Quantum mechanical study of liquid crystals

SUMMARY OF DISSERTATION SUBMITTED FOR THE AWARD OF THE DEGREE OF

Master of Philosophy
in
Physics

By

Sumit Tiwari

Enrolment No.:*1134/16*

Under the supervision of

Dr. Devendra Singh

BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
LUCKNOW
प्रज्ञा शील करुणा
ESTABLISHED 1996

Department of Physics
School of Physical and Decision Sciences
Babasaheb Bhimrao Ambedkar University
(A Central University)
Lucknow – 226025, U.P., (India)

2021

Quantum mechanical study of liquid crystals

Liquid crystals have become increasingly popular due to their immense applications in flat panel displays, bio-sensors, solar cells etc. This dissertation, entitled **“Quantum mechanical study of liquid crystals”**, sums up the results obtained on theoretical research carried out in the Department of Physics, Babasaheb Bhimrao Ambedkar University, Lucknow in between 2019-2021 under the supervision of Dr. Devendra Singh, Assistant Professor, Department of Physics of the University. Structure of liquid crystals has been verified by geometry optimizations. Molecular orbitals have been studied for distribution of electrons and bonding character. To get a glimpse of optical properties of LCs or their response to electric field, polarizability, dielectric constant and band gap have been studied.

This dissertation consists of 4 chapters; summary of each chapter is given as under.

CHAPTER 1

INTRODUCTION

Matter exists in three states; namely solid liquid and gas. It is only a common perception and is not wholly correct. Many organic substances show multiple melting points when heated. Before reaching the phase of an isotropic liquid, they form intermediate phases where they flow like liquids, still possessing some physical properties or characteristics of a crystal. Materials that exhibit such unusual intermediate phases are known as mesogens. They are termed as mesogenic and various phases in which they show their existence are termed as mesophases . Molecules possessing such phases are popularly known as liquid crystals (LC). Another popular name for it is mesomorphic phase (mesomorphic means ‘of intermediate form’).

The solids have both positional and orientational order in crystalline state i.e. the molecules in solids are constrained to a certain direction and position. The molecules in a liquid are also packed together but they do not have a certain positional or orientational order. The liquid crystals on the other hand can flow like the liquids, but the molecules in the liquid crystals are organized and/or in favour of in a crystal-like manner.

The liquid crystals can be categorized in two main categories i.e. Thermotropic and Lyotropic. These categories are further distinguished into various phases depending on the variations in their orientational or positional order under effect of external factors such as temperature . In suitable conditions, the molecules of LCs show orientational direction such that all the axes line up and form a supposed nematic liquid crystal. The molecules are still capable of transferring the world over in the fluid, but their orientation remains the same. It is the least well-arranged LC phase. On the contrary, smectic (S_m) phase displays the orientational order but also positional order. In a smectic phase, the molecular cores of mass are organized in layers and the drive is mainly limited inside the layers. In cholesteric LC phase, molecules express intermolecular forces that rearrange arrangement between molecules at a minor angle to one another.

Lyotropic liquid crystal consists of the components that entertain liquid crystalline properties in certain concentration ranges. Lyotropic Liquid Crystals instead are detected when the concentration of a shape or property anisotropic dispersant in an isotropic solvent is altered. These phases are observed as a function of the amount of amphiphilic molecules in aqua or other solvents. These mesophases are usually comprised of a flexible lipophilic chain (the tail) and a polar (non-ionic or ionic) head group.

Thermotropic LCs are the ones which are extensively recognized due to their influential applications in laptop, flat screen televisions and tablet displays or mobile phones. All these applications depend on the point that LCs reveal elastic behavior and can be addressed via electric or magnetic fields, which alter the orientation of the optic axis and therefore the birefringence.

Thermotropic LCs are additionally distinguished by their degree of order and show more stages of transitions inside the temperature regime of the liquid crystalline state. They tend to show various crystalline phases as a function of temperature. The thermal motion of molecules at the melting point gets increased to such an extent that the material transitions from solid phase to liquid crystal phase. This process takes place below room temperature, on further heating, the liquid crystal gets transformed into other liquid crystal phases and then eventually transforms to an isotropic clear liquid.

For the determination of the type of liquid crystal phases the molecular mass and the low molar mass of the molecule plays a very crucial role. On the basis of geometric shape of the respective mesogenic molecule the classification is done. The liquid crystal phases are observed on the basis of some internal parameters which include the chemical structure of the mesogenic molecule and also some external parameters such as pressure and temperature. The most commonly found variety of the liquid crystal is either calamatic or rod like shaped or either discotic or disk kind shaped. Both discotic and calmatic liquid crystal shows a very high degree of dielectric anisotropy. The mean or effective shape mesogens are represented by these cylinders and these mesogens are free to rotate around their molecular axis.

CHAPTER 2

METHODOLOGY

The system of interest chosen for study is nCB liquid crystal

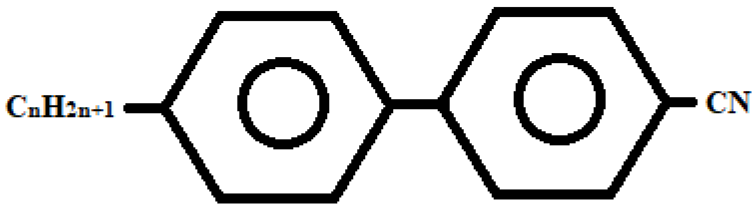

Fig 1 Structure of nCB

All the molecules are optimised by PWscf method using PAW and NC pseudopotentials and the optimised co-ordinates are recorded. Then, SCF calculations of the system are performed. The molecules are chosen to be a monoclinic unit cell as stated in Hanemann et al.

For optimising the coordinates the relax calculations are done using Quantum Espresso software, and then the SCF calculation calculations are performed. Later, phonon calculations are performed for calculating the dielectric constant and polarizability of the system.

The calculations are performed using the plane wave pseudopotential method. The energy cut-off values are properly chosen as a balance between accuracy and time consumed in calculations. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in Fig 2.

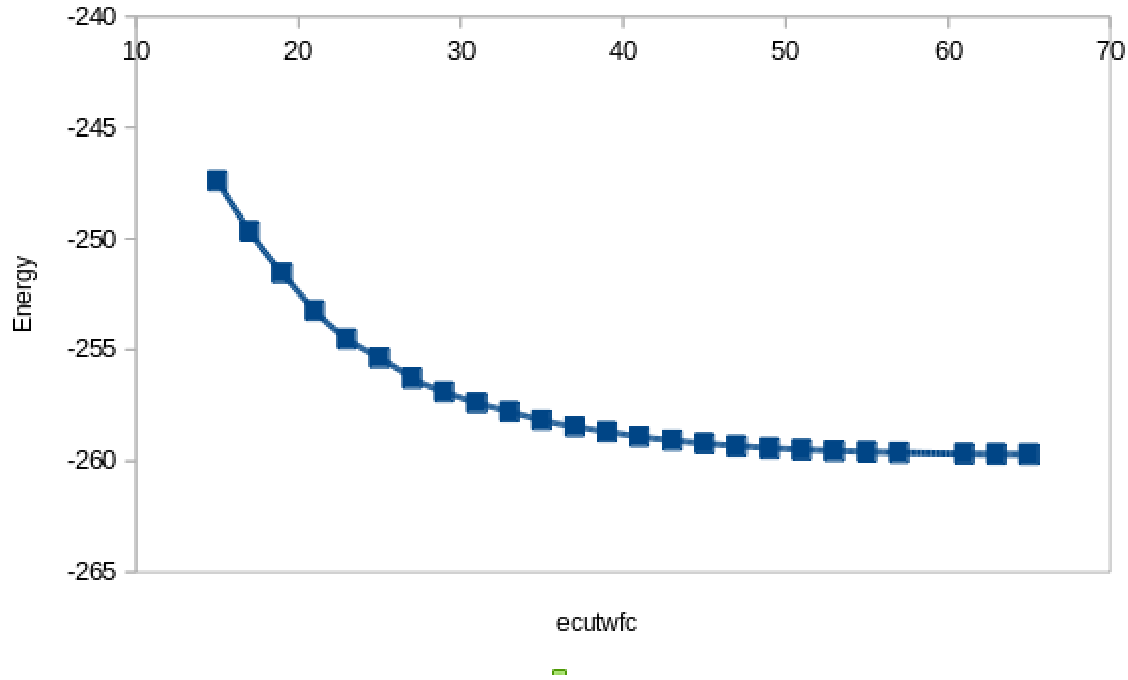

Fig 2 Plot of energy cut-off to total energy of the system

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 4'-methyl-(1, 1'- biphenyl) - 4-carbonitrile (1CB)

The nematic phase of the given molecule is 4'-methyl-(1, 1'- biphenyl) - 4-carbonitrile and it's a nematogenic liquid crystal and is commonly used as a liquid crystal device

The Homo-Lumo of the molecule is shown in fig 3, The energy gap (E_g) of HOMO-LUMO is 2.94 eV (NC) & 3.02 eV (PAW). It can be deduced that that the molecule is dominated by its functional groups. The Humo of the molecule is largely centered around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. Whereas, for Lumo the delocalization of valence orbitals is there throughout the molecule.

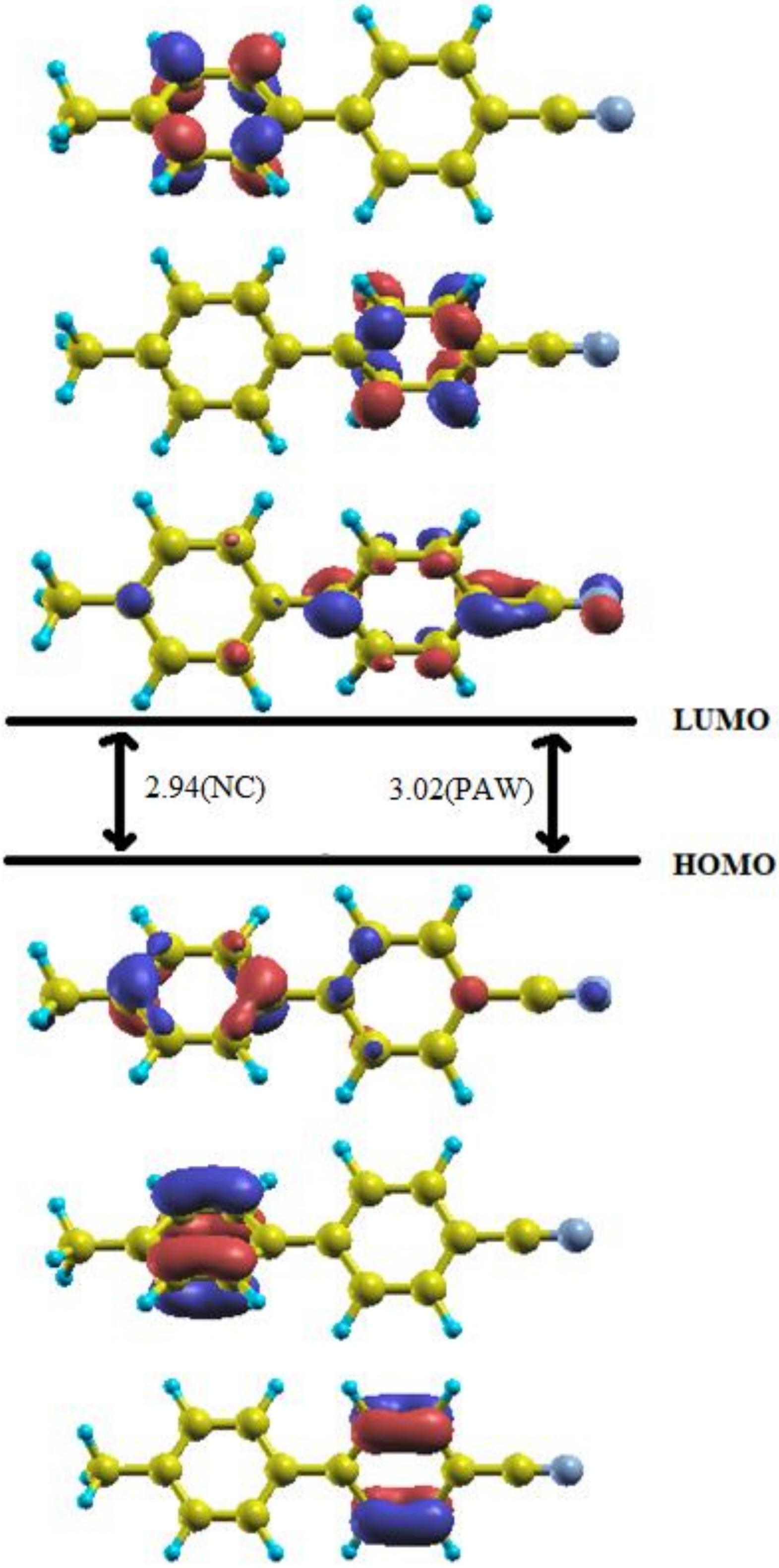

Fig 3 Molecular orbital plot for 1CB

The IR spectra plot of the molecule is given in fig 4.

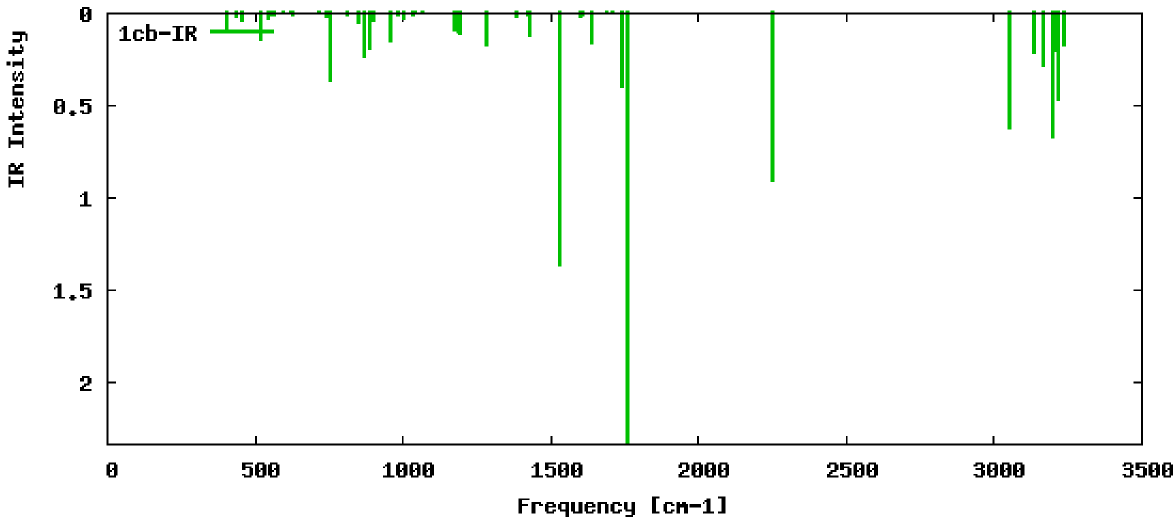

Fig 4 IR spectra plot of 1CB

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.407945032 \\ 1.159207466 \\ 1.107939205 \end{pmatrix},\ \varepsilon_{r(PAW)} = \begin{pmatrix} 1.357350218 \\ 1.146417435 \\ 1.098832143 \end{pmatrix},$$

Average value of dielectric constant comes out to be 1.225 (NC) and 1.201 (PAW).

The value of polarizability comes out to be $\propto = \begin{pmatrix} 420.42 \\ 176.99 \\ 121.98 \end{pmatrix}, \propto = \begin{pmatrix} 373.82 \\ 163.44 \\ 112.98 \end{pmatrix}$ and the average value of polarizability is 239.8 au^3 (NC) and 216.423 au^3 (PAW).

3.2 4'-ethyl-(1,1'- biphenyl)- 4-carbonitrile (2CB)

The nematic phase of the given molecule is 4'-ethyl-(1,1'- biphenyl)- 4-carbonitrile and it's a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The Homo-Lumo of the molecule is shown in fig 5, The energy gap (E_g) 0f HOMO-LUMO is 3.40 eV (NC) & 3.55 eV (PAW). It can be deduced that that the molecule is dominated by its functional groups. The Humo of the molecule is largely centred on the phenyl rings involving the carbon atoms, and the nitrogen that exists at the end is occupied. Whereas, for Lumo the delocalization of valence orbitals is there throughout the molecule.

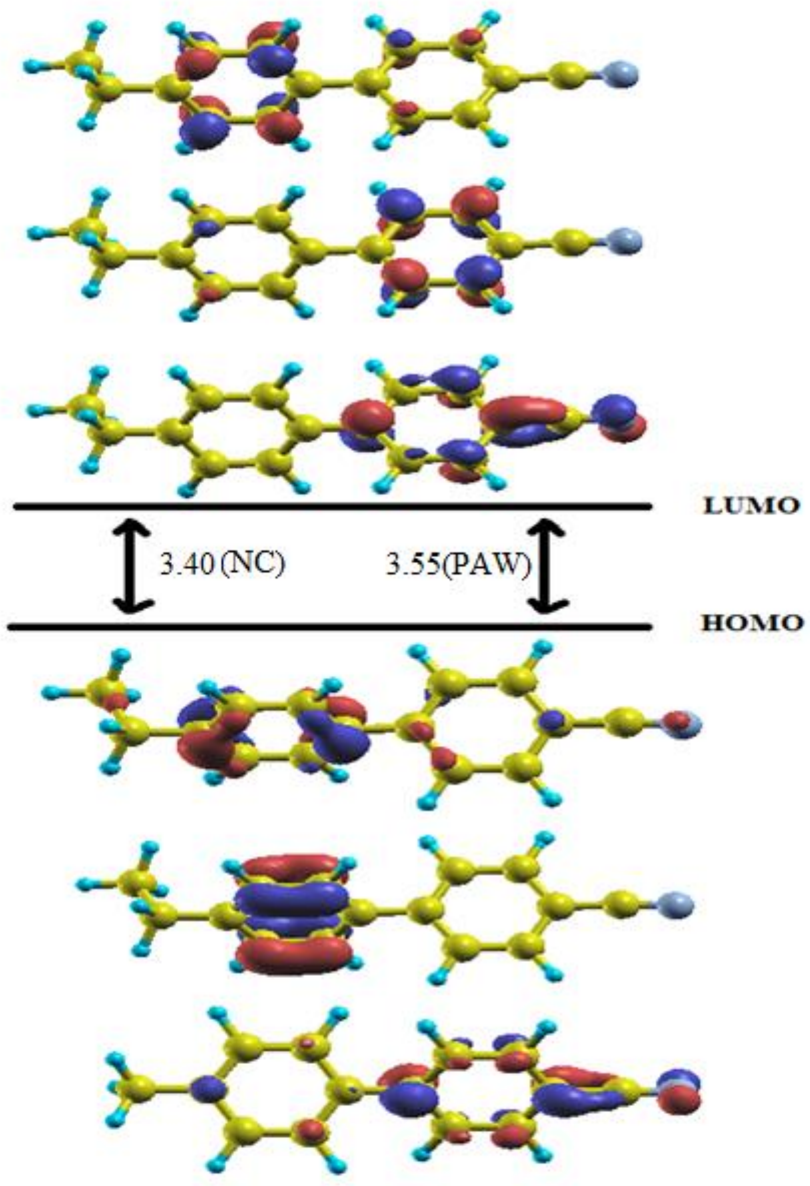

Fig 5 Molecular orbital plot for 2CB

The IR spectra plot of the molecule is given in fig 6

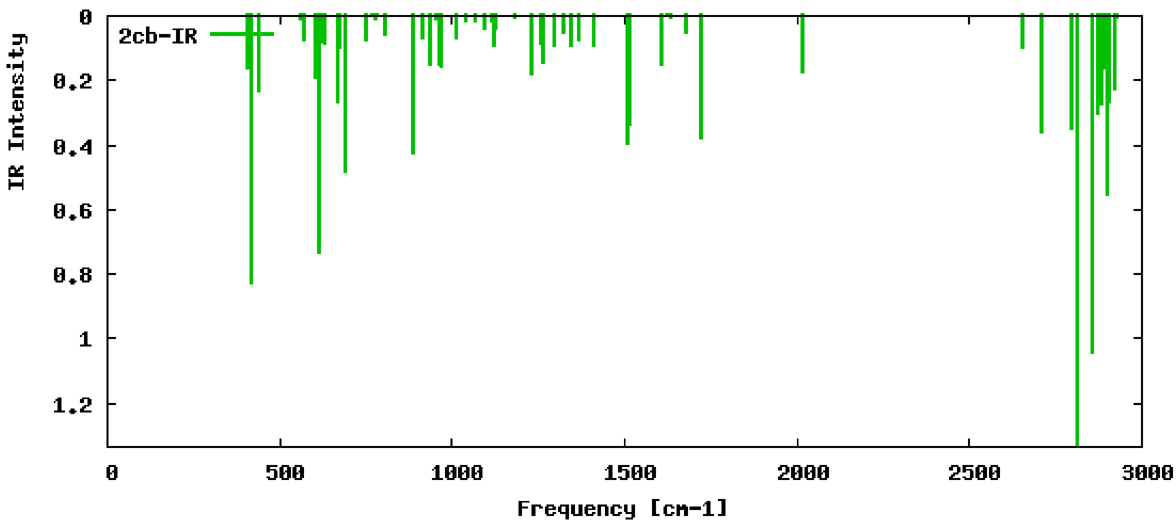

Fig 6 IR spectra plot of 2CB

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.774645132 \\ 1.322363457 \\ 1.541202401 \end{pmatrix}, \ \varepsilon_{r(PAW)} = \begin{pmatrix} 1.659667675 \\ 1.358449148 \\ 1.390910634 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.55(NC) and 1.47(PAW).

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 299.74 \\ 141.72 \\ 223.22 \end{pmatrix}$, $\propto = \begin{pmatrix} 263.27 \\ 155.89 \\ 168.38 \end{pmatrix}$ and the average value of polarizability is 221.56 au^3 (NC) and 195.85 au^3 (PAW).

3.3 4'-propyl-(1,1'- biphenyl)- 4-carbonitrile (3CB)

The nematic phase of the given molecule is 4'-propyl-(1,1'- biphenyl)- 4-carbonitrile and it's a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The Homo-Lumo of the molecule is shown in fig 7, The energy gap (E_g) 0f HOMO-LUMO is 3.10 eV (NC) & 3.55 eV (PAW). It can be deduced that that the molecule is dominated by its functional groups. The Humo of the molecule is largely centered around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. Whereas, for Lumo the delocalization of valence orbitals is there throughout the molecule.

The IR peak intensities spectra plot of the given molecule is given in fig 8.

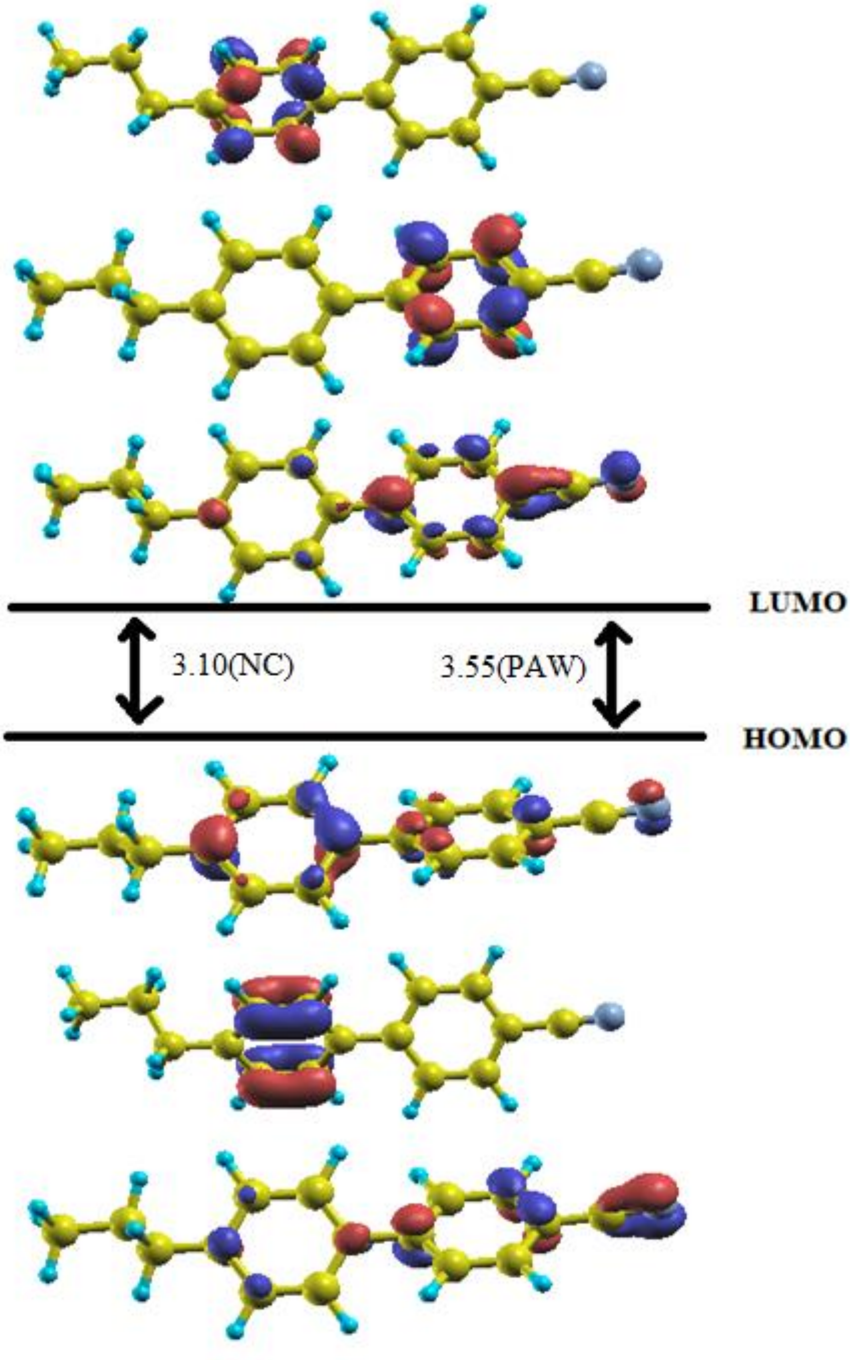

Fig 7 Molecular orbital plot for 3CB

The IR peak intensities spectra plot of the given molecule is given in fig 8.

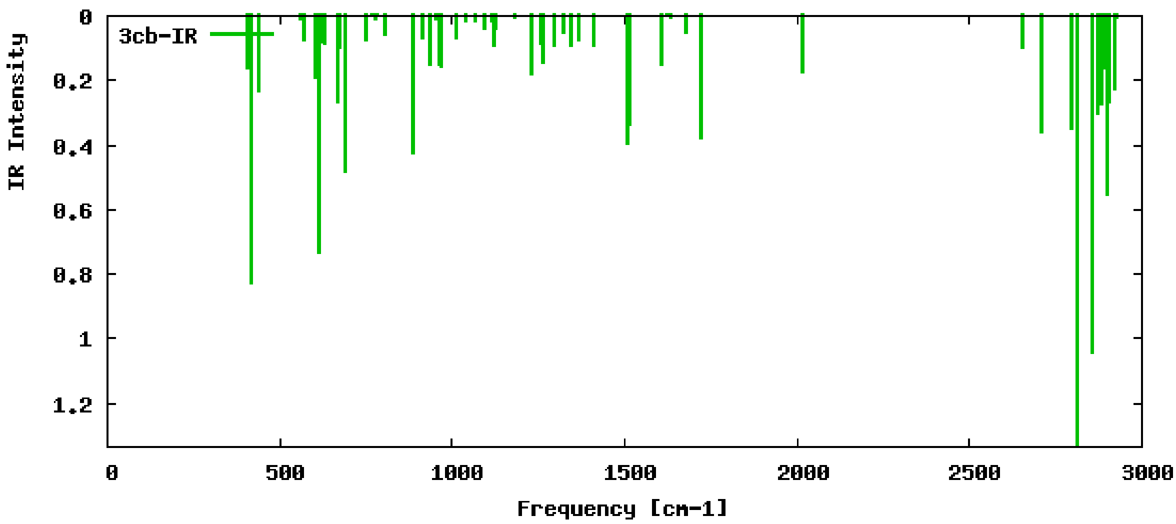

Fig 8 IR spectra of 3CB

The dielectric tensor of the molecule is also calculated and is given as

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.631541829 \\ 1.287090128 \\ 1.272987638 \end{pmatrix}, \varepsilon_{r(PAW)} = \begin{pmatrix} 1.561010322 \\ 1.261360929 \\ 1.272987638 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.4(NC) and 1.36(PAW).

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 370.43 \\ 186.04 \\ 177.66 \end{pmatrix}, \propto = \begin{pmatrix} 335.58 \\ 170.70 \\ 164.55 \end{pmatrix}$ and the average value of polarizability is 244.71 au^3 (NC) and 223.61 au^3 (PAW).

3.4 4'-butyl-(1,1'- biphenyl)- 4-carbonitrile (4CB)

The nematic phase of the given molecule is 4'-Butyl-(1,1'- biphenyl)- 4-carbonitrile and it's a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The Homo-Lumo of the molecule is shown in fig 9, The energy gap (E_g) 0f HOMO-LUMO is 3.20 eV (NC) & 3.24 eV (PAW). It can be deduced that that the molecule is dominated by its functional groups. The Humo of the molecule is largely centered around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. Whereas, for Lumo the delocalization of valence orbitals is there throughout the molecule.

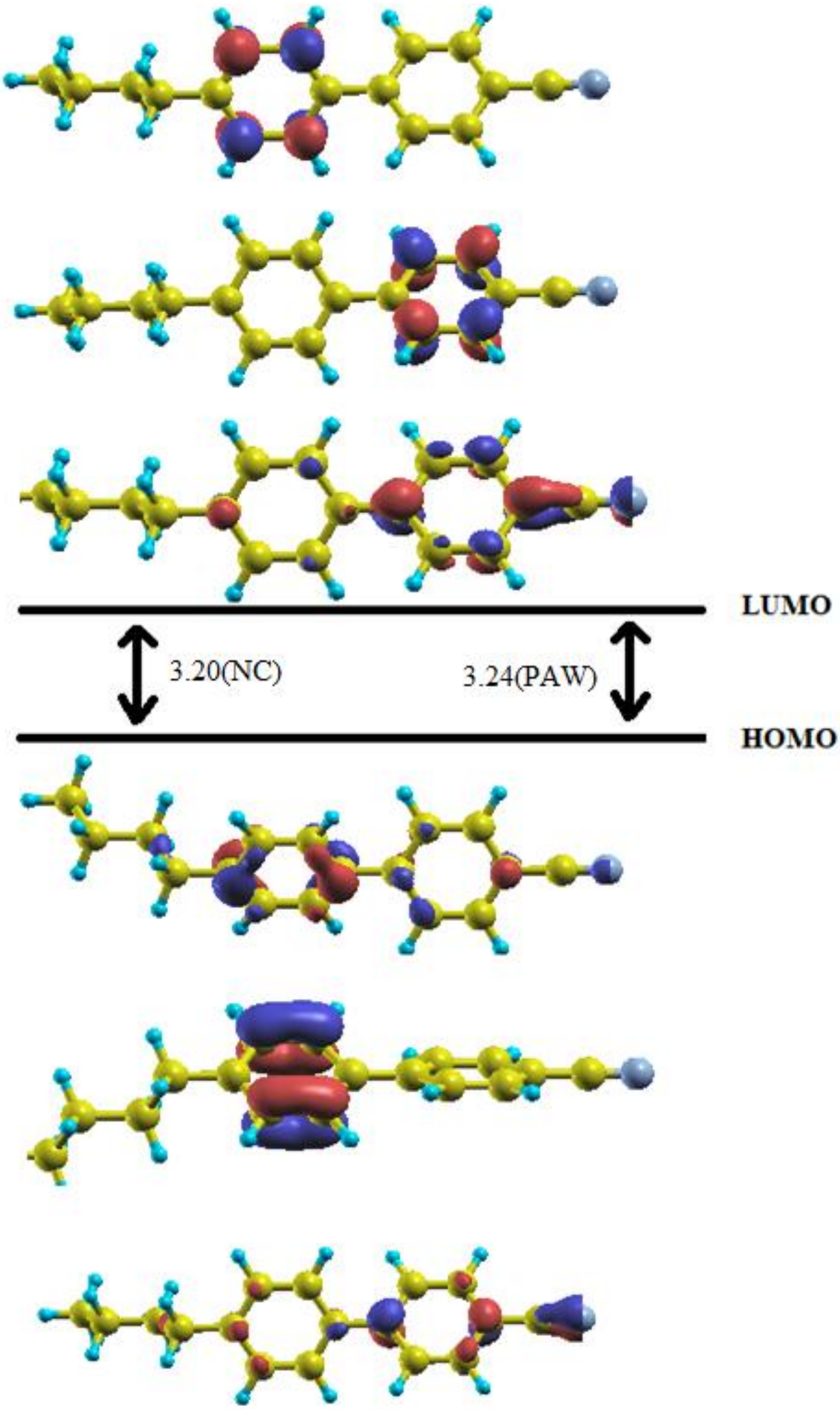

Fig 9 Molecular orbital plot for 4CB

The IR peak intensities spectra plot of the given molecule is given in fig 10.

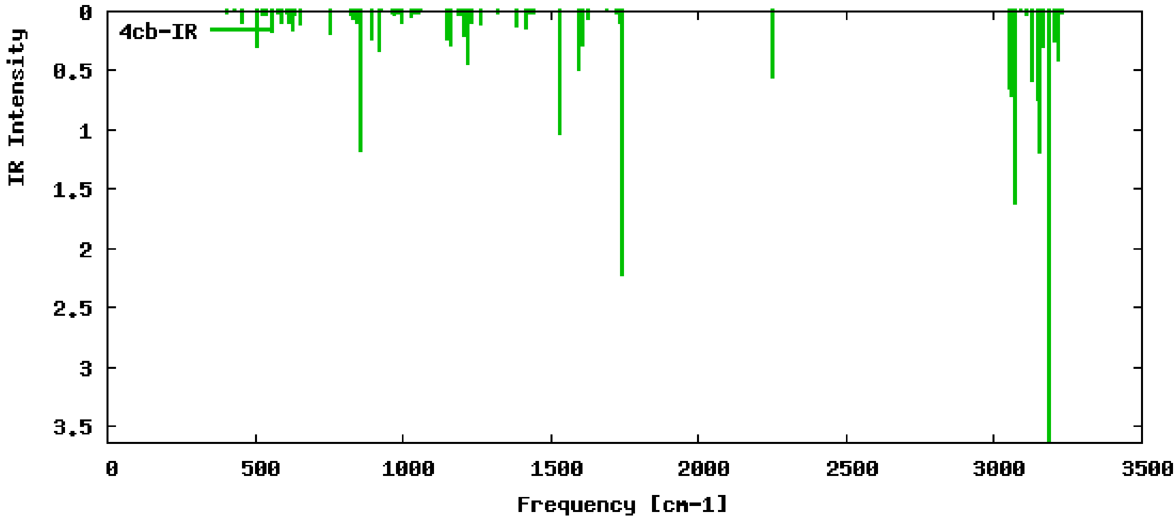

Fig 10 IR spectra of 4CB liquid crystal

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_r = \begin{pmatrix} 2.184657918 \\ 1.688872132 \\ 1.435866804 \end{pmatrix}, \varepsilon_r = \begin{pmatrix} 2.041920365 \\ 1.611658858 \\ 1.395207403 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.77(NC) and 1.68(PAW).

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 337.65 \\ 249.12 \\ 169.23 \end{pmatrix}$, $\propto = \begin{pmatrix} 343.88 \\ 225.92 \\ 155.28 \end{pmatrix}$ and the average value of polarizability is 252(NC) and 241.69(PAW).

3.5 4'-pentyl-(1, 1'- biphenyl) - 4-carbonitrile (5CB)

The nematic phase of the given molecule is 4'-pentyl-(1,1'- biphenyl)- 4-carbonitrile and it's a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The Homo-Lumo of the molecule is shown in fig 3.11, The energy gap (E_g) 0f HOMO-LUMO is 2.98 eV (NC) & 3.05 eV (PAW). It can be deduced that that the molecule is dominated by its functional groups. The Humo of the molecule is largely centered around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. Whereas, for Lumo the delocalization of valence orbitals is there throughout the molecule.

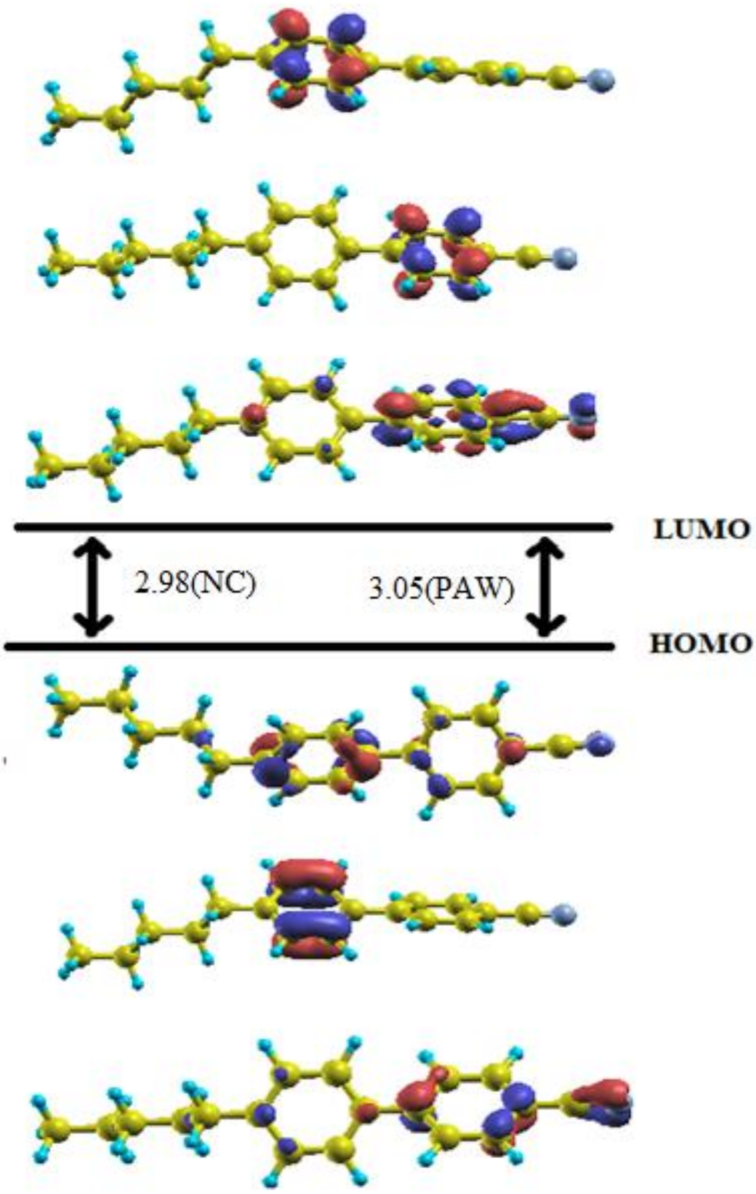

Fig 11 Molecular orbital plot for 5CB

The IR peak intensities spectra plot of the given molecule is given in fig 12.

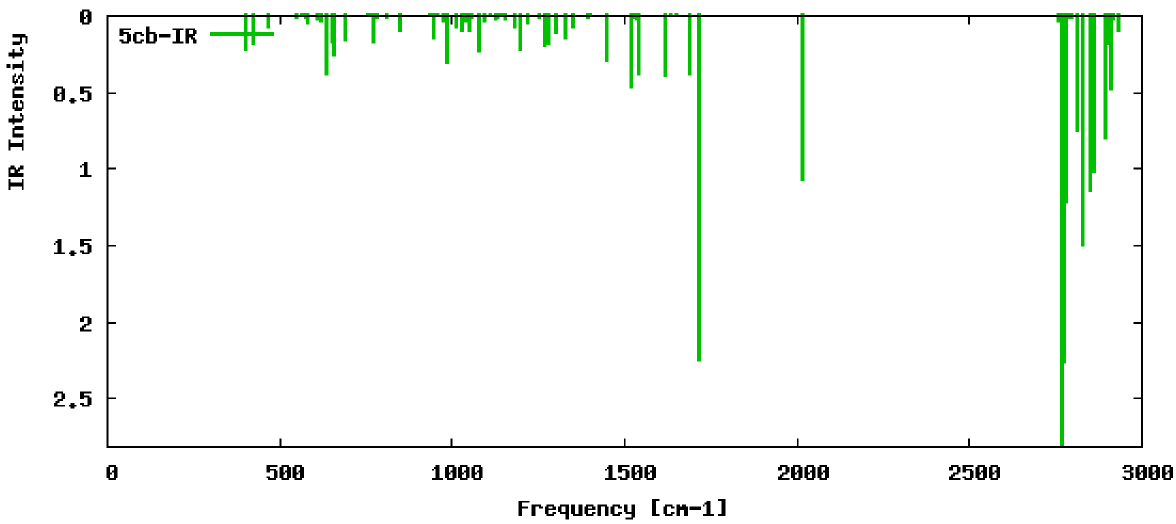

Fig 12 IR spectra plot of 5CB

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.682415153 \\ 1.278595991 \\ 1.240497075 \end{pmatrix}, \varepsilon_{r(PAW)} = \begin{pmatrix} 1.601823295 \\ 1.256839434 \\ 1.217472032 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.4(NC) and 1.36(PAW).

The value of polarizability comes out to be $\propto = \begin{pmatrix} 479.36 \\ 219.80 \\ 191.98 \end{pmatrix}$, $\propto = \begin{pmatrix} 432.21 \\ 203.99 \\ 174.84 \end{pmatrix}$ and the average value of polarizability is 297.0467 au^3 (NC) and 270.34 au^3 (PAW).

3.6 4-Nitrosobenzonitrile (4NB)

The given liquid molecule is 4-Nitrosobenzonitrile is a commonly used liquid crystal device used in LCD’s

The Homo-Lumo of the molecule is shown in fig 13, It can be deduced that that the molecule is dominated by its functional groups.

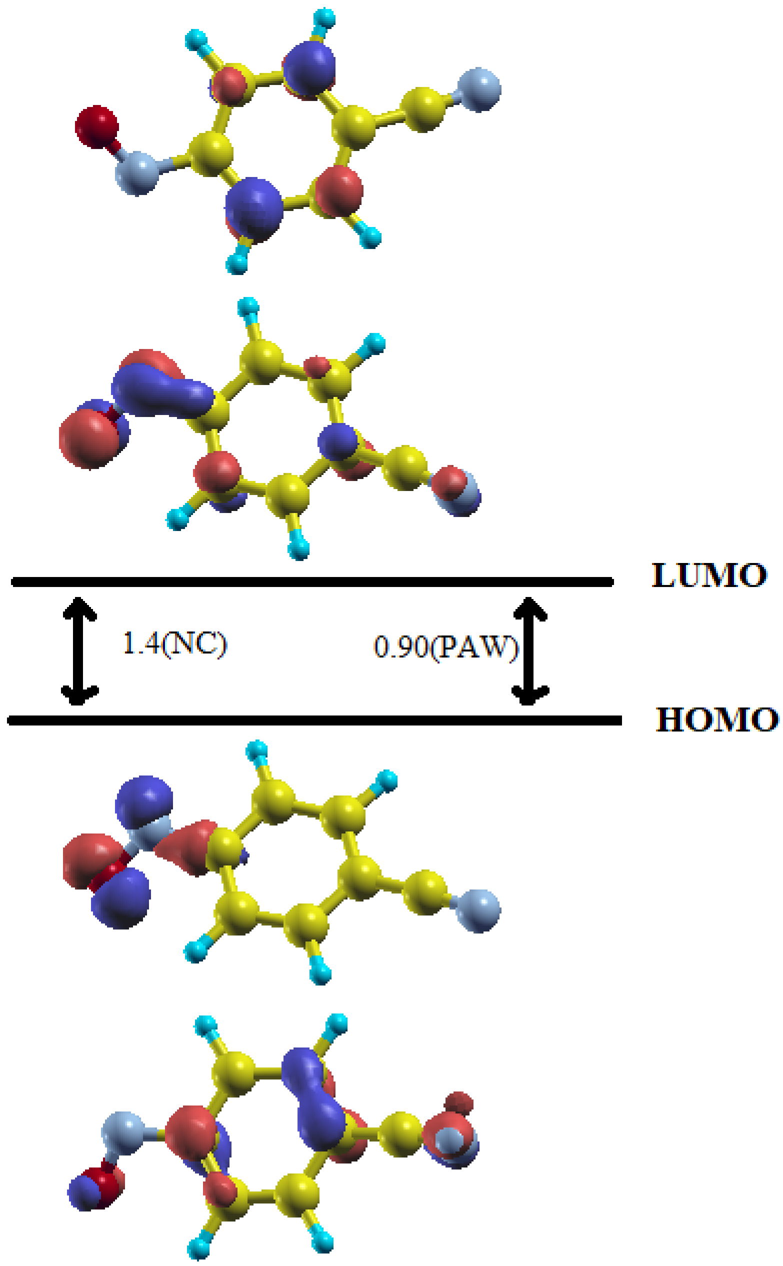

Fig 13 Molecular orbital plot of 4NB

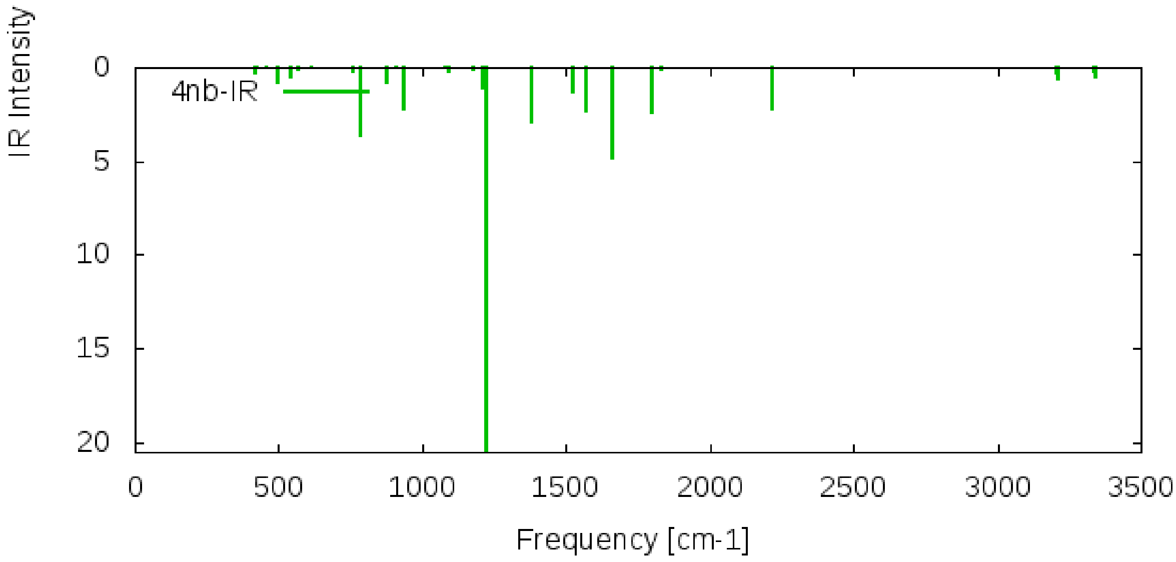

Fig 14 IR spectra plot of 4NB

The dielectric tensor of the molecule is also calculated and is given as

$$\varepsilon_{r(NC)} = \begin{pmatrix} 2.758437298 \\ 1.946325168 \\ 2.952548820 \end{pmatrix}, \varepsilon_{r(PAW)} = \begin{pmatrix} 2.656605588 \\ 2.982627225 \\ 2.696076669 \end{pmatrix}$$

Average value of dielectric constant comes out to be 2.55(NC) and 2.45(PAW).

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 124.36 \\ 80.7 \\ 132.68 \end{pmatrix}$, $\propto = \begin{pmatrix} 119.72 \\ 83.03 \\ 121.54 \end{pmatrix}$and the average value of polarizability is 112.58(NC) and 108.1(PAW).

Discussion

The band gap and dielectric constant show odd-even effect in the n-cynobiphenyl series where n is the number of carbon atoms in the alkyl chain of nCB as reported by Kumar et al., The value of band gap for 1CB is 3.02 eV and for 2CB it increases to 3.55 eV and then decreases for 3CB to 3.17 eV for and then increases for 4CB TO 3.24 eV as shown in Fig 15. The dielectric constant for 1CB is 1.2 and for 2CB it increases to 1.469 and subsequently for 3CB it decreases to 1.36, subsequently increases for 4CB to 1.68 and later decreases to 1.36 for 5CB. The seemingly erroneous pattern may be due to smaller energy cut-off values (ecutwfc).

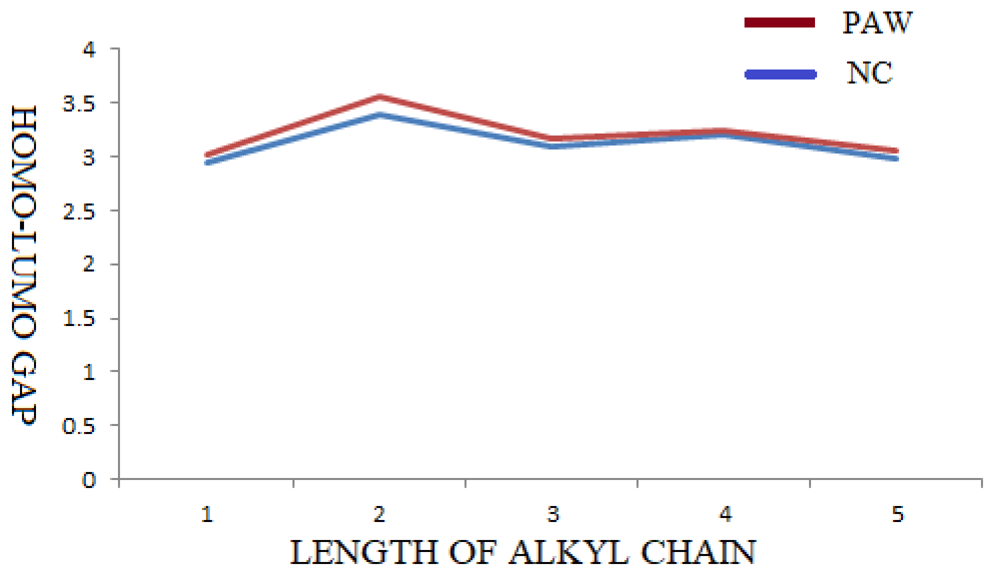

Fig 15 ODD-EVEN effect in HOMO-LUMO gap

The structure of molecule is nearly same for both PAW and Norm Conserving pseudopotentials. The bond lengths vary within nearly 2.3% of each other.

The infra-red spectra wave numbers also lie within nearly 2.25% (for 3CB) to 6.4% (for 2CB) of the experimental values. Higher cut-off wave functions or bigger k-point grid may be used to reduce error. However, it becomes computationally costly.

The Molecular orbital studies are in consonance with the previous theoretical calculated parameters .

CHAPTER 4

CONCLUSIONS

The structure of nCB (n=1-5) has been optimised using PWscf method implemented using Quantum Espresso. The given structures are optimised using PAW and NC Pseudopotentials and the bond length of the given molecules are compared. With the use of optimised co-ordinates, the value of band gap, polarizability and dielectric constant is calculated.

Table 1 **C**alculated parameters of 1-5CB and 4NB

Molecule	HOMO LUMO gap(eV)		Polarizability (a.u^3)		Dielectric constant	
	NC	**PAW**	**NC**	**PAW**	**NC**	**PAW**
1CB	2.94	3.02	239.8	216.42	1.225	1.201
2CB	3.40	3.55	221.56	195.85	1.546	1.47
3CB	3.10	3.17	244.71	223.61	1.397	1.358
4CB	3.20	3.24	252.00	241.69	1.77	1.683
5CB	2.98	3.05	297.05	270.35	1.401	1.359
4NB	1.40	0.90	112.58	108.1	2.552	2.445

It can be deduced that the molecule is dominated by its functional groups. In nCB, the HOMO of the molecule is largely centered on the phenyl rings involving the carbon atoms and the nitrogen that exists at the end is occupied. For LUMO the delocalization of valence orbitals is there throughout the molecule.

Also the HOMO LUMO of 4NB is dominated by the presence of its functional groups.

There could be seen an odd even effect in the nCB series of liquid crystals where n is the number of carbon atoms in the alkyl chain attached to the benzene ring, it increases for the value of even number of carbon atoms and then decreases for the odd number of carbon atoms. The subsequent pattern is visible for the HOMO-LUMO and polarizability of the molecule. The value of HOMO-LUMO gap for 1CB is 2.94 eV (NC) and for 2CB it increases to 3.40 eV (NC) and then decreases for 3CB to 3.10 (NC) and then increases for 4CB to 3.20 eV (NC) and then again decreases for 5CB to 2.98eV (NC). The same pattern is observed for the dielectric constant of the molecules. The given pattern follows for PAW pseudopotentials also.

Future scope

Quantum Espresso does calculations on period structures. The studies presented here assume perfectly crystalline state of liquid crystal. However, the liquid crystals do not show exact periodicity at room temperature. Hence, there is scope of further study of properties at NTP. Since LCs have promising applications in display devices which in turn are governed by birefringence on account of applied electric field applied, therefore, electric field calculations have good scope. Regarding periodicity, a supercell may be constructed with a few LC molecules populated inside it having minimum energy configuration. A cluster formation approach within this supercell of appropriate size must be designed. For this, molecular dynamic stimulations of the molecules may be performed. It is of significance to study the effect of electric field and calculate the electro-optical properties of the molecules which include birefringence, order parameter and refractive index of the molecule. Later, non-linear properties may also be investigated.

In the near future I would like to increase the length of alkyl chain in the nCB series of molecule and wish to calculate the properties of higher order molecules of the biphenyl series. Study of effect of applied electric field to LC molecule is expected to help understand the nature of performance of LC devices at molecular level.