Liouville-space *R*-matrix-Floquet description of atomic radiative processes involving autoionizing states in the presence of intense electromagnetic fields

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Abstract. A reduced-density-operator description is developed for coherent optical phenomena in many-electron atomic systems, utilizing a Liouville-space, multiple-mode Floquet-Fourier representation. The Liouville-space formulation provides a natural generalization of the ordinary Hilbert-space (Hamiltonian) *R*-matrix-Floquet method, which has been developed for multi-photon transitions and laser-assisted electron-atom collision processes. In these applications, the *R*-matrix-Floquet method has been demonstrated to be capable of providing an accurate representation of the complex, multi-level structure of many-electron atomic systems in bound, continuum, and autoionizing states. The ordinary Hilbert-space (Hamiltonian) formulation of the *R*-matrix-Floquet method has been implemented in highly developed computer programs, which can provide a non-perturbative treatment of the interaction of a classical, multiple-mode electromagnetic field with a quantum system. This quantum system may correspond to a many-electron, bound atomic system and a single continuum electron. However, including pseudo-states in the expansion of the many-electron atomic wave function can provide a representation of multiple continuum electrons. The "dressed" many-electron atomic states thereby obtained can be used in a realistic non-perturbative evaluation of the transition probabilities for an extensive class of atomic collision and radiation processes in the presence of intense electromagnetic fields. In order to incorporate environmental relaxation and decoherence phenomena, we propose to utilize the ordinary Hilbert-space (Hamiltonian) *R*-matrix-Floquet method as a starting-point for a Liouville-space (reduced-density-operator) formulation. To illustrate how the Liouville-space *R*-matrix-Floquet formulation can be implemented for coherent atomic radiative processes, we discuss applications to electromagnetically induced transparency, as well

as to related pump-probe optical phenomena, and also to the unified description of radiative and dielectronic recombination in electron-ion beam interactions and high-temperature plasmas.

1. Introduction

Radiative transitions involving autoionizing states of many-electron atomic systems can play an important role in non-linear optical (multi-photon) interactions, in electron-ion beam interactions, and in high-temperature laboratory and astrophysical plasmas. In the otherwise continuous electron and photon spectra above the field-free ionization threshold, autoionizing states can give rise to line-like features with asymmetric profiles. In the presence of intense electromagnetic fields, ordinary bound atomic states can acquire additional widths and shifts due to field-induced (single and multi-photon) ionization processes, which usually exceed the contributions due to spontaneous radiative-decay processes in the isolated atomic system. Accordingly, it is advantageous to treat bound and autoionizing states on an equal footing. The realistic, multi-level quantum-mechanical description of electromagnetic interactions involving excited bound and autoionizing states of many-electron atomic systems has presented significant challenges, not only in the ordinary Hilbert-space (Schrödinger-equation) approach but also in the more general Liouville-space (reduced-density-operator) formulation.

1.1. Electromagnetically induced transparency and related pump-probe optical phenomena

The coherent and resonant non-linear optical phenomenon known as electromagnetically induced transparency was first described by Harris, Field, and Imamoglu (1990) in terms of the quantum-mechanical interference between electromagnetic-transition amplitudes associated with autoionizing states of a many-electron atomic system. Alternatively, this non-linear optical phenomenon can be described by the introduction of "dressed" states, which are eigenstates of the many-electron atomic Hamiltonian operator including the interaction with an electromagnetic field. Due to a rapid frequency dependence of the index of refraction within a narrow spectral range, electromagnetically induced transparency can lead to a substantial reduction in the group velocity of a propagating electromagnetic pulse. This electromagnetic-propagation phenomenon has become know as slow light. The investigation of the slow light produced by electromagnetically induced transparency, as well as by related pump-probe optical phenomena, has become the subject of intense theoretical and experimental activity, because of potential applications for optical delay lines (Lowell and Parra 2005) and for quantum information storage and retrieval (Lukin 2003).

1.2. Radiative and dielectronic recombination

The standard theory of the two-step (resonant) dielectronic recombination process:

$$A_i^{z+} + e^- \to A_j^{(z-1)+} \to A_k^{(z-1)+} + \hbar\omega \,, \tag{1}$$

where z = Z - N is the residual ionic-charge number for the N-electron system with nuclear charge number Z, was first developed in detail by Massey and Bates (1942) and Bates and Massey (1943), who were particularly concerned with recombination processes in the earth's ionosphere. Further pioneering theoretical investigations, which were based on the standard theory, have been carried out by Bates (1962), Bates and Dalgarno (1962), Seaton (1962), and Burgess and Seaton (1964). The application of the standard theory to the dielectronic recombination of multiply-charged many-electron atomic ions A^{z+} in a high-temperature plasma, such as the solar corona or a Tokamak plasma, was first reported by Burgess (1964, 1965). Burgess demonstrated that, in the important temperature region, dielectronic recombination through an entire Rydberg series of autoionizing resonances $A_j^{(z-1)+}$ can be dominant over the ordinary direct (non-resonant) radiative recombination process:

$$A_i^{z+} + e^- \to A_k^{(z-1)+} + \hbar\omega \,. \tag{2}$$

The standard theory of dielectronic recombination has been comprehensively reviewed by Seaton and Storey (1976). As a result of fundamental theoretical investigations (Davies and Seaton 1969, Bell and Seaton 1985, Alber, Cooper and Rau 1984, Jacobs, Cooper and Haan 1987, Haan and Jacobs 1989), it has been firmly established that radiative and dielectronic recombination are most rigorously treated as corresponding to coherent, quantum-mechanically interfering components of a single electromagnetic transition connecting the initial state i and final state k of the electron-recombining-ion system $A^{(z-1)+}$.

The effect of a static electric field on the dielectronic recombination process has been the subject of experimental (Müller et al 1986) and theoretical (Jacobs et al 1976, LaGattuta and Han 1983) investigations. However, the influence of an electromagnetic field has not been extensively studied. Dielectronic recombination in the presence of a microwave field has been observed (Klimenko and Gallagher 2000), and dielectronic recombination in the presence of a laser field has been treated theoretically (LaGattuta 1988). Our investigation of radiative and dielectronic recombination in the presence of an intense electromagnetic field is in part motivated by the possibility that the charged-state distributions and radiative emission spectra of impurity ions in the plasma of the planned International Tokamak Experimental Reactor (ITER) may be significantly influenced by the intense RF fields that have been proposed for the plasma heating and current drive.

1.3. The ordinary Hilbert-space (Hamiltonian) R-matrix-Floquet method

The ordinary Hilbert-space (Hamiltonian) *R*-matrix-Floquet method was first developed by Burke, Francken, and Joachain (1990, 1991), and this method has been extended by Dörr et al (1992) to provide a detailed treatment of the *R*-matrix-Floquet equations where the electromagnetic interaction is transformed from the dipole-length to the velocity representation. The *R*-matrix-Floquet method has been applied to multi-photon transitions, e. g., the n-photon ionization process:

$$A_i + n\hbar\omega \rightarrow A_j^+ + e^- , \qquad (3)$$

by, e. g., Feng and van der Hart (2003), van der Hart (2005, 2006), and van der Hart et al (2005). The *R*-matrix-Floquet method has also been applied to laser-assisted electron-atom collision processes, e. g., the n-photon process:

$$A_i + e^- + n\hbar\omega \rightarrow A_j + e^- , \qquad (4)$$

by, e. g., Charlo et al (1998), Dunseath and Terao-Dunseath (2004), and Terao-Dunseath et al (2001, 2002). The *R*-matrix-Floquet method has been demonstrated to be capable of providing a realistic representation of the complex, multi-level structure of many-electron atomic systems in bound, continuum, and autoionizing states.

A particular advantage of the *R*-matrix-Floquet method is that the basic *R*-matrix techniques and many-electron computer programs have already been developed for the ordinary Hilbert-space (Hamiltonian) description of field-free electron-atom collision processes (Burke, Hibbert and Robb 1971, Berrington et al 1974, Burke and Robb 1975, Berrington et al 1978, Berrington, Eissner and Norrington 1995), single-photon ionization processes (Burke and Taylor 1975), and free-free radiative transitions of atomic systems (Bell et al 1977, Burke and Berrington 1993, Burke, Noble and Burke 2007). The ordinary Hilbert-space (Hamiltonian) formulation of the *R*-matrix-Floquet method can provide a realistic non-perturbative description of the dynamical evolution of the many-electron atomic system in the presence of a classical (possibly multiple-mode) electromagnetic field. The atomic system may consist of bound electrons and a single continuum electron. However, including pseudo-states in the expansion of the many-electron atomic wave function, as introduced by Bartschat et al (1996a, 1996b), can provide a representation of multiple continuum electrons. The "dressed" atomic states thereby obtained can then be used for the systematic investigation of an extensive class of atomic collision and radiation processes in the presence of intense, stationary (continuous-wave) electromagnetic fields. For a description of atomic processes in ultrashort-pulse electromagnetic fields, an alternative time-dependent *R*-matrix method has been developed (Burke and Burke 1997, van der Hart et al 2007, Lysaght et al 2008, and Guan et al 2007, 2008). A comprehensive discussion of the *R*-matrix-Floquet and the time-dependent *R*-matrix methods has been presented in a recent book by Burke (2011).

1.4. The Liouville-space (reduced-density-matrix) Floquet formulation

Relaxation and decoherence phenomena, due to environmental collisional and radiative interactions, can play an important role in the determination of the widths and shifts of spectral lines for ensembles of many-electron atomic systems in warm vapors and in high-temperature plasmas. In particular, the highly-excited bound and doubly-excited Rydberg autoionizing states, which often play the dominant role in dielectronic recombination, can acquire widths and shifts that exceed the contributions from autoionization and spontaneous radiative decay with increasing density and radiation-field intensity. In order to systematically incorporate environmental interactions in the detailed theoretical description of atomic and molecular processes in the presence of stationary (continuous-wave) electromagnetic fields, we propose to adopt the ordinary Hilbert-space (Hamiltonian) formulation of the *R*-matrix-Floquet method as a starting point for a Liouville-space (reduced-density-operator) formulation. The basic framework for our proposed Liouville-space Floquet approach is provided by a previously-developed formulation for multi-level atomic and molecular systems that are resonantly coupled to intense, coherent electromagnetic fields and under the influence of homogeneous relaxation and decoherence processes (Ben-Reuven and Rabin 1979, Rabin and Ben-Reuven 1979). A closely related Liouville-space Floquet framework has also been presented by Chu and Telnov (2004). For detailed applications to electromagnetically induced transparency and related pump-probe optical phenomena, we will be especially interested in atomic processes in the presence of both an intense (possibly multiple-mode) electromagnetic field, which is to be treated classically, and a weak multiple-mode electromagnetic field, which may be treated either as a classical field or as a quantum field. In a future investigation, we will introduce a different Liouville-space (reduced-density-operator) formulation based on the alternative time-dependent *R*-matrix method (van der Hart 2008, Burke 2011), which is expected to be more appropriate for the description of atomic and molecular processes in the presence of ultrashort-pulse electromagnetic fields for which the Floquet-Fourier expansion would involve a very large set of electromagnetic-field modes.

The Liouville-space (reduced-density-operator) formulation in the multiple-mode Floquet-Fourier representation can be implemented using a direct numerical solution of the equation-of-motion for the reduced density operator or a perturbation-theory approach, involving an expansion of the reduced density operator in powers of the weak electromagnetic field. If the weak electromagnetic field is to be treated as a quantum field, the perturbation-theory expansion of the reduced density operator can be expressed in terms of either the photon-number eigenstates or the coherent states. The quantum-field description, which would be rigorously based on an open-systems version of quantum electrodynamics, is expected to be much more difficult than the classical-field description. In this investigation, we propose a semiclassical, non-perturbative description of the electromagnetic interaction, in which the entire (combined) electromagnetic field is treated as a classical field and is represented as a multiple-mode Floquet-Fourier expansion.

1.5. The organization of this paper

The remainder of this paper has been organized in the following manner. In section 2 we present a generalized, multiple-mode version of the *R*-matrix-Floquet method that has been developed for the ordinary Hilbert-space (Hamiltonian) description of atomic processes in the presence of an intense electromagnetic (laser) field. In section 3 we describe the Liouville-space (reduced-density-operator) formulation in the multiple-mode Floquet-Fourier representation, utilizing the ordinary Hilbert-space (Hamiltonian)

R-matrix-Floquet description as a starting-point. In section 4 we discuss the application of the Liouville-space *R*-matrix-Floquet formulation to electromagnetically induced transparency and to related pump-probe optical phenomena involving coherent and resonant non-linear electromagnetic interactions. In section 5 we consider the application of the Liouville-space *R*-matrix-Floquet approach to the unified description of radiative and dielectronic recombination. Our conclusions and future plans are given in section 6.

2. The ordinary Hilbert-space (Hamiltonian) *R*-matrix-Floquet method

2.1. The Hamiltonian description for the many-electron atomic system in the presence of an electromagnetic field

We consider an (N+1)-electron atomic system in the presence of an external electromagnetic (laser) field. The atomic system can be described by the time-dependent Schrödinger equation:

$$\left[\mathrm{H}_{\mathrm{N+1}} + \mathrm{V(t)}\right]\Psi(\mathbf{X}_{\mathrm{N+1}},\mathrm{t}) = \mathrm{i}\hbar\frac{\partial}{\partial \mathrm{t}}\Psi(\mathbf{X}_{\mathrm{N+1}},\mathrm{t}). \qquad (5)$$

In equation (5), $\mathrm{H}_{\mathrm{N+1}}$ is the non-relativistic Hamiltonian operator for the (N+1)-electron atomic system in the absence of the electromagnetic field, $\mathrm{V(t)}$ denotes the operator describing the interaction of the atomic system with the external electromagnetic field, and $\mathbf{X}_{\mathrm{N+1}}$ represents the set $\{\mathbf{x}_{\mathrm{i}}\}$ of the N+1 single-electron spatial and spin coordinates

$\mathbf{x}_i = (\vec{r}_i, \sigma_i)$. The non-relativistic Hamiltonian operator H_{N+1} can be expressed in the form:

$$H_{N+1} = \sum_{i=1}^{N+1} \left(\frac{-\hbar^2}{2m} \vec{\nabla}_i^2 - \frac{Ze^2}{|\vec{r}_i|} \right) + \sum_{i>j=1}^{N+1} \frac{e^2}{|\vec{r}_{ij}|}. \tag{6}$$

In the *R*-matrix expansion of the (N+1)-electron wave function $\Psi(\mathbf{X}_{N+1}, t)$, we will take into account single-electron ionization and scattering processes in the presence of the external electromagnetic field. It should be noted that virtual states corresponding to multiple-electron continua can be represented by a suitable choice of the many-electron expansion basis set, e. g., by the inclusion of pseudo-states (Bartschat et al 1996a, 1996b).

In the *R*-matrix Floquet method, reviewed by Burke (2011), the three-dimensional space of the (N+1)-electron atomic system is sub-divided into three principal regions by the introduction of spheres of radii a_0 and a_p centered on the nucleus, as illustrated in Figure 1. In the internal region, the radial coordinates r_i of all N+1 electrons satisfy the condition:

$$r_i \le a_0, \quad i = 1, 2, \ldots, N+1, \tag{7}$$

where the sphere of radius a_0 is defined to envelop the charge distribution of the bound states that are retained in the expansion of the (N+1)-electron wave function $\Psi(\mathbf{X}_{N+1}, t)$.

In this internal region, the effects of correlation and exchange between the continuum (ejected or scattered) electron and the remaining electrons are important and must be described by the inclusion of appropriate (N+1)-electron basis states in the expansion of the wave function $\Psi(\mathbf{X}_{N+1},t)$. In the external region, one of the (N+1)-electron radial coordinates, corresponding to the continuum electron, lies on or outside of the sphere of radius a_0, and the remaining electrons are confined within this sphere. In the asymptotic region, the continuum-electron radial coordinate lies on or outside of the sphere of radius $a_p > a_0$, where an asymptotic expansion can be introduced for the set of the radial wave functions describing the continuum electron.

2.1.1. The semiclassical description of the electromagnetic interaction

We will treat the electromagnetic interaction using the non-relativistic approximation in the Coulomb gauge, for which the electromagnetic scalar potential may be set equal to zero in the absence of free charges. In addition, we will adopt a semiclassical description of the electromagnetic interaction, in which the external electromagnetic field is treated as a classical field satisfying the Maxwell equations. The semiclassical electromagnetic-interaction operator can be expressed as the sum $V(t) = V^1(t) + V^2(t)$ of a contribution $V^1(t)$ that is linear in the electromagnetic vector potential $\vec{A}(\vec{r},t)$ and a contribution $V^2(t)$ that is quadratic in $\vec{A}(\vec{r},t)$. The linear contribution can be expressed, as a sum of terms involving the single-electron canonical-momentum operators $\vec{p}_i = -i\hbar\vec{\nabla}_i$, in the manifestly Hermitian form:

$$V^1(t) = \left(\frac{e}{2mc}\right)\sum_{i=1}^{N+1}\left[\vec{p}_i \bullet \vec{A}(\vec{r}_i,t) + \vec{A}(\vec{r}_i,t) \bullet \vec{p}_i\right]. \tag{8}$$

We have neglected the relatively small contribution to the electromagnetic interaction arising from the motion of the much heavier nuclei. It should be noted that, in a systematic analysis that is based on the fully relativistic many-electron description of the electromagnetic interaction, an additional linear contribution is obtained involving the single-electron spin operators and the magnetic field. The quadratic contribution to the electromagnetic interaction is given by

$$V^2(t) = \left(\frac{e^2}{2mc^2}\right)\sum_{i=1}^{N+1}\vec{A}(\vec{r}_i,t) \bullet \vec{A}(\vec{r}_i,t)\,. \tag{9}$$

It has been noted that the inclusion of a spatially dependent quadratic contribution is not fully compatible with the non-relativistic description that we have adopted (Burke, Franken, and Joachain 1990, Dörr, Joachain, Potvliege, and Vucic 1994). Consequently, it is more consistent to initially introduce the electric-dipole approximation described below.

In an alternative representation of the electromagnetic interaction $V(t)$, involving the electric and magnetic fields together with the various electromagnetic dipole and multipole moments, the leading contribution can be expressed in the electric-dipole form:

$$V(t)=\left(\frac{e}{2}\right)\sum_{i=1}^{N+1}\left[\vec{r}_i \bullet \vec{E}(\vec{r}_i,t)+\vec{E}(\vec{r}_i,t)\bullet \vec{r}_i\right], \qquad (10)$$

where $\vec{E}(\vec{r},t)=-(1/c)(\partial/\partial t)\vec{A}(\vec{r},t)$ is the electric field. Beyond the electric-dipole approximation, this form of the electromagnetic interaction is not equivalent to that given by the sum of Eqs. (8) and (9). A fully relativistic description of coherent electromagnetic processes in many-electron atomic systems, consistently and systematically taking into account higher multipole contributions, represents a significant challenge. A detailed discussion of the classical, semiclassical, and fully quantum-mechanical descriptions of atomic electromagnetic interactions has been presented by Joachain, Kylstra, and Potvliege (2012).

2.1.2. The multiple-mode representation of the classical electromagnetic field

The general, multiple-mode classical electromagnetic field can be represented as a superposition of single-mode (monochromatic) plane-wave fields in the form:

$$\vec{A}(\vec{r},t) = \sum_j \left\{\vec{A}_j(\vec{k}_j,\omega_j)\exp\left[i(\vec{k}_j \bullet \vec{r}-\omega_j t)\right] + \vec{A}_j(\vec{k}_j,\omega_j)^* \exp\left[-i(\vec{k}_j \bullet \vec{r}-\omega_j t)\right]\right\}, \qquad (11)$$

where the field amplitudes $\vec{A}_j(\vec{k}_j,\omega_j)$ include the polarization vectors and the exponential phase factors. Both positive and negative values of the discrete frequency variables ω_j must be explicitly taken into account within the summation over j. The frequencies ω_j

and wave-vectors $\vec{k}_j$ can be treated as independent variables by extending the form of Eq. (11) to allow for the two independent summations over these variables. This extension may be necessary for the precise description of the electromagnetic interactions in general, dispersive and refractive media. In an addition extension, the field amplitudes $\vec{A}_j(\vec{k}_j,\omega_j)$ can be treated as explicitly time-dependent quantities.

An alternative, explicitly time-dependent approach is expected to be necessary for the accurate description of ultrashort-pulse laser interactions of atomic systems (Day, Piraux and Potvliege 2000), because the frequency-domain description would entail an impractically large set of frequencies. An explicitly time-dependent *R*-matrix theory has been developed (Burke and Burke 1997, van der Hart et al 2007, Lysaght et al 2008, and Guan et al 2007, 2008) for the description of ultrashort-pulse laser interactions with many-electron atomic systems, and the explicitly time-dependent *R*-matrix theory is expected to be advantageous for electromagnetic fields that have rapid time variations.

2.1.3. The multiple-mode Floquet-Fourier expansion of the many-electron wave function

The solution of Eq. (5) can be obtain by introducing the multiple-mode Floquet-Fourier expansion:

$$\Psi(\mathbf{X}_{N+1},t)=\exp\left(-iEt/\hbar\right)\sum_{n}\exp\left(-i\Omega_n t\right)\psi_n\left(\mathbf{X}_{N+1}\right), \tag{12}$$

where E is known as the quasi-energy. The quasi-energy has a negative imaginary part for multi-photon ionization and non-linear optical processes but is real for laser-assisted electron-atom and electron-ion collision processes. The summation over n includes all angular frequencies Ω_n that can be represented as linear combinations of the angular frequencies ω_j of the discrete modes comprising the classical electromagnetic field $\vec{A}(\vec{r},t)$. If the angular frequencies ω_j are assumed to be only in irrational ratios with each other, Eq. (12) may be expressed in terms of the frequency variables $\Omega_{\vec{n}}$ defined by

$$\Omega_{\vec{n}}=\vec{n}\bullet\vec{\omega}=\sum_j n_j\omega_j. \tag{13}$$

The mode number vector $\vec{n}$ represents the infinite set consisting of all positive and negative values of the individual Floquet-Fourier mode numbers n_j corresponding to the irreducible set of the incommensurate angular frequencies ω_j. Eqs. (12) and (13) may then be combined to obtain the following expressions:

$$\begin{aligned}\Psi(\mathbf{X}_{N+1},t)&=\exp\left(-iEt/\hbar\right)\sum_{\vec{n}}\exp\left(-i\Omega_{\vec{n}}t\right)\psi_{\vec{n}}\left(\mathbf{X}_{N+1}\right)\\&=\exp\left(-iEt/\hbar\right)\sum_{n_1,n_2,..}\prod_j\left[\exp\left(-in_j\omega_jt\right)\right]\psi_{n_1,n_2,..}\left(\mathbf{X}_{N+1}\right).\end{aligned} \tag{14}$$

From the quantized-electromagnetic-field viewpoint, the positive values of the individual Floquet-Fourier mode numbers n_j correspond to photon-absorption processes while the negative values of n_j are associated with photon-emission processes.

The extension of the Floquet method for two modes of the classical electromagnetic field has been given by Ho and Chu (1984, 1985) and by Chu and Telnov (2004). Jaron, Mese, and Potvliege (2000) have presented the generalization of the Floquet method for three electromagnetic-field modes, in a form that provides the foundation for our multiple-mode formulation. Since the explicitly time-dependent approach is expected to be most appropriate for short-pulse multiple-mode electromagnetic fields, our multiple-mode Floquet formulation is intended for application primarily for long-pulse electromagnetic fields with incommensurate frequencies. For general multiple-mode fields, the electromagnetic interaction cannot be assumed to be periodic and the basic periodicity condition of the simple single-mode Floquet theory may not be satisfied. Consequently, the multiple-mode Floquet Fourier expansions given by Eqs. (12) and (14) should be understood as representations in terms of a complete basis set corresponding to the various discrete electromagnetic-field modes. A detailed discussion of the Floquet method has been presented by Joachain, Kylstra, and Potvliege (2012).

In the remainder of this section, atomic units will be adopted in order to simply the forms of the equations presented above. In atomic units, $\hbar = \mathrm{m} = \mathrm{e} = 1$.

2.2. The R-matrix-Floquet description of the many-electron atomic system in the internal region

2.2.1. The set of coupled equations for the multiple-mode Floquet-Fourier functions

In the *R*-matrix-Floquet method (Burke, Francken and Joachain 1990, 1991, Burke, Noble and Burke 2007, Burke 2011, and Joachain, Kylstra, and Potvliege 2012), the semiclassical electromagnetic-interaction operator $V(t)$ in the internal region is expressed in the non-relativistic electric-dipole form given by Eq. (10). If the multiple-mode Floquet-Fourier expansion for the (N+1)-electron wave function given by Eq. (14) is substituted into Eq. (5), the following infinite set of coupled time-independent equations is obtained for the time-independent mode functions $\psi_{\vec{n}}\left(\mathbf{X}_{N+1}\right)$:

$$\left(H_{N+1} - E - \vec{n}\bullet\vec{\omega}\right)\psi_{\vec{n}}\left(\mathbf{X}_{N+1}\right) + \sum_{j}\left[V_{N+1,j}(\vec{k}_j,\omega_j)\psi_{\vec{n}_j^-}\left(\mathbf{X}_{N+1}\right) + V^{*}_{N+1,j}(\vec{k}_j,\omega_j)\psi_{\vec{n}_j^+}\left(\mathbf{X}_{N+1}\right)\right] = 0. \quad (15)$$

In the electric-dipole representation, the time-independent, (N+1)-electron semiclassical electromagnetic-interaction operator coefficients $V_{N+1,j}(\vec{k}_j,\omega_j)$ can be expressed in the form:

$$V_{N+1,j}(\vec{k}_j,\omega_j) = \sum_{i=1}^{N+1}\left(\frac{1}{2}\right)\left[\vec{r}_i \bullet \vec{E}_j(\vec{k}_j,\omega_j)\exp\left(i\vec{k}_j \bullet \vec{r}_i\right) + \exp\left(i\vec{k}_j \bullet \vec{r}_i\right)\vec{E}_j(\vec{k}_j,\omega_j)\bullet \vec{r}_i\right]. \quad (16)$$

The modified Floquet-Fourier mode number vectors $\vec{n}_j^{\pm}$ are defined as follows:

$$\vec{n}_j^{\pm} = \left(n_1, n_2, .., n_j \pm 1, ..\right). \quad (17)$$

For a single mode of the classical electromagnetic field, Eq. (15) is in agreement with the original formulation of the *R*-matrix Floquet theory of multi-photon processes by Burke, Francken, and Joachain (1990, 1991). In the long-wavelength approximation, the dependence of the semiclassical electromagnetic-interaction operator coefficients $V_{N+1,j}(\vec{k}_j,\omega_j)$ on the wave-vectors $\vec{k}_j$ can be neglected. The electric-dipole-interaction operator coefficient for an electromagnetic-field mode j can then be expressed in the simplified dipole-length form:

$$V_{N+1,j}(\omega_j) = \vec{E}(\omega_j) \bullet \sum_{i=1}^{N+1} \vec{r}_i = \vec{E}(\omega_j) \bullet \vec{R}_{N+1}, \tag{18}$$

where $\vec{R}_{N+1}$ is the (N+1)-electron coordinate operator. In the remainder of this subsection, which is devoted to the (N+1)-electron wave function expansion in the internal region, we will use the simplified dipole-length representation given by Eq. (18). For the (N+1)-electron wave function expansion in the external and asymptotic regions, alternative velocity and acceleration representations will be introduced.

If the time-independent Floquet-Fourier wave functions $\psi_{\vec{n}}\left(\mathbf{X}_{N+1}\right)$ are regarded as the individual components of the multiple-mode state vector $\left|\vec{\psi}\right\rangle$, Eq. (15) can be expressed in the compact matrix-operator form:

$$\left(\mathbf{H}_F - E\right)\left|\vec{\psi}\right\rangle = 0. \tag{19}$$

The Floquet Hamiltonian operator $\mathbf{H}_F$ is a multi-dimensional matrix operator in the vector space of the Floquet-Fourier modes specified by the number vector $\vec{n}$. The diagonal elements of this matrix are the operators $H_{N+1} - \vec{n} \bullet \vec{\omega}$, while the non-diagonal elements are either the operator coefficients $V_{N+1,j}(\omega_j)$ or the complex-conjugate operator coefficients $V^*_{N+1,j}(\omega_j)$.

2.2.2. The Hermitian form of multiple-mode Floquet-Fourier eigenvalue problem

It has been noted (Burke, Francken and Joachain 1991) that the Floquet Hamiltonian matrix operator $\mathbf{H}_F$ is not Hermitian in the internal region, because the kinetic-energy operator contained in H_{N+1} gives rise to surface terms at the boundary $r_i = a_0$. Consequently, the eigenvalues of $\mathbf{H}_F$ are complex. In order to circumvent this difficulty, Eq. (19) can be re-expressed in the equivalent form:

$$\left(\mathbf{H}_F + \mathbf{L}_b - E\right)\left|\vec{\psi}\right\rangle = \mathbf{L}_b\left|\vec{\psi}\right\rangle, \tag{20}$$

where $\mathbf{L}_b$ is the matrix operator introduced by Bloch (1957). The Bloch matrix operator may be expressed in the explicit form

$$\mathbf{L}_b = \sum_{i=1}^{N+1} \frac{1}{2}\delta\left(r_i - a_0\right)\left(\frac{d}{dr_i} - \frac{b_0 - 1}{r_i}\right)\mathbf{I}, \tag{21}$$

where b_0 is an arbitrary constant and $\mathbf{I}$ is the identity matrix operator. The Bloch matrix operator is diagonal in the space of the Floquet-Fourier mode numbers and is defined to cancel the surface terms. Consequently, the combined matrix operator $\mathbf{H}_F + \mathbf{L}_b$ is Hermitian in the internal region, with real eigenvalues. If the eigenvalues and eigenvectors of the combined matrix operator $\mathbf{H}_F + \mathbf{L}_b$ are denoted by E_k and $|\vec{\psi}_k\rangle$, respectively, the spectral representation of the combined matrix operator $\mathbf{H}_F + \mathbf{L}_b$ can be introduced to formally obtain the linearly independent solutions $|\vec{\psi}_j(E)\rangle$ of Eq. (20) in the internal region, corresponding to the quasi-energy E, as follows:

$$\begin{aligned} |\vec{\psi}_j(E)\rangle &= \sum_{k,k'} |\vec{\psi}_{k'}\rangle\langle\vec{\psi}_{k'}| \frac{1}{\mathbf{H}_F + \mathbf{L}_b - E} |\vec{\psi}_k\rangle\langle\vec{\psi}_k|\mathbf{L}_b|\vec{\psi}_j(E)\rangle \\ &= \sum_k |\vec{\psi}_k\rangle \frac{1}{E_k - E}\langle\vec{\psi}_k|\mathbf{L}_b|\vec{\psi}_j(E)\rangle = \sum_k |\vec{\psi}_k\rangle A_{kj}(E). \end{aligned} \tag{22}$$

It should be noted that the index j in Eq. (22) denotes the linearly independent solutions rather than the electromagnetic-field modes. The multiple-mode state vectors $|\vec{\psi}_k\rangle$ are composed of the energy-independent basis functions $\psi_{\vec{n}k}$ that are defined in the internal region and are described in detail below. The energy-dependent expansion coefficients denoted by $A_{kj}(E)$ must be determined by taking into account the asymptotic boundary conditions that are satisfied by the solutions given by Eq. (22). For the applications in sections 4 and 5, it will be necessary to evaluate the electromagnetic-transition matrix elements for the various atomic processes of interest, utilizing the many-electron *R*-matrix Floquet-Fourier wave functions that are defined throughout all spatial regions and satisfy the appropriate asymptotic boundary conditions (e. g., corresponding to laser-assisted electron-atom or electron-ion scattering or to multi-photon ionization).

2.2.3. The multiple-mode R-matrix-Floquet expansion for the (N+1)-electron eigenfunctions

In the *R*-matrix-Floquet method (Burke, Francken and Joachain 1990, 1991, Burke, Noble and Burke 2007, Burke 2011, and Joachain, Kylstra and Potvliege 2012), the (N+1)-electron eigenvectors $\left|\vec{\psi}_{\mathrm{k}}\right\rangle$, which occur in the spectral decomposition employed in Eq. (22), are expanded in a form analogous to that introduced in the *R*-matrix method in the absence of electromagnetic fields (Burke, Hibbert and Robb 1971, Burke and Robb 1975, Burke and Berrington 1993, Burke, Noble and Burke 2007, and Burke 2011). In the internal region, the *R*-matrix-Floquet expansion may be expressed in a multiple-mode vector representation. The individual components, which are specified by the number vector $\vec{\mathrm{n}}$, may be expanded in the form:

$$\psi_{\vec{\mathrm{n}}\mathrm{k}} = \sum_{\Gamma i \ell} a^{\Gamma}_{i\ell\vec{\mathrm{n}}\mathrm{k}} \zeta^{\Gamma}_{i\ell\vec{\mathrm{n}}} + \sum_{\Gamma i} b^{\Gamma}_{i\vec{\mathrm{n}}\mathrm{k}} \chi^{\Gamma}_{i\vec{\mathrm{n}}}. \tag{23}$$

The (N+1)-electron functions $\zeta^{\Gamma}_{i\ell\vec{\mathrm{n}}}$ are the antisymmetrized combinations of the products $\phi^{\Gamma}_{i}\mathrm{u}^{\Gamma}_{i\ell\vec{\mathrm{n}}}$. In the LS-coupling representation, the (N+1)-electron channel functions ϕ^{Γ}_{i} are formed by coupling the orbital and spin angular momentum states of the N-electron atomic states ϕ_i (and possibly pseudo-states as described below) with the orbital and spin angular momentum states pertaining to the continuum (ejected or scattered) electron. Accordingly, the symbol Γ represents the set of channel quantum numbers, including the total orbital angular momentum L, the total spin angular momentum S, the corresponding magnetic components M_L and M_S, the parity π, and the set of remaining quantum numbers γ that are required to completely specify the (N+1)-electron-state channel. The continuum-electron radial basis functions $u^{\Gamma}_{i\ell\vec{n}}$, where ℓ denotes the orbital angular momentum, are non-vanishing on the boundary of the internal region. The (N+1)-electron basis functions $\chi^{\Gamma}_{i\vec{n}}$, for which *i* does not correspond to a bound-atomic-state index, are quadratically integrable, antisymmetric functions that can be assumed to vanish on the boundary of the internal region. The basis functions $\chi^{\Gamma}_{i\vec{n}}$ are introduced to provide a complete set for the expansion of the (N+1)-electron wave function, as discussed below. The expansion coefficient $a^{\Gamma}_{i\ell\vec{n}k}$ and $b^{\Gamma}_{i\vec{n}k}$ in Eq. (23) are obtained by the diagonalization of the combined matrix operator $\mathbf{H}_F + \mathbf{L}_b$ in the internal region.

In the diagonalization of the combined matrix operator $\mathbf{H}_F + \mathbf{L}_b$, it is necessary to consider only the submatrix eigenvalue problem pertaining to each individual set of indices corresponding to the conserved quantum numbers pertaining to the exact eigenstates, which are represented by the expansion given in Eq. (23). However, it should be emphasized that the index j, designating the linearly independent solutions in Eq. (22), must be permitted to include all members of the complete set specified by the conserved quantum numbers, which are associated with the symmetry operators that commute with the combined matrix operator $\mathbf{H}_F + \mathbf{L}_b$. Because of the presence of the multiple-mode electromagnetic interaction, certain quantum numbers (e. g., the total orbital angular momentum L) pertaining to the field-free (N+1)-electron Hamiltonian operator will no longer be conserved in the presence of an electromagnetic field, as discussed by Burke (2011).

In the *R*-matrix-Floquet computer programs that have been developed for multi-photon transitions and laser-assisted electron-atom collision processes, only a finite number of N-electron bound (target) eigenstates ϕ_i can be included in the first expansion in Eq. (23), which is known as the close-coupling expansion in the theory of electron-atom scattering. In order to provide an expansion of the total wave function that can be systematically extended towards completeness, the first expansion can be augmented with additional terms corresponding to pseudo-states (Bartschat et al 1996a, 1996b) and the second expansion can contain quadratically integrable (N+1)-electron basis functions. These additional contributions can also allow for virtual processes involving two or more continuum electrons, which are expected to play an important role at high energies and in atomic processes occurring in the presence of intense electromagnetic fields.

As discussed by Burke, Francken and Joachain (1991) and Burke (2011), the multi-dimensional *R*-matrix is introduced when Eq. (22) is projected onto the combined (tensor-product) space of the channel states, which are specified by the indices *i* and Γ, together with the Floquet-Fourier modes, which are specified by the single-mode number n. The *R*-matrix appropriate for electron-atom or electron-ion scattering or for multi-photon ionization is defined when this projected relationship is evaluated on the boundary of the internal region at $r_{N+1} = a_0$. In the present investigation, the *R*-matrix is further generalized for multiple Floquet-Fourier modes. This further generalized *R*-matrix, in the combined (tensor-product) space of the channel states and the Floquet-Fourier modes specified by the number vector $\vec{n}$, is introduced in Appendix 1.

2.3. The R-matrix-Floquet description of the many-electron atomic system in the external and asymptotic regions defined in Figure 1

2.3.1. The transformed Hamiltonian eigenvalue problems in the external region

In the external region, where the radial coordinate of only one of the N+1 electrons is greater than or equal to the radius a_0 of the sphere enclosing the internal region, two transformed representations have been introduced in the *R*-matrix-Floquet method (Burke, Francken and Joachain 1991, Burke, Noble and Burke 2007, Burke 2011, and Joachain, Kylstra and Potvliege 2012). In one transformed representation, the velocity (or momentum) form is used for the semiclassical electromagnetic interaction of one of the N+1 electrons, which corresponds to the continuum electron. However, the dipole-length form is retained for the remaining N inner electrons, corresponding to the bound atomic electrons. In the other transformed representation, the acceleration form is introduced for the semiclassical electromagnetic interaction of the continuum electron; while the dipole-length form is again retained for the N bound electrons. In the remainder of this section, we will treat the electromagnetic interaction in the long-wavelength limit, for which the spatial dependence can be neglected.

2.3.2. The velocity representation in the external region

The transformed Hamiltonian eigenvalue problem in the velocity representation (denoted by the superscript V) can be expressed in the form:

$$\left[H^{V}_{N+1} + \vec{E}(t) \bullet \vec{R}_{N}\right] \Psi(\mathbf{X}_{N+1}, t) = i \frac{\partial}{\partial t} \Psi(\mathbf{X}_{N+1}, t). \tag{24}$$

The N-electron coordinate operator $\vec{R}_N$ is obtained from the corresponding (N+1)-electron operator in Eq. (18) by replacing (N+1) with N. The transformed Hamiltonian operator H^{V}_{N+1} can be written, in atomic units, in the form:

$$H^{V}_{N+1} = H_N - \frac{1}{2} \vec{\nabla}^{2}_{N+1} - \frac{Z}{|\vec{r}_{N+1}|} + \sum_{i=1}^{N} \frac{1}{|\vec{r}_{N+1} - \vec{r}_i|} + \frac{1}{c} \vec{A}(t) \bullet \vec{p}_{N+1}. \tag{25}$$

The N-electron Hamiltonian operator H_N is obtained from Eq. (6) by replacing (N+1) with N. In this representation, the dipole-length form is employed for the semiclassical electromagnetic interaction of the N inner (bound) electrons, while the velocity (or momentum) form is adopted for the (N+1)'th (continuum) electron.

After introducing the multiple-mode Floquet-Fourier expansion for the (N+1)-electron wave function $\Psi(\mathbf{X}_{N+1}, t)$ in the external region, assuming that this expansion has the same form as that given by Eq. (14), an infinite set of coupled equations is obtained for the multiple-mode Floquet-Fourier functions $\psi_{\vec{n}}\left(\mathbf{X}_{N+1}\right)$. This set of equations differs from the set given by Eq. (15) in that different forms are introduced for the electromagnetic-interaction operator coefficients $V_{N,j}(\omega_j)$ pertaining to the N inner (bound) electrons and the separated momentum contribution for the (N+1)'th (continuum) electron.

2.3.3. The acceleration representation in the asymptotic region

In the asymptotic region, beyond some large radius a_p, a further transformation can be introduced, in which the semiclassical electromagnetic interaction of the continuum electron is expressed in the acceleration representation. The transformed Hamiltonian eigenvalue problem appropriate for the asymptotic region can then be expressed, in the acceleration form (denoted by the superscript A), as follows:

$$\left[H_{N+1}^{A}+\vec{E}(t)\bullet\vec{R}_{N}\right]\Psi(\mathbf{X}_{N+1},t)=i\frac{\partial}{\partial t}\Psi(\mathbf{X}_{N+1},t). \tag{26}$$

The transformed Hamiltonian operator H_{N+1}^{A} can be written, in atomic units, in the form:

$$H_{N+1}^{A}=H_{N}-\frac{1}{2}\vec{\nabla}_{N+1}^{2}-\frac{Z}{\left|\vec{r}_{N+1}+\vec{\alpha}(t)\right|}+\sum_{i=1}^{N}\frac{1}{\left|\vec{r}_{N+1}+\vec{\alpha}(t)-\vec{r}_{i}\right|}, \tag{27}$$

where the vector $\vec{\alpha}(t)$, which is defined by

$$\vec{\alpha}(t) = \frac{1}{c}\int_{-\infty}^{t} \vec{A}(t')dt' , \qquad (28)$$

has the property that its time derivative corresponds to the classical velocity of a free electron in the electromagnetic field represented by the vector potential $\vec{A}(t)$. This acceleration representation has the advantage that the transformed Hamiltonian operator H^{A}_{N+1} can be reduced to the field-free Hamiltonian operator H_{N+1} in the limit $r_{N+1} \to \infty$. In this case, the radial wave functions describing the (N+1)'th (continuum) electron will be governed by simpler asymptotic boundary conditions, which are analogous to those used for electron-atom or electron-ion collision processes in the absence of an electromagnetic field (Burke 2011). However, due to the presence of the interaction term $\vec{E}(t) \bullet \vec{R}_N$, the full, combined Hamiltonian in Eq. (26) still involves the electromagnetic field in the limit asymptotic $r_{N+1} \to \infty$.

2.3.4. The solution of the Hamiltonian eigenvalue problem in the external region

The solution of the Hamiltonian eigenvalue problem in the external region, expressed in either the velocity or the acceleration representation, is based on the introduction of a Floquet-Fourier expansion of the same form as the expansion for the wave function $\Psi(\mathbf{X}_{N+1}, t)$ that was employed for the internal region. The Hamiltonian eigenvalue problem in the external region can be expressed in the matrix-operator form given by Eq. (19), except that the non-diagonal matrix elements of the Floquet

Hamiltonian operator $\mathbf{H}_{\mathrm{F}}$ are now expressed in terms of the electromagnetic-interaction operator coefficients $\mathrm{V}_{\mathrm{N,j}}(\omega_{\mathrm{j}})$, together with additional terms that arise from the transformed continuum-electron electromagnetic interactions that have been separately incorporated into Eqs. (25) and (27). The electromagnetic-interaction operator coefficients $\mathrm{V}_{\mathrm{N,j}}(\omega_{\mathrm{j}})$ may be obtained from Eq. (16) simply by replacing N+1 with N and taking the long-wavelength limit. If the semiclassical electromagnetic interaction of the continuum electron is described in the acceleration representation, the non-diagonal matrix elements of the Floquet Hamiltonian operator will contain additional contributions that will be generated as a result of an infinite expansion in terms of the mode number vector $\vec{\mathrm{n}}$. Consequently, these non-diagonal elements will exhibit a more complex pattern than in the length or velocity representations.

Following the original introduction of the *R*-matrix-Floquet method (Burke, Francken and Joachain 1990, 1991), new computational methods for solving the *R*-matrix-Floquet equations in the external region in the velocity representation have been developed by Dörr et al (1992). A relatively straightforward procedure, for the transformation from the velocity representation to the acceleration representation at a large radius a_p, has been employed by Charlo et al (1998) and by Terao-Dunseath and Dunseath (2002).

2.3.5. The close-coupling expansion for the (N+1)-electron Floquet-Fourier wave functions

In the external region, the multiple-mode (N+1)-electron wave functions are expanded in the close-coupling form:

$$\psi_{\vec{n}j} = \sum_{\Gamma i} \phi_i^{\Gamma}(r_{N+1}^{-1}) r_{N+1}^{-1} \, G_{i\vec{n}j}^{\Gamma}(r_{N+1}). \qquad (29)$$

In this expansion, the summations over Γ and i cover the same ranges as in the expansion adopted in the internal region, which is given by Eq. (23). The index j in Eq. (29) designates the linearly independent solutions, as in Eq. (22). The symbol $\phi_i^{\Gamma}(r_{N+1}^{-1})$ denotes the (N+1)-electron channel functions, which are formed by coupling the orbital and spin angular-momentum states of the N-electron atomic state ϕ_i with the orbital and spin angular-momentum states of the (N+1)'th (continuum) electron. Unlike the expansion given by Eq. (23), the expansion given by Eq. (29) is not antisymmetrized. This is appropriate for the external region, in which the (N+1)'th (continuum) electron is now assumed to be outside the sphere of radius a_0, while the remaining N (bound) electrons are assumed to be confined within this sphere. Consequently, it is permissible to neglect the exchange interactions between the (N+1)'th electron and the remaining N electrons. The radial wave functions $G_{i\vec{n}j}^{\Gamma}(r_{N+1})$ describing the (N+1)'th (continuum) electron satisfy a set of coupled, second-order differential equations of the close-coupling form. The continuum-electron orbital angular momentum ℓ has not been explicitly indicated, because it has been implicitly included in the channel index Γ.

In the electromagnetically modified close-coupling equations satisfied by the radial wave functions $\mathrm{G}^{\Gamma}_{\vec{n}\mathrm{j}}(\mathrm{r}_{\mathrm{N+1}})$, the long-range potentials coupling the various channels Γ are expressed in different forms in the velocity and acceleration representations. Explicit expressions for these long-range potentials have been presented, for a single-mode electromagnetic field, by Burke, Francken and Joachain (1991). The corresponding multiple-mode expressions can be simply deduced, in a manner similar to the multiple-mode generalization of the set of equations for the time-independent Floquet-Fourier wave functions $\psi_{\vec{\mathrm{n}}}\left(\mathbf{X}_{\mathrm{N+1}}\right)$ given by Eq. (15).

2.3.6. The boundary conditions and the generalized R-matrix

The solutions of the electromagnetically modified close-coupling equations must satisfy the boundary conditions at the sphere radius a_0, where the *R*-matrix is introduced in the dipole-length representation, and also at the larger radius a_p, where the asymptotic expansion is assumed to provide an accurate representation of the continuum-electron radial wave functions $\mathrm{G}^{\Gamma}_{\vec{n}\mathrm{j}}(\mathrm{r}_{\mathrm{N+1}})$. In our investigation, the *R*-matrix is generalized as a multi-dimensional matrix in the vector space of the Floquet-Fourier modes specified by the number vector $\vec{\mathrm{n}}$, as well as in the space of the channel states. In Appendix 1, we discuss the construction of this generalized *R*-matrix in the dipole-length representation from the solutions in the internal region.

For a complete specification of the wave function expansion in the external region, it is necessary to relate, at the boundary $r_{N+1} = a_0$, the reduced radial wave functions and their derivatives that are defined in the internal region to the radial wave functions $G^{\Gamma}_{i\vec{n}j}(r_{N+1})$ and their derivatives that are introduced in the external region. In Appendix 2, these boundary conditions at $r_{N+1} = a_0$ are obtained based on a transformation of the generalized *R*-matrix from the dipole-length representation to the velocity representation. It is also necessary to specify the boundary conditions that must be satisfied by the radial wave functions at $r_{N+1} = a_p$. In order to determine these asymptotic boundary conditions, the radial wave functions $G^{\Gamma}_{i\vec{n}j}(r_{N+1})$ that are introduced in the external region are propagated in the velocity representation from $r_{N+1} = a_0$ to $r_{N+1} = a_p$ and then are transformed to the acceleration representation, as described by Burke, Francken and Joachain (1991) for a single electromagnetic-field mode. This analysis yields an expression for the *R*-matrix in the acceleration representation. The multiple-mode generalization of this analysis is presented in Appendix 3, which is devoted to the construction of the multiple-mode (N+1)-electron wave functions that are continuously defined throughout the entire spatial region and satisfy the asymptotic boundary conditions appropriate for electromagnetically assisted electron-atom and electron-ion collisions and for multi-photon ionization processes. These are the wave functions that will be required for the evaluation of the matrix elements describing the electromagnetic processes that are treated in sections 4 and 5.

3. The Liouville-space (reduced-density-operator) formulation

3.1. The general density-operator and reduced-density-operator approaches

In the density-operator approach, a general statistical state of a combined, interacting (closed) quantum system is represented by the complete density operator ρ. The complete density operator ρ is conventionally assumed to be initially expressible in the uncorrelated, tensor-product form given by $\rho(t_0) = \rho^S \otimes \rho^E$. The density operator ρ^S represents the statistical state of the relevant quantum system of interest at the initial time t_0, while the density operator ρ^E represents the initial quantum-statistical state of the environment. However, the complete density operator representing the final statistical state of the combined, interacting quantum system at an arbitrary time cannot be assumed to be expressible in the simple uncorrelated, tensor-product form that is conventionally adopted for the initial statistical state. The statistical state of the relevant quantum system, at an arbitrary time t, can be represented by means of the reduced, relevant density operator $\rho^r(t)$. The reduced, relevant density operator $\rho^r(t)$ is defined in terms of the average (partial-trace) operation $\rho^r(t) = Tr_E\{\rho(t)\}$, which is taken over the large set of quantum numbers corresponding to the environmental degrees of freedom.

The reduced-density-operator approach (Fano 1957, Cohen-Tannoudji et al 1992) is an advantageous framework for the systematic incorporation of a microscopic description of the collisional and radiative decoherence and relaxation processes (together with the associated spectral-line broadening mechanisms) that arise from the influence of a much larger system, which is designated as the environment. In the conventional reservoir approximation, the environment is assumed to be unaffected by its interactions with the much smaller, relevant quantum system. Consequently, the environment can be represented by a time-independent density operator. The kinetics and spectral phenomena due to the environmental interactions can be systematically and self-consistently investigated in terms of the self-energy corrections that arise in the complementary time-domain and frequency-domain formulations of the reduced-density-operator approach. It should be recognized that the partition of the entire, interacting quantum system into a relevant quantum system and an environment is by no means unique. Furthermore, different partitions are intrinsically inequivalent and will inevitably lead to different approximations. The approach based on this partition of the entire, interacting quantum system is illustrated in Figure 2.

It is convenient to introduce the reduced description by adopting an abstract formalism based on the Zwanzig Liouville-space projection operators (Zwanzig 1961, Fano 1963). The Liouville-space operators (which will be denoted in the following discussion by overbars) are defined within a generalized Hilbert space known as Liouville space. In this generalized space, the ordinary Hilbert-space operators, such as the density operators, play the role of state vectors. The individual members of the Liouville-space basis set $\left\{|\alpha\rangle\langle\beta|\right\}$ may be denoted, in the Liouville-space double-bracket (Dirac) notation, by $|\alpha,\beta\rangle\rangle$. The complete Liouville-space basis set $\left\{|\alpha,\beta\rangle\rangle\right\}$ can be constructed from the complete, elementary Hilbert-space basis sets $\left\{|\alpha\rangle\right\}$ and $\left\{\langle\beta|\right\}$. Since the general density operator ρ is now treated as a general state vector in Liouville space, it may be denoted by $|\rho\rangle\rangle$. The complex inner product $\langle\langle\rho_1|\rho_2\rangle\rangle$ of the two Liouville-space state vectors $|\rho_1\rangle\rangle$ and $|\rho_2\rangle\rangle$ is represented by the trace operation $\mathrm{Tr}(\rho_1^+\rho_2)$, where the superscript "+" indicates the adjoint. A general Liouville-space state vector (e. g., a general density operator) can then be represented in terms of an expansion involving the members of the complete basis set in Liouville space, together with the corresponding expansion coefficients (matrix elements). Accordingly, the density operator $|\rho\rangle\rangle$ can be represented by means of the expansion:

$$|\rho\rangle\rangle=\sum_{\alpha}\sum_{\beta}|\alpha,\beta\rangle\rangle\langle\langle\alpha,\beta|\rho\rangle\rangle=\sum_{\alpha}\sum_{\beta}|\alpha\rangle\langle\alpha|\rho|\beta\rangle\langle\beta|. \tag{30}$$

The corresponding expansion for a general Liouville-space operator is expressed in terms of tetradic matrix elements, which are specified by four ordinary Hilbert-space indices.

3.2. The frequency-domain (resolvent-operator) formulation

In the frequency-domain (resolvent-operator) formulation of the reduced-density-operator description, the electromagnetic-transition rate corresponding to the transition probability per unit time may be expressed in the generalized (Liouville-space) Fermi Golden-Rule form (Ben-Reuven and Rabin 1979, Jacobs, Cooper and Haan 1994):

$$A_R(i\rightarrow f)=-i\lim_{\varepsilon\rightarrow 0}\langle\langle P_f^r|\overline{T}^r(+i\varepsilon)|\rho_i^r\rangle\rangle. \tag{31}$$

The initial and final states of the relevant quantum system are represented by the reduced, relevant density operator ρ_i^r and the projection operator P_f^r, respectively. The reduced, relevant Liouville-space transition operator $\bar{T}^r(+i\varepsilon)$ is a generalization of the ordinary Hilbert-space transition operator, and the conventional asymptotic (scattering-theory) boundary condition is indicated by the $\varepsilon \to 0$ limit. The reduced, relevant Liouville-space transition operator can be evaluated using the Lippmann-Schwinger relationship $\bar{T}^r(+i\varepsilon)=\bar{V}^r+\bar{V}^r\bar{G}^r(+i\varepsilon)\bar{V}^r$. The reduced, relevant Liouville-space resolvent (or Green) operator is expressed by $\bar{G}^r(+i\varepsilon)=[+i\varepsilon-\bar{L}^r-\bar{\Sigma}(+i\varepsilon)]^{-1}$, where $\bar{L}^r$ is the relevant Liouvillian operator and $\bar{\Sigma}(+i\varepsilon)$ is the Liouville-space self-energy operator, which will be defined below. The relevant Liouville-space operator $\bar{L}^r$ can be decomposed as $\bar{L}^r=\bar{L}_0^r+\bar{V}^r$, where the zero-order Liouville-space operator $\bar{L}_0^r$ is the sum of the separate Liouville-space operators for the isolated many-electron quantum system and the free electromagnetic field (in the quantized-field formulation) while $\bar{V}^r$ is the electromagnetic-interaction operator. The relevant Liouvillian operator $\bar{L}^r$ is defined in terms of a commutator relationship involving the relevant-system Hamiltonian operator H^r, which describes the relevant many-electron quantum system in the presence of an electromagnetic field. The tetradic matrix elements $L^r_{\alpha\beta,\gamma\delta}$ of the relevant Liouville-space operator $\bar{L}^r$ may be introduced by means of the following relationships (Ben-Reuven and Rabin 1979):

$$\langle\alpha|\overline{\mathrm{L}}^{\mathrm{r}}\,\rho^{\mathrm{r}}|\beta\rangle=\langle\alpha|(1/\hbar)\left[\mathrm{H}^{\mathrm{r}},\rho^{\mathrm{r}}\right]|\beta\rangle=\sum_{\gamma}\sum_{\delta}\overline{\mathrm{L}}^{\mathrm{r}}_{\alpha\beta,\gamma\delta}\rho^{\mathrm{r}}_{\gamma\delta}=\sum_{\gamma}\sum_{\delta}(1/\hbar)\left(\mathrm{H}^{\mathrm{r}}_{\alpha\gamma}\delta_{\delta\beta}-\delta_{\alpha\gamma}\mathrm{H}^{\mathrm{r}}_{\delta\beta}\right)\rho^{\mathrm{r}}_{\gamma\delta}. \tag{32}$$

The electromagnetic field can be treated as a quantized field by introducing the Liouville-space basis set composed of the tensor products of the individual relevant many-electron quantum-system and photon occupation-number basis states.

The initial statistical state of the relevant quantum system is represented by the reduced, relevant density operator $\rho_i{}^r$. The final state of interest in the electromagnetic transition is formally represented by means of the relevant projection operator $P_f{}^r$. For the description of the single-photon spontaneous-emission process, the initial-state reduced, relevant density operator represents the relevant many-electron quantum system and no photons while the relevant final-state projection operator projects onto the subspace corresponding to the relevant many-electron quantum system in some final state and a single-photon in an observable mode. Natural generalizations can be introduced for the description of single-photon absorption and multi-photon (non-linear optical) processes. It is clear that the quantum-field-theory description of non-linear optical phenomena, in terms of multi-photon components of the initial-state reduced, relevant density operators and the relevant final-state projection operators, is practical only for not-too-intense electromagnetic fields, for which the numbers of photons in the observable field modes are not arbitrarily large. For intense laser fields, one can either adopt a basis set consisting of coherent states or treat the electromagnetic field as a classical field.

3.2.1. The frequency-domain self-energy operator

The Liouville-space self-energy operator $\bar{\Sigma}(+i\varepsilon)$ represents the spectral effects of the decoherence and relaxation processes arising from environmental collisional and radiative interactions. The Liouville-space self-energy operator $\bar{\Sigma}(+i\varepsilon)$ can be formally expressed in terms of the Zwanzig Liouville-space projection operators $\bar{\mathrm{P}}$ and $\bar{\mathrm{Q}}$. The Zwanzig Liouville-space projection operator $\bar{\mathrm{P}}$ has the explicit form $\left|\rho^{\mathrm{E}}\right\rangle\!\!\left\rangle\!\left\langle\!\!\left\langle \mathrm{I}^{\mathrm{E}}\right|\right.\right.$, where the symbol I^{E} occurring as a Liouville-space state vector denotes the environmental identity operator. The action of the projection operator $\bar{\mathrm{P}}$ on the density operator ρ can be illustrated in detail by means of the following operations:

$$\bar{\mathrm{P}}|\rho\rangle\!\rangle=|\rho^{\mathrm{E}}\rangle\!\rangle\langle\!\langle \mathrm{I}^{\mathrm{E}}|\rho\rangle\!\rangle=|\rho^{\mathrm{E}}\rangle\!\rangle\sum_{\gamma}\langle\!\langle\gamma,\gamma|\rho\rangle\!\rangle=|\rho^{\mathrm{E}}\rangle\!\rangle\sum_{\gamma}\langle\gamma|\rho|\gamma\rangle=|\rho^{\mathrm{E}}\rangle\!\rangle\otimes|\mathrm{Tr}_{\mathrm{E}}(\rho)\rangle\!\rangle=|\rho^{\mathrm{E}}\rangle\!\rangle\otimes|\rho^{\mathrm{r}}\rangle\!\rangle. \quad (33)$$

As a result of the average over the environmental degrees of freedom corresponding to the states denoted by $|\gamma\rangle$, the projection operator $\bar{\mathrm{P}}$ projects the density operator ρ for the entire (closed) interacting quantum system onto the subspace of the degrees of freedom for the reduced, relevant system (uncorrelated with the environmental degrees of freedom). The environmental average (partial-trace operation) therefore introduces the reduced, relevant density operator ρ^{r}. The complementary projection operator $\bar{\mathrm{Q}}=1-\bar{\mathrm{P}}$ projects onto the orthogonal subspace of the irrelevant (environmental) degrees of freedom (taking into account the system-environment correlations). With these definitions, the Liouville-space self-energy operator $\bar{\Sigma}(z)$ can be expressed, as a function of the complex variable z, by means of the relationships (Ben-Reuven and Rabin 1979, Jacobs, Cooper and Haan 1994):

$$\bar{\Sigma}(z) = \bar{P}\bar{V}^{ir}\bar{P} + \bar{P}\bar{V}\bar{Q}\frac{1}{z - \bar{Q}\bar{L}\bar{Q}}\bar{Q}\bar{V}\bar{P} = \mathrm{Tr}_E\left[\left(\bar{V}^{ir} + \bar{V}\bar{Q}\frac{1}{z - \bar{Q}\bar{L}\bar{Q}}\bar{Q}\bar{V}\right)\rho^E\right]. \tag{34}$$

The complete Liouville-space operator $\bar{L}$ is defined in terms of the total Hamiltonian operator for the entire (closed) interacting quantum system. The total Liouville-space interaction operator $\bar{V}$ is partitioned as $\bar{V} = \bar{V}^r + \bar{V}^{ir}$, where the irrelevant interaction operator $\bar{V}^{ir}$ includes the environmental interactions. The Liouville-space projection-operator formalism has the advantage that the abstract analysis can be carried out in considerable generality, without the need to initially specify the detailed physical nature of the environmental interactions. We emphasize that the fundamental quantum-mechanical treatment for the Liouville-space self-energy corrections can provide a general theoretical understanding of the influence of the environmental interactions, which are often treated by the introduction of oversimplified assumptions or phenomenological parameters.

3.2.2. Conventional frequency-domain approximations

The general tetradic-matrix expression for the electromagnetic-transition rate given by Eq. (31) can be used to determine the overall spectral-line shape for an arbitrary array of (possibly overlapping) spectral lines due to radiative transitions involving the closely-spaced substates of the relevant many-electron quantum system. The substates can consist of the Stark-Zeeman components that are associated with the individual many-electron atomic energy-level states, which may be specified in the LS, fine-structure (J) or hyperfine-structure (F) representation. In the widely used isolated-line approximation, the expressions for the standard Lorentzian spectral-line shape parameters (the line shifts and widths) can be recovered from the diagonal tetradic matrix elements of the general expression for the Liouville-space self-energy operator $\bar{\Sigma}(+i\varepsilon)$ given by Eq. (34). When the system-environment interactions are sufficiently weak, the Liouville-space self-energy operator $\bar{\Sigma}(+i\varepsilon)$ may be expressed as a perturbation expansion involving increasing powers of the total Liouville-space interaction operator $\bar{V}$. If only the lowest-order non-vanishing contribution is retained in this perturbation expansion (which is often referred to as the Born approximation), the total (isolated-Lorentzian-line) shift and width can be expressed simply as the sums of the partial contributions from the elementary collisional and radiative decoherence and relaxation processes acting alone. Quantum-mechanical interference between the individual transition amplitudes can occur in the high-order contributions to the isolated-Lorentzian-line width and shift, as well as in the more general tetradic-matrix form of the spectral-line profile, which is applicable to overlapping lines. For the description of intense-field (non-linear optical) phenomena, the states of the relevant many-electron quantum system can be taken to be "dressed states" , which are usually determined including the interaction with a classical (possibly multiple-mode) electromagnetic field.

3.3. The time-domain (equation-of-motion) formulation

The time-domain (equation-of-motion) formulation of the reduced-density-operator description is based on the equation of motion for the reduced, relevant density operator $\rho^r(t)$, which describes the dynamics of the relevant many-electron quantum system combined (entangled) with the observable modes of a quantized electromagnetic field. The reduced equation of motion can be derived from the more general quantum Liouville (or Liouville-von Neumann) equation for the combined, complete density operator $\rho(t)$. The reduced equation of motion can be expressed in the generalized-Master-equation form (Burnett, Cooper, Ballagh and Smith 1980, Jacobs, Cooper and Haan 1994):

$$i\frac{\partial}{\partial t}\rho^r(t) = \bar{L}^r(t)\rho^r(t) + \int_{t_0}^{t} dt'\,\bar{\bar{\Sigma}}(t,t')\rho^r(t'). \qquad (35)$$

This is an integro-differential equation, which is expressed in terms of the Liouville-space self-energy operator kernel $\bar{\bar{\Sigma}}(t,t')$. The time-domain (equation-of-motion) formulation provides a general framework for the systematic evaluation of the macroscopic electromagnetic-response functions describing linear and non-linear optical interactions. These electromagnetic-response functions are usually defined within the context of a simpler semiclassical description, in which the dynamical evolution of the relevant many-electron quantum system is investigated using the quantum-open-systems equation of motion for the reduced density operator while the electromagnetic field is treated according to classical electrodynamics (i. e., the Maxwell equations).

The reduction procedure provides a closed-form set of equations for the various matrix elements of the reduced, relevant density operator $\rho^r(t)=\bar{P}\rho(t)$, which represents (at an arbitrary time t) the statistical state of the relevant quantum system. The relevant quantum system may be taken as the ensemble of many-electron atomic systems either combined (entangled) with the relevant modes of a quantized electromagnetic field and/or in the presence of an external classical electromagnetic field. The closed-form result given by Eq. (35) has been obtained by neglecting the initial-state correlations between the relevant and environmental degrees of freedom, which are described by an omitted contribution involving the irrelevant projection $\bar{Q}\rho(t_0)$ (evaluated at the initial time t_0). The initial-state correlations are automatically excluded by the standard approximation of assuming that the entire initial-state density operator $\rho(t_0)$ is expressible as an uncorrelated, tensor product of individual density operators representing the separate (isolated) relevant many-electron quantum system, the free electromagnetic field, and the environment.

3.3.1. The time-domain self-energy operator

In terms of the Zwanzig Liouville-space projection operators $\bar{P}$ and $\bar{Q}$, the Liouville-space self-energy operator kernel $\bar{\Sigma}(t,t')$ can be formally expressed by means of the relationships (Burnett, Cooper, Ballagh and Smith 1980, Jacobs, Cooper and Haan 1994):

$$\bar{\Sigma}(t,t')=-i\bar{P}\bar{V}(t)\bar{Q}\bar{g}_Q(t,t')\bar{Q}\bar{V}(t')\bar{P}=-i\mathrm{Tr}_E\left[\bar{V}(t)\bar{Q}\bar{g}_Q(t,t')\bar{Q}\bar{V}(t')\rho^E\right]. \tag{36}$$

The Q-subspace projection $\bar{g}_Q(t,t')$ of the Liouville-space propagator is defined, in terms of the time-ordering operator *T*, as follows:

$$\bar{g}_Q(t,t')=T\exp\left[-i\int_{t'}^{t}dt''\bar{Q}\bar{L}(t'')\bar{Q}\right]. \tag{37}$$

The Liouville-space operator $\bar{Q}\bar{L}(t)\bar{Q}$ is a non-Hermitian operator, corresponding to the irreversibility resulting from the environmental average (partial-trace operation). Consequently, the Liouville-space propagator defined by Eq. (37) will be a non-unitary operator. The Liouville-space self-energy operator kernel $\bar{\Sigma}(t,t')$, which appears in the time-domain (equation-of-motion) formulation, can be related to the time-independent Liouville-space self-energy operator $\bar{\Sigma}(z)$, occurring in the frequency-domain (resolvent-operator) formulation. This relationship can be most directly derived by invoking the Fourier-transform relationship between the time-domain propagator and corresponding frequency-domain resolvent operator.

3.3.2. The Markov (short-memory-time) approximation

In the commonly adopted Markov (short-memory-time) approximation, the Liouville-space self-energy operator kernel $\bar{\Sigma}(t,t')$ is assumed to be independent of time.

The Markov approximation may be introduced into the equation of motion for the reduced, relevant density operator $\rho^r(t)$ by utilizing the relationship:

$$\bar{\Sigma}(t,t')=\lim_{z\to i0}\bar{\Sigma}(z)\delta(t-t'). \qquad (38)$$

Due to the presence of the component of the Liouville-space operator representing the free electromagnetic field in Eq. (34), the Liouville-space self-energy operator $\bar{\Sigma}(z)$ in the quantized-field formulation will in general be a function of the photon frequency. In the Markov approximation, the frequency-domain Liouville-space self-energy operator $\bar{\Sigma}(i0)$, which will subsequently be denoted by $\bar{\Sigma}$, is independent of the photon frequency. However, if a "dressed – state" basis set is adopted, taking into account the influence of a classical electromagnetic field, the Markov form of the frequency-domain Liouville-space self-energy operator will acquire an implicit dependence on the amplitude and frequency of the external (applied) time-dependent field. For the treatment of ultra-short-pulse electromagnetic interactions, the Markov approximation is not expected to be valid.

3.4. The reduced-density-operator description in the Floquet representation

In this subsection, we present a formulation of the reduced-density-operator description in the Liouville-space multiple-mode Floquet-Fourier representation. Our formulation is essentially based on the formulation that has been introduced by Ben-Reuven and Rabin (1979) and by Rabin and Ben-Reuven (1979). A closely related

Liouville-space multiple-mode Floquet-Fourier formulation has also been presented by Chu and Telnov (2004). As discussed in the introduction, our primary goal is the development of a Liouville-space formulation that incorporates as a starting point the ordinary Hilbert-space (Hamiltonian) *R*-matrix-Floquet description discussed in the preceding section.

We shall consider the interaction of an ensemble of many-electron atomic systems with an intense (possibly multiple-mode) classical electromagnetic field together with a weak multiple-mode electromagnetic field, which may be treated either as a classical field or as a quantum field. The intense electromagnetic field, which is traditionally referred to as the pump or control field, is most appropriately treated non-perturbatively, using the Floquet method or an alternative optical-Bloch-equation approach. In the theory of linear and non-linear optical phenomena, the weak electromagnetic field, which is often referred to as the probe or propagating field, may be treated using a perturbation expansion of the reduced density operator. This perturbation expansion is usually introduced within the framework of a semiclassical description of the electromagnetic interaction, in which the reduced density operator describing the ensemble of many-electron atomic systems is expanded in powers of the classical electromagnetic field. The perturbation-theory formulation for a quantized field, which could be based on the representation corresponding to the complete set of photon-occupation-number (Fock-space) states, is most rigorously developed within the framework of an open-systems extension of quantum electrodynamics. This quantized-field formulation is expected to be much more difficult than the classical-field description and, to the best of our knowledge, has not been fully developed in applications to multi-photon processes and non-linear optical phenomena. In the present investigation, we introduce a semiclassical Liouville-space Floquet formulation, in which the entire, combined electromagnetic field, consisting of the pump field and the probe field, is treated as a classical field and represented within the framework of a multiple-mode Floquet-Fourier expansion of the reduced density operator describing the ensemble of many-electron atomic systems. The present formulation will be applied to specific electromagnetic processes involving ensembles of many-electron atomic systems in the following sections.

The time evolution of the reduced, relevant density operator $\rho^r(t)$ describing the ensemble of many-electron atomic systems may be determined by means of either the generalized (non-Markovian) form (indicated by the equality) or the simplified (Markovian) form (indicated by the symbol $\rightarrow$) of the semiclassical Liouville-space equation of motion:

$$i\partial\rho^r(t)/\partial t = \bar{L}^r(t)\rho^r(t) + \int_{t_0}^{t} dt'\,\bar{\Sigma}(t,t')\rho^r(t') \rightarrow \bar{L}^r(t)\rho^r(t) + \bar{\Sigma}\rho^r(t)\,. \tag{39}$$

The relevant Liouvillian operator $\bar{L}^r$, which is defined by Eq. (32), can be expressed as a sum of an unperturbed Liouvillian operator $\bar{L}_0^r$ and a Liouville-space interaction (perturbation) operator $\bar{V}^r$. The two versions of the semiclassical equation of motion given by Eq. (39) will now be understood to differ from the equation of motion expressed by Eq. (35), which is defined in the more extensive Liouville space corresponding to the tensor-product states of the relevant many-electron quantum system and a quantized electromagnetic field. When the electromagnetic field is treated as a classical field, the reduced, relevant density operator $\rho^r(t)$ is defined entirely within the Liouville subspace of the states of the relevant many-electron quantum system.

The total (relevant) Hamiltonian operator $H^r(t)$, in terms of which the Liouville-space operator $\overline{L}^r$ is defined, can be written as the sum of a zero-order (unperturbed) Hamiltonian operator H_0^r and an electromagnetic-interaction (perturbation) operator $V^r(t)$ as follows:

$$H^r(t)=H_0^r+V^r(t). \tag{40}$$

In the remainder of this section, the superscript "r" will be omitted.

The zero-order (relevant) Hamiltonian H_0 will be taken to be the non-relativistic Hamiltonian operator H_{N+1} occurring in Eq. (5) and expressed by means of Eq. (6). This zero-order Hamiltonian operator describes a single (N+1)-electron atomic system in the absence of the electromagnetic field. The eigenstates of this Hamiltonian operator consist of the complete set of bound, non-resonant continuum, and autoionizing states of the isolated (N+1)-electron atomic system. As discussed above, in our Liouville-space formulation the classical electromagnetic field will be taken to be the entire, combined electromagnetic field, consisting of both the intense (pump or control) field and the weak (probe or propagating) field. In the non-relativistic, Coulomb-gauge representation of the electromagnetic interaction that is expressed in terms of the electromagnetic-field vector potential, it is customary to introduce the decomposition $V(t)=V^1(t)+V^2(t)$, where the linear and quadratic components of the electromagnetic interaction are given by Eqs. (8) and (9), respectively. In this investigation, we will utilize the alternative representation that is expressed in terms of the electric and magnetic fields, together with the corresponding electromagnetic dipole and multipole moments. As discussed in section 2, we will retain only the leading (electric-dipole) contribution given by Eq. (10).

In the applications discussed in sections 4 and 5, we will consider an ensemble of N_0 identical many-electron atomic systems. If the interactions among the different many-electron atomic systems are neglected, the (reduced) density operator representing the statistical state of the entire relevant many-electron quantum system can be expressed in the tensor-product form $\rho=\bigotimes_{i=1}^{N_0}\rho_i$, where ρ_i denotes the (reduced) density operator describing a single many-electron atomic system. In this case, the wave functions representing the entire relevant-quantum-system states can be expressed as tensor products of the individual atomic-state wave functions, each of which pertains to a single many-electron atomic system. The matrix elements involving the various single-electron operators (e. g., the electric-dipole-moment operator) can be reduced to the corresponding matrix elements for a single many-electron atomic system. The final result for an ensemble of identical non-interacting many-electron atomic systems is then obtained by simply multiplying the contribution of each of the identical many-electron atomic systems by their number density in the ensemble. In a future investigation, we will introduce a hierarchical reduced-density-operator formulation, similar to the formulation that has been presented by Ben-Reuven (1980), in which the tensor-product form of the individual (reduced) atomic density operators ρ_i will occur as the lowest-order approximation in the set (hierarchy) of (reduced) density operators describing two or more interacting many-electron atomic systems. This hierarchical formulation will provide a fundamental framework for the systematic description of the interactions among the different many-electron atomic systems, which are expected to play an important role in cooperative electromagnetic phenomena such as superradiance.

3.4.1. The multiple-mode Floquet-Fourier expansion of the reduced density operator

The interaction of the ensemble of many-electron atomic systems with the entire, combined classical electromagnetic field can be treated non-perturbatively by introducing the multiple-mode Floquet-Fourier expansion of the (reduced) density operator (Ben-Reuven and Rabin 1979, Rabin and Ben-Reuven 1979, Chu and Telnov 2004):

$$\left|\rho(t)\right\rangle\!\!\right\rangle=\sum_{\vec{n}}\left|\rho_{\vec{n}}(t)\right\rangle\!\!\right\rangle\exp\left(-i\vec{n}\bullet\vec{\omega}t\right). \tag{41}$$

The product $\vec{n}\bullet\vec{\omega}$ has been defined by Eq. (13) in terms of a summation over the irreducible set of the discrete (incommensurate) Floquet-Fourier modes comprising the classical electromagnetic field. As a result of the multiple-mode Floquet-Fourier expansion, the (reduced) density operator can be expressed in the Liouville-space Floquet representation as follows:

$$\left|\rho(t)\right\rangle\!\rangle=\sum_{a}\sum_{b}\sum_{\vec{n}}\left|ab;\vec{n}\right\rangle\!\rangle\langle\!\left\langle ab;\vec{n}\middle|\rho(t)\right\rangle\!\rangle, \tag{42}$$

where the field-free states of a many-electron atomic system are denoted by the lower case Latin letters a and b. The Liouville-space Floquet representation is obtained as an extension of the field-free Liouville-space representation to include the additional set of indices corresponding to the multiple-mode Floquet-Fourier mode numbers, which are collectively represented by the vector $\vec{n}$. It should be noted that, in the specification of the Liouville-space Floquet tensor-product states $\left|ab;\vec{n}\right\rangle\!\rangle \equiv |a\rangle\langle b|\otimes|\vec{n}\rangle$, the individual components of the composite mode-number vector $\vec{n}$ will corresponding to pairs of the individual mode numbers that have been introduced in the ordinary Hilbert-space Floquet-Fourier wave function expansion given by Eq. (14). As a result of the expansions for the (reduced) density operator given by Eqs. (41) and (42), the individual Floquet-Fourier components $\langle\!\left\langle ab;\vec{n}\middle|\rho(t)\right\rangle\!\rangle$ satisfy an infinite set of coupled equations of motion that involves only explicitly time-independent electromagnetic-interaction coefficients. However, as discussed below, the advantage of this time independence will be fully realized only with the assumption that the Liouville-space self-energy operator can be expressed in a field-independent and Markovian form.

In an alternative, perturbation-theory treatment of the interaction with the weak, multiple-mode classical electromagnetic field, the (reduced) density operator could be represented by means of an additional expansion involving the various powers of the weak field. Accordingly, Eq (42) would then be replaced by a more complicated form, which would be expressed in terms of summations over both the Floquet-Fourier mode numbers corresponding to the intense electromagnetic field and the powers of the weak electromagnetic field. If this alternative approach is adopted in a future extension of this investigation, it might be convenient to extend the set of Floquet-Fourier modes specified by the number vector $\vec{n}$ to include both the intense-field and the weak-field modes, with the understanding that the exclusively weak-field modes should be consistently treated in the ordinary Hilbert-space Floquet-Fourier representation given by Eq. (14). In our Liouville-space formulation, the interaction with the entire, combined classical electromagnetic field will be treated in a non-perturbative manner, on the basis of the multiple-mode Floquet-Fourier expansion of the (reduced) density operator given by Eq. (42).

3.4.2. The coupled equations for the Floquet-Fourier components of the (reduced) atomic density operator

We now introduce into the Liouville equation of motion given by Eq. (39) the (reduced)-density-operator expansion given by Eq. (42), together with the electric-dipole form expressed by Eq. (10) for the interaction of the ensemble of many-electron atomic systems with the entire, combined multiple-mode classical electromagnetic field. We thereby obtain an infinite set of coupled integro-differential equations for the Floquet-Fourier components $\langle\langle ab;\vec{n}|\rho(t)\rangle\rangle$ of the (reduced) atomic density operator. An individual member of this set may be explicitly expressed in the detailed matrix-element form:

$$
\begin{aligned}
&[i(\partial/\partial t)-(\omega_a-\omega_b-\vec{n}\bullet\vec{\omega})]\langle\langle ab;\vec{n}|\rho(t)\rangle\rangle \\
&-\left(\frac{1}{\hbar}\right)\sum_c\sum_j\Big[V_{ac}(\vec{k}_j,\omega_j)\langle\langle cb;\vec{n}_j^-|\rho(t)\rangle\rangle-\langle\langle ac;\vec{n}_j^-|\rho(t)\rangle\rangle V_{cb}(\vec{k}_j,\omega_j)\Big] \\
&-\left(\frac{1}{\hbar}\right)\sum_c\sum_j\Big[V_{ac}^*(\vec{k}_j,\omega_j)\langle\langle cb;\vec{n}_j^+|\rho(t)\rangle\rangle-\langle\langle ac;\vec{n}_j^+|\rho(t)\rangle\rangle V_{cb}^*(\vec{k}_j,\omega_j)\Big] \qquad (43) \\
&=\sum_c\sum_d\sum_{\vec{n}'}\int_{t_0}^{t}dt'\langle\langle ab;\vec{n}|\overline{\Sigma}(t,t')|cd;\vec{n}'\rangle\rangle\langle\langle cd;\vec{n}'|\rho(t')\rangle\rangle .
\end{aligned}
$$

We have omitted the subscripts (N+1) and j on the electromagnetic-interaction operator coefficients $V(\vec{k}_j,\omega_j)$, which are defined by Eq. (16). We have also employed the modified Floquet-Fourier mode number vectors $\vec{n}_j^{\pm}$, which are defined by Eq. (17).

We note that Ben-Reuven and Rabin (1979) have presented an extension of the infinite set of coupled equations of motion for the Floquet-Fourier components $\langle\langle ab;\vec{n}|\rho(t)\rangle\rangle$ of the (reduced) atomic density operator, which can be adopted to incorporate the Doppler effect arising from the translational states associated with the center-of-mass motion of a many-electron atomic system. These translational states can be represented in terms of the position variable $\vec{r}$ and the momentum variable $\vec{p}=m\vec{v}$ corresponding to the center of mass velocity $\vec{v}$. The appropriate extension of Eq. (43) can be obtained by introducing the substitution $\vec{n}\bullet\vec{\omega}\rightarrow\vec{n}\bullet\vec{\omega}-\vec{v}\bullet\vec{k}$, where the multiple-mode wave-vector $\vec{k}$ is defined in terms of the individual wave-vectors $\vec{k}_j$ by $\vec{k}=\sum_j n_j\vec{k}_j$. The "dressed atomic – state" coherences are then specified in the more detailed form $\langle\langle ab;\vec{p}+\hbar\vec{k},\vec{p};\vec{n}|\rho(\vec{r},\vec{v},t)\rangle\rangle$.

Ben-Reuven (1980) has introduced a more general (reduced) density-operator formulation, which can be employed to incorporate the cooperative effects of two or more interacting many-electron atomic systems in the presence of intense electromagnetic fields. In addition to the Master equation for the "dressed atomic – state" coherences pertaining to a single many-electron atomic system, which is expressed by Eq. (43), a Liouville-space Bethe-Salpeter type equation has been derived for the two-atom coherences, incorporating the mutual interaction of a pair of coherently-excited many-electron atomic systems. For higher-rank coherences, involving clusters of three or more interacting many-electron atomic systems, it is necessary to introduce a set (hierarchy) of coupled integro-differential equations in order to obtain the set of coherences pertaining to the various numbers of coherently-excited many-electron atomic systems. Since the number of many-electron atomic systems is very large, it is necessary to introduce an appropriate truncation procedure in order to restrict the description to a small number of coherently-excited many-electron atomic systems.

If the Liouville-space self-energy contribution occurring on the right-hand side is omitted, the set of coupled equations given by Eq. (43) for the (reduced)-density-operator components $\langle\langle ab;\vec{n}|\rho(t)\rangle\rangle$ can be expressed in a form that is entirely equivalent to the set of coupled ordinary Hilbert-space (Hamiltonian) equations given by Eq. (15). The solutions to this set of coupled equations correspond to "dressed" states of the (N+1)-electron atomic system, in the presence of the combined, classical electromagnetic field but in the absence of the environmental collisional and radiative interactions.

The frequency variables that occur in the set of coupled equations given by Eq. (43) are related to the eigenvalues of the unperturbed (N+1)-electron atomic Hamiltonian operator H_{N+1} as follows:

$$E_a = \hbar\omega_a \quad \text{and} \quad E_b = \hbar\omega_b . \tag{44}$$

It should be noted that complex eigenvalues might be obtained from a "dressed – atom" approach, which is based on the set of coupled equations describing the (N+1)-electron atomic system in the presence of the classical electromagnetic field. The real parts can include the electromagnetically induced shifts that correspond to the dynamical Stark energy-level shifts, while the imaginary parts can include the widths due to multi-photon ionization processes from the (N+1)-electron atomic system in the classical electromagnetic field.

3.4.3. The Liouville-space Floquet-Fourier self-energy operator

If the field-dependence of the Liouville-space self-energy operator kernel is neglected, the tetradic matrix elements occurring in Eq. (43) can be simplified by employing the relationship:

$$\left\langle ab;\vec{n}\middle|\overline{\Sigma}(t,t')\middle|cd;\vec{n}'\right\rangle = \overline{\Sigma}_{ab,cd}(t,t')\delta_{\vec{n},\vec{n}'} . \tag{45}$$

As discussed by Ben-Reuven and Rabin (1979), if this simplifying approximation can be justified, then the field-free collisional and radiative decoherence and relaxation rates could be used in the set of coupled equations of motion for the Floquet-Fourier components of the (reduced) atomic density operator. (A less severe approximation, which would permit the incorporation of some intense-field effects, would involve retaining the diagonality with respect to $\vec{n}$ while at the same time allowing the tetradic matrix elements of the Liouville-space self-energy operator kernel to depend on $\vec{n}$.)

In the Markov approximation corresponding to Eq. (38), the relationship given by Eq. (45) can be simply expressed in terms of the tetradic matrix elements of the time-independent and frequency-independent Liouville-space self-energy operator $\overline{\overline{\Sigma}}$. It should be noted that the implementation of the full non-Markovian version of the (reduced)-density-operator formulation, which may be necessary for the precise description of ultra-short-pulse coherent electromagnetic interactions, could be more difficult, because the advantage of the Floquet-Fourier representation, of removing the explicit time dependence of the coefficients in the set of coupled equations given by Eq. (43) for the (reduced)-density-operator components, would not be fully realized. However, the solutions of Eq. (43) will still be functions of time, even if the Liouville-space self-energy operator is assumed to have a field-independent and Markovian form.

3.4.4. The Liouville-space R-matrix-Floquet formulation

We introduce a Liouville-space formulation for the incorporation, as a starting point, of the ordinary Hilbert-space (Hamiltonian) *R*-matrix-Floquet approach that was originally introduced by Burke, Francken, and Joachain (1990, 1991), which has been reviewed in section 2. The objective of our Liouville-space formulation is to provide a fundamental framework for the systematic treatment of the effects of the decoherence and relaxation phenomena due to environmental collisional and radiative interactions, based on a detailed description of the multi-level structure of the (N+1)-electron atomic system in the presence of a multiple-mode classical electromagnetic field. In order to introduce a compact notation for the set of coupled (reduced)-density-operator equations given by Eq. (43), the individual Floquet-Fourier components $\left|\rho_{\vec{n}}(t)\right\rangle\!\rangle$ will now be represented by the multiple-mode Liouville-space state vector $\left|\vec{\rho}\right\rangle\!\rangle$. In a manor analogous to Eq. (19), the set of coupled (reduced)-density-operator equations can be expressed in the compact matrix-operator forms:

$$\left[i\left(\partial/\partial t\right)-\bar{\mathbf{L}}_{\mathbf{F}}\right]\left|\vec{\rho}(t)\right\rangle\!\rangle=\int_{t_0}^{t}dt'\,\bar{\mathbf{\Sigma}}(t,t')\left|\vec{\rho}(t)\right\rangle\!\rangle\rightarrow\bar{\mathbf{\Sigma}}\left|\vec{\rho}(t)\right\rangle\!\rangle. \qquad (46)$$

The Floquet Liouville-space operators $\bar{\mathbf{L}}_{\mathbf{F}}$ and $\bar{\mathbf{\Sigma}}$ are now treated as matrices of Liouville-space operators in the multiple-mode vector space of the incommensurate Floquet-Fourier modes specified by the composite number vector $\vec{n}$. The diagonal elements of this matrix $\bar{\mathbf{L}}_{\mathbf{F}}$ are generated by the modified Liouvillian operator $\bar{\mathbf{L}}_{\mathbf{0}}$ defined as follows:

$$\overline{\mathbf{L}}_{\mathbf{0}} = \overline{\mathrm{L}}_{N+1} - \vec{n} \bullet \vec{\omega}\bar{I}. \qquad (47)$$

The introduction of this modified Liouvillian operator accomplishes the objective of removing the time-dependence of the electromagnetic-interaction coefficients in the set of coupled (reduced)-density-operator equations. The non-diagonal elements of the Floquet Liouvillian matrix operator $\overline{\mathbf{L}}_{\mathbf{F}}$ are either the Liouville-space interaction-operator coefficients $\overline{V}(\vec{k}_j,\omega_j)$ or the complex-conjugate operator coefficients $\overline{V}^{*}(\vec{k}_j,\omega_j)$.

In order to obtain a formal solution to Eq. (46), we would like to introduce a spectral representation for the Floquet Liouvillian matrix operator $\overline{\mathbf{L}}_{\mathbf{F}}$. Since the corresponding Floquet Hamiltonian matrix operator $\mathbf{H}_{\mathbf{F}}$ is in the general case a non-Hermitian operator, it will be necessary to adopt the biorthogonal representation involving the right and left eigenvectors of this matrix operator; as described by Burke (2011), by Fleischer and Moiseyev (2005), and by Joachain, Kylstra, and Potvliege (2012). We will be guided by the Liouville-space formulations based on this biorthogonal representation that have been presented by Chu and Telnov 2004), by Faisal (1987), and by Sauvan and Dalimier (2009).

The right and left eigenvectors of the non-Hermitian Floquet Hamiltonian matrix operator $\mathbf{H}_{\mathbf{F}}$ will be represented by the eigenvector wave functions $\left|\vec{\psi}_{\lambda}\right\rangle$ and $\left\langle\vec{\chi}_{\lambda}\right|$, respectively. The eigenvalue equations satisfied by the right and left eigenvector wave functions can then be written in the forms:

$$\mathbf{H_F}|\vec{\psi}_\lambda\rangle \; = \; E_\lambda|\vec{\psi}_\lambda\rangle \tag{48}$$

and

$$\langle\vec{\chi}_\lambda|\mathbf{H_F} \; = \; E^*_\lambda\langle\vec{\chi}_\lambda|. \tag{49}$$

The right and left eigenvector wave functions can be constructed to satisfy the orthonormalization condition $\langle\vec{\chi}_\lambda|\vec{\psi}_{\lambda'}\rangle \; = \; \delta_{\lambda\lambda'}$. The completeness relationship can be expressed as $\sum_\lambda|\vec{\psi}_\lambda\rangle\langle\vec{\chi}_\lambda| \; = \; 1$. The biorthogonal representation is based on the "dressed – atom" states that are obtained using the ordinary Hilbert-space *R*-matrix-Floquet method. These states may have complex eigenvalues corresponding to the multi-photon ionization and autoionization rates.

If the eigenvalues and eigenvectors of the Floquet Liouvillian matrix operator $\bar{\mathbf{L}}_\mathbf{F}$ are denoted by ω_λ and $|\vec{\rho}_\lambda\rangle\rangle$, respectively, a spectral representation of this Liouville-space matrix operator can be introduced to obtain a formal solution of the set of coupled equation given by Eq. (46). Within the framework of the simplifying Markov and field-independent approximations for the Liouville-space self-energy operator, this formal solution may be expressed, in the frequency-domain formulation, in the form:

$$|\vec{\rho}(\omega)\rangle\rangle=\sum_\lambda|\vec{\rho}_\lambda\rangle\rangle\frac{1}{\omega-\omega_\lambda}\langle\langle\vec{\rho}_\lambda|\bar{\boldsymbol{\Sigma}}|\vec{\rho}(\omega)\rangle\rangle. \tag{50}$$

This Liouville-space frequency-domain formal solution, although analogous to the ordinary Hilbert-space solution given by Eq. (22), differs in that the spectral representation is now based on the right and left eigenvectors of the non-Hermitian Floquet Hamiltonian matrix operator $\mathbf{H_F}$. The Liouville-space frequency-domain formal solution might be most advantageously utilized as a starting point for the introduction of a perturbation expansion in terms of the Liouville-space self-energy matrix operator $\bar{\mathbf{\Sigma}}$. For a non-perturbative approach, Eq. (50) can be employed to obtain a set of coupled algebraic equations for the quantities $\langle\langle\vec{\rho}_\lambda|\bar{\mathbf{\Sigma}}|\vec{\rho}(\omega)\rangle\rangle$. This set of coupled algebraic equations can be written as follows:

$$\sum_{\lambda'} M_{\lambda\lambda'}\langle\langle\vec{\rho}_{\lambda'}|\bar{\mathbf{\Sigma}}|\vec{\rho}(\omega)\rangle\rangle=\sum_{\lambda'}\left[\langle\langle\vec{\rho}_\lambda|\bar{\mathbf{\Sigma}}|\vec{\rho}_{\lambda'}\rangle\rangle\frac{1}{\omega-\omega_{\lambda'}}-\delta_{\lambda\lambda'}\right]\langle\langle\vec{\rho}_{\lambda'}|\bar{\mathbf{\Sigma}}|\vec{\rho}(\omega)\rangle\rangle=0. \tag{51}$$

A solution can be obtained only if the determinant of the matrix M in Eq. (51) vanishes.

The density-operator eigenvectors $|\vec{\rho}_\lambda\rangle\rangle$ of the Floquet Liouvillian matrix operator $\bar{\mathbf{L}}_\mathbf{F}$ are to be constructed from the corresponding ordinary Hilbert-space right and left eigenvector wave functions, which will be denoted by $|\vec{\psi}_{\lambda_i}\rangle$ and $\langle\vec{\chi}_{\lambda_i}|$, respectively, where i = 1 or 2. Because of the omission of the Liouville-space self-energy matrix operator $\bar{\mathbf{\Sigma}}$ from the eigenvalue problem corresponding to the Floquet Liouvillian matrix operator $\bar{\mathbf{L}}_\mathbf{F}$, it is permissible to employ the following relationship:

$$|\vec{\rho}_{\lambda}\rangle\rangle = |\vec{\psi}_{\lambda_1}\rangle\langle\vec{\chi}_{\lambda_2}| . \tag{52}$$

Accordingly, the single Liouville-space state index λ in Eqs. (50), (51), and (52) is introduced to collectively represent the set of the two ordinary Hilbert-space state indices λ_1 and λ_2. The corresponding eigenvalues are related by $\omega_{\lambda} = \omega_{\lambda_1} - \omega^{*}_{\lambda_2}$. The indices λ_1 and λ_2 designate the states pertaining to the right and left eigenvectors of the non-Hermitian Floquet Hamiltonian matrix operator $\mathbf{H_F}$. The right and left eigenvector wave functions are assumed to have been obtained by means of the ordinary Hilbert-space *R*-matrix-Floquet method, which has been reviewed in section 2. The states designated by the indices λ_1 and λ_2, which are defined within the tensor-product space of the unperturbed (field-free) (N+1)-electron atomic states and the multiple-mode Floquet mode numbers, should be distinguished from the states denoted entirely by the indices a and b, which have been used for the unperturbed states of the isolated many-electron atomic system.

The right and left eigenvector wave functions $|\vec{\psi}_{\lambda_i}\rangle$ and $\langle\vec{\chi}_{\lambda_i}|$ are assumed to have been determined by employing the ordinary Hilbert-space *R*-matrix-Floquet method utilizing the procedures described in Appendix 3. These eigenvector wave functions may now be employed for the construction of the density-operator eigenvectors $|\vec{\rho}_{\lambda}\rangle\rangle$ that are defined by Eq. (52). The detailed relationship can be explicitly expressed as follows:

$$\left\langle\left\langle \mathbf{X}_{N+1},\mathbf{X}'_{N+1} \middle| \vec{\rho}_{\lambda} \right\rangle\right\rangle = \left\langle \mathbf{X}_{N+1} \middle| \vec{\psi}_{\lambda_1} \right\rangle \left\langle \vec{\chi}_{\lambda_2} \middle| \mathbf{X}'_{N+1} \right\rangle = \vec{\psi}_{\lambda_1}\left(\mathbf{X}_{N+1}\right)\vec{\chi}^{+}_{\lambda_2}\left(\mathbf{X}'_{N+1}\right). \tag{53}$$

The superscript "+" is used to indicate the required adjoint form of the eigenvector wave function. By means of the relationship given by Eq. (53),the formal solutions for the set of coupled frequency-domain equations given by Eq. (50) can be constructed from the ordinary Hilbert-space right and left eigenvector wave functions that are obtained by means of the *R*-matrix Floquet methods reviewed in section 2.

It should be emphasized that the ordinary Hilbert-space right and left eigenvector wave-function must correspond to the *R*-matrix Floquet wave functions that are continuously defined throughout all spatial regions and also satisfy the asymptotic boundary conditions corresponding to the specific electromagnetic processes of interest. Accordingly, it will be necessary to construct the appropriate linear combinations of the individual wave-functions expansions that have been introduced for the separate spatial regions in section 2. Furthermore, it is apparent that the left eigenvector wave functions should satisfy the time-reversed, incoming-wave boundary conditions (Goldberger and Watson 1964). The required procedures are described in Appendix 3.

We have emphasized that the ordinary Hilbert-space right and left eigenvector wave-function that are to be constructed from the *R*-matrix Floquet wave functions, and the corresponding density-operator eigenvectors $|\vec{\rho}_{\lambda}\rangle\rangle$, pertain to an ensemble of non-interacting many-electron atomic systems. The applications discussed in sections 4 and 5 will be accordingly restricted by this assumption. However, we have pointed out that this assumption is not valid for coherently-excited many-electron systems, where cooperative electromagnetic phenomena can play an important role. In this case, it is necessary to investigate the influence of the interactions amount the many-electron atomic systems. A set (hierarchy) of coupled (reduced) density-operator equations, such as that introduced by Ben-Reuven (1980), can provide a general framework for the systematic investigation of these interactions. Furthermore, this hierarchical (reduced) density-operator formulation can be implemented utilizing a Liouville-space basis set obtained from the ordinary Hilbert-space right and left eigenvector wave-function that are constructed from the *R*-matrix Floquet wave functions.

4. Application of the Liouville-space *R*-matrix-Floquet formulation to electromagnetically induced transparency and related pump-probe optical phenomena

In this section, we consider the application of the Liouville-space *R*-matrix-Floquet formulation presented in the previous section to resonant and coherent non-linear optical processes in many-electron atomic systems, particularly electromagnetically induced transparency and related pump-probe optical phenomena. Our primary objective is to provide a framework for the incorporation of a realistic representation of the many-electron laser-dressed atomic structure, beyond the traditionally adopted (and sometimes oversimplified) few-atomic-level models. In addition to the influence of a more extensive set of bound and autoionizing atomic states, as well as non-resonant continuum states, the Liouville-space *R*-matrix-Floquet formulation should provide a foundation for the systematic description of the spectral effects due to environmental decoherence and relaxation phenomena, together with multi-photon ionization. Specifically, we will allow for the influence of the multi-photon ionization processes described by Eq. (3). The more precise spectral description that can thereby be provided should be applicable to laser powers and frequency detunings for which the few-atomic-level models are inadequate and to environmental decoherence and relaxation phenomena for which simplified optical-Bloch-equation models are incomplete.

4.1 The macroscopic electromagnetic response in the multiple-mode Floquet-Fourier representation

The investigation of electromagnetically induced transparency and related pump-probe optical phenomena is based on the evaluation of the macroscopic electromagnetic response, which provides the source terms in the Maxwell equations describing the propagation of the electromagnetic field in the optical medium. We introduce a Liouville-space multiple-mode Floquet-Fourier description of the macroscopic electromagnetic response, which is motivated by the description presented by Chu and Telnov (2004), who specifically considered a two-level model for the quantized electronic system. Our objective is to provide a systematic framework for the determination of the general, linear and non-linear macroscopic electromagnetic response for an ensemble of many-electron atomic systems interacting with a multiple-mode classical electromagnetic field. In the Maxwell equations describing the propagation of the electromagnetic field, the macroscopic electromagnetic response can be incorporated by introducing the polarization density $\vec{P}(t)$. (For a more general Maxwell-equations description, the magnetization density should also be included.) The macroscopic polarization density can be defined as the Liouville-space inner product (quantum-statistical-ensemble average) involving the microscopic electric-dipole-moment operator $\vec{D}=e\sum_i \vec{r}_i$ for the many-electron atomic system and the (reduced) atomic density operator $\rho(t)$ as follows:

$$\vec{P}(t)=n_0\left\langle \vec{D} \right\rangle = n_0 \left\langle\left\langle \vec{D} \middle| \rho(t) \right\rangle\right\rangle = n_0 \, \mathrm{Tr}\left[\vec{D}\rho(t)\right]. \tag{54}$$

It should be pointed out that the macroscopic electromagnetic response can be alternatively, and equivalently, characterized in terms of the macroscopic charge and current densities, which are defined as the ensemble averages of the microscopic charge-density and current-density operators. The number density of many-electron atomic systems in the ensemble is denoted by n_0, and $\rho(t)$ is the (reduced) density operator for the many-electron atomic system in the presence of an intense classical electromagnetic field. It should be noted that this simple result, involving the microscopic electric-dipole-moment operator pertaining to a single atomic system and the number density n_0, is valid only if the interactions among different atomic systems can be neglected. In order to systematically take into account the interactions among two or more many-electron atomic systems, it will be necessary to employ a hierarchical (reduced) density-operator formulation, such as the formulation introduced by Ben-Reuven (1980) and discussed in section 3. We note that strong dipole-dipole interactions between pairs of many-electron atoms have been found to play an important role in spectral observations and theoretical investigations of electromagnetically induced transparency and coherent population trapping in ensembles of highly-excited Rydberg atoms, where the atomic radii of the outer electrons can become greater than the laser wavelengths (Sevinçli et al 2011).

After substituting the multiple-mode Floquet-Fourier expansion for the (reduced) atomic density operator given by Eq. (41) and introducing the frequency variable $\Omega_{\vec{n}}=\vec{n}\bullet\vec{\omega}$ defined by Eq. (13), a corresponding multiple-mode expansion for the macroscopic polarization density $\vec{P}(t)$ can be obtained as follows:

$$\vec{P}(t)=n_0\left\langle\left\langle\vec{D}\middle|\rho(t)\right\rangle\right\rangle=n_0\sum_{\vec{n}}\left\langle\left\langle\vec{D}\middle|\rho_{\vec{n}}(t)\right\rangle\right\rangle\exp\left(-i\vec{n}\bullet\vec{\omega}t\right)=\sum_{\vec{n}}P_{\vec{n}}\left(\Omega_{\vec{n}}\right)\exp\left(-i\Omega_{\vec{n}}t\right). \qquad (55)$$

The macroscopic polarization density is thereby represented in terms of the set of the multiple-mode Floquet-Fourier polarization-density components $P_{\vec{n}}\left(\Omega_{\vec{n}}\right)=n_0\left\langle\left\langle\vec{D}\middle|\rho_{\vec{n}}(t)\right\rangle\right\rangle$, which can provide a non-perturbative characterization of the macroscopic electromagnetic response to the various frequency components of the classical electromagnetic field (e. g., a pump field, a probe field, and various combinations).

The conventional linear and non-linear optical susceptibility tensors can be defined by introducing an expansion for the macroscopic polarization density $\vec{P}(t)$ in powers m of the electric field associated with the multiple-mode classical electromagnetic field. Wang and Chu (1987) have introduced the concept of an intensity-dependent non-linear optical susceptibility $\chi^{\vec{n}}(\Omega_{\vec{n}})$, which is defined in terms of the multiple-mode Floquet-Fourier polarization-density components $P_{\vec{n}}\left(\Omega_{\vec{n}}\right)=n_0\left\langle\left\langle\vec{D}\middle|\rho_{\vec{n}}(t)\right\rangle\right\rangle$. The general definition for the conventional m'th order contribution to the macroscopic electronic polarization density is a multi-dimensional integral relationship. If only electric fields corresponding to single harmonic modes are considered and spatial dispersion is neglected, the general definition of the conventional m'th order contribution can be reduced to a simple algebraic form involving an intensity-independent rank-(m+1) susceptibility tensor and the tensor product of m electric fields. In a similar manner, the relationship introduced for the intensity-dependent linear (m=1) and non-linear (m>1) optical susceptibilities by Wang and Chu (1987) would be expressible in the tensor form:

$$P_{\vec{n}}\left(\Omega_{\vec{n}}\right)=\chi^{\vec{n}}(\Omega_{\vec{n}})\bullet\vec{E}(n_1\omega_1)\bullet\ldots\vec{E}(n_m\omega_m). \tag{56}$$

In the limit of weak fields, the intensity-dependent linear and non-linear optical susceptibility tensors $\chi^{\vec{n}}(\Omega_{\vec{n}})$ can be reduced to the conventional m'th order intensity-independent rank-(m+1) optical susceptibility tensors χ^{m}, which are obtained from a perturbation expansion of the (reduced) atomic density operator in powers of the multiple-mode classical electric field. However, the intensity-dependent linear and non-linear optical susceptibility tensors $\chi^{\vec{n}}(\Omega_{\vec{n}})$ may exhibit complex field-dependences, and the anticipated weak-field tensor structure of the linear and non-linear susceptibility relationship may not be realized. For simplicity, we shall directly evaluate the multiple-mode Floquet-Fourier polarization-density components $P_{\vec{n}}\left(\Omega_{\vec{n}}\right)=n_0\left\langle\left\langle\vec{D}\middle|\rho_{\vec{n}}(t)\right\rangle\right\rangle$ without reference to the concept of the intensity-dependent linear and non-linear optical susceptibility tensors, and we will defer the treatment in terms of the intensity-dependent susceptibility tensors to a future extension of this investigation.

After introducing the Liouville-space representation based on the tensor-product states $\left|ab;\vec{n}\right\rangle\!\right\rangle \equiv \left|a\right\rangle\!\left\langle b\right| \otimes \left|\vec{n}\right\rangle$ employed in Eq. (42), the multiple-mode Floquet-Fourier polarization-density components $P_{\vec{n}}\left(\Omega_{\vec{n}}\right) = n_0 \left\langle\!\left\langle \vec{D} \middle| \rho_{\vec{n}}(t) \right\rangle\!\right\rangle$ can be evaluated as follows:

$$P_{\vec{n}}\left(\Omega_{\vec{n}}\right) = n_0 \sum_a \sum_b \left\langle\!\left\langle \vec{D} \middle| ab;\vec{n} \right\rangle\!\right\rangle \left\langle\!\left\langle ab;\vec{n} \middle| \rho(t) \right\rangle\!\right\rangle. \tag{57}$$

4.2 The macroscopic electromagnetic response in the multiple-mode Liouville-space R-matrix-Floquet representation

In order to employ the multiple-mode Liouville-space *R*-matrix-Floquet formulation introduced in section 3.4.4, we adopt the definition of the macroscopic electromagnetic response in the alternative frequency-domain representation:

$$\vec{P}(\omega) = n_0 \left\langle \vec{D} \right\rangle = n_0 \left\langle\!\left\langle \vec{D} \middle| \vec{\rho}\left(\omega\right) \right\rangle\!\right\rangle = n_0 \,\mathrm{Tr}\left[\vec{D}\vec{\rho}\left(\omega\right)\right]. \tag{58}$$

After introducing the Liouville-space representation based on the zero-order tensor-product states $\left|ab;\vec{n}\right\rangle\!\right\rangle \equiv \left|a\right\rangle\!\left\langle b\right| \otimes \left|\vec{n}\right\rangle$, the macroscopic electromagnetic response in the frequency-domain representation can be expressed in the form:

$$\vec{P}(\omega)=n_0\sum_a\sum_b\sum_{\vec{n}}\langle\langle\vec{D}|ab;\vec{n}\rangle\rangle\langle\langle ab;\vec{n}|\vec{\rho}(\omega)\rangle\rangle. \tag{59}$$

From a perturbation expansion of the (reduced) density operator $\vec{\rho}(\omega)$ in powers of the classical electromagnetic field, a set (hierarchy) of coupled frequency-domain relationships for the field components of the density operator can be obtained from Eq. (43). The conventional description of the linear and non-linear macroscopic electromagnetic response can be recovered by introducing this perturbation expansion for the density operator into Eq. (59).

If the formal solution obtained as Eq. (50) is introduced into the expression given by Eq. (59) and only the lowest-order contribution is retained arising from the perturbation expansion in terms of the Liouville-space self-energy matrix operator $\bar{\boldsymbol{\Sigma}}$, we obtain the following expression for the macroscopic polarization density in the frequency-domain representation:

$$\vec{P}(\omega)=n_0\sum_a\sum_b\sum_{\vec{n}}\sum_\lambda\langle\langle\vec{D}|ab;\vec{n}\rangle\rangle\langle\langle ab;\vec{n}|\vec{\rho}_\lambda\rangle\rangle\frac{1}{\omega-\omega_\lambda}\langle\langle\vec{\rho}_\lambda|\bar{\boldsymbol{\Sigma}}|\vec{\rho}_\lambda(\omega)\rangle\rangle. \tag{60}$$

For a more balanced Liouville-space representation, the zero-order tensor-product intermediate states $|ab;\vec{n}\rangle\rangle\equiv|a\rangle\langle b|\otimes|\vec{n}\rangle$ in Eqs. (59) and (60) should be replaced by the Liouville-space "dressed $-$ atom" states $|\lambda_1\lambda_2\rangle\rangle$. These states are to be constructed from the solutions that are obtained from the ordinary Hilbert-space *R*-matrix-Floquet approach according to Eqs. (52) and (53), which pertain to the biorthogonal representation involving the right and left eigenvectors of the non-Hermitian Floquet Hamiltonian matrix operator $\mathbf{H_F}$. The summations over the indices a, b, and $\vec{n}$ should then be replaced by summations over the "dressed – atom" intermediate-state indices λ_1 and λ_2, and the Liouville-space intermediate-state index λ is also understood to correspond to two ordinary Hilbert-space "dressed – atom" state indices. The more balanced expression for the macroscopic polarization density is then obtained in the form:

$$\vec{P}(\omega) = n_0 \sum_{\lambda_1}\sum_{\lambda_2}\sum_{\lambda} \left\langle\left\langle \vec{D} \middle| \lambda_1\lambda_2 \right\rangle\right\rangle \left\langle\left\langle \lambda_1\lambda_2 \middle| \vec{\rho}_\lambda \right\rangle\right\rangle \frac{1}{\omega-\omega_\lambda} \left\langle\left\langle \vec{\rho}_\lambda \middle| \bar{\boldsymbol{\Sigma}} \middle| \vec{\rho}_\lambda(\omega) \right\rangle\right\rangle . \qquad (61)$$

For an evaluation of the macroscopic polarization density that is non-perturbative with respect to the Liouville-space self-energy matrix operator $\bar{\boldsymbol{\Sigma}}$, it will be necessary to introduce the solutions to the set of coupled algebraic equations provided by Eq. (51) into the full expression given by Eq. (50). The fully non-linear and non-perturbative "dressed – atom" description of the electromagnetic-field propagation can then be incorporated by including this fully non-perturbative result for the macroscopic polarization density as a source term in the Maxwell equations.

4.3 The role of autoionizing states in the multi-level description of the macroscopic electromagnetic response

The sums over the zero-order states a and b in Eqs. (59) and (60) can include the bound, autoionizing, and non-resonant continuum states of the unperturbed many-electron atomic system, in the absence of the external electromagnetic field. These zero-order states can also be included in the expansions for the *R*-matrix-Floquet wave functions, from which the $"\text{dressed}-\text{atom}"$ Liouville-space states denoted by $|\lambda_1\lambda_2\rangle\rangle$ and $|\vec{\rho}_\lambda\rangle\rangle$ are constructed as described in section 3. Accordingly, the expression obtained for the macroscopic polarization density in the frequency-domain representation (as well as the corresponding result that is non-perturbative with respect to the Liouville-space self-energy matrix operator $\overline{\overline{\mathbf{\Sigma}}}$) can incorporate the coherent contributions corresponding to the quantum-mechanical interference of electromagnetic transition amplitudes associated with the autoionizing states. These coherent contributions play an essential role in the interpretation of electromagnetically induced transparency (EIT) that was originally presented by Harris, Field, and Imamoglu (1990), as well as related pump-probe optical phenomena.

The slow-light propagation phenomenon in the EIT process has most frequently been investigated by evaluating the conventional expression for the linear electrical susceptibility using $"\text{dressed}-\text{atom}"$ states, corresponding to eigenstates of the many-electron Hamiltonian operator including the interaction with the intense (pump or control) electromagnetic field responsible for the coherent excitation of the many-electron atomic system. By means of the approach based on the multiple-mode Liouville-space *R*-matrix-Floquet representation, we can provide an entirely non-perturbative description of the macroscopic electromagnetic response, which can be included in the

Maxwell equations to investigate the linear and non-linear propagation characteristics of the electromagnetic field. Our general Liouville-space *R*-matrix-Floquet formulation should be applicable for the description of a wide variety of pump-probe optical phenomena, for which the simplified few-atomic-level and phenomenological optical-Bloch-equation models may be inadequate.

5. Application of the Liouville-space *R*-matrix-Floquet formulation to the unified description of radiative and dielectronic recombination

This section is devoted to the application of the Liouville-space *R*-matrix-Floquet formulation presented in section 3 to the unified description of radiative and dielectronic recombination in the presence of an external electromagnetic field. Specifically, we will provide a unified description of the two-step (resonant) dielectronic recombination process described by Eq. (1) together with the ordinary direct (non-resonant) radiative recombination process corresponding to Eq. (2), in the presence of an intense classical electromagnetic field. In the introduction, we have emphasized that radiative and dielectronic recombination are most rigorously treated as corresponding to coherent, quantum-mechanically interfering components of a single electromagnetic transition connecting the initial continuum state and the final bound state of the electron-recombining-ion system in the photo-recombination process.

5.1 Investigation of the electron-ion photo-recombination process in the presence of an intense classical electromagnetic field using the frequency-domain (resolvent-operator) formulation of the Liouville-space R-matrix-Floquet description

In the frequency-domain (resolvent-operator) formulation of the reduced-density-operator description, the electron-ion photo-recombination process can be investigated by an evaluation of the generalized (Liouville-space) transition rate given by Eq. (31). The electron-ion photo-recombination process in the presence of an intense classical electromagnetic field can be treated by introducing, for the initial continuum states and the final bound states, the *R*-matrix-Floquet wave functions that are defined within all spatial regions and satisfy the appropriate asymptotic boundary conditions. The intermediate sates will also be represented by *R*-matrix-Floquet wave functions. In the biorthogonal representation introduced in section 3.4.4, the right eigenvector wave functions representing the initial continuum states must satisfy the outgoing-wave boundary conditions pertaining to the electron-ion collision process, as discussed in appendix A3, while the final bound states can be represented by exponentially decaying radial wave functions. However, the left eigenvector wave functions representing the initial continuum states should satisfy the time-reversed, incoming-wave boundary conditions (Goldberger and Watson 1964). If only the lowest-order contribution is retained in the perturbation expansion of the Liouville-space transition matrix operator $\bar{\mathbf{T}}^{\mathrm{r}}$, in powers of the relevant Liouville-space electromagnetic-interaction matrix operator $\bar{\mathbf{V}}^{\mathrm{r}}$, the transition rate for the single-photon spontaneous emission process can be expressed in the form:

$$A_R(i \rightarrow f) = -\, i \lim_{\varepsilon \rightarrow 0} \sum_{\lambda_i} \sum_{\lambda_i'} \sum_{\lambda_f} \left\langle\!\left\langle \lambda_f \lambda_f, 11 \right| \bar{\mathbf{V}}^r\, \bar{\mathbf{G}}_0^r(+i\varepsilon)\, \bar{\mathbf{V}}^r \left| \lambda_i \lambda_i', 00 \right\rangle\!\right\rangle \left\langle\!\left\langle \lambda_i \lambda_i', 00 \right| \rho_i^r \right\rangle\!\right\rangle. \qquad (62)$$

The right eigenvectors representing the initial continuum states and the final bound states are denoted by $|\lambda_i\rangle$ and $|\lambda_f\rangle$, respectively, while the corresponding left eigenvectors are denoted by $\langle\lambda_i|$ and $\langle\lambda_f|$, respectively. In the Liouville-space tensor-product representation based on the many-electron *R*-matrix-Floquet "dressed – atom" states $|\lambda_i\rangle$ and $\langle\lambda_i|$, together with the relevant occupation-number states $|n_{\vec{k}\lambda}\rangle$ of the quantized electromagnetic field in the spontaneous single-photon emission process, we have allowed for non-diagonal matrix elements of the initial-state reduced density operator ρ_i^r corresponding to the coherent excitation of the many-electron atomic system. The relevant final-state projection operator P_f^r has been expressed in terms of Liouville-space tensor-product states corresponding to the many-electron *R*-matrix-Floquet "dressed – atom" states $|\lambda_f\rangle$ and $\langle\lambda_f|$ that can be populated as a result of the spontaneous emission of a single photon with momentum $\hbar\vec{k}$ (and energy $\hbar\omega$) and polarization (or helicity) λ. The zero-order reduced, relevant Liouville-space resolvent (or Green) matrix operator is given by $\bar{\mathbf{G}}_0^r(+i\varepsilon) = [+i\varepsilon - \bar{\mathbf{L}}_0^r - \bar{\mathbf{\Sigma}}(+i\varepsilon)]^{-1}$.

After introducing two sets of intermediate Liouville-space *R*-matrix-Floquet "dressed – atom" and quantized-field tensor-product states, Eq. (62) can be expressed in the expanded form:

$$\begin{aligned} A_R(i \rightarrow f) = -i \lim_{\varepsilon \rightarrow 0} \sum_{\lambda_i} \sum_{\lambda_i'} \sum_{\lambda_f} \sum_{\lambda\lambda'} \sum_{nn'} \sum_{\lambda''\lambda'''} \sum_{n''n'''} \langle\langle \lambda_f \lambda_f, 11 | \bar{\mathbf{V}}^r | \lambda\lambda', nn' \rangle\rangle \\ \times \langle\langle \lambda\lambda', nn' | \bar{\mathbf{G}}_0^r(+i\varepsilon) | \lambda''\lambda''', n''n''' \rangle\rangle \langle\langle \lambda''\lambda''', n''n''' | \bar{\mathbf{V}}^r | \lambda_i \lambda_i', 00 \rangle \langle\langle \lambda_i \lambda_i', 00 | \rho_i^r \rangle\rangle. \end{aligned} \tag{63}$$

This expanded form can be further evaluated by employing the following expression for the tetradic matrix elements of the relevant Liouville-space electromagnetic-interaction matrix operator $\bar{\mathbf{V}}^r$:

$$\begin{aligned} \langle\langle \delta\delta', n''n''' | \bar{\mathbf{V}}^r | \gamma\gamma', nn' \rangle\rangle = & \left(\frac{1}{\hbar}\right)\left[V_{\delta\gamma}(\vec{k}\lambda)\delta_{n'',n-1}\sqrt{n} \right]\delta_{\delta'\gamma'}\delta_{n''',n'} \\ & + \left(\frac{1}{\hbar}\right)\left[V_{\delta\gamma}^{*}(\vec{k}\lambda)\delta_{n'',n+1}\sqrt{n+1} \right]\delta_{\delta'\gamma'}\delta_{n''',n'} \\ & - \left(\frac{1}{\hbar}\right)\left[V_{\gamma'\delta'}(\vec{k}\lambda)\delta_{n'''-1,n'}\sqrt{n'''} \right]\delta_{\delta\gamma}\delta_{n'',n} \\ & - \left(\frac{1}{\hbar}\right)\left[V_{\gamma'\delta'}^{*}(\vec{k}\lambda)\delta_{n'''+1,n'}\sqrt{n'''+1} \right]\delta_{\delta\gamma}\delta_{n'',n}, \end{aligned} \tag{64}$$

where the ordinary-Hilbert-space electromagnetic-interaction matrix elements $V_{\delta\gamma}(\vec{k}_i\lambda_i)$ are defined, in terms of the right and left "dressed – atom" state eigenvectors, by

$$V_{\delta\gamma}(\vec{k}\lambda) = \left(\frac{e}{2m}\right)\sqrt{\frac{2\pi\hbar}{V\omega}}\langle\delta|\sum_i\left[\vec{p}_i \bullet \vec{\varepsilon}_{\vec{k}\lambda} e^{i(\vec{k}\bullet\vec{r}_i)} + e^{i(\vec{k}\bullet\vec{r}_i)}\vec{p}_i \bullet \vec{\varepsilon}_{\vec{k}\lambda}\right]|\gamma\rangle. \tag{65}$$

V denotes the volume in which the electromagnetic field corresponding to the spontaneous single-photon emission process is quantized. The electric-dipole approximation may be introduced by setting $\vec{k}=0$. If the transformation to the position operators is employed, the matrix elements given by Eq. (65) can be expressed in terms of the matrix elements of the total many-electron electric-dipole-moment operator $\vec{D}=e\sum_i \vec{r}_i$ between the many-electron *R*-matrix-Floquet "dressed – atom" state eigenvectors.

Using Eq. (64), the product of the two tetradic matrix elements of the relevant Liouville-space electromagnetic-interaction matrix operator $\bar{\mathbf{V}}^r$ in Eq. (63) will give rise to 16 terms. To complete this evaluation, it will be necessary to introduce an explicit expression for the tetradic matrix elements of the zero-order reduced, relevant Liouville-space resolvent matrix operator $\bar{\mathbf{G}}_0^r(+i\varepsilon)$. In the biorthogonal representation, these tetradic matrix elements satisfy the following set of equations:

$$\begin{aligned}
&\sum_{\gamma}\sum_{\gamma'}\sum_{\bar{n}}\sum_{\bar{n}'}\left\langle\left\langle \delta\delta',n''n''' \middle| \bar{\mathbf{G}}_0^r(+i\varepsilon) \middle| \gamma\gamma',\bar{n}\bar{n}' \right\rangle\right\rangle \\
&\times\left[\left(+i\varepsilon-\omega_\alpha+\omega_\beta^*-n\omega+n'\omega\right)\delta_{\gamma\alpha}\delta_{\gamma'\beta}\delta_{\bar{n}n}\delta_{\bar{n}'n'}-\left\langle\left\langle \gamma\gamma',\bar{n}\bar{n}' \middle| \bar{\boldsymbol{\Sigma}}(+i\varepsilon) \middle| \alpha\beta,nn' \right\rangle\right\rangle\right] \qquad (66)\\
&=\delta_{\delta\alpha}\delta_{\delta'\beta}\delta_{n''n}\delta_{n'''n'}.
\end{aligned}$$

If the isolated-line approximation is introduced and the initial-state atomic coherences are neglected, then this set of equations can be solved, and the electromagnetic transition rate can be obtained as an incoherent superposition of the Lorentzian spectral profiles associated with the individual transitions among the "dressed – atom" states. The detailed evaluation of the tetradic matrix elements Liouville-space self-energy matrix operator

$\bar{\boldsymbol{\Sigma}}(+i\varepsilon)$, giving rise to the spectral-line widths and shifts due to the environmental collisional and radiative interactions, will be deferred to a future investigation. In addition to the systematic evaluation of the Liouville-space self-energy corrections, it may be necessary to include various relativistic and radiative (QED) corrections to the conventional non-relativistic many-electron atomic structure in order to provide accurate spectral simulations that can be compared with high-resolution experimental results.

5.2 The electron-ion photo-recombination cross section in the Liouville-space R-matrix-Floquet description

The electron-ion photo-recombination cross section can be obtained from the transition rate given by Eq. (62) as follows: If the incident continuum-electron state is not normalized per unit electron flux, then the transition rate should be divided by the incident electron flux. The density of final photon states per unit energy and solid angle intervals should be included. If the angular distribution of the emitted photons is not of interest in the observation of the combined electron-ion photo-recombination process, then the differential cross section should be integrated over the photon directions. Finally, sums and averages over the quantum numbers corresponding to degenerate or nearly degenerate atomic sublevels and photon polarizations can be carried out.

5.3 The role autoionizing states in the unified description of radiative and dielectronic recombination

The ordinary Hilbert-space formulation of the unified description of radiative and dielectronic recombination developed by Jacobs, Cooper and Haan (1987) and by Haan and Jacobs (1989) is based on the zero-order representation in terms of eigenstates of the field-free atomic Hamiltonian operator. In this formulation, the total electron-ion photo-recombination cross section can be unambiguously expressed as a sum of the following three distinct contributions: a term representing the direct (non-resonant) radiative-recombination process, a term describing the two-step (resonant) dielectronic-recombination processes involving the intermediate autoionizing states, and a term arising from the interference between the non-resonant and resonant transition amplitudes.

In the Liouville-space formulation presented by Jacobs, Cooper and Haan (1994), the division of the total electron-ion photo-recombination cross section into the three distinct contributions discussed above is complicated, because the complete zero-order Liouville-space basis set must include coherences connecting the autoionizing states with either the electron-continuum or the photon-continuum states. However, a unified description of the combined electron-ion photo-recombination process is still provided.

In the description of autoionization phenomena within the framework of the close-coupling and *R*-matrix approaches to electron-ion scattering processes and photoionization, as reviewed by Burke (2011), the autoionization resonances and the non-resonant electron-continuum states are automatically treated on an equal footing. Furthermore, the spectral-line widths and shifts due to autoionization are implicitly taken into account, and in some calculation the spectral-line widths and shifts associated with spontaneous radiative emission have been incorporated by means of an effective radiation-damping potential. Consequently, the close-coupling and *R*-matrix approaches automatically provide a combined treatment of the autoionization and non-resonant electron-continuum states. Moreover, this combined treatment of the autoionization and non-resonant electron-continuum states has the advantage of providing an inherently non-perturbative description of the complex spectral variation that can be produced by a multitude of overlapping resonant structures. This combined treatment of autoionization and non-resonant electron-ion scattering is also an integral feature in the determination of the *R*-matrix-Floquet wave functions, as reviewed in section 2. In the evaluation of the Liouville-space expression for the transition rate given by Eq. (62) using the *R*-matrix-Floquet right and left eigenvector wave functions, the total electron-ion photo-recombination cross section can not naturally be separated into the three distinct contributions discussed above. Nevertheless, these right and left eigenvector wave functions can provide an advantageous starting point for our Liouville-space formulation, which automatically incorporates a unified description of the combined electron-ion photo-recombination process in the presence of an intense electromagnetic field.

5.4 Investigation of the electron-ion photo-recombination process in the presence of a classical electromagnetic field using the time-domain (equation-of-motion) formulation of the Liouville-space R-matrix-Floquet description

A unified description of radiative and dielectronic recombination in the presence of a classical electromagnetic field can be developed in the alternative time-domain (equation-of-motion) formulation of the Liouville-space *R*-matrix-Floquet description. Ravi and Agarwal (1991) have developed an equation-of-motion formulation that features a diagonalization of the field-free many-electron atomic Hamiltonian operator within the subspace of the autoionizing resonance states and the non-resonant electron-ion continuum states. In our *R*-matrix-Floquet description, this diagonalization is implicitly carried out for the many-electron atomic Hamiltonian operator in the presence of an intense electromagnetic field, as reviewed in section 2. In addition, while Ravi and Agarwal (1991) have allowed for only the environmental interaction corresponding the spontaneous radiative-emission process, the general Liouville-space self-energy operator introduced in our reduced-density-operator description can be evaluated for a wide class of atomic collisional and radiative decoherence and relaxation processes. In order to apply the time-domain (equation-of-motion) formulation described in section 3, the Floquet Liouvillian matrix operator $\bar{\mathbf{L}}_{\mathbf{F}}$ in Eq. (46) must be generalized to include the interaction with the quantized electromagnetic field in the spontaneous radiative-emission processes, in addition to the interaction with the intense classical electromagnetic field. The solution of this generalized equation-of-motion for the reduced density operator $\rho^{r}(t)$ can then be used to evaluate the desired electromagnetic-transition probability as a function of time, which is given by the Liouville-space inner product $\langle\langle P_f|\rho^{r}(t)\rangle\rangle$ of the (reduced) density operator $\rho^{r}(t)$ and the final-state projection operator P_f, and the corresponding transition rate can be obtained as described by Jacobs, Cooper and Haan (1994).

6. Conclusions and future plans

A Liouville-space *R*-matrix-Floquet formulation has been developed with the objective of providing a non-perturbative and unified description for a wide class of resonant and non-resonant coherent optical phenomena involving many-electron atomic systems in the presence of an intense external electromagnetic field. Using the ordinary Hilbert-space *R*-matrix-Floquet description as a starting point, our Liouville-space formulation should be capable of incorporating a realistic representation of the laser-dressed multi-level many-electron atomic structure, including bound states, non-resonant electron-scattering continua, and autoionizing resonances, together with a comprehensive and systematic treatment of the influence of environmental relaxation and decoherence mechanisms, such as spontaneous radiative decay and atomic collision processes.

A particular advantage of the *R*-matrix-Floquet method is that the basic *R*-matrix techniques and many-electron computer programs have already been developed for the ordinary Hilbert-space (Hamiltonian) description of field-free electron-atom and electron-ion collision processes, single-photon ionization processes, and free-free radiative transitions of atomic systems. Moreover, the ordinary Hilbert-space (Hamiltonian) formulation of the *R*-matrix-Floquet method can provide a realistic non-perturbative description of the dynamical evolution of the many-electron atomic system in the presence of a classical (possibly multiple-mode) electromagnetic field. The "dressed" atomic states thereby obtained can be used for the systematic investigation of an extensive class of atomic collision and radiation processes in the presence of intense, stationary (continuous-wave) electromagnetic fields. For a description of atomic processes in ultrashort-pulse electromagnetic fields, an alternative time-dependent *R*-matrix method has been developed, and this alternative method will be adopted in a future investigation as a starting point for a time-dependent Liouville-space *R*-matrix formulation.

We have indicated how the Liouville-space *R*-matrix-Floquet formulation can be applied to resonant and coherent non-linear optical processes in many-electron atomic systems, particularly electromagnetically induced transparency and related pump-probe optical phenomena. Although we have restricted the discussion of these applications to an ensemble of non-interacting many-electron atomic systems, we have indicated that a hierarchical (reduced) density-operator description can be employed for a systematic investigation of cooperative electromagnetic phenomena involving coherently-excited many-electron atomic systems. We have also discussed the application of the Liouville-space *R*-matrix-Floquet formulation to the unified description of radiative and dielectronic recombination in the presence of an external electromagnetic field.

In a future investigation, the tetradic matrix elements of the Liouville-space self-energy matrix operator, which occurs in the expressions for the macroscopic electromagnetic response and the Liouville-space electromagnetic-transition rates, will be explicitly evaluated for environmental collisional and radiative decoherence and relaxation mechanism. Finally, it will be necessary to develop the computer programs for the construction of the right and left eigenvector wave functions of the non-Hermitian Floquet Hamiltonian that are continuously defined within all spatial regions and satisfy the appropriate asymptotic boundary conditions, so that these eigenvector wave functions (in the biorthogonal representation) can be employed in detailed evaluations of the various electromagnetic characteristics within the framework of our Liouville-space *R*-matrix-Floquet formulation. If a more detailed atomic-structure representation (such as that describing the hyperfine structure), beyond what can be practically accommodated in the expansions for the *R*-matrix-Floquet wave functions, is required for an accurate spectral description, then the required electric-dipole matrix elements for the many-electron atomic system can be transformed into the more detailed atomic-structure representation using standard angular-momentum-coupling transformations.

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Appendix 1. Explicit definition for the *R*-matrix in the multiple-mode Floquet-Fourier representation

Burke, Francken and Joachain (1991) have introduced the *R*-matrix by projecting Eq. (22) onto the combined (tensor-product) space of the channel states, which are specified by the indices *i* and Γ, together with the single electromagnetic-field mode specified by the Floquet-Fourier number n. Using Eqs. (21) and (23) and evaluating this projected equation on the boundary of the internal region at $r = a_0$, the following multiple-mode relationship (involving the mode-number vector $\vec{n}$) can be obtained:

$$ {}^{L}F^{\Gamma}_{i\vec{n}j}(a_0) = \sum_{\Gamma' i' \vec{n}'} {}^{L}R^{\Gamma\Gamma'}_{i\vec{n}i'\vec{n}'}(E) \left(r\frac{d}{dr}\,{}^{L}F^{\Gamma'}_{i'\vec{n}'j} - b_0\,{}^{L}F^{\Gamma'}_{i'\vec{n}'j} \right)_{r=a_0} . \qquad \text{(A1.1)} $$

The *R*-matrix in the dipole-length representation, denoted by the pre-superscript L, is thereby further generalized as a higher-dimensional matrix, which is defined within the combined space of the channel states and the Floquet-Fourier modes (involving the mode-number vector $\vec{n}$) as follows:

$$ {}^{L}R^{\Gamma\Gamma'}_{i\vec{n}i'\vec{n}'}(E) = \left(\frac{1}{2a_0} \right) \sum_{k} \left(\frac{{}^{L}w^{\Gamma}_{i\vec{n}k}\,{}^{L}w^{\Gamma'}_{i'\vec{n}'k}}{E_k - E} \right). \qquad \text{(A1.2)} $$

The reduced radial functions ${}^{L}F^{\Gamma}_{i\vec{n}j}(r)$ in the internal region are defined, in terms of the (N+1)-electron channel functions ϕ^{Γ}_{i} and the linearly independent wave functions $\psi_{\vec{n}j}(E)$ that are obtained in the internal region, by means of the relationship:

$$\left(\frac{1}{r}\right){}^{L}F^{\Gamma}_{i\vec{n}j}(r)=\left\langle\phi^{\Gamma}_{i}\middle|\psi_{\vec{n}j}(E)\right\rangle \tag{A1.3}$$

and the surface amplitudes ${}^{L}w^{\Gamma}_{i\vec{n}k}$ are given by

$$\left(\frac{1}{a_0}\right){}^{L}w^{\Gamma}_{i\vec{n}k}=\left\langle\phi^{\Gamma}_{i}\middle|\psi_{\vec{n}k}\right\rangle_{r=a_0} \tag{A1.4}$$

As discussed in Appendix 2, Eq. (A1.1) can be transformed to the velocity representation to provide the boundary conditions at r = a_0 that are required for obtaining the *R*-matrix Floquet-Fourier wave functions in the external region.

Appendix 2. Transformation of the generalized *R*-matrix from the dipole-length representation to the velocity representation

In order to solve the electromagnetically modified close-coupling equations in the external region, it is necessary to introduce the boundary conditions that must be satisfied by the radial wave functions for the continuum electron at the boundary of the internal region at r = a_0. These boundary conditions can be obtained starting from the equation defining the generalized *R*-matrix, which is given by Eq. (A1.1). As described by Burke, Francken and Joachain (1991), it is necessary to transform the reduced radial functions ${}^{\mathrm{L}}\mathrm{F}^{\Gamma}_{\mathrm{i}\vec{\mathrm{n}}\mathrm{j}}(\mathrm{r})$ (which are defined in the internal region in the dipole-length representation) to the velocity representation. The multiple-mode generalization of this transformation can be expressed in the form:

$$ {}^{\mathrm{V}}\mathrm{F}^{\Gamma}_{\mathrm{i}\vec{\mathrm{n}}\mathrm{j}}(\mathrm{a}_0)=\sum_{\Gamma'\mathrm{i}'\vec{\mathrm{n}}'}\mathrm{C}_{\Gamma\mathrm{i}\vec{\mathrm{n}},\Gamma'\mathrm{i}'\vec{\mathrm{n}}'}\,{}^{\mathrm{L}}\mathrm{F}^{\Gamma'}_{\mathrm{i}'\vec{\mathrm{n}}'\mathrm{j}}(\mathrm{a}_0), \tag{A2.1} $$

where the elements of the matrix **C** can be obtained by means of the multiple-mode generalization of the relationship given by Burke, Francken and Joachain (1991). This multiple-mode generalization of the relationship for the elements of the matrix **C** can be explicitly expressed in terms of the matrix elements, between the (N+1)-electron channel functions $\phi^{\Gamma}_{\mathrm{i}}(\mathrm{r}^{-1}_{\mathrm{N+1}})$, of operator functions that arise from the expansion of the transformation of the (N+1)-electron wave function $\Psi(\mathbf{X}_{\mathrm{N+1}},\mathrm{t})$ from the dipole-length representation to the velocity representation. The reduced radial functions ${}^{\mathrm{L}}\mathrm{F}^{\Gamma}_{\mathrm{i}\vec{\mathrm{n}}\mathrm{j}}(\mathrm{r})$ are defined by means of Eq. (A1.3) and the radial functions ${}^{\mathrm{V}}\mathrm{F}^{\Gamma}_{\mathrm{i}\vec{\mathrm{n}}\mathrm{j}}(\mathrm{r})$ in the external region are the radial functions $\mathrm{G}^{\Gamma}_{i\vec{\mathrm{n}}\mathrm{j}}(\mathrm{r}_{\mathrm{N+1}})$ in Eq. (29), which satisfy equations of the close-coupling form and correspond to the asymptotic boundary conditions for the electromagnetic process of interest, as discussed in Appendix 3. From this expression, the transformation of the generalized *R*-matrix from the dipole-length representation to the velocity representation can be obtained in the multi-dimensional (multiple-channel and multiple-mode) form:

$$ {}^{V}\mathbf{R}=a_0^{-1}\mathbf{C}\left[\left(\frac{d\mathbf{C}}{dr}\right)_{r=a_0}+a_0^{-1}\mathbf{C}\,{}^{L}\mathbf{R}^{-1}\right]^{-1}. \qquad \text{(A2.2)} $$

This relationship provides the desired transformation of the generalized *R*-matrix. In a manner analogous to the derivation of Eq. (A1.1), the following multiple-mode relationship (involving the mode-number vector $\vec{n}$) for the derivatives of the radial functions ${}^{V}F^{\Gamma}_{i\vec{n}j}(r)$ can be obtained:

$$ {}^{V}F^{\Gamma}_{i\vec{n}j}(a_0)=\sum_{\Gamma' i'\vec{n}'}{}^{V}R^{\Gamma\Gamma'}_{i\vec{n}i'\vec{n}'}(E)\left(r\frac{d}{dr}\,{}^{V}F^{\Gamma'}_{i'\vec{n}'j}-b_0\,{}^{V}F^{\Gamma'}_{i'\vec{n}'j}\right)_{r=a_0}. \qquad \text{(A2.3)} $$

This relationship can be used in conjunction with (A2.1) to relate the radial wave functions ${}^{V}F^{\Gamma}_{i\vec{n}j}(r)$ and their derivatives on the boundary between the internal and external regions. The desired boundary conditions on the radial wave functions ${}^{V}F^{\Gamma}_{i\vec{n}j}(r)$ at $r = a_0$ are thereby provided.

Appendix 3. Construction of the *R*-matrix multiple-mode Floquet-Fourier wave functions satisfying the asymptotic boundary conditions for various electromagnetic processes

In order to introduce the asymptotic boundary conditions for various electromagnetic processes, we shall assume that the electromagnetically modified close-coupling equations have been transformed to the acceleration representation, as described by Burke, Francken and Joachain (1991), where the external (laser) electromagnetic field is assumed to be monochromatic, linearly polarized, and spatially homogeneous. In addition, we shall follow their procedure and assume that the kinetic-energy and dipole-potential terms in these equations have been diagonalized, corresponding to the electron scattering by an atom or ion that is "dressed" by the electromagnetic field. This analysis yields an expression for the *R*-matrix in the acceleration representation. The multiple-mode generalization of this expression for the *R*-matrix is as follows:

$$ {}^{\mathrm{A}}\mathrm{G}^{\Gamma}_{i\vec{\mathrm{n}}\mathrm{j}}(a_p) = \sum_{\Gamma'\mathrm{i}'\vec{\mathrm{n}}'} {}^{\mathrm{A}}\mathrm{R}^{\Gamma\Gamma'}_{\mathrm{i}\vec{\mathrm{n}}\mathrm{i}'\vec{\mathrm{n}}'}(\mathrm{E}) \left(\mathrm{r}\frac{\mathrm{d}}{\mathrm{dr}}\,{}^{\mathrm{A}}\mathrm{G}^{\Gamma}_{i\vec{\mathrm{n}}\mathrm{j}} - \mathrm{b}_0\,{}^{\mathrm{A}}\mathrm{G}^{\Gamma}_{i\vec{\mathrm{n}}\mathrm{j}} \right)_{\mathrm{r}=a_p} . \tag{A3.1} $$

The radial wave functions $\mathrm{G}^{\Gamma}_{i\vec{\mathrm{n}}\mathrm{j}}$ describing the continuum electron will be governed by simpler asymptotic boundary conditions, which are analogous to those used for electron-atom or electron-ion collision processes in the absence of an electromagnetic field.

For the description of laser-assisted electron-atom and electron-ion collisions, the asymptotic boundary conditions can be expressed as follows:

$$G_{\nu\nu'}(r)\xrightarrow[r\to\infty]{}k_\nu^{-1/2}\left[\sin\left(\theta_\nu\right)\delta_{\nu\nu'}+\cos\left(\theta_\nu\right)K_{\nu\nu'}\right] \quad \text{for } k_\nu^2\geq 0 \tag{A3.2}$$

and

$$G_{\nu\nu'}(r)\xrightarrow[r\to\infty]{}\exp\left(-\left|k_\nu\right|r\right)N_{\nu\nu'} \quad \text{for } k_\nu^2<0\,. \tag{A3.3}$$

The individual asymptotic boundary conditions corresponding to the open and closed channels are described by Eqs. (A3.2) and (A3.3), respectively. It is convenient to adopt an ordering scheme in which the open channels occur first. Furthermore, the set of channel indices $\Gamma, i, \vec{n}$ are now denoted by the single index ν, and the pre-superscript A has been dropped. The quantity θ_ν is defined as follows:

$$\theta_\nu=k_\nu r-\left(\frac{1}{2}\right)\ell_i\pi-\eta_\nu\,\ell n\left(2k_\nu r\right)+\sigma_\nu, \tag{A3.4}$$

$$\eta_\nu=-\left(Z-N\right)/k_\nu, \tag{A3.5}$$

$$\sigma_\nu=\arg\Gamma\left(\ell_i+1+i\eta_\nu\right). \tag{A3.6}$$

Eq. (A3.2) provides the definition of the muti-channel and multiple-mode K-matrix, from which the corresponding multi-dimensional S-matrix can be obtained according to the standard relationship:

$$S=\frac{1+iK}{1-iK}. \tag{A3.7}$$

The multi-dimensional K-matrix can be related to the multi-dimensional *R*-matrix by a generalization of the procedure described for a single electromagnetic-field mode by Burke, Francken and Joachain (1991). In terms of the S-matrix, the asymptotic boundary conditions for the open channels can be expressed in the alternative form:

$$\bar{G}_{\nu\nu'}(r)\xrightarrow[r\to\infty]{}k_{\nu}^{-1/2}\left[\exp\left(-i\theta_{\nu}\right)\delta_{\nu\nu'}-\exp\left(i\theta_{\nu}\right)S_{\nu\nu'}\right]. \tag{A3.8}$$

The transformed radial functions can be obtained as follows:

$$\bar{G}_{\nu\nu'}(r)=\sum_{\mu}\sum_{\mu'}G_{\nu\mu}(r)U_{\mu\mu'}\exp\left(+i\zeta_{\mu'}\right)\cos\left(\zeta_{\mu'}\right)U_{\nu'\mu'}. \tag{A3.9}$$

The U-matrix diagonalizes both the S-matrix and the K-matrix in the forms:

$$\left(U^{T}SU\right)_{\mu\mu'}=\exp\left(2i\zeta_{\mu}\right)\delta_{\mu\mu'}, \tag{A3.10}$$

$$\left(U^{T}KU\right)_{\mu\mu'}=\tan\left(\zeta_{\mu}\right)\delta_{\mu\mu'}. \tag{A3.11}$$

For the description of single-photon ionization processes in the absence of electromagnetic fields, the continuum-electron wave functions have been assumed to satisfy the alternative, (time-reversed) incoming-wave asymptotic boundary conditions. The appropriate modified forms of Eqs. (A3.8) And (A3.9) have been presented by Jacobs (1971, 1972).

For the description of multi-photon ionization processes, the linearly independent solutions of the electromagnetically modified close-coupling equations satisfy the alternative asymptotic boundary conditions:

$$G_{\nu\nu'}(r)\xrightarrow[r\to\infty]{}\exp\left(ik_{\nu}r\right)\delta_{\nu\nu'} \tag{A3.12}$$

In the determination of these solutions, account must be taken that the quasi-energy has real and imaginary parts, due to the dynamical Stark shift and the total ionization rate.

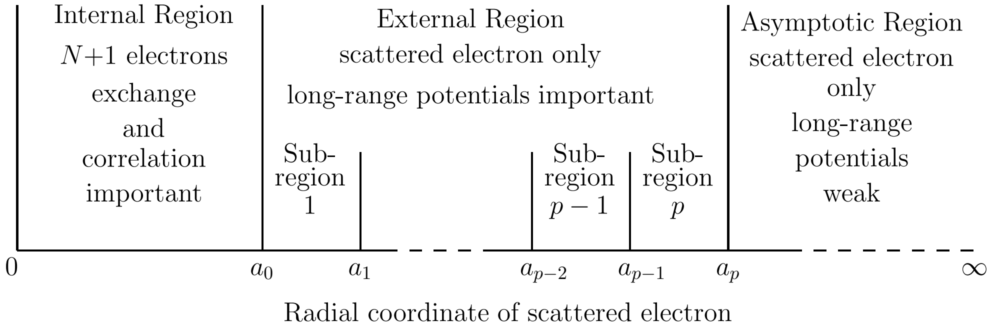
It should be noted that the (time-reversed) incoming-wave boundary conditions (Goldberger and Watson 1964) should be employed for the construction of the left eigenvector wave functions in the biorthogonal representation that has been introduced in section 3.4.4. Incorporating the required asymptotic boundary conditions, together with the boundary conditions at r = a_0 that have been described in Appendices 1 and 2, the multiple-mode (N+1)-electron wave functions that are continuously defined throughout the entire spatial region can be constructed in the forms that are appropriate for the description of electromagnetically assisted electron-atom and electron-ion collisions and for multi-photon ionization processes.

Figure Captions

Fig. 1. The partition of the three-dimensional space of the (N+1)-electron atomic system in the *R*-matrix theory of electron-atom and electron-ion collision processes.

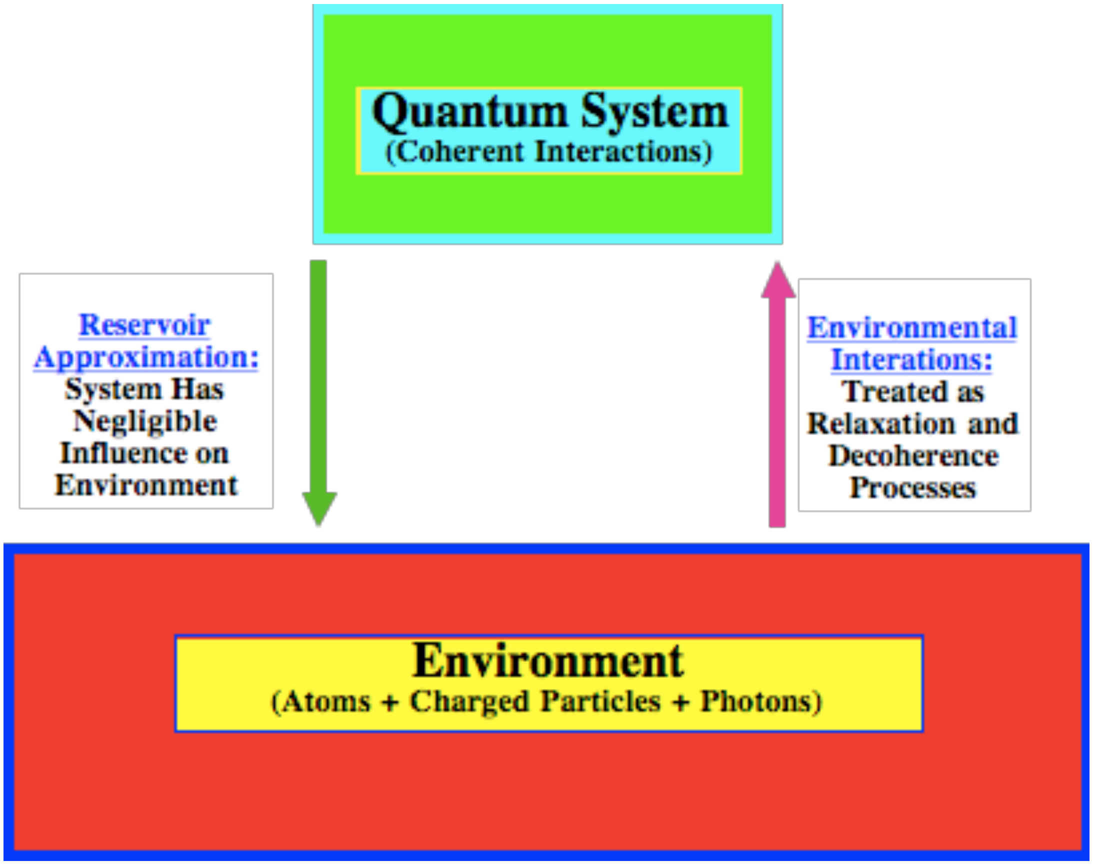
Fig. 2. In the reduced-density-operator description, the partition of the entire, interacting system into a “relevant” quantum system (which may consist of an ensemble of many-electron atomic systems and a set of emitted or observable photons) and an environment (which may consist of many-electron atoms, charged particles, and photons), which is treated using the conventional reservoir approximation. **(color online)**

Figure 1



Internal Region
N+1 electrons
exchange
and
correlation
important
External Region
scattered electron only
long-range potentials important
Sub-
region
1
Sub-
region
$p-1$
Sub-
region
p
Asymptotic Region
scattered electron
only
long-range
potentials
weak
0
a_0
a_1
a_{p-2}
a_{p-1}
a_p
∞
Radial coordinate of scattered electron

Figure 2


Quantum System
(Coherent Interactions)
Reservoir Approximation:
System Has Negligible Influence on Environment
Environmental Interations:
Treated as Relaxation and Decoherence Processes
Environment
(Atoms + Charged Particles + Photons)

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