Exercise 1

1. Go to RMP 32, 245 (1960) to find out the energies of the molecular orbitals for Li_2, C_2, N_2, O_2 and F_2 molecules and order them. Check against the ordering in Table 4.3 of note-3 to see if the order given there should be changed.
  Pay special attention to N_2 and note that the order changes from different calculations.

2. Carefully study the correlation diagram of Fig. 10.14 of BJ for homonuclear diatomic molecules. Work out the united atom limit of the $\sigma_u * 2p$ state from the separated atom limit.

3. Go to the web or any reference books to find out the dissociation energy and the equilibrium distance of H_2^+, H_2, N_2, O_2, CO, and I_2. Express the results in eV's and in angstroms, respectively.
  From the potential curves of H_2 and of H_2^+ calculate the ionization energies, assuming Franck-Condon principle.

Exercise 2:

1. Sketch the molecular orbital **correlation diagram** for FH and FH$^+$. Note that you need to use the binding energy of F and H in the separated atom limit and the orbital energies of the united atom.
    Write down the ground-state configurations of FH and FH$^+$ and the angular momentum designations of the electrons, i.e., in $^{2S+1}\Lambda$.

2. In this exercise we will learn to **count the degeneracy**.

 First we consider the HD molecule.

 (i) Sketch the rotational energy levels in terms of B, the rotational constant. Consider J=0, 1, 2, 3, 4, 5. Draw the levels to the correct scale.
(ii) Recall the selection rules for absorption. Sketch the absorption spectra (i.e., the different lines that you can observe).
(iii) Note that the population of different excited states is governed by the Boltzman factor at each given temperature T. However, for each J, there is a degeneracy of (2J+1). Based on this fact, what is the expected intensity distributions of the rotational spectra?

 Next we will consider H_2.
 There is no pure rotational spectra allowed. We will consider the relative populations of the rotational levels, remembering that we need to consider nuclear spin statistics.
 (iv) Calculate the degeneracy factor for J=0, 1, 2, 3.
 (v) Find the rotational constant of H_2, and calculate the relative fraction of J=1 level with respect to J=0 level at 20 ^{o}K and at room temperature 300 ^{o}K.
 (vi) Repeat (v) but for D_2.

 (vii) Prove that there are no even J rotational levels for $^{16}O_2$.

Problem set -3   (due 3/4/05)

1. (a) A chirped laser field in the time domain can be written in this form

$$\vec{E}_x(t) = Re\{E_{0x}e^{-\sigma(1-i\xi)t^2}e^{i\omega_x t}\vec{e}_x\},$$

Rewrite this expression in the form of

$$E(t) = E_0(t)\cos[\omega_x t + \delta(t)]$$

showing the time dependence of the carrier phase $\delta(t)$. Express the half-width τ_x (defined as the full width at half maximum--FWHM) of the intensity $|E_x(t)|^2$ in the time domain in terms of σ and ξ.

(b) Take the Fourier transform of $E_x(t)$ to find $A(\omega)$. From $|A(\omega)|^2$ calculate the half width $\Delta\omega$ in the frequency domain. Show that

$$\Delta\omega = \frac{4\ln 2}{\tau_x}\sqrt{1+\xi^2}$$

2. Write a program to calculate the superposition of plane waves,

$$\sum_1^n A_i \cos[\phi_i + (2i+1)\omega t]$$

and plot the sum as a function of time. Take ω to be the 800nm Ti-Sapphire laser.

(a) Let the phase of each harmonic in the sum to be zero, **plot** the resulting wave (vs time) and show that it is a pulse train. Consider n=4 and 10 and convince yourself that the width of each pulse in the pulse train is narrower with larger n. You can take A_i to be all equal (=1) in one calculation and then in another calculation make the A_i different (say between 0.5 and 1.5) . Show that in the latter you still get pulse trains.

(b) In the 2nd part, take all the A_i to be equal, but vary the phase ϕ_i to somewhat different values and plot the resulting pulse to show that pulse train does not exist any more. Just do two cases.

3. We will use the result of part (b) of problem 1 to estimate the energy uncertainty of a Gaussian pulse without the chirp ($\xi = 0$). For a pulse with pulse length τ_x of (a) 10 fs, (b) 1 fs (c) 200as, what is the respective energy width of the pulse? Express your results in eV's.

Exercise 4.   A free electron in a monochromatic laser field (due 3/7/05)

1. In this exercise we assume that the electron can be described classically. The acceleration, velocity and displacement are given by

$$\frac{d^2x}{dt^2} = \frac{eE_0}{m} \cos \omega_0 t$$

$$\frac{dx}{dt} = v = \frac{eE_0}{m\omega_0} \sin \omega_0 t + v_i$$

$$x = -\frac{eE_0}{m\omega_0^2} \cos \omega_0 t + v_i t + x_i$$

(a) Assume that the electron becomes free(or born) at t=t₀, with zero velocity at x=0. Calculate analytically the time and the velocity of the electron when it returns to x=0. Determine the kinetic energy of the electron at the return(when x=0 again) vs   the phase angle $\omega_0 t$.

(b) Show that the curve is like this one:
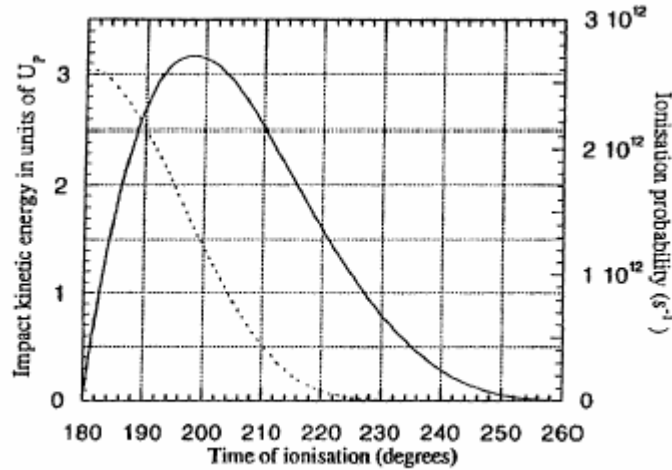
The maximum kinetic energy occurs at 17^0 from the laser peak angle. You can read that the maximum kinetic energy is 3.17 U$_P$. Note that the dashed curve is the tunneling ionization probability and ionization is important only near the peak of the field.

(c) Consider a laser of wavelength 800nm, and intensity of 10^{14} W/cm², calculate and plot the maximum excursion distance of the electron that would return to x=0 for each phase angle $\omega_0 t$ shown in the figure. Note that there are two phase angles (or times) where the electron will return to x=0 with the same kinetic energy. For an electron that returns with 2.5 U$_P$,   identify the two trajectories, i.e., their maximum distance of exersion from x=0. The two paths are called long path and short path, respectively.

(d) Show that if electrons   were born at phase angles less than 180^0 (from Fig above), the electron does not return to x=0. Check your calculation for phase angle of 170 and 160 degrees.

homework-5   (due 3/18/05)

In this exercise we will use the tunneling ionization theory to do a few "realistic"
calculations.
 For atoms:
(1) Assume a linearly polarized laser pulse is of Gaussian form, with *peak* intensity of
3.5×10^{14} W/cm^2. Write down the time-dependence of the electric field if the pulse has a
duration of 30 fs, assuming that the carrier phase is zero and that the electric field is
maximum at t=0.

(2) Use the cycle-averaged ADK rate, eq. (3) in notes-7, to calculate the total ionization
probability if such a pulse is applied to an Ar and a Xe atom. Take the pulse shape into
account. For your convenience, the coefficient C_ℓ for Ar is 2.586 and for Xe is 2.67.

(3) Saturation intensity: Since the total ionization probability of an atom cannot be
greater than 1.0, the atom can be fully ionized before the pulse is over if the laser
intensity is very large. Let us define the saturation intensity is the peak intensity for a
given pulse that the total ionization probability reaches 98%. Calculate the saturation
intensity of Ar and Xe for a 30 fs Gaussian pulse. Calculate the saturation intensity for
each atom if the pulse duration is 8 fs.

(4) For high harmonic generation the atom cannot be fully ionized, thus the highest HHG
cutoff is governed by the saturation intensity. Calculate the highest HHG cutoff (i.e., the
highest harmonic order) for Ar and Xe, respectively. Compare your results with Fig. 1 of
Shan et al PRA66, 061401 (2002). Assume pulse length is 30 fs.

For diatomic molecules:
(5) Use the MO-ADK theory to calculate the alignment-dependent ionization rates for N_2
and O_2 molecules. use peak intensity of 3×10^{14} W/cm^2 for N_2 and 2×10^{14} W/cm^2 for O_2.
Compare your results with the figures shown in the notes-7a handout. All the parameters
needed for your calculation can be found in Tong et al PRA66, 033402 (2002).

(6) Do another calculation with half of the peak intensity for each molecule and show that
the alignment-dependence rates do not change much with laser intensity.

Homework set-6

1. The outermost shell of Ar atom is $3p^6$, i.e., there are six electrons. Consider the ionization of Ar by an intense laser pulse. The laser is linearly polarized with peak intensity 3.5×10^{14} W/cm^2. We will use the ADK theory (or static ionization theory) to calculate the ionization rates. Consult Table II of Tong et al, PRA66, 033402 (2002) for the parameters you need to do the calculations.

(a) Calculate and compare the average ionization rates from the m=0 and m=1 magnetic substates of the 3p electrons.

(b) Look up the binding energy of the 3s subshell of Ar, and estimate if you can neglect the ionization from the 3s electrons.

(c) Assume that you have a 5fs pulse (FWHM) and the pulse shape is Gaussian. Write down the form of the laser's electric field for a carrier envelope phase (cep) of 0 and $\pi/2$. Take t=0 at the peak of the laser's intensity envelope. Write a simple program to calculate the total ionization probability by such a pulse by integrating over the ionization rates over the duration of the pulse. Compare if the probability depends on the cep. Use the static ionization rate at each instant of time.

(d) Repeat the calculation of (c) for an 8fs pulse.

Next, consider circularly polarized laser of FWHM 5fs and mean wavelength 800nm.

(e) For a circularly polarized light of the same peak field strength and pulse duration of 5 fs, write down the expression of the laser's electric field vs time, again assuming Gaussian pulse shape. Consider cep of 0 and $\pi/2$.

(f) Using Static ionization rate, calculate the ionization rate of Ar by this circularly polarized light vs time. What is the total ionization probability at the end of the pulse? How does this probability depend on the cep?

2. More practice of using the Floquet theory for H_2^+ and D_2^+.

This question was asked in the mid-term exam and you complained that you did not have enough time. So here it is again.

(a) This figure was shown in Note-10a, page 2, which gives the kinetic energy release per proton after H_2^+ is dissociated by a 40 fs laser of wavelength of 800nm.
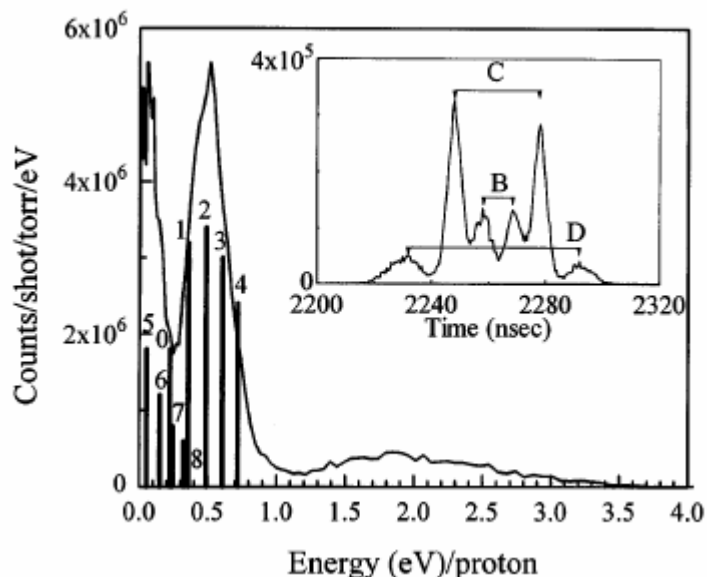
The first peak, at the lowest energy, is attributed to the 1-photon absorption from $v=5-8$ and the second peak at slightly higher energy, is considered to be from the 2-photon absorption from $v=1,4$, both leading to the dissociation. Use the Floquet diagram from Max Sayler, calculate the energies of these lines and show that they are indeed at where they are supposed to be.

(b) If H_2^+ is replaced by D_2^+, what are the vibrational levels that will appear in the 1-photon peaks and in the 2-photon peaks. Calculate the energies of these individual peaks. Estimate your energies from the Floquet diagram given in your notes, i.e., we will neglect the modification of the Floquet energy by the laser field strength.

(c) From part (a), what will be the positions of these peaks if we use a laser that has mean wavelength of 400 nm. (Recall that this experiment is being carried out at JRM.)

(d) The peak near 2.0 eV in this figure is due to CREI. What is CREI? If you used D_2^+ as the target, where is the position of this peak? If the laser is 400nm in wavelength, where do you expect the location of this peak be?

1. In the rescattering theory for the double ionization of H_2 by a laser pulse, we have used this schematic diagram below to discuss the mechanism of double ionization.
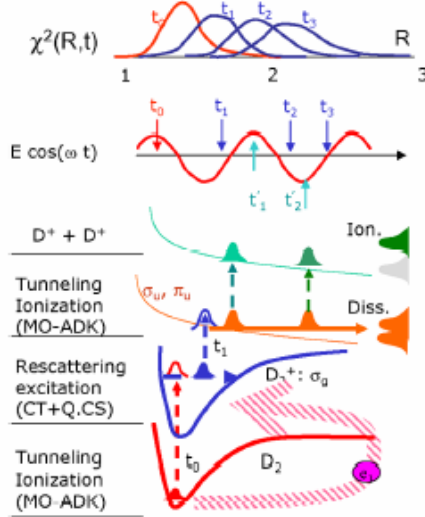(see note-10a)

Fig. 1

In this exercise we will calculate the total kinetic energy release which have been measured by Cocke's group (left) and modelled more accurately by X. M. Tong (right), shown below.
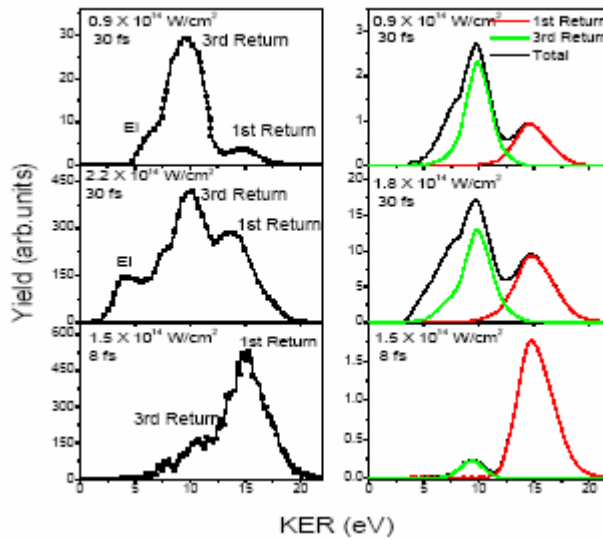

Fig. 2

In the first step, the H_2 is singly ionized, say at time t_0, in the second frame of Fig. 1 near the peak of the laser field. From Frank-Condon principle, a vibrational wave packet is created. This wave packet is very close to the v=5 vibrational state, initially at the left classical turning point. The motion of this wave packet is to be approximated by a

classical harmonic oscillator such the internuclear distance can be followed precisely in time.

  (a) Write down the displacement of this classical harmonic oscillator with the distance measured from the inner turning point of the v=5 vibrational state (which is close to the equilibrium distance of H_2 at 1.4 a.u.). Make sure that you write the equation all in atomic units. You can read the amplitude of this harmonic oscillator from Fig. 3 of note-10 given by Max.
  (b) In the rescattering theory, the second ionization of H_2 is due to the rescattering where the returned electron has enough kinetic energy to ionize the remaining electron. The first time the electron returns to the ion occurs at time t_1. For the 800nm laser pulse, what is the duration between t_1 and t_0?
  (c) At time t_1, what is the internuclear separation according to our classical harmonic oscillator model?
  (d) If the second electron is instantaneously ionized (another Frank-Condon principle) by the returning electron at t_1, the two remaining protons will Coulomb explode to convert the potential energy into the total kinetic energy release. This released energy is then measured experimentally. Calculate this energy in eV and compare your result with the energy of the peak labelled by "1st return" in Fig. 2.
  (e) If the second electron is ionized at time t_3 of Fig. 1, what is the internuclear separation at that time, and what is the expected total kinetic energy release? Compare your result with the experimental data labelled " 3rd return".

  Note that the laser intensity will change the relative size of the peaks only, not the position of the peaks.
 (f) If you change the pulse duration of the laser, would the peak positions change?
  (g) If the mean wavelength of the laser is 1200 nm, what will be the positions of the peaks for the 1st and the 3rd returns, respectively?

Homework-8.   XUV+IR electron spectra

In this exercise we will walk over the experiment of **Kienberger et al Nature 427, 817 (2004)**
where they determined the width of the attosecond pulse to be 250 as.

Recall that the XUV and the laser, if overlapped as shown, the electron spectra will be like this:
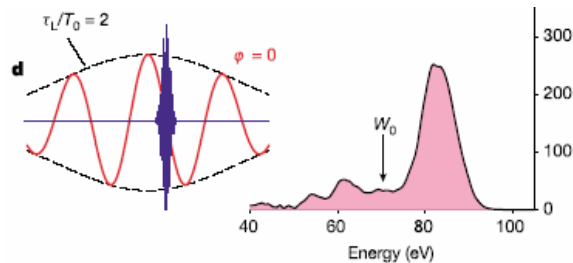
The laser parameters are: 750 nm (1.5 eV, T=2.5 fs), and it is a 5 fs pulse with zero
carrier phase. For the XUV the mean energy is 93.5 eV. The target atom is Ne. The
electrons are measured at zero degrees with respect to the laser polarization.
   Give all of your answers in a.u. unless otherwise indicated.

 (a) Without the laser, what is the mean momentum of the ejected electron?
 (b) The diagram above shows that the electron energy will be shifted if the XUV is
placed at where it is. I would read that the peak position is at about 84 eV. If you assume
that the laser amplitude is constant, from this shift, calculate the peak electric field of the
laser.

   Note that the pulse does not have constant amplitude. Assume that the laser pulse is
Gaussian of 5fs for its FWHM. They say that the peak field is 75 MV/cm. What would
you get?

 (see the next figure)
  Next they measured the electron spectra at the time delay where the vector potential is
zero. The next figure gives the results that were discussed in the class. After a more
elaborate analysis they claimed that the XUV pulse is chirped, and has pulse duration of
250 as. We will see if we can estimate that their results are meaningful.

 (c) Read the width of frame (a) and estimate the width of the photoelectron spectra. If
the attosecond pulse has no chirp and has the pulse duration (always FWHM) of 250 as,
what should be the width in frame (a). Recall there is no laser field in this case.
 (d) Now they have the laser on and the <u>center</u> of the XUV pulse is placed at where the
vector potential is zero. Since the XUV pulse has a width, you still get additional shift
from the laser. Take the XUV pulse to be 250 as as they said (recall that this is measured
from the intensity, not the electric field or vector potential.)
   Estimate what is the vector potential of the laser at the half-width (in time) of the XUV
pulse. Take the peak electric field to be 75 MV/cm.
 (e) Calculate the width of the electron spectra in this case and compare your result that
you can read from (b) or (c).

Legend (within figure):
■ Measurement
— Simulation

Axis labels:
- Y-axis: Electron counts per bin
- X-axis: Electron kinetic energy (eV)

Panel labels: a, b, c