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Floquet-state perturbation theory for the radio-frequency modulation of the Mössbauer resonance

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We study theoretically resonance absorption of γ rays by nuclei exposed to an external radio-frequency (rf) magnetic field. The external field is taken to couple directly to the nuclear magnetic moments. Perturbation theory is developed for Mössbauer spectroscopy in terms of Floquet eigenstates that incorporate the rf field exactly. The present treatment allows for calculation of the conventional time-averaged absorption spectrum, as well as analysis of the time dependence of absorption, resolved on the scale of a period of the rf field. An efficient numerical implementation of the theory is described and comparisons with the equally general approach of Salkola and Stenholm [M. Salkola and S. Stenholm, Phys. Rev. A **41**, 3838 (1990)] are made. We demonstrate that even at off-resonance frequencies a strong modulation leads to shifts of the original static hyperfine lines. Examples of line splittings of NMR's associated with Rabi flopping are also shown.

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I. INTRODUCTION

The isotope ^{57}Fe is the most commonly employed nuclear species in Mössbauer spectroscopy. The iron nuclei may be exposed to an internal magnetic field of up to 30 T. Compared to this, any experimentally applied rf field is minuscule. However, in a magnetically soft material, nuclear magnetization may follow even a rather weak external field (ferromagnetic enhancement). This is why the majority of experiments demonstrating direct electromagnetic influence of externally applied rf fields on nuclear transitions have been carried out with ^{57}Fe. We emphasize, though, that such entanglement of γ and rf transitions is by no means restricted to iron only.

Traditionally, two distinct types of rf modulation have been discussed. In the *longitudinal* (or diagonal) case the rf field is parallel to the average internal field. The effect is to modulate the energies of the Zeeman-split nuclear states and hence to modulate the frequencies of the γ transitions. A harmonic modulation leads to the familiar frequency modulation sidebands with the intensities proportional to $[J_n(\alpha)]^2$, where α is the modulation index. In the case of *transverse* modulation the rf field is perpendicular to the static field. The modulating field then drives transitions between the Zeeman split static field states. At higher rf fields Rabi flopping as well as dynamic Stark shifts and splittings of the Mössbauer lines should emerge.

Early experiments to demonstrate changes in Mössbauer absorption caused by an external rf field were carried out by Perlow [1,2] and Matthias [3]. Later many similar experiments have been performed. Sidebands were observed in addition to the original parent transitions, but the interpretations varied from magnetostriction [4] to domain wall motion [2]. The first conclusive results about the direct coupling of the rf field to the nuclear magnetic moment were obtained in Refs. [5] (^{181}Ta) and [6–8] (^{67}Zn) with nonmagnetic samples.

In the past limitations on the field strength have prevented the observation of effects associated with Rabi oscillations. A review of unsuccessful experiments is given in Ref. [9]. Recently, though, high-field line splittings were observed for the ground [10] and excited [11] state resonances of ^{57}Fe. In rf modulation experiments Mössbauer lines that correspond to ordinarily forbidden nuclear transitions may also appear. This comes about because the transverse modulation field mixes static-field nuclear states with different characters, e.g., z components of angular momentum, and thereby relaxes selection rules. Such lines were present in the experiments of Ref. [10], as pointed out by Olariu *et al.* [12]. The steadily improving understanding and control of the rf field induced effects may pave the way to experiments in which coherent population transfer to a superposition of Zeeman states is needed [13].

On the theoretical side, the initial papers on rf modulation include [14–16]. The rf field is often treated in the rotating-wave approximation (RWA). Salkola and Stenholm [17] have applied a continued-fraction method to the problem and ended up with a formulation in which no RWA approximation is needed for the rf field. While this approach is general, it is developed in terms of density matrices and easily leads to extensive numerical computations.

We have recently introduced a leaner alternative, perturbation theory with respect to Floquet states that already exactly account for the modulating fields [18,19]. In the present paper we expand on our previous brief exposition [19]. In Sec. II we outline our methods. The formal *Floquet state perturbation theory* (FPT) is studied in Sec. II A. At this point the emphasis is on mathematics; we are mainly interested in what goes into the theory. How the approach works in the special case of Mössbauer spectroscopy is the subject of Sec. II B. The computational aspects of our implementation of the theory in Mössbauer spectroscopy are discussed in Sec. II C. All of the experimentally observed phenomena are quantitatively explained by the theory of Salkola and Stenholm [17]. Nonetheless, as an illustration of our method, we present a few additional examples in Sec. III. The remarks in Sec. IV about the benefits of our scheme conclude the paper.

II. NUCLEAR RESPONSE

In this paper we address modulation and transient Mössbauer spectroscopy [6,7] on a high level of generality. We incorporate the environmental magnetic and electric fields, which lead to line splittings in conventional Mössbauer spectroscopy. In addition, we allow for an arbitrarily strong time-dependent coupling between the states within each nuclear spin manifold. A radio-frequency magnetic-field coupling to the magnetic dipole of the nucleus is an example. Another example is afforded by the velocity modulation that is the cornerstone of Mössbauer spectroscopy: the Doppler shift of the γ photons is equivalent to an interaction that shifts all states within an excited nuclear level in unison. Naturally, we also account for the electromagnetic coupling between the nuclear manifolds, and the attendant emission and absorption of γ photons.

The key simplification is that, in the absence of a γ-ray laser, the incoming γ radiation may always be treated perturbatively. It turns out that the perturbation theory for a system with explicit time dependences is an interesting problem in its own right. Here we assume that the unperturbed Hamiltonian underlying the perturbation theory is periodic in time. This allows us to use the Floquet states of the unperturbed Hamiltonian as the basis of the perturbation theory.

A. Floquet-state perturbation theory

In this section we develop the formal FPT from first principles. Along the way we introduce three technical assumptions, which are carefully pointed out.

We consider a system with the Hamiltonian

$$\mathscr{H}(t)=\mathscr{H}_0(t)+\mathscr{V}. \tag{1}$$

In a peculiar reversal of the usual role of these operators, we let the unperturbed Hamiltonian $\mathscr{H}_0$ depend on time and take the perturbation $\mathscr{V}$ to be time independent. Moreover, anticipating the need to incorporate linewidths into the Hamiltonian, we do not require that the operator $\mathscr{H}_0$ be Hermitian. As Hermiticity of the unperturbed Hamiltonian is built into the standard perturbation theory, we have to take a fresh look at the development of perturbation theory itself. Such considerations will make the bulk of our exposition, although it turns out that the resulting changes from the ordinary course of action are minor.

The initial steps toward perturbation theory with respect to the operator $\mathscr{V}$ go as usual. First, we define the unperturbed time translation operator from any initial time t_1 to any final time t_2 through

$$i\hbar\frac{\partial}{\partial t_2}U(t_2,t_1)=\mathscr{H}_0(t_2)U(t_2,t_1),\quad U(t_1,t_1)=1. \tag{2}$$

$\mathscr{H}_0$ need not be Hermitian, so U need not be unitary. However, by taking the time derivative with respect to t_2 in the definition of the inverse of U, $U(t_2,t_1)U^{-1}(t_2,t_1)=1$, one may see that the inverse U^{-1} still satisfies an evolution equation analogous to the corresponding unitary case,

$$i\hbar\frac{\partial}{\partial t_2}U^{-1}(t_2,t_1)=-U^{-1}(t_2,t_1)\mathscr{H}_0(t_2). \tag{3}$$

As U is the evolution operator for a first-order differential operator, it has the familiar group and inverse properties as well,

$$U(t_3,t_2)U(t_2,t_1)=U(t_3,t_1),\quad U^{-1}(t_2,t_1)=U(t_1,t_2). \tag{4}$$

We next define the *interaction picture* version $\tilde{\mathscr{O}}(t)$ of any operator $\mathscr{O}(t)$ with respect to $\mathscr{H}_0$ as

$$\tilde{\mathscr{O}}(t)=U_0^{-1}(t,t_0)\mathscr{O}(t)U_0(t,t_0). \tag{5}$$

Here t_0 is an arbitrary initial time for the interaction picture. Using Eqs. (2) and (3) it may be shown easily that the Liouville–von Neumann equation of motion for the density operator ρ,

$$i\hbar\dot{\rho}=[\mathscr{H}_0+\mathscr{V},\rho], \tag{6}$$

reads in the interaction picture

$$i\hbar\dot{\tilde{\rho}}=[\tilde{\mathscr{V}},\tilde{\rho}]. \tag{7}$$

There is no formal difference from the corresponding unitary theory.

We now introduce our first assumption.

Assumption 1. At some time t' the Schrödinger picture density operator $\rho(t')=\rho$ is such that

$$[\rho,\mathscr{H}_0(t)]=0 \tag{8}$$

holds for all times t.

Equation (8) implies that

$$[\rho,U(t_2,t_1)]=0 \tag{9}$$

is satisfied at all times t_1 and t_2. In the absence of the perturbation $\mathscr{V}$ the density operator of the system would therefore satisfy at all times t the equations

$$\rho(t)=\tilde{\rho}(t)=\rho. \tag{10}$$

Conversely, the requirement that the density operator of the unperturbed system is a constant, call it ρ, implies Eq. (8). Equation (8) therefore is a necessary and sufficient condition that ρ describes a stationary state for the unperturbed system. Given that the Hamiltonian $\mathscr{H}_0$ may depend explicitly on time and may be non-Hermitian, the existence of such a ρ is a nontrivial matter; but if the time evolution of a physical system does lead to a stationary state, the steady state is described by a density operator ρ satisfying Eq. (8).

Assumption 1 together with Eq. (7) validates the standard perturbation series

$$\tilde{\rho}(t)=\rho-\frac{i}{\hbar}\int_{-\infty}^{t}dt_1[\tilde{\mathscr{V}}(t_1),\rho] -\frac{1}{\hbar^2}\int_{-\infty}^{t}dt_2\int_{-\infty}^{t_2}dt_1[\tilde{\mathscr{V}}(t_2),[\tilde{\mathscr{V}}(t_1),\rho]]+\cdots. \tag{11}$$

Let us now consider the perturbation-induced expectation value of an operator $A(t)$. Without loss of generality we assume that $\mathrm{Tr}\{\rho A(t)\}=0$. We have exactly the same first-order result as in conventional perturbation theory,

$$\langle A(t)\rangle=-\frac{i}{\hbar}\int_{-\infty}^{t}dt'\ \mathrm{Tr}\{\rho[\tilde{A}(t),\tilde{\mathscr{V}}(t')]\}. \tag{12}$$

We next bring in the second nontrivial ingredient of our approach.

Assumption 2. The unperturbed Hamiltonian $\mathscr{H}_0(t)$ is periodic in time.

We denote the period by T. The corresponding angular frequency is $\omega=2\pi/T$.

By the Floquet theorem [18] one may find a set of time-dependent state vectors $\{|n,t\rangle\}_n$ and the corresponding eigenfrequencies $\{\epsilon_n\}_n$ in such a way that (i) each vector $|n,t\rangle$ is periodic in t with the period T and (ii) the frequencies and the Floquet eigenstates satisfy the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}(e^{-i\epsilon_n t}|n,t\rangle)=\mathscr{H}_0(t)(e^{-i\epsilon_n t}|n,t\rangle). \tag{13}$$

Even though the quantities ϵ_n have the dimension of frequency in our treatment, to accommodate the standard parlance we will call them "quasienergies." There is an inherent ambiguity in the definition of Floquet states, in that an arbitrary multiple of ω may be added to the quasienergy ϵ_n. Equation (13) then remains valid, provided the original ket $|n,t\rangle$ is multiplied by a suitable oscillating exponential with the period T. We always assume that the quasienergies are chosen in the interval $\epsilon_n\in[0,\omega)$, which renders them unique.

We finally introduce the third, more technical condition.

Assumption 3. At any fixed time t, the vectors $\{|n,t\rangle\}_n$ may be chosen, and have been chosen, to form an orthonormal basis.

This statement is normally valid if $\mathscr{H}_0$ is Hermitian; we have added it as a safeguard against anomalies in the non-Hermitian case.

On the basis of Eq. (13) and Assumption 3, one may write the unperturbed time evolution operator in terms of the Floquet states as

$$U(t_2,t_1)=\sum_n e^{-i\epsilon_n(t_2-t_1)}|n,t_2\rangle\langle n,t_1|. \tag{14}$$

Besides, it follows from Eq. (8) that if $|n,t\rangle$ satisfies Eq. (13), then so does $\rho|n,t\rangle$. Assumption 3 then guarantees that it is possible to construct the Floquet states to be eigenstates of ρ as well. After this has been done, we have

$$\rho=\sum_n p_n|n,t\rangle\langle n,t|. \tag{15}$$

Here p_n evidently is the probability that the system is in the Floquet state n. It may be shown easily from Assumptions 1 and 3 that the numbers p_n must, in fact, be constants in time.

We continue the development by simplifying (12) using (4) and (9), and then insert (14) and (15). This gives

$$\langle A(t)\rangle=-\frac{i}{\hbar}\sum_{m,n}(p_n-p_m)\int_{-\infty}^{t}dt'\,e^{i(\epsilon_n-\epsilon_m)(t-t')} \times\langle n,t|A|m,t\rangle\langle m,t'|\mathscr{V}|n,t'\rangle. \tag{16}$$

As our last simplification we note that the matrix elements of the operators A and $\mathscr{V}$ are, of course, periodic functions of time. We therefore have Fourier series of the form

$$\langle m,t|A|n,t\rangle=\sum_k A_{mn}^{(k)}e^{-ik\omega t}. \tag{17}$$

Combination of (16) and (17) leads to the final result

$$\langle A(t)\rangle=-\frac{i}{\hbar}\sum_{\substack{m,n\\k_1,k_2}}(p_n-p_m) \times e^{-i\omega(k_1+k_2)t}\frac{A_{nm}^{(k_1)}\mathscr{V}_{mn}^{(k_2)}}{i(\epsilon_m-\epsilon_n-k_2\omega)+\eta}. \tag{18}$$

Here $\eta=0^+$ is a convergence factor, in case $\mathscr{H}_0$ is Hermitian. While we have silently assumed the convergence of integrals such as in (12) and (16), this is a delicate issue. We have an example coming up shortly.

All told, Eq. (18) gives the perturbation-induced expectation value of the operator A in the case when the *unperturbed* Hamiltonian depends explicitly on time, while the *perturbation* is time independent. The derivation relied on three nontrivial assumptions, and the final result is expressed in terms of Fourier series of the matrix elements of certain operators between Floquet eigenstates of the unperturbed Hamiltonian. It should be noted that our perturbation theory is different from the usual perturbation theory involving Floquet states. Conventionally, the periodic part of the Hamiltonian is the small perturbation and the aim is to find perturbative expansions for the quasienergies and Floquet eigenstates themselves [18].

It is not clear whether any reasonable physical model exists that satisfies our assumptions; and even if such a model existed, the ensuing computational effort might seem overwhelming. However, in the subsequent sections we are going to argue that modulation Mössbauer spectroscopy fits the requirements, and even introduce a scheme that yields numerical results quite painlessly.

B. Application to Mössbauer spectroscopy

1. Hamiltonian

Our description of Mössbauer spectroscopy starts from two nuclear energy levels g and e, for "ground" and "excited." For an isolated nucleus these would consist of eigenstates of angular momentum, and would possess the conventional $(2I_{g,e}+1)$-fold degeneracies. We refer to the unit projection operators within the nuclear manifolds as 1_g and 1_e. The corresponding dimensions of the manifolds are denoted by $n_{g,e}=\mathrm{Tr}[1_{g,e}]$.

The idea is to build a theory of modulation Mössbauer spectroscopy by refining on the notion of nuclear levels: We add interactions and analyze what becomes of the initially degenerate nuclear energy levels. Our discussion is coached in terms familiar from quantum optics, a discipline concerned with the properties and interactions of electromagnetic fields. The textbooks by Stenholm [20] and Meystre and Sargent [21] are in spirit particularly close to our approach.

We write the first form of the unperturbed Hamiltonian

$$H_0(t)=\hbar\Omega_0 1_e+H_g(t)+H_e(t)+H_F+H_{\mathrm{QED}}. \qquad (19)$$

The nuclear-physics splitting between the ground- and excited-state manifolds has been lumped into $\hbar\Omega_0 1_e$. The terms H_g and H_e stand for Hamiltonians that act completely within the ground-state and excited-state manifolds, respectively. H_g and H_e contain all static electromagnetic fields originating from the environment of the nuclei. Such fields may lift the angular momentum degeneracy of the nuclear levels at least in part, giving rise to the ubiquitous multiline Mössbauer spectra. The operators H_g and H_e also incorporate possible externally applied static or time-dependent fields, such as the sinusoidally oscillating magnetic field in the experiments of Tittonen *et al.* [10].

The remaining terms H_F and H_{QED} stand for the Hamiltonian of the free electromagnetic field and for the QED interactions of the nucleus with the field. Such interactions lead to spontaneous emission, i.e., γ activity. Inasmuch as the changes in the total occupation probabilities of the ground-state and the excited-state nuclear manifolds need not be taken into account, spontaneous emission is correctly described by simply adding an imaginary component $-i\gamma$ to the characteristic frequencies of all excited states, γ is the half width at half maximum of the resonance line. In all experiments until now the excitation probability of an individual nucleus due to the incoming γ radiation has been extremely small, so this approach is acceptable.

For the time being we model the γ radiation from a Mössbauer source as a monochromatic wave of frequency Ω. Far away from the source any electromagnetic field is locally a plane wave, so we might as well think of the incoming radiation as a plane wave. This field couples to some nuclear multipoles that effect transitions between the manifolds g and e. We have an interaction term of the form $\mathscr{V}\cos(\Omega t)$, where $\mathscr{V}$ is a Hermitian operator. We define the raising and lowering parts of the transition operator as

$$\mathscr{V}=\mathscr{V}^{+}+\mathscr{V}^{-}, \quad \mathscr{V}^{+}=1_e\mathscr{V}1_g, \quad \mathscr{V}^{-}=1_g\mathscr{V}1_e \quad (20)$$

and carry out what in quantum optics is known as the rotating-wave approximation,

$$\mathscr{V}\cos(\Omega t)\rightarrow\tfrac{1}{2}\mathscr{V}^{+}e^{-i\Omega t}+\tfrac{1}{2}\mathscr{V}^{-}e^{i\Omega t}. \qquad (21)$$

At this point it is standard practice to remove the explicit time dependence of the external field from the problem by carrying out the unitary transformation generated by $\exp(-i\Omega t 1_e)$ on the Hamiltonian.

After these steps our Hamiltonian is

$$\mathscr{H}(t)=\mathscr{H}_0(t)+\mathscr{V}, \qquad (22a)$$

$$\mathscr{H}_0(t)=H_g(t)+H_e(t)-\hbar[\delta(t)+i\gamma]1_e. \qquad (22b)$$

Here

$$\delta(t)=\Omega-\Omega_0(t), \qquad (23)$$

detuning in the language of quantum optics, is the difference between the frequency of the driving field Ω and the nuclear resonance frequency Ω_0. In (22) we have written a time-dependent detuning. In fact, in Mössbauer spectroscopy frequency scans are usually carried out with the aid of the Doppler effect, which for all practical purposes is equivalent to varying the resonance frequency of either the absorber or the emitter. The time-dependent detuning allows for Doppler shifts, constant or modulated in time.

2. Assumptions of Floquet perturbation theory

It remains to be shown that our description of transient and modulation Mössbauer spectroscopy fits the FPT framework. First, we choose the unperturbed density operator as

$$\rho=\frac{1}{n_g}1_g. \qquad (24)$$

This commutes with $\mathscr{H}_0$ and therewith satisfies Assumption 1. The operator ρ is a legitimate steady-state density operator at least if the energy splittings within the ground-state manifold are small in comparison with thermal energies. Besides, if there is no modulation within the ground-state manifold, one can always improve on (24) by using the thermal density operator, which in such a case commutes with H_g. The most problematic situation occurs when the thermal energy is small compared with the static splittings and time-dependent fields are also present. The modulating fields may then drive transitions between thermally occupied states. Under such circumstances it is not clear whether the thermal relaxation may force a steady state, let alone if the steady state is of the form (24). In other words, there is no guarantee that the steady state (24) is ever attained. To study this question one has to study a model combining thermal relaxation and external driving fields. We deem this to be outside the scope of the present paper and simply apply Eq. (24).

Assumption 2, periodicity, is valid if there is no explicit time dependence. The conventional Mössbauer spectroscopy is thus covered. Also, if the nuclear states are modulated or a time-dependent Doppler shift is involved, the Hamiltonian is periodic as long as all time dependences are periodic and commensurate.

Next, two observations may be made from (22). First, there is no coupling between the ground and the excited levels g and e in $\mathscr{H}_0$, so any Floquet eigenstate may always be chosen to belong entirely to either the ground or the excited nuclear manifold. Second, the Floquet eigenstates of the Hermitian operator $H_e-\hbar\delta(t)$ are also Floquet eigenstates of $\mathscr{H}_0$; the quasienergies simply differ by $-i\gamma$. As the Floquet eigenstates of a Hermitian Hamiltonian ordinarily satisfy Assumption 3, then so do the Floquet eigenstates of our unperturbed Hamiltonian $\mathscr{H}_0$.

A final comment on the RWA in the present context might be in order. The RWA is known to be good when the transition rate due to the driving field and the detuning are both much smaller than the transition frequency itself. This is the case for the γ transitions between nuclear manifolds, at the present time and in the foreseeable future. Radio-frequency transitions within a nuclear manifold stand in pointed contrast. We treat them exactly, without the RWA.

3. Absorption and dispersion

We are now in a position to apply the FPT to Mössbauer spectroscopy. In an experiment the absorption of electromagnetic radiation upon propagation through a macroscopic sample is ultimately measured, while we have pursued the response of a single nucleus. In an optically thin sample the connection is straightforward: absorption is proportional to the out-of-phase component of the expectation value of the perturbation $\mathscr{V}$. The correspondence between microscopic and macroscopic response has been worked out for an optically thick sample as well [22,23]. We do not adapt these discussions to our present case, but proceed under the assumption of an optically thin sample. It should be noted, though, that propagation may intertwine absorption and dispersion. To allow for future generalizations, we show both of these components in Eq. (26) below.

Contrary to the assumptions of the previous sections, no monochromatic Mössbauer source exists. However, it may be shown easily that, inasmuch as linear response of a thin sample is concerned, the finite linewidth of the Mössbauer source may be taken into account simply by using the *sum* of the source and emitter linewidths as the absorptive linewidth γ. Henceforth γ always refers to such a joint linewidth.

To cut down on redundant notation, from now on we treat the ground and excited level labels g and e as state indices that may range over all states in the corresponding nuclear manifolds. Accordingly, we write the Fourier series of the matrix elements between the Floquet states as

$$\langle e,t|\mathscr{V}^+|g,t\rangle \equiv \sum_k e^{-ik\omega t}v_k(e,g). \tag{25}$$

Also, as evident from (22), certain quasienergies acquire the imaginary part $-\gamma$. We prefer to deal with the imaginary part explicitly and denote by $\epsilon_{g,e}$ the real quasienergies that would apply in the absence of spontaneous damping. With these preliminaries, Eqs. (18) and (24) give our main result

$$-\langle \mathscr{V}^-(t)\rangle = \frac{1}{n_g\hbar}\sum_{\substack{g,e\\ k_1,k_2}} e^{i\omega(k_1-k_2)t}\,\frac{i\gamma-[\delta-(\epsilon_e-\epsilon_g-k_2\omega)]}{[\delta-(\epsilon_e-\epsilon_g-k_2\omega)]^2+\gamma^2}\times v^*_{k_1}(e,g)v_{k_2}(e,g). \tag{26}$$

The real and imaginary parts of this expression are proportional to the instantaneous (time dependent) dispersion and absorption, respectively.

Two aspects of (26) call for comments. First, let us, for the sake of the argument, assume electric dipole coupling for the Mössbauer transition. Then the nucleus-field interaction reads $-\mathbf{d}\cdot\mathbf{E}$, whereas the polarization, and hence the susceptibility of the medium, is proportional to the expectation value of the dipole operator $\mathbf{d}$. We have inserted the odd minus sign explicitly into (26). Second, the susceptibility turns out to be proportional to the expectation value of the specific operator $\mathscr{V}^-$. This may seem fortunate, as the integrals in Eqs. (12) and (16) converge neatly with $A=\mathscr{V}^-$ but diverge for $A=\mathscr{V}^+$. On the other hand, the expectation value of $\mathscr{V}^+$ should always equal the complex conjugate of the expectation value of $\mathscr{V}^-$. This is the case if we carry out the integrals formally as

$$\int_0^\infty dt e^{-\alpha t}=\frac{1}{\alpha}, \tag{27}$$

paying no attention to the convergence condition that $\mathrm{Re}(\alpha)>0$. Caveat emptor.

Suppose, for instance, that time-averaged absorption is measured. Then only the time-independent component with $k_1=k_2$ survives in (26) and the imaginary part is to be taken. The time-averaged absorption coefficient is

$$\alpha=K\sum_{g,e,k}\frac{\gamma|v_k(e,g)|^2}{[\delta-(\epsilon_e-\epsilon_g-k\omega)]^2+\gamma^2}. \tag{28}$$

K is a factor that depends on the density of nuclei in the absorber.

The form of Eq. (28) is familiar from numerous occasions in which either the energies of the nuclear states or the (Doppler shifted) γ frequencies are modulated sinusoidally. Then the coefficients v_k are certain Bessel functions; see, e.g., [8]. What is more intriguing is that the same functional form applies to transverse excitation, when an oscillating magnetic field drives transitions between nuclear states rather than moves the states around. Dynamic Stark shifts and Rabi sidebands of resonances enter via the quasienergies. Whenever called for, the full time dependence of absorption is also on hand from Eq. (26).

C. Numerical implementation

We have written a general package of C computer programs to implement the core of our analysis numerically, somewhat along the lines of a similar program system prepared for use in the optical regime [24]. There are two basic differences. First, in quantum optics perturbation theory is not of much use, while in Mössbauer spectroscopy it leads to a major simplification. In particular, the present Mössbauer theory manipulates state vectors rather than density operators, which results in a tremendous reduction of core size and run time compared to the corresponding optical code. Second, in the optical regime electric-dipole interactions dominate so prominently that other multipoles are not supported at all in the programs of Ref. [24]. In contrast, higher multipoles are an essential part of Mössbauer spectroscopy.

The present program system has the entire machinery of multipole operators, Clebsch-Gordan coefficients, rotation matrices, etc., built in. As far as data input is concerned, multipoles are actually the organizing concept. The user sets up the physical system by giving the multipole expansions for H_g, H_e, and $\mathscr{V}$. Specification of the problem also includes the explicit functions that govern the time evolution of H_g, H_e, and δ.

To find the Floquet states and energies, the programs integrate numerically the matrix equation

$$i\hbar \frac{\partial}{\partial t} U = \mathscr{H}_0 U \tag{29}$$

over one period T, starting with the unit matrix as U. The eigenvalues of the resulting matrix U are of the form $e^{-i\epsilon_n T}$ and the corresponding eigenvectors give a snapshot of the Floquet eigenstates $|n,T\rangle$ at the end of the integration period. The time dependence of the Floquet states is obtained by integrating the Schrödinger equation over one more period with the instantaneous eigenvectors $|n,T\rangle$ as the initial conditions. The matrix elements $v_k(e,g)$ are extracted from the time-dependent matrix elements between the Floquet states using the fast Fourier transformation.

The treatment of the nucleus-field interactions is automated with an elaborate software handshaking scheme. However, in a practical experiment one may not have full control over the relative directions of the magnetic fields, polarizations of γ radiation, and so forth. This imposes additional averages over the directions. At the moment it is largely up to the user of the programs to manage such averages.

Salkola and Stenholm [17] have developed a continued-fraction method to calculate Mössbauer spectra to the same degree of generality as achieved in the present work. Their completely different theoretical development is reflected in a completely different numerical implementation. In particular, the code of Salkola and Stenholm manipulates density operators, while our programs deal with state vectors. The size of the linear algebra is *much* smaller in our programs. Although we have not done rigorous benchmarking of both program systems on the same machine, it is our impression that, depending on the particular task, our present scheme may be several orders of magnitude faster.

III. EXAMPLES

We demonstrate the feasibility of our numerical scheme with calculations of a few time-independent as well as time-dependent transmission spectra. The hyperfine parameters of the isotope ^{57}Fe ($I_g = 1/2$ and $I_e = 3/2$) are the same as those used in Ref. [10]. The NMR frequencies for the ground and the excited states have been chosen to be 41.2 MHz and 23.6 MHz, corresponding to the internal magnetic field of 30 T; we discard any electric-field gradients. By convention, the static magnetic field points in the z direction. The natural linewidth of $\gamma = 2\pi \times 1.128$ MHz is assumed for the nuclear transition. The amplitude of the applied rf magnetic field is fixed at 10 T. We assume that the γ radiation propagates in a direction perpendicular to z, call it x, and compute the average of the transmissions for γ radiation with linear polarizations in the y and z directions. This procedure correctly accounts for unpolarized radiation incident on the dipole transition $g \rightarrow e$.

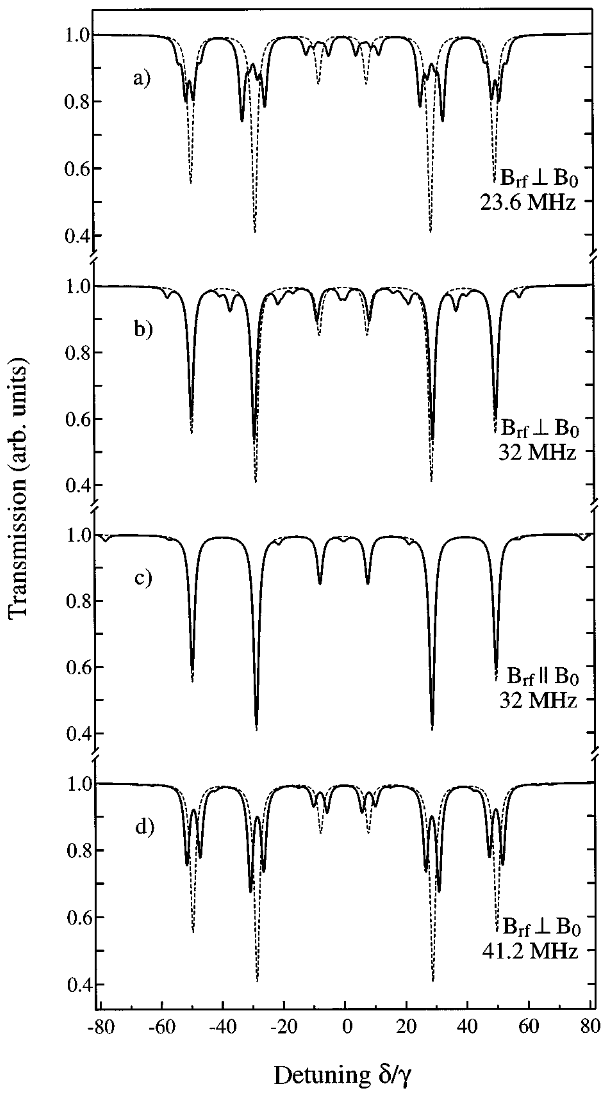

FIG. 1. Calculated Mössbauer spectra with magnetic rf modulation (solid line). For comparison, the unperturbed spectrum is also shown in each case (dashed line). The modulation frequencies are (a) 23.6 MHz (excited state NMR resonance), (b) and (c) 32 MHz (off-resonance frequency between excited- and ground-state resonances), and (d) 41.2 MHz (ground-state resonance). The NMR line splittings as a result of the transverse modulation may be seen in (a) and (d). The differences in sideband formation may be observed between traces (b) (transverse modulation) and (c) (longitudinal modulation).

The effects of varying the modulation frequency and the polarization direction of the rf field on time-averaged transmission are shown in Fig. 1. In Fig. 1(a) a transverse rf field in the y direction is applied at the resonance frequency of the excited level, $\omega = 2\pi \times 23.6$ MHz. Each parent line splits into $2I_e + 1 = 4$ components with unequal intensities (solid line). Here, as in the other traces of Fig. 1, the dashed line shows the original spectrum in the absence of the rf field.

A frequency in between the ground and excited level splittings leads to two kinds of effects. With transverse (off-diagonal) 32-MHz modulation, the nuclear states are no longer pure eigenstates of I_z. Many spectral components that are ordinarily forbidden become allowed. The corresponding sidebands can be seen in Fig. 1(b). In addition, each parent line is slightly shifted. This is also visible in Fig. 1(b) by comparing the solid and the dashed line. This shift was also discussed in Ref. [25]. If longitudinal (diagonal) 32-MHz modulation is applied, the modulation indices are rather small and little change in the spectrum is expected. In fact, we only see a few small sidebands separated by ω from the parent lines [Fig. 1(c)].

If the rf frequency is tuned to the NMR of the ground state and the modulation is transverse, each of the six lines splits into two components with different intensities (since the RWA approximation was not made). The effect of varying the modulation frequency around the resonance was reported earlier in Ref. [10].

One may also measure absorption in time domain synchronized to the phase of the modulating field (transient Mössbauer spectroscopy). First experimental results regarding magnetic modulation have been obtained very recently [26]. A constant Mössbauer drive velocity corresponding to an absorption line can be selected and the dynamic behavior of that particular transition can be followed.

In terms of our theory, we pick a constant detuning and study how the absorption varies during the period of the rf field. Here we choose the detuning of 28.7 MHz corresponding to the strongest transition in the unperturbed spectrum. Figure 2 shows the Mössbauer transmission as a function of the phase of the rf field. In Fig. 2(a) the longitudinal modulation at $\omega = 0.5\gamma$ is applied. Typical transient behavior is seen, because the resonance is passed quite rapidly. A striking difference between the longitudinal and transverse modulations may be observed in Figs. 2(b) and 2(c), computed with $\omega = \gamma$ for transverse [Fig. 2(b)] and longitudinal [Fig. 2(c)] modulations. In the transverse case the dominating behavior is oscillations at the second harmonic of the rf field. This is also the result if measurements were performed at higher frequencies, e.g., the NMR frequency of the ground state. In the longitudinal case the modulation index decreases as the modulation frequency is increased for a fixed modulation amplitude. The transient features are correspondingly much more tempered in Fig. 2(c) than in Fig. 2(a).

IV. CONCLUDING REMARKS

Even though the present calculations were performed for an isotope of iron, it should be understood that this particular hyperfine structure is not hard wired into the programs. On the contrary, the object-oriented C language environment makes routine applications of the present treatment in practical spectroscopy quite straightforward. Normally only the section of the code defining the nuclear level structure need be modified, leaving the parts that solve the dynamics unchanged. Besides, the level scheme may be changed on the fly with a couple of lines of code. The core computation of the nuclear response is also fast enough that the inevitable experimental averages and nonidealities may be taken into account while still retaining comfortable run times on a small computer workstation. Finally, in addition to the time-averaged response of Mössbauer samples to all kinds of rf excitations, transient Mössbauer spectroscopy may be analyzed with equal ease.

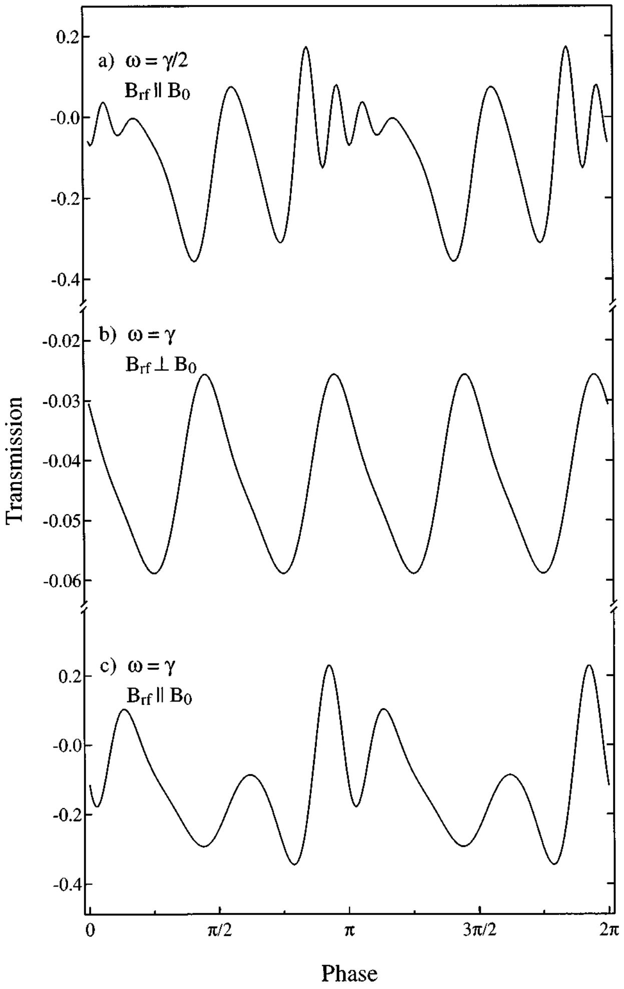

FIG. 2. Time-dependent scans of Mössbauer absorption (transient Mössbauer curves) for rf modulation. A constant velocity ($\delta = 2\pi \times 28.7$MHz) was selected that corresponds to the strongest $m_g = 1/2 \rightarrow m_e = 1/2$ transition. The modulation frequencies are (a) $\omega = 0.5\gamma$ (longitudinal modulation), (b) $\omega = \gamma$ (transverse modulation), and (c) $\omega = \gamma$ (longitudinal modulation).

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