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Indistinguishability and interference in the coherent control of atomic and molecular processes

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The subtle and fundamental issue of indistinguishability and interference between independent pathways to the same target state is examined in the context of coherent control of atomic and molecular processes, with emphasis placed on possible “which-way” information due to quantum entanglement established in the quantum dynamics. Because quantum interference between independent pathways to the same target state occurs only when the independent pathways are indistinguishable, it is first shown that creating useful coherence between nondegenerate states of a molecule for subsequent quantum interference manipulation cannot be achieved by collisions between atoms or molecules that are prepared in momentum and energy eigenstates. Coherence can, however, be transferred from light fields to atoms or molecules. Using a particular coherent control scenario, it is shown that this coherence transfer and the subsequent coherent phase control can be readily realized by the most classical states of light, i.e., coherent states of light. It is further demonstrated that quantum states of light may suppress the extent of phase-sensitive coherent control by leaking out some which-way information while “incoherent interference control” scenarios proposed in the literature have automatically ensured the indistinguishability of multiple excitation pathways. The possibility of quantum coherence in photodissociation product states is also understood in terms of the disentanglement between photodissociation fragments. Results offer deeper insights into quantum coherence generation in atomic and molecular processes.

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I. INTRODUCTION

Interference constitutes one of the most intriguing aspects of quantum mechanics.^{1,2} Specifically, when a target state is accessible by two or more independent pathways, the corresponding probability amplitudes must be added, rather than the corresponding probabilities added, in order to obtain the overall result. The realization that the resulting constructive or destructive interference terms can be altered via experimentally controllable parameters motivated the development of the field of “coherent control.”^{3–5} Considerable theoretical and experimental work has been done in this area, demonstrating our ability to actively control atomic and molecular processes by manipulating quantum interference.

Despite the fact that quantum interference allows for active control, the mystery it contains, however, admittedly remains.^{6–8} This becomes particularly clear if we consider the role of Young’s double-slit interference experiment for atoms or electrons, introduced during the early days of quantum mechanics. Traditional understandings of the double-slit experiment are based largely on Bohr’s complementarity, i.e., wave-particle duality. That is, if we can measure the recoiling slits and successfully determine which slit a particular particle goes through, then the interference will be

necessarily washed out due to the position uncertainty introduced by measurement. As a result, the wavelike property and the particlelike property cannot be observed simultaneously. Modern quantum optical tests further support Bohr’s claim.⁹ For example, in the double-slit experiments using atomic beams, micromaser detectors can determine which path the particle has followed without affecting the atomic spatial wave function by use of the atomic internal degrees of freedom. Doing so, however, causes loss of interference as a consequence of the available which-way information contained in the entanglement between the particles and the measuring apparatus.¹⁰ Other one-photon and two-photon interference experiments¹¹ further demonstrated that quantum interference should be understood as the physical manifestation of the intrinsic indistinguishability of multiple independent pathways, and that once there is some way, even in principle, of distinguishing between independent quantum routes to the same target state, the corresponding probabilities should be added and quantum interference no longer exists.

There exist some useful quantitative treatments that relate quantum interference to the indistinguishability between multiple pathways.^{12–15} Because they are not the focus of this paper, here we briefly introduce only one of them that will be occasionally used below. Let $|\psi_1\rangle$ and $|\psi_2\rangle$ denote the final states associated with two pathways. A measure for distin-

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guishing between these two states can be described by a complete set of commuting orthogonal projection operators $\{P_n \equiv |\xi_n\rangle\langle\xi_n|\}$. The degree of *indistinguishability* can then be defined as

$$U_{P_n}(\psi_1, \psi_2) = \sum_n \sqrt{\frac{\langle\psi_1|P_n|\psi_1\rangle\langle\psi_2|P_n|\psi_2\rangle}{\langle\psi_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle}}, \quad (1)$$

where $U_{P_n}(\psi_1, \psi_2)=1$ represents maximal indistinguishability (e.g., when $|\psi_1\rangle$ differs from $|\psi_2\rangle$ by a phase factor only), and $U_{P_n}(\psi_1, \psi_2)=0$ represents perfect distinguishability. On the other hand, the degree of *interference power* of $|\psi_1\rangle$ and $|\psi_2\rangle$, for a complete set of orthogonal projection operators $\{P'_l \equiv |\eta_l\rangle\langle\eta_l|\}$, is defined as

$$I_{P'_l}(\psi_1, \psi_2) = \sum_l \frac{|\langle\psi_1|P'_l|\psi_2\rangle|}{\sqrt{\langle\psi_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle}}. \quad (2)$$

It has been proven that if $\{P_n\}$ and $\{P'_l\}$ commute, then the degree of interference power is always no larger than that of indistinguishability,¹³ i.e.,

$$U_{P_n}(\psi_1, \psi_2) \geq I_{P'_l}(\psi_1, \psi_2). \quad (3)$$

Equation (3) implies that entangling the initial system wave functions $|1\rangle$ and $|2\rangle$ with measurement apparatus wave functions $|\xi_1\rangle$ and $|\xi_2\rangle$ should unavoidably affect quantum interference contributions.¹⁶ To see this more clearly, let us assume that the decoupled time evolution of the system and the measurement apparatus are described by the unitary operators U_S and U_M , respectively. The corresponding final states for the system and the measurement apparatus are given by $|\psi_1\rangle = U_S|1\rangle \otimes U_M|\xi_1\rangle$ and $|\psi_2\rangle = U_S|2\rangle \otimes U_M|\xi_2\rangle$. Then, the degree of interference power [Eq. (2)] for any measurement P'_l done on the system only is proportional to $|\langle\xi_1|U_M^\dagger U_M|\xi_2\rangle| = |\langle\xi_1|\xi_2\rangle|$. Hence, when $|1\rangle$ and $|2\rangle$ are entangled with orthogonal states $|\xi_1\rangle$ and $|\xi_2\rangle$, there will be no interference because $\langle\xi_1|\xi_2\rangle=0$. Indeed, the degree of indistinguishability [Eq. (1)] between $|\psi_1\rangle$ and $|\psi_2\rangle$ is zero if we choose $P_1 = |\xi_1\rangle\langle\xi_1|$ and $P_2 = |\xi_2\rangle\langle\xi_2|$. That is, the measurement of P_1 and P_2 serves to distinguish between $|1\rangle$ and $|2\rangle$, and thus to distinguish between the two pathways $|1\rangle \rightarrow |\eta_l\rangle$ and $|2\rangle \rightarrow |\eta_l\rangle$. On the other hand, if the states $|\xi_1\rangle$ and $|\xi_2\rangle$ are similar (i.e., their overlap is considerable), then the entanglement between the system and the measuring apparatus is weak enough to allow for quantum interference (i.e., the measurement of P_1 and P_2 will not provide much which-way information about the system and interference will not be lost).¹⁰ Qualitative aspects of the relationship between interference and which-way information are crucial to the entire discussion below.

In the context of coherent control, our appreciation of the usefulness of interference far exceeds our understanding of the fundamental essence of interference. In particular, in laser control of atomic and molecular processes, a laser pulse is usually employed to prepare a superposition state for the subsequent generation of multiple coherent pathways, analogous to the role of a beam splitter in matter-wave interference experiments. Fundamentally interesting questions then arise. For example, why do laser fields provide an important

means of creating molecular coherence for subsequent quantum interference control? Is there any which-way information extractable from the light field after the light-matter interaction is over? Are the independent pathways indeed largely indistinguishable so as to ensure interference? Further, with regard to indistinguishability between multiple excitation pathways, how do we understand the well-known fact that, on one hand traditional interference control scenarios are extremely phase-sensitive, and on the other hand there are also some phase-insensitive interference control scenarios?^{3,4}

Questions such as these have motivated us to examine the issue of indistinguishability and interference in the specific context of the coherent control of atomic and molecular processes. Our goal is to obtain deeper insights into the nature of coherence and interference in coherent control and to establish some foundational concepts in this area.

This paper is organized as follows. Section II presents considerations on the possibility of creating useful quantum coherence via atomic or molecular collisions. We show that, due to indistinguishability requirements, collisions between atoms or molecules prepared in momentum and energy eigenstates cannot, in almost all instances, create useful quantum coherence for subsequent control. Thus, as the first step in most quantum control scenarios, creating a superposition state comprising nondegenerate states is done by coherent laser irradiation. In Sec. III, we (1) compare a fully quantized theory of a two-pulse coherent control scenario with a classical-field treatment, in order to understand conditions under which laser-molecule interaction can create molecular coherence without leaking out which-way information and (2) analyze the differences between phase sensitive and phase insensitive control scenarios in terms of the nature of indistinguishability of multiple excitation pathways. The creation of quantum coherence in photodissociation processes is discussed in Sec. IV. We briefly summarize and conclude this work in Sec. V.

II. ON QUANTUM COHERENCE CREATION BY ATOMIC AND MOLECULAR COLLISIONS

In several important coherent control scenarios,^{3,4} the first step is to create a superposition state that results in multiple coherent pathways to the same target state. Here we examine the possibility of preparing useful quantum superposition states via atomic and molecular collisions. To see that this is a rather fundamental issue, consider first a typical molecular crossed-beam experiment (to be specific we focus below on bimolecular collisions, but these considerations apply to atomic collisions as well). Because the interaction time δt in the crossed-beam experiment is short, in effect each beam is subject to a “pulsed” interaction due to the other beam. It would then appear that such a molecular process is analogous to pulsed laser-molecule interaction and may be able to generate useful quantum superposition states with the characteristic energy coherence width given by $\hbar/\delta t$. However, this turns out to be incorrect even when the total system is perfectly isolated from the environment. As will become evident, this is because different energy or momentum components of the quantum state of one particle of

interest are distinguishable by measuring the quantum state of other particles. This feature is directly related to Einstein–Podolsky–Rosen (EPR) arguments.¹⁷

Consider the bimolecular collision $A+B \rightarrow C+D$, where A , B , C , and D are, in general, molecules of mass m_A , m_B , m_C , and m_D . Their free internal Hamiltonians are H_A^0 , H_B^0 , H_C^0 , and H_D^0 . Here C and D can be identical to A and B (nonreactive scattering) or can differ from A and B (reactive scattering). For a molecule denoted by X , the momentum eigenket (in the laboratory frame) is denoted by $|\mathbf{K}_X\rangle$ with the wave vector $\mathbf{K}_X$, and the internal eigenstate is represented by $|\phi_{E_X, n_X}^X\rangle$, where E_X is the internal energy of particle X and n_X is a set of good quantum numbers accounting for degeneracies. The eigenkets associated with the relative motion and the center of mass of motion of two molecules X and Y are denoted by $|\mathbf{k}_{XY}^{E_X, E_Y}\rangle$ and $|\mathbf{K}_{XY}\rangle$. Now suppose that the preparation of a superposition state of the molecule C is of particular interest. Then other channels not including C can be neglected and all possible states $|\phi_{E_C, n_C}^C\rangle \otimes |\phi_{E_D, n_D}^D\rangle \otimes |\mathbf{k}_{CD}^{E_C, E_D}\rangle \otimes |\mathbf{K}_{CD}\rangle$ form a complete basis set of the Hilbert space of interest.

We assume that initially molecules A and B are in pure internal states $|\phi_{E_A, n_A}^A\rangle$ and $|\phi_{E_B, n_B}^B\rangle$. Under normal circumstances their translational states can be taken as momentum eigenstates if they are created in a molecular beam apparatus.¹⁸ In addition, since one of our goals is to see if coherence between different momentum or energy eigenstates can be created by a collision process, we naturally assume that the initial states are prepared as momentum and energy eigenstates. Thus, before the collision, the quantum state is

$$|\Psi_0\rangle = |\phi_{E_A, n_A}^A\rangle \otimes |\phi_{E_B, n_B}^B\rangle \otimes |\mathbf{k}_{AB}^{E_A, E_B}\rangle \otimes |\mathbf{K}_{AB}\rangle, \quad (4)$$

where $\mathbf{k}_{AB}^{E_A, E_B} = (m_B \mathbf{k}_A - m_A \mathbf{k}_B) / (m_A + m_B)$ and $\mathbf{K}_{AB} = \mathbf{K}_A + \mathbf{K}_B$. After the collision, this initial state evolves to $|\Psi_{CD}\rangle$ for the product channel $C+D$.

Of interest is whether a bimolecular collision of this kind produces any useful coherence in molecule C . By useful coherence we mean coherence in C that could be used for a subsequent coherent control scenario, without reference to molecule D . To address this issue the quantum state composition of $|\Psi_{CD}\rangle$ needs to be examined. Specifically, $|\Psi_{CD}\rangle$ can be written as

$$|\Psi_{CD}\rangle = \int d\Omega \sum_{E_C, n_C} \sum_{E_D, n_D} S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) \times |\phi_{E_C, n_C}^C\rangle \otimes |\mathbf{K}_C\rangle \otimes |\phi_{E_D, n_D}^D\rangle \otimes |\mathbf{K}_D\rangle, \quad (5)$$

where $S_{ABCD}(E_C, n_C; E_D, n_D | \Omega)$ denotes an on-shell scattering matrix, the direction of $\mathbf{k}_{CD}^{E_C, E_D}$ is given by Ω , and the magnitude of $\mathbf{k}_{CD}^{E_C, E_D}$ is uniquely determined by momentum and energy conservation. As is seen clearly from Eq. (5), a collision between A and B can readily produce a superposition state consisting of different translational and/or internal quantum states, but such a superposition state is in the entire product space of C and D , i.e., both the translational and the internal states of C and D are entangled. Such entanglement between molecules C and D can, in principle, provide which-state information about the molecule C . Indeed, if we have obtained the values of $\mathbf{K}_D$ and E_D by measuring D only, then from momentum and energy conservation of the collision process we can infer $\mathbf{K}_C$ and E_C . Hence, a natural set of projection operators for distinguishing between different C states, and thus distinguishing between different pathways associated with these states, are given by

$$P_{\mathbf{K}_D, E_D, n_D} = |\mathbf{K}_D\rangle \langle \mathbf{K}_D| |\phi_{E_D, n_D}^D\rangle \langle \phi_{E_D, n_D}^D|. \quad (6)$$

As one can now readily check, the corresponding degree of indistinguishability between the C states with different E_C or $\mathbf{K}_C$ is zero. The interference power of the C states is hence zero, i.e., the C states with different E_C or $\mathbf{K}_C$ cannot be used for coherent control in a second process that does not involve molecule D .

Clearly, if two particles (C and D) have once interacted with each other, they will never be separable. It is this non-separability, the essence of the EPR argument,¹⁷ that makes which-state information about one molecule available. Thus, the availability of the which-state information about C rules out bimolecular collisions as a rational means of creating indistinguishable multiple pathways (associated with C) to the same target state. To our knowledge, this seemingly straightforward result is not well appreciated even in considerations of atom and molecule interferometry.¹⁹

To further understand the relationship between interference and indistinguishability and to examine whether or not there are useful coherence effects between degenerate internal states of C , we alternatively use below a density matrix approach. The density operator $\hat{\rho}_{CD}$ in the $C+D$ arrangement after the preparation collision is given by

$$\hat{\rho}_{CD} \equiv |\Psi_{CD}\rangle \langle \Psi_{CD}| = \iint d\Omega d\Omega' \sum_{E_C, n_C, E_D, n_D} \sum_{E'_C, n'_C, E'_D, n'_D} S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) S_{ABCD}^*(E'_C, n'_C; E'_D, n'_D | \Omega') |\phi_{E_C, n_C}^C\rangle \otimes |\mathbf{K}_C^{E_C, E_D}\rangle \otimes |\phi_{E_D, n_D}^D\rangle \otimes |\mathbf{K}_D^{E_C, E_D}\rangle \langle \mathbf{K}_D^{E'_C, E'_D}| \otimes \langle \phi_{E'_D, n'_D}^D| \otimes \langle \mathbf{K}_C^{E'_C, E'_D}| \otimes \langle \phi_{E'_C, n'_C}^C|. \quad (7)$$

Consider then a second collision between molecule C and another object F that may be an atom, a molecule, or a photon. The total initial density operator $\hat{\rho}_i$ for the second collision with regard to the entire system is a product of the density operator prepared in the first collision and the density operator $\hat{\rho}_F$ of F , i.e., $\hat{\rho}_i \equiv \hat{\rho}_{CD} \otimes \hat{\rho}_F$. If the second scattering process is described by the scattering operator $\hat{S}'$, then the total density operator after the second process is given by $\hat{S}'^\dagger \hat{\rho}_{CD} \hat{S}'$. Because the second scattering process is assumed

to be independent of molecule D , all operators involving only D commute with the scattering operator $\hat{S}'$. Furthermore, the projector associated with a target state, denoted $|\phi\rangle\langle\phi|$, is also assumed to be independent of molecule D and therefore commutes with operators involving D only. After first tracing over those degrees of freedom associated with D , we then obtain that the probability P_t of reaching the target state is given by

$$P_t = \int d\Omega \sum_{E_C, E_D, n_D} \sum_{n_C, n'_C} S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) S_{ABCD}^*(E_C, n'_C; E_D, n_D | \Omega) \hat{T}_{ND}(\hat{S}'^\dagger | \phi_{E_C, n_C}^C \rangle \otimes |\mathbf{K}_C^{E_C, E_D}\rangle \langle \mathbf{K}_C^{E_C, E_D}| \otimes \langle \phi_{E_C, n'_C}^C | \otimes \hat{\rho}_E \hat{S}' | \phi \rangle \langle \phi |) \equiv \int d\Omega \sum_{E_C, E_D, n_D} \sum_{n_C, n'_C} S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) S_{ABCD}^*(E_C, n'_C; E_D, n_D | \Omega) T_{E_C, E_D, n_D}^{n_C, n'_C}(\Omega), \quad (8)$$

where $\hat{T}_{ND}$ denotes the trace over all degrees of freedom excluding molecule D . Note also that Eq. (8) also defines $T_{E_C, E_D, n_D}^{n_C, n'_C}(\Omega)$.

Note first that $T_{E_C, E_D, n_D}^{n_C, n'_C}(\Omega)$ only contains terms diagonal in the translational motion of C . Hence, useful translational coherence of C is not generated. Likewise, the probability of reaching the target state is diagonal in representation of the nondegenerate internal states of C . Thus, the product of the $C+F$ collision does not see the “quantum coherence” between nondegenerate states of C . Clearly, here one can expect no interference whatsoever between multiple pathways $(E_A, E_B, n_A, n_B, \mathbf{k}_{AB}^{E_A, E_B}) \rightarrow [E_C(E'_C), n_C, \mathbf{K}_C^{E_C, E_D}(\mathbf{K}_C^{E'_C, E'_D})] \rightarrow$ target states.

These results are consistent with the previous discussion based on the indistinguishability requirement. Interestingly, in the derivation here, the degrees of freedom associated with D are traced over since D is not of interest. As such, there are no useful quantum coherences between the C states with different momentum or internal energy, even though we do not make any measurement on D to distinguish between the C states. This observation provides greater insight into the issue. That is, it makes clear that what is fundamentally important is not that we actually distinguish between different C states by use of the projectors $P_{\mathbf{K}_D, E_D, n_D}$ defined in Eq. (6), but rather that there exists the *possibility* of distinguishing between different C states. This is an example that, as far as indistinguishability between independent pathways is concerned, what counts is what you can do, not what you actually do.^{2,20}

The which-state information about C is seen to arise as a direct consequence of the conservation laws of total momentum and total energy of C and D . To “erase” the which-state information afforded by the quantum entanglement (and hence to allow for the possibility of interference), we need to introduce uncertainty in knowing the state of C from mea-

suring D , i.e., it is necessary to introduce some uncertainties in momentum or energy into the system. For example, (1) momentum uncertainties may be easily introduced to molecular systems by collisions between molecules and macroscopic objects that in general have considerable momentum variances as compared with microscopic particles;¹⁹ and (2) as shown below, energy uncertainties can be easily introduced through laser excitation. It is for the second reason that laser technologies are so important to coherent control. Bimolecular collisions themselves are seen not a useful means for producing interesting quantum coherence effects for subsequent manipulation of interference effects.

The above straightforward density matrix formalism also allows us to examine if bimolecular collisions may create quantum coherence between *degenerate* molecular states of C . Interestingly, in Eq. (8), one sees that for each specified set of Ω, E_C, E_D, n_D , the reaction probability contains the diagonal terms $T_{E_C, E_D, n_D}^{n_C, n_C}(\Omega)$, and the cross terms $T_{E_C, E_D, n_D}^{n_C, n'_C}(\Omega)$ ($n_C \neq n'_C$). The cross terms describe interference effects between the pathways $(E_A, E_B, n_A, n_B, \mathbf{k}_{AB}^{E_A, E_B}) \rightarrow [E_C, n_C(n'_C), \mathbf{K}_C^{E_C, E_D}, n_D, \mathbf{K}_D^{E_C, E_D}] \rightarrow$ target states. They refer to identical eigenenergies of internal states and identical translational states of D , consistent with the indistinguishability requirement discussed above. To further ensure such quantum interference, the coefficients associated with these nondiagonal terms, namely, $S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) S_{ABCD}^*(E_C, n'_C; E_D, n_D | \Omega)$ ($n_C \neq n'_C$), should be nonzero. Since n_C and n_D usually refer to quantities such as the parity or the projection of the total angular momentum onto a space-fixed axis, at first glance it may appear that $S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) S_{ABCD}^*(E_C, n'_C; E_D, n_D | \Omega) = 0$ for $n_C \neq n'_C$, because either $n_C n_D$ or $n_C + n_D$ should be conserved in the scattering processes. But this is not true. Instead, we note (1) that the conservation laws of parity and angular momentum only require

$$\int d\Omega S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) S_{ABCD}^*(E_C, n'_C; E_D, n_D | \Omega) = 0, \quad (9)$$

$$n_C \neq n'_C,$$

and (2) that for any particular direction characterized by Ω [e.g., the direction strongly preferred by the second collision via the Ω dependence of $T_{E_C, E_D, n_D}^{n_C, n'_C}(\Omega)$], $S_{ABCD}(E_C, n_C; E_D, n_D | \Omega) S_{ABCD}^*(E_C, n'_C; E_D, n_D | \Omega)$ can be nonzero. Hence, bimolecular collisions can create a certain type of potentially useful quantum coherence between degenerate molecular states, but in a very subtle manner. This result may be of interest to considerations on controlling bimolecular reactions,²¹ where superposition states consisting of degenerate internal states are used. Nevertheless, in general, quantum coherence between degenerate states is of limited use.

We summarize the results to conclude this section. We have considered the collision of $A+B \rightarrow C+D$ at fixed total energy and total momentum, and asked if the coherence created in the products of this collision can be used in a subsequent collisional step to do coherent control. To be experimentally feasible, this would mean that we would be trying to use the coherence established in *one* of the product molecules in the subsequent step. We would call this “useful coherence.” Our results show that (a) bimolecular collisions, such as multichannel collision $A+B \rightarrow C+D$, cannot produce useful molecular translational coherence, (b) bimolecular collisions cannot achieve useful coherence between nondegenerate rovibrational states, (c) bimolecular collisions cannot produce useful coherence between different product states of various translational and rovibrational states, and (d) bimolecular collisions, however, can produce certain useful coherence between degenerate molecular states, such as those with different parities or projections of the total angular momentum onto a space-fixed axis.

III. INDISTINGUISHABILITY AND INTERFERENCE IN COHERENT CONTROL OF PHOTOCHEMICAL PROCESSES

In this section, we consider a representative phase-sensitive coherent control scheme, namely, a particular two-pulse coherent control scenario,^{22,23} to examine the fundamental issue of indistinguishability and interference in the coherent control of photochemical processes. We then carry out similar examinations of two phase-insensitive interference control scenarios.

A. Classical treatment of laser fields in two-pulse coherent control

Consider a classical linearly polarized electric field $E(t)$ incident on an initially bound molecule. The molecule is assumed to be in an eigenstate $|E_0\rangle$ of the molecular Hamiltonian H_M . The overall Hamiltonian, in the dipole approximation, is then given by

$$H = H_M - \hat{d}[E(t) + E^*(t)], \quad (10)$$

where $\hat{d}$ is dipole moment operator along the electric field. In a two-pulse control scenario, the external field consists of two separated Gaussian pulses $E_x(t)$ and $E_d(t)$ centered at $t = t_x$ and t_d , respectively. The Fourier transform of $E_x(t)$ and $E_d(t)$ is given by $E_x(\omega)$ and $E_d(\omega)$. The first pulse $E_x(t)$ induces a transition to a superposition of bound excited molecular states and the second pulse dissociates the molecule by further exciting it to the continuum. Both fields are chosen to be sufficiently weak to apply first-order perturbation theory.

Assuming that the first pulse encompasses only two $|E_1\rangle$ and $|E_2\rangle$ excited states, the superposition state thus prepared is given by

$$|\phi(t)\rangle = |E_0\rangle \exp(-iE_0 t/\hbar) + c_1 |E_1\rangle \exp(-iE_1 t/\hbar) + c_2 |E_2\rangle \exp(-iE_2 t/\hbar), \quad (11)$$

where

$$c_m = \frac{\sqrt{2}\pi}{i\hbar} d_{m,0} E_x(\omega_{E_m E_0}), \quad m = 1, 2, \quad (12)$$

with $\omega_{E_m E_0} \equiv (E_m - E_0)/\hbar$ and $d_{m,0} \equiv \langle E_m | \hat{d} | E_0 \rangle$. This superposition state is subjected to a second pulse after a time delay $(t_d - t_x)$. When the second-pulse is completed, the system wave function is given by

$$|\psi(t)\rangle = |\phi(t)\rangle + \sum_{n,q} \int dE B(E, n, q | t) |E, n, q^-\rangle \exp(-iEt/\hbar), \quad (13)$$

where E , n , and q denote the eigenenergy, the quantum numbers other than the energy, and the arrangement index for the eigenfunction $|E, n, q^-\rangle$ in the continuum. The probability of observing the state $|E, n, q^-\rangle$ in the remote future is given by

$$\begin{aligned} P(E, n, q) &= \lim_{t \rightarrow \infty} \langle \psi(t) | E, n, q^- \rangle \langle E, n, q^- | \psi(t) \rangle \\ &= |B(E, n, q | t = \infty)|^2 \\ &= \frac{2\pi}{\hbar^2} \left| \sum_{m=1,2} c_m \langle E, n, q^- | \hat{d} | E_m \rangle E_d(\omega_{EE_m}) \right|^2 \\ &= \frac{2\pi}{\hbar^2} \{ |c_1|^2 d_{1,1}^q |E_d(\omega_{EE_1})|^2 + |c_2|^2 d_{2,2}^q |E_d(\omega_{EE_2})|^2 \} \\ &\quad + I_{12}(t_d - t_x), \end{aligned} \quad (14)$$

with

$$\langle E_1 | \hat{d} | E_0 \rangle \langle E_0 | \hat{d} | E_2 \rangle \equiv \langle E_1 | \hat{d} | E_0 \rangle \langle E_0 | \hat{d} | E_2 \rangle \exp(i\theta), \quad (15)$$

$$|d_{i,m}^q(E)| \exp[i\alpha_{i,m}^q(E)] \equiv \langle E, n, q^- | \hat{d} | E_i \rangle \langle E_m | \hat{d} | E, n, q^- \rangle, \quad (16)$$

and

$$I_{12}(t_d - t_x) = \frac{4\pi}{\hbar^2} |c_1 c_2^* E_d(\omega_{EE_1}) E_d^*(\omega_{EE_2})| |d_{1,2}^q| \times \cos[\omega_{E_2 E_1}(t_d - t_x) + \alpha_{1,2}^q(E) + \theta]. \quad (17)$$

Clearly, by changing the time delay between the two pulses or the ratio between c_1 and c_2 , one can manipulate the interference term $I_{12}(t_d - t_x)$. Moreover, due to the presence of the molecular phase $\alpha_{1,2}^q$, the interference may be constructive for one arrangement while being destructive for other arrangements. Selectivity can thus be achieved through the manipulation of quantum interference and excellent control has been predicted²² and observed experimentally.²⁴

B. Fully quantized theory of two-pulse coherent control

The above classical treatment of light fields has several advantages. For example, it shows, in a very simple manner, the source of the interference and how it can be manipulated experimentally. It can also be readily extended to cases in which laser incoherence is present. However, as the apparatus for the double-slit experiment is treated quantum mechanically in Bohr's defense of the consistency of quantum mechanics,^{7,12} it is advantageous here to consider a fully quantized theory of the two-pulse coherent control scheme. As will become evident, by also quantizing light fields, we can readily examine the implications of molecule-photon entanglement, the indistinguishability between independent excitation pathways, and hence expose the key difference between bimolecular collisions and laser-molecule interaction.

Consider then a molecule subjected to a quantized electromagnetic field. The total Hamiltonian including the molecular Hamiltonian H_M , the radiation Hamiltonian H_R , and the interaction Hamiltonian H_I , in the Schrödinger picture, is given by²⁵

$$H = H_M + H_R + H_I \equiv H_0 + H_I \\ = \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} + \sum_j E_j |j\rangle \langle j| \\ + i \sum_{\mathbf{k}} \sum_{mn} \sqrt{\frac{\hbar \omega_{\mathbf{k}}}{2\epsilon_0 V}} \cdot d_{mn} (\hat{a}_{\mathbf{k}} - \hat{a}_{\mathbf{k}}^\dagger) |m\rangle \langle n|, \quad (18)$$

where the electrical field is assumed to be in the same direction as the molecular dipole moment, $d_{mn} \equiv \langle E_m | \hat{d} | E_n \rangle$, $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^\dagger$ are the photon annihilation and creation operators for the frequency component $\omega_{\mathbf{k}}$, V is the quantization volume for the quantum field, and ϵ_0 is the permittivity of the vacuum.

Given the Hamiltonian in Eq. (18), first-order perturbation theory gives

$$\exp(-iHt/\hbar) = \exp(-iH_0 t/\hbar) \left\{ 1 + \frac{1}{\hbar} \sum_{\mathbf{k}} \sum_{mn} d_{mn} |m\rangle \langle n| \times \sqrt{\frac{\hbar \omega_{\mathbf{k}}}{2\epsilon_0 V}} \left[\hat{a}_{\mathbf{k}} \frac{\exp[i(\omega_{E_m E_n} - \omega_{\mathbf{k}})t]}{i(\omega_{E_m E_n} - \omega_{\mathbf{k}} - i\epsilon)} - \hat{a}_{\mathbf{k}}^\dagger \frac{\exp[i(\omega_{E_m E_n} + \omega_{\mathbf{k}})t]}{i(\omega_{E_m E_n} + \omega_{\mathbf{k}} - i\epsilon)} \right] \right\}, \quad (19)$$

where ϵ finally goes to 0^+ . We define the time $t=0$ as that after which the first pulse is over. Further, in addition to the assumptions of the classical field treatment, we assume that the quantum state of the first pulse at $t=0$ would be given by $|\psi^x\rangle$ if there were no laser-molecule interaction. Then, the wave function for the entire system at $t=0$ is given by (in the rotating wave approximation)

$$|\Psi(t=0)\rangle = |\psi^x\rangle \otimes |E_0\rangle + \frac{1}{\hbar} (d_{10} \hat{A}_{10} |\psi^x\rangle) \otimes |E_1\rangle \\ + \frac{1}{\hbar} (d_{20} \hat{A}_{20} |\psi^x\rangle) \otimes |E_2\rangle, \quad (20)$$

where operators $\hat{A}_{j0}$ are

$$\hat{A}_{j0} \equiv \sum_{\mathbf{k}} \sqrt{\frac{\hbar \omega_{\mathbf{k}}}{2\epsilon_0 V}} \frac{\hat{a}_{\mathbf{k}}}{i(\omega_{E_j E_0} - \omega_{\mathbf{k}} - i\epsilon)}, \quad j = 1, 2. \quad (21)$$

For the second laser pulse, the quantum state of light is assumed to be $|\psi^d\rangle$ at $t=0$. Applying first-order perturbation theory a second time gives rise to the wave function $|\Psi(t)\rangle$ for the entire system at any time $t \geq 0$. For the sake of comparison with the classical treatment, we also assume that only the $|E_1\rangle$ and $|E_2\rangle$ levels contribute to the photodissociation probabilities. Then one finds

$$\lim_{t \rightarrow +\infty} |\Psi(t)\rangle \rightarrow \exp(-iH_0 t/\hbar) |\Psi(0)\rangle \\ - \exp(-iEt/\hbar) \frac{1}{\hbar^2} \sum_{n,q} \int dE |E, n, q^-\rangle \\ \otimes [d_{E,1}^{n,q} d_{10} (\hat{B}_{E,1} |\psi^d\rangle) \otimes (\hat{A}_{10} |\psi^x\rangle) \\ + d_{E,2}^{n,q} d_{20} (\hat{B}_{E,2} |\psi^d\rangle) \otimes (\hat{A}_{20} |\psi^x\rangle)], \quad (22)$$

where $d_{E,i}^{n,q} \equiv \langle E, n, q^- | \hat{d} | E_i \rangle$, and where $\hat{B}_{E,j}$ is given by

$$\hat{B}_{E,j} \equiv \sum_{\mathbf{k}} \sqrt{\frac{\hbar \omega_{\mathbf{k}}}{2\epsilon_0 V}} \frac{\hat{a}_{\mathbf{k}}}{i(\omega_{EE_j} - \omega_{\mathbf{k}} + i\epsilon)}, \quad j = 1, 2. \quad (23)$$

C. Interference and indistinguishability in two-pulse coherent control

Equation (22) shows that postlaser excitation the molecular state is entangled with both the first and second light fields. It is therefore possible that with this entanglement one can identify the excitation pathway through which the molecule is dissociated, i.e., by either the route $|E_0\rangle \rightarrow |E_1\rangle \rightarrow |E\rangle$ or the route $|E_0\rangle \rightarrow |E_2\rangle \rightarrow |E\rangle$. This could result in the loss of interference. However, unlike the bimolecular collision case analyzed in Sec. II, here the photon states that are

entangled with the molecular states are usually not orthogonal. This suggests that the two independent excitation pathways can still have a high degree of indistinguishability. Specifically, if we define

$$\begin{aligned} |\psi_1\rangle &\equiv \frac{\exp(-iEt/\hbar)}{\hbar^2} \int dE \sum_{n,q} |E, n, q^-\rangle \\ &\quad \otimes d_{E,1}^{n,q} d_{10}(\hat{B}_{E,1}|\psi^d\rangle) \otimes (\hat{A}_{10}|\psi^x\rangle), \\ |\psi_2\rangle &\equiv \frac{\exp(-iEt/\hbar)}{\hbar^2} \int dE \sum_{n,q} |E, n, q^-\rangle \\ &\quad \otimes d_{E,2}^{n,q} d_{20}(\hat{B}_{E,2}|\psi^d\rangle) \otimes (\hat{A}_{20}|\psi^x\rangle), \end{aligned} \quad (24)$$

then the continuum part of $|\Psi(t)\rangle$ is just a superposition of these two states, corresponding to different contributions from independent excitation pathways. The interference of these two states for the measurement of the projector $|E, n, q^-\rangle\langle E, n, q^-|$ is given by

$$\begin{aligned} &\langle \psi_1 | E, n, q^- \rangle \langle E, n, q^- | \psi_2 \rangle + \langle \psi_2 | E, n, q^- \rangle \langle E, n, q^- | \psi_1 \rangle \\ &= \frac{1}{\hbar^4} \sum_n (d_{E,2}^{n,q})^* d_{E,1}^{n,q} d_{20}^* d_{10} \langle \psi^x | \hat{A}_{2,0}^\dagger \hat{A}_{1,0} | \psi^x \rangle \\ &\quad \times \langle \psi^d | \hat{B}_{E,2}^\dagger \hat{B}_{E,1} | \psi^d \rangle + \text{c.c.} \end{aligned} \quad (25)$$

The first observation to be made from Eq. (25) is that an exact correspondence between classical and quantum treatment of the light fields can be made under certain conditions. Suppose both $|\psi^x\rangle$ and $|\psi^d\rangle$ are products of coherent states of light for different frequencies, i.e.,

$$\begin{aligned} \hat{A}_{j0}|\psi^x\rangle &= \sum_{\mathbf{k}} \sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\epsilon_0 V i(\omega_{E_j E_0} - \omega_{\mathbf{k}} - i\epsilon)}} \alpha_{\mathbf{k}} |\psi^x\rangle \\ &\equiv \sqrt{2\pi E_x^q(\omega_{E_j E_0})} |\psi^x\rangle, \\ \hat{B}_{E,j}|\psi^d\rangle &= \sum_{\mathbf{k}} \sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\epsilon_0 V i(\omega_{EE_j} - \omega_{\mathbf{k}} + i\epsilon)}} \beta_{\mathbf{k}} |\psi^d\rangle \\ &\equiv \sqrt{2\pi E_d^q(\omega_{EE_j})} |\psi^d\rangle, \end{aligned} \quad (26)$$

where $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ are the eigenvalues of $\hat{a}_{\mathbf{k}}$ for the first and second light pulses, characterizing the coherent states of light. One can then establish the equivalence between Eqs. (25) and (17) by requiring $E_x^q(\omega_{E_j E_0})$ and $E_d^q(\omega_{EE_j})$ defined in Eq. (26) to be the same as the Fourier components $E_x(\omega_{E_j E_0})$ and $E_d(\omega_{EE_j})$ of the classical light fields. Of even greater interest is the implication of this correspondence condition for the degree of indistinguishability between the two independent excitation pathways ($|E_0\rangle \rightarrow |E_1\rangle \rightarrow E$ and $|E_0\rangle \rightarrow |E_2\rangle \rightarrow E$). Substituting Eq. (26) into Eq. (24), one sees that $|\psi_1\rangle$ is absolutely indistinguishable from $|\psi_2\rangle$ except for a c-number phase factor, i.e., the degree of indistinguishability is one. Thus, subject to the condition of Eq. (26), it is absolutely impossible to tell which excitation pathway the molecule takes, even after making precise measurements of the light fields. In other words, the quantum-classical correspondence condition of Eq. (26) here corresponds to the case

of maximal degree of indistinguishability between the two excitation pathways $|E_0\rangle \rightarrow |E_1\rangle \rightarrow E$ and $|E_0\rangle \rightarrow |E_2\rangle \rightarrow E$. Hence, *coherent states of light for both the preparation and dissociation pulses can first create and then manipulate molecular coherence without leaking out any which-way information.*

It then follows that quantum states of light in general may provide some which-way information in a molecular process that allows for multiple excitation pathways. We find that this is evidently true in some limiting cases. Consider first a case in which the wave function $|\psi^x\rangle$ of the first light field is an eigenstate $|n_{\mathbf{k}}\rangle$ of the photon number operator $\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}}$ for $\omega_{\mathbf{k}} \approx \omega_{E_1 E_0}$ and still a coherent state for other frequency components. Then, one can easily distinguish between the two excitation possibilities $|E_0\rangle \rightarrow |E_1\rangle$ and $|E_0\rangle \rightarrow |E_2\rangle$, by carrying out a measurement of the change in the number of photons with frequency $\omega_{E_1 E_0}$. That is, if the number of photons with frequency $\omega_{E_1 E_0}$ decreases by one, then the molecule must have been excited to $|E_1\rangle$, otherwise it must have been excited to $|E_2\rangle$. According to the indistinguishability requirement for interference, this zero indistinguishability completely destroys the interference. Indeed, if we choose a complete set of distinguishing projectors as $P_{\mathbf{k}} = |n_{\mathbf{k}}\rangle\langle n_{\mathbf{k}}|$, then the corresponding degree of indistinguishability [see Eq. (1)] between $|\psi_1\rangle$ and $|\psi_2\rangle$ in Eq. (24) is zero; and since $\langle n_{\mathbf{k}} | \hat{A}_{20}^\dagger \hat{A}_{10} | n_{\mathbf{k}} \rangle = 0$, the interference power for the projectors $|E, n, q^-\rangle\langle E, n, q^-|$ is also zero. Similarly, for the dissociation pulse, if $|\psi^d\rangle$ is a photon number eigenstate for one frequency component, e.g., ω_{EE_1} , interference will not exist because we can distinguish between $|E_1\rangle \rightarrow |E\rangle$ and $|E_2\rangle \rightarrow |E\rangle$ by measuring the photon number in the second light field.

One could argue that this example could be intuitively understood in terms of the photon number and photon phase uncertainty relation say, $\delta N \delta \phi \approx 1$. That is, a photon number eigenstate ($\delta N = 0$) gives the largest phase uncertainty ($\delta \phi \approx 2\pi$), and a large phase uncertainty destroys phase control. However, it should be stressed that the physics here is in fact more fundamental than is manifest in this oversimplified perspective. For example, consider the two well-known quantum states of light, namely, the even coherent states (ECS) $|\psi^{\text{ECS}}\rangle = [2(1 + \exp(-2\alpha^2))]^{-1/2}(|\alpha\rangle + |-\alpha\rangle)$ and the odd coherent states (OCS) $|\psi^{\text{OCS}}\rangle = [2(1 - \exp(-2\alpha^2))]^{-1/2}(|\alpha\rangle - |-\alpha\rangle)$, where $\hat{a}|\alpha\rangle = \alpha|\alpha\rangle$ and $\hat{a}|-\alpha\rangle = -\alpha|-\alpha\rangle$.²⁶ The photon number distribution P_n^{ECS} for ECS is given by $P_n^{\text{ECS}} = [2\alpha^{2n} \exp(-\alpha^2)] / [n!(1 + \exp(-2\alpha^2))]$ if n is even, and $P_n^{\text{ECS}} = 0$ if n is odd; whereas the photon number distribution P_n^{OCS} for OCS is given by $P_n^{\text{OCS}} = [2\alpha^{2n} \exp(-\alpha^2)] / [n!(1 - \exp(-2\alpha^2))]$ if n is odd and $P_n^{\text{OCS}} = 0$ if n is even. Note that such OCS and ECS can typically have $\delta N \gg 1$, suggesting that the phase uncertainty could be very small ($\delta \phi \ll 1$) if the uncertainty relation $\delta N \delta \phi \approx 1$ is applied. However, here loss of one photon in OCS (ECS) leads to a dramatic change in the quantum states of light, i.e., from only allowing for odd (even) numbers of photons to only allowing for even (odd) numbers of photons. Thus, if the preparation or dissociation pulse is given by an OCS (ECS) for one frequency component (say, $\omega_{E_2 E_0}$), one can, in principle, tell whether or not the molecule has absorbed a

photon of a certain frequency, by a postinteraction measurement of the even/odd property of the photon number distribution. This implies that in these cases there should not be quantum interference, as a result of complete distinguishability of multiple excitation pathways. Indeed, based on the fact that

$$\langle \psi^{\text{ECS}} | \hat{a} | \psi^{\text{ECS}} \rangle = \langle \psi^{\text{OCS}} | \hat{a} | \psi^{\text{OCS}} \rangle = 0, \quad (27)$$

one clearly sees that quantum interference given by Eq. (25) should vanish if either the preparation or the dissociation pulse is given by OCS or ECS.

These results are also relevant to quantum computation. Since quantum computation relies on coherently controlled evolution of atomic and molecular systems, the analysis here suggests that nonclassical light fields may affect the reliability of a quantum computer by leaking out some which-way information. This is consistent with a recent study suggesting that the quantum nature of light may have important implications for the limits of quantum computation.²⁷

Comparing laser-molecule interaction considered here and bimolecular collisions analyzed in Sec. II, we see that their key difference in quantum coherence generation arises from two sources. First, a pulsed laser field itself already carries coherence between different frequency components and such coherence can be directly transferred to create coherence between different molecular eigenstates. Second, a laser field (e.g., when the quantum states of light are close to coherent states) is somewhat of a classical object, thus the interaction between a molecule and a laser field is more or less analogous to the scattering between a molecule and a macroscopic object (e.g., a classical diffraction slit in front of a double-slit plate). This is in contrast to the scattering between two molecules (submicroscopic objects) assumed to be in momentum and energy eigenstates, where quantum entanglement and hence the which-way information can be easily established.

D. Indistinguishability and interference in incoherent control

The physical picture established in the previous subsection applies also to other weak-field coherent control scenarios [e.g., “1 photon+3 photon” control, “1 photon+2 photon” control, “ $\omega_1+\omega_2$ ” versus “ $\omega_3+\omega_4$ ” control ($\omega_{1(2)} \neq \omega_{3(4)}$)] with minor changes.²⁸ However, it remains to examine the issue of indistinguishability and interference in several cases of “incoherent interference control” schemes, where interference between multiple pathways was found to be insensitive to laser phases.^{29,30}

Consider first the so-called “ $\omega_1+\omega_2$ ” versus “ $\omega_2+\omega_1$ ” control.²⁹ In this case, the first pathway starts with the excitation from state $|E_0\rangle$ to an intermediate state $|E_1\rangle$ by absorbing a photon of frequency ω_1 , followed by the excitation from state $|E_1\rangle$ to the target state $|E, n, q^-\rangle$ by a second photon of frequency ω_2 . The second pathway proceeds through another intermediate state $|E_2\rangle$ by first absorbing a photon of frequency ω_2 , and then being excited from $|E_2\rangle$ to $|E, n, q^-\rangle$ by absorbing a second photon of frequency ω_1 . Rigorously describing such laser-molecule interaction requires a general

resonant two-photon photodissociation theory,³¹ by which both level shifts and level widths can be explicitly taken into account. Nevertheless, for the purpose here, it suffices to apply second-order perturbation theory with the fully quantized Hamiltonian (18). Substituting Eq. (18) into the following perturbation series

$$\begin{aligned} \exp(-iHt/\hbar) = \exp(-iH_0t/\hbar) & \left[1 - \frac{i}{\hbar} \int_0^t dt_1 \exp(iH_0t_1/\hbar) H_I \right. \\ & \times \exp(-\epsilon t_1) \exp(-iH_0t_1/\hbar) \\ & - \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \exp(iH_0t_1/\hbar) H_I \\ & \times \exp(-\epsilon t_1) \exp(-iH_0t_1/\hbar) \exp(iH_0t_2/\hbar) H_I \\ & \left. \times \exp(-\epsilon t_2) \exp(-iH_0t_2/\hbar) \right], \quad (28) \end{aligned}$$

neglecting the first-order term (i.e., assuming that this term does not contribute to photodissociation), and applying the rotating wave approximation, one obtains the time-evolving state $|\Psi(t)\rangle$ for the entire molecule-field system. In particular, if initially the state $|\Psi_0\rangle$ is a direct product state of the matter wave function $|E_0\rangle$ and the light field wave function $|\psi\rangle$, we have

$$\begin{aligned} \lim_{t \rightarrow +\infty} |\Psi(t)\rangle = \exp(-iH_0t/\hbar) \\ \times \left[|\Psi_0\rangle - \frac{1}{2\epsilon_0 V \hbar} \sum_{\mathbf{k}\mathbf{k}'} \sum_j \sum_{n,q} \int dE |E, n, q^-\rangle \right. \\ \left. \otimes \frac{\sqrt{\omega_{\mathbf{k}} \omega_{\mathbf{k}'}} d_{Ej}^{mq} d_{j0} \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{k}}}{(\omega_{EE_0} - \omega_{\mathbf{k}} - \omega_{\mathbf{k}'} + 2i\epsilon)(\omega_{EE_j} - \omega_{\mathbf{k}'} + i\epsilon)} |\psi\rangle \right], \quad (29) \end{aligned}$$

where ϵ finally goes to 0^+ , the intermediate states are assumed to be $|E_j\rangle$, and d_{Ej}^{mq} and d_{j0} are the associated transition dipole moments between the intermediate state and initial or final states. As in the two-pulse control case, Eq. (29) indicates that in general the final state is an entangled state between the molecule and the light fields. The molecule-photon entanglement can, in general, decrease the indistinguishability of the multiple pathways associated with different intermediate states. Interestingly, this is not the case in the special situation used in the $\omega_1+\omega_2$ versus $\omega_2+\omega_1$ scheme. In this special case, there are only two near-resonant and dominant intermediate bound states $|E_1\rangle$ and $|E_2\rangle$ of energy E_1 and E_2 , satisfying $\omega_{EE_1} = \omega_{E_2E_0}$. Hence,

$$(\omega_{EE_1} - \omega_{\mathbf{k}'} + i\epsilon) = (\omega_{E_2E_0} - \omega_{\mathbf{k}'} + i\epsilon) = -(\omega_{EE_2} - \omega_{\mathbf{k}} + i\epsilon), \quad (30)$$

where in obtaining the second equality we used $(\omega_{EE_0} - \omega_{\mathbf{k}} - \omega_{\mathbf{k}'} + 2i\epsilon) \approx 0$ due to conservation of total energy. Using Eq. (30) and manipulating the order of the sum in Eq. (29), the E, n, q component of the wave function is found to be

$$\lim_{t \rightarrow +\infty} |\Psi(t)\rangle_{E,n,q} = \frac{\exp(-iEt/\hbar)}{2\epsilon_0 \hbar V} \sum_{\mathbf{k}\mathbf{k}'} \left[\frac{-d_{E1}^{nq} d_{10} \sqrt{\omega_{\mathbf{k}} \omega_{\mathbf{k}'}} |E, n, q^-\rangle \otimes \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{k}} |\psi\rangle}{(\omega_{EE_0} - \omega_{\mathbf{k}} - \omega_{\mathbf{k}'} + 2i\epsilon)(\omega_{EE_1} - \omega_{\mathbf{k}'} + i\epsilon)} + \frac{d_{E2}^{nq} d_{20} \sqrt{\omega_{\mathbf{k}} \omega_{\mathbf{k}'}} |E, n, q^-\rangle \otimes \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{k}} |\psi\rangle}{(\omega_{EE_0} - \omega_{\mathbf{k}} - \omega_{\mathbf{k}'} + 2i\epsilon)(\omega_{EE_1} - \omega_{\mathbf{k}'} + i\epsilon)} \right]. \quad (31)$$

Clearly, the first term on the right hand side of Eq. (31) represents the contribution from the first path through the intermediate state $|E_1\rangle$, and the second term represents the contribution from the second path associated with $|E_2\rangle$. Remarkably, without any restriction on the form of $|\psi\rangle$, the two terms in Eq. (31) arising from two excitation pathways are seen to be identical except the c-number coefficients, i.e., the degree of indistinguishability of these two components is one and the final molecular state $|E, n, q^-\rangle$ is disentangled from the light field. As such, in the peculiar $\omega_1 + \omega_2$ versus $\omega_2 + \omega_1$ control scheme, the final states arising from the two independent pathways happen to be indistinguishable, even after considering any possible molecule-field entanglement. This is in sharp contrast to the two-pulse control case in which only coherent states of light can guarantee the maximal degree of indistinguishability.

Let us now consider a second incoherent interference control example, here in the strong field.³⁰ In this case, the first pathway is simply a direct excitation from an initial state to a target state, and the second pathway begins with an excitation from the initial state to the same target state, followed by back and forth transitions (induced by a strong field) between the target state and a third intermediate state. Evidently, classifying independent pathways in this way is just a convenient zero-field picture for understanding the associated quantum effects. These “back and forth” transitions are simply fictitious excitation pathways in a perturbation theory interpretation of the excitation from the initial state to a dressed target state. Given that it is absolutely impossible to distinguish between fictitious pathways, even in principle, the maximal degree of indistinguishability is automatically guaranteed, as is the associated quantum interference.

To conclude, incoherent interference control is markedly different from traditional coherent control, in that the former utilizes a specific kind of quantum interference that results from the absolute indistinguishability of multiple excitation pathways to the same target state. It can therefore be anticipated that incoherent interference control schemes will be applicable in cases involving highly quantum states of light.

IV. COHERENCE CREATION IN PHOTODISSOCIATION PROCESSES

In this section we apply insights from Secs. III and IV to the related problem of quantum coherence creation in photodissociation processes. On one hand, this problem is similar to quantum coherence creation in bimolecular collisions since usually there are two or more products separating from one another in the photodissociation processes. On the other hand, the physics here involves the creation of molecular coherence using light fields.

Suppose the photodissociation process is $AB \rightarrow (AB)^* \rightarrow C + D$, where $(AB)^*$ represents, after AB absorbs one photon, the excited complex before it breaks apart to form molecules $C + D$. Conventional photodissociation experiments that employ very long monochromatic laser pulses are such that, essentially, $(AB)^*$ has both definite energy and momentum. Hence the process $(AB)^* \rightarrow C + D$ is precisely the same as the second half of a bimolecular collision discussed in Sec. II. It then follows that each photodissociation fragment in this process cannot have useful coherence between different translational states or between nondegenerate rovibrational states.³² This is fundamentally because one can, in principle, obtain which-state information about one fragment by measuring the other fragment since the total momentum and total energy are known. One can then predict that, although it is common to have a broad rovibrational state distribution in a photodissociation fragment, no definite phase relationships between the nondegenerate rovibrational states of one individual product molecule should be expected in traditional photodissociation processes (i.e., that do not incorporate coincidence measurements). This should be the case even when classical correlations in the final state distributions between two fragments are weak.

As in bimolecular collisions, however, conventional photodissociation with monochromatic sources can still generate coherence between *degenerate* internal states of photodissociation fragments. For example, consider a laser field linearly polarized along the x direction and examine the coherence between states of C with different m_z (the quantum number associated with the projection of the angular momentum onto the z -axis). The associated selection rule is $[m_z(C) + m_z(D) - m_z(AB)] = +1$ or $[m_z(C) + m_z(D) - m_z(AB)] = -1$. Apparently then, knowledge of $m_z(D)$ cannot tell us the precise value of $m_z(C)$ since there are still two different possibilities. Thus, a superposition state of C comprising two $m_z(C)$ components can be created in such a photodissociation process.

By contrast to the bimolecular analogy and monochromatic light sources, femtosecond laser technology opens new interference possibilities in photodissociation dynamics. Ultrafast laser pulses directly excite the molecule AB into a coherent superposition state of many rovibrational states embedded in the continuum, on a time scale much less than that of the rovibrational motion. These photodissociation processes are no longer analogous to the second half of bimolecular collisions due to the large energy uncertainty introduced by ultrafast laser pulses. Indeed, these processes are similar to those in various coherent control scenarios where coherence is transferred from light fields to molecules. As such, quantum states of photodissociation fragments C and D can be largely free from entanglement in energy, i.e., by

accurately measuring the energy of one fragment we cannot necessarily specify the energy of the other fragment. Hence, indistinguishability conditions can be satisfied and rovibrational coherence effects of one individual photodissociation fragment may be created and further used for a second molecular process. One can conclude that it is exactly the lack of entanglement between photodissociation fragments that makes possible the previous observation of coherent vibrational motion of photodissociation fragments.^{33–35} Note, however, that under the assumption that we can neglect the momentum carried by photons, useful coherence in the translational motion of a product molecule still cannot be created due to the momentum entanglement between photodissociation fragments.

V. CONCLUDING REMARKS

In this work, we have examined, within in the context of coherent control of molecular processes, the subtle issue of indistinguishability and interference between independent pathways. Interference occurs only when independent pathways are indistinguishable. Due to this indistinguishability requirement, creating a useful superposition state of nondegenerate molecular states or of momentum eigenstates for subsequent coherent control cannot be achieved by collisions between atoms or molecules (initially prepared in energy and momentum eigenstates). Coherence can, however, be conveniently transferred from light fields to molecules. This coherence transfer and the subsequent coherent control based on this coherence transfer (as analyzed in the two-pulse control as an example) are best realized by the most classical states of light, i.e., coherent states of light.

We have shown that quantum states of light may suppress the extent of phase-sensitive coherent control by leaking out some which-way information in quantum processes. By contrast, incoherent interference control schemes are shown to have automatically ensured the maximal degree of indistinguishability between independent excitation pathways. Thus, when extended to a regime where the quantum nature of light becomes important, some of the known optical control scenarios should be effective whereas some others may not work at all.

We have also discussed the implication of the relationship between indistinguishability and interference for understanding coherence creation in photodissociation fragments. It is shown that traditional photodissociation processes with long monochromatic laser pulses cannot create useful molecular coherence between nondegenerate rovibrational states due to the quantum entanglement between photodissociation fragments. New possibilities afforded by femtosecond photodissociation processes are understood in terms of disentanglement in energy between photodissociation fragments.

The essence of coherent laser control of atomic and molecular processes can be often understood in parallel with a double-slit quantum interference experiment. This work further strengthens this analogy. In particular, it now becomes clear that laser fields in coherent phase control play the similar role as the classical diffraction single-slit plate and the classical double-slit plate, in that laser fields first create in-

dependent pathways and then recombine these pathways to generate quantum interference. Though somewhat counterintuitive, we can now conclude that, due to the unavoidable quantum entanglement between quantum systems that have interacted in the past, the successful creation of quantum coherence or interference phenomenon in a quantum system often involves a macroscopic object that is describable by classical physics, such as classical slits in the case of double-slit matter-wave interference experiments, or a sufficiently classical electromagnetic field in the case of coherent interference control experiments. As is now clear, roughly speaking this is because a classical object can remain disentangled with the quantum system of interest and independent pathways are therefore created without leaking out which-way information. Such a role of classical objects in generating useful quantum coherence, we believe, deserves more attention in understanding the connection between classical and quantum worlds.

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