AN EXAMPLE OF CHAOTIC EIGENSTATES IN A COMPLEX ATOM

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Statistically processing a group of excited states with the total angular momentum and parity $J^{\pi} = 1^{+}$ in the cerium atom reveals that their eigenfunctions are random superpositions of some few basic states. A possible dynamical mechanism responsible for the formation of those chaotic states is briefly discussed.

The motion of many dynamical systems in classical mechanics is known to be chaotic, or stochastic (see, e.g., ref. [1]). Among those are many-electron (highly excited) atoms as their autoionization shows, for example. The latter is related, in turn, to the absence of any small perturbation parameter in the atom (unlike the solar system which is similar to a classical atom), and to the singularity of the Coulomb interaction.

In quantum mechanics such a temporal dynamical chaos is impossible because of the discreteness of the energy spectrum. The transition to classical chaos required by the correspondence principle is realized, according to refs. [2,3], on a certain diffusion time scale $T_R \sim D^{-1} = \rho$, where ρ is the mean level density, and $\hbar = 1$. On this scale the quantum system does not yet "feel" (according to the uncertainty relation) the spectrum discreteness, and it is diffusing over an energy surface (generally, an invariant surface (a layer, see below) of all the exact motion integrals) as in the classical limit, provided the perturbation is strong enough to substantially mix up the unperturbed quantum states [4].

As T_R rapidly grows with quantum numbers I, any initial state with sufficiently large I has enough time to relax into the microcanonical distribution. It implies that the corresponding (Wigner) eigenfunctions become ergodic on the energy surface. As $I \to \infty$ this has been rigorously proved by Shnirelman [5] (see also ref. [6]), the quantum ergodicity requiring only the ergodicity of motion in the classical limit. If, however, the classical motion possesses stronger statistical properties, particularly, an exponential correlation decay, it is reasonable to expect the eigenstates to be some random gaussian functions. The gaussian statistic naturally appears due to decorrelation of an evolving quantum state in the process of its would-be classical relaxation on the energy surface. To the best of my knowledge a similar conjecture had been first put forward in ref. [7], although without any relation to the classical dynamical chaos which was discussed in ref. [8] (see also refs. [3,9]).

Specifically, this conjecture may be formulated as follows. Consider an ensemble of eigenfunctions ψ_m with all exact motion integrals, except the energy, fixed, and represent them in the basis of some unperturbed states φ_n:

$$\psi_m = a_{mn}\varphi_n, \quad \varphi_n = \psi_m a_{mn}. \tag{1}$$

Then, the elements of the real orthogonal matrix a_{mn} are assumed to be random with the gaussian statistic of parameters

$$\langle a_{mn}\rangle = 0, \quad \sigma^2(a_{mn}) = \langle a_{mn}^2\rangle - \langle a_{mn}\rangle^2 = N^{-1}. \tag{2}$$

Here $N(E)$ is the eigenfunction dimension in the Hilbert space, i.e. the effective number of basic states coupled into an eigenstate or the width of the energy layer. The elements a_{mn} cannot be, of course, completely independent owing to the conditions of normalization and of orthogonality of ψ_m. However, if $N \gg 1$, the former is apparently insignificant while the latter is also considerably weakened as any two random and independent vectors are almost orthogonal: $a_{mn}a_{m'n}$

$\sim N^{-1/2}$ provided $\langle a_{mn}\rangle = 0$. This implies vanishing a_{mn} correlations as $N \to \infty$ (see, e.g. ref. [10]). We shall call such eigenstates chaotic. They determine the maximal chaos allowed in a closed quantum system or, in brief, the maximal quantum chaos (MQC). Note that MQC is *composition chaos*, e.g. the composition of an eigenfunction out of some basic functions or that of an initial state out of eigenstates. In the latter case MQC does not imply temporal chaos as the system evolution in time is still almost periodic.

The "gibbsian" measure for a_{mn} (2) is also derived in the statistical random matrix theory (RMT) from a "microcanonical" measure for ψ vectors, i.e. from their isotropic distribution in the Hilbert space (see, e.g., ref. [10]). In this respect the MQC conjecture above is equivalent to the main statistical hypothesis in RMT. However, the dynamical approach outlined above allows one, in principle, to find out the conditions of applicability for RMT as well as an important eigenstate characteristic, $N(E)$, which is absent in the statistical theory. The matrix dimension d in the latter is an arbitrary parameter while actually it should satisfy $d \ll N(E)$. Besides, the statistical description turns out to be extended not only to the ensemble of eigenstates of a single system but even to a single eigenstate as $N \to \infty$ (cf. ref. [11]).

The statistical analysis of atomic states has been restricted as yet to their energies (see, e.g. ref. [12], where it is shown that there exist a series of states confirming RMT predictions). Meanwhile, the vast empirical data collected to date and aptly presented in atlas [13] allow one to analyze the atomic eigenfunctions as well.

As an example of chaotic eigenstates a series of 35 excited states in the cerium neutral atom has been chosen having $J^\pi = 1^+$ and energy $E \approx 2$–3 eV (D = 0.027 eV) above the ground state of $J^\pi = 4^-$. The CeI ionization potential is 5.54 eV. The eigenfunctions have been calculated for 31 of 35 states, and they are presented in ref. [13] by the two leading basic states φ_n of largest probabilities in the superposition: $a_1^2 = w_1 \geqslant w_2 = a_2^2$. Altogether, 34 basic states have been recorded for the eigenfunctions in question.

Assuming the MQC conjecture (2) and $N \gg 1$ the w distribution can be shown to be an approximately gaussian one with the parameters (a more detailed statistical analysis will be published elsewhere):

$$\langle w_1\rangle \approx N^{-1}\ln N, \quad \langle w_2\rangle \approx N^{-1}(\ln N - 1),$$
$$\sigma(w_1) \approx \sigma(w_2) \approx N^{-1}. \tag{3}$$

From ref. [13]: $\langle w_1\rangle = 0.177$; $\langle w_2\rangle = 0.111$; whence $N^{(1)} = 15.4 \pm 1.6$; $N^{(2)} = 16.0 \pm 3.8$. The rms standard deviations of the expected distributions are given throughout the paper. The variance and 4th moment of the w_1 distribution are equal (normalized to unity) within their uncertainties

$$(N^{(1)}\sigma)^2 = 1.14 \pm 0.25,$$
$$\langle(w_1 - \langle w_1\rangle)^4\rangle/3\sigma^4 = 1.36 \pm 1.0, \tag{4}$$

which also confirms the gaussian statistic.

The global structure of the eigenstates is presented in fig. 1. It forms a layer shown by two dashed straight lines. Here m is the eigenstate's serial number increasing with E_m, and n is that for basic states ordered according to the mean m of those eigenstates where a given φ_n appears as a leading one. If some φ_n is leading in a single ψ_m only (shaded squares in figure) it has been excluded from further statistical analysis since those φ_n are artificially concentrating near the layer axis. The distribution of the rest of the φ_n in n, that is over an energy surface, is compatible with the homogeneous one ($\chi^2(4) = 2.1$, confidence level CL $\approx 30\%$), the variance being equal to $\sigma_n^2 = 19.6$. Whence, the effective number of basic states on the energy surface is $N_E = \sqrt{12}\,\sigma_n = 15.3 \pm 1.2$. This value is very close to $N^{(1)} = 15.4 \pm 1.6$ above, which implies the ergodicity of eigenstates, each effectively coupling all

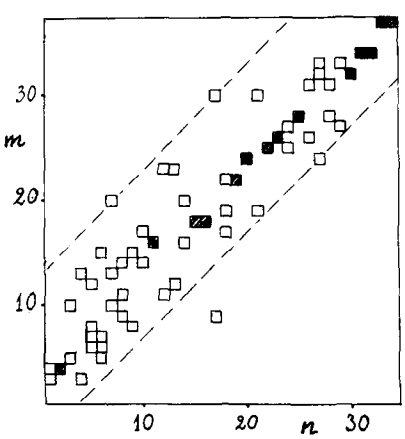

Fig. 1. The global structure of atomic eigenstates ψ_m as given by the distribution of leading basic states φ_n (see text).

basic states on the energy surface.

The distribution of a given φ_n in m also agrees with the homogeneous distribution ($\chi^2(4) = 5.1$; CL $\approx 30\%$). From the variance, $\sigma_m^2 = 17.4$, the energy surface "width" $\Delta E/D = N_\varphi = 14.4 \pm 1.1$. The observed equality $N_\varphi = N_E$ required by normalization of the wavefunctions [see eq. (2)] gives an additional confirmation of the above results.

Some other statistical tests have also been applied and did confirm the MQC conjecture. Particularly, the number of eigenfunctions in which a given φ_n appears as a leading one agrees with the binomial distribution of the parameter $p = 2/N$. This gives also the number of the basic states missed in fig. 1 (and in ref. [13]): 4.5 ± 2.

A relatively small value of the dimension N allows one to observe the global structure of eigenstates in atoms unlike nuclei where $N \sim 10^6$ (see, e.g. ref. [14]). On the other hand, small N imposes some limitations on the RMT applicability in regard to many-level correlations. The principal differences in the excitation of atoms and nuclei were already emphasized by Bohr in his first paper on the compound nucleus [15]. Presently, these differences look quantitative rather than qualitative, yet they are still fairly big.

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