Ionization of Model Atomic Systems by Periodic Forcings of Arbitrary Size

Joel L. Lebowitz

Departments of Mathematics and Physics

Rutgers University

(Joint work with O. Costin, R. Costin, A. Rokhlenko, C. Stucchio and S. Tanveer)

Setting

We study the long time behavior of the solution of the Schrödinger equation in d dimensions (in units such that $\hbar = 2m = 1$),

$$i\partial_t \psi(x,t) = \left[-\Delta + V_0(x) + V_1(x,t)\right] \psi(x,t) \tag{1}$$

Here, $x \in \mathbb{R}^d$, $t \geq 0$, $V_0(x)$ is a binding potential such that $H_0 = -\Delta + V_0$ has both bound and continuum states, and

$$V_1(x,t) = \sum_{j=1}^{\infty} \left[\Omega_j(x) e^{ij\omega t} + c.c\right] \tag{2}$$

is a time-periodic potential. The initial condition, $\psi(x,0) = \psi_0(x)$ is taken to be in $L^2(\mathbb{R}^d)$.

Ionization

Our primary interest is whether the system ionizes under the influence of the forcing $V_1(x,t)$, as well as the rate of ionization if it occurs. Ionization corresponds to delocalization of the wavefunction as $t \to \infty$. We say that the system, e.g. a Hydrogen atom, (fully) ionizes if the probability of finding the electron in any bounded spatial region $B \subset \mathbb{R}^d$ goes to zero as time becomes large, i.e.

$$P(B_R, t) = \int_{|x|<R} |\psi(x,t)|^2 dx \to 0, \tag{3}$$

as $t \to \infty$.

The Floquet Connection

A simple way in which ionization may fail is the existence of a solution of the Schrödinger equation in the form

$$\psi(t, x) = e^{i\phi t} v(t, x) \tag{4}$$

with $\phi \in \mathbb{R}$ and $v \in L^2([0, 2\pi/\omega] \times \mathbb{R}^d)$ time periodic. This leads to the equation:

$$Kv = \phi v \tag{5}$$

where

$$K = i\frac{\partial}{\partial t} - (-\Delta + V_0(x) + V_1(x, t)) \tag{6}$$

is the Floquet operator.(5) with $0 \neq v \in L^2$ means by definition, that $\phi \in \sigma_d(K)$, the discrete spectrum of K.

Somewhat surprisingly, in all systems we studied $\sigma_d(K) \neq \emptyset$ is in fact the *only* possibility for ionization to fail.

A proof of ionization then implies that K does not have any point, or singular continuous, spectrum. This turns out to be a consequence of the existence of an underlying compact operator formulation, the operator being closely related to K.

Ionization is then expected generically since L^2 solutions of the Schrödinger equation of the special form ($e^{i\phi t}v$) are unlikely. One can also use phase space (entropy) arguments in favor of generic ionization. Once the particle manages to escape into the "big world" it will never return as is true for random perturbations (Pillet). Still, mathematical physicists want proofs. We provide such proofs for certain classes of systems and also find some nongeneric counterexamples.

Laplace space formulation

The propagator $U(t,x)$ which solves the Schrödinger equation is unitary and strongly differentiable in t. This implies that for $\psi_0 \in L^2(\mathbb{R}^d)$, the Laplace transform

$$\hat{\psi}(p,\cdot) := \int_0^\infty \psi(t,\cdot)e^{-pt}dt \tag{7}$$

exists for $p \in \mathbb{H}$, the right half complex plane, and the map $p \to \hat{\psi}$ is L^2 valued analytic for Re $p > 0$.

The Laplace transform converts the asymptotic problem (3) into an analytical one involving the structure of singularities of $\hat{\psi}(p,x)$ for Re $p \le 0$. In particular, ionization will occur if $\hat{\psi}(p,\cdot)$ has no poles on the imaginary axis when $V_1 \neq 0$.

When $V_1 = 0$ there will be poles of $\widehat{\psi}$ at $p = -iE_n$, E_n the eigenvalues of the bound states of H_0. As V_1 is turned on these poles are expected to move into the left complex plane, forming resonances. This has in fact been proven rigorously for small enough $V_1 = Ex \cos \omega t$ when V_0 is a dilation analytic potential, by various authors.

In particular Sandro Graffi and Kenji Yajima proved this in 1983 for the Coloumb potential, $V_0 = -b/|x|$, $x \in \mathbb{R}^3$.

This does not imply, however the absence of poles (resonances) on the imaginary axis for finite strength V_1. We rule this out in the cases treated by using the Fredholm alternative on a suitable compact operator. We also find some non-generic examples where ionization fails.

Simple calculations show that $\widehat{\psi}$ satisfies the equation

$$(H_0 - ip)\widehat{\psi}(p,x) = -i\psi_0(x) - \sum_{j\epsilon\mathbb{Z}} \Omega_j(x)\widehat{\psi}(p-i,j\omega,x) \tag{8}$$

Clearly (8) couples two values of p only if $(p_1 - p_2) \in i\omega\mathbb{Z}$, and is effectively an infinite systems of partial differential equations.

Setting

$$p = p_1 + in\omega, \text{ with } p_1 \in \mathbb{C} \text{ mod } i\omega \tag{9}$$

$$y_n(p_1,x) = \widehat{\psi}(p_1 + in\omega, x) \tag{10}$$

(8) now becomes an infinite set of second order equations

$$(H_0 - ip_1 + n\omega)y_n = y_n^0 - \sum_{j\in\mathbb{Z}} \Omega_j(x)y_{n-j} \tag{11}$$

$$y_n^0 = -i\psi_0\delta_{n,0}$$

It is this system on which we carry out our analysis.

Examples: In all cases $V_1(x,t) = V_1(x, t + 2\pi/\omega)$ has zero time average and there are no restrictions on $\omega > 0$ or the strength of V_1.

1. $V_0(x) = -2\delta(x)$, $V_1(x,t) = \eta(t)\delta(x)$, $x \in \mathbb{R}$ or
$V_1(x,t) = r\ [\delta(x-a) + \delta\ (x+a)] \sin \omega t$

Result: ionization occurs generically but fails in some (explicit) cases

2. $V_0(x) = r_0 \chi_D(x), V_1(x,t) = r_1 \chi_D(x) \sin \omega t$, $D \subset \mathbb{R}^d$ a compact domain; χ_D characteristic function

3. $V_0(x) = -2\delta(x)$, $V_1(x,t) = xE(t)$, $x \in \mathbb{R}$

Result: ionization occurs when $E(t)$ is a trigonometric polynomial

4. $V_0(x) = -b/|x|$, $x \in \mathbb{R}^3$

Result: ionization occurs when $V_1(x,t) = \Omega(|x|) \cos \omega t$, Ω is compactly supported and positive.

Parametric perturbation of δ function

$$i\psi_t = \Big(- \partial_{xx} - 2\delta(x) + \delta(x)\eta(t)\Big)\psi, \quad x\epsilon\mathbb{R}$$

Spectrum of H_0

- Discrete spectrum: one bound state $u_b(x) = e^{-|x|}$ with energy $E_b = -\omega_0 = -1$

- Continuous spectrum: $E = k^2 > 0$ with generalized eigenfunctions:

$$u(k,x) = \frac{1}{\sqrt{2\pi}}\left(e^{ikx} - \frac{1}{1+i|k|}e^{i|kx|}\right)$$

We consider solutions of the Schrödinger equation with initial conditions corresponding to the particle being in its bound state,

$$\psi(x, 0) = u_b(x)$$

We then expand $\psi(x;t)$ into the complete set of eigenstates of H_0,

$$\psi(x;t) = \theta(t)u_b(x) + \psi_\perp$$

We find that ionization occurs if $\theta(t) \to 0$ as $t \to \infty$.

The orthogonal component $\psi_\perp$ will decay (as a power law) when $t \to \infty$.

The next few slides show the nature of the decay of $|\theta(t)|^2$. For small r the decay is essentially exponential with the exponent behaving like $r^{2n(\omega)}$ where $n(\omega)$ is the "number of photons" requuired for ionization, in accord with Fermi's "Golden rule" applied to perturbation theory.

Fermi Golden Rule, multiphoton effects

Exponential decay region, $|\theta|^2 \approx e^{-\Gamma t}$.

Using continued fractions Γ can be calculated convergently for any ω and r. For small r we have

$$\Gamma \sim \begin{cases} \sqrt{\omega - 1}\,\frac{r^2}{\omega}; & \text{if } \omega - \varepsilon \in (1, \infty) \\ \frac{\sqrt{2\omega - 1}}{(1 - \sqrt{1 - \omega})^2}\,\frac{r^4}{8\omega}; & \text{if } \omega \pm \varepsilon \in (\frac{1}{2}, 1) \\ \cdots & \cdots \\ \frac{2^{-2n+2}\sqrt{n\omega - 1}}{\prod_{m<n}(1 - \sqrt{1 - m\omega})^2}\,\frac{r^{2n}}{n\omega}; & \text{if } \omega \pm \varepsilon \in (\frac{1}{n}, \frac{1}{n-1}) \end{cases}$$

Definition of exponential decay rate Γ, for small r. Look at time scales of the right order of magnitude. If $\omega \pm \varepsilon \in (\frac{1}{n}, \frac{1}{n-1})$ then

(0.1)
$$\hat{\Gamma} = -T^{-1} \lim_{r \to 0} \ln \left|\theta(r^{-2n}T)\right|^2 = \frac{2^{-2n+2}\sqrt{n\omega - 1}}{n\omega \prod_{m<n}(1 - \sqrt{1 - m\omega})^2}$$

Behavior at resonances is qualitatively different. E.g. when $\omega - 1 = r^2/\sqrt{2}$ we find

$$\Gamma \sim \left(\frac{2^{1/4}}{8} - \frac{2^{3/4}}{16}\right) r^3$$

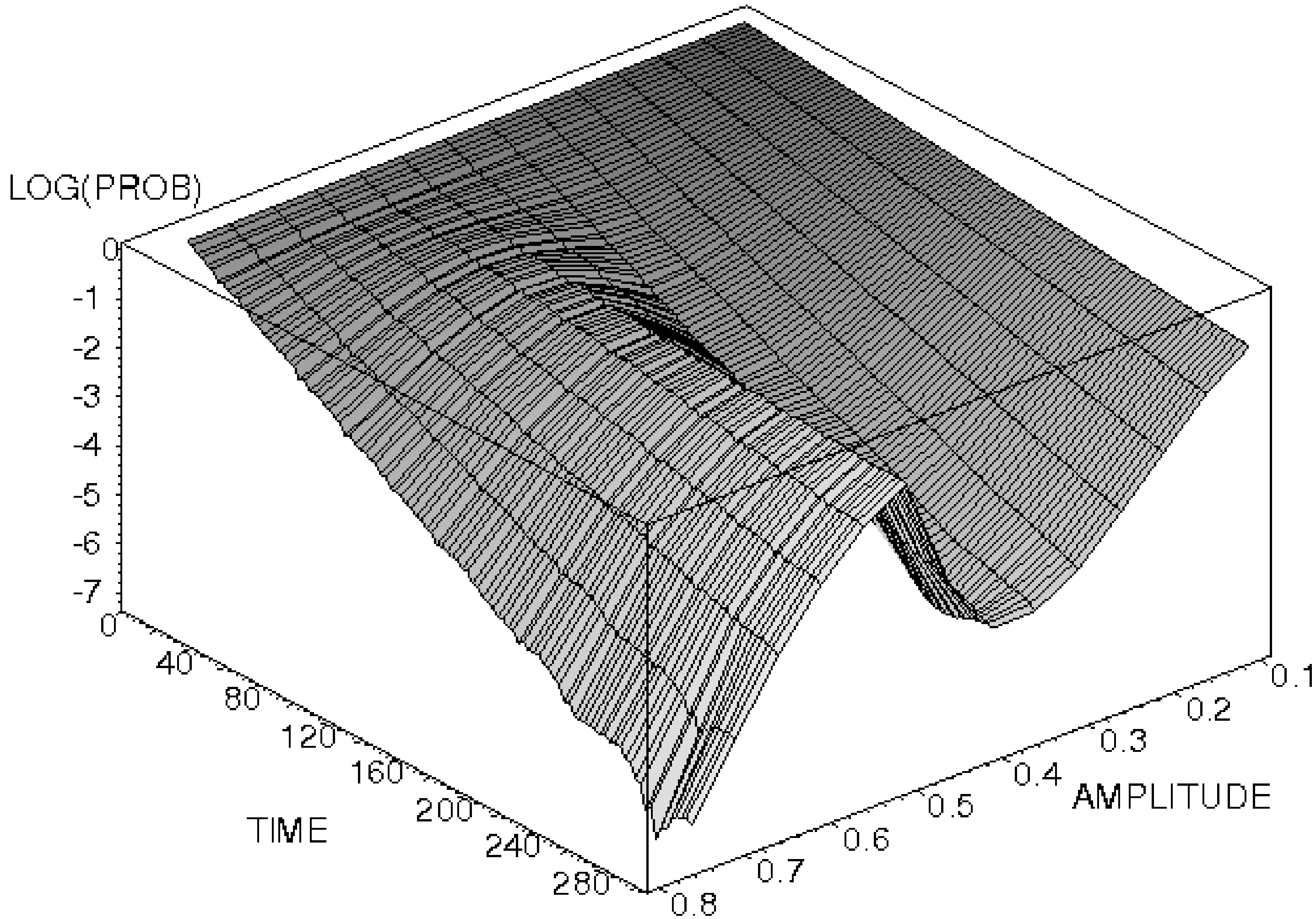
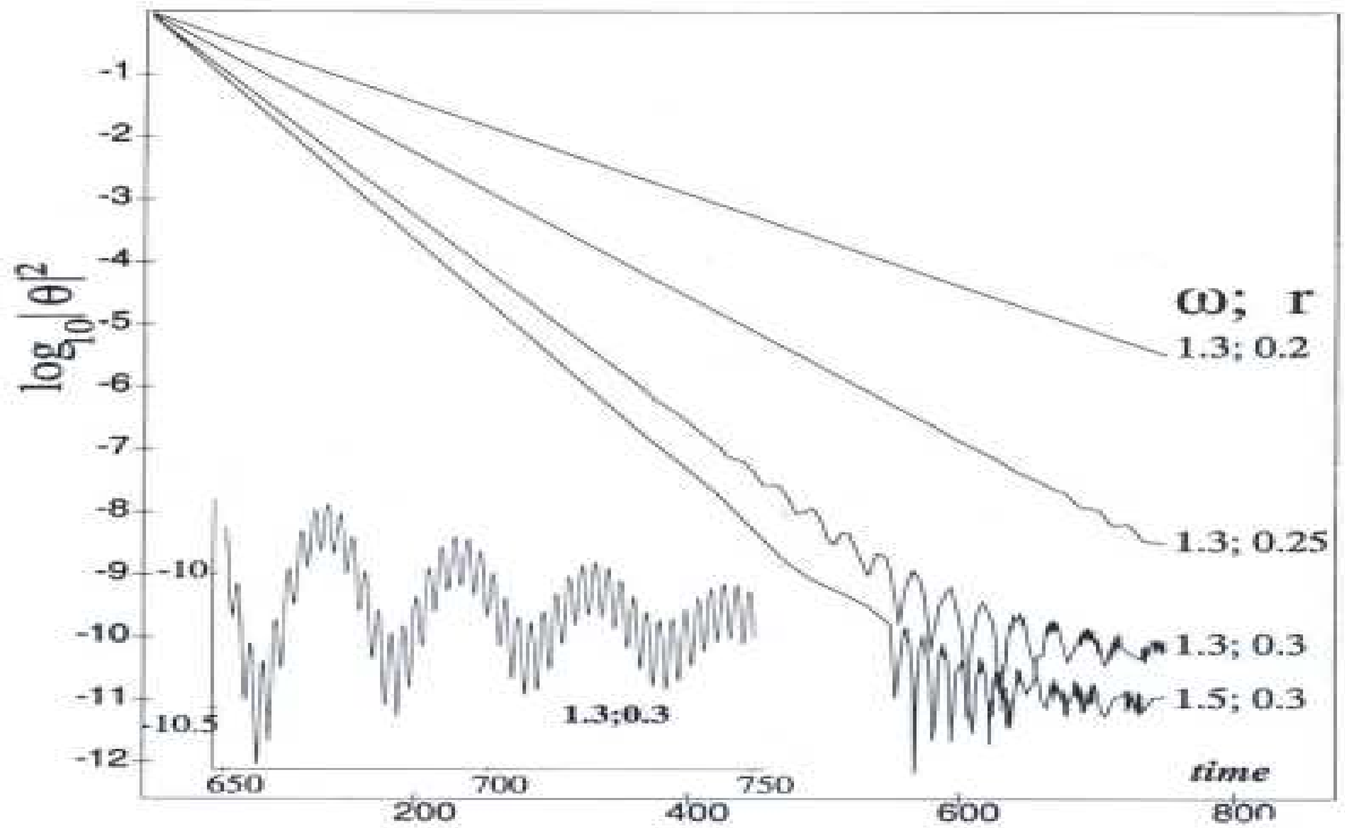
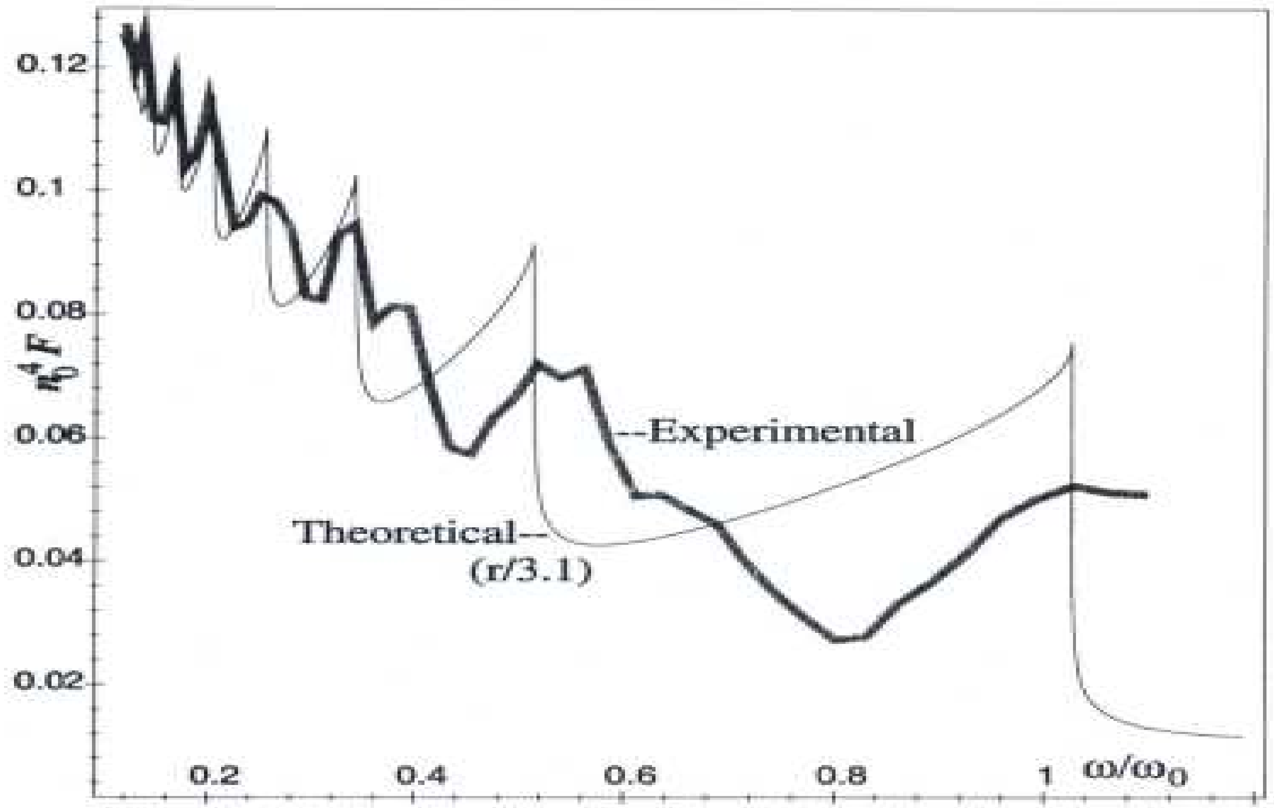


Figure 1: Decay probability versus time versus amplitude in simple model.



Plot of $\log_{10}|\theta(t)|^2$ vs. time in units of ω_0^{-1} for several values of ω and r. Inset shows detail of power-law tail for $\omega = 1.3$, $r = 0.3$.

Note how the exponential decay holds all the way down to $|\theta(t)|^2 \sim 0$ for all practical purposes (FAPP)



Comparison of the theoretical and experimental threshold amplitudes for 50% ionization vs. ω/ω_0. for $t = 700\ 2\pi/\omega$,

Hydrogen atoms in level $n_0 \simeq 24$.

$\omega_0 \sim n_0^{-3}$, microwave field F in units of nuclear field $\sim n_0^{-4}$. We found by rough fitting $r \sim 3\ n_0^4 F$

For experiment: $V_0 = -e^2/|x|$, $V_1 = x F \sin \omega t$

Dynamic Stark shift $\sim [r^2/2\omega] \sqrt{\omega + 1} = \mathrm{Im}\ \Gamma_0$

General $\eta(t)$

$$i\frac{\partial\psi}{\partial t} = \Big(-\partial_{xx} - 2\delta(x) + \eta(t)\delta(x)\Big)\psi$$

Proposition *If* η *is a trigonometric polynomial,*

$$\eta(t) = \sum_{k=1}^{N} \Big\{ C_j e^{ij\omega t} + \overline{C_j} e^{-ij\omega t} \Big\},$$

then $\theta(t) \to 0$ as $t \to \infty$

$*$

"Compelling conjecture". $\theta(t) \to 0$ as $t \to \infty$ for any $\eta(t)$, at least if the C_j decay "reasonably" fast.

FALSE: Ionizing properties depend nontrivially on special property of Fourier coefficients.

Consider a general periodic $\eta(t)$

$$\eta = \sum_{j=1}^{\infty} \left(C_j e^{i\omega jt} + C_{-j} e^{-i\omega jt} \right)$$

Genericity condition (g) The right shift operator T on $l_2(\mathbb{N})$ is given by

$$T(C_1, C_2, ..., C_n, ...) = (C_2, C_3, ..., C_{n+1}, ...)$$

We say that $\mathbf{C} \in l_2(\mathbb{N})$ is *generic with respect to* T if the Hilbert space generated by all the translates of $\mathbf{C}$ contains the vector $e_1 = (1, 0, 0, ...)$ (which is the kernel of T):

$$e_1 \in \bigvee_{n=0}^{\infty} T^n \mathbf{C} \qquad \textbf{(g)}$$

where the right side denotes the closure of the space generated by the $T^n\mathbf{C}$ with $n \geq 0$. This condition is generically satisfied.

A simple example which *fails* $(\mathbf{g})$ is,

$$\tilde{\eta}(t) = 2r\lambda \frac{\lambda - \cos(\omega t)}{1 + \lambda^2 - 2\lambda\cos(\omega t)}$$

for some $\lambda \in (0,1)$. Here $C_n = -r\lambda^n$ for $n \geq 1$.

Theorem $\lim_{t\to\infty} |\theta(t)| = 0$, for all η satisfying (g)

Theorem For $\tilde{\eta}$ with any ω, r there exists λ for which $\liminf_{t\to\infty} |\theta(t)| > 0$.

1. There are infinitely many λ's, accumulating at 1, such that $\liminf_{t\to\infty} |\theta(t)| > 0$.

2. For large t, θ approaches a quasiperiodic function. Floquet operator has a discrete spectrum, in this case.

3. This is *nonperturbative*. $\tilde{\eta}(t)$ cannot be made arbitrarily small.

We have also investigated the case when

$V_0 = -\delta(x)$, $V_1(x,t) = r\,[\delta(x-a) + \delta(x+a)] \sin \omega t$
This also exhibits "stabilization". In fact one can find a two dimensional set of r, ω and a for which ionization fails. This is again nonperturbative.

Surprise: Even when $V_0(x) = 0$, so that there are no bound states, we can find parameter values r, ω and a such that for an initial $\psi_0 \in L^2(R)$ the particle remain localized While this type of behavior is probably peculiar to $V_1(x,t)$ consisting of delta functions there are examples of systems with smooth V_0 and V_1 which fail to ionize. Still, in this problem, proofs are necessary to convince even a "reasonable" person.

I describe now a very special model. Results are a bit more general.

Let $\chi_D(x)$ be the characteristic function of an arbitrary compact set D in $\mathbb{R}^d$, d=1,2,3. Set

$V_0(x) = r_0 \chi_D(x)$, $V_1(x,t) = r_1 \chi_D(x) sin(\omega t)$

Assume also that $\psi_0(x) = 0$ for $x \in D$. Then

$$\psi(x,t) = \sum_{j \epsilon \mathbb{Z}} e^{ij\omega t} h_j(x,t) + \sum_{k=1} P_k(t) e^{-i\sigma_k t} F_k(x,t),$$

with $I_m \sigma_k < 0$ for all k. The $P_k(t)$ are polynomials in t, and the $h_j(x,t)$ have Borel summable power series in $t^{-1/2}$ beginning with $t^{-3/2}$.

Dipole case in one dimension(O. Costin, JLL, C. Stucchio, RMP, 2008)

We consider the time evolution of a particle in one dimension governed by the Schrödinger equation with a delta function attractive potential and a time-periodic dipole field:

$$i\partial_t \psi(x,t) = \left(-\frac{\partial^2}{\partial x^2} - 2\delta(x)\right)\psi(x,t) + E(t)x\psi(x,t)$$

$$\psi(x,0) = \psi_0(x) \in L^2(\mathbb{R})$$

This is a model used by physicists to study ionization. Our results are the first ones (as far as we know) which actually prove ionization for arbitrary strength fields.

Theorem 1. (Ionization) Suppose $E(t)$ is a trigonometric polynomial, i.e.

$$E(t) = \sum_{n=1}^{N} \left(E_n e^{in\omega t} + \overline{E_n} e^{-in\omega t} \right).$$

Then for any $\psi_0(x) \in L^2(\mathbb{R})$ ionization occurs, i.e.

$$\lim_{t \to \infty} \int_{-L}^{L} |\psi(x,t)|^2 dx = 0, \forall L \in \mathbb{R}^+$$

If $\psi_0(x) \in L^1(\mathbb{R}) \cap L^2(\mathbb{R})$, then the approach to zero is at least as fast as t^{-1}.

Theorem 2

Suppose $\psi_0(x)$ is compactly supported and in H^1 and $E(t)$ is smooth and time periodic. Then, the solution $\psi(x,t)$ can be uniquely (for fixed M) decomposed as:

$$\psi(x,t) = \sum_{k=0}^{M} \sum_{j=0}^{n_k} \alpha_{k,j} t^j e^{-i\sigma_k t} \Phi_{k,j}(x,t) + \Psi_M(x,t)$$

The resonance energies σ_k satisfy $\Im \sigma_k \leq 0$, and are ordered according to $\Im \sigma_{k+1} \leq \Im \sigma_k$. The resonant states $(\phi_{k,j}(x,t))$ are Gamow vectors (generalized, if $j > 0$).

In the above expansion, we collect the M resonances with $\Im \sigma_k$ closest to zero, and M must be large enough so that we collect all resonances σ_k with $\Im \sigma_k = 0$. The number of Gamow vectors (and resonances) may be infinite, but we can only include finitely many of them.

The remainder $\Psi_M(x,t)$ has the following asymptotic expansion in time:

$$\Psi_M(x,t) \sim \sum_{j\in\mathbb{Z}} e^{ij\omega t} \sum_{n=1}^{\infty} D_{j,n}(x) t^{-n/2}$$

This expansion is uniform on compact sets in x, but not in L^2. In general, $D_{j,n}(x)$ is not in L^2.

Uniqueness of the decomposition is defined relative to the analytic structure of $\psi(x,t)$: the Zak transform of $\psi(x,t)$ has poles at $\sigma = \sigma_k$ (with residues proportional to $\Phi_{k,j}(x,t)$), while $\Psi_M(x,t)$ has a Zak transform that is analytic in the region $\{\sigma : \Re\sigma \in (0,\omega), \Im\sigma > \Im\sigma_M\}$. The Zak transform is defined as follows.

Definition

Let $f(t) = 0$ for $t < 0$ and $|f(t)| \leq Ce^{\alpha t}$ for some $\alpha > 0$. Then $f(t)$ is said to be Zak transformable. The Zak transform of $f(t)$ is defined (for $\Im\sigma > \alpha$) by:

$$\mathcal{Z}[f](\sigma, t) = \sum_{j \in \mathbb{Z}} e^{i\sigma(t+2\pi j/\omega)} f(t + 2\pi j/\omega)$$

We define $y(\sigma, t)$ as the Zak transform of (essentially) the wave function $\psi(x, t)$ at $x = c(t)$ where $c''(t) = 2E(t)$

$y(\sigma, t)$ is then given by:

$$y(\sigma, t) = [1 - \mathcal{K}(\sigma)]^{-1} y_0(\sigma, t)$$

where $y_0(\sigma, t)$ is known, and $\mathcal{K}(\sigma)$ is a compact integral operator.

The poles of $[1 - \mathcal{K}(\sigma)]^{-1}$ correspond to the resonances σ_k in the decomposition of $\psi(x,t)$ while the $\phi_{k,j}(x,t)$ are related to the residues at the poles of multiplicity j. They satisfy the equations,

$$(\mathcal{K} - \sigma_k)\phi_{k,j} = \phi_{k,j-1}, \qquad \phi_{k,-1} = 0$$

with 'outgoing wave" or radiation boundary conditions: $\phi_{k,0}(x,t)$ must behave like the Green's function near $|x| = \infty$.

Coulomb systems in 3D (O. Costin, S. Tanveer, in preparation)

$H = -\Delta - b/r + V(t,x) = H_C + V$, $x \in \mathbb{R}^3$, $b > 0$,

$i\psi_t = H_C\psi + V(t,x)\psi; \qquad \psi(0,x) = \psi_0(x) \in H^1(\mathbb{R}^3)$

where $V(t,x) = \sum_{j=1}^{\infty} [\Omega_j(x) e^{ij\omega t} + c.c.]$

Assumptions: $\Omega_j(x)$, $j \in \mathbb{Z}$ have a common compact support, chosen to be the ball $B_1 \subset \mathbb{R}^3$ of radius 1, and
$\sum_{j\in\mathbb{Z}} (1 + |j|) \parallel \Omega_j \parallel_{L^2} (B_1) < \infty$.

The homogeneous equation satisfied by the time Laplace transform $\widehat{\psi}(p,x)$ can be written (after some doctoring) as an infinite system of second order equations (see slide 8)

$$(H_C - ip_1 + n\omega)w_n = -\sum_{j\in\mathbb{Z}} \Omega_j(x) w_{n-j},$$

where

$$p = p_1 + in\omega, \text{ with } p_1 \in \mathbb{C} \bmod i\omega.$$

Using rigorous WKB analysis of infinite systems of differential equations we show the following.

Theorem 1

For $V(t,x) = 2\Omega(r)\sin(\omega t - \theta)$, with $\Omega(r) = 0$ for $r > 1$, $\Omega(r) > 0$ for $r \leq 1$ and $\Omega(r) \in C^\infty[0,1]$, $\sigma_d(K) = \emptyset$ and ionization always occurs.

Furthermore, if $\psi_0(x)$ is compactly supported and has only finitely many spherical harmonics, then $\int_B |\psi|^2 dx$ is $O(t^{-5/3})$.

The proof, uses Theorems (2) and (3) and rigorous asymptotics of w_n as $n \to -\infty$.

Theorem 2 Assuming spherical symmetry of the $\Omega_j(x)$, ionization occurs *iff* for all $p_1 \in i\mathbb{R}$, the homogeneous equation has only the trivial solution $\{w_n\}_{n\in\mathbb{Z}} = \mathbf{0}$ in the appropriate Hilbert space. This is true *iff* $\sigma_d(K) = \emptyset$.

This extends results about absence of singular continuous spectrum of the Floquet operator K, to this class of systems, with Coulombic potential and spherical forcings of compact support.

Properties of Floquet bound states for general compactly supported $V(t,x)$.

Theorem 3 If there exists a nonzero solution of the homogeneous equation, $w \in \mathcal{H}$, then w has the further property

$$w_n = \chi_{\mathsf{B}_1} w_n \quad \text{for all} \quad n < 0$$

with χ_A the characteristic function of the set A.

This makes the second order homogeneous system formally overdetermined since the regularity of w in x imposes both Dirichlet and Neumann conditions on $\partial \mathsf{B}_1$ for $n < 0$. Nontrivial solutions are not, in general, expected to exist.

Remark

The results can be extended to systems with H_C replaced by

$$H_W = -\Delta - b/r + W(r)$$

where b may be zero and $W(r)$ decays at least as fast as $r^{-1-\epsilon}$ for large r, $W \in L^\infty(\mathbb{R}^3)$.

Outline of the ideas entering proof As in our previous work on simpler systems, we rely on a modified Fredholm theory to prove a dichotomy: either there are bound Floquet states, or the system gets ionized. Mathematically the Coulomb potential introduces a number of substantial difficulties compared to the potentials considered before due to its singular behavior at the origin and, more importantly, its very slow decay at infinity.

The slow decay translates into potential-specific corrections at infinity and the asymptotic behavior in the far field of the resolvent has to be calculated in detail The accumulation of eigenvalues of increasing multiplicity at the top of the discrete spectrum of H_C produces an essential singularity at zero of the Floquet resolvent. This is responsible for the change in the large time asymptotic behavior of the wave function, from $t^{-3/2}$ to $t^{-5/6}$.