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Application of the variational cellular method to periodic structures. Energy band of sodium

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The first application of the recently proposed variational cellular method (VCM) to periodic structures is reported. The method is applied to the determination of the electronic structure of metallic sodium. The results of these calculations, when compared with previous results obtained through other methods, lead to the conclusion that VCM is an accurate and fast method. Empty-lattice energy eigenvalues for the Δ symmetry line in a body-centered-cubic lattice are found to be correct to 0.001 Ry, when spherical harmonic components up to $l_{\max}=4$ are used in the cellular expansions.

I. INTRODUCTION

It has been shown that the recently proposed variational cellular method (VCM) is a useful approach to the problem of finding the one-electron solutions of the Schrödinger equation for molecules.[1] Previous applications of VCM were concerned with the self-consistent calculations for the ground-state potential curves and ionizaton energies of H_2,$H_2{}^+$ and some covalent diatomic molecules.[2,3] From these results we concluded that VCM is a very precise and fast method. The aim of this paper is to report the results of the first application of the formalism to the case of three-dimensional periodic structures.

Electronic-structure calculations for metallic sodium were carried out within the VCM framework and results are compared with previous calculations. A preliminary report of our work was published elsewhere.[4] In this paper the relevant aspects of the formalism and the details of the calculations are discussed.

The starting point for the VCM goes back to the old cellular method of Wigner and Seitz, one of the earliest attempts to solve the crystal-wave equation for a realistic crystal model.[5] In this classic study of metallic sodium, the crystal volume was decomposed into space-filling atomic polyhedra (Wigner-Seitz cells), then these polyhedra were replaced by equivalent volume spheres and suitable boundary conditions were imposed on the surfaces of these spheres. The cellular wave-function representation was defined by solving a central-field problem in each of these spheres. Soon afterwards Slater applied an improved version of the cellular method to sodium, where the boundary conditions were imposed at a selected number of points on the surfaces of the polyhedron.[6] Schockley showed that Slater's procedure leads to large errors for the free-electron energy eigenvalues of an empty lattice. He concluded that spherical harmonics of higher order than those used in Slater's calculations had to be used.[7] A great improvement on Slater's cellular method was made by taking advantage of the crystal symmetry to increase the order of the spherical harmonics used in the cellular expansion.[8] It was shown that for certain special points in the Brillouin zone (BZ) results of significant accuracy could be obtained for sodium. This calculation was extended to other points in the BZ.[9]

In the earlier cellular calculations based on exact point matching, it was found that the resulting energy levels depend on the choice of matching points and on the related choice of cellular basis functions. These convergence problems and Kohn's demonstration that Slater's cellular method could be derived from a variational principle, prompted other authors to satisfy the boundary conditions in a least-squares sense over a large number of points spanning all the polyhedral faces, instead of at a limited number of points.[10] Altmann and his collaborators have been successfully applying the rigorous cellular method to many metallic crystals.[11] Slater's cellular method or modified versions of it have also been applied to diamond-lattice-type crystals[12–14] and insulators.[15] Recently a modified version of Altmann's rigorous cellular method was applied to calculate the electronic structure of fcc lanthanum and that of a tungsten monolayer.[16] The method was extended to nonspherical cellular potentials and the inclusion of relativistic effects has been reported.[17] On the other hand, the basic concepts of the cellular method have been recently used by several authors to develop new models for molecular and crystal electronic structure calculations.[18–21]

Leite, Herman, and Bennett carried out the band-structure calculations of diamond using Slater's cellular method.[22] The dependence of the energy-level structure on the choice of matching points and cellular basis functions was carefully examined. It was demonstrated that the cellular method based on exact point matching leads to energy levels that are relatively insensitive to the choice and spatial arrangement of a limited number of matching points, provided the cellular wave functions are represented by a sufficiently large number of basis functions. Tetrahedral harmonic expansions including orbital quantum numbers up to $l_{\max}=12$ are necessary to ensure reasonable convergence at the zone points Γ, X, and L. Although it was concluded that the cellular method is an accurate technique even for such loosely packed structures as diamondlike crystals, this severe convergence problem is one of the fundamental weaknesses of the method. In Slater's cellular method the matching points sample only limited portions of the cell surfaces, and therefore it is clear that the eigensolutions cannot be derived from a variational principle. Energy eigenvalues not determined variationally demand wave functions with high-order spherical harmonics. Thus, in VCM an attempt was made to formulate the cellular method in a variational way. The main idea behind the method was to add a much faster convergence to the flexibility of the cellular formalism. The theory of VCM is extremely simple and has the advantage of discarding the muffin-tin approximation of the self-consistent potential, which is the main source of error in methods like the augmented-plane-wave (APW) and Kohn-Korringa-Rostoker (KKR) methods.[23–25]

The electronic structure of sodium has been the subject of calculations for almost fifty years. Since the pioneering work of Wigner and Seitz most of the standard band-structure calculation methods have been applied to the alkali metals.[26–29] Metallic sodium has been a subject of research in most of the classical works in the cellular method. We have undertaken another calculation with the main objective of developing and testing VCM for periodic structures. Our intention was to establish the VCM secular equation and to study the convergence of the energy eigenvalues as a function of the number of the cellular basis functions. Therefore, no attempt was made by us to perform the calculations self-consistently. It has been shown from previous calculations that the general features of the alkali-metals band structure are independent of the precise form of the crystal potential. Thus, although our results are not self-consistent, comparisons with more elaborate calculations were made.

The paper is organized as follows: In Sec. II the theory of VCM is reviewed and applied to a three-dimensional periodic structure with one atom per unit cell. In Sec. III the results of our studies for metallic sodium are discussed. The empty-lattice test is made with VCM and the results are displayed in Sec. IV. Considerable emphasis is placed on comparing the results from exact point matching and VCM calculations regarding the empty-lattice test. Finally the main conclusions are summarized in Sec. V.

II. CELLULAR METHOD APPLIED TO THE SODIUM STRUCTURE

The cellular method has been discussed by many authors.[11,30] The idea of the method is as follows: The crystal is decomposed into space-filling atomic polyhedra (Wigner-Seitz cells), one surrounding each lattice site. The crystal potential is approximated within each polyhedron by its spherical average with respect to the center of the polyhedron. Within each polyhedron i the crystal-wave function corresponding to energy eigenvalue ϵ_0 is expanded as

$$\psi_i(\vec{r})=\sum_{\lambda} A_{i\lambda} f_{i\lambda}(\vec{r}) , \tag{1a}$$

where

$$f_{i\lambda}(\vec{r})=R_l^{\epsilon_0}(r_i)Y_\lambda(\hat{r}_i) . \tag{1b}$$

λ denotes the angular momentum pair lm, $\vec{r}=(r_i,\hat{r}_i)$ is a radius vector whose origin is at lattice site i, the $Y_\lambda(\hat{r}_i)$ are normalized spherical harmon-

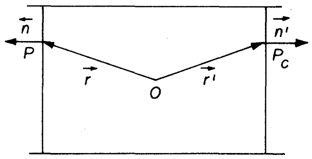

FIG. 1. Notation for cellular boundary conditions.

ics, the $R_l^{\epsilon_0}(r_i)$ are the solutions of the radial Schrödinger equation for energy ϵ_0, and the $A_{i\lambda}$ are undetermined expansion coefficients.

In the periodic lattice ψ_i is a propagating state and exactly satisfies the one-particle Schrödinger equation for the cellular crystal potential. Accordingly, the coefficients $A_{i\lambda}$ in different cells are related by the Bloch theorem. Figure 1 schematically represents the atomic polyhedron (unit cell) of a crystal with one atom per unit cell. The equations which express the crystal periodicity (Bloch) conditions appropriate to the reduced wave vector $\vec{k}$ can be written as follows:

$$\psi_i(\vec{r}\,')=e^{i\vec{k}\cdot\vec{R}}\psi_i(\vec{r}) , \tag{2a}$$

$$\partial_n\psi_i(\vec{r}\,')=-e^{i\vec{k}\cdot\vec{R}}\partial_n\psi_i(\vec{r}) . \tag{2b}$$

The points $\vec{r}$ and $\vec{r}\,'$ (conjugate points) lie on the surface of the polyhedron i and are separated by a direct-lattice vector $\vec{R}$. ∂_n means an outward normal derivative. These equations ensure the continuity of the crystal-wave function and its normal derivative on the surface of the polyhedra. According to Slater's original cellular method, the boundary conditions expressed by Eqs. (2) are exactly satisfied at a limited number of matching points.[6] If the total number of matching points is N ($N/2$ pairs of conjugate points) and the total number of spherical harmonics is N, Eqs. (2) define, for a fixed value of $\vec{k}$, N linear homogeneous equations for the expansion coefficients $A_{i\lambda}$. In order that the boundary conditions are satisfied nontrivially, the corresponding $N\times N$ determinant must vanish. We generate the functions $R_l^{\epsilon_0}(r_i)$ by performing numerical outward integration of the radial Schrödinger equation for each value ϵ_0. Therefore, one evaluates the functions $f_{i\lambda}$ and their nomal derivatives as a function of ϵ_0 at all required matching points, and then searches for the zeros of the determinant as a function of ϵ_0. There will be a set of eigensolutions corresponding to different energy bands, and therefore Eqs. (2) lead to the dispersion relations connecting ϵ_0 and $\vec{k}$.

In principle, one should impose boundary conditions at a large number of points spanning all the polyhedral faces, in order to ensure that the wave function can be derived from a variational principle.[10] If one requires the exact point matching solution for the boundary condition problem, too high a value for the maximum orbital quantum number $l_{\max}$ is needed in the cellular expansion [Eqs. (1)]. To overcome this severe limitation of the cellular method without loosing its flexibility, the VCM was proposed.[1]

The cellular function ψ_i is assumed as a trial function to be used in the following variational expression for the energy ϵ:

$$\sum_i \int d\Omega\, \psi_i^*\psi_i\epsilon=\sum_i \int d\Omega\, \psi_i^*(-\nabla^2+V)\psi_i+\tfrac{1}{2}\sum_{S_{ij}}\int dS(\psi_i-\psi_j)(\partial_n\psi_j^*-\partial_n\psi_i^*)$$
$$+\tfrac{1}{2}\sum_{S_{ij}}\int dS(\psi_i^*+\psi_j^*)(\partial_n\psi_j+\partial_n\psi_i) , \tag{3}$$

where the volume integrals are performed in each cell i and surface integrals in each boundary S_{ij} between cells i and j. The summations run over cells, V is the potential and $\partial_n\psi_i$ denotes the outward normal derivative to the cell surface S_{ij}, from cell i. ϵ is always real for any trial wave function. We can vary ψ_i^* to obtain the conditions for ϵ to be stationary

$$(-\nabla^2+V)\psi_i=\epsilon\psi_i , \tag{4a}$$

$$\psi_i\,|_{S_{ij}}=\psi_j\,|_{S_{ij}} , \tag{4b}$$

$$\partial_n\psi_i\,|_{S_{ij}}=-\partial_n\psi_j\,|_{S_{ij}} . \tag{4c}$$

Equations (4) imply that the wave function and its normal derivative have to be continuous through the cell boundaries. The variational expression for the energy eigenvalue adopted in the VCM derivation [Eq. (3)] is the same one Antoci and Nardelli used in their intersecting sphere model.[31]

If the cellular representation of the wave function [Eqs. (1)] is assumed and the Bloch conditions [Eqs. (2)] are used to relate the coefficients $A_{i\lambda}$ in different cells, we can derive the secular equation for the crystalline structure with one atom per unit cell from the variational expression [Eq. (3)]

$$\sum_{\lambda'}\langle\lambda\,|\,H\,|\,\lambda'\rangle A_{\lambda'}=0 , \tag{5}$$

where

$$\langle\lambda\,|\,H\,|\,\lambda'\rangle=\sum_{\vec{R}}\int dS_{\vec{R}}\, e^{i\vec{k}\cdot\vec{R}}[f_{\lambda'}(\vec{r})\partial_n f_\lambda^*(\vec{r}\,')$$
$$+f_\lambda^*(\vec{r}\,')\partial_n f_{\lambda'}(\vec{r})] , \tag{6}$$

where the sum runs over all the lattice vectors connecting parallel faces of the atomic polyhedron, and the integrals are performed on the surfaces defined by the $\vec{r}$ vectors. We have dropped the cell index i to simplify the notation.

The secular matrix is then parametrized in terms of ϵ_0 and the one-electron energies are also obtained by searching for the zeros of the associated determinant. The surface integrations which define the matrix elements $H_{\lambda\lambda'}$ are performed according to the usual procedure of numerical integration, where the integrand is evaluated at a finite number of points and summed with appropriate weight factors. The practical use of the VCM would be seriously hindered if these surface integrations had to be made with much precision. In that case we would be faced with the difficult problem of establishing the net of points and their respective weights which would permit a precise evaluation of the integrals. It has already been shown that the surface integrations need no special care but can be performed very naively.[1] VCM is also variational with respect to the number and location on the cell surfaces of the points needed to perform the integrations. This is the main reason VCM is as fast as the standard multiple-scattering $X\alpha$ method for molecular calculations.[2] This problem is carefully examined in this paper in order to survey the possibility of the VCM becoming a satisfactory tool for the solution of the Schrödinger equation in crystals.

One important asset of the VCM is the definition of a criterion of precision that permits us to reach conclusions on the accuracy of the calculations without increasing the basis set. The criterion C of precision, defined according to Ref. 1, can be written for the crystalline structure with one atom per unit cell as

$$C=1+\sum_{\lambda\lambda'}\left[A^*_\lambda\frac{d}{d\epsilon}(H_{\lambda,\lambda'})A_{\lambda'}\Big/2A^*_\lambda N_{\lambda\lambda'}A_{\lambda'}\right], \tag{7}$$

where the matrix N is given by

$$N_{\lambda\lambda'}=\int dS\left[\frac{d}{d\epsilon}(f^*_\lambda)\partial_n f_{\lambda'} - f_{\lambda'}\frac{d}{d\epsilon}(\partial_n f^*_\lambda)\right]. \tag{8}$$

We verified that the behavior of C, as a function of the number of spherical harmonics in the cellular expansion and the number of points used to perform the surface integrations, is a reliable criterion of precision of the calculation.

In order to apply the method to metallic sodium we considered the space-filling polyhedra for a body-centered-cubic (bcc) lattice. The Wigner-Seitz cell is a truncated octahedron delimited by eight octahedral faces (hexagons) and six cubic faces (squares). There are seven lattice vectors connecting seven pairs of parallel faces.[6] The crystal potential could be expressed as the sum of a Coulomb term and an exchange term. The former was represented by a spatial superposition of atomic Coulomb potentials, one centered on each atomic site. The spherical average of the crystal Coulomb potential was calculated with respect to the center of the cell. The atomic Coulomb potential and charge density were obtained from a self-consistent Hartree-Fock-Slater atomic calculation with Slater's approximation for the exchange term.[32] The crystal-charge density was also calculated by considering a spatial superposition of free-atom charge densities. The spherical average of the cube root of the crystal charge density was performed within the cell and was used to calculate the spherically averaged Slater-type statistical exchange potential. The crystal potential was determined by taking the atomic contributions of up to 16 shells of neighboring atoms into account. We assumed as the sodium-lattice parameter the value $a_L=4.225$ Å.[33]

III. VCM RESULTS FOR SODIUM

In the general formulation of the VCM no assumption is made *a priori* about the shape of the cells. This is an important asset of the method, which makes it suitable to be applied to a wide range of systems.[1] In order to calculate the secular matrix elements it is necessary to perform the surface integrations numerically. The integral of a generic function $g(\vec{r})$ on a cell surface S can be approximated by the expression

$$\int_S g(\vec{r})\,dS \cong \sum_p w_p g(\vec{r}_p)\ , \tag{9}$$

where we are adding the values of $g(\vec{r})$ at some selected points $\vec{r}_p$ on the surface S, multiplied by the appropriate weight factors w_p. For a three-dimensional periodic structure, the Wigner-Seitz cells are well-defined polyhedra delimited by planar faces. These faces can always be divided into triangles and the w_p can be easily found.[34]

In Fig. 2 the sets of points we selected on the faces of the atomic polyhedron to perform the cal-

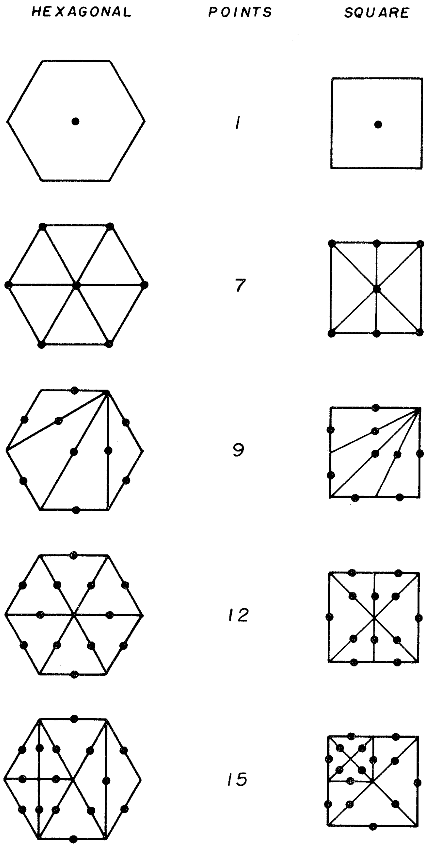

FIG. 2. Different sets of points used to perform the cellular calculations. The square and the hexagon represent the two kind of polyhedral faces.

culations are shown. Once the values of f_λ and $\partial_n f_\lambda$ at these points for the eight hexagonal and six square faces of the polyhedron are known, the matrix elements are calculated using Eq. (9). When only the center of the faces are used as matching points the values of w_p will be the areas of the hexagon and of the square. In order to make a careful study of the convergence properties of VCM, we find it convenient to use cubic harmonics as the basis functions, rather than the standard spherical harmonics. Thus, we are using linear combinations of spherical harmonics which transform according to the irreducible representations of the cubic point group O_h.[35]

In Table I a convergence study of the $\Gamma_{25'}$ level of sodium as a function of the number of terms in the cellular expansion and of the number of points used to perform the numerical surface integrations at hexagons and squares is shown (see Fig. 2). The cellular representation includes cubic harmonics whose maximum angular momentum is $l_{\max}$. The first interesting feature of Table I is that it emphasizes the double variational character of VCM. For a fixed value of $l_{\max}$, the solution converges if enough points are used for the surface integrations. When this number of points is reached, the solution is no longer sensitive to the number and location of the points of the cell surfaces. It is clear then that the lack of precision in the calculation of the surface integrals is not important in the VCM. On the other hand, VCM shows fast convergence with respect to l. The solution is fully convergent for $l_{\max}=6$ and convergent for $l_{\max}=4$ within tenths of eV. Comments should be made with respect to the entries correspondent to $l_{\max}=8$. No solutions were found with one and seven points per face. When nine points per face were considered a solution which deviates from the converged value was found. Finally, with 12 and 15 points we obtained the converged result. This behavior of the energy eigenvalue has a straightforward interpretation. One and seven points are not enough to sample a spherical harmonic whose angular momentum is eight. The inclusion of this harmonic generates a mismatch at the cell boundaries and the solution cannot be found. However, if more points are considered in the calculations, the high-order spherical harmonic is sampled correctly and the converged value is obtained. Accordingly, one point per face is not enough to sample spherical harmonic whose angular momentum is greater than two.

TABLE I. Convergence of the $\Gamma_{25'}$ energy level of metallic sodium. $l_{\max}$ is the maximum spherical harmonic angular momentum in the cellular expansion. "Points" is the number of points used for numerical integration in the hexagonal and square faces of the polyhedron (see Fig. 2). Values are in rydbergs.

Points $l_{\max}$	2	4	6	8
1	0.194			
7	0.385	0.490	0.489	
9	0.368	0.530	0.476	0.477
12	0.430	0.517	0.507	0.507
15	0.429	0.516	0.507	0.507

In Table II we show the calculated values for the criterion C of precision related to the $\Gamma_{25'}$ energy level. We expect C to be small compared to one for converged results. We conclude from the results shown in Table II that a good accuracy is obtained for $l_{\max}=4$ or 6. Table II also shows that the lack of precision in the calculation of the surface integrals is not critical. Twelve points per face is enough to ensure convergence.

TABLE II. Behavior of the criterion C of precision as a function of $l_{\max}$ and "points." The entries correspond to the $\Gamma_{25'}$ level and this table should be compared with Table I. C is defined in the text by Eq. (7).

Points $l_{\max}$	2	4	6	8
1	0.6153			
7	0.2474	−0.0984	−0.1054	
9	0.2645	0.0785	−0.0097	0.0807
12	0.3008	−0.0177	−0.0302	−0.1264
15	0.2996	−0.0231	−0.0342	−0.1090

Thus we conclude that by using twelve points per face and up to $l_{\max}=4$ in the cellular expansion, the sodium energy bands can be calculated by VCM with a good degree of accuracy. All the calculations were then performed within this scheme.

Table III shows the energy levels of sodium at some selected high-symmetry points in the BZ. The Γ_1 level was chosen as the origin. The WSS entries are from a Wigner-Seitz-Slater cellular calculation.[9] The linear combination of atomic orbitals (LCAO) values are from a self-consistent calculation performed using the LCAO method.[28] The APW entries correspond to an APW calculation.[27] The quantum defect method (QDM) values were obtained using the quantum defect method[36] ($a_L=4.3$ Å). Those entries labeled as KKRZ were obtained from a self-consistent calculation using the Kohn-Korringa-Rostoker-Ziman method[37,38] ($a_L=4.3$ Å). Finally, the orthogonalized-plane-wave (OPW) entries are from an OPW calculation.[39] When comparing the results displayed in Table III we have to bear in mind that the potentials used in the methods may have been rather different. Most of the earlier energy-band calculations on sodium were done with the use of the Prokofjew potential.[5,6,8,9] The recent calculations were performed by taking into account more elaborated descriptions of the exchange-correlation potential.[27,28,38] In spite of these observations, a fairly good agreement between the VCM, APW, and OPW calculations is found. It is interesting to observe that the VCM results represent a definite improvement on the WSS values.

Table IV compares the band gap

$$\Delta E_{110}=E(N_1)-E(N_{1'})$$

obtained from VCM with the results of other calculations. The different labels for the entries are the same as those of Table III. The agreement between the VCM, OPW, and APW calculations is

TABLE III. Energy levels of metallic sodium at some selected points in the BZ. The Γ_1 level was taken as reference and placed at the zero of energy. Values are in rydbergs.

Level method	VCM	WSS[a]	LCAO[b]	APW[c]	QDM[d]	KKRZ[e]	OPW[f]
Γ_1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\Gamma_{25'}$	1.125		1.033	1.092	1.028	1.073	1.114
Γ_{12}	1.157		1.202	1.158	1.114	1.135	1.154
Γ_{15}	1.225		1.213	1.218	1.117	1.138	1.268
P_4	0.427	0.498	0.438	0.436	0.437	0.425	0.432
P_1	0.522	0.628	0.526	0.549	0.508	0.499	0.582
H_{12}	0.583	0.595	0.602	0.567	0.573	0.565	0.569
H_{15}	0.592	0.625	0.567	0.594	0.579	0.568	0.593
H_1	0.743	0.708		0.784	0.728		0.846
$N_{1'}$	0.295	0.293	0.297	0.294	0.296	0.284	0.284
N_1	0.343	0.340	0.317	0.325	0.313	0.308	0.335
N_2	0.758		0.813	0.838	0.814	0.829	0.814
$N_{3'}$	0.861		0.866	0.899	0.854		0.916
$N_{4'}$	0.890		0.966	0.907	0.888		0.914
N_1	0.989		0.999	0.985	0.942		

[a] Reference 9.
[b] Reference 28.
[c] Reference 27.
[d] Reference 36.
[e] References 37 and 38.
[f] Reference 39.

TABLE IV. Energy levels at N_1 and $N_{1'}$ and the width of the energy gap $E(N_1)-E(N_{1'})$ for metallic sodium. The references for the data sources are given in Table II. Values are in rydbergs.

Level method	VCM	WSS	LCAO	APW	QDM	KKRZ	OPW
N_1	-0.252	-0.268	0.317	0.325	-0.291	0.270	-0.128
$N_{1'}$	-0.300	-0.315	0.297	0.294	-0.308	0.246	-0.179
$E(N_1)-E(N_{1'})$	0.048	0.047	0.020	0.031	0.017	0.024	0.051

of the order of ±0.01 Ry. The APW value reported in Table IV was obtained by using the Kohn and Sham approximation to the exchange potential. When the Hartree-Fock potential is used the value for the gap is 0.041 Ry.[27] By scaling the statistical-exchange parameter α from 1 to $\frac{2}{3}$ in the $X\alpha$ method it was observed that the gap ΔE_{110} remains constant within 0.005 Ry.[39] Accordingly, the use of a more elaborated treatment for the exchange-correlation potential is out of the scope of the present work.[40] The difference between our result and that of Howarth and Jones (WSS entry) is remarkable in spite of the large cellular expansion used by those authors. VCM is much more accurate and faster than that early version of the cellular method. Somewhat larger discrepancies are observed between the VCM result and those obtained from LCAO, QDM, and KKRZ methods.

The overall result of the energy band of sodium as determined by VCM is shown in Figure 3. Conduction and excited bands are present along the Δ, F, Λ, Σ, and G symmetry directions.

IV. EMPTY-LATTICE TEST

It has been continuously alleged since 1937 that the cellular method does not satisfy the Schockley empty-lattice test. This problem has been an object of investigation for many authors along the history of the cellular method.[7–10,21,41] In the empty lattice the cellular spherical potential is assumed to be constant within the cells. This is an exactly solvable case which can be used as a test for the accuracy of the method.

We have carried out VCM calculations for an empty bcc lattice with the same lattice parameter

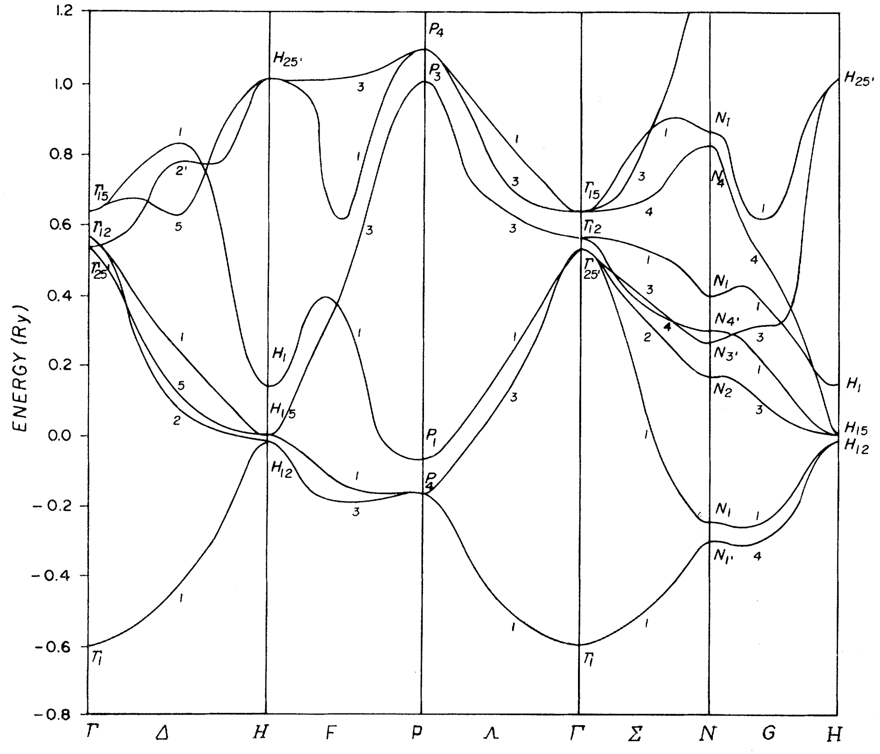

FIG. 3. Energy-band structure of bcc sodium obtained from the VCM calculations.

TABLE V. Convergence of the free-electron energy eigenvalue corresponding to the wave vector $\vec{k}=(2\pi/a_L)\,(\frac{1}{2},0,0)$ in the BZ of the bcc lattice. $l_{\max}$ is the maximum spherical harmonic angular momentum in the cellular expansion. "Points" is the number of points used for numerical integration in the hexagonal and square faces of the polyhedron (see Fig. 2). Values are in rydbergs. The exact value of the energy is 0.154 822 Ry.

Points $l_{\max}$	1	2	3	4	5
1	0.134	0.134	0.149		
7	0.135	0.134	0.154	0.153	0.152
9	0.137	0.137	0.155	0.155	0.155
12	0.137	0.137	0.155	0.155	0.155
15	0.137	0.137	0.155	0.155	0.155

of sodium. The sets of points used in this investigation are the same considered previously and shown in Fig. 2. The cellular method within the framework of the exact point matching approach was also applied to the bcc empty lattice and the results were compared with those obtained from the VCM calculations.

The energy eigenvalue of an electron of wave vector $\vec{k}$ in an empty lattice is k^2, in atomic units. According to the cellular method the functions $R_l^{\epsilon_0}(r)$ are determined from the radial Schrödinger equation, which for an empty lattice is written as

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}R_l^{\epsilon_0}(r)+\left[\epsilon_0-\frac{l(l+1)}{r^2}\right]R_l^{\epsilon_0}(r)=0\ . \tag{10}$$

The solutions of this equation which are regular at the origin are the well-known Bessel functions. They are then used to calculate the matrix elements of VCM and of the Slater cellular method (exact point matching approach).

By applying VCM we performed the convergence study of the free-electron energy eigenvalue at $\vec{k}=(2\pi/a_L)\,(\frac{1}{2},0,0)$ as a function of $l_{\max}$ and "points." Tables V and VI show the results of this study. According to the values obtained for the criterion C of precision, shown in Table VI, the optimal value for the convergence is $l_{\max}=3$. By extending the cellular expansion up to $l_{\max}=5$, C increases while the converged energy eigenvalue remains constant. The inclusion of spherical harmonic of higher order ($l_{\max}>3$) generates a mismatch at the cell boundaries, therefore increasing the value of C. However, due to the variational character of the method, the mismatch has no first-order effect on the energy eigenvalue. It is also observed from Tables V and VI that sets of 9 or 12 points per face of the polyhedron (see Fig. 2) are enough to ensure convergence. The obtained result for the free-electron energy eigenvalue 0.155 Ry, is in good agreement with the exact result, 0.154 822 Ry. In the present calculation we used a more accurate numerical search for the energy eigenvalues than that used in our previous work.[4] This explains the small discrepancies between the results shown in Table V and those already reported by us.[4] Altmann and his collaborators applied the empty-lattice test for the bcc structure and found errors of about 0.0001 Ry for high-symmetry points using the rigorous cellular method.[41] For a general $\vec{k}$ value the errors are of about 0.005 Ry but there are others of greater

TABLE VI. Behavior of the criterion C of precision as a function of $l_{\max}$ and "points." The entries correspond to the free-electron energy eigenvalue at $\vec{k}=(2\pi/a_L)\,(\frac{1}{2},0,0)$. This table should be compared with Table V. C is defined in the text by Eq. (7).

Points $l_{\max}$	1	2	3	4	5
1	1.1207	0.7437	0.5186		
7	1.2641	0.5831	0.0894	0.7818	0.8453
9	1.1976	0.7384	0.0790	0.5692	0.7451
12	1.1972	0.7400	0.0805	0.5465	0.6539
15	1.1978	0.7400	0.0859	0.5457	0.6332

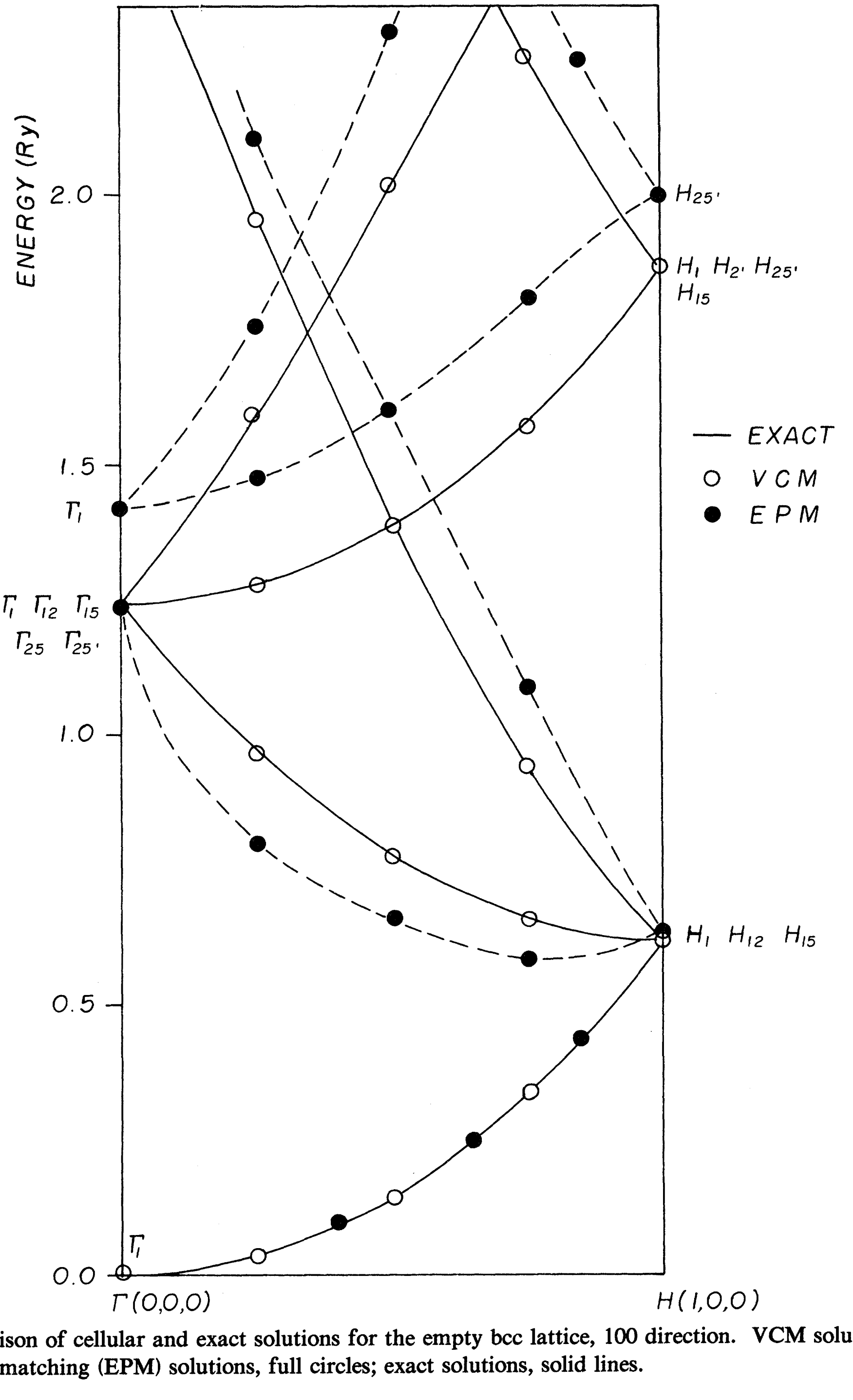

FIG. 4. Comparison of cellular and exact solutions for the empty bcc lattice, 100 direction. VCM solutions, empty circles; exact point matching (EPM) solutions, full circles; exact solutions, solid lines.

magnitude ($\sim$0.02 Ry). In order to reach this agreement the boundary conditions were imposed over a grid of 256 pairs of conjugate points spanning $\frac{1}{48}$ of the Wigner-Seitz cell. The wave function was carried out up to $l_{\max}=12$ for high-symmetry points and $l_{\max}=6$ for a general $\vec{k}$.

In Fig. 4 comparisons of VCM, exact point matching (EPM) and exact solutions for the bcc empty lattice, Δ direction, are made. The empty circles denote the VCM results, the full circles denote the exact point matching results and the exact solutions correspond to the solid lines. The exact point matching solutions were found by selecting points on the square and hexagonal faces of the polyhedron, among those shown in Fig. 2. Cellular components up to $l_{\max}=4$ were considered in the wave-function expansion. Twelve points per face and up to $l_{\max}=4$ were considered in order to perform the VCM calculations.

From the results shown in Fig. 4 we conclude that the agreement between the VCM results and the exact solutions is very good. On the other hand, the exact point matching results present strong deviations from the exact solutions, for values of $\vec{k}$ outside of the first BZ. Very large gaps are observed at the zone boundaries and along the symmetry line. These discrepancies noted by other authors in the past have been quoted in disfavor of the cellular method. No attempt was made by us to compare the exact point matching results with those obtained by other authors. Since we are using a different set of matching points and the solutions are strongly dependent on the number and position of these points on the cell surfaces, the comparison would be meaningless.

V. CONCLUSIONS

The results reported in this paper show that the VCM is an accurate and fast method to determine the electronic structure of solids as well as of molecules. The energy bands of metallic sodium and of an empty bcc lattice were accurately determined by assuming the cellular wave expansion with components up to $l_{\max}=4$ and by using only 12 points per face to perform the numerical integrations. Therefore, the severe convergence problem related to the point matching approach is avoided.

The formulation of the VCM as adapted to three-dimensional periodic structures turns out to be somewhat similar to the method used by Jenkins in the past.[14] However, the procedure adopted by this author to perform the surface integrations seriously hindered the practical use of the method. We believe that even today, when high-speed computers are available, the way used to solve the cellular matching problem would be very time consuming. With the VCM we provide a useful contribution to solve this interesting problem. We conclude that the results are sufficiently encouraging to suggest that the method may be applied to more complex periodic structures.

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