Magnetoeexcitons break antiunitary symmetries

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We show analytically and numerically that the application of an external magnetic field to highly excited Rydberg excitons breaks all antiunitary symmetries in the system. Only by considering the complete valence band structure of a direct band gap cubic semiconductor, the Hamiltonian of excitons leads to the statistics of a Gaussian unitary ensemble (GUE) without the need for interactions with other quasi-particles like phonons. Hence, we give theoretical evidence for a spatially homogeneous system breaking all antiunitary symmetries.

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For more than 100 years one distinguishes in classical mechanics between two fundamentally different types of motion: regular and chaotic motion. Their appearance strongly depends on the presence of underlying symmetries, which are connected with constants of motion and reduce the degrees of freedom in a given system. If symmetries are broken, the classical dynamics often becomes nonintegrable and chaotic. However, since the description of chaos by trajectories and Lyapunov exponents is not possible in quantum mechanics, it has been known for a long time how classical chaos manifests itself in quantum mechanical spectra [1, 2].

The Bohigas-Giannoni-Schmit conjecture [3] suggests that quantum systems with few degrees of freedom and with a chaotic classical limit can be described by random matrix theory [4, 5], and thus show typical level spacings. At the transition to quantum chaos, the level spacing statistics will change from Poissonian statistics to the statistics of a Gaussian orthogonal ensemble (GOE) or a Gaussian unitary ensemble (GUE) as symmetry reduction leads to a correlation of levels and hence to a strong suppression of crossings [1].

To which of the two universality classes a given system belongs is determined by remaining antiunitary symmetries in the system. While GOE statistics can be observed in many different systems like, e.g., in atomic [6, 7] and molecular spectra [8], for nuclei in external magnetic fields [9, 12], microwaves [13, 15], impurities [16], and quantum wells [17], GUE statistics appears only if all antiunitary symmetries are broken [3, 18]. Thus, GUE statistics is observable only in very exotic systems like microwave cavities with ferrite strips [19] or billiards in microwave resonators [20] and graphene quantum dots [21].

There is no example for a system showing GUE statistics in atomic physics. This is especially true for one of the prime examples when studying quantum chaos: the highly excited hydrogen atom in strong external fields. Even though the applied magnetic field breaks time-reversal invariance, at least one antiunitary symmetry, e.g., time reversal and a certain parity, remains and GOE statistics is observed [11, 22, 23].

Excitons are fundamental quasi-particles in semiconductors, which consist of an electron in the conduction band and a positively charged hole in the valence band. Recently, T. Kazimierczuk et al [24] have shown in a remarkable high-resolution absorption experiment an almost perfect hydrogen-like absorption series for the yellow exciton in cuprous oxide (Cu$_2$O) up to a principal quantum number of $n = 25$. This experiment has drawn new interest to the field of excitons experimentally and theoretically [25, 35].

Since excitons in semiconductors are often treated as the hydrogen analog of the solid state but also show substantial deviations from this behavior due to the surrounding solid, the question about their level spacing statistics in external fields arises. First experimental investigations of the level spacing statistics in an external magnetic field give indications on a breaking of antiunitary symmetries, which is, however, attributed to the interaction of excitons and phonons [31].

Very recently, we have shown that it is indispensable to account for the complete valence band structure of Cu$_2$O in a quantitative theory of excitons [28] to explain the striking experimental findings of a fine structure splitting and the observability of $F$ excitons [25]. We have also proven that the effect of the valence band structure on the exciton spectra is even more prominent when treating excitons in external fields [35].

In this Letter we will now show that the simultaneous presence of a cubic band structure and external fields will break all antiunitary symmetries in the exciton system without the need of phonons. This effect is present in all direct band gap semiconductors with a cubic valence band structure and not restricted to Cu$_2$O. We prove not only analytically that the antiunitary symmetry known from the hydrogen atom in external fields is broken in the case of excitons, but also, by solving the Schrödinger equation in a complete basis, that the nearest-neighbor spacing distribution of exciton states reveals GUE statistics. Thus, we give the first theoretical evidence for a spatially homogeneous system which breaks all antiunitary symmetries and demonstrate a fundamental difference between atoms in vacuum and excitons.

Without external fields the Hamiltonian of excitons in direct band gap semiconductors reads [28]

$$H = E_g - e^2/4\pi\varepsilon_0|\mathbf{r}_e - \mathbf{r}_h| + H_c (p_e) + H_h (p_h)$$

with the band gap energy $E_g$, the Coulomb interaction...
which is screened by the dielectric constant \( \varepsilon \), and the kinetic energies of electron and hole. While the conduction band is almost parabolic in many semiconductors and thus the kinetic energy of the electron can be described by the simple expression \( H_0(p_e) = p_e^2/2m_0 \), with the effective mass \( m_e \), the kinetic energy of the hole in the case of three coupled valence bands is given by the more complex expression [28] [29] [30]

\[
H_h(p_h) = H_{so} + \gamma_1 p_e^2/2m_0 - 3\gamma_2 p_h^2 I^2_2 + c.p.)/h^2m_0 - 6\gamma_3 \{p_{h1},p_{h2}\} (I_1, I_2) + c.p.)/h^2m_0.
\]

with \( \{a, b\} = (ab + ba)/2 \). Here \( \gamma_i \) denote the three Luttinger parameters, \( m_0 \) the free electron mass and c.p. cyclic permutation. The threefold degenerate valence band is accounted for by the quasi-spin \( I = 1 \), which is a convenient abstraction to denote the three orbital Bloch functions [36, 42, 45, 46]. In this Letter we want to show that the Hamiltonian (3) breaks all antiunitary symmetries. Hence, we will show that the only remaining antiunitary symmetry mentioned above is broken for the exciton Hamiltonian if the plane spanned by both fields is not identical to one of the symmetry planes of the cubic lattice. Even without an external electric field the symmetry is broken if the magnetic field is not oriented in one of these symmetry planes. Only if the plane spanned by both fields is identical to one of the symmetry planes of the cubic lattice, the antiunitary symmetry \( KS_n \) with \( \hat{n} \) given by Eq. (3) is present.

At first, we will show this analytically. Under time inversion \( K \) and reflections \( S_n \) at a plane perpendicular to a normal vector \( \hat{n} \) the vectors of position \( r \), momentum \( p \) and spin \( S \) transform according to [47]

\[
K r K^\dagger = r, \quad K p K^\dagger = -p, \quad K S K^\dagger = -S.
\]

and

\[
S_n r S_n^\dagger = r - 2\hat{n} (\hat{n} \cdot r), \quad S_n p S_n^\dagger = p - 2\hat{n} (\hat{n} \cdot p), \quad S_n S_n^\dagger = -S + 2\hat{n} (\hat{n} \cdot S).
\]

Let us denote the orientation of \( B \) and \( F \) in spherical coordinates via \( B (\varphi, \theta) = B (\cos \varphi \sin \theta, \sin \varphi \sin \theta, \cos \theta)^T \).
Possible orientations of the fields breaking the antiunitary symmetry are then, e.g., \( B (0, 0) \) and \( F (\pi/6, \pi/2), B (0, \pi/6) \) and \( F (\pi/2, \pi/2) \) or \( B (\pi/6, \pi/6) \) and \( F = 0 \). In all of these cases the hydrogen-like part of the Hamiltonian is invariant under KS\( \hat{n} \) with \( \hat{n} \) given by Eq. (6). However, other parts of the Hamiltonian like \( H_c = (p_1^2 S_2^2 + c.p.) \) [see Eq. (2)] are not invariant. For example, for the case with \( B (0, 0) \) and \( F (\pi/6, \pi/2) \), we obtain

\[
S_n KHcK^\dagger S_n^\dagger - H_c = 1/8 \left[ 2\sqrt{3} \left( S_2^2 - S_1^2 \right) p_1 p_2 \right. \\
+ 3 \left( S_1^2 p_2^2 + S_2^2 p_1^2 \right) - 3 \left( S_1^2 p_1^2 + S_2^2 p_2^2 \right) \\
+ \left. \left( S_1, S_2 \right) \left( 2\sqrt{3} \left( p_2^2 - p_1^2 \right) + 12 p_1 p_2 \right) \right] \neq 0 \quad (9)
\]

with \( \hat{n} = (-1/2, \sqrt{3}/2, 0)^T \). Thus, the generalized time-reversal symmetry of the hydrogen atom is broken for excitons due to the cubic symmetry of the semiconductor.

Since a breaking of all antiunitary symmetries is connected with the appearance of GUE statistics, we now solve the Schrödinger equation corresponding to \( H \) for the arbitrarily chosen set of material parameters \( E_0 = 0, \varepsilon = 7.5, m_e = m_0, \gamma_1 = 2, \) and \( \mu' = 0 \) using a complete basis. We can then analyze the nearest-neighbor spacings of the energy levels [23]. To reduce the size of our basis and thus the numerical effort, we already assumed \( \Delta = 0 \) so that we can disregard the spins of electron and hole.

The cubic part of the Hamiltonian [3] couples the angular momentum \( L \) of the exciton and the quasi spin \( I \) to the total momentum \( G = L + I \) with the \( z \) component \( M_G \). For the radial part of the basis functions we use the Coulomb-Sturmian functions of Refs. [28] with the radial quantum number \( N \) to obtain a complete basis. Hence the ansatz for the exciton wave function reads

\[
|\Psi\rangle = \sum_{NLGM_G} c_{NLGM_G} |N, L, I, G, M_G\rangle, \quad (10)
\]

with complex coefficients \( c \).

Without an external electric field, parity is a good quantum number and the operators in the Schrödinger equation couple only basis states with even or with odd values of \( L \). Hence, we consider the case with \( B (\pi/6, \pi/6) \) and \( F = 0 \) and use only basis states with odd values of \( L \) as these exciton states can be observed in direct band gap, parity forbidden semiconductors [25, 28, 29].

After rotating the coordinate system by the Euler angles \( (\alpha, \beta, \gamma) = (0, \vartheta, \varphi) \) to make the quantization axis coincide with the direction of the magnetic field [45, 49], we write the Hamiltonian in terms of irreducible tensors [37, 50]. Inserting the ansatz [10] in the Schrödinger equation \( H|\Psi\rangle = E|\Psi\rangle \) and multiplying from the left with the state \( |N', L', I', G', M'_G\rangle \), we obtain a matrix representation of the Schrödinger equation of the form \( Dc = EMc \). The vector \( c \) contains the coefficients of the ansatz [10] and the matrix elements entering the matrices \( D \) and \( M \) can be calculated using the relations given in Ref. [28]. The generalized eigenvalue problem is finally solved using an appropriate LAPACK routine [50].

In our numerical calculations, the maximum number of basis states used is limited by the condition \( N + L \leq 29 \) due to the required computer memory.

Before analyzing the nearest-neighbor spacings, we have to unfold the spectra to obtain a constant mean spacing [11, 13, 23, 51]. The number of level spacings analyzed is comparatively small since the magnetic field breaks all symmetries in the system and impedes the convergence of the solutions of the generalized eigenvalue problem with high energies [28]. As in Ref. [28], we furthermore have to leave out a certain number of low-lying sparse levels to remove individual but nontypical fluctuations. Hence, we use about 250 exciton states for our analysis. Owing to this number of states, we do...
for non-interacting energy levels, the Wigner distribution
theory [3, 31]: the Poissonian distribution

to the spacing distributions known from random matrix
show the cumulative distribution function corresponding
ues of the parameter
δ for
we have to note that an evaluation of numerical spectra
not present histograms of the level spacing probability
tics can be observed when neglecting phonons.
function
P(s) but calculate the cumulative
distribution function [52]

$$F(s) = \int_0^s P(x) \, dx.$$ (11)

The function $F(s)$ is shown in Fig. 2 for increasing va-
dues of the parameter $\delta'$ at $B = 3\, \text{T}$. In this figure we also
show the cumulative distribution function corresponding
to the spacing distributions known from random matrix
theory [3, 31]: the Poissonian distribution

$$P_p(s) = e^{-s}$$ (12)

for non-interacting energy levels, the Wigner distribution

$$P_{\text{GOE}}(s) = \frac{\pi}{2} s e^{-\pi s^2/4},$$ (13)

and the distribution

$$P_{\text{GUE}}(s) = \frac{32}{\pi} s^2 e^{-4s^2/\pi}$$ (14)

for systems without any antiunitary symmetry. Note that
the most characteristic feature of GUE statistics is the qua-
 dratic level repulsion for small $s$ and that the
clearest distinction between GOE and GUE statistics can
be taken for $0 \leq s \leq 0.5$. Hence, we see from that there
is clear evidence for GUE statistics. Note that for all
results presented in Fig. 1 we used the constant value of
$B = 3\, \text{T}$ and exciton states within a certain energy range.
It is well known from atomic physics that chaotic effects
become more apparent in higher magnetic fields or by
using states of higher energies for the analysis. Hence,
by increasing $B$ or investigating the statistics of exciton
states with higher energies, GUE statistics could prob-
bly be observed for smaller values of $|\delta'|$. At this point
we have to note that an evaluation of numerical spectra
for $\delta' > 0$ shows the same appearance of GUE statistics.
This is expected since the analytically shown breaking of
all antiunitary symmetries is independent of the sign of the
material parameters.

If the magnetic field is oriented in one of the symmetry
planes of the cubic lattice, only GOE statistics is observ-
able. Indeed, when investigating the exciton spectrum
for, e.g., $B(0, \pi/6)$, the level spacing statistics is best
described by GOE statistics, especially for small values
of $s$, as can be seen from Fig. 2. Very recently, M. Åf-
mann et al [31] have shown experimentally that excitons
in Cu$_2$O show GUE statistics in an external magnetic
field. However, since their experimental spectra were an-
yzed exactly for $B(0, \pi/6)$, there must be another ex-
planation for this observation than the cubic band struc-
ture. M. Åfmann et al [31] have assigned the observa-
tion of GUE statistics to the interaction of excitons and
phonons.

The main advantage of theory over the experiments is
the fact that the exciton-phonon interaction can be left
out. Hence, one can treat the effects of the band struc-
ture and of the exciton-phonon interaction separately.

In conclusion, we have shown analytically and numer-
ically that the cubic symmetry of the lattice and the
band structure leads to a breaking of all antiunitary sym-
metries in the system of magnetoexcitons. This effect
demonstrates a fundamental difference between atoms in
vacuum and excitons and is not limited to certain val-
ues of the material parameters, for which reason it ap-
ppears in all direct band gap semiconductors with a cubic
valence band structure. Furthermore, a closer investiga-
tion of excitons in external fields can lead to a better
understanding of the connection between quantum and
classical chaos.

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