Atoms and Molecules in High Laser Fields --
Physics Beyond Perturbation Theory

With short-pulse lasers it is possible to routinely produce optical fields that exceed the atomic Coulomb field. This is an extremely active field of current research. In this course we will spend a few lectures surveying some of the many new phenomena that have been observed:

A) Generation of high harmonics. We will treat this in some detail, since the physics is readily accessible, at least for "medium-high" power.

B) Excess-photon absorption and related phenomena.

C) Molecular structure in intense fields.

D) Coherent control with tailored pulses.

E) Ultra-precise frequency measurement with free combs.

I will survey a few of the widely used theoretical methods, somewhat casually, and Friedrich's book does much the same. Note that any successful treatment must include a detailed model of the amplitude and phase evolution on an optical time scale, since the behavior of any atom or molecule in fields greater than \(10^9 \text{ V/cm}\) will include dynamics on the single-cycle time scale.

The early guess (wrongly) was that not much would happen except for a "Coulomb explosion." Electrons would be ripped off in a sudden approximation, with the final state determined by free-electron dynamics together with the "shakeup" spectrum of the ionic fragment as it settles into a lower-energy state. This works in certain situations, but in general is not a successful model.
A. Intense - Field Harmonic Generation

Experiments have involved laser pulses from less than 100 fs to 10 ns in duration, with irradiances from $10^5$ to $10^{13}$ W/cm². Theoretical approaches have been nearly as diverse, though only a few have attained the status of complete, detailed calculations.

Refs: 1) See handout on suggested term paper topics.
      2) Friedrich, Ch. 5,

Our discussion generally follows Ref. 3, which gives results for 40 fs Nd:YAG laser pulses, $\lambda = 1064$ nm, $P = 1$ GW max.

(i) "Low" power $I < 5 \times 10^{12}$ W/cm²

Use lowest-order perturbation theory. Then, for generation of $q^{th}$ harmonic from a single atom,

$$I_q = C_q I_0^q,$$

from $q^{th}$-order TDPT

The $q^{th}$ power law causes successive orders to diminish rapidly.
Actually, they fall off even faster than $I_0 \theta^2$, because for $N$ atoms we must also consider phase matching.

For plane waves in an unperturbed medium, $\Delta K = 0$, (momentum conservation)

But here, the beams are focused, and the medium's properties are time-dependent due to laser-induced changes in the refractive index, and the production of increasing numbers of free electrons by ionization. The effects of focusing are taken into account for a Gaussian beam by calculating a "phase matching factor" $F_q (b, \Delta k)$, where $b$ = confocal parameter (length of focal region). In a semiclassical LRT approach,

$$E_b \propto \chi^{(2)} N E_0 \otimes F_q (b, \Delta k)$$

$$F_q (b, \Delta k) = \int e^{-i (\Delta k z + (\Delta - 1) \tan^{-1} \left( \frac{2z}{b} \right) \left( 1 + \frac{4z^2}{b^2} \right)^{-\frac{1}{2}}} b \frac{dz}{b}$$

(First derived by Bjorklund, 1975)

Accumulated surplus phase through focus = $\pi$, relative to a plane wave. This is reflected in the $\tan^{-1}$ term.

In an infinite medium with $\Delta K = 0$, clearly $F_q = 0$. Harmonic radiation generated before focus is cancelled by radiation generated after it.
So optimal phase match is a bit complicated, and generally occurs with \( \Delta k < 0 \), especially in an extended high-pressure medium. It also drops quickly with increasing \( q \), mainly because the width in \( k \) space of the phase-matching region narrows as the harmonic order \( q \) increases (note the two factors of \( q \) in Eq. (2)). So,

\[
\ln I_q \propto q^2 \text{ faster than } \beta I_q^2 \text{ with constant } \beta
\]

For a given harmonic, though, still expect \( I_q \propto I_0 \),

Exception is the near-resonant case,

\[
I \propto I_0^7
\]

(iii) High power \( P > 10^{13} \text{ W/cm}^2 \). Here the situation is completely different. A plateau region is seen, and at \( 1.3 \times 10^{15} \text{ W/cm}^2 \), 15th harmonic is as intense as 5th.

Further, all the highest harmonics have roughly the same scaling, approximately \( I_0^{12} \). In other work, up to the 299th harmonic has been seen! (30 fs, HTW pulses, \( \lambda_{299} \approx 2.7 \mu m \), by Margaret Murnane and co-workers at Michigan.) So both LOST and phase-matching conditions break down. Fig. 1 on the next page, from Ref. 3, shows typical results.
Various quantum and classical models have been constructed to explain this sort of result, including two serious attempts to solve the full problem: Floquet calculations, and direct numerical solution of the Schrödinger equation. I will outline some results from the latter approach, pioneered by Kenneth Kalantar at Livermore.

For a single H atom, in a.u.,

\[ i \frac{\partial \psi}{\partial t} = \left( -\frac{1}{2} \nabla^2 - \frac{1}{r} + E_o \right) \psi(t) \sin(wt) \]

Expand

\[ \psi(r,t) = \sum_{l=0}^{L} \Phi_l(r,t) Y_{lo}(\theta) \]
15th harmonic
Xe

Figure 2.
Intensity of
15th-harmonic
production in
Xe

Figure 3. \( |F_q(b, \Delta k)|^2 \) as a function of the harmonic order \( q \) in xenon at 15 Torr for two focusing geometries: \( b = 1 \text{ mm} \) (circles) and \( b = 4 \text{ mm} \) (squares). The perturbative results are shown by full curves, the non-perturbative results obtained at \( 3 \times 10^3 \text{ W cm}^{-2} \) by broken curves with symbols. The broken curves without symbols indicate the perturbative results obtained by neglecting dispersion (\( \Delta k = 0 \)).
\[ \Phi_j (r, t) \rightarrow \Phi_j (r_j, t) \quad r_j = (j - 0.5) \Delta r \]

write \[ g^j_k = \langle r_j | \Phi_j (r_j, t) \rangle. \]

Then
\[ i \frac{\partial}{\partial t} g^j_k = (H_0 g)^j_k + (H_{ij} g)^j_k \]

atomic Hamiltonian, diagonal in \( k \)
interaction Hamiltonian, diagonal in \( j \)

For multielectron atoms, Kulander substitutes Hartree-Slater potentials.

Solve by numerical integration (on a Cray Y-MP) using something called the "Pencore-Rockford alternating directions implicit scheme". To minimize dependence on pulse shape, calculate photoemission after pulse has built up for \( \sim 10 \) optical cycles. Ionization loss is included. The induced dipole is calculated directly
\[ d(\omega) = \frac{1}{T_1 - T_2} \int_{T_2}^{T_1} dt \int e^{i \omega t} \langle \chi (r, \tau) | \chi (r, \tau) \rangle \]

For an ensemble of atoms, experimentally, one finds the \( N^2 \) scaling rule is followed quite well, so effects of high order on phase matching can't be very important.

Classically, the wave equation gives a set of coupled equations, given in Ref. 3 in cgs units,
\[ \nabla^2 \Phi_q + \left( \frac{2 \nu}{c} \right)^2 \Phi_q = -4\pi \left( \frac{2 \nu}{c} \right)^2 \rho_q, \]

\( \rho_q = \) sum of nonlinear and linear polarizations
Ignore pump depletion, higher-order corrections to refractive indices, but don't go to TDPT limit. Then $P_q$ is given by

$$P_q(r, z) = 2 N_0 \text{d}_q^2(r, z) e^{-i \varphi (\text{tan}^{-1} \frac{2z}{b} - \frac{2K_1 r^2 z}{b^2 + 4z^2} + \text{induced dipole from } S)}$$

The field strength and number of photons are then calculated, and the results are shown in the dotted line on Fig. 2.

Finally, the effective phase-matching factor is found by dividing the number of photons by $N_0\text{d}_q^2$ and appropriate scaling factors for the beam profile. The resulting graphs, shown in Fig. 3, differ from the results of perturbation theory by as much as a factor of $10^6$! The predominant reason is that the amplitude of the harmonic radiation varies spatially much less than in the perturbative case, and this dramatically improves the phase matching.

(iii) Very high power fs/ps pulses, $P > 10^{14}$ W/cm$^2$

Now the field is sufficient to immediately ionize the atom, on a scale that is not slow compared to $\omega_{optical}$. Harmonic generation is due principally to interaction with the "free" electron, which oscillates in the field. Re-collision greatly enhances harmonic generation:

$$\text{oscillation in } \omega_{optical}$$
The husband-wife team of Margaret Murnane and Henry Ketteler has played a leading role in the generation of extremely high harmonics. Some recent references are:


The present record is approx. the 300th harmonic, and photon energies of ~ 500 eV have been produced.

Much of the recent emphasis is on optimizing specific harmonics (1) and on improving spatial coherence (2).

General approach:

![Diagram of gas and pulse](image)

In (1), production of 27th harmonic is optimized by shaping pulse amplitude with a "genetic algorithm" --

![Diagram of waveguide and laser](image)

(See Figs. on next page.)

Procedure: start with 19 random pulse shapes, select "fittest" pulses. Then randomly mutate each slightly, retest, repeat. Sensitivity to pulse shape is so extreme that why it works is unclear!

In (2), narrow fiber and aperture were used to achieve a coherent spatial mode. Results: holograms produced with 31 eV radiation, harmonic orders 17-23.
Shaped-pulse optimization of coherent emission of high-harmonic soft X-rays

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Figure 1 Optimization of a single (27th) harmonic in argon while suppressing adjacent harmonics. The optimization criterion (fitness function) for this run corresponded to

\[ f = \Sigma s_i - \Sigma s_j - \Sigma s_k, \]

where \( s \) corresponds to the signal level of a CCD pixel, and the ranges \( i, j \) and \( k \) represent the pixels corresponding to a 0.5-nm spectral bandwidth centred around the 25th, 27th and 29th harmonic. The peak enhancement for the 27th harmonic is a factor of 8, while the energy enhancement is a factor of 4.6. The contrast ratio between the 27th harmonic and adjacent harmonic increases by a factor of 4.

Figure 2 Laser pulse characteristics. a, b. Amplitude (a) and phase (b) of the transform-limited (dashed line) and optimized (solid line) laser pulses corresponding to Fig. 1. These data were taken using the frequency-resolved optical gating technique (FROG). The energy of the pulse is kept constant.
B. Excess - Molen absorption (FPA)

The first and best region for the determination of the "above-threshold ionization" is the photoabsorption region. In this region the photoabsorption cross section is large enough to ionize the direct excitations, with the result that an effective photoabsorption cross section is obtained.

The resulting field, according to the theory, results in the unperturbed electron energy as a function of the electron energy. The unperturbed electron energy is given by:

\[ E_{\text{unperturbed}} = \frac{2}{\beta + 4z^2} \]

where \( \beta \) is the effective photoabsorption cross section.
The same phenomenon has also been observed in molecular photodissociation and in negative-ion photodetachment, hence the generalized description of these processes as "excess-photon absorption". We will discuss only the case of above-threshold ionization, or ATI.


Typical result with long (x10 psec) pulses at 2 x 10^13 W/cm^2:

\[ \text{Photoelectron energy is measured.} \]

The most probable result is that 2 or 3 extra photons are absorbed! Why? The quantum-mechanical description is quite complicated, but the basic physics is easily seen in a semiclassical account. First, consider a free electron in a strong harmonic field. It will execute an oscillatory or "quiver" motion at velocity

\[ V = \frac{eE}{m} \left( \cos \omega t - \cos \omega t_0 \right) \]

Thus the kinetic energy, averaged over a cycle, is
\[
\langle \frac{1}{2} m v^2 \rangle = \frac{e^2 E^2}{4 mw^2} \left( 1 + 2 \cos^2 \omega t \right)
\]

just the energy at \( t = 0 \)

\[ U_p = \frac{e^2 E^2}{4 mw^2} \]  

Quantum mechanically, solutions of S.E. are "Volkov states", with \( E = \frac{p^2}{2m} + U_p \) (see Friedrich).

At 1064 nm, 10^14 W/cm^2, \( U_p \ll 10 \text{ eV} \) (10 x hv)!

Bound states --

For continuous and high Rydberg states, \( U_p > U_{binding} \), and the free-electron model approximately describes the energy shift:

\[ \Rightarrow \text{all highly excited states shift up by the pondermotive potential (must give electron the extra "wiggle" energy -- this makes sense!)} \]

Deeply bound states -- new field is just a perturbation. It's not hard to show that the wiggle amplitude for a state bound by \( hw_0 \) in an external field \( w \) is reduced by a factor \( \left( \frac{w}{w_0} \right)^2 \), classically.

Hence for deeply bound states, pondermotive shift is

\[ U'_p \approx U_p \left( \frac{w}{w_0} \right)^4 \]  

(very small)  

(quantum mechanically, \( 4 \rightarrow 2 \) for ground state.)

Net effect: \( U_p \) is increased by \( U_p \). But, how do the electrons get back this excess energy, which we see in the detector?

Answer: they are ejected from the laser beam by the pondermotive force gradient; in this process
The quiver energy is regained as kinetic energy, so the detector sees the full energy excess above the zero-field ionization potential.

**Short pulses:**

The time needed for an atom to leave the focal region is determined by its acceleration due to the gradient of the ponderomotive potential. The dominant term is simply

$$\langle \mathbf{m} \mathbf{a} \rangle = - \mathbf{x} \frac{\partial U_p}{\partial x} = - \mathbf{\nabla} U_p \quad (11)$$

along intensity gradient.

If you're bothered by the fact that $U_p$ is not truly a potential energy, a more elaborate treatment by Freeman et al. gives the same result, along with several smaller terms.

If $T$ is sufficiently short, the field turns off before the electron departs the laser. Then the "potential" $U_p$ is not conservative, and we do not recover the original energies (no more ATI).

In the ionization cross-sections we usually see resonant structure, which occurs whenever a bound level is ac Stark-shifted into resonance. The behavior is quite different for short and long pulses:

- Peak correspond to Rydberg states.
- Short pulse exist.
- Long-pulse exist.

Electron energy

Basically, the states ionize at whatever moment in the pulse they are Stark-shifted into resonance, in the short-pulse work. Theory: mostly Floquet methods.