First-Principles calculations of Material properties

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(22PPH101)

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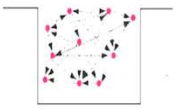
Objective

- 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.

First principles calculation using DFT – overview

$$\hat{H} = -\frac{1}{2}\left[\left(\sum_i \frac{\hbar^2}{m_e}\nabla_i^2 + \sum_\alpha \frac{\hbar^2}{M_\alpha}\nabla_\alpha^2\right) + \left(\sum_{i,\alpha}\frac{2z_\alpha e^2}{|\vec{r_i} - \vec{R_\alpha}|} - \sum_{i\neq j}\frac{e^2}{|\vec{r_i} - \vec{r_j}|} - \sum_{i,\alpha}\frac{z_\alpha z_\beta e^2}{|\vec{R_\alpha} - \vec{R_\beta}|}\right)\right]$$



Many body SH eq method

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

MFT

SCF

PBE

NC-PPs

$$\rho(\boldsymbol{r}) = \langle\psi|\hat{\rho}(\boldsymbol{r})|\psi\rangle$$

$$\hat{\rho}(\boldsymbol{r}) = \sum_{k=1}^{N} n_k|\varphi_k(\boldsymbol{r})|^2$$

$$\hat{\rho}(\boldsymbol{r}) = \sum_{k=1}^{N}\delta(r - r_i)$$

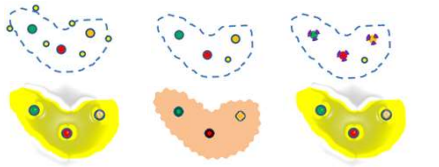
Slater determinant constructed from N orbitals, φ_k with corresponding n_k

Solving the Kohn – sham eq. to obtain charge density and calculate the energy

Interacting electrons Exact Hamiltonian for real molecule

Non-Interacting e^- Apx. Hamiltonian for real molecule

KS non-Interacting e^- Apx. Hamiltonian for fictitious molecule

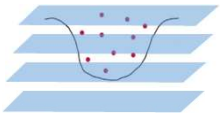


Density of interacting e^- is exact density

Density of non -interacting e^- is apx. density

Density of fictitious *system*is exact density

$$\left(-\frac{\hbar}{2m}\nabla^2 + v_{eff}(r)\right)\varphi_i(r) = E_i\varphi_i(r)$$



The KS particle reduced to one body problem and the potential is calculated using the plane wave basis set

$$E[n] = E_{kin,KS}[n] + E_{Col}[n] + E_{ext}[n] + (E_{kin}[n] - E_{kin,KS}[n]) + E_{xc}[n]$$

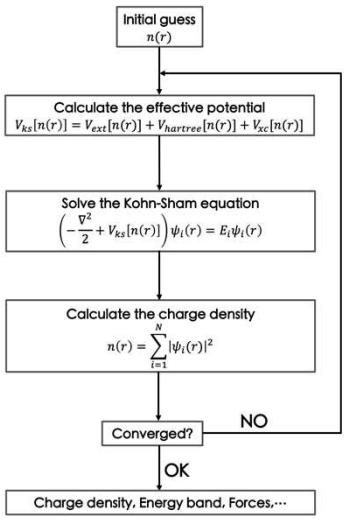
$$E[n] = 2\sum_{i=1}^{\frac{N_{el}}{2}}\int \psi_i^*(r)\left(-\frac{1}{2}\nabla^2\right)\psi_i(r)dr + E_{Col}[n] + E_{ext}[n] + \mathrm{E'_{xc}[n]}$$

Total energy are all functionals of the charge density.

Ion-electron potential energy, Ion-ion potential energy, electron-electron energy, ***kinetic energy, exchange-correlation energy***

First principles calculation – Methods used

- Density functional theory (DFT) using plane-wave (PW) basis set.
- Perdew–Burke– Ernzerhof (PBE) exchange correlation functional for ab initio calculations using QE.
- The core electrons described by Norm-Conserving (NC) PPs in separable (Kleinman-Bylander) form.
- VC-relax calculation for structure optimization.
- High symmetry K paths using XCrySDen.
- Coupled linear-response TDDFPT.
- Quantum Liouville equation using Lanczos algorithm.
- The post processing work of the results are done using Fortran90, python and Origin.



Computational Facilities

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

- Workstation (remote access) - IITH (18 hrs per month)
  - Processor - Intel® Xeon® D-2700
  - RAM –64GB
  - Operating system - Red Hat Enterprise Linux
  - Cores – 8 to 20
  - GPU – 8 GB

Properties calculated

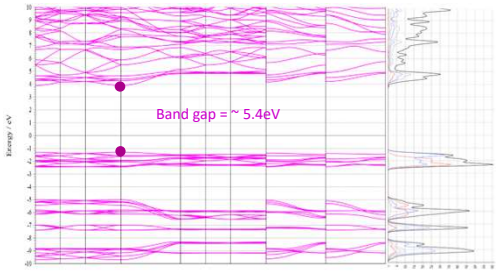
- Structural parameters*
- Bonding *
- Optimized structure*
- Powered XRD pattern*
- Fermi Energy*
- HOMO – LUMO
- Total magnetization
- Pressure and strain
- Total energy*
- Total enthalpy
- Density of states (DOS)*
- High symmetry k- points*
- Electronic band structure*
- Projected density of states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

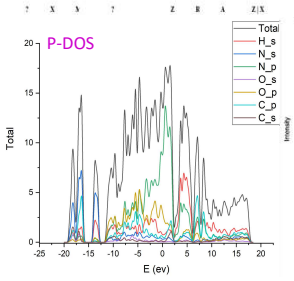
* Calculated for all the materials

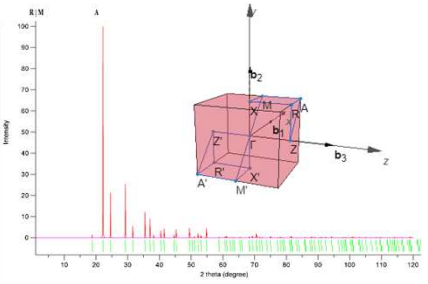
Results – Organic materials

Urea (H_4CN_2O)

Band structure and DOS

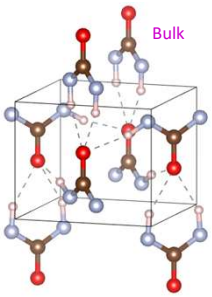






a = 5.56 Å α = 90°
b = 5.56 Å β = 90°
c = 4.65 Å γ = 143.4°

The structure is zero-dimensional and consists of two $CO(NH_2)_2$ clusters. C^{4+} is bonded in a trigonal planar geometry to two equivalent N^{3-} and one O^{2-} atom. Both C-N bond lengths are 1.34 Å. The C-O bond length is 1.27 Å. N^{3-} is bonded in a trigonal planar geometry to one C^{4+} and two H^{1+} atoms. Both N-H bond lengths are 1.01 Å.

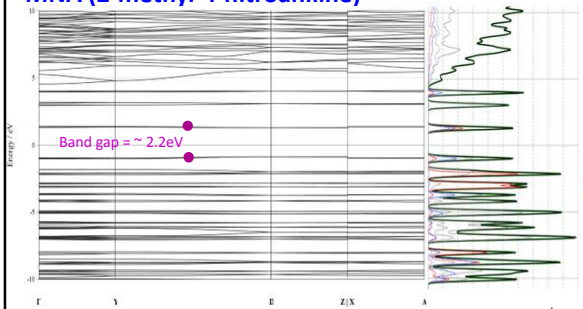


Lattice system : Tetragonal
Space group = $P-4\,2ab$
Volume = 143.40 Å^3
Density = 4.5 gcm^{-3}
Fermi energy = 1.7230 eV
Total energy = -713.21 Ry
Lowest occupied level = 0.2421eV
Highest occupied level = 0.6824 eV

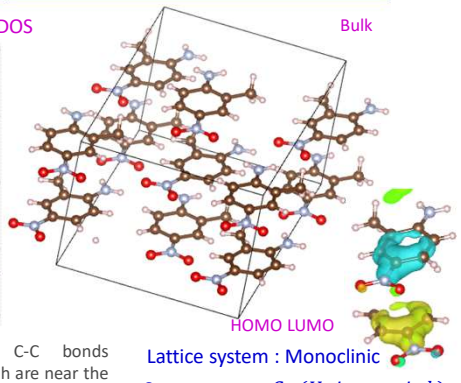
Results – Organic materials

MNA (2-methyl-4-nitroaniline)

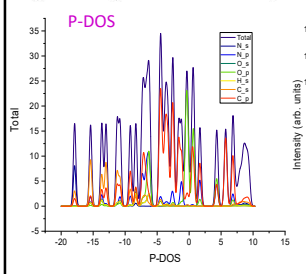
Band structure and DOS



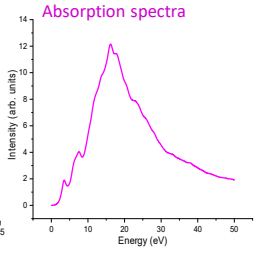
Bulk



HOMO LUMO



Absorption spectra



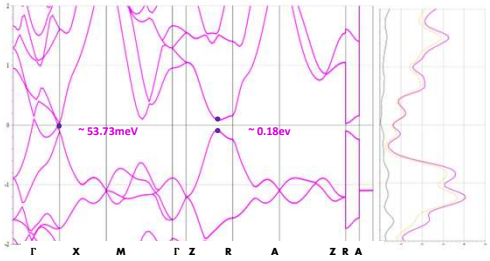
the C-C bonds which are near the amino-group are longer than those which are near the nitro-group .Such differences show that the benzene plays a major role in electron delocalization.

Lattice system : Monoclinic
Space group = Cc $(Unique\ axis\ b)$
a = 10.72 Å α = 90°
b = 11.57 Å β = 130.42°
c = 7.46 Å γ = 90°
Volume = 705.47 Å^3
Fermi energy = 2.1476 eV
Total energy = -785.58 Ry
Lowest occupied level = 4.2974eV
Highest occupied level = 1.6617 eV

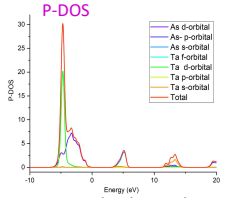
Results – Inorganic material

TaAs (Tantalum Arsenide)

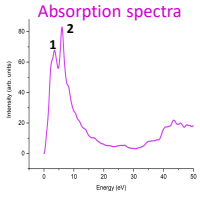
Band structure and DOS



P-DOS

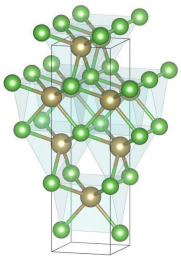


Absorption spectra



maximum orbital contributions to the band structure are provided by the d-orbital of As and d-orbital of Ta. From the absorption spectra it is seen that there are two distinct peaks at 6 eV (1) and 3.6eV (2), which shows that there is an electronic transition between those two states

Ta^{3+} is bonded to six equivalent As^{3-} atoms. As^{3-} is bonded to six equivalent Ta^{3+} atoms to form a mixture of distorted edge, corner, and face-sharing $TaAs_6$ and $AsTa_6$ pentagonal pyramids.



Bonding of atoms

Total pressure = 218.21 kbar

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

Total Bulk Modulus =175 Gpa.

Lattice system : Tetragonal

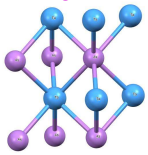
Space group = $I4_1md$

a = 3.44 Å α = 90°

b = 3.44 Å β = 90°

c = 711.75 Å γ = 90°

Volume = 139.17 $Å^3$



Weyl semimetal

Enthalpy = 4964.33 Ry

Fermi energy = 23.4993 eV

Total energy = 4513.88 Ry

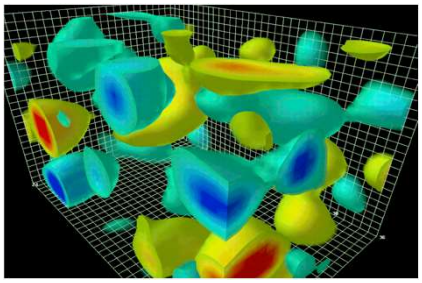
$$\text{Total stress (Ry/}bohr^{-3}) = \begin{matrix} -0.00821 & 0.000000 & 0.000000 \\ 0.000000 & -0.01100 & 0.000000 \\ 0.000000 & 0.000000 & 0.023672 \end{matrix}$$

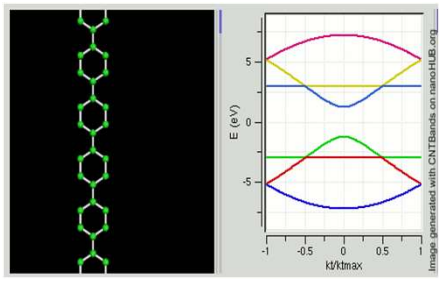
$$\text{Total pressure (Kbar)} = \begin{matrix} -1208.26 & 0.000000 & 0.00000 \\ 0.000000 & -1619.48 & 0.00000 \\ 0.000000 & 0.000000 & 3482.37 \end{matrix}$$

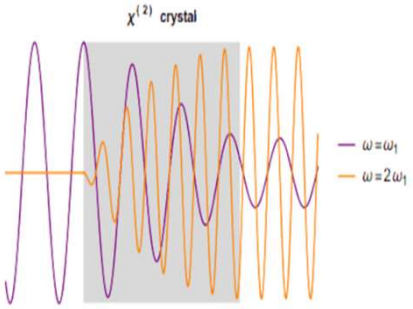
Further work

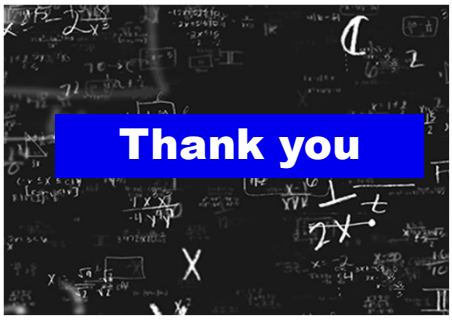
We have extended our work to do the following

- To optimize the code and configure it to the system to perform calculation to avoid memory segmentation problem.
- To calculate the NLO properties (SHG susceptibility) of organic materials and other materials.




E (eV)
5
0
-5
-1
-0.5
0
0.5
1
kt/ktmax
Image generated with CNTBands on nanoHUB.org


$\chi^{(2)}$ crystal
$\omega=\omega_1$
$\omega=2\omega_1$


Thank you