

NOTAS DE FÍSICA

VOLUME XVI

Nº 9

EXCHANGE POTENTIAL IN A PSEUDO-POTENTIAL SCHEME

by

X. A. da Silva and A. A. Gomes

CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Av. Wenceslau Braz, 71 - Botafogo - ZC-82

RIO DE JANEIRO, BRAZIL

1970

## EXCHANGE POTENTIAL IN A PSEUDO-POTENTIAL SCHEME

X. A. da Silva and A. A. Gomes  
*Centro Brasileiro de Pesquisas Físicas*  
*Rio de Janeiro, Brazil*

(Received August 17, 1970)

### 1. INTRODUCTION

The problem of describing the magnetic properties associated to the interaction between localized and conduction electrons involves essentially two steps <sup>1, 2</sup>. Firstly one should obtain the one-electron states (both localized and conduction) from a band theoretical calculation. Secondly, one should derive an effective Hamiltonian, written in terms of spin variables (the relevant parameter defining the localized state), describing the Coulomb scattering of these conduction states by the localized electrons. This effective Hamiltonian must incorporate Pauli-principle requirements.

The general philosophy of the second step is discussed in a quite simple way by Caspers <sup>3</sup>. It should be emphasized however that the second step involves to a certain extent the first one in the sense that the one-electron states (conduction and localized) used in the construction of the effective Hamiltonian should be derived from the same one electron Schrodinger equation. This remark concerning internal consistency of the equivalent Hamiltonian approach becomes more clear if one notes that it is crucial in this model to have well energy separated solu-

tions of the crystal's one-electron problem, in order to be possible a clear distinction between conduction and local states. The case where the one-electron potential is not strong enough to bind the magnetic electrons, and resonance phenomena occurs, must be discussed within Anderson's approach<sup>4</sup>. In particular in the present case the orthogonality condition (apart from these energy considerations) between localized and conduction states will play an essential role in discussing the exchange potential. Once the effective Hamiltonian is obtained, perturbation theory is commonly applied to get the magnetic properties, for instance the spin polarization. It should be mentioned that in applying perturbation theory in this last step, one needs unperturbed Bloch states corresponding to the solution of the first step mentioned above, and which usually is obtained through a rather laborious numerical calculation (for instance Gd,<sup>2</sup>). Recently<sup>5</sup>, the method of pseudo potentials has been widely applied in one-electron calculations, since it enables the use of simple perturbation methods. It is the purpose of this note to introduce the pseudo-potential picture to describe the scattering of conduction electrons by localized spins in presence of the periodic crystal potential; we hope that in doing so, both steps of the calculation can be solved within the framework of perturbation theory, giving then an unified view of the problem. In the first and second parts of this note we rederive Casper's<sup>3</sup> effective potential, paying attention to the precise formulation of one-electron states. The rest of the note is devoted to the pseudo-potential formulation of Casper's approach and the interpretation of the results as compared to usual results.

## II. FORMULATION OF THE TWO ELECTRON PROBLEM

We start assuming that the self-consistent one electron crystal potential  $V(r)$  is given. The conduction and localized states satisfy respectively:

$$(T+V)\psi_k(r) = E_k^0 \psi_k(r) \quad (1-a)$$

$$(T+V)\psi_\beta(r) = E_\beta \psi_\beta(r) \quad (1-b)$$

From the hermiticity of T+V it follows the orthogonality condition:

$$\langle \psi_k | \psi_\beta \rangle = 0 \quad \text{for any } k, E_k^0 \neq E_\beta \quad (1-c)$$

This equality holds because of the explicit assumption that the localized state (carrying the magnetic moment) is well separated in energy from the conduction states  $\psi_k$ . We wish to emphasize this point, since for some rare-earth metals (like Cerium for example) the incomplete f-shell emerges into the conduction band, invalidating then our approach. In the following it will be assumed that the localized state is occupied by a single electron. Starting from  $\psi_k(r)$  and  $\psi_\beta(r)$  obtained in (1), it is possible to write down the zeroth-order wave functions for the electron pair (which serve as a basis set for the calculation of the Coulomb scattering):

$$\psi_{k,\beta,M}^{(+)}(r_1, r_2) = \frac{1}{\sqrt{2}} \{ \psi_k(r_1) \psi_\beta(r_2) \pm \psi_k(r_2) \psi_\beta(r_1) \} |S^{(\pm)}, M\rangle \quad (2)$$

$|S^{(\pm)}, M\rangle$  being the normalized spin functions for the singlet (+) and triplet (-) spin states of the pair, with components (respectively 0, and 1,0,-1) specified by M. In this way, taking the Hamiltonian for the pair as given by:

$$\mathcal{H} = T(r_1) + V(r_1) + T(r_2) + V(r_2) + \mathcal{H}'_{12}, \quad \mathcal{H}'_{12} = \frac{e^2}{|r_1 - r_2|} \quad (3)$$

calculating its matrix elements between states (2) and approximately diagonalizing the secular equation obtained, it is in principle possible to get approximate solutions of the Coulomb scattering problem. However it is also possible (and more simple) to work with unsymmetrized coordinate wave functions, incorporating then the exclusion principle requirements into an effective hamiltonian. One proceeds as follows: firstly one defines the complete set of unsymmetrized

states:

$$\tilde{\psi}_{k,\beta,M}^{(+)}(r_1, r_2) = \psi_k(r_1) \psi_\beta(r_2) |S^{(+)}, M\rangle \quad (4)$$

Secondly one determines the effective hamiltonian  $\tilde{\mathcal{H}}$  such that:

$$\langle \tilde{\psi}_{k',\beta',M'}^{(+)} | \tilde{\mathcal{H}} | \psi_{k,\beta,M}^{(+)} \rangle = \langle \tilde{\psi}_{k',\beta',M'}^{(+)} | \tilde{\mathcal{H}} | \tilde{\psi}_{k,\beta,M}^{(+)} \rangle \quad (5)$$

At this point it is useful to introduce a special notation; one defines operators  $P_{12}^r$  and  $P_{12}^s$  as follows:

$$P_{12}^r \psi(r_1, r_2), \text{ for any function } \psi(r_1, r_2) \quad (6-a)$$

$$P_{12}^s = \frac{1}{2} + 2\vec{S}_1 \cdot \vec{S}_2 \quad (6-b)$$

$\vec{S}_1$  and  $\vec{S}_2$  being respectively the conduction and localized electron spin operators.

From definition (6-b) and the form of the spin states  $|S^{(+)}, M\rangle$  one gets:

$$P_{12}^s |S^{(+)}, M\rangle = \frac{1}{4} |S^{(+)}, M\rangle \quad (6-c)$$

Using these definitions, it follows that:

$$\tilde{\psi}_{k,\beta,M}^{(+)}(r_1, r_2) = \frac{1}{\sqrt{2}} (1 - P_{12}^r P_{12}^s) \tilde{\psi}_{k,\beta,M}^{(+)}(r_1, r_2) \quad (7)$$

From (5) and (7) it turns out that a completely equivalent formulation of the initial problem is provided by:

$$\tilde{\mathcal{H}} \tilde{\psi}_\lambda(r_1, r_2) = (1 - P_{12}^r P_{12}^s) \tilde{\mathcal{H}} \tilde{\psi}_\lambda(r_1, r_2) \quad (8-a)$$

$\tilde{\psi}_\lambda(r_1, r_2)$  being the solution of:

$$\tilde{\mathcal{H}} \tilde{\psi}_\lambda = E_\lambda \tilde{\psi}_\lambda \quad (8-b)$$

where  $\tilde{\mathcal{H}}$  is defined by (5) and  $\tilde{\psi}_\lambda$  is in general a linear combination of the unsymmetrized functions (4). In order to obtain the explicit form of  $\tilde{\mathcal{H}}$  one firstly calculates  $\tilde{\mathcal{H}} \tilde{\psi}_{k,\beta,M}^{(+)}$ ; using equations (3), (2) and the notations (6) one gets:

$$\mathcal{H}\psi_{k,\beta,M}^{(+)} = \left[ (E_k^0 + E_\beta) (1 - P_{12}^R P_{12}^S) + \mathcal{H}'_{12} (1 - P_{12}^R P_{12}^S) \right] \frac{1}{\sqrt{2}} \psi_{k,\beta,M}^{(+)} \quad (9)$$

Using explicitly the orthogonality condition (1-c) it follows from (9) that:

$$\langle \psi_{k',\beta',M'}^{(+)} | \mathcal{H} | \psi_{k,\beta,M}^{(+)} \rangle = \delta_{MM'} \left[ (E_k^0 + E_\beta) \delta_{kk'} \delta_{\beta\beta'} \langle k',\beta' | \mathcal{H}'_{12} | k,\beta \rangle + \langle k',\beta' | \mathcal{H}'_{12} | k,\beta \rangle \right] \quad (10a)$$

where the states  $|k,\beta\rangle$  are simple products  $|\psi_k\rangle|\psi_\beta\rangle$  and the matrix elements of  $\mathcal{H}'_{12}$  are defined by:

$$\langle k_1 \beta_1 | \mathcal{H}'_{12} | k_2 \beta_2 \rangle = e \int \frac{\psi_{k_1}^*(r_1) \psi_{\beta_1}^*(r_2) \psi_{k_2}(r_1) \psi_{\beta_2}(r_2)}{|r_1 - r_2|} dr_1 dr_2 \quad (10b)$$

Since  $\mathcal{H}'_{12}$  is spin independent and using equations (6), equation (10a) may be transformed to:

$$\langle \psi_{k',\beta',M'}^{(+)} | \mathcal{H} | \psi_{k,\beta,M}^{(+)} \rangle = \delta_{MM'} \left[ (E_k^0 + E_\beta) \delta_{kk'} \delta_{\beta\beta'} + \langle \psi_{k',\beta',M'}^{(+)} | \mathcal{H}'_{12} (1 - P_{12}^R P_{12}^S) | \psi_{k,\beta,M}^{(+)} \rangle \right] \quad (11)$$

Introducing now the one electron hamiltonian  $\mathcal{H}_0$  by:

$$\mathcal{H}_0 = T(r_1) + V(r_1) + T(r_2) + V(r_2) \quad (12a)$$

one gets finally:

$$\langle \psi_{k',\beta',M'}^{(+)} | \mathcal{H} | \psi_{k,\beta,M}^{(+)} \rangle = \langle \psi_{k',\beta',M'}^{(+)} | \mathcal{H}_0 + \mathcal{H}'_{12} (1 - P_{12}^R P_{12}^S) | \psi_{k,\beta,M}^{(+)} \rangle \quad (12b)$$

Comparing (12b) to (5), and using for  $P_{12}^S$  its explicit form 6-b one gets for  $\bar{\mathcal{H}}$ :

$$\bar{\mathcal{H}} = \mathcal{H}_0 + \mathcal{H}'_{12} = \mathcal{H}_0 + \mathcal{H}'_{12} \left(1 - \frac{1}{2} P_{12}^R\right) - 2 \mathcal{H}'_{12} P_{12}^R \vec{S}_1 \cdot \vec{S}_2 \quad (13)$$

Expression (13) concludes the derivation of the effective hamiltonian for the electron pair case, and shows clearly the two effects introduced by the exclusion principle requirement: Firstly one has a spin-independent term  $\mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^R)$  which contributes together with the one electron terms to the average energy of the two possible states of the pair (singlet and triplet) and secondly the spin dependent term which splits in energy the singlet of the triplet. Now we intend to apply these ideas to the case of an electron gas in

presence of a localized spin.

### III. THE CONDUCTION ELECTRON GAS CASE

The conduction electron gas in presence of a localized spin has in principle quite different aspects from the preceding case, since one wants to consider it separately from the localized spin. More precisely, what one wants is to describe how conduction states (a filled band up to the Fermi level) are perturbed by a localized spin in a definite spin state (say  $\uparrow$ ). In this sense, one needs to have control on the spin state of the localized electron, and one asks for the response of the conduction electrons to the previously established orientation of the local moment.

In this situation the classification of spin in singlet and triplet states is not the more convenient one for this purpose. It is necessary then to adapt the previous formulation to this situation, and this involves several remarks. Firstly one remembers that in the equivalent formulation approach developed above, all Pauli principle requirements are already incorporated. Although the above analysis involves the states  $|S^{(+)}, M\rangle$ , we consider equation (13) as describing the essential features of the complete Coulomb scattering problem. Next step is then to relax the condition of firstly coupling spins (according to usual rules) and then calculating spatial parts, substituting this procedure by another one which seems more suitable for polarization calculation purposes. One proceeds as follows: firstly one searches solutions for the problem of determining  $\Psi_{\lambda}(r_1, r_2)$  in the form:

$$|\Psi_{\lambda}(r_1, r_2)\rangle = \Psi_{\lambda\sigma}(r_1)\rangle|\psi_{\beta}(r_2)\rangle|S_{\beta}(2)\rangle \quad (14)$$

where  $|S_{\beta}(2)\rangle$  is a definite spin states (say  $\uparrow$ ) of the localized electron, and

now because of the coupling between itinerant and localized states, conduction states become a linear combination (with different spatial parts) of electron spin states. This means for instance that  $|\psi_{\lambda\uparrow}(r_1)\rangle$  is a state of spin mainly  $\uparrow$ , involving also a contribution from  $\downarrow$  spin states (cf. below). The general hamiltonian (13) will then be used in order to determine  $|\psi_{\lambda\sigma}\rangle$  since it is assumed (and this is consistent with the fact that the one electron potential is strong enough to well separate in energy the local state from the conduction states) that the spatial part of the local state remains the same even in presence of Coulomb scattering. The usual approach at this point is to use perturbation theory, expanding the spatial parts of  $|\psi_{\lambda\sigma}(r_1)\rangle$  in terms of eigenstates of the one electron problem (obtained from a previous band-theoretical calculation). It is precisely at this step of the polarization calculation that the pseudo-potential approach of one-electron calculations plays the important role of transforming both steps of the approach in a perturbation problem.

#### IV. FORMULATION OF THE PROBLEM IN A PSEUDO-POTENTIAL SCHEME

The basic idea <sup>7</sup> of the pseudo potential method consists in finding an equivalent one-electron hamiltonian, which reproduces correctly the one-electron eigenvalues and eigenfunctions by the use of a perturbation approach. Although these ideas are commonly used in one-electron problem, through the hypothesis summarized in (14), they can also be applied here. Within the spirit of (14) the problem can be formulated as follows: the pseudo wave function  $|\phi_{\lambda\sigma}\rangle$  (this corresponds more precisely to a mainly  $\sigma$  pseudo wave function) is introduced:

$$|\Psi_{\lambda}(r_1 r_1)\rangle = |\psi_{\lambda\sigma}(r_1)\rangle |\psi_{\beta}(r_2)\rangle |s_{\beta}(2)\rangle \quad (15a)$$

$$E_{\lambda} = E_{\beta} + E_{\lambda\sigma} \quad (15b)$$



$$|\psi_{\lambda\sigma}\rangle = (1 - \sum_{\alpha} |\alpha\rangle\langle\alpha|) |\phi_{\lambda\sigma}\rangle \quad (15c)$$

Some comments are necessary at this point; in equation (15b) it is emphasized that the main effect of Coulomb scattering is felt by the conduction states, the energy of the localized state remaining the same as in (1-b); the states  $\{|\alpha\rangle\}$  are all the core states, including the magnetic state  $\psi_{\beta}$ , and the quantum number  $\alpha$  includes the spin also. It follows then from (15c) that the conduction states (even in presence of Coulomb scattering) are automatically orthogonal to inner shell states. Next step is to substitute equations (15) in (8-b) to get:

$$\begin{aligned} & (\mathcal{H}_0 + \mathcal{H}'_{12}) (1 - \sum_{\alpha} |\alpha(1)\rangle\langle\alpha(1)|) |\phi_{\lambda\sigma}(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle = \\ & = (E_{\beta} + E_{\lambda\sigma}) (1 - \sum_{\alpha} |\alpha(1)\rangle\langle\alpha(1)|) |\phi_{\lambda\sigma}(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle \end{aligned} \quad (16)$$

Remembering that core states satisfy:

$$(T+V) |\alpha\rangle = E_{\alpha} |\alpha\rangle \quad (17)$$

one calculates:

$$\begin{aligned} & \mathcal{H}'_{12} (1 - \sum_{\alpha} |\alpha(1)\rangle\langle\alpha(1)|) |\phi_{\lambda\sigma}(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle = \{(T+V) |\phi_{\lambda\sigma}(1)\rangle\} |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle \\ & + E_{\beta} |\phi_{\lambda\sigma}(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle - \sum_{\alpha} (E_{\alpha} + E_{\beta}) |\alpha(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle \langle\alpha| \phi_{\lambda\sigma} \rangle \end{aligned} \quad (18a)$$

Substituting (18a) in (16) one obtains:

$$\begin{aligned} & \{(T+V) |\phi_{\lambda\sigma}(1)\rangle\} |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle - \sum_{\alpha} E_{\alpha} |\alpha(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle \langle\alpha| \phi_{\lambda\sigma} \rangle \\ & + \mathcal{H}'_{12} (1 - \sum_{\alpha} |\alpha(1)\rangle\langle\alpha(1)|) |\phi_{\lambda\sigma}(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle = \epsilon_{\lambda\sigma} (1 - \sum_{\alpha} |\alpha(1)\rangle\langle\alpha(1)|) |\phi_{\lambda\sigma}(1)\rangle | \\ & \psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle \end{aligned} \quad (18b)$$

which can be rewritten as:

$$\begin{aligned} & \{(T+V) |\phi_{\lambda\sigma}(1)\rangle\} |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle + \sum_{\alpha} (\epsilon_{\lambda\sigma} - E_{\alpha}) |\alpha(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle \langle\alpha| \phi_{\lambda\sigma} \rangle \\ & + \mathcal{H}'_{12} (1 - \sum_{\alpha} |\alpha(1)\rangle\langle\alpha(1)|) |\phi_{\lambda\sigma}(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle = \epsilon_{\lambda\sigma} |\phi_{\lambda\sigma}(1)\rangle |\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle \end{aligned} \quad (18c)$$

Now one multiplies (18c) by  $|\psi_{\beta}(2)\rangle |S_{\beta}(2)\rangle$  to get:

$$\begin{aligned}
& (T+V+\sum_{\alpha} (E_{\lambda\sigma} - E_{\alpha}) |\alpha\rangle\langle\alpha|) |\phi_{\lambda\sigma}\rangle + \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} (1-\sum_{\alpha} |\alpha\rangle\langle\alpha|) | \phi_{\lambda\sigma}(1) \psi_{\beta}(2) S_{\beta}(2) \rangle \\
& = \epsilon_{\lambda\sigma} |\phi_{\lambda\sigma}(1)\rangle
\end{aligned} \tag{19}$$

Now we rewrite in a more convenient way the last term of the left hand side of (19); using the explicit form of  $\mathcal{H}'_{12}$  one gets:

$$\begin{aligned}
& \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} (1-\sum_{\alpha} |\alpha\rangle\langle\alpha|) | \phi_{\lambda\sigma}(1) \psi_{\beta}(2) S_{\beta}(2) \rangle = \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} | \phi_{\lambda\sigma}(1) \psi_{\beta}(2) S_{\beta}(2) \rangle \\
& \quad - \sum_{\alpha} \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} | \alpha(1) \psi_{\beta}(2) S_{\beta}(2) \rangle \langle\alpha | \phi_{\lambda\sigma} \rangle \\
& = \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} (1-\frac{1}{2}P_{12}^r) | \phi_{\lambda\sigma}(1) \psi_{\beta}(2) S_{\beta}(2) \rangle - \sum_{\alpha} \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} (1-\frac{1}{2}P_{12}^r) | \\
& \quad \alpha(1) \psi_{\beta}(2) S_{\beta}(2) \rangle \langle\alpha | \phi_{\lambda\sigma} \rangle - 2 \{ \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} P_{12}^r \vec{s}_1 \cdot \vec{s}_2 | \phi_{\lambda\sigma}(1) \psi_{\beta}(2) S_{\beta}(2) \rangle - \\
& \quad - \sum_{\alpha} \langle\psi_{\beta}(2) S_{\beta}(2) | \mathcal{H}'_{12} P_{12}^r \vec{s}_1 \cdot \vec{s}_2 | \alpha(1) \psi_{\beta}(2) S_{\beta}(2) \rangle \langle\alpha | \phi_{\lambda\sigma} \rangle \}
\end{aligned} \tag{20}$$

Within the spirit of pseudo-potential theory, one searches solutions for  $\phi_{\lambda\sigma}(1)$  as linear combinations of plane waves. Now due to the coupling between localized and itinerant electrons, contrary to one-electron calculations, one searches for solutions which are also linear combinations of spin states; more precisely, taking  $k$  as the  $\lambda$  quantum number one has:

$$|\phi_{k\sigma}(1)\rangle = \sum_{q,\sigma'} a_{q\sigma'}^{\sigma} |k+q,\sigma'(1)\rangle \tag{21}$$

where  $|k+q,\sigma(1)\rangle$  stands for the simple product  $|k+q(1)\rangle |S_{\sigma}(1)\rangle$ ,  $\sigma$  being  $\uparrow$  or  $\downarrow$ . The coefficients  $a_{q\sigma'}^{\sigma}$  will be determined in powers of the perturbations, that means in powers of Harrison's pseudopotential  $W = V + \sum_{\alpha} (E_{k\sigma} - E_{\alpha}) |\alpha\rangle\langle\alpha|$  and the Coulomb coupling. These remarks and equation (21) enable us to rewrite expression (19) in a quite useful way:

$$\begin{aligned}
& (T+W) \sum_{q', \sigma'} a_{q', \sigma'}^{\sigma} |k+q', \sigma'(1)\rangle + \sum_{q', \sigma'} a_{q', \sigma'}^{\sigma} \{ \langle \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^r) | k+q', (1)\sigma'(1) \psi_{\beta}(2) \rangle \\
& - \sum_{\alpha} \langle \alpha | k+q' \rangle \langle \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^r) | \alpha(1) \sigma'(1) \psi_{\beta}(2) \rangle \} \\
& - 2 \sum_{q', \sigma'} a_{q', \sigma'}^{\sigma} \{ \langle \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^r | k+q(1) \psi_{\beta}(2) \rangle - \sum_{\alpha} \langle \alpha | k+q' \rangle \langle \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^r | \alpha(1) \psi_{\beta}(2) \rangle \} \\
& \times \langle s_{\beta}(2) | \hat{S}_1 \cdot \hat{S}_2 | \sigma'(1) s_{\beta}(2) \rangle = \epsilon_{k\sigma} \sum_{q', \sigma'} a_{q', \sigma'}^{\sigma} |k+q', \sigma'(1)\rangle \quad (22)
\end{aligned}$$

### V. SOLUTION OF (22) IN PERTURBATION THEORY

Now we obtain the coefficients  $a_{q', \sigma'}^{(1)}$  where (1) means the i-th order in the perturbations (W and Coulomb interaction), and the energies are written as:

$$\epsilon_{k\sigma} = \epsilon_{k\sigma}^0 + \epsilon_{k\sigma}^{(1)} + \dots \quad (23)$$

The zeroth order terms is simply given by:

$$T | \phi_{k\sigma}^0 \rangle = \epsilon_{k\sigma}^0 | \phi_{k\sigma}^0 \rangle \quad (24a)$$

where  $\epsilon_k^0 = \frac{k^2}{2m}$  and  $| \phi_k^0 \rangle = | k \rangle | \sigma \rangle$ , which corresponds to

$$a_{q', \sigma'}^{(0)} = \delta_{q', 0} \delta_{\sigma \sigma'} \quad (24b)$$

The first order term is obtained from (22) as:

$$\begin{aligned}
& \sum_{q', \sigma''} a_{q', \sigma''}^{\sigma(1)} T | k+q', \sigma''(1) \rangle + \sum_{q', \sigma''} a_{q', \sigma''}^{\sigma(0)} | k+q', \sigma''(1) \rangle + \\
& + \sum_{q', \sigma''} a_{q', \sigma''}^{(0)} \langle \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^r) | k+q'(1) \psi_{\beta}(2) \rangle | \sigma''(1) \rangle \\
& - \sum_{\alpha, q', \sigma''} a_{q', \sigma''}^{\sigma(0)} \langle \alpha | k+q' \rangle \langle \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^r) | \alpha(1) \psi_{\beta}(2) \rangle | \sigma''(1) \rangle \\
& - 2 \sum_{q', \sigma''} a_{q', \sigma''}^{(0)} \{ \langle \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^r | k+q'(1) \psi_{\beta}(2) \rangle -
\end{aligned}$$

$$\begin{aligned}
& - \sum_{\alpha} \langle \alpha | k+q' \rangle \langle \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^F | \alpha(1) \psi_{\beta}(2) \rangle \langle S_{\beta}(2) | \vec{S}_1 \cdot \vec{S}_2 | \sigma''(1) S_{\beta}(2) \rangle \\
& = \varepsilon_{k\sigma}^{(1)} \sum_{q', \sigma''} a_{q', \sigma''}^{(0)} |k+q', \sigma''(1)\rangle + \varepsilon_{k\sigma}^{(0)} \sum_{q', \sigma''} a_{q', \sigma''}^{\sigma(1)} |k+q', \sigma''(1)\rangle \quad (25)
\end{aligned}$$

Now remembering that  $T|k+q', \sigma''(1)\rangle = \frac{(k+q')^2}{2m} |k+q', \sigma''(1)\rangle$  one obtains multiplying (25) by  $|k+q, \sigma'(1)\rangle$  (using in this calculation equation 24-b for  $a_{q', \sigma}^{\sigma(0)}$ ):

$$\begin{aligned}
& a_{q\sigma'}^{\sigma(1)} \left( \frac{(k+q)^2}{2m} - \frac{k^2}{2m} \right) + \langle k+q | W | k \rangle \delta_{\sigma\sigma'} + \delta_{\sigma\sigma'} \{ \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^F) | k(1) \psi_{\beta}(2) \rangle \\
& - \sum_{\alpha} \langle \alpha | k \rangle \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^F) | \alpha(1) \psi_{\beta}(2) \rangle \} \\
& - 2 \{ \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^F | k(1) \psi_{\beta}(2) \rangle - \sum_{\alpha} \langle \alpha | k \rangle \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^F | \alpha(1) \psi_{\beta}(2) \rangle \} \\
& \times \langle \sigma'(1) S_{\beta}(2) | \vec{S}_1 \cdot \vec{S}_2 | \sigma(1) S_{\beta}(2) \rangle = 0
\end{aligned}$$

Now we introduce the following effective matrix elements:

$$\begin{aligned}
\langle k+q | W^* | k \rangle & = \langle k+q | W | k \rangle + \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^F) | k(1) \psi_{\beta}(2) \rangle \\
- \sum_{\alpha} \langle \alpha | k \rangle \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} (1 - \frac{1}{2} P_{12}^F) | \alpha(1) \psi_{\beta}(2) \rangle & \quad (27a)
\end{aligned}$$

and

$$\langle k+q | J^* | k \rangle = \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^F | k(1) \psi_{\beta}(2) \rangle - \sum_{\alpha} \langle \alpha | k \rangle \langle k+q(1) \psi_{\beta}(2) | \mathcal{H}'_{12} P_{12}^F | \alpha(1) \psi_{\beta}(2) \rangle \quad (27b)$$

Using these definitions, one obtains from (26):

$$a_{q\sigma'}^{\sigma(1)} = \frac{\langle k+q | W^* | k \rangle}{k^2/2m - (k+q)^2/2m} \delta_{\sigma\sigma'} - \frac{2 \langle k+q | J^* | k \rangle}{k^2/2m - (k+q)^2/2m} \langle \sigma'(1) S_{\beta}(2) | \vec{S}_1 \cdot \vec{S}_2 | \sigma(1) S_{\beta}(2) \rangle \quad (28)$$

It remains to evaluate the spin matrix element in (28); using

$$2\vec{S}_1 \cdot \vec{S}_2 = S_1^+ S_2^- + S_1^- S_2^+ + 2S_1^z S_2^z \quad (29)$$

it turns out that

$$2\langle\sigma'(1)S_\beta(2)|\vec{S}_1 \cdot \vec{S}_2|\sigma(1)S_\beta(2)\rangle = 2\sigma\delta_{\sigma\sigma'} S_2^z + S_{\sigma'}^z - \sigma S_2^\sigma \quad (30)$$

where  $S_2^\sigma$  is defined as  $S_2^+$ .

Substituting (30) in (28) one obtains finally for the coefficients

$$a_{q\sigma'}^\sigma = \frac{\langle k+q|W^*|k\rangle}{k^2/2m - (k+q)^2/2m} \delta_{\sigma\sigma'} - \frac{\langle k+q|J^*|k\rangle}{k^2/2m - (k+q)^2/2m} \{2\sigma\delta_{\sigma\sigma'} S_2^z + \delta_{\sigma'}^z - \sigma S_2^\sigma\} \quad (31)$$

Finally the pseudo wave function of spin mainly  $\sigma$  reads:

$$|\phi_{k\sigma}^{(1)}(1)\rangle = \sum_{q \neq 0} \frac{\langle k+q|W^*|k\rangle}{k^2/2m - (k+q)^2/2m} |k+q, \sigma\rangle - \sum_{q \neq 0} \frac{\langle k+q|J^*|k\rangle}{k^2/2m - (k+q)^2/2m} \{2\sigma S_2^z |k+q, \sigma\rangle + S_2^\sigma |k+q, -\sigma\rangle\} \quad (32)$$

Combining equations (32) and (15-c) one obtains for the "true" conduction states:

$$|\psi_{k\sigma}^{(1)}(1)\rangle = \sum_{q \neq 0} \frac{\langle k+q|W^*|k\rangle}{k^2/2m - (k+q)^2/2m} (1 - \sum_{\alpha} |\alpha\rangle\langle\alpha|) |k+q, \sigma\rangle - \sum_{q \neq 0} \frac{\langle k+q|J^*|k\rangle}{k^2/2m - (k+q)^2/2m} \{2\sigma S_2^z (1 - \sum_{\alpha} |\alpha\rangle\langle\alpha|) |k+q, \sigma\rangle + S_2^\sigma (1 - \sum_{\alpha} |\alpha\rangle\langle\alpha|) |k+q, -\sigma\rangle\} \quad (33)$$

## CONCLUSION

The spin-polarization problem was thus reduced to a "double" perturbation problem where crystal effects and Coulomb scattering are discussed within the

same perturbation theoretic approach. There are however, apart of these conceptual points, some physical insights that one obtains in paying attention to the orthogonalization requirements. The perhaps most important consequence of this pseudo-potential approach is given by the "effective" matrix elements defined in (27-a, 27-b). In usual perturbation calculations of the spin polarization, starting from a free-electron gas <sup>6</sup>, the "exchange coupling"  $J(k+q,k)$  is given by the first term of (27-b). Now, due to orthogonality effects (involving in particular the magnetic shell  $|\psi_\beta\rangle = |\beta\rangle$ ) one introduces a "reduction" of the exchange coupling given by the second term of (27-b). It should be emphasized that this correction has nothing to do with Coulomb scattering, but only reflects the fact that conduction states near a nucleus looks as atomic-like functions, and one should extract from the plane waves some amount of the spherical harmonics already present as core states in order to calculate the exchange coupling. Finally, we want to remark that some cases occur (for instance noble and transition metals) where apart of deep core states one has filled d-bands near the Fermi level. The main consequence of this (see Harrison <sup>5</sup>) is the occurrence of s-d mixing; consequently one expects that the reduction factor will involve also d-d matrix elements of the Coulomb interaction which are thought to be quite important in discussing these cases. This point will be discussed in a forthcoming note.

\* \* \*

#### REFERENCES

1. G. Bambakidis, J. Phys. Chem. Sols. 31, 503 (1970).
2. T. L. Loucks, "Augmented Plane Wave Method" (Benjamin 1967).
3. W. J. Caspers, Physics I, 45 (1964).
4. B. Coqblin and Schrieffer, Phys. Rev., 185, 847 (1969).
5. W. A. Harrison, "Pseudo-Potentials in the Theory of Metals" (Benjamin 1966).
6. K. Yosida, Phys. Rev. 106, 893 (1957).