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The self-consistent fully relativistic SKKR Green function method: applications to the (100), (110) and (111) surfaces of Au and Pt

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Abstract. The fully relativistic version of the screened Korringa–Kohn–Rostoker (SKKR) method is discussed and applied charge self-consistently to the (100), (110) and (111) surfaces of Au and Pt. In comparison to corresponding semi-relativistic calculations for Au it is found that spectral densities depend very crucially on the inclusion of relativistic effects. In terms of work functions, however, the difference between the semi-relativistic and the relativistic calculations is rather small.

1. Introduction

Many technologically important systems in surface physics are related to noble metals or noble metal alloys. In particular Au and Pt systems are heavily used as catalytic systems. Quite recently the interest in using interface properties such as, for example, oscillatory coupling of magnetic interfaces has seemed to grow almost exponentially. There is therefore a definite need to describe the electronic structure of semi-infinite systems such as surfaces and interfaces on a fully relativistic scale. It will be shown in this paper that 'traditional' semi-relativistic approaches possibly only apply to certain surface properties such as work functions, while failing completely in mapping dispersion relations or spectral properties.

2. Theoretical aspects

In real space scattering the scattering path operator is given by (see e.g. Weinberger 1990)

$$\tau(E) = \left[t(E)^{-1} - G(E)\right]^{-1} \tag{1}$$

where $\tau(E)$ is a supermatrix of angular momentum representations labelled by sites,

$$\tau(E) = \{\tau^{nm}(E)\} \qquad \tau^{nm}(E) = \{\tau^{nm}_{QQ'}(E)\} \tag{2}$$

$t(E)$ contains block-wise the single site t-matrices,

$$t(E) = \{\mathbf{t}^n(E), \delta_{nm}\} \qquad \mathbf{t}^n(E) = \{t^n_{QQ'}(E)\} \tag{3}$$

$G(E)$ refers to a supermatrix of the structure constants,

$$G(E) = \{\mathbf{G}^{nm}(E)\} \qquad \mathbf{G}^{nm}(E) = \{G^{nm}_{QQ'}(E)\} \tag{4}$$

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and Q denotes a pair of relativistic quantum numbers $(\kappa\mu)$. As is well known the relativistic structure constants $\mathbf{G}^{nm}(E)$ are easily obtained from their non-relativistic counterparts $\mathbf{G}^{nm}_{\mathrm{NR}}(E)$ by means of a transformation with Clebsch–Gordan coefficients (see e.g. Rose 1971 or Weinberger 1990)

$$\mathbf{G}^{nm}(E) = \sum_{\sigma=\pm 1/2} C(\sigma)^{\dagger}\mathbf{G}^{nm}_{\mathrm{NR}}(E)C(\sigma) \qquad C(\sigma)_{\ell m,\kappa\mu} = \langle j\ell\tfrac{1}{2};\mu-\sigma,\sigma\rangle\delta_{m,\mu-\sigma} \tag{5}$$

for which the following completeness and orthogonality relations apply

$$\left[\sum_{\sigma=\pm 1/2} C(\sigma)^{\dagger}C(\sigma)\right]_{\kappa\mu,\kappa'\mu'} = \delta_{\kappa\kappa'}\delta_{\mu\mu'} \qquad [C(\sigma)C(\sigma')^{\dagger}]_{\ell m,\ell' m'} = \delta_{\ell\ell'}\delta_{mm'}\delta_{\sigma\sigma'}. \tag{6}$$

The single-site matrices in equation (3) are defined by the usual matching condition for scattering solutions $R^n_Q(E;\boldsymbol{r}_n)$ at the muffin-tin radius R^n_s,

$$R^n_Q(E;\boldsymbol{r}_n) = J_Q(E;\boldsymbol{r}_n) - \mathrm{i}\sqrt{E}\sum_{Q'} H_{Q'}(E;\boldsymbol{r}_n)t^n_{Q'Q}(E)$$
$$\boldsymbol{r}_n = \boldsymbol{r} - \boldsymbol{R}_n \qquad |\boldsymbol{r}_n| = R^n_s \tag{7}$$

in terms of the following bispinors

$$J_{\kappa\mu}(E;\boldsymbol{r}) = \begin{pmatrix} j_\ell(\sqrt{E}r)\chi_{\kappa\mu}(\hat{\boldsymbol{r}}) \\ (\mathrm{i}\sqrt{E}S_\kappa/c)j_{\bar{\ell}}(\sqrt{E}r)\chi_{-\kappa\mu}(\hat{\boldsymbol{r}}) \end{pmatrix} \tag{8}$$

$$H_{\kappa\mu}(E;\boldsymbol{r}) = \begin{pmatrix} h^+_\ell(\sqrt{E}r)\chi_{\kappa\mu}(\hat{\boldsymbol{r}}) \\ (\mathrm{i}\sqrt{E}S_\kappa/c)h^+_{\bar{\ell}}(\sqrt{E}r)\chi_{-\kappa\mu}(\hat{\boldsymbol{r}}) \end{pmatrix} \tag{9}$$

related to Bessel and Hankel functions, where $S_\kappa = \ell - \bar{\ell}$. Note that in equations (5), (7), (8) and (9) the weak relativistic limit and atomic (Rydberg) units are used.

Following now the ideas of the SKKR method (see Szunyogh *et al* 1994), a Dyson equation for the screened non-relativistic structure constants can be formulated,

$$\mathbf{G}^{\alpha,nm}_{\mathrm{NR}}(E) = \mathbf{G}^{nm}_{\mathrm{NR}}(E) + \sum_k \mathbf{G}^{nk}_{\mathrm{NR}}(E)\hat{\alpha}^k_{\mathrm{NR}}(E)\mathbf{G}^{\alpha km}_{\mathrm{NR}}(E) \tag{10}$$

in which site-independent, but ℓ-dependent screening parameters form a diagonal angular momentum representation

$$\hat{\alpha}^n_{\mathrm{NR}}(E) = \{\hat{\alpha}_\ell(E)\delta_{\mathrm{LL}'}\} \qquad \forall n. \tag{11}$$

From equation (5), one can easily see that the screened relativistic structure constants are then given by

$$\mathbf{G}^{\alpha,nm}(E) \equiv \sum_{\sigma=\pm 1/2} C(\sigma)^{\dagger}\mathbf{G}^{\alpha,nm}_{\mathrm{NR}}(E)C(\sigma) \tag{12}$$

and that because of the completeness and orthogonality relations for the Clebsch–Gordan coefficients in equation (6), the relativistic screening parameters trivially reduce to their non-relativistic counterparts:

$$\hat{\alpha}^n(E) \equiv \sum_{\sigma=\pm 1/2} C(\sigma)^{\dagger}\hat{\alpha}^n_{\mathrm{NR}}(E)C(\sigma) \tag{13}$$

i.e.,

$$\hat{\alpha}^n(E) = \{\hat{\alpha}_\ell(E)\delta_{\kappa\kappa'}\delta_{\mu\mu'}\}. \tag{14}$$

The same formal structure pertains therefore in the relativistic version as in the non-relativistic version of the SKKR method, namely that in terms of screened (relativistic) structure constants

$$\mathbf{G}^{\alpha,nm}(E) = \mathbf{G}^{nm}(E) + \sum_k \mathbf{G}^{nk}(E)\hat{\alpha}^k(E)\mathbf{G}^{\alpha,km}(E) \tag{15}$$

and screened (relativistic) single-site t-matrices (see also the discussion in Szunyogh *et al* 1994)

$$\mathbf{t}^{\alpha,n}(E) = \mathbf{t}^n(E) - \hat{\alpha}^n(E) \tag{16}$$

a supermatrix of a screened (relativistic) scattering path operator in real space can be formulated

$$\tau^\alpha(E) = \left[t^\alpha(E)^{-1} - G^\alpha(E)\right]^{-1} \tag{17}$$

such that a block in the unscreened scattering path operator (see equation (2)) is defined by

$$\tau^{nm}(E) = \mathbf{t}^n(E)\mathbf{t}^{\alpha,n}(E)^{-1}\tau^{\alpha,nm}(E)\mathbf{t}^{\alpha,m}(E)^{-1}\mathbf{t}^m(E) - \delta_{nm}\mathbf{t}^n(E)\mathbf{t}^{\alpha,n}(E)^{-1}\hat{\alpha}(E). \tag{18}$$

Because of this formal equivalence between a non-relativistic and a relativistic approach, applications to semi-infinite systems, described at length by Szunyogh *et al* (1994), invoke no new aspects in the relativistic case, and therefore need not be repeated here in detail. It should be recalled, however, that by grouping 'atomic' layers into 'principal' layers, which due to the finite screening length of the structure constants couple only to the next nearest 'principal' layers, the scattering path operator and therefore consequently also the Green function can be viewed as tridiagonal supermatrices labelled by principal layers. In principle therefore inversion of the following infinite matrices $\mathcal{M}$

$$\mathcal{M} = \begin{pmatrix} M_{\mathrm{L,L}} & M_{\mathrm{L,I}} & 0 \\ M_{\mathrm{I,L}} & M_{\mathrm{I,I}} & M_{\mathrm{I,R}} \\ 0 & M_{\mathrm{R,I}} & M_{\mathrm{R,R}} \end{pmatrix} \tag{19}$$

where L and R denote a left and right semi-infinite system, respectively, and I an intermediate interface region, can be performed exactly by recursion. The number of atomic layers per principal layer is of course determined by the screening length of $\mathbf{G}^{\alpha,nm}(E)$. Quite clearly any $k_\parallel$ projection of these matrices $\mathcal{M}$ shows the same tridiagonal structure.

3. Numerical aspects

All calculations were carried out charge self-consistently using the local density functional by Ceperley and Alder (1980) and by solving the Poisson equation as discussed by Szunyogh *et al* (1994) within the atomic sphere approximation (ASA). For the (100) and (111) surfaces the interface region (see equation (19)) consisted of four metal and two vacuum ('atomic') layers, while for the (110) surfaces this region consisted of three metal and three vacuum ('atomic') layers. This different set-up for the interface region of (110) surfaces follows previous experience with the principal surfaces of Cu. The total number of $k_\parallel$ points per irreducible wedge of the (surface) Brillouin zone was 45 in the case of the (100) and (111) surfaces and 49 for the (110) surfaces. In all calculations the maximum angular momentum quantum number is restricted to two.

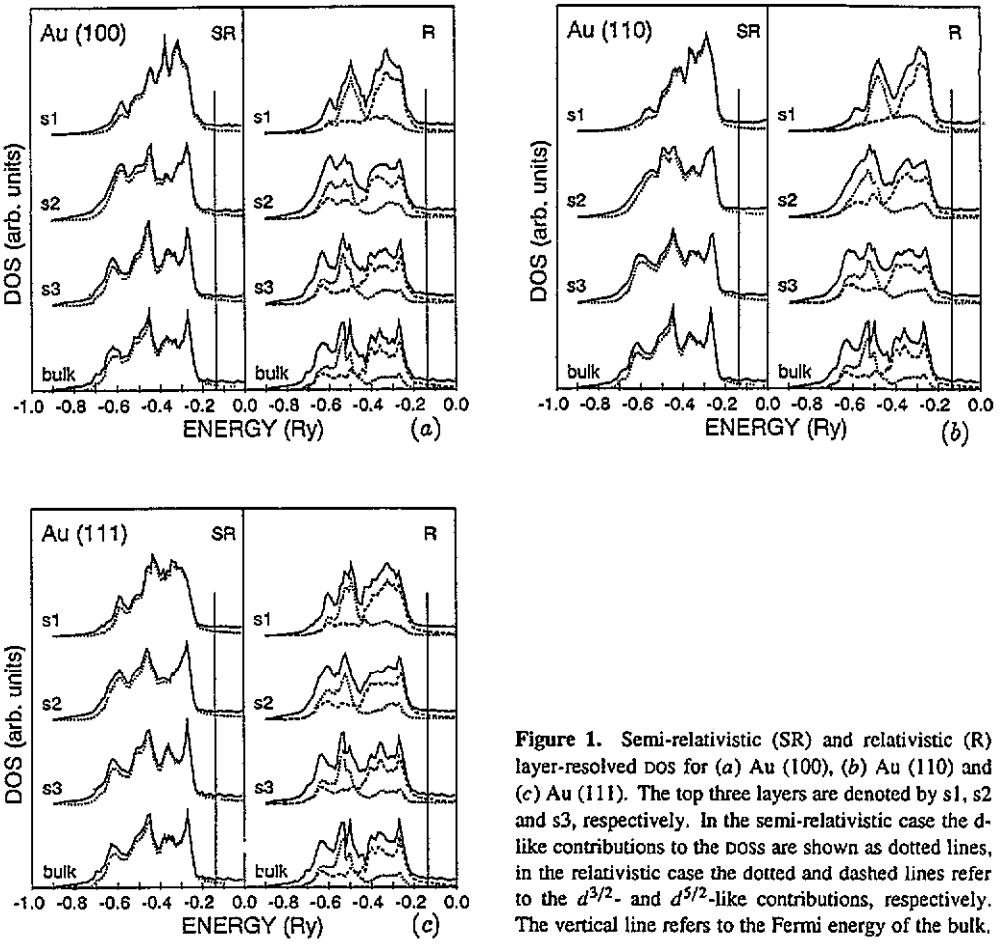

Figure 1. Semi-relativistic (SR) and relativistic (R) layer-resolved DOS for (*a*) Au (100), (*b*) Au (110) and (*c*) Au (111). The top three layers are denoted by s1, s2 and s3, respectively. In the semi-relativistic case the d-like contributions to the DOSs are shown as dotted lines, in the relativistic case the dotted and dashed lines refer to the $d^{3/2}$- and $d^{5/2}$-like contributions, respectively. The vertical line refers to the Fermi energy of the bulk.

4. Application to the (100), (110) and (111) surfaces of Au and Pt

In figures 1(*a*)–(*c*) the relativistic and semi-relativistic (inclusion of the mass velocity and the Darwin term in the radial Schrödinger equation) layer-resolved densities of states (DOSs) are shown for the three principle surfaces of Au. As can be seen from these figures, the semi-relativistic DOSs have very little in common with their relativistic counterparts. Because of the large spin–orbit splitting of Au and the related relativistic crystal field splitting the separation between the $d^{3/2}$- and $d^{5/2}$-like peaks in the DOSs is quite visible. Also visible is that the dispersion is reduced as one approaches the surface: the $d^{3/2}$- and $d^{5/2}$-like peaks sharpen up. Quite clearly a semi-relativistic description yields a completely inappropriate description for the electronic structure of Au surfaces.

Turning now to the relativistic cases, it should be recalled that the different widths of the $d^{3/2}$- and $d^{5/2}$-like peaks in the surface DOS, with respect to the different orientations of the surface, mainly reflect the different number of neighbours for a site in these surface layers. It is interesting to note that the rather sharp top peak in the DOS for the bulk layer (around −0.25 Ryd) is no longer present in the DOS for the surface layer.

For Pt (figures 2(*a*)–(*c*)) this top peak essentially determines the value of the (bulk) density of states at the Fermi energy, which as is well known is rather high. As can be seen from figure 2, this particular peak is completely wiped out in the case of the (111) surface,

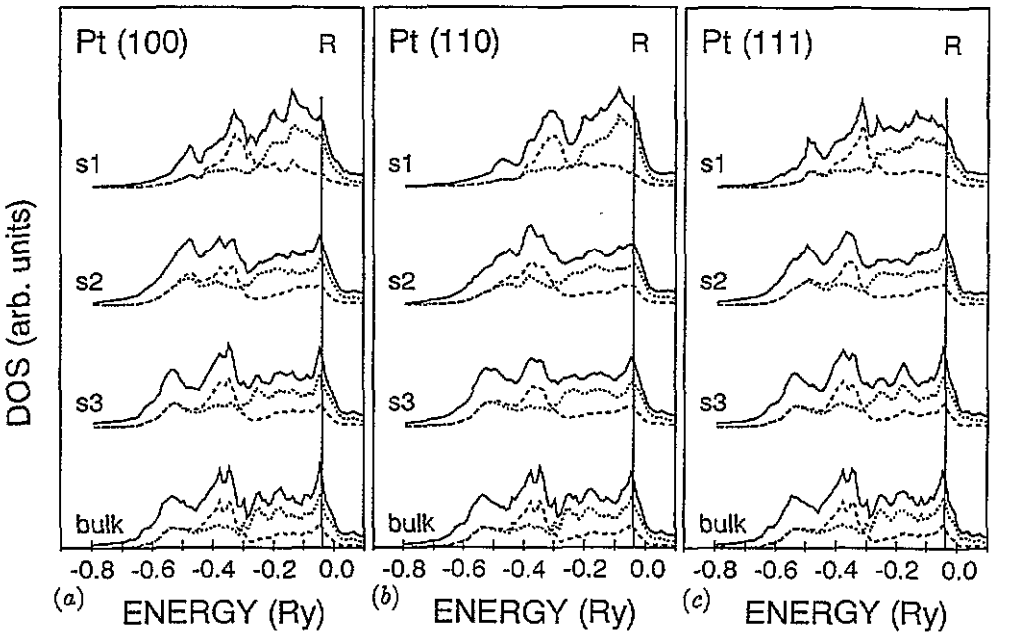

Figure 2. Relativistic (R) layer-resolved DOS for (*a*) Pt (100), (*b*) Pt (110) and (*c*) Pt (111). The top three layers are denoted by s1, s2 and s3, respectively. The dotted and dashed lines refer to the $d^{3/2}$- and $d^{5/2}$-like contributions, respectively, the vertical line to the Fermi energy of the bulk.

and resolved only as a kind of shoulder for the (100) and (110) surfaces. In all three cases the reduction of dispersion near or at the surface can be seen in the shape of the $d^{3/2}$- and $d^{5/2}$-like peaks.

Because of the large relativistic effects in Au and Pt, doubts ought to be expressed as to whether the semi-relativistic DOSs shown by Crampin (1993) for Au (100) have any physical meaning at all. A semi-relativistic approach, however tempting to use in an investigation of the magnetic properties of the Fe/Au(100) system, can be completely misleading in the case of a noble metal surface coated with a magnetic 3d metal, since 'hybridization effects' are described wrongly and also indirect relativistic effects in the 3d overlayer, induced by the host, have to be expected. Quite clearly polarization effects in the Au layer below the overlayer are important, which in turn can only be incorporated properly by using a spin-polarized relativistic approach. For the case of Fe double impurities in Au this was discussed for example by Weinberger *et al* (1990).

Table 1. Work functions (eV) for different surfaces of Au and Pt as calculated semi-relativistically (SR) and relativistically (R). Column A refers to the present calculations, column B to the values of Skriver and Rosengaard (1992).

		(100)		(110)		(111)	
		A	B	A	B	A	B
Au	SR	6.23	6.16	5.85	5.40	6.08	6.01
	R	6.26		5.86		6.13	
Pt	SR	6.93	6.97	6.15		6.67	6.74
	R	6.86		6.10		6.60	

A completely different story emerges when comparing work functions calculated either semi-relativistically or relativistically. From table 1 one can see that for the work functions the differences between these two types of calculation are indeed only marginal, which however was to be expected, since the work function is determined by the difference of the constant vacuum potential level and the bulk Fermi energy. This is also the reason why in general the semi-relativistic values of Skriver and Rosengaard (1992), which are shown in table 1 for comparison, are quite accurate. The only exceptions are perhaps the values for the (110) surfaces, since Skriver and Rosengaard (1992) used in their calculations only two layers of empty spheres to relax the vacuum region, which seems to be too simplistic (see also the discussion in Szunyogh *et al* (1994)).

5. Conclusion

In this paper it was shown that the SKKR method can be extended to a fully relativistic description of the electronic structure of semi-infinite systems. In this sense it is only comparable to the recent fully relativistic TB-LMTO formulation by Drchal *et al* (1994), keeping however all the advantages and disadvantages of a true scattering approach. It was shown that for surfaces of 5d metals the use of a fully relativistic approach is mandatory if one is (also) interested in spectral quantities. Presently the relativistic SKKR method is extended to the spin-polarized case, which in principle allows calculation of surface magnetic anisotropies or for different orientations of the magnetic field in the case of magnetic interface coupling to be dealt with.

Acknowledgments

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