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Screened real-space study of the magnetic properties of Ni

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ABSTRACT

We have implemented screening in the fully relativistic spin-polarized version of the real-space Korringa–Kohn–Rostoker (KKR) band-structure method. Exploiting the resulting sparsity of the KKR matrix, we were able to accelerate the matrix inversions considerably. The factors determining the convergence of the method as a function of atoms in the cluster are discussed, and we show results obtained for the magnetic and orbital moment of elemental Ni.

§1. INTRODUCTION

An accurate real-space electronic structure method is a requirement for performing calculations with relaxations of the atoms in a solid. The Korringa–Kohn–Rostoker (KKR) method, a combination of multiple-scattering theory and Green's function formalism, can be implemented for any arrangement of the atomic positions and therefore allows for the study of both disordered and ordered solids. For a muffin-tin potential, the KKR method is an exact solution of the one-electron Schrödinger equation in a solid. In practice, however, the large amount of linear algebra operations, which have to be performed in the KKR method for the required matrix inversion, limits the method's applicability in real space to small clusters. Recent developments have allowed multiple-scattering equations to be expressed in a tight-binding form. In particular, Zeller *et al.* (1995) have shown that, by exploiting the freedom of choice of reference medium, a set of screened structure constants can be obtained, which are short ranged, and allow supercell calculations to be performed with the KKR method (Zeller 1997).

In this paper we investigate the possibility of evaluating, in the real-space screened representation, all the physical quantities of interest. We do not consider a lattice Fourier transform of the screened structure constants to make the KKR matrices finite, but we tackle the problem of 'infinite' KKR matrices. In the screened representation these matrices become sparse. We show which algorithms to implement, which take into account only the non-zero elements of the sparse matrix and can considerably speed up the matrix inversion. We elucidate the potential of this approach for realistic applications by a study of the spin and orbital moments in elemental Ni. In what follows we describe the theory of screening and show how this can lead to a very efficient evaluation of the multiple-scattering expressions. We discuss problems related to the structure of the screened structure constant matrix. Finally, we show preliminary results obtained for the magnetic moment of Ni.

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§2. Theory

In order to perform real-space calculations, we introduce the concept of a local interaction zone (LIZ) (Wang *et al.* 1995), where a central site, situated at $\mathbf{R}_0$, is surrounded by N sites at positions $\mathbf{R}_i$. For simplicity we describe the LIZ in terms of shells of atoms of constant radius $|\mathbf{R}_i - \mathbf{R}_0|$. The assumption is that the electronic structure of the central site is determined by its interaction with the neigbouring atoms in the LIZ, that is physical quantities, such as the charge density and the magnetic and orbital moments on the central site, are expected to converge with increasing number of atoms in the LIZ. The hope is that between 500 and 1000 atoms will give a reliable result.

In the KKR method, all physical information is contained in the Green's function of the system. Within the relativistic and spin-polarized extension of the method (Strange *et al.* 1991a), the Green's function in the vicinity of the central site is given by

$$G(\mathbf{r} + \mathbf{R}_0, \mathbf{r}' + \mathbf{R}_0) = \sum_{\lambda\lambda'} Z^0_\lambda(\mathbf{r}, E)\tau^{0,0}_{\lambda\lambda'}(E)Z^0_{\lambda'}(\mathbf{r}', E) - \sum_{\lambda} Z^0_\lambda(\mathbf{r}_<, E)J^0_\lambda(\mathbf{r}_>, E). \quad (1)$$

Here λ stands for the pair of relativistic quantum numbers (κ, μ). $\tau^{0,0}_{\lambda\lambda'}(E)$ refers to the (λ, λ') element of the on-site $2(l+1)^2$-dimensional block $\{\tau_{\lambda\lambda'}(E)\}^{0,0}$ of the scattering path matrix

$$\boldsymbol{\tau}(E) = \left[\mathbf{t}^{-1}(E) - \mathbf{G}^0(E)\right]^{-1}. \quad (2)$$

Z^0_λ and J^0_λ are the regular and irregular single-site scattering solutions respectively for the central potential. The amount of numerical work involved in the inversion of equation (2) scales as $O(N^3)$, multiplied by a further factor of eight in the relativistic case. As a result we are limited to a LIZ of about 100 atoms (Beiden *et al.* 1998).

By constructing a new reference medium, consisting of constant repulsive potentials which fill up the muffin-tin spheres inside the LIZ, we obtain a new set of structure constants (Zeller *et al.* 1995) $\mathbf{G}^{sc}(E)$, related to the free-space values $\mathbf{G}^0(E)$ by

$$\mathbf{G}^{sc}(E) = \mathbf{G}^0(E)\left[\mathbf{I} - \mathbf{t}^{sc}(E)\mathbf{G}^0(E)\right]^{-1}. \quad (3)$$

These screened structure constants decay exponentially in space, and the resulting structure constant matrix is sparse. In figure 1 we show the screened structure constant matrix for a LIZ of 17 shells (459 atoms) and a screening cut-off of one shell (13 atoms). Note that the displayed sparsity reflects the tight-binding nature of the screened structure constants.

Given $\Delta\mathbf{t} = \mathbf{t}^{mt} - \mathbf{t}^{sc}$, where $\mathbf{t}^{mt}$ and $\mathbf{t}^{sc}$ are the single-site muffin–tin and reference system scattering matrice respectively, the scattering path operator, in terms of the screened structure constants, becomes

$$\boldsymbol{\tau}_\Delta(E) = \left[(\Delta\mathbf{t})^{-1}(E) - \mathbf{G}^{sc}(E)\right]^{-1}. \quad (4)$$

Inserting the above equation into equation (1), together with the relevant regular and irregular solutions, gives again the Green's function for the system. The advantage of this expression, as we shall see in the following section, is the considerable speed-up related to the sparsity of the matrix that is to be inverted.

Knowing the Green's function (1) we can calculate such quantities as the density of states

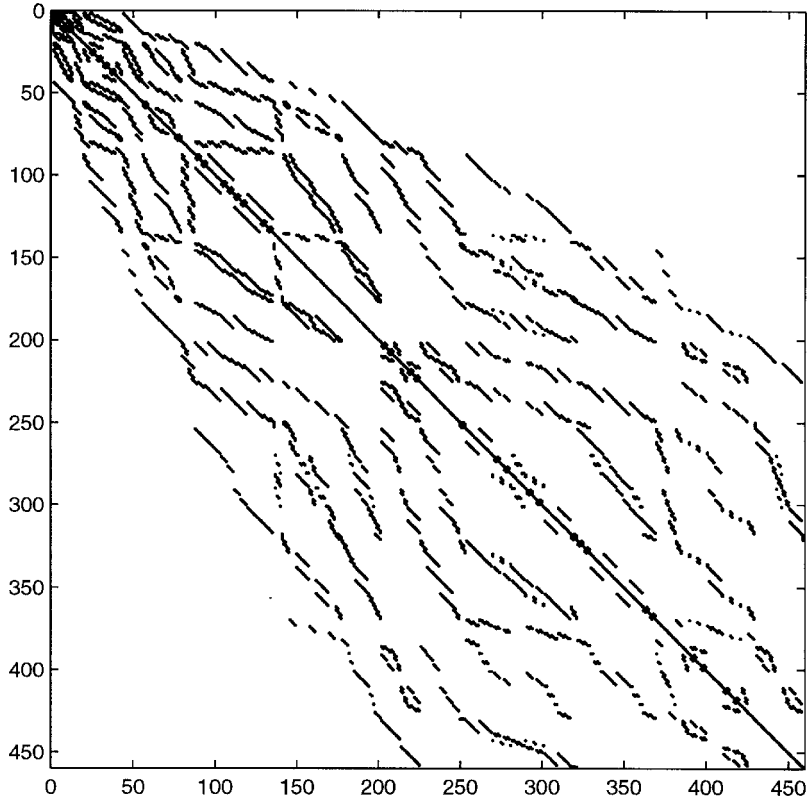

Figure 1. Sparsity pattern of the screened structure constant matrix, for a LIZ of 459 atoms and a screening radius of one shell.

$$n(E) = \frac{-1}{\pi} \operatorname{Im} \int \operatorname{Tr} G(\mathbf{r},\mathbf{r},E)\, \mathrm{d}^3\mathbf{r}, \tag{5}$$

the spin magnetic moment

$$\mathbf{m}_{\mathrm{spin}} = \frac{-\mu_{\mathrm{B}}}{\pi} \operatorname{Im} \int \mathrm{d}^3 r \int^{E_{\mathrm{F}}} \operatorname{Tr} \beta \mathbf{h} G(\mathbf{r},\mathbf{r},E)\, \mathrm{d}E \tag{6}$$

and orbital magnetic moment

$$\mathbf{m}_{\mathrm{orb}} = \frac{-\mu_{\mathrm{B}}}{\pi} \operatorname{Im} \int \mathrm{d}^3 r \int^{E_{\mathrm{F}}} \operatorname{Tr} \beta \mathbf{L} G(\mathbf{r},\mathbf{r},E)\, \mathrm{d}E, \tag{7}$$

where the trace is over spin space and $\mathbf{L}$ is the orbital moment operator.

§3. Sparse matrix inversion

We tested several packages for inverting sparse asymmetric linear systems of equations, and measured the respective speed-up compared with the conventional **LU** decomposition. Most packages work only for very sparse systems, that is with less than 0.1% of non-zero elements. For our less sparse matrices, by far best results were obtained with a package from the Harwell Subroutine Library, ME48 (Duff 1996). The central processing unit (CPU) times, measured for cluster sizes between 13 and 321 atoms, with one shell of screening, are displayed in table 1.

Table 1. A comparison of the CPU times and speed-ups for two different inversion packages for clusters of 13 to 321 atoms, corresponding to different sizes and degrees of sparsity of the KKR matrix.

Matrix dimension	Sparsity (%)	CPU time: **LU**	CPU time: ME48, analyse/factorize/solve	Speed-up
416	55.1	7	0/ 1/ 0	7
1256	84.5	260	4/ 6/ 3	20
2696	93.5	3690	24/ 54/13	42
3284	94.9	5314	45/ 63/14	69
3668	95.7	7444	55/ 84/16	74
4244	96.6	11995	89/199/29	52

ME48 is a direct method, based on a sequence of the following three steps.

(a) The analysis phase is where a good pivot order is determined. The energy dependence of the structure constants implies that the inversion has to be repeated for each energy but, since the sparsity pattern remains unchanged, the analysis step has to be executed only once.
(b) The factorization phase is where the permuted matrix is decomposed into lower and upper triangular matrices **L** and **U** respectively.
(c) The solve phase is where the equations are solved by forward and backward substitution. As we are only interested in the $(0, 0)$ block of the inverted matrix, we need only to solve for $2(l + 1)^2$ equations.

As can be seen from figure 2, the speed-up is really noticeable, in the screened case exhibiting now approximately $O(N)$ behaviour.

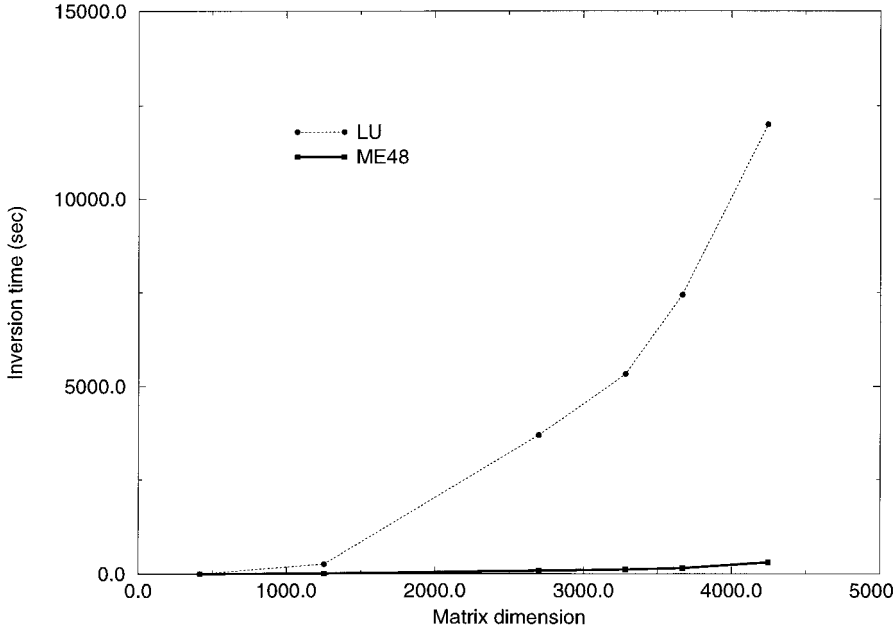

Figure 2. Sparse matrix inversion times as a function of matrix dimension: (···●···), **LU** decomposition; (—■—), ME48

§4. The screened structure constant matrix

It follows from equation (6) that the Green's function has to be calculated for a whole range of energies in order to determine the magnetic and orbital moments. We can replace the integral along the real energy axis by a contour integral in the complex plane (Zeller *et al.* 1982). At these complex energies the Green's function behaves much more smoothly; therefore fewer integration points are needed and, moreover, the screened structure constants can be interpolated with respect to energy.

The free-space reference medium is infinite, and the corresponding structure constants, which join the sites of the LIZ to each other, depend only on the relative distance of the sites, and not on their absolute positions:

$$G^{0;i,j}_{lml'm'}(E) = -4\pi i^{l-l'}(E^{1/2}) \sum_{l''m''} i^{l''} C^{L''}_{LL'} h_{l''}\left[E^{1/2}\left|\mathbf{R}_n - \mathbf{R}_m\right|\right] Y^{m''}_{l''}(\widehat{\mathbf{R}_n - \mathbf{R}_m}). \quad (8)$$

Note that all the sites in the LIZ are equivalent, and the corresponding matrix can be constructed analytically for each energy. Our screened reference medium, on the other hand, has constant repulsive potentials inside the muffin-tin spheres of the LIZ and free space outside. The scattering environment of those reference sites, which are situated at the surface of the zone, is completely different from that of the more central sites. The consequence is that on the surface the screened structure constants for each site depend on the spatial arrangement of the reference potentials in neighbouring shells. As a result the screened structure constants lose the property of translational invariance. This can be visualized by defining a relative quantity

$$\Delta N^{0,J}_{ll'}(\left|\mathbf{R}_i - \mathbf{R}_j\right|; E) = \frac{\left[\sum_{mm'} \left|G^{sc;0,J}_{lm,l'm'}(E) - G^{sc;i,j}_{lm,l'm'}(E)\right|^2\right]^{1/2}}{\left[\sum_{mm'} \left|G^{sc;0,J}_{lm,l'm'}(E)\right|^2\right]^{1/2}}. \quad (9)$$

The above formula is a generalization of a similar formula of Zeller *et al.* (1995). It determines the variation of the screened structure constants at fixed sites at the origin 0 and J with respect to sites i and j, chosen by the condition that $\mathbf{R}_i - \mathbf{R}_j = \mathbf{R}_0 - \mathbf{R}_J$. In figure 3 we display ΔN for different i, in the (100) and (110) directions respectively with J being a site on the first shell around 0. Two sites, situated opposite to each other on the same shell k, are in the figure referred to as $-k$ and k respectively.

The screened structure constants on sites situated within the ten first shells, are more or less equivalent, which is reflected by the fact that ΔN is of the order of 10^{-5}. Therefore, translational invariance of the nearest-neighbour screened structure constants is approximately fulfilled for a region of ten shells out of the total of 17 shells. Moreover, these structure constants can be obtained by inverting equation (3) for as small a cluster, consisting of a central site and its two neighbour shells, as 19 atoms in the case of a fcc structure. We can therefore reconstruct the screened structure constants for the bulk region of the large LIZ by translations of the screened structure constants of the small cluster. On the surface of the LIZ, ΔN can be as large as 0.8 (see figure 3), and the ΔN values are different for different directions. Consequently these structure constants cannot be obtained from translational invariance. These need to be calculated explicitly, taking into account the specific scattering neighbourhood of each site. These clusters are usually small, that is between four and 12 atoms for one shell screening. Furthermore, $l = 3$ is used only for the first three shells of the LIZ; all the others have $l = 2$ or less (Nicholson *et al.* 1994). Therefore it is not time consuming to invert these small matrices.

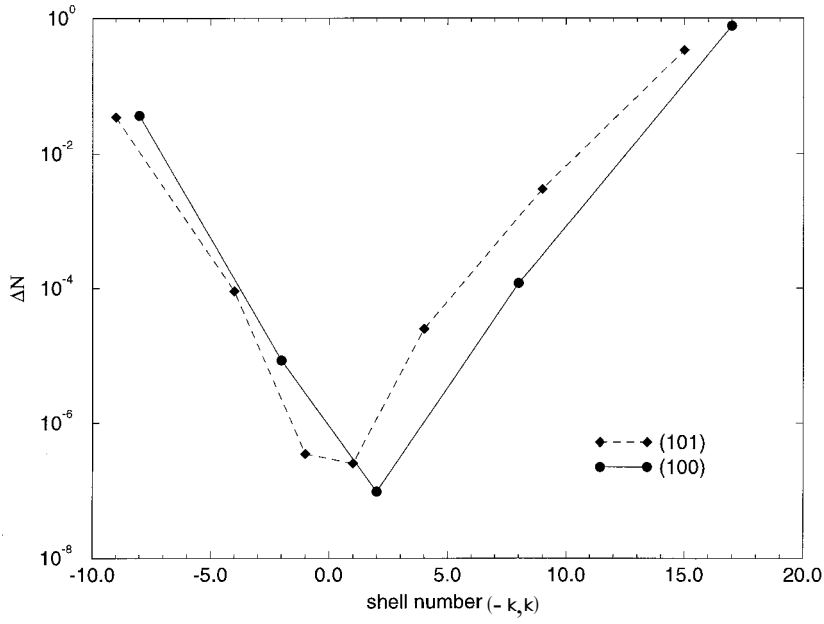

Figure 3. Relative variation in the screened structure constants as a function of shell number. ΔN is measured with respect to the structure constants joining the central site to its nearest-neighbour shell.

Before leaving this section it is useful to compare the present approach with the standard approach of working with screened structure constants. By lattice Fourier transforming the screened structure constants to k space, one solves for the infinite system where the screened structure constants are translationally invariant. The k-space screened KKR method has been successfully applied to large-scale supercell calculations (Zeller 1997) and layered systems (Wilberger *et al.* 1997). It is our consideration of a finite cluster in real space which destroys translational invariance of the screened structure constants. This means, of course, that additional screened structure constants have to be evaluated and in particular all screened structure constants for the sites in the surface region of the cluster need to be calculated.

§5. Results and Discussion

In our calculations with the screened real-space method, we were concerned with the convergence of the magnetic and orbital moments of Ni with respect to the size of the LIZ. First we analysed the relative influence of the surface. When the same screened structure constants were placed on every site of the cluster, including those of the surface, the calculated magnetic moment showed no convergence, even for a cluster of 1200 atoms. This could be assigned to the fact that, even for a cluster of 1000 atoms, what is considered as a surface constitutes more than 50% of the atoms in the cluster. To achieve convergence, the prescription of the preceding section was implemented. The latter takes into account the fact that the finite cluster destroys the translational invariance of the screened structure constants and therefore involves calculating these screened structure constants for every surface atom.

The convergence of the magnetic moment for Ni is shown in figure 4. A screening potential of 4 Ryd was used. Even with nearest-neighbour screening only, the

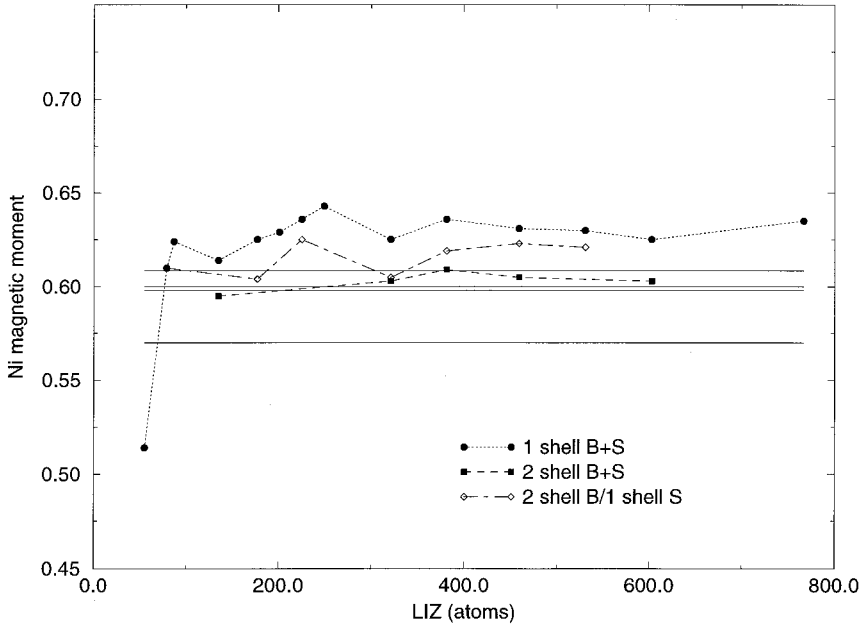

Figure 4. Convergence of the Ni magnetic moment as a function of real-space cluster size: (···●···), screening radius of one shell for all the sites of the cluster; (—■—), screening radius of two shells for all the sites of the cluster; (– - –◇–- –), result obtained for two shells of screening in the bulk, and one shell of screening in the surface area; (——), from top to bottom, lines referring respectively to the results of Trygg *et al.* (1995), Strange *et al.* (1991b) and Guo *et al.* (1991) and to experiment (Wein 1988).

convergence is apparent but does not give an accurate result within a cluster size of 800 atoms. For two shells of screening, implemented for all the sites of the cluster, the result is much more satisfying, concerning both the convergence and the value of the magnetic moment which is in agreement with other calculations (figure 4). The result obtained with a screening radius of two shells for the bulk atoms but only one shell screening for the surface atoms shows unsatisfactory convergence, indicating the overall importance of an accurate evaluation of the screened structure constants for the surface region, which similarly to the bulk also needs two shells of screening.

Another indication for having confidence in the accuracy of these real space calculations, with two nearest neighbour shells of screening, is the calculated value of $0.052\mu_B$ for the orbital moment on the central site of a cluster of 603 Ni atoms. This value is close to the experimental value of $0.05\mu_B$ (Wein 1988). Since, the change in reference medium is simply an identity transformation of the multiple-scattering equations, in the limit of no cut-off, exactly the same results should be found for the screened and unscreened version of our real-space method. A value of $0.545\mu_B$ (Beiden *et al.* 1998) was found for the spin magnetic moment of Ni when calculated with the unscreened real space code, with a cluster size of 135 atoms. Our results for the same cluster size and with respectively one and two shells of screening are $0.614\mu_B$ and $0.595\mu_B$. The result for three shells of screening is around $0.57\mu_B$. Thus the screened result is steadily converging towards the unscreened result. It also shows that for these small cluster sizes, where most atoms can actually be

considered as part of the surface, a higher screening radius is needed if we are to reproduce the unscreened results. Note that in the unscreened calculations it becomes impractical, from a computational point of view, to consider clusters beyond the size of 135 atoms, in which case the magnetic and orbital moments of Ni have not been fully converged (Beiden *et al.* 1998). However, for the screened calculation we readily performed calculations for 603 atoms and could converge the magnetic and orbital moments of Ni to a much higher accuracy.

In conclusion, we have presented a new real-space methodology which allows electronic properties to be calculated to a high accuracy. It is based on the screened representation of the multiple-scattering theory combined with the powerful sparse matrix technology for matrix inversion. It allows one to study systems of more than 600 atoms in a spin-polarized and relativistic multiple-scattering framework. In the latter case we have been able to converge the magnetic and orbital moments of Ni to a higher accuracy than previous unscreened multiple-scattering calculations.

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