

MSc Project presentation
On

First-principles calculations of Urea, MNA and TaAs

By

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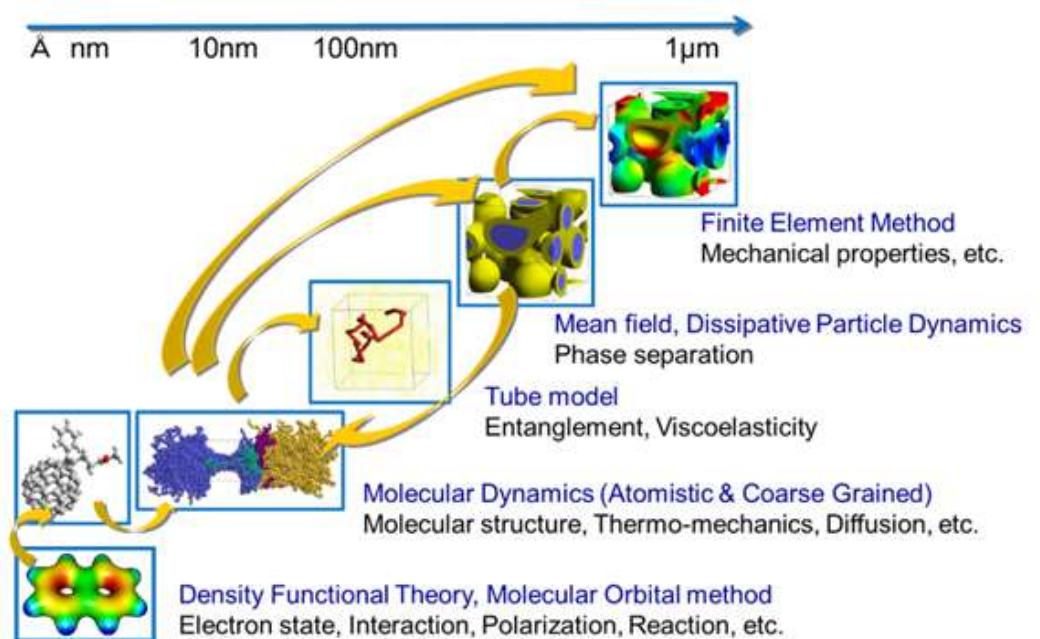
2nd April 2024

Outline

- Material properties prediction
- Objectives
- Materials chosen
- First principles calculation – Theoretical background
- First principles calculation – Methods and tools used
- Computational Facilities
- Properties calculated
- Results
 - Organic Materials
 - Inorganic Materials
- Conclusion
- Further work

Material properties prediction

- Condensed Matter Physics - Explores the behavior of matter in condensed phases.
- Material properties prediction - essential for designing and engineering advanced materials.
- Computational condensed matter physics
 - Utilizes advanced computational techniques to calculate and predict the properties and behaviors of materials in condensed phases.



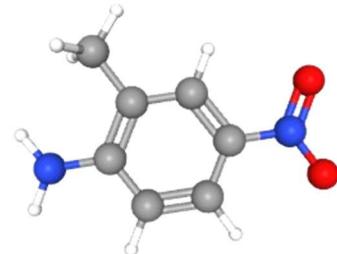
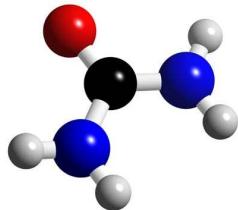
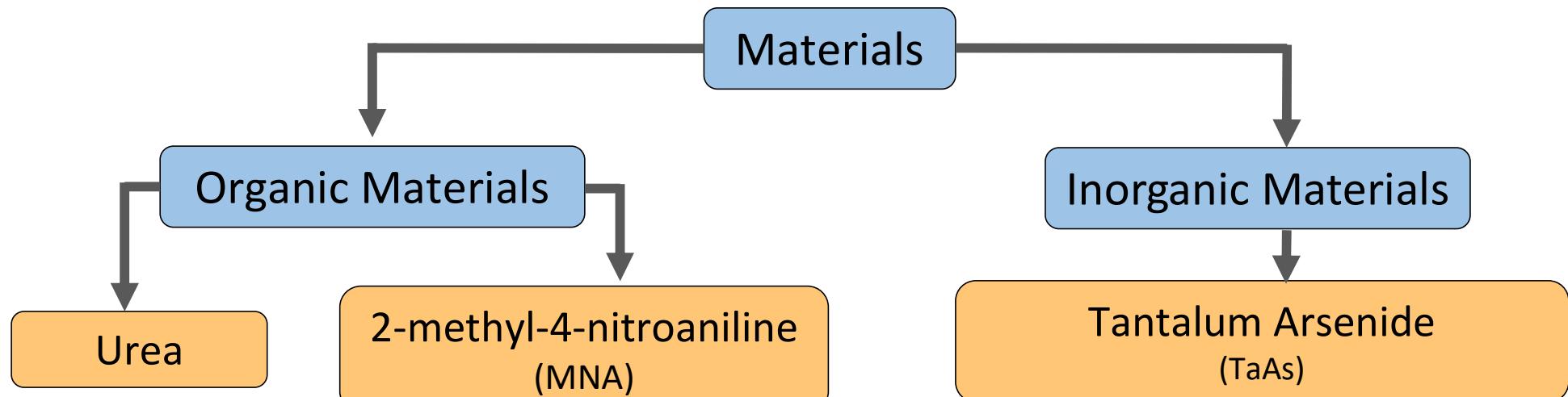
<https://mse.iitd.ac.in/ongoing-research/3>

<https://www.j-octa.com/functions/dft/>

Objectives

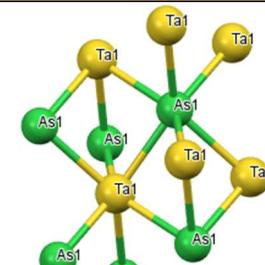
- To Understand the Theoretical framework of first principles calculations using density functional (DFT) theory.
- To develop optimized structure of materials.
- To calculate the various properties of materials.

Material Chosen



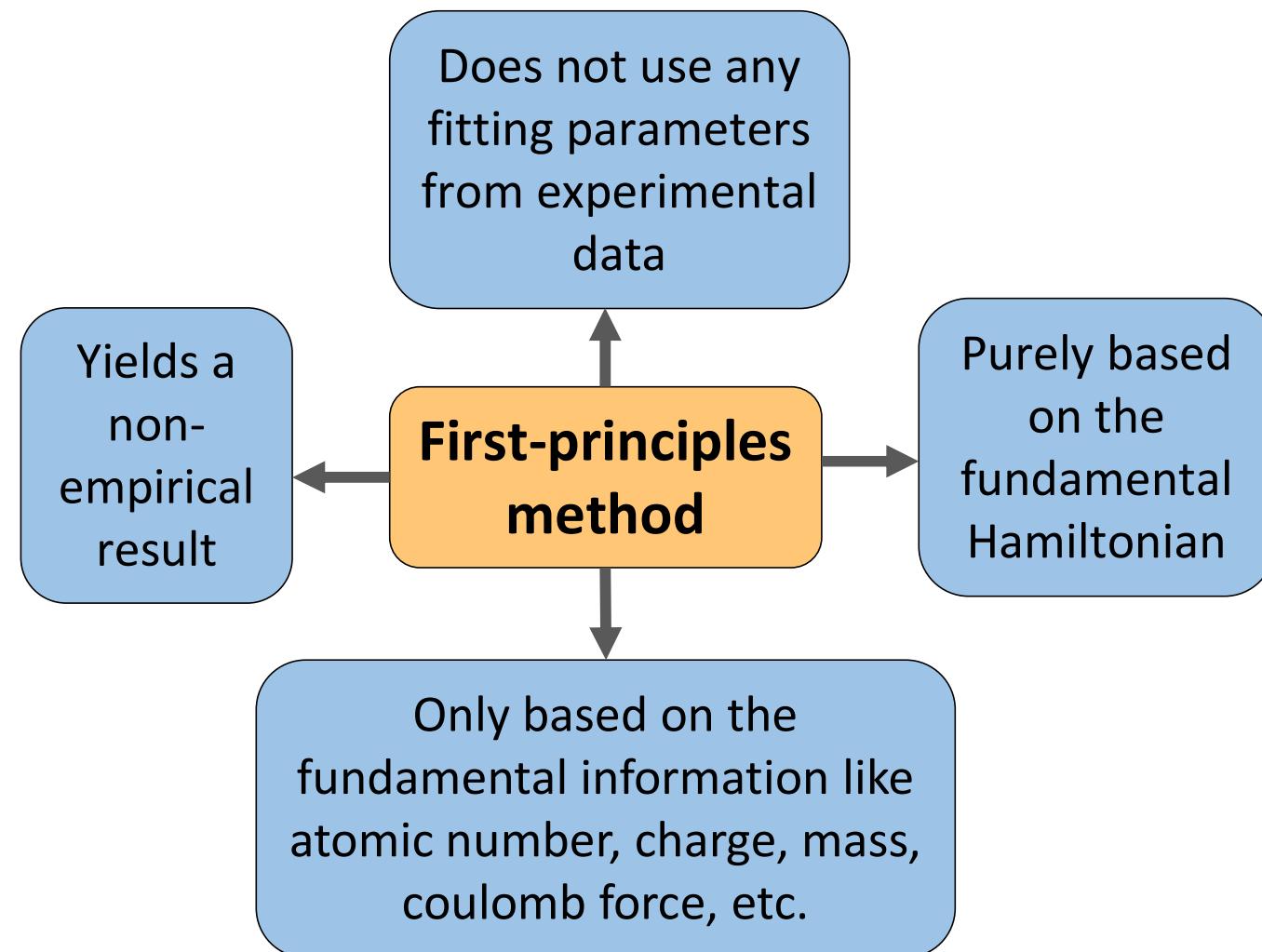
Challenging nature of performing first-principles calculations on organic crystals

All three materials show potential applications in non-linear optics.



Recently developed with Promising applications like Weyl semimetals, topological insulators etc.

First principles calculation – Theoretical background



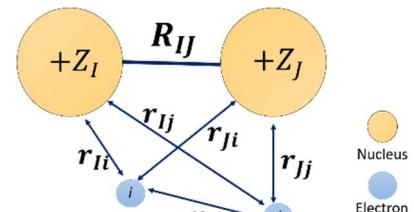
First – principles calculation using DFT

Density Functional Theory (DFT) is a powerful computational method. Used in physics, chemistry, and materials science.

Through the utilization of functionals DFT enables the determination of various properties of multi-electron systems by analyzing electron density.

First principles calculation – Theoretical background

$$\hat{H}\psi = E\psi$$

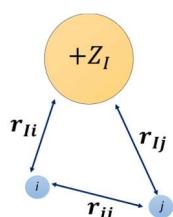


$$\hat{H} = -\frac{1}{2} \left[\left(\sum_I \frac{\hbar^2}{M_I} \nabla_I^2 + \sum_i \frac{\hbar^2}{M_i} \nabla_i^2 \right) + \left(\sum_{i,\alpha} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} - \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \right) \right]$$

The many-body problem

$$\hat{H}_e \psi_e(\vec{r}, \vec{R}) = E_e \psi_e(\vec{r}, \vec{R})$$

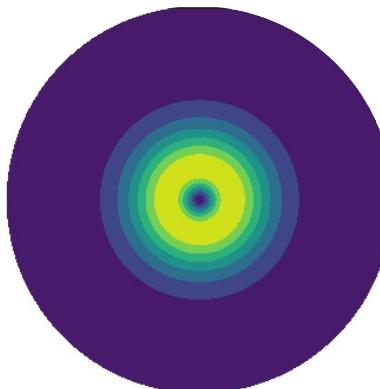
$$\hat{H}_e = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V^{ext}(\vec{r}, \vec{R})$$



BO approximation

$$\left(-\frac{1}{2} \nabla^2 + U_{eff} \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

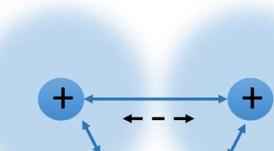
$$n(\vec{r}) = 2 \sum_{i=1}^{\frac{N}{2}} |\psi_i(\vec{r})|^2$$



DFT

Hartree method

$$\psi(x_1, x_2, x_3, \dots, x_p) = \psi_\alpha(x_1) \psi_\beta(x_2) \psi_\gamma(x_3) \dots \psi_\pi(x_p)$$



SCF

$$\begin{aligned} & \left[-\frac{\hbar^2}{2M_I} \nabla_I^2 + V^{ext}(\vec{r}, \vec{R}) + \sum_j \int d\vec{r}' \psi_j^*(\vec{r}') \psi_j(\vec{r}') \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right] \psi_i(\vec{r}') \\ & + \sum_j \int d\vec{r}' \psi_j^*(\vec{r}') \psi_i(\vec{r}') \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \psi_j(\vec{r}) \delta_{sis_j} = \epsilon_i \psi_i(\vec{r}') \end{aligned}$$

HF method

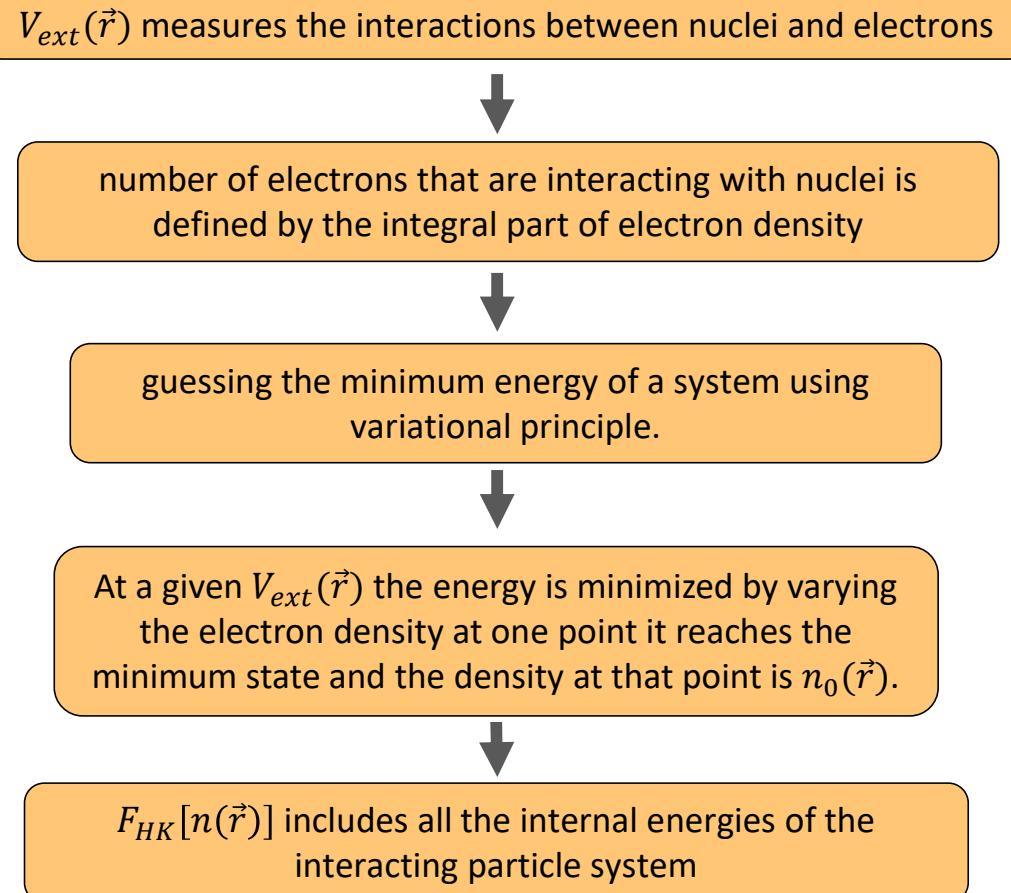
First principles calculation – Theoretical background

Hohenberg and Kohn (HK) theorems

Theorem 1: For any system of interacting particles in an external potential $V_{ext}(\vec{r})$ is determined by unique functional of the ground state of the particle density $n_0(\vec{r})$.

Theorem 2: The energy functional that gives the ground state energy of the system gives the lowest energy only when the input density is in the ground state.

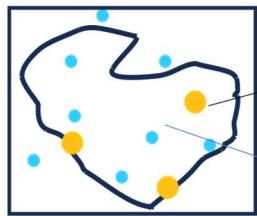
$$E[n(\vec{r})] = F_{HK}[n(\vec{r})] + \int V_{ext}(\vec{r})n(\vec{r})d\vec{r}$$



First principles calculation – Theoretical background

KS ansatz

Interacting electrons



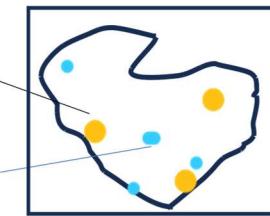
Exact Hamiltonian operator for all electrons together

Exact electron density



Obtained by solving Schrödinger equation (SE) to obtain **exact wavefunction** for interacting electrons

Non-interacting electrons



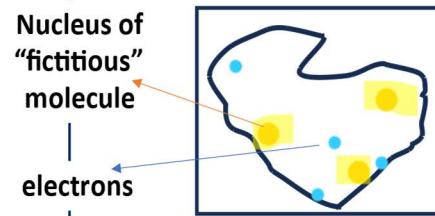
Hamiltonian operator for one electron moving in an “average” potential caused by the rest of the electrons

Approximate electron density



Obtained by solving SE for one electron. Combine **many one electron** wavefunctions (molecular orbitals) to obtain **approximate wave function** for all electrons

Kohn-Sham non-interacting electrons



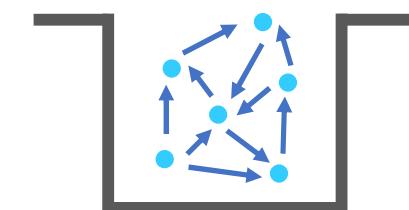
Hamiltonian operator for one electron moving in an “average” potential caused by a special fictitious system of electrons

Exact electron density

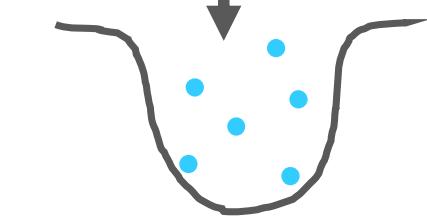


Obtained by solving solve SE for one electron. Combine **one electron** wavefunctions (molecular orbitals) to obtain **approximate wave function** for all electrons

KS equations can be solved using self-consistent field method by providing the exact form of $E_{xc}[n(\vec{r})]$ is given.



Many body SH eq method



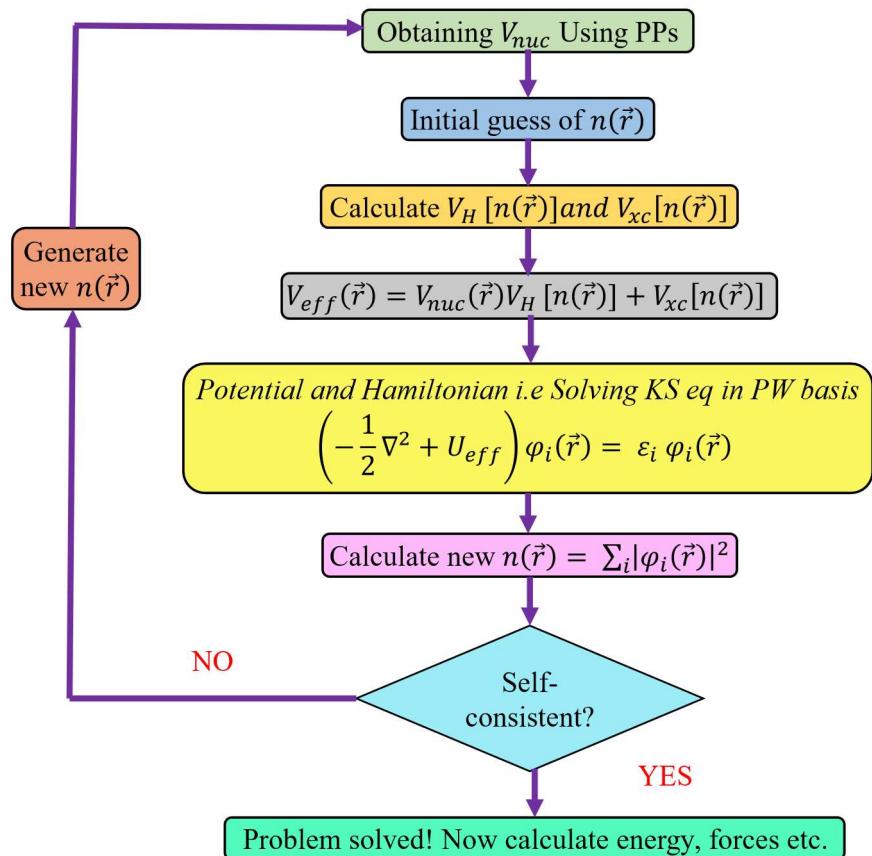
The effective potential modeled using MFT and DFT



basis function to represent the wavefunctions of electrons

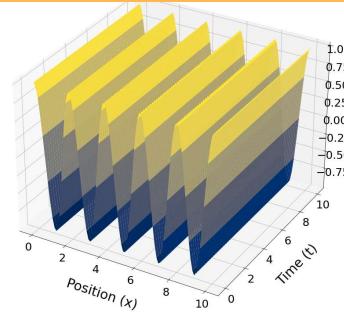
First principles calculation – Methods and tools used

SCF Loop

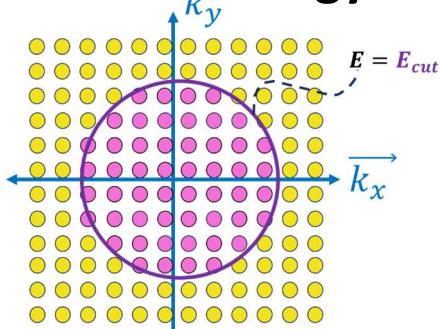


PW Basis set

PW are often used as basis functions to represent the wavefunctions of electrons, where the electronic wavefunctions exhibit translational symmetry



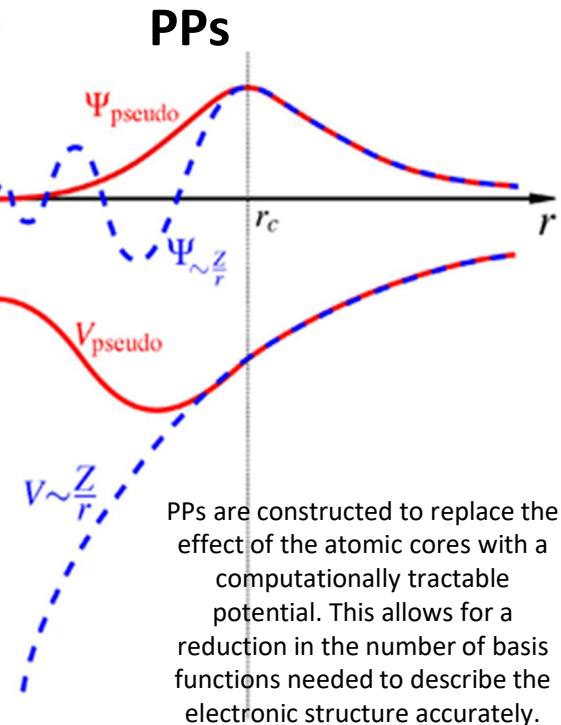
PW cutoff energy



The cut-off energy is a key convergence parameter
 E_{cut} of charge density = 4 E_{cut} of orbitals

$$E_{cut} = \frac{\hbar^2}{2m} |\vec{G}_{max}|^2$$

PPs



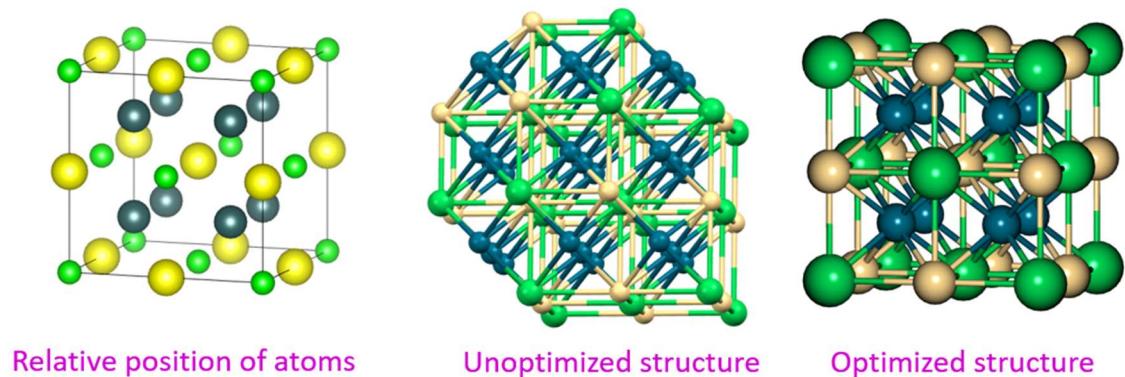
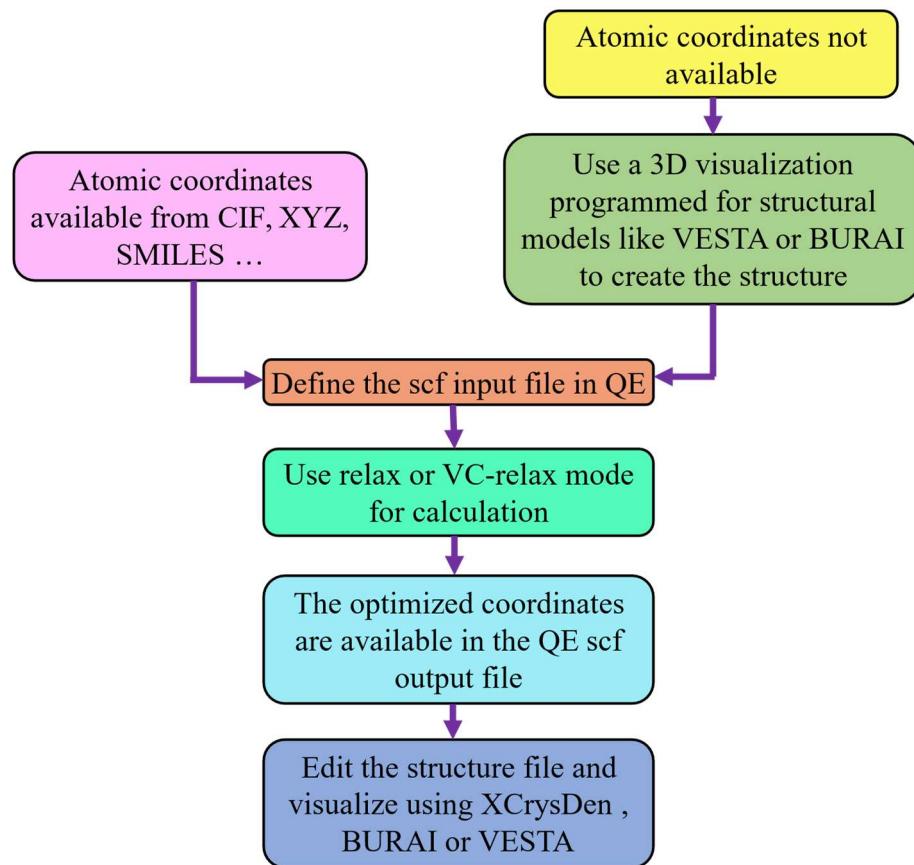
PPs are constructed to replace the effect of the atomic cores with a computationally tractable potential. This allows for a reduction in the number of basis functions needed to describe the electronic structure accurately.

First principles calculation – Methods and tools used

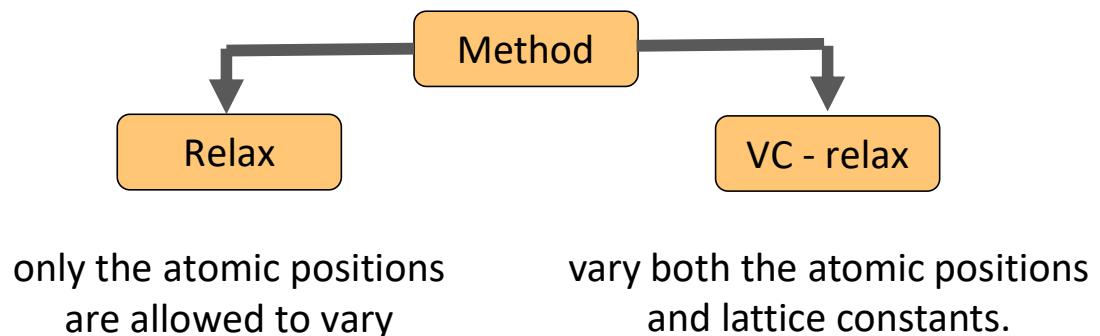
- Density functional theory (DFT) using [plane-wave \(PW\) pseudopotential \(PP\)](#).
- PWscf (Plane-Wave Self-Consistent Field) calculation using [Quantum espresso code](#).
- Gfortron, FFT and LAPACK are used to run the QE code.
- Perdew–Burke–Ernzerhof (PBE) exchange correlation functional for ab initio calculations.
- The core electrons are described by [Norm-Conserving \(NC\) PPs](#) in separable (Kleinman-Bylander) form.
- Structure is fully relaxed in its ground state using [Variable Cell relax \(vc-relax\)](#) calculation and visualized using VESTA.
- The [high-symmetry K paths](#) in the Brillouin zone are found using XCrySDen.
- [BURAI GUI](#) is used to visualize and modify the input files for scf calculation.
- [Coupled linear-response TDDFPT equations](#) and [Quantum liouville equation using Lanczos algorithm](#) to calculate the absorption spectra.
- The post processing work of the results are done using Fortran90, python and Origin.

First principles calculation – Methods and tools used

Structural optimization

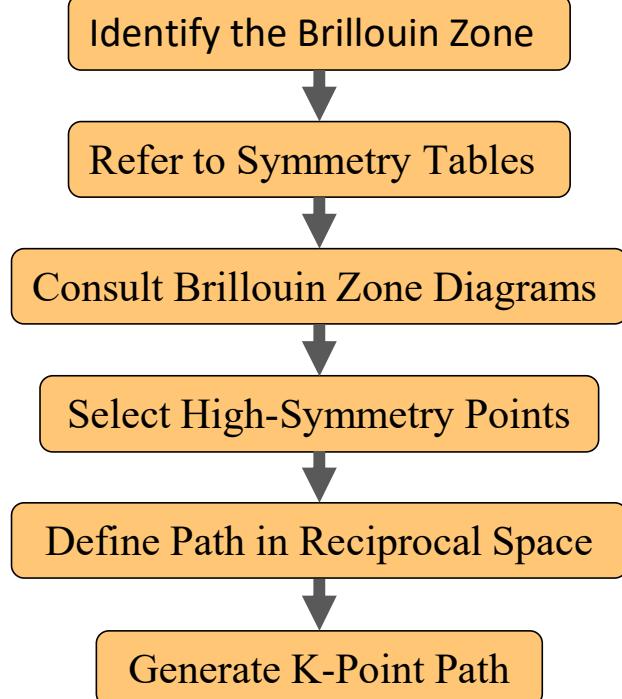
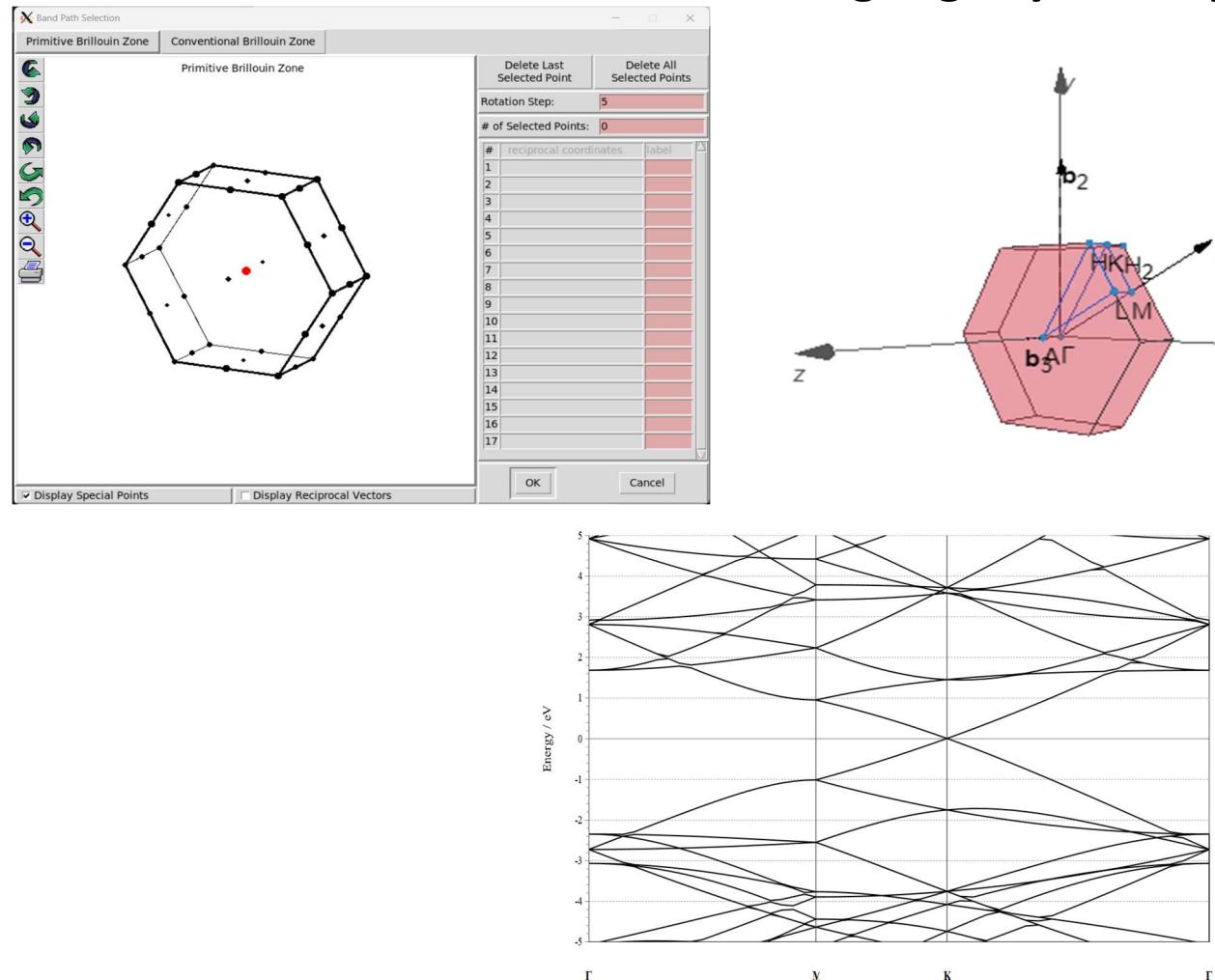


moving the atoms of a molecule to get the most stable structure with the lowest possible ground state energy.



First principles calculation – Methods and tools used

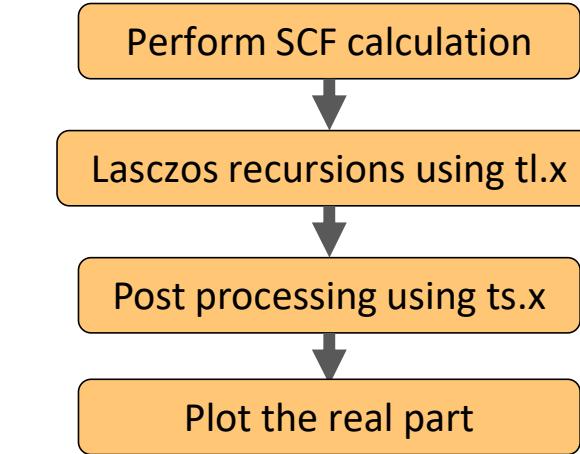
Selecting High symmetry K-points



First principles calculation – Methods and tools used

Calculation of absorption spectra

- The `turbo_lanczos.x` program allows us to calculate absorption spectra of molecules using time-dependent density functional perturbation theory (TDDFPT) without computing empty states.
- The interactions of electrons (Hartree and Exchange-Correlation effects) are considered fully in ab initio and self-consistently.
- The overall absorption spectrum in a wide frequency range can be calculated at once



	\hbar \omega(eV)	Re(chi) (e^2*a_0^2/eV)	Im(chi) (e^2*a_0^2/eV)
chi_1_1=	0.0000000000000E+00	0.367809385681014E+02	- .0000000000000E+00
chi_2_1=	0.0000000000000E+00	-.631858329281267E-04	0.0000000000000E+00
chi_3_1=	0.0000000000000E+00	-.204467248171178E+02	0.0000000000000E+00
chi_1_2=	0.0000000000000E+00	-.631706192483719E-04	0.0000000000000E+00
chi_2_2=	0.0000000000000E+00	0.250012382752616E+02	- .0000000000000E+00
chi_3_2=	0.0000000000000E+00	0.358096420342268E-04	- .0000000000000E+00
chi_1_3=	0.0000000000000E+00	-.204463946327822E+02	0.0000000000000E+00
chi_2_3=	0.0000000000000E+00	0.358450506838120E-04	- .0000000000000E+00
chi_3_3=	0.0000000000000E+00	0.205248428246752E+02	- .0000000000000E+00
chi_1_1=	0.1000000000000E-01	0.367810680070323E+02	0.207145008754846E-01
chi_2_1=	0.1000000000000E-01	-.631868517748287E-04	- .187715955097414E-06
chi_3_1=	0.1000000000000E-01	-.204467950141741E+02	- .112857575489507E-01
chi_1_2=	0.1000000000000E-01	-.631716378970102E-04	- .187509351059613E-06
chi_2_2=	0.1000000000000E-01	0.250012789479554E+02	0.607690777777168E-02
chi_3_2=	0.1000000000000E-01	0.358101583277243E-04	0.954462827239609E-07

Computational facilities

- Personal computer
 - Processor - 11th Gen Intel(R) Core(TM) i5-1135G7
 - RAM – 16GB (SSD)
 - Operating system – UBUNTU (Linux), Windows 11
 - Cores – 4
 - GPU – 2GB

Most of the calculations are run parallelly utilizing the 4 available cores.

- The average time for scf calculations is 10 to 30 min.
- The average time for DOS calculations is 1hr.
- the average time for the bands calculations is 5 to 10 hr. the average time for the absorption spectra is 5 to 10 hr.

This is the minimum configuration for running any DFT code

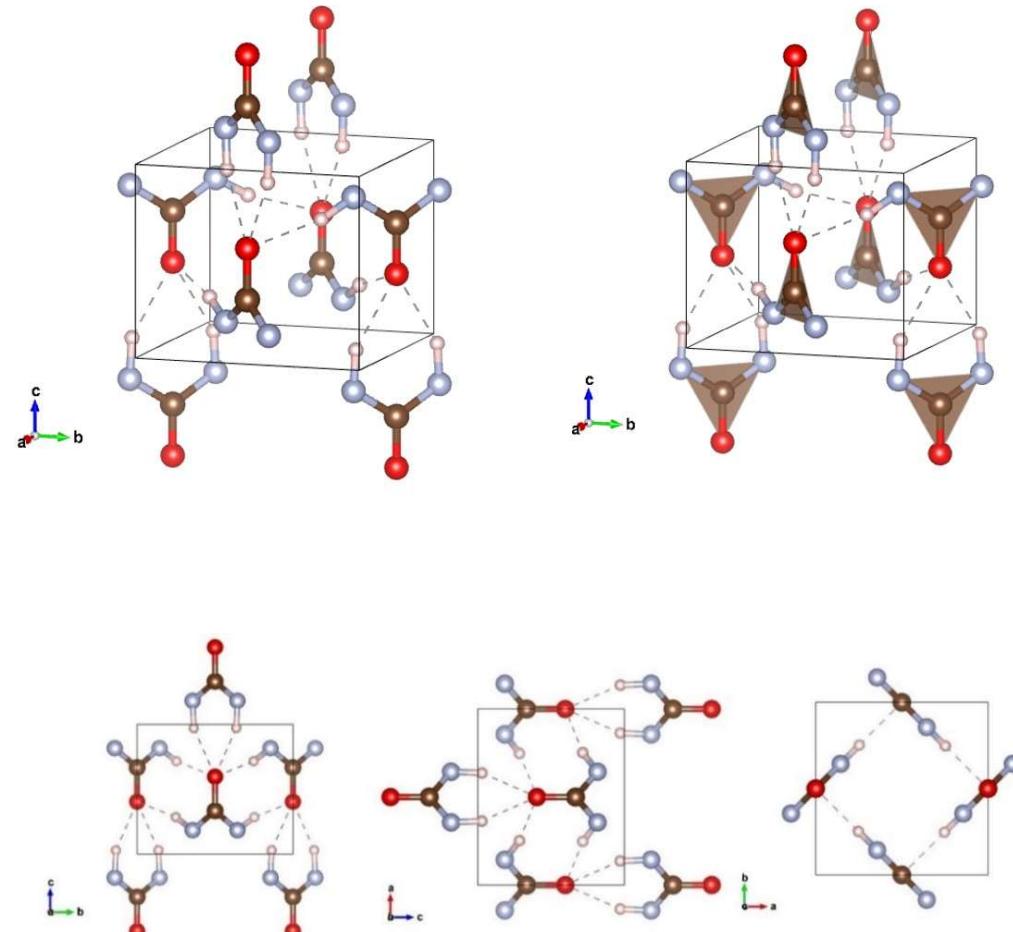
Properties calculated

- Structural parameters*
- Bonding *
- Optimized structure*
- Powered XRD pattern*
- Fermi Energy*
- Total magnetization
- Pressure and strain
- Total energy*
- Density of states (DOS)*
- High symmetry k- points*
- Electronic band structure*
- Projected density of states (PDOS) *
- Absorption spectra*

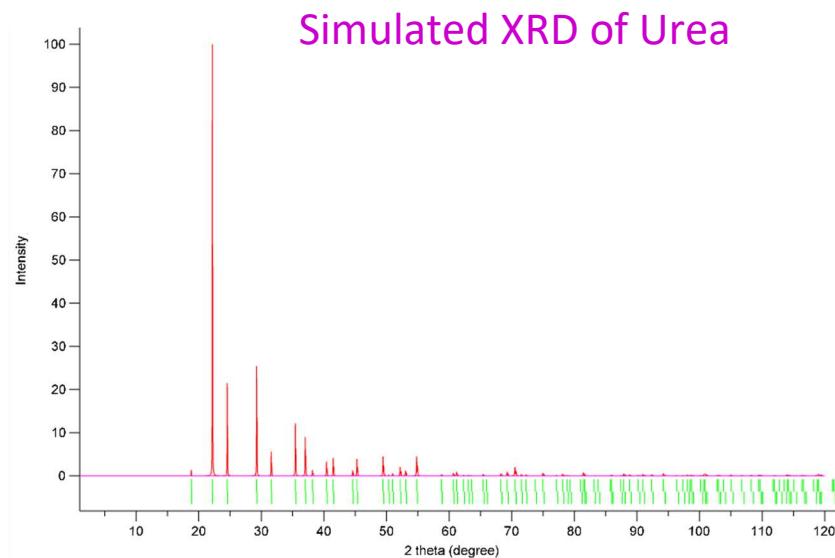
* Calculated for all the materials

Results – Organic materials - Urea

- Urea Crystallizes in the tetragonal P4₂1m space group.
- The consists of two CO(NH₂)₂ clusters. C⁴⁺ is bonded in a trigonal planar geometry to two equivalent N³⁻ and one O²⁻ atom. Both C-N bond lengths are 1.34 Å.
- The C-O bond length is 1.27 Å. N³⁻ is bonded in a trigonal planar geometry to one C⁴⁺ and two H¹⁺ atoms.
- Both N-H bond lengths are 1.01 Å. There are two inequivalent H¹⁺ sites.
- In the first H¹⁺ site, H¹⁺ is bonded in a single-bond geometry to one N³⁻ atom. In the second H¹⁺ site, H¹⁺ is bonded in a single-bond geometry to one N³⁻ atom. O²⁻ is bonded in a single-bond geometry to one C⁴⁺ atom

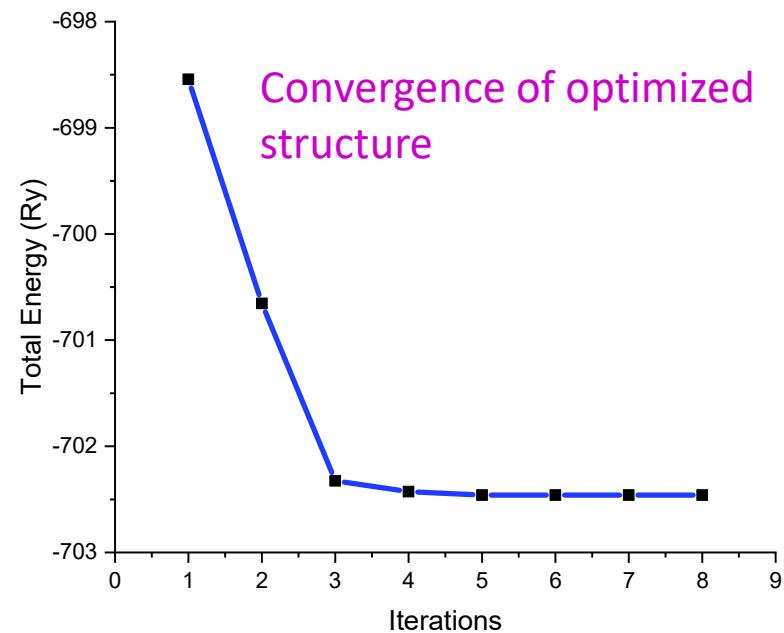


Results – Organic materials - Urea



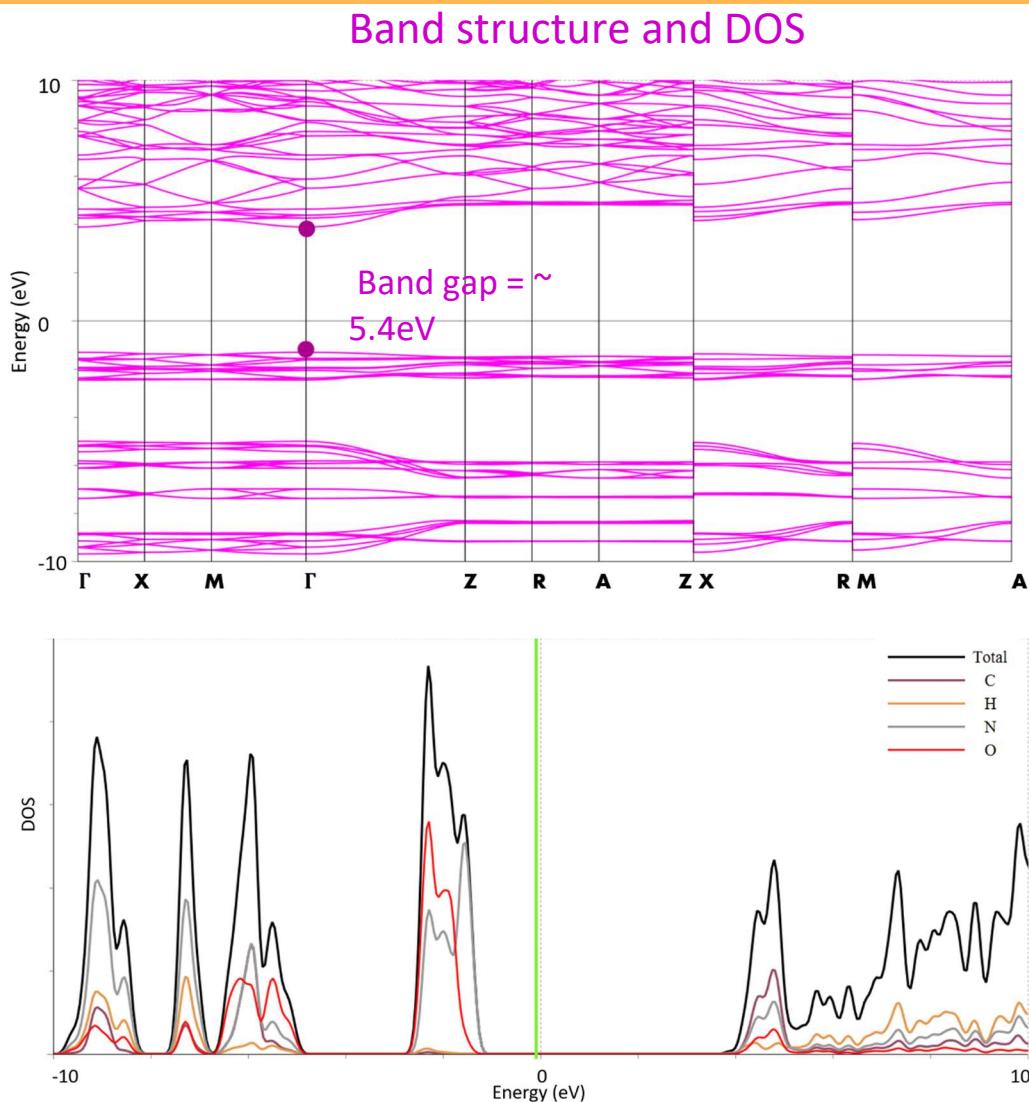
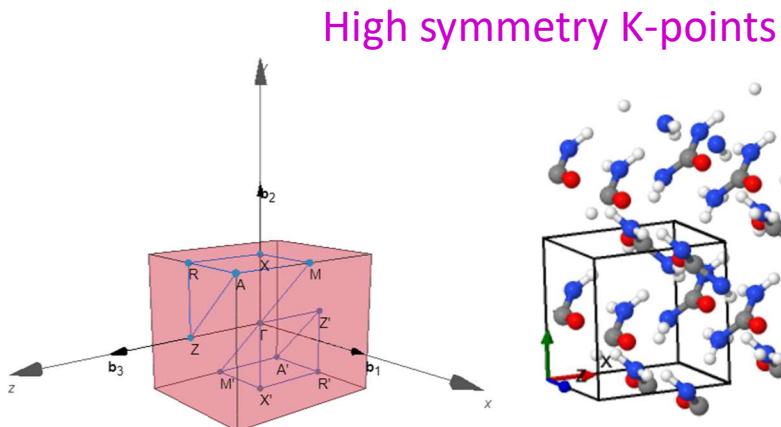
$a = 5.56 \text{ \AA}$ $\alpha = 90^\circ$
 $b = 5.56 \text{ \AA}$ $\beta = 90^\circ$
 $c = 4.65 \text{ \AA}$ $\gamma = 143.4^\circ$
Volume = 143.40 \AA^3
Density = 4.5 g cm^{-3}

Lattice system : Tetragonal
Space group = $P - 4 2ab$
Fermi energy = 1.7230 eV
Total energy = -713.21 Ry



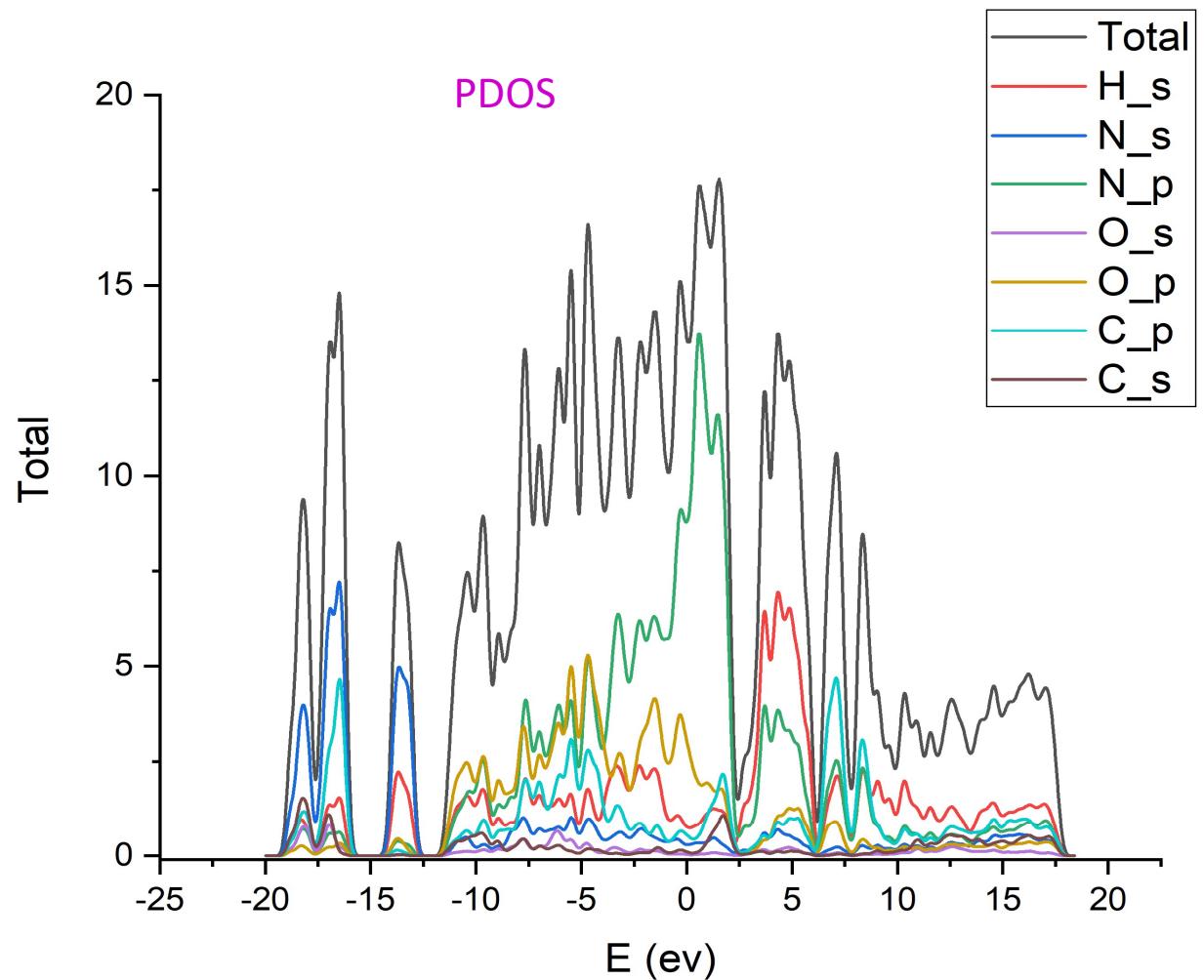
Lowest occupied level = 0.2421eV
Highest occupied level = 0.6824 eV
crystal structure of urea is characterized by its layered arrangement of molecules held together by hydrogen bonding interactions.

Results – Organic materials - Urea



From the DOS plot it is seen that the Oxygen and Nitrogen have the maximum contribution of electrons in both valence band and conduction band. In the conduction band the contribution of carbon is relatively high.

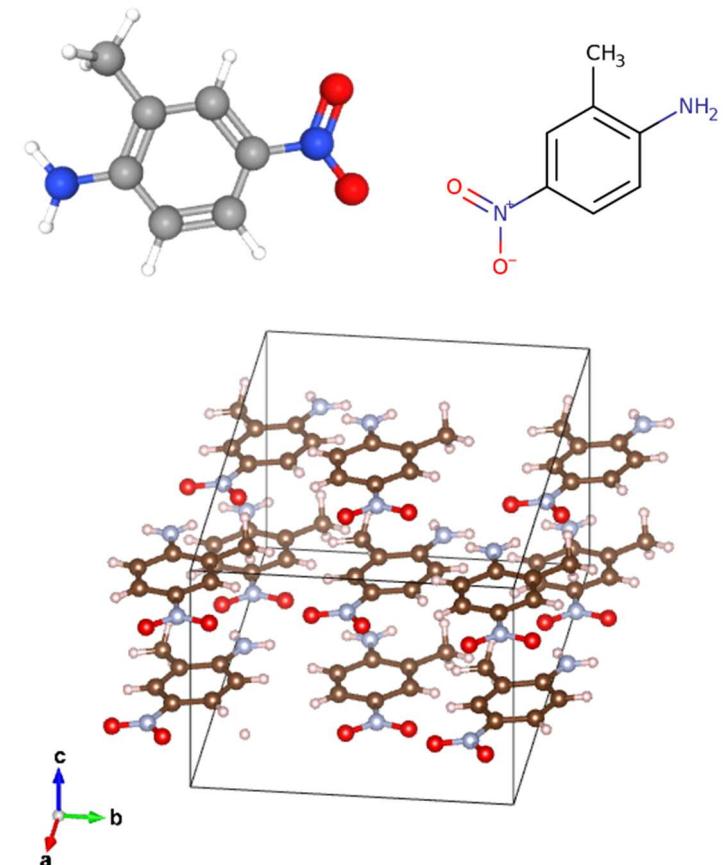
Results – Organic materials - Urea



the p orbital of nitrogen has the maximum contribution in the bonding.
The hydrogen bonding in urea is evident by its contribution in the bonding.

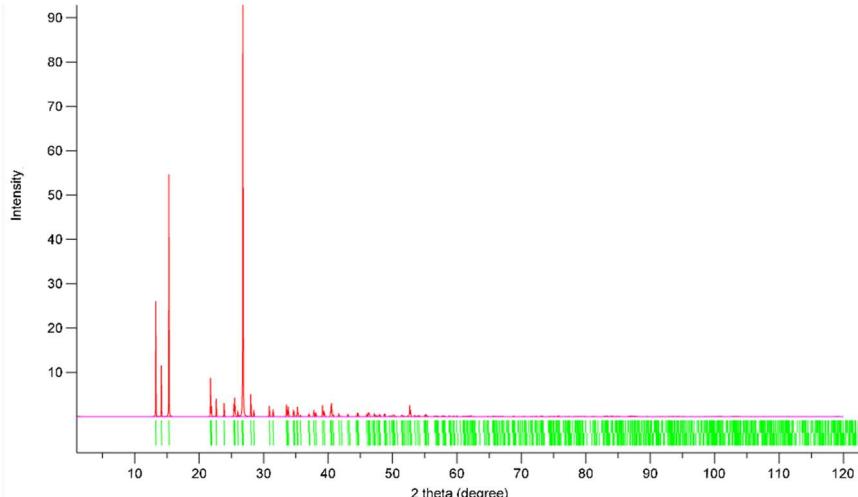
Results – Organic materials - MNA

- The molecule consists of an aniline group, which is a benzene ring with an amino group attached, and it has two substituent groups: a methyl group attached at the 2-position and a nitro group attached at the 4-position.
- The calculated C–H bonds are slightly longer than their experimental counterparts.
- Due to the electron withdrawing effects of the nitro group, those C–C bonds which are along the long molecular axis are shorter than other C–C bonds. In addition, the C–C bonds which are near the amino group are longer than those which are near the nitro-group.
- Such differences show that the benzene ring which acts as a molecular bridge plays a major role in electron delocalization.



Results – Organic materials - MNA

Simulated XRD of Urea



$a = 10.72 \text{ \AA}$ $\alpha = 90^\circ$
 $b = 11.57 \text{ \AA}$ $\beta = 130.42^\circ$
 $c = 7.46 \text{ \AA}$ $\gamma = 90^\circ$
Volume = 705.47 \AA^3

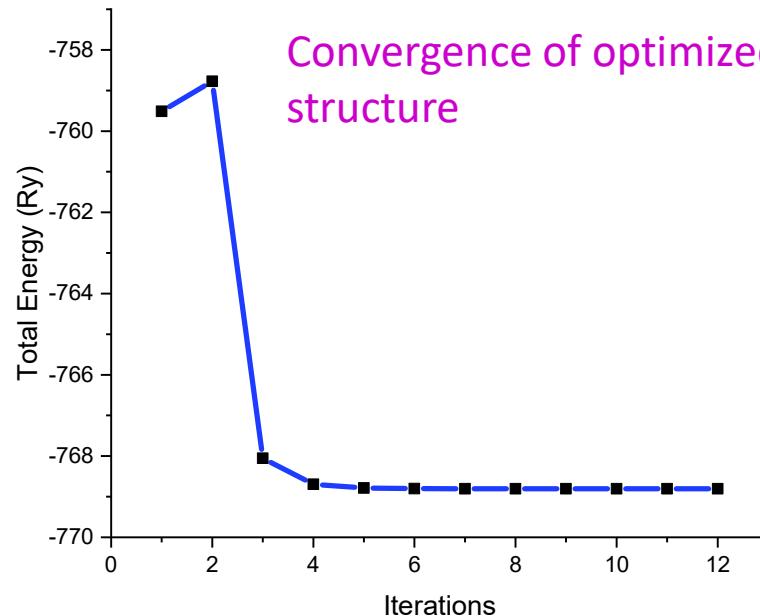
Lattice system : Monoclinic

Space group = Cc (*Unique axis b*)

Fermi energy = 2.1476 eV

Total energy = -785.58 Ry

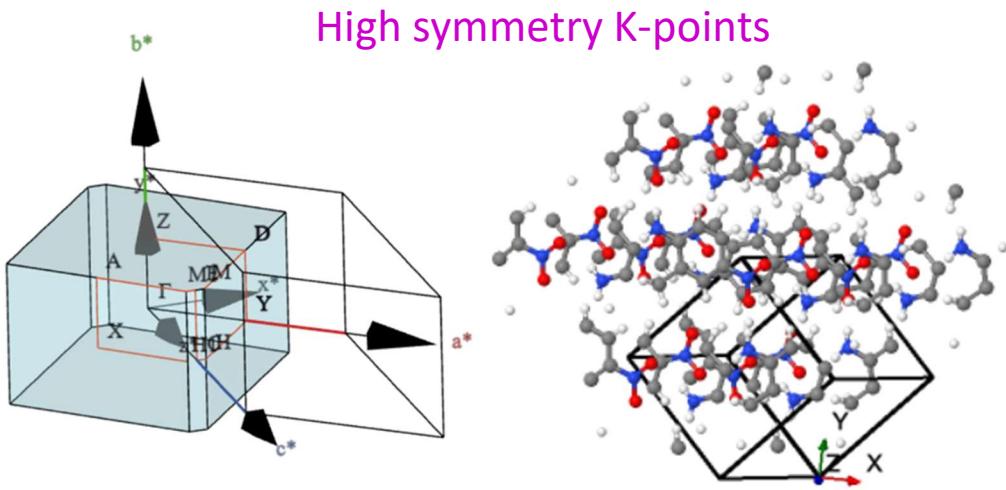
Convergence of optimized structure



Lowest occupied level = 4.2974eV

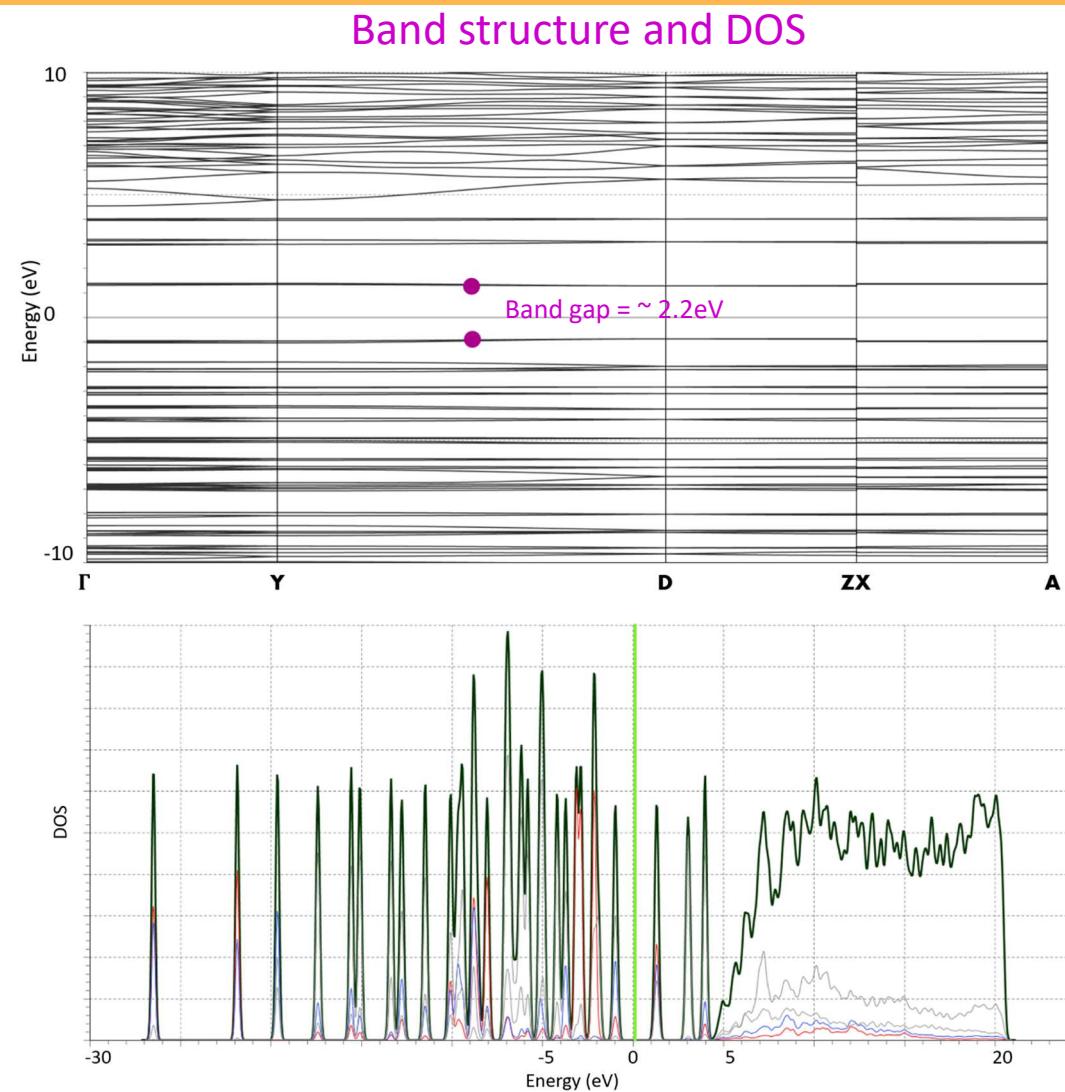
Highest occupied level = 1.6617 eV

Results – Organic materials - MNA

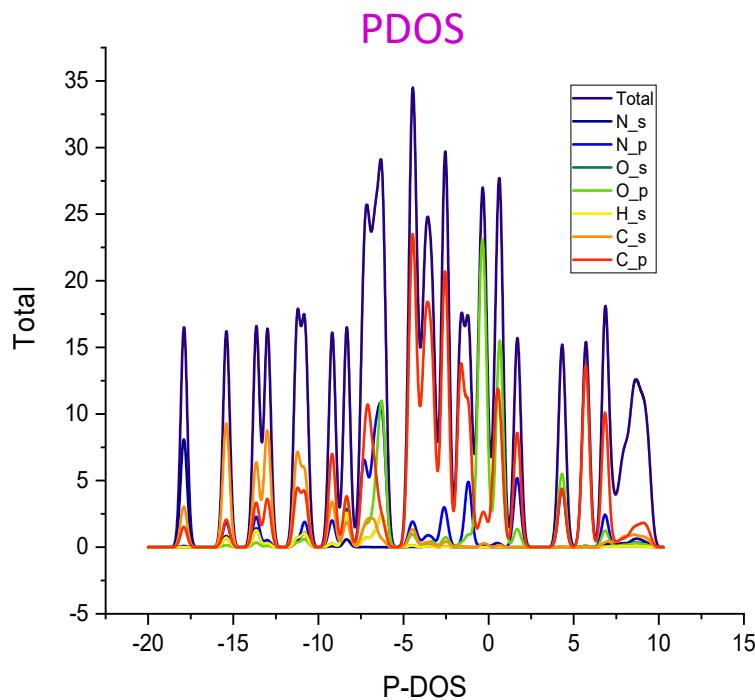


The band structure reveals that MNA is an insulator.
The periodicity of the band structure shows that MNA is a highly crystalline structure.

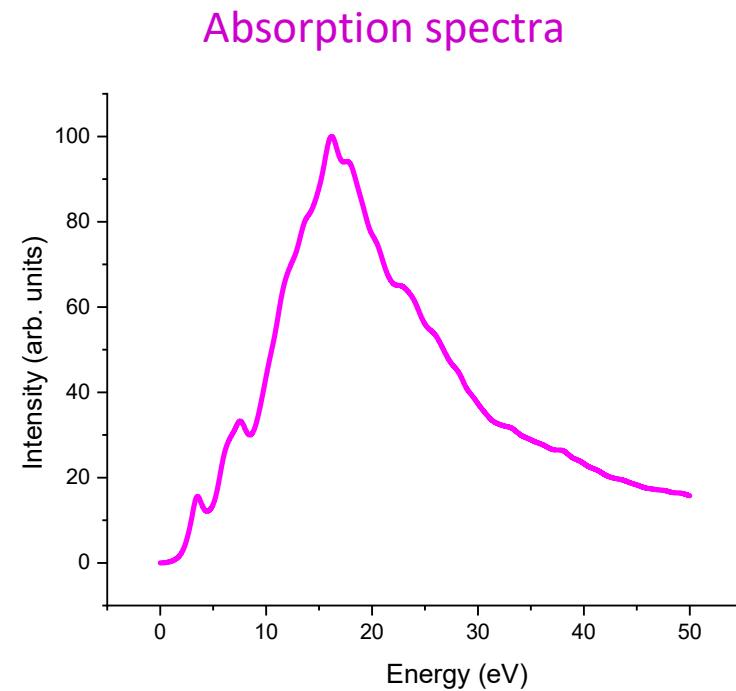
From the DOS plot it is seen that all the elements have relatively equal contribution to the total number of electrons.



Results – Organic materials - MNA



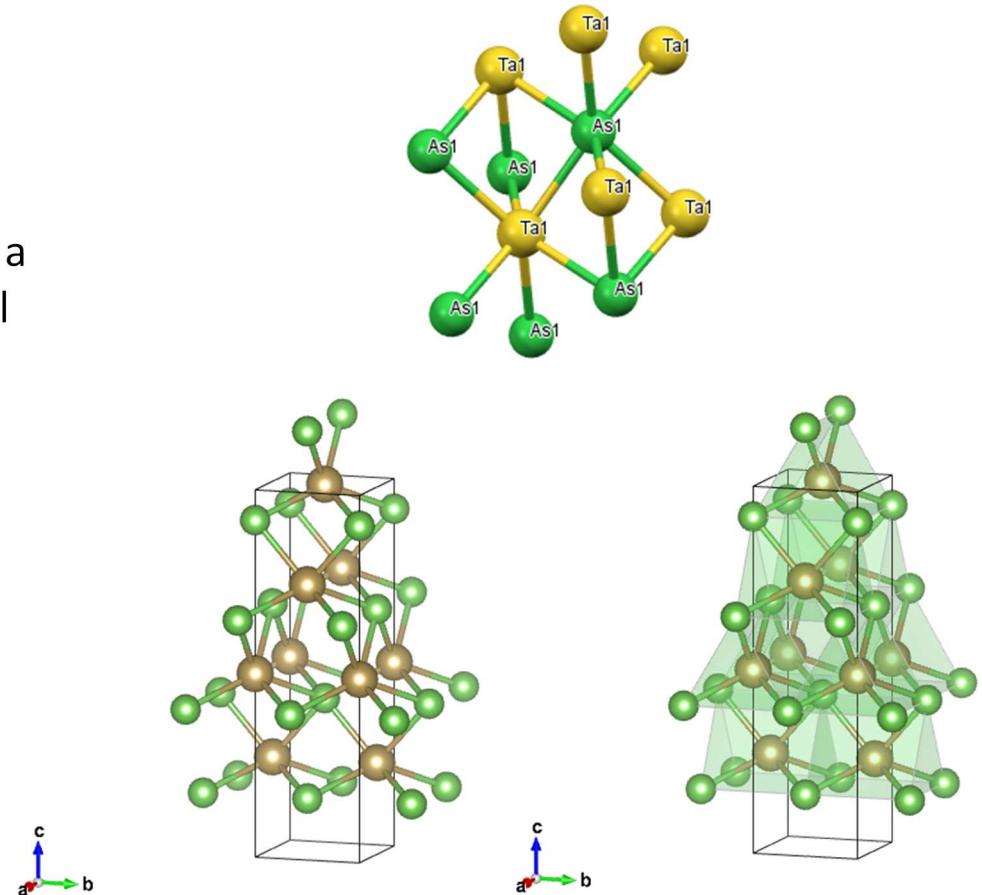
From the PDOS it is found that the p orbital of nitrogen, carbon and oxygen has the maximum contribution in the bonding. The hydrogen bonding in MNA is less as compared to Urea.



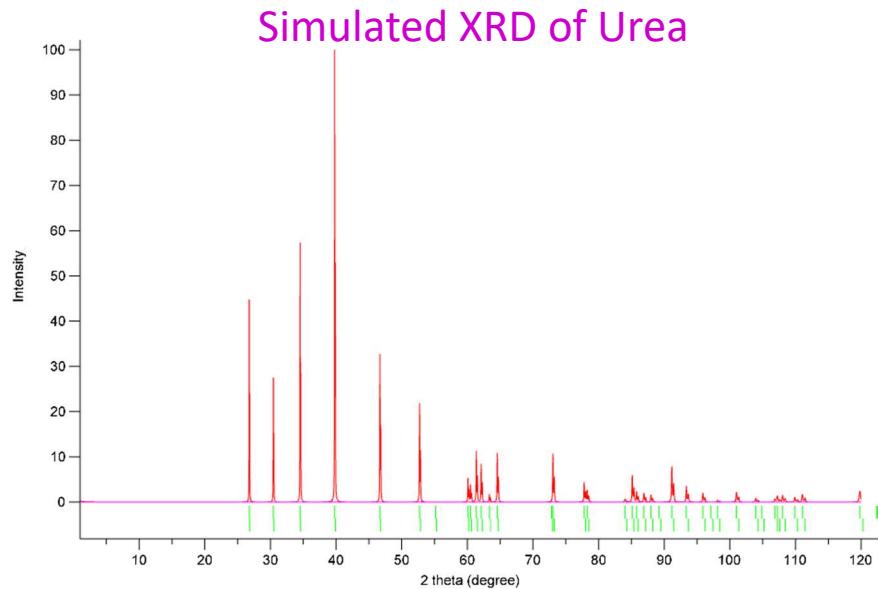
The peaks at 3.6 eV (344.4005nm) and 7.5 eV (167.5462nm) correspond to a lower electronic transition. The peak at 16.17 eV (76.6754nm) corresponds to a higher electronic transition.

Results – Inorganic materials - TaAs

- TaAs (Tantalum Arsenide) is an inorganic compound. It consists of tantalum (Ta) and arsenic (As) elements, which are both inorganic elements. TaAs crystallizes in a non-centrosymmetric structure, making it a topological material .
- TaAs belongs to the family of Weyl semimetals.
- TaAs crystallizes in the tetragonal I4₁md space group. Ta³⁺ is bonded to six equivalent As³⁻ atoms. As³⁻ is bonded to six equivalent Ta³⁺ atoms to form a mixture distorted edge, corner, and face-sharing TaAs₆ and AsTa₆ pentagonal pyramids



Results – Inorganic materials - TaAs

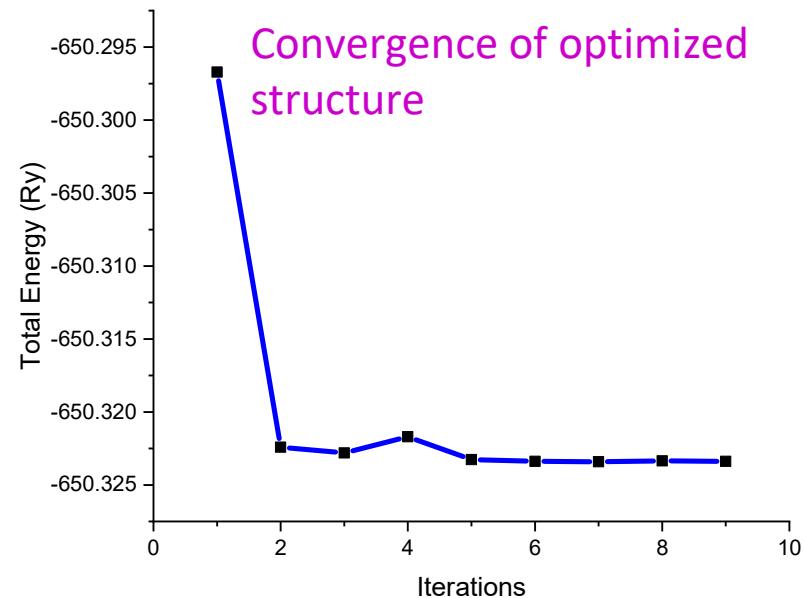


$a = 3.44 \text{ \AA}$
 $b = 3.44 \text{ \AA}$
 $c = 711.75 \text{ \AA}$

$\alpha = 90^\circ$
 $\beta = 90^\circ$
 $\gamma = 90^\circ$

Space group = $I4_1md$
Lattice system : Tetragonal

Fermi energy = 23.4993 eV
Total energy = 4513.88 Ry
Enthalpy = 4964.33 Ry



Results – Inorganic materials - TaAs

Mechanical properties

- Total stress (Ry/ $bohr^3$) =

-0.00821	0.000000	0.000000
0.000000	-0.01100	0.000000
0.000000	0.000000	0.023672

- Total pressure (Kbar) =

-1208.26	0.000000	0.000000
0.000000	-1619.48	0.000000
0.000000	0.000000	3482.37

- Total pressure = 218.21 kbar

- Total density = $61.80720 \frac{g}{cm^3}$

- Total Bulk Modulus = 175 Gpa.

Thermodynamic properties

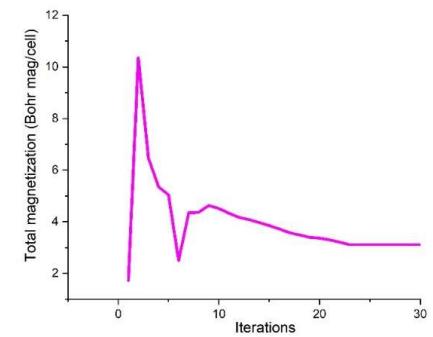
From the experimental results this ground state of the molecule is stable in normal condition even though it has a endothermic energy exchange in a reaction.

- The total energy of the system : -4513.88434915 Ry
- The total internal energy of the system : -4513.87450529 Ry
- The average enthalpy of the system : -4964.3315049892 Ry

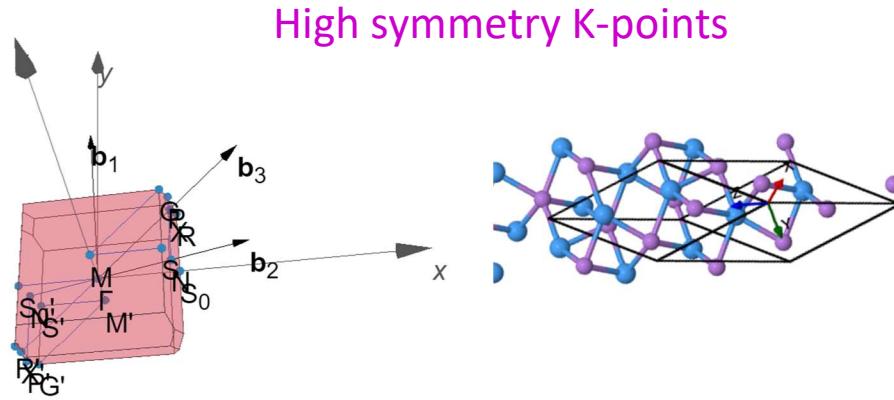
Magnetic properties

The total magnetization = 3.11 Bohr mag/cell.

TaAs exhibit a large topological magneto-electric effect. This effect refers to the generation of an electric polarization in response to an applied magnetic field, and it arises due to the unique electronic band structure of TaAs.

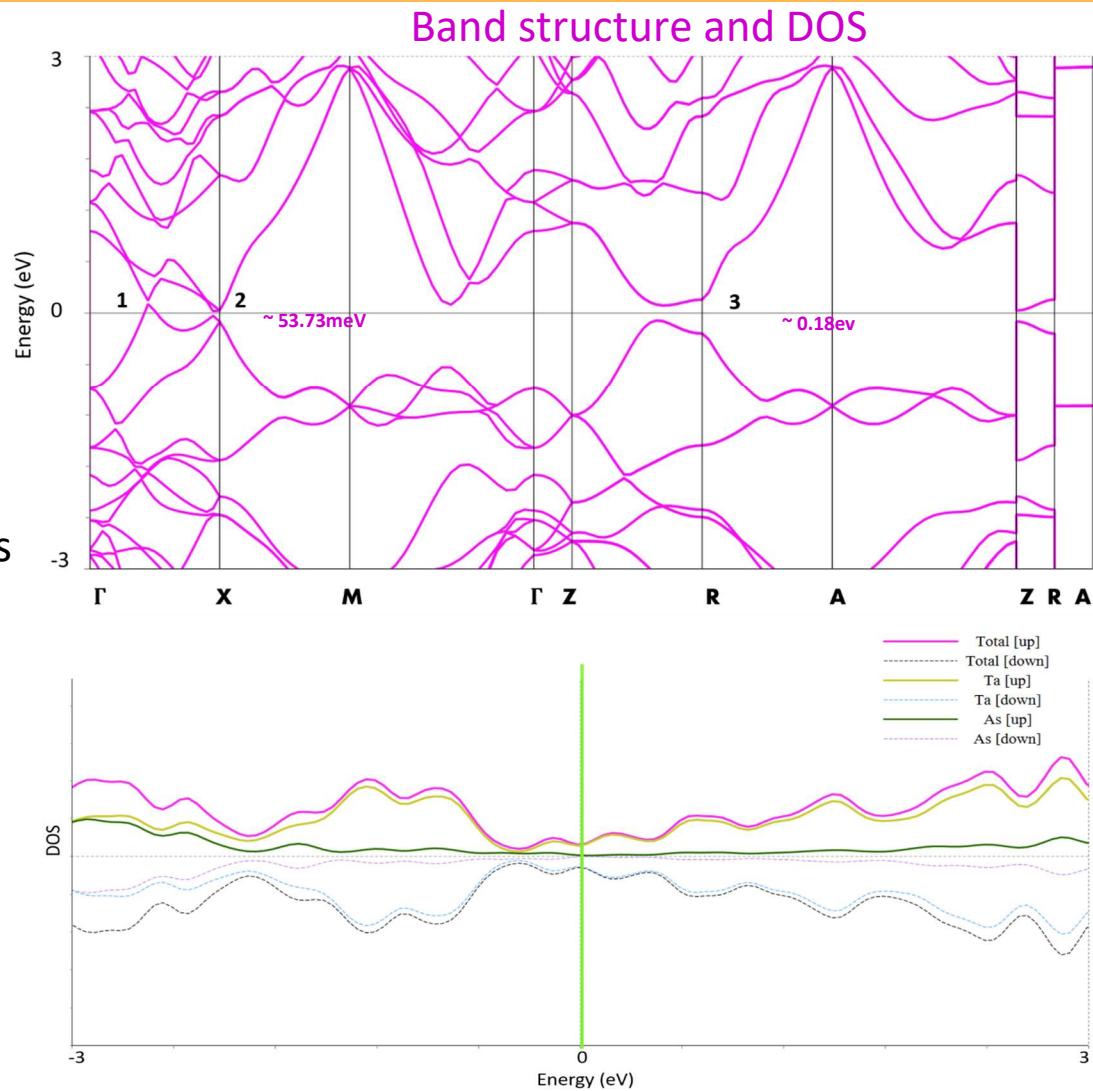


Results – Inorganic materials - TaAs

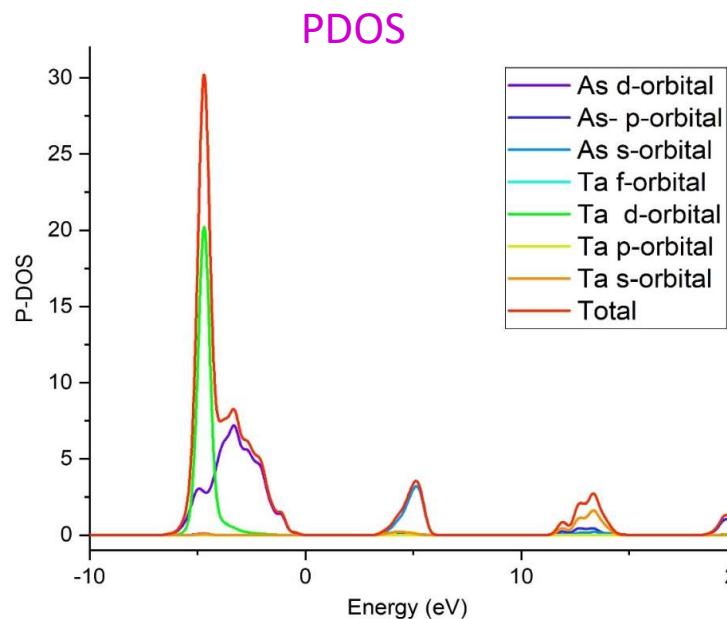


The electronic band dispersion in TaAs typically shows few bands crossing the Fermi level, with distinct characteristics near the Dirac points. Which confirm that it is a Weyl semimetal

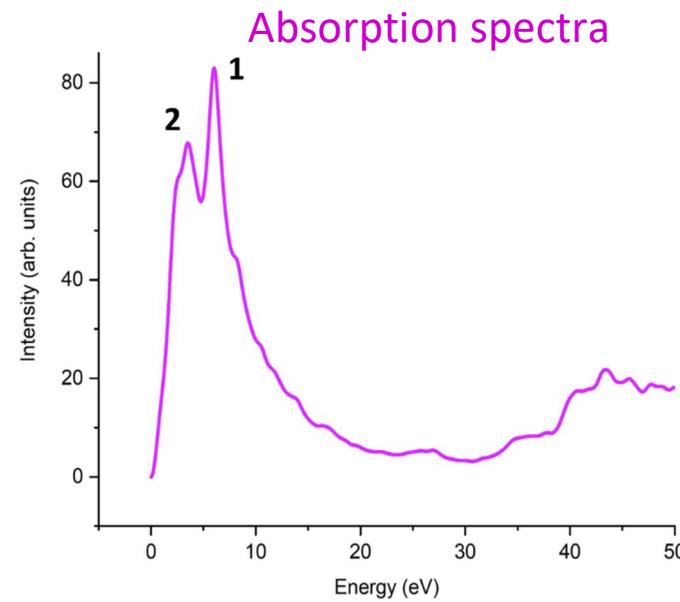
From the DOS plot it is clearly seen that the contribution of Ta is more in the density of states as compared to As.



Results – Inorganic materials - TaAs



The PDOS plot show that the d orbital of Ta and the d orbital of As involve in the maximum bonding. Other orbitals barely involves in bonding.



From the absorption spectra it is seen that there are two distinct peaks at 6 eV (1) (206.6403 nm) and 3.6eV (2) (344.4005 nm), which shows that there is an electronic transition between those two states. This sharp peak in those regions specifies the high probability of electronic transition in that region.

Conclusion

- Employing Density Functional Theory (DFT) using Quantum Espresso the structural, electronic, and optical properties of urea, Methyl-4-nitroaniline (MNA), and Tantalum Arsenide (TaAs) has been calculated.
- The results reveal the band gap values for urea (~ 5.4 eV) and MNA (~ 2.2 eV), elucidating the dominant electron contributions from specific orbitals.
- Additionally, TaAs is identified as a Wely semimetal from its band structure, exhibiting notable bonding involving the d orbitals of Ta and As.
- The absorption spectra of MNA and TaAs unveils distinct electronic transitions.

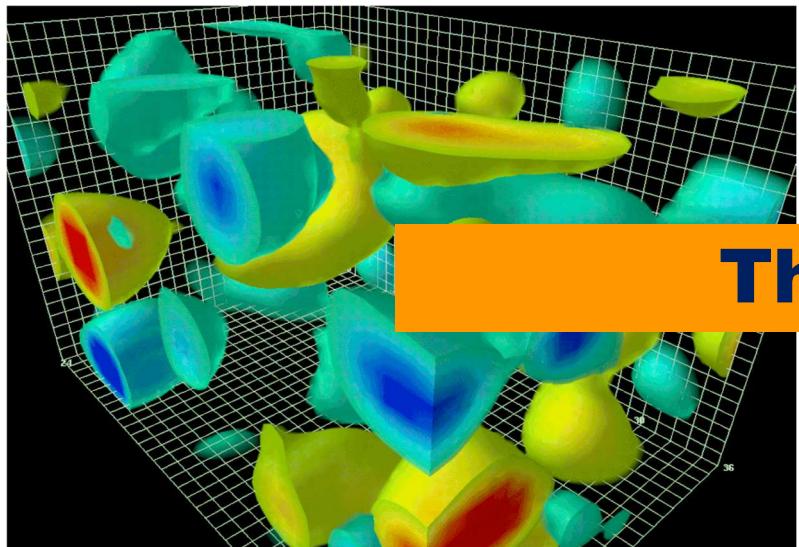
Further work

- The materials chosen i.e. Urea, MNA and TaAs have potential applications in non- linear optics.
- The calculation that are done in this work is the preliminary calculation to find other properties like linear optical response, dielectric function, Nonlinear Susceptibility, Nonlinear Coefficient, hyperpolarizability and other properties using more advanced codes like Elk code, VASP, Materials studio etc.
- Apart from this TaAs has a huge scope of study in other applications like spintronics, photonics, optoelectronics, topological insulators, and energy storage and conversion.
- Using the data and results from this work further calculations can be carried out to find the applied properties.

Reference

- Omidi, A. R. and Dadsetani, M., "Optical properties of phenanthrene: A DFT study for comparison between linear and nonlinear regimes", *Solid State Communications*, vol. 234, pp. 1–9, 2016. doi:10.1016/j.ssc.2016.02.018.
- Lehtola, S., & Karttunen, A. J. (2022). Free and open source software for computational chemistry education. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 12(5), e1610. <https://doi.org/10.1002/wcms.1610>.
- G. C. P. N. Marzari, "atomistic computer modeling of materials (sma 5107)," mit open learning, spring 2005 .
- G. Lee, computational materials science -an introduction second edition, taylor & francis, 2017.
- N. A. B. 6. Castep developers group, "plane waves, unit cell, k-points and all that," castep with support with esu, durham, 2021.
- . B. S. B. N. C. M. C. R. C. C. C. D. C. G. C. M. D. I. A. D. C. A. Giannozzi, "quantum-espresso.org," quantum-espresso, [online]. Available: https://www.quantum-espresso.org/doc/input_pw.html.
- J. J. Paul, "computational-condensed-matter-physics," 2023. [online]. Available: https://github.com/johnpaulj1509/computational-condensed-matter-physics/tree/main/quantum_espresso.
- M. D. A. A. R. Omidi, "a dft study of linear and nonlinear optical properties of 2-methyl-4-nitroaniline and 2-amino-4-nitroaniline crystals," *the journal of physical chemistry c*, vol. 119, no. 28, pp. 16263-16275, 2015.
- M. E. Dadsetani, " optical distinctions between weyl semimetal taas and dirac semimetal na3bi: an ab initio investigation," *j. Electron. Mater*, vol. 45, p. 867–5876, 2016.
- Nelson, J. N., Rice, A. D., Kurleto, R., Shackelford, A., Sierzega, Z., Hao, P., Berggren, B. S., Jiang, C., Norman, A. G., Holtz, M. E., Mangum, J. S., Leahy, I. A., Heinselman, K. N., Ness, H., Van Schilfgaarde, M., Dessau, D. S., & Alberi, K. (2023). Thin-film TaAs: Developing a platform for Weyl semimetal devices. *Matter*, 6(9), 2886-2899. <https://doi.org/10.1016/j.matt.2023.06.018>
- Huang, Xiaochun & Zhao, Lingxiao & Long, Yujia & Wang, Peipei & Chen, Dong & Yang, Zhanhai & Liang, Hui & Xue, Mianqi & Weng, Hongming & Fang, Zhong & Dai, Xi & Chen, Genfu. (2015). Observation of the Chiral-Anomaly-Induced Negative Magnetoresistance in 3D Weyl Semimetal TaAs. <http://xxx.lanl.gov/abs/1503.01304>. 5. 10.1103/PhysRevX.5.031023.

Further work



Thank you

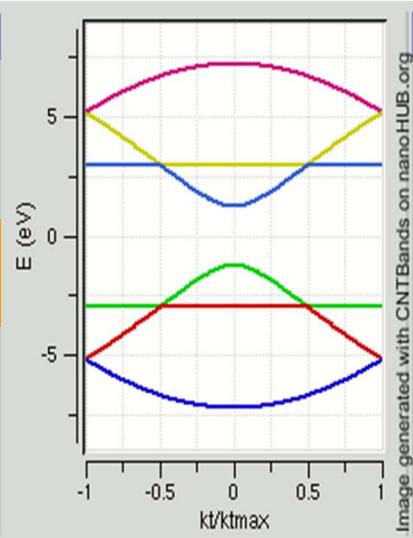
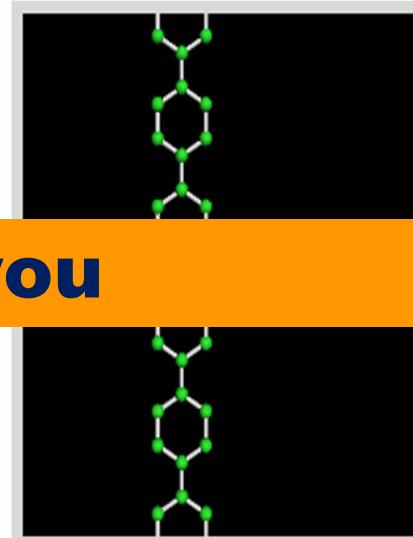


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