On the repulsion of energy eigenstates in the time domain

(level spacings/dephasing/time correlation function/uncertainty principle/statistical spectroscopy)

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ABSTRACT The rate and extent of the exploration of the available phase space of a bound quantum mechanical system are shown to depend on the repulsion of energy eigenstates. Central to the argument is the Fourier transform relating the survival probability (in time) of an initially prepared nonstationary state and the (frequency) autocorrelation function of the excitation spectrum. Strong repulsion of states, as in the Wigner surmise, leads to a rapid dephasing of the initially coherently prepared state. The rate and extent of sampling of phase space depend not only on the pair levels depend but also on the intensity fluctuations. The rate of dephasing is equal to that inferred from the width of the spectral autocorrelation function.

A pair of levels that are degenerate will be split apart by a perturbation. This is the simplest example of the "repulsion" of eigenstates in the energy domain. Even when the two levels are initially nondegenerate, any coupling tends to push them further apart. In a multilevel system, such as a highly excited atom, nucleus, or molecule, the levels cannot get too far apart as they will then approach other levels and be repelled by them. Even so, it is unlikely to observe another level in the immediate vicinity of any given level. This is part of the so-called Wigner surmise (1–3), which plays an essential role in current statistical spectroscopy. Level repulsion is opposite to what is expected for a separable, but anharmonic, multilevel system, where the most probable spacing between adjacent levels is zero (4).

In this article we discuss the manifestation of this repulsion in the time domain. We do so in terms of the temporal evolution of an initially prepared nonstationary state. The adjective "repulsion" is thereby shown to be quite appropriate and descriptive. It is the level spacing distribution (or, more accurately, the spectral autocorrelation) that determines the rate of dephasing of the initial nonstationary state, with the larger spacings determining the earlier stages of the time evolution.

The repulsion of eigenstates in the time domain offers therefore an interpretation of the time–energy uncertainty relation (5) in terms of the temporal evolution of a nonstationary initial state. It is not necessary for the energy spectrum to be continuous, nor is it necessary to invoke the concept of a resonance or to make the Wigner–Weisskopf (6) approximation. As we shall discuss below in detail, it will turn out that there are two distinct aspects that govern the time evolution and these are not easily distinguished when the energy spectrum is continuous.

From an operational point of view, our discussion has the advantage that it is firmly rooted in the concept of an optical spectrum. The spectral correlation function that we use can therefore be simply generated from experimental data. Indeed, our discussion is a natural outgrowth of the dependent approach to spectroscopy as discussed by Heller (7, 8) and others (9–11).

For two reasons our discussion emphasizes the time evolution of quantal systems with discrete energy spectra. The main one is that the concept of repulsion of eigenstates is more natural and more intuitive for a discrete spectrum. Not that states in the continuum do not repel, but there the discussion is best carried out in terms of the scattering matrix (or equivalently, the density of states). The secondary reason is that our discussion contributes, we hope, to an understanding of the factors that are relevant for time evolution in bound quantal systems. Such an understanding is called for since, strictly speaking (12–14), systems with a discrete energy spectra have a quasiperiodic time evolution. Hence one could argue that they do not "evolve." This is true, of course, but misleading. For systems (be they molecules, nuclei, etc.) of realistic complexity, the density of excited states in the energy regime that can be explored by modern spectroscopic techniques is usually high enough that the recurrence time is very, or even exceedingly, long on the scale of experimental interest. Long before that time, an initial nonstationary state will dephase, giving rise to an apparent decay (15–18). This dephasing is the manifestation of the repulsion of eigenstates that is under discussion here.

The Survival Probability

An absorption or excitation spectrum, normalized to unit strength, can be written as

\[ S(\omega) = \sum_n p_n \delta(\omega_n + \omega - \omega_n). \]

The sum is over the discrete levels of the Hamiltonian of the system with the eigenvalues \( \hbar \omega_n \). \( p_n \) is the spectral weight of the \( n \)-th level and normalization of the spectrum implies \( \sum_n p_n = 1 \). \( E_i \) is the initial energy and \( \hbar \omega \) is the energy of the photon. In what follows, we set the energy scale by putting \( E_i = 0 \).

The survival probability, \( |C(t)|^2 \), is defined in terms of the Fourier transform, \( C(t) \), of the spectrum:

\[ C(t) = \int \exp(-i\omega t)S(\omega)d\omega. \]

The spectrum \( S(\omega) \) can only be measured to a finite resolution. Failure to resolve small frequency differences means that the longer time behavior of \( C(t) \) will not be well determined by the experiment. For our purpose, however, it is the short-time behavior of \( C(t) \) that is of interest.

One can regard \( C(t) \) as the time autocorrelation function of the initially prepared nonstationary state \( |\phi(0)\rangle \). To do so one writes, in terms of eigenstates \( |\phi_n\rangle \),

\[ p_n = |\langle \phi_n | \phi(0) \rangle|^2, \]

so that

\[ C(t) = \langle \phi(0) | \phi(t) \rangle. \]
Here \( |\phi(t)\rangle \) is the initial state propagated to the time \( t \) under the full Hamiltonian. The survival probability, \( |C(t)|^2 \), is then the probability of being in the initially prepared state at the time \( t \) after the preparation. If the initial state is not a pure state but is characterized by a density matrix \( \rho(0) \), we define
\[
|C(t)|^2 = \text{Tr}[\rho(t)\rho(0)]. \tag{5}
\]

The survival probability is clearly a measure of excursions of the initial state into other regions of phase space. The simplest example is the canonical two-state system where \( |C(t)|^2 \) manifests “quantum beats” (19). If \( p \) and \( 1-p \) are the intensities of the two eigenstates, which differ by an energy \( \Delta E \),
\[
|C(t)|^2 = p^2 + (1 - p)^2 + 2p(1 - p)\cos(t\Delta E/\hbar). \tag{6}
\]

The envelope of \( |C(t)|^2 \) is \( p \pm (1-p)^2 \) and the amplitude of the oscillation is \( 4p(1 - p) \). Even in this simple case, the temporal evolution is determined not only by the spacing (i.e., \( \Delta E \)) but also by the intensity. If the spectrum is dominated by one (or the other) eigenstate so that \( p \) and \( 1-p \) are very unequal, the initial nonstationary state remains localized, as it does if \( \Delta E \to 0 \). When both transitions are prominent in the spectrum, \( |C(t)|^2 \) is fully modulated, with a frequency determined by the spacing. The dephasing of the initial state depends both on the line positions and on their intensities.

When the spectrum is more congested one may still be able to experimentally resolve the quantum beats (18). At higher excitation energies, when the density of states is higher, \( |C(t)|^2 \) rapidly declines (11, 18, 20, 21).

From a mathematical point of view, \( C(t) \) can be regarded as a “characteristic function” of the probability density \( S(\omega) \). It is a property of the characteristic function (22) that \( |C(t)|^2 \) is also a characteristic function. Our main point is the physical interpretation of this purely mathematical result. In other words, we seek to determine and discuss the physical identity of the probability density whose characteristic function is \( |C(t)|^2 \).

Directly from the definition of \( C(t) \) (Eq. 2), it follows that
\[
|C(t)|^2 = \int_{-\infty}^{\infty} dw \exp(-i\omega t)G(\omega), \tag{7}
\]
where \( G(\omega) \) is the spectral autocorrelation function,
\[
G(\omega) = \int_{-\infty}^{\infty} S(\omega')S(\omega' + \omega)dw'. \tag{8}
\]

This is a known result in the theory of Fourier transforms (23). If the roles of time and frequency are interchanged, it is familiar as the Wiener (24) or the Wiener–Khinchin Theorem. On the other hand, since \( S(\omega) \) can be interpreted as a probability density, it follows from the theory of the characteristic function (22) that \( G(\omega) \), the inverse Fourier transform of \( |C(t)|^2 \), has the interpretation of a probability density as well. Indeed, it is evidently non-negative and normalized:
\[
\int_{-\infty}^{\infty} G(\omega)d\omega = |C(t = 0)|^2 = 1. \tag{9}
\]

The Spectral Correlation Function

The spectral autocorrelation function \( G(\omega) \) has been defined (Eq. 7) as the Fourier transform of the survival probability. It can be determined, via Eq. 8, directly from the observed spectrum. Its physical interpretation as a probability density derives from the corresponding interpretation of the spectrum \( S(\omega) \) itself: we regard \( S(\omega)d\omega \) as the fractional intensity in the frequency interval \( \omega, \omega + d\omega \). In other words, \( S(\omega)d\omega \) is the probability of a transition in the range \( \omega, \omega + d\omega \) (see Eq. 1). \( G(\omega) \) is the autocorrelation of \( S(\omega) \) (see Eq. 8). Thus \( G(\omega)d\omega \) is the joint probability of two transitions separated by the frequency interval \( \omega, \omega + d\omega \). This also follows on introducing Eq. 1 into Eq. 8:
\[
G(\omega) = \sum_{m} n \rho_m \rho_m^* \delta(\omega_n - \omega_m - \omega), \tag{10}
\]
or, since \( \rho_m \) is the intensity of the \( n \)th level and different levels are at different energies,
\[
G(\omega) = \delta(\omega) \sum_{m} \rho_m^2 + \sum_{m \neq n} \rho_n \rho_m^* \delta(\omega_n - \omega_m - \omega). \tag{11}
\]

In Eq. 11, the prime on the second summation indicates that the diagonal, \( m = n \), terms are to be excluded. The Fourier transform relation between the survival probability and \( G(\omega) \) implies that it is the diagonal part that determines the asymptotic, \( t \to \infty \), limit of \( |C(t)|^2 \).

The explicit expressions 10 and 11 serve to emphasize that \( G(\omega) \) is the weighted joint distribution function of spectroscopic spacings, with the weights determined by spectral intensities. \( G(\omega) \) becomes the more familiar distribution function for spacings between levels (irrespective of their intensities) only in the limiting case that all intensities are equal. In that event \( G(\omega)d\omega \) is the probability of finding two lines with a spacing in the interval \( d\omega \) around \( \omega \).

Just as in Dyson’s approach (1–3, 25) to correlations in level spacings, it is convenient to remove from \( G(\omega) \) its diagonal, or the level’s “self-correlation” part. The remainder can then be arranged to vanish when \( \omega \) is much larger than the mean level spacing. The first step in isolating the diagonal part of \( G(\omega) \) was already taken in Eq. 11. The quantity \( \sum_n \rho_n^2 \) is a measure of the “number of lines” in the spectrum (8, 11),
\[
\frac{1}{N} = \sum_n \rho_n^2, \tag{12}
\]
and is the actual number of lines for a spectrum of uniform intensity. For a perfect spectral resolution, the “self” part of \( G(\omega) \) is (see Eq. 11) \( 1/N \), so that
\[
G(\omega) = \frac{1}{N} [\delta(\omega) + (N - 1)P(\omega)]. \tag{13}
\]

Here \( [(N - 1)/N]P(\omega) \) is, by its definition, the fractional intensity at a separation \( \omega, \omega + d\omega \) from a given line, averaged over all lines. Its integrated value over all \( \omega \) must yield \( (N - 1)/N \) so that \( P(\omega) \), as defined, is a normalized probability density. \( P(\omega) \) determines the survival probability at short and intermediate times.

As an example consider the “ultimate” level repulsion, conjectured (26) to be the case when the spacings are all equal. If the intensities are taken all equal too, then
\[
G(\omega) \propto III(\omega/D). \tag{14}
\]

Here
\[
III(\omega) = \sum_{n=-\infty}^{m} \delta(\omega - n) \tag{15}
\]
is the sampling function defined in ref. 23. It follows that \( |C(t)|^2 \),
\[
|C(t)|^2 \propto III(Dt), \tag{16}
\]
is a series of equidistant pulses in time at an interval $D^{-1}$ apart. These correspond to the recurrences mentioned in the Introduction. For $0 < t < D^{-1}$ (i.e., after the initial preparation and before the first recurrence), $|C(t)|^2 = 0$. The extreme repulsion of the eigenstates ‘instantly’ drives the system away from the initially prepared region. Of course, the sudden dephasing is possible only when the spectrum is truly semi-infinite, thereby leading to Eq. 15. For a truncated series of equidistant sharp lines, the initial decline of $|C(t)|^2$ will be as $[\sin(\Omega)/\Omega]^2$, where $\Omega = ND$ is the frequency range of the spectrum.

When the intensities are not all equal, the drop in $|C(t)|^2$ will not be quite to zero. Say $p(\omega)$ is the smooth function of $\omega$ whose values at the integer multiples of $D$ are the intensities $P_n = p(nD)$. Then, for equidistant levels,

$$S(\omega) = D^{-1}p(\omega)III(\omega/D)$$

$$= \sum_n p(nD)\delta(\omega - nD).$$

Then $C(t)$ is the convolution of the Fourier transform $P(t)$ of $p(\omega)$ with $III(Dt)$. In other words $C(t)$ is a replication of $P(t)$ at intervals of $1/D$.

The opposite extreme occurs when the intensity is randomly distributed. Then $P(\omega)$ is a sequence of randomly placed delta functions and it is easier to discuss its ensemble average, which is uniform:

$$\langle P(\omega) \rangle = 1/(N-1).$$

Here $1/\tilde{p}$ is the average (intensity-weighted) spacing. Now

$$G(\omega) = \frac{1}{N} [\delta(\omega) + p]$$

or

$$\langle |C(t)|^2 \rangle = \frac{1}{N} [1 + 2\pi p\delta(t)].$$

In the absence of level repulsion, the ensemble averaged survival probability does not fall below $1/N$.

In the general case we can write

$$G(\omega) = (\delta(\omega) + p + [(N - 1)(P(\omega) - p)],$$

where the constant term $p$ gives rise to a $\delta(t)$ contribution in the survival probability (see Eq. 20), while the deviation of $\langle P(t) \rangle$ from $p/(N-1)$ accounts for the decline of the survival probability prior to the first recurrence (i.e., for $\tilde{p}t < 1$).

An interesting limit occurs when most of the nonuniformity of $P(\omega)$ is due to the fluctuation in the intensities. If one assumes (27) that the intensities have $x^2$ distribution with $\nu$ degrees of freedom,

$$\langle |C(t)|^2 \rangle = [1 + (Dt)^2]^{-\nu}.$$  

To include the nonrandomness in level spacings, Eq. 22 needs to be convoluted with the time dependence due to the spacings distribution. As $\nu \rightarrow \infty$ (the limit of no intensity fluctuations; ref. 27), the time dependence is entirely due to spacings distribution. For $\nu < 1$, which is the regular regime in the spectrum, Eq. 22 shows that the variation in the intensities can prevent the rapid decline of $|C(t)|^2$.

In the general case, neither are the levels equidistant (or, in the opposite extreme, random) nor are the intensities uniform, and the fluctuations of both determine the rate of dephasing of the initially nonstationary state.

The intuitive meaning of level repulsion is that for $\omega < D$, $G(\omega)$ is below its average value and is particularly low near the origin (but not at the origin itself). We can summarize the technical situation by the initial rate of decline of the survival probability:

$$\frac{d^2}{dt^2} |C(t = 0)|^2 = \int \omega^2 G(\omega) d\omega.$$  

The faster is the decline, the more is $G(\omega)$ concentrated away from the origin. A special case of this conclusion is the so-called $(20, 21)$ correlation hole—i.e., the drop to near zero of $|C(t)|^2$ for $t < D^{-1}$ due to the Wigner level repulsion.

Other implications of the Fourier transform relation between the survival probability and the intensity autocorrelation are discussed in the next two sections.

### The Sampling of Phase Space

During its time evolution the initial state can sojourn in other regions of phase space. In the long time limit the number of quantum states that have been visited in this manner is $N$, the effective number of points in the spectrum (Eq. 12). This number is determined, for a sharp line spectrum, by the self part of $G(\omega)$,

$$\frac{1}{N} = \int S^2(\omega) d\omega.$$  

If the spectral resolution of the experiment is finite, say $|\omega| < 1/T$ we can define $N_T$ as the number of states that will be resolved. This number is sensitive to the value of $G(\omega)$ near the origin and, as such, is a useful probe of the short-range $\omega$ dependence of $G(\omega)$. As we shall argue shortly, one can also define $N_T$ by degrading a higher-resolution spectrum. Furthermore, we may also want to probe the short-time behavior of the survival probability [equivalent to the longer-range behavior of $G(\omega)$] and we will introduce $N_0$, as the appropriate measure. The insight provided by these two measures is thus complementary.

We define $N_T$ in terms of the sinc($x$) function, $\text{sinc}(\omega) \equiv \sin(\omega)/\omega$, by

$$\frac{1}{N_T} = \frac{1}{\pi} \int_0^\infty G(\omega)\text{sinc}^2\left(\frac{\omega T}{2}\right) d\omega.$$  

The function $\text{sinc}(\omega T)$ drops rapidly to zero for $|\omega|T > 1$ so that the integration in Eq. 25 is effectively confined to the vicinity of the origin. Since the survival probability is the Fourier transform of $G(\omega)$ and the Fourier transform of $\text{sinc}^2(\omega)$ is the triangular function $\pi(1 - |\omega/2T|)$ for $|\omega| < 1$ and zero otherwise, we have from the power theorem (ref. 23, chapter 6),

$$\frac{1}{N_T} = \frac{2}{T} \int_0^T (1 - t/T)|C(t)|^2 dt.$$  

This measure has been extensively discussed by Heller (7, 8) and others (11) as the number of quantum states sampled up to the time $T$. We see that in the present context it is also a measure of the concentration of $G(\omega)$ at low frequencies, $|\omega|T \approx 1$.

Level repulsion—which means that but for the ‘self’ spike at $\omega = 0$, $G(\omega)$ has a very low value—at low values of $\omega$—means that more states will be sampled at any time $T, DT < 1$, as compared with the uniform limit. Indeed, in the extreme case

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1. We use the notation $N_T$ when the spectral resolution is $1/T$ since the result, Eq. 26, has been previously derived by a different approach (8) and has been denoted $N_T$. 

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of level repulsion, Eq. 14, $G(\omega) = 0$ for $0 < \omega < D$, so that $N_T = N$ for any $DT < 1$.

As the measure of the decline of $|C(t)|^2$ from its initial value of unity we use $N_\Omega$.

$$\frac{1}{N_\Omega} = \frac{1}{2\pi} \int_0^{\infty} |C(t)|^2 \text{sinc}^2 \left( \frac{1}{2} \Omega t \right) dt$$

$$= 2 \int_0^{\infty} (1 - \omega/\Omega) G(\omega) d\omega. \quad [27]$$

Here the integration over $t$ is effectively confined to $\Omega t < 1$, and $1/\Omega$ is the time interval that is sampled.

The measure $N_\Omega$ has not, to our knowledge, been previously discussed. One readily shows that $N_\Omega$ is nondecreasing as the time interval sampled is increasing (i.e., as $\Omega$ is decreasing). $N_\Omega$ tends to unity, as it should, when $\Omega \to \infty$ when only the initial state has been sampled. As $\Omega \to 0$, $N_\Omega \to N$. By analogy to $N_T$, we can also think of $\Omega$ as the frequency resolution of the experiment. $N_\Omega$ is then the number of levels resolved when only levels that are more than $\Omega$ or so apart can be distinguished. Hence, for the perfect resolution we have that $N_\Omega \to N$, whereas at the poorest resolution $N_\Omega \to 1$.

As long as $\Omega < D$, level repulsion means that more levels can be distinguished at any given resolution $\Omega$. This expectation is clearly borne out by either of the expressions in Eq. 27 for $N_\Omega$. A faster decline of $|C(t)|^2$ for $\Omega t < 1$ means that $N_\Omega$ is larger; a lower value of $G(\omega)$ at low $\omega$ means the same.

### Time–Energy Uncertainty Relation

For a strict line spectrum the quantal recurrences will occur indefinitely, thereby precluding any definition of a finite duration of the sampling of phase space. We therefore smooth the line spectrum by convoluting it with a normalized window function, $G_T(\omega)$—e.g., sinc$(\omega)$. We define the smooth envelope by

$$S_T(\omega) = \int_{-\infty}^{\infty} G_T(\omega - \omega') S(\omega') d\omega'$$

$$= \sum_n p_n G_T(\omega - \omega_n). \quad [28]$$

The window function is normalized and, hence, so is $S_T(\omega)$ since we have defined $S(\omega)$ to be normalized. $G_T(\omega)$ is the corresponding autocorrelation function. Unlike $G(\omega)$ itself, $G_T(\omega)$ has a finite value at the origin.

The autocorrelation width of the spectrum is defined by (ref. 23, chapter 6)

$$W_\omega = \int_{-\infty}^{\infty} G_T(\omega) d\omega / G_T(0). \quad [29]$$

Since $G_T(\omega)$ is normalized if $S_T(\omega)$ is,

$$W_\omega = 1/G_T(0). \quad [30]$$

The equivalent width of the survival probability [which is the Fourier transform of $G_T(\omega)$], $W_t$, is defined by

$$W_t = \int_{-\infty}^{\infty} |C_T(t)|^2 dt / |C_T(0)|^2. \quad [31]$$

In our case

$$W_t = \int_{-\infty}^{\infty} |C_T(t)|^2 dt$$

and is clearly proportional to the inverse of $W_\omega$.

$$W_t W_\omega = (2\pi)^{-1}, \quad [33]$$

since

$$G_T(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} |C_T(t)|^2 \exp(i\omega t) dt. \quad [34]$$

One can argue that for a smooth spectrum (i.e., for a window function that is neither too narrow nor so broad as to erase all details), a useful measure of the rate of sampling of phase space is $R$,

$$R = 1/\int_{-\infty}^{\infty} |C_T(t)|^2 dt$$

$$= 1/2\pi G_T(0)$$

$$= 1/2\pi \int_{-\infty}^{\infty} |S_T(\omega)|^2 d\omega. \quad [35]$$

It is interesting to note that $R$ is related to the widths, $R = 1/W_t = W_\omega/2\pi$, just as the rate of the decay of a state prepared in the continuum (5) is.

### Concluding Remarks

The manifestation of level repulsion in the dynamics of a bound quantum mechanical system has been discussed. The paucity of transitions separated by below-average frequency spacings is reflected in a higher initial rate of exploration of phase space. In the extreme limit of a picket-fence spectrum, almost all the available phase space is instantly accessible. In the opposite extreme, when any frequency interval contributes as much intensity, the initial rate of dephasing is slowest. Concrete applications to realistic spectra as well as more detailed implications, such as there being a separation of time scales when the spacing's distribution is multihumped (28, 29), the propagation of an incoherently prepared (i.e., a mixed) state, and the role of intensity fluctuations will be presented elsewhere. We also intend to return to the implications of the present discussion for the interpretation of the time–energy uncertainty principle in bound systems. In turn, we hope to show that the Fourier transform pair as used here to relate probabilities (rather than amplitudes as is usually the case), can also be applied to other pairs of conjugate variables such as momentum and position. This has more than just a formal connection with our discussion, since the repulsion of eigenstates is not unrelated to their orthogonality (i.e., to their mutual exclusion from the same region in phase space).

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