Equilibrium in Periodically Time-Dependent Two-Level Systems

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The Floquet solution for the evolution operator of a periodically time-dependent two-level Hamiltonian provides an effective Hamiltonian that can be used to examine the equilibrium properties of the system. In one example, calculations with a model Hamiltonian show that identical equilibrium properties are predicted in the laboratory frame as in a time-dependent interaction frame. A second example considers the changes that arise when the model Hamiltonian contains an explicit periodic time dependence.

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I report in this Letter on the role played by the effective Hamiltonian for a system of interacting two-level particles subject to periodic, time-dependent external forces. The effective Hamiltonian characterizes the evolution of the system over one period in time and is itself time independent. Thus, one can apply the methods of statistical mechanics to the effective Hamiltonian and thereby elucidate the equilibrium properties of the system. This procedure provides an avenue for studying time-dependent many-body systems.

There exist two main uses for two-level systems as models of nature. In one case the systems do not explicitly depend on time; here one is concerned primarily with the equilibrium properties of many-body systems. In this connection I note the current interest in the effects that a condensed phase has on tunneling dynamics.[1] The second use of the two-level model is as the prototype for the interaction of radiation with matter.[2] Here, in contrast, the Hamiltonian does explicitly depend on time and one is primarily interested in the evolution of the coherently driven system.[3] The question arises: How does one combine the statistical mechanics in the first case with the time dependence of the latter in order to address many-body systems subject to external time-dependent forces?

The question just raised has traditional roots in magnetic resonance, originating with the application by Redfield[4] of spin thermodynamics in the rotating frame. Subsequent developments in magnetic resonance brought about the prospect of high-resolution spectroscopy of solids via pulse techniques.[5] For this purpose one is primarily interested in the short-time ($t \sim T_2$) evolution of the pulsed spin system. However, it is natural to inquire further about the long-time effects of the pulse sequence. This requires extensions of Redfield's ideas and has raised questions regarding the proper way that this should be done.[6,7] These ideas are not limited to spin systems. The methods of magnetic resonance appear in other fields as well, for instance in the studies of electric dipole echoes in glasses.[8] The advent of the femtosecond laser, with pulse lengths short compared to optical dephasing times, will surely see the investigation of the optical properties of condensed phases by multiple-pulse interactions with laser radiation,[9] again raising the above question.

The purpose of this Letter is to examine the equilibrium properties of a model time-independent Hamiltonian in an *interaction reference frame.* The transformation to the interaction frame imparts a periodic time dependence to the Hamiltonian. An application of Floquet's theorem in this frame produces a *time-independent effective Hamiltonian.* It is important here that the equilibrium properties predicted by the effective Hamiltonian are identical to those determined by standard methods in the laboratory frame. This result serves as a basis upon which to examine the effects that are introduced when the laboratory-frame Hamiltonian contains time-dependent terms, due for example to coupling of a radiation field.

Let us consider the model Hamiltonian

$$H = -\omega_1 I_x + H_{20}, \tag{1}$$

containing a field term of magnitude ω_1 and an interaction term

$$H_{20} = \textstyle\sum_{i<j} \omega_{ij} \sqrt{6}(2 I_z^i I_z^j + I_1^i I_{-1}^j + I_{-1}^i I_1^j), \tag{2}$$

that transforms under rotations as the $M = 0$ term of a second-rank spherical tensor. In magnetic resonance terms this represents a dipolar-coupled spin system in a transverse magnetic field. In the laboratory frame it is a straightforward procedure to calculate the equilibrium properties of the system.[10] If we assume that H allows no independent commuting observables besides itself, the equilibrium state is

$$\rho_{\text{eq}} = 1 - \beta_{\text{eq}} H \tag{3}$$

in the high-temperature approximation.[11] Given an initial state $\rho(0) = 1 - \beta_i \omega_0 I_x$, the conservation of energy allows us to determine β_{eq} in terms of β_i and implies an equilibrium magnetization along the x axis of

$$M_{\text{eq}}/M_i = (1 + \omega_{\text{loc}}^2/\omega_1^2)^{-1}, \tag{4}$$

where $\omega_{\mathrm{loc}}^2 = \mathrm{Tr}(H_{20})^2 \mathrm{Tr} I_z^2$.

We seek the analogous result in an interaction frame defined by

$$\rho_R(t) = \exp(i\pi I_y/2)\exp(-i\omega_1 I_x t)\rho(t)\exp(i\omega_1 I_x t)\exp(-i\pi I_y/2). \tag{5}$$

The additional tilt by $\pi/2$ about the y axis is merely for mathematical convenience. The time dependence of this unitary transformation yields

$$H_R(t) = (\tfrac{3}{8})^{1/2} e^{-i\omega_1 2t} H_{22} - \tfrac{1}{2} H_{20} + (\tfrac{3}{8})^{1/2} e^{i\omega_1 2t} H_{2,-2} \tag{6}$$

for the Hamiltonian in the interaction frame. Note that in this frame, the field term no longer appears.

How one determines the equilibrium properties of the system is not clear on account of the time dependence of the Hamiltonian. The periodicity of $H_R(t)$ allows us to write the evolution operator as

$$U(t) = P(t) e^{-i\overline{H}t}, \tag{7}$$

where $P(t)$ has the same periodicity as $H_R(t)$, but $\overline{H}$, the effective Hamiltonian, is *time independent*. This suggests that $\overline{H}$ be used to predict the equilibrium state; however, $\overline{H}$ is not uniquely defined. To any $\overline{H}$ we can add an operator N, obeying $[\overline{H}, N] = 0$ and the constraint that any eigenvalue of N equals $m 2\pi/\tau$ for some integer m, and satisfy Eq. (7) by defining a new operator $P'(t) = P(t) e^{iNt}$. Here τ is the period of $H_R(t)$. The ambiguity of $\overline{H}$ can be resolved[7a] by consideration of the long-time average of an observable Q;

$$\langle Q \rangle = \lim_{T \to \infty} (1/T) \int_0^T \mathrm{Tr}[P^\dagger(t) Q P(t) e^{-i\overline{H}t} \rho(0) e^{i\overline{H}t}]\, dt, \tag{8}$$

where the properties of the trace allow us to alter the occurrence of $P^\dagger(t)$ from its expected position. This has the same form as the time average for a conservative system, except for the periodic time dependence of the apparent observable, $P^\dagger(t) Q P(t)$. For the conservative system, the time average picks out the constant component of the integrand, that is, of the frequency spectrum that the differences, $\lambda_i - \lambda_j$, of the eigenvalues of the Hamiltonian define. Above, not only will the constant component contribute to the time average, but also those components at $\pm k 2\pi/\tau$, *unless* the spectrum of eigenvalue differences lies entirely within the range

$$|\lambda_i - \lambda_j| < 2\pi/\tau. \tag{9}$$

If this is the case then, in analogy with the relationship between time and ensemble averages for a conservative system, we can define the equilibrium state

$$\rho_{\mathrm{eq}} = \exp(-\beta_{\mathrm{eq}} \overline{H}) \tag{10}$$

in which the observable I_z takes on the value[12]

$$M_{\mathrm{eq}} = \mathrm{Tr}\{[P^\dagger(t) I_z P(t)]_{\mathrm{av}} \rho_{\mathrm{eq}}\}. \tag{11}$$

Here, the average represents the constant component of the apparent observable, $P^\dagger(t) Q P(t)$. If $\overline{H}$ does not satisfy the conditions of Eq. (9) then one of two recourses is possible: Either an appropriate N is found so that $\overline{H} + N$ satisfies this condition or a transformation is made to an interaction frame in which the Hamiltonian has a smaller range of eigenvalues.

For the present application it remains to find $\overline{H}$ and therewith M_{eq}. One procedure is to develop a series expansion $\overline{H} = \sum \overline{H}^{(n)}$, the first term of which is the *average Hamiltonian.*[5] A set of recursion relations for the $\overline{H}^{(n)}$ applied to the present problem yields[7b]

$$\begin{aligned} \overline{H}^{(1)} &= \tfrac{1}{2} H_{20}, \\ \overline{H}^{(2)} &= -(3/16\omega_1)[H_{22}, H_{2,-2}] + (1/4\omega_1)(\tfrac{3}{8})^{1/2}[H_{20}, H_{22} - H_{2,-2}], \end{aligned} \tag{12}$$

a series that develops as powers of $\omega_{\mathrm{loc}}/\omega_1$. Equation (11) and the effective Hamiltonian yield $M_{\mathrm{eq}}/M_i = (9\omega_{\mathrm{loc}}^2/16\omega_1^2)(1 + 27\omega_{\mathrm{loc}}^2/8\omega_1^2)^{-1}$ in stark contrast to the laboratory-frame prediction of Eq. (4). This discrepancy can be corrected by the following observation. If, for the moment, we consider only $\overline{H}^{(1)}$ there exists a second operator that commutes with $\overline{H}^{(1)}$—namely I_z. Adding the correction term $\overline{H}^{(2)}$ removes the commutability of I_z; however I_z can itself be corrected so as to commute with $\overline{H}^{(1)} + \overline{H}^{(2)}$. As the n-th order term is added to the series for the effective Hamiltonian, so an n-th order term can be added to I_z to ensure that the two operators commute to order $n+1$. The implication is this: $\overline{H}$ and H are both conserved operators and the assumption that $\overline{H}$ alone determines the equilibrium state is invalid. Furthermore, because H is assumed to allow no other conserved observables, $\bar{H}$ must be *dependent* on H. This being the case, the equilibrium state in the interaction frame is determined by H, just as it is in the laboratory frame. Naturally, the predicted equilibrium properties, such as M_{eq}, are identical in the two frames.

I turn next to a modified version of the Hamiltonian in Eq. (1) that is time dependent:

$$H(t) = -\omega_1(t) I_x + \Delta I_z + H_{20}. \tag{13}$$

One application in which this Hamiltonian arises is for pulsed spin locking in magnetic resonance of solids.[6,7] Here the field is a sequence of pulses, $\omega_1(t) = \theta \sum \delta(t - 2(k-1)\tau)$, with a tip angle of θ and a spacing of 2τ. Again we transform to an interaction frame, the *toggling frame*, via a unitary operator satisfying

$$dU_0/dt = -i[\omega_1(t) - \Delta I_z] U_0. \tag{14}$$

At $t = 2\tau$ the solution is

$$U_0(2\tau) = \exp(i\Delta I_z \tau) \exp(-i\theta I_x) \exp(i\Delta I_z \tau)$$
$$= \exp(i\omega_e \hat{\mathbf{n}} \cdot \mathbf{I} 2\tau), \tag{15}$$

where $\hat{\mathbf{n}}$ represents the effective axis of rotation and the frequency satisfies

$$\cos(\omega_e \tau) = \cos(\Delta\tau) \cos(\theta/2). \tag{16}$$

When $\omega_e = m\pi/n\tau$, m complete rotations are made in n periods of 2τ, and thus the toggling frame is periodic with period $n2\tau$. If for a particular combination of Δ and θ the cyclic condition does not hold, let $\Delta = \Delta_R + \delta$, where Δ_R does satisfy the condition.

In order to simplify the determination of $\bar{H}$, let us tilt the toggling frame by an angle α, with $\tan\alpha = \tan(\theta/2)/\sin(\Delta\tau)$, so as to align $\hat{\mathbf{n}}$ with the z axis. The Hamiltonian in this frame is

$$H_R(k,j) = \sum_L \sum_M d^L_{M0}(\alpha) H_{LM} \exp[i\omega_e M 2\tau (k - 1 + j)], \tag{17}$$

in terms of the Wigner matrix elements and the H_{LM} defined by

$$e^{-i\alpha I_y}(-\delta I_z + H_{20}) e^{i\alpha I_y} = \sum_L \sum_M d^L_{M0}(\alpha) H_{LM}. \tag{18}$$

The discrete nature of the pulses is responsible for the appearance of the Hamiltonian above. The index k labels the kth (of n) period of 2τ that comprises the cycle. The index j equals 0 before and 1 after the pulse that occurs in the middle of each period. The integrations necessary to evaluate the effective Hamiltonian series, via the recursion relations of Ref. 7b, reduce to sums in the present situation and are evaluated following the standard rules for summing power series. The result is

$$\bar{H}^{(1)} = \sum_L d^L_{00}(\alpha) H_{L0} = -\delta \cos\alpha I_z + \tfrac{1}{2}(3\cos^2\alpha - 1) H_{20}, \tag{19}$$

$$\begin{aligned}\bar{H}^{(2)} = {} & \tau \sum_L \sum_{M\neq 0} \sum_{L'} [d^{L'}_{00}(\alpha) H_{L'0}, d^L_{M0}(\alpha) H_{LM}] \cot(\omega_e M \tau) \\ & + \tau \sum_L \sum_{M>0} \sum_{L'} [d^L_{M0}(\alpha) H_{LM}, d^{L'}_{-M,0}(\alpha) H_{L',-M}] \cot(\omega_e M \tau) \\ & + \tau \sum_L \sum_{M\neq 0} \sum_{L'} d^L_{\pm n - M,0}(\alpha) H_{L,\pm n - M}\, d^{L'}_{M0}(\alpha) H_{L'M} \cot(\omega_e M \tau).\end{aligned} \tag{20}$$

We are now in a position to examine the equilibrium state implied by the effective Hamiltonian of Eqs. (19) and (20). The first-order term of $\bar{H}$ allows two constants of the motion, namely I_z and H_{20}, and consequently leads to the prediction of a quasistationary state having separate temperatures for the field and interaction terms. Figure 1 shows the expected dependence of M_{qs} on the pulse angle, in agreement with experimental values.[6a] Upon the addition of $\bar{H}^{(2)}$ to the effective Hamiltonian, these two constants of the motion could be corrected to commute with $\bar{H}^{(1)} + \bar{H}^{(2)}$ if it were not for the third term in Eq. (20). It is because the third term causes n-quantum transitions that the corrections are not possible. This term is *nonzero only for the three-pulse cycle* ($\omega_e - \pi/3\tau$). In this situation the quasistationary state will decay to an equilibrium state characterized by $\bar{H}$ and a single temperature[7a] and will lead to the equilibrium magnetization shown in Fig. 1. The third term in Eq. (20) also governs the decay dynamics and predicts a τ^2 dependence of the relaxation rate for the three-pulse cycle. For longer cycles, the quasistationary state will persist to second order; however, it will decay due to terms in higher-order corrections to $\bar{H}$. For example, with the four-pulse cycle the quasistationary state decays at a rate proportional to τ^4 because of terms in $\bar{H}^{(3)}$.

The pulsed spin-locking experiments of Erofeev, Feldman, and co-workers bear out these predictions.[6] They find that certain combinations of θ and Δ lead to a τ^2 dependence of the relaxation rate, namely those satisfying $\omega_e = \pi/3\tau$, while other combinations lead to τ^4 or τ^6 dependences. In a related area, similar phenomena have been observed in the pulsed spin locking of a nuclear quadrupole resonance by Marino

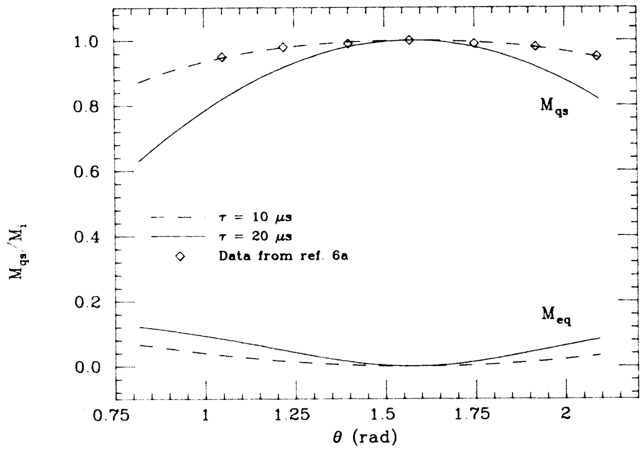

FIG. 1. The dependence of the average value of the observable I_x (i.e., the magnetization) on the pulse angle, θ, for the quasistationary and equilibrium states of a system described by the Hamiltonian of Eq. (13). For this example, $\Delta = 0$ and $\omega_{\rm loc} = 23\,570$ rad/sec.

and Klainer.[13] The above methods provide an explanation of these results as well.[14] In conclusion, the discussion presented in this Letter suggests that these phenomena are general in nature and should be observable in other two-level systems.

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