

# Theory of low-energy electron diffraction for nanomaterials – subclusters, automated searches

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Abstract:

To enable the determination of detailed structures of nanomaterials, we have previously made the theory of low-energy electron diffraction (LEED) much more efficient for complex and disordered systems, calling it NanoLEED: our cluster approach speeds up the computation to scale as  $n \log n$ , rather than the standard  $n^3$  or  $n^2$ , with  $n$  the number of atoms, for example. Strong multiple scattering may occasionally cause poor convergence: this is solved here by treating all scattering within subclusters of a few atoms (e.g. a  $\text{SiH}_3$  group) with accurate matrix inversion. For the structure determination of complex nanostructures, an efficient search method is also essential: for that purpose a modified version of tensor LEED is here adapted to nanostructures, and called NanoTensorLEED.

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## 1. Introduction

In recent publications [1-3], we have introduced efficient new approaches for calculating intensities of low-energy electron diffraction (LEED) for complex nanostructures, which we collectively call NanoLEED, after the name of our computer code. The accuracy, structural sensitivity and performance of the approximations used were demonstrated for ordered structures – pure  $C_{60}$ , endohedral  $C_{60}$ , exohedral  $C_{60}$  and pure carbon nanotubes adsorbed on Cu(111) – and also for disordered finite-sized structures – silicon nanowires – with various shapes and distortions. The performance gain leads to  $n \log n$  scaling of the computational time, instead of the standard  $n^3$  or  $n^2$  scaling, where  $n$  is the number of inequivalent atoms, for example. This allows much more complex structures to be analyzed than with conventional LEED methods.

In this paper we report two further developments of this new method. The first deals with a shortcoming of our approximations, not unfamiliar in other LEED approximations: they occasionally converge poorly for some atomic geometries, presumably also due to very strong multiple scattering. To overcome this limitation, we treat problematic small subclusters of atoms with matrix inversion to guarantee full and accurate inclusion of multiple scattering within them: the result is a (non-diagonal) scattering matrix describing the exact and complete scattering by that subcluster, which can then be included as a non-spherical “pseudo-atom” in the NanoLEED code. This approach uses the idea of one-center expansion applied earlier by Pendry to LEED [4] and follows the cluster approach to LEED developed in the 1980s [5].

The second development addresses the need to automate the structural search for complex nanostructures. With such structures, we may expect to need relatively large atomic displacement steps during a search, compared to the  $\sim 0.01$  nm steps common in past LEED searches [6]. Therefore, the second-order tensor LEED method [7] commonly used in current LEED codes [8] is likely to not be the most appropriate for nanostructures. Furthermore, the conventional tensor LEED approach would be computationally much less efficient for nanostructures, because it requires one “time-reversed” LEED calculation for each exit direction: that can be done efficiently in layered structures like surfaces, but not in non-periodic structures like nanoparticles. Our approach here is therefore a new, simplified version of tensor LEED [9] that omits the “time-reversed” LEED calculations. This allows a more approximate but still fast estimation of the appropriate directions of displacement of the atoms; we then repeat the full NanoLEED multiple-scattering calculation after that collective displacement, iterating until a minimum is found, for example with steepest descent or conjugate gradient methods. Such an approach is analogous to the familiar use of the Hellmann-Feynman theorem in total-energy optimization [10,11].

Our NanoTensorLEED method contrasts with the more common use of the second-order tensor LEED method: in that case most of the search takes place within the range of validity of second-order tensor LEED ( $\sim 0.04$  nm), starting from a single reference structure at which a full multiple-scattering calculation is made; the reference structure itself is rarely updated, and in many analyses it is even never updated [6], because of the

small resulting displacements in the more predictable surface structures to which tensor LEED is normally applied.

In the following, we first summarize the theoretical basis of our NanoLEED method, and then introduce the two new developments that deal with occasional poor convergence and with automated searches.

## 2. Review of the NanoLEED Method

We briefly describe two computationally efficient methods to solve the multiple scattering problem in LEED [1-3]: an approximate grid-based method called Sparse-Matrix Canonical Grid or SMCG method; and the approximate “UV” method. Both approaches are iterative and rely in LEED on sufficient inelastic damping of electron wave amplitudes to compensate for the strong elastic scattering.

First, let’s recall that solving the multiple scattering in LEED can be formulated as the inversion of a matrix  $A$ , which involves computing times that typically scale as  $N^3$  and  $N^2$ , depending on the method, if  $A$  has dimension  $N$ .

In the Sparse-Matrix Canonical Grid (SMCG) method [12], the scaling is improved by Fast Fourier Transform (FFT). This is made possible by changing matrix  $A$  to be strictly periodic (as for a periodic structure), i.e.  $A_{n,m} = A_{n-m}$ , even though the structure may not be periodic at all. For LEED, this requires solving the scattering as if the atoms occupied a periodic, rectangular spatial grid. With an arbitrary non-periodic structure, including any nanostructure, we can construct such a regular grid and refer each atom to its nearest grid point: then the propagation of an electron from an atom  $i$  to an atom  $j$  proceeds via the grid points  $P$  and  $Q$  nearest to atoms  $i$  and  $j$ , resp., i.e. along the path  $i \rightarrow P \rightarrow Q \rightarrow j$ . This method is exact if a sufficient number of partial waves are used, so as to enable the accurate propagation of electrons between each atom and its nearest grid point. The major part of the computation turns out to be the scattering between the regular grid points, which FFT solves in times proportional to  $N_g \log N_g$ , where  $N_g$  is the number of grid points used (in each dimension, FFT requires a number of grid points that is a power of 2): the number  $N_g$  is approximately related to the number of atoms.

An alternative method to SMCG uses Singular Value Decomposition (SVD). If the rank of matrix  $A$  (i.e. the number of its nonzero eigenvalues) is  $r < N$ ,  $A$  can be factored into a product of three matrices,  $A_{N \times N} = U_{N \times r} D_{r \times r} V_{r \times N}$ , where the smaller diagonal matrix  $D$  contains the  $r$  nonzero eigenvalues of  $A$ , while  $U$  and  $V$  are rectangular. LEED does not produce vanishing eigenvalues, but this approach can still be used approximately by equating small eigenvalues to zero: we can then replace  $A$  by  $UDV$ . Thereby, the smaller is the rank  $r$ , the faster is the computation. To efficiently find the rank and the singular values of a matrix, the so-called “UV” method can be used for the SVD decomposition [13]. This approach leads to computation times proportional to

$N \log N$ , with  $N$  the dimension of  $A$ .

We found that the SCMG and UV methods are most efficient in different circumstances. SMCG outperforms UV for large numbers of atoms and large interatomic distances. But we also found that a more conventional approach, the Conjugate Gradient (CG) method [14], is more efficient than either SMCG or UV for small numbers of atoms and small interatomic distances [1-3]. Our NanoLEED code therefore combines these three methods and selects the most efficient one at each stage: a single structure often includes near, intermediate and distant neighbors, so different methods are applied to different pairs of atoms in the same structure.

Our implementation in the code named NanoLEED allows both periodic and non-periodic structures, including isolated nanoclusters.

### 3. Exact Multiple Scattering in Atomic Subclusters

In our applications of NanoLEED, we have found that occasionally the iterations involved in SMCG and UV do not converge well. For example, this happened with  $\text{SiH}_3$  clusters which were used to terminate the surface of a silicon nanowire [3]. Removing the hydrogen solved the non-convergence: it may come as a surprise that hydrogen, usually viewed as a weak scatterer, causes poor convergence in multiple scattering, with only a weak dependence on which phase shifts we used for H! This behavior also occurred at isolated energies in  $\text{C}_{60}$  buckyballs [1,2] (in that case we could fortunately skip such energies and interpolate between well-converged intensities at nearby energies). We believe that this is due to unusually strong multiple scattering between near neighbors, in circumstances that are not easy to predict. As already pointed out by Pendry [15], multiple scattering can be very strong at energies where waves reaching an atom have the same phase, giving strong constructive interference.

A solution to such poor convergence is to treat the multiple scattering by exact matrix inversion in a small subcluster of atoms between which the poor convergence arises. A single-center expansion is then used. The subcluster should remain small to keep the maximum required angular momentum  $l_{\max}$  low (it is roughly proportional to the radius of the subcluster). To connect the previous summary with the scattering from small clusters of atoms, we thus next briefly recall a common formulation of electron scattering in LEED.

The standard LEED method [16,17] calculates matrices  $T_i$ , representing the amplitudes due to scattering paths ending at all relevant atoms  $i$  ( $i = 1, \dots, n$ ), including all partial waves and all multiple scattering paths within a suitably chosen cluster (or layer) of atoms. The matrices  $T_i$  are the solution of the equation  $A\hat{T} = t$ , where  $\hat{T} = (T_1 \ T_2 \ \dots \ T_n)^T$ , while  $t = (t_1 \ t_2 \ \dots \ t_n)^T$  contains the known atomic scattering properties  $t_i$  of each individual atom  $i$ , and  $A = I - tG$  contains, besides  $t$ , the

unit matrix as well as Green's functions  $G$  for propagation between the various atoms. The dimension  $N$  of matrix  $A$  is proportional to the number  $n$  of inequivalent atoms in the cluster or layer and to the number of partial waves needed,  $L = (l_{\max} + 1)^2$ , typically 25 to 100.

We now decouple the electron multiple scattering inside each small subcluster from the multiple scattering occurring outside and solve the multiple scattering problem in two stages: first within each isolated subcluster; then for the whole system where each subcluster has been replaced by a single object with the same scattering properties as the corresponding subcluster.

Earlier, the theoretical approach described above has been developed [18] for an arbitrary cluster of atoms and for arbitrary chemical identities of the cluster's constituents. The main idea is to group atoms together in small clusters that can be replaced by entities with scattering properties equivalent to the original small cluster. Having the atoms grouped as described, a series of efficient embedding algorithms [18,19] can be used to solve the problem of electron multiple scattering in the whole cluster. We only present here how the multiple scattering can be decoupled, the rest of the topic being available in Ref. 18.

In a cluster of scatterers, the individual scattering-related operators (and consequently the corresponding scattering matrices) are expressed with respect to each scatterer, *i.e.* the origins to which the individual operators relate are the geometrical centers of the corresponding atoms. To build a cluster operator one must choose a common origin and relate all the individual operators to it. For example, if the cluster operator  $A$  is a sum of individual operators  $A_i$ , then

$$A = \sum_i \bar{A}_i = \sum_i Tr(\bar{R}_i) A_i Tr(-\bar{R}_i) \quad (1)$$

where  $Tr(\bar{R}_i)$  is a translation operator needed to "shift" atom  $i$  (more precisely, an electronic scattering state related to  $i$ ) onto the common origin, and  $\bar{A}_i$  is the resulting shifted operator. In the following, we will use a bar to denote the shifted atomic operators related to the common origin of the cluster.

With these notations, the cluster's scattering matrix becomes

$$T = \sum_i \bar{T}_i \quad (2)$$

Here  $\bar{T}_i$  includes all the multiple scattering paths ending at atom  $i$ , referred to the common origin. These operators obey the familiar self-consistent equation [15,19]

$$\bar{T}_i = \bar{t}_i + \sum_{j \neq i} \bar{t}_i G_o^{ij} \bar{T}_j \quad (3)$$

where  $\bar{t}_i$  are the atomic scattering matrices ( $\bar{t}_i$  is diagonal when atom  $i$  is not shifted) and  $G_o^{ij}$  is the free-space propagator Green function from atom  $j$  to atom  $i$  (we will generally omit the atom indices  $i$  and  $j$  for readability). This is the equation we usually solve by UV-SMCG.

Now, let us group the atoms in subclusters which will be labeled by Greek letters  $\alpha, \beta, \dots$ . Each one of these small clusters is characterized by its own scattering matrix

$$\tau_\alpha = \sum_{i \in \alpha} \bar{T}_i(\alpha) = \sum_{i \in \alpha} Tr(\bar{R}_i - \bar{R}_\alpha) T_i(\alpha) Tr(-\bar{R}_i + \bar{R}_\alpha) \quad (4)$$

Here  $T_i(\alpha)$  describes all those multiple scattering paths ending at atom  $i$  which never scatter outside the subcluster  $\alpha$ . These operators obey the self-consistent equation

$$\bar{T}_i(\alpha) = \bar{t}_i + \sum_{\substack{j \in \alpha \\ j \neq i}} \bar{t}_j G_o \bar{T}_j(\alpha) \quad (5)$$

or explicitly

$$Tr(\bar{R}_i - \bar{R}_\alpha) T_i(\alpha) Tr(-\bar{R}_i + \bar{R}_\alpha) = Tr(\bar{R}_i - \bar{R}_\alpha) \bar{t}_i Tr(-\bar{R}_i + \bar{R}_\alpha) + \sum_{\substack{j \in \alpha \\ j \neq i}} Tr(\bar{R}_i - \bar{R}_\alpha) \bar{t}_j Tr(-\bar{R}_i + \bar{R}_\alpha) G_o Tr(\bar{R}_j - \bar{R}_\alpha) T_j(\alpha) Tr(-\bar{R}_j + \bar{R}_\alpha) \quad (6)$$

Now equation 5 can be written using the multiple scattering series expansion:

$$\bar{T}_i(\alpha) = \bar{t}_i + \sum_{\substack{j \in \alpha \\ j \neq i}} \bar{t}_j G_o \bar{t}_j + \sum_{\substack{j \in \alpha \\ j \neq i}} \sum_{\substack{k \in \alpha \\ k \neq j}} \bar{t}_j G_o \bar{t}_j G_o \bar{t}_k + \dots \quad (7)$$

If one sums  $\bar{T}_i$  over all the atoms belonging to a certain subcluster  $\alpha$ , the result is an operator describing all the multiple scattering paths ending in the subcluster  $\alpha$ , which we can call  $\bar{T}_\alpha$ . To find the equation it obeys, we sum equation 3 over all the atoms  $i$  belonging to  $\alpha$ .

$$\sum_{i \in \alpha} \bar{T}_i = \sum_{i \in \alpha} \bar{t}_i + \sum_{i \in \alpha} \sum_{j \neq i} \bar{t}_j G_o \bar{T}_j \quad (8)$$

The sum over  $j$  can be split into a sum over atoms that belong to  $\alpha$  and a sum over atoms that don't belong to  $\alpha$ :

$$\sum_{i \in \alpha} \bar{T}_i = \sum_{i \in \alpha} \bar{t}_i + \sum_{i \in \alpha} \left( \sum_{\substack{j \in \alpha \\ j \neq i}} \bar{t}_i G_o \bar{T}_j + \sum_{\substack{j \notin \alpha \\ j \neq i}} \bar{t}_i G_o \bar{T}_j \right) \quad (9)$$

The terms that refer to atoms that don't belong to  $\alpha$  can further be grouped by the subclusters to which they do belong:

$$\begin{aligned} \sum_{i \in \alpha} \bar{T}_i &= \sum_{i \in \alpha} \bar{t}_i + \sum_{i \in \alpha} \left( \sum_{\substack{j \in \alpha \\ j \neq i}} \bar{t}_i G_o \bar{T}_j + \sum_{\beta \neq \alpha} \bar{t}_i G_o \sum_{j \in \beta} \bar{T}_j \right) \\ &= \sum_{i \in \alpha} \bar{t}_i + \sum_{i \in \alpha} \left( \sum_{\substack{j \in \alpha \\ j \neq i}} \bar{t}_i G_o \bar{T}_j + \sum_{\beta \neq \alpha} \bar{t}_i G_o \sum_{\beta} \bar{T}_\beta \right) \end{aligned} \quad (10)$$

If we continue by expanding all  $\bar{T}_j$ ,  $j \in \alpha$ , using equation 3, we are led to

$$\begin{aligned} \bar{T}_\alpha &= \sum_{i \in \alpha} \bar{T}_i = \sum_{i \in \alpha} \left( \bar{t}_i + \sum_{\substack{j \in \alpha \\ j \neq i}} \bar{t}_i G_o \bar{t}_j + \sum_{\substack{j \in \alpha, k \in \alpha \\ j \neq i, k \neq j}} \bar{t}_i G_o \bar{t}_j G_o \bar{t}_k + \dots \right) \\ &\quad + \sum_{\beta \neq \alpha} \sum_{i \in \alpha} \left( \bar{t}_i + \sum_{\substack{j \in \alpha \\ j \neq i}} \bar{t}_i G_o \bar{t}_j + \sum_{\substack{j \in \alpha, k \in \alpha \\ j \neq i, k \neq j}} \bar{t}_i G_o \bar{t}_j G_o \bar{t}_k + \dots \right) G_o \sum_{\beta} \bar{T}_\beta \end{aligned} \quad (11)$$

By looking at equation 7, one can easily identify the quantities inside the brackets as  $\bar{T}_i(\alpha)$  and, taking equation 4 into account, one finally finds the expression

$$\bar{T}_\alpha = \bar{\tau}_\alpha + \sum_{\beta \neq \alpha} \bar{\tau}_\alpha G_o \bar{T}_\beta \quad (12)$$

which is equivalent to equation 3 but written for subclusters seen as entities rather than for individual atoms.

Equations 3, 5 and 12 form the theoretical backbone of our subcluster method. First, equation 3 is solved by matrix inversion for each of the small subclusters, and using equation 5 we get the equivalent scattering matrices corresponding to each subcluster. Finally, equation 12 is solved for the complete system, by the efficient UV-SMCG method.

#### 4. Nano-Tensor-LEED

In applying LEED to nanostructures, whether ordered or not, one faces a relatively large number of structural parameters that must be fit to experiment. The search for the correct structure is thus more difficult than in most structure analyses performed to date for ordered surfaces. For this purpose we apply a minimum-seeking method modeled after that common in total-energy minimizations based on Hellmann-Feynman forces [10,11], where a completely new calculation of total energy and forces is performed after all the

atomic positions have been changed in directions suggested by the forces. In tensor-LEED terminology (and this is the way we implement NanoTensorLEED), this is equivalent to recalculate LEED intensities for a completely new reference structure after all atoms have been moved in directions suggested by the steepest descent of the R-factor for the reference structure, which is calculated using tensor LEED: thus a new reference structure calculation is performed after a single tensor LEED calculation.

Tensor LEED in the past has been used to obtain a relatively accurate approximation of the R-factor hypersurface close to a fixed “reference structure”: using that approximation a nearby R-factor minimum is found by multiple tensor LEED calculations (usually within  $\sim 0.05$  nm of the reference structure, and usually without iterating the reference structure itself); one way to describe this is that tensor LEED gives a relatively accurate direction of steepest descent of the R-factor for the reference structure, leading sufficiently close to the desired minimum, in addition to providing relatively accurate intensities and R-factor values. Instead of this very local approach, we now expect to make larger steps beyond the range of accuracy of tensor LEED, where the direction of steepest descent can have changed substantially from that for the reference structure, and the intensities may be poorly represented by tensor LEED. We will not even attempt to calculate LEED intensities this way, but only the approximate steepest direction. And, since this steepest direction is not accurate far from a reference structure, there is a fortiori no point in calculating it with the usual accuracy. We may therefore use a simplified version of tensor LEED to obtain a rougher and faster estimate for that steepest direction: this is then adequate to move each atom in the proper general direction, after which a new reference structure is calculated, repeating the whole process iteratively. It is important to stress that this simplified version of tensor LEED is only used to obtain a direction of atomic movement, while the LEED intensities in the new reference structure are calculated without tensor LEED and thus without any tensor-LEED related approximations. Thus, our simplified tensor LEED method only affects the effectiveness of the search rather than the accuracy of the resulting optimum structure.

To apply this approach to our NanoLEED formalism, we start with the standard second-order tensor LEED method and assume that an incident electron beam is aimed at the analyzed sample. The incident electron wavefunction is a plane wave and can be written as

$$\phi_{in}(\vec{r}) = \langle \vec{r} | \phi_{in} \rangle = \langle \vec{r} | \vec{k}_{in} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}_{in}\vec{r}} \quad (13)$$

At the analyzer, the recorded electron’s wavefunction is

$$\phi_{sc}(\vec{R}_{sc}) = \langle \vec{R}_{sc} | \phi_{sc} \rangle. \quad (14)$$

The scattered electron state can be written as a function of the incident state and of the transition operator of the cluster:



$$|\phi_{sc}\rangle = (1 + G_o T)|\phi_{in}\rangle. \quad (15)$$

However, as in LEED the electrons reaching the analyzer have all been scattered, the last equation becomes

$$|\phi_{sc}\rangle = G_o T|\phi_{in}\rangle. \quad (16)$$

So the scattered wavefunction of an electron reaching the analyzer can be written as

$$\phi_{sc}(\vec{R}_{sc}) = \langle \vec{R}_{sc} | G_o T | \phi_{in} \rangle. \quad (17)$$

At large  $R_{sc}$ , the asymptotic limit is valid:

$$\langle \vec{R}_{sc} | G_o = \frac{e^{ik_0 R_{sc}}}{k_0 R_{sc}} \langle \vec{k}_{sc} |, \quad (18)$$

where  $k_0 = |\vec{k}_{sc}| = |\vec{k}_{in}|$  and  $\vec{k}_{sc} = k_0 \hat{R}_{sc}$ .

The scattered wavefunction is then

$$\phi_{sc}(\vec{R}_{sc}) = \frac{e^{ik_0 R_{sc}}}{k_0 R_{sc}} \langle \vec{k}_{sc} | T | \vec{k}_{in} \rangle \equiv \frac{e^{ik_0 R_{sc}}}{k_0 R_{sc}} f(\Omega_{sc}). \quad (19)$$

where  $f(\Omega_{sc}) = \frac{1}{k_0} \langle \vec{k}_{sc} | T | \vec{k}_{in} \rangle$  is the angular scattering distribution [20].

As stated in the previous section, the cluster's scattering matrix in the reference configuration (i.e., before atoms are displaced) is

$$T = \sum_i \bar{T}_i = \sum_i Tr(\vec{R}_i) T_i Tr(-\vec{R}_i), \quad (20)$$

while in the modified configuration (i.e., after atoms are displaced) it will be

$$T' = \sum_i \bar{T}'_i = \sum_i Tr(\vec{R}_i + \delta\vec{R}_i) T'_i Tr(-\vec{R}_i - \delta\vec{R}_i). \quad (21)$$

The multiple scattering self-consistent equations are, for the reference and the modified configurations, respectively:

$$\bar{T}_i = \bar{t}_i + \sum_{j \neq i} \bar{t}_j G_o \bar{T}_j, \quad \text{with } \bar{T}_i = Tr(\vec{R}_i) T_i Tr(-\vec{R}_i) \quad (22)$$

and

$$\bar{T}_i = \bar{t}_i + \sum_{j \neq i} \bar{t}_j G_o \bar{T}_j, \text{ with } \bar{T}_i = \text{Tr}(\bar{R}_i + \delta \bar{R}_i) T_i \text{Tr}(-\bar{R}_i - \delta \bar{R}_i). \quad (23)$$

The corresponding expansions in multiple scattering series are

$$\bar{T}_i = \bar{t}_i + \sum_{j \neq i} \bar{t}_j G_o \bar{t}_j + \sum_{j \neq i} \sum_{k \neq j} \bar{t}_j G_o \bar{t}_j G_o \bar{t}_k + \dots \quad (24)$$

and

$$\bar{T}_i = \bar{t}_i + \sum_{j \neq i} \bar{t}_j G_o \bar{t}_j + \sum_{j \neq i} \sum_{k \neq j} \bar{t}_j G_o \bar{t}_j G_o \bar{t}_k + \dots. \quad (25)$$

If we adopt the same approximation level as in second-order tensor LEED [9], the multiple scattering in the reference and in the modified configurations are the same, except for one displaced atom, which we here take to be the last scattering atom. Thus:

$$\begin{aligned} & \bar{t}_i + \sum_{j \neq i} \bar{t}_j G_o \bar{t}_j + \sum_{j \neq i} \sum_{k \neq j} \bar{t}_j G_o \bar{t}_j G_o \bar{t}_k + \dots \\ & \cong \bar{t}'_i + \sum_{j \neq i} \bar{t}_j G_o \bar{t}_j + \sum_{j \neq i} \sum_{k \neq j} \bar{t}_j G_o \bar{t}_j G_o \bar{t}_k + \dots \end{aligned} \quad (26)$$

Since we here only allow the last scattering atom,  $i$ , to be displaced, this approximation includes only those paths that end at a displaced atom. The missing paths are those that start at a displaced atom, such as  $i$ , scatter through the cluster and end at the detector; for reasons of computational cost, to be further explained later, we will neglect these other paths starting at atom  $i$ . Note that in equation 26, if a path scatters from any *displaced* atoms *before* reaching atom  $i$ , we assume that these atoms still have their *undisplaced* location during such earlier scattering.

This means that for the reference and modified structures one has

$$\begin{cases} \bar{T}_i = \bar{t}_i + \sum_{j \neq i} \bar{t}_j G_o \bar{T}_j \\ \bar{T}'_i \cong \bar{t}'_i + \sum_{j \neq i} \bar{t}_j G_o \bar{T}_j \end{cases} \quad (27)$$

In this approximation, the change in angular scattering distribution only depends on  $\delta \bar{t}_i$  and has an expression similar to equation 2 of ref. 8:

$$\delta f(\Omega) = \left\langle \bar{k}_{sc} \left| \sum_i \{(\bar{t}'_i - \bar{t}_i) [1 + \sum_{j \neq i} G_o^{ij} \bar{T}_j]\} \right| \bar{k}_m \right\rangle, \quad (28)$$

where  $|\vec{k}_{in}\rangle$  and  $|\vec{k}_{sc}\rangle$  represent plane waves in our case. Taking into account that

$$Tr(\vec{R}_i + \delta\vec{R}_i) = Tr(\vec{R}_i)Tr(\delta\vec{R}_i) = Tr(\delta\vec{R}_i)Tr(\vec{R}_i) \quad (29)$$

we obtain

$$\begin{aligned} \delta f(\Omega) = & \\ & \sum_i \left\{ \sum_{L,L'} a'_{iL} \langle k_o; L | -t_i + Tr(\delta\vec{R}_i) t_i Tr(-\delta\vec{R}_i) | L' \rangle [a_{iL'} + \sum_{j \neq i} \sum_{L''} G_{o:L,L''}^{ij} (\vec{R}_j - \vec{R}_i) T_{j:L''}(\vec{R}_j)] \right\} \end{aligned} \quad (30)$$

Here  $G_{o:L,L''}^{ij}(\vec{R}_j - \vec{R}_i)$  is a matrix element (in spherical-wave basis set) of the free-space propagator,  $T_{j:L''}(\vec{R}_j) = \langle k_o; L'' | T_j Tr(-\vec{R}_j) | \vec{k}_{in} \rangle$  is the result vector of the UV-SMCG algorithm,

$$\langle k_o; L | -t_i + Tr(\delta\vec{R}_i) t_i Tr(-\delta\vec{R}_i) | k_o; L' \rangle = -t_{iL} \delta_{LL'} + \sum_{L''} J_{L,L''}(\delta\vec{R}_i) t_{iL''} J_{L'',L'}(-\delta\vec{R}_i) \quad (31)$$

and

$$J_{L,L''}(\delta\vec{R}_i) = 4\pi \sum_{L'''} i^{l'''} j_{l'''}(k_o | \delta\vec{R}_i | Y_{L''}(\delta\vec{R}_i) a(L, L', L'''), \quad (32)$$

where  $a(L, L', L''')$  is a Clebsch-Gordan coefficient.

In equation 30, the first term between square brackets,  $a_{iL'}(\vec{k}_{in})$ , is the incident unscattered wave on atom  $i$ , while the second term includes all scattering paths leading to atom  $i$  (note that both these terms exclude scattering by atom  $i$ ).

In conventional tensor LEED,  $a'_{iL}(\vec{k}_{sc})$  represents the fully scattered “time-reversed” LEED state (as if electrons were traveling from the detector to atom  $i$ , including any number of scatterings along the way): this must be calculated for each desired exit direction (each measured beam), which can be done efficiently since the layer-scattering matrices need not be recomputed for each such direction if the surface has two-dimensional periodicity. With NanoLEED, there would be no analogous saving in recomputing  $a'_{iL}(\vec{k}_{sc})$ , since no periodic layers are defined, so that each exit direction would require a complete “time-reversed” NanoLEED calculation, a prohibitive cost. However, we need less accuracy than with tensor LEED (because we only need to find the approximate direction of steepest descent of the R-factor), so we may approximate

$a'_{i:L}(\vec{k}_{sc})$  to be the unscattered wave traveling directly between atom  $i$  and the detector, as we already did in deriving equation 28:

$$a'_{i:L}(\vec{k}_{sc}) \equiv \langle \vec{k}_{sc} | Tr(\vec{R}_i) | k_0; L \rangle = \frac{1}{k_0} e^{-i\vec{k}_{sc}\vec{R}_i} Y_L^*(\hat{k}_{sc}) \quad (33)$$

We have assumed a plane-wave final state in our derivation, since this choice is convenient for a distant detector. But if the detector were a nearby atom (as could happen in techniques like x-ray absorption fine structure), then a single plane wave would not suffice to describe the near-field behavior of the scattered wave: one could then work in the spherical-wave representation from equation 18 onward.

A similar expression holds for  $a_{i:L'}$ :

$$a_{i:L'}(\vec{k}_{in}) \equiv \langle k_0; L' | Tr(-\vec{R}_i) | \vec{k}_{in} \rangle = \frac{1}{k_0} e^{i\vec{k}_{in}\vec{R}_i} Y_{L'}(\hat{k}_{in}) \quad (34)$$

Equation 30 can now be expanded by the same scheme described in Ref. 8 and a tensor can be calculated for NanoTensorLEED. In particular, we can perform the series expansion over Cartesian coordinates shown in equations 23 and 34-35 of Ref. 8. If we further restrict the result to the lowest-order terms of this expansion, we obtain a simplified linear tensor LEED result.

Equation 30 is efficient for determining the change of LEED intensity, and hence change of R-factor, due to a small structural change, because the computationally expensive quantities  $G_{o:L,L'}^{ij}(\vec{R}_j - \vec{R}_i)$  and  $T_{j:L'}(\vec{R}_j)$  are obtained as part of the NanoLEED calculation for the reference structure and do not depend on the structural changes being explored. It is therefore a good basis for automated structural optimization.

## 5. Conclusions

We have described two very useful extensions of our NanoLEED methodology. The first allows overcoming poor convergence of multiple scattering in small atomic subclusters. And the second permits the efficient application of directed search methods based on using a downward sloping target function, the R-factor. These extensions bring the structural determination of nanostructures one step closer: the main challenge ahead is experimental rather than theoretical or computational, as discussed at some length in our earlier papers [1-3].

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