1. Classification *INPE-COM.4-RPE*
C.D.U. 539.2

2. Period

4. Distribution Criterion
internal [ ]
external [X]

3. Key Words (selected by the author)
BAND THEORY
SEMICONDUCTORES

5. Report Nº
INPE-1763-RPE/152

6. Date
June, 1980

7. Revised by
Ronald Ranvaud

8. Title and Sub-title
SELF - CONSISTENT APW $\vec{k}.\vec{p}$ METHOD - I THEORY

9. Authorized by
Nelson de Jesus Parada
Diretor

10. Sector *DEE* Code

11. Nº of Copies *10*

12. Authorship
I.C.da Cunha Lima
A. Ferreira da Silva
N. J. Parada

13. Signature of the responsible

14. Nº of Pages *17*

15. Price

16. Summary/Notes

A first principle method based on an APW-$\vec{k}.\vec{p}$ band structure calculation is derived in order to obtain the self-consistent eigen-energies, cristalline potential and electronic charge density. The simplicity and extensions of the method are discussed, including comparison with the results obtained by the use of Chadi and Cohen special points technique.

17. Remarks *This paper will be submitted to International Journal of Quantum Chemistry.*

SELF-CONSISTENT APW - $\vec{k}.\vec{p}$ METHOD

I THEORY

I.C. da Cunha Lima, A. Ferreira da Silva and N.J. Parada

Instituto de Pesquisas Espaciais - INPE

Conselho Nacional de Desenvolvimento Científico e Tecnológico- CNPq

12200 São José dos Campos - SP - Brazil

ABSTRACT

A first principle method based on an APW-$\vec{k}.\vec{p}$ band structure calculation is derived in order to obtain the self-consistent eigen-energies, cristalline potential and electronic charge density. The simplicity and extensions of the method are discussed, including comparison with the results obtained by the use of Chadi and Cohen special points technique.

1. INTRODUCTION

The Symmetrized Augmented Plane Wave (SAPW) Method, in which this work is based, was first proposed in its simplest form by Slater [1] and since then developed by several authors [2,3]. Later on, relativistic [4] and "non-muffin-tin" [5] corrections were taken into account.

Once the energy levels and the respective wave functions are obtained for each electronic state, then self-consistency may be established to obtain the charge density inside each one of the p spheres of the "muffin-tin" model [3] :

$$\sigma_p(r) = 2er^2 \int_p d\Omega \left\{ \sum_{\vec{k}} \sum_{n,i} b^{\Gamma\alpha}_{n,i}(\vec{k},\vec{r})^* \, b^{\Gamma\alpha}_{n,i}(\vec{k},\vec{r}) \right\}; \quad (r < R_p) \tag{1}$$

In the above expression, $b^{\Gamma\alpha}_{n,i}(\vec{k},\vec{r})$ is a Bloch function belonging to the n^{th} band and transforming like the i^{th} partner of the Γ_α irreducible representation of the group of the wave vector $\vec{k}$. Summation is extended to occupied states only. Factor 2 comes from the fact that in a non-relativistic formulation, each state is doubly degenerate because of the possibility of being occupied by electrons with spin up and spin down. In Eq. (1), a spherically symmetric distribution of charges inside the spheres of radius R_p is assumed. Also

$$\sigma_p(r) = 4\pi r^2 \rho_p(r)$$

where $\rho_p(r)$ is the charge per unit volume.

In order to make the unitary cell neutral, a constant charge density outside spheres (plane waves) $\bar{\rho}$ is imposed such that

$$\bar{\rho} = -\sum_p Q_p / (\Omega_{ws} - \sum_p V_p) \tag{2}$$

Q_p being the total charge inside the p sphere, that is,

$$Q_p = |e| Z_p - \int_0^{R_p} \sigma_p (r)dr$$

and $V_p=4/3\ \pi R_p^3$; Ω_{ws} is the volume of the Wigner-Seitz cell and Z_p the atomic number of the atom, or ion, inside sphere p.

So, at least formally,self-consistency is established. Once the charge density is known,we can, in principle, derive the crystalline potential and recalculate the band structure.

The utilization of Eq. (1)to establish a self-consistent calculation has a great inconvenient: degeneracies in the states corresponding to a wave $\vec{k}$ decrease with decreasing symmetry of the respective point in the Brillouin zone. For this reason, the contribution of a low symmetry $\vec{k}$ point may require too many diagonalizations of the APW secular matrix. One solution in order to avoid this problem would be to assume that the periodic part of the Bloch function does not depend strongly on wave vector $\vec{k}$. This would correspond using the approximate method proposed by Chadi and Cohen[6] and more recently by Mankhorst and Pack [7]. It consists in the utilization of some special points in the Brillouin zone when performing the summation over occupied states in Eq. (1). Using only the value at these special points, multiplied by some weight factors, the approximation solution is obtained. But the accuracy of that method depends on the material under study. Or, accordingly, the number of special points to be considered depends on the localization of the occupied states.

The method to be described later in this paper tries to overcome these difficulties by proposing the use of a $\vec{k}.\vec{p}$ expansion for the

Bloch states in the Brillouin zone. We assume that the SAPW's are calculated at a point of high symmetry, and that the matrix elements of the momentum operator are also obtained. With them, we can derive an expression for the self-consistent charge density and obtain the crystalline potential. No other approximation is assumed in addition to the "muffin-tin" model, which is however only a simplifying hypothesis, not a restriction imposed by the method. Expressions are derived for $T = 0$, but repopulation of states caused by variation of temperature can also be treated directly by considering the partition function. In this case,electron-phonon interaction and variation of lattice parameter with temperature should also be considered.

In Section 2, we derive the main expressions for the charge density and the crystalline potential, assuming Slater's exchange. In Section 3,we add some comments and discuss possible generalizations of the method.

2. ITERATIVE PROCESS

Let's assume that the one-electron eigenenergies and eigenfunctions are known at a point $\vec{k}_0$ of the first Brillouin zone, preferably the Γ point, $2\pi/a$ (0,0,0). Hence, we are able to construct the complete set of Kohn-Luttinger functions and to use it to expand the Bloch function of a generic wave vector $\vec{k}$.The coefficients of the expansion are determined through the diagonalization of the secular matrix, and if all states at point $\vec{k}_0$ are considered, the expansion is exact. For a non-relativistic calculation, off-diagonal terms contain matrix elements of the operator $(\hbar/m)\vec{k}.\vec{p}$ between Bloch functions at $\vec{k}_0$. The wave vector $\vec{K}$ is the difference $(\vec{k} - \vec{k}_0)$ and $\vec{p}$ is the momentum operator. This process is

called $\vec{k}.\vec{p}$ and was first utilized by Cardona and Pollack [9], using some experimental results and adjusting parameters. Later, Parada [10] showed the feasibility of obtaining matrix elements of momentum operators from first principles, without adjusting parameters. In this paper, we will follow Parada's procedure.

Let's first expand the Bloch functions at $\vec{k}_o$ in terms of the Symmetrized Augmented Plane Waves, set as follows:

$$b^{\Gamma\alpha}_{n,i}(\vec{k}_o,\vec{r}) = \sum_{\ell,\vec{K}_s} C^{\Gamma\alpha}_{n,\ell}(\vec{K}_s)\, \psi^{\Gamma\alpha}_{i,\ell}(\vec{k}_o+\vec{K}_s,\vec{r}) \qquad (3)$$

where $\vec{K}_s$ are reciprocal lattice vectors. The SAPW's are obtained by applying to the APW's the projection operator [11]:

$$\rho^{\Gamma\alpha}_{i,\ell} = \sum_R \Gamma^{\alpha}_{i,\ell}(R)^*\, R \qquad (4)$$

where the summation is extended to all symmetry operations of the group of the wave vector $\vec{k}_o$; $\Gamma^{\alpha}_{i,\ell}(R)$ is the (i,ℓ) element of the matrix corresponding to operation R in the Γ_α irreducible representation.

We construct then the Kohn-Luttinger functions

$$X_{n,i}(\vec{k}-\vec{k}_o;\vec{r}) = \exp\left[\, i\,(\vec{k}-\vec{k}_o)\,.\,\vec{r}\,\right] b^{\Gamma\alpha}_{n,i}\,(\vec{k}_o,\vec{r})$$

and make the ansatz

$$b^{\Gamma\beta}_{n,i}(\vec{k},\vec{r}) = \sum_{m,j} A^{m,j}_{n,i}(\vec{k})\, b^{\Gamma\alpha}_{m,j}(\vec{k}_o,\vec{r}) \qquad (5)$$

Taking into account Eq. (5) in the one-electron Schrödinger equation, we obtain after some calculations the secular determinant

$$\det\left\{ \left[E_m(\vec{k}_o) - E_n(\vec{k}) + \frac{\hbar^2\vec{k}^2}{2m} \right] \delta_{mn}\,\delta_{ij} + \frac{\hbar}{m}\,\vec{k}.\vec{p}^{\,i,j}_{n,m} \right\} = 0 \qquad (6)$$

where

$$\vec{p}^{\,i,j}_{n,m} = \int d^3r\; b^{*}_{n,i}\,(\vec{k}_o,\vec{r})\;(-i\hbar\vec{\nabla})\;b_{m,j}\,(\vec{k}_o,\vec{r})$$

Solution of Eq. (6) gives the energies $E_n(\vec{k})$ and the coefficients $A^{m,j}_{n,i}$. Now, we substitute the ansatz (5) in the expression for the charge density. Defining

$$D^{j,j'}_{m,m'} = \sum_{n,i,\vec{k}} A^{m,j}_{n,i}\;(\vec{k})^{*}\;A^{m',j'}_{n,i}(\vec{k}) \tag{7}$$

and

$$I^{j,j'}_{m,m'}(r) = \int_{p} d\Omega\; b^{\Gamma_\alpha}_{m,j}\,(\vec{k}_o,\vec{r})\;b^{\Gamma_\delta}_{m',j'}(\vec{k}_o,\vec{r}) \tag{8}$$

the charge density can be written as:

$$\sigma_p(r) = 2\,e r^2 \sum_{\substack{m,m'\\ j,j'}} D^{j,j'}_{m,m'}\;I^{j,j'}_{m,m'}\;(r) \tag{9}$$

We can see that the use of the $\vec{k}.\vec{p}$ expansion separates expression (1) in to two parts: one that contains only information about the reciprocal space, and other that depends only on the results obtained at point $\vec{k}_o$. Summation in (7) extends to all occupied states. However, levels (m,j) and (m',j') are both occupied and unoccupied states at $\vec{k}_o$. The same occurs in the angular integral centered in sphere p shown in Eq. (8). This difficulty can be overcome in the following way.

Equation (8) being invariant under rotation of the axis obeys the same property of the scalar product of symmetrized functions:

$$\langle f^{\Gamma_\alpha}_{i\ell} \mid g^{\Gamma_\beta}_{i'\ell'}\rangle = \frac{g}{n_\alpha}\,\delta_{\alpha,\beta}\,\delta_{i,i'}\;\langle f \mid g^{\Gamma_\alpha}_{\ell,\ell'}\rangle$$

where g is the order of the group, n_α is the dimension of the Γ_α irreducible representation and f the unsymmetrized function which gives rise to the symmetrized one $f^{\Gamma_\alpha}_{i,\ell}$ through the projection operator $f^{\Gamma_\alpha}_{i\ell} = \rho^{\Gamma_\alpha}_{i\ell} f$. So, matrix I is non-zero only if Γ_α and Γ_δ are the same representation, and j=j'. In addition,it does not depend on the index of the partner j. We can therefore omit index j and use an extra index α to represent Γ_α when defining I. So, instead of $I^{j,j'}_{m,m'}$ we will use $I^{\alpha}_{m,m'}$. The unsymmetrized functions to be considered in Eq. (8) are the linear combinations of APW's

$$\phi^{APW}_E(\vec{K},\vec{r}) = \exp(i\,\vec{K}.\vec{r}_p) \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} 4\pi i^\ell\, j_\ell(KR_p)\, \frac{u_{p,\ell,E}(r)}{u_{p,\ell,E}(R_p)}\, x$$

$$x\; Y^*_{\ell,m}(\Theta_{\vec{K}},\phi_{\vec{K}})\; Y_{\ell,m}(\Theta,\phi)$$

where $\vec{r}_p$ defines the position of the center of the sphere p, whose radius is R_p and $\Theta_{\vec{K}}$ and $\phi_{\vec{K}}$ are angular coordinates of vector $\vec{K}$. We can make use of the orthonormality of spherical harmonics:

$$\int \sin\Theta\, d\Theta\, d\phi\; Y^*_{\lambda,\mu} Y_{\lambda',\mu'} = \delta_{\lambda,\lambda'}\; \delta_{\mu,\mu'}$$

and of the sum rule:

$$\sum_{\mu} Y^*_{\lambda,\mu}(\Theta,\phi) Y_{\lambda,\mu}(\Theta',\phi') = \frac{(2\lambda+1)}{4\pi}\, P_\lambda(\cos\gamma)$$

where γ is the angle between the directions (Θ,ϕ) and (Θ',ϕ') to arrive to the final expression

$$I^{\alpha}_{m,m'} = \sum_{\vec{K}_S} \sum_{\vec{K}_T} \left\{ \sum_{\ell,t} C^{\Gamma_\alpha}_{m,\ell}(\vec{K}_S)^* C_{m',t}(\vec{K}_T) \sum_{\lambda} \bar{u}_{p,\lambda,m'}\; \bar{u}_{p,\lambda,m'}\; B^{\alpha}_{p} \right\} \qquad (10)$$

$$\bar{u}_{p,\lambda,m} = \frac{u_{p,\lambda,m}(r)}{u_{p,\lambda,m}(R_p)}$$

and

$$B_p^{\alpha} = \frac{g}{n_{\alpha}} \; 4\pi \; (2\lambda + 1) \sum_{R} \left\{ \Gamma^{*}_{\ell,t} \; (R) \exp\left[\; i(R\vec{K}_T - \vec{K}_s) \cdot \vec{r}_p \; \right] \; x \right.$$

$$\left. x \; j_{\lambda}(K_s R_p) j_{\lambda} \; (K_T R_p) \; P_{\lambda} \; (\cos\gamma) \right\} \qquad (11)$$

In the above equations, R means the symmetry operation, $R\vec{K}_T$ is the vector resulting from the operation R applied to $\vec{K}_T$ and now γ is the angle between $\vec{K}_s$ and $R\vec{K}_T$. B_p^{α} depends only on the crystal symmetry and is not altered throughout the iterative process.

An important simplification can also be performed on matrix D. Each coefficient of the Kohn-Luttinger expansion at a point $\vec{k}$ inside a certain fraction 1/g of the Brillouin zone is related to another vector $\vec{k}' = R\vec{k}$ [10] through

$$A_{n,i}^{m,j} \; (\vec{k}') = A_{n,i}^{m,j} \; (R\vec{k}) = \sum_{\ell} \Gamma_{\alpha} \; (R)_{j,\ell} \; A_{n,i}^{m,\ell} \; (\vec{k}) \qquad (12)$$

Eq. (12) is a general relation for any vector $\vec{k}$, but some operations R, besides identity, transform $\vec{k}$ into itself. In order to avoid considering several times the same vector into the summation, we take, for each vector in the fraction 1/g, a weight factor $1/W(\vec{k})$.

If the total number of vectors in that fraction is G, we have

$$G = \sum_{\vec{k}}^{ZB/g} g/W(\vec{k})$$

So, making use of the above arguments and of the fundamental theorem of irreducible representations, we obtain for matrix D

$$D_{m,m'}^{\alpha} = \frac{g}{n_{\alpha}} \cdot \frac{1}{G} \sum_{n,i} \sum_{\vec{k}}^{ZB/g} \left\{ \sum_{\ell} A_{n,i}^{m,\ell} \; (\vec{k})^{*} A_{n,i}^{m',\ell} \; (\vec{k}) / W(\vec{k}) \right\} \qquad (13)$$

which does not depend on partner j and is non-zero only if both m and m' belong to the same representation Γ_α (because of this property, we have omitted index j and used an extra index α to represent the common irreducible representation Γ_α).

Eq. (9) can then be rewritten:

$$\sigma_p(r) = 2er^2 \sum_{\substack{m,m',\alpha \\ (m,m')\in\alpha}} n_\alpha D^\alpha_{m,m'} I^\alpha_{m,m'} \qquad (14)$$

where the summation is extended to all m and m' belonging to the same irreducible representation Γ_α.

The charge density obtained is a real quantity as can be observed by the following properties of the matrices involved:

a) Let's write

$B^\alpha_p = B^\alpha_p(\vec{K}_s,\ell,\vec{K}_T,t,\lambda)$. Interchanging $\vec{K}_s$ and $\vec{K}_T,\ell$ and t in Eq. (11), it is easy to show that:

$$B^\alpha_p\ (\vec{K}_T,t,\vec{K}_s,\ell,\lambda)^* = B^\alpha_p\ (K_s,\ell,\vec{K}_T,t,\lambda)$$

b) As a consequence, we obtain

$$I^\alpha_{m,m'}(r) = I^\alpha_{m',m}\ (r)^*$$

c) Direct observation of matrix D shows that

$$D^\alpha_{m,m'} = D^\alpha_{m',m}{}^*$$

and the following expression is obtained for $\sigma_p\ (r)$:

$$\sigma_p(r)=2er^2 \sum_{\substack{m,m' \\ m\geq m'}} n_\alpha \left\{ 2\mathrm{Re}\left[D^\alpha_{m,m'}\ I^\alpha_{m,m'}\ (r)\right] - \delta_{m,m'}\mathrm{Re}\left[D^\alpha_{m,m'} I^\alpha_{m,m'}(r)\right]\right\} \qquad (15)$$

where Re means real part.

Up to now, we have derived the expression for a self-consistent

charge density based on an APW - $\vec{k}.\vec{p}$ calculation and showed that the expression obtained can be separated into a product of two parts: one - matrix I-that depends only on the results at a point of high symmetry, the center of the Brillouin zone preferably; and the other - matrix D - that can be written as a summation in reciprocal space of coefficients obtained from the expansion of Bloch functions in the Kohn-Luttinger set. These coefficients are obtained by diagonalization of the $\vec{k}.\vec{p}$ secular matrix (Eq. (6)), in a collection of points inside a fraction of the Brillouin zone. When obtaining matrix I, the values of B_p^{α} are calculated only for the first iteration; for the others, including the first, we need only to calculate the radial functions for each energy level and the coefficients of the expansion of the Bloch function into symmetrized augmented plane waves.

Once the charge density is obtained inside each one of the "muffin-tin" spheres, and the unitary cell is maintened neutral by imposing a uniform distribution of charge outside the spheres, we can obtain the crystalline potential. We will assume Slater [12] approximation for the exchange term:

$$V_{exch}(r) = -6 \left[3\sigma_p (r)/32\pi^2 r^2 \right]^{1/3} \quad ; \quad r \leq R_p \tag{16}$$

and

$$V_{exch}^{out} = -6 \left(3 \bar{\rho}/8\pi\right)^{1/2} \quad ; \quad r > R_p \tag{16a}$$

The Coulomb part of the potential inside each sphere can be separated into two contributions: the potential due to charges located inside the sphere, and the potential due to charges lying outside the sphere under consideration. The solution of this problem is, generally

speaking, a complicated one, but as we are only interested in the "muffin-tin" approximation, we will use the spherical symmetric average of the potential inside the spheres. Non-spherical corrections are beyond the scope of this paper. The spherically symmetric contribution from a charge element, located outside the sphere to the potential inside the sphere, is independent of r and equal to its value at the center of the sphere. So, the external charges contribute in the average with a constant term to the potential inside the sphere.

Therefore, we obtain from direct integration of $\sigma_p(r)$, the total Coulomb term of the potential inside sphere p.

$$V_p^{Coul} = \frac{2Z_p}{r} + \frac{2}{r}\int_o^r \sigma_p(t)\,dt + 2\int_r^R \frac{\sigma_p(t)}{t}\,dt + C_p \qquad (17)$$

In the above expression, we have made use of atomic units. C_p contains all the contribution coming from external charges, and is determined by an indirect process, as follows.

Starting with the charge density obtained at the end of each iteration, we can calculate the spatial average of the potential outside the spheres, that will be called V_{out}, and in the limit, the average value on the surface of each spheres, i.e, $V(R_p)$. This can be done by using a procedure similar to that of Slater [13], as shown in Appendix A. Assuming that in the whole plane wave region the potential is uniform and equal to V_{out}, according to the "muffin-tin" model, the difference $V(R_p)-V_{out}$ gives the discontinuity observed when crossing the surface of each sphere. As the Coulomb potential in the plane wave region is assumed to be zero, the value of the constant C_p must be such that the potential on the surface of sphere p is equal to the value of the discontinuity. So,

we have the definition of each C_p:

$$-\frac{2Z_p}{R_p} + \frac{2}{R_p}\int_o^{R_p} \sigma_p(r)\,dr + C_p = V(R_p) - V_{out} \qquad (18)$$

It is a common practice to set the whole potential, not only the Coulomb term outside spheres equal to zero. Then, we have to subtract the Slater exchange, Eq. (16a) obtaining:

$$V_p(r) = -\frac{2Z_p}{r} + \frac{2}{r}\int_o^r \sigma_p(t)dt + 2\int_r^R \frac{\sigma_p(t)}{t}\,dt + C_p + V_{exch}(r) - V_{exch}^{out} \qquad (19)$$

The core states are almost unaffected by the crystalline bonding, so we can leave them unaltered through the iterative process and treat only the valence bands. For each iteration i, the total charge density will be

$$\sigma_p^{(i)}(r) = \sigma_{p,core}(r) + \sigma_{p,valence}^{(i)}(r)$$

Also, in order to guarantee a more uniform convergence through the sucessive iterations, we calculate expression (19) using a charge density which is not that obtained from the preceding iteration, but a certain average calculated with densities previously obtained throughout the process.

3. CONCLUSIONS

The self-consistent method for band structure calculation presented in this article shows immediatly some advantages. First of all, the APW calculation is carried out only once in each iteration, preferably at the center of the Brillouin zone, which is the point of highest symmetry; hence, less diagonalizations of the secular matrix are necessary.

A second advantage is that B_p^{α} depends only on the crystal symmetry

and some parameters, such as the sphere radii, that once determined in the beginning of the first iteration, are kept unaltered. Therefore B_p^α, which is the part of the calculation that involves most of the computational time, is calculated only once throughout the self-consistent process.

Finally, information about points in the Brillouin zone other than $\vec{k}$. is completely absorbed by matrix D, which is calculated, for each iteration, with results coming from the $\vec{k}.\vec{p}$ expansion.

Improvements on this method may follow the same sequence of a non-self-consistent one: corrections to the "muffin-tin" model, spin-orbit interaction and others relativistic corrections. But, another advantage of this method is to easily allow the inclusion of temperature effects on repopulation. As matrix D contains all information about the reciprocal space, the effect of temperature T can be considered by redefining D as:

$$D^{\alpha}_{m,m'}(T)=g\, n_{\alpha}^{-1}\, G^{-1} \sum_{n,i} \sum_{\vec{k}}^{ZB/g} \frac{\sum_{\ell} A^{m,\ell}_{n,i}(\vec{k})^{*}\, A^{m';\ell}_{n,i}(\vec{k})}{W(k)\left\{1+\exp\left[(E_{n,i}(\vec{k})-\mu)/K_B T\right]\right\}} \qquad (20)$$

where μ is the chemical potential and K_B is the Boltzmann constant.

In the paper that follows an application to NaCl and an optimization of the method will be presented, but, we can already present a conclusion, which can be used as a simplifying procedure in similar cases. It was observed that matrix D does not vary considerably with the numbers of point in the fraction ZB/g of the Brillouin zone. So, self-consistency can be started with the special points of Chadi and Cohen [6] , leaving the utilization of the others points for the last iterations, where all contributions will be considered.

REFERENCES

[1] J.C.Slater, Phys.Rev. 51, 846 (1937).

[2] J.C.Slater, Phys.Rev. 92, 603 (1953);M.M. Safrem and J.C.Slater, Phys.Rev. 92, 1126 (1953); L.F.Mattheiss, Phys.Rev. 133A 1399 (1964).

[3] For a review on SAPW see, for example, L.F.Mattheiss, J.H.Wood and A.C.Switendick in "Methods in Computational Physics" Vol.8 Chapt. 4, Academic Press (1968).

[4] L.E.Johnson,J.B.Conklin, Jr. and G.W.Pratt, Jr., Phys.Rev.11 538 (1936); J.B. Conklin, Jr, L.E.Johnson and G.W.Pratt, Jr., Phys.Rev. Lett. 14, 1072 (1965); Phys.Rev. 139, A1333 (1965); Phys.Rev. 143,506 (1956).

[5] W.E. Rudge,Phys.Rev. 181, 1020 (1969); Phys.Rev.181 ,1024 (1969); E.O. Kane, Phys.Rev. 4B,1917 (1917).

[6] D.J. Chadi and M.L. Cohen, Phys.Rev.B8, 5747 (1973).

[7] H.J.Mankhorst and J.D. Pack,Phys.Rev.B13, 5188 (1976).

[8] J.M.Luttinger and Kohn,Phys.Rev.97, 869 (1955).

[9] M.Cardona and F.H. Pollack, Phys.Rev. 142, 530 (1966).

[10] N.J.Parada, Phys.Rev.B3, 2042 (1971).

[11] J.F.Cornwell, Group Theory and Electronic Energy Bands in Solids, North Holland Publ. (1969).

[12] J.C. Slater, Phys.Rev. 81, 385 (1951)

[13] J.C. Slater, Quantum Theory of Molecules and Solids, McGraw Hill Vol.1,Appendix 12 (1963).

APPENDIX A

CALCULATION OF V^{out} AND V(Rp)

The Ewald's method is well known and its presentation in an interesting analytic way was done by Slater [13] . Since we have used Slater's scheme in a special way to calculate the expressions $V(R_p)$ and V^{out},we present our results in this Appendix.

First of all,we substitute our "real" charge distribution,consisting of spheres of radius R_p containing a charge density $\sigma_p(r)$ surrounded by a uniform sea of charge with density $\bar{\rho}$,by a new distribution, which will consist of points charges q_p at the points where before the spheres were centered, with values

$$q_p = |e|Z_p + \int_o^{R_p} \sigma_p(r)\ dr - \frac{4\pi}{3}\bar{\rho}\ R_p^3 \qquad (A.1)$$

They will be surrounded by a uniform charge density in order to make the unitary cell neutral. Potentials for points outside the APW spheres will not be disturbed by such redistribution.

Let's assume that we have a NaCl structure. We can separate the fcc structure of anion sites from that of the cations sites and treat them separately.

The Coulomb potential per unit charge due to each substructure can be separated into two contributions

$$\Phi_1(r) = \frac{1}{r} + \frac{8}{3a^3} r^2 + \text{const.} \qquad (A.2a)$$

and

$$\phi_2(r) = \frac{1}{a}\left\{A_4\frac{r^4}{a^6}(\ell^4+m^4+n^4-\frac{3}{5})+A_6\frac{r^6}{a^6}\left[\ell^6+m^6+n^6-\right.\right.$$

$$\left.\left.-\frac{15}{11}(\ell^4+m^4+n^4)+\frac{30}{77}\right]+\ldots\right\} \qquad (A.2b)$$

where $\ell = \frac{x}{r}$, $m = \frac{y}{r}$, $n = \frac{z}{r}$ and a is the lattice parameter. The total potential is $\phi_1 + \phi_2$. Adjusting the parameters in order to fit Ewald's results, we obtain for an fcc structure

$$\phi_1 = \frac{1}{r} + \frac{8\pi}{3a^3}r^2 - \frac{4.58480}{a} \qquad (A.3)$$

and

$A_4 = -18.687$; $A_6 = -1002.05$

The average potential ontside the spheres, V^{out}, is obtained by adding the contributions of the two sublattices.

As the crystalline potential varies weakly in the vicinity of the boundaries of the Wigner Seitz cell, we can substitute this cell by a sphere with radius R and equal volume in order to perform spherical integrations. Let's center our attention on, say, the Cl sublattice. We have to calculate the integral of ϕ_1 inside sphere of radius R, the integral of ϕ_1 inside the sphere of radius R_{Cl} and the integral of ($\phi_1 + \phi_2$) inside the sphere of radius R_{Na} centered at (0,0,a/2). Let's call them I_1, I_2 and I_3 respectively. Since ϕ_2 gives no contribution to the spherical integral around the site of the Cl atom, we conclude that the contribution of Cl to the average potential in the plane wave region is

$$V_{Cl}^{out} = \frac{q_{Cl}}{\Omega_{out}}\left[I_1 - I_2 - I_3\right] \qquad (A.4)$$

where

$$\Omega_{out} = \frac{4\pi}{3} (R^3 - R_{Cl}^3 - R_{Na}^3)$$

The first two integrals are trivial to calculate. The difficulty which arises in the calculation of I_3 can be avoided by fitting Ewald's results with new functions ϕ_1' and ϕ_2' centered at (0,0,a/2), a point with the same symmetry of (0,0,0). In the vicinity of this new origin, aside from the divergence due to the ion Cl, we obtain

$$\phi_1' = \frac{8\pi}{3a^3} r^2 - \frac{1.089730}{a} \qquad (A.5)$$

Again, ϕ_2' gives no contribution to I_3 and we need only calculate the integral of ϕ_1'. The contribution of the Cl sublattice is, then:

$$V_{Cl}^{out} = - q_{Cl} \frac{4\pi}{3\Omega_{out}} \left[\frac{3}{2} (R^2 - R_{Cl}^2) + \frac{8}{5a^3} (R^5 - R_{Cl} - R_{Na}^5) - \right.$$

$$\left. - \frac{4.584850}{a} (R^3 - R_{Cl}^3) + \frac{1.089730}{a} R_{Na}^3 \right] \qquad (A.6)$$

A similar contribution is obtained for the second sublattice interchanging indices Cl and Na.

In order to calculate the average values of the potentials on the surfaces of the "muffin-tin" spheres, we have to consider that each ion contributes to the average on the surface of its own sphere and also to the sphere of the other kind. Once again, let's consider first the Cl sublattice and take one of the q_{Cl} as origin. The contribution of this sublattice to the average potential on the surface of the Cl sphere, using Eq. (A.3), is

$$V_{Cl}(R_{Cl}) = q_{Cl} \left(\frac{1}{R_{Cl}} + \frac{8\pi}{3a^3} R_{Cl}^2 - \frac{4.584850}{a} \right) \qquad (A.7)$$

We can use Eq. (A.5) to obtain the contribution of the Cl sublattice to the sphere centered on q_{Na}

$$V_{Cl}(R_{Na}) = -q_{Cl} \left(\frac{8\pi}{3a^3} R_{Na}^2 - \frac{1.089730}{a} \right) \qquad (A.8)$$

Conversely, we can establish the contribution of the second sublattice to $V(R_{Cl})$

$$V_{Na}(R_{Cl}) = q_{Na} \left(\frac{8\pi}{3a^3} R_{Cl}^2 - \frac{1.089730}{a} \right) \qquad (A.9)$$

Finally,

$$V(R_{Cl}) = V_{Cl}(R_{Cl}) + V_{Na}(R_{Cl})$$

with similar equation for $V(R_{Na})$.

Although we have used this method specifically for the NaCl structure, it can be applied to all structures composed by superposition of fcc sublattices. The parameters appearing in the Eqs. (A.2a) and (A.4), for each case, appear in the table presented by Slater [13].