

# Control of Chemical and Physical Processes using Phase and Amplitude-Shaped Laser Pulses

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When two or more photons are required to excite a transition in an atom or molecule, the phase between those photons can play a role that is as important as the frequency of the photons. In fact, the phase difference is liable to modulate the probability of the excitation between 0 and 100%. The interest in phase-related (coherent) control stems in part from research focusing on quantum information sciences, controlling chemical processes and developing new optical technologies such as biophotonics and imaging cellular materials. The use of the coherent properties of radiation to control physical processes is the modern offspring of the famous double slit experiment of Young in 1884. In that experiment, Young demonstrated that when light passes through two slits spaced on the order of the wavelength of the radiation an interference pattern is created. Even when single photons pass through two slits, the correlation function between individual the photon diffraction events is consistent with the classical interference pattern. In an interferometry experiment (e.g., a Michelson interferometer), the position of the fringes depends sensitively on the difference in phase between the two interfering pathways. One can completely modulate the intensity at a certain position by simply changing the length (phase) of one of the paths. In 1930s Davisson and Germer demonstrated that electrons<sup>1</sup>, too, could interfere and recently Zeilinger<sup>2</sup> observed diffraction when buckyballs (60 carbon atoms arranged in the shape of a soccer ball) interacted with two slits!

Given the fact that the wave properties of matter are well-established, we can consider the use of the wave properties of light interacting with matter to control physical and chemical processes driven by absorption of light. And we can do this even if we do not fundamentally understand how the photon, electron, or buckyball interact with two slits simultaneously! Perhaps the first mention of the concept of phase control in the optical regime can be traced Manykin and Afanas'ev's to investigations<sup>3</sup> in Russia in the early sixties where in the interference between a one and three photon path was theoretically proposed as a means to modulate a two photon absorption. This idea lay dormant until the reality of controlling the relative phase of two distinct frequencies was achieved in the laboratory (using gas phase pressure modulation) for frequency domain experiments many years later, as described later.

The goal in all quantum control experiments can be expressed in the following<sup>4</sup> notion:

$$|\psi_i\rangle \rightarrow |\psi_f\rangle \quad (2)$$

where an initial quantum state  $|\psi_i\rangle$  is transferred to a specified final state  $|\psi_f\rangle$  by virtue of an interaction with an electromagnetic field. The propagation of the initial state to the final state is governed by the time-dependent Schrödinger equation for the molecule coupled to the driving field via:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = [H_0 - \mu \cdot \varepsilon(t)] |\psi\rangle \quad (3)$$

where  $\mu$  is the transition dipole,  $H_0$  is the Hamiltonian for the molecule and  $\varepsilon(t)$  is the electromagnetic field. The key is to find the time dependent electric field that will enable

the transition and this depends intimately on the Hamiltonian for the molecule. We will see that certain simple Hamiltonians and objectives can be solved analytically, but for chemically interesting problems, where the solution to Hamiltonian is complicated, novel solution strategies must be employed.

Electronic states within a molecule are coupled through dipole transitions and, since the electromagnetic driving field is a wave, Brumer and Shapiro<sup>5</sup> suggested in 1985 that interference effects should be observable in the probability for transferring population in a molecule as a function of the phase of the driving fields.. The key notion in all quantum interference phenomena is that any two states that are coupled by indistinguishable paths will interfere, and that interference can be modulated as the phase difference between those paths is altered. For example, in an atom or molecule, a one photon path has a one photon transition probability,  $f_{qd}$ , given by:

$$f_{qd}^{(1)} e^{i\delta_{qd}^{(1)}} = \langle d | D^{(1)} | E, \hat{k}_1, q^- \rangle \quad (1)$$

$$D^{(1)} = \mu \cdot e$$

where  $e^{i\delta}$  is an arbitrary phase,  $q$  represents the initial state,  $d$  represents the target state and  $D$  is the transition dipole moment, which is a function of the transition dipole  $\mu$  and electric field vector  $e$ . A three photon excitation process has a transition probability,  $f^{(3)}$ , given by:

$$f_{qd}^{(3)} e^{i\delta_{qd}^{(3)}} = \langle g | D^{(3)} | E, \hat{k}_1, q^- \rangle \quad (2)$$

$$D^{(3)} = \sum_i \sum_j \frac{\mu \cdot e_1 |i\rangle \langle i| \mu \cdot e_1 |i'\rangle \langle i'| \mu \cdot e_1}{(\hbar\omega_1 - E_i)(2\hbar\omega_1 - E_{i'})}$$

The amplitude for transferring population from state 1 to state 3 is then given by:

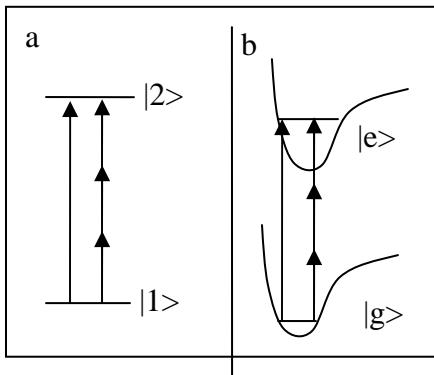


Figure 1, A schematic of two state control in the case of **a**, a two-state atom; and **b**, a molecule. In each case, the and lower and upper state are coupled by a one and three photon path.

$$W^q = \left| f_{qd}^{(1)} e^{i\delta_{qd}^{(1)}} + e^{i\phi} f_{qd}^{(3)} e^{i\delta_{qd}^{(3)}} + f_{qd}^{(3)} e^{i\delta_{qd}^{(3)}} + f_i f_{qr}^{(3)} e^{i(\delta_{qr}^{(3)} - \delta)} \right|^2$$

$$W^q = W_1^q + W_3^q + 2W_{13}^q \cos(\phi + \delta_{13}^q) \quad (3)$$

The cross term,  $W_{13}$  can completely modulate the population in the excited state even if the individual amplitudes would correspond to 100% transfer. Note that there is a phase in each of the expressions which is normally of no consequence. In the case of excitation of the atom or molecule in the presence of two or more pathways, the phase difference of the pathways is not only important, but it can dominate the excitation allowing complete transfer or completely shutting off the transition!

The experimental realization of the two path method was first demonstrated by the Elliott group in 1988 for an atomic transition<sup>6</sup>. The trick was the implementation of precise phase control

by the frequency dependent retardance for an the  $\omega$  vs.  $3\omega$  interaction in a gas cell. Since  $3\omega$  is closer to an electronic transition, the index of refraction is greater. Upon increasing the pressure of the gas cell, the relative phase of the one and three photon transition can be modulated many times as the pressure is increased. The Gordon group employed this phase control method in 1991 to control the control of the dissociative ionization of HI<sup>7</sup>. The two color, two path control method has been extended to larger molecules, but has not produced the general applicability level that time-dependent, ultrafast laser pulse shaping methods have demonstrated. In part this is due to the fact that the pressure tuning method, while well-suited to 1 vs. 3 photon control had limited applicability for creating the complex pulse shapes necessary to control processes in polyatomic molecules.

### Time and Frequency; the Complementary Control Basis Sets

The majority of the initial control experiments have been realized by manipulating laser pulses to create specialize shapes in the time domain rather than relying on the frequency domain control described in references 6 and 7. In one implementation of the time domain approach, a pulse of laser light is used to initiate a process and a second, time-delayed pulse is used to probe the dynamics of the system. This is perhaps the simplest example of time domain control. In the simplest example of frequency domain control, two “continuous wave” lasers are manipulated with respect to their relative phase to control population transfer for instance. In the Elliott experiment described for 1 vs.  $3\omega$  control the shaping occurred in the frequency domain, by directly altering the phase difference between  $\omega$  and  $3\omega$  by pressure manipulation. Note that the overlap of the continuous waves in the time domain will lead to periodic temporal structure in the electric field as the two waves interfere, and this suggests that there is a correspondence between time and frequency domain control. Note also that this interference structure will depend on the relative phase delay between the 1 and  $3\omega$  beams.

Formally, there is a one to one correspondence between control in the frequency domain and control in the time domain<sup>8</sup>. The two approaches are Fourier transforms of each other. The time-domain approach can be thought of as the analog of the traditional pump-probe method wherein a time-dependent wave packet,  $\Psi(t)$ , is created from time-independent eigenstates by constructing a superposition of time-independent wave functions:

$$\Psi(t) = \sum_i a_i \psi_i e^{i\omega t} e^{i\phi_i} \quad (4)$$

where  $a_i$  is the coefficient for the amount of eigenfunction,  $\psi_i$ , in the superposition state,  $\omega_i$  is the energy of  $\psi_i$ , and  $\phi_i$  is the phase of the eigenfunction. In an eigenstate, the phase of the wave function plays no role physics of the system, but in the superposition state (or in a nonlinear process), phase shares equal importance with the magnitude of the coefficient  $a_i$ .

In the vast majority of the time domain control experiments the objective is to interrogate the dynamics of a physical or chemical process, rather than to control the available product channels of the system. Perhaps this is just semantics, but the bulk of the time-domain pump probe experiments are focused on the characterization, rather than the creation of new products and distributions of products<sup>9</sup>. To manipulate the product distributions in a flexible way, one typically employs a shaped laser pulse, rather than a

simple pump probe excitation scheme. In the shaped pulse control approach, an ultrafast, time-dependent pulse is Fourier transformed from time to frequency. To accomplish this, the laser pulse is spectrally dispersed, typically by a grating or prism and collimated by a lens. The spectrally dispersed beam passes through a focus at the Fourier plane and is then imaged onto a second grating or prism. In the Fourier plane of the 4f spectrometer, a phase and amplitude mask is applied to modulate the pulse in the spectral domain. After re-imaging, the phase and amplitude modulated beam becomes a temporally modulated laser pulse. This method for pulse shaping was first proposed in 1988 by Andrew Weiner.<sup>10</sup> As described in Chapters X and Y there are several designs to accomplish such 4f pulse shaping using acousto-optic, liquid crystal and deformable mirror masks. More effective control of product channels can be obtained using these laser pulse shaping techniques because up to 1000 individual frequency bands can be phase controlled, providing hundreds of sub-pulses. Compare this with the two frequencies controlled in the gas cell phase control experiment or the two pulses available in a pump probe method.

Perhaps the reason why the multi-path laser pulse shaping control approach found in pump-probe and shaped laser pulse control experiments has dominated the control literature is that there are many more interfering pathways available. The two path, frequency space control method described above can be realized by simply using two elements of the spatial light modulation scheme. In the case where one desires to control complicated processes in a complicated system, like the breaking of bonds in a polyatomic molecule, one intuitively suspects that more slits (control knobs, sub pulses or time-frequency structure) will give a higher degree of control. In the case where the eigenstates of the system are not resolved, this use of multiple pathways or slits is necessary to achieve control. This intuitive picture is born out by experiment.

Multiple slits can easily be introduced into the path of a laser beam by the use of a spatial light modulator. In this case, up to one thousand effective slits are available in the case of acousto-optic modulation and a typical modulator might employ 128 independent pixels or slits. If one considers the products of a chemical reaction to be a distribution of product states, then one requires the highest resolving power to localize intensity on a single product. This is typically accomplished by using a number of slits, scattering centers or grating lines. In the case of optical radiation, one device for selecting a specific frequency is a diffraction grating. One can calculate the resolution of a diffracting system as a function of the number of point sources by:

$$R = n m \quad (5)$$

where  $n$  is the number of scattering rulings and  $m$  is the order. Clearly, as  $n$  increases, the angular spread of the diffracted wave decreases, providing higher resolution. Thus to control a super position state for greater spatial or temporal resolution more scattering centers improve the spatial resolution. That is, the resolution of the super position state in state space scales with the number of waves that can be super-imposed. The message for the control of complex systems is that two slits can not possibly achieve the sort of control possible with hundreds to thousands of slits either qualitatively or quantitatively.

Since the coordinates of time and frequency are Fourier pairs, the control concepts proposed for pump-dump and two path interference are intrinsically linked. One

can show that what ever scheme one proposes in one coordinate space can be formulated in the other and this is a direct consequence of the wave nature of matter and radiation.

### Calculating the Optimal Pulse Shape for Control

Given the powerful pulse shaping ability in the time-frequency domain, one might propose that all we need perform is a calculation to specify the laser pulse shape that will provide the desired product distribution. Unfortunately, the available computational power and algorithms are not sufficient to gain predictive ability from quantum calculations for real, complex systems at the present time. In fact, sufficient computing does not presently exist to calculate the time-dependent laser pulse shapes for even the simplest of chemical reactions. Calculations have been performed for controlling molecules, but the level of approximation employed is such that no experimental implementation has been performed yet. One counter example, however, is a calculation predicting the outcome of a laser induced chemical reaction where the Cl-Cl bond in chlorine was cleaved by spinning chlorine molecules from the ground to  $J = 420$  states using a shaped laser pulse.<sup>11</sup> In this experiment, the shape was a dual chirp that induced Raman ladder climbing through the rotational manifold. Rotational wave functions are also known to sufficiently high accuracy that time-dependent rotational alignment can be predicted. In such rotational excitation experiments, however, bonds are typically not broken. Rather a rotational alignment is prepared. In most such experiments there is no pulse shaping, rather the degree of alignment is calculated as a function of time after an impulsive alignment pulse is applied. However, recent calculations suggest that the degree of alignment can be enhanced if shaped laser pulses are employed<sup>12</sup>.

### Closed Loop Control

When one desires control over a more complicated outcome, such as manipulating laser induced bond dissociation dynamics, the preferred solution at the present time is to use closed loop methods to determine a suitable laser pulse shape. The reason for the necessity of such an “engineering” approach can be understood by considering the Hamiltonian for the control experiment. The overall Hamiltonian for the system,  $H_{\text{system}}$ , is given by:

$$H_{\text{system}} = H_{\text{molecule}} + H_{\text{radiation}} + H_{\text{interaction}}, \quad (6)$$

where  $H_{\text{molecule}}$  is the Hamiltonian for the molecule,  $H_{\text{radiation}}$  is the Hamiltonian for the radiation and  $H_{\text{interaction}}$  is the Hamiltonian for the interaction between the radiation and the molecule. Unfortunately, the solution to the molecular Hamiltonian interacting with radiation is only in approximate form and for intense laser field, many excited states of the molecule must be known to allow a “first principles” solution (as in equations 1-3) for the necessary electric field to drive a chemical transformation. At the present time such excited states are not calculable for polyatomic molecules. In fact the lower electronic and vibrational states are often zero-order-bright-states rather than the eigenstates necessary for the calculation. In the weak field limit, the interaction Hamiltonian is the well-known  $\mu \cdot E$ , but at higher laser intensities, the solution involves higher order interactions, making the calculation even more challenging. In this event, one can

consider the use of adaptive engineering methods to refine the time dependent field that will be suitable for controlling the desired molecular process<sup>13</sup>.

In the adaptive engineering approach, the system itself is used to screen and refine the laser pulse shape required for optimal control. The experiment has marked similarities to nature's method of optimizing an enzyme to perform a desired task. For example, in the immune system response to a pathogen, a series of evolutionary operations are performed to deliver an array of antibodies to be screened for effective binding to an antigen. The antibodies are specified through a series of crossover and mutation operations to the DNA used to produce the peptides in the antibody pool<sup>14</sup>. In a similar fashion, we encode the DNA of the laser pulse shape in a series of phase and amplitude functions that are used to control the voltages applied to the liquid crystal pixels in the spatial light modulator. We begin with a collection of 40 randomly generated laser pulse shapes and screen for the desired outcome of the photonic reagent using an appropriate detection system. The detection systems include mass spectrometry, UV-visible absorption, coherent anti-Stokes Raman spectroscopy (CARS), stimulated Raman and extreme UV emission spectroscopy. The signal measured by the detection system is fed back to the algorithm to generate a fitness value describing the suitability of that particular photonic reagent for the desired process.

The general requirement for feedback detection is that the detector be rapid on the time scale of updates to the pulse shaping system. Once the pulse shape is applied to the molecular system, the result of the photonic reagent interacting with the system is measured and a fitness value is calculated. The fitness value is stored with the genome specifying the phase and amplitude mask and is used to determine the probability that the genome will be used to produce the next generation. The actual selection of genomes occurs through the process of proportional selection, a process wherein the probability of use in the next generation is proportional to the fitness of the genome. Thus there is not a threshold for incorporation or exclusion, rather there is a probability factor determining the likelihood of incorporation. The next generation is created from a series of cloning, crossover and mutation operations. The crossover operations allow useful characteristics of one pulse shape to be combined with useful characteristics of another pulse shape. Mutation allows new phase and amplitude values to be incorporated into a given pulse shape and cloning refers to the duplication of the best genomes into the population to preserve stability.

### Strong Field Control

To control chemical processes (bond breaking and bond making in molecules and materials) with photonic reagents, one has to excite the system using the available vibrational and electronic manifolds of states. (The rotational manifold may also be employed to align the molecules to increase reaction probability, but except in the extreme example of the molecular centrifuge, there is no chemistry (bond breaking and making) at rotational levels of excitation. Currently, separate laser sources must be employed to excite the vastly different energy ranges of vibration and electronic states. Rotations occur in the microwave region, vibrations occur in the infrared and electronic excitation occurs in the visible/UV range. At the present time, there is no laser system

that can span such a large frequency range, thus providing a major limitation to control schemes in the weak field regime. Supercontinuum fibers are providing a first example of a technology that can excite a molecule over a large wavelength range, although the excitation would occur in the weak field limit. The weak field regime encompasses the perturbative regime where the eigenstates of the field free system form the natural basis states for control. In the weak field limit (e.g. CW lasers), there is a spectroscopic restriction that the radiation resonantly excite the molecule. Thus if a series of 10 vibrations and five excited electronic states are important, perhaps 15 to 50 separate, phase locked laser lines are required for control. In the weak field regime, this is no trivial task as no methods have been demonstrated for such a synthesis of electromagnetic radiation. For ultrafast laser pulses, the bandwidth restriction is reduced somewhat because of the Fourier relationship between pulse duration and bandwidth. Rather than having the  $10^{-8}$  eV line width in a typical CW laser, the line width is more like  $10^{-2}$  eV. Since vibrational energy level spacings are on this order, one can coherently excite many rotational and perhaps two or three vibrational lines in a molecule using the CO stretching frequency ( $\sim 0.2$  eV) as an example. This is typically not enough bandwidth to control any but the simplest of chemical reactions, for instance  $I_2 \rightarrow 2I$ . However to control the chemical reactivity of more complex polyatomic molecules, more comprehensive control mechanisms are necessary.

In the strong field regime, the laser intensities approach the atomic unit of field strength. Thus the laser interaction itself can modify the electronic structure of the molecule and this effectively causes a massive increase in effective bandwidth from tens to hundreds of meV for a 40 fs duration laser pulse to 10 eV when Stark shifting and broadening of energy levels is accounted for. A schematic of such bandwidth enhancing phenomena is shown in Figure X. The stark shifting will produce energy level shifts on the order of electronic energy level spacing between the HOMO and LUMO of most molecules as the laser intensity approaches  $10^{14}$  W  $\text{cm}^{-2}$ . In addition, broadening of the levels due to nonadiabatic excitation will also be on the order of the electronic energy level spacings. This produces a quasicontinuum that is under investigation at the present time to discern new mechanisms of control.

With the availability of the enhanced band width in the strong field regime, a number of interesting experiments have been performed. These include the the control of bond dissociation, and rearrangement, and the control of filamentation in the solution phase.

Problems:

1 Calculate the number of outcomes when **a**, a coin is flipped twice, three times, n times; **b**, three coins are flipped two times, n times; **c**, 128 liquid crystals have 1 degree of phase control.

2 Describe the procedure that nature employs for evolution where in information is stored in a genome, and progress is made by always comparing to an ensemble that remembers the past through that genome.

3 Calculate the pulse shape resulting when  $w$  and  $2w$  interfere as a function of the relative phase between the waves.

4 Calculate the interference between an  $w$  and  $3w$  interfering pathway as a function of relative phase using equations 1-3.

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