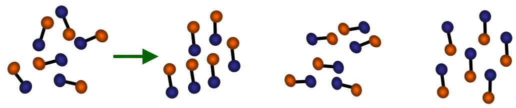
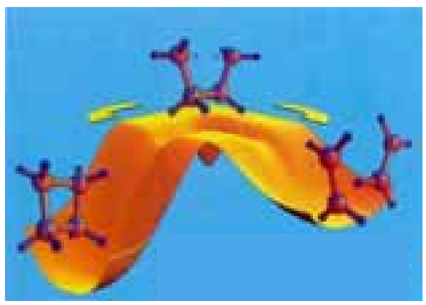
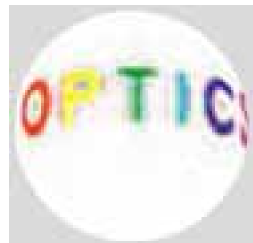
Quantum Control:

Using Lasers to Redesign Atoms and Molecules







Atoms and molecules are the fundamental building blocks of all matter. Due to their incredibly small size and quantum nature, understanding and controlling these tiny systems presents enormous challenges but also tremendous opportunities for designing and controlling matter at all scales.

Outline:

A. Control - General Considerations
B. Waves – Properties
C. Light – Standard Sources
D. Atomic Structure – Observations and Quantum Interpretation
E. Wavepackets – Making it all move
F. Lasers – A special kind of light
G. Observation – Destructive Viewing and Reproducibility
H. Examples

Control

1. Observe and Learn as much as possible about system

2. Identify/Develop Tools for Changing system

3. Maintain Feedback

1. Example: Driving a Car, playing a video game – need to know how to play the game

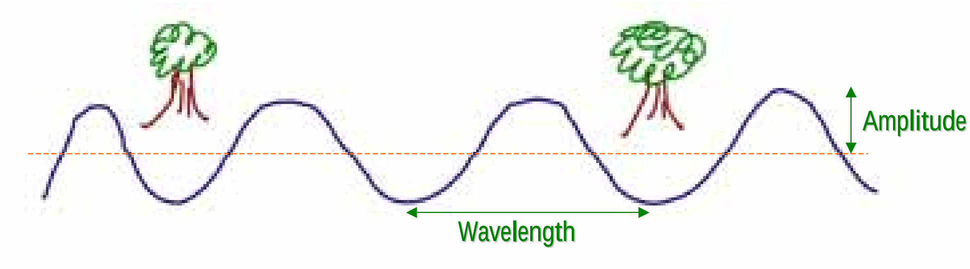
2. Fast – Must be able to change the system as fast as it can change itself

3. Fast and interpretable – Even if you know the road well, the system can change (rock slide, child retrieving a ball, stalled car, drunk driver,…) your vision is feed back. When you see something happen, you have to be able to interpret and react correctly to control the situation. In some cases, there is a minimum of unforeseen events and system behaves very predictably. Ex: airport tram, jet far from airports, and feedback can be minimized or eliminated.

Note that all three of criteria can be incredibly hard to meet when we are dealing with matter at the atomic scale (1/10 nm – diameters of 1 millionth a human hair) whose behavior is described by quantum rather than macroscopic classical physics, whose motion can be very fast (with changes occurring over times as short at 10-16 sec (10 billion milliion times per second), and whose motion cannot be predicted or monitored with certainty until the system is destroyed.

A Wave…

…Is a disturbance in a (quasi-) continuous medium



Frequency: # of crests that pass in 1 second

Energy: Proportional to amplitude squared

Waves are very familiar to us – water waves, sound waves, light waves,…

They all have characteristic properties…

Waves contain energy and travel at a speed that is a characteristic of the medium

The wave’s energy determines how hard it hits you, how loud the sound is, how bright the light is

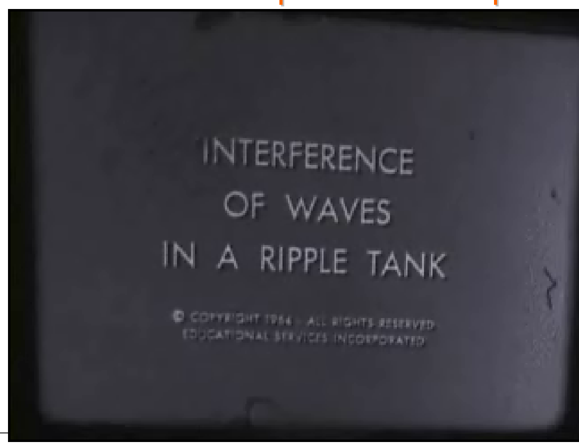
Superposition and Interference

...Put 2 waves together – you get different wave!

Examples:

A. 2 waves with different frequencies ... loudness "beats" in time

B. Two separated sources ... quiet and loud positions in space



< click to play movie.

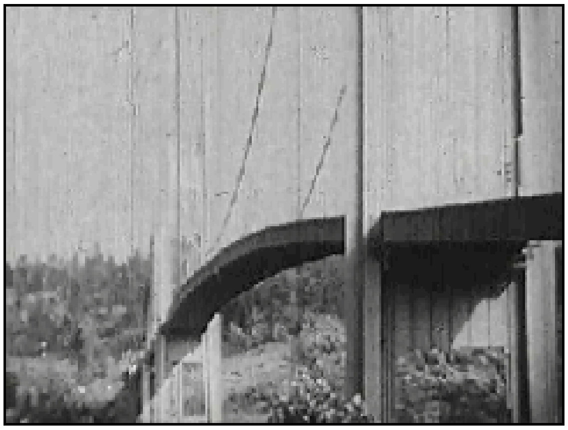
Waves have crests and troughs. If you put two waves with equal amplitude together so that their crests and troughs coincide, then the resultant wave will have 2x the amplitude and 4x the energy (power) of either wave alone. This is constructive interference.

If the crests of one wave coincide with the troughs of the other, then the resultant amplitude is zero. This is destructive interference. (Where does the energy go?)

Show beat demo with tuning forks. A convenient method for tuning a piano or other stringed instrument.

Standing Waves

_ Found in systems with boundaries
_ "Normal Mode" waves fit between boundaries
_ Superposition of multiply reflected traveling waves
_ Energy does not propagate, but can be stored



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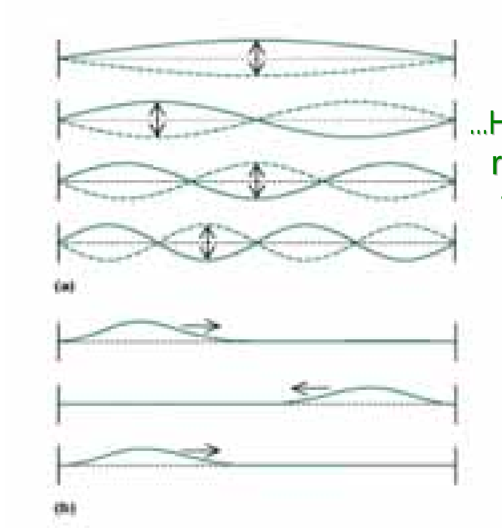
Examples: Musical instruments, Strings, organ pipes, ...

Different normal modes for different shapes/types of systems

Show standing waves in spring. Large amplitude motion develops by pumping energy into system- at just the right frequency - over a long period of time. Large force is not required - energy is stored

Wave Synthesis and Pulse Generation

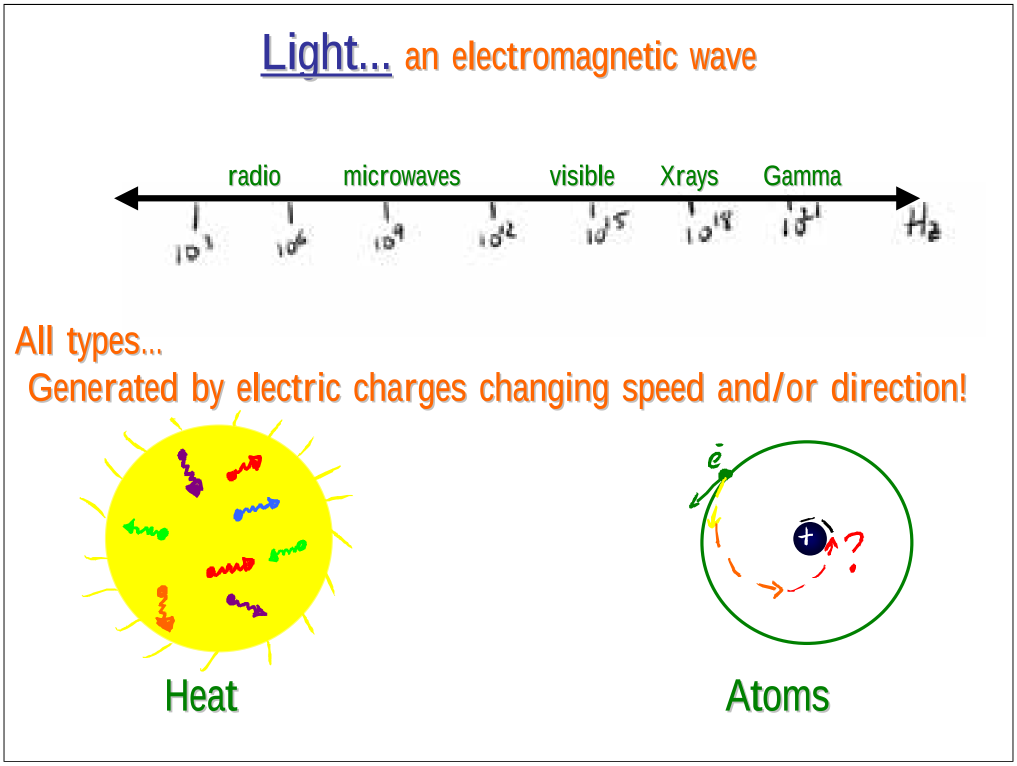
You can build any waveform from other waves but...



...High resolution in time (or position) requires broad range of frequencies (or wavelengths)

"The Uncertainty Principle"

The idea of synthesizing waveforms is well known in music. By their nature, the energy in these waves will propagate in time. They are non-stationary and do not have a well defined frequency! Show pulses in spring. You can't pinpoint where (or when) a wave is and still specify its frequency or wavelength.



Light exhibits all the properties and characteristics of waves ... interference, superposition, energy propagation,... but it requires no medium!! Show two slit interference with light. The only difference between visible light and other types of electromagnetic waves is the frequency. Faster motional changes of charges give higher frequencies.

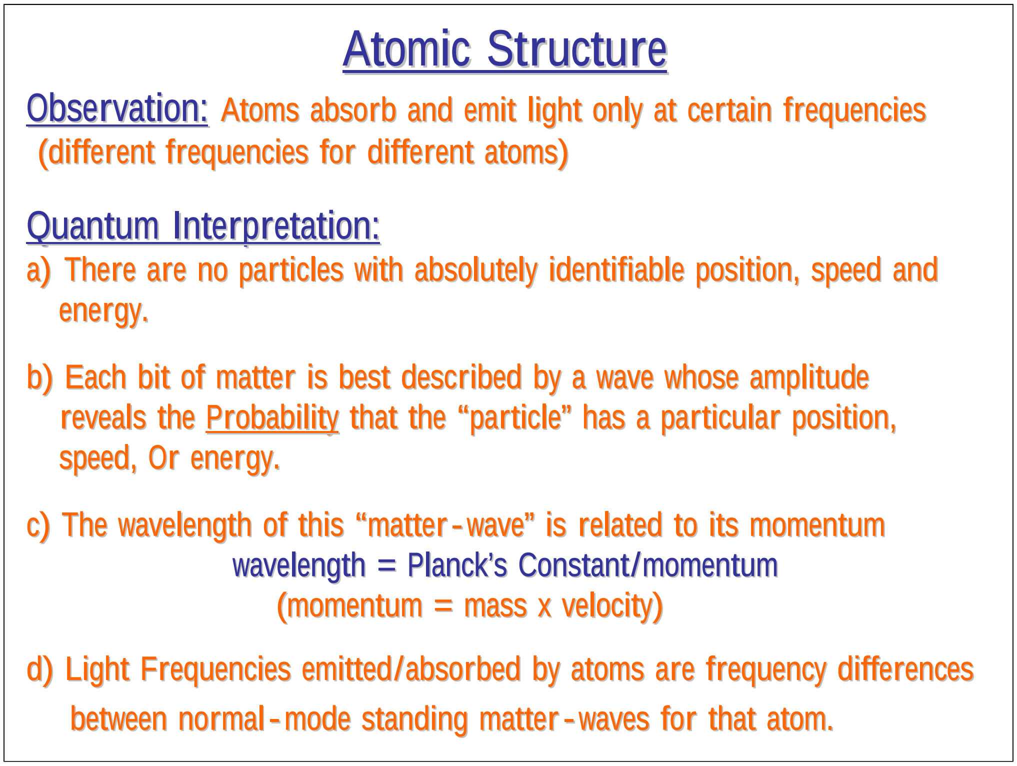
Electrons and ions in hot objects jiggle around (this is what heat is) and radiate . The hotter the object, the higher the frequencies that are emitted. Light bulbs are cooler than the sun and do not have as much blue (high frequency content). But electrons in atoms must change their velocity as they move around the nucleus (picture the planets in orbit around the sun). If so, they should radiate, and eventually the electron orbit should decay as it "cools". This suggests the collapse of atoms - which doesn't seem to happen. Why not?

Show spectra from light bulb and from tubes. Atoms bombarded by electrons in the discharge only seem to emit light at certain colors. Why?

Light is a wave…
Generated by electric charges changing speed and/or direction!

The time-varying amplitude of the light wave…
Subjects charges to an electric force – the same type of force that holds atoms and molecules together – Causing the charges to change their speed and/or direction

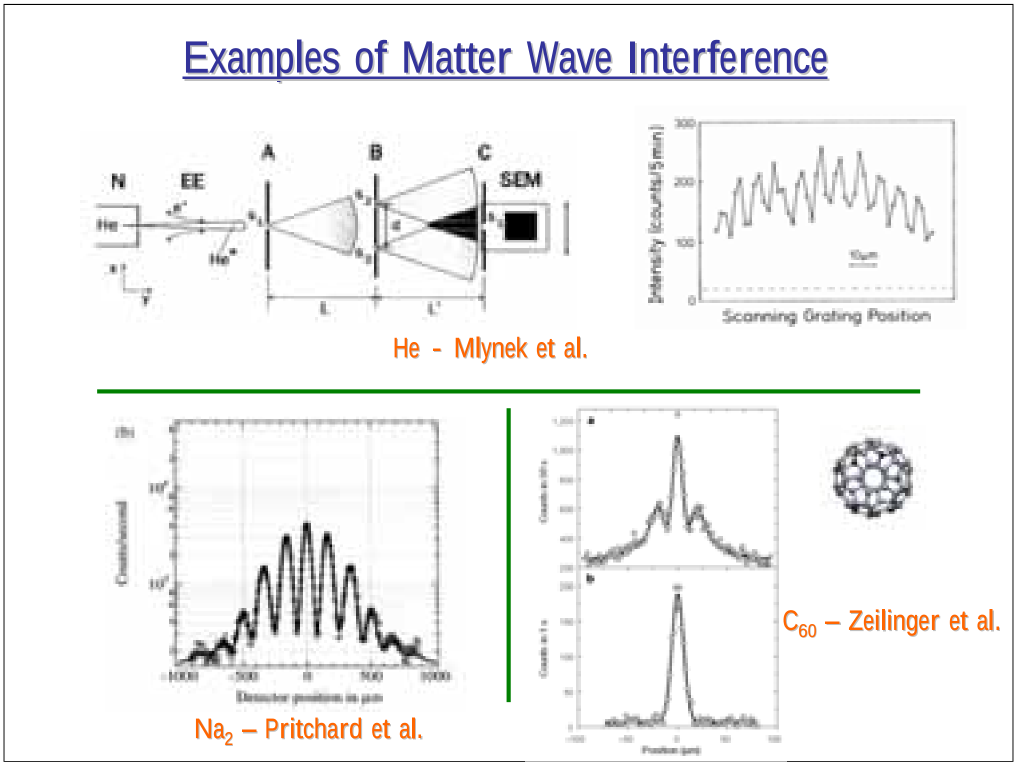
Light is a tool…
for manipulating the position and motion of the charged particles that make up atoms and molecules!



The most successful known theory for describing the physical universe

c) deBroglie’s hypothesis has now been confirmed many times over

d) Show standing waves in spring again – you must shake the spring at different frequencies to excite different modes.



The wave nature of matter was confirmed using electron diffraction nearly immediately after deBroglie's hypothesis

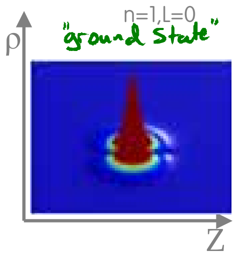
However, more recently people have gotten much better at making very small devices "slits" through which the matter waves can pass.

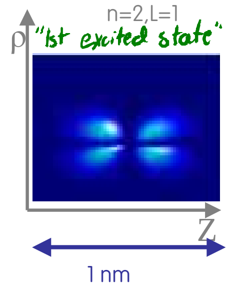
The larger the particles, the smaller the deBroglie wavelength, and the smaller the slits must be to observe the effect. Rather large chunks of matter, e.g. C60 have now been seen to exhibit multiple slit interference – just like any other wave.

Stationary States...

...Well-Defined frequency (i.e. energy) - position/momentum uncertain

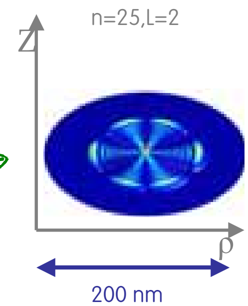
Hydrogen





Absorption/Emission spectrum
Reveals "normal-modes" for
Each atom or molecule (molecular
Rotations and vibrations too!)

Highly excited state

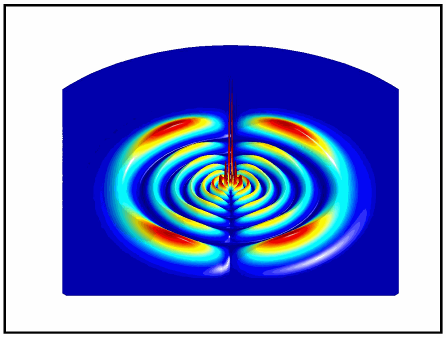


Recall the uncertainty principle. Well defined frequency means the wave has existed for a long time (not a short pulse).

Wavepacket Synthesis ...

... specifying particle position or momentum (rather than energy).

Atomic Examples



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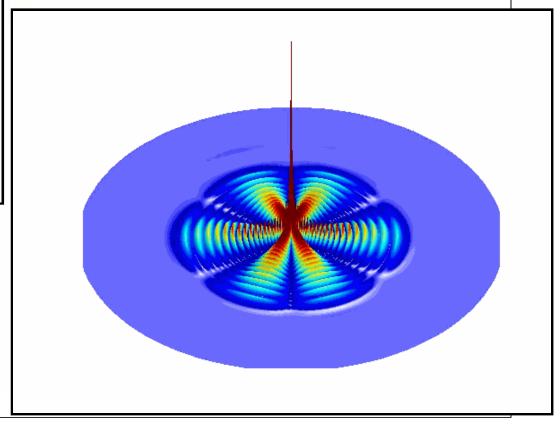


Analogous possibilities for molecular
Rotations and vibrations too!

click to play movie. >

Can we control how probable it is that the system is in a particular spatial configuration, or has particles moving at certain speeds at a particular time? Yes! All we need to do is superpose the correct standing waves and we can design a matter "wavepacket." Just like we design pulses on the spring. We superpose these standing waves by simultaneously exciting the atom to multiple standing waves using a specially designed light pulse.

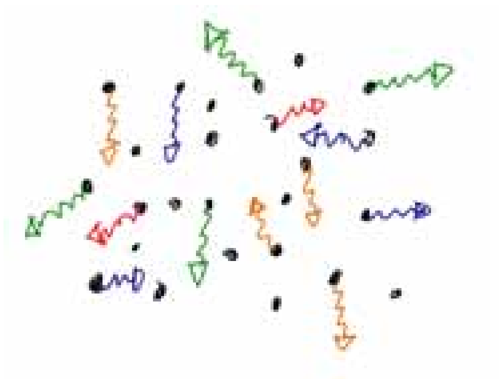
We can think of the light pulse as exciting the normal modes with just the right amplitude and phase, or equivalently, that the light field shakes the system and forces the system into a particular non-stationary mode.

Note that the relative positions or motions of particles can be very important for determining various types of reactivity. Thus, controlling wavepacket excitation and motion is a key method for manipulating atomic scale interactions.

But how controllable are our light tools?

Incoherent Light Sources…

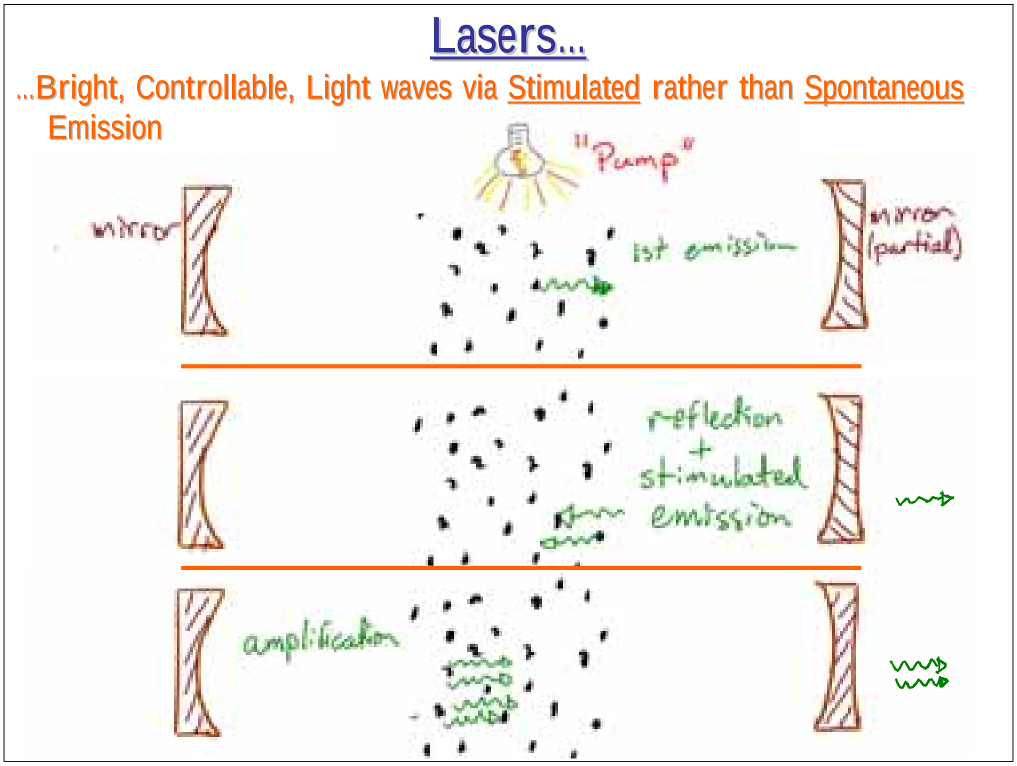
…Broad Spectrum, Low energy at any frequency, non-directional, uncontrollable



Atomic or Thermal – No communication between emitters

Sun, lightbulbs, LEDs, atomic discharges, etc.

We have no control over the frequency and phase, of this type of light. No generated waves are reproducible. Not useful for controlling matter.



Laser means LIGHT AMPLIFICATION BY STIMULATED EMISSION OF RADIATION

The first emitted light wave keeps bouncing back and forth in the cavity until it comes into contact with another excited atom. It jiggles that electron to emit *in-phase* in the same direction as the first wave. Those two waves stimulate more in-phase emission along the laser cavity. Light leaks out through the partial mirror. The light in the cavity has memory of the correct phase. The light leaving the cavity remains perfectly coherent. Feedback provided by mirrors is key

Pump light can be pulsed or continuous.

Lasers…

…Many different output characteristics

a) continuous or pulsed (pulse durations ~ 5 x 10^{-15} seconds)
b) coherent frequency spreads from < 1 Hz to > 10^{15} Hz
c) primary frequencies from infrared to visible to ultraviolet
d) average powers of > 1 million Watts
e) peak pulsed powers > 10^{15} Watts with peak electric forces 1000x greater than those that hold atoms and molecules together
f) prices from a few dollars to a few billion dollars

Enable extremely accurate spectroscopy (measurement of structure) and arbitrary(?) manipulation of atoms and molecules

Viewing Motion Within Atoms and Molecules

Typical Observation Requirements:

A) Fast shutter or strobe to “freeze” motion for viewing
electrons – $< 10^{-16} – 10^{-9}$ sec
molecular vibrations $\sim 10^{-15} – 10^{-9}$ sec
molecular rotations $\sim 10^{-13}$ – ?? Sec

B) Very high spatial resolution (< 0.1 nm)

C) Can't Disturb system
(Oops! – All measurements of quantum systems are destructive - if you interact with the system to learn something about it, you change it irreversibly)

So now, in principle, we know how to understand our system – use spectroscopy and quantum mechanics to determine normal-modes.

In principle, we have coherent laser tools that can be used to subject the charges in atoms and molecules to forces and control our system.

What about feedback? How do we keep an eye on our system?

In many cases, requirement A is not an issue. Current lasers are fast enough to capture many types of motion in atoms and molecules. However, B) and C) are HUGE Problems!

Let’s skip B) for now.

C) Requires that we change our whole approach. We obviously cannot continuously watch our system evolve.

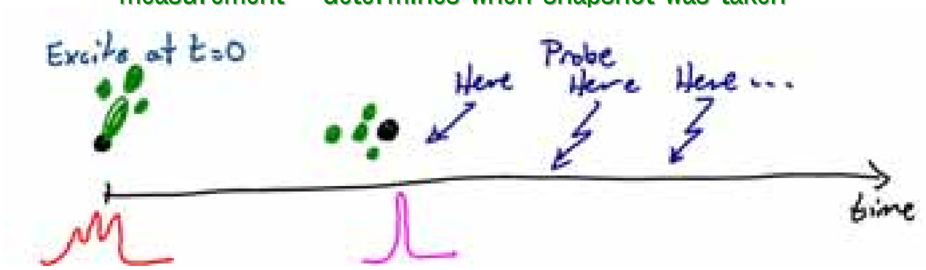
Viewing with Destructive Measurements

Take “snapshots” of system at well defined time during evolution

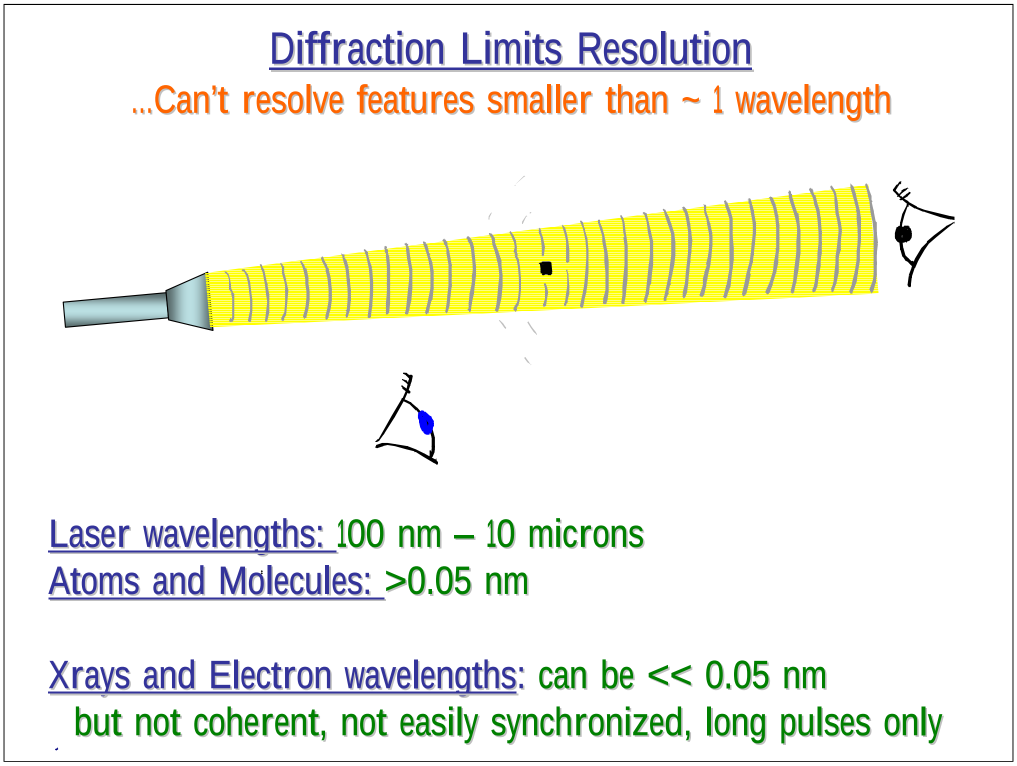
Each snapshot is a frame for a movie iff:

A) System is identically prepared before every measurement

B) Precise synchronization between start “event” and destructive measurement – determines when snapshot was taken



Clearly, the identical preparation and the synchronization issues require that we use lasers to create our wavepackets at a particular time, and other lasers to probe how the system has evolved.



How do we see the state of the system during any snapshot?

Waves do not reflect from or get shadowed by objects that are smaller than a wavelength. Think about yourself in the ocean as waves roll past you. Could someone tell that you were in the ocean by looking at the waves that passed you or were reflected back by you? You leave no trace. However, a large jetty or piece of land can block/reflect waves.

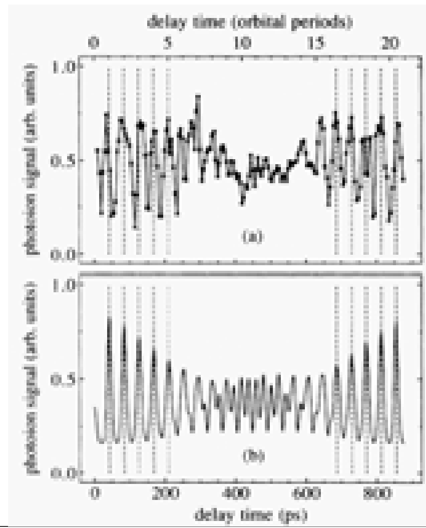
We can't use reflection or absorption of visible light to give us information and electron/Xray pulses are not short and not well synchronized with lasers (best laser generated electron pulses ~ 10^-12 sec but not very bright). Similarly, laser generated Xray pulses can be short and relatively well synchronized, but are not very bright. Its hard to see in the dark.

Laser Solution…

Exploit optical interactions that depend critically on particle position, speed, energy, …..

Examples:

A) Much more likely to ionize Atomic Electrons if they are near the nucleus during a short pulse of laser light… ionization probability is equivalent to probability that electron is near nucleus at that instant



Stroud et al

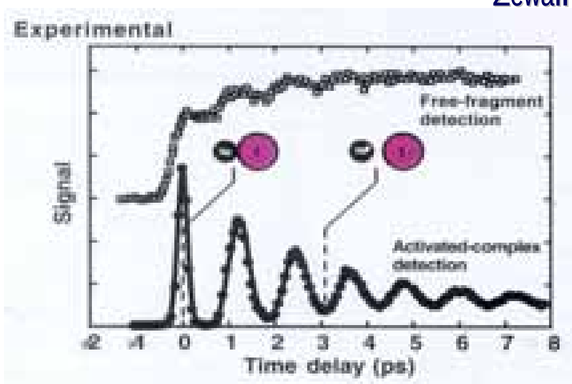
In the picture, a short laser pulse quickly excites an electron on an atom from its ground state, giving it almost enough energy to escape the atom. The electron periodically returns to the nucleus giving the peaks in the data and simulation. Viewing the motion of this type of electron packet is sort of the standard “eye chart” for new methods being developed to view electron dynamics. Analogously, you check that your vision is sound before driving on the interstate.

Note that if the normal modes of the system are known, one can use measurements of the time-dependent probability for finding the electron at one point in space to determine the full wave motion – but difficult to do in practice.

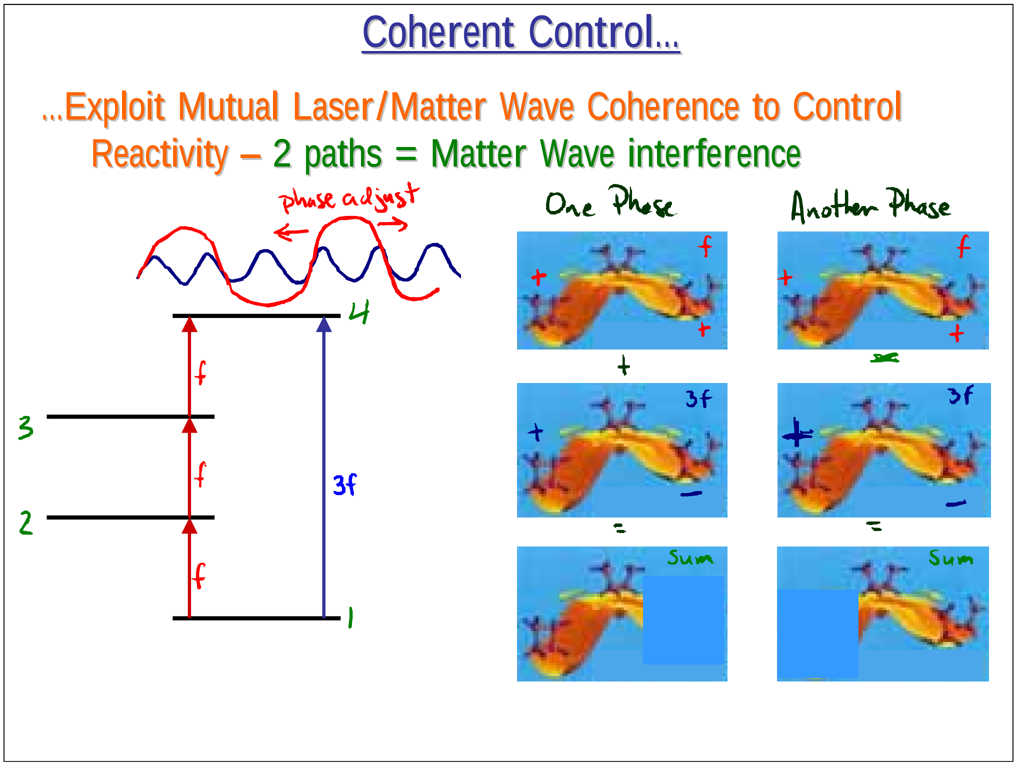
Probe Technique Examples (continued):

B) Electron excitation/ionization in molecules depends on relative positions of nuclei...Ionization Probability due to short laser pulse depends on its frequency and the molecular configuration at that instant.

Zewail et al.



Here the molecule is excited so that its energy is more than sufficient to dissociate the covalent bond. However, the dissociation is not immediate. Some of the outgoing matter waves remain ionically bound and bounce back toward each other a few times before finally parting for good. (Ionic is bound covalent is free here)



So by exploiting our knowledge of the normal mode structure of atoms and molecules we can still follow motion within atoms and molecules even using probe wavelengths >> the size of the system. To some degree, we have satisfied the control criteria (information, tools, feedback) as well as possible. What are some control examples

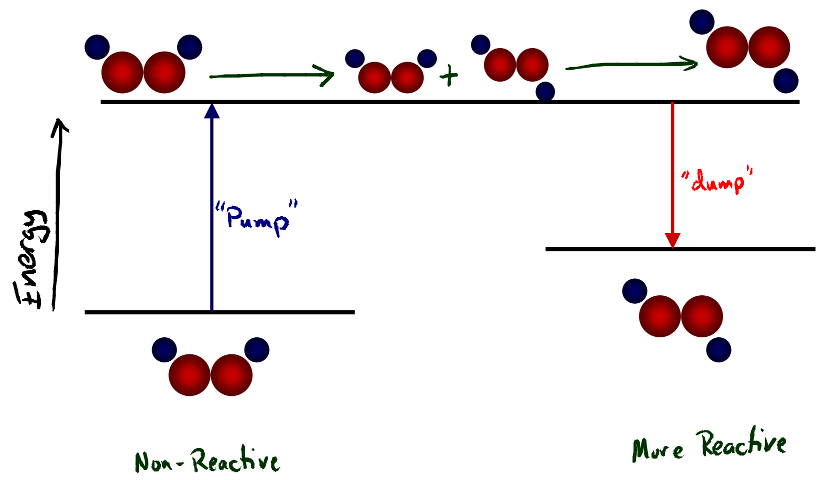
A standard approach is standard two slit (or two path) interference. What two paths might be exploited in almost any system. Two different – coherent- excitation paths.

We can excite the molecule using two different frequencies of light – one an integer multiple (or harmonic) of the other. The excited state can move along two paths. The matter wavepackets for the different excitations can have different signs for these two paths. Depending on the relative phase of the two light beams, the two waves headed to the right can interfere constructively or destructively.

The reaction is for illustrative purposes only, and the control experiment suggested has not been performed.

Left is cyclobutane right is 2x ethylene.

Pump - Dump Wavepacket Control



This method does not rely on relative coherence between the two laser pulses (pump and dump) but does rely on coherent wavepacket evolution from one conformation to another within the molecule. At low energies, there can be an energy barrier preventing a molecule from changing its confirmation to a reactive one. At higher energies, there is no barrier and the normal mode is a superposition of both confirmations. Immediately after excitation, the excited wavepacket resembles the initial conformer. But over time the wave evolves into the reactive conformer and can be efficiently de-excited using the dump pulse.

Significant Problems

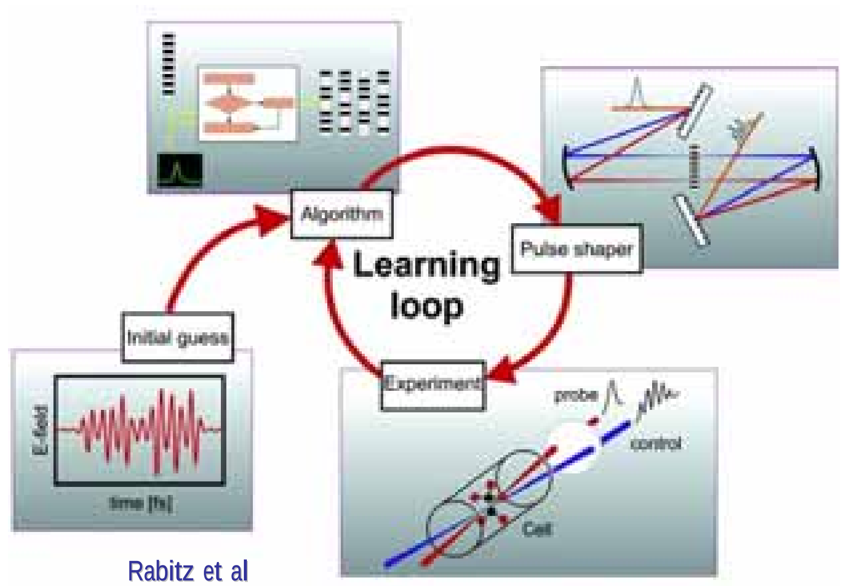
Very Complex Systems
Not Well Characterized

Strong Lasers Required
To Maximize Yield will
Change the System

How do I determine the correct control parameters – frequency, phase, time-delay, etc...?

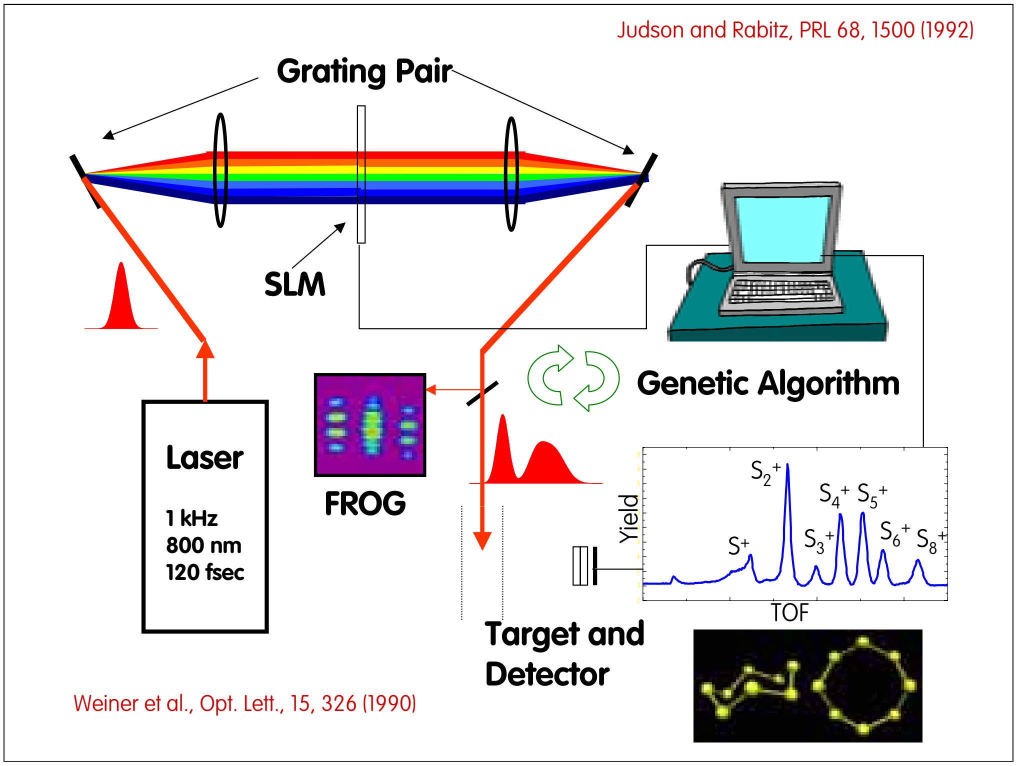
Feedback or "Learning" Control…

…The system always knows what's best !

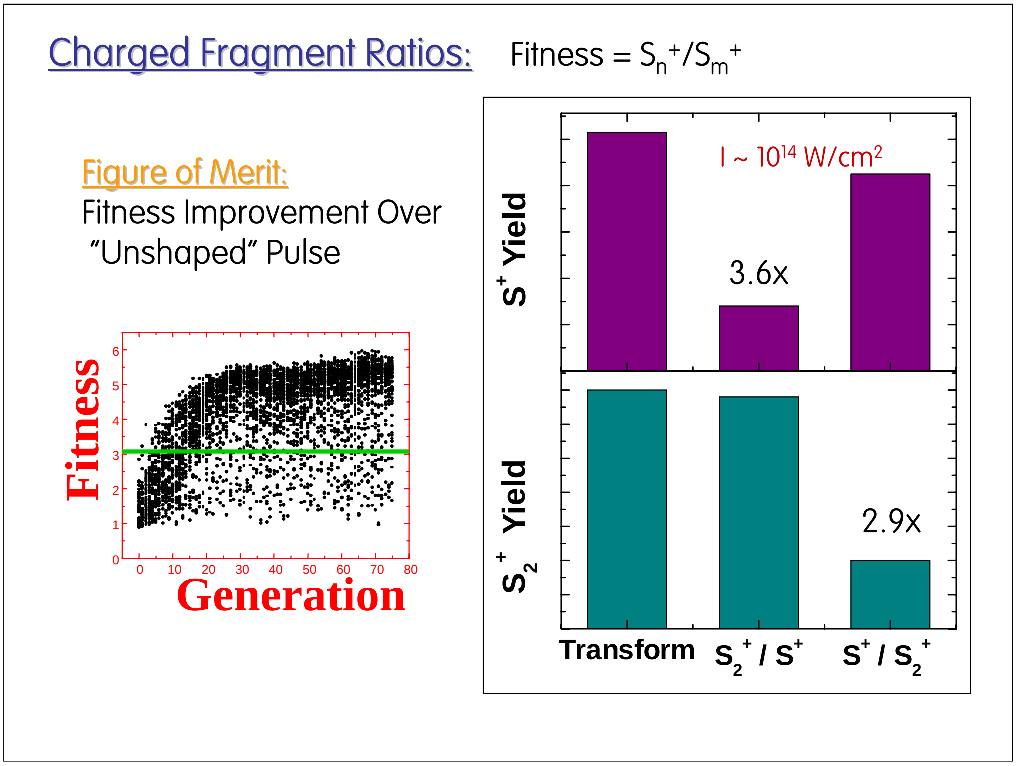


You don't know what laser fields to apply so start off with a few random ones. Use a pulse shaper, diffraction gratings spatially separate colors (like the one used on the demo camera). Once separated we can change the amplitude and phase of the waves at each color using a liquid crystal display (similar to the one on my laptop or in the projector) A second diffraction grating puts all the colors back together again. This is an optical waveform synthesizer (a digital keyboard for light). In the genetic language each waveform is an individual, and the amplitudes and phases of each of its composite frequencies are its genes.

We run an experiment using each of the 50 or so individual pulses. Pulses compete for mating rights based on their performance in obtaining the desired result of our experiment. We splice and mutate the genes of offspring of mating individuals. We form 50 new individuals and run the experiment again. We don't know (and perhaps don't care) what pulse shape works the best – we just want results. We rapidly search a large phase-space for the best result. The algorithm converges on a set of individuals that, on average, perform as well as possible.



One of our tries at this type of experiment. Here we wanted to use a very intense laser to blow up a sulfur ring molecule. We tried to optimize the production of certain ions while minimizing the production of others.



It works quite well. We almost always do better using the algorithm than if we had just used an unshaped pulse straight out of our laser and the system is too complicated to determine a priori what pulse shape would be optimal.

Beyond Laser Controlled Chemistry

A) Coherent target preparation…
isolate specific phenomena that are intrinsic to more complex, processes
e.g. controlled collisions

B) Storing and Processing quantum information within atoms and molecules

Future Progress Rests on Technology

Controllable Coherent spectra from THz regime to X-rays.

- Optical Arbitrary Waveform Generator Currently Under Investigation
- Pulses as short as 10^{-16} seconds have now been produced and are being used as the ultimate fast probes