New Perturbative Approach to the Application of Low-Energy Electron Diffraction—the t-Matrix Formalism*

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We present a new t-matrix formulation of the perturbation approach to the theory of low-energy electron diffraction. Good agreement is obtained between theory and experiment for the (100) and (110) clean surfaces of aluminum and nickel. Speed and good convergence make it particularly suited to the analysis of overlayer structures.

Recently, there have been significant advances[1-9] in the formulation of a microscopic theory of low-energy electron diffraction (LEED) for clean metal surfaces. The realization of the importance of the microscopic ion-core scattering potential in defining the details of intensity-energy spectra is one such result. It has been shown that, when the ion-core potential is adequately provided for,[10] large improvements are obtained in the agreement between theory and experiment for both the primary and secondary structures of the intensity spectra. Both Fermi-energy potentials[2,4,8] and potentials constructed specifically to treat scattering at higher energies[1,3,6,9] have been effectively used in various microscopic models.

Because a microscopic model treats the many-body coherent and incoherent interactions of a large number of particles, such calculations typically involve matrix inversions of large dimensions. The importance of the ion-core potential requires that a large number of phase shifts be included to achieve a good representation of the scattering potential. An additional time-consuming factor is that the electron wave field inside the crystal is represented by a basis set of Bloch waves requiring a large number of Bloch waves (or beams) in the calculation. An unavoidable requirement is that the computation time for major parts of the computation goes up as L^3 and N^3, where L is the square of the number of phase shifts and N is the number of Bloch waves.

It is the purpose of this Letter to propose a new t-matrix approach of the perturbative method which is equally applicable to small (near normal) and to large (glancing) angles of incidence. A unique feature of the new method is that it contains no time-consuming matrix-inversion steps and can easily be extended to complicated overlayer systems. Inclusion of as many as 49 Bloch waves does not pose serious computer time or core-size problems.

The need for a fast computational method becomes particularly critical when structure-analysis applications are made to systems of overlayers on metals in which the existence of a smaller reciprocal lattice for the overlayer, the possibility of a smaller d spacing, or the addition of more planar structures (particularly in the case of reconstructed overlayers) greatly complicate

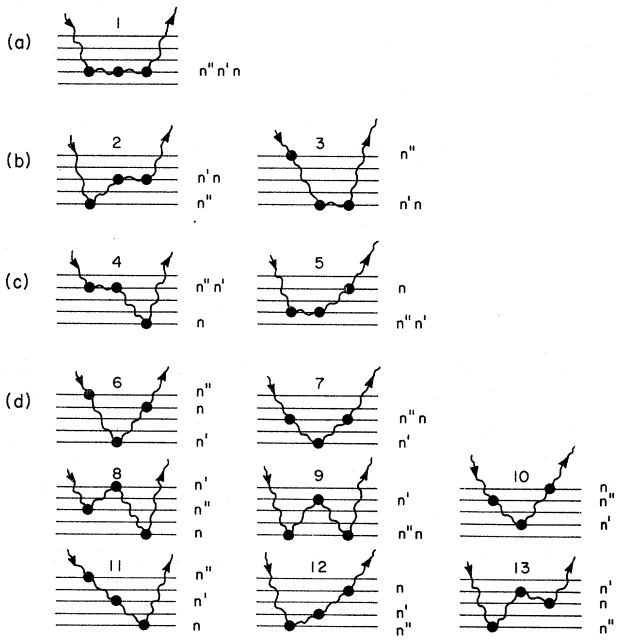

FIG. 1. Diagramatic presentation of all third-order scattering events defined in Eq. (3); n'', n', and n correspond to the sequence of scattering from each plane. The diagrams indicate all combinations of scattering events without specifying the number of planes between any two interplanar events.

computation. Recent developments in the analysis of inelastic LEED[11] also place a premium on the use of a fast method of general applicability.

In a recent communication, Pendry[7] proposed a perturbative approach to LEED spectra intensities. Taking only a finite number of scattering layers and summing over all orders of forward scattering events, his method appears to be best suited for normal or near-normal angles of incidence. In his method, matrix inversions for the planar scattering matrices are retained. Hence, in the case of complicated planar structures or reconstructed layers, the major portion of the computation time still increases as L^3.

Our new perturbation approach is based on a reformulation of Beeby's multiple scattering approach.[12] The inclusion of the electron self-energy, the quasiparticle renormalization, and temperature corrections are provided for in a manner previously described.[3] For the total scattering T matrix, we have the exact expression

$$[T_n]_{LL'}=[t_n]_L\,\delta_{LL'}+\sum_{L''}([t_n]_L\sum_{n'=0}^{\infty}[G^{nn'}]_{LL''}[T_{n'}]_{L''L'}), \tag{1}$$

where $[t_n]_L\delta_{LL'}$ is the diagonal core-scattering matrix for ion cores in the plane n.[3] $[G^{nn'}]_{LL'}$ is the propagator describing propagation of an electron from plane n' to plane n and involves lattice sums of damped Bloch waves. If we now iterate Eq. (1) in terms of the ion-core matrices $[t_n]_L\delta_{LL'}$ to third order, this step shortens the computation time considerably. For a given order, the magnitude of a given sequence of scattering events is determined by the number of forward and backward scattering matrix elements as well as the sequence of events in the scattering process. A sequence containing more forward scattering matrix elements is not necessarily larger than one containing more backward matrix elements. Our method is to keep, to third order, *all* terms in the intraplanar and interplanar scattering.

The sums over lattice planes in Eq. (1) can be transformed[13] into sums over the reciprocal lattice of the two-dimensional surface mesh, and after carrying out this transformation there are a total of thirteen third-order terms. We show all the third-order events diagramatically in Fig. 1 where each dot denotes a scattering event occurring anywhere in the plane of the dot and the sequence of events follows the path indicated in each case. A typical third-order term in the amplitude corresponding to the eleventh diagram [Fig. 1(d)] has the following form:

$$\begin{aligned}A\propto\frac{1}{\kappa^2}\sum_{\vec{g}_1,\vec{g}_2}\frac{1}{k_\perp(\vec{g}_1)k_\perp(\vec{g}_2)}\sum_{LL'L''}&\{Y_L(\vec{k}_\parallel+\vec{g}_0-k_\perp(\vec{g}_0)\hat{e}_\perp)[t]_L\,Y_L{}^*(\vec{k}_\parallel+\vec{g}_2+k_\perp(\vec{g}_2)\hat{e}_\perp)\\&\times Y_{L'}(\vec{k}_\parallel+\vec{g}_2+k_\perp(\vec{g}_2)\hat{e}_\perp)[t]_{L'}\,Y_{L'}{}^*(\vec{k}_\parallel+\vec{g}_1+k_\perp(\vec{g}_1)\hat{e}_\perp)\,Y_{L''}(\vec{k}_\parallel+\vec{g}_1+k_\perp(\vec{g}_1)\hat{e}_\perp)[t]_{L''}\\&\times Y_{L''}{}^*(\vec{k}_\parallel+k_\perp(\vec{0})\hat{e}_\perp)\Big\}\Big[\frac{1}{1-\exp\{[k_\perp(\vec{0})+k_\perp(\vec{g}_0)]d_z-\vec{g}_0\cdot\vec{d}\}}\\&\times\frac{\exp\{[k_\perp(\vec{0})+k_\perp(\vec{g}_2)]d_z-\vec{g}_2\cdot\vec{d}\}}{1-\exp\{[k_\perp(\vec{0})+k_\perp(\vec{g}_2)]d_z-\vec{g}_2\cdot\vec{d}\}}\,\frac{\exp\{[k_\perp(\vec{0})+k_\perp(\vec{g}_1)]d_z-\vec{g}_1\cdot\vec{d}\}}{1-\exp\{[k_\perp(\vec{0})+k_\perp(\vec{g}_1)]d_z-\vec{g}_1\cdot\vec{d}\}}\Big],\end{aligned} \tag{2}$$

where we have put $[t_n]_L=[t]_L$, and $\vec{k}_\parallel$ and $\vec{k}_\parallel+\vec{g}_0$ are the components of the incident and reflected wave vectors parallel to the surface, $\hat{e}_\perp$ is the inward normal to the surface and $(\vec{k}_\parallel+\vec{g})^2+k_\perp^2(\vec{g})]=(2m/\hbar^2)\times[E-\Sigma^*(\vec{k},E)]$, where E is the energy of the incoming electron, $\vec{g}$ is the reciprocal lattice vector of the two-dimensional mesh, and Σ^* is the renormalized self-energy.[3] $Y_L(\theta,\varphi)$ is a spherical harmonic of complex argument, and $\vec{d}$ is the vector displacement of plane $n+1$ from plane n. The first factor in braces in Eq. (2) comes from ion-core scatterings. The factor in large brackets comes from the summation over lattice planes and depends on the sequence of scattering events.

In addition to the considerations of speed and core size, the critical consideration of any perturbation method is that of convergence. In order to estimate the degree of convergence obtained by the elimination of terms of higher order than third, we sum to infinite order the events occurring in the same plane to give the planar scattering matrix $[\tau]_{LL'}=[t(1-G^{nn}t)]_{LL'}{}^{-1}$. The third-order result in the planar scattering,

$$[t]_{LL'}=[t]_L\delta_{LL'}+[t]_L[G^{nn}]_{LL'}[t]_{L'}+\textstyle\sum_{L''}[t]_L[G^{nn}]_{LL''}[t]_{L''}[G^{nn}]_{L''L'}[t]_{L'}, \tag{3}$$

is compared with that of infinite order for the (100) faces of aluminum and nickel. The results

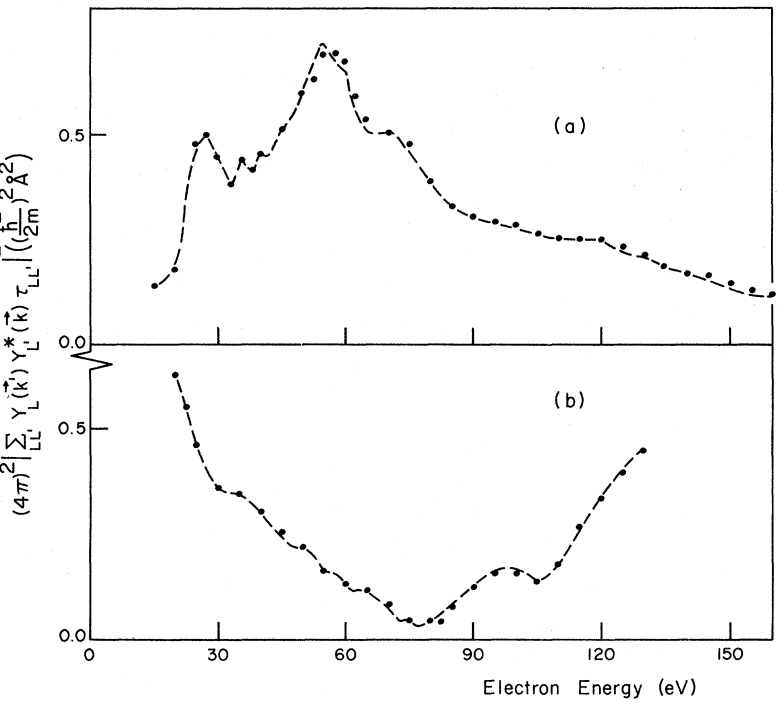

FIG. 2. Convergence of the third-order t-matrix formalism from a comparison of the planar scattering intensity for infinite order (broken lines) to the corresponding intensity for third order (dots). Calculations are made for normal incidence at $T = 300°K$ using six phase shifts for (a) Al(100), (b) Ni(100).

are shown in Figs. 2(a) and 2(b), respectively. We note that, for the energy ranges and metal face considered, the convergence is good. For the great majority of points in the indicated energy ranges, the convergence is within 2 – 4%. This qualifies use of this method as an effective and rapid means for quantitative interpretation of LEED intensity-energy spectra.

This overall convergence is probably not as good as that obtained from Pendry's method[7] where all forward scattering events are summed and terms kept only to third order in back scattering. The chief advantages of using the ion-core t-matrix approach, on the other hand, are in the achievement of faster time and greater ease in extension of the calculation to more complicated systems. It has a definite advantage in the handling of reconstructed surfaces and systems with adsorbates having small d spacings normal to the surface layer. The computational accuracy of the t-matrix method is well within the limits of uncertainties that exist in defining contributions to scattering from damping strength, inner potential, and surface screening.

We have applied the third-order t-matrix method to intensity-energy spectra calculations on clean surfaces of aluminum and nickel. The com-

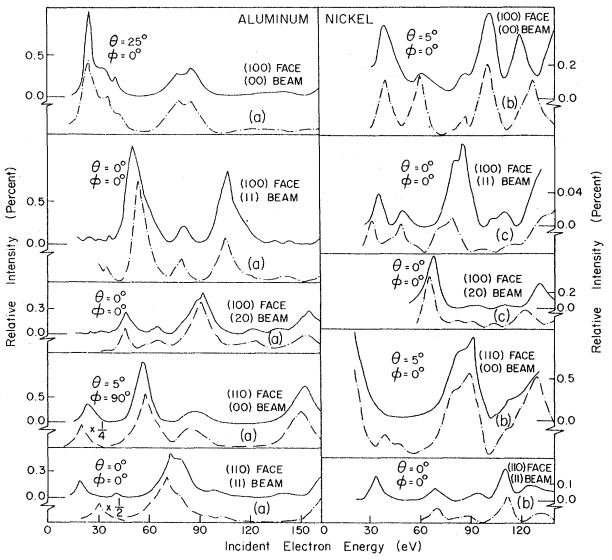

FIG. 3. Comparison between third-order t-matrix results (solid lines) and experiments (broken lines) for the specular and nonspecular beams for clean surfaces of Al(100), Al(110), Ni(100), and Ni(110). Calculations are made for six phase shifts at $T = 300°K$. Experimental curves are taken from room-temperature results of (a) Ref. 14, (b) Ref. 15, and (c) Ref. 16. The experimental curves for Al(110) (Ref. 14) are shifted a constant 12 eV to lower energies to facilitate comparison.

parisons between theoretical results and experimental data[14-16] are shown in Fig. 3. Details of the use of potential, energy-dependent electron self-energy, and quasiparticle renormalization are to be reported elsewhere.[13] In these calculations, six phase shifts and 29 beams are used, and each energy point takes 18 sec on an IBM 360/65. We believe that this is faster than any existing method in terms of a comparable degree of convergence. Our results for aluminum (100) and (110) for the specular and nonspecular beams, using the t-matrix method, agree very well with a recent exact calculation of Laramore and Duke.[8]

In conclusion, a new fast perturbative approach to LEED theory is proposed which gives adequate convergence and involves no matrix inversion routines. The extremely fast computation time and general applicability of the method make possible the realization of applying microscopic models to the interpretation of LEED intensity spectra of complicated surfaces such as those associated with overlayers and reconstructed structures.

Reference to the LEED intensity measurements on nickel by J. E. Demuth prior to publication is appreciated. We are also grateful to C. B. Duke, G. E. Laramore, D. W. Jepsen, P. M. Marcus, and F. Jona for knowledge of their works prior to publication.

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Oscillatory Behavior of g Values and Magnetic Circular Dichroism in a Jahn-Teller Coupled System

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We report on the oscillatory behavior of the reduction factors for the electronic orbital angular momentum of Jahn-Teller coupled non-Kramers doublets, which comes from the diagonal matrix elements of the orbital angular momentum. The calculated envelope of the magnetic circular dichroism for the parity-allowed transition $A \rightarrow E$ also exhibits an oscillatory behavior, which is given by the nondiagonal matrix elements of the orbital angular momentum.

In recent years, a considerable amount of theoretical and experimental work[1,2] has been reported on static and dynamical Jahn-Teller effects. Ham[3] in particular has revealed that, when a triplet state belonging to the T_{1g} and/or T_{2g} representation[4] of the cubic symmetry couples to the E_g vibration, the dynamical Jahn-Teller coupling may reduce the values of the nondiagonal matrix elements of the electron orbital angular momentum. Furthermore, he[5] has shown that, in the orbital doublet state, the Jahn-Teller coupling reduces values of the electronic parameters in the spin Hamiltonian for the vibronic ground state by factors precisely analogous to the orbital reduction factors which describe partial quenching of the off-diagonal operators in the