

Effective action for a nonadiabatic quantum process

Aurel Bulgac

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6396

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A sum rule for the so-called quantum phases is established, without assuming adiabatic evolution. By considering two interacting quantum systems, conventionally designated as a boson and a fermionic one, we evaluate the effective bosonic action after integrating out the fermionic variables. This effective action contains a nontrivial topological part, which has the same origin as the quantum adiabatic phase. However, the derivation does not rely on any adiabatic assumption.

INTRODUCTION

Recently, there has been an extensive interest in the so-called quantum adiabatic or Berry's phase, mainly after the papers of Berry¹ and Simon.² The fact that during an adiabatic evolution of a quantum system the wave function acquires an additional phase besides the natural one (often called the dynamical phase) was known for quite a long time in molecular dynamics.³ This additional phase was merely an annoying factor, which complicated the analysis of the molecular processes in the Born-Oppenheimer approximation. The relevance of this additional phase to different fields of physics has become evident only during the last few years.⁴⁻⁷ Recently Aharonov and Anandan⁶ have shown that if there is a periodic solution (up to a phase factor) of the time-dependent Schrödinger equation, then Berry's result is always valid.

For illustrative purposes only we shall first describe a simple two-level system, a spin- $\frac{1}{2}$ particle in a uniformly rotating magnetic field. From this example one can see explicitly that the adiabatic result obtained by Berry¹ is actually an exact one. The adiabatic assumption is not needed. In the case studied by Berry and others the evolving state is an eigenstate of the Hamiltonian at the initial moment and will evolve in time as an eigenstate of the instantaneous Hamiltonian. In the general case the initial state is not an eigenstate of the instantaneous Hamiltonian at the initial moment, but an eigenstate of the evolution operator after the completion of a cycle. Even if this reminds one of the adiabatic result, the meaning is rather different. In the adiabatic limit the trajectory of the system is independent of the rate with which the system evolves in time (provided the adiabatic requirement is met) and consequently, Berry's phase is independent of the velocity with which the system is driven by external forces along such a trajectory.

The time dependence of the Schrödinger equation usually come from some external driving force. If the rate of change of this driving force changes, the shape of the quantum trajectory changes as well (this will be evident from the analytic example we give) and this will induce a different quantum phase. One of the consequences of the appearance of such a phase is the occurrence of an equivalent Aharonov-Bohm effect³ in molecular systems due to the appearance of an effective gauge field. More-

over, Wilczek and Zee⁵ showed that even non-Abelian effective gauge fields appear in the treatment of molecular systems in the adiabatic approximation if there is a degeneracy in the electronic structure. We would like to point to the fact that such non-Abelian gauge fields are present always, whether or not a degeneracy occurs. When one treats a physical system as two interacting subsystems the appearance of non-Abelian effective gauge fields is rather a rule than an exception.

Finally, we compute the effective action for a bosonic system in interaction with a fermionic one, after integrating out the fermionic degrees of freedom. As in the adiabatic case, the effective action contains an additional term, the nonadiabatic quantum phase. The rules for the evaluation of the effective action are completely different from the case of adiabatic evolution. Determining in a consistent way the fermionic periodic solutions proves to be crucial in computing the effective bosonic action.

A SIMPLE ANALYTIC EXAMPLE

Let us consider the following Schrödinger equation:

$$i\hbar \frac{\partial \varphi}{\partial t} = H(t)\varphi = \mu B \begin{bmatrix} \cos\theta & \sin\theta \exp(-i\omega t) \\ \sin\theta \exp(i\omega t) & -\cos\theta \end{bmatrix} \varphi \quad (1)$$

for a spin- $\frac{1}{2}$ particle in a magnetic field precessing uniformly around the Oz axis,

$$\mathbf{B}(t) = B(\sin\theta \cos(\omega t), \sin\theta \sin(\omega t), \cos\theta) . \quad (2)$$

We choose units such that $\mu B = \hbar$. In the adiabatic limit the angular frequency $\omega \rightarrow 0$. Obviously, $H(0) = H(T)$, where $\omega T = 2\pi$. The instantaneous eigenfunctions and eigenvalues of the above Hamiltonian are (up to an irrelevant phase factor)

$$\begin{aligned} \phi_+(t) &= \begin{bmatrix} \cos(\theta/2) \exp(-i\omega t/2) \\ \sin(\theta/2) \exp(i\omega t/2) \end{bmatrix}, \\ \phi_-(t) &= \begin{bmatrix} -\sin(\theta/2) \exp(-i\omega t/2) \\ \cos(\theta/2) \exp(i\omega t/2) \end{bmatrix}, \\ \epsilon_{\pm} &= \pm \frac{\mu B}{\hbar} = \pm 1 . \end{aligned}$$

They correspond to the orientation of the spin along and against the instantaneous magnetic field. Under the adiabatic assumption, these two states will evolve independently in time. The remarkable fact is that these states will acquire after one period T , besides the expected dynamical phase $\exp(-i\varepsilon_{\pm}T)$, an additional phase $\exp(i\gamma_{\pm})$, exactly equal to half the solid angle subtended at the center by the circle traced on a sphere by the instantaneous spin.

The general solution to Eq. (1) is, however, in general, different. There are two linearly independent solutions, which have the form

$$\psi_{\pm}(t) = \begin{pmatrix} a_{\pm} \exp[-(i\omega t/2) - i\varepsilon_{\pm}t] \\ b_{\pm} \exp[(i\omega t/2) - i\varepsilon_{\pm}t] \end{pmatrix},$$

where

$$\varepsilon_{\pm} = \pm \left[1 - \omega \cos\theta + \frac{\omega^2}{4} \right]^{1/2}$$

and

$$\begin{pmatrix} \cos\theta - (\omega/2) - \varepsilon_{\pm} & \sin\theta \\ \sin\theta & -[\cos\theta - (\omega/2)] - \varepsilon_{\pm} \end{pmatrix} \begin{pmatrix} a_{\pm} \\ b_{\pm} \end{pmatrix} = 0,$$

$$a_{\pm}^2 + b_{\pm}^2 = 1.$$

The constants a_{\pm} , b_{\pm} can be chosen to be real. The instantaneous value of the energy is

$$\langle \varepsilon_{\pm} \rangle = \varepsilon_{\pm} + \frac{\omega}{2}(a_{\pm}^2 - b_{\pm}^2)$$

and the momentary value of the spin is

$$\mathbf{s}_{\pm}(t) = \frac{1}{2}(2a_{\pm}b_{\pm} \cos\omega t, 2a_{\pm}b_{\pm} \sin\omega t, a_{\pm}^2 - b_{\pm}^2). \quad (3)$$

Obviously, $\psi_{\pm}(t)$ are not eigenvectors of the instantaneous Hamiltonian $H(t)$. Also, the angle between the momentary magnetic field and the spin is different from 0 or π . However, these two vectors, while evolving in time, rotate with the same frequency and the angle between them is constant in time [compare relations (2) and (3)]. For these particular choices of initial conditions, the spin is slaved by the magnetic field as in the case of adiabatic evolution. For any other choice, the evolution is not periodic (unless the ratio ε_{\pm}/ω is a rational number). After one period, not only does the magnetic field return to its initial value, but so does the spin. The wave functions $\psi_{\pm}(t)$ acquire a phase

$$\psi_{\pm}(T) = \psi_{\pm}(0) \exp[-i(\pi + \varepsilon_{\pm}T)].$$

It is trivial to check that

$$\delta_{\pm} = \pi + \varepsilon_{\pm}T = \langle \varepsilon_{\pm} \rangle T + \frac{1}{2}\Omega_{\pm},$$

where $\langle \varepsilon_{\pm} \rangle T$ is the dynamical phase and

$$\Omega_{\pm} = 2\pi(1 - a_{\pm}^2 + b_{\pm}^2)$$

is the solid angle at the center subtended by the circle traced by the spin on a sphere, which is exactly the adia-

batic result. The difference is not only that the process is not adiabatic, but the initial state is now a superposition of instantaneous eigenstates. If $\omega \rightarrow 0$ then $\psi_{\pm}(0) \rightarrow \phi_{\pm}(0)$ and we recover the adiabatic result. It is interesting to note that

$$\delta_{+} + \delta_{-} = 2\pi = 0 \pmod{2\pi},$$

$$\Omega_{+} + \Omega_{-} = 4\pi = 0 \pmod{2\pi},$$

and

$$\mathbf{s}_{+}(t) + \mathbf{s}_{-}(t) = 0.$$

This is indicative of the fact that one can establish some kind of sum rule for the quantum phases. At least for any other value of the spin in a precessing magnetic field this result can be established in a straightforward manner as above.

GENERAL CASE

We will show now that the above result is a general one. This is merely a repetition of the result established in Ref. 6, which shall be needed later on to establish the form of the effective action. Let us consider a time-dependent Hamiltonian $H(t)$ and the corresponding Schrödinger equation

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H(t)\psi(t), \quad H(T) = H(0).$$

The condition that the Hamiltonian is a periodic operator includes also the case of time-independent Hamiltonians, but in such a case the period could be chosen arbitrarily. Let us consider the time evolution of a complete linearly independent set of wave functions. The formal solution can be written as ($\hbar = 1$)

$$\psi_k(t) = T \exp \left[-i \int_0^t dt' H(t') \right] \psi_k(0) = U(t) \psi_k(0).$$

The subscript k stands for the whole set of quantum numbers necessary to distinguish different wave functions. Since $U(t)$ is a unitary operator, it can be brought to the diagonal form by a suitable unitary transformation at any intermediate time. At least such a statement seems to hold for any finite dimensional Hilbert space, which is the only case when one can hope to make a real computation. The author is not aware of any difficulties in the general case. A unitary operator would have in general both discrete and continuous spectra. The simplest example is the case corresponding to a Schrödinger equation for a time-dependent Hamiltonian. Strictly speaking, the wave functions corresponding to the continuous spectrum are not proper eigenvectors. This fact can generate standard mathematical difficulties in diagonalizing the evolution operator, which, however, can be overcome in a variety of ways (e.g., by confining the physical system into a sufficiently large box). In nuclear physics, periodic solutions have been studied both theoretically and numerically for some time.⁸

When one deals with a level crossing or quasicrossing between two electronic terms in a molecule, the adiabatic assumption is clearly inadequate and one has to take into

account nonadiabatic effects arising from transitions between the two terms near the level crossing, which depends drastically on the rate of the time evolution. We shall be interested in diagonalizing $U(T)$ only. Suppose $\psi_k(0)$ form a complete set of eigenvectors of $U(T)$, i.e.,

$$U(T)\psi_k(0) = \exp(i\delta_k)\psi_k(0) = \psi_k(T).$$

In the theory of differential equations with periodic coefficients the numbers δ_k are shown as Floquet's indices. Consequently, for any periodic Hamiltonian one can find a set of functions, which under time evolution return to their initial values, after one period, up to a phase factor. The same is true also for time-dependent Hamiltonians, but with arbitrary period. We will show that modulo 2π this phase always can be represented as a sum of the dynamical and geometric phases.

One can always introduce an arbitrary phase $\delta_k(t)$, such that $\delta_k(0) = 0$, $\delta_k(T) = \delta_k$, and the functions

$$\bar{\varphi}_k(t) = \exp[-i\delta_k(t)]\psi_k(t),$$

which are periodic, $\bar{\varphi}_k(T) = \bar{\varphi}_k(0)$. We have

$$\varepsilon_k(t) = \langle \psi_k(t) | H(t) | \psi_k(t) \rangle \equiv \langle \bar{\varphi}_k(t) | H(t) | \bar{\varphi}_k(t) \rangle.$$

Let us write

$$\delta_k(t) = \gamma_k(t) - \int_0^t dt' \varepsilon_k(t').$$

It is straightforward to establish that

$$\gamma_k(t) = \int_0^t dt' \left\langle \bar{\varphi}_k(t') \left| i \frac{\partial \bar{\varphi}_k(t')}{\partial t'} \right. \right\rangle,$$

and consequently,

$$\delta_k = \gamma_k(T) - \int_0^T dt \varepsilon_k(t).$$

The geometric part of the phase $\gamma_k(T)$ is given actually by a contour integral, since $\bar{\varphi}_k(T) = \bar{\varphi}_k(0)$. Such an integral is gauge invariant, i.e., if we multiply the functions $\bar{\varphi}_k(t)$ by $\exp[i\alpha_k(t)]$, with the restriction $\alpha_k(0) = \alpha_k(T)$, the value of $\gamma_k(T)$ will remain unchanged. Therefore, the geometric part of the phase acquired by the wave function under a cyclic evolution depends only on the path (which is closed under such circumstances), but not on the velocity with which this path in Hilbert space is traced. However, the path itself is determined by the time evolution and will change if the period is changed. One can see from this proof that the value of the so-called Floquet's index is determined not only by the energy spectrum of the instantaneous Hamiltonian along the path, but contains also a geometric part which will give rise to important corrections⁷ to the usual semiclassical Bohr-Sommerfeld quantization rule.⁸ There is a major difference between the adiabatic limit and the general case. In the adiabatic limit, during the entire evolution the state remains at all times, during the evolution, an instantaneous eigenstate of the instantaneous Hamiltonian. In the general case, the quantum state, which after a full period returns to its initial value, is an eigenvalue of the evolution operator at the time $t = T$. If one knows the period of the motion, one has to diagonalize this operator in order to find the truly periodic solutions of the time-

dependent Schrödinger equation.

We will show now that the quantum phases satisfy a simple sum rule, which is a generalization of the result mentioned at the end of the preceding section. Let us consider for simplicity that the Hilbert space is finite-dimensional and that

$$\begin{aligned} \text{Tr}[H(t)] &= \sum_{n=1}^N \langle n | H(t) | n \rangle \\ &= \sum_{n=1}^N \varepsilon_n(t) = 0. \end{aligned}$$

As one can easily see, one can always subtract from the Hamiltonian a time-dependent constant $\text{Tr}[H(t)]$, which corresponds to a common phase factor $\exp\{-i \int_0^t dt' \text{Tr}[H(t')]\}$ for all wave functions. Let us consider now the N -particle wave function

$$\Phi(1, \dots, N, t) = \frac{1}{\sqrt{N!}} \det[\psi_n(l, t)],$$

where

$$i\hbar \partial_t \psi_n(l, t) = H(l, t) \psi_n(l, t).$$

This wave function satisfies the following time-dependent Schrödinger equation:

$$\begin{aligned} i\hbar \frac{\partial \Phi(1, \dots, N, t)}{\partial t} &= \sum_{n=1}^N H(n, t) \Phi(1, \dots, N, t) \\ &\equiv \text{Tr}[H(t)] \Phi(1, \dots, N, t) \equiv 0. \end{aligned}$$

In doing so, we actually consider a mapping of the given Hamiltonian and Hilbert spaces into a different Hamiltonian, with the same matrix elements, which describes a fictitious fermion field with N states available. The state described by the above wave function corresponds to an N -fermion state, n labeling the single-particle states in this new Hilbert space and l the coordinates. Consequently, this wave function is time independent; it does not undergo any time evolution, according to the above equation. Such a wave function corresponds to N noninteracting fermions which fill all the available single-particle states and thus there is nothing left in the Hilbert space into which such a state can transform, but itself. The only thing which can change is the phase, which after a period is

$$\sum_{n=1}^N (\gamma_n - \int_0^T dt \varepsilon_n) = \sum_{n=1}^N \gamma_n = 0,$$

which establishes the sum rule for the quantum phases.

As we mentioned in the Introduction, Wilczek and Zee⁵ extended Berry's analysis to the case of degenerate levels and introduced instead of a phase factor a unitary matrix which characterized the time evolution of a group of degenerate levels, which, in complete analogy with the case studied by Berry, supports a similar simple geometrical interpretation. The degeneracy considered by these authors was arising due to a symmetry of the Hamiltonian. Berry's analysis did not encompass this case, since in his expression for the quantum phase, which included a

certain sum over the whole spectrum, there is an energy denominator, which, in the case of degenerate levels, vanishes. As one can see, however, from the general result, the fact that there is or not a degeneracy in the spectrum does not reveal itself in any way. Moreover, the quantum system can have in general a very complicated time evolution, which can include level crossing as well (such a degeneracy does not arise from a symmetry of the Hamiltonian). In their treatment, Wilczek and Zee⁵ were able to show evidence of the appearance of effective non-Abelian fields in the effective Hamiltonian for nuclear motion. Do the effective non-Abelian gauge fields appear only when one deals with a system with degenerate levels? Several explicit examples, when this is not the case, have been worked out in Ref. 9. Even if one does not have a degeneracy in the electronic spectrum, one can easily imagine that there are situations when including only one electronic term will be a bad approximation. The simplest example is the case of level crossing, when during the time evolution two electronic terms cross or approach so closely that a transition between the corresponding states cannot be neglected. This is the famous Landau-Zener effect, where the occupation probability of one or another electronic term drastically depends on the rate of the time evolution. Even when most of the time evolution is adiabatic, near the level crossing the adiabaticity is broken and one has to consider nonadiabatic effects. The character of the periodic solutions in such a case surely will drastically change with the period of the quantum evolution and one has to consider from the very beginning at least two electronic terms.

Let us turn to the canonical example, namely, a molecular system. The Hamiltonian is

$$H = -\frac{\hbar^2}{2M} \nabla_R^2 + h(R, r),$$

where the first term describes the relative nuclear motion and the second one the electrons and the Coulomb interaction between electrons and nuclei. The total wave function can be represented in the form

$$\Psi(R, r) = \sum_n \phi_n(R) \varphi_n(r, R),$$

where

$$h(R, r) \varphi_n(r, R) = \varepsilon_n \phi_n(R) \varphi_n(r, R)$$

are the so-called instantaneous electron eigenstates and eigenvalues which depend parametrically on R , the nuclear configuration, and

$$\begin{aligned} \sum_{ln} -\frac{\hbar^2}{2M} (\nabla_R \delta_{kl} + \langle \varphi_k(R) | \nabla_R | \varphi_l(R) \rangle) \\ \times (\nabla_R \delta_{ln} + \langle \varphi_l(R) | \nabla_R | \varphi_n(R) \rangle) \phi_n(R) \\ + \sum_l \langle \varphi_k(R) | h(R) | \varphi_l(R) \rangle \phi_l(R) = \varepsilon \phi_k(R). \end{aligned}$$

In passing, we would like to point out the fact that in the case of any realistic calculation, the nondiagonal matrix elements $\langle \varphi_k(R) | h(R) | \varphi_l(R) \rangle$ are different from zero (unless they vanish due to some symmetry reasons) and have to be taken into account since it is practically impossible to exactly solve the electronic problem.

In the Born-Oppenheimer approximation one usually retains only one term in the expression for the total wave function, or, if there are degenerate electronic terms, only the corresponding electronic wave functions. If the sum extends over the whole spectrum it is completely irrelevant how one chooses the electronic wave functions, once the set is complete. The total wave function must be invariant under the following unitary transformation:

$$\tilde{\varphi}_n(r, R) = U_{nm}(R) \varphi_m(r, R),$$

$$\tilde{\phi}_n(R) = U_{nm}^* \phi_m(R),$$

irrespective of whether one includes a complete set of electronic wave functions. In the case of only one term, the unitary matrix $U_{nm}(R)$ becomes simply an arbitrary complex number of modulus unity. Due to such a gauge invariance of the total wave-function effective gauge fields $\mathbf{A}_{ln}(\mathbf{R}) = \langle \varphi_l(\mathbf{R}) | i \nabla_R | \varphi_n(\mathbf{R}) \rangle$ appear in the nuclear Hamiltonian.^{3,5} Generally speaking, there are non-Abelian fields, which couple in a nontrivial way different components of the nuclear wave functions and cannot be transformed away by a suitably chosen unitary transformation.^{3,9}

Let us consider now two interacting quantum systems, conventionally designated as bosonic and fermionic systems (or depending on the physical content, nuclear and electronic or collective and intrinsic systems), with the Hamiltonian

$$\hat{H} = \hat{H}_B(\mathbf{P}, \mathbf{Q}) + \hat{H}_F(\mathbf{P}, \mathbf{Q}),$$

where \mathbf{P} and \mathbf{Q} are the canonically conjugate bosonic coordinates and momenta. The corresponding fermionic variables are not shown. The path-integral method applied to the bosonic degrees of freedom only leads to the following expression for the trace of the evolution operator ($\hbar = 1$):

$$\begin{aligned} K(T) = \text{Tr} \exp(-i\hat{H}T) = \sum_k \int \prod_t d\mu(\mathbf{Q}(t), \mathbf{P}(t)) \exp\{i[\mathbf{P}(t) \cdot \dot{\mathbf{Q}}(t) - H_B(\mathbf{P}(t), \mathbf{Q}(t))]\} \\ \times \langle \tilde{\varphi}_k(\mathbf{Q}(0), \mathbf{P}(0), 0) | T \exp[-i\hat{H}_F(\mathbf{P}(t), \mathbf{Q}(t))] | \tilde{\varphi}_k(\mathbf{Q}(0), \mathbf{P}(0), 0) \rangle, \end{aligned}$$

where $\mathbf{Q}(0) = \mathbf{Q}(T)$, $\mathbf{P}(0) = \mathbf{P}(T)$, and $\tilde{\varphi}_k(\mathbf{Q}(0), \mathbf{P}(0), 0)$ are the eigenvectors of the fermionic evolution operator

$$T \exp \left[-i \int_0^T dt \hat{H}_F(\mathbf{P}(t), \mathbf{Q}(t)) \right] \tilde{\varphi}_k(\mathbf{Q}(0), \mathbf{P}(0), 0) = \exp(i\delta_k) \tilde{\varphi}_k(\mathbf{Q}(0), \mathbf{P}(0), 0) = \tilde{\varphi}_k(\mathbf{Q}(T), \mathbf{P}(T), T).$$

Now the fermionic wave functions $\bar{\varphi}_k(\mathbf{Q}(t), \mathbf{P}(t), t)$ play the same role as the instantaneous eigenvectors of the fermionic part of the Hamiltonian in the adiabatic approximation. After some simple manipulations one ends up with the following expression:

$$K(T) = \sum_k \int \prod_t d\mu(\mathbf{Q}(t), \mathbf{P}(t)) \exp\{i[\mathbf{P}(t)\dot{\mathbf{Q}}(t) - H_B(\mathbf{P}(t), \mathbf{Q}(t))]\} \\ \times \exp \left[i \left[-\langle \bar{\varphi}_k(\mathbf{Q}(t), \mathbf{P}(t), t) | \hat{H}_F(\mathbf{P}(t), \mathbf{Q}(t)) | \bar{\varphi}_k(\mathbf{Q}(t), \mathbf{P}(t), t) \rangle \right. \right. \\ \left. \left. + i \left\langle \bar{\varphi}_k(\mathbf{Q}(t), \mathbf{P}(t), t) \left| \frac{\partial \bar{\varphi}_k(\mathbf{Q}(t), \mathbf{P}(t), t)}{\partial t} \right. \right\rangle \right] \right].$$

The expectation value of the fermionic Hamiltonian plays the role of additional potential energy for the bosonic system as one would expect. However, there is an additional term and one will be inclined to simply discard this term in a semiclassical treatment of the bosons. As we already know from the adiabatic result, this is not the case and this term has to be taken properly into account in a quantum description. Consequently, the effective action for the bosonic degrees of freedom acquires a topological contribution (the last term in the exponent) formally similar to the one obtained in the adiabatic approximation.⁶ The simple form of the effective action is due to the special choice of the fermionic wave functions, described above.

CONCLUSIONS

Whenever a physical system is split into two parts in order to simplify the analysis and part of the variables are integrated out, an additional term appears in the effective action. This term has a geometrical (sometimes called topological) nature. The meaning is simple. A subsystem can reach a final quantum state following different paths, which cannot be deformed continuously one into another. The effect of the fast variables on the slow ones cannot be described in terms of potential energy only and, in general, one has to take into account effective gauge fields generated by the fast subsystem. Upon quantization, one will observe the appearance of additional terms in the standard Bohr-Sommerfeld rule, which do not have the usual interpretation as arising from classical turning

points. These terms manifest themselves as additional phases. We showed that such terms are present always, the adiabatic assumption being unnecessary. In addition to that, we established a sum rule for the quantum phases.

One can use the present result for studying situations, when there is a real or avoided level crossing, as in the famous Landau-Zener effect, or when there are several close electronic terms, and the energy separation among them is small enough to prevent the adiabatic approximation from being applied. The simplest approach will be as follows: Include relevant electronic configurations, represent the electronic wave function as a superposition of only these configurations, and find the corresponding periodic solutions for a given period. With the electronic wave function found in this manner, compute the effective nuclear action and apply to it the Bohr-Sommerfeld quantization rule, which will give an equation for the period.

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