Calculation of statistical entropic measures in a model of solids

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Abstract

In this work, a one-dimensional model of crystalline solids based on the Dirac comb limit of the Kröning-Penney model is considered. From the wave functions of the valence electrons, we calculate a statistical measure of complexity and the Fisher-Shannon information for the lower energy electronic bands appearing in the system. All these magnitudes present an extremal value for the case of solids having half-filled bands, a configuration where in general a high conductivity is attained in real solids, such as it happens with the monovalent metals.

Key words: Crystalline solid models; Electronic band structure; Statistical indicators
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The application of information theory measures to quantum systems is a subject of interest in the last years \cite{1,2,3}. Some relevant properties of the hierarchical organization of atoms \cite{4,5} and nuclei \cite{6} are revealed when these indicators are calculated on these many-body systems. On the one hand, they display an increasing trend with the number of particles, electrons or nucleons. On the other hand, they take extremal values on the closure of shells. Moreover, in the case of nuclei, the trace of magic numbers is displayed by these entropic products such as the Fisher-Shannon information \cite{7} and a statistical complexity measure \cite{8}. Also these statistical quantifiers have revealed a connection with physical measures, such as the ionization potential and the static dipole polarizability \cite{9} in atomic physics. All of them, theoretical and

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physical magnitudes, are capable of unveiling the shell structure of atoms, specifically the closure of shells in the noble gases.

A strategy to calculate these indicators is to quantify the discrete hierarchical organization of these multiparticle systems through the fractional occupation probabilities. These probabilities capture the filling of the shell structure of these systems. From them, the different statistical magnitudes are derived. The metallic clusters is another system that has also been studied with this method [10]. As in the case of atoms and nuclei, the shell structure of the valence electrons is well displayed by the spiky behavior of the statistical complexity and the magic numbers are unveiled by relevant peaks of the Fisher-Shannon information.

A different strategy to compute these entropic magnitudes is to use the probability density of the quantum system as the basic ingredient. This can be analytically obtained in some cases such as the H-atom [3] or numerically derived in other cases from a Hartree-Fock scheme [11,12] or a density functional-theory for atoms and molecules [13].

In this work, we address the problem to calculate these statistical indicators in a solid by this last strategy. For this purpose, the band structure of the solid has to be determined. The Krönig-Penney (KP) model [14] is a one-dimensional model of crystalline solids that presents a band structure sharing many properties with band structures of more sophisticated models. Moreover, it also has the advantage that allows to analytically find such electronic band structure.

The KP model considers that electrons move in an infinite one-dimensional crystal where the positive ions are located at positions $x = na/2$ with $n = \pm 1, \pm 2, \ldots$, generating a periodic potential of period $a$. A simplified version of the KP model is obtained when this periodic potential is taken with the form of the Dirac comb [15]:

$$V(x) = \frac{\hbar^2}{m} \Omega \sum_{n=-\infty}^{+\infty} \delta(x + na),$$

(1)

where $\hbar$ is the Planck constant, $m$ is the electronic mass and $\Omega$ is the intensity of the potential. In this case, the spatial part $\Psi(x)$ of the electronic wave function is determined from the time independent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right]\Psi(x) = E\Psi(x),$$

(2)

where the eigenvalue $E$ is the energy of the eigenstate $\Psi(x)$.

For a periodic potential, the Bloch’s theorem [16] establishes the form of the
general solution of the Eq. (2). This is a plane wave, with wave number $K$, modulated by a periodic function, $u_K(x)$:

$$\Psi(x) = e^{iKx}u_K(x),$$

(3)

where $u_K(x)$ has the periodicity of the crystal lattice: $u_K(x) = u_K(x + a)$. It implies the following translation property,

$$\Psi(x + a) = e^{iKa}\Psi(x).$$

(4)

Let us observe that we have the case of free electrons when $V(x) = 0$ and the solutions of type (3) recover the plane wave form with a total wave number $k = K$, with $u_K(x) = \text{constant}$. It suggests that the solution of Eq. (2) in the region $0 < x < a$, where $V(x) = 0$, can be associated in some way with a wave number $k$ and then written in the general form:

$$\Psi(x) = A\sin kx + B\cos kx,$$

(5)

and, by the translation property (4), this solution in the region $a < x < 2a$ is

$$\Psi(x) = e^{iK\alpha}[A\sin k(x - a) + B\cos k(x - a)],$$

(6)

with $A, B$ complex constants and $k = \sqrt{2mE/h^2}$.

Two boundary conditions must be fulfilled by $\Psi$ at the point $x = a$: on the one hand, the continuity of the wave function and, on the other hand, the jump in the derivative provoked by the Delta function (1). This gives the relations:

$$\Psi(a + 0) = \Psi(a - 0),$$

(7)

$$\Psi'(a + 0) = \Psi'(a - 0) + 2\Omega\Psi(a).$$

(8)

From these boundary conditions applied to the wave functions (5-6), the following homogeneous linear system is obtained for the unknowns $A$ and $B$:

$$\begin{pmatrix}
\sin ka & \cos k\alpha - e^{iK\alpha} \\
(ke^{iK\alpha} - k\cos ka - 2\Omega \sin ka) & (k\sin ka - 2\Omega \cos ka)
\end{pmatrix}
\begin{pmatrix}
A \\
B
\end{pmatrix}
= \begin{pmatrix}
0 \\
0
\end{pmatrix}.$$  

(9)

To have a non-trivial solution, the determinant of this $2 \times 2$ matrix has to be zero. Then, the following quantization relation for $k$ is obtained [15]:

$$\cos Ka = \cos ka + \frac{\Omega}{k}\sin ka.$$  

(10)

The electronic band structure of the one-dimensional crystal is contained in this equation. When $K$ varies its value in the different Brillouin zones, given by $(m - 1)\pi \leq |Ka| \leq m\pi$, with $m = 1$ for the first Brillouin zone, $m = 2$ for
the second Brillouin zone, etc., only certain intervals of \( k \) are allowed. These intervals for \( k \) are the energy bands of the electronic system. The positive and negative parts of these intervals correspond with the positive and negative parts of the Brillouin zones, respectively. In the limit \( \Omega a = 0 \), the free electron problem is recovered, then the solutions are the plane waves with \( k = K \). In the limit \( \Omega a = \infty \), we have the square well problem, then the wave number of the eigenstates verify \( \sin ka = 0 \). For an intermediate case, \( 0 < \Omega a < \infty \), Eq. (10) has to be solved. Concretely, for the particular value \( \Omega a = 4 \), that has also been used in Ref. [15], the lower energy bands obtained in this system for \( k > 0 \) are:

\[
\begin{align*}
2.154 \leq ka &\leq \pi \quad \text{(1st band)}, \\
4.578 \leq ka &\leq 2\pi \quad \text{(2nd band)}, \\
7.287 \leq ka &\leq 3\pi \quad \text{(3rd band)}, \\
10.174 \leq ka &\leq 4\pi \quad \text{(4th band)}.
\end{align*}
\]

The bands are symmetrically found for \( k < 0 \). Observe that, to finally get the wave function of the electronic states, we additionally need the normalization condition to completely determine \( \Psi(x) \), except a global phase factor. For our calculations, by taking \( \Omega a = 4 \), we will perform this normalization in the unit cell \([0, a]\).

The basic ingredient to calculate the statistical entropic measures in which we are interested is the probability density of the electronic states. This is given by \( \rho(x) = |\Psi(x)|^2 \). From this density, we proceed to compute the statistical complexity and the Fisher-Shannon information. Notice that the wave function \( \Psi(x) \) for a given \( k \) is transformed in \( -\Psi(x) \) for \( -k \), therefore all the magnitudes depending on the density are the same in both cases, and then we reduce our study to the positive part \((k > 0)\) of the electronic bands.

Let us recall the definition of the statistical complexity \( C \) [8,17], the so-called \( LMC \) complexity, that is defined as

\[
C = H \cdot D ,
\]

where \( H \) represents the information content of the system and \( D \) gives an idea of how much sharp is its spatial distribution. As a quantifier of \( H \), we take a version used in Ref. [17]. This is the simple exponential Shannon entropy [18], that has the form,

\[
H = e^S ,
\]

where \( S \) is the Shannon information entropy [19],

\[
S = - \int_0^a \rho(x) \log \rho(x) \, dx .
\]
Fig. 1. Shannon entropy, $S$, vs. the adimensional wave number, $ka$, for $k > 0$. Only the four lower electronic bands given in expression (11) are shown.

For the disequilibrium we take the form originally introduced in Refs. [8,17], that is,

$$D = \int_0^a \rho^2(x) \, dx .$$

(15)

The entropy, $S$, and the statistical complexity, $C$, for the lower electronic bands of the present one-dimensional crystalline solid are given in Fig. 1 and Fig. 2, respectively. When this hypothetical solid is in a situation of high conductivity, i.e. when it contains a band that is partially filled and partially empty, it can be observed in the figures that the more energetic electrons attain the highest entropy and the lowest complexity in the vicinity of the half-filled band. This is the point where in general the highest conductivity is also attained. Take, for instance, the real case of the monovalent metals, that include the alkali metals (Li, Na, K, Rb, Cs) and the noble metals (Cu, Ag, Au). These metals present all the bands completely filled or empty, except an only half-filled conduction band [20]. Compared with other solids, these metals display a very high conductivity, that in the cases of Ag and Cu it is the highest in nature. Then, it is remarkable this coincidence at the point of half-filled band where, on the one hand, the entropy and the statistical complexity are extrema for this model of solids and, on the other hand, the conductivity reaches its upper values for the real cases of monovalent metals.

Now, we check that other statistical entropic measures also display this behavior when the solid has half-filled bands. Let us take, for instance, the
Fig. 2. Statistical complexity, $C$, vs. the adimensional wave number, $ka$, for $k > 0$. Only the four lower electronic bands given in expression (11) are shown.

Fisher-Shannon information, $P$, that has been applied in different contexts \cite{7,21} for atomic systems. This quantity is given by

$$P = J \cdot I,$$  \quad (16)

where the first factor

$$J = \frac{1}{2\pi e} e^{2S/3},$$  \quad (17)

is a version of the exponential Shannon entropy \cite{18}, and the second factor

$$I = \int_a^0 \frac{[d\rho(x)/dx]^2}{\rho(x)} \, dx ,$$  \quad (18)

is the so-called Fisher information measure \cite{22}, that quantifies the stiffness of the probability density. Observe in Fig. 3 the confirmation of the previous results obtained in Figs. 1 and 2 for $S$ and $C$, in the sense that the extremal values of $P$ for this model of solids are also reached at the half-filling band points.

The former calculations are done orbital by orbital, i.e. thinking that the solid is a set of individual and independent orbitals, each one identified by its own wave number $k$. We can change the point of view of the problem and to think that the solid stands in some kind of collective state whose probability density $\rho_t(x)$ is the normalized sum of all the allowed electronic densities obtained from
Fig. 3. Fisher-Shannon entropy, $P$, vs. the adimensional wave number, $ka$, for $k > 0$. Only the four lower electronic bands given in expression (11) are shown.

The orbitals with wave numbers in the interval $[k_{\text{min}}, k_{\text{max}}]$; $k_{\text{min}}$ will be the minimal electronic wave number of the solid, i.e. the lowest $k$ obtained in the first band, and $k_{\text{max}}$ will be the upper $k$ corresponding to the most energetic electron of the solid. The expression for $\rho_t(x)$ is

$$\rho_t(x) = \frac{\int_{k_{\text{min}}}^{k_{\text{max}}} \rho_k(x) \, dk}{\int_{k_{\text{min}}}^{k_{\text{max}}} dk}. \quad (19)$$

Observe that $\rho_t(x)$ is normalized in the interval $[0, a]$, $\int_0^a \rho_t(x) \, dx = 1$, and that in the present model of solid $k_{\text{min}} = 2.154$ as given in formulas (11).

The calculation of the statistical complexity $C_t$ for this $\rho_t(x)$ is presented in Fig. 4. In this case, the minimal values of $C_t$ are also located in the vicinity of the half-filled electronic bands such as the behavior of $C$ for the individual orbitals shown in Fig. 2. In the hypothetical limit case of a solid where $k_{\text{max}}a \gg 1$, let us remark that the density $\rho_t(x)$ will tend to the uniform density and then the lowest value of complexity, $C_t = 1$, can be reached, as it can be seen in Fig. 4.

In summary, this work puts in evidence that certain conformational properties of many-body systems are reflected by the behavior of the statistical complexity $C$ and the Fisher-Shannon information $P$. In the present study, the electronic band structure of a model of solids has been unfolded and the
measurement of these magnitudes for such a model has been achieved. It is remarkable the fact that the extremal values of $C$ and $P$ are attained on the configurations with half-filled bands, which is also the electronic band configuration displayed by the solids with the highest conductivity, let us say the monovalent metals. Therefore, the calculation of these statistical indicators for a model of solids has unveiled certain physical properties of these systems, in the same way that these entropic measures also reveal some conformational aspects of other quantum many-body systems.

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