Non-resonant driving of an H atom with broken time-reversal symmetry

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Abstract. The dynamics of atomic hydrogen placed in a static electric field and illuminated by elliptically polarized microwaves is studied in the range of small field amplitudes where perturbation calculations are applicable. For a general configuration of the fields any generalized time-reversal symmetry is broken and, as the classical dynamics is chaotic, the level statistics obeys the random matrices prediction of a Gaussian unitary ensemble.

Bohigas et al’s conjecture [1] that a general quantum system with underlying chaotic classical dynamics has statistical properties of energy levels described by random matrix theory has been confirmed by theoretical studies of numerous chaotic systems (see, e.g., [2, 3]). Experimental verifications, on the other hand, are much less abundant [4, 5] and, as far as we know, concern only systems possessing anti-unitary (generalized time-reversal) symmetry, where the level statistics can be modelled by random matrices of the Gaussian orthogonal ensemble (GOE) [6]. Realization of a quantum system with quadratic level repulsion as is typical for matrices from the Gaussian unitary ensemble (GUE) [6] requires breaking of any anti-unitary symmetry invariance. For example, for atomic or molecular systems it means one would have to apply an inhomogeneous magnetic field across the molecule and it be well experimentally controlled on such a small scale [2]. Such a requirement is rather unattainable even in the Rydberg regime of excitation. While a real quantum system with GUE statistics has not been realized experimentally, there are experiments with microwave cavities (so-called wave chaos experiments) where anti-unitary symmetry can be broken by applying some ferrite devices [7, 8].

Recently, however, it has been shown [9, 10] that to break anti-unitary symmetry invariance, in atomic systems, it is not necessary to employ a magnetic field. Indeed, a combination of elliptically polarized microwaves with a static electric field applied to, for example, hydrogen (H) atoms can do this work as well. In previous studies [9, 10] we have restricted ourselves to a case when the microwave field is resonant with the classical motion of the electron, i.e. the ratio of the microwave frequency, \( \omega \), to the Kepler frequency, \( \omega_K = 1/n_0^3 \) (where \( n_0 \) is the principal quantum number of the H atom), is an integer number. It has been found that such a system can reflect level statistics very close to that of the GUE prediction.

In this paper we study a more general situation of non-resonant driving of the atoms and show that an appropriate choice of the system parameters allows us to reach statistical
properties expected for matrices of the GUE. We consider the weak-field limit where quantum results may be obtained by the lowest orders of perturbation theory. A classical investigation of the system behaviour is also carried out in terms of the perturbation calculations. It allows us to find out for what system parameters the secular motion of the electronic ellipse reveals chaotic dynamics.

The Hamiltonian of a realistic three-dimensional H atom placed in a static electric field and driven by an elliptically polarized microwave field in atomic units, neglecting relativistic effects, assuming infinite mass of the nucleus, and employing the dipole approximation reads as

$$H = \frac{p^2}{2} - \frac{1}{r} + F(x \cos \omega t + ay \sin \omega t) + E \cdot \mathbf{r} \quad (1)$$

where $F$, $\alpha$ and $\omega$ are, respectively, the amplitude, degree of elliptical polarization and frequency of the microwave field, while $E$ denotes the static electric field vector. As the external perturbation is time periodic, one may apply Floquet formalism and look for quasi-energy levels of the system.

We assume very small field amplitudes which allows us to include only the lowest non-vanishing terms in the quantum effective Hamiltonian [11] describing the dynamics of a given $n_0$ hydrogenic manifold. The static electric field contributes already in the first order of $E$ as the states with fixed $n_0$ are coupled among each other by the $E \cdot \mathbf{r}$ operator. On the other hand, there is no direct coupling between the states due to the microwave perturbation. Indeed, the states can be coupled only indirectly by the process of absorption and emission of microwave photons. Thus the first non-vanishing term is second order in $F$. The final matrix (with dimension $n_0^2$) of the quantum effective Hamiltonian, i.e. the Hamiltonian is first order in $E$ and second order in $F$, is then diagonalized by standard routines. The details of the quantum perturbation calculations can be found in [10], here we would only like to stress that the whole physically realistic problem is reduced to the analysis of the finite $n_0^2$-dimensional Hilbert space where $1/n_0$ plays the role of the effective Planck constant.

We now turn to a classical analysis of the system. The range of our interests is the high-frequency regime, i.e. $\omega > \omega_K$, which means that for weak external fields we have two fast degrees of freedom in the system, i.e. the position of the electron on an elliptical orbit and the phase of the microwave field, while two slow degrees of freedom corresponding to the orientation of the elliptical trajectory. One can get rid of the fast degrees of freedom by means of classical perturbation theory [12] which results in the classical effective Hamiltonian describing slow precession of an electronic ellipse. The perturbation calculation can be easily carried out employing the Lie method [12], actually it closely follows a similar procedure applied in [13] to the H atom perturbed by a linearly polarized microwave field. The first stage is to express the Hamiltonian (1) in terms of the action-angle variables of the unperturbed hydrogen atom. The new pairs of canonically conjugate variables are $(J, \Theta)$, i.e. the principal action (the analogue of the principal quantum number, $n_0$) and the position of the electron on an ellipse, respectively; $(L, \Psi)$, i.e. the angular momentum of the electron and the conjugate angle; and finally $(M, \Phi)$, i.e. the angular momentum projection on the z-axis and the angle of rotation around this axis [14]. Averaging the resulting Hamiltonian over $\Theta$ and $t$ immediately gives the first-order contribution to the classical effective Hamiltonian,

$$H^{(1)}(L, \Psi, M, \Phi) = \frac{3}{2} n_0^2 \left[ 1 - \frac{L^2}{n_0^2} \right] E_{\lambda} \left[ \cos \Phi \cos \Psi - \frac{M}{L} \sin \Phi \sin \Psi \right]$$

$$+ E_{\lambda} \left[ \sin \Phi \cos \Psi + \frac{M}{L} \cos \Phi \sin \Psi \right] + E_{\lambda} \sqrt{1 - \frac{M^2}{L^2} \sin \Psi}. \quad (2)$$
The second-order contribution of the microwave field requires calculating the generating function, \( w \) [12], which is the solution of the following equation:
\[
\frac{\partial w}{\partial t} + \omega K \frac{\partial w}{\partial \Theta} = -H_{\text{micro}}
\] (3)
where \( H_{\text{micro}} \) is the microwave part of the Hamiltonian (1) expressed in the action-angle variables (an explicit expression for \( H_{\text{micro}} \) as a Fourier series can be found in [14]). The solution for \( w \) is given as an infinite series with terms containing \( 1/(\omega \pm m\omega_K) \), where \( m \) is an integer number. For resonant driving, i.e. \( \omega/\omega_K \approx m \), one faces the small-denominators problem [12], but here we are not affected by this problem as we are interested in a non-resonant perturbation. Having calculated \( w \) it is a straightforward task to obtain the second-order contribution to the effective Hamiltonian by averaging the Poisson bracket of \( w \) and \( H_{\text{micro}} \) over \( \Theta \) and \( t \), i.e.
\[
H^{(2)}(L, \Psi, M, \Phi) = \frac{1}{2} \langle \{ w, H_{\text{micro}} \} \rangle_{\Theta,t}
\] (4)
we omit the lengthy explicit formula for \( H^{(2)} \) here). The final classical effective Hamiltonian reads
\[
H^{\text{eff}}(L, \Psi, M, \Phi) = -\frac{1}{2n_0^2} + H^{(1)} + H^{(2)}.
\] (5)
This is the classical counterpart of the quantum effective Hamiltonian, namely first order in the static electric field and second order in the microwave field. The classical Hamiltonian (5) possesses scaling symmetry, i.e. one can get rid of one of the parameters of the system. Introducing \( F_0 = n_0^2 F, E_0 = n_0^2 E, \omega_0 = n_0^2 \omega, L = L/n_0, M = M/n_0 \) and \( H^{\text{eff}}_0 = n_0^2 H^{\text{eff}} \), the dynamics becomes independent of the particular choice of the \( n_0 \) hydrogenic manifold.

For a general fields configuration the secular motion in the \( (L, \Psi, M, \Phi) \) phase space is not integrable and to investigate classical dynamics we have to perform numerical integration of the equations of motion generated by the Hamiltonian (5). For the linear microwave polarization without an additional static electric field considered in [13] the secular motion was one dimensional and employing the WKB quantization rule [2] the authors were able to get semiclassical predictions for quasi-energy levels in very good agreement with exact quantum numerical data.

For elliptically polarized microwaves and general orientation of the static field vector the anti-unitary symmetry invariance is broken. Only when either \( E_x = 0 \) or \( E_y = 0 \) is the system invariant with respect to the time-reversal combined with \( x \to -x \) or \( y \to -y \) transformations, respectively, see (1). As an example of a general elliptical polarization case we have (later on in this paper) analysed the degree of the polarization \( \alpha = 0.4 \). The microwave frequency has been chosen as \( \omega_0 = 1.304 \) and the amplitude as \( F_0 = 0.02 \), which is well in the range where, for the linear microwave polarization, the WKB calculations give good agreement with the exact numerical results [13]. Then by investigating the Poincaré surface of section we have found that the amplitude \( E_0 = 0.00028 \) and the orientation of the static field vector \( \phi \approx 0.3\pi \), \( \theta \approx \pi/4 \) (where \( \theta, \phi \) are the usual spherical angles) correspond to chaotic dynamics in the energy interval \( H^{\text{eff}}_0 \in [-0.500 32, -0.500 08] \). Putting \( \phi = 0 \) (\( E_y = 0 \)) one recovers the anti-unitary symmetry of the system, then the classical dynamics is found to be predominantly chaotic for \( H^{\text{eff}}_0 \in [-0.500 16, -0.499 92] \). Figure 1 shows examples of the phase space structures for both \( \phi = 0 \) and \( 0.3\pi \).

Having done the classical analysis we can switch to quantum calculation results. In order to get reasonable statistics for quasi-energy levels we have diagonalized the matrix of the quantum effective Hamiltonian for different \( n_0 \) manifolds in the range \( n_0 = 50–59 \). From
each diagonalization we have separated and unfolded the spectrum in the energy intervals corresponding to chaotic classical dynamics. This procedure has been applied to the anti-unitary invariant case ($\phi = 0$) and to the case with broken anti-unitary symmetry ($\phi = 0.3\pi$). Figure 2 shows histograms of the nearest-neighbour spacing (NNS) distributions of the quasi-energy levels (there are about $10^4$ spacings in each of the data sets) together with the plots of the Wigner surmises [3] for the GOE and GUE. The figure also shows the spectral rigidities, i.e. $\Delta_3$ statistics [3]. The qualitative agreement of the data with random matrix theory is apparent, especially for the case with broken anti-unitary symmetry.

To focus on quantitative measure we have fitted theoretical NNS distributions to the data (to avoid the dependence of the results on bin size the distributions have been fitted to the cumulative histograms [15]). For the anti-unitary invariant case the best-fitting Berry–Robnik distribution (i.e. the distribution for an independent superposition of Poisson and GOE spectra [16]) results in the parameter value (a relative measure of the chaotic part of the phase space) $q = 0.98$ with $\chi^2/N = 0.3$, i.e. chi-squared divided by the number of spacings $N$. Employing the Izrailev distribution [17, 18] we get the value of the level repulsion parameter $\beta = 0.96$ with $\chi^2/N = 0.8$. For the spectral rigidity the best-fitting $\Delta_3$ statistics corresponding to an independent superposition of Poisson and GOE spectra [3] results in $q = 0.99$ which is in agreement with the value obtained from the Berry–Robnik distribution fit.

In the case with broken anti-unitary symmetry one obtains the following parameter values: Berry–Robnik statistics (now it corresponds to an independent superposition of the Poisson and GUE spectra [19]) $q = 1$ with $\chi^2/N = 0.2$, Izrailev distribution $\beta = 2.05$ with $\chi^2/N = 0.3$ and from the spectral rigidity fit $q = 1$.

The presented results show undoubtedly that the system under consideration can reflect Bohigas et al’s conjecture both with or without anti-unitary symmetry. The question is whether such a behaviour can be observed experimentally? In this respect let us consider the case with broken generalized time-reversal symmetry. As there is no discrete symmetry in the system
one has no problem with separation of overlapping spectra. On the other hand, it results in a high density of states and requires high experimental resolution. We have presented the data for hydrogenic manifolds in the range $n_0 = 50–59$ in order to have good statistics but our results for $n_0 = 40–49$ reveal the very same behaviour. For example, for $n_0 = 40$ and $F = 40$ V cm$^{-1}$, $\omega = 2\pi \times 134$ GHz, $E = 0.56$ V cm$^{-1}$ the average level spacing is of the order of $10^{-4}$ cm$^{-1}$ and a measurement in the energy range between $-68.628$ and $-68.595$ cm$^{-1}$ provides about 500 levels. It sounds feasible experimentally.

Previous studies [9, 10] have been devoted to resonant microwave driving of H atoms placed in a static electric field. This paper deals with general non-resonant driving and shows that intra-manifold chaotic dynamics [9, 10, 20–22], i.e. the situation when states corresponding to a fixed principal quantum number $n_0$ are mixed significantly only among each other and the underlying classical dynamics is irregular, is not restricted to a particular resonant case but exists widely in the frequency domain. The presented behaviour is field-amplitude independent, i.e. if $F \to 0$ and $E \to 0$ but $E/F^2 = \text{constant}$, the structure of the phase space corresponding to secular motion remains unchanged as do the statistical properties of quasi-energy levels. This is a signature of inapplicability of the Kolmogorov–Arnold–Moser theorem [12] to a highly degenerate Coulomb problem. For high field amplitudes when hydrogenic manifolds cannot be considered as isolated and the inter-manifold mixing becomes relevant, our perturbation approach, obviously, becomes irrelevant. However, this regime, for a realistic three-dimensional problem, still constitutes a challenge for the theory.
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