Spectral theory and x-ray diffraction

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Crystallographers use x-ray spectra to understand the structure of solids and ergodic theorists use spectra of abstract dynamical systems for structural studies; the relation of the two is shown here.

I. INTRODUCTION

In x-ray diffraction one analyzes quantities like the unit scattering power of a sample of $N$ scatterers in a volume $V$. If the scatters are distributed with a density $\rho(u), u \in V$, then the total scattering power for the sample is given by

$$I_N(s) = \int_V P(u) \exp(-2\pi i s \cdot u) du,$$

where $P(u) = \int V \rho(u' + u) \rho(u') du'$ is the autocorrelation of $\rho$; $I_N(s)$ is the measured intensity in the direction $S$, of radiation diffracted from a beam of wavelength $\lambda$ propagating in the direction $S_0$, with $s = (S-S_0)/\lambda$ [Eq. (2.11) in Guinier].$^1$I$_N(s)$ clearly depends on the configuration of the given sample through $P(u)$, and thus on the separations of scatterers and the relative frequencies of such separations. Ergodic theory enables us to relate $I_N(s)$ to part of the spectrum of a certain group of unitary operators acting on a Hilbert space. In this paper we prove that

$$I_N(s) ds = |V| d\langle E \tilde{f}, \tilde{f} \rangle$$

with equality in the limit of an infinite sample, where $E_s$ is a spectral family of projection operators of those unitary operators acting on a certain Hilbert space, $\tilde{f}$ is an element of this space, and $ds$ is a volume element of $R^3$ (the radial direction corresponding to the wavelength $\lambda$). In this way ergodic theory demonstrates a link between $I_N(s)$ and $E_s$.

II. THE THEORY

Let $X$ be the set of all "configurations with hard core restrictions," that is, the set of all sets of countably many points in $R^3$ (points representing the positions of scatterers) such that the distance between any two points is at least one. Define a metric on $X$ as follows. Enumerate the countable set of all finite collections of open balls in $R^3$ such that for each finite set: (1) the configuration of their centers satisfies the hard core condition, (2) all centers have rational coordinates, and (3) all radii are rational and less than 1/2. Let $B_c(e)$ be the open ball with center $c$ and radius $e$, and to each such ball define the continuous function $f_{c,e}: R^3 \rightarrow R$ by

$$f_{c,e}(u) = \begin{cases} e - ||u-c||, & \text{if } u \in B_c(e) \\ 0, & \text{otherwise} \end{cases}$$

where $||u||$ denotes the usual Euclidean norm in $R^3$. Let $C_n$ denote the set of open balls in the $n$th collection in the enumeration above, and let $\delta_j(x)$ be the position of the $j$th particle of $x$. Define the function $f_n:X \times X \rightarrow R$ as follows: $f_n(x) = \prod_{c \in C_n} \Sigma_j f_{c} (\delta_j(x))$. Finally, define the metric $d:X \times X \rightarrow R$ by $d(x,y) = \sup_n |f_n(x) - f_n(y)|/n$. To prove $X$ is compact in the metric...
topology one need only show it has the property that any sequence of configurations has a
subsequence which converges.\(^2\) This is straightforward using Cantor diagonalization and the
Bolzano–Weierstrass theorem applied to bounded cubes, as follows.

**Lemma:** The space \(X\) is compact.

**Proof:** Given a configuration \(x \in X\) we may enumerate the points of \(x\) as follows. Form a
lattice in \(\mathbb{R}^3\) from the vectors \(n_1(1/\sqrt{3},0,0), n_2(0,1/\sqrt{3},0), n_3(0,0,1/\sqrt{3})\), where \(n_1,n_2,n_3 \in \mathbb{Z}\).
Enumerate the corresponding lattice boxes \(\{(u_1,u_2,u_3) \in \mathbb{R}^3 | 1/\sqrt{3}u_i < u_i < 1/\sqrt{3}(n_i+1)\}, i=1,2,3\) so as to spiral outward from the origin. Then in each copy (translate) of the half-
open–half-closed box \([0,1/\sqrt{3}) \times [0,1/\sqrt{3}) \times [0,1/\sqrt{3})\) there exists at most one point of
the configuration \(x\) (by hard core condition). Define \(x(j)\) as the position of the particle of \(x\) in \(j\thinspace\)th box, \(B_j\) [let \(x(j) = \{\eta\}\) if no such particle exists]. Let \(\bar{B}_j\) be the closure of \(B_j\) and assign
\(B_j = \bar{B}_j \cup \{\eta\} \) the usual product topology. Let \(x_i\), \(i \geq 1\), be any sequence of configurations in \(X\).
Then \(x_i(1)\) is a sequence in \(B_1\). By the Bolzano–Weierstrass theorem\(^2\) there exists a convergent
subsequence, \(x_j^i\), such that \(x_j^i(1) \rightarrow x^i \in B_1\) as \(i \rightarrow \infty\). Again by the Bolzano–Weierstrass theorem
we may take a subsequence of \(x_j^i\), call it \(x_j^r\), such that \(x_j^r(j) \rightarrow x^j \in B_j\) for \(j = 1,2\) as \(i \rightarrow \infty\).
Continuing in this way we obtain subsequences \(x_j^m\) such that \(x_j^m(j) \rightarrow x^m \in B_j\) for \(j = 1,\ldots,m\) as
\(i \rightarrow \infty\). Taking the diagonal subsequence \(x_j^m\) we have that \(x_j^m(j) \rightarrow x^j \in B_j\) for all \(j = m \rightarrow \infty\).
Note this gives rise to an allowed configuration \(x = \{x^j | j \geq 1\}\) (that is, the hard core condition
is satisfied by the collection of points \(x^j, j \geq 1\). The fact that \(x_j^m \rightarrow x\) in the metric on \(X\) follows
simply.

Consider the group of translations of \(\mathbb{R}^3\) acting on \(X\) in the usual way: that is, every particle
of a given configuration is translated by \(t\) for all \(x \in X, t \in \mathbb{R}^3\). Since \(X\) is compact and \(\{t | t \in \mathbb{R}^3\}\) is a group of commuting homeomorphisms on \(X\),
there exists a Borel probability measure \(\mu\) on \(X\) invariant under \(t\) for all \(t \in \mathbb{R}^3\) (Markov–
Kakutani theorem).\(^3\) We assume the action is ergodic, that is, \(t(A) = A\) for all \(t \in \mathbb{R}^3\) implies
\(\mu(A) = 0\) or 1. Let \(L = L^2(X,\mu)\) be the Hilbert space of complex valued functions on \(X\) which
are square integrable with respect to \(\mu\). Define the group of unitary operators \(\{T^t \mid t \in \mathbb{R}^3\}\) on \(L\) by
\([T^t(f)](x) = f[t(x)]\). Let \(\delta(x) \in \mathbb{R}^3\) be any point in the configuration \(x\) closest to the origin,
and for each \(f : \mathbb{R}^3 \rightarrow \mathbb{R}\) define \(f(x) = f[-\delta(x)]\). Take \(f\) to be any positive, real valued function
on \(\mathbb{R}^3\) such that: \(\text{supp}(f) \subseteq B_0(\epsilon)\) (that is, \(f = 0\) outside a ball of radius \(\epsilon\) centered at the
origin), and \(\int_{B_0(\epsilon)} f^2(s)ds = 1\). (For example, we may take \(f\) to be the constant function
\(1/\text{vol}[B_0(\epsilon)]\) on \(B_0(\epsilon)\), 0 otherwise.) Furthermore suppose \(\epsilon > 0\) is sufficiently small (e.g.,
\(\epsilon < 1/2\)) such that given any \(x \in X\) there exists at most one point of \(x\) contained in \(B_0(\epsilon)\). It
then follows from the hard core condition that \(\tilde{f}(x) = \sum_{j \geq 1} f[-\delta_j(x)]\), where \(\delta_j(x) = \text{position}
of \(j\)th particle of \(x\). Thus

\[
T^s \tilde{f}(x) = \sum_{j \geq 1} f[s - \delta_j(x)].
\]

Consider the quantity:

\[
\langle T^s \tilde{f}, \tilde{f} \rangle = \int_X [T^s \tilde{f}(x)] [\tilde{f}(x)] \, d\mu(x)
\]

which by Birkhoff's pointwise ergodic theorem\(^4\) satisfies, for \(\mu\)-almost every \(x \in X\),

\[
\langle T^s \tilde{f}, \tilde{f} \rangle = \lim_{\nu \rightarrow \infty} \frac{1}{V} \int_V [T^{s+\nu} \tilde{f}(x)] [T^s \tilde{f}(x)] \, du
\]

and so.
Alternately, from Naimark's generalization of Stone's theorem \(^5\) we know that
\[
\langle T' f, f \rangle = \int_{\mathbb{R}^3} \exp(i2\pi s \cdot t) d\langle E_{T'}, f \rangle,
\] (5)

where \(E_{T'}: \mathbb{L} \to \mathbb{L}\) is a spectral family of operators corresponding to the group of operators \(\{ T' | t \in \mathbb{R}^3 \}\). Now if we have \(N\) identical scatterers, centered at \(N\) points \(\delta_j(x)\) in the configuration \(x\) of (4) which are in a volume \(V\), each scatterer represented, not by a delta-function mass (or charge), but a mass (charge) distributed by a density \(f(u - \delta_j(x))\), they produce a total intensity \(I_N\) which satisfies [taking the inverse Fourier transform of Eq. (2.11) in Guinier],
\[
\int_{\mathbb{R}^3} \sum_{j,k} f(t+u - \delta_j(x)) f(u - \delta_k(x)) du = \int_{\mathbb{R}^3} \exp(i2\pi s \cdot t) I_N(s) ds.
\] (6)

Comparing Eqs. (4), (5), and (6) we have that
\[
\lim_{N \to \infty} \frac{I_N(s)}{N^2} ds = |V_0| d\langle E_{T'}, f \rangle,
\] (7)

where \(|V_0| = V/N = \text{average volume available to a scatterer.} \) Alternately we have approximately:
\[
I_N(s) ds \approx |V| d\langle E_{T'}, f \rangle.
\] (8)

### III. CONCLUDING REMARKS

It is perhaps useful to mention the observation motivating the application of ergodic theory to the study of the unit scattering power. Consideration of the quantity \(\langle T' f, f \rangle\) was central to the above development and arose quite naturally in the context of averaging. By Eq. (4), \(\langle T' f, f \rangle\) is related to the separation of scatterers as can readily be seen in the case where \(f\) is uniformly supported over the ball of radius \(\epsilon\) [that is, \(f(u) = 1/\text{vol}[B_0(\epsilon)]\) for \(u \in B_0(\epsilon)\), 0 otherwise]. In this case when \(x \in X\) is a lattice (as in the case of a simple crystal) and \(t = \delta_j(x)\) \(\delta_k(x)\) is a lattice vector, then \(\langle T' f, f \rangle\) is the density of pairs separated by the vector \(t\). If \(t' \approx t\) (say \(|t' - t| < 2\epsilon\)) then \(\langle T' f, f \rangle\) will be nonzero, so indeed this quantity is related to the densities of pair separations.

It is hoped that the interplay between the two spectra will be of use to both crystallographers and ergodic theorists.

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