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Band-structure calculations of BN by the self-consistent variational cellular method

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The electronic band-structure calculations of zinc-blende–structure BN is carried out with use of a self-consistent version of the local-density variational cellular method. The crystal potential and charge density are approximated within atomic and interstitial space-filling cells by their spherical average. We find that the values obtained for the valence-band widths and minimum band gaps of BN are in good agreement with the results of recent *ab initio* calculations.

There have been in the last few years successful attempts to use the basic ideas of the cellular method, as originated by Wigner, Seitz, and Slater,[1,2] to develop new methods of investigating the electronic structure and related properties of molecules, crystals, finite cluster of atoms, etc.[3-8] Several applications have shown that these new versions of the cellular method are fast and accurate schemes of electronic-state calculations. What makes these recent improvements on the original cellular method so reliable is the use of variational principles to solve the boundary-condition problem on the surface of the cells.[3-5]

The variational cellular method (VCM), as proposed by Ferreira and Leite,[3] was initially applied to perform self-consistent-field (SCF) calculations of one-electron energy spectra, binding energies, and bond lengths of diatomic molecules.[6,9] Shortly thereafter the method was extended to periodic structures with an arbitrary number of atoms per unit cell, and non-SCF results were reported for the band structure of metallic sodium[7] and lithium[10] and of the elemental semiconductors diamond and silicon.[11] In this paper we present the consolidated SCF version of the method and report on the results of its application to calculate the band structure of the zinc-blende–structure BN crystal.

In order to implement the SCF version of the VCM for periodic structures we have combined the non-SCF formulation of the method[11] with the procedure described by Ferreira and Leite[3] to calculate the electronic charge density within the cells. According to the VCM, the crystal space is partitioned into space-filling atomic (interstitial) polyhedra, the crystal potential is approximated within each polyhedron by its spherical average, and the one-electron wave function with wave vector $\mathbf{k}$ and energy ε^0 is expanded within each polyhedron i as a linear combination of partial waves $R_{il}(r)Y_\lambda(\hat{\mathbf{r}})$. $rR_{il}(r)$ is the solution $p_{il}(r)$ of the radial Schrödinger equation and $Y_\lambda(\hat{\mathbf{r}})$ is the spherical harmonic corresponding to the angular-momentum quantum numbers l,m. Using the cellular representation of the wave function, the Bloch conditions and a variational expression,[3] Ferraz *et al.* have derived the VCM secular equation for periodic structures.[11] In order to obtain the secular matrix, H, which is parametrized in terms of ε^0, numerical integrations on the surfaces of the polyhedra are required. The one-electron energies ε are obtained by searching for the zeros of the determinant of H.

We follow now the work of Ferreira and Leite[3] for molecules to calculate the spherical average $\rho_i(r)$ of the electronic charge density in the polyhedron i. We start by first normalizing the radial functions so that

$$p_{il}(0)=0,\quad p_{il}(R)=1\ , \tag{1}$$

where R is the radius of the inscribed sphere in the polyhedron i. We search for the second linearly independent solutions $q_{il}(r)$ of the radial Schrödinger equation on which are imposed the conditions

$$q_{il}(0)=0,\quad \left.\frac{dq_{il}(r)}{dr}\right|_{r=R}=1\ . \tag{2}$$

A Q matrix is obtained from the secular matrix H, by replacing p_{il} by q_{il} and making zero the elements of H that do not contain p_{il}. The charge density in each polyhedron i can readily be obtained by

$$4\pi r^2\rho_i(r)=-\frac{2}{N}\sum_{\nu}\sum_{\mathbf{k}}\sum_{l}p_{il}^2(r)d_\nu C_{il}\ , \tag{3}$$

with

$$C_{il}=-\sum_{j}\sum_{\lambda}\sum_{\lambda'}\langle i\lambda|Q|j\lambda'\rangle\langle j\lambda'|H^{-1}|i\lambda\rangle\Big/\sum_{j'}\sum_{j''}\sum_{\lambda'}\sum_{\lambda''}\frac{\partial}{\partial\varepsilon}\langle j'\lambda'|H|j''\lambda''\rangle\langle j''\lambda''|H^{-1}|j'\lambda'\rangle\ .$$

In Eq. (3), ν runs over occupied levels, d_ν is the space degeneracy of the level, N is the number of unit cells of the crystal, and the labels j, j', and j'' refer to atomic polyhedra belonging to an arbitrary unit cell. Equation (3) is the extension of Eq. (37) in Ref. 3 for periodic structures.

One can improve considerably on the cellular representation of the crystal potential by introducing interstitial (empty) polyhedra into the crystal space partitioning.[12] In this way it is possible to handle open structures within the framework of closely packed lattices. If the polyhedra have approximately spherical shape, we can assume that Eq. (3) is valid even for $r > R$. Thus, the Poisson's equation, which determines the Coulomb potential, can be integrated for all values of r inside of each polyhedron. It has been verified that this procedure leads to better results when compared to the use of the standard "muffin-tin" approximation for the charge density.[13]

The secular equation derived by Ferraz *et al.*,[11] Eq. (3), and the Hohenberg-Kohn-Sham local-density-functional approximation are the basic ingredients of the SCF VCM formulation. We report now on the results obtained by applying the method to calculate the band structure of zinc-blende–structure BN.

The properties of BN have deserved a great deal of attention from both technological and basic points of view.[14] Although there are few experimental works in the literature concerned about the electronic structure of this compound, several theoretical calculations have been reported.[14] Until recently these calculations were not able to provide a clear picture of the electronic structure of the material. Their results for the energy levels and for the transition assignments differ significantly. However, recent rigorous calculations have lead to a consistent description of the BN band structure.[14–16] One of our goals is to compare the results of these recent calculations with those obtained from the SCF VCM for BN.

In this work we handle the BN structure within the framework of a closely packed bcc lattice. The crystal unit cell is then partitioned into four equivalent truncated octahedra, two of which locate the B and N atoms, and the two others, the interstitial positions (empty cells).[11,12] The value 3.615 Å was taken for the lattice parameter[17] and the Hedin-Lundqvist[18] expression for the local-density functional was used to describe the exchange-correlation effects.

In order to perform the first interaction in the SCF scheme we follow the procedure described by Ferraz *et al.* in their fourfold-partioning non-SCF VCM calculations for silicon and diamond.[11] A crystal potential is built from the spatial superpositions of Coulomb potentials and charge densities of the B and N atoms.[12] From this potential, which is spherically symmetric in each polyhedron, we determine the partial waves and the secular H matrix. The evaluation of the elements of H requires surface integrations at the hexagonal and square faces of the four octahedra. The calculations are carried out numerically by selecting sets of 10 points on each face of the polyhedra. The cellular representation of the wave function includes symmetrized cubic harmonics whose maximum angular momentum is $l_{\max}$. We have verified that for BN the valence bands are fully convergent for $l_{\max}=4$, and the lower conduction bands converge for $l_{\max}=5$. As we have pointed out previously,[7] once the convergence in the cellular expansion is reached, the solution is no longer sensitive to the number and location of the points used to perform the integrations on the cell surfaces.

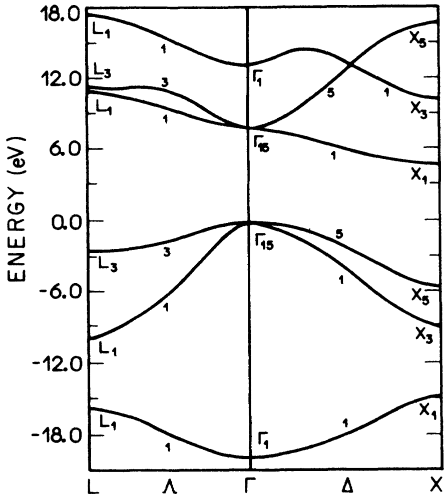

FIG. 1. Energy bands of zinc-blende–structure BN as calculated by SCF VCM. The zero of energy was placed at the top of the valence band.

The Q matrix, which is basic to determine the cellular potential for the next SCF cycle, depends on the particular polyhedron considered and on the particular value of the orbital quantum number l. Since the Q matrix is obtained directly from the secular H matrix, it also contains the Bloch phase factor $\exp(i\mathbf{k}\cdot\mathbf{R})$ where $\mathbf{R}$ are direct-lattice vectors separating conjugate points on the surfaces of the polyhedra.[11] Thus, each non-null matrix element of Q is obtained by performing a sum running over all the lattice vectors connecting two parallel faces, each one belonging to one polyhedron.

Once the H and Q matrices are known, the calculations of the C_{il} coefficients given in Eq. (3) are carried out by constructing the inverse matrix H^{-1} and performing the energy derivatives numerically. The sum over $\mathbf{k}$ occupied

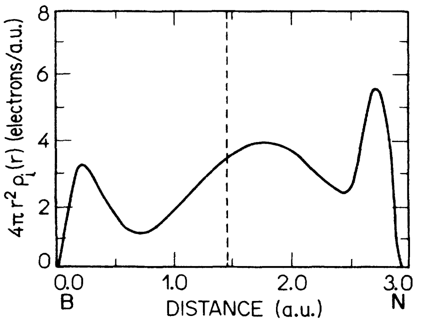

FIG. 2. Valence radial electronic charge distribution along the BN bonding direction. The origin of the distance is taken at the B site. The N site is at 2.96 a.u. The r coordinate is measured from each nucleus to the border of the corresponding cell at half way of the bond length (dashed line).

TABLE I. Comparison of the zinc-blende–structure BN valence-band widths and minimum band gaps (in eV) from the SCF VCM calculations with the experimental results and the recent theoretical calculations.

	Valence-band width			Minimum band gaps	
Ref.	Upper	Lower	Full	Direct[a]	Indirect[b]
			Theory		
this work	10.1	5.3	19.7	7.9	5.0
14	10.8	5.9	20.3	8.6	4.2
15	9.7	5.5	19.9	9.9	7.0
16	10.7	5.9	20.1	8.8	4.4
			Experiment		
20			<22.0		<6.0
21					$\simeq 6.4$

[a] All the theoretical values correspond to $\Gamma_{15}^{v} \rightarrow \Gamma_{15}^{c}$.

[b] All the theoretical values correspond to $\Gamma_{15}^{v} \rightarrow X_{1}^{c}$.

states required to calculate the radial charge density $\rho_i(r)$ is performed using three special **k** points in the Brillouin zone (BZ).[19] Since the electronic charge density is spherically symmetric in each polyhedron, the integration of the Poisson's equation is straightforward, leading to the cellular potential to be used in the next SCF cycle. Suitable mixtures of potentials have ensured a rapid convergence of the calculations for BN.

In Fig. 1 the calculated SCF VCM band-structure of zinc-blende–structure BN, along high-symmetry lines in the BZ, is shown. Table I compares the valence-band widths and minimum energy gaps obtained from SCF VCM with the results of the most recent calculations. The entries in Table I include results of an *ab initio* pseudopotential local-density calculations,[14] a minimum-basis linear-combination-of-atomic-orbitals (LCAO) approach with an adjusted indirect gap[15] and a full-potential linear augmented-plane-wave calculation.[16] The experimental results are from soft-x-ray spectroscopy[20] and uv-absorption[21] measurements.

It is gratifying to conclude that the SCF VCM results are in fairly good agreement with those obtained from recent rigorous calculations. The symmetry of the lowest conduction-band state of BN, as it arises from theory, has been subject of controversy in the past. The assignment of the X_1^c point in the BZ for the conduction-band minimum is a common feature of all the calculations compared in Table I. Particularly, the SCF VCM leads to an X_3^c level at 5.6 eV above the X_1^c. This value is also in good agreement with the results obtained from an *ab initio* relativistic pseudopotential method (4.77 eV) and from a relativistic linear-muffin-tin-orbital method (4.93 eV).[22]

Figure 2 shows the total valence radial electronic charge density along the bond direction of BN. The variational solution of the boundary-condition problem in the VCM leads to negligible wave-function mismatch on the cell surfaces. As a consequence, SCF charge densities and potentials are continuous through the cell boundaries. From Fig. 2 we can extract the total valence charge inside the spheres surrounding each atom. These are touching spheres with radii equal to 1.48 a.u. The values $2.33e$ and $4.61e$ were found for the B and N spheres, respectively, leaving about one electronic charge (e) distributed within the two interstitial polyhedra in the unit cell. The total charge density $\rho(r)$ along the bond displays a local maximum within the polyhedron corresponding to N. Although this asymmetric distribution of charge along the bond indicates an ionic character for the BN compound, our results show that the B atom is losing less charge than that inferred from the pseudopotential[14] and (LCAO) (Ref. 15) calculations.

In this report we have presented the SCF version of the VCM and investigated its virtue by carrying out the band-structure calculations of zinc-blende–structure BN.

This paper complements our previous works where the non-SCF version of the method was applied to metallic and covalently bound crystals. The theoretical formulation of the SCF VCM is conceptually simple and the results obtained for zinc-blende–structure BN indicate that the method is fast and accurate.

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[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[2] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[3] L. G. Ferreira and J. R. Leite, Phys. Rev. A **18**, 335 (1978).

[4] M. Farjam and H. B. Shore, Phys. Rev. B **37**, 1059 (1988).

[5] R. K. Nesbet, Phys. Rev. B **30**, 4230 (1984); **33**, 8027 (1986); **38**, 4955 (1988).

[6] L. G. Ferreira and J. R. Leite, Phys. Rev. Lett. **40**, 49 (1978); Phys. Rev. A **20**, 689 (1979).

[7] A. C. Ferraz, E. K. Takahashi, and J. R. Leite, Phys. Rev. B **26**, 690 (1982).

[8] L. G. Ferreira and M. L. De Siqueira, J. Phys. B **16**, 3111 (1983); Phys. Rev. B **34**, 5315 (1986).

[9] L. M. Brescansin, J. R. Leite, and L. G. Ferreira, J. Chem. Phys. **71**, 4923 (1979).

[10] A. C. Ferraz, E. K. Takahashi, and J. R. Leite, Solid State Commun. **44**, 1569 (1982).

[11] A. C. Ferraz, M. I. T. Chagas, E. K. Takahashi, and J. R. Leite, Phys. Rev. B **29**, 7003 (1984); J. R. Leite, A. C. Ferraz, and L. G. Ferreira, Int. J. Quantum Chem. S **13**, 395 (1979); in *Proceedings of the International Symposium on Atomic, Molecular, and Solid-State Theory, Collision Phenomena, Quantum Statistics, and Computational Methods, Flagler Beach, Florida,* edited by Per-Olov Löwdin and Yngve Öhrn (Wiley, New York, 1979).

[12] J. R. Leite, B. I. Bennett, and F. Herman, Phys. Rev. B **12**, 1466 (1975).

[13] A. T. Lino, J. R. Leite, A. C. Ferraz, and E. Takahashi, J. Phys. Chem. Solids **48**, 911 (1987).

[14] R. M. Wentzcovitch, K. J. Chang, and M. L. Cohen, Phys. Rev. B **34**, 1071 (1986), and references therein; R. M. Wentzcovitch, M. L. Cohen, and P. K. Lam, *ibid.* **36**, 6058 (1987).

[15] M. Z. Huang and W. Y. Ching, J. Phys. Chem. Solids **46**, 977 (1985).

[16] K. T. Park, K. Terakura, and N. Hamada, J. Phys. C **20**, 1241 (1987).

[17] D. R. Wiff and R. Keown, J. Chem. Phys. **47**, 3113 (1967).

[18] L. Hedin and B. J. Lundqvist, J. Phys. C **4**, 2064 (1971).

[19] A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973).

[20] V. A. Fomichev and M. A. Rumsh, J. Phys. Chem. Solids **29**, 1015 (1968).

[21] R. M. Chrenko, Solid State Commun. **14**, 511 (1974).

[22] R. M. Wentzcovitch, M. Cardona, M. L. Cohen, and N. E. Christensen, Solid State Commun. **67**, 927 (1988).