# Controlling the Future of Matter

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Ever since the development of the laser, the quest to use light to control the future of matter has been one of the Holy Grails of chemistry.[1-9] Can we develop general ways to use lasers to specifically manipulate the quantum behavior of atoms and molecules? Can we control the nature and products of chemical reactions by, for example, breaking a selected bond in a polyatomic molecule? Can we develop novel synthetic methods to produce exotic new molecules, states of molecules, or even molecular devices, such as programmable optics or nanomachines? Can we extend these ideas beyond the gas phase to applications in solids, clusters, or liquids or on surfaces?

Ultimately, the ability to control matter with light depends on a close interplay between theory and experiment. The first step is to choose a target, or final outcome, that we wish our sample of matter to attain. Next, we must design the optimal way to use light to drive the sample to that goal. Then we need to create as well as we can the experimental conditions to produce the appropriate light in the laboratory. Finally, we must have a way to measure how well we have attained our goal. In the past, some success has been achieved by controlling the frequency or intensity of light.[3,10] The product yield in a photoinitiated reaction, for example, depends on how long we wait after the initiation of the reaction to measure the yield. Similarly, tuning the laser frequency to a vibrational or electronic resonance can alter the outcome of a reaction. Bond, or mode, selective chemistry has now been demonstrated experimentally by several groups.[11-14]

In this paper, we concentrate on methods that can be broadly grouped under the rubric of "quantum control". These methods achieve selectivity by exploiting the quantum mechanical constructive and destructive interference in matter induced by light. For example, Brumer and Shapiro have shown[4] that, in a system with two or more independent routes to the same degenerate final state, varying the relative phase of these paths can be used to exert control over the outcome of chemical events. An alternative set of methods attempts to design the light pulse or train of pulses to attain a given goal.[5,7-9,15-20] One way to do this, as first demonstrated by Rabitz and co-workers,[21,22] is by the use of optimal control theory. Tannor and Rice[8] developed a scheme for control of product formation in a chemical reaction via time delay between a pair of femtosecond pulses and introduced a variational formulation for the optimal pulse sequence. The control in all of these methods derives from the explicit attempt to tailor the coherence of light to modify the natural dynamics of matter.

While the theoretical side of this field is currently more advanced than the experimental, several groups

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The Wilson Group, in the Department of Chemistry at the University of California, San Diego, combines analytical and computational theory with ultrafast experiments to study the quantum control of matter with light. Researchers in the group have a variety of backgrounds, from chemistry and physics to optics.

Kent Wilson (Ph.D., Berkeley, 1964) is the group leader. Wilson's research interests have spanned archaeology, air pollution, computer animation and graphics, molecular dynamics, and ultrafast diffraction and spectroscopy. The group's computational theorists, Jeff Krause (Ph.D., Chicago, 1987) and Rob Whitnell (Ph.D., Chicago, 1988), work on classical, semiclassical, and quantum approaches to control. YiJing Yan (Ph.D., Rochester, 1989) develops analytical theories of nonlinear spectroscopies. On the experimental side, Bern Kohler (Ph.D., MIT, 1990) and Vlad Yakovlev (Ph.D., Moscow State University, 1990) designed and built the ultrafast laser system used in the experiments. Ferenc Raksi (Ph.D., JATE University, Hungary, 1989) concentrates on experimental ultrafast X-ray techniques for quantum control.

have now successfully demonstrated control in the laboratory. Control of atomic ionization has been accomplished by Elliot and co-workers,[23] and of molecular ionization by Gordon and co-workers.[24] The directionality of photoelectron emission has been controlled by Muller et al. in the gas phase[25] and by Baranova et al. in a semiconductor.[26] Warren and co-workers[27] have shown that electronic population can be inverted in a gas and that population transfer can be enhanced with frequency swept pulses.[28] The products of a chemical reaction have been controlled by Zewail and co-workers using a series of short timed pulses.[29] The control of vibrational dynamics in a diatomic molecule has been achieved by Scherer et al. using phase-locked pulses[30] and by by Kohler et al. using specially tailored pulses.[31,32] There have also been reports of the control of angular distributions of photoelectrons by Yin et al.,[33] atomic products by Hepburn and co-workers,[34] and the total yield of atomic final states by Shapiro and co-workers.[35]

In this Account, we will focus mainly on speculating about the future, rather than on recounting the past. We will begin with only enough examples of what has already been accomplished to ground the discussion in reality. We will then set off upon a knightly quest for the Holy Grail. We will dream of conceivable futures for matter that we would like to achieve. These will be the late night dreams of the mercurial quantum dynamicist. Like all dreams they may not come to pass. In the end, all of them may prove impractical to achieve. The Holy Grail itself was never found, but its quest inspired many works of art and literature. We hope that the process of our dreaming, and the progress of our search, may lead us to outcomes that are of value, even if they are not our original goals.

The theory of quantum control allows us, in principle, to compute the optimal light field required to reach any specified target for a sample of matter. There is, however, no guarantee in practice that we know enough about the sample, or have enough computer time, to perform the computation, or that having computed the optimal light field, we can make it in the laboratory. In what follows, we will discuss various targets, or goals for matter, beginning with an illustrative case for which both theory and experiment have now been performed.

We hope that the reader will indulge us for myopically focusing in what follows almost exclusively upon our own work and dreams. This has the advantage

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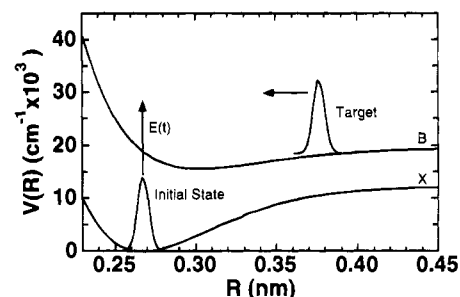


**Figure 1.** Schematic diagram of the $I_2$ molecular reflectron described in the text. The iodine molecule begins in its ground X state, and the object is to find the electric field $E(t)$ that creates a wave packet on the electronically excited B state with the best possible overlap with the target, at the target time. For the reflectron, the target is a minimum uncertainty Gaussian distribution centered about a position of 0.372 nm, with a momentum directed toward the center of mass corresponding to an energy of 403 cm$^{-1}$. The target time is 550 fs.

that the blame for conceits and misjudgments may be clearly placed.

## Controlling Where Atoms Are, and Where They Are Going

When a molecule is excited by a short pulse of light of the appropriate center frequency, a localized wave packet can be created on an electronically excited state. Because molecular potential surfaces are anharmonic, these matter packets tend to spread in both position and momentum. One simple goal for quantum control is to counteract this natural tendency to spread, or defocus, and to require that the matter packet be localized at a certain time, about a chosen position and momentum.[18-21,36-39] In particular, we can specify that the quantum distribution should be as tightly localized as possible within the bounds prescribed by quantum mechanics. That is, the matter packet should be of minimum uncertainty (i.e., $\Delta p \delta q = \hbar/2$, where $\Delta p$ is the variance in momentum and $\Delta q$ is the variance in position). One way to do this is to use a laser source to produce light pulses whose coherence properties we can control. By interacting this light with a sample of material, the coherence of the light can be transformed into the coherence of the material quantum wave function, such that the wave packet evolves to maximum overlap with the chosen target at the chosen time.

As a first example, consider the control of the vibrational dynamics of the $I_2$ molecule, as illustrated schematically in Figure 1.[19] The target, in this case, is a minimum uncertainty Gaussian distribution on the electronically excited B state, centered about a position of 0.372 nm, with its momentum directed toward the center of mass (that is, the iodine atoms are moving toward each other with a selected mean velocity). We have termed this example the "molecular reflection", since the wave packet must reflect from the outer wall of the potential to reach the target region with a negative momentum.[19] The goal is to find that laser pulse, or electric field $E(t)$, that excites the molecule from its ground state to form a vibra-
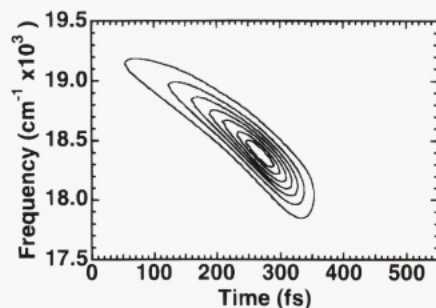
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**Figure 2.** Globally optimal field, in the weak response limit, for the molecular reflectron shown in Figure 1, in a Wigner time–frequency representation.

tional wave packet with the best possible overlap with the target at the chosen target time (550 fs, in this case).

To compute the optimal laser field for a particular scenario such as that in Figure 1, we have developed and implemented a theory combining a density-matrix, Liouville space approach with optimal control theory.[18,19] In the weak response (i.e., perturbative) limit, the theory involves computing a specially constructed material response function, or control kernel, that depends only on material properties, such as the potential energy surfaces, dipole moments or other couplings, and the target, but not explicitly on the electric field. The eigenvectors of the material response function are the optimal electric fields, and the eigenvalues are the target yields, which measure how well the target has been achieved. The eigenvector associated with the largest eigenvalue is the globally optimal field, in the weak response limit.[18] Thus, the desired laser pulse $E(t)$ is obtained by simply diagonalizing the appropriate matrix.

The globally optimal field for the reflection is shown in Figure 2 in a Wigner, or time–frequency, representation. The field is simple and smooth, and its dominant characteristic is the presence of a significant negative chirp, visible as the overall negative slope of the contours in the figure. In a negatively chirped pulse, the high-frequency components arrive before the low-frequency components. This causes the higher energy parts of the wave packet to be excited before the lower energy parts. The higher energy parts must travel "further" on the anharmonic B state before reaching the target region, at which point they interfere constructively with the lower energy parts to produce the required narrow, minimum uncertainty distribution in position and momentum. If we choose a target with an outgoing momentum, or a "cannon", the globally optical field has a positive chirp, instead of a negative chirp.[19] We see, then, that it is the coherence, in the sense of the time–frequency correlation of the optimal field, that is responaible for the control.

The underlying physics governing the globally optimal field in Figure 2 is easy to understand. In fact, several groups have used, or proposed to use, chirped pulses to control various dynamical processes.[39,40] We emphasize, however, that our formalism does not enforce a priori that the field have a specified functional form. In fact, the shape of the electric field is totally unconstrained in the allotted time interval. The system discovers the simple chirped form for the reflection field automatically, and without prejudice.

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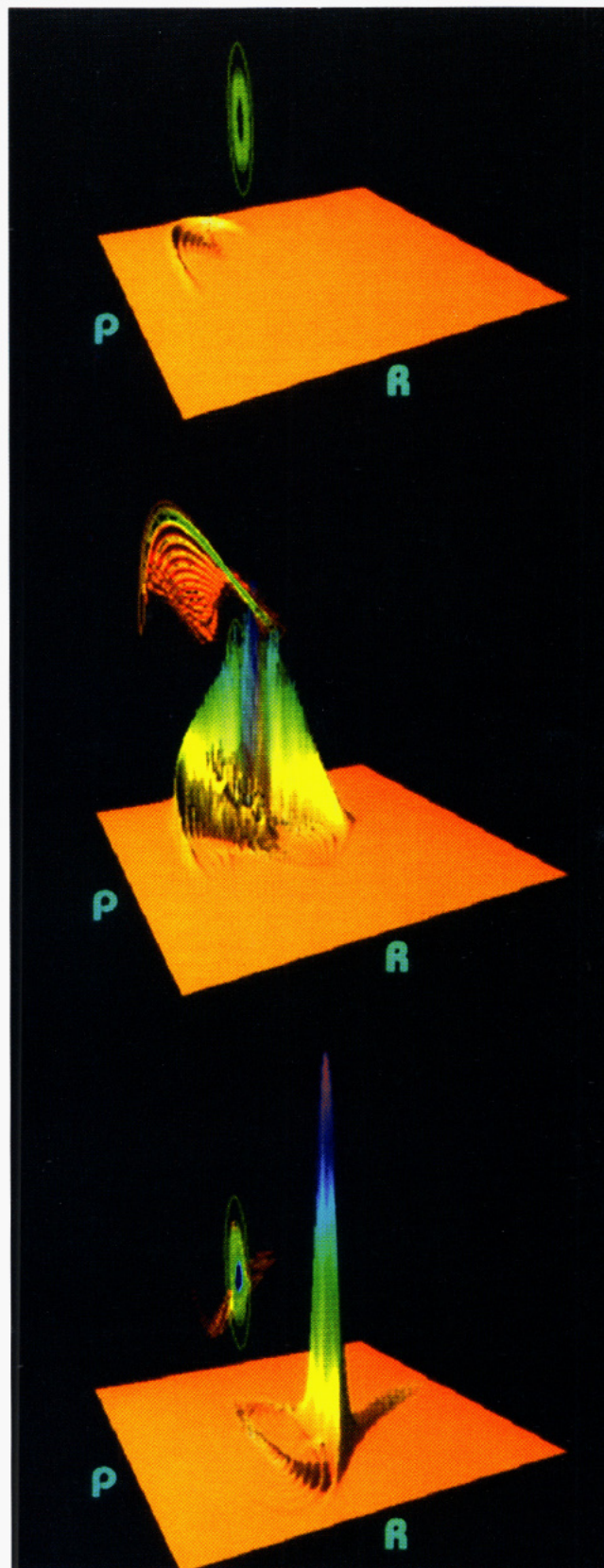


**Figure 3.** Time evolution of the vibrational wave packet created by the globally optimal field in Figure 2, for the molecular reflectron. The evolution is presented in a Wigner phase space (position $R$ and momentum $P$) representation. Two views of the evolution are shown, a three-dimensional representation (foreground), in which the height is mapped to the color, and a two-dimensional, contour representation (background). The green contours depict the target. The propagation time is (top to bottom) 110 fs, 330 fs, and the target time, 550 fs, when the wave packet is focused into a nearly minimum uncertainty distribution in position and momentum.
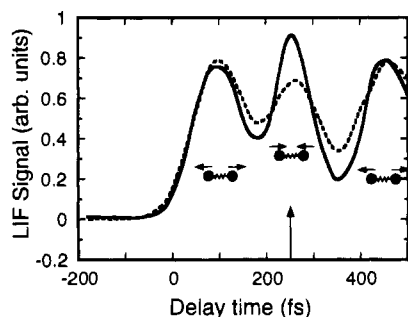
**Figure 4.** Experimental realization of the quantum control of the vibrational dynamics of $I_2$. The target is a minimum uncertainty Gaussian distribution with momentum directed toward the center of mass (i.e., a reflectron), as illustrated in Figure 1. The solid line shows the laser-induced fluorescence (LIF) signal as a function of the delay time between the pump and probe pulses for a pump field with a negative chirp such as that in Figure 2. The dashed line shows the signal obtained with an approximately time-reversed pump pulse (that is, a positively chirped pulse). The probe pulses had a temporal duration of ~45 fs and were transform limited (zero chirp). The target time, at which the wave packet focuses or defocuses depending upon the chirp of the pump pulse, is indicated by the vertical arrow.

We also note that the optical fields are not limited by the method to solutions consisting of a single pulse. In general, multiple-pulse solutions are obtained if the allotted time interval is long enough to support them.[19] Of course, there is no reason to expect in the general case that the optimal fields will be as simple as that in Figure 2, especially in a complicated multimode system.

Figure 3 shows the time evolution of the $I_2$ molecule in phase space (i.e., in both internuclear position and internuclear momentum) as it is driven by the globally optimal field toward the target. The wave packet is quite complicated at early times in the evolution and is extended in both position and momentum over much of its available phase space. As the target time approaches, the quantum interference collapses the wave packet onto the minimum uncertainty target. The achievement, measured as the overlap of the vibrational wave packet with the target at the target time, is 0.97, which is not perfect, but as good as nature allows in the weak response limit. The wave packet produced at the target time is well localized in both position and momentum. However, the wave packet produced by an identical laser pulse, with just the sign of the chirp reversed, produces a vibrational wave packet at the target time that is considerably more delocalized in both position and momentum. This is another indication that control in this case is due to quantum interference. The positively and negatively chirped pulses that produce such different results are identical in both their frequency spectra and time−intensity profiles. In fact, they are simply time reversals of each other.

We have performed an experiment[31,32] in which we have synthesized a pulse resembling the globally optimal field in Figure 2. We have experimentally demonstrated, as shown in Figure 4, that a negatively chirped pulse does indeed produce a localized wave packet at the target time, while a positively chirped pulse produces a much less localized wave packet. To observe the vibrational dynamics experimentally, we use the pump−probe approach pioneered for $I_2$ gas phase dynamics by Zewail.[41] By exciting the wave packet with a probe pulse to a third electronic state,

or probe state, we open a window in internuclear distance in which the probability of finding the wave packet at a certain time is related to the observed laser−induced fluorescence from the probe state as a function of the delay time between the tailored pump and probe pulses.

It is important to realize that, having gained the ability to control the vibrational dynamics of a molecule, we can also exert this power, in principle, to control chemical reactions. By exciting the system with a laser pulse at the target time, we can force the localized matter packet onto a chosen excited state that, for example, dissociates to desired products. The theoretical and experimental example discussed above shows that we can use pulses of light to robustly control wave packets, and thus the positions and momenta of the nuclei in molecules. Thus, we have the potential to control the course of photoinduced processes by altering the coherence of a pulse of light, or train of pulses, in analogy with experiments controlling nuclear spin systems using pulsed NMR.[42]

A number of techniques are available for synthesizing ultrafast laser pulses for quantum control. In our initial experiment[31,32] demonstrating the control of vibrational dynamics in the iodine molecule, we used a kilohertz Ti:sapphire-driven, optical parametric amplifier to provide tunable ultrafast pulses[43] followed by an adjustable prism system to control the chirp. More sophisticated pulse tailoring, suitable for synthesizing more complex wave forms, have been demonstrated by several groups using liquid crystal display technology[44−47] and acousto-optical tailoring.[48] As these techniques continue to evolve, they promise to significantly increase the range and complexity of feasible experiments, in both the strong and weak response regimes.

## Controlling Bonding

Controlling the future of matter requires the control of electron dynamics, as well as the control of nuclear dynamics discussed above. We would like, ideally, to be able to control chemical bonding, which is a considerable challenge, both theoretically and experimentally. In the general case, this might require light pulses on the attosecond ($10^{-18}$ s) time scale of electronic motion, but there are special cases in which femtosecond and picosecond pulses may suffice.

Control of the dynamics of electrons in atoms can readily be achieved. One can easily compute, given a known light pulse, the time evolution of an electron in a potential. Many experiments in atomic physics have demonstrated the ability to excite an electron with a short light pulse and to create a wave packet with a simple, or complicated, form at a certain

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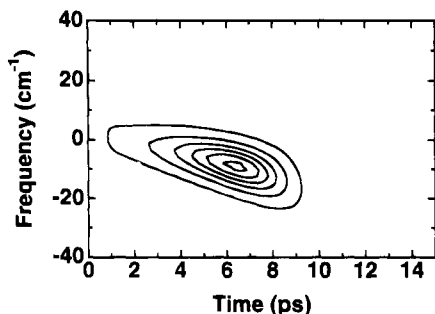
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**Figure 5.** Globally optimal field, in the weak response limit, for the electronic reflectron in the hydrogen atom. The target in this case is a minimum uncertainty Gaussian distribution centered about a position of 212 nm, with a momentum directed toward the center of mass corresponding to an energy of 2.2 $cm^{-1}$. The target time is 17 ps, and the frequency is measured relative to the energy of the $n = 50$ level of hydrogen.

time.[49-52] The goal of quantum control is to invert this process. In other words, choosing a desired outcome for the electron at a future time, what is the ideal light field to reach that goal?

For the hydrogen atom, we can give just such an example of quantum control.[51] A minimum uncertainty target is chosen in the radial distance of the electron from the nucleus and in the corresponding radial momentum. Just as in the molecular case, the target is chosen to be a Gaussian distribution with a negative momentum. The computed globally optimal light pulse, shown in Figure 5, is simple and smooth, and on the picosecond time scale. For the analogous pseudo-one-electron experiment in an alkali atom, the necessary visible light pulse could be synthesized easily in the laboratory.

The light pulse in Figure 5 creates a wave packet which is a coherent superposition of several electronic Rydberg states of the H atom, all with p-orbital angular symmetric, and, in this example, centered about the principle quantum number $n = 50$. The time evolution of this electron packet is shown in Figure 6. As can be seen in the figure, the packet evolves in time through complex patterns of quantum interference, to arrive almost perfectly in the target region, at the target time. Notice also that, while we usually think of electrons as traveling very rapidly over very short distances, the electrons in Rydberg packets can have quite long periods (~20 ps, in this case), with large excursions from the nucleus (~260 nm, in this case). In this situation, the behavior of the electron can be understood reasonably well with classicl mechanics.[49]

## Synthesis with Light

Given the ability, as discussed above, to focus atoms in space and time, combined with the ability to control the motions of electrons, one can imagine the development of a new tool for chemical synthesis. Nuclear quantum control would be used to manipulate the atoms into a desired pattern, followed by electronic quantum control to bond the atoms into the desired molecular conformation. Exotic new molecules might

be made in this way, or highly strained species such as transient moieties located on the saddle points of potential energy surface, far removed from the Franck–Condon region.

## Big Systems

We have discussed in detail so far only the quantum control of atoms and diatomic molecules, and therefore the reader might wonder if quantum control can ever by extended to bigger systems, and if so, what are likely to be the limits. Can we ever hope to control the quantum dynamics of macromolecules, such as proteins and nucleic acids? The author's crystal ball is clouded, but we can at least express some hopes and some thoughts on how one might proceed.

First of all, consider the question of large molecules in the gas phase. Several difficulties must be overcome. The first is the lack of sufficient knowledge about the detailed properties of large molecules and their Hamiltonians, in particular how the potential energy and the strength of the interaction with a light field vary with the positions of the nuclei. This makes a priori calculation of the optimal light field inexact at best. A possible approach to this problem is discussed below.

A second difficulty, even assuming that we have complete knowledge of the Hamiltonian, is that the calculation of the optimal light field for a large molecule with many degrees of freedom may be impractical, or impossible. Exact quantum methods are currently limited to 3 or 4 degrees of freedom and are likely, for computational reasons, to remain limited to relatively small systems for the foreseeable future. Thus, computing the optimal light field for a macromolecule might seem a hopeless task. Fortunately, quantum control often requires only short times, so approximations to exact quantum dynamics such as (almost) classical,[53-55] or semiclassical,[56] approaches that might be accurate for a vibrational period or less may still prove to be useful.

A third difficulty is the large number of occupied vibrational and rotational quantum states found in a sample of large molecules at room temperature. It is likely that no single light pulse can control such a diverse set of initial conditions. Cooling the molecules in a molecular beam or trap might provide a partial solution to this problem, as would using an initial laser pulse to prepare the sample in a single quantum state by, for example, adiabatic half-passage,[57] or the use of tailored infrared pulses.[58-60]

As a partial way around some of these diffficulties, let us consider quantum control in crystals. Crystals are easy to cool to very low temperatures, and thus

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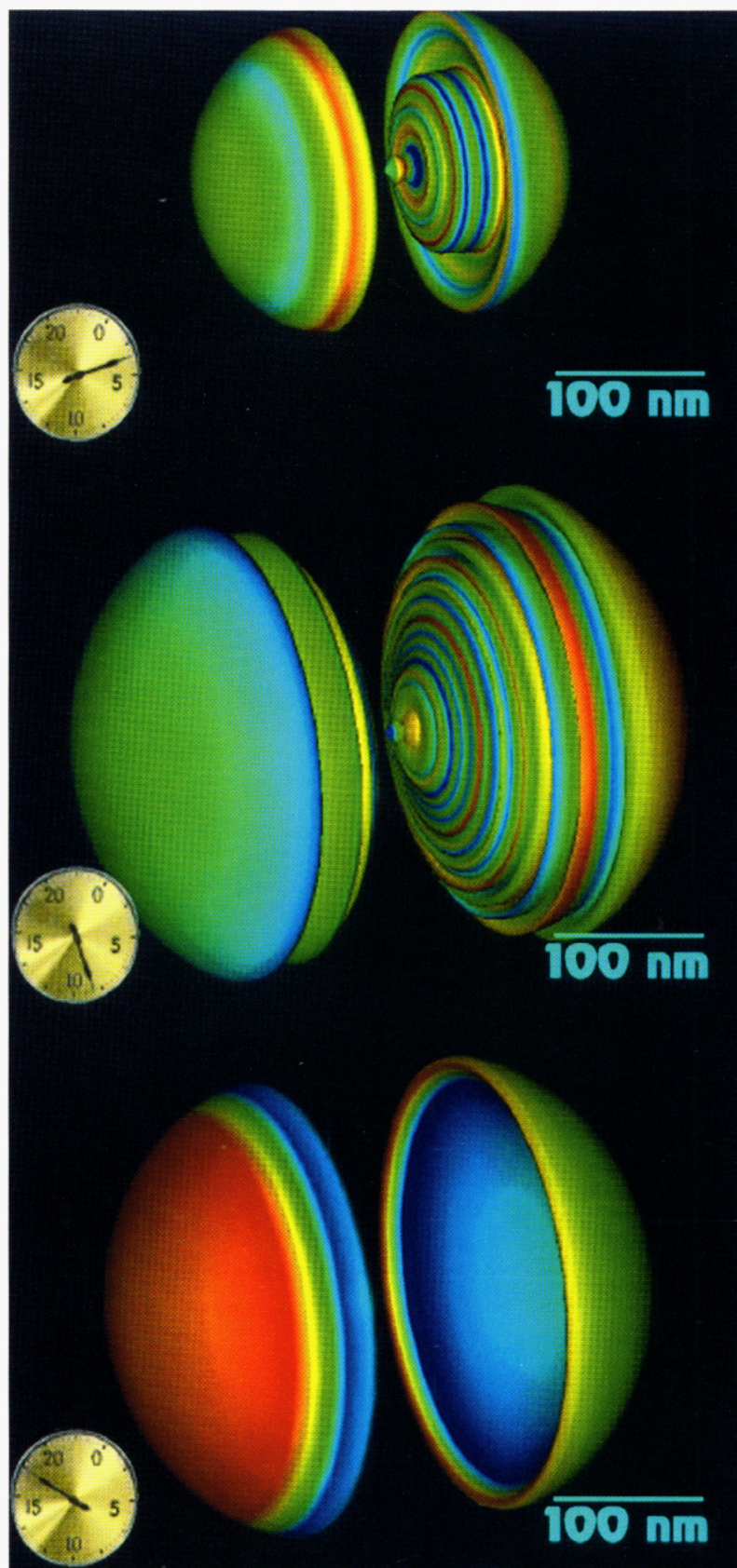(56) Messina, M.; Wilson, K. R. Unpublished.
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**Figure 6.** Creation of an electronic reflectron in the hydrogen atom. Shown is the calculated time evolution of the electronic Rydberg wave packet in the hydrogen atom created by the globally optimal field in Figure 5. The clock in the lower left-hand corner shows the propagation time in picoseconds, and the scale in the lower right-hand corner shows the length scale. The atom begins in its ground 1s state and is excited to a manifold of Rydberg states with p-orbital symmetry. The isosurface represents a constant value of the magnitude of the electronic wave function in spherical coordinates, and the colors are mapped to the complex phase.

the number of initial states can be considerably reduced from a room temperature distribution. Furthermore, crystals are homogeneous, in the sense that in a perfect crystal the unit cells are exactly the same.

With this in mind, we intend to attempt to control the photodissociation of $I_2$ in a cold rare gas matrix, in collaboration with A. Apkarian, R. Zadoyan, and C. Martens.
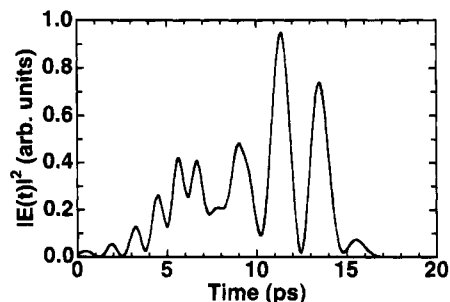
**Figure 7.** Globally optimal field for a target consisting of five peaks in the radial electronic coordinate in the hydrogen atom, with the momentum directed away from the center of mass.

Perhaps the most important case from a chemical point of view is control in liquid solutions. Liquids are heterogeneous, in that the surroundings of each chromophore are different, even at low temperatures (glasses). Furthermore, cooling leads, in general, to crystallization, and so very cold temperatures are usually incompatible with the liquid state. Nonetheless, in a simulation of the photodissociation of $I_2$ in room temperature argon at liquid-like density, we found that some quantum control could still be achieved if one acts quickly, that is, within a half vibrational period.[53,54]

## Programmable Holographic Optics

Can we attain more complex targets than the simple Gaussian minimum uncertainty targets in phase space described above? The answer is clearly yes, but again has two parts. The first involves whether we can compute the optimal light fields for complex targets, and the second is whether we can actually make the computed fields in the laboratory.

Let us investigate this question with an example, again drawn from the hydrogen atom. We choose in this case to make a target with five peaks in the radial position of the electron distribution and a mean momentum directed away from the nucleus.[61] The intensity of the electric field as a function of time, $|E(t)|^2$, that best drives the H atom to this target is shown in Figure 7. This field seems, at first, too complex to be synthesized in the laboratory. However, a closer study reveals that the field is composed of a superposition of five independent, nearly Gaussian chirped pulses with nearly the same center frequency and with fixed phase relations.[61] Individual pulses in the visible of such nature (which might be useful for related alkali metal experiments) have already been synthesized and used for quantum control.[31,32] It may be possible to combine such pulses to produce a wave form such as that in Figure 7 to produce transient structures with features on the nano- to picometer length scales.

Figure 8 shows the wave packet created by the globally optimal field in Figure 7, at the target time. As in Figure 6, the packet is depicted in spherical coordinates, with p-orbital symmetry. The packet consists of five concentric shells, representing the five radial peaks in the target. The overlap with the target at the target time is nearly perfect. We have also shown computationally that complex targets in nuclear

(in contrast to the electronic example just discussed) position and momentum may also be produced by similar methods.[61] This result suggests that the design of very complicated structures might be reduced to the formation and placement of simple building blocks that are comparatively easy to synthesize.

It is intriguing to speculate that the ability to design and construct time-dependent transient electronic and nuclear structures might lead to the possibility of controlling the subsequent course of light (e.g., X-rays) or matter (e.g., electrons). As a first example, the interference of light or matter waves scattered from different parts of a structure such as that in Figure 8 would lead to light or matter patterns varying in space and time. Since the optical pulses required to produce any desired pattern in matter can be computed, in principle, this method might be used to design programmable diffractive or holographic optical elements.[62] Another possibility would be to control the absorption of light by building diffraction patterns into the internuclear distance distribution of a molecule. For example, the absorption by molecules of ionizing light might be controlled by enhancing constructive or destructive interference between direct electron emission and scattering of photoelectrons from a neighboring atom. In this way, an ultrafast modulator for X-rays might be constructed.

## Building and Running Nanomachines

Eric Drexler has proposed building nanomachines whose basic building blocks are individual atoms.[63] One example is a planetary gear system, whose teeth are made of individual atoms. Left unsolved are the practical details of how to manufacture such interesting creations and how to run them once they are produced. One can consider the synthesis of such nanomachines as a conceivable application of quantum control, using nuclear control to place the atoms and electronic control to form the needed chemical bonds to hold them in place. In addition, since it is as easy to control momentum as position, quantum control might also be useful in designing an energy, or fuel, source for nanomachines, by controlling the coupling of light to matter.

## Further Dreams

As we discussed above, one difficulty with quantum control is that computing the optimal light field to control matter requires more detailed knowledge about the properties of matter (for example, the potential energy surfaces and couplings to the light field as functions of atomic positions) than is usually available. One way around this is to build a feedback loop which includes theory (embodied in an attached computer) and experiment.[22,64,65] Given a chosen

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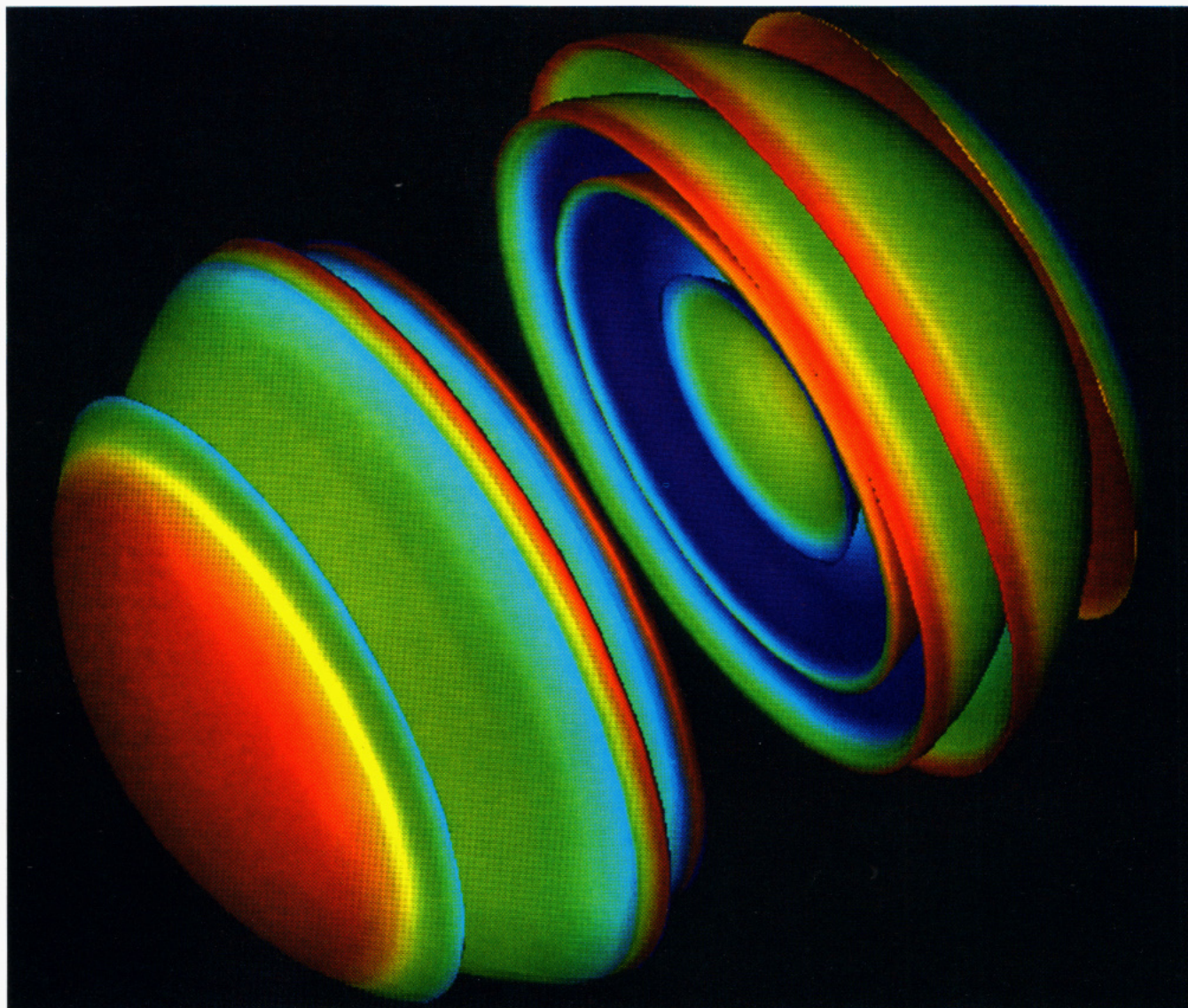(63) Drexler, K. E. *Nanosystems*; Wiley: New York, 1992.
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**Figure 8.** Creation of an electronic structure in the electronic wave function of the hydrogen atom. Shown is the electronic wave packet created by the field in Figure 7. The five peaks in the radial coordinate are visible as five concentric shells. The isosurface represents a constant value of the magnitude of the electron wave function in spherical coordinates, and the colors are mapped to the complex phase.

target and imperfect knowledge of the material system, we estimate the optimal light field on the computer and then send its specifications to a computer-controlled light pulse synthesizer which makes and focuses the pulse on the sample. The results of the experiment, which indicate how closely the system has been driven to the desired target, are then transmitted back to the computer handling the theory, which uses this measurement (and previous ones) to further improve the estimate of the properties of the material system. From this improved knowledge of the system, a better estimate of the optimal light field can be computed. Repetition of this cycle, it is hoped, will lead to convergence both with respect to knowledge about the material properties of the system and with respect to the ability to control its evolution to the desired target.

## Conclusions

This has been a quick look at the Holy Grail of using lasers to control matter, and at goals for quantum control to entice us onward into the future. Realistically, some of these dreams will come true, and others will not. But the quest to achieve the goals discussed here will likely lead us to unanticipated discoveries, which may in the end be worth more to us than the original goals.

For more information, the reader might wish to consult our World Wide Web site (http://www-wilson.ucsd.edu), which contains many more illustrations of theory and experiment in the form of words, images, computer animations, and videos.

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