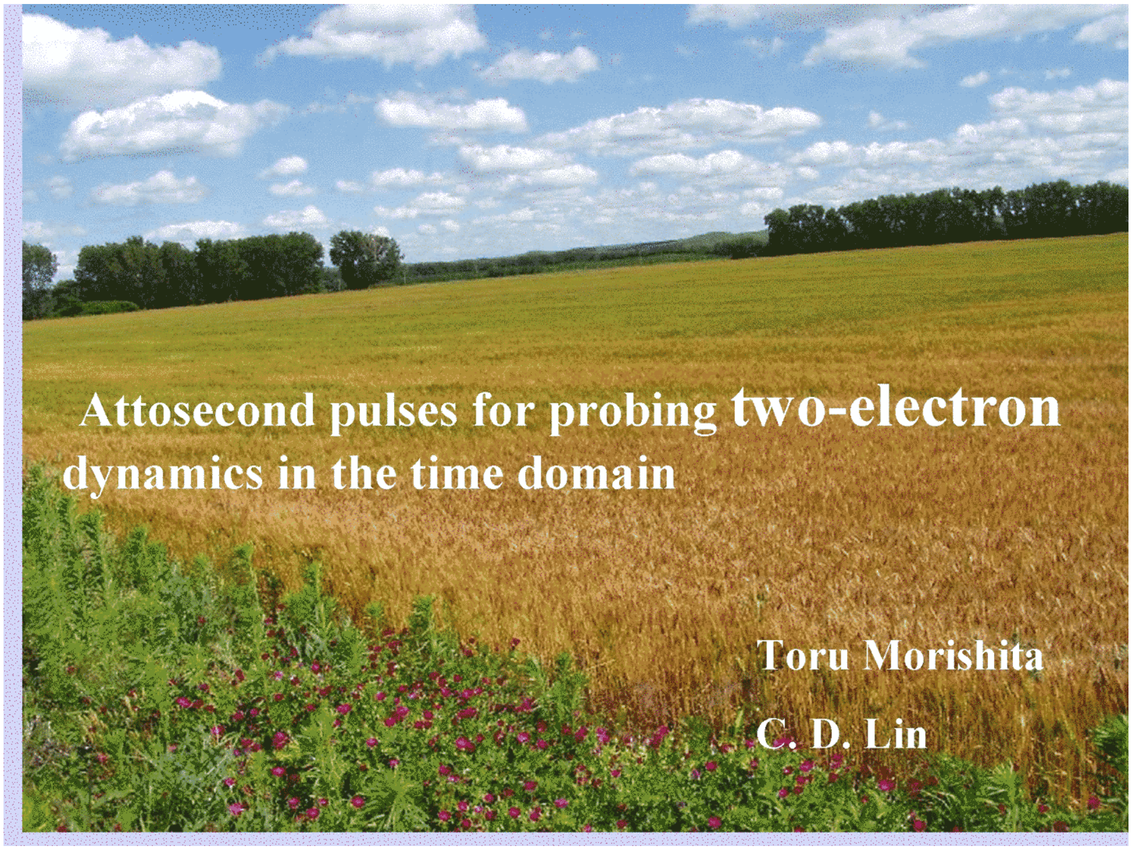


"Movies" of Microscopic Events

??

need fast clocks

femtosecond Chemistry– Zewail 1999

Time scales …

Radiative lifetimes	nanoseconds (10^{-9} s)
rotation of molecules	picoseconds (10^{-12} s)
Vibration of molecules	femtoseconds (10^{-15}s)
electronic motion	**attoseconds (10^{-18}s)**

To probe electronic motion in the time domain

– need to create electronic wave packets

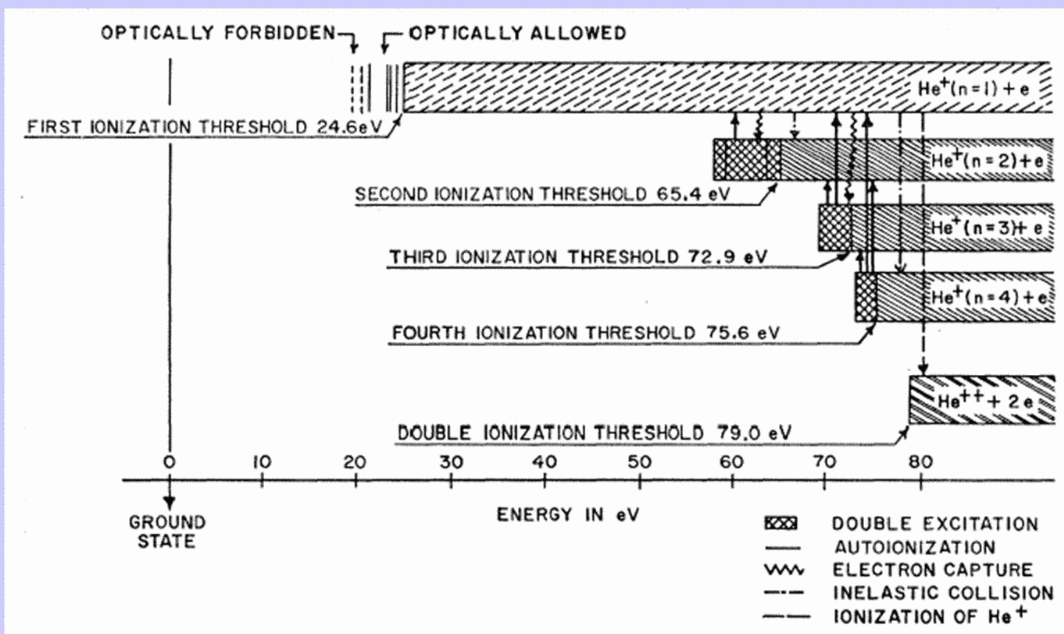
1. Single-electron wave packet –Rydberg atoms

- time scale: in nano- or pico-seconds
- designer's wave packet– radial/angular localization

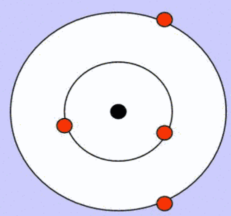
2. Multi-electron wave packet– (our goal)

Probing true electron-electron interaction dynamics in the time domain

Helium Spectrum



Atoms vs molecules



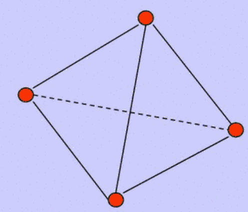
Hartree-Fock

(mean field)

orbitals, Shell structure

$(1s)^2\,(2s)^2\,\ldots$

$\Psi = \psi(r_1)\,\psi(r_2)\ldots$



Born-Oppenheimer

(adiabatic approximation)

rotation, vibration, molecular orbitals

$T_h\,,\ v,\ \ j,\ \ldots$

$\Psi = F_\mu(R)\,\Phi_\mu(R;\Omega)$

Time-Domain physics:

Need to **create** wave packets ← A designer's wave packet?

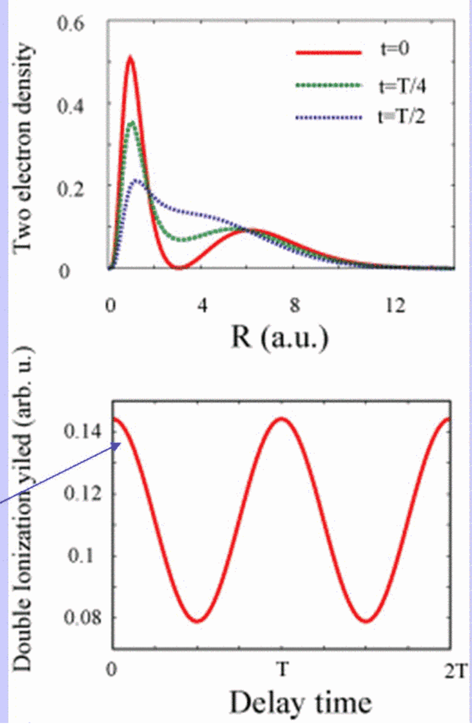
Need to **probe** wave packets ↑ A probe to reveal the dominant features?

Example:

- A simple wave packet made of singly excited states
- Probed by double ionization

Simple case: $1s^2\ {}^1S^e + 1s2s\ {}^1S^e$

20.6eV T=200as



wave packet vs time

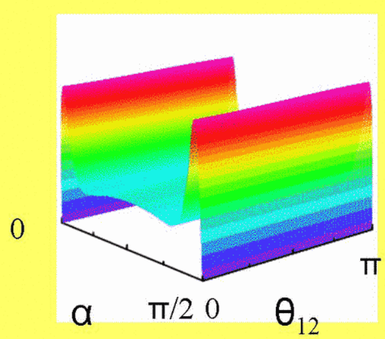
Probe pulse: 95.2eV/100as

Double Ionization yield vs time delay

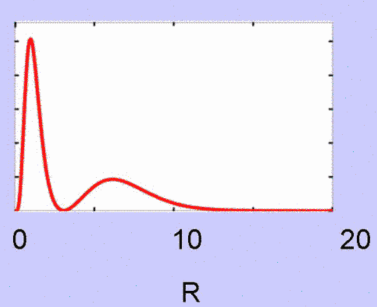
Two electrons are closer together at t=0

Coherent singly excited states: Radial motion of a single electron

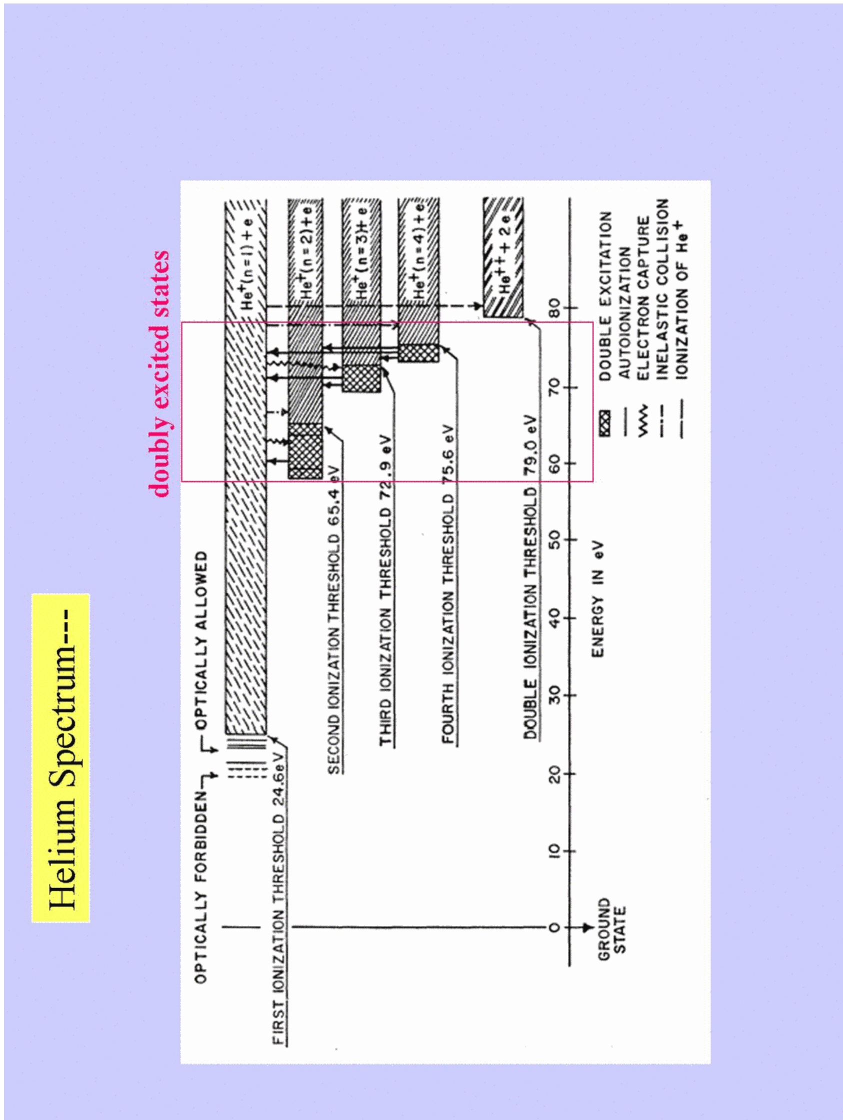
- $1s1s\ {}^1S^e + 1s2s\ {}^1S^e$

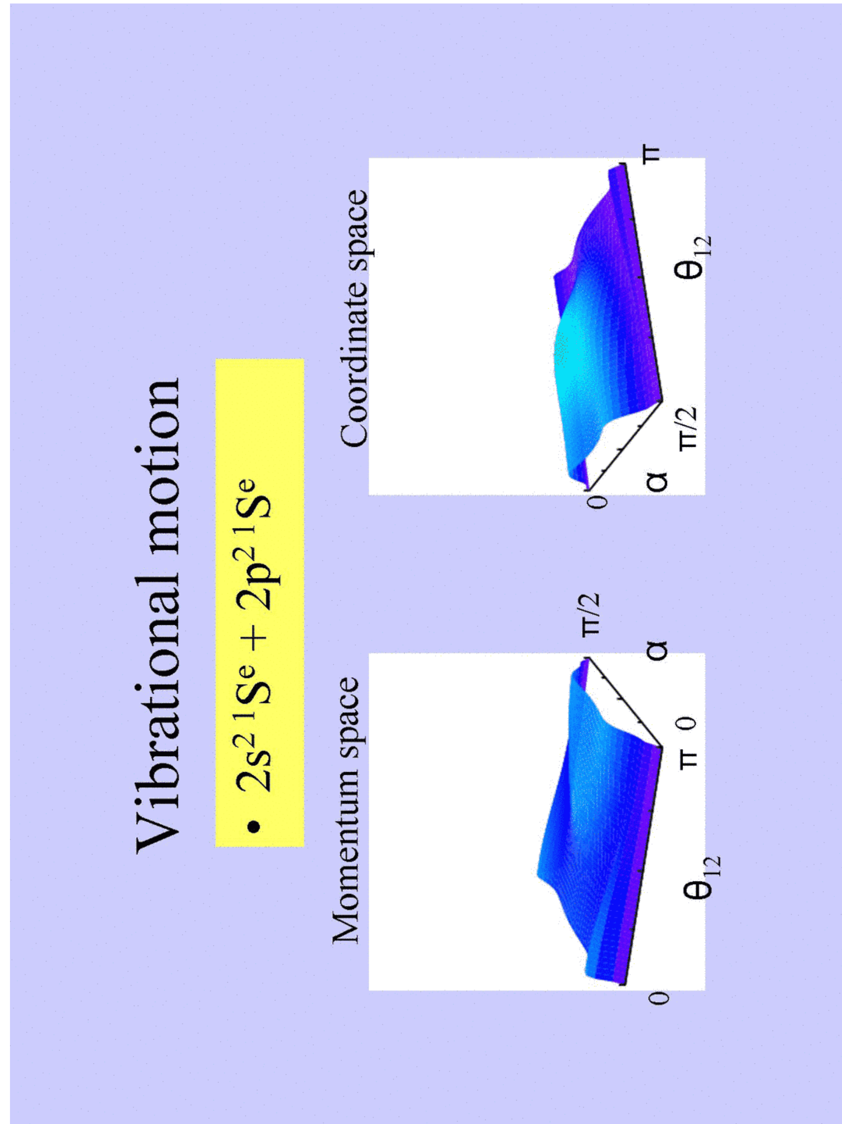


Coordinate space



Radial motion of the outer electron only


Helium Spectrum---
doubly excited states
OPTICALLY FORBIDDEN
OPTICALLY ALLOWED
FIRST IONIZATION THRESHOLD 24.6 eV
SECOND IONIZATION THRESHOLD 65.4 eV
THIRD IONIZATION THRESHOLD 72.9 eV
FOURTH IONIZATION THRESHOLD 75.6 eV
DOUBLE IONIZATION THRESHOLD 79.0 eV
ENERGY IN eV
GROUND STATE
DOUBLE EXCITATION
AUTOIONIZATION
ELECTRON CAPTURE
INELASTIC COLLISION
IONIZATION OF He+


Vibrational motion
• 2s² ¹Se + 2p² ¹Se
Momentum space
Coordinate space
α
θ12
π/2
π
0

Coherent **Doubly** excited states of Helium atoms

-- dynamics in other (?) degrees of freedom

How to describe doubly excited states?

↑ shell model fails

"Accurate" wave functions –

showing strong configuration mixing

$|3s3s\ ^1S^e\rangle = 0.72\,|3s3s\rangle + 0.61\,|3p3p\rangle + 0.15\,|3d3d\rangle + \ldots$

$|3s3p\ ^3P^o\rangle = 0.87\,|3s3p\rangle + 0.39\,|3p3d\rangle + \ldots.$

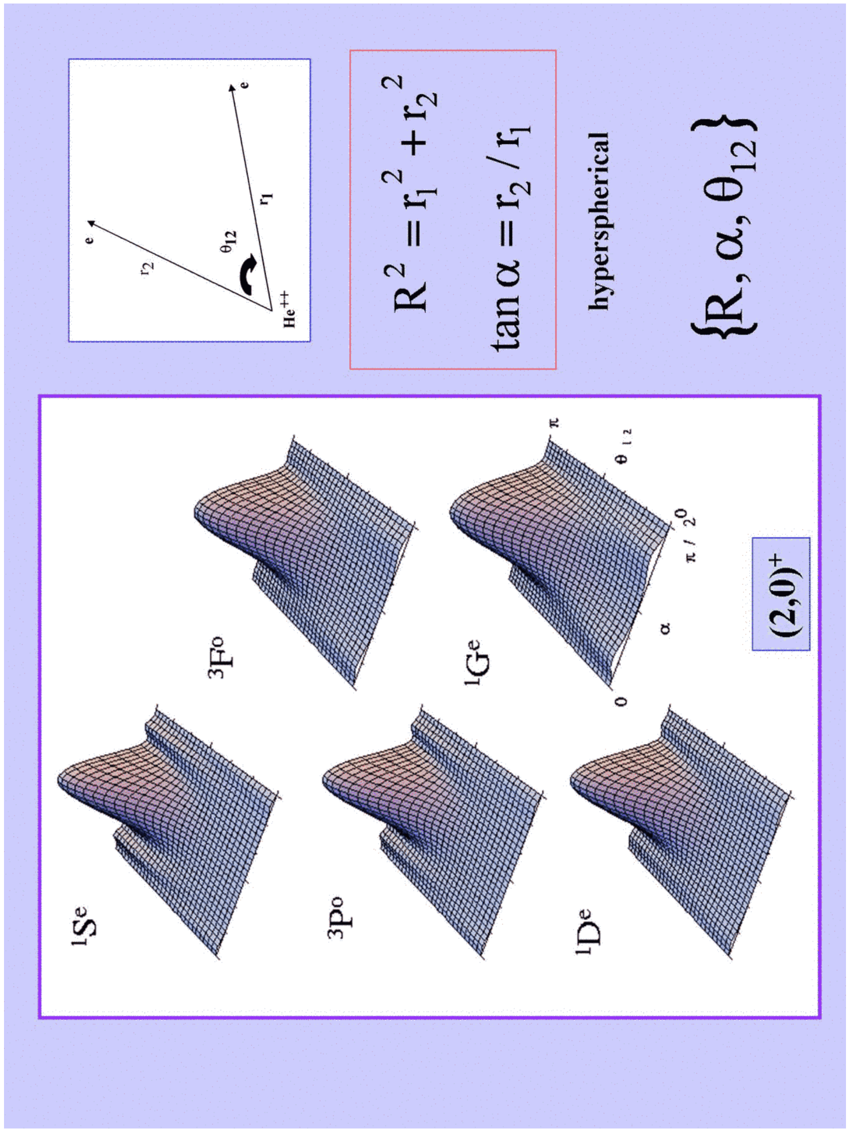
$|3p3p\ ^1D^e\rangle = 0.71|3p3p\rangle - 0.58\,|3s3d\rangle + 0.15|3d3d\rangle + \ldots$

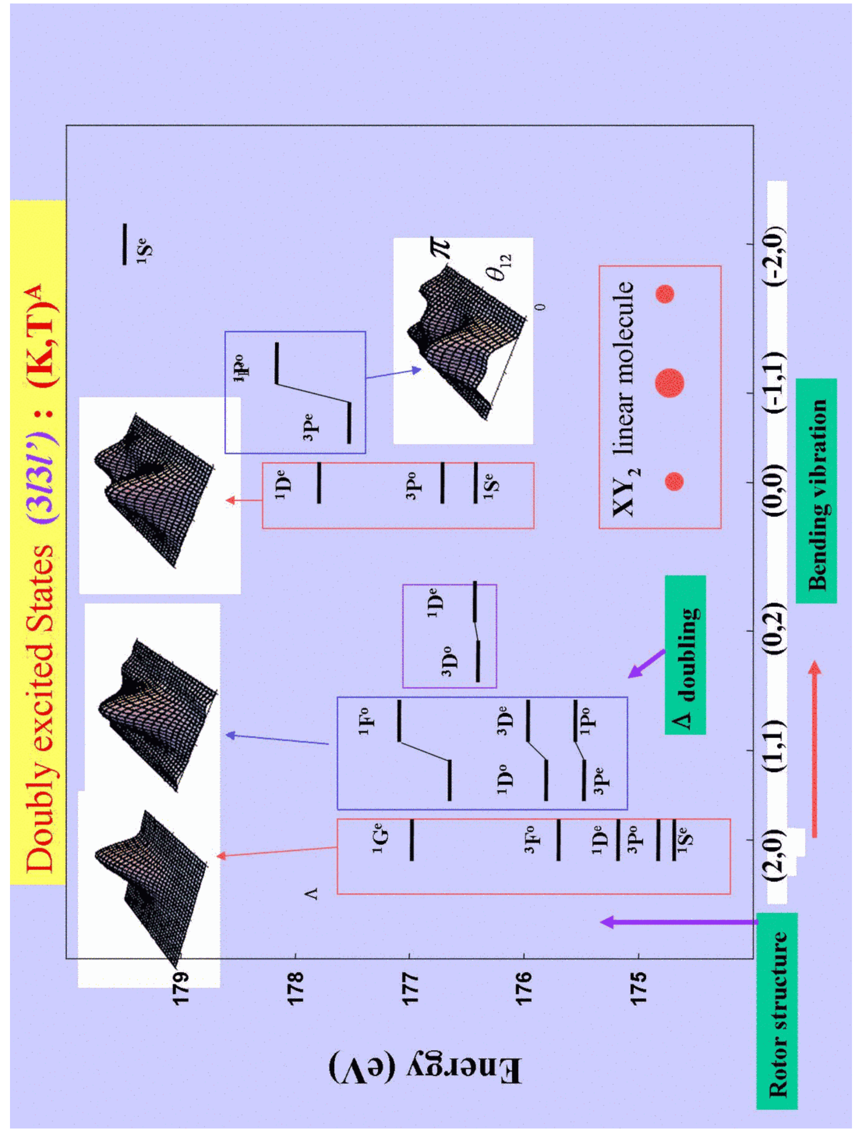
$|3p3d\ ^3F^o\rangle = 0.91|3p3d\rangle + \ldots\ldots\ldots$

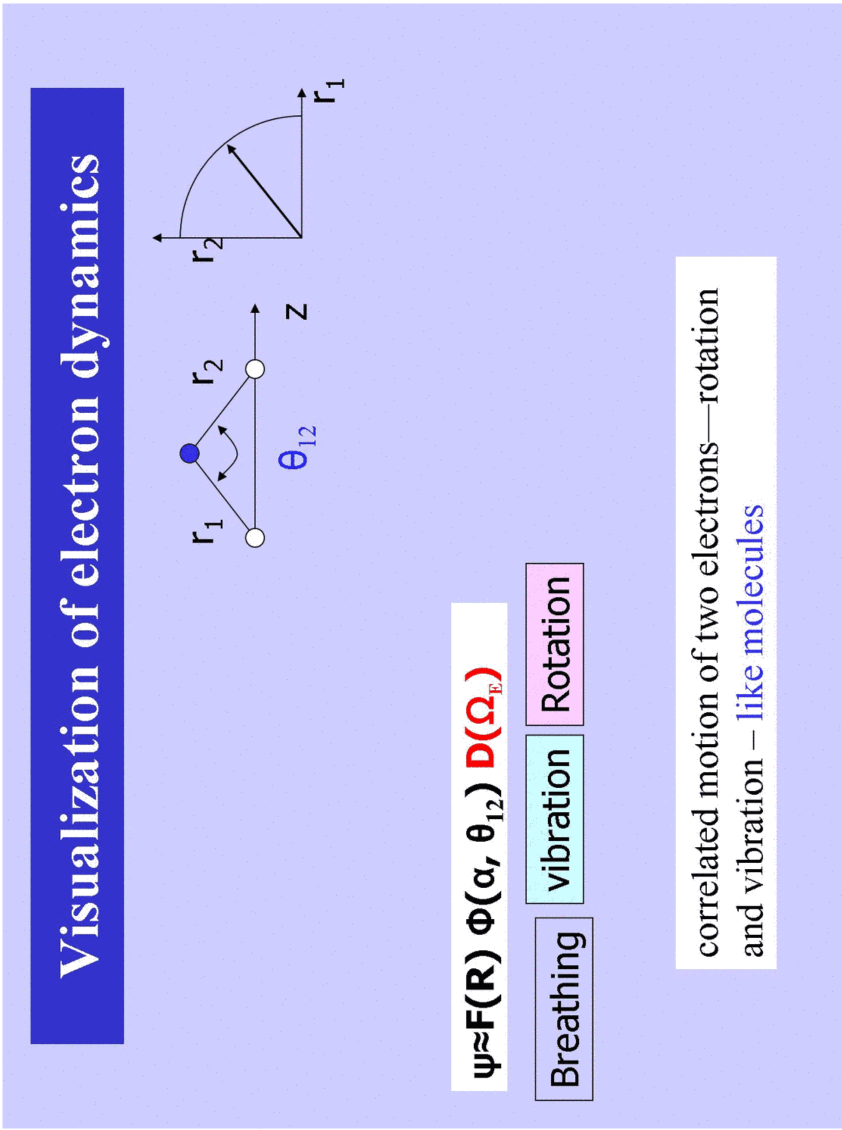
$|3d3d\ ^1G^e\rangle = 0.80\,|3d3d\rangle + \ldots.$

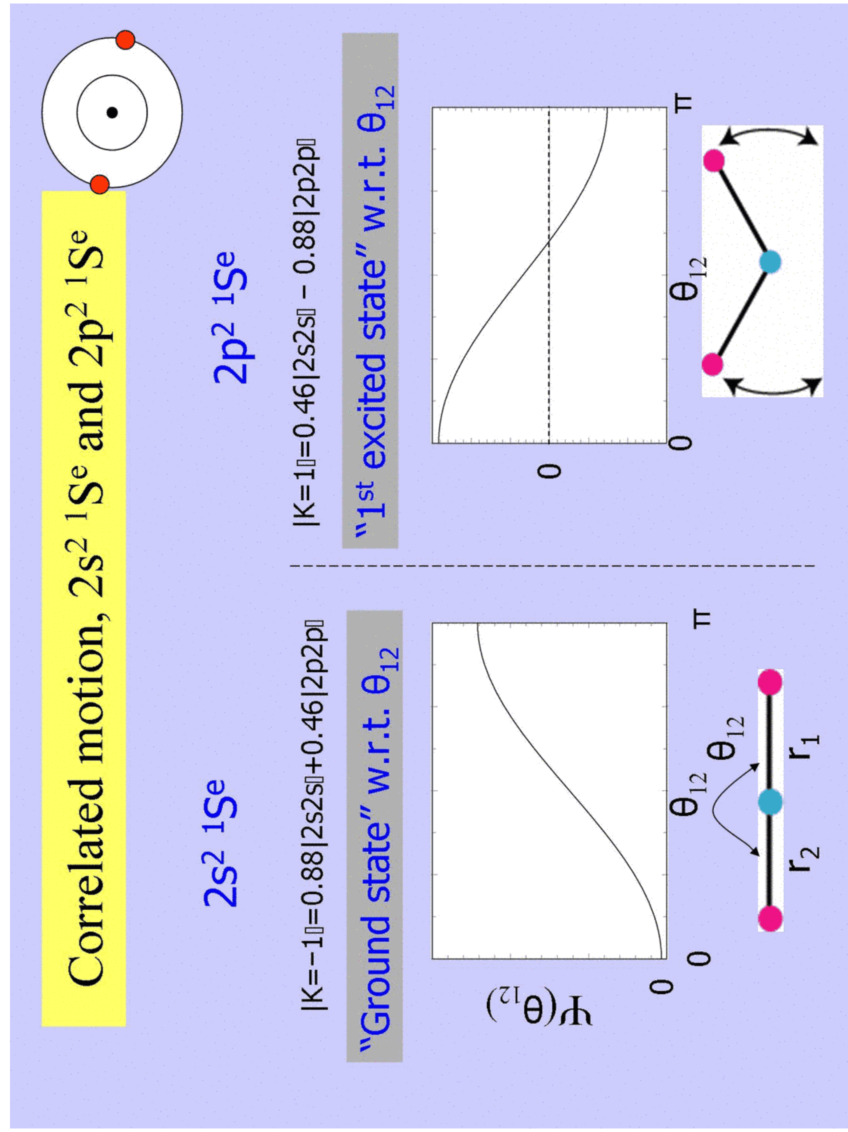
They have Identical correlation quantum numbers:

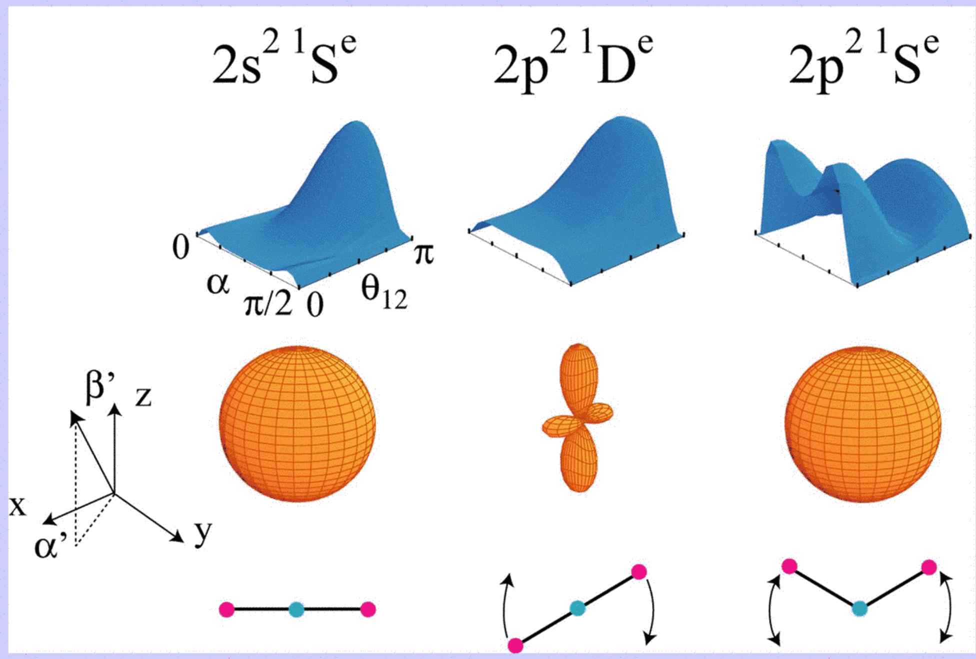
$(K, T)^A = (2,0)^+$


R^2 = r1^2 + r2^2
tan α = r2 / r1
hyperspherical
{R, α, θ12}
1Se
3Fo
3Po
1Ge
1De
(2,0)+

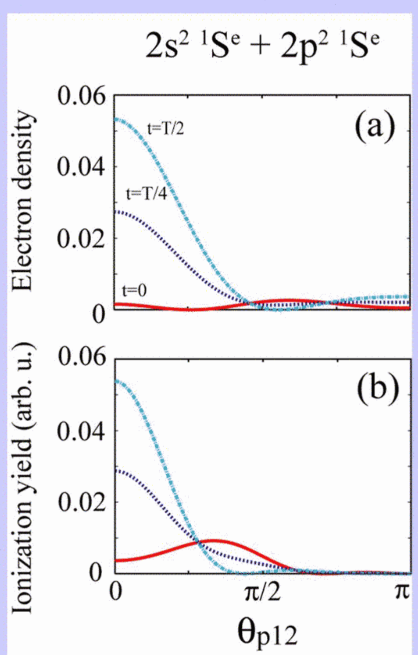

Doubly excited States (3l3l') : (K,T)A
Energy (eV)
XY2 linear molecule
Λ doubling
Bending vibration
Rotor structure
(2,0)
(1,1)
(0,2)
(0,0)
(-1,1)
(-2,0)


Visualization of electron dynamics
r_1
r_2
z
θ_{12}
$\psi \approx F(R)\ \Phi(\alpha, \theta_{12})\ D(\Omega_E)$
Breathing
vibration
Rotation
correlated motion of two electrons—rotation
and vibration – like molecules


Correlated motion, $2s^2\ ^1S^e$ and $2p^2\ ^1S^e$
$2s^2\ ^1Se$
$2p^2\ ^1Se$
|K=−1⟩=0.88|2s2s⟩+0.46|2p2p⟩
|K=1⟩=0.46|2s2s⟩ − 0.88|2p2p⟩
"Ground state" w.r.t. θ_{12}
"1st excited state" w.r.t. θ_{12}
$\Psi(\theta_{12})$
0
π
θ_{12}
r_1
r_2



Dynamics of a simple coherent state



Initial state at t=0

T=980 as

time-dependence of the wave packet in momentum space, in angle θ_{12}

time-dependence from the **double ionization** signal

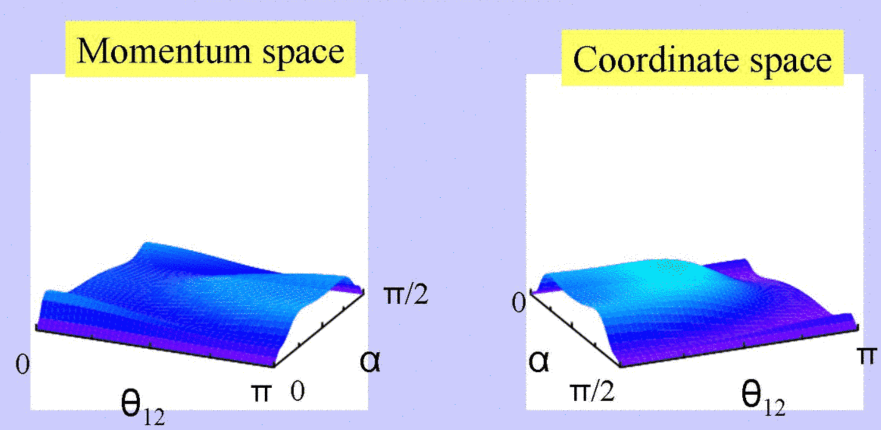
200 asec-27.2 eV

"Technical" computational issues—

- Attosecond pulse has intensity of the order 10^{12} W/cm^2
- Use first order perturbation theory
- Initial state wavefunctions are Configuration Interaction wave functions
- Final two-electron continuum wave functions are symmetrized product of Coulomb functions with charge=1. (not sensitive to this effective charge)
- Analysis in hyperspherical coordinates

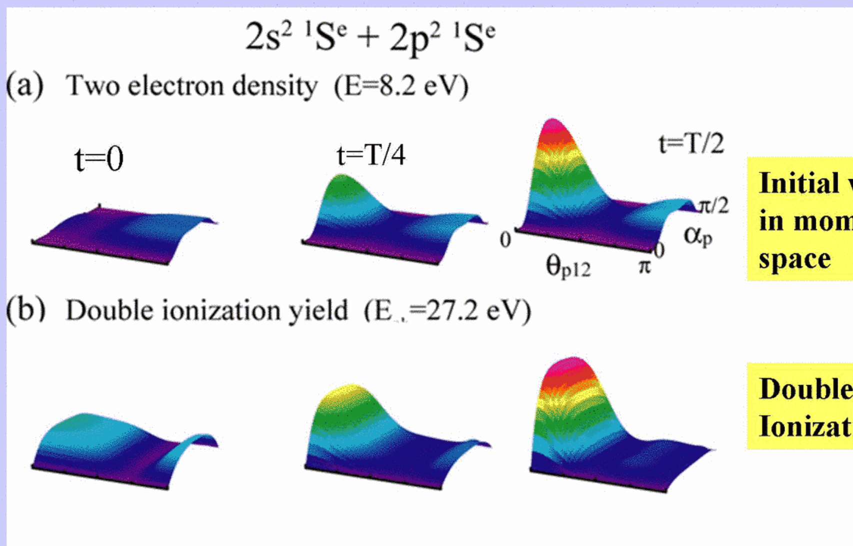
Vibrational motion

- $2s^2\,{}^1S^e + 2p^2\,{}^1S^e$



Ionization signal revealing the time dependence of a two-electron wave packet

200 asec- 27.2 eV



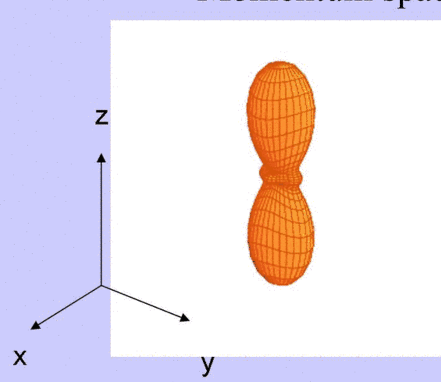
Initial wave packet in momentum space

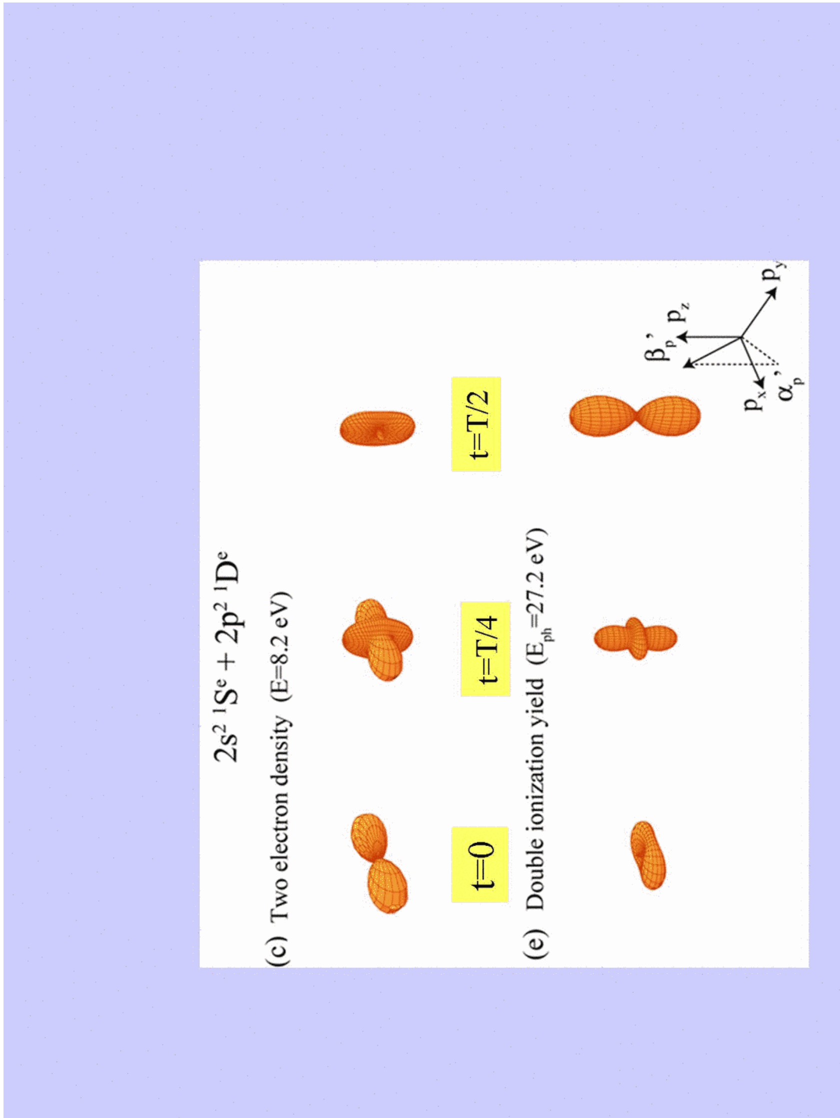
Double Ionization signal

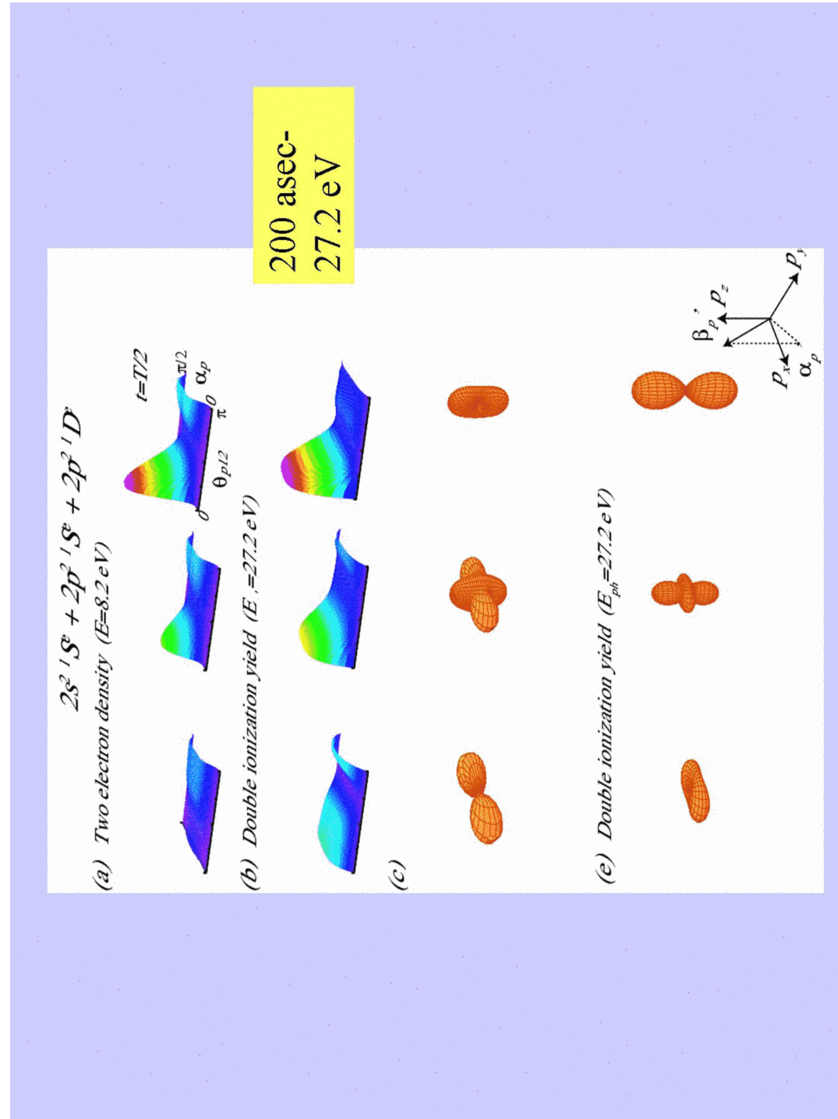
Rotational wave packet

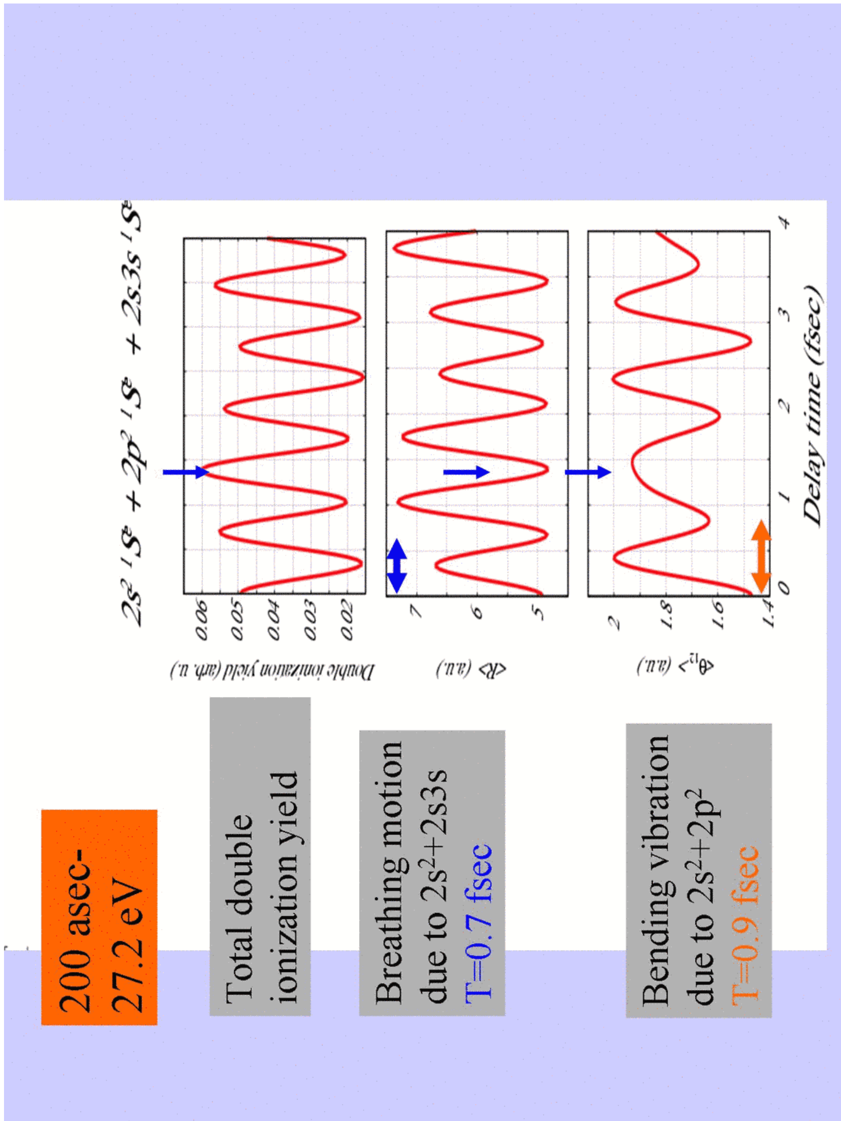
- $2s^2\ {}^1S^e + 2p^2\ {}^1D^e$

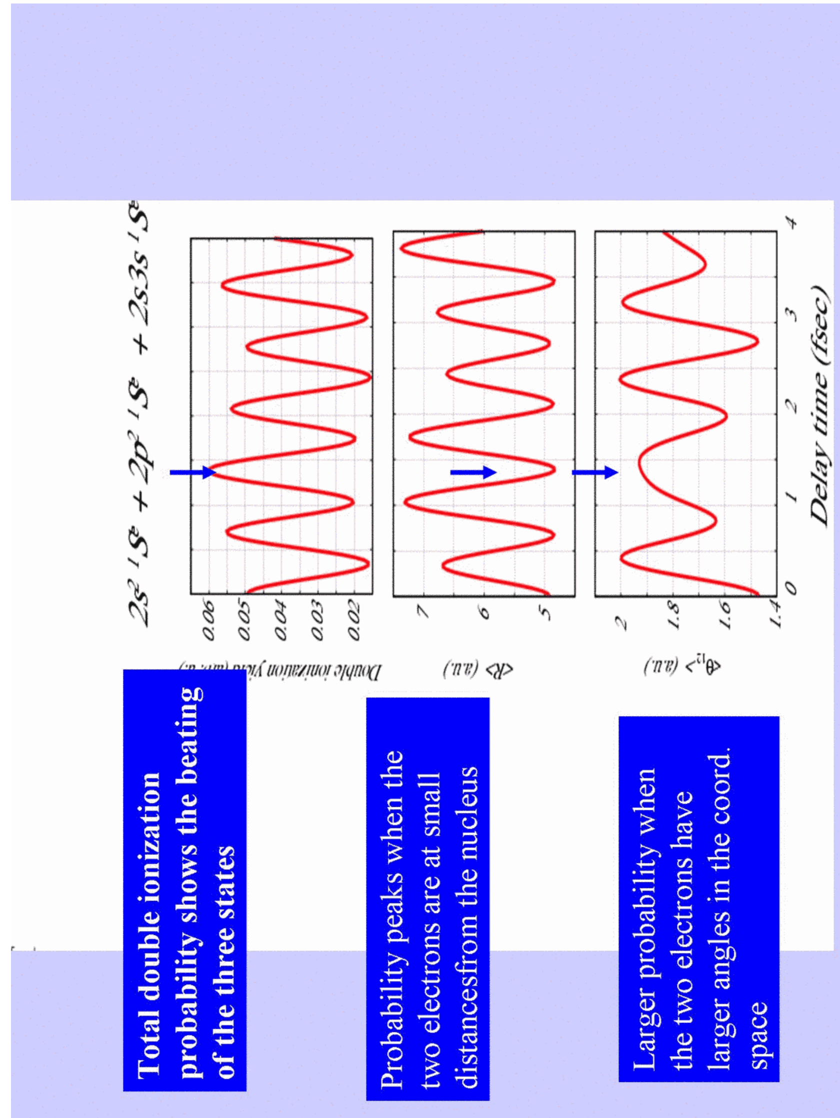
Momentum space




2s2 1Se + 2p2 1De
(c) Two electron density (E=8.2 eV)
t=0
t=T/4
t=T/2
(e) Double ionization yield (Eph=27.2 eV)
px
py
pz
βp'
αp'


200 asec-
27.2 eV
2s2 1Se + 2p2 1De
(a) Two electron density (E=8.2 eV)
t=T/2
(b) Double ionization yield (E ,=27.2 eV)
(c)
(e) Double ionization yield (Eph=27.2 eV)
px
py
pz
βp'
αp


200 asec-
27.2 eV
Total double
ionization yield
Breathing motion
due to 2s²+2s3s
T=0.7 fsec
Bending vibration
due to 2s²+2p²
T=0.9 fsec
2s² ¹Sᵉ + 2p² ¹Sᵉ + 2s3s ¹Sᵉ
Double ionization yield (arb. u.)
<R> (a.u.)
<θ₁₂> (a.u.)
Delay time (fsec)


Total double ionization
probability shows the beating
of the three states
Probability peaks when the
two electrons are at small
distancesfrom the nucleus
Larger probability when
the two electrons have
larger angles in the coord.
space
2s² ¹Sᵉ + 2p² ¹Sᵉ + 2s3s ¹Sᵉ
<R> (a.u.)
<θ₁₂> (a.u.)
Delay time (fsec)

Major Features of two-electron dynamics in the time domain

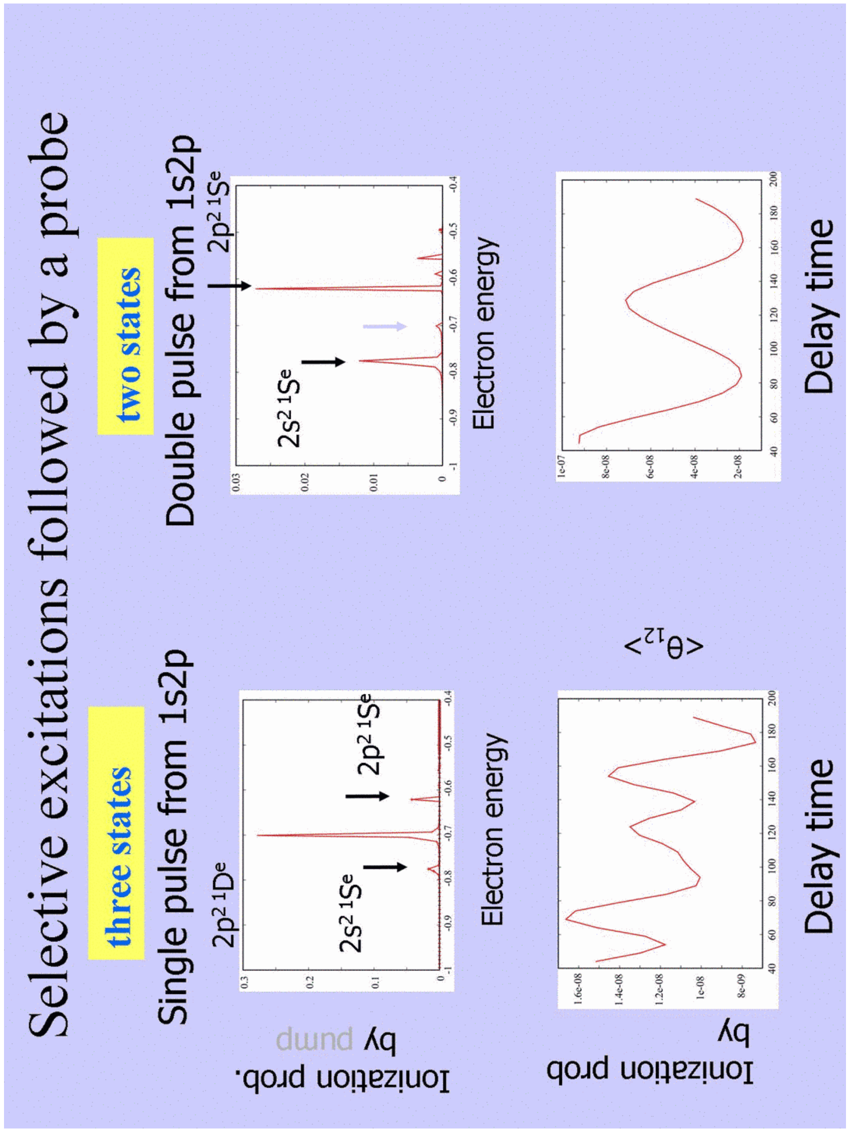
1. Their correlated motions can be described in terms of stretching, bending vibrational and rotational modes.
2. Special wave packets may reveal the time dependence of one of these modes only.
3. Double ionization of such a wave packet may reveal main features of the time-dependence of such a wave packet.
4. Visualization of such time dependence from the momentum spectra of the two electrons requires special sampling of the experimental data

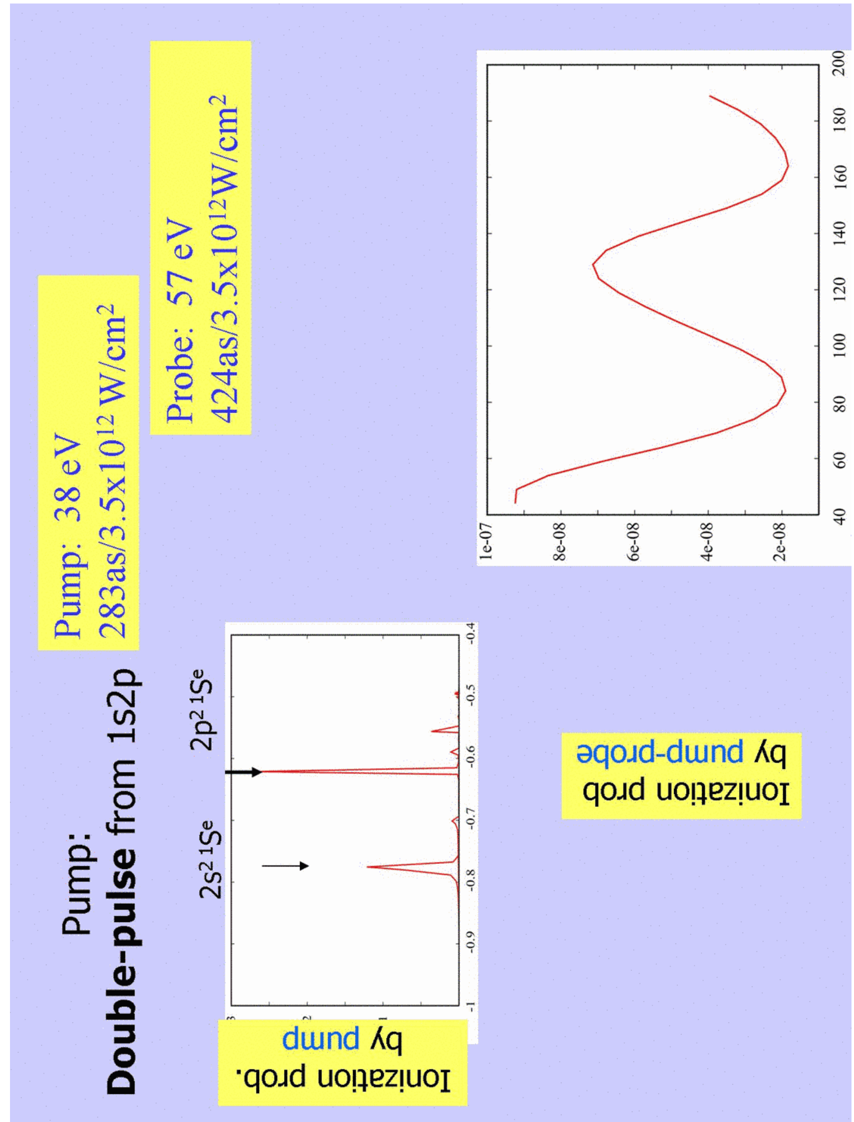
Pump-Probe experiments

- How to create wave packets of doubly excited states with some desired properties?

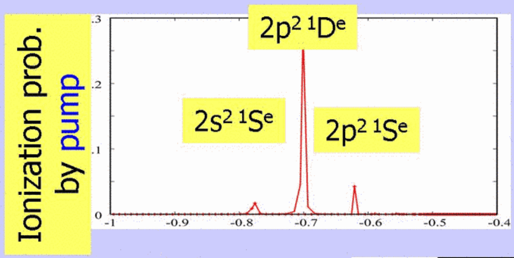
General method– I don't know.

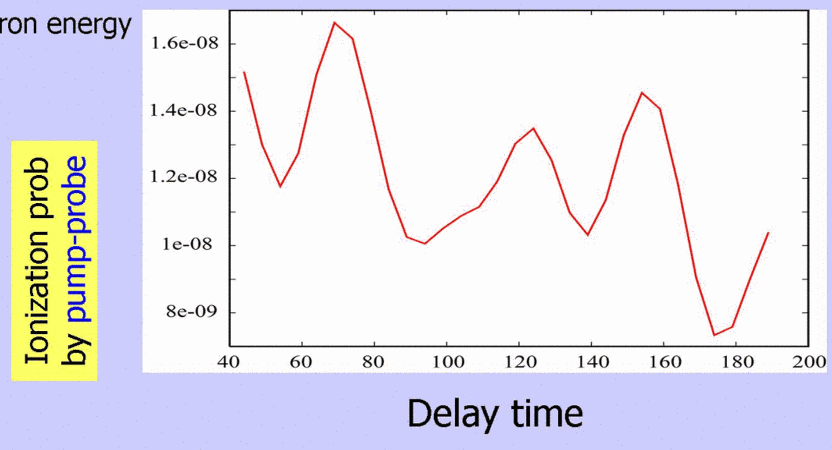
Special simple examples– some offered here.


Selective excitations followed by a probe
three states
Single pulse from 1s2p
two states
Double pulse from 1s2p
2p2 1De
2s2 1Se
2p2 1Se
Ionization prob. by pump
Electron energy
Ionization prob by
Delay time
<θ12>
2s2 1Se
2p2 1Se
Electron energy
Delay time


Pump:
Double-pulse from 1s2p
Pump: 38 eV
283as/3.5x10^12 W/cm^2
Probe: 57 eV
424as/3.5x10^12W/cm^2
2s2 1Se
2p2 1Se
Ionization prob. by pump
Ionization prob by pump-probe

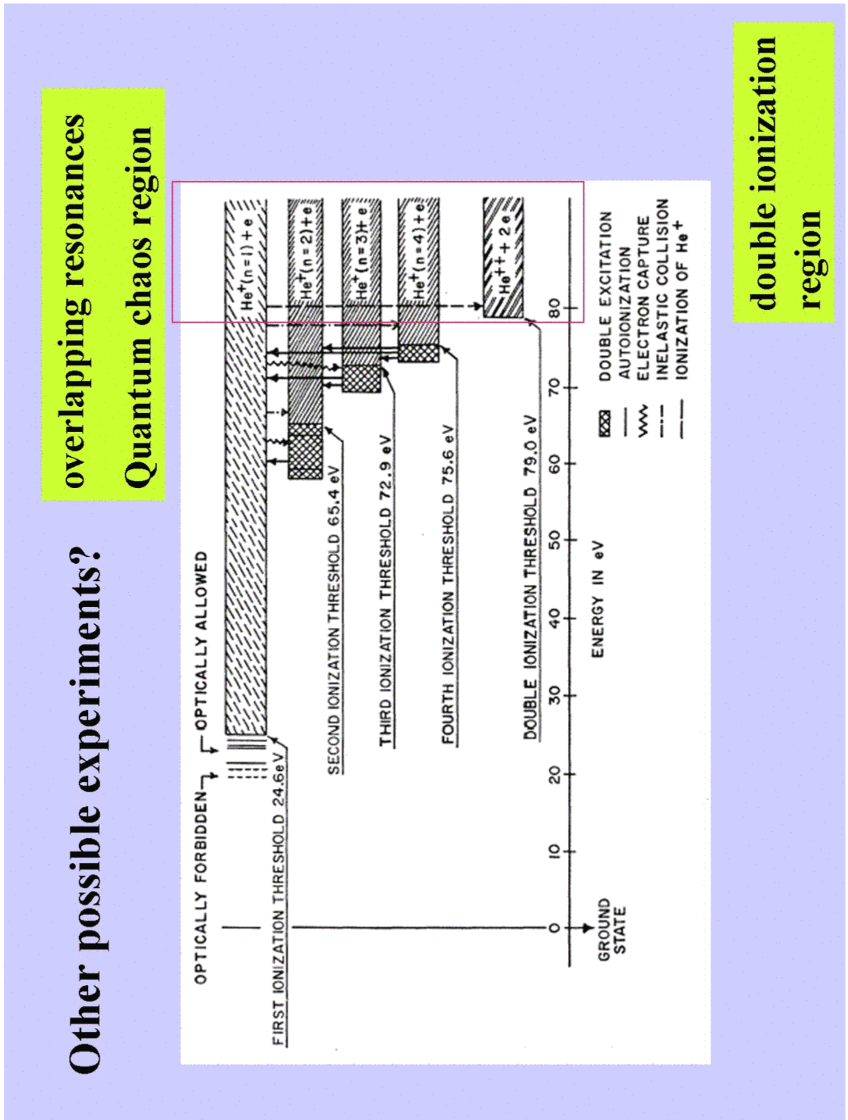
Single pulse from 1s2p





Comments—

- Rich physics to be explored by creating two-electron wave packet
- Dynamics can be probed by double Ionization– six-dimensional momentum spectra of the two electrons
- Analysis of the data is challenging
- Can the experiments be done with current attosecond pulses?
- Measurements of total ionization probability in pump-probe experiments are easier--- interpretation would need help from theory


Other possible experiments?
overlapping resonances
Quantum chaos region
double ionization region
OPTICALLY FORBIDDEN
OPTICALLY ALLOWED
FIRST IONIZATION THRESHOLD 24.6 eV
SECOND IONIZATION THRESHOLD 65.4 eV
THIRD IONIZATION THRESHOLD 72.9 eV
FOURTH IONIZATION THRESHOLD 75.6 eV
DOUBLE IONIZATION THRESHOLD 79.0 eV
He+(n=1)+e
He+(n=2)+e
He+(n=3)+e
He+(n=4)+e
He++ + 2e
0
10
20
30
40
50
60
70
80
GROUND STATE
ENERGY IN eV
DOUBLE EXCITATION
AUTOIONIZATION
ELECTRON CAPTURE
INELASTIC COLLISION
IONIZATION OF He+