Quantum mechanics of systems periodic in time

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Some expressions for the time evolution of quantum-mechanical systems with Hamiltonians periodic in time, derivable from the work of Shirley and applied by Young, Deal, and Kestner and Haeberlen and Waugh—all for finite-basis-set systems—are derived for a general system (possibly infinite Hilbert space). These results suggest a new type of approximation to the time-evolution operator, one which is exact at multiples of the period of the Hamiltonian. Comparison is made to an exactly soluble problem, namely, a nonrelativistic hydrogen atom in a circularly polarized monochromatic field.

I. INTRODUCTION

Knowledge of the quantum dynamics of systems with Hamiltonians periodic in time has played an enormously important role in understanding the various phenomena which arise when light interacts with matter. The importance of periodic Hamiltonians is due mainly to the fact that the semiclassical radiation theory—in which the matter system is treated quantum mechanically and radiation is considered to be an externally provided classical electromagnetic field—usually leads to Hamiltonians periodic in time through an assumed sinusoidal time variation of the electromagnetic field. Also contributing is the fact that this semiclassical theory is considerably more tractable than the fully quantized theory.

However, rarely is the periodic property of the Hamiltonian exploited to any great extent in determining the time evolution of such systems. More often than not the temporal behavior of the system of interest is predicted using time-dependent perturbation theory to first order.[1] Alternately (for two-level systems), the effects of a sinusoidally oscillating electromagnetic field may be approximately calculated by transforming to the so-called rotating coordinate frame by a unitary transformation. This familiar rotating-wave approximation leads to the Rabi formula for the behavior of a two-level system in an oscillating field.[2] In the first case, no explicit use is made of the periodicity of the Hamiltonian and in the second case the method only works for sinusoidal time variation.

There was a time when available light sources were so weak and/or incoherent that the first-order perturbation-theory treatment was entirely adequate. For sufficiently weak excitation other processes not included in the theory— such as spontaneous radiative decay, intermolecular collisions, etc.—prevent any appreciable accumulation of probability in excited states so that questions concerning long-term behavior within the framework of the semiclassical theory are purely academic. In fact, it has occasionally been deemed necessary to demonstrate how the perturbation-theory result may be obtained from the Rabi formulation.[3]

The advent of laser light sources, with their various combinations of high intensity, spectral purity, and long correlation times, has provided a host of new and interesting phenomena and has given new merit to the question of the long-term behavior of a harmonically driven quantum-mechanical system.[4] Our principal interest is in the long-term behavior of such harmonically driven quantum systems; however, the result which we shall establish in this paper depends only on the periodicity of the Hamiltonian in time and not on the detailed functional form of that periodicity.

Quantum-mechanical systems with Hamiltonians periodic in time have been studied by Shirley[5] and Young, Deal, and Kestner,[6] within the framework of truncated basis sets and many interesting results have been established. In their work attention is directed toward calculating and discussing the properties of the so-called quasiperiodic states. These are states which evolve back into themselves (possibly multiplied by a phase factor of modulus 1) in one period of the Hamiltonian. In other words, if the period is τ and $U(\tau, 0)$ is the unitary time-evolution operator which takes a state from time zero to time τ, the quasiperiodic states are the eigenfunctions of $U(\tau, 0)$. It can be rigorously demonstrated only for finite Hilbert spaces that such quasiperiodic states exist. Whether or not quasiperiodic states exist for systems with infinite Hilbert spaces is not known; however, Young, Deal and Kestner give a physical argument to support a conjecture that they do not. Still within the framework of finite basis sets, Haeberlen and Waugh[7] employed similar formulas in their theoretical treatment of multiple pulse NMR experiments for the high-resolution NMR of solids.

Sambe[8] has recently given an extensive discussion of the quantum mechanics of systems with a periodic Hamiltonian, beginning, however, with the assumption that eigenstates for what he calls the "Hamiltonian for steady states" exist.

Whether or not quasiperiodic states exist for systems with infinite Hilbert spaces, relations similar to those established and used for finite-basis-set systems may be proven for infinite-Hilbert-space systems, and it is the purpose of this paper to set them forth. In Sec. II we shall prove the principal result of this paper; in Sec. III we will show that this suggests an entirely new type of approximation method for describing the long-term behavior of systems with periodic Hamiltonians and discuss the relationship of the present work to that of Shirley and Young, Deal, and Kestner. In Sec. IV we compare the approximate solution for a nonrelativistic hydrogen atom interacting in the dipole approximation—with a circularly polarized monochromatic electromagnetic field—with the exact solution to the same problem. In addition, we consider the existence of quasiperiodic states for this same model.

II. TIME-EVOLUTION OPERATORS FOR PERIODIC SYSTEMS

Hamiltonians in the semiclassical radiation theory generally have the form

$$H(t)=H_0+V(t)-i\gamma\,, \tag{1}$$

where H_0 is the time-independent Hamiltonian operator for the unperturbed atom or molecule, etc., $V(t)$ describes the coupling of the atoms to the externally provided electromagnetic field, and γ is an optional diagonal matrix for the approximate inclusion of damping effects.[9] When $V(t)$ is periodic in time with period τ, we have

$$H(t+\tau)=H(t)\,.$$

We consider the time-evolution operator $U(t,t_0)$ which converts a state at t_0 into its state at t, i.e.,

$$|\psi(t)\rangle=U(t,t_0)|\psi(t_0)\rangle\,.$$

$U(t,t_0)$ satisfies the boundary condition

$$U(t_0,t_0)=1$$

and, in the usual case where the γ term is omitted, $U(t,t_0)$ is unitary. $U(t,t_0)$ is a solution of the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}U(t,t_0)=H(t)U(t,t_0)$$

with formal solution obtained in the usual way by integrating once and then iterating[10]:

$$U(t,t_0)=1+\frac{1}{i\hbar}\int_{t_0}^{t}dt'\,H(t')+\frac{1}{(i\hbar)^2}\int_{t_0}^{t}dt'\,H(t')\int_{t_0}^{t'}dt''\,H(t'')+\cdots. \tag{2}$$

We shall assume without further ado that the formal solution (2) exists (i.e., the expansion converges); however, we note that the expansion does not manifestly diverge.[11] This may be seen as follows: Let H_m be the maximum value of $H(t)$ chosen by selecting the maximum absolute value of each matrix element of $H(t)$ throughout its period (we exclude periodicities such as $\sec\omega t$); then each matrix element in each term of (2) is certainly less than the corresponding element in the expansion obtained from (3) by replacing $H(t)$ by H_m. In the latter case the nth term in the expansion is $(1/n!)\,(H_m t/i\hbar)^n$ so that the expansion converges to $e^{-iH_m t/\hbar}$.

We will now prove that

$$U(t+\tau,0)=U(t,0)U(\tau,0)\,. \tag{3}$$

To do this we will first show that

$$U(t+\tau,\tau)=U(t,0) \tag{4}$$

from which (3) follows immediately. From the formal solution (2), we may write

$$U(t+\tau,\tau)=1+\frac{1}{i\hbar}\int_{\tau}^{t+\tau}dt'\,H(t')+\frac{1}{(i\hbar)^2}\int_{\tau}^{t+\tau}dt'\,H(t')\int_{\tau}^{t'}dt''\,H(t'')+\cdots \tag{5}$$

and make the variable changes $s'=t'+\tau$, $s''=t''+\tau$, etc. in every term. By virtue of the periodicity of $H(t)$, the expansion (5) becomes

$$U(t+\tau,\tau)=1+\frac{1}{i\hbar}\int_{0}^{t}ds'\,H(s')+\frac{1}{(i\hbar)^2}\int_{0}^{t}ds'\,H(s')\int_{0}^{s'}ds''\,H(s'')+\cdots$$
$$=U(t,0)\,.$$

Multiplying from the left by $U(\tau,0)$ gives the required result. Note that $U(t,0)$ does not commute with $U(\tau,0)$ except at $t=n\tau$ so that a variation of (3) with the right-hand-side product reversed does not hold.

III. DISCUSSION

The most immediate consequence of (3) is that $U(\tau, 0)$, the time evolution over one period, provides essentially all the information we ever need about the long-term behavior of the system with Hamiltonian (1). That is [now suppressing the $t_0 = 0$ index and writing $U(t) \equiv U(t, 0)$]

$$U(2\tau) = U(\tau)U(\tau) = U(\tau)^2 ,$$

or

$$U(n\tau) = U(\tau)^n .$$

It is rare that any information is required about the time evolution of a system over time scales comparable to τ. In most cases [where the interaction term $V(t)$ is weak relative to H_0] the interesting behavior occurs on time scales many orders of magnitude larger than τ. If we know $U(\tau)$ we may then calculate $U(t)$ exactly at $t = n\tau$ which is much more fine-grained information than usually desired.

If the Hilbert space of the problem is finite (e.g., a truncated basis set), then $U(\tau)$ may be diagonalized by some unitary transformation S.[12] That is,

$$S^\dagger U(\tau) S = e^{-iD} , \tag{6}$$

where D is a diagonal matrix. With the definition $H' = (\hbar/\tau)D$ we may rewrite (6) as

$$S^\dagger U(\tau) S = e^{-i\tau H'/\hbar}$$

and consequently

$$U(\tau) = S e^{-i\tau H'/\hbar} S^\dagger ,$$

whereupon

$$U(n\tau) = U(\tau)^n = S e^{-in\tau H'/\hbar} S^\dagger . \tag{7}$$

Defining the constant Hermitian matrix

$$G = SH' S^\dagger$$

allows us to write (7) as follows:

$$U(n\tau) = e^{-in\tau G/\hbar}$$

which suggests an approximation for $U(t)$ which we call $U_p(t)$ (with p standing for periodic since this approximate time-evolution operator will be exact for $t = n\tau$):

$$U_p(t) = e^{-itG/\hbar} . \tag{8}$$

That the above is consistent with previous work may be shown as follows: Define a time-dependent matrix $A(t)$ by

$$A(t) = U(t) e^{itG/\hbar} .$$

$A(t)$ is periodic with period τ since

$$\begin{aligned} A(t+\tau) &= U(t+\tau) e^{iG(t+\tau)/\hbar} \\ &= U(t) U(\tau) e^{iG\tau/\hbar} e^{iGt/\hbar} \\ &= U(t) e^{iGt/\hbar} \\ &= A(t) \end{aligned}$$

by virtue of the fact that $U(\tau) = e^{-iG\tau/\hbar}$. Then $U(t)$ may be written in the form

$$U(t) = A(t) e^{-iGt/\hbar} \tag{9}$$

with $A(t)$ periodic in time as established by Shirley.

As long as the Hilbert space of the problem is finite, a unitary transformation S may always be found which diagonalizes $U(\tau)$; however, when the Hilbert space is infinite a unitary transformation S does not necessarily exist which will bring $S(\tau)$ into diagonal form. The arguments which led to writing $U(t)$ in the form (9) and which gave the approximation (8) are then not available for the derivation of equivalent expressions for infinite-Hilbert-space systems. Nevertheless, Eqs. (8) and (9) hold for infinite systems. The proof of this statement is a straightforward application of three theorems in Hilbert-space theory (regarding spectral decompositions of unitary and Hermitian operators regardless of their diagonalizability).[13] The first two theorems simply prove that a spectral decomposition may be found for every unitary and every Hermitian operator. From the spectral decomposition of $U(\tau)$, we can construct a one-parameter family of unitary operators which may be written $U(\tau)^{t/\tau}$ for shorthand, with

$$U(\tau)^{t/\tau} U(\tau)^{s/\tau} = U(\tau)^{(t+s)/\tau} . \tag{10}$$

(See the discussion preceding Stone's theorem in Ref. 13.) Stone's theorem then declares that $U(\tau)^{t/\tau}$ may be written generally in the form

$$U(\tau)^{t/\tau} = e^{-iGt/\hbar} ,$$

where G is a Hermitian operator. [Note that this does not imply that $U(\tau)^{t/\tau}$ is equal to $U(t, 0)$. $U(t, t_0)$ is a two-parameter unitary transformation so that condition (10) for applying Stone's theorem does not hold.]

One of the principal results of this paper is to prove that an approximation (8) exists for infinite- as well as finite-Hilbert-space systems. Finding the Hermitian operator G in terms of H_0 and V, however, is a formidable problem that has not yet been solved in general.

The question of the existence of quasiperiodic states [eigenstates of $U(\tau)$] may be posed in terms of the Hermitian operator G; if G can be brought into diagonal form by a unitary transformation, then quasiperiodic states exist. Within the framework of the quantum mechanics of atoms and molecules, it is usually the case that those operators with a purely discrete spectrum of eigenvalues can be transformed into diagonal form and those with a continuous eigenvalue spectrum cannot. Then presumably if G has an entirely discrete spectrum it can be diagonalized.

IV. EXAMPLE

Consider a nonrelativistic hydrogen atom with unperturbed Hamiltonian H_0 and electron coordinates x, y, z interacting with a circularly polarized monochromatic field of vector potential

$$A = (E_0 c/\omega)\,(\hat{x}\cos\omega t + \hat{y}\sin\omega t)\,, \tag{11}$$

where we have assumed the wavelength to be long compared to the size of the atom. In the dipole approximation the interaction is $e\vec{r}\cdot\vec{E}(t)$ with $\vec{E}(t)$ derived from (11):

$$\vec{E}(t) = E_0(\hat{x}\sin\omega t - \hat{y}\cos\omega t)\,,$$

where $\hat{x}$ and $\hat{y}$ are unit vectors. The Hamiltonian for this model system is then

$$H(t) = H_0 + eE_0(x\sin\omega t - y\cos\omega t)\,. \tag{12}$$

It is shown elsewhere[14] that the time-evolution operator for this problem may be obtained in closed form and is given by

$$U(t) = e^{-i\omega t L_z/\hbar}\, e^{-it(H_0 - \omega L_z + eE_0 x)/\hbar}\,, \tag{13}$$

where L_z is the operator for the z component of angular momentum.

For comparison we can calculate $U(\tau)$:

$$U(\tau) = e^{-i\tau(H_0 - \omega L_z + eE_0 x)/\hbar}\,, \tag{14}$$

and the operators A and G of Sec. III are readily identified:

$$A = e^{-i\omega t L_z/\hbar} \tag{15}$$

and

$$G = H_0 - \omega L_z + eE_0 x\,. \tag{16}$$

The exact $U(t)$ differs from the approximate time-evolution operator $U_p(t)$ [Eq. (8)] only by a unitary factor which is diagonal in the eigenvectors of H_0. Clearly transition probabilities calculated from $U(t)$ and $U_p(t)$ will be identical so that in this respect the use of $U_p(t)$ entails no loss of information. The only circumstances in which $U_p(t)$ gives different results from $U(t)$ is when the detailed relative phases of the wave functions is important, for example, in determining the time evolution of some physical quantity whose operator is nondiagonal in the eigenvectors of H_0. A case in point is the time evolution of the dipole moment operator (written here as $-e\vec{r}=\vec{\mu}$) where

$$\vec{\mu}(t) = U^+(t)\vec{\mu}\,U(t) \tag{17}$$

contains time-dependent phase factors not present in the corresponding expression using $U_p(t)$.

Quasiperiodic states do not exist for this model (as defined) since the operator G, (16), cannot be brought to diagonal form. G is similar in this respect to the nonrelativistic Stark-effect Hamiltonian for hydrogen and is not diagonalizable for the same reasons as in this latter problem. However, it is important that the nonexistence of quasiperiodic states is not a consequence of the periodicity of the driving field but rather of the detailed form of the interaction operator. It is easy to imagine similar models—for example, with a spatially limited driving field—which would give a diagonalizable G operator, and for which quasiperiodic states would exist.

The periodic operator A, (15), is simpler for this model than might have been expected, being diagonal in the eigenvectors of H_0. However, there seems to be no reason why one would expect such simplicity in all cases.

One further comment needs to be made: we have made an especially fortuitous choice of phase of the driving field (11). We would not expect the phase to have an effect on any physical quantity. However, it may be shown by the methods of Ref. 14 that if ωt is replaced by $\omega t+\delta$ in Eq. (11), $U(\tau)$ takes the form

$$U(\tau) = e^{-i\delta L_z/\hbar}\, e^{-i\tau G/\hbar} \tag{18}$$

with the same G as before. In fact, this must still be representable as $e^{-i\tau G'/\hbar}$ but since L_z and G do not commute, the operator G' will be some complicated function of L_z, G, and their various commutators.[15] Thus, although the physical properties must be independent of the phase δ, the *form* of the solution is very much simpler for a particular choice of phase.

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[1]See, for example, L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw-Hill, San Francisco, 1968), Chap. 11.

[2]I. I. Rabi, Phys. Rev. 51, 652 (1937). For a discussion of rotating-wave transformations in infinite-Hilbert-space systems see W. R. Salzman, Phys. Rev. A 5, 789 (1972).

[3]See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, England,

1970), Chap. II, Sec. D.

[4]For a general review of this and related topics see P. W. Langhoff, S. T. Epstein, and M. Karplus, Rev. Mod. Phys. 44, 602 (1972).

[5]J. H. Shirley, Phys. Rev. 138, B979 (1965).

[6]R. H. Young, W. J. Deal, and N. R. Kestner, Mol. Phys. 17, 369 (1969).

[7]V. Haeberlen and J. S. Waugh, Phys. Rev. 175, 453 (1968) (see also footnote 10).

[8]H. Sambe, Phys. Rev. A 7, 2203 (1973).

[9]Inclusion of the γ damping term in (1), which makes the Hamiltonian non-Hermitian, is not intended to imply that such inclusion is usual, or even desirable. It is included only to indicate that our result holds even when it is included. The time-evolution operator obtained from such a Hamiltonian is nonunitary and so does not conserve probabilities.

[10]See, for example, S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Harper and Row, New York, 1961), Sec. 11f. It is tempting to try to work with the even more formal solution

$$U(t,t_0)=P\exp\left(\frac{1}{i\hbar}\int_{t_0}^{t}dt'\,H(t')\right),$$

where P is the Dyson time-ordering operator, as in Ref. 7. However, any result based on this formal solution must be justified term by term in (2), since it is only a shorthand expression for (2). Note that the integral inside the exponential can in many cases be done in closed form, whereupon P has no effect and one gets an incorrect result.

[11]The present paper is intended for application to atomic and molecular problems for which the usual domain of H (and H_m below) consists of antisymmetrized products of one-electron functions. In this domain H may be unbounded.

[12]From here on we drop the γ damping term so that $U(\tau)$ is unitary.

[13]F. Riesz and B. Sz.-Nagy, *Functional Analysis*, translated by L. F. Boron (Ungar, New York, 1955). Theorems on pp. 281, 320, and theorem and discussion of Sec. 137.

[14]W. R. Salzman, Chem. Phys. Lett. 25, 302 (1974).

[15]See, for example, W. Magnus, Comm. Pure Appl. Math. 7, 649 (1954).