

Corrections and parametrization of semiempirical large unit cell method for covalent semiconductors

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Self-consistent Hartree-Fock within the framework of large unit cell (LUC) formalism using complete and intermediate neglect of differential overlap (INDO) is used to simulate electronic band structure of covalent crystalline semiconductors. Correlation corrections are added via second-order Moller-Plesset perturbation method. Other corrections such as relativistic spin-orbit effects on the band gap and zero-point energy are also included. Cohesive energy, band gap, valence-band width, and hybridization orbitals are obtained from band calculations. Bulk modulus, charge distribution, and x-ray form factors are also calculated. These calculations are directed toward large scale or defected systems. Results show that the effects of some of these corrections are indispensable to obtain a clear view of semiempirical parameters used to fit band structure of covalent semiconductors. Correlation and INDO corrections removed some electronic cloud from the bonding region to the spherical region around the atom. Correlation corrections with its long time and limited improvements are not advised for large scale calculations. Solid parameters are compared with those of molecules and free atoms to understand the rules of parametrization in solids. Resemblance with size-dependent nanocluster properties is established for present calculations such as the decrease of band gap with increasing size of LUC. The major difference of the present calculations from previous nanocluster calculations is the use of the same element atom of the cluster to cap surface dangling bonds.

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I. INTRODUCTION

Different models of band structure of solids are used nowadays that vary from empirical to *ab initio* models.¹ In quantum chemistry of molecules, certain semiempirical methods had gained spectacular attention in the 1970s because of their simplicity and applicability to wide molecular species.² Among these are the complete (CNDO) and intermediate (INDO) neglect of differential overlap. However, the use of Gaussian orbitals^{3,4} and the increasingly faster computation facilities made the use of more accurate *ab initio* methods a better choice for performing such calculations for molecules. On the other hand, the high number of atoms and electrons in solids created some limitations in performing these accurate methods especially for defected solid systems without resorting to some approximations. A shift of priorities of semiempirical methods to more demanding calculations such as large and defected systems is made.

The extension of the semiempirical calculations to solids had begun in approximately one decade after its application to molecules.⁵⁻¹⁰ The extension made use of the large unit cell (LUC) method to implement periodic boundary of solid. LUC-CNDO or LUC-INDO calculations have the ability to include large number of atoms including surfaces, interstitials, or vacancies. Previous LUC-CNDO and LUC-INDO calculations for semiconductors had focused on diamond and silicon.^{7,9,11} Other calculations applied the method to LiF and KCl crystals,¹⁰ copper oxide crystalline compounds,¹² F centers,¹³ titanium oxides,¹⁴ zirconium oxides,¹⁵ etc.

In this work, several corrections including correlation using Moller-Plesset perturbation method¹⁶ and zero-point motions of the nuclei¹⁷ are added. The calculations are extended to include all elementary semiconductors (diamond, silicon,

germanium, and α -tin). No previous calculations are reported for germanium or α -tin using LUC method. Other corrections had to be added to high atomic number elements such as relativistic spin-orbit splitting correction for the band gap.¹⁸ Sensitivity analysis of the present method at CNDO level was performed in Ref. 9. The same analysis is well applicable to the INDO case. Scaling to a larger number of carbon and silicon atoms has also been discussed in Refs. 9 and 11. The results showed that although small differences in predicted properties are observed as the size of the LUC varies, it should be possible in many cases to establish required semiempirical parameter set using small unit cell and then transfer it to a larger unit cell for defect-type calculations. Reference 11 used different \mathbf{k} points (\mathbf{k} is the lattice wave vector). However, the authors asserted that limited improvements were gained.

II. THEORY

In the method of linear combination of atomic orbitals, basis states that are combined to form molecular or solid eigenvectors are the wave functions of the atoms that form the molecule or the solid,

$$\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}. \quad (1)$$

Here, $C_{\mu i}$ are the combination coefficients. The determination of the expansion coefficients is based on the variational methods in quantum mechanics. After selecting the basis states, the coefficients $C_{\mu i}$ may be adjusted to minimize the expectation value of the total energy. The variation of these coefficients leads to a set of algebraic equations which are called Roothan-Hall equations.³

$$\sum_{\nu} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) C_{\nu i} = 0. \quad (2)$$

In the above equation, $S_{\mu\nu}$ is the overlap integral defined by

$$S_{\mu\nu} = \int \varphi_{\mu}(1) \varphi_{\nu}(1) d\tau_1. \quad (3)$$

$F_{\mu\nu}$ is the Fock operator matrix given by³

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\lambda|\nu\sigma) \right]. \quad (4)$$

$H_{\mu\nu}$ is the matrix element of the core Hamiltonian of a single electron in the field of the nuclei. Its operator representation is given by

$$H_{\mu\nu} = \int \varphi_{\mu}(1) \left(-\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{r} \right) \varphi_{\nu}(1) d\tau_1. \quad (5)$$

Here, Z_A is the charge of nucleus A and the summation is over all nuclei. The quantity in parentheses in Eq. (4) is the two-electron integral defined by the equation

$$(\mu\nu|\lambda\sigma) = \int \int \varphi_{\mu}(1) \varphi_{\nu}(1) \frac{1}{r_{12}} \varphi_{\lambda}(2) \varphi_{\sigma}(2) d\tau_1 d\tau_2. \quad (6)$$

In Eq. (4), the two-electron integrals are multiplied by the density matrix $P_{\mu\nu}$ which is defined by

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} \tilde{C}_{\mu i}^* \tilde{C}_{\nu i}. \quad (7)$$

The summation is over occupied orbitals only for closed shell systems which is the case in the present work.

Empirical parameters in CNDO and INDO methods include orbital exponent (ζ) of the Slater-type orbital, bonding parameter (β^0), and the average energy of ionization and affinity of valence orbitals [$\frac{1}{2}(I\mu + A\mu)$] (μ refers to s or p orbitals in the present case). The main assumptions of these methods can be summarized² by considering only valence electrons, replacing the overlap matrix by unit matrix, neglecting differential overlap in two-electron repulsion integrals, reducing the remaining set of two-electron integrals to one value per atom pair, neglecting monatomic differential overlap in the interaction integrals involving the cores of other atoms, and finally taking diatomic off-diagonal core matrix elements to be proportional to the corresponding overlap integrals. Partial account of exchange integrals is considered in INDO formalism. Applying the above approximations to Fock Hamiltonian of Eq. (4) with the $\mathbf{k}=0$ approximations for the LUC method results with the following equations for LUC-INDO formalism:¹⁹

$$\begin{aligned} F_{\mu\mu} &= U_{\mu\mu 00} - \frac{1}{2} \sum_{\nu \neq 0} P_{\mu\nu} f(x) \gamma_{AA0\nu} - \frac{1}{2} \sum_{\lambda \text{ on } A} P_{\lambda\lambda} (\mu\lambda|\mu\lambda) \\ &- \sum_{C \neq A} \sum_{\nu} Z_C \gamma_{AC0\nu} + \sum_{C \neq A} \sum_{\nu} P_C \gamma_{AC0\nu} \\ &+ \sum_{\nu} \beta_A^0 (S_{\mu\mu 0\nu} - \delta_{0\nu}), \end{aligned} \quad (8)$$

$$\begin{aligned} F_{\mu\nu} &= \sum_{\nu \neq 0} \beta_A^0 S_{\mu\nu 0\nu} - \frac{1}{2} P_{\mu\nu} \sum_{\nu \neq 0} f(x) \gamma_{AA0\nu} \\ &+ P_{\mu\nu} \left[1.5(\mu\nu|\mu\nu) - \frac{1}{2} (\mu\mu|\nu\nu) \right], \\ &\mu \text{ and } \nu \text{ on atom } A, \end{aligned} \quad (9)$$

$$\begin{aligned} F_{\mu\nu} &= \sum_{\nu} \frac{1}{2} (\beta_A^0 + \beta_C^0) S_{\mu\nu 0\nu} \\ &- \frac{1}{2} P_{\mu\nu} \sum_{\nu} f(x) \gamma_{AC0\nu}, \quad \mu \text{ on atom } A \text{ and } \nu \text{ on atom } C. \end{aligned} \quad (10)$$

Here, $U_{\mu\mu 00}$ is the energy of an electron in atomic orbital μ in the electrostatic field of its own core and the inner-shell electrons in the central lattice (0), $\gamma_{AC0\nu}$ is the two-electron integral between atom A in the central lattice (0) and atom C in the ν lattice, and P_C is the total electronic density at atom C . A final correction is made by Evarestov and Smirnov²⁰ and Szymanski¹⁹ to avoid divergence when including large number of neighbors by the introduction of the modulating function $f(x)$ which has the form

$$f(x) = \left(\frac{\sin(x)}{x} \right)^2. \quad (11)$$

Here, x is given by

$$x = \frac{\pi R_{AB0\nu}}{a}, \quad (12)$$

where $R_{AB0\nu}$ is the distance between atom A at the central lattice 0 and atom B at the ν lattice. This form of the Fock Hamiltonian will be used in the calculations of the band structure and physical properties of covalent semiconductors in the next section.

The main deficiency of Hartree-Fock theory is the lack of correlation between motions of electrons. Correlation energy is defined as the difference between the Hartree-Fock and exact (nonrelativistic) energy,³

$$E(\text{exact}) = E(\text{Hartree-Fock}) + E(\text{correlation}). \quad (13)$$

The correlation correction to the initial error inhibited in Hartree-Fock calculations is due to the fact that only one single determinant is included in Hartree-Fock calculations. Several methods were designed to overcome this deficiency. One of these methods, which can be applied to molecular and solid calculations, is the Moller-Plesset perturbation method.³ The second-order contribution (MP2) to the energy in this theory is given by

$$E^{(2)} = \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{virt}} (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)^{-1} |(ij|ab)|^2. \quad (14)$$

Here, i and j represent occupied orbitals, a and b represent virtual orbitals, and $(ij|ab)$ is the perturbative Hamiltonian

which is related to the two-electron integrals [Eq. (6)] over spin coordinates:

$$(ij|ab) = \int \int \chi_i^*(1)\chi_j^*(2) \frac{1}{r_{12}} [\chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2)] d\tau_1 d\tau_2. \quad (15)$$

Here, χ is a spin-orbital. This method will be applied in the present work.

Experimentally measured spin-orbit splitting will be used to obtain the original nonsplit levels. This method is usually used when trying to add relativistic corrections for high Z elements.¹⁸ As an example, the Γ_{25} symmetry point with spin-orbit interaction split to the Γ_8^+ and Γ_7^+ states as follows:

$$\begin{aligned} E(\Gamma_8^+) &= E(\Gamma_{25}) + \lambda, \\ E(\Gamma_7^+) &= E(\Gamma_{25}) - 2\lambda. \end{aligned} \quad (16)$$

Here, λ is given by

$$\lambda = \frac{\Delta_0}{3}. \quad (17)$$

Experimental spin-orbit splitting Δ_0 is given the values 0.0, 0.04, 0.29, and 0.80 for diamond, silicon, germanium, and α -tin respectively.¹⁸

III. CALCULATIONS AND RESULTS

The calculations are carried out by forming a cube of side $3a$, where a is the lattice constant of the LUC lattice. In the present work, conventional eight atom diamond structure lattice is used as the LUC. This size of LUC is selected in order to be able to add correlation corrections. The time taken by correlation corrections is several times the time taken by CNDO or INDO band-structure calculations itself. The interaction of the atoms in the central lattice with the surrounding atoms up to the fourth neighbors is included. These calculations require the determination of wave functions and positions of 864 electrons and 216 nuclei. The selection of the suitable semiempirical parameters is made after correlation corrections are added to the final Hartree-Fock wave functions.

The convergence of the LUC-INDO calculations is fast. As an example, Table I shows the successive electronic energies calculated for each iteration for silicon lattice needed to obtain the final Hartree-Fock results in the present work parameter set of Table II. The tolerance of the cohesive energy of one atom is set to 0.0017 eV, which is better than the previous LUC calculations.^{9,10} One of the difficulties faced in the present method is divergence and oscillation in self-consistent procedure when surveying some combination of parameters. One of the helpful remarks is the suitable choice of initial guess states of first iteration that reduces the number of self-consistent cycles.

The four semiempirical parameters are varied first so as to give nearly the exact values of the equilibrium lattice constant and cohesive energy and to compensate between the

TABLE I. The successive electronic energy and difference between steps (in eV) calculated in each iteration for silicon lattice in the present work parameter set of Table II.

Iteration No.	Total energy (eV)	Difference (eV)
0	-857.5255479	
1	-858.6123549	1.086807
2	-858.8306718	0.2183169
3	-858.8731226	0.0424508
4	-858.8812418	0.0081192

direct band gap and valence-band width. The remaining of the output data of the calculations is a result of the theory that is used in the present work.

The cohesive energy is calculated from the total energy of the LUC. Since the large unit cell is composed of eight atoms, the cohesive energy is given by

$$E_{\text{coh}} = E_T/8 - E_{\text{free}} - E_0. \quad (18)$$

Here, E_{free} is the experimental free atom sp shell energy.²¹ The use of experimental free sp shell energy is due to the fact that semiempirical parameters which are fitted to solid band structure might be inappropriate to describe atomic energy with the same level of theory. The cohesive energy is also corrected for the zero-point motion of the nuclei.¹⁷ This correction is due to the fact that unlike the classical harmonic oscillator, the vibrational ground state is not equal to zero but equal to E_0 . This is a pure quantum-mechanical effect and is directly related to the uncertainly principle.⁴ This correction had not been taken into account in the previous LUC calculations. Its value is 0.18, 0.07, 0.04, and 0.03 eV for the four elements C, Si, Ge, and α -Sn, respectively.¹⁷

The experimental direct band gap and valence-band width are corrected for spin-orbit splitting as described by Eqs. (16) and (17) of the last section. This correction increases the experimental value of the band gap by a certain amount depending on the states that bound this gap. The energy bands at high-symmetry points are set relative to the Γ_{25} (highest occupied state), as is the usual procedure used by most of the other works.^{9,11}

Although there are many results for diamond and silicon band structure using different methods, Hartree-Fock results for germanium and tin are rare.²²⁻²⁴ Using the procedure outlined above, the band structure and electronic properties of covalent semiconductors are listed in Table III in comparison with other LUC (Ref. 9) and other Hartree-Fock results (Ref. 24). The eigenvalues of the high-symmetry points (Γ and X points) are shown in Table IV.

It is interesting to see the effect of INDO and correlation corrections on CNDO calculations. This is shown in Table V using our parameter set of Table II. It can be seen that the effect of INDO corrections or INDO+correlation corrections is not trivial. In addition to this, the INDO and correlation corrections are in the same direction in some of the listed results and in opposite direction in the others.

TABLE II. Present parameter sets of covalent semiconductors for LUC-INDO with correlation corrections in comparison with previous CNDO parameters (Ref. 9).

		ζ (a.u. ⁻¹)	β^0 (eV)	$-\frac{1}{2}(I_s+A_s)$ (eV)	$-\frac{1}{2}(I_p+A_p)$ (eV)
C	Ref. 9	1.765	-10.2	7.0	5.5
	Present work	1.83	-10.00	5.57	4.39
Si	Ref. 9	1.54	-6.4	6.3	4.4
	Present work	1.635	-5.45	7.25	4.95
Ge	Present work	1.98	-5.35	9.35	5.4
α -Sn	Present work	2.05	-5.35	9.46	4.96

One of the good tests for the present theory is bulk modulus:

$$B = V \left(\frac{d^2 E_T}{dV^2} \right)_{V=V_0}. \quad (19)$$

Here, V_0 is the equilibrium lattice volume. Table VI shows the present work comparison with other LUC results.⁹

In Fig. 1, a comparison is made for the different values of the orbital exponent (ζ) in atoms, molecules, and solids, while Fig. 2 shows a comparison of solid and molecular values for the bonding parameter β^0 . Figure 3 shows the electronic density along the line joining two first-neighbors atoms. In order to check the validity of charge distribution, the present work results are used to calculate x-ray atomic form (scattering) factors after adding the standard core charges.³⁹ These form factors are plotted against experiment in Fig. 4.

Vast bibliography exists especially for diamond and less for silicon and germanium and even more rare for tin. The coverage of all this literature is so difficult that we tried to restrict our comparison to previous LUC results⁹ and Hartree-Fock results that included all four covalent semiconductors.²⁴ In addition, the results here are what one can expect from semiempirical methods. As an example,

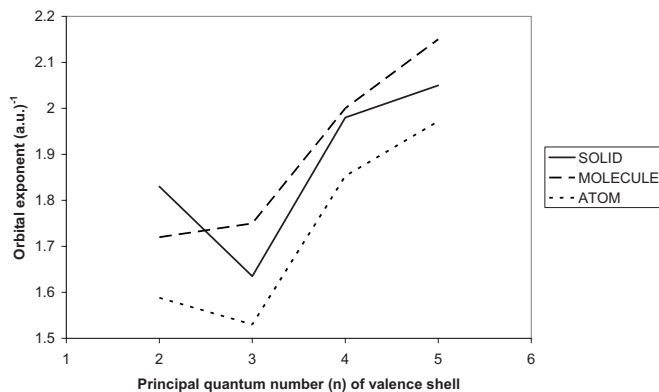


FIG. 1. The values of ζ in this work for the diamond structure elements (solid) compared with single zeta that are given by Clementi and Roetti (Ref. 39) for atoms (atom) and that given to molecules (molecule) (Ref. 3).

more accurate methods including GW approximation, local-density approximation, and quasiparticle band-structure calculations can give better results than that given in present work tables.^{29,44,45} The present work is aimed to find the best way to parametrize the semiempirical calculations applied to large scale or defected systems that cannot be handled by the more accurate *ab initio* methods because of the lack of sufficient computer resources or speeds.

Finally, we performed calculations for a larger LUC that contains 64 atoms at the INDO level which is eight times the size of our initial LUC. Correlation corrections are discarded because of computer time requirements. $3 \times 3 \times 3$ supercell that contains 64 atoms in each cell is widely used in surface and vacancy calculations.^{46,47} The results are shown in Table VII. These results should be compared with the INDO column results of Table V. Cohesive energy of diamond remains the same, while that of the rest of the elements increases. Valence-band width and s orbital occupation in hybridized states increase for all four elements. Three of the investigated properties with the exception of band gap are still in good and sometimes better agreement with experimental data listed in Table III. The band gap of diamond 64 atom LUC is in good agreement with recent values.⁴⁸⁻⁵⁰

The band gap of tin slightly decreased. Low values for the gap are obtained for Ge and Si. For germanium, the experimental band gap is the average of 8 and 64 gap calculations that are of equal distance from the experimental value. Re-

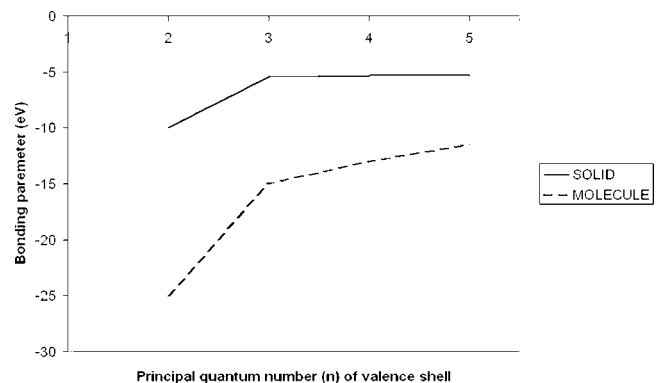


FIG. 2. The values of the bonding parameter β^0 for covalent semiconductors in the present work compared with the same quantity for molecules suggested by Boca (Ref. 40).

TABLE III. The band structure and electronic properties of diamond, silicon, germanium and α -tin in this work compared with other LUC results (Ref. 9), other Hartree-Fock methods (Ref. 24) and experimental data. Note that cohesive energy of Ref. 1 is corrected for zero-point motion energy (Ref. 17).

	Reference 24	Reference 9	Present work	Expt.	Reference
C					
Lattice constant A^0	3.56	3.56	3.56	3.56	1
Cohesive energy (eV/atom)	5.3	7.68	7.55	7.55	1
Valence-band width (eV)	29.9	22.4	20.17	21.0	25
Direct band gap (eV)	23.7	9.4	8.71	7.3	24
Hybridization state		$s^{0.6}p^{3.4}$	$s^{0.926}p^{3.074}$		
Neighbors included		2	4		
Si					
Lattice constant A^0	5.43	5.45	5.43	5.43	1
Cohesive energy (eV/atom)	2.9	4.7	4.68	4.70	1
Valence-band width (eV)	18.0	13.2	11.87	12.4	26
Direct band gap (eV)	9.3	7.0	3.50	3.44	27
Hybridization state		$s^{0.93}p^{3.07}$	$s^{1.256}p^{2.744}$		
Neighbors included	2	2	4		
Ge					
Lattice constant A^0	5.65		5.65	5.65	1
Cohesive energy (eV/atom)	1.2		3.85	3.89	1
Valence-band width (eV)	18.9		12.47	12.9	28
				12.6	29
Direct band gap (eV)	4.3		1.67	0.99	30
Hybridization state			$s^{1.487}p^{2.513}$		
Neighbors included			4		
α -Sn					
Lattice constant A^0	6.46		6.46	6.46	1
Cohesive energy (eV/atom)	0.1		3.00	3.17	1
Valence-band width (eV)	16.0		12.21		
Direct band gap (eV)	2.6		1.27	0.26	1
				-0.15	31
				-0.37	32
Hybridization state			$s^{1.544}p^{2.456}$		
Neighbors included			4		

adjustment of the parameters of 64 atom LUC is needed to fit the experimental data at least to account for the band gap and trend of results. Here we reach the same conclusion of Ref. 9 mentioned earlier in the Introduction that although differences in predicted properties are observed as the size of the LUC varies, it should be possible in many cases to establish required semiempirical parameter set using small unit cell and then transfer it to a larger unit cell.

All band gaps of the four elements decrease in going from 8 to 64 LUC calculations. This decrease resembles that of nanoclusters with increasing size. In fact, the present LUC calculations can also be seen from another point of view as nanoclusters of varying size with the surface dangling bonds capped or passivated with atoms of the same element of the cluster. The decrease of band gap with increasing nanocluster size is in agreement with both recent experimental and the-

oretical investigations of most of elemental semiconductors.⁴⁸⁻⁵² α -tin nanocluster band gaps are not yet partially reported because of missing experimental evidence.⁵³

IV. CONCLUSIONS

Table III shows that the calculated values of the direct-band-gap energy decrease with increasing atomic number. As is the usual trend in Hartree-Fock calculations,²⁴ the calculated values are always greater than the experimental values. INDO corrections are found to be dependent on the kind of states that bound this gap, while correlation corrections always increase it. The reason that MP2 correlation correction did not improve the results of the direct band gap is that CNDO or INDO methods neglect a large number of two-electron integrals. MP2 method depends crucially on two-

TABLE IV. Energy of high-symmetry points of diamond, silicon, germanium, and α -tin in (eV) at Γ and X high-symmetry points with respect to Γ_{25} point compared with Ref. 9 for CNDO calculations, Hartree-Fock calculations (Ref. 24), and available experimental data.

	Reference 24	Reference 9	Present work	Expt.	Reference
C					
Γ_1	-29.9	-22.4	-20.17	-21.0	25
X_{1V}	-18.6	-13.2	-9.03	-13.0	33
X_{4V}	-9.3	-7.6	-4.92	-5.00	33
Γ_{25}	0.0	0.0	0.0	0.0	
Γ_{15}	14.6	9.4	8.71	7.3	24
X_{1C}	13.3	13.9	9.97	6.0	33
Γ_2	23.7	9.69	9.98	15.0	24
X_{4C}		14.1	11.23		
Si					
Γ_1	-18.0	-13.2	-11.87	-12.4	26
X_{1V}	-11.5	-7.5	-6.22	-2.9	33
X_{4V}	-3.85	-4.8	-2.63		
Γ_{25}	0.0	0.0	0.0	0.0	
Γ_{15}	8.7	7.0	5.91	3.44	27
Γ_2	9.3	7.1	3.50	4.2	34
X_{1C}	5.8	8.6	5.25	1.13	33
X_{4C}		9.8	7.36		
Ge					
Γ_1	-18.9		-12.47	-12.9	28
				-12.6	29
X_{1V}	-13.0		-7.30	-9.3	28
X_{4V}	-4.2		-2.37	-3.15	28
Γ_{25}	0.0		0.0	0.0	
Γ_2	4.3		1.67	0.99	30
X_{1C}	5.4		4.90	1.3	29
Γ_{15}	7.9		6.07	3.0	30
X_{4C}			7.60		
α -Sn					
Γ_1	-16.0		-12.38		
X_{1V}	-11.2		-7.37		
X_{4V}	-3.9		-2.75		
Γ_{25}	0.0		0.0	0.0	
Γ_2	2.6		1.27	0.26	1
				-0.15	31
				-0.37	32
X_{1C}	4.39		4.6		
Γ_{15}	6.6		6.12	2.3	24
X_{4C}			7.34		

electron integrals, as can be seen from Eqs. (14) and (15). In fact, all three- and four-center integrals and many of two- and one-center integrals are neglected or approximated in CNDO and INDO theories. Another reason is the poor quality of conduction-band levels. In order to reduce the value of the band gap, one must resort to *ab initio* theory so that a complete set of two-electron integrals is evaluated. Correla-

tion corrections with its large time and limited improvements are not advised for large scale defected systems. Instead, using semiempirical parameters that embody correlation corrections for a limited number of physical properties is a better choice. The valence-band width is well represented by the present method. The addition of higher orbitals is needed for the description of the conduction band which is beyond the

TABLE V. The band structure and electronic properties of diamond, silicon, germanium, and α -tin using the parameters of present work (Table II) for CNDO calculations and the same parameters for INDO and INDO+correlation corrections.

		CNDO	INDO	INDO+ correlation
C	Cohesive energy (eV/atom)	18.99	7.02	7.55
	Valence-band width (eV)	16.01	20.47	20.17
	Direct band gap (eV)	7.85	7.85	8.71
	Hybridization state	$s^{0.72}p^{3.28}$	$s^{0.92}p^{3.08}$	$s^{0.926}p^{3.074}$
Si	Cohesive energy (eV/atom)	11.69	4.25	4.68
	Valence-band width (eV)	10.08	12.11	11.87
	Direct band gap (eV)	4.82	2.80	3.50
	Hybridization state	$s^{1.089}p^{2.911}$	$s^{1.251}p^{2.749}$	$s^{1.256}p^{2.744}$
Ge	Cohesive energy (eV/atom)	10.59	3.43	3.85
	Valence-band width (eV)	11.99	12.80	12.47
	Direct band gap (eV)	1.45	0.64	1.67
	Hybridization state	$s^{1.396}p^{2.608}$	$s^{1.438}p^{2.562}$	$s^{1.487}p^{2.513}$
Sn	Cohesive energy (eV/atom)	8.89	2.68	3.00
	Valence-band width (eV)	11.85	12.44	12.21
	Direct band gap (eV)	0.979	0.386	1.270
	Hybridization state	$s^{1.421}p^{2.579}$	$s^{1.452}p^{2.548}$	$s^{1.544}p^{2.456}$

present CNDO or INDO theories. Table IV shows that the order of the high-symmetry points is also well represented with the exception of the lowest conduction-band levels of silicon.

Hybrid crystal orbitals show an increasing s state occupancy with the increasing atomic number of the elements. This reflects the tendency of these elements to retain their atomic configuration s^2p^2 and the weakening of the directional character of the solid bonds represented by the sp^3 hybridized orbitals. Extrapolating s state occupancy for Pb shows that Pb configuration will be near the atomic configuration $6s^26p^2$. Thus, we expect that this reason less favors Pb from

crystallizing in diamond structure in comparison with the more stable fcc structure.⁵⁴ Table V shows that both INDO and correlation corrections increase the s state occupancy. This shows that the effect of INDO and correlation corrections is to transform some of the electron cloud from the bonding region between two atoms to the spherical region around the nucleus.

The calculated bulk modulus values from total energy curve⁵⁵ presented in Table VI show the correct experimental trend of decreasing bulk modulus with increasing atomic number. The calculated values are always greater than those of the experiments as is the trend of other semiempirical results.⁹ From Fig. 1, we can see that the values of the orbital exponent (ζ) in the present work for solids are closer to

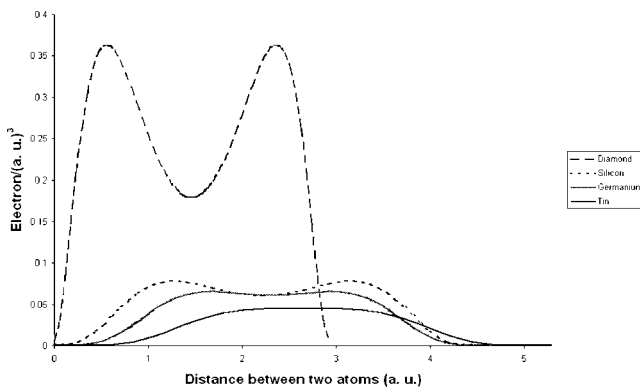


FIG. 3. The valence electronic charge density along the line joining two first-neighbor covalent semiconductor atoms. Note that diamond has the shortest bond length and the highest charge density followed by Si and Ge. α -Sn has the longest bond length and the lowest charge density.

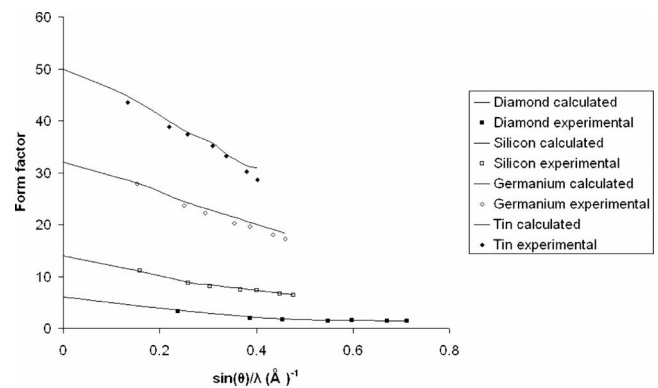


FIG. 4. Calculated atomic form factors for covalent semiconductors in comparison with experimental data (Refs. 41–43). θ is the x-ray radiation incidence angle and λ is the wavelength.

TABLE VI. The calculated values of bulk modules (present work) compared with the results of Ref. 9 and the experimental values. Values are in 10^{11} N/m².

	Reference 9	Present work	Expt.	Reference
C	9.73	8.08	5.45 4.42	1 35
Si	2.1	1.495	0.988 0.97	1 36
Ge		1.378	0.772 0.758	1 37
α -Sn		0.966	1.11 0.53	1 38

standard *ab initio* molecular values. However, these values take the trend of atomic exponents of single zeta of Clementi and Roetti.³⁹ This behavior can be attributed to INDO embodied approximations keeping in mind that molecular exponent is for *ab initio* calculations and that core orbital effects (that increase with the atomic number) are neglected in the present INDO theory. On the other hand, Fig. 2 shows that the absolute value of bonding parameter for molecules is always two to three times that for solids. This can be attributed to the distributed electronic cloud in all directions for solids. In molecules, this electronic cloud is directed to one or two directions in most of the cases. The transformation of semiempirical parameters to defected systems will require the use of hybrid parameters. As an example, surfaces will require the use of bonding parameters that are in between molecular and solid parameters at least for the atoms at the surface. This shows parameter dependence on bond order and coordination number. The absolute values of the average of ionization and affinity parameters always increase for *s* and *p* orbitals with increasing atomic number with the exception of *p* orbital for Sn. This trend of parameters was found to give the best fit to experimental values. These parameters are not unique but follow the above-mentioned trends. From Fig. 3, we can see two humps on the line joining two first-neighbor atoms. Those two humps almost unite for Sn. These shapes were indicated for diamond and silicon in Ref. 56 and for Sn in Ref. 57. We can notice from these figures that the electronic charge decreases in this region for higher atomic number elements. In fact, the highest electronic charge density is about $0.36 e/a.u.^3$ for diamond and decreases to $0.045 e/a.u.^3$ for Sn. The same values for the highest electronic charge density for diamond and silicon as in the present work are also given in Ref. 56. These calculated shapes and values use methods different from the methods in the present work. Reference 56 uses nonlocal exchange Hartree-Fock approximation, while Ref. 57 uses local-density approximation. The comparable results show that the present charge-density distribution might be found in

TABLE VII. Properties of 64 atom LUC at INDO level using present work parameter set of Table II.

	C	Si	Ge	Sn
Cohesive energy (eV)	7.02	4.35	3.82	3.04
Valence-band width (eV)	22.08	13.29	13.82	13.27
Band gap (eV)	5.98	0.71	0.19	0.35
Hybridization state	$s^{1.03}p^{2.97}$	$s^{1.45}p^{2.55}$	$s^{1.67}p^{2.33}$	$s^{1.65}p^{2.35}$

experimental data. Experimental x-ray form factors are a mirror that reflects the accuracy of the shape of total charge distribution. Charge density of the present work is used to evaluate x-ray atomic scattering factors after adding standard core charge distribution.³⁹ The present work form factors agree well with the experimental values as in Fig. 4, which confirms the validity of the present charge distribution.

Increasing the size of LUC will lead to generally acceptable values of electronic properties with experiment with some exceptions as in Table VII. Readjustment is needed to account for the band gap and trend of results.

A by-product of the process of increasing LUC size is the resemblance with size-dependent nanocluster properties. All 64 atom LUC's have smaller band gaps, in agreement with recent investigations of semiconductor nanoclusters.⁴⁸⁻⁵² The major difference of the present calculations from previous theoretical and experimental works on nanoclusters is the use of the same element atom to cap the surface dangling bonds instead of hydrogen or other atoms.⁴⁸⁻⁵⁰

V. SUMMARY

The present self-consistent semiempirical theory can be applied successfully to account for the band structure and physical properties of all elementary semiconductors using appropriate parameters. These parameters are bond order and coordination number dependent. Several corrections can also be applied to the calculations to approach the real physical situation. Some of these corrections are difficult to apply especially when transforming the calculations to large scale systems. Transforming the calculations to larger unit cells gives generally acceptable results. However, the empirical parameters that are designed to fit 8 atom LUC with experimental data have to be readjusted to be suitable for 64 atom LUC. Using larger sizes of LUC resembles nanoclusters with increasing size and decreasing band gap.

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