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Abraham Szöke

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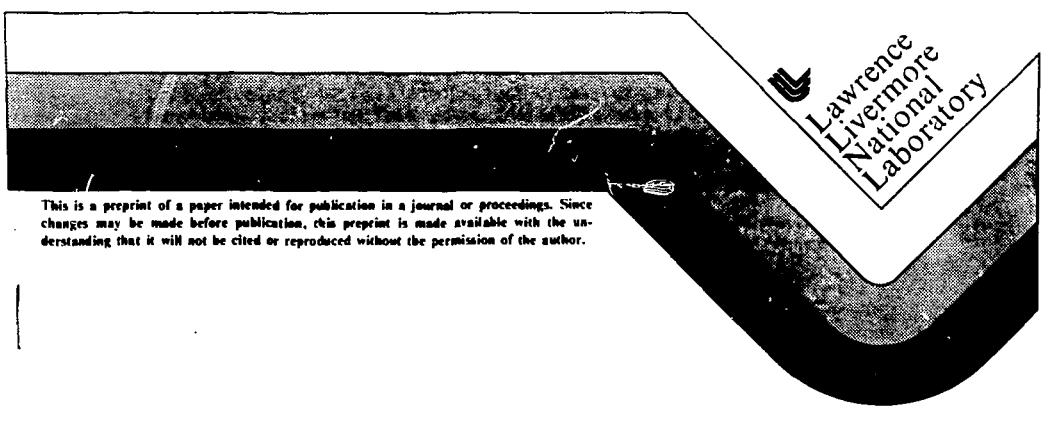

THEORY OF MULTIPHOTON IONIZATION OF ATOMS

Abraham Szöke
Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

ABSTRACT

A non-perturbative approach to the theory of multiphoton ionization is reviewed. Adiabatic Floquet theory is its first approximation. It explains qualitatively the energy and angular distribution of photoelectrons. In many-electron atoms it predicts collective and inner shell excitation.

INTRODUCTION

Picosecond visible and ultraviolet laser pulses of high intensity do violent things to atoms. In the last few years some spectacular results were obtained: above-threshold ionization, multiple ionization, striking angular distributions of photoelectrons, short wavelength lasers. The theoreticians not only did not provide guidance to the experimentalists, but there is a profound lack of agreement even on the approaches to be used to understand the phenomena.

In this paper I will review the particular approach I have been pursuing.[1-4] I hope to clarify some of the concepts that are incontroversial (or at least should be so) and point out where are the main unsolved problems (at least in my opinion).

Multiphoton ionization of atoms can be formulated as a scattering problem. On the incoming side there is an atom, and a large number of (more or less coherent) photons from the laser. On the outgoing side, most of the incoming photons go unhindered, some get scattered, some get absorbed, and the atom may get excited, singly or multiply ionized or all of the above. This is many-body scattering theory, so one cannot make too much progress. The fist simplification is to neglect all scattered photons, and spontaneously emitted ones. As the external field is strong, it can be represented by a classical field. Also, we are only interested in ionization by pulsed fields, whose spectrum is narrow compared to their frequency. These assumptions translate the problem to a solution of a time dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \tag{1}$$

where the Hamiltonian is

$$H = \sum_i^Z \frac{1}{2m}(\bar{p}_i + \frac{e}{c}\bar{A}(\bar{r}_i, t))^2 + \sum_{i\neq j}^Z \frac{e^2}{r_{ij}} - \sum_i Z\frac{e^2}{r_i} \tag{2}$$

with obvious notation [$e > 0$, $\bar{p}_i = -i\hbar\bar{\nabla}_i$, no electronic spin, and no relativity]. The external vector potential is an

almost periodic function, with slowly varying amplitude and frequency (SVEA).

$$\bar{A}\,(\bar{r},\,t) = \bar{A}_0(\tau_1)\,\cos\,[\int^t \omega(\tau_1')\,dt' - \bar{K}.\bar{r}]. \tag{3}$$

where we assumed a plane wave, and wrote τ_1 for the (slow) timescale of the pulse. It is natural to expand the solution of Eq. 1 in multiple timescales.[2,5] Defining the dimensionless fast time (actually it is the optical phase)

$$\tau_0 = \int^t \omega(\tau_1')\,dt' \approx \omega t \tag{4}$$

and formally defining the slow time (also dimensionless) as

$$\tau_1 = \varepsilon\tau_0 \quad , \quad \varepsilon = \text{const} << 1 \tag{5}$$

a hierarchy of equations is obtained for $\Psi \equiv \Psi(\bar{r}_i,\,\tau_0,\,\tau_1)$

$$\Psi = \Psi^{(0)} + \varepsilon\,\Psi^{(1)} + \varepsilon^2\,\Psi^{(2)} + \ldots \quad , \tag{6}$$

The first two are,

$$i\hbar\,\omega(\tau_1)\,\frac{\partial\Psi^{(0)}}{\partial\tau_0} - H\,\Psi^{(0)} = 0 \tag{7}$$

$$i\hbar\omega(\tau_1)\,\frac{\partial\Psi^{(1)}}{\partial\tau_0} - H\Psi^{(1)} = i\hbar\omega\,\frac{\partial\Psi^{(0)}}{\partial\tau_1} \tag{8}$$

The first one, Eq. (7), produces the wave functions and states of "Floquet theory": the Hamiltonian is exactly 2π periodic in τ_0, the states contain $A_0(\tau_1)$ and $\omega(\tau_1)$ as parameters. This provides a natural (if not always convenient) basis set for the solution. The slow time dependence of Ψ^0 is obtained from the second equation by eliminating secular terms from it. [As shown by J. Garrison recently, one obtains as a bonus Berry's phase.[6]] The result is particularly clear when the pulse turns on adiabatically. The wave function is a "succession" of Floquet states,

$$\Psi_j^{(0)} = \exp\,[-\,i\,\int\,\Omega_j\,d\tau_0]\,\phi_j^{(0)}(A_0,\,\tau_0)$$

$$\phi_j^{(0)}(A_0,\,\tau_0 + 2\pi) = \phi_j^{(0)}(A_0,\,\tau_0) \quad , \tag{9}$$

where state j correlates adiabatically to the (j'th) state, the unperturbed atom started from the beginning of the optical pulse. This should be properly called "adiabatic" Floquet theory. Extensive calculations were done on many systems of interest by Reinhardt, Chu and coworkers.[7]

I will now review informally the lessons and limitations of this theory. First, Eq. 7 has no "real" bound states, every state decays, i.e., ionizes (however slowly).[8] If outgoing wave boundary conditions are imposed on the wave function, the imaginary part of

the eigenvalue, the so called quasi energy ($\Omega\hbar\omega$ in Eq. 9) gives the total ionization rate.[7] Second, the theory is not perturbative in the electromagnetic field strength, though its limitations will be discussed below. Third, it can be shown by model calculations that appreciable above threshold ionization is obtained.[2] Fourth, the absence of ponderomotive shifts in the observed electron energies and the sudden disappearance of low energy electrons due to "closure .. channels" can be explicitly traced in the calculations,[2] in accordance with conservation energy arguments.[1]

The two main limitations to the validity of adiabataic Floquet theory are resonances and non-adiabaticity. As a blanket statement, when the first order theory breaks down most probably quantum chaos is obtained.[9] Non-linear resonances occur, when a multiple of the incident frequency approaches an energy level difference of the adiabatic Floquet states. These states, as a function of the field strength, can have avoided crossings. There are two complicating factors: the first one, mentioned above, is that all Floquet states belong to the continuum, and the second one that the quasi energies should properly be restricted to a finite range, $0 \leq E_F < \hbar\omega$.[7] Even disregarding the complications, at these crossings the adiabatic states "exchange" the character of their wave functions, so if the passage is adiabatic, there is really a "transition" and vice versa. The simplest way to estimate the conditions for adiabaticity is by the Landau-Zener formula,[10]

$$W = \frac{2\pi}{\hbar} \left| V_{nm} \right|^2 \left| \frac{\partial}{\partial \tau} (E_m - E_n) \right|^{-1}_{E_m = E_n}$$

where E_m, E_n are the quasi energies of the diabatic levels, and $2 \left| V_{nm} \right|$ is the minimum energy separation at the avoided crossing. When $W \gtrsim 1$ the passage is adiabatic and vice versa. Thus it can be seen that both the strength of the laser field (through V_{nm}, and the dependence of E_n, E_m on it) and the shortness of the pulse is important. If many level crossings occur, the actual behavior of the atom may become quite uncalculable, and unpredictable.

Several aspects of multiphoton ionization are correctly given by adiabatic Floquet theory. The electron spectrum, as measured outside the laser field, consists of peaks corresponding to the absorption of a fixed (N) number of photons. These states correlate adiabatically to states close to the atom (inside the field!) that have their translational energy diminished by the ponderomotive potential, and "dressed" by a variable number of photons. In a linearly polarized field this number has a strong maximum when the electron's translational motion is parallel to the field's polarization. This implies that if an electron is emitted with a number of virtual photons attached to it, its energy spectrum (as measured outside the laser field) shows "above

threshold ionization." Also, when the number of virtual photons becomes sizable (at low laser frequencies) we expect a strongly peaked angular distribution parallel to the laser's polarization.

C. Cerjan of LLNL has done computor solutions of simple model systems,[11] (without the adiabatic approximation) and the author attempted to get a "finite element" solution of the same model in the adiabatic Floquet approximation. These should be very useful to assess the importance (or unimportance) of detailed level structures of atoms in multiphoton ionization, and the presence or absence of non-linear resonances, non-adiabaticity and possible chaos.

Many electron atoms are more interesting but even more difficult to treat. Multiple scale expansion can be used to simplify time dependent Hartree Fock (TDHF) theory in almost periodic fields. The first approximation is then analogous to adiabatic Floquet theory and can be viewed as its extension to many electron systems.[3] The solution is again a succession of adiabatic states. Thus it is interesting to investigate their nature.

TDHF theory restricts the (properly antisymmetric) wave function to a single configuration. Denoting it by $|g\rangle^n$, (e.g., $|5p\rangle^6$ for the ground state of xenon) we can see that it includes both single-electron excitations, $|g\rangle^{n-1}|e\rangle$. (e.g., $|5p\rangle^5|6s\rangle$) and what we call collective excitations, $(\alpha|g\rangle + \beta|e\rangle)^n$, (e.g., $(1/\sqrt{2}\ |5p\rangle + 1/\sqrt{2}\ |6s\rangle)^6$). In a pure collective excitation, each electron is "dressed" coherently by the same number of photons. Ionization occurs when some electron's wave function has a component from the continuum. As a general rule, collective excitations occur when the atom is driven off resonance.

Collective excitations, if they don't decay, (see below) allow to put a large amount of energy into an outer shell of a many electron atom. This in turn can excite the inner shell of the same atom, possibly producing short wavelength lasers. Recently the rate for this process was estimated assuming collective excitation.[4,12]

The first hard question is whether, how strongly, and under what circucmstances are collective excitations excited. All the caveats raised for the single electron theory apply here too: there are problems with resonances, and non-adiabaticity. There are even serious questions as how to observe such a state if it is excited. The second hard question is the decay of these states. There are two main routes for their decay: autoionization, and the conversion of the internal energy into non-collective motion. In nuclear physics this is analogous to the decay of a giant dipole resonance into single nuclear emission or into a compound nuclear state (the latter is also called spreading).

The excitation question is within TDHF theory, it is being investigated through numerical solution (without an adiabatic approximation) by K. Kulander at LLNL.[13] The second problem, an even more difficult one may be addressed using diagrammatic

perturbation with the adiabatic Floquet - TDHF states as a starting point.[14]

In summary, a non-perturbative theory of atomic multiphoton processes starts with adiabatic Floquet theory as its first approximation. Even at that stage, it predicts from first principles above threshold ionization, the closing of channels, collective excitation, and the transfer of energy to inner shells. The possible (and very probable) breakdown of the theory is due to resonances, non-adiabaticity and the decay of collective excitations due to electron-electron interaction (the same as collisions, the same as correlations). If these processes are dominant, we may end up with statistical concepts, similar to RRKM theory and quasi-continua in multiphoton dissociation of large molecules.

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