Photon echoes and Berry's phase

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We prove a theorem linking the phase associated with the ballistic evolution of a coherent state of a harmonic oscillator about a jumping vertex to that associated with its adiabatic migration along straight lines connecting the initial and the final points of each ballistic arc to the vertex on which the arc is centered. This equivalence allows one to determine the ballistic phase by Berry's prescription. The method facilitates both the visualization and the calculation of modulation effects (quantum beats) in photon-echo experiments.

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I. INTRODUCTION

Photon-echo experiments are potentially sensitive detectors of Berry phase [1] effects. In the stimulated echo configuration, where three excitation pulses are applied at t_1, $t_2 = t_1 + \tau$, and $t_3 = t_1 + T$, an echo is observed at $t_4 = t_1 + \tau + T$, which is the result of an interference from contributions associated with two distinct pairs of atomic state trajectories [2,3]. Associated with each pair is a phase, and since there is an interference, any difference in the phases can be detected. For simple two-level atoms this difference vanishes, but in more complicated molecules it may receive nonzero contributions from the degrees of freedom (vibronic) associated with nuclear motion. An example is the typical organic dye molecule. Although basically a two-level (electronic) system, it is subject to a multitude of vibronic excitations that complicate the formation of the echo [4–9].

The distinct pairs of trajectories we referred to are distinguished by their electronic state histories following the second excitation pulse. In one pair it is the excited electronic state superposition states that evolve to produce a coherent dipole moment; in the other it is the ground state superposition states.

Each of these contributions is influenced by vibronic evolution. Fortunately the analysis of the vibronic evolution is considerably simplified by using coherent states parametrized by a complex number α and defined as

$$|\alpha\rangle \equiv D(\alpha)\ |0\rangle = e^{-\frac{1}{2}|\alpha|^2} e^{\alpha a^\dagger}\ |0\rangle\ , \qquad (1.1)$$

where $D(\alpha) = e^{\alpha a^\dagger - \alpha^* a} = e^{-\frac{1}{2}|\alpha|^2} e^{\alpha a^\dagger} e^{-\alpha^* a}$ is the displacement operator, $[a,\, a^\dagger] = 1$, and $|0\rangle$ is the lowest vibronic state [10]. These states satisfy

$$a\ |\alpha\rangle = \alpha\ |\alpha\rangle\,. \qquad (1.2)$$

For each vibronic mode there is a simple trajectory in α space that describes the coherent state evolution. We have found that the diagrams showing these trajectories, which we call α diagrams, directly give the contribution of the vibronic mode to the magnitude and phase of the stimulated echo [11]. For the stimulated echo there are two diagrams whose results must be combined. They yield identical magnitudes but differ in phase. This phase difference thus contributes to the echo modulation.

In a previous paper we have called this phase a Berry phase [11]. The aim of the present paper is to justify this usage by a theorem that states that this phase is identical to the Berry phase associated with a related adiabatic process. The phase is therefore given by an area rule. We shall use the term radial adiabatic simulation (RAS) for the replacement of a ballistic trajectory in α space by the appropriate adiabatic trajectory, as the latter trajectory consists of the radii bounding the angles subtended by the ballistic arcs.

In Sec. II we shall review the theory of a harmonic oscillator with a variable equilibrium point and shall obtain an expression whose integral over time determines the phase of the wave function. In Sec. III we shall present and prove our theorem linking our problem to that of the Berry phase. In Sec. IV we shall use Berry's formula to obtain an area rule for the relative phase of two trajectories. In Sec. V we shall derive the same area rule directly from our formula of Sec. II. In Sec. VI we illustrate the application of our theorem to the stimulated echo problem. The application of the area rule to the trilevel echo problem is also briefly considered.

II. DISPLACED HARMONIC OSCILLATOR

Let a be the standard lowering operator, with

$$[a,\, a^\dagger] = 1, \qquad (2.1)$$

and let $\delta = \delta(t)$ be some time-dependent c-number "displacement." We are interested in the evolution of a system under the Hamiltonian

$$H = H(t) = \hbar\omega\ [a - \delta(t)]^\dagger\ [a - \delta(t)]\,. \qquad (2.2)$$

If δ is real, this Hamiltonian represents an oscillator with its equilibrium point displaced in position space. The

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spectrum of H is taken to be time independent. The solution of Schrödinger's equation

$$i \frac{d}{dt} |t\rangle = \omega \{a^\dagger - [\delta(t)]^*\} [a - \delta(t)] |t\rangle \qquad (2.3)$$

is readily seen, by substitution of Eq. (1.1), to be

$$|t\rangle = e^{i\phi} |\alpha\rangle , \qquad (2.4)$$

where ϕ (real) and α (complex) depend on time according to

$$i\dot{\alpha} = \omega [\alpha - \delta(t)] \qquad (2.5)$$

and

$$-\dot{\phi} - \tfrac{i}{2} (\dot{\alpha}\alpha^* + \alpha\dot{\alpha}^*) = -\omega [\delta(t)^*] [\alpha - \delta(t)] . \qquad (2.6)$$

By repeated application of Eq. (2.5), we may transform Eq. (2.6) into

$$\dot{\phi} = \mathrm{Im}\,(\dot{\alpha}^* \delta) . \qquad (2.7)$$

Now, if δ remains constant over an interval of time, the increment of ϕ over that time is

$$\Delta\phi = \mathrm{Im}\,(\Delta\alpha^* \delta) , \qquad (2.8)$$

which is twice the area of a triangle in the complex plane two of whose sides are $\Delta\alpha$ and δ. The appearance of such an area brings the Berry phase to mind. We therefore leave Eq. (2.7) for the moment and turn to a general theorem relating ballistic to adiabatic changes of a harmonic oscillator.

III. EQUIVALENCE THEOREM

Suppose that an oscillator is prepared in the state $|\alpha_0\rangle$ at the time t_0 and evolves from t_0 to t under the Hamiltonian Eq. (2.2). Then at time t the state is $U_\delta(t, t_0) |\alpha_0\rangle$, where

$$U_\delta(t, t_0) \equiv \mathcal{T} \exp \int_{t_0}^{t} -i\omega \left[a^\dagger - \delta^*(\tau)\right] \left[a - \delta(\tau)\right] d\tau \qquad (3.1)$$

and $\mathcal{T}$ denotes time ordered.

The system might, however, have been prepared in a different state $|\alpha'_0\rangle$ at t_0 and evolved under a Hamiltonian determined by a different function $\delta'(\tau)$. Then its final state at time t would be $U_{\delta'}(t, t_0) |\alpha'_0\rangle$.

Our interest is in the effect of these parallel evolutions on the relative phase of the two wave functions. That is, we want to find

$$\Phi \equiv \arg \langle\alpha'_0| U^\dagger_{\delta'}(t, t_0)\, U_\delta(t, t_0) |\alpha_0\rangle - \arg \langle\alpha'_0 \mid \alpha_0\rangle . \qquad (3.2)$$

Our theorem applies most conveniently to the case where $\delta(\tau)$ and $\delta'(\tau)$ are multiple step functions changing only at discrete times. That is, we suppose that

$$\delta(\tau) = \delta_n, \qquad (3.3)$$

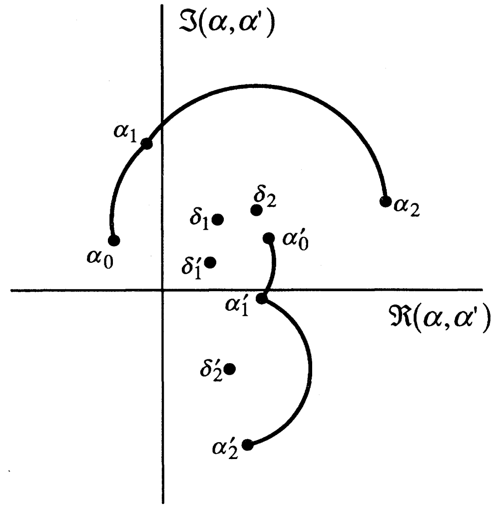

FIG. 1. Pair of ballistic trajectories corresponding to Hamiltonians H_δ and $H_{\delta'}$ (case $N = 2$ of the text) where $\delta(t) = \delta_1$ during the first (shorter) time interval and $\delta(t) = \delta_2$ during the second (longer) interval. During these same intervals $\delta'(t) = \delta'_1$ and δ'_2. The corresponding trajectories follow the arcs $\alpha_0 \to \alpha_1 \to \alpha_2$ and $\alpha'_0 \to \alpha'_1 \to \alpha'_2$. Note that $\alpha_0 \to \alpha_1$ is centered on δ_1, etc.

$$\delta'(\tau) = \delta'_n \qquad (3.4)$$

in the interval $t_{n-1} < t < t_n$, where $t_0 < t_1 < \cdots < t_N = t$.

It is clear from Eqs. (2.4) and (2.5) that

$$U_\delta(t, t_0) |\alpha_0\rangle = e^{i\phi_\delta} |\alpha_N\rangle \qquad (3.5)$$

for some phase ϕ_δ, where α_N is a complex number obtained from α_0 by executing a series of circular arcs $\alpha_0 \to \alpha_1 \to \cdots \to \alpha_N$. The arc from α_{n-1} to α_n has center δ_n and runs clockwise through an angle of $\omega(t_n - t_{n-1})$ radians (see Fig. 1). A similar formula holds for the primed trajectory. Obviously

$$\Phi = \phi_\delta - \phi_{\delta'} + \arg \langle\alpha'_N \mid \alpha_N\rangle - \arg \langle\alpha'_0 \mid \alpha_0\rangle . \qquad (3.6)$$

Let us now consider an oscillator prepared in the state $|\alpha_0\rangle$ and subjected to the Hamiltonian

$$H_\gamma = \hbar\omega\, (a - \gamma)^\dagger\, (a - \gamma) , \qquad (3.7)$$

where the complex parameter γ changes adiabatically by migrating along the closed polygon in the complex plane whose vertices are successively α_0, δ_1, α_1, ... , α_{N-1}, δ_N, α_N, α'_N, δ'_N, α'_{N-1}, ... , α'_1, δ'_1, α'_0, α_0. That is, each arc $\alpha_{n-1} \to \alpha_n$ is replaced by a pair of straight lines $\alpha_{n-1} \to \delta_n \to \alpha_n$; the primed evolution is treated similarly and run backward and the polygon is closed by straight lines $\alpha_N \to \alpha'_N$ and $\alpha'_0 \to \alpha_0$ (see Fig. 2). This polygonal trajectory is the RAS path (see Sec. I) corresponding to the given pair of ballistic trajectories represented by $U_\delta(t, t_0)$ and $U_{\delta'}(t, t_0)$.

The equivalence theorem then states that the RAS

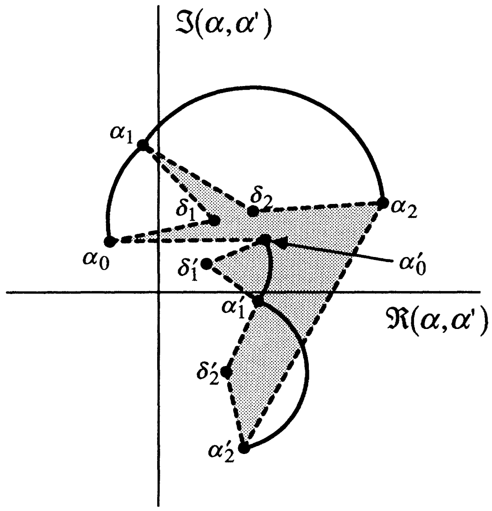

FIG. 2. Same as Fig. 1 with the addition of dotted lines showing the RAS or equivalent Berry trajectory. Each pair of radii ($\alpha_0 \to \delta_1 \to \alpha_1$, etc.) adiabatically simulates the corresponding arc ($\alpha_0 \to \alpha_1$, etc.) and the whole closed (dotted) polygon produces a Berry phase (equal to twice the shaded area) identical to the phase difference introduced between the unprimed and the primed states by their simultaneous evolution under H_δ and H'_δ.

evolution under Eq. (3.7) will carry the state $|\alpha_0\rangle$ to $e^{i\Phi}\,|\alpha_0\rangle$, where Φ is the same phase as given by Eq. (3.2). Therefore Berry's theorem for adiabatic closed paths (see Sec. IV) can be used to evaluate Eq. (3.2).

To prove the theorem we introduce some simple notation. Under the Hamiltonian (2.2), with γ migrating adiabatically *along a straight line* from γ_i to γ_f, an initial state $|i\rangle$ will evolve to some final state $|f\rangle$; it is understood that the kets $|i\rangle$, $|f\rangle$ *include the right phase factors.* We express such a fact by writing

$$|i\rangle \underset{\gamma_i\to\,\gamma_f}{\longrightarrow} |f\rangle\,. \tag{3.8}$$

Under this notation it can be shown (see Appendix A) that for any complex Γ, $|0\rangle \underset{0\to\Gamma}{\longrightarrow} |\Gamma\rangle$ *with no phase factor missing.* Likewise $|\Gamma\rangle \underset{\Gamma\to 0}{\longrightarrow} |0\rangle$. Putting these results together, for any complex Γ and real τ, we can write

$$|\Gamma\rangle \underset{\Gamma\to 0\to\Gamma e^{-i\omega\tau}}{\longrightarrow} |\Gamma e^{-i\omega\tau}\rangle\,, \tag{3.9}$$

where the adiabatic process consists of two straight-line migrations, from $\gamma = \Gamma$ to $\gamma = 0$ to $\gamma = \Gamma e^{-i\omega\tau}$.

Now consider the nth interval in our ballistic process, characterized by an evolution operator

$$U_n = U_\delta(t_n, t_{n-1}) = D(\delta_n)U_0(t_n - t_{n-1})D^{-1}(\delta_n), \tag{3.10}$$

where $U_0(\tau) = e^{-i\omega a^\dagger a(\tau)}$. It is evident from Eqs. (2.4), (2.5), and (2.7) with $\delta = 0$ that $U_0\,(\tau)\,|\Gamma\rangle = |\Gamma e^{-i\omega\tau}\rangle$ for arbitrary complex Γ. Applying (3.9) we then have

$$|\Gamma\rangle \underset{\Gamma\to\;0\to\Gamma e^{-i\omega\tau}}{\longrightarrow} U_0\,(\tau)\;|\Gamma\rangle\,. \tag{3.11}$$

In view of (2.5) we have $\alpha_n - \delta_n = e^{-i\omega(t_n - t_{n-1})}(\alpha_{n-1} - \delta_n)$; therefore, setting $\Gamma = \alpha_{n-1} - \delta_n$, we have

$$|\alpha_{n-1} - \delta_n\rangle \underset{\alpha_{n-1}\to 0\to\alpha_n-\delta_n}{\longrightarrow} U_0\,(t_n - t_{n-1})\;|\alpha_{n-1} - \delta_n\rangle\,. \tag{3.12}$$

We now observe that any adiabatic process can be subjected to a unitary transformation and therefore any statement of the form $|i\rangle \underset{\Gamma_i\to\Gamma_f}{\longrightarrow} |f\rangle$ can be transformed to $D\,(\delta)\;|i\rangle \underset{\Gamma_i+\delta\to\Gamma_f+\delta}{\longrightarrow} D\,(\delta)\;|f\rangle$. Applying this transformation to (3.12) we find

$$\begin{aligned} &D\,(\delta_n)\,|\alpha_{n-1} - \delta_n\rangle \\ &\underset{\alpha_{n-1}\to\delta_n\to\alpha_n}{\longrightarrow} D\,(\delta_n)\;U_0\,(t_n - t_{n-1})\;|\alpha_{n-1} - \delta_n\rangle \\ &\quad = U_n D(\delta_n)|\alpha_{n-1} - \delta_n\rangle. \end{aligned} \tag{3.13}$$

Finally, since $D(\delta)|\alpha - \delta\rangle$ is the same as $|\alpha\rangle$ apart from a phase factor, we have

$$|\alpha_{n-1}\rangle \underset{\alpha_{n-1}\to\delta_n\to\alpha_n}{\longrightarrow} U_n\;|\alpha_{n-1}\rangle\,; \tag{3.14}$$

the same phase factor has been dropped from both sides of the arrow.

Equation (3.13) shows that the ballistic evolution from $|\alpha_{n-1}\rangle$ to $U_n|\alpha_{n-1}\rangle$ is correctly simulated, *including the right phase factor,* by the RAS adiabatic evolution from α_{n-1} to δ_n to α_n. Since, moreover, $|\alpha_{n-1}\rangle$ is the same, apart from a phase factor, as $U_\delta(t_{n-1}, t_0)|\alpha_0\rangle$, we can again drop this factor from both sides and obtain $U_\delta\,(t_{n-1},\, t_0)\;|\alpha_0\rangle \underset{\alpha_{n-1}\to\delta_n\to\alpha_n}{\longrightarrow} U_\delta\,(t_n,\, t_0)\;|\alpha_0\rangle$.

In this form it is clear that the n intervals can be concatenated so as to yield

$$|\alpha_0\rangle \underset{\alpha_0\to\delta_1\to\cdots\to\alpha_N}{\longrightarrow} U_\delta\,(t_N,\, t_0)\;|\alpha_0\rangle = e^{i\,\phi_\delta}\;|\alpha_N\rangle\,. \tag{3.15}$$

Likewise

$$e^{i\,\phi'_\delta}\;|\alpha'_N\rangle \underset{\alpha'_N\to\delta'_N\to\cdots\to\alpha'_0}{\longrightarrow} |\alpha'_0\rangle\,. \tag{3.16}$$

We now consider the connecting links from α_N to α'_N and from α'_0 to α_0. It is shown in Appendix B that the adiabatic path straight from Γ_i to Γ_f takes $|\Gamma_i\rangle$ to $e^{i\phi}|\Gamma_f\rangle$ where ϕ is just the phase of $\langle\Gamma_f|\Gamma_i\rangle$; that is,

$$|\Gamma_i\rangle \underset{\Gamma_i\to\Gamma_f}{\longrightarrow} e^{i\,\arg\langle\Gamma_f|\Gamma_f\rangle}\;|\Gamma_f\rangle\,. \tag{3.17}$$

With $\Gamma_i = \alpha'_0$, $\Gamma_f = \alpha_0$, we obtain

$$|\alpha'_0\rangle \underset{\alpha'_0\to\alpha_0}{\longrightarrow} e^{i\,\arg\langle\alpha_0|\alpha'_0\rangle}\;|\alpha_0\rangle\,. \tag{3.18}$$

With $\Gamma_i = \alpha_N$, $\Gamma_f = \alpha'_N$, and using (3.15) and (3.16), we obtain

$$|\alpha_0\rangle \underset{\alpha_0\to\delta_1\to\cdots\to\alpha'_N\to\delta'_N\to\cdots\to\alpha'_0}{\longrightarrow} e^{(i\,\phi_\delta - i\,\phi_{\delta'})}\, e^{i\,\arg\langle\alpha'_N|\alpha_N\rangle}\, |\alpha'_0\rangle\,. \tag{3.19}$$

Combining this with (3.18) we have the equivalence theorem.

IV. AREA LAW FROM BERRY'S THEOREM

To apply Berry's theorem to our RAS path in the α plane, we start from Eq. (7b) of [1], which gives the phase Φ [there called $\gamma_n(C)$] as

$$\gamma_n(C) = -\mathrm{Im}\iint_C dS\,\langle\nabla n|\times|\nabla n\rangle, \tag{4.1}$$

which we shall write as

$$\Phi = -\mathrm{Im}\iint dxdy\,\langle\alpha|\,\overleftarrow{\nabla}\times\vec{\nabla}\,|\alpha\rangle. \tag{4.2}$$

Here $\alpha = x+i\,y$, $\vec{\nabla} = \hat{\vec{x}}\,\frac{\partial}{\partial x}+\hat{\vec{y}}\,\frac{\partial}{\partial y}$ acting on the ket to the right, and $\overleftarrow{\nabla}$ is the same operator acting on the bra to the left. The symbol $\times$ denotes the (scalar) cross product in two dimensions; thus (using arrows also to indicate the action of $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial y}$)

$$\begin{aligned}\overleftarrow{\nabla}\times\vec{\nabla} &= \frac{\overleftarrow{\partial}}{\partial x}\frac{\vec{\partial}}{\partial y} - \frac{\overleftarrow{\partial}}{\partial y}\frac{\vec{\partial}}{\partial x}\\ &= 2\,i\left(\frac{\overleftarrow{\partial}}{\partial\alpha^*}\frac{\vec{\partial}}{\partial\alpha} - \frac{\overleftarrow{\partial}}{\partial\alpha}\frac{\vec{\partial}}{\partial\alpha^*}\right)\end{aligned} \tag{4.3}$$

by the chain rule. The integral ranges over the portion of the x-y plane enclosed by the adiabatic path.

Now, $|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}\,e^{\alpha\,a^\dagger}\,|0\rangle$ and therefore

$$\frac{\partial}{\partial\alpha}\,|\alpha\rangle = \left(-\tfrac{1}{2}\,\alpha^* + a^\dagger\right)\,|\alpha\rangle\ , \tag{4.4a}$$

$$\frac{\partial}{\partial\alpha^*}\,|\alpha\rangle = -\tfrac{1}{2}\,\alpha\,|\alpha\rangle = \left(+\tfrac{1}{2}\,\alpha - a\right)\,|\alpha\rangle\,; \tag{4.4b}$$

see Eq. (1.2). It follows that

$$\begin{aligned}&\langle\alpha|\left(\frac{\overleftarrow{\partial}}{\partial\alpha^*}\frac{\vec{\partial}}{\partial\alpha} - \frac{\overleftarrow{\partial}}{\partial\alpha}\frac{\vec{\partial}}{\partial\alpha^*}\right)|\alpha\rangle\\ &\quad= \langle\alpha|\,\left[\left(-\tfrac{1}{2}\,\alpha + a\right),\,\left(-\tfrac{1}{2}\,\alpha^* + a^\dagger\right)\right]\,|\alpha\rangle\\ &\quad= 1.\end{aligned} \tag{4.5}$$

This gives Berry's phase as

$$\Phi = \iint dx\,dy\;(-2), \tag{4.6}$$

which is twice the area on the complex plane enclosed by the path. Since Berry's formula was derived from Stokes's law, which assumes that the area is enclosed counterclockwise, the negative sign tells us to assign a positive phase to area encircled clockwise.

V. DIRECT DERIVATION OF THE AREA LAW

Here we shall derive the area law directly from Eq. (2.7), for the case in which $\delta(t)$ is a multiple step function as described by Eqs. (3.3) and (3.4). Integrating Eq. (2.7), with constant $\delta = \delta_n$, we find that the ballistic evolution of $\alpha(t)$ from α_{n-1} to α_n produces a phase $\mathrm{Im}\left[\left(\alpha_n^* - \alpha_{n-1}^*\right)\,\delta_n\right]$. Now $\mathrm{Im}\,(\alpha_n^*\,\delta_n)$ is twice the area enclosed (all areas will be counted as positive when encircled clockwise) by a triangular path from 0 to δ_n to α_n to 0. Likewise $-\mathrm{Im}\,\left(\alpha_{n-1}^*\,\delta_n\right)$ corresponds to the triangle $0\to\alpha_{n-1}\to\delta_n\to 0$. Therefore $\mathrm{Im}\left[\left(\alpha_n - \alpha_{n-1}\right)^*\,\delta_n\right]$ is twice the area enclosed by $0\to\alpha_{n-1}\to\delta_n\to 0\to\delta_n\to\alpha_n\to 0$, which can be shortened to $0\to\alpha_{n-1}\to\delta_n\to\alpha_n\to 0$.

Now, by adding together N steps, we find that ϕ_δ, defined by Eq. (3.5), is twice the area enclosed by

$$\begin{aligned}&0\to\alpha_0\to\delta_1\to\alpha_1\to 0\to\alpha_1\to\delta_2\to\cdots\\ &\quad\to\delta_N\to\alpha_N\to 0\end{aligned} \tag{5.1}$$

or, more shortly, by

$$\begin{aligned}&0\to\alpha_0\to\delta_1\to\alpha_1\to\delta_2\to\alpha_2\to\cdots\\ &\quad\to\alpha_{N-1}\to\delta_N\to\alpha_N\to 0\ .\end{aligned} \tag{5.2}$$

Likewise $-\phi_{\delta'}$ is twice the area enclosed by

$$0\to\alpha'_N\to\delta'_N\to\ \cdots\ \to\delta'_1\to\alpha'_0\to 0. \tag{5.3}$$

The inner product $\langle\alpha'\mid\alpha\rangle = e^{-\frac{1}{2}|\alpha'-\alpha|^2}\,e^{\frac{1}{2}(\alpha'^*\alpha - \alpha'\alpha^*)}$ carries a phase $-\mathrm{Im}\,(\alpha'\,\alpha^*)$, which is twice the area enclosed by

$$0\to\alpha\to\alpha'\to 0\ . \tag{5.4}$$

Now the net phase Φ defined by Eq. (3.2) is, by Eqs. (5.2)–(5.4), just twice the area enclosed by

$$0\to\alpha_0\to\delta_1\to\ \cdots\ \to\delta_N\to\alpha_N\to 0\to\alpha_N\to\alpha'_N\to 0\to\alpha'_N\to\delta'_N\to\ \cdots\ \to\delta'_1\to\alpha'_0\to 0\to\alpha'_0\to\alpha_0\to 0.$$

But again by canceling out the retraced paths, we eliminate the point 0 and obtain

$$\alpha_0 \to \delta_1 \to \cdots \to \delta_N \to \alpha_N \to \alpha'_N \to \delta'_N \to \cdots$$
$$\to \delta'_1 \to \alpha'_0$$
$$\to \alpha_0 .$$

This is the same polygon whose area appeared in Berry's theorem in Sec. IV.

Inasmuch as we have derived the area law here without referring to RAS paths or Berry's theorem, the whole equivalence theorem may be deemed superfluous. We remind the reader, though, that the argument traced in Secs. III and IV bypasses the algebraic manipulations that lie behind the general solution Eqs. (2.5)–(2.7) of the ballistic problem. Our chief motive for introducing Berry's theorem, however, is not to make the area law easier to derive, but rather to understand it in the light of the deeper insights associated with the Berry phase.

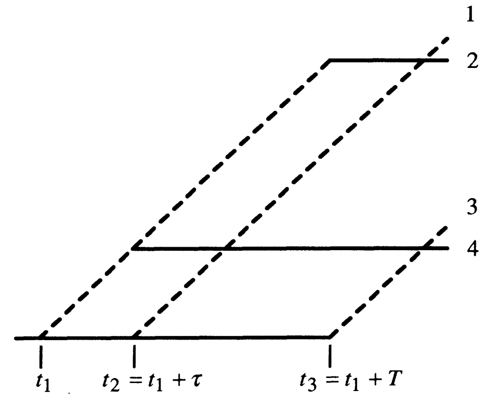

FIG. 3. Familiar recoil or excitation diagram describing a stimulated echo with copropagating beams. The echo amplitude at time $T+\tau$ is the sum of two terms associated with the path crossings 1-2 and 3-4. Normally each term can be read off from the diagram by rules given elsewhere [2]. In the presence of vibronic excitation each term receives an additional factor whose phase is the subject of this paper.

VI. APPLICATION OF THE AREA LAW

As an example we calculate the amplitude of the stimulated echo in a two-level (transition frequency Ω) electronic system with one vibronic mode (vibronic frequency ω). The Hamiltonian, including the interaction with the radiation field, is

$$H = H_\Omega + H_\omega + H_{\rm int}, \tag{6.1}$$

where

$$H_\Omega = -\tfrac{1}{2}\,\hbar\Omega\, |g\rangle\langle g| + \tfrac{1}{2}\,\hbar\Omega\, |e\rangle\langle e| , \tag{6.2}$$

$$H_\omega = \hbar\,\omega\left(a^\dagger a + \tfrac{1}{2}\right)\, |g\rangle\langle g| + \hbar\,\omega\left(b^\dagger b + \tfrac{1}{2}\right)\, |e\rangle\langle e| , \tag{6.3}$$

and

$$H_{\rm int} = -{\rm Re}\left[E\,(t)\; e^{i\,(k\cdot r - \Omega\, t)}\right]\{P_{eg}\; |e\rangle\langle g| + P_{ge}\; |g\rangle\langle e|\} \;, \tag{6.4}$$

where $b = a - \delta$, $[a,\, a^\dagger] = [b,\, b^\dagger] = 1$, $P_{ij} = \langle i|\,\mathbf{P}\cdot\hat{\mathbf{e}}\;|j\rangle$, and the wave function follows $\dot\Psi = -\frac{i}{\hbar}\,H\,\Psi$. Here δ is a fixed number that measures the strength of the Franck-Condon effect. The radiation field amplitude $E\,(t)$ consists of a series of short pulses of area θ_1, θ_2, and θ_3 applied at t_1, $t_2 = t_1 + \tau$, and $t_3 = t_1 + T$. These pulses put each atom's wave function into a linear superposition of states so that overall

$$\Psi = \prod_j \sum_p \Psi_p^j \;, \tag{6.5}$$

where j runs over the atoms and p the states (or paths). The atoms are taken to be identical so we drop the index j. The vibronic and electronic states factor, and we write

$$\Psi_p = |\psi_{\rm vib},\, \psi_{\rm elec}\rangle_p \,. \tag{6.6}$$

The electronic evolution is best visualized by using a recoil diagram (in the case of a gas) or an excitation diagram (for a solid) (see Fig. 3). For sensibly collinear excitation pulses the two kinds of diagrams are similar. Only the trajectory pairs labeled 1,2 and 3,4 cross at $t = T + \tau$ to form the stimulated echo. The dipole moment, which in general is given by

$$\langle\Psi|\,\mathbf{P}\,|\Psi\rangle = N\sum_{p,p'}\langle\Psi_p|\,\mathbf{P}\,|\Psi'_p\rangle \;, \tag{6.7}$$

therefore reduces to

$$\begin{aligned}
\langle\Psi|\;\mathbf{P}\;|\Psi\rangle &= N\;\{{}_2\langle\psi_{\rm vib}\mid\psi_{\rm vib}\rangle_1\;{}_2\langle\psi_{\rm elec}|\;\mathbf{P}\;|\psi_{\rm elec}\rangle_1 \;+\; {}_4\langle\psi_{\rm vib}\mid\psi_{\rm vib}\rangle_3\;{}_4\langle\psi_{\rm elec}|\;\mathbf{P}\;|\psi_{\rm elec}\rangle_3\}\\
&= N\;\langle\mathbf{P}\rangle\; f\,(t)\;{}_2\langle\psi_{\rm vib}\mid\psi_{\rm vib}\rangle_1\\
&\quad\times\left\{\cos\tfrac{\theta_1}{2}\; i\,\sin\tfrac{\theta_2}{2}\;\cos\tfrac{\theta_3}{2}\; e^{-i\,\Omega\,(t-\tau)}\; e^{-i(\mathbf{k}-\mathbf{k_2})\cdot\mathbf{r}}\right\}\left\{i\,\sin\tfrac{\theta_1}{2}\;\cos\tfrac{\theta_2}{2}\; i\,\sin\tfrac{\theta_3}{2}\; e^{-i\,\Omega\,T}\; e^{i\,(\mathbf{k_1}-\mathbf{k_3})\cdot\mathbf{r}}\right\}^* + \text{c.c.}\\
&\quad+N\;\langle\mathbf{P}\rangle\; f\,(t)\;{}_4\langle\psi_{\rm vib}\mid\psi_{\rm vib}\rangle_3\\
&\quad\times\left\{\cos\tfrac{\theta_1}{2}\;\cos\tfrac{\theta_2}{2}\; i\,\sin\tfrac{\theta_3}{2}\; e^{-i\,\Omega\,(t-T)}\; e^{-i(\mathbf{k}-\mathbf{k_3})\cdot\mathbf{r}}\right\}\left\{i\,\sin\tfrac{\theta_1}{2}\; i\,\sin\tfrac{\theta_2}{2}\;\cos\tfrac{\theta_3}{2}\; e^{-i\,\Omega\,\tau}\; e^{i\,(\mathbf{k_1}-\mathbf{k_2})\cdot\mathbf{r}}\right\}^* + \text{c.c.}\\
&= \tfrac{N}{2^3}\;\langle\mathbf{P}\rangle\; f\,(t)\;\{{}_2\langle\psi_{\rm vib}\mid\psi_{\rm vib}\rangle_1 + {}_4\langle\psi_{\rm vib}\mid\psi_{\rm vib}\rangle_3\}\;\sin\theta_1\;\sin\theta_2\;\sin\theta_3\, e^{-i\,\Omega\,(t-T-\tau)}\; e^{-i\,(\mathbf{k}-\mathbf{k_3}-\mathbf{k_2}+\mathbf{k_1})\cdot\mathbf{r}}.
\end{aligned} \tag{6.8}$$

The complex function $f(t)$ peaks in magnitude at $T+\tau$ and has a phase that is dependent on the phases of the excitation pulses. The electronic contributions constructively interfere. We have used θ_j and k_j to denote the areas and k vectors, respectively, of the first, second, and third excitation pulses. In the previous sections the labeling of the vibronic α was associated with the $(n-1)$ th excitation pulse.

It now remains to evaluate the vibronic matrix elements. Each state $|\psi_{\rm vib}\rangle_p$, $p = 1,\ldots,4$, is arrived at by an evolution under a Hamiltonian of the form Eq. (2.2), where in accordance with Eq. (6.3) the value of $\delta(t)$ is $\delta_g \equiv 0$ or $\delta_e \equiv \delta$, depending on whether the path p puts the molecule in the electronic state g or e at time t. For ease of notation, in discussing the matrix element $V_{pp'} \equiv {}_{p'}\langle\psi_{\rm vib} \mid \psi_{\rm vib}\rangle_p$ we shall let α_t and β_t describe respectively the ket and the bra at time t. Then the magnitude of the matrix element is

$$|V_{pp'}| = e^{-\frac{1}{2}|\alpha_t-\beta_t|^2} \tag{6.9}$$

and its argument is given by the area rule; therefore the matrix element can be found entirely from the α-diagram of the two trajectories p and p'.

Consider first the matrix element $V_{12} = |V_{12}|\, e^{i\,\Phi_{12}}$. The evolution of $|\psi_{\rm vib}\rangle_1$ can be described in a modification of the schematic notation of Sec. III as

$$\alpha_0 = 0 \underset{\delta_g}{\overset{\text{ballistic}}{\longrightarrow}} \alpha_\tau = 0 \underset{\delta_e}{\overset{\text{ballistic}}{\longrightarrow}} \alpha_t = \delta(1-e^{-i\omega(t-\tau)})$$

and that of $|\psi_{\rm vib}\rangle_2$ as

$$\beta_0 = 0 \underset{\delta_e}{\overset{\text{ballistic}}{\longrightarrow}} \beta_T = \delta(1-e^{-i\omega T})$$

$$\underset{\delta_g}{\overset{\text{ballistic}}{\longrightarrow}} \beta_t = \beta_T e^{-i\omega(t-T)},$$

where t is any time later than all the pulses. Thus from Eq. (6.9) we have

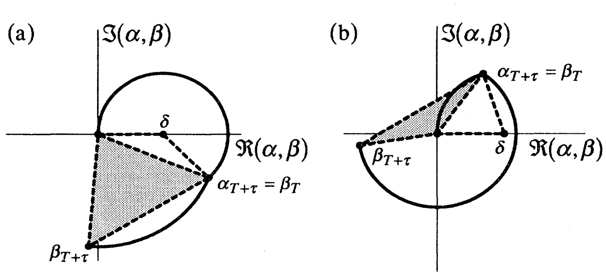

FIG. 4. α trajectories associated with (a) paths 1 and 2 and (b) paths 3 and 4 are shown along with the RAS path (dotted lines) in the manner of Fig. 2. The RAS polygons in (a) $\alpha_0 = \alpha_\tau \to \delta \to \alpha_{T+\tau} \to \beta_{T+\tau} \to 0 \to \beta_T \to \delta \to \beta_0 = \alpha_0$ and (b) $\alpha_0 = \alpha_T \to \delta \to \alpha_{T+\tau} \to \beta_{T+\tau} \to 0 \to \beta_\tau \to \delta \to \beta_0 = \alpha_0$ have a common edge $|\alpha_{T+\tau} - \beta_{T+\tau}|$. The enclosed (shaded) areas represent half the Berry phase. The areas in (a) and (b) are clearly different.

$$\begin{aligned}|V_{12}| &= e^{-\frac{1}{2}|\alpha_t-\beta_t|^2} \\ &= e^{-\frac{1}{2}|\delta|^2\left|\left(1-e^{-i\omega(t-\tau)}\right)-\left(1-e^{-i\omega T}\right)e^{-i\omega(t-T)}\right|^2} \\ &= e^{-\frac{1}{2}|\delta|^2\left|1+e^{-i\omega t}-e^{-i\omega(t-\tau)}-e^{-i\omega(t-T)}\right|^2}\,, \end{aligned} \tag{6.10}$$

which at $t = T+\tau$, the time of the echo, reduces to

$$|V_{12}| = e^{-8|\delta|^2 \sin^2(\omega\tau/2)\sin^2(\omega T/2)}. \tag{6.11}$$

The phase Φ_{12} is twice the area enclosed clockwise by the RAS trajectory [see Fig. 4(a)]

$$\alpha_0 \to \delta_g \to \alpha_\tau \to \delta_e \to \alpha_t \to \beta_t \to \delta_g \to \beta_T \to \delta_e \to \beta_0 \to \alpha_0\,,$$

which is just

$$0 \to \delta \to \alpha_t \to \beta_t \to 0 \to \beta_T \to \delta \to 0.$$

At the time of the echo we have a fortuitous degeneracy $\alpha_{t=T+\tau} = \beta_T$, so that the RAS path can be written as

$$0 \to \delta \to \alpha_{T+\tau} \to \beta_{T+\tau} \to 0 \to \alpha_{T+\tau} \to \delta \to 0,$$

which is just

$$0 \to \alpha_{T+\tau} \to \beta_{T+\tau} \to 0.$$

Therefore

$$\begin{aligned}\Phi_{12} &= \mathrm{Im}\,(\alpha_{T+\tau},\, \beta_{T+\tau}) \\ &= |\delta|^2\, \mathrm{Im}\left[\left(e^{-i\omega T}-1\right)\left(e^{i\omega T}-1\right)e^{i\omega\tau}\right] \\ &= \arg_1\langle\psi_{\rm vib} \mid \psi_{\rm vib}\rangle_2 \\ &= 8\,|\delta|^2 \sin^2(\omega T/2)\sin(\omega\tau/2)\cos(\omega\tau/2)\,. \end{aligned} \tag{6.12}$$

For the matrix element V_{34} the excitation diagram [Fig. 4(b)] shows that we should simply interchange the times T and τ obtaining

$$\begin{aligned}|V_{34}| &= e^{-\frac{1}{2}|\alpha_t-\beta_t|^2} \\ &= e^{-\frac{1}{2}|\delta|^2\left|\left(e^{-i\omega(t-T)}-1\right)-\left(e^{-i\omega\tau}-1\right)e^{-i\omega(t-\tau)}\right|^2} \\ &= e^{-\frac{1}{2}|\delta|^2\left|1+e^{-i\omega t}-e^{-i\omega(t-T)}-e^{-i\omega(t-\tau)}\right|^2} \\ &= |V_{12}| \end{aligned} \tag{6.13}$$

and

$$\begin{aligned}\Phi_{34} &= \mathrm{Im}\left(\alpha_{T+\tau}\,\beta^*_{T+\tau}\right) \\ &= |\delta|^2\, \mathrm{Im}\left[\left(e^{-i\omega\tau}-1\right)\left(e^{i\omega\tau}-1\right)e^{i\omega T}\right] \\ &= 8\,|\delta|^2 \sin^2(\omega\tau/2)\sin(\omega T/2)\cos(\omega T/2)\,. \end{aligned} \tag{6.14}$$

Thus the vibronic elements are the same except for the phase. The phase difference is given by

$$\begin{aligned}\langle\psi_{\rm vib} \mid \psi_{\rm vib}\rangle\,\Delta\Phi &= \Phi_{12} - \Phi_{34} \\ &= 8\,|\delta|^2 \sin(\omega T/2) \\ &\quad \times \sin(\omega\tau/2)\,\sin[\omega\,(T-\tau)/2]\,. \end{aligned} \tag{6.15}$$

This is a major contribution to the echo modulation.

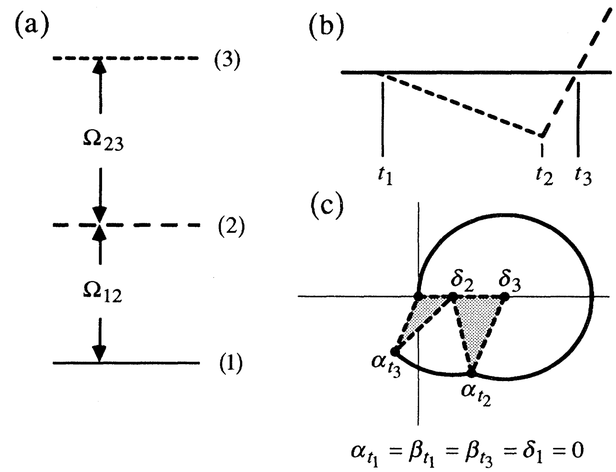

FIG. 5. Application of Berry's theorem to a trilevel echo in a vibronic molecule with two Franck-Condon displacements: (a) level scheme, (b) recoil diagram showing manner of excitation and time of echo, and (c) α diagram showing α and β trajectories and the RAS polygon. The shaded area is now the sum of two triangles and cannot be found simply from the inner product $\langle \beta_{t_3} | \alpha_{t_3} \rangle$, which has no imaginary part since $\beta_{t_3} = 0$.

The example given above, while chosen because it relates to a commonly performed experiment, does not fully illustrate the power of the area method because the matrix elements in this case are identical to

$$\langle \beta_t \mid \alpha_t \rangle = e^{-\frac{1}{2} |\alpha_t - \beta_t|^2} \, e^{-\frac{1}{2} (\alpha_t \beta_t^* - \alpha_t^* \beta_t)}. \tag{6.16}$$

The phase is simplified here by the fact that the RAS trajectories for α and β are identical until the last step ($\alpha_{T+\tau} = \beta_T \to \delta_g \to \beta_{T+\tau}$ or $\alpha_{T+\tau} = \beta_\tau \to \delta_g \to \beta_{T+\tau}$) so that the Berry area consists only of the triangle formed by $\alpha_{T+\tau}$, $\beta_{T+\tau}$, and $\delta_g = 0$.

As a less trivial illustration we may consider a trilevel echo in a gas of molecules subject to Franck-Condon displacements of δ_2 and δ_3 for the second and the third level, respectively [12]. The first pulse at t_1 consists of two counterpropagating parts: one traveling "forward" at frequency Ω_{12}, the other "backward" at frequency Ω_{23}. Since $\Omega_{23} > \Omega_{12}$ the wave packet associated with level (3) recoils backward with a momentum $|\hbar \mathbf{k}| = |\hbar\,(\mathbf{k}_{12} + \mathbf{k}_{23})| = \hbar\,(\Omega_{12} - \Omega_{23})/c$. The second pulse, at t_2, at frequency Ω_{23} travels backward and stimulates emission to generate the wave packet associated with level (2). This wave packet recoils forward with momentum $|\hbar \mathbf{k}| = |\hbar\,(\mathbf{k}_{12} + \mathbf{k}_{23} - \mathbf{k}_{23})| = \hbar \Omega_{12}/c$. The wave packet associated with level (1) remains fixed in position throughout. A trilevel echo is formed when the recoil trajectories associated with levels (1) and (2) cross. This echo carries a vibronic factor whose phase, according to Sec. III is twice the area enclosed by $0 = \alpha_0 \equiv \alpha_{t_1} \to \delta_3 \to \alpha_{t_2} \to \delta_2 \to \alpha_{t_3} \to \beta_{t_3} \to \delta_1 \to \beta_{t_1} \equiv \beta_0 = 0$, or more simply $0 \to \delta_3 \to \alpha_{t_2} \to \delta_2 \to \alpha_{t_3} \to 0$. This is a pair of triangles as shown in Fig. 5 (c). Since there is only a single crossing, this phase does not modify the echo amplitude. If, however, one uses phase sensitive detection, then the effect of the Berry phase should be apparent.

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APPENDIX A

Consider an adiabatic process in which γ migrates on a straight line from 0 to Γ. If the initial state is $|0\rangle$, the final state will be $|\Gamma\rangle$.

Proof. Let the state at any time be

$$|t\rangle = e^{i\phi}\, |\gamma(t)\rangle + |\varepsilon\rangle_t \, , \tag{A1}$$

where $|\gamma\rangle = D(\gamma)\,|0\rangle$ and $|\varepsilon\rangle$ is a ket of small magnitude, proportional to $\dot\gamma$. Then Schrödinger's equation gives

$$H(t)\,|\varepsilon\rangle_t = -\hbar\dot\phi\, e^{i\phi}\, |\gamma\rangle + i\,\hbar\, e^{i\phi} \frac{d}{dt}\, |\gamma\rangle + i\,\hbar \frac{d}{dt}\, |\varepsilon\rangle_t \tag{A2}$$

since $H(t)\,|\gamma\rangle = 0$ by Eq. (3.7). In the adiabatic limit we can drop $\frac{d}{dt}\,|\varepsilon\rangle_t$ and have $\dot\phi\,|\gamma\rangle = i\,\frac{d}{dt}\,|\gamma\rangle - \frac{1}{\hbar}\, e^{-i\phi}\, H\,|\varepsilon\rangle$ or, on multiplying by $\langle\gamma|$,

$$\dot\phi = i \left\langle \gamma \middle| \frac{d}{dt} \middle| \gamma \right\rangle \tag{A3}$$

since $\langle\gamma|\; H = 0$.

Now it is given that $\gamma(t) = \Gamma\,\xi(t)$, where ξ is real. Therefore

$$|\gamma\rangle = D(\gamma)\,|0\rangle = e^{\xi\,(\Gamma a^\dagger - \Gamma^* a)}\,|0\rangle \tag{A4}$$

and

$$\frac{d}{dt}\,|\gamma\rangle = \dot\xi\,\left(\Gamma\, a^\dagger - \Gamma^*\, a\right)\,|\gamma\rangle\,, \tag{A5}$$

$$\left\langle \gamma \middle| \frac{d}{dt} \middle| \gamma \right\rangle = \dot\xi\,\left(\Gamma\,\gamma^* - \Gamma^*\,\gamma\right) = \dot\xi\,\xi\,\left(|\Gamma|^2 - |\Gamma|^2\right) = 0 \tag{A6}$$

since $a\,|\gamma\rangle = \gamma\,|\gamma\rangle$ and $\langle\gamma|\; a^\dagger = \langle\gamma|\;\gamma^*$. Therefore $\dot\phi = 0$; since $\phi = 0$ at the beginning of the migration, it remains zero at the end. A similar argument applies with 0 and Γ interchanged.

APPENDIX B

Here we show that $|\Gamma_i\rangle \underset{\Gamma_i \to \Gamma_f}{\longrightarrow} e^{i\phi}\,|\Gamma_f\rangle$, where $\phi = \arg\langle\Gamma_f|\Gamma_i\rangle$. Let D stand for $D(\Gamma_i)$ and Δ for $\Gamma_f - \Gamma_i$. Then we have

$$D|0\rangle = |\Gamma_i\rangle \tag{B1}$$

and $D|\Delta\rangle$ is the same as $|\Gamma_f\rangle$ apart from a phase. The latter statement can be rendered neatly as

$$D|\Delta\rangle\langle\Delta|D^\dagger = |\Gamma_f\rangle\langle\Gamma_f|. \tag{B2}$$

Consequently, we have the identity

$$\begin{aligned} |\Gamma_f\rangle\langle\Gamma_f|\Gamma_i\rangle &= D|\Delta\rangle\langle\Delta|D^\dagger D|0\rangle \\ &= D|\Delta\rangle\langle\Delta|0\rangle. \end{aligned} \tag{B3}$$

But from Eq. (1.1), since $\langle 0|e^{\alpha a^\dagger} = \langle 0|$, we have $\langle\Delta|0\rangle = e^{-\frac{1}{2}\Delta^2}$, which is real. Hence if we take $\phi = \arg\langle\Gamma_f|\Gamma_i\rangle$, then we have

$$|\Gamma_f\rangle e^{i\phi} = D|\Delta\rangle. \tag{B4}$$

On the other hand, Appendix A shows that $|0\rangle \underset{0\to\Delta}{\longrightarrow} |\Delta\rangle$, and by a unitary transformation this becomes

$$D\;|0\rangle \underset{\Gamma_i\to\Gamma_f}{\longrightarrow} D\;|\Delta\rangle\,. \tag{B5}$$

Applying (B1) and (B4), we have the desired result.

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