T}^r(z)\bar{P}_\varepsilon=\bar{P}_\omega\bar{\Lambda}^r(z)\bar{P}_\varepsilon+\bar{P}_\omega\bar{\Lambda}^r(z)\bar{P}_a\bar{G}^r(z)\bar{P}_a\bar{\Lambda}^r(z)\bar{P}_\varepsilon\ , \qquad (84)$$

where we have now invoked the assumptions expressed by Eqs. (47) and (49) for the initial and final continuum states and have accordingly introduced the relevant Liouville-space line-shift or vertex operator

$$\bar{\Lambda}^r(z)=\bar{V}^r+\bar{V}^r\bar{P}_c\bar{\Phi}(z)\bar{P}_c\bar{V}^r\ . \qquad (85)$$

Equation (84) provides a natural separation of the projected relevant Liouville-space transition operator into a direct nonresonant continuum contribution, which is represented by $\bar{P}_\omega\bar{\Lambda}^r(z)\bar{P}_\varepsilon$, and a discrete resonant contribution, in which $\bar{P}_a\bar{G}^r(z)\bar{P}_a$ plays the role of a resolvent operator within the Liouville subspace of the discrete resonance states and the resonance-state coherences. The resonance term, however, differs from the conventional expression for the resonant transition amplitude, such as that given by the traditional theory of dielectronic recombination, because of our inclusion of the effects associated with the coupling between the zeroth-order relevant electron- and photon-continuum states, together with relaxation phenomena.

In our treatment of radiative transitions of the electronic subsystem, we can assume that the total relevant Liouville-space interaction $\bar{V}^r$ does not have tetradic matrix elements that directly couple stationary single-photon-continuum states with other stationary single-photon-continuum states. When considering tetradic matrix elements involving these states, we can assume that the projected relevant Liouville-space interaction satisfies the condition $\bar{P}_\omega\bar{V}^r\bar{P}_\omega=0$. For general relevant Liouville-space states, which may include the mixed nonstationary states or coherences in the definitions of the relevant projection operators, we cannot be restricted by this assumption. In a similar manner, we can assume that the relevant Liouville-space interaction of stationary single-electron-continuum states with other stationary single-electron-continuum states, which would be described by the projected interaction $\bar{P}_\varepsilon\bar{V}^r\bar{P}_\varepsilon$, has already been incorporated into the relevant zeroth-order Liouvillian $\bar{P}\bar{L}^0\bar{P}$, in the same way as in the ordinary Hilbert-space description presented by Haan and Jacobs [4]. We have defined the single-electron-continuum projection operator $\bar{P}_\varepsilon$ in such a way as to satisfy the condition $\bar{P}_\varepsilon\bar{V}^r\bar{P}_\varepsilon=0$. For tetradic matrix elements involving these stationary states, $\bar{V}^r$ can now be treated as the sum of the Liouville-space interactions leading to bound-free radiationless electron emission (e.g., autoionization or dechanneling) and to spontaneous radiative decay (e.g., stabilizing radiative transitions in dielectronic recombination or bound-bound transitions in electron channeling radiation). The tetradic matrix elements describing the bound-free and free-bound radiative transitions will be generated by the term involving the continuum-space resolvent operator in Eq. (85) and also by the mixed, nonstationary intermediate states in the general definition of the single-photon-continuum projection operator $\bar{P}_\omega$, which involve the direct product of ordinary Hilbert-space single-electron-continuum and single-photon-continuum states. It should be emphasized that the electron-continuum eigenstates of the relevant Liouville-space operator $\bar{P}\bar{L}^0\bar{P}$ are not composed of plane-wave states appropriate for free electrons, but are instead represented by scattering eigenstates satisfying the appropriate incoming-wave or outgoing-wave boundary conditions (specified by the corresponding limit of the complex variable z) in the absences of both the relevant Liouville-space interactions included in $\bar{V}^r$ and the bath interactions represented by $\bar{\Sigma}(z)$.

Following the ordinary Hilbert-space analysis of Haan and Jacobs [4], we can formulate a general procedure for evaluating the tetradic matrix elements of the projected relevant Liouville-space transition operator $\bar{P}_\omega\bar{T}^r(z)\bar{P}_\varepsilon$, which is given by Eq. (84). The evaluation of the desired tetradic matrix elements of $\bar{P}_\omega\bar{T}^r(z)\bar{P}_\varepsilon$ will involve finding explicit expressions for the tetradic matrix elements of the relevant Liouville-space line-shift operator $\bar{\Lambda}^r(z)$, which is given by Eq. (85). The desired tetradic matrix elements of $\bar{\Lambda}^r(z)$ can be obtained from a knowledge of the various tetradic matrix elements of the relevant continuum-space resolvent operator $\bar{\Phi}(z)$. Introducing the effective Liouville-space interaction operator $\bar{V}_{\text{eff}}(z)=\bar{V}^r+\bar{\Sigma}(z)$, which incorporates the collisional and radiative relaxation effects on an equal footing with the relevant interactions, the definition of $\bar{\Phi}(z)$ given by Eq. (80) can be rewritten to obtain the relationship

$$\begin{aligned}[\bar{z}-\bar{P}_c\bar{L}^0\bar{P}_c]\bar{\Phi}(z)=\bar{P}_c&+\bar{P}_\varepsilon\bar{V}_{\text{eff}}(z)\bar{P}_\varepsilon\bar{\Phi}(z)\\&+\bar{P}_\omega\bar{V}_{\text{eff}}(z)\bar{P}_\omega\bar{\Phi}(z)\\&+\bar{P}_\varepsilon\bar{V}_{\text{eff}}(z)\bar{P}_\omega\bar{\Phi}(z)\\&+\bar{P}_\omega\bar{V}_{\text{eff}}(z)\bar{P}_\varepsilon\bar{\Phi}(z)\ .\end{aligned}\tag{86}$$

Because of the presence of the mixed, nonstationary intermediate Liouville-space states in the general definition of the relevant continuum-space projection operators, we cannot utilize the assumptions expressed by Eqs. (47) and (49) to eliminate the terms involving the Liouville-space self-energy $\bar{\Sigma}(z)$. After taking the various orthogonal projections of Eq. (86), which involve the relevant continuum-space projection operators $\bar{P}_\varepsilon$ and $\bar{P}_\omega$, we obtain the following results for the required projections of the relevant continuum-space resolvent operator $\bar{\Phi}(z)$:

$$\begin{aligned}\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon=\bar{P}_\varepsilon\{\bar{P}_\varepsilon[&z-\bar{L}^0-\bar{V}_{\text{eff}}(z)\\&-\bar{V}_{\text{eff}}(z)\bar{P}_\omega\bar{G}^e(z)\bar{P}_\omega\bar{V}_{\text{eff}}(z)]\bar{P}_\varepsilon\}^{-1}\bar{P}_\varepsilon\ ,\end{aligned}\tag{87}$$

$$\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\varepsilon=\bar{P}_\omega\bar{G}^e(z)\bar{P}_\omega\bar{V}_{\text{eff}}(z)\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon\ ,\tag{88}$$

$$\begin{aligned}&\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega\\&\quad=\bar{P}_\omega\{\bar{P}_\omega[z-\bar{L}^0-\bar{V}_{\text{eff}}(z)\\&\qquad-\bar{V}_{\text{eff}}(z)\bar{P}_\varepsilon\bar{G}^e(z)\bar{P}_\varepsilon\bar{V}_{\text{eff}}(z)]\bar{P}_\omega\}^{-1}\bar{P}_\omega\ ,\end{aligned}\tag{89}$$

$$\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\omega=\bar{P}_\varepsilon\bar{G}^e(z)\bar{P}_\varepsilon\bar{V}_{\text{eff}}(z)\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega\ ,\tag{90}$$

where

$$\bar{P}_\varepsilon\bar{G}^e(z)\bar{P}_\varepsilon=\bar{P}_\varepsilon\{\bar{P}_\varepsilon[z-\bar{L}^0-\bar{V}_{\text{eff}}(z)]\bar{P}_\varepsilon\}^{-1}\bar{P}_\varepsilon\ ,\tag{91}$$

$$\bar{P}_\omega\bar{G}^e(z)\bar{P}_\omega=\bar{P}_\omega\{\bar{P}_\omega[z-\bar{L}^0-\bar{V}_{\text{eff}}(z)]\bar{P}_\omega\}^{-1}\bar{P}_\omega\ .\tag{92}$$

The general procedure for evaluating the tetradic matrix elements of the reduced, relevant Liouville-space transition operator $\bar{T}^r(z)$ which are appropriate for the description of radiative transitions of the electronic subsystem in the presence of relaxation processes can now be described in a manner analogous to that given for electron-ion photorecombination processes by Haan and Jacobs [4], which was based on the ordinary Hilbert-space transition operator. First, the tetradic matrix elements of $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon$, $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\omega$, $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\varepsilon$, and $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega$ are evaluated, using Eqs. (87)–(90) and noting that $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\varepsilon$ and $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\omega$ have been expressed in terms of $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon$ and $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega$, respectively. In a practical calculation, it may be necessary to approximate the projections of $\bar{G}^e(z)$, which are defined by Eqs. (91) and (92), by the corresponding projections of $\bar{G}^0(z)$, which are obtained by omitting $\bar{V}_{\text{eff}}(z)$. Next, the tetradic matrix elements of $\bar{P}_\omega\bar{\Lambda}^r(z)\bar{P}_\varepsilon$, $\bar{P}_\omega\bar{\Lambda}^r(z)\bar{P}_a$, $\bar{P}_a\bar{\Lambda}^r(z)\bar{P}_\varepsilon$, and $\bar{P}_a\bar{\Lambda}(z)\bar{P}_a$ are determined, using Eqs. (81) and (85), respectively. The tetradic matrix corresponding to the projected relevant operator $\bar{P}_a[z-\bar{L}^0-\bar{\Lambda}(z)]\bar{P}_a$, which is defined within the Liouville subspace of the discrete resonance states and the resonance-state coherences, must now be inverted to obtain the projected relevant resolvent operator $\bar{P}_a\bar{G}^r(z)\bar{P}_a$. Finally, the tetradic matrix elements of the projected relevant Liouville-space transition operator $\bar{P}_\omega\bar{T}^r(z)\bar{P}_\varepsilon$ can now be evaluated for various radiative transitions involving initial single-electron-continuum states and final single-photon-continuum states, which may be associated with bound levels of the electronic subsystem. While both the resonant and nonresonant transition amplitudes are influenced by the coupling between the relevant electron and photon continua, which is described by the relevant Liouville-space vertex operator $\bar{\Lambda}^r(z)$, one might expect that the resonant contribution, involving the projected relevant Liouville-space resolvent operator $\bar{P}_a\bar{G}^r(z)\bar{P}_a$, will be most significantly affected by the inclusion, by means of $\bar{\Sigma}(z)$, of the effects due to the multitude of collisional and radiative relaxation processes. The occurrence of the mixed, nonstationary intermediate Liouville-space states in the general definitions of the relevant projection operators gives rise to the additional influence of these relaxation processes on the various projections of the relevant continuum-space resolvent operator $\bar{\Phi}(z)$ and, consequently, on the nonresonant contribution. If this complication could be ignored, then the entire procedure of obtaining the required projections of the relevant continuum-space resolvent operator would be substantially simplified, because then $\bar{G}^e(z)$ could be replaced by $\bar{G}^0(z)$ and $\bar{\Sigma}(z)$ could be omitted in Eqs. (87)–(90).

2. *Time-dependent formulation*

The time-dependent approach to the unified treatment of resonant and nonresonant radiative transitions can be provided by combining Eq. (61), which is the equation of motion for the reduced, relevant part $\bar{P}\rho^I(t)$ of the interaction-picture density operator $\rho^I(t)$, with the partition of the relevant Liouville space, which is formally indicated by Eq. (71). If we neglect the last term in Eq.(61), which describes the effects of initial-state correlations, the equation of motion for the reduced relevant part of the density operator $\bar{P}\rho^I(t)$ can be rewritten in the form

$$\frac{\partial}{\partial t}[\bar{P}\rho^I(t)] = -i\bar{P}\bar{V}^I(t)\bar{P}\rho^I(t) - i\int_{t_0}^{t} dt'[\bar{P}\bar{\Sigma}^I(t,t')\bar{P}\rho^I(t')] \ , \tag{93}$$

where the right-hand side of this equation represents the combined action of the relevant Liouville-space interaction operator $\bar{P}\bar{V}^I(t)\bar{P}$ and the Liouville-space self-energy operator $\bar{\Sigma}^I(t,t')$. A substantial simplification of Eq. (93) can be achieved by introducing the Markov short-memory-time approximation, expressed by Eq. (67), which allows the right-hand side of this equation to be represented simply in the form $-i\bar{P}\bar{V}^I_{\text{eff}}(t)\bar{P}\rho^I(t)$. Since this approximation is not generally valid for all of the collisional and radiative interactions included in the Liouville-space self-energy operator $\bar{\Sigma}^I(t,t')$, we shall postpone the introduction of this approximation until the appropriate applications of the general theory.

The projected Liouville-space interaction operator $\bar{P}\bar{V}^I(t)\bar{P}$ will now be taken to include the interaction-picture operator corresponding to the relevant interaction that was denoted by $\bar{V}^r$ in the time-independent formulation. Specifically, $\bar{P}\bar{V}^I(t)\bar{P}$ will include the sum of the interaction responsible for autoionization and the interaction leading to the radiative transition of the electronic subsystem of interest.

Expressions for the four required projections of the reduced, relevant time-dependent Liouville-space propagator $\bar{P}\bar{g}^I(t,t')\bar{P}$ can be derived, which are analogous to the time-independent results given by Eqs. (76)–(79). We first outline the derivation of $\bar{P}_a\bar{P}\bar{g}^I(t,t')\bar{P}\bar{P}_a$ in order to illustrate the procedure. After introducing the partition of the relevant Liouville space into discrete resonant and nonresonant continuum subspaces and forming the two orthogonal projections, resulting from the successive action, from the left, of the relevant Liouville-subspace projection operators $\bar{P}_a$ and $\bar{P}_c$, we obtain

$$\begin{aligned}\frac{\partial}{\partial t}[\bar{P}_a\bar{P}\rho^I(t)] = {} & -i\bar{P}_a\bar{V}^I(t)\bar{P}_a\bar{P}\rho^I(t) - i\int_{t_0}^{t} dt'[\bar{P}_a\bar{\Sigma}^I(t,t')\bar{P}_a\bar{P}\rho^I(t')] \\ & -i\bar{P}_a\bar{V}^I(t)\bar{P}_c\bar{P}\rho^I(t) - i\int_{t_0}^{t} dt'[\bar{P}_a\bar{\Sigma}^I(t,t')\bar{P}_c\bar{P}\rho^I(t')]\end{aligned} \tag{94}$$

and

$$\begin{aligned}\frac{\partial}{\partial t}[\bar{P}_c\bar{P}\rho^I(t)] = {} & -i\bar{P}_c\bar{V}^I(t)\bar{P}_a\bar{P}\rho^I(t) - i\int_{t_0}^{t} dt'[\bar{P}_c\bar{\Sigma}^I(t,t')\bar{P}_a\bar{P}\rho^I(t')] \\ & -i\bar{P}_c\bar{V}^I(t)\bar{P}_c\bar{P}\rho^I(t) - i\int_{t_0}^{t} dt'[\bar{P}_c\bar{\Sigma}^I(t,t')\bar{P}_c\bar{P}\rho^I(t')] \ .\end{aligned} \tag{95}$$

Following the analysis that lead to the derivation of Eq. (61), we introduce the Liouville-space propagator identity

$$\begin{aligned}\bar{P}\bar{g}^I(t,t_0)\bar{P} = {} & \bar{g}^I_{P_c}(t,t_0) - i\int_{t_0}^{t} dt'[g^I_{P_c}(t,t')\bar{P}_c\bar{V}^I(t')\bar{P}_a\bar{P}\bar{g}^I(t',t_0)\bar{P}] \\ & -i\int_{t_0}^{t} dt'[\bar{g}^I_{P_c}(t,t')\int_{t_0}^{t'} dt''[\bar{P}_c\bar{\Sigma}^I(t',t'')\bar{P}_a\bar{P}\bar{g}^I(t'',t_0)\bar{P}] \ ,\end{aligned} \tag{96}$$

which applies to the projection of the interaction-picture propagator $\bar{P}\bar{g}^I(t,t_0)\bar{P}$, defined within the Liouville-subspace of the relevant degrees of freedom. The propagator $\bar{g}^I_{P_c}(t,t_0)$ is defined within the relevant Liouville-subspace of the continuum projection operator $\bar{P}_c$ and may be formally expressed as

$$\bar{g}^I_{P_c}(t,t_0) = \mathcal{T}\exp\left[-i\int_{t_0}^{t} dt'\bar{P}_c\bar{V}^I(t')\bar{P}_c - i\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''[\bar{P}_c\bar{\Sigma}^I(t',t'')\bar{P}_c]\right] \ . \tag{97}$$

It can be seen that the Liouville-space propagator $\bar{g}^I_{P_c}(t,t_0)$ plays a role that is analogous to that of the continuum-space resolvent operator $\bar{\Phi}(z)$, which was introduced in the time-independent formulation. The propagator identity given by Eq. (96) can be employed to obtain a formal solution to Eq. (95), which may be written in the form

$$\begin{aligned}\bar{P}_c\bar{P}\rho^I(t) = {} & \bar{P}_c\bar{g}^I_{P_c}(t,t_0)\bar{P}_c\bar{P}\rho^I(t_0) - i\int_{t_0}^{t} dt'[\bar{P}_c\bar{g}^I_{P_c}(t,t')\bar{P}_c\bar{V}^I(t')\bar{P}_a\bar{P}\rho^I(t')] \\ & -i\int_{t_0}^{t} dt'[\bar{P}_c\bar{g}^I_{P_c}(t,t')\int_{t_0}^{t'} dt''\bar{P}_c\bar{\Sigma}^I(t',t'')\bar{P}_a\bar{P}\rho^I(t'')] \ .\end{aligned} \tag{98}$$

After Eq.(98) is substituted into Eq. (94), the desired equation of motion for $\bar{P}_a\bar{P}\rho^I(t)$ is obtained in the form

$$\begin{aligned}\frac{\partial}{\partial t}[\bar{P}_a\bar{P}\rho^I(t)] = {} & -i\bar{P}_a\bar{\Lambda}^I(t)\bar{P}_a\bar{P}\rho^I(t) - i\bar{P}_a\bar{V}^I(t)\bar{P}_c\bar{g}^I_{P_c}(t,t_0)\bar{P}_c\bar{P}\rho^I(t_0) \\ & -i\int_{t_0}^{t} dt'\bar{P}_a\bar{\Sigma}^I(t,t')\bar{P}_c\bar{g}^I_{P_c}(t',t_0)\bar{P}_c\bar{P}\rho^I(t_0) \ ,\end{aligned} \tag{99}$$

where

$$\begin{aligned}\bar{P}_a\bar{\Lambda}^I(t)\bar{P}_a\bar{P}\rho^I(t)\equiv{}&\bar{P}_a\bar{V}^I(t)\bar{P}_a\bar{P}\rho^I(t)+\int_{t_0}^{t}dt'\bar{P}_a\bar{\Sigma}^I(t,t')\bar{P}_a\bar{P}\rho^I(t')\\&-i\int_{t_0}^{t}dt'[\bar{P}_a\bar{V}^I(t)\bar{P}_c\bar{g}^I_{P_c}(t,t')\bar{P}_c\bar{V}^I(t')\bar{P}_a\bar{P}\rho^I(t')]\\&-i\int_{t_0}^{t}dt'\left[\int_{t_0}^{t}dt''\bar{P}_a\bar{\Sigma}^I(t,t'')\bar{P}_c\bar{g}^I_{P_c}(t'',t')\bar{P}_c\bar{V}^I(t')\bar{P}_a\bar{P}\rho^I(t')\right]\\&-i\int_{t_0}^{t}dt'\left[\bar{P}_a\bar{V}^I(t)\bar{P}_c\bar{g}^I_{P_c}(t,t')\int_{t_0}^{t'}dt''\bar{P}_c\bar{\Sigma}^I(t',t'')\bar{P}_a\bar{P}\rho^I(t'')\right]\\&-i\int_{t_0}^{t}dt'\left[\int_{t_0}^{t}dt'''\bar{P}_a\bar{\Sigma}^I(t,t''')\bar{P}_c\bar{g}^I_{P_c}(t''',t')\int_{t_0}^{t'}dt''\bar{P}_c\bar{\Sigma}^I(t',t'')\bar{P}_a\bar{P}\rho^I(t'')\right]\,.\end{aligned}\tag{100}$$

It can be seen that the Liouville-space operator $\bar{\Lambda}^I(t)$ defined by Eq. (100) plays a role analogous to that of the line-shift operator $\bar{\Lambda}(z)$, which was introduced in the time-independent formulation. In contrast to the argument that was provided to justify the neglect of the initial-correlation term in Eq. (61), it is not generally valid to offer an analogous argument to justify the neglect of the last two terms in Eq. (99). If the initial conditions involve a specification of the nonresonant continuum part of the density operator $\bar{P}_c\bar{P}\rho^I(t)$, then this would influence the equation of motion for the discrete resonant part of the density operator $\bar{P}_a\bar{P}\rho^I(t)$. Accordingly, it will be necessary to obtain a separate equation of motion for the nonresonant continuum part.

The equation of motion for the nonresonant continuum part of the density operator $\bar{P}_c\bar{P}\rho^I(t)$ can be obtained by a procedure analogous to the derivation of Eq. (99). We first introduce the Liouville-space propagator identity that is obtained from Eq. (96) after interchanging the roles of the projection operators $\bar{P}_a$ and $\bar{P}_c$. The Liouville-space propagator $\bar{g}^I_{P_a}(t,t_0)$, which appears in this identity, is defined by the result obtained after replacing $\bar{P}_c$ with $\bar{P}_a$ in Eq. (97). By means of this procedure, a formal solution to Eq. (94) can be obtained. The introduction of this formal solution into Eq. (95) gives the desired equation of motion for $\bar{P}_c\bar{P}\rho^I(t)$ in the form

$$\begin{aligned}\frac{\partial}{\partial t}[\bar{P}_c\bar{P}\rho^I(t)]={}&-i\bar{P}_c\bar{V}^I(t)\bar{P}_c\bar{P}\rho^I(t)-i\int_{t_0}^{t}dt'\bar{P}_c\bar{\Sigma}^I(t,t')\bar{P}_c\bar{P}\rho^I(t')\\&+(-i)^2\int_{t_0}^{t}dt'[\bar{P}_c\bar{V}^I(t)\bar{P}_a\bar{g}^I_{P_a}(t,t')\bar{P}_a\bar{V}^I(t')\bar{P}_c\bar{P}\rho^I(t')]\\&+(-i)^2\int_{t_0}^{t}dt'\left[\int_{t_0}^{t}dt''\bar{P}_c\bar{\Sigma}^I(t,t'')\bar{P}_a\bar{g}^I_{P_a}(t'',t')\bar{P}_a\bar{V}^I(t')\bar{P}_c\bar{P}\rho^I(t')\right]\\&+(-i)^2\int_{t_0}^{t}dt'\left[\bar{P}_c\bar{V}^I(t)\bar{P}_a\bar{g}^I_{P_a}(t,t')\int_{t_0}^{t'}dt''\bar{P}_a\bar{\Sigma}^I(t',t'')\bar{P}_c\bar{P}\rho^I(t'')\right]\\&+(-i)^2\int_{t_0}^{t}dt'\left[\int_{t_0}^{t}dt'''\bar{P}_c\bar{\Sigma}^I(t,t''')\bar{P}_a\bar{g}^I_{P_a}(t''',t')\int_{t_0}^{t'}dt''\bar{P}_a\bar{\Sigma}^I(t',t'')\bar{P}_c\bar{P}\rho^I(t'')\right]\\&-i\bar{P}_c\bar{V}^I(t)\bar{P}_a\bar{g}^I_{P_a}(t,t_0)\bar{P}_a\bar{P}\rho^I(t_0)-i\int_{t_0}^{t}dt'\bar{P}_c\bar{\Sigma}^I(t,t')\bar{P}_a\bar{g}^I_{P_a}(t',t_0)\bar{P}_a\bar{P}\rho^I(t_0)\,.\end{aligned}\tag{101}$$

Now if the recombination or other radiation process under investigation in the scattering-theory description involves an initial condition characterized by $\bar{P}_c\bar{P}\rho^I(t_0)$, then the last two terms in Eq.(101) containing the initial discrete resonant part $\bar{P}_a\bar{P}\rho^I(t_0)$ can be neglected. In contrast to the discussion dealing with the interpretation of the last term in Eq. (61), the selection of the appropriate closure of the dynamical equations resulting from the introduction of the relevant Liouville-subspace projection operators $\bar{P}_a$ and $\bar{P}_c$ requires that the initial conditions be carefully specified.

Following the procedure employed in the derivation of Eq. (64), we can obtain from Eqs. (99) and (101), respectively, the more abstract relationships

$$\frac{\partial}{\partial t}[\bar{P}_a\bar{P}\bar{g}^I(t,t_0)\bar{P}\bar{P}_a]=-i\bar{P}_a\bar{\Lambda}^I(t)\bar{P}_a\bar{P}\bar{g}^I(t,t_0)\bar{P}\bar{P}_a\tag{102}$$

and

$$
\begin{aligned}
\frac{\partial}{\partial t}[\bar{P}_c\bar{P}\bar{g}^I(t,t_0)\bar{P}\bar{P}_c] = & -i\bar{P}_c\bar{V}^I(t)\bar{P}_c\bar{P}\bar{g}^I(t,t_0)\bar{P}\bar{P}_c \\
& -i\int_{t_0}^{t}dt'\bar{P}_c\bar{\Sigma}^I(t,t')\bar{P}_c\bar{P}\bar{g}^I(t',t_0)\bar{P}\bar{P}_c \\
& +(-i)^2\int_{t_0}^{t}dt'[\bar{P}_c\bar{V}^I(t)\bar{P}_a\bar{g}^I_{P_a}(t,t')\bar{P}_a\bar{V}^I(t')\bar{P}_c\bar{P}\bar{g}^I(t',t_0)\bar{P}\bar{P}_c] \\
& +(-i)^2\int_{t_0}^{t}dt'\left[\int_{t_0}^{t}dt''\bar{P}_c\bar{\Sigma}^I(t,t'')\bar{P}_a\bar{g}^I_{P_a}(t'',t')\bar{P}_a\bar{V}^I(t')\bar{P}_c\bar{P}\bar{g}^I(t',t_0)\bar{P}\bar{P}_c\right] \\
& +(-i)^2\int_{t_0}^{t}dt'\left[\bar{P}_c\bar{V}^I(t)\bar{P}_a\bar{g}^I_{P_a}(t,t')\int_{t_0}^{t'}dt''\bar{P}_a\bar{\Sigma}^I(t',t'')\bar{P}_c\bar{P}\bar{g}^I(t'',t_0)\bar{P}\bar{P}_c\right] \\
& +(-i)^2\int_{t_0}^{t}dt'\left[\int_{t_0}^{t}dt'''\bar{P}_c\bar{\Sigma}^I(t,t''')\bar{P}_a\bar{g}^I_{P_a}(t''',t')\int_{t_0}^{t'}dt''\bar{P}_a\bar{\Sigma}^I(t',t'')\bar{P}_c\bar{P}\bar{g}^I(t'',t_0)\bar{P}\bar{P}_c\right] . \quad (103)
\end{aligned}
$$

If the Liouville-space interaction $\bar{V}$ is assumed to be independent of time, the Laplace-transform techniques that were used in the derivation of Eq. (65) may be employed to establish that Eq. (102) is the time-dependent Liouville-space interaction-picture equivalent of the Liouville-space resolvent-operator result given by Eq. (76). In order to establish the corresponding connection between Eqs. (103) and (79), it is necessary to introduce various Liouville-space propagator identities, in order to eliminate $\bar{g}^I_{P_a}(t,t')$ in favor of $\bar{g}^I_{P_c}(t,t')$. Lambropoulos and Zoller [40,41] have presented both time-dependent and time-independent approaches to the description of multiphoton autoionization, employing the ordinary Hilbert-space Feshbach projection operators. In contrast, Ravi and Agarwal [68] have introduced a density-operator approach, without the explicit introduction of projection operators, in a unified treatment of radiative and dielectronic recombination. The present investigation may be viewed as providing a synthesis of these two previously reported approaches.

The time-dependent transition probability has been defined by Eq. (68), in terms of the projection of the Liouville-space interaction-picture propagator $\bar{P}\bar{g}^I(t,t_0)\bar{P}$ onto the subspace of the relevant degrees of freedom. In analogy with Eq. (84) for the projected relevant Liouville-space transition operator, the projected relevant Liouville-space propagator $\bar{P}_\omega\bar{P}\bar{g}^I(t,t_0)\bar{P}\bar{P}_\varepsilon$ describes the time-dependent transition in which the relevant subsystem evolves from a single-electron-continuum state (in the Liouville subspace of $\bar{P}_\varepsilon$) into a single-photon-continuum state (in the Liouville subspace of $\bar{P}_\omega$). The partial differential equation satisfied by $\bar{P}_\omega\bar{P}\bar{g}^I(t,t_0)\bar{P}\bar{P}_\varepsilon$ can be obtained by introducing into Eq. (103) the decomposition of the continuum projection operator $\bar{P}_c$ into the components $\bar{P}_\varepsilon$ and $\bar{P}_\omega$. After elimination of $\bar{g}^I_{P_a}(t,t_0)$ in favor of $\bar{g}^I_{P_c}(t,t_0)$, a procedure analogous to that employed in connection with Eqs. (87)–(90) can be formulated to provide a general time-dependent unified treatment of resonant and nonresonant radiative transitions of an electronic subsystem, which is simultaneously undergoing a multitude of collisional and radiative relaxation processes. The introduction of the Markov short-memory-time approximation given by Eq. (67) will, when valid, provide a substantial simplification in the treatment of the relaxation processes. We emphasize that only in limiting cases can one introduce a transition probability per unit time which is time independent.

B. Explicit forms for the projections of the continuum-space resolvent operator $\bar{\Phi}(z)$

We now present a general procedure for deriving explicit expressions for the projections $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon$ and $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega$ of the relevant Liouville-space continuum resolvent operator $\bar{\Phi}(z)$. These projections, which are formally expressed by means of Eqs. (87) and (89), are required during the preliminary stages of the general procedure that we have developed for evaluating the tetradic matrix elements of the reduced, relevant Liouville-space transition operator $\bar{T}^r(z)$ describing radiative transitions involving initial electron-continuum states and final photon-continuum states. Because the Liouville-space self-energy operator $\bar{\Sigma}(z)$, which incorporates the effects of the multitude of collisional and radiative relaxation processes, cannot in general be excluded in the formal expressions for the projections of the relevant Liouville-space continuum resolvent operator $\bar{\Phi}(z)$, we cannot further postpone the detailed specification of the structure of $\bar{\Sigma}(z)$ until the applications to specific transitions in particular electronic systems. A procedure that is analogous to the one developed in this subsection will be needed in the time-dependent scattering-theory formulation, which is based on the equations of motion for the relevant projections of the density operator or of the Liouville-space propagator. This time-dependent version will be developed in a future extension of this investigation.

In deriving explicit forms for the projections $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon$ and $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega$, the central problem is the accomplishment of the inversions that are indicated in the formal expressions given by Eqs. (87) and (89). Following the ordinary Hilbert-space analysis presented by Haan and Jacobs [4], we investigate how the corresponding Liouville-space inversions can be performed in a general application featuring a limited number of discrete resonance states together with a limited number of single-electron and single-photon continua. We find that the required inversions can be performed after approximating the projections of $\bar{G}^e(z)$, which are given by Eqs. (91) and (92), with the corresponding projections of $\bar{G}^0(z)$ and introducing the Liouville-space version of the pole approximation [17] on both the electron and photon continua. This is a more restrictive procedure than was necessary in the ordinary Hilbert-space analysis, where the inversions could be carried out directly in terms of $\underline{G}^0(z)$ and the pole approximation could be introduced for the photon continua alone, without the necessity of imposing it on the electron continua.

The subdivision of the relevant subspace associated with the Liouville-space continuum projection operators $\bar{P}_\varepsilon$ and $\bar{P}_\omega$ can be spanned by a basis set consisting of single-electron-continuum states denoted by $|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle$, single-photon-continuum states denoted by $|\beta\beta',\Omega\Omega'\rangle\rangle$, and mixed states or coherences of the types $|\mu\Upsilon,\beta;0\Omega\rangle\rangle$ and $|\beta,\mu\Upsilon;\Omega0\rangle\rangle$. Here we have introduced the total frequency variables

$$\Upsilon=\omega_\mu+\varepsilon/\hbar, \quad \Omega=\omega_\beta+\omega , \tag{104}$$

where $\hbar\omega_\mu$ and $\hbar\omega_\beta$ are bound-state energies of the electronic subsystem, ε is the continuum-electron energy, and $\hbar\omega$ is the photon energy. The continuum electron is treated as part of the electronic subsystem rather than as a member of the multitude of perturbing particles whose effects are incorporated, together with those of the remaining photon modes, by means of the Liouville-space self-energy operator $\bar{\Sigma}(z)$. Accordingly, the state with energy $\hbar\omega_\beta$ represents a system having one additional electron in comparison with the system corresponding to the energy $\hbar\omega_\mu$. For simplicity, we will assume that the electron-spin-projection and photon-helicity quantum numbers have been included in the discrete space specifications μ and β. The electron and photon directions may also be specified together with the discrete indices, by means of partial-wave decompositions and multipole expansions. It should be emphasized that the relevant Liouville-space basis set introduced in this subsection is appropriate only for processes involving a single-electron continuum and a single-photon continuum, although these continua may be otherwise multichannel in nature. For multiple-electron and/or multiphoton transitions, additional types of continuum states would be required in order to provide a complete basis set for the relevant Liouville space.

We will assume that the relevant Liouville-space electron- and photon-continuum states satisfy orthogonality and normalization conditions that are analogous to the corresponding ordinary Hilbert-space relationships. For the discrete indices these conditions are expressed in terms of the Kronecker δ function, while for the continuous variables the Dirac δ function must be employed. We reexpress our definitions for the Liouville-space continuum projection operators $\bar{P}_\varepsilon$ and $\bar{P}_\omega$ as follows:

$$\begin{aligned}\bar{P}_\varepsilon&=\sum_\mu\sum_{\mu'}\int d\Upsilon\int d\Upsilon'|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle\langle\langle\mu\Upsilon,\mu'\Upsilon';00| ,\\ \bar{P}_\omega&=\sum_\beta\sum_{\beta'}\int d\Omega\int d\Omega'|\beta\beta',\Omega\Omega'\rangle\rangle\langle\langle\beta\beta',\Omega\Omega'|\\ &\quad+\sum_\mu\sum_\beta\int d\Upsilon\int d\Omega|\mu\Upsilon,\beta;0\Omega\rangle\rangle\langle\langle\mu\Upsilon,\beta;0\Omega|\\ &\quad+\sum_\mu\sum_\beta\int d\Upsilon\int d\Omega|\beta,\mu\Upsilon;\Omega0\rangle\rangle\langle\langle\beta,\mu\Upsilon;\Omega0| .\end{aligned} \tag{105}$$

A complete operator basis set is obtained for the relevant Liouville space when these continuum projection operators are combined with the discrete-resonance projection operator $\bar{P}_a$, which will be defined in terms of the Liouville-space states $|\alpha\alpha',00\rangle\rangle$, $|\alpha\beta,0\Omega\rangle\rangle$, $|\alpha,\mu\Upsilon;00\rangle\rangle$, $|\beta\alpha,\Omega0\rangle\rangle$, and $|\mu\Upsilon,\alpha;00\rangle\rangle$.

1. *Explicit form for the projection $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon$*

It is convenient to rewrite the exact result for $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon$, which is given by Eq. (87), in the form

$$\begin{aligned}&\bar{P}_\varepsilon[\bar{P}_\varepsilon\bar{G}^e(z)\bar{P}_\varepsilon]^{-1}\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon\\ &\quad=\bar{P}_\varepsilon+[\bar{P}_\varepsilon\bar{V}_{\mathrm{eff}}(z)\bar{P}_\omega\bar{G}^e(z)\bar{P}_\omega\bar{V}_{\mathrm{eff}}(z)\bar{P}_\varepsilon]\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon ,\end{aligned} \tag{106}$$

where $\bar{P}_\varepsilon\bar{G}^e(z)\bar{P}_\varepsilon$ and $\bar{P}_\omega\bar{G}^e(z)\bar{P}_\omega$ are defined by Eqs. (91) and (92), respectively. We now approximate these projections of $\bar{G}^e(z)$ by the corresponding projections of $\bar{G}^0(z)$, which are obtained after omitting the effective Liouville-space interaction operator $\bar{V}_{\mathrm{eff}}(z)$. We postpone to a future investigation the treatment of the higher-order corrections that are obtained by retaining $\bar{V}_{\mathrm{eff}}(z)$ in the expressions for the projections of $\bar{G}^e(z)$. Taking tetradic matrix elements between different states within the Liouville subspace of the projection operator $\bar{P}_\varepsilon$, we obtain

$$\begin{aligned}&(z-\Upsilon+\Upsilon')\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar{\Phi}(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\\ &\quad=\delta(\mu,\mu'')\delta(\mu',\mu''')\delta(\Upsilon-\Upsilon'')\delta(\Upsilon'-\Upsilon''')\\ &\qquad+\sum_{\bar{\mu}}\sum_{\bar{\mu}'}\int d\bar{\Upsilon}\int d\bar{\Upsilon}'\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\mathrm{eff}}(z)\bar{P}_\omega\bar{G}^0(z)\bar{P}_\omega\bar{V}_{\mathrm{eff}}(z)|\bar{\mu}\bar{\Upsilon},\bar{\mu}'\bar{\Upsilon}';00\rangle\rangle\\ &\qquad\qquad\times\langle\langle\bar{\mu}\bar{\Upsilon},\bar{\mu}'\bar{\Upsilon}';00|\bar{\Phi}(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle ,\end{aligned} \tag{107}$$

where we have employed Eqs. (10) and (13).

The matrix elements of $\bar{V}_{\mathrm{eff}}(z)\bar{P}_\omega\bar{G}^0(z)\bar{P}_\omega\bar{V}_{\mathrm{eff}}(z)$, which appear in Eq. (107), can be expanded, in terms of the Liouville-space operator basis set that we have adopted for the photon-continuum projection operator $\bar{P}_\omega$, as

$$
\begin{aligned}
&\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\rm eff}(z)\bar{P}_\omega\bar{G}^0(z)\bar{P}_\omega\bar{V}_{\rm eff}(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle\\
&\quad=\sum_{\beta,\beta'}\biggl\{\int d\Omega\int d\Omega'\frac{\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\rm eff}(z)|\beta\beta',\Omega\Omega'\rangle\rangle\langle\langle \beta\beta',\Omega\Omega'|\bar{V}_{\rm eff}(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle}{z-\Omega+\Omega'}\biggr\}\\
&\qquad+\sum_{\bar\mu'',\beta}\int d\bar\Upsilon''\int d\Omega\,\biggl[\frac{\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\rm eff}(z)|\bar\mu''\bar\Upsilon'',\beta;0\Omega\rangle\rangle\langle\langle \bar\mu''\bar\Upsilon'',\beta;0\Omega|\bar{V}_{\rm eff}(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle}{z-\bar\Upsilon''+\Omega}\\
&\qquad\qquad+\frac{\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\rm eff}(z)|\beta,\bar\mu''\bar\Upsilon'';\Omega0\rangle\rangle\langle\langle \beta,\bar\mu''\bar\Upsilon'';\Omega0|\bar{V}_{\rm eff}(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle}{z-\Omega+\Upsilon''}\biggr]\;. \qquad (108)
\end{aligned}
$$

Dividing Eq. (107) by $(z-\Upsilon+\Upsilon')$, multiplying by $\langle\langle\beta\beta',\Omega\Omega'|\bar{V}_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle$, summing over μ and μ', and integrating over Υ and Υ', we obtain

$$
\begin{aligned}
&\sum_{\mu,\mu'}\int d\Upsilon\,d\Upsilon'\langle\langle \beta\beta',\Omega\Omega'|\bar{V}_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\\
&\quad=\sum_{\mu,\mu'}\int d\Upsilon\,d\Upsilon'\frac{\langle\langle \beta\beta',\Omega\Omega'|\bar{V}_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle}{z-\Upsilon+\Upsilon'}\\
&\qquad\times\biggl[\delta(\mu,\mu'')\delta(\mu',\mu''')\delta(\Upsilon-\Upsilon'')\delta(\Upsilon'-\Upsilon''')\\
&\qquad\quad+\sum_{\bar\beta,\bar\beta'}\biggl\{\int d\bar\Omega\,d\bar\Omega'\biggl[\frac{\langle\langle \mu\Upsilon,\mu'\Upsilon'';00|\bar{V}_{\rm eff}(z)|\bar\beta\bar\beta',\bar\Omega\bar\Omega'\rangle\rangle}{z-\bar\Omega+\bar\Omega'}\\
&\qquad\qquad\times\sum_{\bar\mu,\bar\mu'}\int d\bar\Upsilon\,d\bar\Upsilon'\langle\langle \bar\beta\bar\beta',\bar\Omega\bar\Omega'|\bar{V}_{\rm eff}(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle\\
&\qquad\qquad\quad\times\langle\langle \bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\biggr]\biggr\}\\
&\qquad\quad+\sum_{\bar\mu'',\bar\beta}\biggl\{\int d\bar\Upsilon''d\bar\Omega\biggl[\frac{\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\rm eff}(z)|\bar\mu''\bar\Upsilon'',\bar\beta;0\bar\Omega\rangle\rangle}{z-\bar\Upsilon''+\bar\Omega}\\
&\qquad\qquad\times\sum_{\bar\mu,\bar\mu'}\int d\bar\Upsilon\,d\bar\Upsilon'\langle\langle \bar\mu''\bar\Upsilon'',\bar\beta;0\bar\Omega|\bar{V}_{\rm eff}(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle\\
&\qquad\qquad\quad\times\langle\langle \bar\mu\bar\Upsilon,\bar\mu'\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\biggr]\biggr\}\\
&\qquad\quad+\sum_{\bar\mu'',\bar\beta}\biggl\{\int d\Upsilon''d\bar\Omega\biggl[\frac{\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\rm eff}(z)|\bar\beta,\bar\mu''\bar\Upsilon'';\bar\Omega0\rangle\rangle}{z-\bar\Omega+\bar\Upsilon''}\\
&\qquad\qquad\times\sum_{\bar\mu,\bar\mu'}\int d\bar\Upsilon\,d\bar\Upsilon'\langle\langle \bar\beta,\bar\mu''\bar\Upsilon'';\bar\Omega0|\bar{V}_{\rm eff}(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle\\
&\qquad\qquad\quad\times\langle\langle \bar\mu\Upsilon,\bar\mu'\bar\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\biggr]\biggr\}\biggr]\;, \qquad (109)
\end{aligned}
$$

where Eq. (108) has been employed. In order to obtain a closed set of equations, it is necessary to repeat the above procedure two additional times, using the multiplying factors $\langle\langle\beta,\bar\mu'''\bar\Upsilon''';\Omega0|\bar{V}_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle$ and $\langle\langle\bar\mu'''\bar\Upsilon''',\beta;0\Omega|\bar{V}_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle$. After using Eqs. (107) and (108), the desired tetradic matrix elements of the projection $\bar{P}_\varepsilon\bar\Phi(z)\bar{P}_\varepsilon$ can be explicitly expressed in terms of the quantity occurring on the left-hand side of Eq. (109), together with those on the left-hand sides of the additional two equations of the closed set [see Eq. (125)].

Our goal of obtaining a finite-dimensional matrix-inversion problem, whose solution would provide explicit expressions for the Liouville-space matrix elements $\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle$, is hindered by the presence in Eq. (109) of the integrations over the continuous frequency variables $\bar{\Omega}$, $\bar{\Omega}'$, and $\bar{\Upsilon}''$. In order to obtain a finite-dimensional matrix-inversion problem, without the introduction of a discretization procedure for these intermediate continua, it is necessary to employ the Liouville-space analog of the pole approximation, which has been introduced in the context of the ordinary Hilbert-space resolvent-operator analysis [4,17]. Accordingly, we write (with $z=\Delta\Omega_p+i\varepsilon$)

$$(z-\bar{\Omega}+\bar{\Omega}')^{-1}=\mathrm{P}(\Delta\Omega_p-\bar{\Omega}+\bar{\Omega}')^{-1}-i\pi\delta(\Delta\Omega_p-\bar{\Omega}+\bar{\Omega}')\;, \tag{110}$$

where P denotes the Cauchy principal-value part and the $\varepsilon\rightarrow+0$ limit has been taken. The Liouville-space version of the pole approximation involves the neglect of the principal-value part of the integral over the continua. The application of the Liouville-space pole approximation to $(z-\bar{\Omega}+\bar{\Omega}')^{-1}$, $(z-\bar{\Upsilon}''+\bar{\Omega})^{-1}$, and $(z-\bar{\Omega}+\bar{\Upsilon}'')^{-1}$ leads to the appearance of δ functions and the corresponding elimination of one of the frequency integrations in each of the final three contributions on the right-hand side of Eq. (109).

Another integration over the continuous frequency variables can be eliminated from each of the final three terms in Eq. (109) by investigating the detailed structure of the various tetradic matrix elements of the effective Liouville-space interaction operator $\bar{V}_{\mathrm{eff}}(z)$. We first consider the contributions included in $\bar{V}^r$, which describe radiative transitions and autoionization processes in atoms and channeling radiation and a few dechanneling processes for energetic electrons in crystals. It is clear that only the radiative interaction in $\bar{V}^r$ will contribute to the tetradic matrix elements in Eq. (109), because in all three cases there is a change in the occupation numbers of the relevant photon modes. The matrix elements of the ordinary Hilbert-space interaction operator $V_{\mathbf{k}\lambda}^{SR}$ may be evaluated by introducing the expansion

$$V_{\mathbf{k}\lambda}^{SR}|\gamma,n\rangle=\sum_{\gamma'}[V(\gamma'\gamma;\mathbf{k},\lambda)\sqrt{n}\,|\gamma',n-1\rangle+V(\gamma'\gamma;-\mathbf{k},\lambda)\sqrt{n+1}|\gamma',n+1\rangle]\;. \tag{111}$$

For a many-electron system, the coefficient $V(\gamma'\gamma;\mathbf{k},\lambda)$ is given in its relativistic form by [69]

$$V(\gamma'\gamma;\mathbf{k},\lambda)=-e\left[\frac{2\pi\hbar}{\omega}\right]^{1/2}\left\langle\gamma'\left|\sum_j c\boldsymbol{\alpha}_j\cdot\hat{\boldsymbol{\varepsilon}}_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}_j}\right|\gamma\right\rangle\;, \tag{112}$$

where $\boldsymbol{\alpha}_j$ denotes the Dirac matrices. We emphasize that γ and γ' may refer to discrete or continuum states of the electronic subsystem. Note that only a single relevant photon mode $\mathbf{k},\lambda$ is assumed to contribute to each term in the sum over γ' in Eq. (111).

Using Eq. (13), we find that the tetradic matrix elements of the Liouville-space interaction operator $\bar{V}_{\mathbf{k}\lambda}^{SR}$ which appear in Eq. (109) can be obtained from the form

$$\begin{aligned}\langle\langle\beta\beta',nn'|\bar{V}_{\mathbf{k}\lambda}^{SR}|\gamma\gamma',00\rangle\rangle&=\frac{1}{\hbar}[V(\beta\gamma;-\mathbf{k},\lambda)\delta(n,1)\delta(\beta',\gamma')\delta(n',0)\\&\quad-\delta(\beta,\gamma)\delta(n,0)V(\gamma'\beta';\mathbf{k},\lambda)\delta(n',1)]\;.\end{aligned} \tag{113}$$

We must also employ the relation

$$\langle\langle\gamma\gamma',00|\bar{V}_{\mathbf{k}\lambda}^{SR}|\beta\beta',nn'\rangle\rangle=\langle\langle\beta\beta',nn'|\bar{V}_{\mathbf{k}\lambda}^{SR}|\gamma\gamma',00\rangle\rangle^*\;, \tag{114}$$

which follows from the general relationship expressing Hermitian conjugation in tetradic notation [12]. The nonvanishing contributions of $\bar{V}_{\mathbf{k}\lambda}^{SR}$ can be obtained from the results

$$\begin{aligned}\langle\langle\bar{\mu}''\bar{\Upsilon}'',\bar{\beta};0\bar{\Omega}|\bar{V}_{\mathbf{k}\lambda}^{SR}|\bar{\mu}\bar{\Upsilon},\bar{\mu}'\bar{\Upsilon}';00\rangle\rangle&=\frac{-1}{\hbar}\delta(\bar{\mu}'',\bar{\mu})\delta(\bar{\Upsilon}''-\bar{\Upsilon})V(\bar{\mu}'\bar{\Upsilon}',\bar{\beta};\mathbf{k},\lambda)\;,\\ \langle\langle\bar{\beta},\bar{\mu}''\bar{\Upsilon}'';\bar{\Omega}0|\bar{V}_{\mathbf{k}\lambda}^{SR}|\bar{\mu}\bar{\Upsilon},\bar{\mu}'\bar{\Upsilon}';00\rangle\rangle&=\frac{1}{\hbar}V(\bar{\beta},\bar{\mu}\bar{\Upsilon};-\mathbf{k},\lambda)\delta(\bar{\mu}'',\bar{\mu}')\delta(\Upsilon''-\bar{\Upsilon}')\;,\end{aligned} \tag{115}$$

together with their respective Hermitian conjugates. It may be noted that Eqs. (115) can be related by the condition expressing Liouville conjugation [12]. The matrix elements $V(\mu\Upsilon,\beta;\mathbf{k},\lambda)$ and $V(\beta,\mu\Upsilon;-\mathbf{k},\lambda)$ respectively describe photoionization and ordinary radiative recombination in atomic systems or bound-free and free-bound transitions in the context of channeling radiation of energetic electrons in crystals. If the relaxation effects, which are incorporated by means of the Liouville-space self-energy operator $\bar{\Sigma}(z)$, could be neglected, the application of Eqs. (115), together with the Liouville-space version of pole approximation, would result in a finite-dimensional matrix inversion problem for the required tetradic matrix elements of $\bar{P}_\varepsilon\bar{\Phi}(z)\bar{P}_\varepsilon$. We will now show that a finite-dimensional matrix inversion problem can also be achieved when relaxation effects are taken into account in a lowest-order approximation.

In order to incorporate the effects of the collisional and radiative relaxation processes, it is necessary to investigate the structure of the tetradic matrix elements of the Liouville-space self-energy operator $\bar{\Sigma}(z)$. We consider only the lowest-order approximation, which is obtained from Eq. (40) after replacing $\bar{L}$ with $\bar{L}^0$ in the Liouville-space resolvent operator. We also introduce the Liouville-space version of the pole approximation, with $z=x+i\varepsilon$, which involves retaining only the δ-function contribution to the resolvent operator. Finally, we employ the approximation $\bar{Q}=\bar{1}$, which is related to the binary-collision approximation and whose justification has been discussed by Ben-Reuven [65]. With these approximations, effects of the multitude of collisional and radiative relaxation processes can be incorporated into Eq. (109) by including tetradic matrix elements of the Liouville-space self-energy operator $\bar{\Sigma}(z)$ of the type

$$\langle\langle \beta\beta',nn'|\bar{\Sigma}(z)|\gamma\gamma',00\rangle\rangle$$
$$=-i\pi\langle\langle \beta\beta',nn'|\bar{P}\bar{V}\delta(x-\bar{L}^0)\bar{V}\bar{P}|\gamma\gamma',00\rangle\rangle$$
$$=-i\pi\langle\langle \beta\beta',nn';I_B|\bar{V}\delta(x-\bar{L}^0)\bar{V}|\gamma\gamma',00;\rho_B\rangle\rangle \ , \tag{116}$$

where we have utilized the definition of the Zwanzig projection operator $\bar{P}$ given by Eq. (51) together with the inner-product relationship given by Eq. (9). In the application of our general formulation to particular electronic systems, we will evaluate tetradic matrix elements of $\bar{V}\delta(x-\bar{L}^0)\bar{V}$ which will provide the lowest-order nonvanishing contributions to the spectral linewidths occurring in the isolated-line approximation.

In order to evaluate the Liouville-space matrix elements expressed by Eq. (116), it is necessary to introduce expansions for the bath density operator ρ_B and the identity operator I_B, in terms of the eigenstates of $\bar{L}^0$, which are analogous to Eqs. (53) and (54). The unperturbed Liouville-space states that refer to the combined system, which are formed from the corresponding relevant states and bath states, may be denoted by $|\beta\beta',nn';pp,mm\rangle\rangle$, where p and m are abbreviations for many-body quantum states representing the system of perturbing particles and the multitude of remaining modes of the radiation field, respectively. The electron-phonon interactions in a crystal lattice, which can contribute to the spectral line widths of bound-bound transitions in electron channeling radiation, may be incorporated by considering the set of perturbing particles to include the phonon modes. Accordingly, Eq. (116) may be expanded in the form

$$\langle\langle \beta\beta',nn'|\bar{\Sigma}(z)|\gamma\gamma',00\rangle\rangle=-i\pi\sum_{p,p'}\sum_{m,m'}\rho_{p'}\rho_{m'}\langle\langle \beta\beta',nn';pp,mm\,|\bar{V}\delta(x-\bar{L}^0)\bar{V}|\gamma\gamma',00;p'p',m'm'\rangle\rangle \ , \tag{117}$$

where $\rho_{p'}$ and $\rho_{m'}$ denote the elements of the diagonal density matrices representing the perturbing particles and the remaining modes of the quantized radiation field. In our application to specific electronic systems, these density-matrix elements will be approximated by introducing the single-particle (or quasiparticle) velocity-distribution functions, together with the spectral-intensity distribution for the radiation field.

To facilitate the evaluation for the tetradic matrix elements of the Liouville-space operator product $\bar{V}\delta(x-\bar{L}^0)\bar{V}$ in the preceding equation, we consider the general tetradic matrix element denoted by $\langle\langle ab|\bar{V}\delta(x-\bar{L}^0)\bar{V}|a'b'\rangle\rangle$, where $|a\rangle$, $|b\rangle$, $|a'\rangle$, and $|b'\rangle$ are eigenstates of the ordinary Hilbert-space Hamiltonian H^0 referring to the composite system. These unperturbed eigenstates can be expressed as direct-product states, in the manner discussed in Sec. II. After inserting a complete set of intermediate unperturbed Liouville-space states, which may be labeled in the compressed notation by $|a''b''\rangle$, and utilizing the relationship given by Eq. (13), we obtain

$$\langle\langle ab|\bar{V}\delta(x-\bar{L}^0)\bar{V}|a'b'\rangle\rangle=\left[\frac{1}{\hbar}\right]^2\sum_{a'',b''}\langle\langle ab|V\otimes I^*-I\otimes V^*|a''b''\rangle\rangle\langle\langle a''b''|V\otimes I^*-I\otimes V^*|a'b'\rangle\rangle\delta(x-\omega_{a''}+\omega_{b''})$$
$$=\left[\frac{1}{\hbar}\right]^2\left\{\sum_{a''}\langle a|V|a''\rangle\langle a''|V|a'\rangle\delta(b,b')\delta(x-\omega_{a''}+\omega_b)\right.$$
$$+\sum_{b''}\langle b|V|b''\rangle^*\langle b''|V|b'\rangle^*\delta(a,a')\delta(x-\omega_a+\omega_{b''})$$
$$\left.-\langle a|V|a'\rangle\langle b|V|b'\rangle^*[\delta(x-\omega_{a'}+\omega_b)+\delta(x-\omega_a+\omega_{b'})]\right\} \ , \tag{118}$$

where $\hbar\omega_a=\langle a|H^0|a\rangle$, etc.

The application of Eq. (118) to the evaluation of Eq. (117) for the tetradic matrix elements of Liouville-space self-energy $\bar{\Sigma}(z)$ leads to the result

$$\langle\langle \beta\beta',nn'|\bar{\Sigma}(z)|\gamma\gamma',00\rangle\rangle$$
$$=\frac{-i\pi}{\hbar^2}\sum_{\alpha''}\sum_{p,p''}\sum_{m,m''}\rho_p\rho_m\langle\beta,n;p,m|V|\alpha''p''m''\rangle\langle\alpha''p''m''|V|\gamma,0;p,m\rangle$$
$$\times\delta(\beta',\gamma')\delta(n',0)\delta(x-\omega_{\alpha''}-\omega_{p''}-\omega_{m''}+\omega_{\beta'}+n'\omega'+\omega_p+\omega_m)$$
$$-\frac{i\pi}{\hbar^2}\sum_{\beta''}\sum_{p,p''}\sum_{m,m''}\rho_p\rho_m\langle\beta',n';p,m|V|\beta''p''m''\rangle^*\langle\beta''p''m''|V|\gamma',0;p,m\rangle^*$$
$$\times\delta(\beta,\gamma)\delta(n,0)\delta(x-\omega_\beta-n\omega-\omega_p-\omega_m+\omega_{\beta''}+\omega_{p''}+\omega_{m''})$$
$$+\frac{i\pi}{\hbar^2}\sum_{p,p'}\sum_{m,m'}\rho_{p'}\rho_{m'}\langle\beta,n;p,m|V|\gamma,0;p',m'\rangle\langle\beta'n';p,m|V|\gamma',0;p',m'\rangle^*$$
$$\times[\delta(x-\omega_\gamma-\omega_{p'}-\omega_{m'}+\omega_{\beta'}+n'\omega'+\omega_p+\omega_m)+\delta(x-\omega_\beta-n\omega-\omega_p-\omega_m+\omega_{\gamma'}+\omega_{p'}+\omega_{m'})] \ . \tag{119}$$

It should be noted that, in this equation, the intermediate states denoted by m'' are many-photon Fock-space states that include both the relevant modes and the remaining modes.

Using Eq. (119), the required tetradic matrix elements of the Louiville-space self-energy operator $\bar{\Sigma}(z)$ can be expressed, in terms of Dirac δ functions, in the same manner as in Eqs. (115). The three distinct contributions may be written in the forms

$$\begin{aligned}
&\langle\langle \bar\beta\bar\beta',\bar\Omega\bar\Omega'|\bar\Sigma(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle=[\delta(x-\bar\Upsilon+\bar\Omega')+\delta(x-\bar\Omega+\Upsilon')]\Sigma'(\bar\beta\bar\beta';\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';11,\mathbf{k},\lambda)\ ,\\
&\langle\langle \bar\mu''\bar\Upsilon'',\bar\beta;0\bar\Omega|\bar\Sigma(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle\\
&\qquad=\delta(\bar\mu'',\bar\mu)\delta(\bar\Upsilon''-\bar\Upsilon)\Sigma(\bar\beta,\bar\mu'\bar\Upsilon';\mathbf{k},\lambda,z)+[\delta(x-\bar\Upsilon+\bar\Omega)+\delta(x-\bar\Upsilon''+\bar\Upsilon')]\Sigma'(\bar\mu''\bar\Upsilon'',\bar\beta;\bar\mu\bar\Upsilon,\bar\mu'\Upsilon';01,\mathbf{k},\lambda)\ ,\\
&\langle\langle \bar\beta,\bar\mu''\bar\Upsilon'';\bar\Omega 0|\bar\Sigma(z)|\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';00\rangle\rangle\\
&\qquad=\delta(\bar\mu'',\bar\mu')\delta(\bar\Upsilon''-\bar\Upsilon')\Sigma(\bar\beta,\bar\mu\bar\Upsilon;\mathbf{k},\lambda,z)+[\delta(x-\bar\Upsilon+\bar\Upsilon'')+\delta(x-\bar\Omega+\bar\Upsilon')]\Sigma'(\bar\beta,\bar\mu''\bar\Upsilon'';\bar\mu\bar\Upsilon,\bar\mu'\bar\Upsilon';10,\mathbf{k},\lambda)\ ,
\end{aligned}\tag{120}$$

where the various coefficients denoted by Σ and Σ' can be obtained from Eq. (119) by identifying the δ functions that have been explicitly exhibited in the results given above. We must also employ the relationship $\bar\Sigma^{\dagger}(z)=\bar\Sigma(z^*)$, where $\langle\langle ab|\bar\Sigma^{\dagger}(z)|cd\rangle\rangle=\langle\langle cd|\bar\Sigma(z)|ab\rangle\rangle^*$.

We are now able to derive a reduced form of Eq. (109). When this reduced form is combined with the analogous reduced forms of the other two equations comprising the closed set, we will have achieved our goal of obtaining a finite-dimensional matrix-inversion problem for the tetradic matrix elements of $\bar P_\varepsilon\bar\Phi(z)\bar P_\varepsilon$.

Using Eqs. (115) and (120), together with the corresponding Hermitian conjugation relationships, the tetradic matrix elements of $\bar V_{\rm eff}(z)$, which are needed in order to obtain the reduced form of Eq. (109), can be expressed as

$$\begin{aligned}
&\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar V_{\rm eff}(z)|\bar\beta\bar\beta',\bar\Omega\bar\Omega'\rangle\rangle=[\delta(x-\Upsilon+\bar\Omega')+\delta(x-\bar\Omega+\Upsilon')]\Sigma'(\mu\Upsilon,\mu'\Upsilon';\bar\beta\bar\beta';11,\mathbf{k},\lambda)\ ,\\
&\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar V_{\rm eff}(z)|\bar\mu''\bar\Upsilon'',\bar\beta;0\bar\Omega\rangle\rangle=\delta(\mu,\bar\mu'')\delta(\Upsilon-\bar\Upsilon'')[-(1/\hbar)V(\mu'\Upsilon',\bar\beta;\mathbf{k},\lambda)^*+\Sigma(\bar\beta,\mu'\Upsilon';\mathbf{k},\lambda,z^*)^*]\\
&\qquad\qquad+[\delta(x-\Upsilon+\bar\Omega)+\delta(x-\bar\Upsilon''+\Upsilon')]\Sigma'(\mu\Upsilon,\mu'\Upsilon';\bar\mu''\bar\Upsilon'',\bar\beta;01,\mathbf{k},\lambda)\ ,\\
&\langle\langle \mu\Upsilon,\mu'\Upsilon';00|\bar V_{\rm eff}(z)|\bar\beta,\bar\mu''\bar\Upsilon'';\bar\Omega 0\rangle\rangle=\delta(\mu',\bar\mu'')\delta(\Upsilon'-\bar\Upsilon'')[(1/\hbar)V(\bar\beta,\mu\Upsilon;-\mathbf{k},\lambda)^*+\Sigma(\bar\beta,\mu\Upsilon;\mathbf{k},\lambda,z^*)^*]\\
&\qquad\qquad\qquad\qquad+[\delta(x-\Upsilon+\bar\Upsilon'')+\delta(x-\bar\Omega+\Upsilon')]\Sigma'(\mu\Upsilon,\mu'\Upsilon';\bar\beta,\bar\mu''\bar\Upsilon'';10,\mathbf{k},\lambda)\ .
\end{aligned}\tag{121}$$

The quantities that play the role of the unknowns in the matrix-inversion problem may be abbreviated as follows:

$$\begin{aligned}
&I(\beta\beta',\Omega\Omega';\mu''\Upsilon'',\mu'''\Upsilon''';z)=\sum_{\mu,\mu'}\int d\Upsilon\,d\Upsilon'\langle\langle\beta\beta',\Omega\Omega'|\bar V_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\ ,\\
&I(\bar\mu''\bar\Upsilon'',\beta;0\Omega;\mu''\Upsilon'',\mu'''\Upsilon''';z)\\
&\qquad=\sum_{\mu,\mu'}\int d\Upsilon\,d\Upsilon'\langle\langle\bar\mu''\bar\Upsilon'',\beta;0\Omega|\bar V_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\ ,\\
&I(\beta,\bar\mu''\bar\Upsilon'';\Omega 0;\mu''\Upsilon'',\mu'''\Upsilon''';z)\\
&\qquad=\sum_{\mu,\mu'}\int d\Upsilon\,d\Upsilon'\langle\langle\beta,\bar\mu''\bar\Upsilon'';\Omega 0|\bar V_{\rm eff}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\rangle\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar\Phi(z)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\ .
\end{aligned}\tag{122}$$

Using the Liouville-space version of the pole approximation given by Eq. (110), together with the expressions for the tetradic matrix elements of $\bar V_{\rm eff}(z)$ given by Eq. (121), the $z\rightarrow+i0$ limit of the reduced form of Eq. (109) can be written as

$$\begin{aligned}
&I(\beta\beta',\Omega\Omega';\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\quad=-i\pi\langle\langle\beta\beta',\Omega\Omega'|\bar V_{\rm eff}(+i0)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\delta(\Upsilon''-\Upsilon''')\\
&\qquad+\sum_{\bar\beta,\bar\beta'}[2\sigma'(\beta,\beta',\bar\beta,\bar\beta';\Omega,11,11,\mathbf{k},\lambda)I(\bar\beta\bar\beta',\Omega\Omega;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad\qquad+2\sigma'(\beta,\beta',\bar\beta,\bar\beta';\Omega',11,11,\mathbf{k},\lambda)I(\bar\beta\bar\beta',\Omega'\Omega';\mu''\Upsilon'',\mu'''\Upsilon''';+i0)]\\
&\qquad+\sum_{\bar\beta,\bar\mu''}[2\sigma'(\beta,\beta',\bar\mu'',\bar\beta;\Omega,11,\mathbf{k},\lambda)I(\bar\mu''\Omega,\bar\beta;0\Omega;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad\qquad+2\sigma'(\beta,\beta',\bar\mu'',\bar\beta;\Omega,11,01,\mathbf{k},\lambda)I(\bar\mu''\Omega,\bar\beta;0\Omega;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad\qquad+2\sigma'(\beta,\beta',\bar\mu'',\bar\beta;\Omega',11,\mathbf{k},\lambda)I(\bar\mu''\Omega',\bar\beta;0\Omega';\mu''\Upsilon'',\mu'''\Upsilon''';+i0)
\end{aligned}$$

$$\begin{aligned}
&\qquad +2\sigma'(\beta,\beta',\bar{\mu}'',\bar{\beta};\Omega',11,01,\mathbf{k},\lambda)I(\bar{\mu}''\Omega',\bar{\beta};0\Omega';\mu''\Upsilon'',\mu'''\Upsilon''';+i0)]\\
&+\sum_{\bar{\beta},\bar{\mu}''}[2\sigma'(\beta,\beta',\bar{\beta},\bar{\mu}'';\Omega,11,\mathbf{k},\lambda)I(\bar{\beta},\bar{\mu}''\Omega;\Omega 0;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad +2\sigma'(\beta,\beta',\bar{\beta},\bar{\mu}'';\Omega,11,10,\mathbf{k},\lambda)I(\bar{\beta},\bar{\mu}''\Omega;\Omega 0;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad +2\sigma'(\beta,\beta',\bar{\beta},\bar{\mu}'';\Omega',11,\mathbf{k},\lambda)I(\bar{\beta},\bar{\mu}''\Omega';\Omega'0;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad +2\sigma'(\beta,\beta',\bar{\beta},\bar{\mu}'';\Omega',11,10,\mathbf{k},\lambda)I(\bar{\beta},\bar{\mu}''\Omega';\Omega'0;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)]\ ,
\end{aligned}\tag{123}$$

where

$$\begin{aligned}
&\sigma'(\beta,\beta',\bar{\beta},\bar{\beta}';\Omega,11,11,\mathbf{k},\lambda)=-\pi^2\sum_{\mu,\mu'}\Sigma'(\beta\beta';\mu\Omega,\mu'\Omega;11,\mathbf{k},\lambda)\Sigma'(\mu\Omega,\mu'\Omega;\bar{\beta}\bar{\beta}';11,\mathbf{k},\lambda)\ ,\\
&\sigma'(\beta,\beta',\bar{\mu}'',\bar{\beta};\Upsilon,11,\mathbf{k},\lambda)=-\pi^2\sum_{\mu,\mu'}\delta(\mu,\bar{\mu}'')\Sigma'(\beta\beta';\mu\Upsilon,\mu'\Upsilon;11,\mathbf{k},\lambda)[(-1/\hbar)V(\mu'\Upsilon,\bar{\beta};\mathbf{k},\lambda)^*+\Sigma(\bar{\beta},\mu'\Upsilon;\mathbf{k},\lambda,-i0)^*]\ ,\\
&\sigma'(\beta,\beta',\bar{\mu}'',\bar{\beta};\Upsilon,11,01,\mathbf{k},\lambda)=-\pi^2\sum_{\mu,\mu'}\Sigma'(\beta\beta';\mu\Upsilon,\mu'\Upsilon;11,\mathbf{k},\lambda)\Sigma'(\mu\Upsilon,\mu'\Upsilon;\bar{\mu}''\Upsilon,\bar{\beta};01,\mathbf{k},\lambda)\ ,\\
&\sigma'(\beta,\beta',\bar{\beta},\bar{\mu}'';\Upsilon,11,\mathbf{k},\lambda)=-\pi^2\sum_{\mu,\mu'}\delta(\mu',\bar{\mu}'')\Sigma'(\beta\beta';\mu\Upsilon,\mu'\Upsilon;11,\mathbf{k},\lambda)[(1/\hbar)V(\bar{\beta},\mu\Upsilon;-\mathbf{k},\lambda)^*+\Sigma(\bar{\beta},\mu\Upsilon;\mathbf{k},\lambda,-i0)^*]\ ,\\
&\sigma'(\beta,\beta',\bar{\beta},\bar{\mu}'';\Upsilon,11,10,\mathbf{k},\lambda)=-\pi^2\sum_{\mu,\mu'}\Sigma'(\beta\beta';\mu\Upsilon,\mu'\Upsilon;11,\mathbf{k},\lambda)\Sigma'(\mu\Upsilon,\mu'\Upsilon;\bar{\beta},\bar{\mu}''\Upsilon;10,\mathbf{k},\lambda)\ .
\end{aligned}\tag{124}$$

The two additional reduced equations, which can be derived in a manner analogous to Eq. (123), must be employed to provide the closed set of equations for the quantities defined by Eq. (122). After these quantities have been obtained, the required tetradic matrix elements of $\bar{P}_\varepsilon\bar{\Phi}(+i0)\bar{P}_\varepsilon$ can be expressed, in the Liouville-space version of the pole approximation, by means of Eqs. (107), (108), and (110), as

$$\begin{aligned}
&\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar{\Phi}(+i0)|\mu''\Upsilon'',\mu'''\Upsilon''';00\rangle\rangle\\
&\quad=-i\pi\delta(\mu,\mu'')\delta(\mu',\mu''')\delta(\Upsilon-\Upsilon'')\delta(\Upsilon'-\Upsilon''')\delta(\Upsilon-\Upsilon')\\
&\qquad -i\pi\sum_{\beta,\beta'}[\Sigma'(\mu\Upsilon,\mu'\Upsilon',\beta,\beta';11,\mathbf{k}\lambda)\{I(\beta\beta',\Upsilon\Upsilon;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)+I(\beta\beta',\Upsilon'\Upsilon';\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\}]\\
&\qquad -i\pi\sum_{\bar{\mu}'',\beta}\{\delta(\mu,\bar{\mu}'')[(-1/\hbar)V(\mu'\Upsilon',\beta;\mathbf{k}\lambda)^*+\Sigma(\beta,\mu'\Upsilon';\mathbf{k},\lambda,-i0)^*]I(\bar{\mu}''\Upsilon,\beta;0\Upsilon;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad\qquad +\Sigma'(\mu\Upsilon,\mu'\Upsilon';\bar{\mu}''\Upsilon,\beta;01,\mathbf{k}\lambda)I(\bar{\mu}''\Upsilon,\beta;0\Upsilon;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad\qquad +\Sigma'(\mu\Upsilon,\mu'\Upsilon';\bar{\mu}''\Upsilon',\beta;01,\mathbf{k}\lambda)I(\bar{\mu}''\Upsilon',\beta;0\Upsilon';\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\}\\
&\quad -i\pi\sum_{\bar{\mu}'',\beta}\{\delta(\mu',\bar{\mu}'')[(1/\hbar)V(\beta,\mu\Upsilon;-\mathbf{k}\lambda)^*+\Sigma(\beta,\mu\Upsilon;\mathbf{k},\lambda,-i0)^*]I(\beta,\bar{\mu}''\Upsilon';\Upsilon'0;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad\qquad +\Sigma'(\mu\Upsilon,\mu'\Upsilon';\beta,\bar{\mu}''\Upsilon;10,\mathbf{k}\lambda)I(\beta,\bar{\mu}''\Upsilon;\Upsilon 0;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\\
&\qquad\qquad +\Sigma'(\mu\Upsilon,\mu'\Upsilon';\beta,\bar{\mu}''\Upsilon';10,\mathbf{k}\lambda)I(\beta,\bar{\mu}''\Upsilon';\Upsilon'0;\mu''\Upsilon'',\mu'''\Upsilon''';+i0)\}\ .
\end{aligned}\tag{125}$$

2. *Explicit forms for the projection* $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega$

In order to derive explicit expressions for the tetradic matrix elements of $\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega$, we first rewrite the exact result, which is given by Eq. (89), in the form

$$\bar{P}_\omega[\bar{P}_\omega\bar{G}^e(z)\bar{P}_\omega]^{-1}\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega=\bar{P}_\omega+[\bar{P}_\omega\bar{V}_{\text{eff}}(z)\bar{P}_\varepsilon\bar{G}^e(z)\bar{P}_\varepsilon\bar{V}_{\text{eff}}(z)\bar{P}_\omega]\bar{P}_\omega\bar{\Phi}(z)\bar{P}_\omega\ .\tag{126}$$

Following the procedure used in the preceding subsection, we now approximate the projections of $\bar{G}^e(z)$ by the corresponding projections of $\bar{G}^0(z)$. As a consequence of the definition of the photon-continuum projection operator given in the second part of Eq. (105), which includes mixed Liouville-space states or electron-photon coherences, it is necessary to obtain expressions for several distinct sets of tetradic matrix elements involving photon-continuum states $|\beta\Omega\rangle$. Taking tetradic matrix elements between different sets of Liouville-space states within the subspace of the projection operator $\bar{P}_\omega$, we obtain

$$
\begin{aligned}
&(z-\Omega+\Omega')\langle\!\langle\beta\beta',\Omega\Omega'|\bar{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\!\rangle\\
&\quad=\delta(\beta,\beta'')\delta(\beta',\beta''')\delta(\Omega-\Omega'')\delta(\Omega'-\Omega''')\\
&\qquad+\sum_{\bar{\beta},\bar{\beta}'}\int d\bar{\Omega}\int d\bar{\Omega}'[\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'\rangle\!\rangle\langle\!\langle\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'|\bar{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\!\rangle]\\
&\qquad+\sum_{\bar{\mu},\bar{\beta}}\int d\bar{\Upsilon}\int d\bar{\Omega}[\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}\rangle\!\rangle\langle\!\langle\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}|\bar{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\!\rangle]\\
&\qquad+\sum_{\bar{\mu},\bar{\beta}}\int d\bar{\Upsilon}\int d\bar{\Omega}[\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0\rangle\!\rangle\langle\!\langle\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0|\bar{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\!\rangle]\ ,\\
&(z-\Omega+\Omega')\langle\!\langle\beta\beta',\Omega\Omega'|\bar{\Phi}(z)|\beta'',\mu\Upsilon;\Omega''0\rangle\!\rangle\\
&\quad=\sum_{\bar{\beta},\bar{\beta}'}\int d\bar{\Omega}\int d\bar{\Omega}'[\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'\rangle\!\rangle\langle\!\langle\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'|\bar{\Phi}(z)|\beta'',\mu\Upsilon;\Omega''0\rangle\!\rangle]\\
&\qquad+\sum_{\bar{\mu},\bar{\beta}}\int d\bar{\Upsilon}\int d\bar{\Omega}[\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}\rangle\!\rangle\langle\!\langle\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}|\bar{\Phi}(z)|\beta'',\mu\Upsilon;\Omega''0\rangle\!\rangle]\\
&\qquad+\sum_{\bar{\mu},\bar{\beta}}\int d\bar{\Upsilon}\int d\bar{\Omega}[\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0\rangle\!\rangle\langle\!\langle\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0|\bar{\Phi}(z)|\beta'',\mu\Upsilon;\Omega''0\rangle\!\rangle]\ ,\\
&(z-\Omega+\Upsilon)\langle\!\langle\beta,\mu\Upsilon;\Omega0|\bar{\Phi}(z)|\beta',\mu'\Upsilon';\Omega'0\rangle\!\rangle\\
&\quad=\delta(\beta,\beta')\delta(\mu,\mu')\delta(\Omega-\Omega')\delta(\Upsilon-\Upsilon')\\
&\qquad+\sum_{\bar{\beta},\bar{\beta}'}\int d\bar{\Omega}\int d\bar{\Omega}'[\langle\!\langle\beta,\mu;\Omega0|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'\rangle\!\rangle\langle\!\langle\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'|\bar{\Phi}(z)|\beta',\mu'\Upsilon';\Omega'0\rangle\!\rangle]\\
&\qquad+\sum_{\bar{\mu},\bar{\beta}}\int d\bar{\Upsilon}\int d\bar{\Omega}[\langle\!\langle\beta,\mu\Upsilon;\Omega0|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}\rangle\!\rangle\langle\!\langle\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}|\bar{\Phi}(z)|\beta',\mu'\Upsilon';\Omega'0\rangle\!\rangle]\\
&\qquad+\sum_{\bar{\mu},\bar{\beta}}\int d\bar{\Upsilon}\int d\bar{\Omega}[\langle\!\langle\beta,\mu\Upsilon;\Omega0|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0\rangle\!\rangle\langle\!\langle\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0|\bar{\Phi}(z)|\beta',\mu'\Upsilon';\Omega'0\rangle\!\rangle]\ .
\end{aligned}
\tag{127}
$$

Similar relationships can be given for the tetradic matrix elements $\langle\!\langle\mu\Upsilon,\beta;0\Omega|\bar{\Phi}(z)|\mu'\Upsilon',\beta';0\Omega'\rangle\!\rangle$, $\langle\!\langle\beta,\beta';\Omega\Omega'|\bar{\Phi}(z)|\mu\Upsilon,\beta'';0\Omega''\rangle\!\rangle$, and $\langle\!\langle\beta,\mu\Upsilon;\Omega0|\bar{\Phi}(z)|\mu'\Upsilon',\beta';0\Omega'\rangle\!\rangle$.

The tetradic matrix elements of $\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)$, which appear in Eqs. (127), can be expanded, using the first part of Eq. (105), as

$$
\begin{aligned}
&\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'\rangle\!\rangle\\
&\qquad=\sum_{\mu,\mu'}\int d\Upsilon\int d\Upsilon'\frac{\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\!\rangle\langle\!\langle\mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\mathrm{eff}}(z)|\bar{\beta}\bar{\beta}',\bar{\Omega}\bar{\Omega}'\rangle\!\rangle}{z-\Upsilon+\Upsilon'}\ ,\\
&\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}\rangle\!\rangle\\
&\qquad=\sum_{\mu,\mu'}\int d\Upsilon\int d\Upsilon'\frac{\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\!\rangle\langle\!\langle\mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\mathrm{eff}}(z)|\bar{\mu}\bar{\Upsilon},\bar{\beta};0\bar{\Omega}\rangle\!\rangle}{z-\Upsilon+\Upsilon'}\ ,\\
&\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)\bar{P}_{\varepsilon}\bar{G}^{0}(z)\bar{P}_{\varepsilon}\bar{V}_{\mathrm{eff}}(z)|\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0\rangle\!\rangle\\
&\qquad=\sum_{\mu,\mu'}\int d\Upsilon\int d\Upsilon'\frac{\langle\!\langle\beta\beta',\Omega\Omega'|\bar{V}_{\mathrm{eff}}(z)|\mu\Upsilon,\mu'\Upsilon';00\rangle\!\rangle\langle\!\langle\mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\mathrm{eff}}(z)|\bar{\beta},\bar{\mu}\bar{\Upsilon};\bar{\Omega}0\rangle\!\rangle}{z-\Upsilon+\Upsilon'}\ .
\end{aligned}
\tag{128}
$$

After combining the first part of Eq. (127) with Eqs. (128) and following a procedure analogous to the one that lead to Eq. (109), we obtain

$$\begin{aligned}
&\sum_{\beta,\beta'}\int d\Omega\int d\Omega'\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\overline{V}_{\text{eff}}(z)|\beta\beta',\Omega\Omega'\rangle\rangle\langle\langle\beta\beta',\Omega\Omega'|\overline{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle \\
&\quad=\sum_{\beta,\beta'}\int d\Omega\int d\Omega'\frac{\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\overline{V}_{\text{eff}}(z)|\beta\beta',\Omega\Omega'\rangle\rangle}{z-\Omega+\Omega'} \\
&\qquad\times\Bigg[\delta(\beta,\beta'')\delta(\beta',\beta''')\delta(\Omega-\Omega'')\delta(\Omega'-\Omega''') \\
&\qquad\quad+\sum_{\overline{\mu},\overline{\mu}'}\int d\overline{\Upsilon}\int d\overline{\Upsilon}'\frac{\langle\langle\beta\beta',\Omega\Omega'|\overline{V}_{\text{eff}}(z)|\overline{\mu}\overline{\Upsilon},\overline{\mu}'\overline{\Upsilon}';00\rangle\rangle}{z-\overline{\Upsilon}+\overline{\Upsilon}'} \\
&\qquad\qquad\times\Bigg\{\sum_{\overline{\beta},\overline{\beta}'}\int d\overline{\Omega}\int d\overline{\Omega}'\langle\langle\overline{\mu}\overline{\Upsilon},\overline{\mu}'\overline{\Upsilon}';00|\overline{V}_{\text{eff}}(z)|\overline{\beta}\overline{\beta}',\overline{\Omega}\overline{\Omega}'\rangle\rangle \\
&\qquad\qquad\qquad\times\langle\langle\overline{\beta}\overline{\beta}',\overline{\Omega}\overline{\Omega}'|\overline{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle \\
&\qquad\qquad+\sum_{\overline{\mu}'',\overline{\beta}}\int d\overline{\Upsilon}''\int d\overline{\Omega}\langle\langle\overline{\mu}\overline{\Upsilon},\overline{\mu}'\overline{\Upsilon}';00|\overline{V}_{\text{eff}}(z)|\overline{\mu}''\overline{\Upsilon}'',\overline{\beta};0\overline{\Omega}\rangle\rangle \\
&\qquad\qquad\qquad\times\langle\langle\overline{\mu}''\overline{\Upsilon}'',\overline{\beta};0\overline{\Omega}|\overline{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle \\
&\qquad\qquad+\sum_{\overline{\mu}'',\overline{\beta}}\int d\overline{\Upsilon}''\int d\overline{\Omega}\langle\langle\overline{\mu}\overline{\Upsilon},\overline{\mu}'\overline{\Upsilon}';00|\overline{V}_{\text{eff}}(z)|\overline{\beta},\overline{\mu}''\overline{\Upsilon}'';\overline{\Omega}0\rangle\rangle \\
&\qquad\qquad\qquad\times\langle\langle\overline{\beta},\overline{\mu}''\overline{\Upsilon}'';\overline{\Omega}0|\overline{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle\Bigg\}\Bigg]\ .
\end{aligned}\tag{129}$$

A similar procedure must be followed, using the second and third parts of Eqs. (127) together with the equations for the remaining three classes of tetradic matrix elements involving photon-continuum states. The result will be a closed set of equations for the quantities in terms of which the desired tetradic matrix elements of the projection $\overline{P}_{\omega}\overline{\Phi}(z)\overline{P}_{\omega}$ can be explicitly expressed.

In order to obtain a finite-dimensional matrix-inversion problem, whose solution would lead to explicit expressions for the various tetradic matrix elements of $\overline{P}_{\omega}\overline{\Phi}(z)\overline{P}_{\omega}$, it is necessary to employ the Liouville-space pole approximation together with the approximate results for the tetradic matrix elements of $\overline{V}_{\text{eff}}(z)$, which are given by Eqs. (121).

The quantities that play the role of the unknowns in the matrix-inversion problem associated with Eq. (129) may be abbreviated as

$$\begin{aligned}
&I(\mu\Upsilon,\mu'\Upsilon';\beta''\beta''',\Omega''\Omega''';z)=\sum_{\beta,\beta'}\int d\Omega\int d\Omega'\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\overline{V}_{\text{eff}}(z)|\beta\beta',\Omega\Omega'\rangle\rangle\langle\langle\beta\beta',\Omega\Omega'|\overline{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle\ , \\
&I'(\mu\Upsilon,\mu'\Upsilon';\beta''\beta''',\Omega''\Omega''';z)=\sum_{\overline{\mu}'',\overline{\beta}}\int d\overline{\Upsilon}''\int d\overline{\Omega}\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\overline{V}_{\text{eff}}(z)|\overline{\mu}''\overline{\Upsilon}'',\overline{\beta};0\overline{\Omega}\rangle\rangle\langle\langle\overline{\mu}''\overline{\Upsilon}'',0\overline{\Omega}|\overline{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle\ , \\
&I''(\mu\Upsilon,\mu'\Upsilon';\beta''\beta''',\Omega''\Omega''';z) \\
&\qquad=\sum_{\overline{\mu}'',\overline{\beta}}\int d\overline{\Upsilon}''\int d\overline{\Omega}\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\overline{V}_{\text{eff}}(z)|\overline{\beta},\overline{\mu}''\overline{\Upsilon}'';\overline{\Omega}0\rangle\rangle\langle\langle\overline{\beta},\overline{\mu}''\overline{\Upsilon}'';\overline{\Omega}0|\overline{\Phi}(z)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle\ .
\end{aligned}\tag{130}$$

Analogous definitions must be introduced in the analysis of the second and third relationships given by Eq. (127), which will lead to matrix-inversion problems similar to that associated with Eq. (129). The result will be a closed set of equations for the desired unknown quantities.

After introducing the Liouville-space pole approximation, together with the approximate expressions for the tetradic matrix elements of $\overline{V}_{\text{eff}}(z)$, the $z\rightarrow+i0$ limit of the reduced form of Eq. (129) can be written

$$
\begin{aligned}
&I(\mu\Upsilon,\mu'\Upsilon';\beta''\beta''',\Omega''\Omega''';z)\\
&\quad=-i\pi\langle\langle\mu\Upsilon,\mu'\Upsilon';00|\bar{V}_{\text{eff}}(+i0)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle\delta(\Omega''-\Omega''')\\
&\qquad+\sum_{\bar{\mu},\bar{\mu}'}\{2\sigma'(\mu\Upsilon,\mu'\Upsilon';\bar{\mu}\Upsilon,\bar{\mu}'\Upsilon;11,11,\mathbf{k},\lambda)\\
&\qquad\qquad\times[I(\bar{\mu}\Upsilon,\bar{\mu}'\Upsilon;\beta''\beta''',\Omega''\Omega''';+i0)+I'(\bar{\mu}\Upsilon,\bar{\mu}'\Upsilon;\beta''\beta''',\Omega''\Omega''';+i0)\\
&\qquad\qquad\quad+I''(\bar{\mu}\Upsilon,\bar{\mu}'\Upsilon;\beta''\beta''',\Omega''\Omega''';+i0)]+2\sigma'(\mu\Upsilon,\mu'\Upsilon';\bar{\mu}\Upsilon',\bar{\mu}'\Upsilon';11,11,\mathbf{k},\lambda)\\
&\qquad\qquad\quad\times[I(\bar{\mu}\Upsilon',\bar{\mu}'\Upsilon';\beta''\beta''',\Omega''\Omega''';+i0)+I'(\bar{\mu}\Upsilon',\bar{\mu}'\Upsilon';\beta''\beta''',\Omega''\Omega''';+i0)\\
&\qquad\qquad\qquad+I''(\bar{\mu}\Upsilon',\bar{\mu}'\bar{\Upsilon}';\beta''\times[I(\bar{\mu}\Upsilon',\beta''',\Omega''\Omega''';+i0)]\}\ ,
\end{aligned}
\tag{131}
$$

where

$$
2\sigma'(\mu\Upsilon,\mu'\Upsilon';\bar{\mu}\Upsilon,\bar{\mu}'\Upsilon;11,11,\mathbf{k},\lambda)=-\pi^{2}\sum_{\beta,\beta'}\Sigma'(\mu\Upsilon,\mu'\Upsilon';\beta\beta';11,11,\mathbf{k},\lambda)\Sigma'(\beta\beta';\bar{\mu}\Upsilon,\bar{\mu}'\Upsilon;11,11,\mathbf{k},\lambda)\ .
\tag{132}
$$

Similar forms are obtained for the reduced equations associated with the second and third parts of Eq. (127).

Two additional reduced equations, which can be derived by following the same procedure used in the derivation of Eq. (131), must be included in order to provide a closed set of equations for the quantities defined by Eqs. (130). After these quantities have been obtained, the tetradic matrix elements of $\bar{P}_{\omega}\bar{\Phi}(z)\bar{P}_{\omega}$, which appear on the left-hand side of the first part of Eq. (127), can be expressed, in the Liouville-space pole approximation, by means of Eqs. (110) and (128), as

$$
\begin{aligned}
&\langle\langle\beta\beta',\Omega\Omega'|\bar{\Phi}(+i0)|\beta''\beta''',\Omega''\Omega'''\rangle\rangle\\
&\quad=-i\pi\delta(\beta,\beta'')\delta(\beta',\beta''')\delta(\Omega-\Omega'')\delta(\Omega'-\Omega'')\delta(\Omega-\Omega')\\
&\qquad-i\pi\sum_{\mu,\mu'}\{\Sigma'(\beta\beta',\mu\Omega,\mu'\Omega;11,\mathbf{k},\lambda)[I(\mu\Omega,\mu'\Omega;\beta''\beta''',\Omega''\Omega''';+i0)\\
&\qquad\qquad+I'(\mu\Omega,\mu'\Omega;\beta''\beta''',\Omega''\Omega''';+i0)+I''(\mu\Omega,\mu'\Omega;\beta''\beta''',\Omega''\Omega''';+i0)]\\
&\qquad\qquad+\Sigma'(\beta\beta',\mu\Omega',\mu'\Omega';11,\mathbf{k},\lambda)[I(\mu\Omega',\mu'\Omega';\beta''\beta''',\Omega''\Omega''';+i0)+I'(\mu\Omega',\mu'\Omega';\beta''\beta''',\Omega''\Omega''';+i0)\\
&\qquad\qquad\quad+I''(\mu\Omega',\mu'\Omega';\beta''\beta''',\Omega''\Omega''';+i0)]\}\ .
\end{aligned}
\tag{133}
$$

Results similar to Eq. (133) can be obtained for the tetradic matrix elements that occur on the left-hand sides of the second and third parts of Eq. (127), as well as for the remaining sets of tetradic matrix elements of $\bar{\Phi}(z)$ involving photon-continuum states.

IV. CONCLUSIONS

In this paper, a density-matrix approach has been developed to treat the effects of collisional and radiative relaxation processes in the unified description of resonant and nonresonant radiative transitions of a complex electronic system. This work provides a generalization of the ordinary Hilbert-space projection-operator and resolvent-operator approach presented by Haan and Jacobs [4], which was applied to the unified description of radiative and dielectronic recombination of electrons with many-electron ions in a high-temperature plasma. In this paper, we have emphasized the applicability of the generalized unified description to a diverse class of radiative transitions in complex electronic systems. In addition to the problem of radiative and dielectronic recombination, we have referred to the application of this approach to the unified description of transverse free-bound and bound-bound transitions in the context of channeling radiation emitted by energetic electrons moving nearly along a symmetry direction in a crystal lattice. In future papers, we will present the detailed applications of the general formulations that have been developed in this paper.

The density-matrix description and Liouville-space operator formalism have been introduced in Sec. II. The fundamental starting point for the investigation of radiative transitions in interacting quantum-mechanical systems is provided by Eq. (24), which expresses the transition probability per unit time as a Liouville-space inner-product involving the tetradic time-evolution operator or propagator. If the asymptotic time limit can be taken, one obtains an expression for the transition rate in terms of the tetradic transition operator. The effects of the collisional and radiative relaxation processes have been incorporated by introducing the Zwanzig projection-operator approach, in which the complete Liouville space is partitioned into a reduced relevant subspace, corresponding to the uncorrelated electronic subsystem together with the relevant modes of the quantized radiation field, and an orthogonal subspace, in which the electronic-subsystem and relevant radiation-field states are dynamically correlated with the multitude of bath degrees of freedom. The central result of the Zwanzig projection-operator approach is that the radiative transition of the electronic subsystem of interest, in the presence of relaxation processes, is completely described by either a reduced, relevant tetradic transition operator or a reduced, relevant tetradic propagator, which is defined within the Liouville subspace of the unperturbed electronic subsystem and the relevant photon modes.

The time-independent formulation of the density-matrix description has been developed in terms of the reduced relevant projection of the Liouville-space transition operator, which is expressed in terms of the relevant projections of the resolvent operator and the interaction operator, by means of the tetradic Lippmann-Schwinger relationship that is given by Eq. (46). The reduced relevant projection of the Liouville-space resolvent operator, which is defined by Eq. (41), is expressed in terms of a Liouville-space self-energy operator, which incorporates the effects of the collisional and radiative relaxation processes. The time-dependent formulation is based on the equation of motion for the reduced relevant part of either the density operator, in the form expressed by Eq. (61), or the Liouville-space time-evolution operator, which is given by Eq. (64). In the time-dependent formulation, the effects of the relaxation processes are described by the self-energy operator that is defined by Eq. (62), which plays the role of a kernel in a time-integral appearing in the equation of motion for the reduced relevant projection of the density operator or of the Liouville-space propagator.

In Sec. III we have adapted the Liouville-space projection-operator formalism to the unified treatment of resonant and nonresonant radiative transitions of an electronic subsystem that is simultaneously interacting with a multitude of perturbing particles and quantized-radiation-field modes. We have thereby provided a generalization of the ordinary Hilbert-space projection-operator approach that was developed by Haan and Jacobs [4], which was applied to the unified treatment of electron-ion radiative and dielectronic recombination in the absence of relaxation processes. In order to accomplish the generalization to incorporate relaxation effects, it has been necessary to introduce a partition of the reduced, relevant Liouville space into discrete resonant and nonresonant continuum subspaces. This partition of the reduced Liouville space is introduced only after the average over the bath degrees of freedom has been performed. Consequently, the discrete resonant and nonresonant continuum projection operators can be represented in terms of a basis set of Liouville-space states referring only to the relevant degrees of freedom. The continuum projection operator has been further decomposed as a sum of a single-electron-continuum projection operator and a single-photon-continuum projection operator. We have indicated that the introduction of these relevant projection operators is complicated by the occurrence of mixed, nonstationary unperturbed Liouville-space states or coherences. Although the initial and final Liouville-space states in the radiative transition are assumed to be stationary states of the Liouville operator corresponding to the unperturbed Hamiltonian, which can be represented by diagonal elements of an initial-state density operator and by a diagonal final-state projection operator, the mixed, nonstationary Liouville-space states must be included in order to provide a complete set of intermediate states in the relevant Liouville subspace.

The time-independent formulation of the generalized unified treatment has been presented in terms of a rearrangement of the tetradic Lippmann-Schwinger relationship for the appropriate projection of the reduced, relevant Liouville-space transition operator. This rearrangement is expressed by Eq. (84), in terms of various projections of a relevant Liouville-space line-shift or vertex operator and the projection of the relevant Liouville-space resolvent operator onto the subspace of the discrete resonance states and the resonance-continuum coherences. Even with the occurrence of the mixed, nonstationary Liouville-space states, the discrete and continuum relevant projection operators can be defined in such a manner as to provide a natural separation of the projected reduced, relevant transition operator into a nonresonant continuum part and a discrete resonant contribution. The discrete resonant contribution differs from the conventional expression for the resonant transition amplitude because of our inclusion of relaxation phenomena on an equal footing with the autoionization and spontaneous radiative decay processes, as well as effects associated with the coupling between the zeroth-order electron- and photon-continuum states. This partition of the reduced, relevant Liouville space has also been introduced into the time-dependent formulation. We have thereby obtained separate equations of motion for the discrete resonant and nonresonant continuum parts of either the reduced density operator, as given by Eqs. (99) and (101), or the reduced Liouville-space time-evolution operator, in the form expressed by Eqs. (102) and (103).

A substantial effort has been devoted to providing a general procedure for deriving explicit expressions for the various (electron and photon) continuum projections of the Liouville-space continuum resolvent operator. These projections, which are formally expressed by means of Eqs. (87) and (89), are required in our general procedure for evaluating the tetradic matrix elements of the reduced, relevant Liouville-space transition operator describing radiative transitions involving initial electron-continuum states and final photon-continuum states. In order to develop this procedure for the required projections of the relevant continuum-space resolvent operator, it has been necessary to consider the detailed structure of the Liouville-space self-energy operator, which incorporates the effects of the collisional and radiative relaxation processes by means of an average over the bath degrees of freedom. We have demonstrated that the tetradic matrix inversions, which occur in the formal expressions for the desired Liouville-space projections, can be reduced to finite-dimensional matrix-inversion problems, in a general application featuring a limited number of discrete resonance states and a limited number of single-electron and single-photon continua. This reduction to finite-dimensional matrix-inversion problems can be accomplished by introducing the Liouville-space pole approximation and employing the lowest-order perturbation-theory approximations for the self-energy contributions in the reduced, relevant Liouville-space resolvent operator. It would be useful to know if this reduction could still be carried out in the general form when higher-order corrections are included and we hope to investigate the possibility of providing a nonperturbative Liouville-space reduction procedure in a future extension of this work.

Future papers will be devoted to the detailed application of our general formalism to the unified description of specific radiative transitions in various electronic systems, which are simultaneously interacting with a multitude of perturbing particles and radiation-field modes. In particular, we will provide analyses of radiative and dielectronic recombination and of free-bound and bound-bound transitions in channeling radiation. The starting point for these applications will be the general Liouville-space expressions for the radiative transition probability which we have obtained in both the time-independent and the time-dependent formulations of the density-matrix approach. It will be necessary to compare the results obtained from the scattering-theory approach, in which the system is described as evolving from an initial single-electron-continuum state into a final single-photon-continuum state, with the results obtained from the relaxation-theory approach, in which one investigates radiative transitions that occur directly from the discrete resonances states in the presence of relaxation processes. In both approaches, it is necessary to determine the populations of the initial states in the radiative transition of interest by considering an entire sequence of collisional and radiative processes. At an appropriate stage in these analyses, we will introduce the isolated-line approximation and the lowest-order perturbation-theory expressions for the various contributions to the Liouville-space self-energy operator whose imaginary parts represent the partial linewidths arising from the individual collisional and radiative relaxation processes. These contributions to the Liouville-space self-energy operator will be treated on an equal footing with the relevant interactions representing autoionization and spontaneous radiative decay. The zeroth-order basis sets employed in these applications may consist of states of either the isolated electronic subsystem or the electronic subsystem in the presence of a classical static or electromagnetic field.

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