Quasi-classical Determination of Electronic Energies and Vibration Frequencies in Boron Compounds

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Substance is a quasi-classical system in sense of Maslov criterion. The interatomic potential is an algebraic function of distance in the first quasi-classical approximation, and molecular or crystalline electronic structure is obtained by solving the secular equation in which matrix elements are expressed by volumes of intersections of the classically accessible areas for electron states of atoms. The quasi-classical estimates of electron orbital energies and vibration frequencies for diatomic molecules B_2, BC, BN, and BO are found. The band gap of 0.14 au was established as a result of the quasi-classical calculations of the density of states for *h*-BN layered crystal. © **2000 Academic Press**

The atomic potential $U(r)$ in general does not meet the standard Wenzel–Kramers–Brillouin (WKB) quasi-classical requirement on spatial smoothness, $|dl(r)/dr| \ll 2\pi$ ($l(r)$ is the electron de Broglie wave length at the distance of r from the center) (1), due to Coulomb singularity in the nucleus position, as well as for electronic shell effects. However, beginning from Bohr's fundamental work (2) up to nowadays the semiclassical analysis of the electronic spectrum is widely used for light atoms and their complexes (see, for instance, (3,4)). Besides, substances can be treated within the local density approximation by using the total energy functional in the form of quasi-classical expansion (5).

Success of quasi-classical approaches is explained by the diffusion of atomic potentials. The solution of the Riccaty-type Schrödinger equation is expressed by the series in terms of powers of the parameter $x = 1/r_0 (2u_0)^{1/2}$ (all relations are given in atomic units), where potential is written as $U(r) = u_0 F(r/r_0)$ (the parameters u_0 and r_0 have the dimensions of energy and distance respectively, whereas function F is nondimensional), and the quasi-classical expression for bounded states energies obtained by Maslov (6) yields that precise and WKB spectra are close to one another

independently from the potential smoothness properties if $x^2 \ll 1$ (7). The presence of electron exchange within the atom determines its finite sizes (8): the behavior of the electron density $n(r)$ in the asymptotic region $r > R$ can be correctly parameterized by the form $n(r) = 0$, where R is the certain finite parameter ($R < \infty$) several times larger than Bohr radius, $R \gg 1$ (9). Consequently in this region atomic potential practically equals 0, and in the region $0 \le r \le R$ it can be written as $U(r) = (Z/R)(f(r/R)/(r/R))$. Here Z is the atomic number, $Z \ge 1$, and $f(r/R)$ is the electron screening factor for the nuclear potential Z/r, $0 \le f(r/R) \le 1$, $f(0) = 1$, $f(1) = 0$. This form indicates that $u_0 \sim Z/R$ and $r_0 \sim R$. Therefore, in the case of atomic potential $x^2 \sim 1/2ZR \ll 1$, and both the atoms and polyatomic structures (molecules and crystals) are quasi-classical systems in sense of Maslov criterion.

On this basis the quasi-classical approach to the description of molecular and crystalline electronic structures has been elaborated (10, 11).

Since the screening factor is an analytic function defined on the finite interval it can be approximated by the polynomial. Using the quadratic approximation we obtain the potential $U_i(r)$ affecting the given ith electron,

$$U_i(r) = 1/r + (Z_i - 1)(1 - r/R_i)^2/r, \qquad [1]$$

where Z_i is the effective charge number of the screened nucleus and R_i is the effective radius of the charge cloud of other electrons. By its substitution into the quantization rule and further simplification we get the classical turning points radii,

$$r_{i1} = n(n - (n^2 - l(l+1))^{1/2})/Z_i,$$
$$r_{i2} = n(n + (n^2 - l(l+1))^{1/2})/Z_i. \qquad [2]$$

Here n and l are the principal and orbital quantum numbers respectively. The values of Z_i and R_i can be obtained by fitting quasi-classical energetic levels E_i and mean orbital radii of electrons $\bar{r}_i$,

$$E_i = -Z_i^2/2n^2 + 2(Z_i - 1)/R_i$$
$$- (1 - 1/Z_i)(3n^2 - l(l+1))/2R_i^2, \qquad [3]$$

$$\bar{r}_i = 3n^2(2n^2 - l(l+1))/(4n^2 - l(l+1))Z_i, \qquad [4]$$

to the Hartree-Fock ones.

The semiclassical limit means truncation of electronic state exponential tails in the classically forbidden regions. In this case space-averaged orbital wave function $\psi_i(r)$ of the ith electron equals 0 outside the classical turning points and a nonzero constant within the range between them,

$$\psi_i(r) = 0 \qquad\qquad (0 < r < r_{i1})$$
$$= (3/4\pi(r_{i2}^3 - r_{i1}^3))^{1/2} \quad (r_{i1} < r < r_{i2})$$
$$= 0 \qquad\qquad (r > r_{i2}). \qquad [5]$$

The spherical layers $r_{i1} < r < r_{i2}$ include corresponding classical orbits.

The full atomic potential in general can be written in the form

$$U(r) = \sum_{i=1}^{z} u_i(r) + Z/r = U_i(r) + u_i(r), \qquad [6]$$

where $u_i(r)$ denotes the potential of the ith electron. Using Eqs. [1] and [6] and the Poisson equation, the radial dependencies of the full atomic potential $U(r)$ and atomic charge density $n(r)$ can be expressed by piecewise analytical functions

$$U(r) = \sum_{i=k+1}^{z} \frac{Z_i - 1}{Z - 1}(1 - r/R_i)^2/r = A_k/r + B_k + C_k r,$$

$$n(r) = \sum_{i=k+1}^{z} \frac{Z_i - 1}{Z - 1}(\delta(\hat{r}) - 1/2\pi R_i r) = A_k \delta(\hat{r}) - C_k/2\pi r$$

$$(R_k \le r < R_{k+1}, k = 0, 1, 2, \ldots, Z), \qquad [7]$$

where $R_0 = 0$ and $R_{Z+1} = \infty$; $U(r) = 0$ and $n(r) = 0$ for $r > R_Z$; A_k, B_k, and C_k denote constants that depend on the parameters Z, Z_i, and R_i; while δ is a delta function.

According to Eq. [7] electron density drops at the points $r = R_k$, $k \ge 1$. Consequently $n(r)$ and $U(r)$ may be approximated by a step-like functions if substituted by the space-averaged values inside each of the (R_k, R_{k+1}) regions,

$$U(r) = 3A_k(R_{k+1}^2 - R_k^2)/2(R_{k+1}^3 - R_k^3) + B_k$$
$$+ 3C_k(R_{k+1}^4 - R_k^4)/4(R_{k+1}^3 - R_k^3) = U_k,$$

$$n(r) = A_k\delta(\hat{r}) - 3C_k(R_{k+1}^2 - R_k^2)/4\pi(R_{k+1}^3 - R_k^3)$$
$$= A_k\delta(\hat{r}) + n_k$$

$$(R_k \le r < R_{k+1}, k = 0, 1, 2, \ldots, S), \qquad [8]$$

where k stands for electronic subshells (and not electrons); S is the total number of subshells in an atom; again $R_0 = 0$, $R_{S+1} = \infty$; and U_k and n_k denote known parameters.

The association of atoms into the molecular and crystalline structures somewhat modifies the spatial distribution of the valence electrons. The configuration of atomic core electrons practically does not change. Thus, initial molecular and crystalline potentials can be approximated by the superposition of the atomic potentials. In the case of expressing atomic and consequently molecular or crystalline potential in terms of step-like functions, where the linear combinations of the piecewise-constant atomic orbitals are chosen as the basis set, the molecular and crystalline electronic structures are 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 finite radius of R_k, r_{k1}, or r_{k2} centered at the atomic sites.

Two main conclusions emerge from the above discussion. First, the matrix elements contain a finite number of summands without series termination. Secondly, one can regard the task of nonzero terms calculation solved if the universal function $V = V(r_1, r_2, r_3; D_{12}, D_{13}, D_{23})$ is known which expresses the volume dependence of the three-sphere intersection region upon their radii r_1, r_2, r_3 and intercentral distances D_{12}, D_{13}, D_{23}. So, the proposed version of the quasi-classical approach reduces the physical problem of the molecular and crystalline electronic structures calculation to a geometrical one.

The volume V of the intersection region is expressed as a continuous piecewise analytical combination of algebraic and inverse trigonometric functions (the explicit solution will be published as a separate paper),

$$V = V_i + V_j + V_k, \qquad [9]$$

$$V_i = 0 \qquad (\cos(t_i) \le \cos(t_i'))$$
$$= W_i \qquad (\cos(t_i') \le \cos(t_i) \le \cos(t_i''))$$
$$= W_{ij} \qquad (\cos(t_i) \ge \cos(t_i''), d_{ij} \ge d_{ik})$$
$$= W_{ik} \qquad (\cos(t_i) \ge \cos(t_i''), d_{ik} \ge d_{ij}), \qquad [10]$$

$$W_{ij} = 0 \qquad\qquad (D_{ij} \leq r_i - r_j)$$

$$= 4\pi r_i^3/3 \qquad\qquad (D_{ij} \leq r_j - r_i)$$

$$= (\pi/3)(2r_i + d_{ij})(r_i - d_{ij})^2 \quad (|r_i - r_j| \leq D_{ij} \leq r_i + r_j)$$

$$= 0 \qquad\qquad (r_i + r_j \leq D_{ij}), \qquad [11]$$

$$W_i = (h/3 \sin(t_i))(2d_{ij}d_{ik} - (d_{ij}^2 + d_{ik}^2)\cos(t_i))$$

$$- d_{ij}(r_i^2 - d_{ij}^2/3)\arccos((d_{ik} - d_{ij}\cos(t_i))/r_{ij}\sin(t_i))$$

$$- d_{ik}(r_i^2 - d_{ik}^2/3)\arccos((d_{ij} - d_{ik}\cos(t_i))/r_{ik}\sin(t_i))$$

$$+ (2r_i^3/3)\arccos((d_{ij}d_{ik} - r_i^2\cos(t_i))/r_{ij}r_{ik}), \qquad [12]$$

$$h^2 = ((r_i^2r_j^2 + r_k^2D_{ij}^2)(D_{ik}^2 + D_{jk}^2 - D_{ij}^2)$$

$$+ (r_i^2r_k^2 + r_j^2D_{ik}^2)(D_{ij}^2 + D_{jk}^2 - D_{ik}^2)$$

$$+ (r_j^2r_k^2 + r_i^2D_{jk}^2)(D_{ij}^2 + D_{jk}^2 - D_{jk}^2)$$

$$- (r_i^2D_{jk}^4 + r_j^2D_{ik}^4 + r_k^2D_{ij}^4)$$

$$- D_{ij}^2D_{ik}^2D_{jk}^2)/(2(D_{ij}^2D_{ik}^2 + D_{ij}^2D_{jk}^2 + D_{ik}^2D_{jk}^2)$$

$$- (D_{ij}^4 + D_{ik}^4 + D_{jk}^4)), \qquad [13]$$

$$\cos(t_i) = (D_{ij}^2 + D_{ik}^2 - D_{jk}^2)/2D_{ij}D_{ik}, \qquad [14]$$

$$\cos(t_i') = (d_{ij}d_{ik} - r_{ij}r_{ik})/r_i^2, \qquad [15]$$

$$\cos(t_i'') = (d_{ij}d_{ik} + r_{ij}r_{ik})/r_i^2, \qquad [16]$$

$$r_{ij}^2 = (2(r_i^2r_j^2 + r_i^2D_{ij}^2 + r_j^2D_{ij}^2) - (r_i^4 + r_j^4 + D_{ij}^4))/4D_{ij}^2, \qquad [17]$$

$$d_{ij} = (r_i^2 - r_j^2 + D_{ij}^2)/2D_{ij}, \qquad [18]$$

$$(ijk) = (123), (321), (231). \qquad [19]$$

Now we can calculate the quasi-classical interatomic potential $P(d)$ as a function of internuclear distance d,

$$P(d) = \frac{1}{2}\int d\hat{r}(n'(r)U''(|\hat{r} - \hat{d}|) + n''(|\hat{r} - \hat{d}|)U'(r)). \quad [20]$$

In the previous and next equations single- and double-primed symbols denote the first and second atoms respectively. Using Eqs. [7] and [8], Eq. [20] gives

$$2P(d) = \sum_{k'=0}^{S'}\sum_{k''=0}^{S''}(n_{k'}'U_{k''}'' + n_{k''}''U_{k'}')(W(R_{k'+1}', R_{k''+1}'', d)$$

$$+ W(R_{k'}', R_{k''}'', d) - W(R_{k'+1}', R_{k''}'', d)$$

$$- W(R_{k'}', R_{k''+1}'', d)) + A_0'\sum_{k''=0}^{S''}(A_{k''}''/d$$

$$+ B_{k''}'' + C_{k''}''d)\theta(d - R_{k''}'')\theta(R_{k''+1}'' - d)$$

$$+ A_0''\sum_{k'=0}^{S'}(A_{k'}'/d + B_{k'}' + C_{k'}'d)\theta(d - R_{k'}')$$

$$\times \theta(R_{k'+1}' - d). \qquad [21]$$

TABLE 1
Quasi-classical Parameters of the Potential and Charge Distributions in Atoms

Atom	k	n	l	$Z_k{}^a$	R_k(au)	A_k(au)	$-B_k$(au)	C_k(au)	U_k(au)	$-n_k$(au)	r_{k1}(au)	r_{k2}(au)
B	0			5	0	3.151	2.078	0.3864	0.6342	0.03982		
	1	1	0	4.601	2.317	1.351	0.523	0.0509	0.0332	0.00213	0	0.435
	2	2	0	3.035	4.964	0.333	0.113	0.0096	0.0005	0.00028	0	2.636
	3	2	1	2.332	5.890						0.502	2.928
C	0			6	0	3.749	2.728	0.5697	0.9622	0.06883		
	1	1	0	5.597	1.976	1.911	0.867	0.0988	0.0574	0.00490	0	0.357
	2	2	0	3.776	4.176	0.800	0.335	0.0351	0.0009	0.00125	0	2.119
	3	2	1	3.001	4.773						0.390	2.276
N	0			7	0	3.910	3.237	0.7643	1.140	0.1052		
	1	1	0	6.579	1.734	2.492	1.312	0.1732	0.085	0.0100	0	0.304
	2	2	0	4.505	3.588	1.324	0.661	0.0824	0.001	0.0035	0	1.776
	3	2	1	3.647	4.007						0.321	1.872
O	0			8	0	3.990	3.666	0.9464	1.238	0.1427		
	1	1	0	7.538	1.583	3.029	1.843	0.2807	0.102	0.0182	0	0.265
	2	2	0	5.254	3.159	1.814	1.074	0.1590	0.001	0.0077	0	0.523
	3	2	1	4.174	3.377						0.281	1.636

$^a Z_0 = Z$.

TABLE 2
Bond Orbital Energies in Diatomic Molecules

Molecule	$-e_1$(au)	$-e_2$(au)	$-e_3$(au)	Method	Reference
B_2	0.7079	0.2321		Theoretical	This work
	0.6776^a	0.3412^b		Theoretical	(12)
	—	0.3495^c		Theoretical	(12)
BC	0.9639	0.3531		Theoretical	This work
	—	0.386 ± 0.039^d		Experimental	(13)
BN	1.1636	0.4018		Theoretical	This work
BO	1.3164	0.7453	0.4323	Theoretical	This work
	1.3038^e	0.8855^f	0.4960^g	Theoretical	(14)
	1.3535^h	0.9674^i	0.5387^j	Theoretical	(14)
	—	—	0.496 ± 0.050^d	Experimental	(13)

$^a 2\sigma_g$.
$^b 1\pi_u$.
$^c 2\sigma_u$.
^{d} Ionization potential.
$^e 0.428(sp^{0.71})_B + 0.904(sp^{1.17})_O$.
$^f (sp^{1.11})_O$.
$^g 0.481(p)_B + 0.877(p)_O$.
$^h 0.422(sp^{2.09})_B + 0.907(sp^{0.88})_O$.
$^i (sp^{0.84})_O$.
$^j 0.325(p)_B$.

$W = W(R', R'', D)$ is the universal algebraic function,

$$W = 0 \quad (R' + R'' \leq D))$$

$$= \pi(R' + R'' - D)^2((R' + R'' + D)^2$$

$$- 4(R'^2 + R''^2 - R'R''))/12D \quad (|R' - R''| \leq D \leq R' + R'')$$

$$= 4\pi R'^3/3 \qquad (D \leq R'' - R')$$

$$= 4\pi R''^3/3 \qquad (D \leq R' - R''), \qquad [22]$$

which expresses the volume dependence of two spheres' intersection region upon their radii R' and R'', and intercentral distance D. θ is the step function. The integral has been calculated for the step-like approximation except for the terms with delta functions where piecewise analytical expression has been used for the potential.

The vibration frequency w can be determined by adjusting the $P(d)$ curve to the harmonic potential in the vicinity of $d = d_{\min}$,

$$P(d) - P(d_{\min}) = Mw^2(d - d_{\min})^2/2, \qquad [23]$$

where M is the reduced mass.

In the present work the elaborated quasi-classical method is applied to some boron compounds. As it is known, this class contains many important molecular compounds and crystalline materials with extremely wide variations of electronic structure types. Namely, electron energy spectra and vibration frequencies of B_2, BC, BN, and BO diatomic molecules have been studied, and also the density of states (DOS) of h-BN crystal has been obtained.

Preliminarily we have calculated the requisited quasi-classical parameters of the potential and charge distribu-
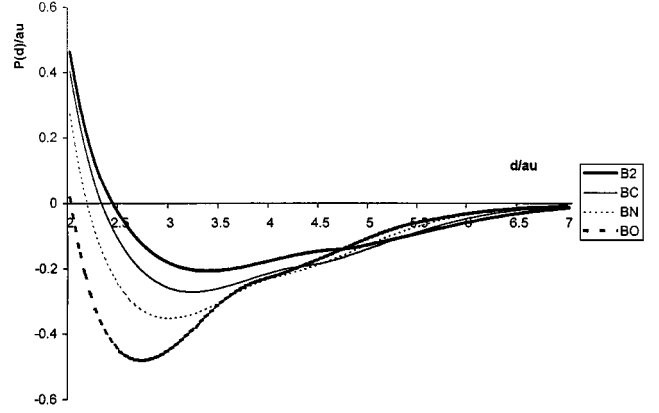

FIG. 1. Quasi-classically calculated interatomic potentials for diatomic molecules B_2, BC, BN, and BO versus internuclear distances.

tions in the constituent atoms B, C, N, and O. The values are presented in Table 1. For h-BN $(r_{32})_B + (r_{32})_N = 4.800$ au < 6.294 au $= c/2$ ($c/2$ is the distance between neighboring layers). Thus the quasi-classical B and N atomic orbitals of different layers do not overlap, and h-BN must be considered as a two-dimensional crystal. In a semiclassical limit, the three-dimensional structure of the h-BN crystal influences the electron spectrum only through the potential.

Energies e_1, e_2, and e_3 of the quasi-classically calculated bond orbitals in diatomic molecules, as well as available theoretical and experimental data, are listed in Table 2. One can recognize that the expected errors of the quasi-classical approach to the determination of low-lying valent states of boron compounds make up a few percent.

The results from analyzing the obtained $P(d)$ curves (Fig. 1), together with some earlier data, are summarized in Table 3.

We have applied the valence orbital basis set ($k = 2, 3$) and obtained solutions for the secular equation for a mesh of 7351 points in a quarter of the first Brillouin zone for layered h-BN crystal. Calculated DOS $N(E)$ with respect to the Fermi level is presented in Fig. 2. The quasi-classical approach reveals that h-BN is an insulator with band gap of

TABLE 3
Vibration Frequencies of Diatomic Molecules

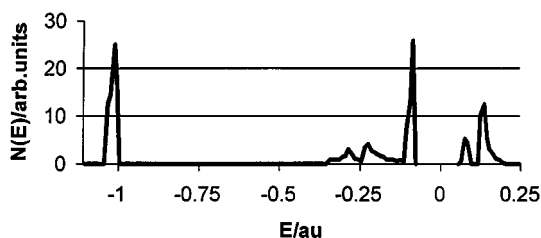| Molecule	w (10^{-3} au)	Method	Reference
B_2	4.80	Theoretical	This work
	4.7900	Experimental	(13)
BC	6.03	Theoretical	This work
	5.194	Theoretical	(15)
BN	6.54	Theoretical	This work
	6.9010	Experimental	(13)
BO	9.17	Theoretical	This work
	8.59176	Experimental	(13)
	8.821	Theoretical	(14)

FIG. 2. Quasi-classically calculated DOS for layered *h*-BN crystal.

$E_g = 0.14$ au. This value does not contradict the theoretical and experimental data reported earlier (16), which lie over wide ranges from 0.09 to 0.47 au and from 0.12 to 0.26 au respectively. $E_g = 0.14$ au is somewhat less than the band gap of 0.17 au obtained in (17) using the full-potential linear augmented-plane-wave method, but it coincides with *h*-BN electronic structure calculations that take into account interlayer interaction (18). In outline our *h*-BN valence band structure is similar to the DOS histograms calculated using tight-binding approximation for hexagonal crystal layers (19) and the orthogonalized-plane-wave method (20) modified on the basis of X-ray experimental data (21).

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