

Self-Consistent Field Variational Cellular Method as Applied to the Band Structure Calculation of Sodium

A.T. LINO, E.K. TAKAHASHI

Universidade Federal de Uberlândia, Caixa Postal 593, Uberlândia, 38400, MG, Brasil

and

JR. LEITE, AC. FERRAZ

Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, São Paulo, 01498, SP, Brasil

Recebido em 6 de maio de 1987; versão revista em 11 de setembro de 1987

Abstract The band structure of metallic sodium is calculated, using for the first time the self-consistent field variational cellular method. In order to implement the self-consistency in the variational cellular theory, the crystal electronic charge density was calculated within the muffin-tin approximation. The comparison between our results and those derived from other calculations leads to the conclusion that the proposed self-consistent version of the variational cellular method is fast and accurate.

1. INTRODUCTION

The cellular *method* of Wigner-Seitz-Slater^{1,2}, ever since it was proposed in 1933, has been recognized by many workers in band structure theory of solids as one that holds the more predominant features of a first principle method, chiefly due to its very simple and quite intuitive formulation and by the use of a non muffin-tin potential. The main difficulties of the method were the convergence of the eigenvalues and the excessive computational efforts in the solution of a great secular equation³⁻⁷. These difficulties led the cellular method to be abandoned during several decades. The great number of points per face required for the surface integration at each cell did not permit competition with other methods. These drawbacks, in their major part, were eliminated after the variational formulation of the cellular method by Ferreira and Leite^{8,9}. In this new version, the convergence of the eigenvalues was obtained with a rather small number of basis functions and the eigenvalues were, to first order, insensitive with respect to the errors in the surface integration

Self-consistent calculations for diatomic molecules were accomplished with enough success using the Variational Cellular Method (VCM) by Ferreira and Leite⁹, Brescansin *et al*¹⁰, and Leite *et al*¹¹. The method was shortly thereafter extended for poliatomic molecules by Ferreira and De Siqueira¹² and its more recent applications were accomplished by Kinoshita *et al*^{13a} in calculations for the SF₆ molecule, and by Ferreira and De Siqueira^{13b} who made a successful use of the method to calculate the electronic structure of defects in solids within the framework of the molecular cluster model. The applications for crystal were performed by Ferraz *et al*¹⁴ for sodium and lithium, in a first test of the VCM applied to crystalline structures with one atom per unit cell. The generalization to crystalline structures with an arbitrary number of atoms per unit cell was accomplished, for diamond and silicon (four atoms per unit cell) by Ferraz *et al*¹⁵.

In this work we develop the self-consistent version of the VCM (SCVCM) as applied to crystals with one atom per unit cell. The use of Group Theory at points of high symmetry of the Brillouin zone and the application of the *mean value point theory* of Baldereschi¹⁶ and Chadi-Cohen¹⁷ lead to a rapid convergence using a relatively small number of points \vec{k} in the Brillouin zone.

In order to apply the self-consistent theory developed here, we have calculated the electronic states of metallic sodium (BCC structure). The band structure of sodium has been calculated by several authors, using almost all theoretical techniques available for the investigation of electronic states in solids. On the other hand, the fact that it has a very simple crystal structure, with a single atom per unit cell, makes it a suitable test for the first application of the SCVCM.

2. THE SELF-CONSISTENCY PROCESS

Accordingly to the original idea of the self-consistent central field of Hartree-Fock¹⁸, each electron of the atom is subjected to the action of a spherically symmetric potential composed by three main terms:

(a) An attractive potential $V_N(r) = -Ze^2/r$ due to the nucleus of charge Ze , e being the charge of the electron at distance r from the nucleus.

(b) A repulsive potential $V_e(r)$ generated by the electronic cloud, obtained by solving Poisson's equation

$$\nabla^2 V_e(r) = -4\pi e^2 \rho(r) , \quad (1)$$

where $\rho(r)$ is the spherically symmetric electronic density

$$\rho(r) = \sum_{\nu\ell} \left[\frac{1}{r} p_{\nu\ell}^2(r) \right]^2 \frac{w_{\nu\ell}}{4\pi} . \quad (2)$$

$p_{\nu\ell}(r)$ is the solution of the radial Schrödinger equation

$$\left[-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + V(r) \right] p_{\nu\ell}(r) = \epsilon_{\nu} p_{\nu\ell}(r) \quad (3)$$

and $w_{\nu\ell}$ is the occupation of the $(\nu\ell)$ orbital.

(c) An attractive potential $V_X(\vec{r}_i, -\vec{r}_j)$, non local, called exchange potential, which depends on the relative positions of electrons i, j . In the Slater approximation¹⁹, this potential is made local with the value

$$V_X(r) = -6\alpha \left(\frac{3}{8\pi} \rho(r) \right)^{1/3} , \quad (4)$$

where the parameter usually assumes values between 2/3 and 1.

Thus, once term (a) is well known, the potential can be found if the electronic charge density is given. Once we know the potential $V(r)$, eq. (3) can be solved and a new electronic charge density can be determined, which leads to another potential. The accepted solution of the many body problem, within the framework of the one particle model, is the one that is obtained self-consistently by an iterative process. We begin with a trial potential $V_1(r)$, preferably closer to that one we believe to be the true potential. In a crystal, the first trial is made, in general, by taking the superposition of atomic potentials and performing the spherical average, since we need a potential with spherical symmetry. Eq. (3) is solved and the density $\rho(r)$ arises as well as the potential, $v_2(r)$. In order to generate the potential for the next iteration we perform a suitable mixing between $V_1(r)$ and $V_2(r)$. Usually we

adopt $V_3(r) = \beta_1 V_1(r) + \beta_2 V_2(r)$, with $\beta_1 + \beta_2 = 1$. The potential $V_3(r)$ is then injected in eq. (3), repeating the process, until the input and output potentials differ only by a suitable criterion.

Since we are dealing with metallic sodium, the wave functions must represent the electronic states of a crystal. Therefore they are limited to a special class, subjected to conditions established by Bloch's theorem and continuity requirements. The boundary conditions imposed depend on the adopted model. Wigner-Seitz^{1,2} cellular model is the one used in this work and the conditions imposed on the wave functions are extracted from a variational principle. We start from the functional of Schlösser and Marcus²⁰, adapted by Ferreira and Leite^{8,9} and Ferraz *et al*^{14,15}

3. SELFCONSISTENT VARIATIONAL CELLULAR METHOD

We will briefly show here the general ideas present in detail in the work of Ferreira and Leite⁹, who developed the secular equation which leads to the energy eigenvalues in the cellular method. The authors have formulated the theory to be applied to molecules. The adaptation for crystals is presented here.

3.1 - The secular equations

According to the original idea of the cellular method, one starts by decomposing the molecular or crystal space into cells with arbitrary but suitable form. The potential within each cell is assumed spherically symmetric. The conditions of continuity for the wave functions and their first derivative are imposed at the boundary of the cells. Since the potential has spherical symmetry, the wave functions for each level ϵ_v , in each cell i , can be expanded in spherical harmonics (omitting the index v)

$$\Psi_i(\vec{r}) = \sum_{\lambda} A_{i\lambda} f_{i\lambda}(\vec{r}), \quad (5)$$

where

$$f_{i\lambda}(\vec{r}) = R_{\lambda}(r_i) Y_{\lambda}(\hat{r}_i). \quad (6)$$

l corresponds to the pair (l, m) specifying the angular momentum and $R_R = p_R/r$ is obtained from eq. (3) for each energy level ϵ_v . $A_{i\lambda}$ are coefficients to be determined by a variational method.

The variational version of the cellular method proposed by Ferreira and Leite^{8, 9} uses the following functional of the energy

$$F = \sum_{S_{ij}} \int dS \left[(\psi_i - \psi_j) (\partial_n \psi_j^* - \partial_n \psi_i^*) + (\psi_i^* + \psi_j^*) (\partial_n \psi_j + \partial_n \psi_i) \right]. \quad (7)$$

The integrals are performed at the surfaces S_{ij} separating the cells i and j . $\partial_n \psi_i$ is the normal derivative outward from the cell i . By varying the coefficients $A_{i\lambda}$ and imposing the condition that F is stationary ($\delta F=0$) one arrives at the secular equation

$$\sum_{j\lambda'} \langle i\lambda | H | j\lambda' \rangle A_{j\lambda'} = 0, \quad (8)$$

where the matrix elements of H are

$$\langle i\lambda | H | j\lambda' \rangle = (1 - \delta_{ij}) \int dS_{ij} (f_{i\lambda}^* \partial_n f_{j\lambda'} + \partial_n f_{i\lambda}^* f_{j\lambda'}) . \quad (9)$$

In dealing with crystals, the calculations can be reduced to a single unit cell using the Bloch conditions

$$\psi_i(\vec{r}') = e^{i\vec{k} \cdot \vec{R}} \psi_j(\vec{r}), \quad (10a)$$

$$\partial_n \psi_i(\vec{r}') = e^{i\vec{k} \cdot \vec{R}} \partial_n \psi_j(\vec{r}), \quad (10b)$$

with $\vec{r}' = \vec{r} + \vec{R}$, \vec{R} being a translation vector of the lattice. In a crystal with one atom per cell, the secular equation reduces to

$$\sum_{\lambda'} \langle \lambda | \bar{H} | \lambda' \rangle A_{\lambda'} = 0, \quad (11)$$

with

$$\langle \lambda | \bar{H} | \lambda' \rangle = \sum e^{i\vec{k} \cdot \vec{R}} \int dS (f_{\lambda}^*(\vec{r}') \partial_n f_{\lambda'}(\vec{r}) + \partial_n f_{\lambda}^*(\vec{r}') f_{\lambda'}(\vec{r})) . \quad (12)$$

Since the functions $f_{i\lambda}$ are parametrized in terms of the energy ϵ_V , the determinant of the \bar{H} matrix depends on ϵ_V . The eigenvalues can be found varying ϵ_V until the determinant of \bar{H} vanishes. In practice we work with the inverse of the trace of the inverse matrix (ITIM). ITIM goes to zero when the determinant of the matrix goes to zero. One can show that the physical solutions are acceptable only when the first derivative with respect to the energy is negative⁹.

3.2 - Electronic density

For the calculation of the electronic density $\rho_i(r)$ in a general cell i , for each energy level ϵ_V , we use the expression derived by Ferreira and Leite

$$4\pi r^2 \rho_i(r) = - \sum_{\lambda} p_{i\lambda}^2(r) C_{i\lambda} \quad , \quad (13)$$

with

$$C_{i\lambda} = \frac{\sum_{j'\lambda'} \sum_{j''\lambda''} \langle j'\lambda' | Q | j''\lambda'' \rangle \langle j''\lambda'' | H^{-1} | j'\lambda' \rangle}{\sum_{j'\lambda'} \sum_{j''\lambda''} \frac{\partial}{\partial \epsilon} \langle j'\lambda' | H | j''\lambda'' \rangle \langle j''\lambda'' | H^{-1} | j'\lambda' \rangle} \quad . \quad (14)$$

The functions $p_{i\lambda}(r)$ are normalized so that $p_{i\lambda}(R) = 1$, R being the radius of the inscribed sphere in the cell. In expression (14) the Q matrix has elements

$$\begin{aligned} \langle j'\lambda' | Q | j''\lambda'' \rangle = & (1 - \delta_{j'\lambda', j''\lambda''}) \int dS_{j', j''} \left[(g_{j'\lambda'}^* \partial_n f_{j''\lambda''} + \partial_n g_{j'\lambda'}^* f_{j''\lambda''}) \delta_{i_j'} \delta_{\ell\ell''} \right. \\ & \left. + (f_{j'\lambda'}^* \partial_n g_{j''\lambda''} + \partial_n f_{j'\lambda'}^* g_{j''\lambda''}) \delta_{i_j''} \delta_{\ell\ell''} \right] \quad , \quad (15) \end{aligned}$$

where

$$g_{j\lambda} = q_{j\lambda}(\vec{r}) Y_{\lambda}(\hat{r}) \quad . \quad (16)$$

The functions $q_{j\lambda}(r)$ correspond to a second linearly independent solution of the radial Schrödinger equation, for which the following boundary conditions are imposed:

$$q_{j\ell}(R) = 0 \quad , \quad \left. \frac{dq_{j\ell}(x)}{dx} \right|_{x=R} = 1 \quad .$$

As we can see from eq. (15), the Q matrix has similar structure to the H matrix and can be obtained from this, replacing the functions $p_{i\ell}(x)$ by $q_{i\ell}(x)$ and equating to zero the elements of H that not contain $p_{i\ell}(x)$.

The adaptation of expressions (13) and (14) to the calculation of the electronic charge in crystals containing one atom per unit cell is rather simple. Since the cells are identical, one needs only to know the charge density in a general cell i . H is then replaced by \bar{H} and the matrix \bar{Q} is derived from \bar{H} by using the same procedure that was used to derive Q from H. The summation in the numerator of eq. (14) reduces to two terms and the denominator contains N identical terms, N being the number of cells in the crystal. Each one of the functions $p_{i\ell}(r)$ or $q_{i\ell}(x)$ depends on the wave vector \vec{k} . Suppressing the index i , the expression (13) becomes

$$4\pi r^2(x, \vec{k}) = -\frac{2}{N} \sum_{\vec{k}} p_{\ell}^2(x, \vec{k}) c_{\ell}(\vec{k}) + \text{c.c.} \quad , \quad (18)$$

with

$$c_{\ell}(\vec{k}) = \frac{\sum_{\lambda} \sum_{\lambda'} \langle \lambda | \bar{Q} | \lambda' \rangle \langle \lambda' | \bar{H}^{-1} | \lambda \rangle}{\sum_{\lambda'} \sum_{\lambda''} \frac{\partial}{\partial \epsilon} \langle \lambda' | \bar{H} | \lambda'' \rangle \langle \lambda'' | \bar{H}^{-1} | \lambda' \rangle} \quad . \quad (19)$$

c.c. is the conjugate complex of the expression. In expression (19), the element $\langle \lambda | \bar{Q} | \lambda' \rangle$ has the form

$$\langle \lambda | \bar{Q} | \lambda' \rangle = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \int dS (g_{\lambda}^*(\vec{r}') \partial_{\vec{r}} f_{\lambda'}(\vec{r}) + \partial_{\vec{r}} g_{\lambda}^*(\vec{r}') f_{\lambda'}(\vec{r})) \quad . \quad (20)$$

The factor 2 appearing in expression (18) for each state \vec{k} takes into account the spins degeneracy. The total charge density is obtained by summing over \vec{k} and over the occupied levels

$$4\pi r^{\text{tot}}(x) = -\frac{2}{N} \sum_{\nu \ell \vec{k}} p_{\ell}^2(x, \vec{k}) d_{\nu}(\vec{k}) c_{\ell}(\vec{k}) \quad (21)$$

$d_{\nu}(\vec{k})$ is the degeneracy of the level.

3.3 - Mean value points in the Brillouin zone

The electronic charge density calculated by some authors^{22, 23} in self-consistent band calculations is obtained through the contribution of a great number of vectors \vec{k} in the Brillouin zone. This is the way suggested by expression (21). The accuracy of the calculations increases with the increase of the number N of vectors \vec{k} taken into account. The computational efforts, in this way become very demanding. So we have made an option for a simplification due to Baldereschi¹⁶ and Chadi-Cohen¹⁷. The mean value point of Baldereschi is representative of all the vectors of the Brillouin zone. The charge density can be obtained with a reasonable approximation if it is calculated only for this value of \vec{k} . The approximation is improved if several representative points are considered. In this work, we use the approximation due to Chadi-Cohen, which considers more than one point. Formally, consider $\vec{k}_1, \vec{k}_2, \vec{k}_3, \dots, \vec{k}_s$, the vectors that represent $N_1, N_2, N_3, \dots, N_s$ vectors of the Brillouin zone with $N_1 + N_2 + N_3 + \dots + N_s = N$. Accordingly, we have

$$\rho^{\text{tot}}(r) = \sum_{n\nu} N_n \rho(r, \vec{k}_n) d_\nu(\vec{k}_n) \quad (22)$$

where $n = 1, 2, 3, \dots, s$ and ν runs over the occupied levels. Defining

$$\alpha_n = \frac{N_n}{N}$$

and using eq.(18) in eq.(22), we obtain

$$4\pi r^2 \rho^{\text{tot}}(r) = -2 \sum_{n\nu\ell} \alpha_n p_\ell^2(r, \vec{k}_n) d_\nu(\vec{k}_n) c_\ell(\vec{k}_n) . \quad (23)$$

For each type of lattice, the weights are determined theoretically.

We have applied expression (23) only for valence and conduction states. The total charge density was obtained by adding this result to the electronic charge density corresponding to the low-lying core states (ρ^{core}). ρ^{core} remains unaltered during the self-consistency process.

3.4 - The Wigner-Seitz polyhedron and the interstitial electronic density

For a BCC structure like that of sodium, the suitable choice for

the cell is the Wigner-Seitz polyhedron shown in figure 1. It is composed by six squares and eight hexagonal faces. Expression (23) was used to calculate the electronic density only for points $\mathbf{r} < R$, R being the radius of the inscribed sphere in the polyhedron. To preserve the spherical symmetric character of the electronic charge density, it was taken as a constant for points \mathbf{r} greater than R and smaller than R_E the radius of a sphere with the same volume as the polyhedron. In this interstitial region $\rho^{\text{tot}}(\mathbf{r}) = \rho_0$ reads

$$\rho_0 = \frac{Z - 4\pi \int_0^R \rho^{\text{tot}}(r) r^2 dr}{\Omega^{\text{int}}}$$

where Ω^{int} is the volume of the interstitial region and Z is the atomic number. The Coulomb potential for each new iteration was obtained by the solution of Poisson's eq. (1) and the total potential was given by adding the nuclear potential, the Coulomb potential and the exchange term

$$V(\mathbf{r}) = V_N(\mathbf{r}) + V_e(\mathbf{r}) + V_x(\mathbf{r}) .$$

In this work we use for the exchange term, the local approximation of Kohn-Sham²¹ ($\alpha = 2/3$ in expression (3)).

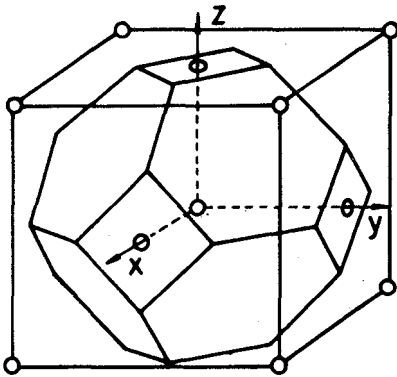


Fig.1 - The Wigner-Seitz cell for metallic sodium.

4. THE FERMI LEVEL

The Fermi level corresponds to the energy of the electron of highest energy in the ground state at the temperature $T = 0^0\text{K}$. For alkali metals like sodium, we can associate to each state \vec{k} the corresponding energy that increases with the increase of \vec{k} . In this way, if we span the Brillouin zone with a certain number of points \vec{k} , the Fermi level will be estimated if we calculate the energy of all states and dispose the energies in increasing order. The Fermi level is equal to that energy for which the fraction of the number of points \vec{k} taken into account is equal to the occupation of the band. The number of points \vec{k} considered must be large enough in order to assure good precision.

Let us assume a scheme by which we realize a partition of the Brillouin zone for a BCC lattice. The unit cell is a cube of edge $4\pi/a$, a being the lattice parameter. We divide each edge into an integer number n_0 with origin at the center of the cube. Each point of the mesh has coordinates $\frac{4\pi}{an_0} (m, n, p)$, with $m, n, p = 0, \pm 1, \pm 2, \pm 3, \dots, \pm n_0/2$. We must discard points that differ mutually by a translation vector of the reciprocal lattice. In this way, points of the form $4\pi/an_0 (n_0/4, n_0/4, n_0/4)$ and $4\pi/an_0 (-n_0/4, -n_0/4, n_0/4, n_0/4)$ are equivalent because they differ by $2\pi/a (1, 1, 0)$. We conclude that the number of points in the cube is n_0^3 . The Brillouin zone has a volume equal to one quarter of the reciprocal unit cell. So the number of points is $N_0 = n_0^3/4$. Taking $n_0 = 16$, we have $N_0 = 1024$ points. Points related by a symmetry operation of the punctual group have the same energy. For a certain vector \vec{k} , the application of all operations generates its star, from which it is enough to calculate the energy for a representative vector. So $\frac{4\pi}{16a} (0, 1, 0)$ is the representative vector of $\frac{4\pi}{16a} [(0, \bar{1}, 0), (1, 0, 0), (\bar{1}, 0, 0), (0, 0, 1), (0, 0, \bar{1})]$, since all belong to the same star. Table 1 shows the representative points for $n_0 = 16$, in units of $4\pi/16a$. n_e is the number of elements in each star.

5. RESULTS FOR SODIUM

The sodium lattice parameter is $a = 4.22508 \text{ \AA}$. The matrix elements were obtained by considering the value of the angular momentum

Table 1 - Coordinates of \vec{k} vectors in units of $\pi/4a$, representative of 1024 vectors that span the Brillouin zone. n_e is the number of components of each star.

\vec{k}	n_e	\vec{k}	n_e	\vec{k}	n_e	\vec{k}	n_e
(0,0,0)	1	(0,1,6)	24	(1,2,4)	48	(2,2,3)	24
(0,0,1)	6	(0,1,7)	12	(1,2,5)	48	(2,2,4)	24
(0,0,2)	6	(0,2,2)	12	(1,2,6)	24	(2,2,5)	24
(0,0,3)	6	(0,2,3)	24	(0,2,5)	24	(2,2,6)	8
(0,0,4)	6	(0,2,4)	24	(0,2,6)	12	(2,3,3)	24
(0,0,5)	6	(0,3,3)	12	(0,3,5)	12	(2,3,4)	48
(0,0,6)	6	(0,3,4)	24	(1,1,5)	24	(2,3,5)	24
(0,0,7)	6	(0,4,4)	6	(1,1,6)	24	(2,4,4)	12
(0,0,8)	1	(1,1,1)	8	(1,1,7)	8	(3,3,3)	8
(0,1,1)	12	(1,1,2)	24	(1,3,3)	24	(3,3,4)	24
(0,1,2)	24	(1,1,3)	24	(1,3,4)	48	(3,3,5)	8
(0,1,3)	24	(1,1,4)	24	(1,3,5)	24	(3,4,4)	12
(0,1,4)	24	(1,2,2)	24	(1,4,4)	12	(4,4,4)	2
(0,1,5)	24	(1,2,3)	48	(2,2,2)	8		

$$\sum n_e = 1024$$

up to $\ell_{\max} = 4$ in expression (5) and the surface integrations were performed by using 7 points per face*** The starting potential, constructed as the spherical average of the superposition of atomic potentials, as well as the core density, were furnished as input data for r values in the mesh defined by Herman-Skillman²⁵. All calculations were performed in this mesh of points. For metallic elements, the valence band is not completely filled and the use of the mean value point theory for the calculation of the charge density is not very useful¹⁷. Nevertheless, for sodium we can use the fact that the functions contributing to the valence band are 3s-like functions and so they differ little from plane waves. In this way, the charge density can be considered nearly constant. The mean value of the charge density can be taken only in the occupied

Table 2 - Two-point and eight-point scheme of Chadi-Cohen for a BCC structure. Weights α_n and energy for each \vec{k} .

	\vec{k} (units of $2\pi/a$)	α_n	energy (Ry)
two-point scheme	(1/4, 1/4, 1/4)	0.5	-0.2118
	(3/4, 1/4, 1/4)	0.5	0.0602
eight-point scheme	(1/8, 1/8, 1/8)	0.0625	-0.3000
	(3/8, 1/8, 1/8)	0.1875	-0.2217
	(3/8, 3/8, 1/8)	0.0625	-0.1448
	(3/8, 3/8, 3/8)	0.1875	-0.0707
	(5/8, 1/8, 1/8)	0.1875	-0.0711
	(5/8, 3/8, 1/8)	0.1875	0.0232
	(5/8, 3/8, 3/8)	0.0625	0.0583
	(7/8, 1/8, 1/8)	0.0625	0.1252

Table 3 - Comparison between self-consistent potentials for some points of the mesh, obtained with the two and eight-point scheme.

	Two-point scheme	Eight-point scheme
$r(a_0)$	$V(r)$ (Ry)	$V(r)$ (Ry)
0.102	-168.208	-168.200
0.406	- 22.898	- 22.889
0.900	- 4.709	- 4.701
1.300	- 2.110	- 2.100
1.712	- 1.123	- 1.116
2.125	- 0.681	- 0.679
2.508	- 0.492	- 0.491
2.890	- 0.400	- 0.398
3.145	- 0.366	- 0.362
3.400	- 0.345	- 0.341

fraction of the band. For sodium, this fraction is one half. In using expression (23) to calculate the charge density, we have considered separately two points and eight points of Chadi-Cohen. Table 2 shows the \vec{k} vectors used with the corresponding weights and eigenvalues. Table 3 shows values of the self-consistent potentials for some points of the mesh, using the two-point and eight-point schemes. The maximum percentual deviation between the potentials obtained is 0.5%. This leads us to conclude that the use of the *mean value point theory* is a good approach.

For the charge q^{sph} within the inscribed sphere we have obtained

$$q^{\text{sph}} = 4\pi \int_0^R \rho^{\text{tot}}(r) r^2 dr = 10.6070 ,$$

where the radius of the inscribed sphere is $R = 3.4583 a_0$. The volume of the interstitial region is

$$\Omega^{\text{int}} = \frac{a^3}{2} - \frac{4\pi}{3} R^3 = 81.4694 a_0^3$$

So, the charge density, assumed constant in the interstitial region resulted

$$\rho_0 = \frac{11 - q^{\text{sph}}}{\Omega^{\text{int}}} = 4.8239 \times 10^{-3} a_0$$

Figure 2 shows the variation of the total charge density with the distance to the center of the polyhedrum. We can verify that the value for ρ_0 is almost the same as the one which converges the charge density $\rho^{\text{tot}}(r)$.

Table 4 shows some self-consistent energy levels in good agreement with results obtained by other methods. The energy levels shown correspond to points of high symmetry in the Brillouin zone:

$$\Gamma \equiv \frac{2\pi}{a} (0,0,0) ; H \equiv \frac{2\pi}{a} (0,1,0) ; P \equiv \frac{2\pi}{a} (1/2,1/2,1/2).$$

We note that according to the present work, the level Γ_{12} is placed below Γ_{2s} , a result which is notably different from the nonself consistent Variational Cellular Method (VCM). We do not have an ex-

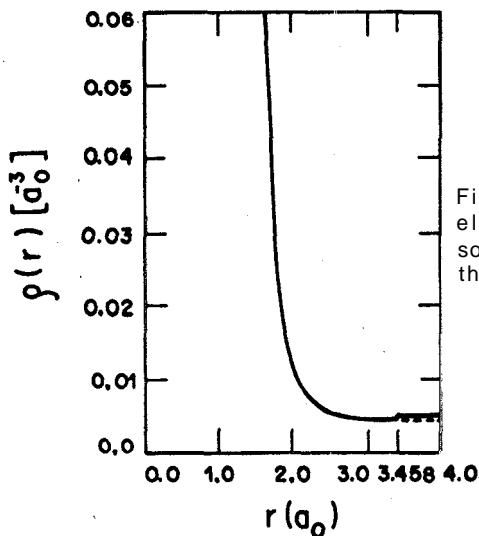


Fig.2 - Variation of the total electronic charge density of sodium with the distance to the center of the polyhedrum.

Table 4 - Comparison between the energy levels (eV) for sodium calculated in the present work with those obtained by other methods.

Method Level	SCVOM	VOM	LCAO	APW	QDM	KKRZ	OPW
Γ_1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$\Gamma_{25'}$	15.246	15.300	14.198	14.851	13.981	14.593	15.150
Γ_{12}	15.014	17.735	16.429	15.749	15.150	15.436	15.694
Γ_{15}	16.524	16.660	16.674	16.565	15.191	15.477	17.245
P_4	5.754	5.807	6.038	5.930	5.943	5.780	5.875
P_1	7.602	7.099	7.086	7.466	6.909	6.786	7.915
H_{12}	7.358	7.929	8.269	7.711	7.793	7.684	7.738
H_{15}	8.092	8.051	7.806	8.078	7.874	7.725	8.065
H_1	10.744	10.105	-	10.662	9.901	-	11.506

SCVOM: self-consistent variational cellular method (present work); VOM: non self-consistent variational cellular method (ref. 14); LCAO: linear combination of atomic orbitals (ref.26); APW: augmented plane waves (ref. 27); QDM: quantum defect method (ref.28); KKRZ: method of Green's function - Ziman version (ref. 29); OPW: orthogonalized plane waves (ref. 30).

planation for this fact. We note, nevertheless, that the results obtained by us for these two levels can be considered an improvement relative to the calculations of VCM when compared with other methods. Similar discrepancy was found by Ching and Callaway²⁶ who found level H_{12} above H_{15} . The self-consistent band structure of sodium is shown in figure 4 for directions ΓH and ΓP (energy in eV).

In figure 3 the product $rV(r)$ as a function of r compares the self-consistent potential, the superposition of atomic potentials and the atomic potential. We see that the self-consistent potential converges to values closer to the atomic one than the superposition of atomic potentials. This result could be predicted if we recall the fact that the electron for the conduction band of sodium is quite free, an evidence of its metallic character.

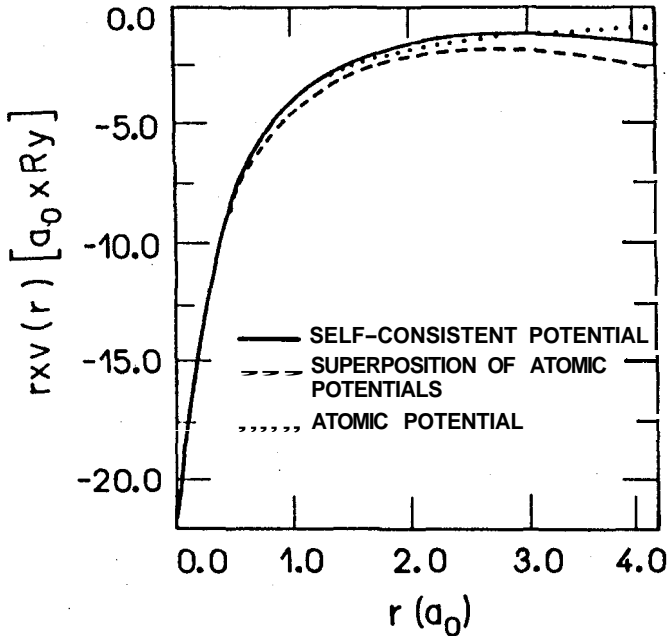


Fig.3 - Comparison between the self-consistent potential, the superposition of atomic potentials and the atomic potential for sodium.

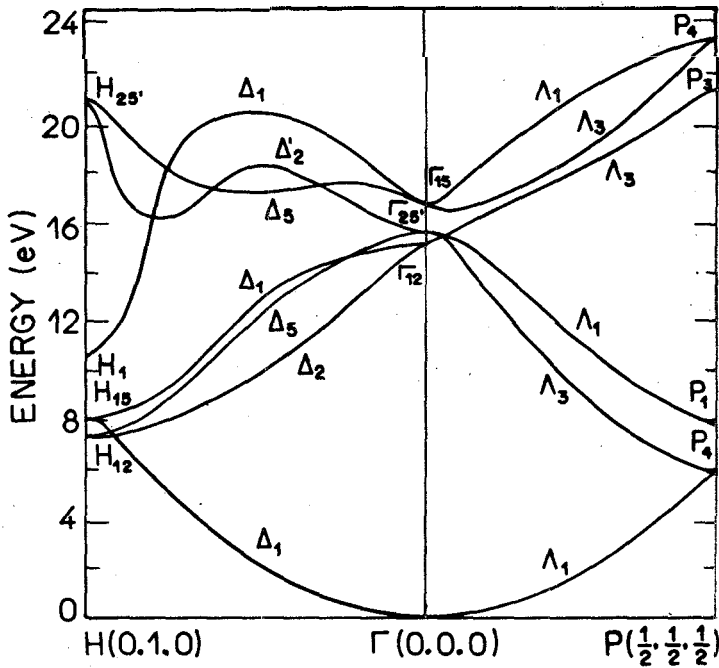


Fig.4 - Band structure of sodium in directions ΓH and ΓP (energies in eV). The origin of energies was placed at the bottom of the conduction band.

In the calculation of the Fermi [leve] for sodium we can make some considerations that simplify the work. The Fermi surface for sodium does not differ very much from a sphere and so the vector \vec{k}_m , which characterizes its Fermi level, is very close to the \vec{k}_F of free electrons. For free electrons we have $\epsilon_F = k_F^2$ (Rydbergs units). In this approximation for sodium the number of accessible states from $k = 0$ to $k = k_F$ is $2 \times \frac{4\pi}{3} k_F^3$, equal to the volume of the Brillouin zone in \vec{k} space

$$2 \times \frac{4\pi}{3} k_F^3 = \frac{1}{4} \left(\frac{4\pi}{3}\right)^3 .$$

In units of $2\pi/\alpha$ we have

$$k_F = \left(\frac{3}{4\pi}\right)^{1/3} = 0.6203505 .$$

For free electrons, the energy increases with the square of k and we hope that this is approximately true for sodium, so we do not need to calculate energies for values of \vec{k} with magnitude much smaller than that of k_F calculated above. Table 5 shows the vectors extracted from table 1, which are needed to obtain the Fermi level. They are disposed in

Table 5 - Self-consistent energy levels for sodium calculated from the 438th to the 512th vector in the Brillouin zone. The number of \vec{k} vectors in a star is indicated in brackets.

\vec{k} (units of $\pi/4a$)	energy (Ry)
(2,3,3) [24]	-0.1167
(0,1,5) [24]	-0.1002
(0,0,5) [6]	-0.0984
(1,3,4) [48]	-0.0881
(0,3,4) [24]	-0.0787
(2,2,4) [24]	-0.0747
(1,1,5) [24]	-0.0699

order of increasing energy (Ry) starting from the 438th vector. The magnitude of the preceding vector is noticeable smaller than k_F . From this table we see that the Fermi level is determined by the energy value of any one of the 48 vectors of the star (1,3,4), since among them we can locate the 512th energy. For the vector (0,0,0) we have obtained the eigenvalue -0.3314 Ry. So we find

$$\epsilon_F(N\alpha) = (0.3314 - 0.0967) \text{ Ry} = 0.2347 \text{ Ry} = 3.1919 \text{ eV}$$

This value is very close to the Fermi level for sodium according to the free electron gas model (3.23 eV) and comparable to the one found by Lawrence²⁹ in his calculation by self-consistent KKRZ for sodium.

REFERENCES

1. E.Wigner and F.Seitz, Phys. Rev. 43, 804 (1933).
2. J.C.Slater, Phys. Rev. 45, 794 (1934).
3. S.L.Altmann, Proc.Cambridge Phyl.Soc. 53, 343 (1957).
4. S.L.Altmann and N.V.Cohan, Proc.Phys.Soc. 71, 383 (1958).
5. S.L.Altmann and C.J.Bradley, Phys.Rev.A135, 1253 (1964).
6. S.L.Altmann and A.P.Cracknell, Rev.Mod.Phys. 37, 19 (1965).
7. S.L.Altmann, A.R.Harford and R.G.Blake, J.Phys. F1, 791 (1971).
8. L.G.Ferreira and J.R.Leite, Phys.Rev.Lett. 40, 49 (1978).
9. L.G.Ferreira and J.R.Leite, Phys.Rev. A18, 335 (1978); Phys. Rev. A20, 689 (1978).
10. L.M.Bregancansin, L.G.Ferreira, J.Chem.Phys. 71, 4923 (1979).
11. J.R.Leite, A.Fazzio, M.A.P.Lima, A.M.Dias, A.Rosato and E.Segre, Int. J.Quantum Chem. S15, 401 (1981).
12. L.G.Ferreira and M.L.De Siqueira, J.Phys. B16, 3111 (1983).
13. (a) D.L.Kinoshita, L.G.Ferreira and M.L.De Siqueira, Int.J. Quantum Chem. 28, 85 (1985); (b) L.G.Ferreira and M.L.De Siqueira, Phys. Rev. B34, 5315 (1986).
14. A.C.Ferraz, E.K.Takahashi and J.R.Leite, Phys.Rev.B26, 690 (1982).
15. A.C.Ferraz, M.I.T.Chagas, E.K.Takahashi and J.R.Leite, Phys. Rev. 829, 7003 (1984).
16. A.Baldereschi, Phys. Rev. 87, 5212 (1973).
17. D.J.Chadi and M.L.Cohen, Phys. Rev. 87, 692 (1973); Phys. Rev. B8, 5747 (1973).
18. DR .Hartree, *The Calculation of Atomic Structures*, John Wiley & Sons (1957).
19. J.C.Slater, Phys. Rev. 81, 385 (1951).
20. H.Schölösson and P.M.Marcus, Phys. Rev. 131, 2529 (1963).
21. W.Kohn and L.J.Sham, Phys. Rev. A140, 1133 (1965).
22. A.C.Switendick, J.Appl.Phys. 37; 1022 (1966).
23. E.C.Snow and J.T.Waber, Phys. Rev. 157, 570 (1967).
24. W.B.Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, vol.2, Pergamon Press, Oxford (1967).

25. F.Herman and S.Skillman, *Atomic Structure Calculations*, Prentice Hall, New Jersey (1963).
26. W.Y.Ching and J.Callaway, *Phys.Rev.* B11, 1324 (1975).
27. L.Dagens and F.Perrot, *Phys.Rev.* B8, 1281 (1973).
28. F.S.Ham, *Phys.Rev.* 128, 82 (1962).
29. M.J.Lawrence, *J.Phys.* F1, 836 (1971).
30. Y.Muda, *J.Phys.Soc.Japan* 31, 1329 (1971).

Resumo

O método celular variacional auto consistente é aplicada pela primeira vez no cálculo da estrutura de faixas de energia do sódio. A formulação auto consistente da teoria celular variacional em cristais é apresentada topando-se a aproximação ruffin-tin para a densidade de carga. Comparando nossos resultados com aqueles obtidos por outros métodos concluímos que a versão auto consistente do método celular desenvolvida neste trabalho é um esquema computacional rápido de obter-se resultados precisos para as bandas.