

## New, Real-Space, Multiple-Scattering-Theory Method for the Determination of Electronic Structure

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We introduce a new method for the exact and unified treatment of the Schrödinger equation and the calculation of the electronic density of states of materials with reduced symmetry (e.g., surfaces and interfaces) many of which are outside the reach of methods based on Bloch's theorem. This method is based on a self-consistent equation determining the  $t$  matrices of those parts of a system characterized by semi-infinite periodicity, without recourse to reciprocal space. The method is illustrated through a calculation of the density of states for bulk Cu and for a (100)/(111) planar Cu interface.

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In the calculation of electronic structure and the study of materials properties, the solution of the Schrödinger equation corresponding to a periodic potential can be achieved through the use of Bloch's theorem and the associated lattice Fourier transforms. This theorem allows the diagonalization of the Hamiltonian in reciprocal ( $\mathbf{k}$ ) space, and has led to the development of powerful and accurate first-principles methods for the calculation of the band structure,  $E(\mathbf{k})$ , and related properties of many materials, particularly metals<sup>1</sup> and metallic alloys.<sup>2</sup>

The conceptual as well as practical appeal of Bloch's theorem is so powerful that the theorem has often been invoked in a somewhat artificial manner to treat materials lacking full translational invariance. As a simple example, we may cite<sup>3</sup> the use of periodically repeating supercells to treat impurities and grain boundaries. In spite of the accuracy of the results obtained through the applications of such methods to specific cases, the use of artificial boundary conditions in general lacks conceptual rigor, can become essentially impractical in cases of even moderate structural complexity (e.g., a few impurities near an incoherent interface), and fails to provide well defined and practical prescriptions for obtaining converged results.

It is the purpose of this Letter to introduce a formalism which greatly alleviates the conceptual and the practical difficulties in the calculation of the electronic structure of systems with reduced symmetry, providing a unified, exact treatment of pure bulk materials and those containing defects of a local or extended nature, such as impurities (substitutional or interstitial), and surface and interface regions (grain boundaries). This formalism is constructed within multiple-scattering theory (MST) in real, rather than reciprocal space, and is based on the fundamental concept of *semi-infinite periodicity* (SIP), and the associated *removal invariance*<sup>4</sup> property of systems characterized by SIP. Specifically, this property al-

lows one to replace the use of Bloch's theorem and of lattice Fourier transforms with a self-consistent equation determining the  $t$  matrix and the associated Green's function of any material with SIP. The power of this new method is illustrated through the reproduction of existing results for the density of states (DOS) of bulk elemental Cu, and the calculation of the DOS of a (100)/(111) Cu interface. Following that, we give a brief discussion of some of the formal and computation aspects of this formalism, its advantages and limitations compared to existing techniques, and our future plans in regard to code development. A much more detailed discussion along these lines is reserved for a future publication.

Quite generally, we define "semi-infinite periodicity" as the periodic repetition of a basic unit along a given direction. As examples of systems of SIP, we may consider a linear, semi-infinite periodic arrangement of atoms, and one of the two parts formed upon severing a periodic material along a cleavage plane. In the first case the basic repeating unit is an atom, while in the second one the repeating unit is either an atomic monolayer or a set of such layers. Clearly, a broad range of systems, from periodic bulk materials to twist and tilt grain boundaries, can be viewed as consisting of parts characterized by SIP. In fact, this view encompasses all structures with the exception of those characterized by structural disorder (amorphous materials), or quasi-periodicity.

The ensuing MST formalism is based on the following "removal invariance" property of systems with SIP: *The  $t$  matrices of any such system remain invariant (within a trivial phase factor) when any number of basic scattering units is removed from the free end of the system.* This property gives rise to a self-consistent equation which allows the determination of the  $t$  matrix and the Green's function in real space.

Within the single-particle approximation, the electron-

ic structure of an assembly of scatterers can be obtained from the single-particle Green's function,  $G(\mathbf{r}, \mathbf{r}')$ , which can be expressed in terms of the complete scattering matrix,  $T$ , of the assembly,

$$G(\mathbf{r}, \mathbf{r}') = G_0(\mathbf{r}, \mathbf{r}') + \int G_0(\mathbf{r}, \mathbf{r}_1) T(\mathbf{r}_1, \mathbf{r}_2) \times G_0(\mathbf{r}_2, \mathbf{r}') d^3 r_1 d^3 r_2, \quad (1)$$

with  $G_0(\mathbf{r}, \mathbf{r}')$  being the free-particle propagator. By decomposing the on-the-energy-shell components of  $T$  in the angular momentum ( $L$ ) representation,  $L = (l, m)$ , with  $T$  centered at the origin,  $o$ , we have

$$T_{LL'} = \sum_{L_1 L_2} \sum_{i, j} g_{LL_1}(-\mathbf{R}_{oi}) \tau_{L_1 L_2}^{ij} g_{L_2 L'}(-\mathbf{R}_{jo}). \quad (2)$$

Here,  $\mathbf{R}_{oi}$  denotes the position of the center cell  $i$ ,  $g(\mathbf{R})$  is the  $L$  representation of the translation operator<sup>5</sup> associated with vector  $\mathbf{R}$ , and  $\tau_{LL'}^{ij}$  are the site angular momentum matrix elements of the scattering path operator<sup>6</sup> between unit cells  $i$  and  $j$ . The elements  $\tau_{LL'}^{ij}$  are given in terms of the  $t$  matrices,  $t_i$ , of individual cells and the intercell free-particle propagator  $G(\mathbf{R}_{ij})$  by the inverse of the MST matrix

$$M_{ij} = t_i^{-1} \delta_{ij} - G(\mathbf{R}_{ij})(1 - \delta_{ij}). \quad (3)$$

It has been shown<sup>6</sup> that Eq. (1) can be written in the form

$$G(\mathbf{r}, \mathbf{r}') = \sum_{LL'} Z_L^i(\mathbf{r}_i) \tau_{LL'}^{ij} Z_{L'}^j(\mathbf{r}_j') - \sum_L S_L^i(\mathbf{r}_i) Z_L^j(\mathbf{r}_j') \delta_{ij}, \quad |\mathbf{r}_i| > |\mathbf{r}_j'|, \quad (4)$$

where  $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_i$  is confined to cell  $i$  and the functions  $Z_L^i, S_L^i$  are appropriately defined<sup>2</sup> regular and irregular solutions of the Schrödinger equation inside unit cell  $i$ , respectively. In most applications, e.g., determination of charge density and the DOS, one is interested only on the diagonal part of  $G(\mathbf{r}, \mathbf{r})$  which can be obtained from the site-diagonal elements,  $\tau^{ii}$ , alone.

For systems with translational invariance, Eq. (3) can be transformed to reciprocal space through the use of Bloch's theorem, and in that form leads to the well-known secular equation of Koringa,<sup>7</sup> and of Kohn and Rostoker<sup>8</sup> (KKR) for the calculation of the band structure of a material. In more general cases of systems lacking translational invariance and characterized only by SIP, we introduce a real-space, multiple-scattering-theory (RS-MST) formalism which can be used in determining  $\tau^{ij}$ , and hence  $G(\mathbf{r}, \mathbf{r}')$ . This method consists in treating exactly a cluster of a finite number of cells, a number of which are bare cells characterized by the individual cell  $t$  matrices, surrounded by certain "renormalized" cells characterized by  $t$  matrices constructed so as to properly represent the infinite medium surrounding the cluster of bare cells. These renormalized cells can be appropriately chosen so that each represents a part of the system characterized by SIP. The determination of the

renormalized cell  $t$  matrices can then be carried out in an iterative way as follows.

First, determine the renormalized cell  $t$  matrix,  $T_1$ , associated with a one-dimensional semi-infinite periodic arrangement of atoms, with  $T_1$  centered at the free end of the semi-infinite line. Because of the removal invariance property, we can use Eq. (3) with the unknown  $T_1$  placed at the end of a line of  $N$  bare cells, invert the corresponding matrix  $M_{ij}$ , and insert that inverse,  $\tau_{ij}$ , in Eq. (2) to obtain a self-consistent equation for  $T_1$ :

$$T_{1, LL'} = \sum_{L_1 L_2} \sum_{i, j} g_{LL_1}(-\mathbf{R}_{oi}) \tau_{L_1 L_2}^{ij}(T_1) g_{L_2 L'}(-\mathbf{R}_{jo}). \quad (5)$$

This equation when solved by iteration or other means determines  $T_1$  for the semi-infinite line. Second, use the angular momentum representation of the rotation operations to obtain the  $t$  matrix of a semi-infinite line extending along a different direction. Third, to determine the renormalized cell  $t$  matrix,  $T_2$ , for a two-dimensional arrangement of atoms, such as a quarter of a monolayer or half of a monolayer, we set up a matrix  $M_{ij}$  for the unknown  $T_2$  and a repeating unit consisting of bare cells and previously determined renormalized cell  $t$  matrices representing half-lines, insert the inverse  $M_{ij}$  into Eq. (2), and solve the resulting self-consistent equation. Finally, the renormalized cell  $t$  matrix for a three-dimensional semi-infinite periodic arrangement of atoms can be determined using the same process with an appropriately chosen cluster of bare cells and renormalized cells representing semi-infinite parts of lower dimensions. In short, at each stage of this process, a number of bare cells along with previously determined renormalized  $t$  matrices are used to form the basic iterating unit to obtain a  $t$  matrix for a higher-dimensional arrangement of cells.

We now consider a system, such as one containing a grain boundary, as consisting of  $N_b$  bare cells, described by individual  $t$  matrices, properly surrounded (dressed) by the  $N_r$  renormalized cells representing various one-, two-, or three-dimensional parts characterized by SIP. The final expression for the Green's function is obtained by considering Eqs. (3) and (4) in connection with the  $N_b$  bare cells and the  $N_r$  renormalized cells. It is to be noted that by changing appropriately the manner in which the renormalized cells are determined, and the characteristics of the bare cells, one can treat a wide spectrum of systems, such as surface relaxation, impurities with lattice relaxation, etc., without undue increase in computational effort.

As it may have become clear through the foregoing discussion, the RS-MST method introduced in this Letter utilizes the properties of SIP allowing for the first time the treatment of infinite systems without recourse to Bloch's theorem and lattice Fourier transforms. We should note that the elimination of reciprocal space from the formalism has three additional beneficial effects. First, it eliminates the need for searching for appropriate grids of points in  $\mathbf{k}$  space to perform rather cumbersome

integrals over the first Brillouin zone of a reciprocal lattice. Second, it eliminates the need to set up the so-called structure constants, replacing them by an easily constructed input file specifying the coordinates of the cluster to be used and the appropriate sequence for determining the renormalized cell  $t$  matrices. Finally, the size of the cluster used is essentially determined by the convergence of the free-particle propagator independently of the number of atoms per unit cell, leading to an approximately linear relation of the computational time to the number of atoms per cell in a charge self-consistent calculation, in contrast with the cubic relation for methods based on reciprocal space. Because of these effects, no significant increase in computational labor results when treating fairly complex structures with low symmetry or with many atoms per unit cell.

An exact application of Eqs. (3) and (5) would involve infinite-dimensional matrices in  $L$  space. For practical applications, a truncation in  $l$  is necessary, and the convergence with respect to the maximum  $l$  used must be considered [especially for the internal summations in Eq. (5)]. Clearly, one can always expect these summations to converge using sufficiently large-size clusters, and check the convergence through calculations truncated at different maximum  $l$ 's. Our numerical studies indicate that convergence can be achieved with moderate size clusters and truncation at relatively small values of  $l$ . Thus, the present method provides a feasible and well-defined approach for obtaining and checking convergence.

Results of numerical calculations carried out within the RS MST introduced here are presented in Fig. 1. In this figure, the heavy solid line depicts the DOS for bulk elemental Cu obtained by Moruzzi, Janak, and Williams (MJW)<sup>1</sup> through the familiar method of KKR. The shaded regions of Fig. 1 represent the local DOS's obtained using the potential functions of MJW at the center of a bare cluster of 117 sites, 1(a), at the center of a 117-site cluster whose boundary sites were appropriate-

ly renormalized using the RS-MST method to simulate the infinite surrounding medium, 1(b), and the DOS at a (100)/(111) planar interface, 1(c), respectively. The bare cluster DOS, shaded region in 1(a), reveals a number of expected features. It is sharper and narrower than that corresponding to the bulk material, and provides only a partial reproduction of the sharp edge of the DOS of Cu at the top of the  $d$  band. By contrast, the RS-MST calculation, shaded region in 1(b), reproduces essentially exactly the results of the  $\mathbf{k}$ -space calculations; any remaining differences with the exact calculations could be attributed to the lack of convergence (the RS-MST calculations were carried out only to  $l=2$  while the MJW calculations included up to  $l=4$ ), or to the use of the atomic-sphere approximation in performing the integrals of the cell wave functions. Finally, the interface DOS in 1(c) exhibits an essentially complete loss of structure and has a somewhat narrower bandwidth than that of the bulk DOS. The first effect is expected due to the loss of translational invariance, while the second is a reflection of the decreased coordination of the site at which the DOS's were calculated: This site was located on the (100) side of the interface and had only nine (rather than twelve) nearest neighbors. It is to be pointed out that this last structure cannot be treated properly within any method relying on reciprocal space (and Bloch's theorem).

It is to be pointed out that the formalism presented here provides the answer to a rather long standing problem in electronic structure calculations, quite concisely stated by Faulkner<sup>9</sup>: how to modify the boundary conditions on a cluster of free sites to represent properly the infinite medium surrounding the cluster. With a cluster of 117 sites this modification is rather small, allowing us to achieve convergence with a very small value of  $l$  ( $=2$ ). The same degree of convergence can also be achieved with small clusters but sufficiently high values of  $l$ , although it is in general computationally more difficult to increase the value of  $l$  rather than the number

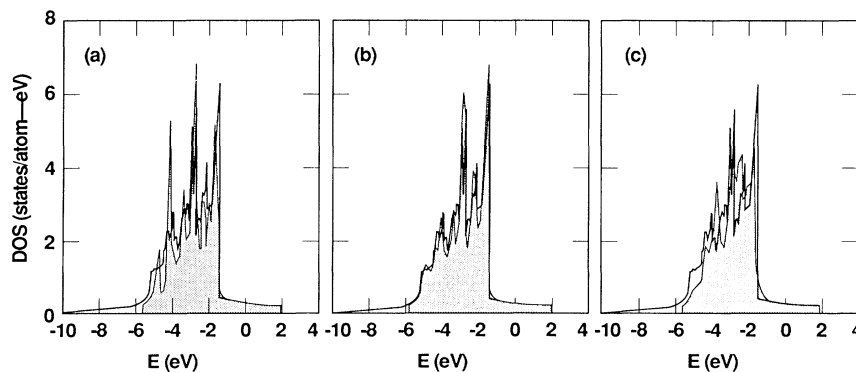


FIG. 1. Local densities of states of bulk Cu calculated through the KKR method, heavy solid line in all panels, at the center of a bare 117-site cluster, shaded region in (a), using the RS-MST method, shaded region in (b), and at a (100)/(111) interface using the RS-MST method, shaded region in (c).

of sites. Detailed examination of the convergence properties of the RS-MST method to be reported in a forthcoming publication indicate strongly the trade off which exists between expansions in real space (number of sites) and in angular momentum states.

Having illustrated the applicability of our method, it is fair to point out its disadvantage in comparison to techniques based on Bloch's theorem. Namely, the RS-MST method does not allow the determination of the dispersion relation,  $E(\mathbf{k})$ , for periodic systems. In addition, as it is true of all other first-principle methods, it cannot be applied to systems with structural disorder of infinite extent (amorphous materials) or quasicrystals. With the exception of these cases, this method provides a treatment of the Schrödinger equation with the proper boundary conditions for all other structures. Calculations are currently under way aimed at examining the rate of convergence with respect to increasing  $l$  and/or cluster size, and at determining optimum dressed cluster arrangements for various structures.

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<sup>1</sup>V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

<sup>2</sup>J. S. Faulkner, in *Progress in Materials Science*, edited by J. W. Christian, P. Haasen, and T. B. Massalski (Pergamon, New York, 1982), Nos. 1 and 2, and references therein.

<sup>3</sup>Space limitations prevent the citing of even a representative list of the vast number of works in the field. An extensive list of references will be given in forthcoming publications.

<sup>4</sup>R. K. Nesbet who coined the term "removal invariance" (private communication).

<sup>5</sup>M. Danos and L. C. Maximon, *J. Math. Phys.* **6**, 766 (1965).

<sup>6</sup>B. L. Györfly and M. J. Stott, in *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and D. M. Watson (Academic, New York, 1973), p. 385.

<sup>7</sup>J. Koringa, *Physica* **13**, 392 (1947).

<sup>8</sup>W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 1111 (1954).

<sup>9</sup>J. S. Faulkner, *J. Phys. C* **10**, 4661 (1977).