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GENERALIZED PHASE SHIFTS FOR A CLUSTER OF MUFFIN - TIN POTENTIALS

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I n t r o d u c t i o n

As is well-known the conception of the so-called muffin-tin potential (mt-potential) led to an essential progress in the qualitative understanding of the electron structure of metals:

1. Owing to the constant potential between the mt-spheres the crystal structure and the potential within the mt-spheres only via its phase shifts enter into the equation determining the band structure by separated quantities (KKR-method/1,2/).

2. For the simple and transition metals the phase shifts have a characteristic behaviour allowing the introduction of model potentials (for simple metals), respectively model Hamiltonians (for transition metals)/3/.

In the mentioned cases the use of the scattering properties of single atoms (only) has been proved useful for understanding the electronic properties. But the discussion of Fletscher, McGill and Klima/4/ using general considerations of Ziman, Lloyd and Berry/5/ shows, that in the case of amorphous semiconductors the in-fluence of the short range order on the electron structure (more precisely on the density of states)is most conveniently described by means of the scattering properties of appropriate (for example tetrahedral) clusters of atoms. Therefore a proper description of the scattering properties of such clusters should be of interest. Our hope is, that the scattering point of view may be really deepened by introducing generalized phase shifts for appropriate clusters of mt-potentials and that such generalized phase shifts play a similar characteristic role for the calculation of the electron structure of amorphous states as the ordinary phase shifts do it for the calculation of the electron structure of the crystalline state. We furthermore hope, that such generalized phase shifts are also of interest for the electron structure of lattices with characteristic coordination properties (for example intermetallic compounds).

The main question in this connection is, how to describe the scattering of a non-spherically symmetric potential (in our case of a cluster of mt-potentials). Now Demkov and Rudakov have recently generalized the well-known method of partial waves, so this method is now applicable also to non-spherically symmetric potentials /6/. In section 1 the Demkov/Rudakov - formalism is shortly summarized. In section 2 the calculation of the generalized phase shifts of the cluster is analogous to the KKR-method reduced to a purely algebraic problem namely to the solution of a system of homogeneous linear equations. In section 3 general properties of these equations are discussed: the number of non-vanishing cluster phase shifts, the qualitative behaviour of the cluster phase shifts, the evaluation of bound state and limits for the possible number of bound states.

1. Generalized Method of Partial Waves for Non-Spherically Symmetric Potentials

As Demkov and Rudakov have shown [6] the solution of the Schrödinger equation describing scattering states $E > 0$ of a local, but non-spherically symmetric potential $V(\vec{r})$

$$[\Delta + \kappa^2 - V(\vec{r})]\phi_\lambda(\vec{r}) = 0, \qquad \kappa \equiv \sqrt{E} \tag{1.1}$$ [x]

can be characterized by the following asymptotic behaviour

$$\phi_\lambda(\vec{r} \to \infty) \to -\frac{1}{2i\kappa r}[A_\lambda(\vec{n})e^{+i(\kappa r + \eta_\lambda)} - A_\lambda^*(\vec{n})e^{-i(\kappa r + \eta_\lambda)}], \; \vec{n} \equiv \frac{\vec{r}}{r} \tag{1.2}$$

with generalized phase shifts $\eta_\lambda(\kappa)$ and partial wave amplitudes $A_\lambda(\vec{n};\kappa)$. These functions $A_\lambda(\vec{n})$ form a complete and orthogonal set on the unit sphere. The quantities η_λ and $A_\lambda(\vec{n})$ describe all scattering phenomena of the potential $V(\vec{r})$ in a completely similar manner as η_L and $Y_L(\vec{n})$ do it for spherically symmetric potentials $V(r)$. For a symmetric scatterer the amplitudes $A_\lambda(\vec{n})$ transform themselves according to the irreducible representation of the corresponding point group.

As an example Demkov and Rudakov calculated the phase shifts for a cluster of zero range potentials. In the following the scattering problem for an arbitrary cluster of non-overlapping mt-potentials is reduced to a ourely algebraic problem.

2. Derivation of the Algebraic Equation Determining η_λ and $A_\lambda(\vec{n})$

By means of an appropriate Green's function(GF)the Schrödinger equation (1.1) including the asymptotic behaviour (1.2) may be

[x] All energies are measured in units $\hbar^2/2m$.

replaced by an integral equation (dropping the index λ)

$$\phi(\vec{r}) = \int d\vec{r}\,' G(\vec{r}-\vec{r}\,') V(\vec{r}\,') \phi(\vec{r}\,'). \tag{2.1}$$

In our case

$$G(\vec{r}-\vec{r}\,') = -\frac{\kappa}{4\pi}\left[\frac{\cos\kappa|\vec{r}-\vec{r}\,'|}{\kappa|\vec{r}-\vec{r}\,'|} + ctg\,\eta\,\frac{\sin\kappa|\vec{r}-\vec{r}\,'|}{\kappa|\vec{r}-\vec{r}\,'|}\right] \tag{2.2}$$

is such an appropriate GF , because it fulfills the equation

$$(\Delta+\kappa^2)\,G(\vec{r}-\vec{r}\,') = \delta(\vec{r}-\vec{r}\,') \tag{2.3}$$

and has the desired asymptotic behaviour

$$G(\vec{r}-\vec{r}\,') \to -\frac{\kappa}{4\pi}\,\frac{1}{2i\kappa r\sin\eta}\left[e^{i(\kappa r+\eta)}e^{-i\kappa\vec{n}\vec{r}\,'} - e^{-i(\kappa r+\eta)}e^{i\kappa\vec{n}\vec{r}\,'}\right] \tag{2.4}$$

for $r\to\infty$. For non-overlapping mt-potentials (with centres $\vec{R}_i$ and radii r_{i0} , $i = 1,\dots, N$) the integral equation (2.1) may be treated in a way completely analogous to the Kohn/Rostoker-method /2/. By means of the Schrödinger equation (1.1) each mt-potential may be replaced by $(\Delta'+\kappa^2)$. After twofold partial integration one obtains surface integrals over the mt-spheres ($|\vec{r}\,'-\vec{R}_i| = r_{i0}$):

$$\sum_{i=1}^{N}\int d\vec{f}_i{}'\left[G(\vec{r}-\vec{r}\,')\frac{\partial\phi(\vec{r}\,')}{\partial\vec{r}\,'} - \frac{\partial G(\vec{r}-\vec{r}\,')}{\partial\vec{r}\,'}\phi(\vec{r}\,')\right] = \begin{cases} 0 & \text{within mt} \\ & \text{for } \vec{r} \\ \phi(\vec{r}) & \text{outside mt}\end{cases} \tag{2.5}$$

The remaining integrals can be easily evaluated, if the wave and Green's functions are expanded in spherical harmonics.

Using the abbreviations (L stands for the quantum numbers of the angular momentum)

(2.6) $n_L(\vec{r}) \equiv n_\ell(\kappa r) Y_L(\vec{n}), \qquad i_L(\vec{r}) \equiv i_\ell(\kappa r) Y_L(\vec{n}),$ (2.6)[x]

$n_L(\vec{r}, \eta) \equiv \sin\eta \, n_L(\vec{r}) - \cos\eta \, i_L(\vec{r})$

the wave function in the immediate surrounding of the i -th sphere has the form

$$\phi^i(\vec{r}) = \sin\eta \sum_L a_L^i \, n_L(\vec{r}_i, \eta_L^i), \quad \vec{r}_i \equiv \vec{r} - \vec{R}_i \tag{2.7}$$

owing to the constant potential outside the spheres. The i -th mt-potential is (for a given energy $E = \kappa^2$) characterized by a set $\mathfrak{L}_i$ of certain angular momenta $L_1, L_2, \ldots$ with non-vanishing mt-phase shifts $\eta_{L_1}^i, \eta_{L_2}^i, \ldots$, the number of which is D_i. Thus the whole cluster has $D \equiv \sum_i D_i$ non-vanishing mt-phase shifts η_L^i; in the special case of only s -scattering ($D_i = 1$), discussed by Demkov/Rudakov/6/, we have $D = N$.

With respect to the expansion of $G(\vec{r}-\vec{r}')$ one has to distinguish the cases: $\vec{r}$ lying within one of the mt-spheres and $\vec{r}$ lying outside the mt-spheres.

For $\vec{r}$ lying within the i -th mt-sphere and $\vec{r}'$ lying on the surface of the j -th mt-sphere (see Fig.) one obtains

$$G(\vec{r}-\vec{r}') = \kappa \sum_{L,L'} i_L(\vec{r}_i) \{ [N_{LL'}^{ij} - \operatorname{ctg}\eta \, J_{LL'}^{ij}] \, i_{L'}(\vec{r}_j{}') + \delta_{ij} \delta_{LL'} n_{L'}(\vec{r}_j{}') \} \tag{2.8}$$

---

x/ $i_\ell(\kappa r)$ and $n_\ell(\kappa r)$ are the spherical Bessel and Neumann functions, respectively (see for example Messiah/7/). The n_ℓ used here differs from Messiah's definition by a minus sign.

as shown in the Appendix 1. The structure, that means the set of the mt-centres $\vec{R}_1,\dots,\vec{R}_N$, is contained in the quantities

$$N^{ii'}_{LL'}=(1-\delta_{ii'})4\pi\sum_{L''}C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, n_{L''}(\vec{R}_{ii'})$$
$$J^{ii'}_{LL'}=4\pi\sum_{L''}C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, j_{L''}(\vec{R}_{ii'})=i^{\ell-\ell'}\int d\Omega\; Y_L(\vec{n})\, e^{i\kappa\vec{n}\vec{R}_{ii'}}\, Y_{L'}(\vec{n}) \tag{2.9}$$

with $\vec{R}_{ii'}=\vec{R}_i-\vec{R}_{i'}$. Using real orthonormal linear combinations $Y_L(\vec{n})$ of the spherical harmonics with the total angular momentum ℓ and with

$$C_{LL'L''}=\int d\Omega\, Y_L(\vec{n})Y_{L'}(\vec{n})Y_{L''}(\vec{n}) \tag{2.10}$$

as generalized Clebsch-Gordon coefficients the structure constants $N^{ii'}_{LL'}$ and $J^{ii'}_{LL'}$ are real symmetric matrices.

Setting (2.7) and (2.8) into (2.5) for $\vec{r}$ inside the i-th mt-potential, performing the surface integration, using the orthogonality of the Y_L and the Wronskian relation of the spherical Bessel functions for $L\in\mathfrak{L}_i$ a system of D homogeneous linear equations for the coefficients a^i_L is obtained,

$$\sum_{i',L'}[\sin\eta_\lambda N^{ii'}_{LL'}-\cos\eta_\lambda J^{ii'}_{LL'}+\delta_{ii'}\delta_{LL'}\sin\eta_\lambda\operatorname{ctg}\eta^i_L]\sin\eta^{i'}_{L'}a^{i'}_{L'\lambda}=0, \tag{2.11}$$

the solutions of which we characterize by an index λ. (2.11) is the condition for that an ansatz of the form (2.7) being valid for each of the mt-spheres. (2.11) has, of course, only solutions if

$$\boxed{\det\|N^{ii'}_{LL'}-\operatorname{ctg}\eta_\lambda J^{ii'}_{LL'}+\delta_{ii'}\delta_{LL'}\operatorname{ctg}\eta^i_L\|=0.} \tag{2.12}$$

(2.12) determines D cluster phase shifts η_λ in dependence of the quantities $\eta^1_L(\kappa),\dots,\eta^N_L(\kappa)$ and $\kappa\vec{R}_1,\dots,\kappa\vec{R}_N$, the latter contained only in the structure constants $N^{ii}_{LL'}$ and $J^{ii}_{LL'}$. Because the symmetric matrices $N^{ii}_{LL'}$ and $J^{ii}_{LL'}$ and the mt-phase shifts η^{i}_{L} are real, also the coefficients $a^{i}_{L\lambda}$ and the phase shifts η_{λ} are real.

The same procedure, which led for $L \in \mathfrak{L}_i$ to (2.11), yields for $L \notin \mathfrak{L}_i$ the coefficients

$$\sin\eta_\lambda \cos\eta^i_L \, a^i_{L\lambda} = \sum_{i,L'} (\cos\eta_\lambda \, J^{ii}_{LL'} - \sin\eta_\lambda \, N^{ii}_{LL'}) \sin\eta^i_{L'} \, a^i_{L'\lambda}, \tag{2.13}$$

which occur (only) in the expression (2.7) for the wave function $\phi^i_\lambda(\vec{r})$ in the immediate surrounding of the i-th mt-sphere.

The solutions of (2.11) determine the wave function not only in the immediate surrounding of each mt-sphere, but also in the whole space outside the mt-spheres. To show this, $G(\vec{r}-\vec{r}\,')$ for $\vec{r}$ lying outside the spheres and $\vec{r}\,'$ lying on the surface of the i-th mt-sphere is needed (see Appendix 1):

$$G(\vec{r}-\vec{r}\,') = \frac{\kappa}{\sin\eta_\lambda} \sum_L n_L(\vec{r}_i, \eta_\lambda) j_L(\vec{r}_i\,'). \tag{2.14}$$

Setting (2.7) and (2.14) into (2.5) for $\vec{r}$ outside the mt-spheres, performing the surface integrations, using again the orthogonality of the Y_L and the Wronskian relation, the following expression for the wave function outside the mt-spheres is received:

$$\phi_\lambda(r) = \sum_{i,L} \sin\eta^i_L \, a^i_{L\lambda} \, n_L(r_i, \eta_\lambda). \tag{2.15}$$

(2.15) is valid in the whole space outside the mt-spheres, especially also at large distances $r \to \infty$. Owing to the asymptotic behaviour of the spherical Bessel functions /7/ the wave function (2.14) has really the demanded asymptotic behaviour (1.2) with amplitudes

$$\boxed{A_\lambda(\vec{n}) = \sum_{l,L} \sin\eta_L^l \, a_{L\lambda}^l (-i)^\ell \, e^{-iK\vec{n}\vec{R}_l} \, Y_L(\vec{n}).} \tag{2.16}$$

(2.15) and (2.16) show how to calculate the wave function outside the spheres and especially the asymptotic behaviour from given cluster-phase shifts η_λ and coefficients $a_{L\lambda}^l$ .Because η_λ , $a_{L\lambda}^l$ and $Y_L(\vec{n})$ are real, the amplitudes $A_\lambda(\vec{n})$ have the property $A^*(\vec{n}) = A\ (-\vec{n})$. The amplitudes $A_\lambda(\vec{n})$ are also orthogonal

$$\int d\Omega A_\lambda^*(\vec{n})A_{\lambda'}(\vec{n}) = \sum_{\substack{l,L,\\ l,L'}} \sin\eta_L^l \, a_{L\lambda}^l \, J_{LL'}^{ll'} \sin\eta_{L'}^{l'} a_{L'\lambda'}^{l'} = \delta_{\lambda\lambda'}, \tag{2.17}$$

as can be shown easily by combining (2.11) for different eigenvalues $ctg\,\eta_\lambda$ in the usual way.

By means of the system of equations (2.11) the different expressions for the wave function (2.7) and (2.15) are equivalent in the immediate surrounding of each mt-sphere. Namely the following is true (for $r_l < R_{ll'(\neq l)}$ and outside the spheres)

$$\phi_\lambda(\vec{r}) - \phi_\lambda^l(\vec{r}) = \sum_L j_L(\vec{r}_l) \sum_{l,L'} [(\sin\eta_\lambda N_{LL'}^{ll'} - \cos\eta_\lambda J_{LL'}^{ll'}) \sin\eta_{L'}^{l'} + \delta_{ll'} \delta_{LL'} \sin\eta_\lambda \cos\eta_L^l] a_{L'\lambda}^{l'} \tag{2.18}$$

as shown in the Appendix 2 using only an appropriate addition theorem about the spherical Neumann functions $n_L(\vec{r})$, also derived in the Appendix 2.

Owing to (2.11) and (2.13) the right hand side of (2.18) is vanishing, showing the equivalence of (2.7) and (2.15). Of course,this conclusion may be inverted, considering (2.15) as an ansatz for the wave function in the whole space outside the spheres and demanding the equivalence of $\phi_\lambda(\vec{r})$ and $\phi_\lambda^l(\vec{r})$ in the immediate surrounding of each mt -sphere, that is demanding the left hand side of (2.18) to be zero ; then (2.11) and (2.13) follow. In this way the system of equations (2.11) determining η_λ and $a^{l}_{L\lambda}$ is derived without Green's functions using only the mentioned additional theorem for the $n_L(\vec{r})$. This way is analogous to Korringa's treatment of the band structure of an ideal mt-lattice /1/.

3. Discussion of the Algebraic Equations Determining η_λ and $A_\lambda(\vec{n})$

The considered mt-phase shifts η^{l}_{L} , the number of which is assumed to be D , produce via (2.11) D non-trivial solutions $a^{l}_{L1}, \ldots, a^{l}_{LD} (L \subset \mathfrak{L}_l)$; the corresponding eigenvalues $tg\eta_1, \ldots, tg\,\eta_D$ don't vanish (for $\kappa \neq 0$), because the case $tg\,\eta_\lambda = 0$ owing to $\det \| J^{ll'}_{LL'} \| > 0$ appears only for trivial solutions $a^{l}_{L\lambda} = 0 (L \subset \mathfrak{L}_l)$. The coefficients $a^{l}_{L\lambda}$ for $L \subset \mathfrak{L}_l$ are not determined by (2.11); they correspond to purely homogeneous, non-scattering wave functions with $\eta_\lambda = 0$ and can be used to complete the set of amplitudes $A_1(\vec{n}), \ldots, A_D(\vec{n})$ by an orthogonalizing procedure.

If one of the mt-phase shifts passes $tg\,\eta^{l}_{L} = 0$ for a certain energy κ_0 , then the number of equations (2.11) reduces to $D-1$. Therefore also one of the cluster phase shifts η_λ passes $tg\,\eta_\lambda = 0$ at the point $\kappa = \kappa_0$.

In the limiting case of large distances between the mt-potentials, $\vec{R}_l \to a\vec{R}_l$ and $a \to \infty$, owing to $N^{ll'}_{LL'} \to 0$ and $J^{ll'}_{LL'} \to \delta_{ll'}\, \delta_{LL'}$ we obtain $ctg\,\eta_\lambda \to ctg\,\eta^{l}_{L}$ from (2.11). Therefore turning reversely to finite distances $R_{ll'}$, each cluster-phase shift η_λ remains within the stripe

$n\pi < \eta_\lambda < (n+1)\pi$ determined by the corresponding mt-phase shift η^{i}_{L}, because (2.11) possesses for $\kappa \neq 0$ no non-trivial solutions with $tg\,\eta_\lambda = 0$.

With this result, with the low energy property $tg\,\eta_\lambda \approx \kappa^{2\ell+1}$ (see /6/) and with the Levinson theorem limits for the number of bound states, $Z = (1/\pi)\Sigma\,\eta_\lambda(0)$, can be obtained:

$$\frac{1}{\pi}\sum_{i,L}[\eta^{i}_{L}(0) + \delta^{i}_{L}\pi] \geq Z \geq \frac{1}{\pi}\sum_{i,L}[\eta^{i}_{L}(0) - (1-\delta^{i}_{L})\cdot\pi], \tag{3.1}$$

at which $\delta^{i}_{L} = 1$ or 0 for $tg\,\eta^{i}_{L}(0) = \pm 0$.

Also bound states $E < 0$ can be calculated by means of (2.11) and (2.12). To this purpose it is only necessary to choose $ctg\,\eta$ (dropping now the index λ) in such a way, that the wave function for κ being imaginary is normalizable; that means $G(\vec{r}-\vec{r}')$ cannot contain exponentially increasing terms for $\kappa = i\bar{\kappa} = i\sqrt{-E}$. This property is evidently given by $\eta = i$ (see (2.2)). Splitting appropriately imaginary units

$$N^{ii'}_{LL'} \equiv i^{\ell-\ell'+1}\,\bar{N}^{ii'}_{LL'},\quad J^{ii'}_{LL'} \equiv i^{\ell-\ell'}\,\bar{J}^{ii'}_{LL'},\quad ctg\,\eta^{i}_{L} \equiv i\,\Delta^{i}_{L} \tag{3.2}$$

we introduce real quantities $\bar{N}^{ii'}_{LL'}, \bar{J}^{ii'}_{LL'}, \Delta^{i}_{L}$. Then (2.12) changes into

$$D^{ii'}_{LL'}(\bar{\kappa}) \equiv \bar{N}^{ii'}_{LL'} - \bar{J}^{ii'}_{LL'} + \delta_{ii'}\,\delta^{i}_{L}\quad \Delta^{i},\quad det\,\|D^{ii'}_{LL'}(\bar{\kappa}_n)\| = 0. \tag{3.3}$$

(3.3) means, that one has to look for the zeros of the determinant, considered as a function of $\bar{\kappa}$. The solutions $\bar{\kappa}_n = \sqrt{-E_n}$ depend on the geometry via the structure constants $\bar{N}^{ii'}_{LL'}, \bar{J}^{ii'}_{LL'}$ and on the mt -potentials via the "phase shifts" $(\bar{j}_\ell(\rho) \equiv i^\ell j_\ell(i\rho),\ \bar{n}_\ell(\rho) \equiv i^{\ell-1} n_\ell(i\rho))$

$$\Delta^l_L = \frac{\bar{n}_\ell(\bar{\kappa} r) R^{l\,\prime}_\ell(r) - \bar{n}'_\ell(\bar{\kappa} r) R^l_\ell(r)}{\bar{j}_\ell(\bar{\kappa} r) R^{l\,\prime}_\ell(r) - \bar{j}'_\ell(\bar{\kappa} r) R^l_\ell(r)}\Big|_{r=r_{l0}}, \tag{3.4}$$

the latter determined essentially by the logarithmic derivatives $R^{l\,\prime}_r / R^l_r$ at the mt-boundaries $r = r_{l0}$. To obtain also the wave function the replacement $\sin\eta\, \sin\eta^l_L a^l_L \to a^l_{Ln}$ is suitable. Then, with the solution κ_n and with the abbreviations

$$a^l_{Ln} \equiv -i^{\ell+1} \bar{a}^l_{Ln},\quad n_L(\vec{r}) - i j_L(\vec{r}) \equiv i^{-\ell+1} \bar{h}_L(\vec{r}) \tag{3.5}$$

introducing again real quantities $\bar{a}^l_{Ln}$, $\bar{h}_L(\vec{r})$, the equations (2.11) and (2.15) change into

$$\sum_{l,L'} D^{ll}_{LL'}(\kappa_n) \bar{a}^l_{L'n} = 0, \qquad \phi_n(\vec{r}) = \sum_{l,L} \bar{a}^l_{Ln} \bar{h}_L(\vec{r}_l), \tag{3.6}$$

showing how to evaluate the wave function outside the spheres also for bound states. Similarly as in the case of scattering states the matrix $D^{ll}_{LL'}$ has a finite order, if the number of non-trivial "phase shifts" Δ^l_L is limited.

The eigenvalues of (2.11) can be written in the form of "expectation values"

$$ctg\,\eta_\lambda = \frac{\sum_{l,L} \sum_{l,L'} \sin\eta^l_L a^l_{L\lambda} [N^{ll}_{LL'} + \delta_{ll}\, \delta_{LL'} ctg\,\eta^l_L] \sin\eta^l_{L'} a^l_{L'\lambda}}{\sum_{l,L} \sum_{l,L'} \sin\eta^l_L a^l_{L\lambda} J^{ll}_{LL'} \sin\eta^l_{L'} a^l_{L'\lambda}}, \tag{3.7}$$

showing its stationary property with respect to small variations of $a^l_{L\lambda}$ around the solutions of the (2.11). Hence for variations of the cluster phase shifts η_λ with respect to the mt-phase shifts (or to the mt-centres $\vec{R}_l$) the coefficients can be treated as constants:

$$\frac{\partial \eta_\lambda}{\partial \eta^{i}_{L}} = (\sin \eta_\lambda \, a^{i}_{L\lambda})^{2} \geq 0. \tag{3.8}$$

If the i -th mt-potential is changed in such a way, that one of its phase shifts η^{i}_{L} increases (decreases), then owing to (3.8) also all cluster phase shifts η_λ increase (decrease).

Conclusion

The phase shifts and the centres of (non-overlapping) mt-potentials, forming an mt-cluster, determine purely algebraically the generalized phase shifts of the cluster. We hope that such generalized phase shifts are useful for the discussion of the electron structure of mt-ensembles with characteristic coordination properties (amorphous semiconductors, intermetallic compounds); the proposed scheme should be also useful for the discussion of the scattering properties of molecules.

Acknowledgement

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Appendix 1

Expansion of $G(\vec{r}-\vec{r}\,')$ in spherical harmonics

To obtain (2.8) and (2.14) from (2.2) we need

$$-\frac{\cos \kappa |\vec{r}_1 + \vec{r}_2|}{\kappa |\vec{r}_1 + \vec{r}_2|} = 4\pi \sum_L (-1)^{\ell} [\theta(r_1 - r_2) n_L(\vec{r}_1) j_L(\vec{r}_2) + \theta(r_2 - r_1) j_L(\vec{r}_1) n_L(\vec{r}_2)], \tag{A1.1}$$

$$\frac{\sin \kappa|\vec{r}_1+\vec{r}_2|}{\kappa|\vec{r}_1+\vec{r}_2|} = 4\pi \sum_L (-1)^{\ell}\, j_L(r_1) j_L(r_2) \tag{A1.2}$$

as a generalization of (A1.2)

$$i^{\ell}\, j_L(\vec{r}_1+\vec{r}_2) = 4\pi \sum_{L_1,L_2} C_{LL_1L_2}\, i^{\ell_1+\ell_2}\, j_{L_1}(\vec{r}_1) j_{L_2}(\vec{r}_2). \tag{A1.3}$$

Moreover, $j_L(-\vec{r}) = (-1)^{\ell} j_L(\vec{r})$ and $(-i)^{\ell} = i^{-\ell}$ will be used.

According to the situation at Fig. we may write $\vec{r}-\vec{r}\,' = \vec{r}_i - \vec{r}_j\,' + R_{ij}$ with $R_{ij} > |\vec{r}_i - \vec{r}_j\,'|$ for $j \neq i$ and $\vec{r}-\vec{r}\,' = \vec{r}_i - \vec{r}_i\,'$ with $r_i' > r_i$ for $j = i$. Therefore the inhomogeneous part of (2.2) may be expanded in the following way, using (A1.1) and (A1.3) in the 1st step and (2.9) in the 2nd step

$$-\frac{\cos \kappa|\vec{r}-\vec{r}\,'|}{\kappa|\vec{r}-\vec{r}\,'|} = 4\pi \sum_{L,L'} [(1-\delta_{ij}) 4\pi \sum_{L''} C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, j_L(\vec{r}_i) j_{L'}(\vec{r}_j\,')\, n_{L''}(\vec{R}_{ij}) + \tag{A1.4}$$
$$+\delta_{ij}\, \delta_{LL'}\, j_L(\vec{r}_i) n_L(\vec{r}_i\,')] = 4\pi \sum_{L,L'} j_L(\vec{r}_i)[N^{ij}_{LL'} j_{L'}(\vec{r}_j\,') + \delta_{ij}\, \delta_{LL'}\, n_{L'}(\vec{r}_j\,')].$$

With (A1.2), (A1.3) and (2.9) the homogeneous part of (2.2) may be expanded in the following way

$$\frac{\sin \kappa|\vec{r}-\vec{r}\,'|}{\kappa|\vec{r}-\vec{r}\,'|} = 4\pi \sum_{L,L'} 4\pi \sum_{L''} C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, j_L(\vec{r}_i) j_{L'}(\vec{r}_j\,') j_{L''}(\vec{R}_{ij}) = \tag{A.1.5}$$
$$= 4\pi \sum_{L,L'} j_L(\vec{r}_i) J^{ij}_{LL'}\, j_{L'}(\vec{r}_j\,').$$

Setting (A1.4) and (A1.5) into (2.2) then (2.8) turns out, q.e.d.

For $\vec{r}$ outside mt-spheres we have $r - r' = r_i - r_i'$ with $r_i > r_i'$. Therefore the inhomogeneous part of (2.2) may be written as

$$-\frac{\cos \kappa|\vec{r}-\vec{r}\,'|}{\kappa|\vec{r}-\vec{r}\,'|} = 4\pi \sum_L n_L(\vec{r}_i) j_L(\vec{r}\,'_i) \tag{A1.6}$$

using (A1.1). The homogeneous part of (2.2) has the expansion

$$\frac{\sin\kappa|\vec{r}-\vec{r}\,'|}{\kappa|\vec{r}-\vec{r}\,'|}=4\pi\sum_{L} i_L(\vec{r}_1)\,i_L(\vec{r}\,'_1) \tag{A1.7}$$

using (A1.2). Setting (A1.6) and (A1.7) into (2.2), then (2.14) is obtained, q.e.d.

Appendix 2

Addition theorem about the spherical Neumann functions

The generalization of (A1.1) (A2.1)

$$i^{\ell} n_L(\vec{r}_1+\vec{r}_2)=4\pi\sum_{L_1,L_2} C_{LL_1L_2}\, i^{\ell_1+\ell_2}\,[\theta(r_1-r_2)\,n_{L_1}(\vec{r}_1)\,i_{L_2}(\vec{r}_2)+\theta(r_2-r_1)\,i_{L_1}(\vec{r}_1)\,n_{L_2}(\vec{r}_2)]$$

may be derived in the following way. Using (see Messiah/7/)

$$i_\ell(\rho)=(-\rho)^\ell\left(\frac{d}{\rho\, d\rho}\right)^\ell\frac{\sin\rho}{\rho},\quad n_\ell(\rho)=(-\rho)^\ell\left(\frac{d}{\rho\, d\rho}\right)^\ell(-1)\,\frac{\cos\rho}{\rho} \tag{A2.2}$$

and (P = Cauchy principle value)

$$\cos\kappa r=\frac{1}{\pi}\int dk\,\frac{P}{k^2-\kappa^2}\,k\sin kr \tag{A.2.3}$$

we have

$$n_\ell(\kappa r)=\frac{1}{\pi}\int\frac{dk}{\kappa}\,\frac{P}{k^2-\kappa^2}\,k^2\left(\frac{k}{\kappa}\right)^\ell i_\ell(kr) \tag{A.2.4}$$

and therefore by means of (2.6) and (A1.3)

$$i^\ell n_L(r_1+r_2)=4\pi\sum_{L_1,L_2} D_{LL_1L_2}\, i^{\ell_1+\ell_2}\, Y_{L_1}(\vec{n}_1)\,Y_{L_2}(\vec{n}_2) \tag{A2.5}$$

$$D_{LL_1L_2}=C_{LL_1L_2}\,\frac{1}{\pi}\int\frac{dk}{\kappa}\,\frac{P}{k^2-\kappa^2}\,k^2\left(\frac{k}{\kappa}\right)^\ell i_{\ell_1}(kr_1)\,i_{\ell_2}(kr_2). \tag{A2.6}$$

The integral can be evaluated easily by means of closing the contour in the complex k-plane. To this purpose it is necessary to replace the Bessel functions $i_\ell(kr)$ partially by Hankel functions

$$h^1_\ell(\rho)=(-\rho)^\ell\left(\frac{d}{\rho\, d\rho}\right)^\ell \frac{e^{i\rho}}{i\rho}\,,\quad h^2_\ell(\rho)=(-\rho)^\ell\left(\frac{d}{\rho\, d\rho}\right)^\ell \frac{e^{-i\rho}}{-i\rho}\,. \qquad \text{(A2.7)}$$

Replacing at first $j_{\ell_1}(kr_1)$ and using

$$h^2_\ell(\rho)=(-1)^\ell h^1_\ell(-\rho)\,,\quad (-1)^{\ell+\ell_1+\ell_2}\, C_{LL_1L_2}=C_{LL_1L_2} \qquad \text{(A2.8)}$$

we obtain

$$D_{LL_1L_2}=C_{LL_1L_2}\,\frac{1}{2\pi}\int_{C_1+C_2}\frac{dk}{\kappa}\,\frac{k^2}{k^2-\kappa^2}\left(\frac{k}{\kappa}\right)^\ell h^1_{\ell_1}(kr_1)\, j_{\ell_2}(kr_2) \qquad \text{(A2.9)}$$

with contours C_1 and C_2 in the upper and lower k-plane, respectively, parallel to the real axis. Owing to the asymptotic behaviour $(k\to\infty)$

$$h^1_{\ell_1}(kr_1)\, j_{\ell_2}(kr_2)\approx(-1)^{\ell_2}\; e^{ik(r_1+r_2)}-e^{ik(r_1-r_2)} \qquad \text{(A2.10)}$$

we can close both contours C_1 and C_2 only for $r_1>r_2$ in the upper k-plane. Closing C_1 yields nothing, closing C_2 only the poles at $k=\pm\kappa$ contribute:

$$D_{LL_1L_2}=C_{LL_1L_2}\,\frac{1}{2i}\left[h^1_{\ell_1}(\kappa r_1)-(-1)^{\ell+\ell_2}\, h^1_{\ell_1}(-\kappa r_1)\right] j_{\ell_2}(\kappa r_2) \qquad \text{(A2.11)}$$

With (A2.8) this can be written as

$$D_{LL_1L_2}=C_{LL_1L_2}\, n_{\ell_1}(\kappa r_1)\, j_{\ell_2}(\kappa r_2) \quad \text{for} \quad r_1>r_2\,. \qquad \text{(A2.12)}$$

If we replace $j_{\ell_2}(kr_2)$ in (A2.6) by Hankel functions we obtain similarly

$$D_{LL_1L_2}=C_{LL_1L_2}\, j_{\ell_1}(\kappa r_1)\, n_{\ell_2}(\kappa r_2) \qquad \text{for} \quad r_2>r_1\,. \qquad \text{(A2.13)}$$

Putting (A2.12) and (A2.13) into (A2.5) really (A2.1) turns out, q.e.d.

As an application of (A2.1) we prove (2.18). We discuss the "Neumann part" and the "Bessel part" of the left hand side of (2.18) separately. With $\vec{r}_l = \vec{r}_l + \vec{R}_{ll}$ and $r_l < R_{ll(\neq l)}$ we can write using (A2.1) and (2.9)

$$\sum_{l,L'} a^{l}_{L'\lambda}\, n_{L'}(\vec{r}_l) - \sum_{L} a^{l}_{L\lambda} n_L(\vec{r}_l) = \sum_{l,L'} a^{l}_{L\lambda}(1-\delta_{ll})\, n_{L'}(\vec{r}_l), \qquad \text{(A.2.14)}$$

$$(1-\delta_{ll})\, n_{L'}(\vec{r}_l) = (1-\delta_{ll})\, 4\pi \sum_{L,L''} C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, j_L(\vec{r}_l)\, n_{L''}(\vec{R}_{ll}) = \sum_L j_L(\vec{r}_l) N^{ll}_{LL'}.$$

The "Bessel part" of $\phi(\vec{r})$ can be treated with (A1.3) and (2.9) in the following way (again $\vec{r}_l = \vec{r}_l + \vec{R}_{ll}$)

$$j_{L'}(\vec{r}_l) = 4\pi \sum_{L,L''} C_{LL'L''}\, i^{\ell-\ell'+\ell''}\, j_L(\vec{r}_l)\, j_{L''}(\vec{R}_{ll}) = \sum_L j_L(\vec{r}_l) J^{ll}_{LL'}. \qquad \text{(A2.15)}$$

Essentially the difference between (A2.14) and (A2.15) yields (2.18), q.e.d.

References

1. J.Korringa. Physica, 13, 392 (1947).
2. W.Kohn and N.Rostoker. Phys.Rev., 94, 1111 (1954).
3. J.M.Ziman. Proc.Phys.Soc., 86, 337 (1965) and 91, 701 (1967);
   V.Heine. Phys.Rev., 153, 673 (1967);
   J.Hubbard. Proc.Phys.Soc. , 92, 921 (1967);
   R.L.Jacobs. J.Phys., C1, 492, (1968);
   D.G.Pettifor. J.Phys., C2, 1050 (1969).
4. N.G.Fletscher. Proc. Phys.Soc., 91 , 724 (1967) and 92, 265 (1967);
   T.C. McGill and J. Klima. J.Phys., C3 , L163 (1970).

5. J.M.Ziman. Proc.Phys.Soc., 88, 387 (1966);
P.Lloyd. Proc.Phys.Soc., 90, 207 and 217 (1967);
P.Lloyd and M.V.Berry. Proc.Phys.Soc., 91, 678 (1967).
6. Yu.N.Demkov and V.S.Rudakov. Zh.exp.teor.Fiz., 59, 2035 (1970).
7. A.Messiah. Quantum Mechanics, North-Holl.Publ.Comp., Amsterdam, 1961 , vol. 1, p. 488.

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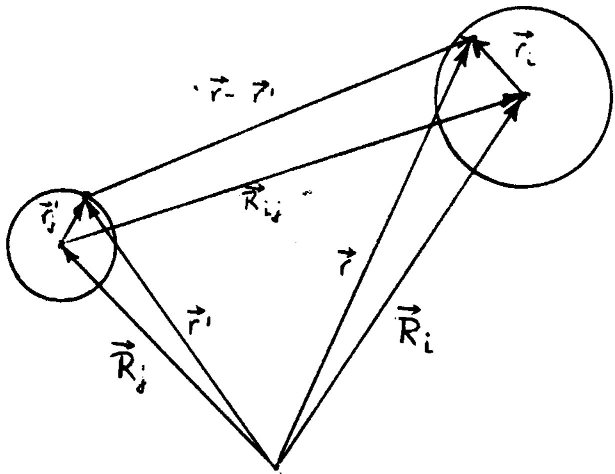

Sites of the *GF*-variables $\vec r, \vec r'$ for $\vec r$ inside the i-th *mt*-sphere.