Nonstationary Dressed States and Effects of Decay in Nonadiabatic Crossing of Decaying Levels

V. V. KOCHAROVSKY, VL. V. KOCHAROVSKY, E. A. DERISHEV,
S. A. LITVAK AND I. A. SHERESHEVSKY
Institute of Applied Physics, Russian Academy of Science
46 Ulyanov Str., 603600 Nizhny Novgorod, Russia

S. TASAKI
Institute for Fundamental Chemistry
34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan

Abstract—The rigorous equations for a nonadiabatic coupling of the amplitudes of decaying discrete states dressed by a continuum are derived by means of the complex spectral decomposition method developed by the Brussels-Austin group. The limitations of the previously used phenomenological equations are shown within the scope of the time-dependent $N$-level Friedrichs-Fano model. The novel nonadiabatic effects owing to the decay of discrete levels into a continuum are found:

(i) nonunitary nonadiabaticity caused from unitary one,
(ii) nonadiabaticity via time dependent coupling with a reservoir, and
(iii) additional cross-decay due to nonadiabaticity.

Reasonable generalization of Berry's phase for decaying eigenstates and regeneration of driven decaying states via coherent mixing with reservoir are discussed. General results are applied to the quasienergy-state dynamics of a three-level molecule driven by DC and AC fields and to the nonsteady Born-Oppenheimer approach of molecules electronically excited to decaying states. Also, a "resonance" approximation leading to the true non-Hermitian Hamiltonian, similar to the phenomenological one (used in quantum optics in the stationary case) and applicable to the nonstationary case, is formulated explicitly.

Keywords—Decaying states, Nonadiabatic phenomena, Quantum optics, Quantum chemistry.

1. STATUS OF THE PROBLEM

Let us begin with very general remarks. As emphasized in the earlier works of the Brussels-Austin group (see, e.g., [5]), there is an asymmetry in the quantum mechanical description of states or particles: stable states or particles are defined as eigenstates of the total Hamiltonian of the system, while unstable states or particles cannot be treated in the same way. Indeed, as

The authors thank I. Prigogine for his continuous interest, valuable comments, critical reading of the manuscript and hospitality during their stay in Brussels. They also thank I. Antoniou, A. Bohm, and E. C. G. Sudarshan for several fruitful discussions and useful comments. Particularly, I. Antoniou kindly provided the historical remarks on Livsic's method (after equation (23)). S.T. is grateful to K. Fukui and M. Nagaoka for their encouragement and valuable comments and for turning the authors' attention to [1-4]. This work is partly supported by the Belgian Government (under the contract "Pole d'attraction interuniversitaire"), the European Communities Commission DG III/ESPRIT—Project ACTCS 9282 and the Contract No. 27155.1/BAS, the U.S. Department of Energy, Grant No. FG05-88ER13897, the Robert A. Welch Foundation and the Ministry of Education, Science and Culture of Japan (a Grant-in-Aid for Scientific Research and a grant under the International Scientific Research Program).
is seen in the works, e.g., of Friedrichs [6] and Fano [7], the total Hamiltonian of the system with discrete decaying states admits only the eigenstates corresponding to the real continuous spectrum and there exist no counterparts corresponding to the unstable discrete states. Usually unstable (decaying) states or particles are assumed to be proper described by the eigenstates of an unperturbed Hamiltonian. This convention is satisfactory only in the lowest-order approximation with respect to the interaction responsible for the decay. There are, however, many phenomena where more accurate treatments of unstable states or particles and, thus, full consideration of the dressing effects are required. Nonadiabatic coupling of unstable discrete states is one such phenomenon.

Recently, several theories [3,4,8–18] have been proposed where the decaying discrete states are described as the eigenstates of the Hamiltonian corresponding to the complex eigenvalues. It is even possible to construct a complete set of basis vectors involving such decaying eigenstates [11,12,17]. These approaches open a new possibility of treating unstable states on the same basis as the stable ones. The complex spectral theory ([19,20] and references therein) developed by the Brussels-Austin group was first formulated for the generator of motion of the density matrices (Liouville-von Neumann operator) to deal with the irreversible phenomena and also was applied to the Hamiltonian of the one-level Friedrichs-Lee model [17,18]. In the present paper, the complex spectral theory is used to study the nonadiabatic coupling of unstable (decaying) discrete levels for the most general N-level Friedrichs-Fano model.

The nonadiabatic coupling of discrete states has been analyzed extensively in quantum mechanics, especially after Landau [21] and Zener [22] (see, e.g., [23–43]), and in the theory of wave propagation, particularly in plasma physics, acoustics and inhomogeneous-waveguide theory (e.g., see [42–49]). In these theories, the time evolution of the probability amplitudes of different levels or the spatial change of the amplitudes of different field-modes (e.g., with different polarizations) are described by a set of linear ordinary differential equations with coefficients depending on time or on a coordinate along propagation path, respectively. If the coefficients are constant, those equations possess a set of linearly independent harmonic solutions (in a nondegenerate case); so there are eigenstates with definite energies. When the coefficients vary in time or space, the mixing of these solutions takes place. The mixing is exponentially small if the coefficients vary slowly enough, so that the adiabatic approximation is applicable [46–53]. Otherwise, nonadiabatic coupling of levels or eigenmodes causes new phenomena.

For decaying discrete states, the problem of nonadiabatic coupling is particularly interesting because understanding it is crucial for solving various physical problems, e.g., collisions of excited molecules [23–29], multiphoton ionization of atoms [50–53], dynamics of spins (or dipole momenta responsible for quantum transitions) driven by a coherent field [30–43], chemical reactions involving excited molecules, etc. Usually, this problem is studied by phenomenological methods such as those using the non-Hermitian Hamiltonian or nonadiabatic coupling equations for decaying partial states. However, the validity of different phenomenological equations and the limits of their applicability have not yet clearly been formulated.

In the following, we derive consistently, for the first time, the fundamental equations of nonadiabatic coupling of decaying discrete levels for the N-level Friedrichs-Fano model and discuss the validity of the existing treatments as well as expected new features. As we shall see, this approach does not require any phenomenological non-Hermitian Hamiltonians, but rather shows how they can be obtained as a specific approximation.

The Friedrichs-Fano model consists of discrete (partial) states, |α⟩ (α = 1,..., N), and continuum reservoir states, |k⟩, with energy ωk (0 ≤ ωk < +∞). The total Hamiltonian is then a sum of

1. the part $h(t)$ governing the evolution of the dynamical subsystem of the discrete states, |α⟩,

2. the interaction $v(t)$ between the discrete subsystem and the reservoir, and
(3) the reservoir energy \( \sum_k \omega_k |k\rangle \langle k| \):

\[
H(t) = h(t) + v(t) + \sum_k \omega_k |k\rangle \langle k| ,
\]

where

\[
v(t) = \sum_{\alpha=1}^N \sum_k [V_{\alpha k}(t)|\alpha\rangle \langle k| + V_{\alpha k}^*(t)|k\rangle \langle \alpha| ,
\]

\[
h(t) = \sum_{\alpha, \alpha'=1}^N h_{\alpha \alpha'}(t)|\alpha\rangle \langle \alpha'| \equiv \sum_{\alpha=1}^N \nu_{\alpha}(t)|\phi_{\alpha}\rangle \langle \phi_{\alpha}| .
\]

The coupling parameters between two discrete levels, \( h_{\alpha \alpha'}(t) \), and between a discrete level and the reservoir, \( V_{\alpha k}(t) \), depend on time explicitly. A \( k \)-dependence of an interaction, \( V_{\alpha k} \), allows one to consider any type of reservoir energy spectrum, e.g., band-type spectrum; cf. [54–57]. For simplicity, we use summations \( \sum_k \cdots \) instead of integrations \( \int d\omega_k \cdots \) bearing in mind the standard limit of infinite quantization box [17,58], \( L^3 \rightarrow \infty \). In this convention, the matrix element of the interaction between discrete states and the reservoir, \( V_{\alpha k} \), is of order \( L^{-3/2} \). In equation (3), \( \nu_{\alpha}(t) \) and \( |\phi_{\alpha}\rangle \) are, respectively, eigenvalues and eigenvectors for the partial Hamiltonian, \( h(t) \), and both depend on time explicitly. If the reservoir is absent, the coupling among the discrete states is described by the subsystem Hamiltonian, \( H(t) \), and the level coupling is described by the time evolution of the probability amplitudes corresponding to the instantaneous eigenfunctions, \( |\phi_{\alpha}(t)\rangle \).

As discussed in Section 2, the complex spectral theory [17] leads to the following decomposition of the total Hermitian Hamiltonian, \( H(t) \):

\[
H(t) = \sum_{\alpha=1}^N \omega_{\alpha}(t)|\phi_{\alpha}\rangle \langle \phi_{\alpha}| + \sum_k \omega_k |\varphi_k\rangle \langle \varphi_k| ,
\]

where \( |\varphi_{\alpha}\rangle \), \( |\varphi_k\rangle \) and \( \langle \phi_{\alpha}| \), \( \langle \varphi_k| \) are, respectively, right and left generalized eigenvectors of \( H(t) \). The states \( |\phi_{\alpha}\rangle \) represent renormalized discrete states dressed by the definite superposition of continuum states, and the corresponding eigenfrequencies, \( \omega_{\alpha}(t) \), are complex. The other states \( |\varphi_k\rangle \) of the reservoir with real eigenenergies, \( \omega_k (0 \leq \omega_k < +\infty) \), are not important if a reservoir memory time scale is less than a time scale of the variation of the Hamiltonian. Thus, the dynamics of the complex amplitudes of the generalized eigenstates, \( |\phi_{\alpha}\rangle \), yields a closed treatment of the nonunitary evolution of the discrete states in the presence of decay. It is the whole point of the present approach to nonadiabatic phenomena. In addition, it could provide a deeper insight on decaying states, because the nonsteady one-level Friedrichs model [6] or the steady \( N \)-level Fano model [7] cannot describe the interaction among decaying states.

This approach reveals novel nonadiabatic effects due to a time variation of the renormalization in generalized eigenstates, which were missed in previous phenomenological schemes [23–31, 50–53]. For the \( N \)-level Friedrichs-Fano model, we can explicitly treat the discrete-state redressing due to the time dependence of the subsystem Hamiltonian (3), \( h(t) \), as well as the interaction (2), \( v(t) \), between the subsystem and the reservoir. Note that the Friedrichs-Fano model does not include the so-called counter-rotating terms [59–61] in the subsystem-reservoir interaction. However, we expect that the main results of the present work are unaffected even if these effects are included.

In Section 2, we construct the complex spectral decomposition of the Hamiltonian for the \( N \)-level Friedrichs-Fano model (1)–(3). The fundamental equations of nonadiabatic crossing of decaying levels are derived in Section 3. Section 4 is devoted to a discussion of the novel
nonadiabatic effects arising from a decay of discrete levels and to a ‘resonance’ approximation leading to the non-Hermitian Hamiltonian similar to phenomenological ones. A generalization of Berry’s phase for decaying states is given in Section 5. The time evolution of Lyapunov-type quantity and regeneration of driven decaying states are discussed in Section 6. In Sections 7 and 8, two basic problems in quantum optics and in quantum chemistry are treated as examples of the present theory: in Section 7, novel nonadiabatic effects are discussed in quasienergy-state dynamics of a three-level molecule driven by nonsteady DC and AC electric field and, in Section 8, we formulate a generalization of the Born-Oppenheimer approach to the case with decaying electronic states and briefly discuss expected new features. The main conclusions are summarized in Section 9.

2. COMPLEX SPECTRAL DECOMPOSITION AND GENERALIZED EIGENSTATES OF N-LEVEL FRIEDRICHS-FANO MODEL

The problem of the diagonalization of the total Hamiltonian (1) was put forward in connection with the problem of atomic autoionization [62,63] and was solved by Friedrichs [6,64] for N = 1 and by Fano [7] for an arbitrary N with several continua. A similar model was considered [65] in the context of neutral kaon decay. However, there was found only the real spectral decomposition, \( H(t) = \sum_k \omega_k |\phi_k^F\rangle \langle \phi_k^F| \), which “dilutes” discrete states throughout the continuum of new eigenstates, \( |\phi_k^F\rangle \), with the unperturbed spectrum, \( 0 < \omega_k < +\infty \). Taking into account the orthonormalization, \( \langle \phi_k^F | \phi_{k'}^F \rangle = \delta_{kk'} \), we find the following state (cf. [7,66]):

\[
|\phi_k^F\rangle = |k\rangle + \sum_{\alpha=1}^{N} a_{k\alpha}(t) \left[ |\alpha\rangle + \sum_{k'} \frac{V_{\alpha k'}(t)}{\omega_k - \omega_{k'} + i\epsilon} |k'\rangle \right],
\]

and the mixing coefficient, \( a_{k\alpha} \),

\[
a_{k\alpha}(t) = \sum_{\beta=1}^{N} \left[ (\omega_k I - K(\omega_k))^{-1} |\alpha\beta\rangle V_{\beta k}^* \right] \xi_{\alpha\beta}(\omega_k) \xi_{\beta\alpha}^{-1}(\omega_k) V_{\alpha k},
\]

where the symbol \( \epsilon(+ \to +0) \) indicates the usual Landau’s rule of evaluating the pole contribution [17,18,41–43,58], \( I \) is the unit \( N \times N \) matrix, and \( K(\omega) \) stands for the time- and frequency-dependent \( N \times N \) matrix

\[
K(\omega)_{\alpha\alpha'} = \hbar \alpha + \sum_{k'} \frac{V_{\alpha k}^* V_{\alpha' k'}^*}{\omega - \omega_{k'} + i\epsilon}.
\]

In equation (7), \( \mathcal{H}(\omega) \) (with \( \alpha = \beta \)) is the eigenvalue of the matrix \( K(\omega) \), and \( \xi_{\alpha\alpha}(\omega) \) and \( \xi_{\alpha\alpha}^{-1}(\omega) \) are components of its right and left eigenvectors:

\[
K(\omega)|u_{\alpha}(\omega)\rangle = \mathcal{H}(\omega)|u_{\alpha}(\omega)\rangle; \quad \langle v_{\alpha}(\omega)|K(\omega) = \mathcal{H}(\omega)\langle v_{\alpha}(\omega)|,
\]

\[
|u_{\alpha}(\omega)\rangle = \sum_{\alpha'=1}^{N} \xi_{\alpha'\alpha}(\omega)|\alpha'\rangle, \quad \langle v_{\alpha}(\omega)| = \sum_{\alpha'=1}^{N} \xi_{\alpha\alpha'}^{-1}(\omega)\langle \alpha'|.
\]

Here we assume that, for any value of \( \omega \), the matrix (7) has \( N \) different eigenvalues. Then the right and left eigenvectors \( \{|u_{\alpha}(\omega)\rangle, \langle v_{\alpha}(\omega)|\} \) form a complete biorthogonal basis in the dynamical subspace spanned by \( \{|\alpha\rangle\} \).

When the transition-matrix element, \( V_{\alpha k} \), as well as the unperturbed continuum state, \( |k\rangle = |\omega\rangle \), depend only on the energy \( \omega_k \), i.e., \( |k\rangle = |\omega_k\rangle \), and equation (5) takes a familiar form

\[
|\phi_k^F\rangle = |\omega\rangle + \sum_{\mu=1}^{N} a_{\omega \mu}(t) \left[ |\mu\rangle + \sum_{\nu} \frac{V_{\mu \nu}(t)}{\omega - \omega' + i\epsilon} |\nu\rangle \right],
\]
Nonstationary Dressed States

$$a_{\omega \mu} = \frac{\tilde{V}_{\mu \omega}^*}{(1 - i\pi / \zeta)(\omega - \tilde{\omega}_{\mu \omega})}, \quad \frac{1}{\zeta} = \sum_{\mu=1}^{N} \frac{\left| \tilde{V}_{\mu \omega} \right|^2}{\omega - \tilde{\omega}_{\mu \omega}},$$

where |\(\mu\)| is the eigenvector of the Hermitian matrix

$$\left( \hbar_{\alpha \alpha'} + V_{\alpha \omega} \sum_{\omega'} \frac{V_{\alpha' \omega'}^* V_{\omega' \omega}}{\omega - \omega'} \right),$$

\(\tilde{\omega}_{\mu \omega}\) is the corresponding eigenvalue, and \(\tilde{V}_{\mu \omega}(t) \equiv \langle \omega | v(t) | \mu \rangle\) is the transition amplitude between the new discrete state |\(\mu\)| and the continuum state |\(\omega\)|. In this nondegenerate case, the eigenstates |\(\psi_{\alpha}^F\rangle\) differ from Fano’s ones [3] only by phase factors.

Note that, because the matrix \(K(\omega)\) is not Hermitian, its right and left eigenvectors are not Hermitian conjugations:

$$\xi_{\alpha \alpha'}^{-1}(\omega) \neq \xi_{\alpha' \alpha}^*(\omega).$$

As mentioned in Section 1, this real spectral decomposition does not contain the parts corresponding to the unstable states and there is no well-defined manner to describe the level crossing phenomena involving unstable states. For the one-level Friedrichs-Lee model [6,64], Nakanishi [67] introduced a generalized eigenstate corresponding to a complex eigenvalue of the total Hamiltonian. Sudarshan, Chiu and Gorini [11,12] then showed that there exists a complete set of left and right generalized eigenstates of the total Hamiltonian (involving Nakanishi’s state), which provides a complex spectral decomposition of the total Hamiltonian. The equivalent complete set was constructed perturbatively by the complex spectral theory developed by the Brussels-Austin group [17,18]. For the \(N\)-level Friedrichs-Fano model, the complex spectral decomposition can be obtained as in the one-level Friedrichs model. One can derive it by a perturbation method adopting a time-ordered boundary condition [17,18]: small denominators relating to the transition from discrete to continuum states are regularized as retarded propagators and those relating to the transition from continuum to discrete states as advanced propagators (of course, other methods, for example, the resolvent method, will lead to the same result).

The calculations are similar to the case of \(N = 1\) [17] and here we only list the results:

$$H(t)|\varphi_{\alpha}\rangle = \omega_{\alpha}|\varphi_{\alpha}\rangle, \quad \langle \tilde{\varphi}_{\alpha}|H(t) = \omega_{\alpha}\langle \tilde{\varphi}_{\alpha}|, \quad (11)$$

$$H(t)|\varphi_{\kappa}\rangle = \omega_{\kappa}|\varphi_{\kappa}\rangle, \quad \langle \tilde{\varphi}_{\kappa}|H(t) = \omega_{\kappa}\langle \tilde{\varphi}_{\kappa}|, \quad (12)$$

where

$$|\varphi_{\alpha}\rangle = g_{\alpha}[\eta_{\alpha}(\omega_{\alpha})]^{-1/2} \sum_{\alpha'=1}^{N} \xi_{\alpha \alpha'}(\omega_{\alpha}) \left\{ |\alpha'\rangle + \sum_{k'} \frac{V_{\alpha \kappa'}^*}{[\omega_{\alpha} - \omega_{k'}]^+} |k'\rangle \right\}, \quad (13)$$

$$\langle \tilde{\varphi}_{\alpha}| = g_{\alpha}^{-1}[\eta_{\alpha}'(\omega_{\alpha})]^{-1/2} \sum_{\alpha'=1}^{N} \xi_{\alpha' \alpha}(\omega_{\alpha}) \left\{ \langle \alpha'| + \sum_{k'} \langle k'| \frac{V_{\alpha \kappa'}^*}{[\omega_{\alpha} - \omega_{k'}]^+} \right\}, \quad (14)$$

$$|\varphi_{\kappa}\rangle = |\phi_{\kappa}^F\rangle - \sum_{\alpha'=1}^{N} \langle \varphi_{\alpha'}| \langle \tilde{\varphi}_{\alpha'}| \phi_{\kappa}^F\rangle = |k\rangle + \sum_{\alpha=1}^{N} \tilde{a}_{\kappa \alpha}(t) \left\{ |\alpha\rangle + \sum_{k'} \frac{V_{\alpha \kappa'}(t)}{\omega_{\kappa} - \omega_{k'} + i\epsilon} |k'\rangle \right\}, \quad (15)$$

$$\langle \tilde{\varphi}_{\kappa}| = \langle \phi_{\kappa}^F|,$$

with

$$\tilde{a}_{\kappa \alpha} = \sum_{\beta \gamma} \frac{\xi_{\gamma \alpha}(\omega_{\kappa}) \xi_{\beta \gamma}^{-1}(\omega_{\kappa})}{\eta_{\beta}(\omega_{\kappa})} V_{\beta \kappa}^*.$$

(17)
The complex eigenvalues, \( \omega_\alpha \), are obtained as the solutions of the dispersion relations,

\[
\omega_\alpha = \mathcal{H}_\alpha(\omega_\alpha), \quad (\alpha = 1, \ldots, N),
\]

which are assumed to have unique solutions (in the lower half-plane for decaying levels). The factor \( \eta_\alpha \) is a normalization constant to be discussed in Sections 4 and 5, and \( \eta_\alpha'(\omega) \) is the derivative given by

\[
\eta_\alpha'(\omega) \equiv \frac{d}{d\omega} \{ \omega - \mathcal{H}_\alpha(\omega) \}. \tag{19}
\]

The expression \( 1/|\omega_\alpha - \omega_{k'}|_+ \) stands for the analytic extension from the upper half-plane with respect to \( \omega_\alpha \) and, for \( \text{Im} \omega_\alpha < 0 \), can be written in terms of the delta function with complex arguments \([11-18,67-69]\)

\[
\frac{1}{|\omega_\alpha - \omega_{k'}|_+} = \frac{1}{\omega_\alpha - \omega_{k'}} - 2\pi i \delta(\omega_{k'} - \omega_\alpha). \tag{20}
\]

The distributions, \( 1/\eta_\alpha(\omega) \), appearing in formula (17) can also be expressed in terms of the delta functions with complex arguments

\[
\frac{1}{\eta_\alpha(\omega)} \equiv \frac{1}{\omega - \mathcal{H}_\alpha(\omega)} + 2\pi i \frac{\delta(\omega - \omega_\alpha)}{\eta_\alpha'(\omega_\alpha)}. \tag{21}
\]

As verified by direct calculations, the new eigenstates form a complete biorthonormal system:

\[
\langle \tilde{\varphi}_\alpha | \varphi_{\alpha'} \rangle = \delta_{\alpha \alpha'}, \quad \langle \tilde{\varphi}_\alpha | \varphi_k \rangle = 0, \quad \langle \varphi_k | \varphi_{\alpha'} \rangle = \delta_{kk'}, \quad \langle \varphi_k | \varphi_\alpha \rangle = 0, \tag{22}
\]

\[
\sum_{\alpha = 1}^{N} |\varphi_\alpha\rangle\langle \tilde{\varphi}_\alpha| + \sum_{k} |\varphi_k\rangle\langle \tilde{\varphi}_k| = I. \tag{23}
\]

According to equations (8), (9), and (18), the complex eigenvalue problem of the total Hamiltonian is related to the eigenvalue problem of an “eigenvalue-dependent” operator \( K(\omega) \) of equation (7). Operators like \( K(\omega) \) arise naturally in the projection operator or partitioning techniques and are known as Livsic operators \([70,71]\) or collision operators \([19,72-74]\). The eigenvalue problem of such eigenvalue-dependent operators was first discussed by Lowdin \([72]\), and Bartlett and Brändas \([73]\). Grecos, Guo, and Guo \([74]\), and Petrosky and Frigogine \([19]\) used this method in the context of the subdynamics theory to define generalized eigenvectors. Also, Chiu and Sudarshan \([65]\) and independently Khalilin \([75]\) used it in the context of the kaon decay problem to extract the evolution of the subsystem consisting of the neutral kaon and its antiparticle.

Because the generalized eigenstates (13)–(15) contain the delta functions with complex arguments, they cannot be given in the usual Hilbert space. Such objects acquire mathematical meaning as linear functionals over a restricted class of Hilbert-space vectors (test vectors) \([11-18,76]\), i.e., through the use of generalized functions theory (e.g., \([68,69]\)). For the \( N \)-level Friedrichs-Fano model, as in the one-level Friedrichs model \([18]\), the states \( |\varphi_\alpha| \) and \( |\tilde{\varphi}_\alpha| \) can be defined as linear functionals over the spaces \( \Phi_+ \) and \( \Phi_- \), respectively, where \( \Phi_\pm \) is the space of all wave functions \( |\psi\rangle \) such that the component \( \langle k | \psi \rangle \) belongs, as a function of \( \omega_k \), to the intersection between the Schwartz class and the upper or lower Hardy class, \( \mathcal{S} \cap \mathcal{H}_\pm \), respectively. In other words, they belong to the topological duals of the test spaces: \( \langle \varphi_\alpha | \in \Phi^+_\alpha \) and \( \langle \tilde{\varphi}_\alpha | \in \Phi^+_- \). Mathematically speaking, it is this extension to the non-Hilbert generalized space that enables the Hermitian operator in the Hilbert space to admit complex eigenvalues (the notion of Hermiticity is well defined only for the Hilbert space operators).

Because a one-to-one correspondence exists between the complex eigenstates and the unperturbed states, one can introduce a transformation connecting the two \([17]\): \( \Lambda^{-1}|\beta\rangle = |\varphi_\beta\rangle \), \( (\beta = 1, \ldots, N, k) \), where

\[
\Lambda \equiv \sum_{\alpha = 1}^{N} |\alpha\rangle\langle \tilde{\varphi}_\alpha| + \sum_{k} |k\rangle\langle \tilde{\varphi}_k|, \quad \Lambda^{-1} \equiv \sum_{\alpha = 1}^{N} |\varphi_\alpha\rangle\langle \alpha| + \sum_{k} |\varphi_k\rangle\langle k|. \tag{24}
\]
If the system is integrable, such transformation is always unitary. However, as clearly seen from equations (24), the transformation $\Lambda$ is not unitary as a result of the nonintegrability of the system. In case of time-independent systems, the nonunitary transformation $\Lambda$ intertwines the total Hamiltonian with a diagonal dissipative operator $[17]$ (see also $[76]$) where the total Hamiltonian is intertwined with a comparison Hamiltonian, instead of the unperturbed one.

The $N \times N$-matrix (7), $K(\omega)$, which provides complex eigenvalues, is not Hermitian. Thus, the matrix may not be diagonalizable and may admit the Jordan block structure. This structure will be transferred to the complex spectral decomposition of the Hamiltonian. Clearly, the appearance of the Jordan blocks in the generator of motion implies a deviation from the purely exponential and/or oscillatory behaviors; namely, there appears a polynomial factor $t^n \exp(i\omega_\alpha t)$, where $n$ is an integer and $\omega_\alpha$ may be complex. In the time-independent case, Arecchi and Courtens $[78]$ have considered a simple model which exhibits nonexponential decay of the form $t \exp(-\gamma t)$. To our knowledge, the physical examples of such a nonexponential decay have not yet been considered for explicitly time-dependent Hamiltonians, $H = H(t)$.

3. DYNAMICAL ANSATZ AND FUNDAMENTAL EQUATIONS

We now have dressed unstable (decaying) states which are expected to provide a consistent description of the level coupling involving decay into a continuum. We shall derive the coupling equations for these states in the most interesting case where the total Hamiltonian varies slowly over the oscillation periods of all discrete eigenstates, $2\pi/\nu_\alpha$ for $|\phi_\alpha\rangle$ in equation (3) or $2\pi/\omega_\alpha$ for $|\varphi_\alpha\rangle$ in equation (4), but nevertheless nonadiabatic effects appear due to a crossing, or even a transitory approach, of some levels:

$$|\omega'_\alpha(t) - \omega''_\alpha(t)| \ll \frac{(\omega'_\alpha + \omega''_\alpha)}{2}; \quad \omega'_\alpha \equiv \text{Re} \omega_\alpha(t). \quad (25)$$

A decay yields nontrivial effects upon a nonadiabatic coupling if a crossing lasts longer than inverse decay rates. Otherwise, all decay rates can be neglected in the coupling equations. Therefore, we only deal with the case where the change of the Hamiltonian is relatively slow, i.e., where the following inequality holds during some period, at least for some levels:

$$\tau^{-1} \equiv \left| \left( \frac{dH}{dt} \right) H^{-1} \right| \ll -\omega''_\alpha; \quad \omega''_\alpha \equiv \text{Im} \omega_\alpha(t). \quad (26)$$

Then, a decay of generalized eigenstates $|\varphi_\alpha\rangle$ can be treated as exponential with current decay rates $\omega''_\alpha(t)$. Of course, we assume that $-\omega''_\alpha \ll \omega'_\alpha$; otherwise the concept of discrete levels is physically meaningless.

In the situation stated above, dressing of generalized eigenstates can set up adiabatically in spite of nonadiabatic level crossing. (An analogous situation is well known for a transient radiation of moving charges in electrodynamics of continuous inhomogeneous media $[79,80]$.) As a result, the complex spectral decomposition (4) allows one to take into account consistently time dependence both of a dynamical subsystem and of its interaction with a reservoir, as well as to keep a closed form of equations of a nonadiabatic discrete-level coupling. The decisive step is the introduction of the complex amplitudes, $f_\alpha(t)$ and $f_k(t)$, of time-dependent generalized eigenstates, $|\varphi_\alpha\rangle$ and $|\varphi_k\rangle$, respectively, in a rigged Hilbert space (cf. equation (23) and also $[11-18,58]$):

$$|\psi(t)\rangle = \sum_{\alpha=1}^{N} b_\alpha(t)|\alpha\rangle + \sum_{k} b_k(t)|k\rangle = \sum_{\alpha=1}^{N} f_\alpha(t)|\varphi_\alpha\rangle + \sum_{k} f_k(t)|\varphi_k\rangle, \quad (27)$$

$$f_\alpha(t) = \sum_{\alpha'=1}^{N} \langle \varphi_\alpha | \alpha' \rangle b_{\alpha'} + \sum_{k'} \langle \varphi_\alpha | k' \rangle b_{k'}. \quad (28)$$
The Schrödinger equation, \( \frac{d\psi}{dt} = -iH\psi \), yields the exact equations for the amplitudes

\[
\dot{f}_\alpha + i\omega_\alpha(t)f_\alpha = -\sum_{\alpha'=1}^{N} \langle \check{\varphi}_\alpha | \varphi_{\alpha'} \rangle f_{\alpha'} - \sum_{k'} \langle \check{\varphi}_\alpha | \varphi_{k'} \rangle f_{k'},
\]

(29)

\[
\dot{f}_k + i\omega_k f_k = -\sum_{\alpha'=1}^{N} \langle \check{\varphi}_k | \varphi_{\alpha'} \rangle f_{\alpha'} - \sum_{k'} \langle \check{\varphi}_k | \varphi_{k'} \rangle f_{k'},
\]

(30)

where the dot stands for the time derivative, \( \frac{d}{dt} \).

For the general situations stated above, it is possible, as a natural approximation, to neglect the last continuous sum of equation (29) as compared to the first discrete sum; even if nonadiabatic effects are small, e.g., \( |[\varphi_\alpha | \varphi_{\alpha'}]|, |\langle \check{\varphi}_\alpha | \varphi_{\alpha'} \rangle| \ll |\omega_\alpha - \omega_{\alpha'}| \) (see [49]), the last term of equation (29) may be negligible as compared to the left-hand side, \( i\omega_\alpha f_\alpha \). In this case, the time evolution of the discrete amplitudes, \( f_\alpha \), is independent of the amplitudes of the (generalized) reservoir eigenstates, \( f_k(t) \), and thus their evolution (30) is not necessary to be considered. Under this approximation, the bare amplitudes, \( b_\alpha \) and \( b_k \), are related to the generalized amplitudes as

\[
b_\alpha = \sum_{\alpha'=1}^{N} \langle \alpha | \varphi_{\alpha'} \rangle f_{\alpha'}, \quad b_k = \sum_{\alpha'=1}^{N} \langle k | \varphi_{\alpha'} \rangle f_{\alpha'}.
\]

(31)

Physically speaking, the reduction to the closed description in the dynamical subspace, \( \tilde{\mathcal{H}} \), spanned by the generalized eigenstates \( |\varphi_\alpha\rangle \) results from a random, incoherent distribution of reservoir-eigenstate amplitudes, \( f_k \), when they have no time for mutual phasing during a nonadiabatic crossing (such a case may take place, e.g., if the reservoir state is close to the vacuum). In other words, the present approximation takes into account the reservoir effects arising from a discrete-state decay into a continuum, but excludes an effect of macroscopic dynamics of the reservoir (e.g., coherent wave packet propagation) as well as the non-Markovian effects arising from the reservoir dynamics in the initial Zeno and final polynomial-decay stages [54,81–87]. Moreover, as the generalized discrete states, \( |\varphi_\alpha\rangle \), correspond to the Gamow vectors (e.g., [14–16]), the coordinate representation of their field parts has exponentially growing terms with respect to the coordinates and, as a result, the present approximation, where only the generalized discrete states are retained, cannot correctly treat field propagation effects. In this paper, we focus only on the nonadiabatic decaying-level coupling, where this approximation is expected to be valid. We are not going to discuss the precise validity conditions of this approximation as well as more general situations, where the full set of equations (29)–(30) is necessary.

In conclusion, we find the fundamental set of equations taking into account an exponential decay of generalized discrete states:

\[
\dot{f}_\alpha + i\omega_\alpha(t)f_\alpha = -\sum_{\alpha'=1}^{N} \langle \check{\varphi}_\alpha | \varphi_{\alpha'} \rangle f_{\alpha'}.
\]

(32)

Then, through equation (31), one can find the amplitudes, \( b_\alpha \), of the initial partial states, \( |\alpha\rangle \), in which we are often interested. This corresponds to the analogous set of equations for linear mode coupling in a wave-propagation theory [49]. (An introduction of bras different from kets corresponds to an introduction of so called “transfer” modes which possess polarizations different from those of primary modes [44,45].) The matrix of coupling coefficients, \( i\langle \varphi_\alpha | \varphi_{\alpha'} \rangle \), is not Hermitian in general and is evaluated in the following sections. Indeed, by differentiating the biorthogonality condition for the generalized basis (see equations (22)), we obtain

\[
[i\langle \varphi_\alpha | \varphi_{\alpha'} \rangle]^* = -i\langle \varphi_{\alpha'} | \varphi_\alpha \rangle = i\langle \varphi_\alpha | \varphi_{\alpha'} \rangle \neq i\langle \varphi_\alpha | \varphi_{\alpha'} \rangle,
\]

(33)
where the star is the complex conjugation. One can always choose a basis with zero diagonal elements \([49,50]\), \(\langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle = -\langle \tilde{\varphi}_\alpha | \tilde{\varphi}_\alpha \rangle = 0\); that is, one can always normalize the time-dependent amplitudes so that the snapshot eigenfrequencies do not depend explicitly on the time derivatives of the Hamiltonian parameters (1). As shown in Section 5, this choice takes into account complex Berry's phase.

In a simple phenomenological approach \([23-31,50-53]\), one starts from the equations for amplitudes, \(\tilde{f}_\alpha\), corresponding to the partial states, \(|\varphi_\alpha\rangle\), which are analogous to equations (32),

\[
\tilde{f}_\alpha + i\nu_\alpha(t)\tilde{f}_\alpha = -\sum_{\alpha'}^N \langle \varphi_\alpha | \tilde{\varphi}_{\alpha'} \rangle \tilde{f}_{\alpha'},
\]

and adds an imaginary part to the normal frequencies, \(\nu_\alpha(t)\), or to the partial frequencies, \(h_{\alpha\alpha}(t)\) (i.e., the diagonal components of the Hamiltonian (3)), in order to take into account the decay. In this approach, the coupling-coefficient matrix, \((i\langle \tilde{\varphi}_\alpha | \tilde{\varphi}_{\alpha'} \rangle\)), does not include the reservoir effects and thus the interplay between the nonadiabatic coupling and reservoir effects is treated inconsistently. As discussed in the next section, the reservoir dependence of the coupling-coefficient matrix, \((i\langle \tilde{\varphi}_\alpha | \varphi_{\alpha'} \rangle\)), is the very origin of the novel nonadiabatic effects of decay-level coupling.

Moreover, the relation (28) indicates the necessity of going out of the usual dynamical subspace spanned by discrete partial states, \(|\alpha\rangle\), and introducing their nontrivial superpositions with the continuous partial states, \(|k\rangle\) (see equations (31)), to obtain the closed set of equations (32), i.e., to construct the correct non-Hermitian time-dependent Schrödinger equation. This result is very difficult to guess phenomenologically, that is, without using the complex spectral decomposition (4) and introducing explicitly dressed discrete decaying levels; cf. \([30,31,50]\).

The presence of a nonadiabatic behavior is shown in equations (32) explicitly through the time derivatives, \(|\tilde{\varphi}_{\alpha'}\rangle\). Once we know their time dependence, as well as that of the eigenfrequencies, several methods are available for solving the fundamental equations (32). Usually, two different cases have been studied: the case where the Hamiltonian is a periodic function of time and the case where the Hamiltonian changes only during some finite time interval, \([0, t_s]\). In the former, the problem is to find a monodromy matrix and quasienergies of the set of equations (32) \([32-41,88]\). In the latter, one usually considers the so-called depletion problem, i.e., the calculation of final amplitudes, \(f_{\alpha}(t_s)\), of all discrete states starting from any given state, \(|\varphi_{\alpha_0}\rangle: f_{\alpha}(0) = \delta_{\alpha_0\alpha}\). The simplest method of solving the depletion problem is based on a perturbation theory in the case of weak (but nonadiabatic) coupling, when \(|f_{\alpha}(t)| \gg |f_{\alpha}(t)|\) for all \(\alpha \neq \alpha_0\) \([28-31,41,47-49]\). Concerning this and other methods, see reviews \([46-49]\) and the references therein.

4. NONADIABATIC EFFECTS DUE TO DECAY

First, we remark that the nonadiabatic terms in equations (32) (r.h.s.) exist even for noncrossing levels whose complex energies are constant or almost constant in time, \(\omega_\alpha(t) \approx \text{const}\). This is because of the redressing of the time-dependent reservoir states. To extract systematically all the effects missed in the previous phenomenological approaches, we calculate the coupling-coefficient matrix, \((i\langle \tilde{\varphi}_\alpha | \varphi_{\alpha'} \rangle\)), explicitly from the formula for the complex eigenstates (13) and (14). Tedious but straightforward calculation for \(\alpha \neq \beta\) gives

\[
\langle \tilde{\varphi}_\alpha | \varphi_\beta \rangle = C_{\alpha\beta} \sum_{\alpha',\beta'}^{N} \xi^{-1}_{\alpha\alpha'}(\omega_\alpha)\xi_{\beta\beta'}(\omega_\beta) \left\{ h_{\alpha',\beta'} + \sum_{k'} V^*_{\alpha'k'}V_{\beta'k'} \right\} + \sum_{k'} V^*_{\alpha'k'}V_{\beta'k'} \langle \omega_\alpha - \omega_{k'} \rangle, \]

where the dots stand for the derivative with respect to the time and the constant factor, \(C_{\alpha\beta}\), is given by

\[
C_{\alpha\beta} = \frac{1}{\omega_\beta - \omega_\alpha} \left( \frac{\eta_\alpha(\omega_\alpha)}{\eta_\beta(\omega_\beta)} \right) \frac{1}{\sqrt{\eta^*_{\alpha}(\omega_\alpha)\eta_{\beta}(\omega_\beta)}}. \]
The matrix (35) depends on the reservoir not only explicitly, but also implicitly through the normalization constants, $g_a, \gamma_{a'}(\omega_a)$, and the matrix elements, $\xi_{a'\alpha'}(\omega_a), \xi_{\alpha\beta'}(\omega_\beta)$; cf. equations (8), (9), (18), and (19). Note that when there is no interaction with the reservoir, $V_{a'k'} = 0$, only the first term of equation (35) remains and the matrix $\xi_{aa'}$ is determined by the dynamical (partial) Hamiltonian, $h_{aa'}$, being unitary and frequency independent. In this case, according to the definitions (7)–(9), we have

$$|\varphi_a\rangle = g_a|\phi_a\rangle \equiv g_a|u_a\rangle, \quad \langle \varphi_{a'}| = g_{a'}^{-1}\langle \phi_{a'}| \equiv g_{a'}^{-1}\langle v_{a'}|,$$

so that equations (32) coincide with equations (34), where $f_a = g_a f_a$, and $g_a$ can be chosen such that no diagonal coupling coefficients appear, e.g., $g_a = 1$ or $g_a = g_a$ with

$$\frac{\dot{g}_a}{g_a} = -\langle \phi_a | \phi_a \rangle \equiv - \sum_{\alpha'=1}^{N} \xi_{a'\alpha'}^{-1} \xi_{\alpha'\alpha}.$$

As explained in the previous section, in the phenomenological approaches, decay is taken into account by adding imaginary parts to the partial energies, $h_{aa}(t)$, or normal energies, $\nu_a(t)$. But the unperturbed coupling coefficients, $\langle \phi_{a'}| \phi_a \rangle$, are still used. On the contrary, formula (35) takes into account, consistently, the effects of decay even on the coupling coefficients and yields the following possibilities.

(i) Let us assume that the interaction has the property that the second and third terms of equation (35) are much smaller than the first. Usually, only this case is considered, and the interaction with the reservoir is supposed to be time independent. In spite of this assumption, the decay rates acquire time dependence induced by the time dependence of the subsystem Hamiltonian (3), $h(t)$. And this time dependence, $-\omega_a'(t)$, can yield the nonadiabatic effects by itself. On the other hand, since the matrix elements $\xi_{aa'}$ depend on the interaction between the subsystem and the reservoir, even the first term of equation (35) produces nonadiabatic effects, the order of which is $O(V^2)f_a$, or the same order of the decay term, $-\omega_a'(t)$. As a result, the nonadiabatic effects of decay cannot be discussed separately from the unitary nonadiabatic effects, even if only the subsystem changes in time, $h_{aa'} = h_{aa}(t)$.

(ii) Let the dynamical partial coupling, $h_{aa'}$, and normal frequencies, $\nu_a$, be constant or vary adiabatically slowly, so that the unitary nonadiabatic coupling between eigenstates is absent in the usual approximation. In fact, nonadiabatic effects are still possible, owing to the time dependence of the interaction with reservoir, $V_{ak}(t)$, i.e., to the second and third terms of equation (35). In other words, the time-dependent reservoir-subsystem coupling induces time-dependent redressing of the generalized eigenstates and time-dependent decay rates, $-\omega_{a'}(t)$. As a result, nonadiabatic effects will come out. (If the redressing is neglected, one has $\langle \tilde{\phi}_a | \phi_{a'} \rangle = 0$, that is, according to equations (32), independent eigenstates, even if the decay rates strongly depend on time. Such a situation would be unphysical and, thus, is impossible.)

(iii) Let the eigenfrequencies, $\omega_a$, decay rates, $\omega_{a'}$, and the matrix of coupling coefficients, $i\langle \tilde{\phi}_a | \phi_{a'} \rangle$, be constant or vary slowly enough in certain time interval. Then the coupling equations (32) possess $N$ linearly independent solutions characterized by new complex eigenfrequencies, $\Omega_a = \Omega_a' + i\Omega_a''$. Ignoring the reservoir, i.e., assuming the matrix of coupling coefficients to be Hermitian, one finds only corrections to the real parts, $\Omega_a' - \omega_a \neq 0$, of the initial eigenfrequencies, $\omega_a = \nu_a$, and, hence, the nonadiabatic effects appear as a harmonic beating, that is, the periodic exchange of populations (and energies) among generalized eigenstates, $|\varphi_a\rangle$. Furthermore, in the phenomenological approach, the decay term, $-\omega_{a'} f_a$, is introduced to the l.h.s. of equations (34) independently. On the other hand, the consistent approach based on equations (32) reveals, in addition, the existence
of the corrections to the imaginary parts of the eigenfrequencies, $\tilde{\Omega}_0^\prime - \Omega_0^\prime \neq 0$, due to the non-Hermiticity of the coupling-coefficient matrix, $i\langle \tilde{\phi}_\alpha | \phi_\beta \rangle$ (cf. equation (33)). Thus, side by side with beating, an additional cross-relaxation of generalized eigenstates appears. When a harmonic beating is suppressed, simple acceleration or slowing down of the decay of a certain superposition of generalized eigenstates is possible.

For concrete calculations, we need further auxiliary variables, namely, the eigenvalues of the $N \times N$-matrix $K(\omega)$, $\mathcal{H}(\omega)$, the matrix elements diagonalizing $K(\omega)$, $\xi_{\alpha\alpha'}$, and the complex eigenvalues, $\omega_{\alpha}$. We obtain all these in Section 7 for the simplest example in quantum optics, namely, for a system with two crossing levels ($N = 2$), which is already suitable for most of the applications. (The phenomenological approach in this case had been improved slightly in [27], but it is not sufficient to describe rigorously the nonadiabatic effects due to level mixing via reservoir.)

Finally, we discuss a ‘resonance’ approximation implicitly used in the previous works on level crossing, where relaxation is taken into account via a perturbation method; cf., e.g., [23–29, 42,43,59]. This approximation does not hold unless the condition explained in the first paragraph of Section 3 is satisfied, i.e., unless all coupled levels are relatively close to each other and their decay is not too strong,

$$-\omega_0^\prime(t), \quad |\omega_\alpha(t) - \omega_\delta(t)| \ll \omega_0(t) = \frac{1}{N} \sum_{\beta=1}^{N} \omega_\beta(t).$$

(39)

Now we show that, under an appropriate approximation, the consistent formulas (35) and (7)–(9) lead to the “resonance” approximation with a new explicit form of a true non-Hermitian Hamiltonian. Bearing in mind a smooth dependence of the molecule-reservoir coupling, $V_{\alpha k}$, on a mode frequency, $\omega_k$, the frequency in the matrix (7), $K(\omega)$, can be fixed to the average energy of coupling levels, $\omega = \omega_0(0)$, and a small difference between the dispersive parameters (19) and unity can be ignored: $\eta_\alpha(\omega_0) \approx 1$. Then, using a tilde to denote the solutions of the eigenvalue problem (8), (9) for the fixed non-Hermitian matrix $\tilde{K}_{\alpha\alpha'} = K_{\alpha\alpha'}(\omega_0)$,

$$\tilde{\omega}_{\alpha} = \mathcal{H}_{\alpha}(\omega_0), \quad |\tilde{u}_{\alpha} = |u_{\alpha}(\omega_0)|, \quad \langle \tilde{u}_{\alpha} \rangle = \langle u_{\alpha}(\omega_0) \rangle, \quad \tilde{\xi}_{\alpha\alpha'} = \xi_{\alpha\alpha'}(\omega_0) \neq \tilde{\xi}_{\alpha\alpha'}^{-1},$$

(40)

we can write the approximate formula for the matrix of coupling coefficients (35) for $\alpha \neq \beta$:

$$\langle \tilde{\phi}_\alpha | \phi_\beta \rangle \simeq g_\beta g_{\alpha}^{-1} \langle \tilde{u}_{\alpha} | \tilde{u}_{\beta} \rangle = \frac{1}{\tilde{\omega}_\beta - \tilde{\omega}_\alpha} \left( \frac{g_\beta}{g_{\alpha}} \right) \sum_{\alpha',\beta'} \tilde{\xi}_{\alpha',\alpha}^{-1} \tilde{K}_{\alpha',\beta'} \tilde{\xi}_{\beta'},$$

(41)

This result corresponds to the proper neglect of the reservoir degrees of freedom and the approximate substitution

$$|\varphi_{\alpha'} \rangle \rightarrow g_{\alpha'} |\tilde{u}_{\alpha'} \rangle, \quad \langle \tilde{\phi}_{\alpha} | \rightarrow g_\alpha^{-1} \langle \tilde{u}_{\alpha} |, \quad h_{\alpha\alpha'} \rightarrow \tilde{K}_{\alpha\alpha'}(t)$$

(42)

(cf. equations (37)), and thus, to the replacement of the total Hermitian Hamiltonian (1) $\equiv (4)$ with the non-Hermitian Hamiltonian

$$\tilde{K}(t) = K(\omega_0, t) \equiv \sum_{\alpha=1}^{N} \tilde{\omega}_{\alpha}(t) |\tilde{u}_{\alpha}(t) \rangle \langle \tilde{u}_{\alpha}(t) |,$$

(43)

which acts on the $N$-dimensional Hilbert space spanned by a complete biorthogonal basis $\{ |\tilde{u}_{\alpha} \rangle, \langle \tilde{v}_{\alpha} | \}$. Note that, in general, non-Hermitian corrections appear in all $N \times N$ elements of the dynamical (partial) Hermitian Hamiltonian (3), $h_{\alpha\alpha'}$. So, even in the ‘resonance’ approximation (39)–(41), the coupling equations (32) for decaying eigenstates are different from the phenomenological equations (34) with improved normal $(v_{\alpha} \rightarrow \tilde{\omega}_{\alpha})$ or partial $(h_{\alpha\alpha} \rightarrow \tilde{K}_{\alpha\alpha})$ frequencies,
because such improvements cannot take the proper coefficients of a nonadiabatic coupling (41) into account. The normalization factors, \( g_\alpha \), in equations (41) and (42) may be chosen arbitrarily, for example, \( g_\alpha = 1 \), but, as in the case without reservoir (38), there is a choice, \( g_\alpha = \tilde{g}_\alpha \), which reduces the diagonal coupling coefficients in equations (32) to zero:

\[
\frac{\dot{\tilde{g}}_\alpha}{\tilde{g}_\alpha} = -\langle \tilde{\psi}_\alpha | \dot{\tilde{\psi}}_\alpha \rangle \equiv - \sum_{\alpha' = 1}^{N} \xi_{\alpha\alpha'}^{-1} \xi_{\alpha'\alpha} \simeq - \sum_{\alpha' = 1}^{N} \xi_{\alpha\alpha'}^{-1}(\tilde{\omega}_0) \xi_{\alpha'\alpha}(\tilde{\omega}_0).
\] (44)

The accuracy of the ‘resonance’ approximation mainly relies on the smallness of the parameters in (39), but its detail depends on the concrete oscillograms of the functions (35) and (41), so that the accuracy should be examined case by case.

5. ON THE GENERALIZED COMPLEX BERRY’S PHASE

Let us show that the present method provides a generalization of the Berry’s phase. As mentioned before, the generalized eigenfunctions (13)-(14), \{\|\varphi_\alpha\rangle, \langle \varphi_\alpha |\}, contain an arbitrary normalization constant \( g_\alpha \), which can always be determined so that \( \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle = 0 \). This relation means, according to equations (27)-(29), that for each instantaneous eigenstate, \( I_\varphi = \tilde{\varphi}_\alpha I_\alpha \), the local phase shift is determined by the solution of the dispersion relation (18) via \( \tilde{f}_\alpha f_\alpha = -i\omega_\alpha(t) \) and does not depend explicitly on any time derivative. Now we shall show that \( \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle = 0 \). Straightforward calculation gives

\[
\langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle = \frac{d}{dt} \ln g_\alpha + \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle_1,
\] (45)

where

\[
\langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle_1 \equiv \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle |_{g_\alpha = 1} = \sum_{\alpha' = 1}^{N} \xi_{\alpha\alpha'}^{-1}(\omega_\alpha) \left\{ \frac{d}{dt} \frac{\xi_{\alpha'\alpha}(\omega_\alpha)}{\eta_{\alpha}(\omega_\alpha)^{1/2}} \right\} - \sum_k \frac{V_{\alpha'k}^*}{|\omega_\alpha - \omega_k|^2} \sum_{\beta' = 1}^{N} \frac{V_{\beta'k}\xi_{\beta'\alpha}(\omega_\alpha)}{\eta_{\alpha}(\omega_\alpha)^{1/2}} \frac{d\omega_\alpha}{dt} + \sum_k \frac{V_{\alpha'k}^*}{|\omega_\alpha - \omega_k|^2} \frac{d}{dt} \sum_{\beta' = 1}^{N} \frac{V_{\beta'k}\xi_{\beta'\alpha}(\omega_\alpha)}{\eta_{\alpha}(\omega_\alpha)^{1/2}} \right\}.
\] (46)

Therefore, the condition \( \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle = 0 \) leads to the equation for \( g_\alpha \) [49],

\[
\frac{d}{dt} \ln g_\alpha = -\langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle_1,
\] (47)

which admits an exponential function of some complex phase as a solution:

\[
g_\alpha = \exp i\Delta_\alpha(t), \quad \Delta_\alpha = i \int_0^t \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle_1 dt'.
\] (48)

The quantity \( \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle_1 \) can also be expressed as

\[
\langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle_1 = \frac{1}{2\omega_\alpha} \left\{ \langle \tilde{\varphi}_\alpha | \dot{H}(t) | \varphi_\alpha \rangle - \langle \tilde{\varphi}_\alpha | \dot{\tilde{H}}(t) | \varphi_\alpha \rangle \right\} |_{g_\alpha = 1}.
\] (49)

Therefore, if the eigenfrequency, \( \omega_\alpha \), is real and the right and left eigenstates coincide, \( |\varphi_\alpha \rangle = |\varphi_\alpha \rangle \), the quantity \( \langle \tilde{\varphi}_\alpha | \varphi_\alpha \rangle_1 \) becomes purely imaginary and thus the phase \( \Delta_\alpha \) becomes real (as discussed, e.g., in [39,40,89]). However, decay exists, the phase \( \Delta_\alpha \) becomes complex. (This result may be understood by comparing equations (38) and (44) which are the approximate versions of equation (47).)
The phase $\Delta_a$ provides a generalization of the Berry's phase, $\Delta_a(t_*)$, if one supposes that an adiabatic approximation is valid and a Hamiltonian returns to the initial value, $H(t_*) = H(0)$, at some moment $t_*$ [89] (see also [90]). In this case, the Schrödinger equation

$$i \frac{\partial}{\partial t} \psi(t) = H(t) \psi(t), \quad |\psi(0)\rangle = |\varphi_0(0)\rangle, \quad g_0 \equiv 1,$$

(50)

together with the adiabatic assumption $|\psi(t)\rangle = a_\alpha(t) |\varphi_\alpha(t)\rangle$ gives a closed equation for the amplitude $a_\alpha$:

$$a_\alpha(t) + i \omega_\alpha(t) a_\alpha(t) = -\langle \tilde{\varphi}_\alpha | \dot{\varphi}_\alpha \rangle a_\alpha(t), \quad a_\alpha(0) = 1,$$

(51)

which leads to

$$a_\alpha(t_*) = \exp \left[ -i \int_0^{t_*} \omega_\alpha(t') dt' \right] \exp \left[ - \int_0^{t_*} \langle \tilde{\varphi}_\alpha | \dot{\varphi}_\alpha \rangle dt' \right].$$

(52)

Factor (48) characterizes that variance of a complex amplitude of the generalized eigenvector $|\varphi_\alpha\rangle$, which takes place in addition to the usual time dependence, $f_\alpha(0) \exp[-i \int_0^{t_*} \omega_\alpha(t') dt']$, i.e., in addition to a dynamical rotation of the wave-function phase and an exponential decay of the amplitude determined by equations (32). Thus, we find a rigorous justification for the phenomenological approach to the Berry’s phase in the system with non-Hermitian Hamiltonian [91–93].

The present analysis (cf. equation (46)) shows that a decay yields a nontrivial dependence of a generalized complex Berry’s phase on a trajectory of a generalized eigenstate, $|\varphi_\alpha\rangle$, in the extended Hilbert space. It can be shown that the Berry-phase construction for nonadiabatic unclosed trajectories suggested in [94–96] is still valid for decaying generalized states. We are not going to discuss a similar generalization of the formula (48), because for a nonadiabatic crossing, a total complex amplitude of the discrete-level-occupation probability is of physical interest, but not its separate factor, $g_\alpha$. Exhaustive information is contained in a solution of coupling equations (32), where a generalized-eigenstate normalization is so chosen that the normalization factor $g_\alpha$ takes into account the generalized complex Berry’s phase (48).

6. DISCRETE SUBSPACE POPULATION AND TIME EVOLUTION OF LYAPUNOV-TYPE QUANTITY

For the time-independent one-level Friedrichs model [17], using the complex spectral decomposition, one can introduce a representation, where the dynamics is manifestly irreversible, and find a Lyapunov-type quantity which decreases monotonically. Here we discuss changes in these aspects caused by the explicit time dependence of the Hamiltonian.

As in the time-independent Friedrichs model [17], we introduce a new representation in the $N$-level case through

$$|\Psi_\Lambda\rangle \equiv \Lambda |\Psi\rangle,$$

(53)

where the nonunitary transformation, $\Lambda$, is defined in equation (24). Then the Schrödinger equation becomes

$$i \frac{\partial}{\partial t} |\Psi_\Lambda\rangle \equiv i \frac{\partial}{\partial t} \Lambda |\Psi\rangle = \Lambda H(t) \Lambda^{-1} |\Psi_\Lambda\rangle + i \left( \frac{\partial \Lambda}{\partial t} \right) \Lambda^{-1} |\Psi_\Lambda\rangle \equiv H_\Lambda(t) |\Psi_\Lambda\rangle,$$

(54)

where the transformed Hamiltonian, $H_\Lambda(t)$, is given by

$$H_\Lambda(t) = \sum_{\alpha=1}^N \omega_\alpha(t) |\alpha\rangle \langle \alpha | + \sum_k \omega_k |k\rangle \langle k | + i \left( \frac{\partial \Lambda}{\partial t} \right) \Lambda^{-1}.$$

(55)
Note that the transformed Hamiltonian is not diagonal because of the third term, which arises from the nonadiabatic behavior. Indeed, the third term, restricted to the dynamical subspace spanned by $\{|\alpha\rangle\}$, precisely corresponds to the nonadiabatic coupling term of equations (32):

$$
 i \frac{\partial \Lambda^{-1}}{\partial t} \bigg|_{\text{dis}} = P_d \left( i \frac{\partial \Lambda^{-1}}{\partial t} \right) P_d = \sum_{\alpha,\alpha'}^N i \langle \dot{\varphi}_\alpha | \varphi_{\alpha'} \rangle |\alpha\rangle \langle \alpha'| \equiv - \sum_{\alpha,\alpha'}^N i \langle \dot{\varphi}_\alpha | \varphi_{\alpha'} \rangle |\alpha\rangle \langle \alpha'|, \quad (56)
$$

where $P_d \equiv \sum_{\alpha=1}^N |\alpha\rangle \langle \alpha|$ is the projection operator to the space of partial discrete states.

The appearance of the nondiagonal part to the transformed Hamiltonian due to the nonadiabatic effects suggests the qualitative change of the dynamics as compared with the time-independent case. Thus it is interesting to see the behavior of the Lyapunov-type variable defined similarly to that of the one-level Friedrichs model [17]:

$$
 \mathcal{Y} \equiv \Lambda^{\dagger} \Lambda - I = \sum_{\alpha=1}^N |\dot{\varphi}_\alpha \rangle \langle \dot{\varphi}_\alpha|, \quad (57)
$$

Its expectation value for a given state, $|\psi(t)\rangle$, is

$$
 \mathcal{Y}_\psi \equiv \langle \psi(t) | \mathcal{Y} | \psi(t) \rangle = \sum_{\alpha=1}^N |f_\alpha(t)|^2, \quad (58)
$$

which also represents the total population of the subspace of the generalized discrete states. Within the range of their validity, the level-coupling equations (32) lead to

$$
 \frac{d\mathcal{Y}_\psi}{dt} = 2 \sum_{\alpha=1}^N \text{Im} \omega_\alpha(t)|f_\alpha|^2 - \sum_{\alpha,\alpha'=1}^N \{ \langle \dot{\varphi}_{\alpha'} | \dot{\varphi}_\alpha \rangle + \langle \dot{\varphi}_{\alpha'} | \dot{\varphi}_\alpha \rangle \} f_\alpha f_{\alpha'}. \quad (59)
$$

As $\text{Im} \omega_\alpha(t) < 0$ for decaying levels, the first term always drives $\mathcal{Y}_\psi$ to monotonic decrease. The second term resulting from the nonadiabatic effects may cause a qualitative change of the evolution of the Lyapunov-type quantity $\mathcal{Y}_\psi$.

Hence, the nonadiabatic interaction between the discrete subsystem and the reservoir can alter the qualitative behavior of the net decay property of the discrete subsystem. In particular, the population of some levels may even be regenerated via faster and deeper depletion of other discrete levels and their redressing with the reservoir states. So, the nonadiabatic coupling among discrete levels can change their lifetimes and provide a way to investigate the very nature of unstable states (or particles). In a wave-propagation theory, an analogous formula gives a variation law of the wave-field energy [42-49]. It cannot be seen in the nonsteady (driven) one-level Friedrichs model, although in this case the monotonicity of the evolution of the Lyapunov-type quantity may also be destroyed by a time-dependent (e.g., periodic) external force, as was shown by Rosenberg and Petrosky [97].

7. STARK EFFECT AND LINEAR COUPLING OF EXCITED QUASIERGY STATES IN A THREE-LEVEL MOLECULE DRIVEN BY NONSTEADY DC AND AC FIELDS

To illustrate the general theory of Sections 3 and 4, let us study nonadiabatic effects of spontaneous decay in the coherent dynamics of a three-level molecule with nondegenerate energy levels, $E_0, E_1$ and $E_2$ ($E_0 < E_1 < E_2$) under external electric fields. The external fields which we consider consist of nonstationary DC and AC components: the former affects the dipole momenta and energy levels via usual Stark effect and the latter is nearly in resonance with the transition between two excited levels, $E_2 - E_1$ (optical Stark effect). A three-level scheme is the basic one in quantum optics and proves its value in treating the resonance interaction of a molecule with quasi-monochromatic electromagnetic fields which interact mainly with three transitions: $E_2 - E_1, E_1 - E_0$, and $E_2 - E_0$. 
7.1. Reduction to the Friedichs-Fano Model

A nonstationary (pulse-like) DC field, \( E_d(t) \), causes temporal changes of three dipole momenta, \( \vec{\mu}(t) \), \( \vec{\mu}_1(t) \), and \( \vec{\mu}_2(t) \), corresponding to the transitions \( E_2 - E_1 \), \( E_1 - E_0 \), and \( E_2 - E_0 \), respectively, and of three energy levels, \( E_{0,1,2}(t) \), via the Stark effect. For simplicity, we assume that the Stark effect for the excited levels 1 and 2 is quadratic. It is realized if the energy states \( |1\rangle \) and \( |2\rangle \) are in opposite parity eigenstates and, hence, have zero constant dipole momenta. Furthermore, if the ground state \( |0\rangle \) is in a parity eigenstate, one optical transition, \( 1 \rightarrow 0 \) or \( 2 \rightarrow 0 \), is forbidden in the dipole approximation (as \( \vec{\mu}_1 \) or \( \vec{\mu}_2 \) is zero) and a spontaneous decay of the mixed excited states takes place through another optical transition, e.g., \( 2 \rightarrow 0 \).

A nonsteady external AC field,

\[
\vec{E}_a(t) = \frac{1}{2} \vec{E}(t) \exp \left[ -i \int_0^t \Omega(t') \, dt' \right] + \text{c.c.,} \quad \left| \frac{\Omega}{\Omega} \right| \ll \Omega,
\]

is assumed to mix two excited levels, that is, to be nearly in resonance with the transition \( 1 \rightarrow 2 \):

\[
|E_2 - E_1 - \Omega| \ll \Omega \sim E_2 - E_1 \ll E_{2,1} - E_0.
\]

In equation (61), we further assume that the transition frequency between excited levels is much lower than the optical frequencies of the transitions to the ground level, \( E_0 \). Then, as is well known, one may ignore the spontaneous transition between excited levels, \( 1 \leftrightarrow 2 \), because the probability of the transition, i.e., Einstein coefficient, is proportional to the cube of the transition frequency, \( A(\omega) \propto \omega^3 \).

In addition, the spontaneous optical transitions to the ground level (\( 2 \rightarrow 0 \), \( 1 \rightarrow 0 \)) are taken into account because of their principal role. This process arises from the interaction between excited molecular states and the vacuum of optical modes, which is described by the second quantized electric field,

\[
\vec{E}_V = i \sum_{p=1}^2 \sum_k \sqrt{\frac{2\pi\omega_k}{L^3}} \vec{e}_k^{(p)} \left( \hat{b}_k^{(p)} A_k - \hat{b}_k^{(p)\dagger} A_k^* \right),
\]

where \( \hat{b}_k^{(p)} \) and \( \hat{b}_k^{(p)\dagger} \) \( (p = 1, 2) \) are annihilation and creation operators of a mode, \( A_k = \exp(ik \cdot r) \) (in a free space), with a frequency \( \omega_k \) and a (unit) polarization vector, \( \vec{e}_k^{(p)} \perp k \) \((\vec{e}_k^{(1)} \perp \vec{e}_k^{(2)})) \). We show that, under the influence of the nonsteady Stark effect, the spontaneous decay can cause a nontrivial effect on the evolution of level populations. In particular, there is a possibility of speeding up (or slowing down) the decay rate of some level through the nonadiabatic interaction with other levels which decay faster (or slower).

Now we consider the Hamiltonian of the system. Because we are not interested in the induced molecular emission and, hence, in many-optical-photon states, the total Hilbert space may be restricted to the direct sum of one-photon states with ground molecular level 0, \( |kp\rangle \), and two different molecular excited states without photons, \( |1\rangle \) and \( |2\rangle \). Under the well-known rotating wave approximation \([41,58,59]\), we obtain a time-dependent Hamiltonian describing the interaction between two excited levels \( (N = 2) \):

\[
\begin{align*}
\hat{H} &= \hat{E}_1(t)|1\rangle\langle 1| + \hat{E}_2(t)|2\rangle\langle 2| \\
&\quad - \gamma(t) \exp \left( -i \int_0^t \Omega \, dt' \right) |2\rangle\langle 1| - \gamma^*(t) \exp \left( i \int_0^t \Omega \, dt' \right) |1\rangle\langle 2| \\
&\quad + \sum_{\beta=1}^2 \sum_{p=1}^2 \sum_k i \sqrt{\frac{2\pi\omega_k}{L^3}} \left[ (\vec{\mu}_\beta(t) \cdot \vec{e}_k^{(p)}) \exp(-ik \cdot r(t)) |kp\rangle\langle \beta| \\
&\quad - (\vec{\mu}_\beta(t) \cdot \vec{e}_k^{(p)}) \exp(ik \cdot r(t)) |\beta\rangle\langle kp| \right] \\
&\quad + \sum_{p=1}^2 \sum_k \omega_k |kp\rangle\langle kp|.
\end{align*}
\]
Here \( \hat{E}_{1,2} = E_{1,2} - E_0 \) denote energy differences between excited and ground levels and we introduce the Rabi frequency, \( \gamma(t) = \hat{E}(t) \cdot \vec{\mu}(t)/2 \), which corresponds to the energy of the interaction between the molecule and the AC field, \( \hat{E} \). The Rabi frequency can always be made real by properly redefining the time-dependent frequency \( \Omega(t) \) in equation (60). The interaction between the molecule and the nonstationary DC field, \( \hat{E}_d(t) \), is taken into account implicitly in the time-dependent parameters \( \hat{E}_{1,2}(t) \) and \( \vec{\mu}_{1,2}(t), \vec{\mu}(t) \). Note that the interaction between the molecule and optical modes depends on the position of the molecule, \( r(t) \).

The rapid oscillations of the dynamical (partial) molecular Hamiltonian can be removed by rotating a phase of one excited state with frequency \( \Omega(t) \), that is, by introducing new states, e.g., \( |1\rangle = \exp(i \int_0^t \Omega dt') |1\rangle \) and \( |2\rangle = |2\rangle \). Then, the Hamiltonian, \( \hat{H}(t) \), reduces to that, \( \hat{H}(t) \), of the Friedrichs-Fano model (1)-(3), with the parameters

\[
\begin{align*}
    h_{11} &= \hat{E}_1 \equiv \Omega_1(t), & h_{22} &= \hat{E}_2 \equiv \Omega_2(t), & h_{21} &= h_{12}^* = -\gamma(t); \\
    V_{\text{akp}}(t) &= i \sqrt{\frac{2 \pi \omega_k}{L^3}} \left( \vec{\mu}_{1}^*(t) \cdot \vec{e}_k^{(p)} \right) \exp \left( i \delta_{1a} \int_0^t \Omega \, dt' - i k \cdot r(t) \right).
\end{align*}
\]

In the absence of an interaction with the reservoir, the dynamical (partial) Hamiltonian (3), \( \hat{h}(t) \), admits real eigenvalues known as quasienergies:

\[
\nu_{1,2} = \frac{1}{2} \left[ \Omega_1^2 + \Omega_2^2 \mp \sqrt{(\Omega_2^2 - \Omega_1^2)^2 + 4|\gamma|^2} \right].
\]  

7.2. Coupling Equations for Decaying Discrete States

Because the system under consideration is equivalent to the two-level Friedrichs-Fano model, the evolution of amplitudes of the decaying discrete states is described by equations (32) derived in Section 3. To write down the equations, we need instantaneous discrete eigenvalues of the total Hamiltonian, \( \omega_\alpha \), and mixing matrix elements, \( \{ \langle \phi_\alpha | \phi_\beta \rangle \} \).

As discussed in Section 2 (cf. equations (7)-(9) and (18)), the discrete eigenvalues are determined from the matrix, \( \{ K(\omega)_{\alpha \alpha} \} \), defined in equation (7). To avoid the QED ultraviolet divergences in the integrals involved in the matrix, \( K \), we assume that the dipole momenta \( \vec{\mu}_\beta \) have additional dependence on the photon frequency \( \omega_k \) in such a way that they are constant in relatively narrow frequency intervals, \( 2\omega \), and zero otherwise: \( \vec{\mu}_{1,2}(\omega) = \text{const. for } \omega \in (\hat{E}_{1,2} - \omega, \hat{E}_{1,2} + \omega) \) and \( \vec{\mu}_{1,2}(\omega) = 0 \) for \( \omega \notin (\hat{E}_{1,2} - \omega, \hat{E}_{1,2} + \omega) \). Note that the auxiliary band width, \( 2\omega \), does not enter the final results when the condition \( \hat{E}_2 - \hat{E}_1 \ll \omega \ll \hat{E}_1 + \hat{E}_2 \) is satisfied.

Then, integrating over orientations of a wave vector \( k \) and over frequency \( \omega = c|k| \), we have

\[
K(\omega, t)_{11,22} \simeq \Omega_1^2(t) - i \frac{2}{3} \left( \frac{\omega}{c} \right)^3 |\vec{\mu}_{1,2}(t)|^2 \equiv \Omega_1^2(t) - i \gamma_{1,2}(\omega, t),
\]

\[
K(\omega, t)_{12} + \gamma(t) = -(K(\omega, t)_{21} + \gamma(t)) \simeq i \frac{2}{3} \left( \frac{\omega}{c} \right)^3 (\vec{\mu}_1^*(t) \cdot \vec{\mu}_2(t)) \exp \left( +i \int_0^t \Omega \, dt' \right).
\]

So, we have

\[
(K(\omega, t)_{\alpha \alpha'}) = \begin{pmatrix} \Omega_1^*(t) - i \Gamma_1(\omega, t), & -\gamma^*(t) \\ -\gamma(t), & \Omega_2^*(t) - i \Gamma_2(\omega, t) \end{pmatrix},
\]

and, assuming further, for simplicity, that the dipole momenta of optical transitions are almost orthogonal, \( \vec{\mu}_1^* \cdot \vec{\mu}_2 \simeq 0 \), or

\[
|\vec{\mu}_1^* \cdot \vec{\mu}_2| \ll |\vec{\mu}_1|^2 - |\vec{\mu}_2|^2,
\]
we can diagonalize the matrix (69) by the non-Hermitian matrix of the frequency-dependent
transformation (9), \( \xi_{\alpha\alpha'} \),
\[
\left( \xi_{\alpha\alpha'} \right) = \frac{1}{\sqrt{\theta^2 + |\gamma|^2}} \begin{pmatrix} \gamma^* & -\theta \\ \theta & \gamma \end{pmatrix}, \quad \left( \xi_{\alpha\alpha'}^{-1} \right) = \frac{1}{\sqrt{\theta^2 + |\gamma|^2}} \begin{pmatrix} \gamma & \theta \\ -\theta & \gamma^* \end{pmatrix};
\]
\[
\theta(\omega) = \frac{1}{2} \left\{ \Omega'_1 - i\Gamma_1(\omega) - \Omega'_2 + i\Gamma_2(\omega) + \sqrt{(\Omega'_2 - i\Gamma_2(\omega) - \Omega'_1 + i\Gamma_1(\omega))^2 + 4|\gamma|^2} \right\}. \quad (72)
\]
The eigenvalues of the matrix (69) are complex: \( \mathcal{H}_1(\omega) = \Omega'_1 - i\Gamma_1(\omega) - \theta(\omega) \) and \( \mathcal{H}_2(\omega) = \Omega'_2 - i\Gamma_2(\omega) + \theta(\omega) \). They enter the characteristic equation (18), which we have to solve.

Under the ‘resonance’ approximation explained at the end of Section 4, which is valid here because the condition (61) is fulfilled, the discrete eigenvalues of the total Hamiltonian, i.e.,
generalized quasienergies (cf. [32–41]), are given by
\[
\omega_{1,2}(t) \simeq \omega_{1,2}(t) = \frac{1}{2} \left[ \Omega_1 + \Omega_2 \mp \sqrt{(\Omega_2 - \Omega_1)^2 + 4|\gamma|^2} \right],
\]
\[
\Omega_{1,2}(t) \equiv \Omega_{1,2}(t) - i\Gamma_{1,2}(t), \quad \Gamma_{1,2} = \Gamma_{1,2} \left( \frac{(\Omega'_1 + \Omega'_2)}{2} \right) \simeq \Gamma_{1,2} \left( \Omega_{1,2} \right). \quad (73)
\]
The relaxation rates, \( \Gamma_{1,2} \), are equal to the one half of the Einstein’s coefficients. \( A(\Omega_{1,2}) \), at the partial (optical) transition frequencies, \( \Omega_{1,2} \). In this case, the corresponding generalized eigenstates, i.e., quasienergy states, are given in terms of equations (13) and (14) of Section 2 by replacing \( \eta_\alpha(\omega)^{\dagger} \) to \( \xi_{\alpha\alpha'} \) to \( \hat{\xi}_{\alpha\alpha'} \) and \( \xi_{\alpha\alpha'}^{-1} \) to \( \hat{\xi}_{\alpha\alpha'}^{-1} \), where \( \hat{\xi}_{\alpha\alpha'} \) and \( \hat{\xi}_{\alpha\alpha'}^{-1} \) are obtained from equations (71) by changing \( \theta(\omega) \) to
\[
\theta_0 = \frac{1}{2} \left[ \Omega_1 - \Omega_2 + \sqrt{(\Omega_2 - \Omega_1)^2 + 4|\gamma|^2} \right]. \quad (74)
\]
We now consider the mixing matrix elements, \( \langle \hat{\phi}_\alpha | \hat{\phi}_\beta \rangle \). Using the regularization explained above, the integrals appearing in the mixing matrix elements are calculated as
\[
\sum_{p=1}^{2} \sum_{k} \frac{V_{akp}^* V_{bkp}}{\omega_{ak} - \omega_{bk}^k} \simeq -\frac{i}{3} \left( \frac{\omega_\alpha}{c} \right)^3 \left( \bar{\mu}_\alpha \cdot (i\delta_{1\beta} \bar{\mu}_\beta) \right) \exp \left\{ i(\delta_{1\beta} - \delta_{1\alpha}) \int_0^t \Omega dt' \right\}. \quad (75)
\]
Assuming the validity of the ‘resonance’ approximation, the mutual orthogonality of excited dipole momenta as before, and in addition, a slow enough change of the parameter such that
\[
\left| \frac{\bar{\mu}_{1,2}}{\bar{\omega}_{1,2}} \right| \ll \Omega,
\]
we have
\[
\langle \hat{\phi}_1 | \hat{\phi}_2 \rangle = \frac{g_2}{g_1} \left[ \frac{\theta_0^2 \gamma - \gamma^2 \gamma^* + \theta_0 \gamma \left( \Omega_2 - \Omega_1 \right)}{(\theta_0^2 + |\gamma|^2) \sqrt{(\Omega_2 - \Omega_1)^2 + 4|\gamma|^2}} + \frac{3\Omega \theta_0 \gamma \Gamma_1}{(\theta_0^2 + |\gamma|^2) \Omega_1} \right],
\]
\[
\langle \hat{\phi}_2 | \hat{\phi}_1 \rangle = \frac{g_1}{g_2} \left[ \frac{\theta_0^2 \gamma - \gamma^2 \gamma^* + \theta_0 \gamma \left( \Omega_2 - \Omega_1 \right)}{(\theta_0^2 + |\gamma|^2) \sqrt{(\Omega_2 - \Omega_1)^2 + 4|\gamma|^2}} - \frac{3\Omega \theta_0 \gamma \Gamma_1}{(\theta_0^2 + |\gamma|^2) \Omega_1} \right].
\]
When the Rabi frequency, \( \gamma \), is real, the mixing matrix elements can be rewritten in a compact form:
\[
\langle \hat{\phi}_1 | \hat{\phi}_2 \rangle = -\frac{g_2}{g_1} \left[ \frac{\hat{q}}{2(1 + q^2)} - \frac{3\Omega \gamma \Gamma_1}{2\Omega_1 |\gamma| \sqrt{1 + q^2}} \right], \quad (77')
\]
\[
\langle \hat{\phi}_2 | \hat{\phi}_1 \rangle = \frac{g_1}{g_2} \left[ \frac{\hat{q}}{2(1 + q^2)} + \frac{3\Omega \gamma \Gamma_1}{2\Omega_1 |\gamma| \sqrt{1 + q^2}} \right], \quad (78')
where \( q \equiv (\Omega_1 - \Omega_2)/(2\gamma) \). The coupling equations of the decaying levels are then given by equations (32):
\[
\dot{f}_1 + i\omega_1 f_1 = -\langle \phi_1 \mid \phi_2 \rangle f_2, \quad \dot{f}_2 + i\omega_2 f_2 = -\langle \phi_2 \mid \phi_1 \rangle f_1.
\] (79)

The conditions assumed above are equivalent to those assumed in the phenomenological approaches leading to equations (34). However, the latter treat the nonadiabatic level-mixing inconsistently, and we discuss the possible differences between the phenomenological and present approaches in the next section.

7.3. Novel Nonadiabatic Effects—Comparison with Phenomenological Approach

The novel nonadiabatic effects discussed in Section 4 have not been taken into account by the phenomenological approach based on equations (34) where the mixing matrix elements are calculated in terms of the unperturbed eigenvectors. When the Rabi frequency \( \gamma \) is real (which is assumed hereafter), they are given by
\[
\dot{\phi}_2 - i\omega_2 \phi_2 = -i\gamma' (\phi_1 \mid \phi_2 - \phi_2 \mid \phi_1),
\] (80)

Note that \( \gamma' \) coincides with the real part of \( q \) defined just after equation (78'). Therefore, these effects can clearly be understood either by comparing the numerical solutions of the phenomenological equations (34) and our equations (32), or as the deviation of the experiments from the prediction based on the phenomenological equations (34). There is no doubt that the experiments will confirm the predictions based on the correct equations (32). In the rest of this section, we investigate the observability of the expected difference between the phenomenological and our approach. Note that because of the explicit lifetime dependence of the mixing matrix elements seen in equations (77) and (78), all cases (i)–(iii) explained in Section 4 are possible.

The new effects would be observable if the difference between the mixing matrix elements of the phenomenological and the present approach is greater than or of the same order as the phenomenological matrix elements:
\[
|\langle \phi_2 \mid \phi_1 \rangle - \langle \phi_2 \mid \phi_1 \rangle| \gtrsim |\langle \phi_2 \mid \phi_1 \rangle|.
\] (81)

First to observe the populations of and the mixing between the two excited levels, their linewidths should be smaller than both the Rabi frequency and the detuning. Because \( \Gamma_{1,2} \sim |\Gamma_2 - \Gamma_1| \), this implies
\[
2|\gamma| \sim |\Omega_2 - \Omega_1| \gtrsim |\Gamma_2 - \Gamma_1|, \quad \text{i.e., } |q'| \sim 1 \gtrsim |q''|,
\] (82)

where \( q'' \equiv (\Gamma_2 - \Gamma_1)/(2\gamma) \) is the imaginary part of \( q \) defined in equation (78'). Therefore, by approximating \( g_2/g_1 \approx 1 \) and by keeping the terms up to the first order in \( q'' \), we have
\[
\langle \phi_2 \mid \phi_1 \rangle - \langle \phi_2 \mid \phi_1 \rangle \approx i\gamma' - iq'' q'd, \quad \text{for } q'' \approx 1 \gtrsim \gamma',
\] (83)

which reduces the observability condition (81) to the following in the lowest order in \( q'' \):
\[
|q''| \gtrsim |q'|.
\] (84)

The condition (84) is satisfied in the following cases:
\[
|\hat{\Gamma}_1 - \hat{\Gamma}_2| \gtrsim |\Omega_1 - \Omega_2|, \quad \text{for } \frac{|\Omega_1 - \Omega_2|}{|\Omega_1 - \Omega_2|} > \frac{\gamma}{\gamma}, \quad (85)
\]
\[
|\hat{\Gamma}_1 - \hat{\Gamma}_2| \gtrsim 2|q'|, \quad \text{for } \frac{|\Omega_1 - \Omega_2|}{|\Omega_1 - \Omega_2|} < \frac{\gamma}{\gamma}, \quad (86)
\]
\[
|\hat{\Gamma}_1 - \hat{\Gamma}_2| \gtrsim \frac{1 - (\Omega_2 - \Omega_1)/\gamma}{(\Omega_2 - \Omega_1)/\gamma}, \quad \text{for } \hat{\Gamma}_1 - \hat{\Gamma}_2 \approx 0. \quad (87)
\]
By comparing the solutions to the phenomenological equations and to the present equations (79), we can show that the nonadiabatic effects of decay may be of the order of unity. Also, further possibilities for realization and optimization of the observability condition (84) will be discussed elsewhere. Here we mention just one example: if the time evolution of the resonance detuning, \( \Omega'_2 - \Omega'_1 = \tilde{E}_2 - \tilde{E}_1 - \Omega \), is synchronized with that of the Rabi frequency, \( \gamma = \tilde{E} \cdot \tilde{\mu}_2 / 2 \), such that their ratio \( q \) is (nearly) constant in time, the phenomenological mixing matrix (nearly) vanishes and the novel nonadiabatic effects are observable under a weaker condition, that is, whenever the time evolution of the difference of the lifetime, \( \tilde{\Gamma}_2 - \tilde{\Gamma}_1 \), is not synchronized with that of the Rabi frequency. Note that the conditions discussed above are derived under the assumption of (approximate) orthogonality (69) of the dipole momenta of the two excited levels. If this assumption is violated, the expressions of the mixing matrix elements become more complicated than equations (77) and (78), but the results discussed above are still expected to be valid.

To realize the situations (85)–(87) experimentally, one needs a tuning among the time evolutions of

1. the DC field, \( \tilde{E}_d(t) \), which controls the decay rates, \( \tilde{\Gamma}_{1,2} \propto |\tilde{\mu}_{1,2}|^2 \), the Rabi frequency, \( \gamma \propto \mu \), and the discrete level energies, \( \Omega'_{1,2} \sim \tilde{E}_{1,2} \),
2. the AC field, \( \tilde{E}(t) \), which controls the mixing of the excited levels, i.e., the Rabi frequency, \( \gamma \propto \mathcal{E} \), and
3. the frequency, \( \Omega \), of the AC field, which controls the partial energy, \( \Omega'_1 = \tilde{E}_1 + \Omega \), and, thus, the detuning frequency, \( \Omega'_1 - \Omega'_2 \simeq \text{const.} \)

For example, an appropriate synchronization between \( \tilde{E}(t) \) and \( \tilde{E}_d(t) \) would lead to a constant Rabi frequency, \( \gamma \simeq \text{const.} \), and between \( \Omega(t) \) and \( \tilde{E}_d(t) \) to a constant detuning frequency, \( \Omega'_1 - \Omega'_2 \simeq \text{const.} \).

Now let us give typical figures of the parameters. The typical values of the optical dipole momenta are \( \mu, \mu_{1,2} \simeq 1 \) Debye \( = 10^{-18} \) cgs units, and the electric static field in the range of \( |\tilde{E}_d| \simeq 1 - 100 \text{ MV/cm} \) can mix molecular (at least vibrational-rotational) eigenstates and change optical dipole momenta. The typical frequencies of optical transitions, natural bandwidths, and vibrational-rotational splitting of electronic levels are, respectively,

\[
\Omega'_{1,2} \simeq 2 \cdot 10^{15} \text{ sec}^{-1}, \quad \tilde{\Gamma}_{1,2} \simeq 2 \cdot 10^5 \text{ sec}^{-1}, \quad \Omega \simeq E_2 - E_1 \simeq 10^{13} \text{ sec}^{-1}.
\]

Then, according to the observability (82) of mixing of the two excited levels, the Rabi frequency should have a value of \( \gamma \gtrsim 10^5 \text{ sec}^{-1} \), which corresponds to the field strength of \( \mathcal{E} \gtrsim 0.06 \text{ V/cm} \). All of these values are experimentally accessible. Also, it is not difficult to create a nonsteady electrostatic field, \( \tilde{E}_d(t) \), which varies in a few microseconds. For example, it can be realized for a molecule moving with thermal velocity, \( v_T \sim 10^5 \text{ cm/sec} \), through an inhomogeneous static field with millimeter length-scale.

The main experimental difficulties are preparing of identically oriented and excited molecules in a small given region with nonsteady DC and AC fields, and performing accurate spectroscopic measurements of populations of decaying quasienergy levels before and after the crossing which is separated by a few microseconds. However, we expect that recent rapid progress in the quantum optical experiments of a single molecule would remove such difficulties and allow us to detect the nonadiabatic effects experimentally.

8. ELECTRONIC DECAYING STATES AND NONADIABATIC EFFECTS IN MOLECULES—BORN-OPPENHEIMER APPROACH

Nonadiabatic crossing of discrete levels is also important in the Born-Oppenheimer approach, where the effective dynamics for the slow nuclear motion is derived by separating it from the fast electronic motion [98,99] and the former plays the role of a slowly varying external field on
the latter. The original Born-Oppenheimer approach, which takes into account only the stable electronic states, has been generalized to deal with decaying electronic states by several authors (see, e.g., [1-4] and the references therein). In this section, which emphasizes on a geometrical-phase contribution [100], we deal with the system described by the following Hamiltonian:

\[ H_{\text{tot}} = \sum_j \frac{-1}{2M_j} \nabla^2_j + W(R) + H_{\text{FF}}(R), \]  

(89)

where \( M_j \) is the mass of \( j^{\text{th}} \) nuclear, \( \nabla_j \) the derivative with respect to its coordinate, \( R_j \); \( W(R) \) is the interaction energy among nuclei, with \( R \) the abbreviation of a set of nuclear coordinates, \( (R = \{R_j\}) \), and \( H_{\text{FF}}(R) \) the electronic Hamiltonian of Friedrichs-Fano type (1) with \( R \)-dependent parameters (i.e., \( h_{\alpha\alpha'} = h_{\alpha\alpha'}(R), \omega_k = \omega_k(R), \) and \( V_{\alpha k} = V_{\alpha k}(R) \)). According to Section 2, for each parameter \( R \), the electronic Hamiltonian, \( H_{\text{FF}}(R) \), admits a complex spectral decomposition,

\[ H_{\text{FF}}(R) = \sum_{\alpha=1}^N \omega_\alpha(R) |\varphi_\alpha(R)\rangle \langle \varphi_\alpha(R)| + \sum_k \omega_k(R) |\varphi_k(R)\rangle \langle \varphi_k(R)|, \]

(90)

where the right and left eigenvectors \( \{|\varphi_\alpha(R)\rangle, |\varphi_k(R)\rangle\} \) form a complete biorthonormal basis (cf. equations (22), (23)) and the discrete eigenvalues \( \omega_\alpha(R) \) can have a nonzero imaginary part \( \text{Im} \omega_\alpha \neq 0 \).

Along the line of the Born-Oppenheimer approach, we look for a solution of the Schrödinger equation,

\[ i \frac{\partial}{\partial t} \Psi = H_{\text{tot}} \Psi, \]

(91)

which is of the following form:

\[ \Psi = \sum_{\alpha=1}^N \Phi_\alpha(R,t) |\varphi_\alpha(R)\rangle + \sum_k \Phi_k(R,t) |\varphi_k(R)\rangle. \]

(92)

Dirac’s notation is used here to express the electronic wave functions and the coordinate representation is used for the nuclear parts. By substituting equations (89) and (92) into equation (91) and using equation (90), one obtains the equation of motion for the nuclear part, \( \Phi_\alpha \):

\[ i \frac{\partial}{\partial t} \Phi_\alpha(R,t) = \left[ \sum_j \frac{-1}{2M_j} \nabla^2_j + W(R) + \omega_\alpha(R) \right] \Phi_\alpha(R,t) \]

\[ + \sum_j \frac{-1}{M_j} \left[ \sum_{\beta=1}^N \langle \varphi_\alpha(R) | \nabla_j | \varphi_\beta(R) \rangle \nabla_j \Phi_\beta(R,t) + \sum_k \langle \varphi_\alpha(R) | \nabla_j | \varphi_k(R) \rangle \nabla_j \Phi_k(R,t) \right] \]

\[ + \sum_j \frac{-1}{2M_j} \left[ \sum_{\beta=1}^N \langle \varphi_\alpha(R) | \nabla^2_j | \varphi_\beta(R) \rangle \Phi_\beta(R,t) + \sum_k \langle \varphi_\alpha(R) | \nabla^2_j | \varphi_k(R) \rangle \Phi_k(R,t) \right]. \]

(93)

The function \( \Phi_k \) satisfies the similar equation. As before, we neglect the contributions from the continuum parts \( \Phi_k \) as well as the transitions between discrete and continuum parts. Then, because

\[ \langle \tilde{\varphi}_\alpha(R) | \nabla^2_j | \varphi_\beta(R) \rangle \simeq \nabla_j (\langle \tilde{\varphi}_\alpha(R) | \nabla_j | \varphi_\beta(R) \rangle) + \sum_{\gamma=1}^N \langle \tilde{\varphi}_\alpha(R) | \nabla_j | \varphi_\gamma(R) \rangle \langle \tilde{\varphi}_\gamma(R) | \nabla_j | \varphi_\beta(R) \rangle, \]

equation (93) leads to

\[ i \frac{\partial}{\partial t} \Phi_\alpha(R,t) = \sum_j \frac{1}{2M_j} \sum_{\beta=1}^N \left[ \delta_{\alpha\beta} \frac{1}{i} \nabla_j - A^j_{\alpha\beta}(R) \right] \left[ \delta_{\beta\gamma} \frac{1}{i} \nabla_j - A^j_{\beta\gamma}(R) \right] \Phi_\gamma(R,t) \]

\[ + \left[ W(R) + \omega_\alpha(R) \right] \Phi_\alpha(R,t), \]

(94)
where the "vector potential" $A^j_{\alpha\beta}$ is given by

$$A^j_{\alpha\beta}(R) \equiv i\langle \dot{\varphi}_\alpha(R) | \nabla_j | \varphi_\beta(R) \rangle. \quad (95)$$

Equation (94) is a fundamental equation which governs the molecular motion, including the effects of the decay of discrete levels and provides a generalization of the Born-Oppenheimer equation. As in the case of stable electronic states [100], the "vector potentials" $A^j_{\alpha\beta}(R)$ correspond to (complex) Berry's phase, which is discussed in Section 5.

Some remarks are in order about the boundary conditions posed on $\Phi_\alpha$. The total wave function $\Psi$ should be single-valued with respect to the nuclear coordinates, $R$, and be symmetric (antisymmetric) with respect to any exchange of a pair of identical Bosonic (Fermionic) nuclei. The same condition should be satisfied by the product $\Phi_\alpha(R,t) | \varphi_\alpha(R) \rangle$. This requirement and the symmetry properties of the electronic wave function, $| \varphi_\alpha(R) \rangle$, determine boundary conditions for the nuclear part, $\Phi_\alpha(R,t)$, under which the equation of motion (94) should be solved. For example, if the electronic wave function $| \varphi_\alpha(R) \rangle$ is double-valued with respect to $R$, one should find a solution to equation (94) which is also double-valued so that the product $\Phi_\alpha(R,t) | \varphi_\alpha(R) \rangle$ becomes single-valued. It is then convenient to redefine electronic wave functions, $| \varphi_\alpha(R) \rangle$, such that they are single-valued in the nuclear coordinates, $R$, and are symmetric with respect to the exchange of any pair of identical nuclei. Using this convention, one can solve the equation of motion (94) under the usual boundary conditions: $\Phi_\alpha(R)$ is single-valued in $R$ and is symmetric (antisymmetric) with respect to any exchange of a pair of identical Bosonic (Fermionic) nuclei. For stable electronic states, this requirement is essential to understand the appearance of a "vector potential" in the presence of conical intersections [100].

The potential $\omega_\alpha(R)$ induced by the electronic motion is, in general, complex and produces the decay of nuclear motion. This fact has been attracting many researchers' attention (e.g., [1,3,4]). Here we remark that the molecular-configuration dependence of the imaginary part of $\omega_\alpha(R)$ would play a significant role in the wave packet propagation. Suppose that there are two different wave packet motions, and one passes a molecular configuration with large $| \text{Im} \omega_\alpha(R) |$, but the other does not. Then the latter motion is more stable than the former. Because wave packet motions can be controlled by lasers, such differences may be measurable experimentally.

Corresponding to the novel nonadiabatic effects discussed in Section 4, the effects of decay also appear in the "vector potentials," $A^j_{\alpha\beta}(R)$, with different electronic indices ($\alpha \neq \beta$), and are responsible for nonadiabatic transitions between different electronic states.

Moreover, the decay would cause a new feature even in the adiabatic approximation, where equation (94) reduces to

$$i \frac{\partial}{\partial t} \Phi_\alpha(R,t) = \left\{ \sum_j \frac{1}{2M_j} \left[ \frac{1}{i} \nabla_j - A^j_{\alpha\alpha}(R) \right]^2 + W(R) + \omega_\alpha(R) \right\} \Phi_\alpha(R,t). \quad (96)$$

For stable electronic states, one can make electronic wave functions real-valued (except with such complications as conical intersections and magnetic fields) [100]. In these cases, the "vector potentials" $A^j_{\alpha\alpha}(R)$ vanish. In the presence of decay, however, the electronic wave functions are not real-valued, and nonvanishing complex "vector potentials" $A^j_{\alpha\alpha}(R)$ appear generically, even without complications such as conical intersections and magnetic fields.

Applications to concrete systems will be reported elsewhere.

9. CONCLUDING REMARKS

We demonstrate a modification of nonadiabatic effects in a time-dependent Friedrichs-Fano model due to the presence of the decay of discrete states into a continuum. The phenomena described here arise from the nonunitary subsystem dynamics and are connected with a renormalization and redressing of unstable (decaying) discrete states. We argue that this nonunitary
evolution can be accounted for using the closed set of nonadiabatic equations (32), provided that a reservoir does not contain any artificially induced macroscopic structures like coherent wave packets. It is remarkable that, in this model, all nonadiabatic effects can be treated via the evolution of pure decaying states.

A consistent analysis of the problem is carried out on the basis of the complex spectral decomposition of the whole Hamiltonian. We find a series of novel nonadiabatic effects missed in the previous phenomenological decay theories:

(i) a time dependence of a Hermitian Hamiltonian of a discrete subsystem can cause a nonadiabaticity not only of a unitary evolution, but also of a nonunitary evolution;

(ii) the nonadiabatic effects can arise from a time dependence of an interaction with a reservoir, even if the Hamiltonian of the discrete subsystem is constant in time;

(iii) a cross-relaxation of dressed states is possible owing their nonadiabatic coupling.

A nonadiabatic crossing of decaying levels may play an important role in quantum optics and in quantum chemistry of excited molecules. In this paper, we have shown a nontrivial role of spontaneous emission in the course of the coherent evolution of quasienergy states for a three-level molecule driven by nonsteady DC and AC fields and have investigated the condition of its experimental observability. Also, we have discussed a modification of the Born-Oppenheimer approach and its outcomes in the presence of the decay of electronic states. Other aspects will be studied in the forthcoming papers.

As mentioned in Section 2, the complex spectral decomposition of the Hamiltonian, contrary to the real (Hilbert-space) spectral decomposition, may admit Jordan blocks reflecting the degeneracy of decaying eigenstates due to a symmetry of the Hamiltonian, \( H(t) \). If the Jordan block structure appears during a finite time interval in the course of the level crossing, the nonadiabatic dynamics (32) will change significantly. In such a case, one more new nonadiabatic effect can be expected, and the basic equations (32), (79) as well as the Born-Oppenheimer equation (94) have to be reconsidered.

REFERENCES