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A NEW APPROACH TO THE AB INITIO CALCULATION OF ELECTRONIC STRUCTURE OF TRANSITION METALS AND THEIR ALLOYS

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Résumé. — La méthode de calcul de la fonction de Green utilisant un système surcomplet de fonctions, qui a été étudiée par les auteurs antérieurement, est appliquée dans le cas de l'alliage dilué de Ni contenant des éléments non de transition. La décroissance rapide de l'aimantation de Ni produite par l'impureté doit provenir d'une anti-résonance qui est produite par l'interférence d'états liés virtuels avec des états OPW dans l'écran de la charge de l'impureté.

Abstract. — The method of calculating the Greenian by use of an overcomplete set of functions which was developed previously by the authors is applied to dilute alloys of Ni containing non-transition elements as impurity. The rapid decrease of magnetization of Ni caused by the impurities is explained as arising from an anti-resonance which is due to the interference of the d virtual states with OPW states in the shielding of the impurity charge.

We developed previously a general method of calculating the Greenian by use of an overcomplete set of functions [1]. When applied to the band structure calculation, the method yields a rapid convergence similar to that obtained by several theories [2-5] which bring the 3 d resonance orbitals explicitly into the ab initio calculation on the basis of the Korringa-Kohn-Rostoker-Ziman method. The resonance orbitals, however, should be useful for a wide variety of problems. As an example we discuss in this paper Ni-base alloys containing a small amount of non-transition element such as Zn, Al, etc...

Suppose we have a complete set of functions |g> with the eigenfunctions of an unperturbed Hamiltonian; in addition we prepare a set of auxiliary orbitals |j> which may correspond to the core or resonance orbitals. We can prove the following expression of the Greenian for a given Hamiltonian $H$ [1]:

$$(E - H)^{-1}_{gg'} = L^{-1}_{gg'} + L^{-1}_{gg'} \Phi_{g'j} A^{-1}_{jj} \times \times (M_{jj} - S_{jj} \langle \gamma \gamma' \rangle L^{-1}_{gg'}) L^{-1}_{gg'}$$

with

$$(E - H)^{-1}_{gg'} = \Phi_{gj} S_{jj'},$$

$$A_{jj'} = A_{jj'} - M_{jj} L^{-1}_{gg'} \Phi_{gj'},$$

and $M_{jj} = (E - H)_{jj} - A_{jj} S_{jj'}$, where $S_{jj}$ is the overlap integral between $|j>$ and $|g>$; $\Phi$ and $A$ are arbitrary operators which may come into the expression because of the overcompleteness of the functions $|g>$ and $|j>$; the summation is taken over those subscripts which appear twice.

It is possible to set up a variational principle to determine the best choices of $\Phi$ and $A$, though the discussion will be given elsewhere. In this paper we assume simply $A_{jj'} = (E - H)_{jj'}$, choosing $|j>$'s to be such that they satisfy the Schroedinger equation within each muffin-tin sphere with the eigenvalues $E_j$'s determined by a boundary condition on the surface of the sphere. An example of the boundary condition which turns out to be most convenient is $|j> = 0$ on the surface. Since so chosen $|j>$'s make a complete set within each sphere, we can cancel the potential $V$ of the Hamiltonian by choosing $\Phi_{uj} = - V_{uj}$ in $L$ to make $E^{-1}$ equal to the Greenian of free electron. Another choice of $\Phi$ is to cancel the potential difference between different atoms in an alloy; in this case $E^{-1}$ is the Greenian of an average Hamiltonian. As was discussed in [1], Eq. (1) leads us to

$$\text{Im} \text{Trace} \left( (E - H)^{-1} \right) =$$

$$= (\partial/\partial E) \text{Im} \{ \text{log det} (L_{gg'}) + \text{log det} (A_{jj'}) \}.$$  \hspace{1cm} (2)

So far the discussion is purely formal. Useful approximations are obtained by truncating $A$ to retain the submatrix spanned by a finite number of $|j>$'s, for example, core and resonance orbitals. As was discussed in [1], the d part of the phase shift due to a transition element atom embedded in a free electron sea can be calculated quite accurately with Eq. (2) by taking into account the contribution of the 3 d orbitals only. An example of the off-resonance case is shown in figure 1, where the phase shifts due to Al in a free electron sea are calculated in a similar approximation; agreement with the exact calculation is satisfactory even in this case.

Table I lists the decrease of magnetization of Ni caused by a non-transition element impurity measured by Crangle and Martin [6]. The data indicate that

<table>
<thead>
<tr>
<th>Element</th>
<th>Decrease of magnetization per solute atom [6]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.14 µm</td>
</tr>
<tr>
<td>Zn</td>
<td>2.11</td>
</tr>
<tr>
<td>Al</td>
<td>2.80</td>
</tr>
<tr>
<td>Si</td>
<td>3.77</td>
</tr>
<tr>
<td>Ge</td>
<td>3.70</td>
</tr>
<tr>
<td>Sn</td>
<td>4.22</td>
</tr>
<tr>
<td>Sb</td>
<td>5.31</td>
</tr>
</tbody>
</table>

Fig. 1. — Phase shifts caused by an atom of Al.

TABLE I

Decrease of magnetization per solute atom [6]

<table>
<thead>
<tr>
<th>Element</th>
<th>Decrease</th>
<th>Decrease</th>
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most of the valence electrons of the impurity atom go into the d band of minority spin [7]. In fact the neutron experiment by the Harwell group [8] shows that the magnetic moments of surrounding Ni are decreased in a wide range. In a simple metal, however, the shielding of the impurity charge is expected to occur mostly at the impurity site with the phase shifts satisfying the Friedel sum rule. We propose the following two step shielding mechanism for the Ni alloys. First we shall show that the number of states below the Fermi level in Ni does not change very much by the potential difference at the impurity site even when a deep impurity potential is present, if one put aside the decrease of 5 states per each spin arising from the absence of the 3 d resonance at the impurity site. The change of the number of states below the Fermi level, which may be called phase shift, becomes small because of an interference with the d band. Nevertheless the number of electrons at the impurity site will be such that the impurity atom is almost electrically neutral. This means that the amplitudes of the wave functions should decrease at the surrounding Ni atoms to produce an electron deficit there; the amount of the deficit should be approximately equal to the number of excess valence electrons brought in by the impurity because the number of states does not change. As the second step the electron deficit thus produced at surrounding Ni sites will be shielded by the d electrons of minority spin. Since it is known both experimentally and theoretically that Fe and Co as impurity in Ni produce a very small perturbation at neighboring sites, this second step can be considered to be approximately independent of the first step [9].

In order to substantiate the above mentioned explanation, we calculate the phase shifts caused by Al in Ni as an example. In Eq. (1) we assume that $\Phi$ is equal to the potential difference $V(Ni) - V(Al)$ at the muffin-tin sphere of the impurity site and $\Phi = 0$ at Ni sites. Then $L^{-1}$ is the Greenian of pure Ni. As $|j > |$'s we adopt those orbitals of Al which are defined within the muffin-tin sphere of the impurity site with the condition $|j > | = 0$ on the surface. The phase shifts are calculated with Eq. (2) by integrating to the Fermi level $E$ and taking the difference with pure Ni. In the energy range of interest, we can truncate $A$ to retain only the 3 s, p, d contributions, although the following argument is valid even when we need more orbitals. The 3 s contribution to the phase shift, for example, can be expressed as

$$- (1/\pi) \ln \log [(E_t - E_{3s}) - \Sigma_{3s}]$$

with

$$\Sigma_{3s} = M_{3s} L_{3s}^{-1} \Phi_{3s}$$

where $L^{-1}$ is the Greenian of pure Ni. $L^{-1}$ is calculated in turn by use of the 3 d resonance orbitals on the basis of the present method; in the wave vector representation the Greenian is calculated for 203 points in a 1/48 of the Brillouin zone. The calculated $\ln \Sigma_{3s}$ and $L \Sigma_{3p}$ for majority spin are shown in figure 2 together with the

![Figure 2](image-url)

**Figure 2.** The full lines 1 and 2 represent $\ln \Sigma_{3s}$ and $L \Sigma_{3s}^{OPW}$, respectively; the broken lines 3 and 4 $\ln \Sigma_{3p}$ and $L \Sigma_{3p}^{OPW}$; the dotted line 5 is the density of states whose scale is shown on the right. All lines are for majority spin.

density of states of pure Ni obtained from the knowledge of $L^{-1}$. Figure 2 shows also $\ln \Sigma_{3s}^{OPW}$ and $L \Sigma_{3s}^{OPW}$; they are calculated by replacing $L^{-1}$ by the Greenian of OPW, that is, the states whose wave functions are orthogonalized to the core and 3 d orbitals of Ni. $\ln \Sigma^{OPW}$ corresponds to what we would expect if Ni were a simple metal.

The difference between $\ln \Sigma^{OPW}$ and $\ln \Sigma$ corresponds to the interference effect of the d band. Figure 2 tells us that $\ln \Sigma$ becomes small near the top of the d band. This phenomenon is similar to the anti-resonance observed in the optical absorption. The latter occurs, for example, in the case where a discrete excited level to which the transition is forbidden lies in a continuum to which the transition is allowed; the discrete level which corresponds to the d band interferes with the continuum corresponding to OPW states through the mixing between them [10,11]. The anti-resonance does not depend on the species of the impurity, since it is a characteristic of $L^{-1}$. Thus figure 2 confirms our assertion that the phase shifts at $E = E_t$ are small in Ni. Details and further calculations will be published elsewhere.

**References**


[6] CRANGLE (J.) and MARTIN (M. J. C.), Phil. Mag., 1959, 4, 1006.


