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MULTIPLE SCATTERING WITHIN FINITE SYSTEMS OF GENERAL MUFFIN-TIN POTENTIALS

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1. Introduction.

Recently an algebraic scheme has been derived, allowing the calculation of generalized phase shifts η_λ and corresponding partial wave amplitudes $A_{L\lambda}$ of a special non-spherically symmetric potential, consisting of a cluster of non-overlapping muffin-tin (MT) potentials. The case of pure s-scatterers, next to considered by Demkov and Rudakov (1970), has been generalized by John and Ziesche (1971) to scatterers with arbitrary angular momenta, using the analogy to the KKR method for band structure calculations (Korringa 1947, Kohn and Rostoker 1954). The mentioned quantities η_λ and $A_{L\lambda}$ are determined only by the sites $\vec{a}_n$ and the phase shifts η_λ^n of the scatterers. The proposed scheme is useful for problems not only of the theory of molecules (electron scattering at molecules (Demkov and Rudakov 1970), bound states of molecules (Smith and Johnson 1969)), but also of solid state theory. It was for example possible, to derive the Lloyd-formula for the density of states of arbitrary, extended MT-systems in a very simple way via a generalized Friedel sum rule (John and Ziesche 1971 b). The use of general properties of the cluster phase shifts η_λ (with respect to their dependence of the MT-phase shifts η_l^n) allows the derivation of new gap criteria of Saxon-Hutner type also for three-dimensional binary alloys (John 1972). Also the application of the proposed method to band structure calculations of lattices with several atoms per unit cell has been discussed recently

(John, Lehmann and Ziesche 1972). Clusters of MT-potentials have been used to describe shortrange order and pseudogaps in elemental amorphous covalent semiconductors (Mc Gill and Klima 1972).

Non-spherically symmetric potential (within the MT-spheres) are important also in transition metals with partially filled d - bands (Jacobs 1972) or semiconductors with covalent bonds (Kane 1971). For such potentials (coupling finite sets of angular momenta) Evans and Keller (1972) recently generalized the usual methods for band structure calculations (KKR,KKRZ,APW). They also used generalized, but slightly otherwise defined phase shifts $\gamma_L(\vec{\kappa})$. In (John, Lehmann and Ziesche 1972) it has been shown, that the use of phase shifts γ_λ and amplitudes $A_{L\lambda}$, which by the way correspond to the eigenstates of the S-, T- or K- matrix, represents probably the more appropriate and natural description. So certain complications can be avoided for example (John, Lehmann and Ziesche 1972), obtained in (Evans, Keller 1972) with respect to the generalization of the APW method.

In the following a more general type of non-spherically symmetric potentials will be considered, being non-zero within an arbitrary volume (Section 2). The application of such potentials to the band structure calculations of lattices within a generalized KKR method allows one in prinoiple, to take into account a non-constant potential within the whole cell.

But here (Section 3) next to only finite clusters of such generalized (of course,non-overlapping) MT-potentials are considered. The cluster equations, determining the scattering properties of the cluster, are obtained by an appropriate ansatz of the wave function (linear combination of MT-orbitals), similar to the original approach of Korringa (1947) and as recently again used (John and Ziesche 1971 a, Andersen and Kasowski 1971, Andersen 1971). In this connection a generalization of recently derived addition theorems for the spherical Bessel (Ziman 1966) and Neumann (John and Ziesche 1971, Ziesche 1972, Andersen 1971) functions is needed (Appendix 2). The decoupling of structure (MT-sites) and potential (MT-phase shifts), which is characteristic of clusters of spherically symmetric MT-potentials,is generally unfortunately lost, although the cluster equations are of the same type. This decoupling appears only in the case, that the envelopping spheres don't overlap. Only in this case the MT-potentials are completely characterized by their asymptotic scattering properties, that means by their far fields. Otherwise, also the near fields appear (mathematically via integrations over pairs of more or less complicated MT-surfaces) , hindering the mentioned decoupling. As a first simple example of generalized MT-potentials (sub-) clusters of usual MT-potentials are considered (Section 4). The elimination of the quantities, describing the scattering properties of the subcluster, yields just the equation for the whole cluster. This shows the consistency of the developed

formalism and means, that a cluster can be divided arbitrarily into subclusters if one takes into account fully the multiple scattering between the subclusters. Such divisions are of interest also for practical calculations, because generally some subcluster phase shifts are small for a given not too high energy (Demkov and Rudakov 1970). This allows to reduce the dimension of the whole cluster problem. - Finally, finite sets of angular momenta coupling potentials $V_{LL'}(r)$ are discussed as a second simple example of generalized MT-potentials (Section 5). Clusters of such potentials are of interest for the band structure of covalent semiconductors with their more open structures of diamand type, because within a generalized KKR-method both the non-sphericity of the MT-potentials at the lattice sites (due to the covalent bonds) and the non-constant potential in the interstitial region can be taken into account. The latter has been approximated by Keller (1971), installating additional spherically symmetric MT-potentials at interstitial sites. But generally these interstitial potentials are non-spherically symmetric.

2. Non-spherically symmetric muffin-tin potentials

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

$$\varphi_\lambda(\vec{r}) = \sum_L \left[j_L(\vec{r})\, A_{L\lambda} \cos\eta_\lambda - n_L(\vec{r})\, A_{L\lambda} \sin\eta_\lambda \right], \qquad (2.1)^{2)}$$

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

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

$$\varphi_\lambda(\vec{r}) = \int_V d\vec{r}' \int_V d\vec{r}'' \; G(\vec{r}-\vec{r}') V(\vec{r}',\vec{r}'')\, \varphi_\lambda(\vec{r}''),$$
$$G(\vec{r}-\vec{r}') \equiv \frac{\varkappa}{4\pi} \left[n_0(\varkappa|\vec{r}-\vec{r}'|) - ctg\,\eta_\lambda\, j_0(\varkappa|\vec{r}-\vec{r}'|) \right]. \qquad (2.3)$$

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

With the usual expansions

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

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

and demanding

$$(j_L, V\varphi_\lambda) = A_{L\lambda}\left(-\frac{1}{\varkappa}\right) \sin\eta_\lambda \tag{2.5}$$

(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 .

This is seen rewriting (2.3) as

$$\varphi_\lambda(\vec{r}) = \varphi_\lambda^0(\vec{r}) + \int_V d\vec{r}' \int_V d\vec{r}'' \, G^+(\vec{r}-\vec{r}') V(\vec{r}',\vec{r}'') \varphi_\lambda(\vec{r}'') , \tag{2.6}$$

$$\varphi_\lambda^0(\vec{r}) \equiv \sum_L j_L(\vec{r})\, A_{L\lambda} \cos\eta_\lambda , \quad G^+(\vec{r}-\vec{r}') \equiv \frac{\varkappa}{4\pi} n_0(\varkappa|\vec{r}-\vec{r}'|)$$

and introducing via

$$\int_V d\vec{r}' \, V(\vec{r},\vec{r}') \varphi_\lambda(\vec{r}') = \int_V d\vec{r}' \, K(\vec{r},\vec{r}') \varphi_\lambda^0(\vec{r}') \tag{2.7}$$

the K -matrix corresponding to the potential V . Really, inserting (2.7) and φ_λ^0 from (2.6) into (2.5)

$$\sum_{L'} (j_L, K j_{L'}) A_{L'\lambda} = A_{L\lambda}\left(-\frac{1}{\varkappa}\right) tg\,\eta_\lambda \tag{2.8}$$

turns out, showing the amplitudes $A_{L\lambda}$ and phase shifts η_λ to be determined as eigenstates of the K-matrix in its L-representation on the energy shell. As a consequence of the finite range r_o the amplitudes $A_{L\lambda}$ are small for $\ell > \varkappa r_o$, as shown for a simple example in Appendix 1. Because the K-matrix is real and symmetric the (real) amplitudes $A_{L\lambda}$ form an orthogonal and complete set

$$\sum_L \tilde{A}_{\lambda L} A_{L\lambda'} = \delta_{\lambda\lambda'} \quad , \quad \sum_\lambda A_{L\lambda} \tilde{A}_{\lambda L'} = \delta_{LL'} . \tag{2.9}$$

Into the completeness relation of course also the trivial scattering states (with $\sin\eta_\lambda = 0$) must be included, which can be obtained by a successive orthogonalizing procedure.

While the asymptotic or far field (2.1) outside the envelopping sphere and related to its centre is determined according to (2.8) by the K-matrix only on the energy shell, these matrix elements $(j_L, K j_{L'})$ are not sufficient for the wave function inside the envelopping sphere. Namely, inserting (2.7) into (2.6) yields

$$\varphi_\lambda(\vec{r}) = j_\lambda(\vec{r})\cos\eta_\lambda - n_\lambda(\vec{r})\sin\eta_\lambda \tag{2.10}$$

with the abbreviations

$$\hat{j}_\lambda(\vec{r}) \equiv \sum_L \hat{j}_L(\vec{r})\, A_{L\lambda}\,,$$

(2.11)

$$\eta_\lambda(\vec{r}) \equiv \int_{\mathcal{V}} d\vec{r}' \int_{\mathcal{V}} d\vec{r}''\, \frac{1}{4\pi}\, n_0(\varkappa|\vec{r}-\vec{r}'|)\, K(\vec{r}',\vec{r}'') \sum_L \hat{j}_L(\vec{r}'')\, A_{L\lambda}(-\varkappa)\, ctg\, \eta_\lambda\,.$$

Indeed, expanding n_0 according to (2.4), for $r < r_0$ also expressions $\langle n_L, K\hat{j}_L \rangle$ appear, involving matrix elements off the energy shell, because the integral representation of $n_L(\varkappa r)$ includes $\hat{j}_L(\varkappa' r)$ for all positive energies $E' = \varkappa'^2$. This is related to the fact, that in the near field region outside the volume $\mathcal{V}$ and inside the envelopping sphere the wave function (although describing only free particle motion as in the far field region outside the envelopping sphere) is determined not only by the asymptotic quantities η_λ and $A_{L\lambda}$, but also by the details of the distribution of scattering centres inside $\mathcal{V}$.

In the following, it is useful to assume, that besides η_λ and $A_{L\lambda}$ also the wave function φ_λ and its normal derivative at the surface of $\mathcal{V}$ is known (via (2.10) and (2.11)). These surface quantities determine then the wave function φ_λ outside $\mathcal{V}$ via the equation

$$\oint\limits_{(\vartheta)} d\vec{f}'\left[\left(\frac{\partial}{\partial \vec{r}'}\right)_{\psi} - \left(\frac{\partial}{\partial \vec{r}'}\right)_{G}\right] G(\vec{r}-\vec{r}')\,\varphi_\lambda(\vec{r}') = \begin{cases} 0 & \vec{r} \in \vartheta \\ \varphi_\lambda(\vec{r}) & \vec{r} \notin \vartheta, \end{cases} \tag{2.12}$$

following itself from (2.3) by means of partial integration. Really, from (2.12) follows, that the wave function outside ϑ is again of the form (2.10) but with

$$\dot{a}_\lambda(\vec{r}) = \varkappa \oint\limits_{(\vartheta)} d\vec{f}'\left[\left(\frac{\partial}{\partial \vec{r}'}\right)_{\dot{a}} - \left(\frac{\partial}{\partial \vec{r}'}\right)_{\psi}\right] \frac{1}{4\pi} \dot{a}_\ell(\varkappa|\vec{r}-\vec{r}'|)\,\varphi_\lambda(\vec{r}')\,\frac{1}{\sin\eta_\lambda}, \tag{2.13}$$

$$n_\lambda(\vec{r}) = \varkappa \oint\limits_{(\vartheta)} d\vec{f}'\left[\left(\frac{\partial}{\partial \vec{r}'}\right)_{n} - \left(\frac{\partial}{\partial \vec{r}'}\right)_{\psi}\right] \frac{1}{4\pi} n_\ell(\varkappa|\vec{r}-\vec{r}'|)\,\varphi_\lambda(\vec{r}')\,\frac{1}{\sin\eta_\lambda}.$$

These expressions are via (2.7) and (2.5) of course equivalent with (2.11). Finally, using the expansions (2.4), from (2.13) and the first line of (2.12) the relations

$$A_{\ell\lambda}\sin\eta_\lambda = \varkappa \oint\limits_{(\vartheta)} d\vec{f}\left[\left(\frac{\partial}{\partial \vec{r}}\right)_{j} - \left(\frac{\partial}{\partial \vec{r}}\right)_{\psi}\right] \dot{a}_\ell(\vec{r})\,\varphi_\lambda(\vec{r}), \tag{2.14}$$

$$A_{\ell\lambda}\cos\eta_\lambda = \varkappa \oint\limits_{(\vartheta)} d\vec{f}\left[\left(\frac{\partial}{\partial \vec{r}}\right)_{n} - \left(\frac{\partial}{\partial \vec{r}}\right)_{\psi}\right] n_\ell(\vec{r})\,\varphi_\lambda(\vec{r}) \tag{2.15}$$

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3) The index at $\partial/\partial\vec{r}$ shows, on which function it only acts.

are obtained, connecting the asymptotic quantities η_λ , $A_{\ell\lambda}$ with the surface quantities φ_λ , $\partial\varphi_\lambda/\partial n$. (2.14) follows also directly from (2.5) by partial wave integration.

By the way, with $ctg\,\eta_\lambda = i$ and $\varkappa = i\bar{\varkappa}$ also bound states $E = -\bar{\varkappa}^2$ can be included into the discussion.

3. Cluster

Now we consider a cluster of such muffin-tins within non-overlapping volumes $\mathcal{V}_i$,each having orbitals $\varphi^i_\lambda(\vec{r})$, from which the cluster wave function $\varphi^i_\mu(\vec{r})$ within $\mathcal{V}_i$ and in the immediate environment of $\mathcal{V}_i$ follows by an appropriate linear combination

$$\varphi^i_\mu(\vec{r}) = \sum_\lambda \left[j^i_\lambda(\vec{r})\cos\eta^i_\lambda - n^i_\lambda(\vec{r})\sin\eta^i_\lambda \right] \mathcal{B}^i_{\lambda\mu} \sin\eta_\mu \,. \qquad (3.1)$$

The cluster wave function $\varphi_\mu(\vec{r})$ in the whole space is given by

$$\boxed{\varphi_\mu(\vec{r}) = \sum_{i,\lambda} \left[j^i_\lambda(\vec{r})\cos\eta_\mu - n^i_\lambda(\vec{r})\sin\eta_\mu \right] B^i_{\lambda\mu} .} \qquad (3.2)$$

This can be considered as an ansatz, corresponding to the

wished asymptotic behaviour, but is also easily obtained from the integral equation (2.3).

Similar as in the case of spherically symmetric muffin-tins (John and Ziesche 1971 a, Andersen and Kasowski 1972) we get the cluster equations for η_μ , $B^i_{\lambda\mu}$ and $\delta^i_{\lambda\mu}$ demanding $\psi_\mu = \psi^i_\mu$ in the surrounding of ϑ_i . To this purpose the expansion of $j^{i'}_{\lambda'}$ and $n^{i'}_{\lambda'}$ around another volume ϑ_i is necessary

$$j^{i'}_{\lambda'}(\vec{r}) = \sum_{\lambda} j^{i}_{\lambda}(\vec{r})\, \mathcal{J}^{ii'}_{\lambda\lambda'} ,$$

$$(1-\delta_{ii'})\, n^{i'}_{\lambda'}(\vec{r}) = \sum_{\lambda} j^{i}_{\lambda}(\vec{r})\, N^{ii'}_{\lambda\lambda'} , \qquad (3.3)$$

defining structure matrices $\mathcal{J}^{ii'}_{\lambda\lambda'}$, $N^{ii'}_{\lambda\lambda'}$, which are determined only by the wave functions ψ^i_λ and $\psi^{i'}_{\lambda'}$ and their normal derivatives on the surfaces of the volumes ϑ_i and $\vartheta_{i'}$, respectively (See Appendix 1, eq . (A2.3)). While the expansion (3.3) of $j^{i'}_{\lambda'}$ is valid for all $\vec{r}$, the corresponding expansion (3.3) of $n^{i'}_{\lambda'}$ holds only within the volume ϑ^*_i and a certain environment of ϑ_i , described in more detail after (4.8). If to each volume ϑ_i itis attached a site $\vec{R}_i$ and if the partial wave amplitudes $A^i_{l\lambda}$ are related to these sites $\vec{R}_i$, then $\mathcal{J}^{ii'}_{\lambda\lambda'}$ can be reduced to a simpler

structure matrix $\mathcal{J}^{ii'}_{LL'}$, containing only these sites $\vec{R}_i$:

$$\mathcal{J}^{ii'}_{\lambda\lambda'} = \sum_{L,L'} \tilde{A}^{i}_{\lambda L}\, \mathcal{J}^{ii'}_{LL'}\, A^{i'}_{L'\lambda'} \tag{3.4}$$

with $\tilde{A}^{i}_{\lambda L} \equiv A^{i}_{L\lambda}$. While (3.4) always holds, is the corresponding relation for $N^{ii'}_{\lambda\lambda'}$, namely

$$N^{ii'}_{\lambda\lambda'} = \sum_{L,L'} \tilde{A}^{i}_{\lambda L}\, N^{ii'}_{LL'}\, A^{i'}_{L'\lambda'} \tag{3.5}$$

valid only, if the volumes ϑ_i are within non-overlapping spheres [4] around the sites $\vec{R}_i$ (see Appendix 2, eq . (A.2.4)). As in (John and Ziesche 1971 a) the structure matrices appearing in (3.4) and (3.5) are defined by

$$\mathcal{J}^{ii'}_{LL'} \equiv 4\pi \sum_{L''} C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, \mathcal{J}_{L''}(\vec{R}_{ii'}) = i^{\ell-\ell'} \int d\Omega\; Y_L(\vec{n})\, e^{i\alpha\pi \vec{R}_{ii'}\vec{n}}\, Y_{L'}(\vec{n}) \tag{3.6}$$

$$N^{ii'}_{LL'} \equiv (1-\delta_{ii'})\, 4\pi \sum_{L''} C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, n_{L''}(\vec{R}_{ii'})$$

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[4] In fact this restriction can be softened slightly. It is only necessary , that the "essential" part of the generalized muffin-tins is within non-overlapping spheres. Let us consider a cluster of ordinary muffin-tins at sites $\vec{a}_n$ as an example for a generalized muffin-tin. Then the asymptotic behaviour (2.1) is correct not only for $r > r_s$, but also for $r > max(a_n)$ and outside the muffin-tin spheres. That means, in this case

with $\vec{R}_{ii'} \equiv \vec{R}_i - \vec{R}_{i'}$ and with

$$C_{LL'L''} \equiv \int d\Omega \; Y_L(\vec{n})\, Y_{L'}(\vec{n})\, Y_{L''}(\vec{n}) \tag{3.7}$$

as Gaunt coefficients.

Inserting (3.3) into (3.2) and demanding $\varphi_\mu = \varphi^i_\mu$ we immediately obtain (see Appendix 2, eq . (A2.6))

$$\boxed{\sum_{i',\lambda'} \left[\delta_{ii'}\delta_{\lambda\lambda'} + tg\,\eta^i_\lambda \left(N^{ii'}_{\lambda\lambda'} - ctg\,\eta_\mu J^{ii'}_{\lambda\lambda'}\right)\right] B^{i'}_{\lambda'\mu} = 0 \quad \text{for } \sin\eta^i_\lambda \neq 0} \tag{3.8}$$

and

$$B^i_{\lambda\mu} = \begin{cases} \dfrac{1}{\sin\eta^i_\lambda}\, B^i_{\lambda\mu} & \text{for } \sin\eta^i_\lambda \neq 0 \\[2ex] \displaystyle\sum_{i',\lambda'} \left[ctg\,\eta_\mu J^{ii'}_{\lambda\lambda'} - N^{ii'}_{\lambda\lambda'}\right] B^{i'}_{\lambda'\mu} & \text{for } \sin\eta^i_\lambda = 0 . \end{cases} \tag{3.9}$$

These cluster equations, determining as many non-trivial cluster scattering states (with $\sin\eta_\mu \neq 0$) as non-trivial MT-phase shifts η^i_λ exist , can be derived of course also by means of a Kohn/Rostoker (1954) treatment.

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only the spheres envelopping the sites of the ordinary muffin-tins must not overlap.

(3.8) and (3.9) are the conditions for that the wave functions (3.1) in the immediate surrounding of each muffin-tin have the *same continuation* (3.2) *into the whole space* (outside the volumes ϑ_i) with an asymptotic behaviour described by cluster phase shifts η_μ and cluster amplitudes $B^i_{\lambda\mu}$.

Similar as in the case of spherically symmetric muffin-tins (Demkov and Rudakov 1970) the eigenvalues $ctg\,\eta_\mu$ of (3.8) can be written in the form of expectation values, the stationary properties of which with respect to small variations of the MT-phase shifts η^i_λ directly leads to

$$\frac{\partial \eta_\mu}{\partial \eta^i_\lambda} = \left(B^i_{\lambda\mu} \sin \eta_\mu \right)^2 \geq 0 . \qquad (3.10)$$

This means, if one of the MT-phase shifts η^i_λ is increased (decreased), then also all cluster phase shifts η_μ increase (decrease).

Again similar as in the case of spherically symmetric muffin-tins (John and Ziesche 1971 a, Smith and Johnson 1969) (3.8) determines with $ctg\,\eta_\mu = i$ and also the bound states $E = -\varkappa^2 < 0$.

If the single muffin-tins have special forms and if they are just touching along parts of their surfaces, forming in this way a total (connected) volume $\vartheta = \sum_i \vartheta_i$ as shown in Fig. 2, then the thin skins of zero potential along the

touching surface parts are of course artificial. These skins therefore can be eliminated, showing the consistency of the developed formalism. To prove this we rewrite (3.2) by means of the recently proved addition theorems for the spherical Bessel (Ziman 1966) and Neumann (John and Ziesche 1971 a, Ziesche 1972, Andersen 1971) functions in the following way (for $r > r_0$)

$$\varphi_\mu(\vec{r}) = \sum_L \left[j_L(\vec{r}) \cos\eta_\mu - n_L(\vec{r}) \sin\eta_\mu \right] B_{L\mu} \tag{3.11}$$

with

$$B_{L\mu} = \sum_{i'L'\lambda'} J^{oi'}_{LL'} A^{i'}_{L'\lambda'} B^{i'}_{\lambda'\mu} \,. \tag{3.12}$$

(3.11) corresponds to (2.1). Using the definition of $\varphi^i_\mu(\vec{r})$, (3.1) and the Wronski relation (A2.2), we obtain (in the last step the skins are eliminated)

$$\begin{aligned} B_{L\mu} \sin\eta_\mu &= \sum_i \varkappa \oint\limits_{(\vartheta_i)} d\vec{f} \left[\left(\frac{\partial}{\partial \vec{r}}\right)_j - \left(\frac{\partial}{\partial \vec{r}}\right)_\varphi \right] j_L(\vec{r})\, \varphi^i_\mu(\vec{r}) \\ &= \varkappa \oint\limits_{(\vartheta)} d\vec{f} \left[\left(\frac{\partial}{\partial \vec{r}}\right)_j - \left(\frac{\partial}{\partial \vec{r}}\right)_\varphi \right] j_L(\vec{r})\, \varphi_\mu(\vec{r}) \end{aligned} \tag{3.13}$$

corresponding to (2.14). To obtain also the formula, corresponding to (2.15), with (3.12), (3.8) and (3.9), we can write:

$$B_{L\mu} \cos\eta_\mu = \sum_{\substack{i'\lambda'\lambda \\ i,i'}} J^{oi}_{LL'} A^{i}_{L'\lambda} \left[N^{ii'}_{\lambda\lambda'} \sin\eta^{i'}_{\lambda'} + \delta_{ii'}\delta_{\lambda\lambda'} \cos\eta^{i'}_{\lambda'} \right] B^{i'}_{\lambda'\mu} \sin\eta_\mu \tag{3.14}$$

Using again (3.1) and (A2.2), really

$$B_{L\mu}\cos\eta_\mu = \varkappa \oint\limits_{(v)} d\vec{f}\left[\left(\frac{\partial}{\partial \vec{r}}\right)_n - \left(\frac{\partial}{\partial \vec{r}}\right)_\varphi\right] n_L(\vec{r})\,\varphi_\mu(\vec{r}) \qquad (3.15)$$

turns out, q.e.d.

If on the other hand the muffin-tins are far enough from each other, so that the envelopping spheres of the muffin-tins (or at least of its " essential part", see footnote 4) don't overlap (see Fig. 3) then (3.5) is valid. That means, the muffin-tins enter into the cluster equations (3.8) only via the asymptotic behaviour of its scattering states φ^i_λ , described by η^i_λ and $A^i_{L\lambda}$. These properties of the far field (2.1) are sufficient, no near field properties (2.11) are necessary. This peculiarity allows also to transform the $i-\lambda$ -representation (3.8) into an $i-L$ -representation by means of (3.4) and (3.5):

$$\sum_{i',L',L''} P^i_{LL'}\left[\delta_{ii'}\delta_{L'L''} + \sum_{L'''}(tg\,\eta)^i_{L'L'''}\left(N^{ii'}_{L'''L''} - ctg\,\eta_\mu\,\delta^{ii'}_{L'''L''}\right)\right] B^{i'}_{L''\mu} = 0 \qquad (3.16)$$

with $B^i_{L\mu} = \sum_{\lambda'(\sin\eta^i_\lambda \neq 0)} A^i_{L\lambda}\,B^i_{\lambda\mu}$ and

$$P^i_{LL'} = \sum_{\lambda(\sin\eta^i_\lambda \neq 0)} A^i_{L\lambda}\,\tilde{A}^i_{\lambda L'} \qquad (3.17)$$

$$(tg\,\eta)^i_{LL'} = \sum_\lambda A^i_{L\lambda}\; tg\,\eta^i_\lambda\; \tilde{A}^i_{\lambda L'} .$$

$P^i_{\ell\ell'}$ projects the non-trivial scattering states ($\sin\eta^i_\lambda \neq 0$). Assuming all MT-phase shifts η^i_λ non-trivial, that is $P^i_{\ell\ell'} = \delta_{\ell\ell'}$, a system of equations (3.18), arises very similar to the equations for a cluster of spherically symmetric muffin-tins (John and Ziesche 1971 a). The only differences are, that the scattering properties of the single muffin-tins are here described by non- diagonal matrices $(tg\,\eta)^i_{\ell\ell'}$, instead of $\delta_{\ell\ell'}\, tg\,\eta^i_\ell$ and that the dimension of the system of equations, (3.16), is in principle infinite. Numerical calculations require of course the restriction to finite numbers of angular momenta. But, because (3.16) breaks down, if the envelopping spheres overlap, the influence of the parts of a single muffin-tin i is described the worse the more far they are from their corresponding site $\vec{R}_i$. That means for a better approximation more angular momenta are necessary than it corresponds to the linear dimension owing to the combination of $(tg\,\eta)^i_{\ell\ell'}$ with $N^{ii}_{\ell\ell'}$ and $J^{ii'}_{\ell\ell'}$. - If we have only a few non-trivial MT-phase shifts η^i_λ, that is $P^i_{\ell\ell'} \neq \delta_{\ell\ell'}$, then the solutions of

$$\sum_{i',\ell'}\left[\delta_{ii'}\,\delta_{\ell\ell'} + \sum_{\mu}(tg\,\eta)^i_{\ell\mu}\,(N^{ii'}_{\mu\ell'} - ctg\,\eta_\mu\, J^{ii'}_{\mu\ell'})\right] B^{i'}_{\ell'\mu} = 0 \qquad (3.18)$$

owing to the definition of $B^i_{\ell\mu}$

must obtain the additional condition $\sum_{L'} P^{i}_{LL'} B^{i}_{L'\mu} = B^{i}_{L\mu}$, separating physical and unphysical solutions. - The advantage of the $L - L$ -representation (3.16) compared with the $L - \lambda$ -representation (3.8) consists in that the MT-potentials enter in a compact menner only via the quantities (3.17).

4. First example: *Cluster of subclusters*

As a first simple example of non-spherically symmetric muffin-tins we consider clusters of usual muffin-tins with phase shifts $\eta_L^{in_i}$ and centres $\vec{R}_{in_i} = \vec{R}_i + \vec{\alpha}_{in_i}$ (see Fig. 4). In this case the surface integrations (2.13) yield [5]

$$\begin{aligned} d^{i}_{\lambda}(\vec{r}) &= \sum_{n_i, L} d^{i}_{L}(\vec{r}_{in_i})\, A^{in_i}_{L\lambda} \\ n^{i}_{\lambda}(\vec{r}) &= \sum_{n_i, L} n_L(\vec{r}_{in_i})\, A^{in_i}_{L\lambda} \end{aligned} \qquad (4.1)$$

[5] Because the non-trivial scattering states ($\sin \eta^{i}_{\lambda} \neq 0$) have only non-vanishing near field amplitudes $A^{in_i}_{L\lambda}$ for the angular momenta L with non-trivial MT-phase shifts $\eta^{in_i}_{L}$, the sums over L in (4.1...5) and (4.10,11) are correspondingly restricted.

with near field amplitudes $A^{in_i}_{L\lambda}$ determined together with the subcluster phase shifts η^i_λ by (see John and Ziesche 1971 a)

$$\sum_{n'_i L'} \left[ctg\,\eta^{in_i}_L M^{n_i n'_i}_{LL'} - ctg\,\eta^i_\lambda \delta^{n_i n'_i}_{LL'} \right] A^{in'_i}_{L'\lambda} = 0 , \tag{4.2}$$

$$M^{n_i n'_i}_{LL'} \equiv \delta_{n_i n'_i}\ \delta_{LL'} + tg\,\eta^{in_i}_L N^{n_i n'_i}_{LL'} .$$

The amplitudes $A^{in_i}_{L\lambda}$ are "orthogonal" and " complete" in the following sense

$$\sum_{n_i L} \tilde{A}^{in_i}_{\lambda L}\ \delta^{n_i n'_i}_{L L'}\ A^{in'_i}_{L'\lambda'} = \delta_{\lambda\lambda'} ,$$

$$\sum_{\lambda(sin\eta^i_\lambda \neq 0)} A^{in_i}_{L\lambda}\ \tilde{A}^{in'_i}_{\lambda L'} = (\delta^{-1})^{n_i n'_i}_{LL'} \tag{4.3a}$$

allowing the following reformulation of (4.2)

$$\sum_\lambda A^{in_i}_{L\lambda}\ tg\,\eta^i_\lambda\ A^{in'_i}_{\lambda L'} = (M^{-1})^{n_i n'_i}_{LL'}\ tg\,\eta^{in'_i}_{L'} , \tag{4.3b}$$

The details are given in Appendix 3. The " surface" structure matrices of the whole cluster defined in (3.3) or (A2.3) reduces via

$$\delta^{ii'}_{\lambda\lambda'} = \sum_{\substack{n_i, L \\ n'_{i'}, L'}} \tilde{A}^{in_i}_{\lambda L}\ \delta^{in_i\, i'n'_{i'}}_{L\ L'}\ A^{i'n'_{i'}}_{L'\lambda'} ,$$

$$N^{ii'}_{\lambda\lambda'} = (1-\delta_{ii'}) \sum_{\substack{n_i, L \\ n'_{i'} L'}} \tilde{A}^{in_i}_{\lambda L}\ N^{in_i\, i'n'_{i'}}_{L\ L'}\ A^{in'_{i'}}_{L'\lambda'} \tag{4.4}$$

to the "point" structure matrices defined ir (3.6).

The consistency of the developed formalism is to be seen in the following way: Elimination of the quantities η_λ^i, $A_{i\lambda}^{in_i}$, describing the subclusters, lead by means of (4.3) to equations for the whole cluster

$$\sum_{i'n_{i'}i'} \left[ctg\,\eta_l^{in_i} M_{l\ l'}^{in_i\ i'n_{i'}} - ctg\,\eta_\mu\, \delta_{l\ l'}^{in_i\ i'n_{i'}} \right] B_{i\mu}^{i'n_{i'}} = 0, \quad (4.5)$$

$$M_{l\ l'}^{in_i\ i'n_{i'}} \equiv \delta_{ii'}\,\delta_{n_i n_{i'}}\,\delta_{ll'} + tg\,\eta_l^{in_i} M_{l\ l'}^{in_i\ i'n_{i'}},$$

which are of the same type as the equations (4.2) for the subclusters only with a (now of course artificial) double enumeration of the single muffin-tins by a subcluster index i and an index n_i within the subcluster. In (4.5) the abbreviation $B_{l\mu}^{in_i} \equiv \sum_{\lambda(\sin\eta_\lambda' \neq 0)} A_{i\lambda}^{in_i} B_{\lambda\mu}^{i}$ is used.

This consistency property of the cluster equations should be of interest also for practical calculations, because generally the subcluster phase shifts η_λ^i are in part very small for a given (not too high) energy. The number of the essentially non-zero phase shifts η_λ^i is determined via $\varkappa a_i'$ by the energy $E = \varkappa^2$ and by the linear dimension $a_i' = max(a_{in_i})$ of the subcluster. Therefore the dimension of the whole cluster equations (3.8) reduces.

Now, we discuss the expressions of the wave functions, especially $\varphi_\mu^i(\vec{r})$. The region in which (3.1) holds,

is determined by the validity of the expansion (3.3) of $n_\lambda^{i'}(\vec{r})$. The latter can be written with (4.1), (A3.2) and (4.4) as

$$(\Lambda-\delta_{ii'})n_L(\vec{r}_{in_{i'}}) = \sum_{\substack{n_i',L_1\\ n_i'',L_2}} j_{L_1}(\vec{r}_{in_i'})(J^{-1})^{n_i'n_i''}_{L_1L_2} N^{in_i''i'n_{i'}}_{L_2L'} = \sum_{L} j_L(\vec{r}_{in_i}) N^{in_i i'n_{i'}}_{LL'} \quad . \tag{4.6}$$

In the last step $j_{L_1}(\vec{r}_{in_i'})$ has been expanded around the muffin-tin n_i. From the addition theorem of the spherical Neumann functions follows, that (4.6) is valid within a sphere around $\vec{R}_{in_i}$ just touching $\vec{R}_{i'n_{i'}}$. Because this consideration is valid for each muffin-tin n_i of the subcluster i and because in (3.3) the muffin-tins $n_{i'}$ of the subcluster i' are summed up, holds the expansion (3.3) of $n_\lambda^{i'}(\vec{r})$ within that region, which consists of spheres around the muffin-tins n_i of the subcluster just touching one of the muffin-tin centres of the subcluster i'. - Therefore in the general case of Section 3 we have to blow up spheres around each surface point of $\mathcal{V}_i$, so that it just touches one of the surface points of $\mathcal{V}_{i'}$. The sum of all these spheres is exactly that part of space, in which the expansion (3.3) of $n_\lambda^{i'}(\vec{r})$ is valid. - Returning again to the special case of subclusters we can write the wave function in the described surrounding of the subcluster i in the following way:

$$\varphi_\mu^i(\vec{r}) = \sum_{n_i,L}\Big\{\Big[n_L(\vec{r}_{in_i}) - \sum_{n_i',L'} j_{L'}(\vec{r}_{in_i'})(J^{-1}N)_{L'L}^{n_i'n_i}\Big]\sin\eta_L^{in_i}$$

$$- \sum_{n_i',L'} j_{L'}(\vec{r}_{in_i'})(J^{-1})_{L'L}^{n_i'n_i}\cos\eta_L^{in_i}\Big\}\,\beta_{L\mu}^{in_i} \qquad (4.7)$$

with

$$\beta_{L\mu}^{in_i} = \begin{cases} \frac{1}{\sin\eta_L^{in_i}}\, B_{L\mu}^{in_i} & \text{for } \sin\eta_L^{in_i} \neq 0 \\ \sum_{i',n_i',L'} \Big[\operatorname{ctg}\zeta_\mu\, J_{LL'}^{in_i i'n_i'} - N_{LL'}^{in_i i'n_i'}\Big] B_{L'\mu}^{i'n_i'} & \text{for } \sin\eta_L^{in_i} = 0 \end{cases} \qquad (4.8)$$

This results from (3.1), (3.9) and (3.9) eliminating the quantities ζ_λ^i and $A_\lambda^{in_i}$ with (4.1), (4.2) and (A3.2). If we expand $\varphi_\mu^i(\vec{r})$ around the muffin-tin n_i, then

$$\varphi_\mu^{in_i}(\vec{r}) = \sum_L \Big[n_L(\vec{r}_{in_i})\sin\eta_L^{in_i} - j_L(\vec{r}_{in_i})\cos\eta_L^{in_i}\Big]\beta_{L\mu}^{in_i}\sin\zeta_\mu \qquad (4.9)$$

turns out, again with the eliminable double enumeration i,n_i (4.9) is valid within a sphere around $\vec{R}_{in_i}$ just touching the next muffin-tin centre (belonging to the

subcluster i or not). This shows the consistency of the formalism also with respect to the wave function .

Finally we consider the special case of subclusters being so far from each other, that the spheres with radii a_o^i around the subcluster sites $\vec{R}_i$ don't overlap. In this case the far field properties of the subcluster described by ζ_λ^i and

$$A_{L\lambda}^{i} = \sum_{n_i' L'} \mathcal{J}_{L\,L'}^{o\,n_i'} A_{L'\lambda}^{i\,n_i'} \tag{4.10}$$

are sufficient, no near field properties as described by $A_{L\lambda}^{i\,n_i'}$ are necessary. This allows - as discussed in Section 3 - to pass from the $i-\lambda$ -representation (3.8) to the $i-L$-representation (3.16) or (3.18), which contains the subcluster quantities in the more compact form (3.17). By the way these quantities (3.17) can be calculated straightforwardly (see Appendix 3)

$$P_{LL'}^{i} = \sum_{\substack{n_i, L_1 \\ n_i', L_2}} \mathcal{J}_{L L_1}^{o\,n_i} \left(\mathcal{J}^{-1}\right)_{L_1 L_2}^{n_i n_i'} \mathcal{J}_{L_2 L'}^{n_i' o} \quad , \tag{4.11}$$

$$\left(t g \eta\right)_{LL'}^{i} = \sum_{\substack{n_i, L_1 \\ n_i', L_2}} \mathcal{J}_{L L_1}^{o n_i} \left(M^{-1}\right)_{L_1 L_2}^{n_i n_i'} t g l_{L_2}^{i\,n_i'} \mathcal{J}_{L_2 L'}^{n_i' o} \quad ,$$

avoiding an extra calculation of h_λ^L and $A_{L\lambda}^{L'}$ (but requiring the inversion of the matrices $\mathcal{J}$ and M). - In the considered case also the $in_i - L$ -representation (4.5) simplifies itself, because the structure matrices split in the following way

$$\mathcal{J}^{in_i\, i'n_{i'}}_{L\quad L'} = \sum_{L_1 L_2} \mathcal{J}^{n_i o}_{L\, L_1}\, \mathcal{J}^{i i'}_{L_1 L_2}\, \mathcal{J}^{o n_{i'}}_{L_2 L'}\,, \tag{4.12}$$

$$N^{in_i\, i'n_{i'}}_{L\quad L'} = \sum_{L_1 L_2} \mathcal{J}^{n_i o}_{L L_1}\, N^{i i'}_{L_1 L_2}\, \mathcal{J}^{o n_{i'}}_{L_2 L'} + \delta_{ii'}\, N^{n_i n_{i'}}_{L L'}\,,$$

separating the cluster structure ($\vec{R}_i$) and the subcluster structure ($\vec{a}_{in_i}$) from each other. - A certain advantage of all three representations is, that variations of the sites or potential within the subcluster can be treated easily.

5. Second example: Cluster of potentials with finite sets of angular momenta.

As a second simple example of a non-spherically symmetric muffin-tin we consider the following (generally non-local) potential

$$V(\vec{r},\vec{r}') = \begin{cases} \sum_{L_1 L'} Y_L(\vec{r})\, V_{LL'}(r,r')\, Y_{L'}(\vec{r}') & \text{for } r<r_o \\ 0 & \text{for } r>r_o \end{cases} \tag{5.1}$$

as recently with respect to band structure calculations discussed by Evens and Keller (1972). The sums over L, L' are running up to a certain maximum angular momentum ℓ_o. Then the Schrödinger equation is transformed with an ansatz $\psi(\vec{r}) = \sum_L Y_L(\vec{n})\, R_L(r)$ into a set of $(\ell_o+1)^2$ coupled differential equations

$$\left[\frac{1}{r}\frac{d^2}{dr^2}r - \frac{\ell(\ell+1)}{r^2} + \varkappa^2\right] R_L(r) = \sum_{L'} \int_0^{r_o} r'^2 dr'\, V_{LL'}(r,r')\, R_{L'}(r'), \qquad (5.2)$$

Demanding regularity at $r = 0$, from (5.2) a set of $(\ell_o+1)^2$ linearly independent solutions $R_{Ln}(r)$ next to arises, having outside the MT-sphere the behaviour

$$R_{Ln}(r) = j_\ell(\varkappa r)\alpha_{Ln} - n_\ell(\varkappa r)\beta_{Ln} \qquad \text{for } r > r_o \qquad (5.3)$$

with coefficients

$$\alpha_{Ln} = \varkappa r_o^2 \left[\frac{dn_\ell}{dr} R_{Ln} - n_\ell \frac{dR_{Ln}}{dr}\right]_{r=r_o},$$

$$\beta_{Ln} = \varkappa r_o^2 \left[\frac{dj_\ell}{dr} R_{Ln} - j_\ell \frac{dR_{Ln}}{dr}\right]_{r=r_o}. \qquad (5.4)$$

From this the scattering states $\psi_\lambda(\vec{r})$ are obtained by an appropriate linear combination $\sum_n \psi_n \gamma_{n\lambda}$ demanding

$$\sum_n \alpha_{Ln}\gamma_{n\lambda} = A_{L\lambda}\cos\eta_\lambda, \quad \sum_n \beta_{Ln}\gamma_{n\lambda} = A_{L\lambda}\sin\eta_\lambda. \qquad (5.5)$$

Therefore a set of algebraic equations arises

$$\sum_{n} (\alpha_{\ell n} - ctg\,\eta_\lambda\, \beta_{\ell n})\, \gamma_{n\lambda} = 0, \qquad (5.6)$$

yielding $(\ell_0+1)^2$ solutions η_λ and $A_{\ell\lambda}$.- By the way of course also bound state $E<0$ can be obtained; only the replacements $x \to i\,\bar{x}$ and $ctg\,\eta_\lambda \to i$ are necessary, the latter guaranteeing the wave function to remain finite. Then (5.6) determines certain energies $E_n = -\bar{x}_n^2$.

Now we consider a cluster of such potentials (5.1), each characterized by quantities η_λ^i and $A_{\ell\lambda}^i$, which are obtained from the matrices $\alpha_{\ell n}^i$ and $\beta_{\ell n}^i$. Because the potentials don't overlap, besides (3.4) also (3.5) is valid. That means, the structure matrices $\mathcal{J}_{\lambda\lambda'}^{ii'}$ and $N_{\lambda\lambda'}^{ii'}$ appearing in the cluster equations (3.8) completely reduce to the matrices $\mathcal{J}_{\ell\ell'}^{ii'}$, $N_{\ell\ell'}^{ii'}$,containing only the centres $\bar{R}_i$ of the potentials, and the (asymptotic or far field) amplitudes $A_{\ell\lambda}^i$. Because the potentials (5.1) involve only finite sets of angular momenta, the sums over ℓ in (3.4) and (3.5) are correspondingly restricted.- Passing from the $i-\lambda-$ representation (3.8) to the $i-\ell-$ representation (3.16), there are no difficulties with respect to the projection operator $P_{\ell\ell'}^i$, because the amplitudes $A_{\ell\lambda}^i$, obtained from (5.5) and (5.6), form itself (that is,

without the trivial scattering states) a complete set. That means we have $P^i_{ll'} = \delta_{ll'}$ in difference to the situation discussed in Section 4. Besides this, the only potential depending quantity $(tg\,\eta^i_{ll'})$, entering into (3.18), can be obtained directly from the original matrices α^i_{ln} and β^i_{ln}

$$(tg\,\eta)^i_{ll'} = \sum_n \beta^i_{ln} \left[(\alpha^i)^{-1}\right]_{nl'} , \qquad (5.7)$$

avoiding an extra calculation of η^i_λ and $A^i_{l\lambda}$ (but requiring the inversion of the matrices α^i_{ln}). (5.7) follows immediately from (5.5).

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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 (4.2) produce only two non-trivial scattering states $\lambda = \pm$

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

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

yielding with respect to the centre the following far field amplitudes

$$A_{L,\pm} = \sum_{n'L'} \mathcal{J}^{0n'}_{LL'} A^{n'}_{L'\pm} = \left[1 \pm (-1)^\ell\right] \delta_{m_\ell 0} \frac{\sqrt{2\ell+1}\; j_\ell(\varkappa a/2)}{\sqrt{2[1 \pm j_0(\varkappa a)]}}\,. \qquad (A1.2)$$

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

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

Appendix 2. Wronski relations and addition theorems of non-spherically symmetric muffin-tin orbitals.

Next to we define with the amplitudes $A_{L\lambda}$ of the trivial scattering states arising from an orthogonalizing procedure a function

$$\chi_\lambda(\vec{r}) = \begin{cases} n_\lambda(\vec{r}) & \text{for } \sin\eta_\lambda \neq 0 \\ \sum_L n_L(\vec{r}) A_{L\lambda} & \text{for } \sin\eta_\lambda = 0. \end{cases} \qquad \text{(A2.1)}$$

Then $\dot{J}_\lambda(\vec{r})$ and $\chi_\lambda(\vec{r})$ fullfill relations

$$\mathcal{R}e \oint_{(\vartheta)} d\vec{f}\left[\left(\frac{\partial}{\partial\vec{r}}\right)_\lambda - \left(\frac{\partial}{\partial\vec{r}}\right)_{\lambda'}\right] \dot{J}_\lambda(\vec{r})\,\dot{J}_{\lambda'}(\vec{r}) = 0 \,, \qquad \text{(A2.2a)}$$

$$\mathcal{R}e \oint_{(\vartheta)} d\vec{f}\left[\left(\frac{\partial}{\partial\vec{r}}\right)_\lambda - \left(\frac{\partial}{\partial\vec{r}}\right)_{\lambda'}\right] \chi_\lambda(\vec{r})\,\chi_{\lambda'}(\vec{r}) = 0 \,, \qquad \text{(A2.2b)}$$

$$\mathcal{R}e \oint_{(\vartheta)} d\vec{f}\left[\left(\frac{\partial}{\partial\vec{r}}\right)_\lambda - \left(\frac{\partial}{\partial\vec{r}}\right)_{\lambda'}\right] \chi_\lambda(\vec{r})\,\dot{J}_{\lambda'}(\vec{r}) = \delta_{\lambda\lambda'} \,, \qquad \text{(A2.2c)}$$

which correspond to and generalize the well-known Wronski relations of the spherical Bessel and Neumann functions. This is proved in the following way: Using, that $\dot{J}_\lambda$ and χ_λ are solutions of the homogeneous equation, we can deform the integration surface (ϑ) into the envelopping sphere

$r = r_0$. Now $n_\lambda = \sum_L n_L A_{L\lambda}$ holds also for $\sin \eta_\lambda \neq 0$. Then with the orthogonality of the Y_L and $A_{L\lambda}$ and with the ordinary Wronski relations immediately (A2.2) results.

With these relations explicit expressions of the structure matrices defined in (3.3) can be obtained. Really from (3.3) follows with (2.13), (A2.2a and c) for $\sin \eta_\lambda^i \neq 0$ (needed in (3.8))

$$N_{\lambda\lambda'}^{ii'} = (1 - \delta_{ii'}) \varkappa \oint_{(V)} d\vec{f} \left[\left(\frac{\partial}{\partial \vec{r}}\right)_\lambda - \left(\frac{\partial}{\partial \vec{r}}\right)_{\lambda'} \right] \frac{\varphi_\lambda^i(\vec{r})}{\sin \eta_\lambda^i} n_{\lambda'}^{i}(\vec{r}) \qquad \text{(A2.3a)}$$

and with (A2.1) and (A2.2c) for $\sin \eta_\lambda^i = 0$ (needed in (3.9))

$$N_{\lambda\lambda'}^{ii'} = (1 - \delta_{ii'}) \varkappa \oint_{(V)} d\vec{f} \left[\left(\frac{\partial}{\partial \vec{r}}\right)_L - \left(\frac{\partial}{\partial \vec{r}}\right)_{\lambda'} \right] \sum_L \tilde{A}_{\lambda L}^{i} n_L(\vec{r}_i) n_{\lambda'}^{i'}(\vec{r}) \qquad \text{(A2.3b)}$$

$n_{\lambda'}^{i'}(\vec{r})$ is given generally by the surface integral (2.13), but in the case of non-overlapping envelopping spheres (2.13) reduces simply with (2.4), (2.14) and (2.15) to $(\vec{r}_i \equiv \vec{r} - \vec{R}_i)$

$$n_{\lambda'}^{i'}(\vec{r}) = \sum_{L'} n_{L'}(\vec{r}_{i'}) A_{L'\lambda'}^{i'} = \sum_{L,L'} j_L(\vec{r}_i) N_{LL'}^{ii'} A_{L'\lambda'}^{i'} . \qquad \text{(A2.4)}$$

In the second step the addition theorem of the spherical Neumann fucntions has been used. Inserting (A2.4) into (A2.3) then (3.5) turns out. Because

there are *no restrictions* for the expansion (2.4) of $\mathcal{J}_o$, the corresponding expression of $\mathcal{J}^{i'}_{\lambda'}(\vec{r})$ is always true; therefore the "homogeneous" structure matrices $\mathcal{J}^{ii'}_{\lambda\lambda'}$ are given by (3.4), also in the case of overlapping envelopping spheres.

By the way, with

$$\mathcal{R}\oint_{(\mathcal{V})} d\vec{f}'\left[\left(\frac{\partial}{\partial \vec{r}'}\right)_o - \left(\frac{\partial}{\partial \vec{r}'}\right)_\lambda\right]\frac{1}{4\pi} n_o(\mathcal{R}|\vec{r}-\vec{r}'|)\mathcal{J}^i_{o\lambda}(\vec{r}') = \begin{cases} \mathcal{J}^i_\lambda(\vec{r}) & \text{for } \vec{r}\in\mathcal{V} \\ o & \text{for } \vec{r}\notin\mathcal{V}, \end{cases}$$

$$\mathcal{R}\oint_{(\mathcal{V})} d\vec{f}'\left[\left(\frac{\partial}{\partial \vec{r}'}\right)_\lambda - \left(\frac{\partial}{\partial \vec{r}'}\right)_o\right]\frac{1}{4\pi} n_o(\mathcal{R}|\vec{r}-\vec{r}'|)\chi_\lambda(\vec{r}') = \begin{cases} 0 \text{ for } \vec{r}\in\mathcal{V} \\ \chi_\lambda(\vec{r}) \text{ for } \vec{r}\notin\mathcal{V}, \end{cases} \qquad (A2.5)$$

which is proved by appropriate deformations of the integration surface, the function $\varphi_\lambda/\sin\vartheta_\lambda$ in (2.13) and (A2.3a) can be replaced by $-n_\lambda$.

Finally, (3.8) and (3.9) are derived from $\varphi_\mu = \varphi^i_\mu$ by means of (A2.2). The difference takes the form

$$\varphi_\mu(\vec{r}) - \varphi^i_\mu(\vec{r}) = \sum_\lambda n^i_\lambda(\vec{r})\alpha_{\lambda\mu} + \sum_\lambda \mathcal{J}^i_\lambda(\vec{r})\beta_{\lambda\mu}. \qquad (A2.6)$$

With (A2.2) immediately follows $\alpha_{\lambda\mu} = 0$ and $\beta_{\lambda\mu} = 0$;

these are the equations (3.8) and (3.9).

Appendix 3: Orthogonality and completeness of the partial wave amplitudes of a cluster.

Owing to the relation between far field amplitudes $A_{L\lambda}$ and near field amplitudes $A^n_{L\lambda}$,

$$A_{L\lambda} = \sum_{n'L'} \mathcal{J}^{nn'}_{LL'} A^{n'}_{L'\lambda} \qquad (A3.1)$$

from the orthogonality and completeness of the far field amplitudes $A_{L\lambda}$ there follow immediately corresponding relations for the near field amplitudes $A^n_{L\lambda}$:

$$\sum_{\substack{n'L'\\ n''L''}} \bar{A}^{\,n}_{\lambda L} \mathcal{J}^{nn'}_{LL'} A^{n'}_{L'\lambda'} = \delta_{\lambda\lambda'} \ , \quad \sum_{\lambda} A^n_{L\lambda} \bar{A}^{\,n'}_{\lambda L'} = (\mathcal{J}^{-1})^{nn'}_{LL'} . \qquad (A3.2)$$

Because the near field amplitudes $A^n_{L\lambda}$ of the non-trivial scattering states are non-zero only for angular momenta with non-trivial phase shifts η^n_L (this can be explicitly expressed by $A^n_{L\lambda} = \sin\eta^n_L \, a^n_{L\lambda}$),

$$A^n_{L\lambda} = 0 \quad \text{for } \sin\eta_\lambda \neq 0 \quad \text{and} \quad \sin\eta^n_L = 0, \qquad (A3.3)$$

the amplitudes of the trivial scattering states fulfill

the following condition as a consequence of the orthogonality:

$$\sum_{n'L'} \partial^{nn'}_{LL'} A^{n'}_{L'\lambda} = 0 \quad \text{for} \quad \sin\zeta_\lambda = 0 \quad \text{and} \quad \sin\zeta^n_\lambda \neq 0 , \qquad \text{(A3.4)}$$

From (A3.3) and (A3.4) follows, that the projection operator of the non-trivial scattering states can be written as

$$\sum_{\lambda(\sin\zeta_\lambda \neq 0)} A_{L\lambda} \tilde{A}_{\lambda L'} = \sum_{\substack{n_{1,2} \\ L_{1,2}(\sin\zeta^{n_{1,2}}_{L_{1,2}} \neq 0)}} \partial^{0n}_{LL_1} (\partial^{-1})^{n_1 n_2}_{L_1 L_2} \partial^{n_2 0}_{L_2 L'} . \qquad \text{(A3.5)}$$

Inserting (A3.1) into (A3.5) yields this projection operator in $n-L$ -representation

$$\sum_{\substack{\lambda \\ (\sin\zeta_\lambda \neq 0)}} A^n_{L\lambda} \tilde{A}^{n'}_{\lambda L'} = \begin{cases} (\partial^{-1})^{nn'}_{LL'} & \text{for } \sin\zeta^n_L \neq 0 \text{ and } \sin\zeta^{n'}_{L'} \neq 0 \\ 0 & \text{for } \sin\zeta^n_L = 0 \text{ or } \sin\zeta^{n'}_{L'} = 0 . \end{cases} \qquad \text{(A3.6)}$$

Finally, with the orthogonality (first equation of (A3.2)) and the "incompleteness" (A3.6) the cluster equations (4.2) can be reformulated as

$$\sum_{\lambda} A^{n}_{L\lambda}\ tg\,\gamma_{\lambda}\,\tilde{A}^{n'}_{\lambda L'} = (M^{-1})^{nn'}_{LL'}\,tg\,\gamma^{n'}_{L'} \qquad \text{(A3.7)}$$

or with (A3.1) as

$$\sum_{\lambda} A_{L\lambda}\,tg\,\gamma_{\lambda}\tilde{A}_{\lambda L'} = \sum_{\substack{n_1 n_2 \\ (\sin\gamma^{n_1 n_2}_{L_1 L_2}\neq 0)}} J^{0n_1}_{LL_1}(M^{-1})^{n_1 n_2}_{L_1 L_2}\,tg\,\gamma^{n_2}_{L_2}\,J^{n_2 0}_{L_2 L'} \,. \qquad \text{(A3.8)}$$

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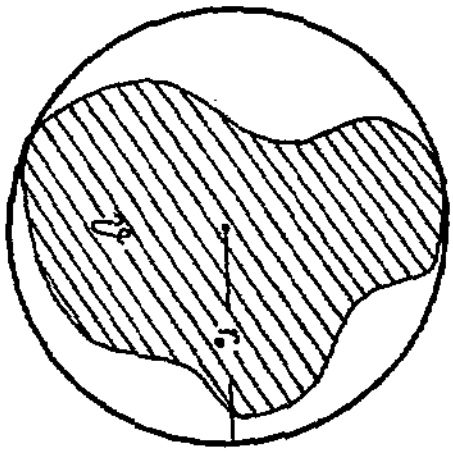

Fig. 1. A general MT-potential and its envelopping sphere with respect to an arbitrary centre.

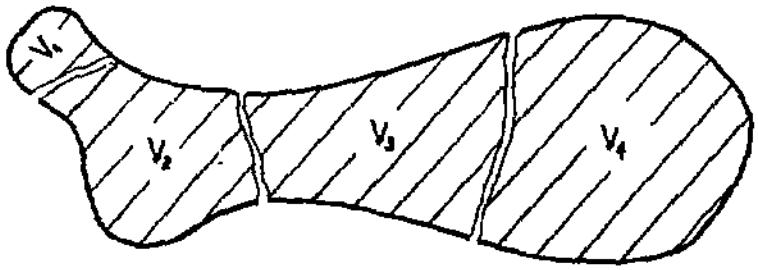

Fig. 2. A cluster of general MT-potentials, touching along parts of their surfaces.

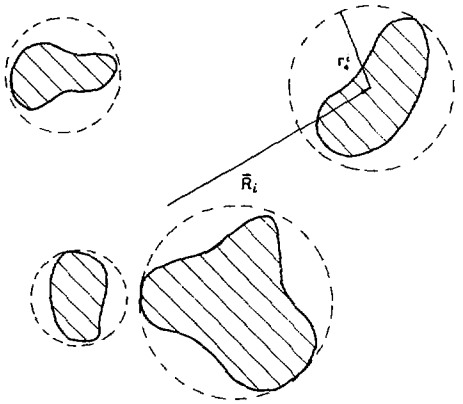

Fig. 3. A cluster of general MT-potentials with non-overlapping envelopping spheres.

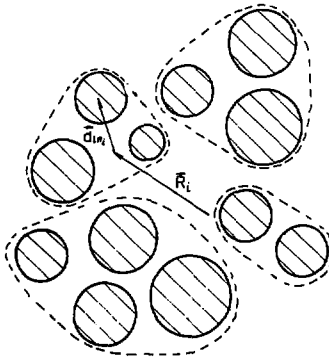

Fig. 4. A cluster of subclusters.