

Semi-empirical LUC-INDO calculations for the effect of pressure on the electronic structure of diamond

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A self-consistent LUC (Large Unit Cell) formalism on the basis of semi-empirical INDO (Intermediate Neglect of Differential Overlap) Hamiltonians has been used to study the electronic properties of diamond and to investigate the pressure dependence of these properties. The calculated properties are in good agreement with the experiments except the conduction band width. The increase of pressure on diamond is predicted to cause the following effects; an increase of the valence and conduction band widths with a decrease of the direct band gap, an increase of the electronic occupation probability for the p orbital with a decrease of this probability for the s orbital, and a decrease of the x-ray scattering factor.

1 Introduction

The band theory of solids is usually employed to consider characteristics of the electronic structure of a crystal which are associated with the potential periodicity and the corresponding electronic-state delocalization over the crystal, namely, the electronic energy bands, effective masses, etc. The electronic and structural properties of solids are a subject of considerable interest in both fundamental and applied physics. Even though remarkable progress has been achieved in a wide variety of problems, determination of the electronic and structural properties remains a theoretical challenge. Up to present, band structure calculations are still subject to immense numerical efforts. Among the methods used in this field is the self-consistent LUC-INDO method in the linear combination of atomic orbitals (LCAO) approximation. This method, which had been already successfully employed for a long time in molecular theory, has gained wide acceptance in calculations of the electronic structure of crystals. The LUC-INDO method compares well in accuracy with other approaches while being at the same time, the best starting approximation to take into account electronic correlations [1]. This method has been used in the present work to study the electronic properties of diamond and to investigate the effect of pressure on these properties.

The electronic structure, lattice constant, bulk modulus, and other physical properties of diamond have been extensively studied and are well-known [2-11]. Recently, Occelli et al. [12] have measured experimentally very accurate values of the lattice constant, bulk modulus, and pressure derivative of the bulk modulus. The present work aims to theoretically determine the energy bands, orbital hybridization, bulk modulus, x-ray scattering factors, valence charge distribution, and then to investigate the effect of pressure on these properties using the self-consistent LUC formalism on the basis of semi-empirical INDO Hamiltonians.

2 Theoretical and computational details

Quantum mechanics offers the only possible way for the solution of many problems in physics and chemistry. A quantum-chemical semi-empirical INDO method developed especially for crystals [13] is used in the present work. This quantum computational formalism has been used with great success especially exploiting the so-called LUC (Large Unit Cell) model [14]. Within the method each molecular orbital is constructed as a linear combination of atomic orbitals [13] in order to express the wave function of the system. Each energy value is calculated by the HF self-consistent field method and the total energy of the system is obtained. The basic idea of LUC is in computing the electronic structure of the unit cell extended in a special manner at $k=0$ in the reduced Brillouin zone. This equivalent to a band structure calculation at those k points; which transform to the Brillouin zone center on extending the unit cell [14].

Using the LCAO, the crystal wave function in the LUC-INDO formalism is written in the following form:

$$\Psi_{\alpha}(k, r) = \sum_u \sum_p^{\text{cells basis}} \exp(ik \cdot R_u) C_{p\alpha}(k) \phi_p(r - R_u) \quad (1)$$

where $C_{p\alpha}$ are the orbital expansion coefficients and R_u is the lattice translation vector. The atomic orbitals used for the LCAO procedure form the basis set of the calculation. Slater-type orbitals (STO) [13] are used in the present work. These orbitals have the radial form

$$R_{nl}(r) = \frac{(2\zeta)^{n+1/2}}{(2n!)^{1/2}} r^{n-1} \exp(-\zeta r) \quad (2)$$

where ζ is the orbital exponent. The expectation value of the electronic energy is given by

$$\varepsilon = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \quad (3)$$

The total Hamiltonian for a microcrystal consisting of \tilde{N} electrons may be written as

$$H = \sum_{\alpha}^{\tilde{N}} \left(-\frac{1}{2} \nabla_{\alpha}^2 - \sum_A^{n_A} Z_A r_{AA}^{-1} \right) + \frac{1}{2} \sum_{\alpha}^{\tilde{N}} \sum_{\beta}^{\tilde{N}} r_{\alpha\beta}^{-1} + \sum_A^{n_A} \sum_B^{n_B} Z_A Z_B R_{AB}^{-1} \quad (4)$$

where Z_A is the core charge, R_{AB} is the distance between the atom A and the atom B, and the summation is over all nuclei. Applying the condition for a stationary state ($\delta\varepsilon = 0$), the Roothan-Hall equations can be obtained [15]:

$$\sum_p (F_{pq}(k) - \varepsilon_{\alpha}(k) S_{pq}(k)) C_{p\alpha}(k) = 0 \quad (5)$$

F_{pq} represents the Fock matrix elements and S_{pq} is the overlap integral for atomic functions Φ_p and Φ_q , and written as

$$S_{pq}(k) = \sum_u \langle \phi_p(r - R_0) | \phi_q(r - R_u) \rangle \exp(ik \cdot R_u) \quad (6)$$

The Fock matrix elements may be expressed as the sum of one and two-electron components:

$$F_{op,uq} = \left\langle \phi_p^o(1) \left| -\frac{1}{2} \nabla_1^2 - \sum_a Z_a r_{1a}^{-1} \right| \phi_q^u(1) \right\rangle + \sum_{v,\lambda} \sum_{rs}^{\text{all cells functions}} P_{rs}^{v\lambda} \left((\phi_p^o \phi_q^u | \phi_r^v \phi_s^\lambda) - \frac{1}{2} (\phi_p^o \phi_r^v | \phi_s^\lambda \phi_q^u) \right) \quad (7)$$

$P_{rs}^{v\lambda}$ is a density matrix element with the form:

$$P_{rs}^{v\lambda} = 2 \sum_k \sum_{\alpha}^{\text{occ}} C_{r\alpha}^*(\mathbf{k}') C_{s\alpha}(\mathbf{k}') \exp[i\mathbf{k}' \cdot (\mathbf{R}_\lambda - \mathbf{R}_v)] \quad (8)$$

Substituting $\mathbf{k}=0$ in Eq. (5) yields

$$\sum (F_{pq}(0) - \epsilon_\alpha(0) S_{pq}(0)) C_{p\alpha}(0) = 0 \quad (9)$$

At this stage there are no approximations in the Fock matrix. However, in the INDO approximation one can utilize the fact that many of the integrals are very small or zero and begin to neglect systematically some of the matrix elements and many approximations can be made. The Fock matrix elements in their final forms in the LUC-INDO formalism are taken from Refs. [16, 17] and used in the present work in the following form:

$$F_{pp}(0) = U_{op,op} - \sum_{B \neq A} \sum_v Z_B \gamma_{AB}^{ov} + \sum_v \beta_A^o (S_{op,vp} - \delta_{ov}) + \sum_r \sum_v P_{rv}(0) \gamma_{AB}^{ov} - \frac{1}{2} \sum_{v \neq o} P_{pp}(0) f(x) \gamma_{AA}^{ov} - \frac{1}{2} \sum_{r \text{ on } A} P_{rv}(0) (\phi_p^o \phi_r^o / \phi_p^o \phi_r^o) \quad (10)$$

$$F_{pq}(0) = \sum_v \beta_{AB}^o S_{op,vq} - \frac{1}{2} P_{pq}(0) \sum_v f(x) \gamma_{AB}^{ov} \quad (11)$$

for p and q on different atomic centers and

$$F_{pq}(0) = \sum_{v \neq 0} \beta_{AB}^o S_{op,vq} - \frac{1}{2} P_{pq}(0) \sum_{v \neq 0} f(x) \gamma_{AA}^{ov} + \frac{1}{2} P_{pq}(0) [3(\phi_p^o \phi_q^o / \phi_p^o \phi_q^o) - (\phi_p^o \phi_p^o / \phi_q^o \phi_q^o)] \quad (12)$$

for p and q on the same atomic center. Where β_{AB}^o is the bonding parameter and γ_{AB} is the average electrostatic repulsion between any electron on atom A and any electron on atom B and can be written as,

$$\gamma_{AB} = \iint \phi_p(1) \phi_q(1) \frac{1}{r_{12}} \phi_p(2) \phi_q(2) d\tau_1 d\tau_2 \quad (13)$$

$U_{\mu\mu}$ is the local core matrix element and given by

$$U_{pp} = -\frac{1}{2} (I_p + A_p) - (Z_A - \frac{1}{2}) \gamma_{AA} \quad (14)$$

where I_μ and A_μ are the ionization potential and electron affinity respectively. $f(x)$ is the modulating function and given by [17]

$$f(x) = \left(\frac{\sin(x)}{x} \right)^2 \quad (15)$$

where x for the 8 atom LUC is given by

$$x = \frac{\pi R_{AB}^{ov}}{a} \quad (16)$$

R_{AB}^{ov} is the distance between the atom A at the central lattice o and the atom B at the ν lattice. The modulating function is multiplied by the density matrix and two electron integral when a summation on the LUCs is made to avoid divergence when including large number of neighbors.

The Roothan-Hall equation are solved by first assuming an initial set of the linear expansion coefficient ($C_{p\alpha}$), generating the density matrix ($P_{rs}^{v\lambda}$), and computing the overlap integral and the first guess of the Fock matrix elements (F_{pq}). Then one can calculate the electronic energy (ϵ_i), and a new matrix of $C_{p\alpha}$ coefficients can be obtained. This procedure is continued until there is no significant variation between the calculated value of $C_{p\alpha}$ and ϵ of the successive iterations. The INDO parameters are optimized by minimizing the deviation between available experimental data and the theoretical results of the final calculations.

The computational procedure and programming of the present work takes the following steps [18]:

1. The positions of atoms and the kind of states associated with every atom are given as input data.
2. The overlap, core Hamiltonian, and two-electron integrals are calculated from the initial basis set.
3. The Fock Hamiltonian is calculated from the initial guess of the wave function, using Slater-type orbitals [13], together with the calculated integrals of step 2.
4. The new eigenvalues are used to calculate the density matrix.
5. The density matrix is used to calculate the total energy.
6. The new eigenvalues are used to calculate a new Fock Hamiltonian.
7. Steps 4 and 5 are repeated and the new electronic energy is compared with the previous one.
8. If the new electronic energy differs from the preceding one by more than a given tolerance (5×10^{-3} eV), steps 6, 4, and 5 are repeated. Otherwise, step 9 is executed.
9. Final Hartree-Fock wave functions are used to calculate the correlation corrections [15,19]. Then the correlated wave functions are obtained.
10. The correlated wave functions are used to obtain the band structure and other physical properties of diamond.

The effect of pressure on the aforementioned properties is investigated by using appropriate input data and executing the above steps.

The initial guess of the wave function is important since the optimum guess reduces the number of iterations performed to obtain the converged electronic energy. A large number of iterations will result in an accumulation of computational errors. The sp^3 initial guess of the wave function is given as an expected linear combination of the atomic states of one cell. We have used a LUC of eight atoms which is the conventional Bravais lattice of diamond having a volume of a^3 , where a is the lattice constant of the Bravais lattice of diamond. Interactions of the atoms in the central Bravais lattice with the surrounding atoms up to the fourth neighbors are included. There are 32 k points within this LUC. The special symmetry points in the Brillouin zone, which are effectively taken into account in the band structure calculations, are Γ_{25} , Γ_1 , Γ_{15} , and X_{4C} . It should be pointed out that the increase of the LUC size will result in an increase of the results accuracy [5], but this complicates the calculations and needs very long time in comparison with the time needed for 8-atom LUC calculations.

3 Results and discussion

3.1 Optimum parameter set

The empirical parameters included in the LUC-INDO method are the orbital exponent ζ , the bonding parameter β^o , $\frac{1}{2}(I_s + A_s)$, and $\frac{1}{2}(I_p + A_p)$. The optimum values of these empirical parameters used for diamond in the present work are listed in Table 1 in comparison with the corresponding values of Harker and Larkins [5].

Table 1 Parameter sets of diamond used in the present work and by Harker and Larkins [5].

Parameter	Ref. [5] value	Present work value
ζ (a.u. ⁻¹)	1.765	1.82
β^o (eV)	-10.2	-10.24
-1/2 (I_s+A_s) (eV)	7.0	6.221
-1/2 (I_p+A_p) (eV)	5.5	4.352

The value of the orbital exponent ζ determines the charge distribution of electrons around the nucleus. This parameter is varied till the total energy reaches its minimum value. Comparing the ζ value for diamond with that given by Clementi and Roetti [20] for atoms and Hehre et al. [15] for molecules, shows that the ζ value for solids and molecules is larger than that for atoms. This indicates the contracted charge distribution in solids and molecules and the diffuse charge distribution in atoms. The value of bonding parameter β^o of diamond is seen to be very much less than that for molecules [21]. This can be explained by noting that the number of bonds in solids is usually higher, then the interaction energy is distributed over these bonds. The value of $\frac{1}{2}(I_s + A_s)$ of diamond is less than the corresponding value of the free atom [22]. This shows that the s orbitals of solids are less connected to their atoms than in the free atom. The same observation is true for the value of $\frac{1}{2}(I_p + A_p)$ for diamond, but it is not the case for other solids [18].

3.2 Electronic and structural properties

Using the computational procedure described in section (2), electronic and structural properties of diamond are determined at 0 K and zero pressure by pure INDO calculations and by INDO calculations with the inclusion of correlation contribution as shown in Table 2 in comparison with other computational and experimental results.

Table 2 Electronic and structural properties of diamond at 0 K and zero pressure determined by the present work ((I) pure INDO and (II) INDO with correlation correction) in comparison with other computational and experimental results.

Property	Computational value				Exp.
	Ref.[5]	Others	Present work		
			(I)	(II)	
Lattice constant (a.u.)	6.73	6.73 [11]	6.73	6.73	6.74 [23] 6.743 [12]
Cohesive energy (eV / atom)	-7.68	-10.16 [24]	-7.35	-7.36	-7.37 [25]
Valence band width (eV)	22.40	24.07 [10]	22.20	22.19	21.0 [26] 24.2 [10]
Conduction band width (eV)	4.70	-	2.67	2.63	8 [27]
Direct band gap (eV)	9.40	7.42 [10]	7.89	7.94	7.3 [10]
Hybridization state	$s^{0.6} p^{3.4}$	-	$s^{0.954} p^{3.046}$		-

It is interesting to note that there is no significant difference between the values extracted from the pure INDO calculations and the corresponding values obtained from the INDO calculations with the inclusion of correlation contribution. This is because that the adopted semi-empirical procedure in some way already includes correlation effects where the INDO calculations are generally fitted to experimental data. The equilibrium lattice constant (a_0) is determined by plotting the total energy as a function of lattice parameter, as shown in Fig.1. The calculated value of the equilibrium lattice constant is in very good agreement with the experimental value [23].

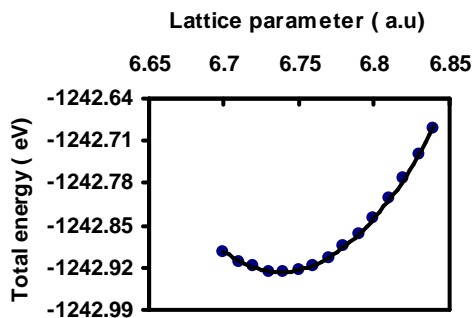


Fig.1 Total energy of diamond as a function of lattice parameter in the present work.

The cohesive energy is calculated from the total energy of the LUC. Since the large unit cell in our calculations is composed of 8 atoms, the cohesive energy can be determined from the following expression:

$$-E_{coh} = E^T / 8 - E_{free} - E_o. \quad (17)$$

where E_{free} is the free atom sp shell energy. The cohesive energy is corrected for the zero-point motion of the nuclei [28]. This correction is due to the fact that unlike the classical harmonic oscillator, the vibrational ground state is not equal to zero but

equals to E_o . This is a pure quantum mechanical effect and is directly related to the uncertainty principle. The cohesive energy value of the present work has better agreement with the experimental value [25] than the Harker and Larkins [5] value. This is because of the including of the exchange integrals, correlation correction, and zero-point energy in our analysis. The correlation correction is the correction included to take into account the fact that the motions of electrons are correlated pairwise to keep electrons apart. This correction is calculated to be 0.012 eV. The zero-point energy is the vibrational ground state energy which is equal to 0.18 eV [28] for diamond. The calculated valence band width is in good agreement with the experimental values [26, 10]. The calculated conduction band width differs markedly from the experimental value [27]. This can be attributed to that not all the excited states are considered, so deep and more precise analysis should be done in this respect. The direct band gap extracted from the present work agrees well with the experimental value [10]. The small difference is due to the neglect of the core states and to the approximations incorporated with the computational formalism. The hybridization states determined by this work show an increase of the s state occupation in comparison with the result of Harker and Larkins [5], and there is a tendency to reach the sp^3 state of diamond. The eigenvalues of the high symmetry points used to determine the band structure are shown in Table 3.

Table 3 Energy bands of diamond at Γ and X high symmetry points with respect to Γ_{25} point, compared with other results.

Symmetry point	Eigenvalue (eV)		
	Ref [5]	Present work	Exp.
Γ_1	-20.60	-22.20	-24.20 [10]
X_{IV}	-9.60	-10.01	-13.00 [29]
X_{4V}	-5.40	-5.33	-5.00 [29]
Γ_{25}	0.00	0.00	-
Γ_{15}	11.80	7.89	7.30 [10]
Γ_2	15.40	8.48	15.30 [30]
X_{1C}	15.20	8.87	6.00 [29]
X_{4C}	14.40	10.56	-

Many physical properties of a solid can be obtained using the wave functions obtained in the preceding section, such as the bulk modulus, x-ray scattering factor, and electronic charge density. The bulk modulus (B) is defined as [31]:

$$B = V \left(\frac{d^2 E^T}{dV^2} \right)_{V=V_o..} \quad (18)$$

where V_o is the equilibrium lattice volume. The bulk modulus can be obtained numerically by calculating the lattice energy at three different volumes; V_o , $V_o + \Delta V$, and $V_o - \Delta V$, and applying the second derivative formula:

$$\left(\frac{d^2 E^T}{dV^2} \right)_{V=V_o} = \lim_{\Delta V \rightarrow 0} \frac{E^T(V_o + \Delta V) + E^T(V_o - \Delta V) - 2E^T(V_o)}{(\Delta V)^2} \quad (19)$$

The calculated bulk modulus of diamond is 5.20×10^{11} N/m², which is in good agreement with the experimental values of 5.45×10^{11} N/m² [32], 4.43×10^{11} N/m² [23], and 4.46×10^{11} N/m² [12].

The x-ray scattering factor (f_j) is defined by [32]

$$f_j = \int \rho_e(r) \exp(-iG \cdot r) dV \quad (20)$$

where $\rho_e(r)$ denotes the atomic charge density expressed as

$$\rho_e = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \Psi_{\mu}(r) \Psi_{\nu}(r) \quad (21)$$

and G is the reciprocal lattice vector. Table 4 shows the calculated x-ray scattering factors for diamond at 0 K and zero pressure, in comparison with experiments [33] and HF calculations [34].

Table 4 X-ray scattering factors of diamond (atomic units) compared with other results.

hkl	X-ray scattering factor value		
	HF [34]	Present work	Experimental [33]
111	3.249	3.49	3.321
220	1.960	2.15	1.972
311	1.693	1.86	1.663
400	1.543	1.62	1.480
331	1.526	1.54	1.539
422	1.427	1.43	1.443
511	1.381	1.38	1.418
333	1.376	1.37	1.418

The valence electrons charge density is also investigated in the present work. Fig.2 displays this charge density for the (001), (400), and (200) planes.

3.3 Effect of pressure on diamond properties

The pressure dependence of the electronic structure and other properties can be determined from the present theory and computational procedure. The pressure dependence of the lattice parameter of diamond is determined using the Murnaghan [35] equation of state:

$$a = a_0 \left(1 + B^- \frac{P}{B_0}\right)^{\frac{1}{3B^-}} \quad (22)$$

where a is the lattice parameter at pressure p , a_0 is the lattice constant at zero pressure which has a computed value of 6.73 a.u and an experimental value of 6.74 a.u [23] and 6.743 a.u [12], B_0 is the bulk modulus at zero pressure which was computed to be 520 GPa and was determined experimentally to be 443 GPa [23] and 446 GPa [12], and B^- represents the pressure derivative of the bulk modulus and has an experimental value of 4.07 [36] and 3.0 [12]. The computed value of a_0 is in good agreement with the experimental values, whereas the agreement is fair concerning the B_0 value. The B^- value was not computed in the present analysis. So the experimental values of B_0 (443 GPa) and B^- (4.07) are adopted to plot the pressure dependence of the lattice parameter as depicted in Fig.3. This figure agrees very well with that published by Xie et al.[9]. It is interesting to mention that using the accurate value of B_0 (446 GPa) and B^- (3.0) reported by Occelli et al. [12] yields a very small difference (less than 0.1%) in the calculated values of the lattice parameter from the corresponding values shown in Fig.3.

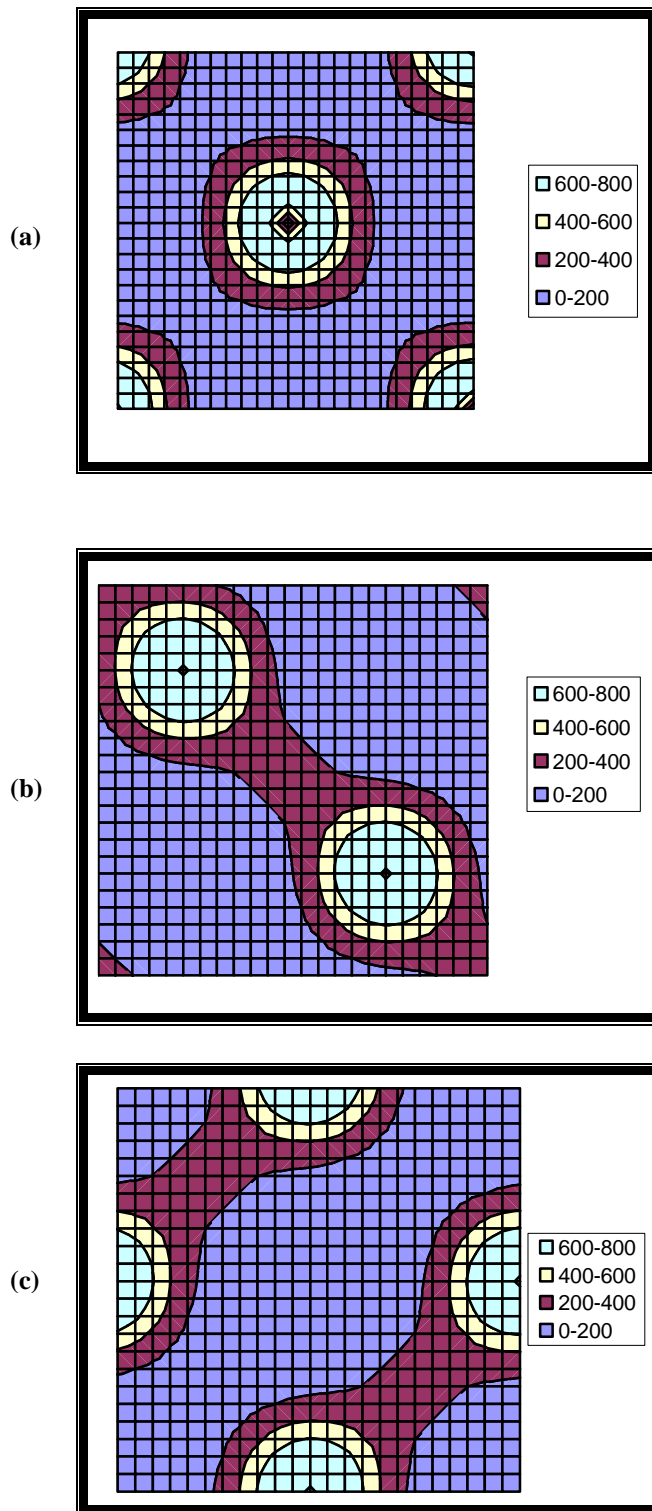


Fig.2 Valence electrons charge density (10^{-5} atomic unit) at 0 K and zero pressure for (a) (001) plane, (b) (400) plane, and (c) (200) plane.

The pressure dependence of the direct band gap is illustrated in Fig.4. A similar behavior has been recently observed by Scandolo et al. [37]. The pressure dependence of the band gap of diamond has been widely investigated. For instance, Fahy and Louie [38] and Van Camp et al. [39] have computed the pressure derivative of the fundamental band gap to be 0.006 and 0.0062 eV/GPa respectively. Whereas, the present work is concerned with the direct band gap and its pressure derivative is computed to be -0.002 eV/GPa in the pressure range (0-20) GPa. It is shown from the

present analysis that the increase of pressure causes a decrease of the absolute value of the cohesive energy. This means that the C-C bond decreases with the increase of pressure. The predicted effect of pressure on valence band width and conduction band width is displayed in Fig.5 and Fig.6 respectively.

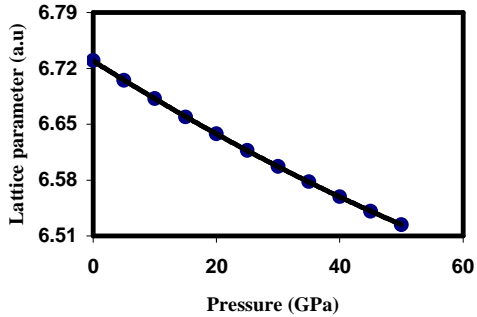


Fig.3 Lattice parameter versus pressure for diamond.

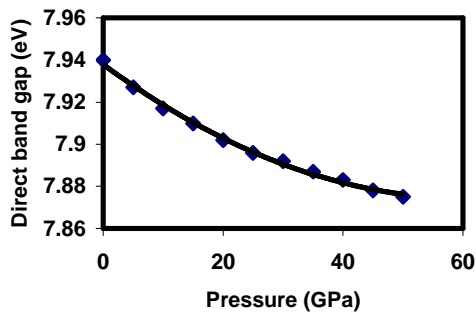


Fig.4 Pressure dependence of the direct band gap of diamond.

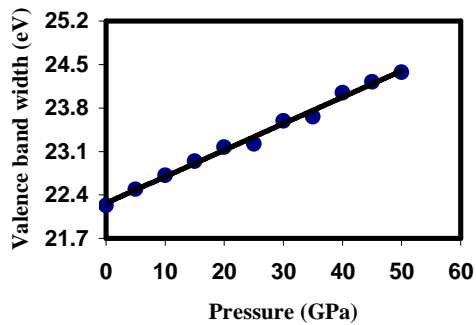


Fig.5 Calculated valence band width of diamond as a function of pressure.

The effect of pressure on the hybridization state of the s orbital is shown in Fig. 7. As obvious from this figure, the increase of pressure causes an increase of the probability of electrons transition from s orbital to p orbital. This is in agreement with the observation of Takemura and Syassen [40].

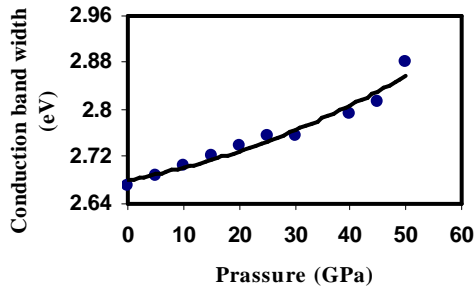


Fig.6 Calculated conduction band width of diamond as a function of pressure.

It is noted that the increase of pressure causes, in general, a decrease of the x-ray scattering factor as shown in Fig.8 for (331), (422), and (511) planes. This can be interpreted as follows; increasing the pressure decreases the inter planer distance (d_{hkl}), and this increases the Bragg scattering angle (Bragg's law), and this in turn causes a decrease of the scattering wave intensity.

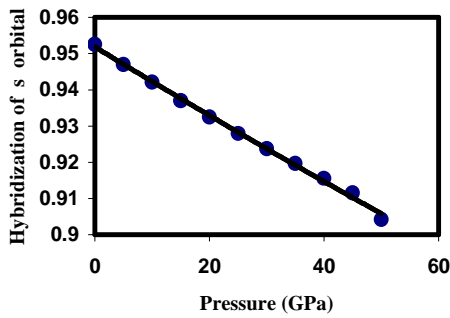


Fig.7 Predicted effect of pressure on the hybridization state of s orbital in diamond.

The effect of pressure (40 GPa) on the valence charge distribution is depicted in Fig.9. Comparing this figure with Fig.2, one can note that pressure causes an increase of the charge density around the nuclei and a decrease of this density at the intermediate distance between the nuclei. The pressure causes an orbitals overlap. A measure of the percentage orbitals overlap ratio can be written as $(d/r_{nn}\%)$, where r_{nn} represents the distance between two neighboring nuclei and it equals $\sqrt{3}/4 a$ for diamond structure, and d represents the distance between two charge density peaks and it can be written as

$$d = r_m - 2 r_{max} \quad (23)$$

where r_{max} is the radial distance at which the charge density peak appears and given by

$$r_{max} = \frac{n-1}{\zeta} \quad (24)$$

Hence, d is now written as

$$d = \frac{\sqrt{3}}{4} a - \frac{2(n-1)}{\zeta} \quad (25)$$

Table 5 shows the effect of pressure on a , r_{nm} , d , and the percentage orbitals overlap ratio.

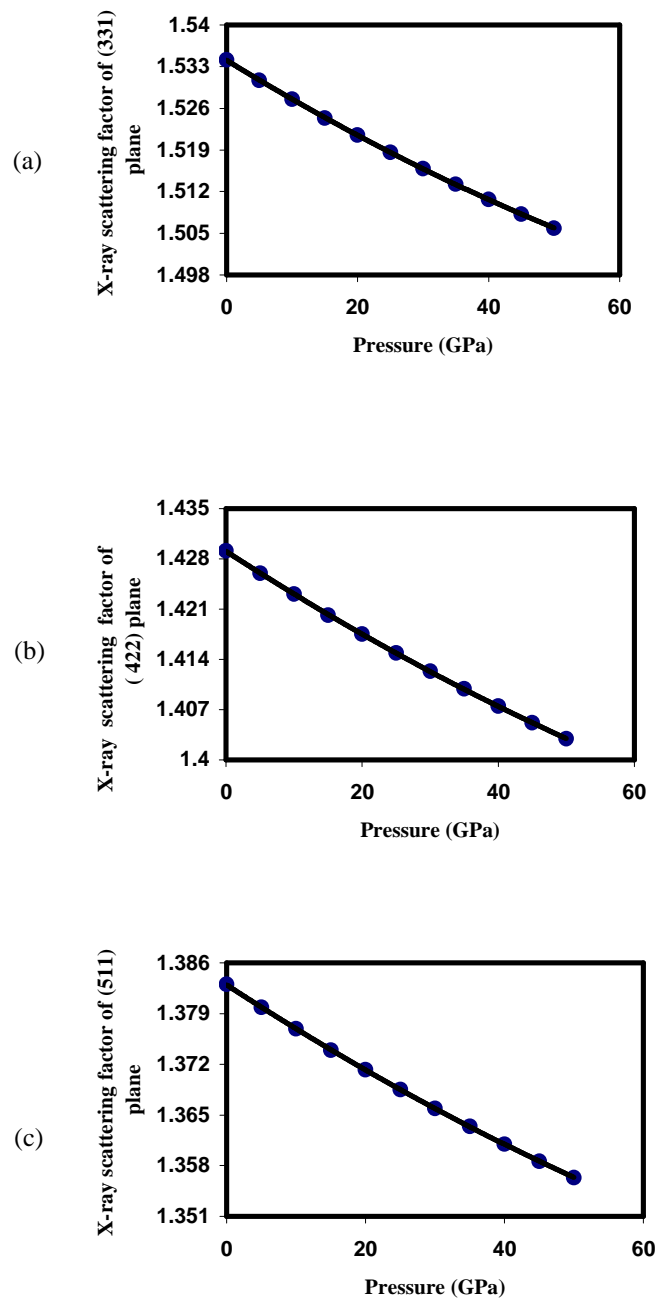


Fig.8 X-ray scattering factor against pressure for (a) (331) plane, (b) (422) plane, and (c) (511) plane of diamond.

Table 5 Predicted effect of pressure on the lattice parameter (a), nearest neighbor distance (r_{nn}), charge density peak to peak distance (d), and the percentage orbitals overlap ratio ($d/r_{nn}\%$).

P (GPa)	a (a.u)	r_{nn} (a.u)	d (a.u)	$d/r_{nn}\%$
0	6.730	2.91	1.82	62.29
5	6.705	2.90	1.80	62.15
10	6.682	2.89	1.79	62.02
15	6.659	2.88	1.78	61.89
20	6.638	2.87	1.78	61.77
25	6.617	2.87	1.77	61.65
30	6.597	2.86	1.76	61.53
35	6.578	2.85	1.75	61.42
40	6.559	2.84	1.74	61.30
45	6.541	2.83	1.73	61.20
50	6.524	2.82	1.73	61.10

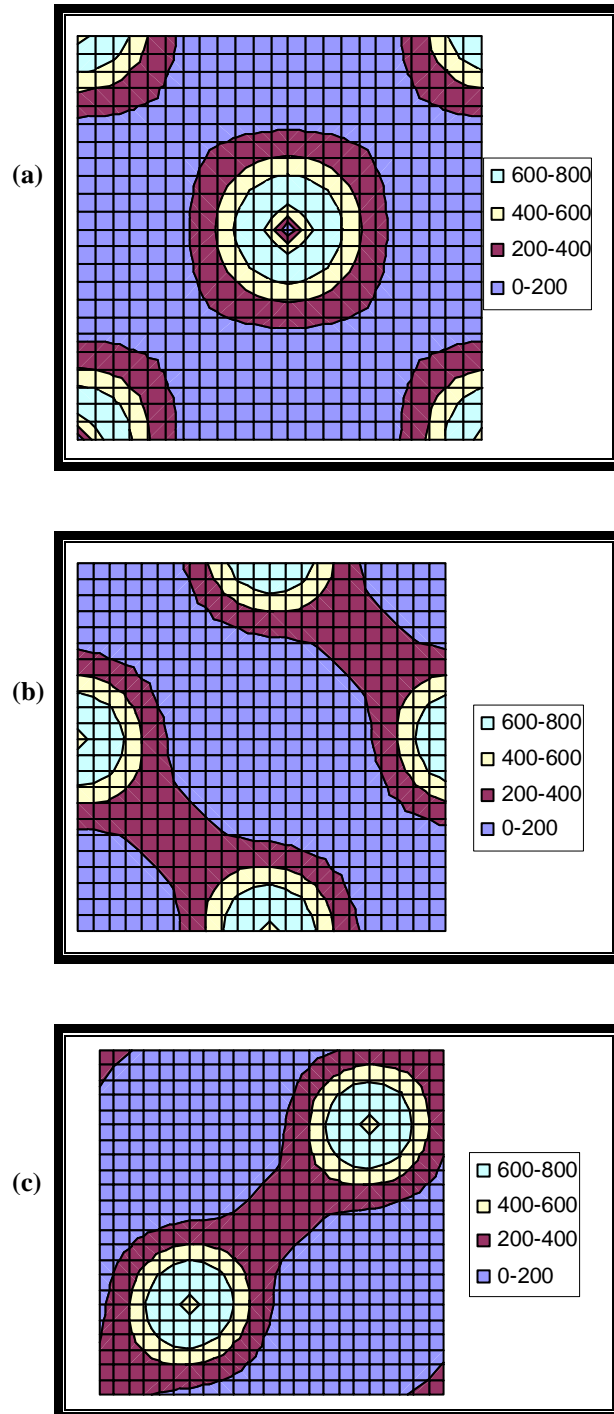


Fig. 9 Predicted effect of a 40 GPa pressure on the valence charge density (10^{-5} atomic unit) of (a) (001) plane, (b) (400) plane, and (c) (200) plane.

4 Conclusions

The success of the LUC-INDO approach depends on the optimum choice of the empirical parameter set. Adding the zero-point and correlation corrections has enhanced the calculated properties. In view of our results, the model can be used to simulate solids in a practical manner, because it is reasonably economical to use. Increasing the LUC size is expected to improve the results accuracy and reliability, as it was also confirmed by Harker and Larkins [5]. The calculated values of the diamond properties are in good agreement with the experimental results except the conduction band width. The increasing of pressure on diamond is predicted to cause the following effects; an increase of the valence and conduction band widths, a decrease of the direct band gap, an increase of the electronic occupation probability for the p orbital with a decrease of this probability for the s orbital, and a decrease of the x-ray scattering factors.

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