Comparative DFT Study of Adsorption of Superheavy Elements Cn and Fl, and Their Lighter Homologs Hg and Pb on Selenium Surface

presented by
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and
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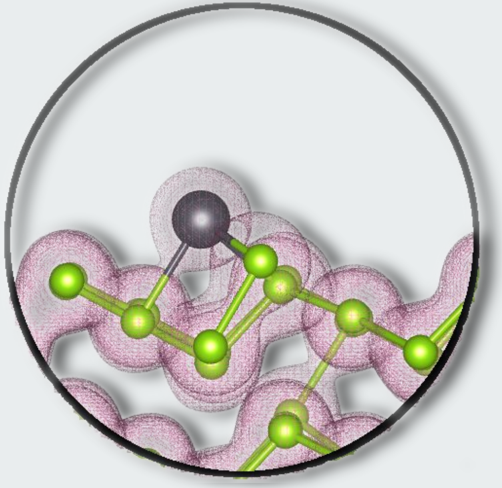

Research experience

Ph. D in Physics, Jadavpur University, Kolkata, India, 15/10/2015
Thesis title: "*Ab-Initio Study of Adsorption and Related Properties for Some Planar Nanostructures*"

Senior UPE Fellow, Jadavpur University, Kolkata, India, 2016-2017

Junior Researcher, Palacký University, Olomouc, Czech Republic, 2017-2019

Postdoctoral Fellow, University of Calcutta, Kolkata, India, 2019-2022

Research Associate, S. N. Bose National Centre for Basic Sciences, 2022-2024

Senior Researcher, BLTP, Joint Institute for Nuclear Research, Dubna (Moscow Region), Russia, 2025 - present

CASTEP
(CAmbridge Serial Total Energy Package)
Adsorption and doping, 2D materials - graphene/ h-BN, surface reaction, electrocatalysis

VASP
(Vienna Ab initio Simulation Package)
(a) photo-catalysis, carbon quantum dot, doping and band-edge alignment
(b) van der Waals crystals, 2D magnetism

QUANTUMESPRESSO
Quantum ESPRESSO (QE)
Topical plan 03-5-1130-2017, theoretical study, superheavy elements - Cn/ Fl

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- Periodic Density Functional Theory (DFT) codes: CASTEP, VASP, Quantum ESPRESSO
- *Ab Initio* crystal structure prediction (USPEX)
- *Ab Initio* (DFT based) Molecular Dynamics

Status and availability of some popular periodic DFT codes

BAND

- All electron code, atomic-orbital basis
- Commercial license as Part of Amsterdam Modeling Suite (AMS)
- All electrons. No pseudopotential necessary
- Dispersion parameters of SHEs taken from homologs
- We had license upto September 2025. But they refused to renew or support

✗

VASP

- Pseudopotential based, plane wave basis
- Commercial license for source code
- SHE pseudopotential available[2]
- Supports DFT-D4 dispersion model, both by native build and ASE[3]
- Refused to sell us

✗

CASTEP

- Pseudopotential based, plane wave basis
- Free academic license for source code
- Can use ONCVPSP pseudopotentials, available for SHE[4]
- Supports DFT-D4 dispersion model by ASE[3]
- We enquired if we can obtain an academic license. They did not reply

✗

QUANTUMESPRESSO

- Pseudopotential based, plane wave basis
- Free and open source
- Can use ONCVPSP pseudopotentials, available for SHE[4]
- Supports DFT-D4 dispersion model by ASE[3]

✓

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[2] L. Trombach et al., Phys. Chem. Chem. Phys., 2019, **21**, 18048-18058

[3] Atomic Simulation Environment (ASE)

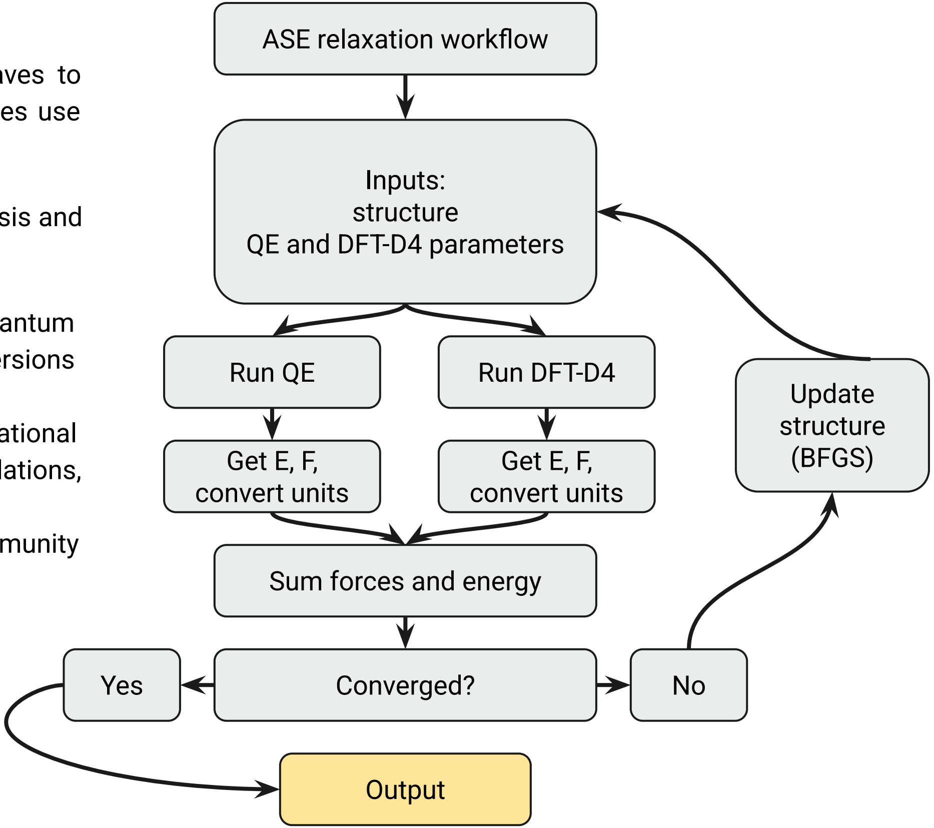
[4] ONCVPSP: Optimized Norm-Conserving Vanderbilt Pseudopotentials, C. Tantardini et al., 2024, **295**, 109002

Atomic Simulation Environment (ASE)

Plane wave basis set codes use Fourier-expanded periodic waves to treat bulk systems with periodicity. Atomic orbital basis set codes use localized atom-centered functions for molecules and clusters.

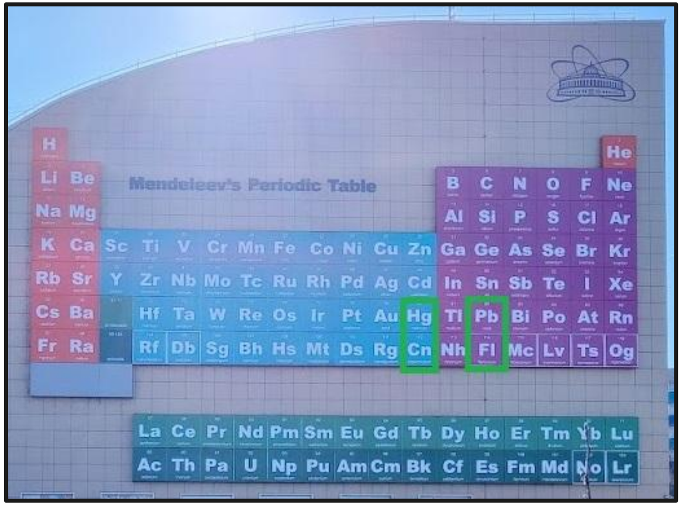
ASE supports 30+ electronic structure codes with both type of basis and for both all electron and pseudopotential based implementations.

- **Multi-calculator integration** - Combines different quantum codes (QE, VASP, MOPAC) and handles unit conversions between them automatically
- **Workflow automation** - Automates multi-step computational processes like structure relaxation, SCF and NSCF calculations, and vibrational analysis by finite differences.
- **Python library** - Free and open-source with active community development and extensive documentation



Adsorption of superheavy elements (SHEs)

- Adsorption of ^{197}Hg $^{183\text{-}185}$Hg on red amorphous selenium (a-Se) and trigonal selenium (t-Se) using gas chromatographic methods - Chiera et al.[1]
- Adsorption enthalpy on a-Se > -0.881 eV
- Adsorption enthalpy on t-Se < -0.622 eV
- Plan for theoretical studies: Adsorption of Mercury ($_{80}$Hg, valence: $5s^2 5p^6 5d^{10} 6s^2$) Copernicium ($_{112}$Cn, valence: $6s^2 6p^6 6d^{10} 7s^2$) Lead ($_{82}$Pb, valence: $5d^{10} 6s^2 6p^2$) and Flerovium ($_{114}$Fl, valence: $6s^2 6p^6 6d^{10} 7s^2 7p^2$) on t-Se surface.
- Identify differences between Cn and Fl adsorption as a precursor to experiments.



Computational Requirements:

- 4-component (ψ_L and ψ_S up and down) spinor description derived from the Dirac equation - though many practical codes use approximate 2-component approaches with added SOC terms.
- All electron treatment or availability of relativistic pseudopotentials.
- Must account for dispersion corrections, as van der Waals forces are omnipresent and often dictate the stability of the adsorbate-substrate interface.

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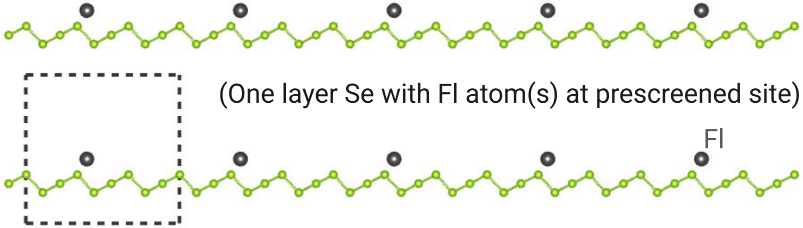
[1] N. M. Chiera et al., J Radioanal Nucl Chem DOI 10.1007/s10967-016-5018-8

Preliminary considerations: surface, periodicity and prescreening

- We selected the t-Se (100) surface based on previous surface energy calculations confirming it as the most stable - Data calculated by my colleague and co-author Dr. Miroslav Ilias, and is currently in the publication process.
- 3×3×1 supercell allows 12-14 Å gap between adatoms - sufficient to ward of spurious interactions from periodic images
- Minimum 10 Å vacuum separation is necessary
- Prescreening of the adsorption sites were done using a python based ASE implementation that maps the available adsorption sites using computationally cheap Lennard-Jones (LJ) model and predicts the most stable adsorption sites - **developed for International Student Practice: Stage 2, held in September - October 2025, JINR, Russia**; Project title: “Simple atomistic modeling of adsorptions on various surfaces”

Atom	ε (eV)	σ (Å)
Hg	0.10	2.40
Cn	0.03	2.80
Pb	0.15	2.60
Fl	0.05	3.00

Empirical LJ parameters used for pre-screening of adsorption sites



(One layer Se with Fl atom(s) at prescreened site)

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

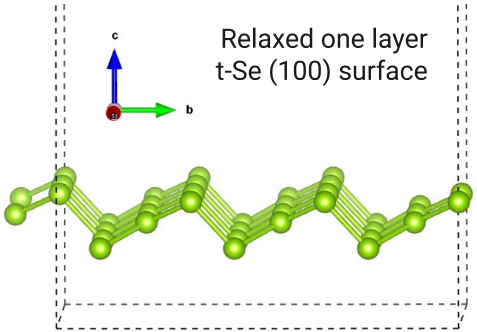
ε: depth of the potential well, σ: distance where potential is zero, r: distance between atoms

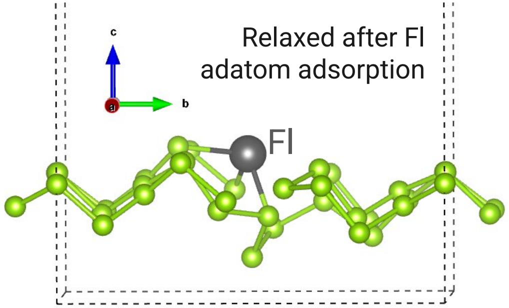
Preliminary considerations: spin orbit coupling (SOC)

- SOC splits and reshapes (heavy and superheavy) atomic orbitals; contracts and localises electron density. Without SOC, strong chemisorption and bonding occurs.
- From experimental trend, we expect weak physisorption
- Preliminary tests were carried out with one layer t-Se (100) surface, with scalar-relativistic pseudopotentials, without SOC and without dispersion corrections

System (adatom on 1 layer t-Se)	E_{ads} (eV)
Fl	-3.148
Pb	-2.728

$$E_{ads} = E_{system} - E_{slab} - E_{adatom}$$


Relaxed one layer t-Se (100) surface


Relaxed after Fl adatom adsorption

Without SOC

Production results: comparison of adsorption energies (E_{ads})

System	BAND (eV)[5]	VASP (eV)[6]	QE-PBE (eV)	QE-PBEsol (eV)
Hg	-0.642	-0.377	-0.385	-0.584
Cn	-0.676	-0.320	-0.400	-0.653
Pb	-1.291	-1.639	-1.435	-1.887
Fl	-0.850		-0.372	-0.569

Computational parameters[7]:

- 3×3×1 supercell of (100) surface of two layer t-Se containing 54 Se atoms.
- Lattice parameters of the selenium slabs were fully optimized. All atomic positions, including the bottom layer, were unconstrained during relaxation.
- All structural relaxations incorporated spin-orbit coupling (non-magnetic) and dispersion corrections
- BAND: SOC with ZORA , BLYP-D3 functional, TZP basis (small-core)
- VASP: PBE functional, PAW-PBE potentials, 1225 eV cut off, 2×2×1 k-point mesh (without symmetry)
- QE: PBE and PBEsol functionals, ONCVPSP PBE and PBEsol potentials, 90 Ry cut off, 2×2×1 k-point mesh (without symmetry). For PBEsol calculations, PBEsol functional with PBEsol ONCVPSP potentials for Se slab and PBE ONCVPSP potentials for the adsorbates were used.

QE allows mixing and matching

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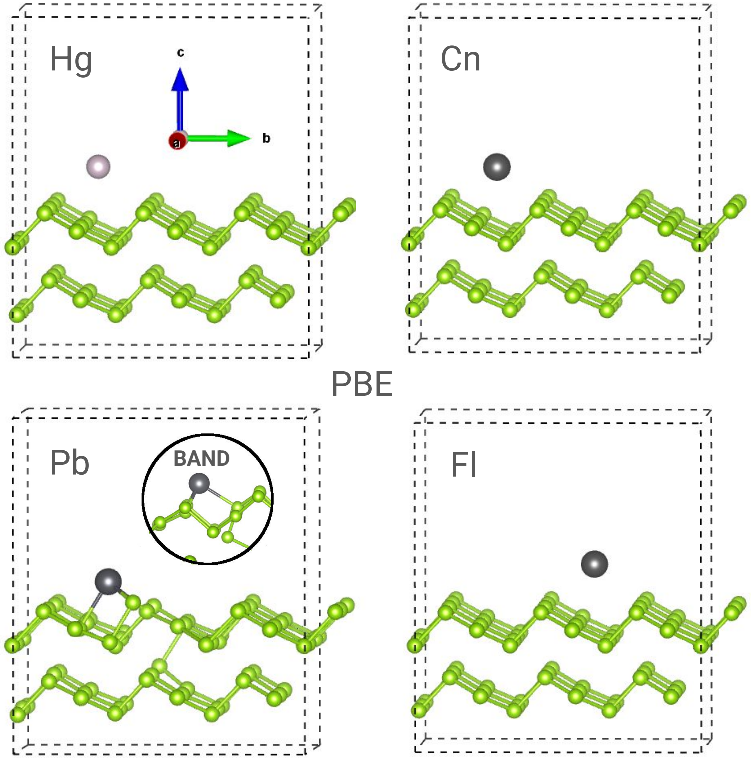
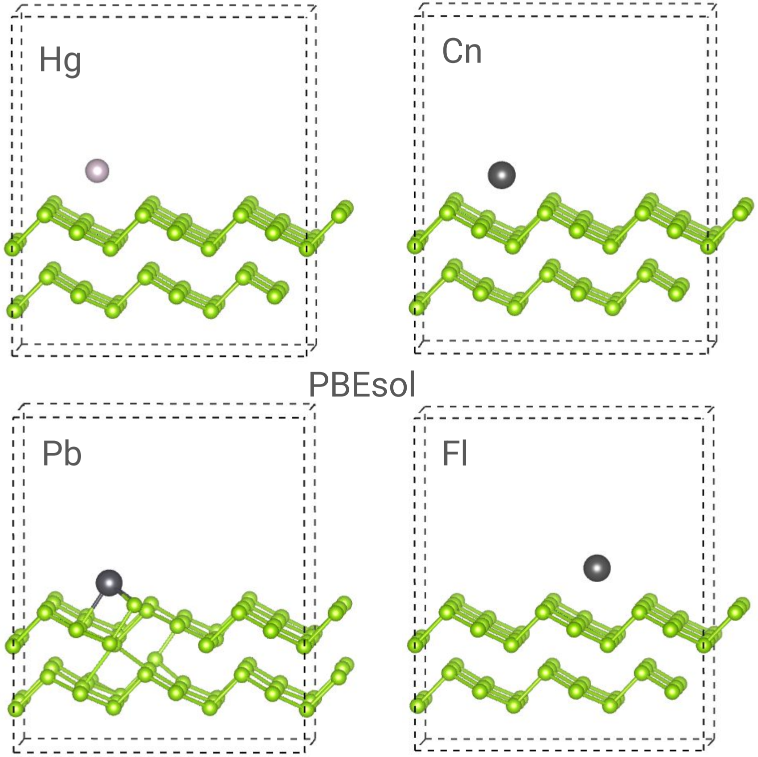
5. Results obtained before our license expired, by my colleague and co-author Dr. Miroslav Ilias, and is currently in the publication process.
6. Data obtained from collaborators, for benchmarking only
7. ZORA: Zero Order Regular Approximated Hamiltonian; BLYP-D3: Becke, Lee, Yang, Parr functional combined with D3 dispersion correction; TZP: Triple-zeta basis; PBE: Perdew, Burke, Ernzerhof GGA functional; PAW: Projector Augmented Wave method; PBEsol: PBE for solids; ONCVPSP: Optimized Norm-Conserving Vanderbilt Pseudopotential

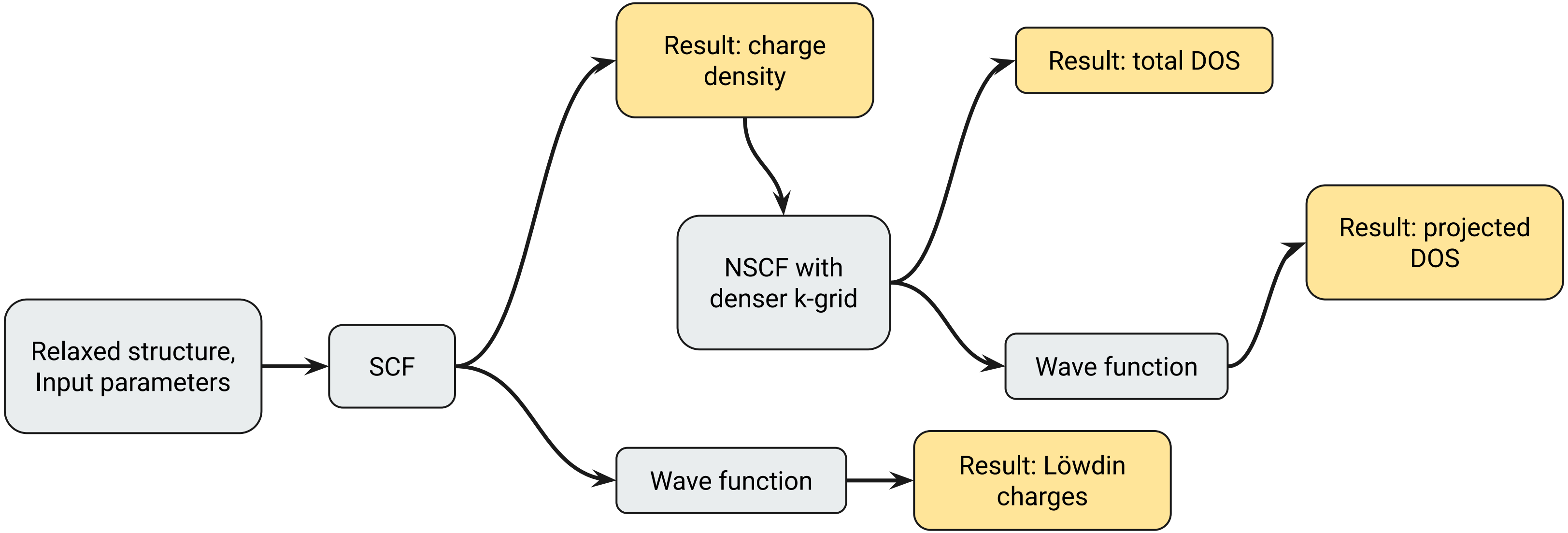
Relaxed structures





Electronic properties

- Calculating electronic properties like charge and DOS involves multiple steps with individual pre and post processing input files and execution sequences But ASE streamlines this complex workflow into a single, cohesive Python code block.
- SCF (Self-Consistent Field) iteratively solves Kohn-Sham equations until electron density converges. NSCF (Non-Self-Consistent Field) uses fixed charge density from SCF to calculate properties at denser k-points grids without re-converging.
- We used 2×2×1 k-point for SCF and 4×4×1 k-point grid for NSCF



Relaxed structure, Input parameters

SCF

Result: charge density

NSCF with denser k-grid

Result: total DOS

Wave function

Result: projected DOS

Wave function

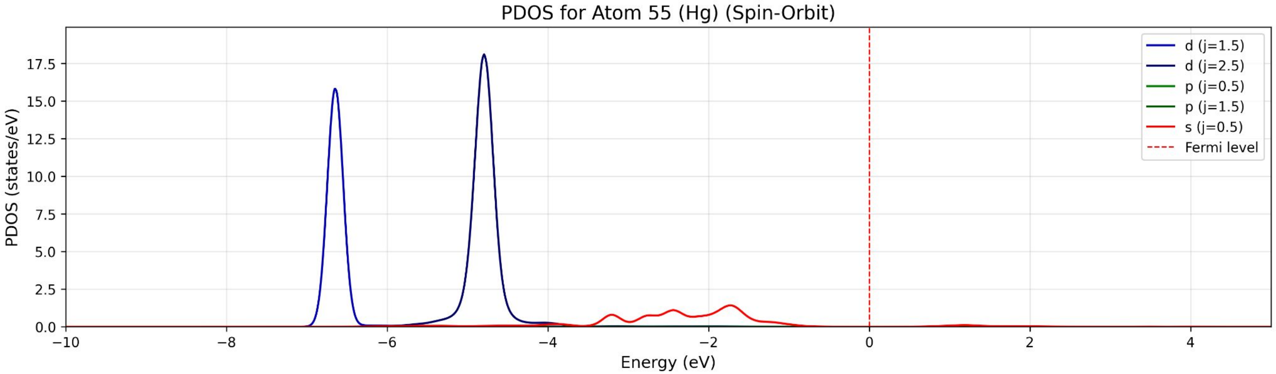
Result: Löwdin charges

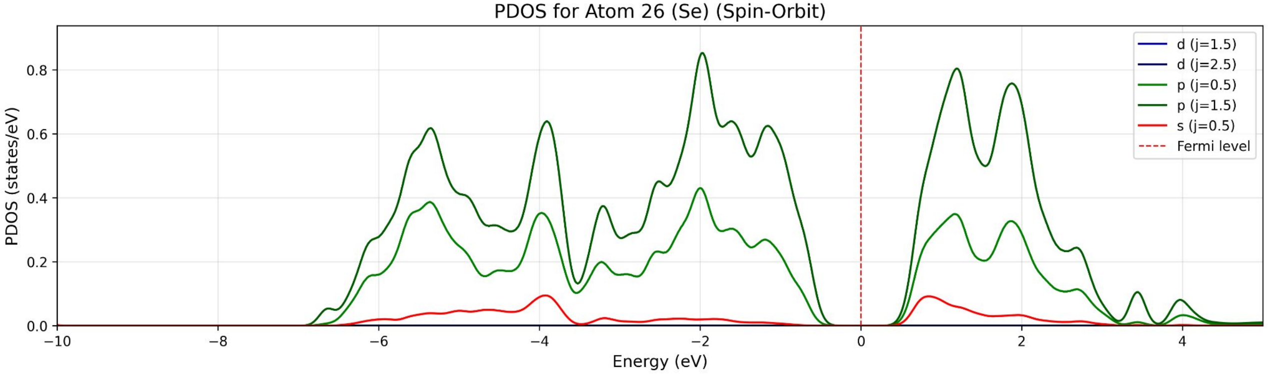
Charge transfer to adsorbates

- Partial Charge is an estimate of the electron count associated with a specific atom or orbital in a molecule, and it helps to quantify charge transfer and chemical bonding.
- Quantum Espresso has tools for Löwdin Population Analysis, which partitions the electron density and calculates partial charges of atoms
- Charge transfer Δe = Z_{val} - Löwdin charge.
- A +ve value of Δe implies electron loss, and -ve value of Δe implies electron gain

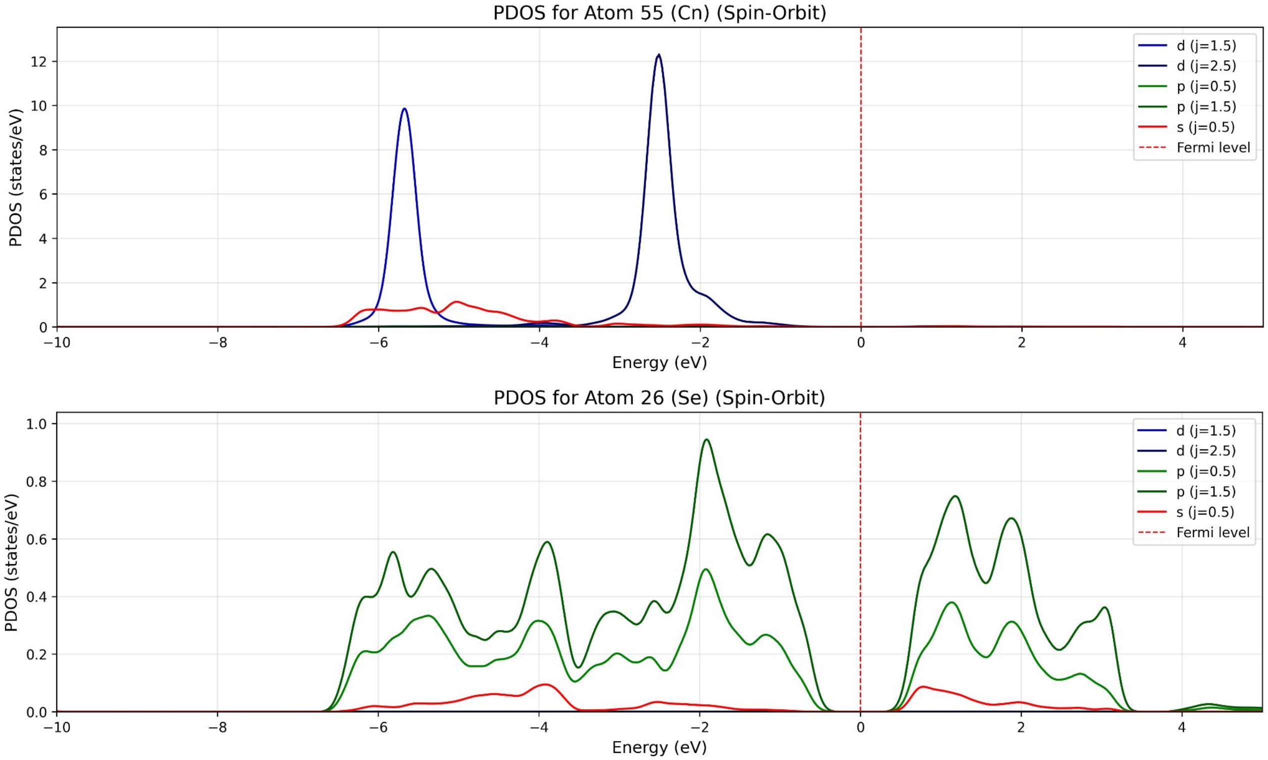
System	Δe (PBE) (e)	Δe (PBEsol) (e)
Hg	0.099	0.110
Cn	0.081	0.135
Pb	0.323	0.298
Fl	-0.018	-0.025

Projected density of states (PBE): Hg and nearest Se atom

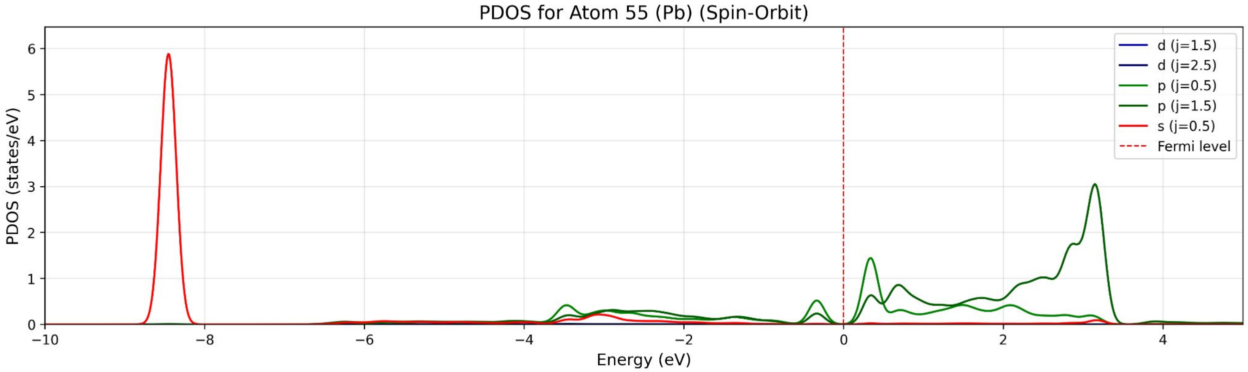


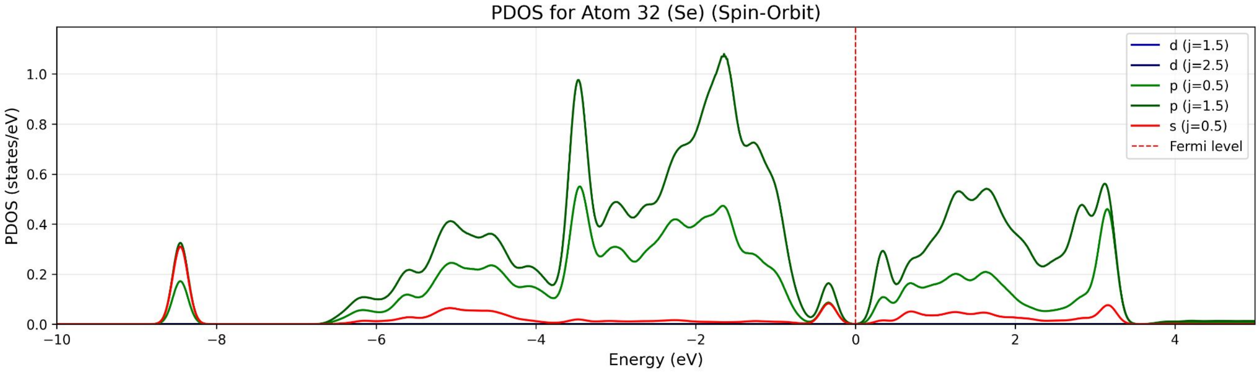


Projected density of states (PBE): Cn and nearest Se atom

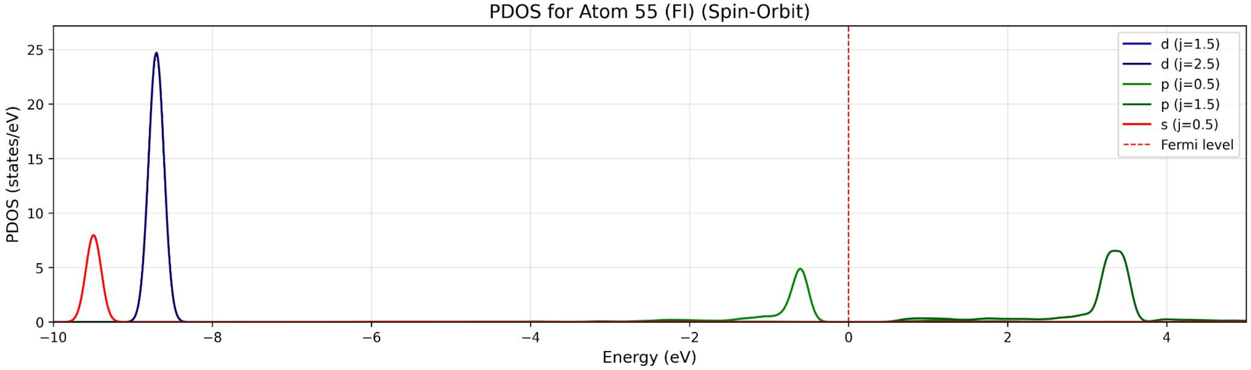


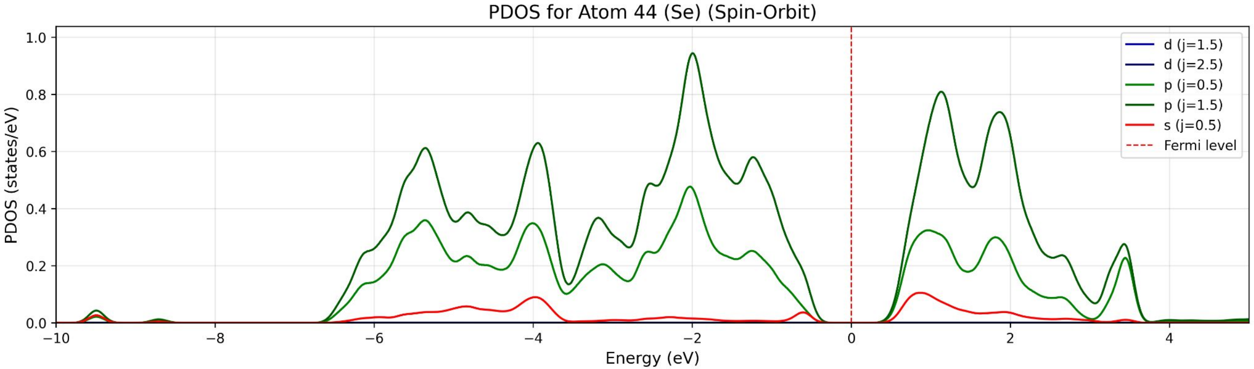
Projected density of states (PBE): Pb and nearest Se atom





Projected density of states (PBE): Fl and nearest Se atom





Finite-temperature effects

- Standard DFT provides electronic energies at 0 K only.
- To predict stability at finite temperatures, zero-point energy and thermal vibrational contributions must be supplemented to the static DFT energies.
- ΔG_{ads} is change in Gibbs free energy (G = H - TS) when an adsorbate atom absorbs onto the slab at T starting from a gas phase. ΔG_{ads} determines whether adsorption is thermodynamically favorable at a given temperature.

$$\Delta G_{ads} = G_{slab+adsorbate} - G_{slab} - \mu_{adsorbate}(P)$$

We have to use a few approximations, but it can be simplified as:

$$\Delta G_{ads} = E_{dft\_adsorption\_energy} + F_{vib} - k_B T$$

- We used ASE's finite displacement module to calculate force constants, then used harmonic approximation to predict vibrational modes and the temperature-dependent free energies (F_{vib}, includes both zero-point energy and thermal vibrational contributions).
- Due to computational constraints, we employed a simplified model with a frozen Se slab, vibrating only the adsorbate to estimate thermodynamic corrections.

ΔG_{ads} at 300 K

System	F_{vib} (PBE) (eV)	ΔG_{ads} (PBE) (eV)	F_{vib} (PBEsol) (eV)	ΔG_{ads} (PBEsol) (eV)
Hg	-0.016	-0.427	0.033	-0.577
Cn	-0.033	-0.459	-0.002	-0.681
Pb	0.100	-1.360	0.107	-1.805
Fl	-0.030	-0.428	-0.012	-0.607

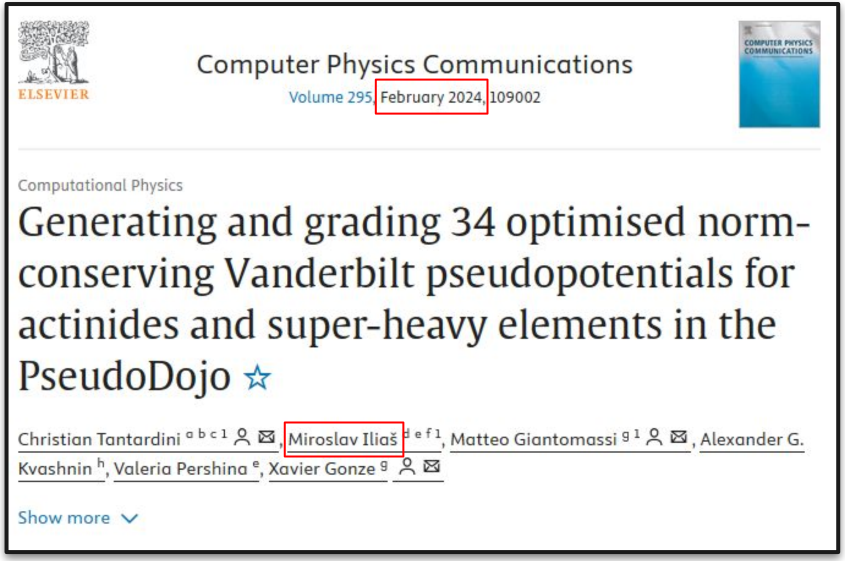
All adsorbates are expected to remain stable on the t-Se (100) surface even at 300 K

Summary of results

- PBE estimates of Hg, Cn, Pb and Fl adsorptions on t-Se by VASP and Quantum ESPRESSO (QE) matches well.
- PBE functional, both in VASP (PAW-PBE) and QE (ONCVPSP), systematically underestimates adsorption energies. However using PBEsol functional with PBEsol Se potentials and PBE adsorbate potentials yield ‘better’ results.
- Using PBEsol functional with PBEsol potentials for both Se and adsorbates produced similar forces, and no further changes in adsorption energies were found. Treating the bulk Se layer with PBEsol is sufficient.
- BAND predicts Fl on t-Se to have 0.17 eV lower adsorption energy than Cn. However QE predicts Fl to have 0.03-0.08 eV higher adsorption energies than Cn on the same.
- Observed discrepancies between BAND and QE likely arise from three key methodological differences: (1) atomic orbital versus plane wave basis sets (2) BAND's more accurate all-electron treatment versus pseudopotentials based approach of QE, and (3) QE-ASE's superior DFT-D4 dispersion corrections versus BAND's DFT-D3 using approximated parameters (taken from previous row) for superheavy elements.
- QE predicts Cn to loss small amount of electrons and gaining a net +ve charge (+0.081 e); and Fl to gain small amount of electrons and gaining a net -ve (-0.018 e) charge. However no formation of strong chemical bonds were observed in either cases.
- Stable adsorptions predicted at 300 K

Status of pseudopotentials

- We used ONCVPSP potentials by C. Tantardini et al., 2024, 295, 109002
- Valence shells (PBE) in the published work (1) Cn: $5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 6d^{10} 7s^2$ (2) Fl: $6s^2 6p^6 6d^{10} 7s^2 7p^2$
- Inclusion of semi-core 5 states and f orbital complicates convergence.
- To keep parity with the treatment of Fl, we generated a ‘lighter’ Cn pseudopotential with the configuration $6s^2 6p^6 6d^{10} 7s^2$ for this work.
- The published Fl PBE pseudopotential has a highly-localized positive energy ghost state.
- Highly-localized positive energy ghost state(s) appear at energies sampled by the valence electrons. They may cause unphysical forces, incorrect total energies, and lead to convergence issues.
- Generating better pseudopotentials and further testing might be necessary



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Computer Physics Communications

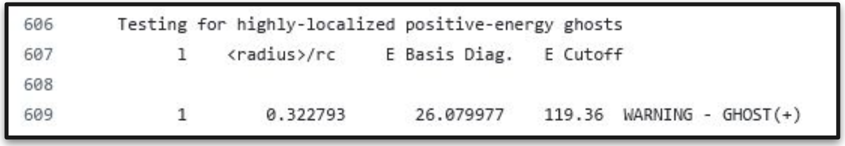
Volume 295, February 2024, 109002

Computational Physics

Generating and grading 34 optimised norm-conserving Vanderbilt pseudopotentials for actinides and super-heavy elements in the PseudoDojo ☆

Christian Tantardini [a b c 1], Miroslav Iliaš [d e f 1], Matteo Giantomassi [g 1], Alexander G. Kvashnin [h], Valeria Pershina [e], Xavier Gonze [g]

Show more



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        Testing for highly-localized positive-energy ghosts
            1     <radius>/rc      E Basis Diag.    E Cutoff

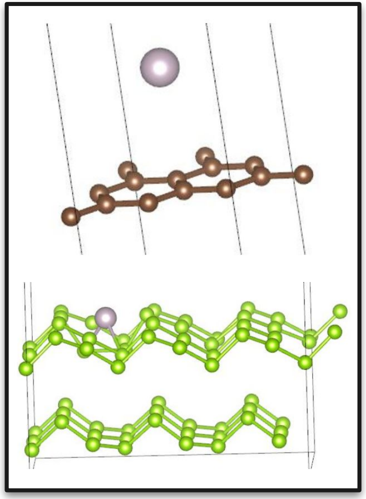
            1         0.322793        26.079977     119.36  WARNING - GHOST(+)
```

Ghost in Fl PBE potential

8. https://github.com/gmatteo/pseudos_ac_she/blob/main/114_Fl/Fl-6spd_r.out

Further scopes: machine-learned interatomic potentials

- We utilized ASE driven CHGNet calculator, and compared the results against QE computed values of adsorption energies.
- Hg adatom adsorption on graphene: CHGNet E_{ads} = -2.499 eV, QE E_{ads} = -2.541 eV
- Hg adatom adsorption on 3×3×1 supercell of (100) surface of two layer t-Se containing 54 Se atoms: CHGNet E_{ads} = -2.370 eV, QE E_{ads} = -0.584 eV
- Although CHGNet generates reasonable geometries, its accuracy is limited to scalar-relativistic level.
- To enhance performance, we have to retrain the model on a QE dataset incorporating SOC and dispersion corrections.
- We also aim to test other neural network tools for adsorption studies, including ALIGNN, DeePMD-kit, Fairchem, MatGL, MACE, orb-models, and SevenNet.



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9. https://chgnet.lbl.gov/

Thank you

Colleagues and staffs at the Bogoliubov Laboratory of Theoretical Physics (BLTP), and The Laboratory of Information Technologies (LIT) team for their help and support.

Team of Dr. N. V. Aksenov at FLNR for feedback regarding experiments.

Quantum ESPRESSO development community for discussions.