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MULTIPLE SCATTERING WITHIN FINITE AND INFINITE SYSTEMS OF GENERALIZED MUFFIN-TIN POTENTIALS. GENERALIZATIONS OF THE CLUSTER EQUATIONS, THE LLOYD-FORMULA AND THE KKR EQUATIONS

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1. Introduction

The well-known concept of so-called muffin-tin potentials (MT-potentials) is used often and in different fields. In solid state theory it is of interest for bandstructure calculations (APW, KKR), for the derivation of model hamiltonians (pseudopotentials for simple metals, hybridized nearly free electron tight binding schemes for transition metals) and for the discussion of the electron density of states in disordered systems (pseudogaps in semiconductors with definite short range order; see Mc Gill and Klima 1972, Keller 1972 and John 1973). In the electron theory of molecules this MT-concept is used both for bound states (see Johnson and Smith 1972) and for the elastic electron scattering on molecules (Demkov and Rudakov 1970, John and Ziesche 1971). An essential advantage of this MT-concept consists in that structure (atomic sites $\vec{R}_i$) and atomic potential, the latter only via its phase shifts η_L^i enter into the theory by separated quantities. On the other hand the accuracy of calculations is restricted by the use of the MT-approximation, simplifying the potential in the following way:

1. The potential within the muffin-tin spheres is assumed to be spherically symmetric. Deviations from this assumption arise for instance from partially filled d-bands in transition metals (Jacobs 1970) or from covalent bands in semiconductors (Kane 1971).

2. The potential between non-overlapping spheres, centered at the atomic sites is assumed to be constant. This is of course reasonable only for close packed structures, but leads for more open structures as diamond to essential errors (Kane 1971).

There are several attempts to overcome both restrictions. Evans and Keller (1971) and John et al. (1972) discuss non-spherically symmetric potentials in the band structure calculation methods (KKR, APW), while Pettifor (1972) investigates such potentials in molecular problems (bound states). The APW method is generally not limited to MT-potentials and in the last two years several authors have studied corrections of the original MT concept within this method. For the KKR method the situation is not so simple. Andersen and Kasowski (1971) use MT-orbitals to overcome both restrictions. Bross and Anthony (1967) as well as Beleznay and Lawrence (1968) have generalized the KKR method, taking into account a non-zero potential between the MT-spheres. Unfortunately this destroys the simple structure of the KKR equations, which may be conserved by another approach, namely by the installation of additional MT-potentials at interstitial sites, as first performed by Keller (1971 b). This of course increases the number of scatterers in the unit cell. Besides there are attempts to extent the KKR method also to the case of overlapping spheres, enveloping the spherically or non-spherically symmetric atomic potentials (Williams 1970, Ball 1972, Williams and Morgan 1972). Here it is shown, that only in the case of non-overlapping enveloping MT-spheres the simple structure of the original KKR method is conserved owing to otherwise divergent angular momenta expansions. To discuss this in more detail, generalized MT-potentials are introduced, being non-zero within an arbitrary volume $\mathcal{V}$ (see Fig.1). In Section 2 the scattering states of such a single generalized MT-potential are described by generalized phase shifts η_λ and corresponding partial wave

amplitudes $A_{L\lambda}$ as recently introduced by Demkov and Rudakov (1970) and furtherly studied by John and Ziesche (1971a) and differently applied (generalized Friedel sum rule and Lloyd-formula: John and Ziesche 1971a, Saxon-Hutner gap criteria for alloys: John 1971, KKR- and AFW-method for non-spherically symmetric MT-potentials: John et al. 1972, localized defects in metals: Lehmann 1973a,b, Rennert and Ziesche 1972). In Section 3 finite clusters of such generalized (of course non-overlapping) MT-potentials, the scattering states of which are assumed to be known, are considered. If certain structure matrices determined by integrations along the surfaces of pairs of these MT-volumes, are known, a purely algebraic scheme for the cluster phase shifts η_μ and their amplitudes $\vartheta_{L\mu}$ holds. In Sections 4 and 5 infinite systems are discussed. Using the cluster equations derived in Section 3, a generalized Lloyd-formula is obtained immediately for the density of states in disordered systems and generalized KKR-equations for the band structure of crystals. In the latter case there are included also potentials non-zero within the whole unit cell and therefore separated only by thin skins of zero potential along the boundaries of the unit cells, so that the envelopping spheres of immediately neighboured unit cells overlap. As a consequence of this in the KKR-structure matrices only the unit cells, far enough from each other, can be treated in the usual manner, while for the immediately neighboured unit cells the near fields of their scattering states must be taken into account, which cannot be described only by the asymptotic or far field characteristics. Therefore KKR equations appear, modified generally not only by the replacement $tg\eta_L \delta_{LL'} \to (tg\eta)_{LL'}$ but

also by at least a partial change in the structure matrices, splitting into a simple far field and a rather complicated near field part.

2. A single generalized muffin-tin potential

A generalized MT-potential is defined here to be non-zero only within a certain volume $\mathcal{V}$ (see Fig. 1). The scattering states $\varphi_\lambda(\vec{r})$ of such a MT-potential are characterized by a behaviour outside the envelopping sphere ($r > r_0$)

$$\varphi_\lambda(\vec{r}) \sim \sum_L \left[j_L(\vec{r}) A_{L\lambda} \cos\eta_\lambda - n_L(\vec{r}) A_{L\lambda} \sin\eta_\lambda \right], \qquad (2.1)$$

containing generalized phase shifts η_λ and real partial wave amplitudes $A_{L\lambda}$. As in (John and Ziesche 1971a) the abbreviations

$$j_L(\vec{r}) \equiv j_\ell(\varkappa r)\, Y_L(\vec{n}), \quad n_L(\vec{r}) \equiv n_\ell(\varkappa r)\, Y_L(\vec{n}), \quad \vec{n} \equiv \frac{\vec{r}}{r} \qquad (2.2)$$

are used. j_ℓ and n_ℓ are the usual spherical Bessel and Neumann functions, respectively. Y_L are real spherical harmonics, $L \hat{=} (\ell, m_\ell)$.

The non-trivial scattering states (characterized by $\sin\eta_\lambda \neq 0$) are determined by the Schrödinger integral equation

$$\varphi_\lambda(\vec{r}) = \int_{\mathcal{V}} d\vec{r}' \int_{\mathcal{V}} d\vec{r}'' \, G(\vec{r}-\vec{r}') V(\vec{r}', \vec{r}'')\, \varphi_\lambda(\vec{r}''), \qquad (2.3)$$

$$G(\vec{r}-\vec{r}') \equiv \frac{\varkappa}{4\pi} \left[n_0(\varkappa|\vec{r}-\vec{r}'|) - \operatorname{ctg}\eta_\lambda\, j_0(\varkappa|\vec{r}-\vec{r}'|) \right].$$

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2) The φ_λ used here differ from those used in (John and Ziesche 1971a) by a minus sign .

With the help of the usual expansions

$$\frac{1}{4\pi} j_0(\varkappa|\vec{r}-\vec{r}'|) = \sum_L j_L(\vec{r})\, j_L(\vec{r}') \quad \text{for } r \gtrless r', \tag{2.4}$$

$$\frac{1}{4\pi} n_0(\varkappa|\vec{r}-\vec{r}'|) = \sum_L n_L(\vec{r})\, j_L(\vec{r}') \quad \text{for } r > r' \tag{2.5}$$

and demanding

$$(j_L, V\varphi_\lambda) = A_{L\lambda}\left(-\frac{1}{\varkappa}\right)\sin\eta_\lambda \tag{2.6}$$

(2.3) realizes the asymptotic behaviour (2.1). For a given energy $E = \varkappa^2$ the equation (2.3) possesses solutions only for certain phase shifts η_λ. By the way, from (2.3) and (2.6) it follows, that $K_\lambda \equiv (-1/\varkappa)\operatorname{tg}\eta_\lambda$ and $A_{L\lambda}$ are the eigenvalues and the eigenvectors of the K-matrix

$$K = V + VG^{\circ}K, \qquad G^{\circ}(\vec{r}-\vec{r}') \equiv \frac{\varkappa}{4\pi} n_0(\varkappa|\vec{r}-\vec{r}'|) \tag{2.7}$$

in its L-representation on the energy shell, $K_{LL'} = (j_L, K j_{L'})$. Because the K-matrix is real and symmetric, the amplitudes are also real and form an orthogonal and complete set. As a consequence of the finite range r_0 the amplitudes $A_{L\lambda}$ are small for $l \gg \varkappa r_0$, as it is shown for a simple example in Appendix 1.

In the following it is necessary to assume, that besides η_λ and $A_{L\lambda}$ also the wave function φ_λ and its normal derivative $\partial\varphi_\lambda/\partial n$ along the surface of $\mathcal{V}$ are known. These latter quantities determine the wave function outside $\mathcal{V}$ and inside the envelopping sphere $r < r_0$ ("near field"), while η_λ and $A_{L\lambda}$ determine only the "far field" beyond the envelopping sphere $r > r_0$. This is seen, rewriting (2.3) by means of partial integration as (here the index λ is dropped and the index at $\partial/\partial\vec{r}$ shows on which function it only acts):

$$\oint_{(\mathcal{V})} d\vec{f}' \left[\left(\frac{\partial}{\partial \vec{r}'}\right)_{\varphi} - \left(\frac{\partial}{\partial \vec{r}'}\right)_{G}\right] G(\vec{r}-\vec{r}')\,\varphi_\lambda(\vec{r}') = \begin{cases} 0 & \vec{r} \in \mathcal{V} \\ \varphi_\lambda(\vec{r}) & \vec{r} \notin \mathcal{V} \end{cases} \tag{2.8a}$$

(2.8b)

Really, from (2.8) it follows, that the wave function outside $\mathcal{V}$ takes the form

$$\varphi_\lambda(\vec{r}) = j_\lambda(\vec{r})\cos\eta_\lambda - n_\lambda(\vec{r})\sin\eta_\lambda \tag{2.9}$$

with (for $\vec{r} \notin \mathcal{V}$)

$$j_\lambda(\vec{r}) = \sum_L j_L(\vec{r})\, A_{L\lambda} \,,$$

$$n_\lambda(\vec{r}) = \varkappa \oint_{(\mathcal{V})} d\vec{f}' \left[\left(\frac{\partial}{\partial \vec{r}'}\right)_n - \left(\frac{\partial}{\partial \vec{r}'}\right)_{\varphi}\right] \frac{1}{4\pi} n_0(\varkappa|\vec{r}-\vec{r}'|)\varphi_\lambda(\vec{r}') \,. \tag{2.10}$$

Using the expansion (2.5), the comparison with (2.1) for $r > r_0$ yields the relation

$$A_{L\lambda}\sin\eta_\lambda = \varkappa \oint_{(\mathcal{V})} d\vec{f}' \left[\left(\frac{\partial}{\partial \vec{r}'}\right)_j - \left(\frac{\partial}{\partial \vec{r}'}\right)_{\varphi}\right] j_L(\vec{r}')\varphi_\lambda(\vec{r}') \,, \tag{2.11}$$

following also directly from (2.6) by partial integration.
In addition (2.8a) yields with (2.4) and (2.5)

$$A_{L\lambda}\cos\eta_\lambda = \varkappa \oint_{(\mathcal{V})} d\vec{f}' \left[\left(\frac{\partial}{\partial \vec{r}'}\right)_n - \left(\frac{\partial}{\partial \vec{r}'}\right)_{\varphi}\right] n_L(\vec{r}')\varphi_\lambda(\vec{r}') \,. \tag{2.12}$$

(2.11) and (2.12) connect the asymptotic quantities with the surface quantities φ_λ , $\partial\varphi_\lambda/\partial n$.

By the way, with the replacements $\varkappa \to i\varkappa$ and $\operatorname{ctg}\eta_\lambda \to i$, the latter guaranteeing the wave function to remain finite, also bound states $E = -\hbar^2\varkappa^2$ can be included into the discussion.

3. Finite systems

Now we consider a cluster of such muffin-tins within non-overlapping volumes $\mathcal{V}_i$, to each of which is attached a site $\vec{R}_i$.

The asymptotic properties of η_λ^i and A_{LA}^i are related to these sites $\vec{R}_i$. The cluster wave function $\varphi_\mu^i(\vec{r})$ in the immediate environment of $\mathcal{V}_i$ follows from an appropriate linear combination of the MT-orbitals $\varphi_\lambda^i(\vec{r})$

$$\varphi_\mu^i(\vec{r}) = \sum_\lambda \left[j_\lambda^i(\vec{r}) \cos\eta_\lambda^i - n_\lambda^i(\vec{r}) \sin\eta_\lambda^i \right] b_{\lambda\mu}^i \sin\eta_\mu . \tag{3.1}$$

The cluster wave function in the whole space, $\varphi_\mu(\vec{r})$, and the cluster-equations, determining the cluster phase shifts η_μ and the cluster amplitudes $b_{\lambda\mu}^i$, are obtained directly from (2.8), taking into account only the replacement $\mathcal{V} \to \sum \mathcal{V}_i$. Really (2.8b) yields with the help of (3.1) immediately the cluster wave functions (outside the volumes $\mathcal{V}_i$)

$$\boxed{\varphi_\mu(\vec{r}) = \sum_{i,\lambda} \left[j_\lambda^i(\vec{r}) \cos\eta_\mu - n_\lambda^i(\vec{r}) \sin\eta_\mu \right] B_{\lambda\mu}^i .} \tag{3.2}$$

with $B_{\lambda\mu}^i = \sin\eta_\lambda^i \, b_{\lambda\mu}^i$. Again using (3.1) from (2.8a) there follow the cluster equations (for $\sin\eta_\lambda^i \neq 0$)

$$\boxed{\sum_{i,\lambda} \left[\delta_{ii'} \delta_{\lambda\lambda'} + \mathrm{tg}\eta_\lambda^i \left(N_{\lambda\lambda'}^{ii'} - \mathrm{ctg}\eta_\mu \right]_{\lambda\lambda'}^{ii'} \right) B_{\lambda'\mu}^{i'} = 0,} \tag{3.3}$$

namely acting on (2.8a) by

$$\sum_{(\mathcal{V}_i - \mathcal{E})} \oint\!\!\!\oint d\vec{f} \left[\left(\frac{\partial}{\partial \vec{r}} \right)_\varphi - \left(\frac{\partial}{\partial \vec{r}} \right)_G \right] \varphi_\lambda^i(\vec{r}).$$

If one uses in this operation instead of $\varphi_\lambda^i(\vec{r})$ the function $\sum_L n_L(\vec{r}_i) A_{L\lambda}^i$ with λ corresponding to the trivial MT-states (with $\sin\eta_\lambda^i = 0$), then the coefficients $b_{\lambda\mu}^i$ for such λ ,

$$b_{\lambda\mu}^i = \sum_{i',\lambda'} \left[\mathrm{ctg}\eta_\mu \right]_{\lambda\lambda'}^{ii'} - N_{\lambda\lambda'}^{ii'} \Big], \tag{3.4}$$

appear, needed in the expression (3.1) for $\varphi_\mu^i(\vec{r})$. The first term in (3.3) arises from

$$\approx \oint_{(U_i-\varepsilon)} d\vec{f}\left[\left(\frac{\partial}{\partial \vec{r}}\right)_{\varphi}-\left(\frac{\partial}{\partial \vec{r}}\right)_{n_0}\right]\varphi^{i}_{\lambda}(\vec{r}) \times \oint_{(U_i)} d\vec{f}'\left[\left(\frac{\partial}{\partial \vec{r}'}\right)_{\varphi}-\left(\frac{\partial}{\partial \vec{r}'}\right)_{n_0}\right]\varphi^{i}_{\lambda'}(\vec{r}')\frac{1}{4\pi} n_0(\varkappa|\vec{r}-\vec{r}'|)$$

$$= \sin\eta^{i}_{L\lambda}\ \ \delta_{\lambda\lambda'}\cos\eta^{i}_{L'\lambda'}\ , \qquad (3.5)$$

which is seen, deforming the integration surfaces appropriately, using (2.5), (2.11), (2.12) and the orthogonality of $A_{L\lambda}$. The left-hand side of (3.4) is similarly defined. The second term in (3.3) and (3.4) contains a structure matrix $N^{ii'}_{\lambda\lambda'}$ defined as

$$N^{ii'}_{\lambda\lambda'}=(1-\delta_{ii'})\frac{\varkappa}{\sin\eta^{i}_{L\lambda}}\oint_{(U_i)} d\vec{f}\left[\left(\frac{\partial}{\partial \vec{r}}\right)_{\varphi}-\left(\frac{\partial}{\partial \vec{r}}\right)_{n_0}\right]\varphi^{i}_{\lambda}(\vec{r})\frac{\varkappa}{\sin\eta^{i'}_{L'\lambda'}}\oint_{(U_{i'})} d\vec{f}'\left[\left(\frac{\partial}{\partial \vec{r}'}\right)_{\varphi}-\left(\frac{\partial}{\partial \vec{r}'}\right)_{n_0}\right]\varphi^{i'}_{\lambda'}(\vec{r}')\times$$

$$\times\frac{1}{4\pi} n_0(\varkappa|\vec{r}-\vec{r}'|). \qquad (3.6)$$

If as in (3.4) λ is a trivial MT-state (with $\sin\eta^{i}_{\lambda}=0$), then $\varphi^{i}_{\lambda}(\vec{r})$ must be replaced by $\sum_{L}\tilde{A}^{i}_{\lambda L} n_L(\vec{r}_i)$. The structure matrix $J^{ii'}_{\lambda\lambda'}$ in the third term of (3.3) is similarly defined, only with $j_0(\ldots)$ instead of $n_0(\ldots)$. Owing to the restriction of the expansion (2.5), the complicated expression (3.6) can be reduced to the asymptotic quantities $A^{i}_{L\lambda}$ and a much more simple matrix $N^{ii'}_{LL'}$, containing only the point structure $\vec{R}_i$, only if the volumes U_i are within non-overlapping spheres around their corresponding sites $\vec{R}_i$:

$$N^{ii'}_{\lambda\lambda'}=\sum_{L,L'}\tilde{A}^{i}_{\lambda L}N^{ii'}_{LL'}A^{i'}_{L'\lambda'}\ . \qquad (3.7)$$

Otherwise, that is for overlapping envelopping spheres, the asymptotic properties are not sufficient and near field properties as in (3.6) must be taken into account. The corresponding relation

$$J^{ii'}_{\lambda\lambda'}=\sum_{L,L'}\tilde{A}^{i}_{\lambda L}J^{ii'}_{LL'}A^{i'}_{L'\lambda'} \qquad (3.8)$$

always holds, because the expansion (2.4) is valid without restrictions. Deriving (3.7) and (3.8), the relation (2.11) and the addition theorems for j_L $(\vec{r}_1+\vec{r}_2)$ (see Ziman 1966) and

$n_L(\vec{r}_1+\vec{r}_2)$ (see Lloyd 1969, 1972, Andersen 1971, John and Ziesche 1971a, Ziesche 1972) have been used. The point structure matrices appearing in (3.7) and (3.8) are defined by

$$\begin{aligned} \mathcal{J}^{ii'}_{LL'} &\equiv 4\pi \sum_{L''} C_{LL'L''} i^{L-L'+L''} j_{L''}(\vec{R}_{ii'}) = i^{L-L'} \int d\Omega\, Y_L(\vec{n}) e^{i\kappa\vec{n}\vec{R}_{ii'}} Y_{L'}(\vec{n}), \\ \mathcal{N}^{ii'}_{LL'} &\equiv (1-\delta_{ii'})\, 4\pi \sum_{L''} C_{LL'L''} i^{L-L'-L''} n_{L''}(\vec{R}_{ii'}) \end{aligned} \tag{3.9}$$

with $\vec{R}_{ii'} \equiv \vec{R}_i - \vec{R}_{i'}$ and with $C_{LL'L''} \equiv \int d\Omega\, Y_L(\vec{n}) Y_{L'}(\vec{n}) Y_{L''}(\vec{n})$ as Gaunt coefficients.

The cluster equations (3.3) have been derived here analogously with Kohn/Rostoker (1954). Of course they can be obtained also by a Rayleigh treatment a la Korringa 1947, considering (3.2) as an ansatz and demanding $\psi_\mu = \psi'_\mu$ in the surrounding of each $\mathcal{V}_i$ as the "Rayleigh-Huygens" self-consistency condition for diffraction (Ziesche 1973). (3.3) then is the condition for that all wave functions (3.1) have the same continuation (3.2) into the whole space (outside the volumes $\mathcal{V}_i$) with an asymptotic behaviour ($r > r_0$)

$$\psi_\mu(\vec{r}) = \sum_L \left[j_L(\vec{r})\, B_{L\mu} \cos\eta_\mu - n_L(\vec{r})\, B_{L\mu} \sin\eta_\mu \right], \tag{3.10}$$

following from (3.2) by means of the mentioned addition theorems for j_L and n_L. The asymptotic behaviour is described by cluster phase shifts η_μ and asymptotic or far field amplitudes $B_{L\mu}$, resulting from the near field amplitudes $B'_{L\mu}$ by

$$B_{L\mu} = \sum_{i\lambda} \mathcal{J}^{oi}_{L\lambda} B'_{\lambda\mu}, \qquad \mathcal{J}^{oi}_{L\lambda} \equiv \sum_{L'} \mathcal{J}^{oi}_{LL'} A^{i}_{L'\lambda}. \tag{3.11}$$

As a consequence of (3.3) the amplitudes are orthogonal to each other for different cluster scattering states μ

$$\sum_L \tilde{B}_{\mu L} B_{L\mu'} = \sum_{i'\lambda} \tilde{B}^{i}_{\mu\lambda} \mathcal{J}^{ii'}_{\lambda\lambda'} B^{i'}_{\lambda'\mu'} = \delta_{\mu\mu'}, \tag{3.12}$$

with $\widetilde{B}_{\mu L} \equiv B_{L\mu}$. Here

$$\sum_{L} j^{i0}_{lL}\, \widetilde{j}^{i0}_{Lk'} = \delta^{ii'}_{\lambda\lambda'} \qquad (3.13)$$

has been used, which follows again from the mentioned addition theorem for j_L .

Just as in the case of spherically symmetric MT's (John and Ziesche 1971a) the cluster equations (3.3) determine as many non-trivial cluster scattering states (with $\sin\eta_\mu \neq 0$) as non-trivial MT-phase shifts η^i_λ (with $\sin\eta^i_\lambda \neq 0$) exist. Also $\partial\eta_\mu / \partial\eta^i_\lambda > 0$ holds as for spherically symmetric MT's. Finally with $\operatorname{ctg}\eta_\mu = i$ and $\varkappa = i\bar{\varkappa}$ also bound states $E = -\bar{\varkappa}^2 < 0$ are determined by (3.3).

Similarly as in(John and Ziesche 1971b) the cluster- K-matrix in its L-representation on the energy shell

$$K_{LL'} = \sum_{\mu} B_{L\mu} K_\mu \widetilde{B}_{\mu L'} \quad , \qquad K_\mu \equiv -\frac{1}{\varkappa} \operatorname{tg}\eta_\mu \qquad (3.14)$$

is obtained from the cluster equations (3.3) as

$$\boxed{\begin{aligned} K_{LL'} &= \sum_{i,i',\lambda,\lambda'} j^{i0}_{L\lambda} \left(M^{-1}\right)^{ii'}_{\lambda\lambda'} K^{i'}_{\lambda'} j^{i'0}_{\lambda' L'} \\ M^{ii'}_{\lambda\lambda'} &\equiv \delta_{ii'}\,\delta_{\lambda\lambda'} - \varkappa K^{i}_{\lambda} N^{ii'}_{\lambda\lambda'} \end{aligned}} \qquad (3.15)$$

This follows of course also directly from (2.7) (see Ziesche 1973b).If the envelopping spheres do not overlap, then (3.6) applies and (3.15) takes the form

$$\boxed{\begin{aligned} K_{LL'} &= \sum_{i,i',\lambda_1,\lambda_2,\lambda_3} j^{i0}_{L\lambda_1} \left(M^{-1}\right)^{ii'}_{\lambda_2\lambda_3} K^{i'}_{\lambda_2} j^{i'0}_{\lambda_3 L'} \\ M^{ii'}_{LL'} &\equiv \delta_{ii'}\,\delta_{LL'} - \varkappa \sum_{\lambda_1} K^{i}_{L\lambda_1} N^{ii'}_{\lambda_1 L'} \end{aligned}} \qquad (3.16)$$

in agreement with Lloyd (1969, 1972), only with the difference, that the single scatterer K-matrices on the energy shell here are expressed explicitly by their eigenvalues $K^i_\lambda = (-1/\varkappa)\operatorname{tg}\eta^i_\lambda$ and their eigenvectors $A^i_{L\lambda}$, that is $K_{LL'} = \sum_\lambda A^i_{L\lambda} K^i_\lambda \widetilde{A}^i_{\lambda L'}$. In the

special case of spherically symmetric scatterers their K-matrices are diagonal, $K^{i}_{LL'} = \delta_{LL'} K^{i}_{L}$, and (3.15) simplifies itself, in agreement with John and Ziesche (1971b) and Mc Gill and Klima (1972).

By the way, the amplitudes form a complete set, if the trivial scattering states (characterized by $K_\mu = 0$) are also included. From (3.15) it follows, that they obey the condition

$$\sum_{L} \rfloor^{i0}_{\lambda L} B_{L\mu} = 0 \qquad \text{for } K'_\lambda \neq 0 \tag{3.17}$$

allowing to represent the projection operator of the non-trivial scattering states in the following form

$$\sum_{\substack{\mu \\ (K_\mu \neq 0)}} B_{L\mu} \widetilde{B}_{\mu L'} = \sum_{\substack{i\lambda \\ i'\lambda' (K'_\lambda \neq 0)}} \rfloor^{0i}_{L\lambda} \left(\rfloor^{-1}\right)^{ii'}_{\lambda\lambda'} \rfloor^{i'0}_{\lambda' L'} \tag{3.18}$$

as proved in the Appendix 2. While for the far fields amplitudes (3.17) holds, the near field amplitudes obey

$$\sum_{\substack{\mu \\ (K_\mu \neq 0)}} B^{i}_{\lambda\mu} \widetilde{B}^{i'}_{\mu\lambda'} = \left(\rfloor^{-1}\right)^{ii'}_{\lambda\lambda'} \tag{3.19}$$

following from (3.18) together with (3.11).

4. Infinite disordered systems

Now we consider an extended system of non-overlapping generalized MT's. For such a system the integrated density of states N(E) is connected via a generalized Friedel sum rule (John and Ziesche 1971b) with the phase shifts η_μ, the number of which is proportional to the volume $\mathcal{V}$ of the system:

$$N(E) - N^0(E) = \frac{2}{\pi} \mathcal{V} \sum_{\mu} \eta_\mu(E). \tag{4.1}$$

N (E) corresponds to the free electron case. The following derivation is similar as in (John and Ziesche 1971b), but owing

to certain peculiarities connected with the resonances of the MT-phase shifts η^i_λ a more careful treatment is necessary as mentioned by Lehmann (1973b)[3].

Using the identity

$$\eta_\mu = -\mathrm{Im}\ \ln \exp(-i\eta_\mu) = -\mathrm{Im}\ \ln(\mathrm{ctg}\,\eta_\mu - i) - \mathrm{Im}\ \ln(\sin\eta_\mu) \qquad (4.2)$$

(4.1) splits into two terms, namely

$$-\mathrm{Im}\ \ln \det\|(\mathrm{ctg}\,\eta_\mu - i)\,\delta_{\mu\mu'}\| = -\mathrm{Im}\ \ln \det\|\mathrm{ctg}\,\eta^i_\lambda\,\delta_{ii'}\,\delta_{\lambda\lambda'} + N^{ii'}_{\lambda\lambda'} - i\,\delta^{ii'}_{\lambda\lambda'}\| \qquad (4.3)$$

and

$$-\mathrm{Im}\ \ln \det\|\sin\eta_\mu\,\delta_{\mu\mu'}\| = -\mathrm{Im}\ \ln \det\|\sin\eta^i_\lambda\,\delta_{ii'}\,\delta_{\lambda\lambda'}\|. \qquad (4.4)$$

(4.3) is based on the cluster equations (3.3) and on $\mathrm{Im}\ \ln \det\|\mathcal{J}\| = 0$, following from $\det\|\mathcal{J}\| > 0$. This latter property affects also, that if one of the MT-phase shifts η^i_λ passes through $n\pi$ at a certain energy, then also one of the cluster-phase shifts η_μ passes through $n\pi$ in the same sense. Therefore also (4.4) holds. Altogether a generalization of the Lloyd-formula (1967) is obtained

$$\boxed{N(E) - N^0(E) = -\frac{2}{\pi\Omega}\,\mathrm{Im}\ln \det\|\cos\eta^i_\lambda\,\delta_{ii'}\,\delta_{\lambda\lambda'} + \sin\eta^i_\lambda\,(N^{ii'}_{\lambda\lambda'} - i\,\delta^{ii'}_{\lambda\lambda'})\|.} \qquad (4.5)$$

If with $N^{ii'}_{\lambda\lambda'} \approx 0$ one completely neglects the multiple scattering between the MT's, then (again with $\det\|\mathcal{J}\| > 0$ and $\mathcal{J}^{ii}_{\lambda\lambda} = 1$)

$$N(E) - N^0(E) \approx \frac{2}{\pi\Omega}\sum_{i,\lambda} \eta^i_\lambda \qquad (4.6)$$

approximately results in. This is the approximation of independent non-spherically symmetric scatterers as used by Mc Gill and Klima (1972) and Keller (1971) in their cluster theory of amorphous covalent semiconductors. The matrix N describes therefore the

3) The author is grateful to Dr.Lehmann for pointing this out.

multiple scattering. To its elements $N^{ii'}_{\lambda\lambda'}$ the simplification (3.7) applies, only if the scatterers are far enough from each other, so that their envelopping spheres do not overlap ($R_{ii'} > r_0^i + r_0^{i'}$). Otherwise the complicated near field formula (3.5) must be applied.

5. Infinite ordered systems

If all the MT's are equal and arranged regularly, then a lattice appears, the periodicity of which is described by

$$\sin\eta_\mu \, B^i_{\lambda\mu} = e^{-i\vec{k}\vec{R}_i} C_{\lambda\vec{k}} \,. \tag{5.1}$$

Therefore with Fourier transformation of the structure matrices

$$N_{\lambda\lambda'}(\vec{k}) \equiv \sum_i e^{-i\vec{k}\vec{R}_{ii'}} N^{ii'}_{\lambda\lambda'} \quad , \quad \rfloor_{\lambda\lambda'}(\vec{k}) \equiv \sum_i e^{-i\vec{k}\vec{R}_{ii'}} \rfloor^{ii'}_{\lambda\lambda'} \tag{5.2}$$

(3.3) changes into generalized KKR-equations

$$\boxed{\sum_\lambda \left\{ \delta_{\lambda\lambda'} + \operatorname{tg}\eta_\lambda \left[N_{\lambda\lambda'}(\vec{k}) - i \rfloor_{\lambda\lambda'}(\vec{k}) \right] \right\} C_{\lambda\vec{k}} = 0 \,,} \tag{5.3}$$

determining the bandstructure $\varkappa(\vec{k})$, while the wave function in the cell at the origin takes according to (3.1) and (3.4) the form

$$\varphi^0_{\vec{k}}(\vec{r}) = \sum_\lambda \left[j_\lambda(\vec{r}) \cos\eta_\lambda - n_\lambda(\vec{r}) \sin\eta_\lambda \right] C_{\lambda\vec{k}} \,,$$

$$C_{\lambda\vec{k}} = \begin{cases} \dfrac{1}{\sin\eta_\lambda} C_{\lambda\vec{k}} & \text{for } \sin\eta_\lambda \neq 0 \\ \left\{ \sum_{\lambda'} \left[i \rfloor_{\lambda\lambda'}(\vec{k}) - N_{\lambda\lambda'}(\vec{k}) \right] C_{\lambda'\vec{k}} \right. & \text{for } \sin\eta_\lambda = 0 \,. \end{cases} \tag{5.4}$$

For negative energies $\operatorname{ctg}\eta_\mu$ in (3.3) and (3.4) must be replaced by i guaranteeing the wave functions to remain finite. For positive energies $\operatorname{ctg}\eta_\mu$ can be chosen arbitrarily, because $\rfloor_{\lambda\lambda'} = 0$ for $\varkappa \neq |\vec{k} + \vec{K}|$. This is due to (3.8) and (3.9) and $\sum_i \exp(i\vec{k}\vec{R}_i) = 0$ for $\vec{k}$ is not a reciprocal lattice vector $\vec{K}$.

According to (3.7) and (3.8) a complete reduction to the

simple point structure matrices of the ordinary KKR-method,

$$\varkappa\left[N_{LL'}(\vec{k})-\delta_{LL'}(\vec{k})\right]=A_{LL'}(\vec{k}) \text{ or } i^{l-l'}B_{LL'}(\vec{k}), \tag{5.5}$$

is possible only in the case of non-overlapping, envelopping spheres. This means a non-zero potential only within the sphere inscribed in the Wigner-Seitz-cell and just touching the boundaries. This case has been considered recently by John et al. (1972). Passing from the λ-representation (5.3) to the L-representation, the ordinary KKR-equations emerge, only $tg\eta_L\delta_{LL'}$ is replaced by the matrix $(tg\eta)_{LL'}=\sum_\lambda A_{L\lambda}tg\eta_\lambda A_{\lambda L'}$, the non-diagonality of which comes from the non-spherically symmetric potential within the inscribed sphere. If this potential arises from a cluster of MT-potentials at sites $\vec{d}_n$, then the non-overlapping condition for the applicability of (3.7) can be softened slightly, because it is sufficient, that only the sites belonging to a cluster are within a sphere not overlapping with the corresponding spheres of the neighboured clusters (see Ziesche 1973a). In this case the KKR-equations for a lattice with several atoms per unit cell appear in such a way that the structure of the cluster and the structure of the corresponding Bravais lattice are described by separated quantities (see Lehmann 1970, John et al 1972).

If the potential is non-zero in the whole Wigner-Seitz-cell, thus seperated only by thin skins of zero potential along the bounderies of the unit cell, then the lattice sum in $N_{\lambda\lambda'}(\vec{k})$ splits into one (far field) part of unit cells, being far enough from each other and allowing again the reduction (3.7),

$$N^{>}_{\lambda\lambda'}(\vec{k})\equiv\sum_{L,L'}\tilde{A}_{\lambda L}N^{>}_{LL'}(\vec{k})A_{L\lambda'}\,,\quad N^{>}_{LL'}(\vec{k})\equiv\sum_{i\,(R_i>R_s)}e^{i\vec{k}\vec{R}_i}\,N^{oi}_{LL'}\,, \tag{5.6}$$

and a second (near field) part of the immediately neighboured unit cells, which can be calculated only via (3.6),

$$\Delta N_{\lambda\lambda'}(\vec{k}) \equiv \sum_{(\vec{R}_i \leq R_0)} e^{i\vec{k}\vec{R}_i} N^{0i}_{\lambda\lambda'} \quad . \tag{5.7}$$

R_0 is the length of the smallest lattice vector outside the sphere, enveloping the unit cell. Passing again to the L -representation modified KKR-equations

$$\boxed{\sum_{L''} \left\{ \delta_{LL''} + \sum_{L'} (tg\eta)_{LL'} \left[N^{>}_{L'L''}(\vec{k}) + \Delta N_{L'L''}(\vec{k}) - i\delta_{L'L''} \right] \right\} C_{L''\vec{k}} = 0} \tag{5.8}$$

appear with $C_{L\vec{k}} \equiv \sum_{\lambda} A_{L\lambda} C_{\lambda\vec{k}}$ and

$$\Delta N_{LL'}(\vec{k}) \equiv \sum_{\lambda,\lambda'} A_{L\lambda} \Delta N_{\lambda\lambda'}(\vec{k}) \bar{A}_{\lambda' L'} \quad . \tag{5.9}$$

In difference to the ordinary KKR-method not only $tg\eta$ but also ΔN contains via (3.6) the potential within the unit cell. That means the separation of potential and structure, as characteristic for the ordinary KKR-method, is modified in the considered case. That the near field part $\Delta N_{\lambda\lambda'}$ is not factorized into the asymptotic or far field properties $A_{L\lambda}$ and point structure, is physically due to an old statement of wave theory, namely, that the near field (see second line of (2.10)) generally cannot be determined completely by the far field characteristics only, but rather depends on the details of the distribution of the scattering centres. The mathematical background is essentially the restriction in the expansion (2.5) of $n_0(\varkappa|\vec{r} - \vec{r}'|)$, meaning, that (2.5) diverges if $r \leq r'$. The analogous expansion of $n_l(\vec{r}-\vec{r}')$is restricted in the same way (see John and Ziesche, 1971, Ziesche 1972). Consequently divergent series occur, if one factorizes $\Delta N_{\lambda\lambda'}$ in the same way as $N^{>}_{\lambda\lambda'}$, trying to set up the ordinary KKR-equations also for overlapping enveloping spheres. Of course this divergence disappears formally if one truncates the KKR-matrices with respect

to L as is usually made. Clearly such a treatment is in principle incorrect. In this case the truncation of L acts as an effective restriction to a potential non-zero only within the inscribed sphere.

There are yet two remarks with respect to the near field part ΔN describing the "mixing" or "interaction" between potential and structure:

1. Although the factorization (3.7) is not completely applicable, there are nevertheless parts of the surfaces, which are far enough from each other to allow this factorization at least partially. Namely, the unit cells $\mathcal{U}_i$ appearing in (5.7) and surrounding the central unit cell $\mathcal{U}_0$, form as a whole a certain volume $\mathcal{V} = \sum_i \mathcal{U}_i$ with an interior and an exterior surface (see fig.2). Only those surface parts of the surrounding unit cells $\mathcal{U}_i$ contribute via (3.6) to $\Delta N_{\lambda\lambda'}$ which belong either to the interior or to the exterior surface of $\mathcal{V}$. We denote these surface parts of $\mathcal{U}_i$ by F_i^{in} and F_i^{ex}. The contribution of F_i^{ex} really factorizes. Therefore $\Delta N_{\lambda\lambda'}$ splits into two parts

$$\Delta N_{\lambda\lambda'}(\vec{k}) = \sum_{(R_i \neq R_0)} e^{i\vec{k}\vec{R}_i} N^{(i)}_{\lambda\lambda'} + \tilde{A}_{\lambda L} \sum_{(R_i \neq R_0)} e^{i\vec{k}\vec{R}_i} N^{0,}_{LL'} A^{(i)}_{L'\lambda} \qquad (5.10)$$

$N^{(i)}_{\lambda\lambda'}$ is that part of $N^{0,}_{\lambda\lambda'}$ in (3.6) with the second surface integration only along F_i^{in} and $A^{(i)}_{L'\lambda}$ is that part of $A_{L'\lambda}$ in (2.11) with the surface integration along F_i^{ex}. Even in $N^{(i)}_{\lambda\lambda'}$ are further certain surface parts allowing again this partial factorization.

2. It is assumed, that a (generally non-real) potential

$$V(\vec{r},\vec{r}') = \begin{cases} \sum_{L,L'} Y_L(\vec{r}) V_{LL'}(r,r') Y_{L'}(\vec{r}') & \text{for } r < r_0 \\ 0 & \text{for } r > r_0 \end{cases} \qquad (5.11)$$

coupling a finite set of angular momenta $\ell < \ell_0$ describes the

crystal potential of one single unit cell. Then the Schrödinger equation is transformed with an ansatz $\Psi(\vec{r})=\sum_L Y_L(\vec{r})R_L(r)$ into a set of $(\ell_0+1)^2$ coupled differential equations for the radial parts $R_L(r)$ (see Evans and Keller 1971). Demanding regularity at $r=0$, a set of $(\ell_0+1)^2$ linearly independent solutions $R_{Ln}(r)$ arises, having outside the envelopping sphere the behaviour

$$R_{Ln}(r)=j_\ell(\varkappa r)\alpha_{Ln}-n_\ell(\varkappa r)\beta_{Ln} \qquad \text{for } r>r_0 . \tag{5.12}$$

Now the scattering states $\Psi^0_\lambda(\vec{r})$ are obtained by an appropriate linear combination $\sum_n \psi_n(\vec{r})\,\gamma_{n\lambda}$, demanding

$$\sum_n \alpha_{nL}\gamma_{n\lambda}=A_{L\lambda}\cos\eta_\lambda \quad , \quad \sum_n \beta_{Ln}\gamma_{n\lambda}=A_{L\lambda}\sin\eta_\lambda , \tag{5.13}$$

as it follows from the comparison with the asymptotic behaviour (2.1). Therefore a set of algebraic equations arises

$$\sum_n (\alpha_{Ln}-\operatorname{ctg}\eta_\lambda\beta_{Ln})\gamma_{n\lambda}=0 , \tag{5.14}$$

yielding $(\ell_0+1)^2$ solutions η_λ and $A_{L\lambda}$. By the way, if one passes to the L-representation (5.9), then the calculation of η_λ and $A_{L\lambda}$ can be avoided, because the needed quantities can be expressed directly by α_{Ln} and β_{Ln} :

$$\sum_\lambda \gamma_{n\lambda}\frac{1}{\sin\eta_\lambda}\tilde{A}_{\lambda L}=(\beta^{-1})_{nL} \quad , \quad (\operatorname{tg}\eta)_{LL'}=\sum_n \beta_{Ln}(\alpha^{-1})_{nL'} . \tag{5.15}$$

Here the completeness of $A_{L\lambda}$ has been used. With the first equation of (5.15) from (5.10) there follows

$$\Delta N_{LL'}(\vec{k})=\sum_{\substack{i,\vec{R}_i\neq\vec{R}_0\\ n,n'}} e^{i\vec{k}\vec{R}_i}N^{0i}_{LL'}A^{(i)}_{L'n}(\beta^{-1})_{nL'}+\sum_{n,n'}(\beta^{-1})_{Ln}\sum_{\vec{R}_i\neq\vec{R}_0} e^{i\vec{k}\vec{R}_i}N^{(i)}_{nn'}(\beta^{-1})_{n'L'} , \tag{5.16}$$

Here $A^{(i)}_{Ln}$ and $N^{(i)}_{nn'}$ are defined in the same manner as $A^{(i)}_{L\lambda}$ and $N^{(i)}_{\lambda\lambda'}$ only using the primary functions $\psi_n=\sum_L Y_L R_{Ln}$ instead of ψ_λ .

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Appendix 1: Angular momentum dependence of the partial wave amplitudes

As a simple example we consider two S -scatterers with equal phase shifts η_0 and a distance a . Then the cluster equations (3.3) produce only two non-trivial scattering states $\lambda = \pm$

$$ctg\,\eta_\pm = -\frac{ctg\,\eta_0 + n_0(\varkappa a)}{1 \pm j_0(\varkappa a)}\,,$$

$$A^1_{0\pm} = \frac{1}{\sqrt{2}[1 \pm j_0(\varkappa a)]}\,, \qquad A^2_{0\pm} = \pm A^1_{0\pm} \tag{A1.1}$$

yielding with respect to the centre the following far field amplitudes

$$A_{L\pm} = \sum_{\ell'} \beta^{\ell\ell'}_{L0} A^{\ell'}_{0\pm} = [1 \pm (-1)^\ell]\, d_{m_\ell 0}\, \frac{\sqrt{2\ell+1}\; j_\ell(\varkappa a/2)}{\sqrt{2}[1 \pm j_0(\varkappa a)]}\,. \tag{A1.2}$$

The ℓ -dependence of $A_{L\pm}$ is essentially determined by $j_\ell(\varkappa a/2)$, which tends for $\ell \gg \varkappa a/2$ to zero as

$$j_\ell(\varkappa a/2) \to \frac{(\varkappa a/2)^\ell}{(2\ell+1)!!} \to e^{-\ell \ln \ell}\,. \tag{A1.3}$$

Appendix 2: The projection operator of the non-trivial scattering states

(3.18) is proved in the following way: Abbreviating the right-hand side of (3.18) by $P_{LL'}$ and acting on a trivial scattering state $B_{L\mu}$ (characterized by $K_\mu = 0$), yields really $\sum_{L'} P_{LL'} B_{L'\mu} = 0$ owing to (3.17). The non-trivial scattering states $B_{L\mu}$ (characterized by $K_\mu \neq 0$) obey the relation

$$\sum_{L'} P_{LL'} B_{L'\mu} = \sum_{L'} P_{LL'} B_{L'\mu} \frac{K_\mu}{K_\mu} = \sum_{L',L''} P_{LL'} K_{L'L''} B_{L''\mu} \frac{1}{K_\mu}$$
$$= \sum_{L''} K_{LL''} B_{L''\mu} \frac{1}{K_\mu} = \hat{B}_{L\mu} \,. \qquad \text{(A2.1)}$$

Here P K = K has been used, following directly from the definitions of K and P and from (3.13).

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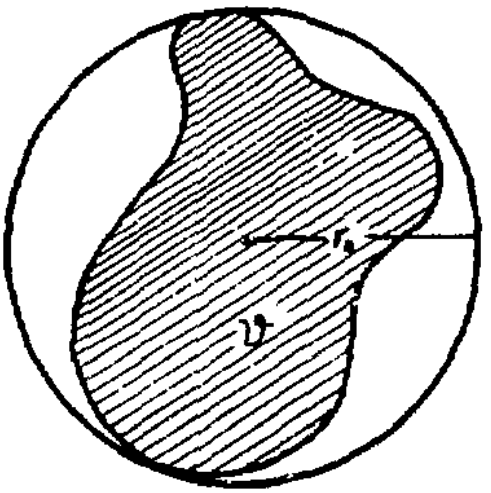

Fig. 1. A general MT-potential and its enveloping sphere with respect to an arbitrary centre.

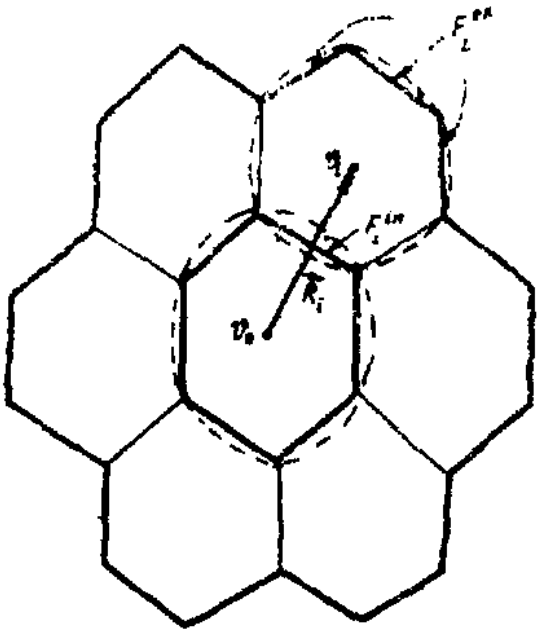

Fig. 2. A simple two-dimensional example, to explain the contributions to the near field part of the generalized KKR-structure matrix.