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Treatment of thermal vibrations and local static disorder within tensor LEED

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A general formalism is developed to include thermal vibrations and local static disorder into tensor-LEED calculations. The given expression for the averaged t matrix is based on a cumulant expansion for the probability distribution of atomic displacements. The method is a generalization of the concept of temperature-dependent scattering phase shifts and allows an efficient description of both anisotropy and anharmonicity of thermal motions, which are important in particular for adsorbate atoms and substrate atoms in the topmost layers.

I. INTRODUCTION

Thermal vibrations have a considerable effect on low-energy electron diffraction (LEED). As the temperature of the sample is increased, the intensity of the LEED beams becomes weaker, the spots are slightly broadened, and the background intensity between the spots is enhanced.[1–3] In a single scattering theory the influence of harmonic lattice vibrations can be described by Debye-Waller factors, as they are used for x-ray diffraction. Within a multiple scattering situation, which is characteristic for LEED, it is much more complicated to include thermal vibrations correctly into the scattering theory. The standard procedure in dynamical LEED calculations is to use temperature-dependent scattering phase shifts, which describe the scattering properties of a vibrating atom. This approach relies on the assumption that the thermal vibrations of different atoms are uncorrelated, which is certainly not true for near neighbors. Only isotropic harmonic vibrations can be treated within this framework. Obviously, much of the difficulties one encounters by generalizing this concept to arbitrary thermal motions result from the fact that anisotropic vibrations disturb the spherical symmetry of the atomic potentials and lead to nondiagonal t matrices for the scattering atoms.

From local electron diffraction techniques such as surface extended x-ray-absorption fine structure (SEXAFS) and photoelectron diffraction, it is well known that the anisotropy in the thermal vibrations of surface atoms can have a measurable influence on the spectra. Vibrational components parallel and perpendicular to the surface have been investigated in several adsorbate systems by SEXAFS (Refs. 4-7) and by scanned-energy mode photoelectron diffraction.[8,9]

The traditional restriction to isotropic harmonic vibrations can certainly be the reason for a number of bad R factors in LEED structure determinations. There are only a few attempts to go beyond this barrier and to consider anisotropic vibrations: A direct method has been developed in Ref. 10 by which a probability distribution of the surface atoms can be obtained from LEED measurements. For CO on Ru(0001) it has been shown in Ref. 11 that the inclusion of anisotropic vibrations of the molecule by means of a "split position" method can improve the R factor significantly. The standard LEED codes[2] offer only the possibility that the layer diffraction matrices are multiplied by anisotropic Debye-Waller factors, whereas the anisotropy of thermal motions has to be neglected for all intralayer scattering events.

In recent years, the tensor-LEED method has been established as a new basis for LEED data analysis.[12–15] This perturbation technique is designed to treat nondiagonal t matrices, which originate from atomic displacements. Many recent structure determinations for complex surfaces have shown that tensor-LEED works very efficient as long as the displacement vectors are within the range of validity of this approximation.

In the present paper, we develop a general expression for an averaged t matrix, which is based on a cumulant expansion. Hence, arbitrary probability distributions of atomic positions can be described. The new method provides a numerically efficient way to include anisotropic vibrations into a multiple scattering theory and, in particular, into existing tensor-LEED codes. Furthermore, also anharmonic contributions can be taken into account. These terms have proven to be important in EXAFS and SEXAFS spectroscopy.[16–26]

II. AVERAGED t MATRIX

The LEED wave field is given by a sum over all possible scattering paths which the electron can take hypothetically on its way through the sample. These contributions consist of terms such as

$$\ldots t_k G_{kj} t_j G_{ji} \ldots \;, \tag{1}$$

where t_j describes the scattering properties of the atom at position $\mathbf{R}_j$ and G_{ji} is the free electron propagator between the atoms $\mathbf{R}_i$ and $\mathbf{R}_j$. The Green function of free electrons with a given kinetic energy $E=(\hbar k)^2/2m$ can be expressed by an integral over the eigenvalues and eigenfunctions:

$$G(\mathbf{R}_j+\mathbf{r}',\mathbf{R}_i+\mathbf{r}) = \int \frac{d^3k'}{(2\pi)^3}\, \frac{e^{i\mathbf{k}'\cdot(\mathbf{R}_{ji}+\mathbf{r}'-\mathbf{r})}}{k^2-k'^2+i\varepsilon} \;, \tag{2}$$

where the limit $\varepsilon \to 0$ has to be taken so that ε is always a real positive quantity. $\mathbf{R}_{ji} = \mathbf{R}_j - \mathbf{R}_i$ is the vector between the two atomic positions. We transform this two-center representation of the Green function G_{ji} with the help of

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_L i^l j_l(kr) Y_L^*(\mathbf{k}) Y_L(\mathbf{r}) \tag{3}$$

into

$$\begin{aligned} G(\mathbf{R}_j + \mathbf{r}', \mathbf{R}_i + \mathbf{r}) \\ &= \sum_{L''} i^{l''} Y_{L''}^*(\mathbf{R}_{ji}) \\ &\quad \times \int \frac{d^3k'}{2\pi^2} j_{l''}(k'R_{ji}) Y_{L''}(\mathbf{k}') \frac{e^{i\mathbf{k}'\cdot(\mathbf{r}'-\mathbf{r})}}{k^2 - k'^2 + i\varepsilon} \ , \end{aligned} \tag{4}$$

where the abbreviation $L = (l, m)$ has been used. Under the condition $r + r' < R_{ji}$ we can calculate the integral over the modulus of $\mathbf{k}'$ using Cauchy's residue theorem. The result is

$$\begin{aligned} G(\mathbf{R}_j + \mathbf{r}', \mathbf{R}_i + \mathbf{r}) = \frac{-ik}{4\pi} \sum_{L''} i^{l''} h_{l''}(kR_{ji}) Y_{L''}^*(\mathbf{R}_{ji}) \\ \times \int d\Omega_{\mathbf{k}} Y_{L''}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})} \ , \end{aligned} \tag{5}$$

from which we obtain immediately by means of Eq. (3) the standard expression for a two-center angular-momentum representation of the Green function:

$$\begin{aligned} G(\mathbf{R}_j + \mathbf{r}', \mathbf{R}_i + \mathbf{r}) = -ik \sum_{L'L} j_{l'}(kr') Y_{L'}(\mathbf{r}') \\ \times G_{L'L}(\mathbf{R}_{ji}) j_l(kr) Y_L^*(\mathbf{r}) \end{aligned} \tag{6}$$

with

$$\begin{aligned} G_{L'L}(\mathbf{R}) = 4\pi \sum_{L''} i^{l'-l+l''} h_{l''}(kR) Y_{L''}^*(\mathbf{R}) \\ \times \int d\Omega Y_{L'}^* Y_{L''} Y_L . \end{aligned} \tag{7}$$

If the scattering atoms are displaced from their positions $\mathbf{R}_j^0$ in a reference system, i.e., for

$$\mathbf{R}_j = \mathbf{R}_j^0 + \mathbf{u}_j \ , \tag{8}$$

the matrix $G_{L'L}(\mathbf{R}_{ji})$ can be factorized into

$$\underline{G}(\mathbf{R}_{ji}) = \underline{J}(\mathbf{u}_j) \underline{G}(\mathbf{R}_{ji}^0) \underline{J}(-\mathbf{u}_i) \ , \tag{9}$$

where underlined quantities denote matrices in the L space. In order to derive this result, we start from Eq. (5),

$$\begin{aligned} G(\mathbf{R}_j + \mathbf{r}', \mathbf{R}_i + \mathbf{r}) = \frac{-ik}{4\pi} \sum_{L''} i^{l''} h_{l''}(kR_{ji}^0) Y_{L''}^*(\mathbf{R}_{ji}^0) \\ \times \int d\Omega_{\mathbf{k}} Y_{L''}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{u}_j+\mathbf{r}'-\mathbf{u}_i-\mathbf{r})}, \end{aligned} \tag{10}$$

and rewrite the plane waves under the integral using the completeness relation of the spherical harmonics as

$$e^{i\mathbf{k}\cdot(\mathbf{u}_j+\mathbf{r}')} = \int d\Omega_{\mathbf{k}'} \sum_L Y_L^*(\mathbf{k}') Y_L(\mathbf{k}) e^{i\mathbf{k}'\cdot(\mathbf{u}_j+\mathbf{r}')}, \tag{11}$$

where the modulus of $\mathbf{k}'$ is equal to the wave number k. Finally, we obtain Eq. (9) and

$$J_{L'L}(\mathbf{u}) = i^{l'-l} \int d\Omega_{\mathbf{k}} Y_{L'}^*(\mathbf{k}) Y_L(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{u}} \ . \tag{12}$$

The LEED wave field, Eq. (1), can now be expressed by propagators between the positions in the reference system $\mathbf{R}_j^0$ and modified t matrices which have the displacements $\mathbf{u}_j$ built in,

$$\underline{t}_j(\mathbf{u}_j) = \underline{J}(-\mathbf{u}_j) \underline{t}_j^0 \underline{J}(\mathbf{u}_j) \ . \tag{13}$$

Usually, the scattering potentials are assumed to be spherical symmetric. Then the matrix $\underline{t}_j^0$ is diagonal with respect to the quantum numbers l and m and the matrix elements are determined by the scattering phase shifts η_l:

$$t_{L'L}^0 = t_l^0 \delta_{L',L} = i \sin \eta_l e^{i\eta_l} \delta_{L',L} \ . \tag{14}$$

However, any displacement $\mathbf{u}_j$ destroys this spherical symmetry of the scatterer so that the matrix $\underline{t}_j(\mathbf{u}_j)$ of the shifted muffin-tin potential will contain off-diagonal terms which are nonzero.

The influence of thermal motions or local static disorder on LEED intensities can be taken into account by using averaged t matrices in the calculation of the wavefield,

$$\underline{T}_j = \langle \underline{t}_j(\mathbf{u}_j) \rangle_{\mathbf{u}_j} = \langle \underline{J}(-\mathbf{u}_j) \underline{t}_j^0 \underline{J}(\mathbf{u}_j) \rangle_{\mathbf{u}_j} \ . \tag{15}$$

If the vibrations are harmonic and isotropic, the matrix $\underline{T}_j$ has the same structure as $\underline{t}_j^0$, i.e., it is diagonal in the indices l and m (see Sec. V). Hence, one can simply use $\underline{T}_j$ instead of $\underline{t}_j^0$ in the multiple scattering programs. This is the standard technique by which thermal vibrations are included into dynamical LEED calculations.[1-3]

Obviously, this approach is only an approximation, since all correlations between the displacements of different atoms as well as the self-correlation of an atom which occurs in more than one factor of an intensity contribution are neglected. There is little chance to go beyond this concept within the framework of a full multiple scattering theory. The errors which may result in LEED intensities from the assumption that the atomic displacements are totally uncorrelated have been discussed in more detail in Ref. 1.

In the following sections we describe a technique, which allows an efficient calculation of the averaged t matrix, defined in Eq. (15), for an arbitrary distribution of atomic displacements $\mathbf{u}_j$.

III. CALCULATION TECHNIQUE

The matrix $\underline{J}(\mathbf{u})$ obeys the differential equations

$$\frac{\partial}{\partial u_\alpha}\underline{J}(\mathbf{u}) = ik\underline{M}^\alpha \underline{J}(\mathbf{u}) \,, \tag{16}$$

where u_α is one of the Cartesian coordinates of $\mathbf{u}$. This set of equations is obtained from Eq. (12) by expressing the coordinates k_α in terms of $Y_{(1,m)}(\mathbf{k})$ and using the completeness relation for spherical harmonics. The matrices $\underline{M}^\alpha$ are given by

$$M^z_{L'L} = i^{l'-l}\sqrt{\frac{4\pi}{3}}\int d\Omega\; Y^*_{L'}Y_L Y_{1,0}, \tag{17}$$

$$\underline{M}^x = \frac{1}{\sqrt{2}}(\underline{M}^- - \underline{M}^+), \tag{18}$$

$$\underline{M}^y = \frac{i}{\sqrt{2}}(\underline{M}^- + \underline{M}^+), \tag{19}$$

with

$$M^\pm_{L'L} = i^{l'-l}\sqrt{\frac{4\pi}{3}}\int d\Omega\; Y^*_{L'}Y_L Y_{1,\pm 1} \,. \tag{20}$$

It can be shown that these matrices commute with each other,

$$[\underline{M}^\alpha, \underline{M}^\beta] = 0 \,. \tag{21}$$

The set of linear differential equations for $\underline{J}(\mathbf{u})$, Eq. (16), has a unique solution which is determined by the initial value. Obviously,

$$\underline{J}(\mathbf{u}) = \exp\left(ik\sum_\alpha u_\alpha \underline{M}^\alpha\right) \tag{22}$$

satisfies both Eq. (16) and the condition imposed by Eq. (12) for the initial value at $\mathbf{u} = \mathbf{0}$,

$$\underline{J}(\mathbf{0}) = \underline{I} \,. \tag{23}$$

The resulting expression for the t matrix of a displaced atom, Eq. (13),

$$\underline{t}(\mathbf{u}) = \exp\left(-ik\sum_\alpha u_\alpha \underline{M}^\alpha\right)\underline{t}^0 \exp\left(ik\sum_\beta u_\beta \underline{M}^\beta\right) \,, \tag{24}$$

can be simplified using the Cambell-Baker-Hausdorff theorem

$$\begin{aligned}\exp(x\underline{A})\underline{B}\exp(-x\underline{A}) &= \underline{B} + x[\underline{A},\underline{B}] + \frac{x^2}{2!}\,[\underline{A},[\underline{A},\underline{B}]] \\ &\quad + \frac{x^3}{3!}\,[\underline{A},[\underline{A},[\underline{A},\underline{B}]]] + \dots \\ &= \exp\left(x[\underline{A},\bullet]\right)\underline{B}.\end{aligned} \tag{25}$$

Since we have

$$[\underline{M}^\alpha,[\underline{M}^\beta,\underline{A}]] = [\underline{M}^\beta,[\underline{M}^\alpha,\underline{A}]] \,, \tag{26}$$

this leads directly to

$$\underline{t}(\mathbf{u}) = \exp\left(-ik\sum_\alpha u_\alpha\,[\underline{M}^\alpha,\bullet]\right)\underline{t}^0 \,. \tag{27}$$

This formula has been used by Oed *et al.* for an expansion of tensor-LEED in Cartesian coordinates.[27] The matrix $\underline{t}(\mathbf{u})$ has to be calculated by a series of commutators as shown in Eq. (25). Computationally this procedure is very efficient, since the majority of matrix elements in the $\underline{M}^\alpha$ is zero. Explicit expressions for the nonvanishing elements are given below:

$$\begin{aligned}M^\pm_{L'L} &= i\sqrt{\frac{(l\mp m)(l\mp m-1)}{2(2l-1)(2l+1)}}\,\delta_{l,l'+1}\delta_{m,m'\mp 1} \\ &\quad + i\sqrt{\frac{(l\pm m+1)(l\pm m+2)}{2(2l+1)(2l+3)}}\,\delta_{l,l'-1}\delta_{m,m'\mp 1},\end{aligned} \tag{28}$$

$$\begin{aligned}M^z_{L'L} &= -i\sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}}\,\delta_{l,l'+1}\delta_{m,m'} \\ &\quad + i\sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}}\,\delta_{l,l'-1}\delta_{m,m'}.\end{aligned} \tag{29}$$

IV. HARMONIC VIBRATIONS

If $\mathbf{u}$ is the time-dependent amplitude of an harmonic vibration around the mean value $\langle\mathbf{u}\rangle = \mathbf{0}$, then the average over a phase factor is determined by the mean square displacements (see, e.g., Ref. 28),

$$\left\langle \exp\left(-i\sum_\alpha k_\alpha u_\alpha\right)\right\rangle = \exp\left(-\frac{1}{2}\sum_{\alpha,\beta}\langle u_\alpha u_\beta\rangle\, k_\beta k_\alpha\right) \,. \tag{30}$$

This result can be generalized to the matrix expression of $\underline{t}(\mathbf{u})$, Eq. (27), and we obtain for the averaged t matrix:

$$\underline{T} = \exp\left(-\frac{1}{2}k^2\sum_{\alpha,\beta}\langle u_\alpha u_\beta\rangle\,[\underline{M}^\beta,[\underline{M}^\alpha,\bullet]]\right)\underline{t}^0 \,. \tag{31}$$

The analogy between these two equations is essentially based on the commutative law for the matrices $\underline{M}^\alpha$ in commutator expressions, Eq. (26). The mean square displacement tensor $\langle u_\alpha u_\beta\rangle$ is symmetric with respect to the indices α and β, and we can find a coordinate system (principal axes) in which it is diagonal,

$$\langle u_\alpha u_\beta\rangle = \langle u_\alpha^2\rangle\delta_{\alpha,\beta} \,. \tag{32}$$

In practical calculations $\underline{T}$ is evaluated by a series of commutators,

$$\underline{T} = \sum_n \underline{T}^{(n)} , \tag{33}$$

where the $\underline{T}^{(n)}$ are obtained by the recurrence relation

$$\underline{T}^{(n+1)} = -\frac{k^2}{2(n+1)} \sum_\alpha \langle u_\alpha^2 \rangle (\underline{M}^\alpha \underline{M}^\alpha \underline{T}^{(n)} + \underline{T}^{(n)} \underline{M}^\alpha \underline{M}^\alpha - 2\underline{M}^\alpha \underline{T}^{(n)} \underline{M}^\alpha) . \tag{34}$$

The recursion starts with the t matrix of the nonvibrating atom,

$$\underline{T}^{(0)} = \underline{t}^0 . \tag{35}$$

The value of n needed for convergence in Eq. (33) depends essentially on the argument $k^2\langle \mathbf{u}^2 \rangle/3$. The first term $\underline{T}^{(0)}$ is diagonal in the indices l and m. As the order n increases, however, more and more off-diagonal positions in $\underline{T}$ will be occupied by nonvanishing elements. All nonzero values of $T^{(n)}_{L'L}$ occur in a region near the diagonal which is determined by the condition $|l - l'| \leq 2n$.

V. ISOTROPIC HARMONIC VIBRATIONS

In this section, we will show that $\underline{T}$ is a diagonal matrix for isotropic harmonic vibrations and we will recover the formula for the diagonal elements which usually has been used in LEED theory[1–3] from the results given above.

For isotropic vibrations we have

$$\langle u_\alpha u_\beta \rangle = \langle u^2 \rangle \delta_{\alpha,\beta} . \tag{36}$$

The first step of the recursion, Eq. (34), gives

$$\underline{T}^{(1)} = -\frac{k^2 \langle u^2 \rangle}{2} \sum_\alpha (\underline{M}^\alpha \underline{M}^\alpha \underline{t}^0 + \underline{t}^0 \underline{M}^\alpha \underline{M}^\alpha - 2\underline{M}^\alpha \underline{t}^0 \underline{M}^\alpha) . \tag{37}$$

From the definition of $\underline{M}^\alpha$ in Sec. III follows

$$\sum_\alpha \underline{M}^\alpha \underline{M}^\alpha = \underline{I} , \tag{38}$$

where $\underline{I}$ is the identity matrix in the L space. The last term in Eq. (37),

$$\sum_\alpha \sum_{L''} M^\alpha_{L'L''} t^0_{l''} M^\alpha_{L''L} = \sum_{\mu=-1}^{1} \sum_{L''} \frac{4\pi}{3} i^{l'-l} t^0_{l''} \int d\Omega \, Y^*_{L'} Y_{L''} Y_{1\mu} \times \int d\Omega \, Y^*_{L''} Y_L Y^*_{1\mu}, \tag{39}$$

can be simplified using $3j$ symbols. With

$$\int d\Omega \, Y^*_L Y_{L'} Y_{L''} = (-1)^m \sqrt{\frac{(2l+1)(2l'+1)(2l''+1)}{4\pi}} \times \begin{pmatrix} l & l' & l'' \\ -m & m' & m'' \end{pmatrix} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \tag{40}$$

and

$$\sum_{m_1 m_2} \begin{pmatrix} l_1 & l_2 & l \\ -m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l' \\ -m_1 & m_2 & m' \end{pmatrix} = \frac{\delta_{ll'} \delta_{mm'}}{2l+1} , \tag{41}$$

we obtain

$$T^{(1)}_{L'L} = -k^2 \langle u^2 \rangle \left[t^0_l - \sum_{l''} (2l''+1) t^0_{l''} \times \begin{pmatrix} l & l'' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \right] \delta_{L',L} . \tag{42}$$

This proves that $\underline{T}^{(1)}$, and subsequently all other $\underline{T}^{(n)}$ are diagonal with respect to the quantum numbers l and m.

In order to transform the diagonal elements of $\underline{T}$ into the familiar form, we introduce two submatrices of $\underline{J}$ and $\underline{M}^\alpha$, which describe one-dimensional displacements along the z axis of the coordinate system:

$$j_{l'l}(ku) = J_{l'0,l0}(u\mathbf{e}_z) , \tag{43}$$

$$m_{l'l} = M^z_{l'0,l0} . \tag{44}$$

According to Eq. (22) they are connected by

$$\underline{j}(ku) = \exp(iku\underline{m}) . \tag{45}$$

Similar formulas have been used earlier in EXAFS theory.[21]

An explicit expression for $\underline{m}$ is

$$m_{l'l} = i^{l'-l} \sqrt{(2l'+1)(2l+1)} \begin{pmatrix} l' & l & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 , \tag{46}$$

where Eq. (40) has been used. Now, we can write the diagonal elements of the first term, given in Eq. (42), with the help of $\underline{m}$ and an additional transformation matrix $\underline{a}$:

$$T^{(1)}_{L'L} = T^{(1)}_l \delta_{l',l} \delta_{m',m} , \tag{47}$$

$$T^{(1)}_{l'} = -k^2 \langle u^2 \rangle \sum_l \{\underline{I} - \underline{a}^{-1} \underline{m}\, \underline{a}\}_{l'l} t^0_l , \tag{48}$$

where $\underline{a}$ is defined by

$$a_{l'l} = i^l \sqrt{2l+1} \delta_{l'l} . \tag{49}$$

From Eq. (31) follows for the total averaged t matrix of an isotropically vibrating muffin-tin potential:

$$T_{L'L} = T_l \delta_{l',l} \delta_{m',m} , \tag{50}$$

$$T_{l'} = \sum_{l} \{\exp[-k^2\langle u^2\rangle(\underline{I} - \underline{a}^{-1}\underline{m}\,\underline{a})]\}_{l'l} t_l^0 \ . \tag{51}$$

Application of Eq. (45) leads to

$$T_{l'} = e^{-k^2\langle u^2\rangle} \sum_{l} \{\underline{a}^{-1}\underline{j}(-ik^2\langle u^2\rangle)\underline{a}\}_{l'l} t_l^0 \ . \tag{52}$$

The integral representation for $\underline{J}(\mathbf{u})$ given in Eq. (12) can be transformed into

$$J_{L'L}(\mathbf{u}) = 4\pi \sum_{L''} i^{l'-l+l''} j_{l''}(ku) Y^*_{L''}(\mathbf{u}) \times \int d\Omega \, Y^*_{L'} Y_{L''} Y_L \tag{53}$$

by expanding the plane wave with the help of Eq. (3). We need only the special case

$$j_{l'l}(ku) = \sum_{l''} i^{l'-l+l''} (2l''+1) j_{l''}(ku) \times \sqrt{(2l'+1)(2l+1)} \begin{pmatrix} l' & l'' & l \\ 0 & 0 & 0 \end{pmatrix}^2 \tag{54}$$

to obtain finally for the diagonal elements

$$T_{l'} = e^{-k^2\langle u^2\rangle} \sum_{ll''} i^{l''} j_{l''}(-ik^2\langle u^2\rangle) \times (2l''+1)(2l+1) \begin{pmatrix} l' & l'' & l \\ 0 & 0 & 0 \end{pmatrix}^2 t_l^0, \tag{55}$$

which is the standard formula used in LEED theory.[1]

VI. ARBITRARY PROBABILITY DISTRIBUTION

The results of Sec. IV can be extended to the case that we have to average the t matrix over a more general probability distribution of atomic displacements, which describes for instance anharmonic vibrations or a structural disorder with some kind of asymmetry. For this purpose we use the method of cumulants[29] (see the Appendix for basic formulas). The cumulants of a three-dimensional distribution function $P(\mathbf{u})$ are defined by

$$\Phi(\mathbf{k}) = \exp\left({\sum_{n_x n_y n_z}}' \frac{(-i)^{n_x+n_y+n_z}}{n_x! n_y! n_z!} \langle u_x^{n_x} u_y^{n_y} u_z^{n_z} \rangle_c \times k_x^{n_x} k_y^{n_y} k_z^{n_z} \right) , \tag{56}$$

where

$$\Phi(\mathbf{k}) = \langle e^{-i\mathbf{k}\cdot\mathbf{u}} \rangle = \int d^3u \, P(\mathbf{u}) e^{-i\mathbf{k}\cdot\mathbf{u}} \tag{57}$$

is the generating or characteristic function. ${\sum}'_{n_x n_y n_z}$ means a summation $\sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty}$ from which the term $n_x = n_y = n_z = 0$ is excluded. The cumulants $\langle u_x^{n_x} u_y^{n_y} u_z^{n_z} \rangle_c$ are denoted by the subscript c in order to distinguish them from the ordinary moments.[29] From a given set of cumulants we can obtain the probability distribution simply by a Fourier transform,

$$P(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3k \, e^{i\mathbf{k}\cdot\mathbf{r}} \Phi(\mathbf{k}) \ . \tag{58}$$

If we use cumulants to characterize the distribution of displacements, the averaged t matrix follows in analogy to Eq. (31):

$$\underline{T} = \exp\left({\sum_{n_x n_y n_z}}' \frac{(-ik)^{n_x+n_y+n_z}}{n_x! n_y! n_z!} \langle u_x^{n_x} u_y^{n_y} u_z^{n_z} \rangle_c \times [\underline{M}^z, [\underline{M}^y, [\underline{M}^x, \bullet]_{n_x}]_{n_y}]_{n_z} \right) \underline{t}^0 \ , \tag{59}$$

where $[\underline{A}, \underline{B}]_n$ is defined by

$$[\underline{A}, \underline{B}]_n = [\underline{A}, [\underline{A}, \underline{B}]_{n-1}] \tag{60}$$

and

$$[\underline{A}, \underline{B}]_0 = \underline{B} \ . \tag{61}$$

This formula contains static displacements $\langle u_\alpha \rangle = \langle u_\alpha \rangle_c$, the mean square displacements of harmonic vibrations, and all types of higher order corrections.

VII. DISCUSSION

We have presented a new method for averaging an atomic t matrix over an arbitrary distribution of displacements. The resulting averaged t matrix can be used in any multiple scattering formalism for LEED, photoelectron diffraction, and EXAFS.

An application to tensor-LEED seems to be particularly promising, since here the full multiple scattering problem is solved only once for a reference system, and all displacements of scattering atoms can be treated by a perturbation theory. This concept opens the possibility to vary a large number of structural parameters at relatively low costs. This has been demonstrated by many structure determinations of complex systems. The described cumulant expansion for the t matrix extends the parameter space beyond static structure models to all types of thermal and local static disorder at surfaces. On the basis of high-quality LEED data, possibly temperature dependent, such a comprehensive fit between theory and experiment will certainly provide new insights into the dynamics of surface atoms. A recent study of surface atom vibrations, although restricted to isotropic harmonic vibrations, has shown that tensor LEED is a suitable basis for these investigations.[30]

The described concept has much in common with the direct method proposed by Pendry and co-workers.[10,27] The essential difference is, however, that the direct method is based on an expansion into moments, whereas the present theory makes use of cumulants. An obvious disadvantage of moments is that harmonic vibrations give rise to a series of higher order moments, as briefly shown in the Appendix. If harmonic vibrations with large amplitudes are present in the system, a user of the direct method would first have to determine a lot of higher order moments as independent parameters from the theory-experiment comparison and then to find out the correlations between them. In the cumulant expansion, only one parameter is required to describe a one-dimensional harmonic vibration, which allows a much better control of the fit between theory and experiment.

The newly derived formulas are a natural extension of the concept of temperature-dependent scattering phase shift. For isotropic harmonic vibrations they give the same results as the standard calculation technique used in existing LEED codes.

We propose to include the cumulants step by step into the fit procedure. First one should get the structure right (first order cumulants). Then one could include harmonic vibrations with anisotropic amplitudes (second order cumulants). Finally one can extend the optimization to selected anharmonic contributions. Anisotropy and anharmonicity will be important in particular for the adsorbate atoms, so that these effects will be concentrated in the fractional order beams. In general, we expect the harmonic contributions to be dominant. Therefore, the cumulants determined by the fit will give a probability distribution, Eq. (58), which is essentially a Gaussian function with small distortions and corrections.

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APPENDIX: METHOD OF CUMULANTS

The generating function

$$\Phi(k) = \langle e^{-ikx} \rangle = \int_{-\infty}^{+\infty} dx'\, P(x') e^{-ikx'} \ , \qquad \text{(A1)}$$

in which $P(x')$ is an arbitrary probability distribution, can be expanded either into moments

$$\Phi(k) = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle \qquad \text{(A2)}$$

or cumulants

$$\Phi(k) = \exp\left(\sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle_c \right) \ . \qquad \text{(A3)}$$

Obviously, the cumulants $\langle x^n \rangle_c$ can be expressed by moments $\langle x^{n'} \rangle$ with $n' \leq n$ and vice versa.

For a Gaussian distribution

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2} \right) \qquad \text{(A4)}$$

we get the moments

$$\langle x^{2m} \rangle = \frac{(2m)!}{m! 2^m} \left(\sigma^2\right)^m \ , \qquad \text{(A5)}$$

$$\langle x^{2m+1} \rangle = 0 \ , \qquad \text{(A6)}$$

and the generating function

$$\Phi(k) = \exp\left(-\frac{1}{2}\sigma^2 k^2 \right) \ , \qquad \text{(A7)}$$

which means that all cumulants higher than second order vanish (unlike the moments).

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