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Reduced-Density-Matrix Description of Decoherence and Relaxation Processes for Electron-Spin Systems: Applications to Trapped Atomic Systems in Optical Lattices, Semiconductor Quantum Dots, and Vacancy Defect Centers in Solids

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ABSTRACT

The quantum dynamics of many-electron spin systems is investigated using a reduced-density-matrix description. Applications of interest include trapped atomic systems in optical lattices, semiconductor quantum dots, and vacancy defect centers in solids. Complimentary time-domain (equation-of-motion) and frequency-domain (resolvent-operator) formulations are self-consistently developed. The general non-perturbative and non-Markovian formulations provide a fundamental framework for systematic evaluations of corrections to the standard Born (lowest-order-perturbation) and Markov (short-memory-time) approximations. Particular attention is given to decoherence and relaxation processes, together with spectral-line broadening phenomena, that are induced by interactions of many-electron spin systems with photons, phonons, nuclear spins, external electric, magnetic, and electromagnetic fields. Within the framework of a quantum-open-systems (reduced-density-operator) approach, these processes are treated either as coherent interactions or as environmental interactions. The environmental interactions are incorporated by means of the general expressions that are derived for the time-domain and frequency-domain Liouville-space self-energy operators, for which the tetradic-matrix elements are explicitly evaluated in the diagonal-resolvent, lowest-order, and Markov (short-memory time) approximations.

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I. INTRODUCTION

Individual many-electron spin systems or ensembles of many-electron spin systems have been extensively investigated for use as quantum bits (qubits), with applications to quantum computation, quantum communication, quantum metrology, and quantum sensing [1-4]. In order to model the propagation of electromagnetic fields in quantum states, in particular entangled photon states, during electromagnetic interactions with many-electron spin systems, it is necessary to provide a quantum dynamical description that takes into account the various coherent interactions as well as the dominant decoherence and relaxation processes. The decoherence and relaxation processes, which are usually viewed as being detrimental for quantum information applications, are the result of the interactions of the many-electron spin system with the environment. The magnetic fields generated by the nuclear-spin environment have been considered to provide the dominant decoherence mechanism. However, the results of a number of theoretical investigations have lead to the prospect that the detrimental effects of the nuclear-spin environment can be minimized by coherent control using applied electric, magnetic, and electromagnetic fields [5, 6, 7]. In order to provide a comprehensive description of both the coherent interactions and the environmental interactions, it will be necessary to systematically take into account the fundamental interactions of the many-electron spin system with photons, phonons, nuclear spins, applied electric, magnetic, and electromagnetic fields. Utilizing the highly developed understanding of the electronic structure of many-electron atomic systems [8], we should

be able to provide realistic representations for the many-electron spin states of trapped atomic systems, semiconductor quantum dots, and vacancy defect centers in solids.

A. Reduced-Density-Matrix Approach

Using a reduced-density-matrix approach, fundamental descriptions of the various decoherence and relaxation processes can be systematically incorporated. Since the results of various theoretical investigations have lead to the suggestion that specific decoherence and relaxation processes can be advantageously controlled or minimized by applied electric, magnetic, and electromagnetic fields [5, 6, 7], it is desirable to develop the reduced-density-matrix approach in a manner such that coherent electromagnetic interactions and environmental interactions can be treated on a nearly equal footing. In the presence of environmental interactions characterized by rapid time variations, it may be necessary to employ a non-Markovian description, for which the various self-energy corrections will be functions of time (or functions of frequency in the frequency-domain formulation) and the corresponding decay mechanisms cannot be described in terms of the standard exponential time dependence. By generalizing previous investigations, a reduced-density-matrix description will be developed for the dynamical evolution of the populations and coherences of a many-electron spin system in a general optical medium, together with the dynamical description of the quantized electromagnetic fields that are interacting with the system of electron spins.

B. Electron-Spin Systems

The many-electron spin systems of interest can be excited, controlled, and interrogated by means of electric, magnetic, and electromagnetic fields. Particular attention has been directed to nitrogen-vacancy defect centers in diamond [6, 7] and similar vacancy defect centers in silicon carbide [9]. The nitrogen-vacancy defect center in diamond is negatively charged and has six electrons, five of which are from the nitrogen atom and the three carbon atoms surrounding the vacancy. Many-electron spin systems in optically trapped atomic systems [10] and semiconductor quantum dots [11] have also been investigated.

C. Organization of this Paper

In section II, we provide a systematic discussion of the various coherent interactions involving the many-electron spin quantum system, together with the environmental interactions. In Section III, the reduced-density-operator description is presented, and the complimentary time-domain (equation-of-motion) and frequency-domain (resolvent-operator) formulations are self-consistently developed. In Section IV, general expressions are derived for the decoherence and relaxation rates for the various fundamental environmental interactions. In Section V, the lowest-order non-vanishing contributions to these decoherence and relaxation rates are explicitly evaluated. In Section VI, general expressions for the single-photon and multi-photon transition rates are presented. Finally, our conclusions and future plans are given in Section VII.

II. FUNDAMENTAL INTERACTIONS

In order to investigate the roles of the various coherent interactions, together with those of the dominant environmental decoherence and relaxation mechanisms, within the framework of a reduced-density-operator approach, we introduce a partition of the entire interacting (closed) light-matter system into a relevant quantum system, which may consist of the many-electron spin system of interest, and an environment. We can then treat the coherent interactions of a many-electron spin system with electromagnetic fields, together with applied electric and magnetic fields, on a fully quantum-mechanical level, while incorporating other interactions stochastically, as environmental processes. By means of a self-consistent development of the time-domain (equation-of-motion) and frequency-domain (resolvent-operator) formulations of the reduced-density-operator description, we can provide a unified framework for the systematic investigation of the decoherence and relaxation processes, together with the associated spectral-line broadening phenomena.

A. Partition of the Total Hamiltonian for the Interacting Light-Matter System

The total Hamiltonian operator H describing the combined, interacting (closed) light-matter system can be partitioned as $H=H_0+V$, where H_0 includes the Hamiltonian operator describing the zero-order (isolated) many-electron spin system (treated either individually or as a member of an ensemble) together with the Hamiltonian operator pertaining to the separate environmental system. The total interaction operator V can then

be subdivided as $V=V^C+V^E$, into a fully quantum-mechanically treated coherent-interaction operator V^C and a stochastically treated environmental-interaction operator V^E . The partition of the entire, interacting quantum system into a coherent (or relevant) quantum system and an environment is inherently arbitrary and is by no means apparent. In the ordinary Hilbert-space description, different divisions of the total Hamiltonian operator into a zero-order (unperturbed) Hamiltonian operator and an interaction (or perturbation) operator would be equivalent if the interaction could be incorporated to all orders. In contrast, different partitions in the reduced-density-operator description are fundamentally inequivalent and will inevitably lead to dissimilar predictions. This difference is primarily the result of the neglect of correlations between the relevant system and the environment. It has been pointed out [7] that the entire set of nuclear spins may be treated as separated into two subsets, the first of which can be considered as coherently coupled to the many-electron spin system of interest while the second and much larger set of nuclear spins can be regarded as giving rise to environmental decoherence and relaxation phenomena. In this investigation, we consider different partitions for electron-spin systems interacting with coherent and environmental fields.

The many-electron spin system of interest will be a many-electron system that can be represented in terms of the individual electron-spin operators $\vec{S}_j$ or the total electronic spin operator $\vec{S}=\sum_j \vec{S}_j$, while the nuclear spins will be represented in terms of the individual nuclear-spin operators $\vec{I}_n$. The index j denotes the individual electron spins in the qubit system. The index n labels the individual nuclei in the atomic or solid-state

structure, and this index can be generalized if necessary to designate different isotopes or different nuclei. The Hamiltonian for the entire interacting system consisting of electron spins and nuclear spins includes the electron-nuclear hyperfine interaction and the various intrinsic nuclear-nuclear interactions [6, 7, 8, 12, 13]. Additional interactions that can play important roles include those involving crystal fields and deformations of the surrounding lattice. In the treatment of ensembles of many-electron spin systems, the inherent dissimilarities of the individual many-electron spin systems in vacancy-defect centers and semiconductor quantum dots will give rise to inhomogeneous mechanisms. We shall defer the treatment of inhomogeneous mechanisms to a future investigation.

B. Coherent-Interaction Operator

The leading (lowest-order) contribution to the spin-dependent component of the coherent-interaction operator V^C pertaining to a system of electron spins, which may be referred to as the spin-Zeeman interaction, can be expressed in the manifestly Hermitian form [8, 16]:

$$V_s^C = \left(\frac{eg_s}{4mc} \right) \sum_j [\vec{s}_j \cdot \vec{B}(\vec{r}_j, t) + \vec{B}(\vec{r}_j, t) \cdot \vec{s}_j] = \left(\frac{\gamma_s}{2} \right) \sum_j [\vec{s}_j \cdot \vec{B}(\vec{r}_j, t) + \vec{B}(\vec{r}_j, t) \cdot \vec{s}_j], \quad (1)$$

where $\vec{B}(\vec{r}_j, t)$ is the total coherent magnetic field acting on the electron spin system located at the position $\vec{r}_j$, including the magnetic component of the control electromagnetic field and any additional applied magnetic field. The nuclear spins $\vec{I}_n$ are

also coupled to the total magnetic field by a coherent interaction operator of the form [8, 16]:

$$V_N^C = \sum_n \vec{B}(\vec{r}_n, t) \cdot \gamma_n \cdot \vec{I}_n, \quad (2)$$

where the matrix elements of the coupling tensors γ_n may vary according to the nuclear positions, the isotope type, and the nuclei type. This interaction does not directly involve the relevant electron-spin system. However, a small subset of the nuclear spins can be treated as playing an important role in the coherent control of the system of electron spins, as discussed above [7]. Consequently, the interaction pertaining to this subset may be included in the total zero-order Hamiltonian operator pertaining to the combined electron-spin and environmental systems.

The leading contribution in the multi-pole expansion of the coherent interaction among the electron spins is given by the magnetic dipolar contribution, which can be expressed in the form [8, 16]:

$$V_{SS}^C = \sum_{i \neq j} \vec{S}_i \cdot \left(\frac{\gamma_s \gamma_s}{|\vec{r}_{ij}|^3} \right) \left(1 - \frac{3 \vec{r}_{ij} \cdot \vec{r}_{ij}}{|\vec{r}_{ij}|^2} \right) \cdot \vec{S}_j \quad (3)$$

In the treatment of an ensemble of many-electron spin systems, one may want to include the coherent interaction among the individual many-electron spin systems in the total

zero-order Hamiltonian operator pertaining to the combined electron-spin and environmental systems.

The individual charge particles in the relevant many-electron spin system can interact with the electromagnetic fields, as well as with the various applied electric and magnetic fields. We treat the system-field interaction using a 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. The interaction of the many-electron spin system with an external magnetic field $\vec{B}_{\text{ext}}(\vec{r}, t)$ will be included by expressing the combined vector potential as the sum of the electromagnetic vector potential $\vec{A}(\vec{r}, t)$ and the external vector potential $\vec{A}_{\text{ext}}(\vec{r}, t)$. The manifestly Hermitian form of the total linear contribution to the system-field interaction, including an external magnetic field $\vec{B}_{\text{ext}}$, can be written as follows [7]:

$$\begin{aligned}
 V_{\text{SF}}^1(t) = & \left(\frac{e}{2mc} \right) \sum_j \left[\vec{p}_j \cdot \vec{A}(\vec{r}_j, t) + \vec{A}(\vec{r}_j, t) \cdot \vec{p}_j \right] + \left(\frac{eg_s}{4mc} \right) \sum_j \left[\vec{s}_j \cdot \vec{\nabla}_j \times \vec{A}(\vec{r}_j, t) + \vec{\nabla}_j \times \vec{A}(\vec{r}_j, t) \cdot \vec{s}_j \right] \\
 & + \left(\frac{e}{4mc} \right) \sum_j \left[\vec{p}_j \cdot \vec{B}_{\text{ext}}(\vec{r}_j, t) \times \vec{r}_j + \vec{B}_{\text{ext}}(\vec{r}_j, t) \times \vec{r}_j \cdot \vec{p}_j \right] + \left(\frac{eg_s}{4mc} \right) \sum_j \left[\vec{s}_j \cdot \vec{B}_{\text{ext}}(\vec{r}_j, t) + \vec{B}_{\text{ext}}(\vec{r}_j, t) \cdot \vec{s}_j \right].
 \end{aligned}
 \tag{4}$$

Our detailed expression for the single-electron canonical-momentum operators $\vec{p}_j$ is given by:

$$\vec{p}_j = -i\hbar\vec{\nabla}_j = m\left(\frac{d\vec{r}_j}{dt}\right) - \left(\frac{e}{c}\right)\vec{A}(\vec{r}_j, t) - \left(\frac{e}{2c}\right)\vec{B}_{\text{ext}}(\vec{r}_j, t) \times \vec{r}_j. \quad (5)$$

The single-electron spin operators may be expressed, in terms of the Pauli operators $\vec{\sigma}_j$, in the form $\vec{s}_j = (\hbar/2)\vec{\sigma}_j$. The external magnetic field $\vec{B}_{\text{ext}}(\vec{r}, t)$ is often assumed to be spatially uniform on the scale of the dimensions of the many-electron spin system and stationary relative to the relevant interaction times. The external vector potential is then given by $\vec{A}_{\text{ext}}(\vec{r}, t) = (1/2)\vec{B}_{\text{ext}}(\vec{r}, t) \times \vec{r}$. The magnetic field associated with the electromagnetic vector potential $\vec{A}(\vec{r}, t)$ is given by $\vec{B}(\vec{r}, t) = \vec{\nabla} \times \vec{A}(\vec{r}, t)$. The sums over j include all electrons (with charge $-e$) in the electron-spin system. For long-wavelength (e. g., infrared) radiation, the contributions involving the nuclear canonical-momentum and nuclear-spin operators can play an important role and should also be considered. The terms involving the electron spin operators $\vec{s}_j$ have already been incorporated in Eq. (1) and therefore may be omitted in Eq. (4). The contributions involving the nuclear-spin operators are assumed to be included in Eq. (2). The quadratic (diamagnetic) contribution to the system-field interaction has been omitted, since the consistent incorporation of this contribution would entail the systematic inclusion of higher-order relativistic interactions involving the electron and nuclear spins and the electric and magnetic fields.

C. Environmental-Interaction Operator

We now consider various contributions to the environmental-interaction operator V^E . The dipolar contribution arises from the hyperfine interaction between the many-electron spin system and the nuclear spins and can be expressed as follows [8, 16]:

$$V_{SN}^E = \sum_n \vec{S} \cdot \mathbf{A}_n \cdot \vec{I}_n = \sum_n \vec{S} \cdot \left(\frac{\gamma_s \gamma_n}{|\vec{r}_n|^3} \right) \left(1 - \frac{3\vec{r}_n \vec{r}_n}{|\vec{r}_n|^2} \right) \cdot \vec{I}_n, \quad (6)$$

where the hyperfine coupling constants are given by the matrix elements of the tensors $\mathbf{A}_n$. This interaction can be considered as an electron-spin Zeeman interaction involving the combined magnetic field produced by the nuclear spins. The dominant contribution to the interaction coupling the nuclear spins is given by the magnetic dipolar contribution [8, 16]:

$$V_{NN}^E = \sum_{m \neq n} \vec{I}_m \cdot \mathbf{C}_{mn} \cdot \vec{I}_n = \sum_{m \neq n} \vec{I}_m \cdot \left(\frac{\gamma_m \gamma_n}{|\vec{r}_{mn}|^3} \right) \left(1 - \frac{3\vec{r}_{mn} \vec{r}_{mn}}{|\vec{r}_{mn}|^2} \right) \cdot \vec{I}_n, \quad (7)$$

where the dipolar coupling constants are given by the elements of the tensor $\mathbf{C}_{mn}$. This interaction may have an important indirect effect on the many-electron spin system as a result of the role of a small subset of the nuclear spins in the coherent control of the system of many-electron spins, as discussed above. Accordingly, it may be necessary to redefine the partition of the entire interacting quantum system in such a manner that a small subset of nuclear spins can be treated as part of the relevant quantum system, while the remaining much larger subset of nuclear spins can be included in the environment.

The dipolar interaction among the relevant electron spins and the small subset of nuclear spins, which is contained in the expression given by Eq. (3), accordingly should be included in the total zero-order Hamiltonian for the combined system of electron and nuclear spins. In the present investigation, we shall preliminarily include all nuclear spins in the environment.

We shall also consider contributions to the interaction operator arising from the coupling of the electron-spin system with environmental photons and phonons. The contribution arising from photons in the environmental electromagnetic field, which will be described by an environmental vector potential $\vec{A}^E$, can be expressed by means of the following interaction operator:

$$V_{SF}^E = \left(\frac{e}{2mc} \right) \sum_j \left[\vec{p}_j \cdot \vec{A}^E(\vec{r}_j, t) + \vec{A}^E(\vec{r}_j, t) \cdot \vec{p}_j \right] + \left(\frac{eg_s}{4mc} \right) \sum_j \left[\vec{s}_j \cdot \vec{\nabla}_j \times \vec{A}^E(\vec{r}_j, t) + \vec{\nabla}_j \times \vec{A}^E(\vec{r}_j, t) \cdot \vec{s}_j \right]. \quad (8)$$

The contribution V_{SV}^E arising from phonons corresponding to quantized vibrational modes (V) can be expressed in a form that is analogous to the result given above for the spin-independent part of the electron-photon interaction. Following the formulations given by Ashcroft and Mermin [14] and by Mahan [15], this contribution can be expressed in terms of the following electronic parts (to be combined with the terms arising from the phonon creation and annihilation operators):

$$V_{sv}^E = \left(\frac{\hbar}{2NM\omega_v} \right)^{1/2} \sum_j \sum_{\vec{R}} \left[\frac{\partial}{\partial \vec{Q}_{\vec{R}}} V_0(\vec{r}_j) \cdot \vec{\epsilon}_{\vec{q}_v \lambda_v} e^{i(\vec{q}_v \cdot \vec{R})} \right]. \quad (9)$$

In this expression, the phonon modes labeled by v are specified in terms of the wave-vectors $\vec{q}_v$, the frequencies ω_v , and the polarizations λ_v . The effective local single-electron potential $V(\vec{r}_j)$ experienced by the electron j in the many-electron quantum system has been expanded around the equilibrium positions of the nuclei, and only the lowest-order contribution has been retained. The effective local single-electron potential at these equilibrium positions is denoted by $V_0(\vec{r}_j)$. The displacements of the nuclei from the equilibrium positions $\vec{R}$ are denoted by $\vec{Q}_{\vec{R}}$. N is either the number of unit cells in a crystal lattice or the number of atoms in a molecule, and M is the atomic mass. An index may be included on M to distinguish the different atoms in the unit cell of a crystal lattice or the different atoms in a molecule. The polarization unit vectors $\vec{\epsilon}_{\vec{q}_v \lambda_v}$ are introduced when the nuclear displacements $\vec{Q}_{\vec{R}}$ are expressed in terms of the coordinates of the phonon modes labeled by v . Higher-order (anharmonic) contributions in the expansion of the effective local single-electron potential would represent multi-phonon interactions. In addition, spin-dependent contributions to the electron-phonon interaction have been discussed in other theoretical investigations.

The unperturbed many-electron states can be represented as sums of anti-symmetrized products (Slater determinants) of single-electron wave-functions from a complete basis set. The matrix elements of the various interaction operators between the

unperturbed many-electron states can then be evaluated as sums involving the matrix elements of the single-electron interaction operators between the active single-electron basis states in the transition. In order to take into account the influence of a crystal field, linear combinations of the unperturbed many-electron system states can be constructed using the transformation coefficients pertaining to the irreducible representation appropriate to the relevant crystallographic point group [16]. Finally, it may be necessary to take into account the contact hyperfine interaction between the electron-spin states and the nuclear spins,

III. REDUCED-DENSITY-OPERATOR APPROACH

A density-operator approach can provide an advantageous starting point for a non-perturbative and non-equilibrium quantum-statistical description of many-electron spin systems under the influence of coherent and environmental interactions. The quantum-open-systems (reduced-density-operator) approach [17-22] can serve as a general framework for a fundamental microscopic description of the decoherence and relaxation processes, which arise from the influence of the environment. In the conventional reservoir approximation, the environment is assumed to be essentially unaffected by its interactions with the relevant (many-electron spin) quantum system of interest. Accordingly, in the conventional reservoir approximation, the environment can be represented by a time-independent density operator.

A. Reduced-Density-Operator Description

Within the framework of the reduced-density-operator approach, the influence of the environment on the relevant (many-electron spin) quantum system of interest is treated stochastically, in terms of decoherence and relaxation processes together with the associated spectral-line broadening mechanisms. These stochastic kinetics and spectral phenomena can be systematically and self-consistently investigated in terms of the Liouville-space self-energy corrections that are introduced in the complimentary time-domain (equation-of-motion) and frequency-domain (resolvent-operator) formulations of the reduced-density-operator approach [17].

A statistical state of the combined, interacting (closed) quantum system is conventionally assumed to be initially expressible as the uncorrelated, tensor-product $\rho(t_0) = \rho^S \otimes \rho^E$ of the separate density operators representing the relevant quantum system (S) of interest, which may be composed of the many-electron spin system together with the coherent fields, and the environment (E). The quantum-statistical state of the relevant quantum system, at an arbitrary time t , can be represented by means of the reduced, relevant density operator defined by $\rho^r(t) = \text{Tr}_E\{\rho(t)\}$, where the quantum-statistical average (partial-trace operation) indicated by Tr_E is to be taken over the large set of quantum numbers corresponding to the environmental degrees of freedom.

The reduced-density-operator description can be presented in compact forms by adopting the Liouville-space operator representation [23-28]. The Liouville-space operators are defined within a generalized Hilbert space, in which ordinary Hilbert-space

operators, such as density operators, play the role of state vectors. The complete set of elementary Hilbert-space (density) operators of the form $|\alpha\rangle\langle\beta|$ provides a complete Liouville-space basis set. The elements of the complete Liouville-space basis set may be denoted, in terms of the two Hilbert-space state indices α and β , using the Liouville-space Dirac notation $|\alpha,\beta\rangle\rangle$. In this basis, the Liouville-space operators (which will be denoted by overbars in the following analyses) are represented by tetradic matrices, which are specified by four ordinary Hilbert-space state indices. The complex inner product $\langle\langle\rho_1|\rho_2\rangle\rangle$ of two Liouville-space state vectors $|\rho_1\rangle$ and $|\rho_2\rangle$ is defined as the trace operation $\text{Tr}(\rho_1^+\rho_2)$, where the superscript “+” indicates the adjoint.

B. Reduced-Density-Operator Description in the Schrödinger picture

We will adopt the Schrödinger picture, for which the reduced density operator is treated as a time-dependent operator, and either a frequency-domain (resolvent-operator) formulation or a time-domain (equation-of-motion) formulation can be employed. However, the operators such as those representing the quantized electromagnetic field are treated as time-independent operators. For open quantum systems, composed of a relevant quantum system and an environment, the results obtained using the alternative Heisenberg picture will not necessarily be equivalent.

1. Frequency-Domain (Resolvent-Operator) Formulation

The experimental investigation of the many-electron spin decoherence and relaxation usually involves the analysis of the spectral-line shapes associated with single-photon and multi-photon transitions, e. g, photoluminescence. In the frequency-domain formulation of our reduced-density-operator description, the electromagnetic-transition rate for a general multi-photon transition can be expressed, in terms of the reduced, relevant Liouville-space transition operator $\bar{T}^r(+i\epsilon)$, the initial-state reduced density operator ρ_i^r , and the relevant final-state projection operator P_f^r , in the generalized Fermi Golden-Rule form [17, 26-28]:

$$A_R(i \rightarrow f) = -i \lim_{\epsilon \rightarrow 0} \langle \langle P_f^r | \bar{T}^r(+i\epsilon) | \rho_i^r \rangle \rangle = -i \lim_{\epsilon \rightarrow 0} \langle \langle P_f^r | \bar{V}^r + \bar{V}^r \bar{G}^r(+i\epsilon) \bar{V}^r | \rho_i^r \rangle \rangle. \quad (10)$$

The reduced, relevant Liouville-space resolvent (or Green) operator is expressed by $\bar{G}^r(+i\epsilon) = [+i\epsilon - \bar{L}^r - \bar{\Sigma}(+i\epsilon)]^{-1}$, where $\bar{L}^r$ is the relevant Liouvillian operator (which is defined in terms of the relevant Hamiltonian operator H^r) and $\bar{\Sigma}(z)$ is the Liouville-space self-energy operator. The tetradic-matrix elements of the relevant Liouvillian operator $\bar{L}^r$ may be obtained by means of the following commutation relationships:

$$\langle \alpha | \bar{L}^r | \rho^r | \beta \rangle = \langle \alpha | (1/\hbar) [H^r, \rho^r] | \beta \rangle = \sum_{\gamma} \sum_{\delta} \bar{L}_{\alpha\beta\gamma\delta}^r \rho_{\gamma\delta}^r = \sum_{\gamma} \sum_{\delta} (1/\hbar) (H_{\alpha\gamma}^r \delta_{\delta\beta} - \delta_{\alpha\gamma} H_{\delta\beta}^r) \rho_{\gamma\delta}^r. \quad (11)$$

The relevant Hamiltonian operator H^r describes the many-particle quantum system of interest together with the quantized electromagnetic field and possibly applied electric and magnetic fields. The relevant Liouvillian operator $\bar{L}^r$ can be decomposed as

$\bar{L}^r = \bar{L}_0^r + \bar{V}^r$, where $\bar{L}_0^r$ is the zero-order (unperturbed) relevant Liouvillian operator corresponding to the zero-order relevant Hamiltonian operator H_0^r and the Liouville-space perturbation operator $\bar{V}^r$ describes the relevant electromagnetic interaction.

The reduced, relevant Liouville-space transition operator can be more conveniently evaluated, in terms of the zero-order reduced, relevant Liouville-space resolvent (or Green) operator $\bar{G}_0^r(+i\varepsilon) = [+i\varepsilon - \bar{L}_0^r - \bar{\Sigma}(+i\varepsilon)]^{-1}$, as a perturbation expansion in powers of $\bar{V}^r$:

$$\bar{T}^r(+i\varepsilon) = \bar{V}^r + \bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r + \bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r + \bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r \dots \quad (12)$$

As a first approximation, we may retain only the lowest-order non-vanishing contribution to the electromagnetic-transition rate for a specific n -photon process of interest. Higher-order contributions will give rise to QED radiative corrections. For a single-photon transition, the lowest-order contribution will be given by $\bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r$. In the case of a two-photon transition, the lowest-order contribution will be provided by $\bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r \bar{G}_0^r(+i\varepsilon) \bar{V}^r$. In the kinetic and spectral descriptions of electromagnetic interactions involving many-electron spin systems, it may be necessary to take into account an extensive class of elementary single-photon and multi-photon transitions.

a. Frequency-Domain Liouville-Space Self-Energy Operator

The frequency-domain Liouville-space self-energy operator $\bar{\Sigma}(z)$ can be expressed in terms of the Zwanzig Liouville-space projection operators $\bar{P} = |\rho^E\rangle\langle\langle I^E|$ and $\bar{Q} = 1 - \bar{P}$, where I^E denotes the environmental identity operator [26, 28]. The projection operator $\bar{P}$ projects onto the subspace of states for the relevant-system degrees of freedom (uncorrelated with the environmental degrees of freedom), while complementary projection operator $\bar{Q}$ projects onto the orthogonal subspace of states for the irrelevant (environmental) degrees of freedom (taking into account the system-environment correlations). The frequency-domain Liouville-space self-energy operator can then be expressed in the forms [17, 26, 28]:

$$\bar{\Sigma}(z) = \bar{P}\bar{V}^{\text{ir}}\bar{P} + \bar{P}\bar{V}\bar{Q}\frac{1}{z - \bar{Q}\bar{L}\bar{Q}}\bar{Q}\bar{V}\bar{P} = \text{Tr}_E \left[\left(\bar{V}^{\text{ir}} + \bar{V}\bar{Q}\frac{1}{z - \bar{Q}\bar{L}\bar{Q}}\bar{Q}\bar{V} \right) \rho^E \right]. \quad (13)$$

The complete Liouvillian 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 is partitioned as $\bar{V} = \bar{V}^{\text{r}} + \bar{V}^{\text{ir}}$, where the irrelevant Liouville-space interaction operator $\bar{V}^{\text{ir}}$ includes the environmental interactions. A major advantage of the Liouville-space operator representation is that a fundamental microscopic treatment can be provided for the environmental interactions, on an equal footing with the QED radiative corrections, which arise from virtual transitions involving the creation and annihilation of electron-positron pairs together with photons. In many descriptions, the environmental interactions are described by the introduction of phenomenological parameters.

b. Initial and Final States in the Electromagnetic Transitions

In our description of an extensive class of single-photon ($n = 1$) and multi-photon ($n > 1$) processes, the initial-state reduced density operator ρ_i^r can be represented in terms of the tensor-product eigenstates $|\alpha\rangle = |a, \{n_i\}\rangle = |a\rangle \otimes |\{n_i\}\rangle$. The relevant final-state projection operator P_f^r projects onto the subspace of tensor-product eigenstates formed from the unperturbed many-electron eigenstates $|b\rangle$ that can be created as a result of an electromagnetic transition from the initial many-electron state a . Accordingly, the required operator eigenstate decompositions can be expressed as follows:

$$|\rho_i^r\rangle\rangle = \sum_a \sum_{a'} \sum_{\{n_i\}} \sum_{\{n'_i\}} |aa', \{n_i\} \{n'_i\}\rangle\rangle \langle\langle aa' | \rho_i^s \rangle\rangle \langle\langle \{n_i\} \{n'_i\} | \rho_i^r \rangle\rangle, \quad (14)$$

$$|P_f^r\rangle\rangle = \sum_b \sum_{\{n'_i\}} |bb, \{n'_i\} \{n'_i\}\rangle\rangle. \quad (15)$$

Note that the indices that are used as subscripts on the reduced density operator and on the projection operator are intended to denote, respectively, the initial and final states of the relevant many-particle and many-photon quantum system in the electromagnetic transition, while the index i that is used as a subscript on the photon occupation numbers n and n' will be understood to denote the various modes of the quantized electromagnetic field. The many-electron states a and b in the electromagnetic transition may also be

specified in terms of sets of single-electron-state occupation numbers. The many-electron states may also be taken to be eigenstates in the presence of applied electric and magnetic fields. We emphasize that the general reduced-density-operator description is applicable to non-equilibrium quantum-statistical distributions for the charged particles and the electromagnetic fields, which can be obtained starting from the time-domain (equation-of-motion) formulation of our reduced-density-operator description presented below.

Eq. (14) has been simplified by introducing the conventional assumption that the initial-state reduced density operator can be expressed as a tensor product of the separate initial-state density operators for the isolated many electron spin system (S) and for the relevant electromagnetic radiation field (R), i. e., $\rho_i^r = \rho_i^S \otimes \rho_i^R$. Note that, in this eigenstate decomposition, both the initial matter-state coherences (corresponding to the non-diagonal reduced-density-matrix elements pertaining to the electron-spin with $a \neq a'$) and the analogous initial-state electromagnetic-field correlations (involving non-diagonal reduced-density-matrix elements with $\{n_i\} \neq \{n'_i\}$) have been taken into account. This will be necessary for the treatment of various coherent interactions.

When the system-environment interactions are sufficiently weak, the Liouville-space self-energy operator $\bar{\Sigma}$ may be expanded in a perturbation series involving increasing powers of the total Liouville-space interaction operator $\bar{V}$. Retaining only the lowest-order non-vanishing contribution, which corresponds to the Born approximation, the total spectral-line shift and width in the diagonal-resolvent approximation can be reduced to the sums of the partial contributions from elementary collisional and radiative

processes acting alone [17]. Interference between transition amplitudes can occur in the high-order contributions to the width and shift, as well as in our general tetradic-matrix expression, which is valid for overlapping spectral lines.

2. Time-domain (Equation-of-Motion) Formulation

The decoherence and relaxation rates pertaining to the many-electron spin system are most generally defined within the framework of a quantum-kinetics (equation-of-motion) formulation of the reduced-density-operator description, featuring an equation-of-motion for the reduced density operator. The time-domain (equation-of-motion) formulation of the reduced-density-operator description is based on the generalized Master equation [17, 26, 28]:

$$\frac{\partial}{\partial t} \rho^r(t) = -i \bar{L}^r(t) \rho^r(t) - i \int_{t_0}^t dt' \bar{\Sigma}(t, t') \rho^r(t'). \quad (16)$$

This closed-form equation of motion for the reduced, relevant density operator $\rho^r(t) = \bar{P} \rho(t)$ has been derived by neglecting the initial-state correlations. Initial-state correlations are automatically excluded by the conventional assumption that the entire initial-state density operator for the combined, interacting light-matter system can be represented as an uncorrelated, tensor product of individual density operators for the separate, isolated subsystems.

a. Time-Domain Self-Energy Operator

The time-domain Liouville-space self-energy operator kernel $\bar{\Sigma}(t, t')$ can be formally expressed by means of the relationships [17, 26, 28]:

$$\bar{\Sigma}(t, t') = -i\bar{P}\bar{V}(t)\bar{Q}\bar{g}_Q(t, t')\bar{Q}\bar{V}(t')\bar{P} = -i\text{Tr}_E[\bar{V}(t)\bar{Q}\bar{g}_Q(t, t')\bar{Q}\bar{V}(t')\rho^E]. \quad (17)$$

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:

$$\bar{g}_Q(t, t') = T \exp \left[-i \int_{t'}^t dt'' \bar{Q}\bar{L}(t'')\bar{Q} \right]. \quad (18)$$

In contrast to the propagator $\bar{g}(t, t')$ corresponding to the total Liouvillian operator $\bar{L}$ for the closed interacting light-matter system, which describes unitary (reversible) time evolution, the Q-subspace projection defined by Eq. (18) describes non-unitary (irreversible) time evolution. 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 may be viewed in terms of the connection between the time-domain propagator and corresponding frequency-domain resolvent operator, which can be most generally expressed in the contour-integration form:

$$\bar{g}(t, t') = \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi i} \oint dz \exp[-iz(t-t')] \bar{G}(z+i\varepsilon), \quad (19)$$

where the general contour integration can be evaluated as a Fourier or a Laplace transformation.

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

$$\bar{\Sigma}(t, t') = \lim_{z \rightarrow i0} \bar{\Sigma}(z) \delta(t-t'). \quad (20)$$

In the Markov approximation, the corresponding frequency-domain Liouville-space self-energy operator $\bar{\Sigma}(i0)$, which will be denoted simply by $\bar{\Sigma}$, is independent of the frequency. In the Markov approximation, the set of relaxation and decoherence rates that is obtained from the time-domain formulation will also provide the set of spectral-line widths and shifts that can be derived using the frequency-domain formulation. For a completely consistent treatment of the non-Markovian dynamics, it may be necessary to retain the initial-state correlation term that was excluded in the derivation of the generalized Master equation. In this case, the results obtained from the two different formulations will not be simply related.

b. Many-Particle-System and Electromagnetic-Field Equations

An equation of motion for the many-particle-system (the many-electron spin system) density operator can be derived from Eq. (16) by performing the additional average (partial-trace) operation over the photon states. On the other hand, the dynamical equation for the density operator representing the quantum-statistical state of the electromagnetic field can be obtained from Eq. (16) by carrying out the complimentary additional average (partial-trace) operation over the many-particle-system states. In this investigation, we consider only the equation of motion for the electron-spin system and defer to a separate investigation the treatment of the dynamics of the quantized electromagnetic field.

Quantum-mechanical interference terms will be encountered in the evaluation of the tetradic matrix elements of the Liouville-space self-energy operator kernel that appears in the equation of motion for the many-particle-system density operator. After introducing the Born (lowest-order) and Markov (short-memory-time) approximations, the set of dynamical equations for the many-particle-system state-population densities (corresponding to the diagonal density-matrix elements) can be expressed in terms of the familiar (lowest-order) radiative and non-radiative transition rates that are obtained from an evaluation of the standard Fermi Golden-Rule formula of ordinary Hilbert-space perturbation theory. The optical Bloch equations are usually understood to correspond to

the extended set of density-matrix equations, taking into account the many-particle-system state coherences (corresponding to the non-diagonal density-matrix elements).

C. Hierarchical Reduced-Density-Operator Formulations for Many-Body Systems

In the treatment of many-electron quantum correlations within the framework of the reduced-density-operator approach, it may be necessary to introduce a correlation (or cluster) decomposition for the reduced density operator, together with a set (hierarchy) of coupled equations of motion for the various correlation components. For example, the equation of motion for the single-electron-spin reduced density operator would be coupled to that for the two-electron-spin reduced density operator. This coupling is obviously a consequence of the interaction. The introduction of a set (hierarchy) of coupled reduced-density-operator equations of motion is expected to be essential for the practical description of solid-state systems, for which the number of electrons is very large in comparison with that for atomic systems, and also for the treatment of the subset of nuclear spins that are coherently controlled. In order to treat a quantized electromagnetic field on an equal footing with the quantized matter system, it will be necessary to introduce a generalized correlation (or cluster) decomposition, together with a generalized correlation hierarchy of coupled reduced-density-operator equations of motion. In this generalization, quantum correlations involving the photons would be included, on an equal footing with the charged-particle correlations. A further generalization would be necessary to take into account correlations involving phonons. In the reduced-density-matrix approach, it will be necessary to separate the many-body

correlations that must be treated as a part of a fully correlated quantum system from those interactions (if any) that can be adequately treated as environmental effects.

IV. GENERAL EXPRESSIONS FOR THE DECOHERENCE AND RELAXATION RATES FOR THE VARIOUS FUNDAMENTAL ENVIRONMENTAL INTERACTIONS

In this section, explicit expressions for the tetradic-matrix elements of the frequency-domain Liouville-space self-energy operator defined by Eq. (13) will be derived, with account taken of the contributions associated with various fundamental environmental interactions, on a nearly equal footing with the various coherent interactions involving the many-electron spin system. In the Markov (short-memory-time) approximation, this Liouville-space self-energy operator is independent of frequency and is equivalent to the corresponding time-domain Liouville-space self-energy operator, representing the decoherence and relaxation rates.

A. Explicit Expressions for the Zwanzig Liouville-Space Projections Operators

The zero-order tensor-product quantum states of the combined system, consisting of the relevant many-electron system and the environment, will now be denoted by $|\alpha\rangle = |a, \{n_i\}\{n_i\}\{m_v\}\rangle = |a\rangle \otimes |\{n_i\}\rangle \otimes |\{n_i\}\rangle \otimes |\{m_v\}\rangle$. The zero-order quantum states of the many-electron spin system, including the electron-spin quantum numbers s , will be specified by a . The entire set of nuclear-spin occupation numbers, a small subset of which

may be included in the relevant quantum system, are denoted by $\{n_i\}$. The set of photon-mode occupation numbers, including the relevant and the environmental electromagnetic-field modes, will be denoted by $\{n_i\}$. Finally, the set of phonon-mode occupation numbers will be denoted by $\{m_v\}$. The Zwanzig Liouville-space projection operators $\bar{P} = |\rho^E\rangle\langle\langle I^E|$ and $\bar{Q} = 1 - \bar{P}$ can then be generally expressed in explicit forms by using the following environmental-eigenstate decompositions:

$$|\rho^E\rangle\langle\langle I^E| = \sum_{\{n_i\}} \sum_{\{n_i\}} \sum_{\{m_v\}} |\{n_i\}\{n_i\}\{n_i\}\{n_i\}\{m_v\}\{m_v\}\rangle\langle\langle \{n_i\}\{n_i\}|\rho^I\rangle\langle\langle \{n_i\}\{n_i\}|\rho^R\rangle\langle\langle \{m_v\}\{m_v\}|\rho^V\rangle\langle\langle, \quad (21)$$

$$|I^E\rangle\langle\langle I^E| = \sum_{\{n_i\}} \sum_{\{n_i\}} \sum_{\{m_v\}} |\{n_i\}\{n_i\}\{n_i\}\{n_i\}\{m_v\}\{m_v\}\rangle\langle\langle \{n_i\}\{n_i\}|\rho^I\rangle\langle\langle \{n_i\}\{n_i\}|\rho^R\rangle\langle\langle \{m_v\}\{m_v\}|\rho^V\rangle\langle\langle, \quad (22)$$

We have introduced the conventional assumption that the environmental density operator ρ^E can be expressed, as the tensor product of the individual density operators for the nuclear spin system (I), for the electromagnetic radiation field (R), and for the vibrational field (V), in the form $\rho^E = \rho^I \otimes \rho^R \otimes \rho^V$. In contrast to the relevant photons that are taken into account in the coherent relevant electromagnetic interaction, which could be produced by incident lasers or other coherent radiation sources, the environmental photons and phonons may be represented by the diagonal density-matrix elements corresponding to thermal-equilibrium distributions and the non-diagonal elements can then be assumed to vanish.

B. Tetradic-Matrix Elements of the Liouville-Space Environmental-Interaction Operator

The total Liouville-space interaction operator $\bar{V}$ can be represented in the general form:

$$\begin{aligned}
 \bar{V} = & \sum_{bb'} \sum_{aa'} \sum_{\{n_i\}\{n'_i\}} \sum_{\{n''_i\}\{n'''_i\}} \sum_{\{m_v\}\{m'_v\}} \left| bb'; \{n''_i\}\{n'''_i\}\{n_i\}\{n'_i\}, \{m_v\}\{m'_v\} \right\rangle \rangle \\
 & \times \left\langle \left\langle bb'; \{n''_i\}\{n'''_i\} \right| \bar{V}^I \left| aa'; \{n_i\}\{n'_i\} \right\rangle \right\rangle \left\langle \left\langle aa'; \{n_i\}\{n'_i\}\{n_i\}\{n'_i\}, \{m_v\}\{m'_v\} \right| \right. \\
 & + \sum_{bb'} \sum_{aa'} \sum_{\{n_i\}\{n'_i\}} \sum_{\{n''_i\}\{n'''_i\}} \sum_{\{m_v\}\{m'_v\}} \left| bb'; \{n_i\}\{n'_i\}\{n''_i\}\{n'''_i\}, \{m_v\}\{m'_v\} \right\rangle \rangle \\
 & \times \left\langle \left\langle bb'; \{n''_i\}\{n'''_i\} \right| \bar{V}^R \left| aa'; \{n_i\}\{n'_i\} \right\rangle \right\rangle \left\langle \left\langle aa'; \{n_i\}\{n'_i\}\{n_i\}\{n'_i\}, \{m_v\}\{m'_v\} \right| \right. \\
 & + \sum_{bb'} \sum_{aa'} \sum_{\{n_i\}\{n'_i\}} \sum_{\{n''_i\}\{n'''_i\}} \sum_{\{m_v\}\{m'_v\}} \left| bb'; \{n_i\}\{n'_i\}\{n_i\}\{n'_i\}, \{m_v\}\{m'_v\} \right\rangle \rangle \\
 & \times \left\langle \left\langle bb'; \{m_v\}\{m'_v\} \right| \bar{V}^V \left| aa'; \{m_v\}\{m'_v\} \right\rangle \right\rangle \left\langle \left\langle aa'; \{n_i\}\{n'_i\}\{n_i\}\{n'_i\}, \{m_v\}\{m'_v\} \right| \right.
 \end{aligned} \tag{23}$$

The total Liouville-space interaction operator has been taken to be the sum of the individual Liouville-space operators describing the electron-nuclear-spin (I), electron-photon (R), and electron-phonon (V) interactions, i. e., $\bar{V} = \bar{V}^I + \bar{V}^R + \bar{V}^V$.

The tetradic-matrix elements of the Liouville-space interaction operator describing the electron-nuclear-spin interactions can be obtained from Eq. (6). The tetradic-matrix elements of the Liouville-space interaction operator describing the electron-photon interactions can be obtained from Eq. (8). The tetradic-matrix elements

of the Liouville-space interaction operator describing the electron-phonon interactions can be obtained, in a form that is analogous to Eq. (8), by replacing the photon occupation numbers with the phonon occupation numbers. The ordinary Hilbert-space matrix elements $V_{ba}(\vec{q}_v \lambda_v)$ describing the electron-phonon interactions can be expressed in a form that is analogous to the result given for the electron-photon interactions by means of Eq. (9).

C. Tetradic-Matrix Elements of the Liouville-Space Self-Energy Operator

It will now be convenient to introduce the Liouville-space relaxation operator:

$$\bar{R}(z) = \bar{V} + \bar{V} \bar{Q} \frac{1}{z - \bar{Q} \bar{L} \bar{Q}} \bar{Q} \bar{V} = \bar{V} + \bar{V} \bar{Q} \frac{1}{z - \bar{Q} \bar{L}_0 \bar{Q}} \bar{Q} \bar{R}(z) \quad (24)$$

The second of the two equivalent forms has been more conveniently expressed in terms of the zero-order Liouvillian operator $\bar{L}_0$ for the combined system, without the total Liouville-space interaction operator $\bar{V}$. Since we will include all photon modes and will preliminarily also include all nuclear spins in the representation of the Liouville-space environmental (irrelevant) interaction operator $\bar{V}^{\text{ir}}$, the distinction between Liouville-space environmental (irrelevant) interaction operator $\bar{V}^{\text{ir}}$ and the total Liouville-space interaction operator $\bar{V}$ will not be necessary. Consequently, the Liouville-space self-energy operator $\bar{\Sigma}(z)$ defined by Eq. (13) can be expressed as follows:

$$\bar{\Sigma}(z) = \bar{P}\bar{R}(z)\bar{P} = \text{Tr}_E[\bar{R}(z)\rho^E] \quad (25)$$

Since the number of the relevant photon modes is very small in comparison with the total number of the photon modes, we can introduce the conventional approximation $\bar{Q}=1-\bar{P}=1$.

The Liouville-space self-energy operator $\bar{\Sigma}(z)$ can be conveniently expressed, in terms of the Liouville-space shift and width operators $\bar{\Delta}(x)$ and $\bar{\Gamma}(x)$, as follows [29, 30]:

$$\lim_{\eta \rightarrow 0} \bar{\Sigma}(x \pm i\eta) = \bar{\Delta}(x) \mp i \frac{\bar{\Gamma}(x)}{2}. \quad (26)$$

In the diagonal-resolvent approximation, the diagonal tetradic-matrix elements of $\bar{\Delta}(x)$ correspond to the shifts associated with the individual spectral lines $a \rightarrow b$ and the diagonal tetradic-matrix elements of $\bar{\Gamma}(x)$ can be interpreted as the full widths at the half maxima.

Using Eqs. (25) - (26) and approximation $\bar{Q}=1-\bar{P}=1$, the lowest-order non-vanishing contribution to the Liouville-space line-width operator can be expressed as follows:

$$\bar{\Gamma}(x) = 2\pi \bar{P} \bar{V} \delta(x - \bar{L}_0) \bar{V} \bar{P} = 2\pi \text{Tr}_E \left[\bar{V} \delta(x - \bar{L}_0) \bar{V} \rho^E \right] \quad (27)$$

The Liouville-space line-shift operator can be evaluated as follows:

$$\bar{\Delta}(x) = \text{Re}(\bar{V}) + \frac{P}{2\pi} \int_{-\infty}^{\infty} \frac{dx' \bar{\Gamma}(x')}{x - x'}, \quad (28)$$

where Re denotes the real part and P indicates the Cauchy principal value.

V. LOWEST-ORDER NON-VANISHING CONTRIBUTION TO THE LIOUVILLE-SPACE LINE-WIDTH OPERATOR

The tetradic-matrix elements of the lowest-order non-vanishing contribution to the Liouville-space line-width operator can be generally expressed as follows:

$$\langle \langle ab; \{n_i\} \{n'_i\} | \bar{\Gamma}(x) | a'b'; \{n''_i\} \{n'''_i\} \rangle \rangle = 2\pi \text{Tr}_E \sum_{\alpha''} \sum_{\beta''} \langle \langle \alpha, \beta | \bar{V} \delta(x - \bar{L}_0) | \alpha'', \beta'' \rangle \rangle \langle \langle \alpha'', \beta'' | \bar{V} \rho^E | \alpha', \beta' \rangle \rangle. \quad (29)$$

The states α , α' , α'' , β , β' , and β'' are formed from the relevant many-electron and multi-photon states appearing on the left-hand side by including a complete set of environmental nuclear-spin, photon, and phonon states $\{\bar{n}_l\} \{\bar{n}_i\} \{\bar{m}_v\}$, which will be denoted by $\square$. The relevant photon modes will be included in the set of the environmental

photon modes. The photon density operator that we have denoted by ρ^R in Eq. (16) should accordingly be understood as the sum of the photon density operator representing the incident (laser) electromagnetic field and the environmental-photon density operator, which may correspond to a thermal-equilibrium distribution.

If we preliminarily include all nuclear spins in the environment, then we can assume that the operators $\bar{L}_0$ and ρ^E are diagonal in the representation based on the tensor-product quantum states of the combined system. We expand the tetradic matrix elements of the Liouville-space interaction operator $\bar{V}$ in terms of the matrix elements of the total ordinary Hilbert-space interaction operator V , and we introduce the detailed tensor-product state specifications. We then introduce the separate electron-nuclear-spin, electron-photon, and electron-phonon interaction operators and also the individual environmental nuclear-spin, photon, and phonon density operators. Taking into account that the trace of each of the individual environmental density operators is unity, we obtain a detailed general result for the tetradic-matrix elements of the lowest-order non-vanishing contribution to the Liouville-space line-width operator.

A. Tetradic-Matrix Elements of the Lowest-Order Non-Vanishing Contribution to the Liouville-Space Line-Width Operator in the Diagonal-Resolvent Approximation

We now introduce the diagonal-resolvent approximation, keeping in mind that the complete analysis of the decoherence and relaxation phenomena will require the evaluation of the non-diagonal tetradic matrix elements of the Liouville-space self-energy

operator. In the diagonal-resolvent approximation, it is necessary to consider only the diagonal tetradic-matrix elements of the Liouville-space line-width operator, which are given by:

$$\begin{aligned}
 & \langle \langle \mathbf{ab}; \{n_i\} \{n'_i\} | \bar{\Gamma}(x) | \mathbf{ab}; \{n_i\} \{n'_i\} \rangle \rangle \\
 &= \left(\frac{2\pi}{\hbar^2} \right) \text{Tr}_E \sum_{\alpha'} \langle \alpha | V | \alpha' \rangle \langle \alpha' | V | \alpha \rangle \delta(x - \omega_{\alpha'} + \omega_{\alpha}) \langle \varepsilon | \rho^E | \varepsilon \rangle \\
 &+ \left(\frac{2\pi}{\hbar^2} \right) \text{Tr}_E \sum_{\beta''} \langle \beta | V | \beta'' \rangle \langle \beta'' | V | \beta \rangle \delta(x - \omega_{\beta''} + \omega_{\beta}) \langle \varepsilon | \rho^E | \varepsilon \rangle \\
 &- \left(\frac{2\pi}{\hbar^2} \right) \text{Tr}_E \langle \alpha | V | \alpha \rangle \langle \beta | V | \beta \rangle \delta(x - \omega_{\alpha} + \omega_{\beta}) \langle \varepsilon | \rho^E | \varepsilon \rangle \\
 &- \left(\frac{2\pi}{\hbar^2} \right) \text{Tr}_E \langle \alpha | V | \alpha \rangle \langle \beta | V | \beta \rangle \delta(x - \omega_{\alpha} + \omega_{\beta}) \langle \varepsilon | \rho^E | \varepsilon \rangle.
 \end{aligned} \tag{30}$$

The first two terms describe electron-nuclear-spin, electron-photon, and electron-phonon interactions corresponding to inelastic transitions that produce a change of the relevant many-electron quantum states, while the last two terms describe elastic transitions that may contribute to the dephasing (decoherence) rate. In the analysis below, we will evaluate only the contributions due to the inelastic transitions. The off-diagonal tetradic elements of the Liouville-space line-width operator, which will be needed in the detailed description of the decoherence mechanisms, will involve interference terms among the interaction matrix elements.

B. Tetradic Matrix Elements of the Lowest-Order Non-Vanishing Contribution to the Liouville-Space Line-Width Operator in the Diagonal-Resolvent Approximation for Single-Photon Emission Processes

We now specialize the result for a single-photon emission process, which might be observed by photo-luminescence. (The photo-luminescence process can also be treated as a photon scattering process.) These tetradic matrix elements can be expressed, as sums of the partial contributions associated with the electron-nuclear-spin (I), the electron-photon (R), and the electron-phonon (V) interactions, as follows:

$$\begin{aligned} \langle\langle ab; n, n+1 | \bar{\Gamma}(x) | ab; n, n+1 \rangle\rangle = & \langle\langle ab; n, n+1 | \bar{\Gamma}^I(x) | ab; n, n+1 \rangle\rangle \\ & + \langle\langle ab; n, n+1 | \bar{\Gamma}^R(x) | ab; n, n+1 \rangle\rangle + \langle\langle ab; n, n+1 | \bar{\Gamma}^V(x) | ab; n, n+1 \rangle\rangle \end{aligned} \quad (31)$$

1. Tetradic Matrix Elements of the Lowest-Order Electron-Nuclear-Spin Contribution to the Liouville-Space Line-Width Operator in the Diagonal-Resolvent Approximation for Single-Photon Emission Processes

For a single-photon emission process, the lowest-order contribution to the diagonal width from the electron-nuclear-spin (I) interactions can be expressed, in terms of the interaction operator given by Eq. (6), as follows:

$$\begin{aligned} \langle\langle ab; n, n+1 | \bar{\Gamma}^{SN}(x) | ab; n, n+1 \rangle\rangle = & \left(\frac{2\pi}{\hbar^2} \right) \sum_{a' \neq a} \sum_{\{n_I\}} \sum_{\{n_I''\}} \left| \langle a, \{n_I\} | V_{SN}^E | a'', \{n_I''\} \rangle \right|^2 \\ & \times \delta(x - \omega_{a'} + \omega_b + \omega - \omega_{\{n_I\}} + \omega_{\{n_I''\}}) \langle n_I | \rho^I | n_I \rangle \\ & + \left(\frac{2\pi}{\hbar^2} \right) \sum_{b' \neq b} \sum_{\{n_I\}} \sum_{\{n_I''\}} \left| \langle b, \{n_I\} | V_{SN}^E | b'', \{n_I''\} \rangle \right|^2 \\ & \times \delta(x - \omega_a + \omega_{b'} + \omega + \omega_{\{n_I\}} - \omega_{\{n_I''\}}) \langle n_I | \rho^I | n_I \rangle \end{aligned} \quad (32)$$

The density operator ρ^I may be taken as a first approximation to correspond to a thermal equilibrium distribution. If we assume as a preliminary approximation that the nuclear spins are uncorrelated, in which case the density operator for the uncorrelated ensemble may be expressed as the tensor product of the density operators for the individual nuclear spins, this expression can be reduced to sums involving matrix elements involving the single nuclear-spin interaction operator multiplied by the density operator pertaining to a single nuclear spin. To obtain the final result for an uncorrelated ensemble of nuclear spins, it is necessary only to multiply by the number of nuclear spins. The average nuclear-spin occupation number (with respect to the single nuclear-spin distribution given by $\langle n_i | \rho^I | n_i \rangle$) will be denoted by $\langle n_i \rangle$. This contribution to the line width may be evaluated in the Markov (short-memory-time) approximation by setting $x = 0$. We have not explicitly included the contact hyperfine interaction, but this contribution should be considered.

2. Tetradic Matrix Elements of the Lowest-Order Radiative Contribution to the Liouville-Space Line-Width Operator in the Diagonal-Resolvent Approximation for Single-Photon Emission Processes

For a single-photon emission process, the lowest-order partial contribution to the diagonal width from the electron-photon (R) interactions can be expressed, in terms of separate components from spontaneous (SR) and induced (IR) radiative transitions, as follows:

$$\langle\langle ab; n, n+1 | \bar{\Gamma}^R(x) | ab; n, n+1 \rangle\rangle = \langle\langle ab; n, n+1 | \bar{\Gamma}^{SR}(x) | ab; n, n+1 \rangle\rangle + \langle\langle ab; n, n+1 | \bar{\Gamma}^{IR}(x) | ab; n, n+1 \rangle\rangle \quad (33)$$

Introducing the explicit form for the electron-photon interaction operator, together with the matrix elements $V_{aa''}(\vec{k}_1, \lambda_1)$ of the electron-photon interaction operator given by Eq. (8), we obtain the following result for the lowest-order separate component of the diagonal width from single-photon spontaneous emission processes:

$$\begin{aligned} \langle\langle ab; n, n+1 | \bar{\Gamma}^{SR}(x) | ab; n, n+1 \rangle\rangle = & \left(\frac{2\pi}{\hbar^2} \right) \sum_{a'' \neq a} \sum_{\vec{k}_1} \sum_{\lambda_1} |V_{aa''}(\vec{k}_1, \lambda_1)|^2 \delta(x - \omega_{a''} + \omega_b + \omega - \omega_{\vec{k}_1, \lambda_1}) \\ & + \left(\frac{2\pi}{\hbar^2} \right) \sum_{b'' \neq b} \sum_{\vec{k}_1} \sum_{\lambda_1} |V_{bb''}(\vec{k}_1, \lambda_1)|^2 \delta(x - \omega_a + \omega_{b''} + \omega + \omega_{\vec{k}_1, \lambda_1}). \end{aligned} \quad (34)$$

The lowest-order separate component of the diagonal width from single-photon absorption and induced emission processes is given by:

$$\begin{aligned} \langle\langle ab; n, n+1 | \bar{\Gamma}^{IR}(x) | ab; n, n+1 \rangle\rangle = & \left(\frac{2\pi}{\hbar^2} \right) \sum_{a'' \neq a} \sum_{\vec{k}_1} \sum_{\lambda_1} |V_{aa''}(\vec{k}_1, \lambda_1)|^2 \delta(x - \omega_{a''} + \omega_b + \omega - \omega_1) \langle n_{\vec{k}_1, \lambda_1} \rangle \\ & + \left(\frac{2\pi}{\hbar^2} \right) \sum_{a'' \neq a} \sum_{\vec{k}_1} \sum_{\lambda_1} |V_{aa''}(\vec{k}_1, \lambda_1)|^2 \delta(x - \omega_{a''} + \omega_b + \omega + \omega_1) \langle n_{\vec{k}_1, \lambda_1} \rangle \\ & + \left(\frac{2\pi}{\hbar^2} \right) \sum_{b'' \neq b} \sum_{\vec{k}_1} \sum_{\lambda_1} |V_{bb''}(\vec{k}_1, \lambda_1)|^2 \delta(x - \omega_a + \omega_{b''} + \omega + \omega_1) \langle n_{\vec{k}_1, \lambda_1} \rangle \\ & + \left(\frac{2\pi}{\hbar^2} \right) \sum_{b'' \neq b} \sum_{\vec{k}_1} \sum_{\lambda_1} |V_{bb''}(\vec{k}_1, \lambda_1)|^2 \delta(x - \omega_a + \omega_{b''} + \omega - \omega_1) \langle n_{\vec{k}_1, \lambda_1} \rangle. \end{aligned} \quad (35)$$

The average photon occupation number (with respect to the photon distribution given by $\langle n_{\vec{k}_i\lambda_i} | \rho^R | n_{\vec{k}_i\lambda_i} \rangle$) is denoted by $\langle n_{\vec{k}_i\lambda_i} \rangle$. For spectral simulations, the line width expressed by Eq. (35) will be evaluated as the sum of the contributions from both the incident (laser) photon distribution and the environmental (thermal-equilibrium) photon distribution. Since in either case the photon occupation number can be assumed to be very large, the distinction between $\langle n_{\vec{k}_i\lambda_i} \rangle$ and $\langle n_{\vec{k}_i\lambda_i} \pm 1 \rangle$ has been ignored. The total radiative line width may be evaluated in the Markov (short-memory-time) approximation by setting $x = 0$. In addition, we can employ the relationship between the average photon occupation number per unit angular frequency $\langle n_{\vec{k}\lambda} \rangle$ and the corresponding specific photon intensity $I(\vec{k}, \lambda)$, which may be expressed in the form:

$$\langle n_{\vec{k}\lambda} \rangle = \left(\frac{8\pi^3}{\hbar c |\vec{k}|^3} \right) I(\vec{k}, \lambda) \quad (36)$$

In order to systematically include the QED radiative corrections, which involve the virtual creation and annihilation of electron-positron pairs and/or photons, it will be necessary to consider the high-order contributions to the Liouville-space line-width and line-shift operators.

3. Tetradic Matrix Elements of the Lowest-Order Vibrational Contribution to the Liouville-Space Line-Width Operator in the Diagonal-Resolvent Approximation for Single-Photon Emission Processes

For a single-photon emission process, the lowest-order partial contribution to the diagonal width from the electron-phonon (V) interactions can be expressed, in terms of separate components from spontaneous (SV) and induced (IV) vibrational transitions, as follows:

$$\langle\langle ab; n, n+1 | \bar{\Gamma}^V(x) | ab; n, n+1 \rangle\rangle = \langle\langle ab; n, n+1 | \bar{\Gamma}^{SV}(x) | ab; n, n+1 \rangle\rangle + \langle\langle ab; n, n+1 | \bar{\Gamma}^{IV}(x) | ab; n, n+1 \rangle\rangle \quad (37)$$

Introducing the explicit form for the electron-phonon interaction operator, together with the matrix elements $V_{aa^*}(\vec{q}_1, \lambda_1)$ of the operator defined by Eq. (9), the lowest-order separate component of the diagonal width from single-phonon spontaneous emission processes is obtained as follows:

$$\begin{aligned} \langle\langle ab; n, n+1 | \bar{\Gamma}^{SV}(x) | ab; n, n+1 \rangle\rangle = & \left(\frac{2\pi}{\hbar^2} \right) \sum_{a^* \neq a} \sum_{\vec{q}_1} \sum_{\lambda_1} |V_{aa^*}(\vec{q}_1, \lambda_1)|^2 \delta(x - \omega_{a^*} + \omega_b + \omega - \omega_{\vec{q}_1, \lambda_1}) \\ & + \left(\frac{2\pi}{\hbar^2} \right) \sum_{b^* \neq b} \sum_{\vec{q}_1} \sum_{\lambda_1} |V_{bb^*}(\vec{q}_1, \lambda_1)|^2 \delta(x - \omega_a + \omega_{b^*} + \omega + \omega_{\vec{q}_1, \lambda_1}). \end{aligned} \quad (38)$$

Note that ω is the relevant photon frequency while $\omega_{\vec{q}_1, \lambda_1}$ is the phonon frequency.

The lowest-order separate component of the diagonal width from single-phonon absorption and induced emission processes is obtained in the following form:

$$\begin{aligned}
\langle\langle ab; n, n+1 | \bar{\Gamma}^{IV}(x) | ab; n, n+1 \rangle\rangle = & \left(\frac{2\pi}{\hbar^2} \right) \sum_{a'' \neq a} \sum_{\vec{q}_1} \sum_{\lambda_1} |V_{aa''}(\vec{q}_1, \lambda_1)|^2 \delta(x - \omega_{a''} + \omega_b + \omega - \omega_{\vec{q}_1, \lambda_1}) \langle m_{\vec{q}_1, \lambda_1} \rangle \\
& + \left(\frac{2\pi}{\hbar^2} \right) \sum_{a'' \neq a} \sum_{\vec{q}_1} \sum_{\lambda_1} |V_{aa''}(\vec{q}_1, \lambda_1)|^2 \delta(x - \omega_{a''} + \omega_b + \omega + \omega_{\vec{q}_1, \lambda_1}) \langle m_{\vec{q}_1, \lambda_1} \rangle \\
& + \left(\frac{2\pi}{\hbar^2} \right) \sum_{b'' \neq b} \sum_{\vec{q}_1} \sum_{\lambda_1} |V_{bb''}(\vec{q}_1, \lambda_1)|^2 \delta(x - \omega_a + \omega_{b''} + \omega + \omega_{\vec{q}_1, \lambda_1}) \langle m_{\vec{q}_1, \lambda_1} \rangle \\
& + \left(\frac{2\pi}{\hbar^2} \right) \sum_{b'' \neq b} \sum_{\vec{q}_1} \sum_{\lambda_1} |V_{bb''}(\vec{q}_1, \lambda_1)|^2 \delta(x - \omega_a + \omega_{b''} + \omega - \omega_{\vec{q}_1, \lambda_1}) \langle m_{\vec{q}_1, \lambda_1} \rangle.
\end{aligned}
\tag{39}$$

The average environmental (thermal-equilibrium) phonon occupation number (with respect to the phonon distribution given by $\langle m_{\vec{q}_1, \lambda_1} | \rho^V | m_{\vec{q}_1, \lambda_1} \rangle$) is denoted by $\langle m_{\vec{q}_1, \lambda_1} \rangle$. Since the phonon occupation number can be assumed to be very large, the distinction between $\langle m_{\vec{q}_1, \lambda_1} \rangle$ and $\langle m_{\vec{q}_1, \lambda_1} \pm 1 \rangle$ has been ignored. The vibrational line width may be evaluated in the Markov (short-memory-time) approximation by setting $x = 0$. In addition, we can employ the relationship between the average phonon occupation number per unit angular frequency $\langle m_{\vec{q}, \lambda} \rangle$ and the corresponding specific phonon intensity $I(\vec{q}, \lambda)$, which is analogous to that for the case of a thermal-equilibrium radiation field. In order to systematically treat the anharmonic effects, which are associated with multi-phonon transitions, it will be necessary to consider higher-order contributions to the Liouville-space line-width and line-shift operators.

VI. GENERAL EXPRESSIONS FOR THE SINGLE-PHOTON AND MULTI-PHOTON TRANSITION RATES

The frequency-dependent single-photon and multi-photon transition rates, which are obtained from Eq. (10) and Eq. (12), can be evaluated in further detail by introducing unperturbed-eigenstate decompositions for the zero-order reduced, relevant Liouville-space resolvent operators and the relevant Liouville-space electromagnetic-interaction operators.

A. Single-Photon Emission

The single-photon emission rate, which can serve as the basis for the analysis of the photo-emission process, can be expanded as follows:

$$A_R^1(i \rightarrow f) = -i \lim_{\varepsilon \rightarrow 0} \sum_a \sum_{a'} \sum_b \sum_n \sum_{cc'} \sum_{\bar{n}\bar{n}'} \sum_{dd'} \sum_{\bar{n}''\bar{n}'''} \langle \langle bb; n+1, n+1 | \bar{V}^r | cc', \bar{n} \bar{n}' \rangle \rangle \times \langle \langle cc', \bar{n} \bar{n}' | \bar{G}_0^r(+i\varepsilon) | dd', \bar{n}'' \bar{n}''' \rangle \rangle \langle \langle dd', \bar{n}'' \bar{n}''' | \bar{V}^r | aa', n n \rangle \rangle \langle \langle aa', n n | \rho_i^r \rangle \rangle. \quad (40)$$

We employ the expression for the tetradic matrix elements of the relevant Liouville-space electromagnetic-interaction operator given by Eq. (8), neglecting the spin-Zeeman contribution for simplicity, for a single-photon transition. We have also ignored the initial-state photon coherences for this simple illustration, keeping in mind that this approximation should be reconsidered in the detailed investigation of the decoherence and relaxation processes. We thereby obtain a sum of products, each of which will give rise to 16 terms.

Using the expression for the tetradic-matrix elements of the zero-order relevant Liouvillian for a single-photon transition, the required tetradic-matrix elements of the zero-order reduced, relevant Liouville-space resolvent operator $\bar{G}_0^r(+i\varepsilon)$ for a single-photon transition are found to satisfy the following set of equations:

$$\sum_c \sum_{c'} \sum_{\bar{n}} \sum_{\bar{n}'} \langle \langle dd', n'' n''' | \bar{G}_0^r(+i\varepsilon) | cc', \bar{n} \bar{n}' \rangle \rangle \times \left[(+i\varepsilon - \omega_a + \omega_b - n\omega + n'\omega) \delta_{ca} \delta_{c'b} \delta_{\bar{n}\bar{n}'} \delta_{n''n'''} - \langle \langle cc', \bar{n} \bar{n}' | \bar{\Sigma}(+i\varepsilon) | ab, nn' \rangle \rangle \right] = \delta_{da} \delta_{d'b} \delta_{n''n'''} \delta_{n''n'''} \quad (41)$$

B. Diagonal-Resolvent Approximation

In the diagonal-resolvent approximation, the set of equations for the tetradic matrix elements of the zero-order reduced, relevant Liouville-space resolvent operator for a single-photon transition, which is given by Eq. (41), can be solved to obtain the following closed-form expression:

$$\langle \langle ab, nn' | \bar{G}_0^r(+i\varepsilon) | cd, n'' n''' \rangle \rangle = \delta_{ca} \delta_{db} \delta_{n''n'''} \delta_{n''n'''} \left[(+i\varepsilon - \omega_a + \omega_b - n\omega + n'\omega) - \langle \langle cd, n'' n''' | \bar{\Sigma}(+i\varepsilon) | ab, nn' \rangle \rangle \right]^{-1}. \quad (42)$$

We now specialize the analysis further by neglecting the initial electronic-state coherences, keeping in mind that these coherences, together with the initial-state photon coherences, must be included for a detailed dynamical description of the various decoherence and relaxation mechanism. We also introduce the assumption that the initial-

state reduced density operator can be expressed as a tensor product of the separate initial-state density operators for the isolated electronic system (S) and the relevant electromagnetic radiation field (R), i. e., $\rho_i^r = \rho_i^S \otimes \rho_i^R$. After expressing the Liouville-space self-energy operator in terms of the corresponding Liouville-space line-width and line-shift operators, as indicated by Eq. (26), the expression for the single-photon emission rate can then be conveniently expressed, as an incoherent superposition of the Lorentzian spectral profiles associated with the individual transitions of the many-electron spin system $a \rightarrow b$, in the standard form:

$$A_R^1(i \rightarrow f) = \left(\frac{2\pi}{\hbar^2} \right) \sum_a \sum_b V_{ab}^*(\vec{k}\lambda) V_{ba}(\vec{k}\lambda) \langle \langle aa | \rho_i^S \rangle \rangle \left(\frac{1}{2\pi} \right) \langle \langle ab; n, n+1 | \bar{\Gamma}(+i\varepsilon) | ab; n, n+1 \rangle \rangle \\ \times \left[\left(\omega_a - \omega_b - \omega + \langle \langle ab; n, n+1 | \bar{\Delta}(+i\varepsilon) | ab; n, n+1 \rangle \rangle \right)^2 + \left(\frac{1}{4} \right) \left(\langle \langle ab; n, n+1 | \bar{\Gamma}(+i\varepsilon) | ab; n, n+1 \rangle \rangle \right)^2 \right]^{-1}. \quad (43)$$

The diagonal-resolvent approximation is therefore appropriate for the spectral representation of a set of isolated lines, with separations that are large compared with their widths.

VII. CONCLUSIONS AND FUTURE PLANS

A reduced-density-operator description has been developed for decoherence and relaxation processes in many-electron spin systems. Based on a derivation of precise

expressions for the tetradic-matrix elements of the time-domain and frequency-domain self-energy operators, a fundamental microscopic quantum-mechanical framework has been provided for a comprehensive determination of the quantum kinetics together with spectral-line shapes. Introducing a perturbation expansion for the frequency-domain Liouville-space self-energy operator, in powers of the environmental-interaction operator, the spectral-line widths and shifts have been systematically and explicitly evaluated in the diagonal-resolvent, short-memory-time (Markov), and lowest-order (Born) approximations. In the Markov approximation, the spectral-line widths also provide the decoherence and relaxation rates. We also have indicated how our general reduced-density-operator description can be employed to obtain the full tetradic-matrix form of the spectral distribution, which is applicable to complex spectra consisting of a multitude of overlapping lines and to the more general investigation of the decoherence and relaxation processes. In a future extension of this investigation, the predictions of our reduced-density-operator description will be compared with experimental observations on specific electron-spin systems.

The spectral-line shapes, which may be analyzed in photoluminescence, are influenced by the incident electromagnetic fields that may be generated by lasers or other coherent radiation sources, and are affected by the various environmental interactions. The environmental interactions taken into account in this investigation are electron-nuclear-spin, electron-photon and electron-phonon interactions. The spectral-line widths and shifts due to these environmental interactions can be evaluated by assuming thermal-equilibrium (Bose-Einstein) distributions for the environmental nuclear spins, photons,

and phonons. However, we have emphasized that our general reduced-density-operator approach can be implemented for non-equilibrium distributions, which can be determined from separate kinetic-theory (equation-of-motion) descriptions for the environmental nuclear spins, photons, and phonons. Accordingly, which can provide a comprehensive framework for realistic and systematic computer simulations of the spectral distributions under general excitation conditions.

The frequency-dependent rate for a single-photon emission process, which may be analyzed in photoluminescence, has been explicitly evaluated, as an unperturbed-eigenstate decomposition, in terms of the tetradic-matrix elements of the zero-order reduced, relevant Liouville-space resolvent operators and the matrix elements of the ordinary Hilbert-space electromagnetic-interaction operators connecting the many-electron spin states. We have indicated that similar expressions can be derived for the rates of processes involving general (higher-order) multi-photon transitions.

The frequency-dependent single-photon rate has been expressed in simplified form by introducing the diagonal-resolvent approximation. From a general expression for the tetradic-matrix elements of the lowest-order non-vanishing contribution to the Liouville-space line-width operator, we have obtained detailed expressions for the various contributions to the line width in the diagonal-resolvent approximation for a single-photon emission process. We have also indicated how the corresponding results can be obtained for the various contributions to the line shifts, as well as for the line widths and shifts associated with general (higher-order) multi-photon processes.

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