Formulation of a New Exchange-Correlation Potential for Better Band Gaps in Density Functional Theory

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INTRODUCTION

Density functional theory (DFT) is a clever and convenient way of solving the complex schrödinger equations for many-electron systems (K. Burke et al, 2007). Clever and convenient in the sense that the solution of complex many-body Schrödinger equation with N-number of electrons which depends on 3N coordinates is abandoned in favour of the density which depends on three spatial coordinates only (K. Burke et al, 2007).

The total energy is now a function of this function (density), hence the name density functional.

DFT has its foundation in the two theorems formulated by Hohenberg and Kohn in 1964: The first one says that the external potential of an interacting system is unique functional of the density and the second one shows that there is a universal functional for the energy which can be defined in terms of the density. The methodology of DFT is applied in many fields such as Condensed Matter Physics, Quantum Chemistry, Materials Science, many branches of Engineering etc and to many different problems, with the ground-state electronic structure problem being the most common. DFT is accurate in the prediction of some properties of many materials, such as shapes and sizes of molecules, crystal structures, ionization energies, band structures, electron affinities, binding or atomisation energies, static response functions, etc. One major limitation of practical DFT however is that it underestimates the size of the gap between the energy of the highest occupied single particle state and the lowest unoccupied single particle state.

THEORETICAL BACKGROUND

The time-independent Schrödinger equation for many-electron complex system which we are to solve is:

$$[-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{\alpha}^{M}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + \frac{1}{2}\sum_i\sum_j\frac{e^2}{4\pi\epsilon_0|r_i-r_j|} - \sum_i\sum_\alpha\frac{(Ze)e}{|R_\alpha-r_i|}$$
$$+\frac{1}{2}\sum_\alpha\sum_\beta\frac{(Z_\alpha)(Z_\beta)(e^2)}{4\pi\epsilon_0|R_\alpha-R_\beta|}]\psi = E\psi \tag{1}$$

The first term on the LHS is the kinetic energy of the electrons, the second is the kinetic energy of the nuclei, the third is the coulomb interaction between electrons, the last two terms are respectively the coulomb interaction between the nuclei and the electrons and the nuclear-nuclear interactions. The variable r_i is the position of the ith electron, m is the electron mass, R_α is the position of the α_{th} nucleus, M_α is the mass of the nucleus, Z_α is the charge on the α_{th} nucleus and the factor ($\frac{1}{2}$) preceeding the electron-electron and nuclear-nuclear interactions is there to avoid double counting

From a pragmatic point of view, problems involving quantum manybody systems are very difficult to track down; they are much more difficult than classical mechanical problems. The reason is that for N electrons, the manybody wavefunction ψ is a function of 3N variables, $\psi = \psi(r_1,...,r_N)$, where r_i, $(i=1,...,N)$ is a 3-dimensional position vector. Highly accurate numerical representation of such functions is close to impossible for $N > 2$ hence approximated in electronic structure methods.

- The first approximation is known as Bohn-oppenheimer Approximation, it comes by considering that the electrons are moving very fast while the nuclei are moving very slowly. Thus, we consider the mass of the nuclei as infinite compared with that of electrons. Thus, as a result of that, the kinectic energy part for the nuclei in the equation vanishes. The equation now becomes (M. Born and J.R. Oppenheimer,1927).

$$\{-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_i\sum_j\frac{1}{|r_i-r_j|} - \sum_i\sum_\alpha\frac{z}{|R_\alpha-r_i|}$$
$$+\frac{1}{2}\sum_\alpha\sum_\beta\frac{(z_\alpha)(z_\beta)}{|R_\alpha-R_\beta|}\}\psi = E\psi \tag{2}$$

where we have used atomic units $\hbar = e^2 = m = 4\pi\epsilon_0 = 1$.

- The last term of (2) i.e. the nuclear-nuclear interaction is a constant. In density functional theory (DFT) formalism, the nuclear-nuclear interaction is irrelevant so it is neglected for convinience sake. we take $r_{ij} \equiv |r_i - r_j|$ so that the Schrödinger equation for a many electron system becomes:

$$\{-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}\frac{1}{|r_{ij}|} + \sum_i^N v_{ext}(r_i)\}\psi = E\psi \tag{3}$$

where $v_{ext}(r_i) = \sum_\alpha\frac{Z_\alpha}{|R_\alpha-r_i|}$ (typically) is the external potential between the electrons and the nuclei.

- In the Kohn-Sham approach, the kinetic energy of the system of interacting particles is assumed to be non-interacting, so using one-electron orbital, they gave a beautiful equation for non-interacting system as follows;

$$(-\frac{1}{2}\nabla^2 + v_s(r))\phi_i(r) = \epsilon_i\phi_i(r) \tag{4}$$

where $\phi_i(r)$ are the one-electron orbitals and ϵ_i are the eigenvalues of the Kohn-Sham one-electron orbitals.

ABSTRACT

In Density Functional Theory formalism, the total energy functional of a system consists of known and unknown parts, the known part consists of kinetic energy of the non-interacting system, the external potential energy and the Hartree or classical coulomb interaction between the electrons. The existence of the unknown part was established by P. Hohenberg and W. Kohn in 1964 and it is known as the Exchange-Correlation Energy which is the major component necessary for accurate prediction of properties of materials.

The true mathematical form of this exchange-correlation Energy is not known, hence, approximations are made for it which reduces the accuracy of DFT, particularly in the case of energy band gaps. In this work, an exchange-correlation potential functional is formulated which is the modification of Hanke and Sham functional in 1998.

The functional was incorporated into the Quantum espresso software package and was used to perform plane-wave based calculation and energy band gaps of some systems were predicted from the formulated functional.

From our functional, we got band gap for Silicon to be 1.10eV which is closer to the experimental value of 1.12eV than that of LDA which is 0.47eV, for Silicon Carbide, experimental value is 2.40eV and we obtained 2.27eV with our functional which is more accurate than 1.35eV from LDA. For Aluminium Phosphide, our method gave 2.28eV while the experimental value is 2.45eV. All these are of error of approximately 6 percent, comparing with the experimental values and LDA results, the exchange-correlation functional in this work has given better predictions of energy band gaps than LDA.

METHODOLOGY

The new exchange-correlation potential functional proposed in this work is shown in equation (5) below and termed as the "UI exchange-correlation potential:

$$v_{xc}^{ins} = -e^2(\frac{2\pi}{3}n(r))^{\frac{1}{3}}[1 - \frac{2\omega_p}{N_{val}(\omega_p + cE_p)}] \tag{5}$$

It differs from Hanke and Sham exchange-correlation functional (Hanke and Sham 1998) in the introduction of an empirical parameter "c" multiplying the Penn gap E_p. In this expression, E_p, ω_p N_{val}, V_0 e and m are, respectively, the Penn gap (D. R. Penn,1962), plasma frequency, number of valence electrons per primitive unit cell, volume of the primitive unit cell, electronic charge and electron mass.

$$ui_\alpha = [1 - \frac{2\omega_p}{N_{val}(\omega_p + cE_p)}] \tag{6}$$

the parameter c included is an enhancement factor which is constant throughout our calculation.

In the contribution, the local density approximation for ω_p, the plasma frequency was used:

$$\omega_p = \sqrt{\frac{4\pi N_{val}e^2}{mV_0}}. \tag{7}$$

We work in atomic units, so that $4\pi\epsilon_0 = m = e = \hbar = 1$ The new exhange-correlation functional was used with LDA pseudopotential (e.g Perdew-Zurger type of pseudopotential) and Self Consistent Field (scf) calculations were done. The Kohn-Sham equations were solved using plane-wave basis sets. For all the systems considered, the Brillouin zone was sampled with an unshifted $4 \times 4 \times 4$ in Quantum Espresso (Monkhost-Pack grid of k-points) and kinetic energy cut-off (ecutwfc) of $60Ry$. Optimization of the functional were carried out for different values of λ, in order to obtain corresponding values of average energy gaps which we denote as $cEp - perl$. From the expression for the λ,

$$ui_\alpha = [1 - \frac{2\omega_p}{N_{val}(\omega_p + cE_p)}],$$

making the cE_p the subject of the relation of equation (5) yields our $cE_p^{analytic}$ to be:

$$cE_p^{analytic} = \omega_p(\frac{2}{N_{val}(1-ui_\alpha)} - 1) \tag{8}$$

where the plasma frequency ω_p were calculated analytically by using equation(7). The $cE_p^{analytic}$ for each value of ui_α by substituting the values of ω_p and the $Nval$ for each system. The two values, $cE_p^{analytic}$ and cE_p^{perl} were plotted on the same graph against the corresponding values of ui_α. The optimal values of ui_α for the different systems considered were obtained and recorded. The optimal $ui_\alpha's$ were now used to run our band structure calculations for each system and the band gaps were calculated.

RESULTS

our calculations were done for different values of ui_α, the corresponding values cE_p^{perl} were generated while $cE_p^{analytic}$ was calculated analytically. Some of the plots are shown below. The intersections of the two curves were noted which give the values of the optimal ui_α. The value of the optimal ui_α were then used to run our band structure calculations. We have calculated the band gaps of each system as $E_{LUMO} - E_{HOMO}$, where E_LUMO is energy of the lowest unoccupied molecular orbital and E_HOMO is the energy of the highest occupied molecular orbital.
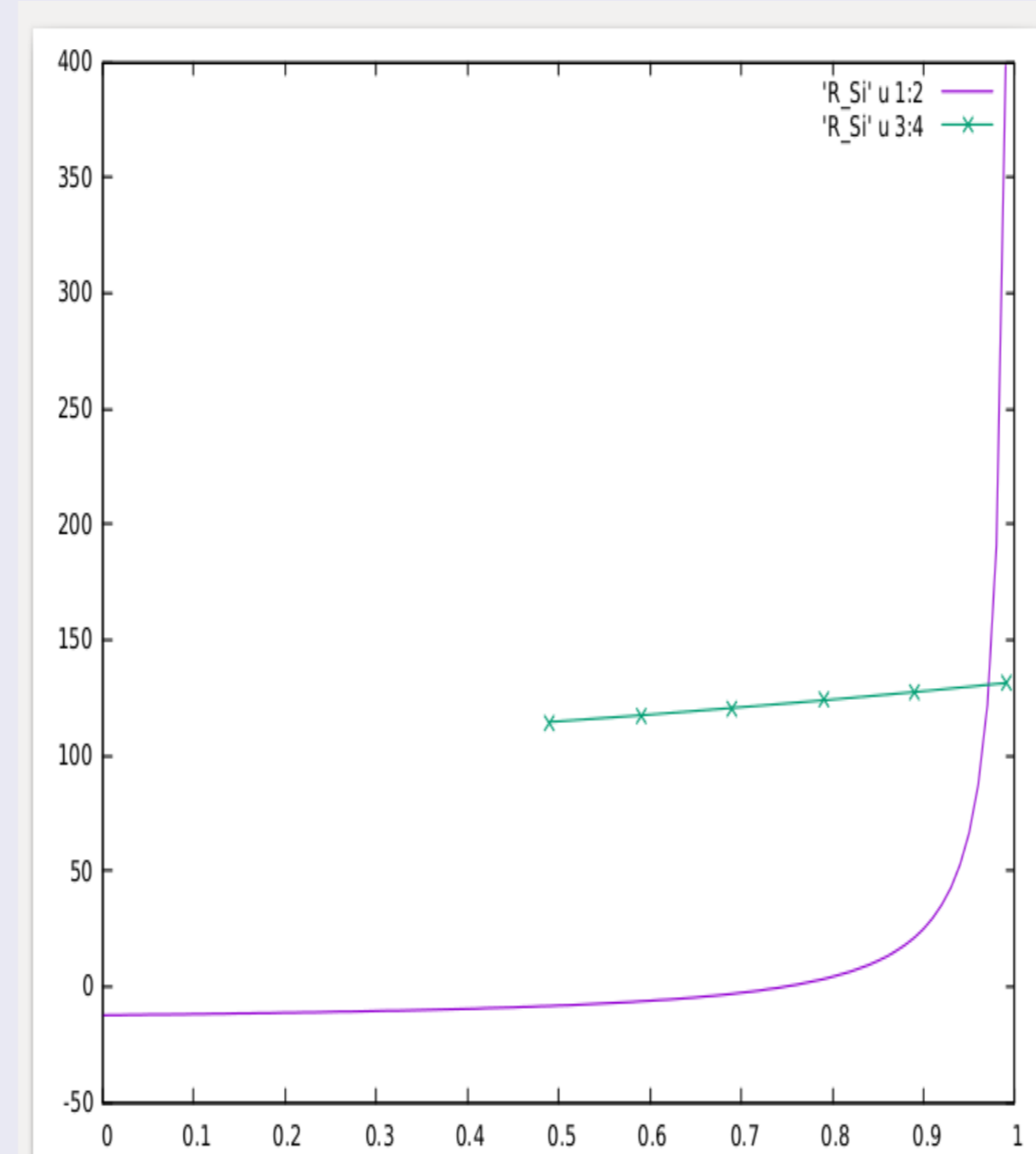

Figure: Plot of cE_p-analytic (purple line), cE_p-perl (green line with points) vs ui-alpha for Silicon

Optimal $ui_\alpha = 0.97$
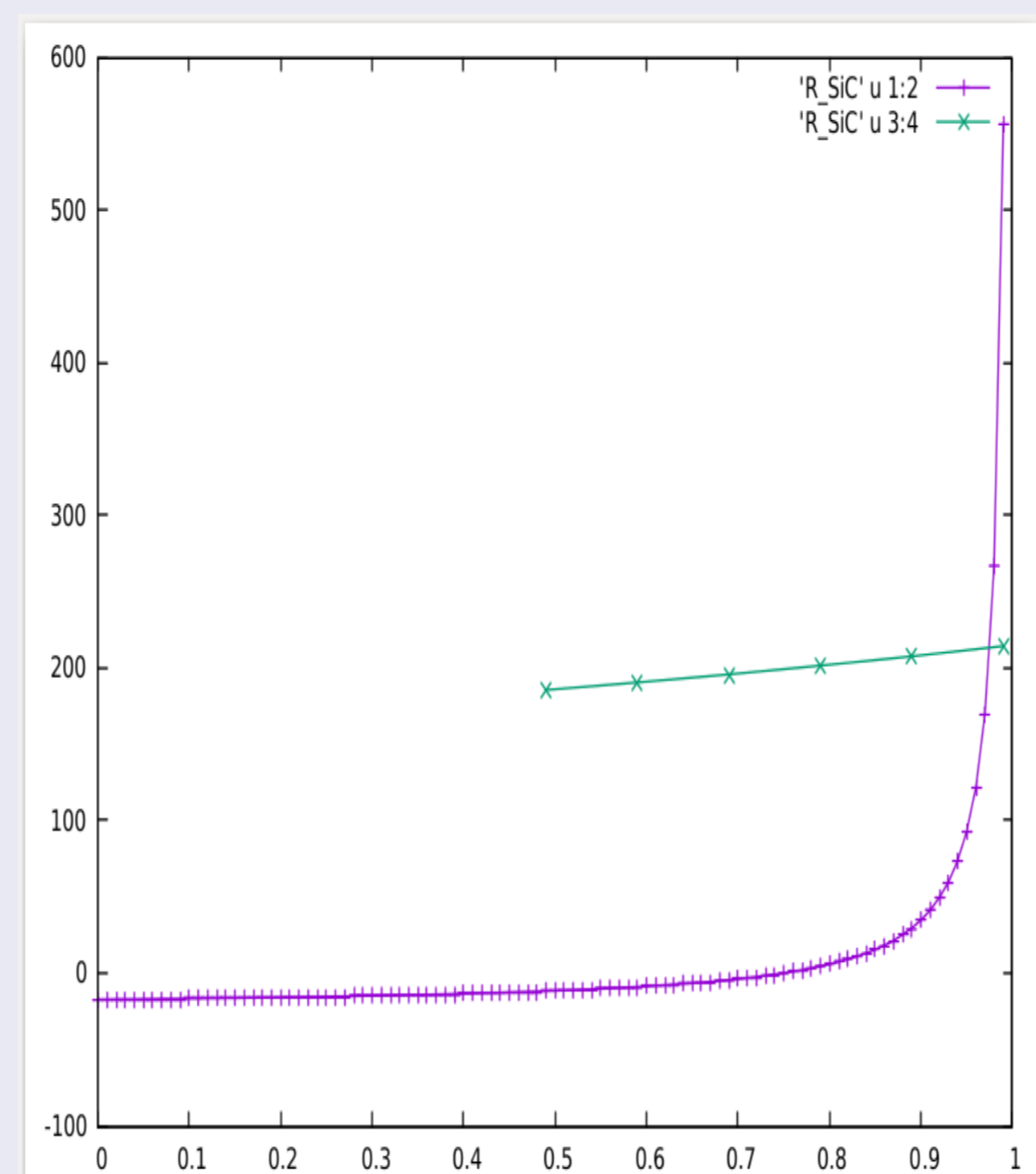

Figure: Plot of cE_p-analytic (purple line), cE_p-perl (green line with points) vs ui-alpha for SiC

Optimal $ui_\alpha = 0.98$

Table: Table of results for the calculation of band gaps

Solid	Exp.	LDA (Lit.)	Error(%)	LDA (this work)	Optimal ui_α	X_α	Error(%)
Si	1.17	0.47	59.8	0.47	0.97	1.10	5.98
BN	6.25	4.39	29.76	4.36	0.98	5.66	9.40
SiC	2.40	1.35	43.75	1.36	0.98	2.27	5.40
AIP	2.45	1.46	40.41	1.43	0.97	2.28	6.90
GaN	3.20	1.63	49.06	2.16	0.94	2.79	12.80
Ar	14.20	8.16	42.54	8.12	0.99	10.67	24.90
GaAs	1.52	0.30	80.26	1.24	0.97	1.70	11.80
LiCl	9.40	6.06	35.53	5.90	0.98	7.21	23.30

RESULTS

our calculations were done for different values of ui_α, the corresponding values cE_p^{perl} were generated while $cE_p^{analytic}$ was calculated analytically. The plots are shown below. The intersections of the two curves were noted which give the values of the optimal ui_α. The value of the optimal ui_α were then used to run our band structure calculations. We have calculated the band gaps of each system as $E_{LUMO} - E_{HOMO}$, where E_{LUMO} is energy of the lowest unoccupied molecular orbital and E_HOMO is the energy of the highest occupied molecular orbital.
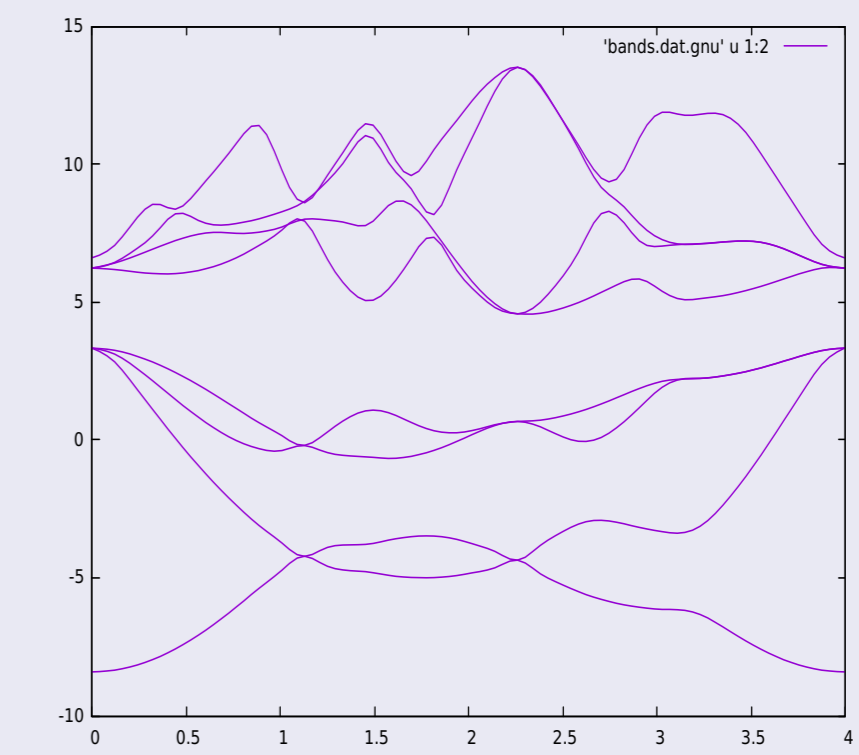

Figure: Band structure of Silicon using the method in this work

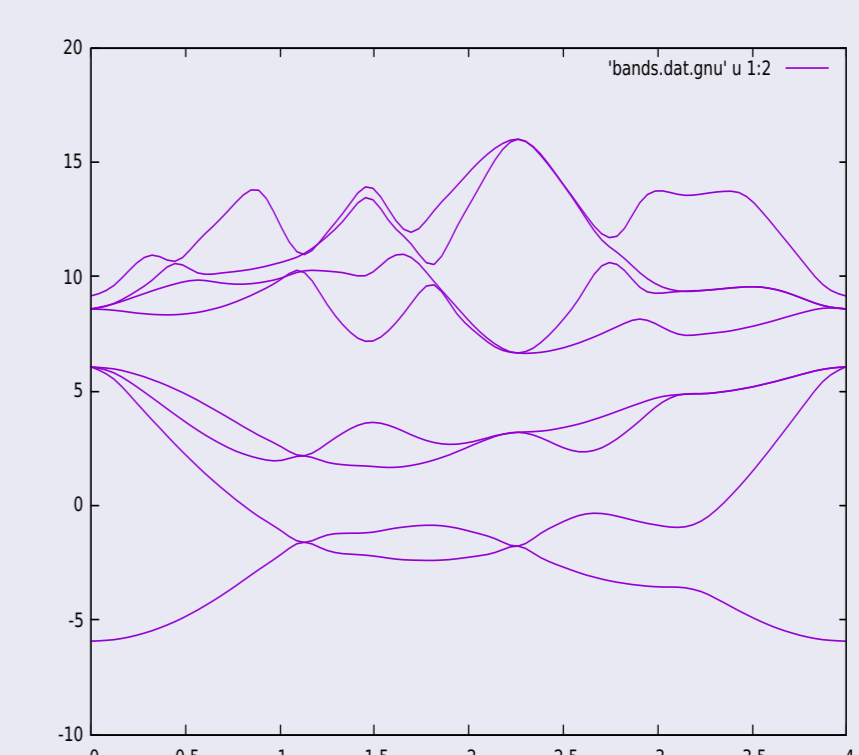$E_{LUMO} \approx 4.50$, $E_{HOMO} \approx 3.30$, $E_g \approx 1.2$

Figure: Band structure of Silicon using LDA method

$E_{LUMO} \approx 6.50$, $E_{HOMO} \approx 5.91$, $E_g \approx 0.59$

DISCCUSION

The results for our calcalations of band gaps (a.k.a X_α) for the systems considered above were compared with experimental values and that of LDA in literature (F. Tran and P. Blaha Phys. 2009). As mentioned earlier that LDA is the first approximation in DFT, it gives underestimation especially in the case of band gaps. As depicted in the tables (1) there is a bit enormous disparities between LDA calculations and experimental values of the band gaps. It is noted that there is atleast some agreement between the experimental values and the calculations in this work for many of the systems considered.

It shows that there is a better agreement between our calculations and experimental values compared to LDA results. This means our formulated exchange-correlation functional has better predictive power of band gaps than LDA. Thus, a major setback in DFT, mentioned earlier in the previous chapter has been partly overcome.

CONCLUSION

The new exchange-correlation potential has been formulated as presented above and incorporated into Quantum espresso software. This functional is easy-to-work-with (less bulky) compare to some functionals and computationally cost effective. Approximation of the total energy and the band structure calculations of some solids have been done using this functional and the results for the calculation of their band gaps are presented in the table (1) which are in very good agreement with the experiment for some of the solids considered especially in case of Si, BN, SiC and AIP with respectively percentage error of 5.98%, 9.4%, 5.4% and 6.9%. therefore we have improved upon LDA at very little additional costs.

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