CONFIGURATION AVERAGING CALCULATION OF THE
ELECTRONIC STRUCTURE OF ALLOYS WITH
ARBITRARY DEGREES OF LONG-RANGE ORDER, USING
THE LATTICE SITE DISTRIBUTION FUNCTION

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We present a new derivation of the t-site scattering operator in terms of the atomic distribution function over
lattice sites. The operator path is presented in a form that avoids a double average (over the crystal potential
and the t-site operator). In configuration averaging of an over-determined path operator one can introduce
sampling coefficients of averages, making it possible to compute changes in symmetry during a structural
order-disorder transition. These coefficients reflect the conformity of the atom-sublattice type to the
characteristics of the single-electron energy spectrum of the alloy, averaged over the configurations. In this
approach the limiting cases are automatically satisfied, and the secular equation reduces to the correct form.

INTRODUCTION

Development of theoretical models of the electronic subsystem of alloys with arbitrary degrees of long-range order
requires an explanation of a number of experimental observations. In some cases an ordered state ensures unique alloy
properties, and even small amounts of disorder (due to doping, introduction of light elements, etc.) can produce significant
changes in system properties.

Today there are a number of methods for calculating the electronic structure of ordered and completely disordered
alloys [1]. However, for partially ordered alloys the available methods do not provide the desired results; therefore, it is of
interest to develop a theoretical description of their electronic subsystems to study and predict alloy properties.

One of the most promising candidate methods for partially disordered systems is based on the formal theory of multiple
scattering as applied to configuration averaging (proposed in [2]). This procedure, which has a profound influence on the
results, is based on averaging over the distribution function, determined by the number of Ising lattice sites filled by atoms of
a given type. This approach has also been extended in [3-8].

The occupation numbers have these values [2]:

\[
c^s(R^t_i) = \begin{cases} 
1, & \text{if for a given configuration on atom of type } s \text{ is at the site } R^t_i = R^t_n + a^t_i; \\
0, & \text{otherwise}. 
\end{cases}
\]  

A configuration average is carried out in this manner [2]:

\[
\langle c^s_{ni} \rangle = n^s_i, \\
\langle c^s_{ni} c^s_{nj} \rangle = \delta^s_{ij} n_{nm} (n^s_i - n^s_i n^s_j) + n^s_i n^s_j,
\]

where \( c^s_{ni} = c^s(R^t_i) \), and \( n^s_i \) is the probability of observing an s-type atom at site i.
TABLE 1

<table>
<thead>
<tr>
<th>τ</th>
<th>i</th>
<th>s</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>Same</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>Different</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>Different</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>Same</td>
<td></td>
</tr>
</tbody>
</table>

We can use these coefficients to write the crystal potential as [2]

\[
V(\vec{r}) = \sum_{s=1}^{N} c^s (\vec{R}_n^s) \varphi^s (|\vec{r} - \vec{R}_n^s|),
\]

where \(\varphi^s (|\vec{r} - \vec{R}_n^s|) = v_{ni}^s\) is the site potential. By analogy with Eq. (4) of reference [8], the total scattering operator can be written in terms of path operators that, in turn, are expressed in terms of t-site operators defined as follows [8]:

\[
t_{ni}^s = v_{ni}^s + v_{ni}^s G_0 t_{ni}^s.
\]

In the L representation a path operator takes the form [8]

\[
\langle T_{LL'}^{s's'}(x) \rangle = \langle [T(x)]^{-1} - \bar{\Gamma}(x) \bar{n}^{-1} \rangle_{L'L'},
\]

Note that, to obtain a formal solution for the structural matrix \(\bar{\Sigma}\), we must expand; in essence, this reduces to adding the indices \(s\) and \(s'\) without any additional changes.

In [2] similar operators have a somewhat different form:

\[
t_{ni}^s = v_{ni}^s + v_{ni}^s G_0 c_{ni} t_{ni}^s.
\]

In this case the transition from averaging the T operator to averaging the path operator is made with no decoupling. However, for the operator \(\tau\) we must decouple the t-site operator (and its associated coefficients \(c_{ni}^s\)) and use the site approximation. The result is a double averaging: t-site operator averages, and averaging over potential [3].

If the order \(N \approx 0.1\), the \(n\) matrix is not degenerate; therefore, Eq. (6') can be transformed into Eq. (6) by taking the matrix \(\bar{n}\) out of the denominator. In this instance the methods of [5] and [8] are equivalent, and in both cases one must use artificial means to obtain the limiting transitions to complete order and complete chaos. This fact arises from the explicit need to account for symmetry changes during order—disorder transitions because the secular equation contains an expansion over the types of atoms in the structural matrix.

Thus, our goal is to develop a formalism for calculating the electronic structure of alloys with arbitrary degrees of long-range order. We do not want the final expressions to contain double averages, and we want them to automatically converge to the correct expressions for the limiting transitions.

**FORMALISM FOR PROPOSED APPROACH**

To correctly perform a configuration average using the smallest possible number of decouplings, we include all configuration dependencies only when finding a single quantity, which is the t-site scattering operator. We redefine it as follows:

\[
t_{ni}^s = c_{ni}^s v_{ni}^s [1 + G_0 t_{ni}^s],
\]