

Quasi-classical approach: Electronic structure of cubic boron nitride crystals

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Abstract

Using the new version of the quasi-classical parameterization based on the screened Coulomb-like atomic potentials the band structure and the unit cell total energy are obtained for boron nitride cubic crystal (c -BN). The calculated density of electron states of the upper valence and lower conduction bands reveals that c -BN is an insulator with band gap of $E_g = 7.1$ eV. The quasi-classical estimation of lattice constant is found to be $a = 3.588$ Å.

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1. Introduction

Boron nitride with the general formula BN exists in the form of diatomic molecule, fullerene-like nanoparticles and some crystalline modifications. Among them the dense cubic zinc-blende phase (c -BN) is of special scientific and technological interest. The present work is aimed to establish without ambiguity the c -BN electronic structure's main features as such kind theoretical investigation is the indispensable step on the knowledge of its properties making this material useful for applications.

The paper is organized as follows. At first we review the quasi-classical approach used. Then results of constituent atoms parameters, c -BN density of electron states, and its lattice constant calculations are presented in comparison with earlier data. Finally, brief conclusions are given concerning the method accuracy.

2. Quasi-classical approach

The quasi-classical expression for bounded states energies obtained by Maslov [1] yields [2] that for the atomic potential the precise and quasi-classical electronic spectra are close to one another. On this basis the

quasi-classical approach to the calculation of molecular and crystalline electronic structures has been developed [3–7]. Its essential content can be described as follows.

The quasi-classical limit means the truncation of electron state exponential tails in the classically forbidden regions. In this case space-averaged orbital charge density $\rho_i(r)$ of the i th electron equals zero outside the classical turning points and a nonzero constant within the range between them (all relations are given in atomic units (au)),

$$\begin{aligned}\rho_i(r) &= 0 \quad (r < r'_i), \\ &= \frac{3}{4\pi(r_i''^3 - r_i'^3)} \quad (r'_i < r < r_i''), \\ &= 0 \quad (r_i'' < r),\end{aligned}$$

$$i = 1, 2, 3, \dots, Z.$$

Here r denotes the distance from the center of atom, r'_i and r_i'' are the electron classical turning points radii ($r'_i < r_i''$), and Z is the atomic number. At the ground state atomic nucleus inner turning point coincides with the center (its radius $r'_0 = 0$) and thus space-averaged nucleus charge density $\rho_0(r)$ equals

$$\begin{aligned}\rho_0(r) &= \frac{3Z}{4\pi r_0''^3} \quad (r < r_0''), \\ &= 0 \quad (r_0'' < r),\end{aligned}$$

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where r_0'' is the nucleus outer turning point radius. Consequently full atomic charge density $\rho(r)$ is expressed by the step-like radial function,

$$\rho(r) = \rho_k \quad (R_{k-1} < r < R_k) \quad k = 1, 2, 3, \dots, q.$$

ρ_k and R_k denote known constants that depend on the electrons and nucleus classical turning points radii ($R_0 = 0, R_0 < R_1 < R_2 < \dots < R_q, R_q < \infty$), and q is the number of charge spherical layers in atom ($q \leq 2Z$).

Using the Poisson equation the radial dependence of the full atomic potential $\varphi(r)$ also can be approximated by the step-like function if substituted by the space-averaged values φ_k inside each of the $R_{k-1} < r < R_k$ regions,

$$\varphi(r) = \varphi_k \quad (R_{k-1} < r < R_k) \quad k = 1, 2, 3, \dots, q,$$

$$\varphi_k = \frac{3A_k(R_k^2 - R_{k-1}^2)}{2(R_k^3 - R_{k-1}^3)} + \frac{3B_k(R_k^5 - R_{k-1}^5)}{5(R_k^3 - R_{k-1}^3)} + C_k,$$

$$A_k = \sum_{i=1}^{k-1} \frac{4\pi\rho_i(R_i^3 - R_{i-1}^3)}{3} - \frac{4\pi\rho_k R_{k-1}^3}{3},$$

$$B_k = -\frac{2\pi\rho_k}{3},$$

$$C_k = \sum_{i=k+1}^q 2\pi\rho_i(R_i^2 - R_{i-1}^2) + 2\pi\rho_k R_k^2.$$

In quasi-classical limit in the region $r > R_q$ charge density and potential vanish identically ($\rho(r) \equiv 0$ and $\varphi(r) \equiv 0$). Thus finite parameter R_q is the quasi-classical atomic radius.

In the case of expressing crystalline (molecular) potential by the superposition of the step-like atomic potentials the crystalline (molecular) electronic structure is determined by solving the secular equation in which matrix elements are the linear combinations of the overlapping volumes for every possible triad of spheres with radii R_k centered at the atomic sites. These matrix elements are calculated using the universal function $V = V(r_1, r_2, r_3; d_{12}, d_{13}, d_{23})$, which expresses the dependence of the three spheres' intersection region volume V upon their radii r_1, r_2, r_3 and inter-central distances d_{12}, d_{13}, d_{23} . The explicit solution of this geometrical problem has been obtained in Ref. [8]: V is the continuous piecewise analytical combination of algebraic and inverse trigonometric functions.

The quasi-classical static and vibration energies of crystal (molecule) are calculated using another universal function $W = W(r_1, r_2; d_{12})$ and its partial derivative $\partial W(r_1, r_2; d_{12})/\partial d_{12}$. W expresses the dependence of two spheres' intersection region volume upon their radii r_1, r_2 and inter-central distance d_{12} . W and $\partial W/\partial d_{12}$ are the continuous piecewise algebraic functions (see Ref. [8]).

The elaborated quasi-classical method was applied to some boron compounds. Namely electron energy spectra and vibration frequencies of B_2 , BC , BN and BO diatomic molecules, and also the density of states of hexagonal boron nitride ($h-BN$) layered crystal were obtained [9–11]. For this purpose the screening factor of the potential $\varphi_i(r)$ affecting the given i th electron in constituent atom was approximated by the radial polynomial.

3. Parameters of constituent atoms

In the present work we investigate cubic phase of boron nitride ($c-BN$) using the new version of the quasi-classical parameterization based on the Coulomb-like atomic potentials,

$$\varphi_i(r) = Z_i/r.$$

The values of effective charge numbers of the screened nucleus Z_i can be obtained by fitting quasi-classical energetic levels to the Hartree-Fock ones E_i (see Ref. [12]),

$$Z_i = n_i \sqrt{-2E_i},$$

where n_i is the i th electron principal quantum number. The Coulomb-like potential is less detailed, but after its substitution into the quasi-classical quantization rule further simplification is not needed and we get exact formulas for the electron classical turning point radii,

$$r_i' = \frac{n_i - \sqrt{n_i^2 - l_i(l_i + 1)}}{\sqrt{-2E_i}},$$

$$r_i'' = \frac{n_i + \sqrt{n_i^2 - l_i(l_i + 1)}}{\sqrt{-2E_i}}.$$

Here l_i is the i th electron orbital quantum number.

In this case the electron cloud effective potential $\varphi_0(r)$ affecting the nucleus is Coulomb-like as well,

$$\varphi_0(r) = -\frac{1}{Z-1} \left(Z^2 - \sum_{i=1}^Z Z_i \right) / r$$

and consequently the nucleus classical turning point radius equals

$$r_0'' = \frac{2(Z-1)}{Z^2 \left(Z^2 - \sum_{i=1}^Z Z_i \right)}.$$

Table 1
Nucleus and electrons classical turning points radii in atoms B and N

	B		N	
	r_i' (au)	r_i'' (au)	r_i' (au)	r_i'' (au)
Nucleus	0	0.027585	0	0.009446
1s	0	0.509802	0	0.357724
2s	0	4.021346	0	2.909074
2p	0.744122	4.337060	0.549803	3.204489

Table 2

Quasi-classical parameters of the charge density and potential distributions in atoms B and N

k	B			N		
	R_k (au)	ρ_k (au)	φ_k (au)	R_k (au)	ρ_k (au)	φ_k (au)
1	0.027585	56865.14	210.5468	0.009446	1982589	878.4581
2	0.509802	-3.61095	8.882329	0.357724	-10.4497	20.22523
3	0.744122	-0.00734	3.652920	0.549803	-0.01939	8.464698
4	4.021346	-0.01028	0.206072	2.909074	-0.04127	0.509668
5	4.337060	-0.00294	0.000614	3.204489	-0.02188	0.003993

Using the stated relations we have calculated the requested quasi-classical parameters of the constituent atoms B and N . The values are listed in Tables 1 and 2.

4. Density of electron states

On the ground of above-described quasi-classical approach (choosing the B and N atoms piecewise-constant valence orbitals as basis set) the solutions for the secular equation have been obtained. Quasi-classically calculated density of electron states (DOS) for the $c - BN$ with respect to the Fermi level is presented in Fig. 1. It reveals that $c - BN$ is an insulator with band gap of $E_g = 7.1$ eV.

In outline it is similar to the DOS calculated for this material earlier using OPW [13–15], tight-binding [16], variational APW [17], orthogonalized LCAO [18], full-potential linear APW [19], and LDA orthogonalized LCAO [20] methods. However, the available experimental and theoretical data do not agree with each other in the value of the band gap. One can recognize this inconsistency from Table 3 where our result is reported in comparison to other selected works. Some of these theoretical methods underestimate the band gap of $c - BN$ ($E_g < 6$ eV) whereas others overestimate its value ($E_g > 8$ eV). Nevertheless both of discrepancies may be attributed to the uncertainties in the knowledge of the crystalline potential. Namely when the self-interaction-corrected potential is employed E_g increases [33] and when the appropriate bond ionicity is included E_g decreases [17]. It seems that value of band gap for $c - BN$ lies over range from 6 to 8 eV which does not contradict the experimental data. The quasi-classically calculated band gap falls in same energy region.

5. Lattice constant

The quasi-classically calculated total energy of $c - BN$ crystal unit cell E plotted as function of lattice constant a is shown in Fig. 2. Before us the total and cohesive energies of boron nitride in the cubic structure

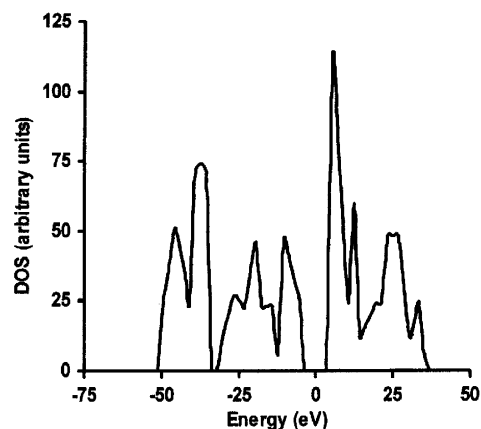


Fig. 1. Quasi-classically calculated density of electron states for $c - BN$ crystal.

Table 3

$c - BN$ band gap

E_g (eV)	Method	Reference
8.0	Reflection spectra	[21]
7.2	Semi-empirical APW	[22]
6.0 ± 0.5	X-ray K-emission and quantum yield spectra	[23]
6.4 ± 0.5	Ultraviolet absorption spectra	[24]
8.7	LCAO- $X\alpha$	[25]
8.0	Empirical PP	[26]
11.3	Exact-exchange HF	[27]
9.16	Variational APW without ionicity	[17]
8.60	Variational APW with fractional ionicity	[17]
7.0	Orthogonalized LCAO	[18]
4.4	Full-potential linear APW	[19]
4.20	KS equations using non-local PP	[28,29]
5.18	LDA orthogonalized LCAO	[20]
6.272	Optical-absorption edge	[30]
6.2	Soft-X-ray and total photon yield spectra	[31]
4.4	LDA with uncorrected PP	[32]
6.1	LDA with self-interaction and relaxation-corrected PP	[32]
6.0	Optical band gap	[33]
6.1–6.4	Linear MTO method with X-ray emission and absorption spectra	[34]
7.1	Quasi-classical approximation	This work

versus lattice constant or unit cell volume were determined applying LDA nonlocal PP [28], LDA orthogonalized LCAO [20], linear MTO [35], and LDA plane-wave PP [36,37] methods. Our $E - a$ dependence and all these curves are similar in shape: parabolic in the vicinity of minimum but with different slopes far right and far left from this point.

The equilibrium structure of $c - BN$ was obtained by minimization of such energy functions with respect to the lattice constant. The results from analyzing the $E - a$ curves together with other theoretical values of the parameter a are summarized in Table 4. These

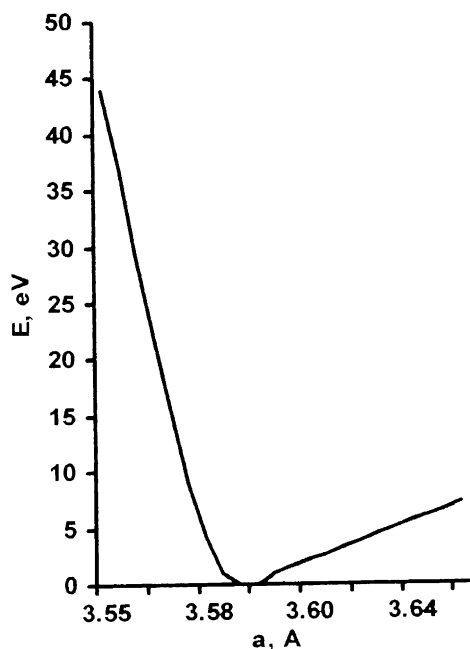


Fig. 2. Quasi-classically calculated c – BN crystal unit cell energy versus lattice constant (with respect to the ground state energy).

Table 4
 c – BN theoretical lattice constant

a (Å)	Method of calculation	Reference
3.59	Full-potential linear APW	[19]
3.6492	LDA non-local PP	[28]
3.625	Linear MTO first basis set	[38]
3.618	Linear MTO second basis set	[38]
3.62	Linear MTO	[35]
3.593	LDA plane-wave PP for static lattice	[36]
3.611	LDA plane-wave PP with zero-point vibration contributions	[36]
3.658	GGA	[36]
3.57	LDA uncorrected PP	[32]
3.68	LDA self-interaction-corrected PP	[32]
3.591	LDA plane-wave PP	[37]
3.58 ± 0.04	Variational Monte Carlo	[39]
3.627	LDA orthogonalized LCAO	[20]
3.62	Short-range force-field modeling	[40]
3.588	Quasi-classical approximation	This work

theoretical data concerned c – BN lattice constant lie over the wide range from 3.54 to 3.68 Å. The quasi-classically calculated lattice constant, $a = 3.588$ Å, is in good agreement with the measured value, $a = 3.615$ Å [41], with a deviation of $\sim 0.7\%$.

The quasi-classical estimation of zero-point vibration energy for this lattice constant is found to be 0.33 eV/mol which is exactly the same value that was obtained [38] from the Debye empirical model and very close to 0.32 eV/mol evaluated [36] from theoretical phonon spectra. It should be noted that quasi-classical lattice constant of c – BN only slightly affected by the zero-point vibrations.

6. Conclusions

As the quasi-classical atomic radii are the finite parameters the quasi-classical matrix elements in secular equation for the crystalline electronic structure and the quasi-classical energy of crystal contain a finite number of summands. Thus this approach is free from ambiguous errors arisen from series termination. Besides the nonzero terms can be calculated analytically using universal geometrical functions. The results of present study of c – BN electronic structure show that the expected accuracy of the quasi-classical determinations of energetic and structural parameters would be especially good in case of boron compounds.

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