Accelerating *ab initio* real-space electronic structure calculations for low-dimensional materials using an atom-sphere grid truncation method

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Outline

Hohenberg–Kohn Theorem

If E is the lowest energy of the system, then E is a functional of the electron density:

$$E = F[n]$$

- We avoid solving the full many-electron wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and work with the electron density function $n(\mathbf{r})$

DFT (Hohenberg–Kohn):

$$E = F[n(\mathbf{r})]$$

Kohn–Sham Equation

Kohn–Sham equation is a single-particle equation
electron–electron interactions are included through the density

$$\hat{H}_{\mathrm{KS}}[\rho]\,|\psi_n\rangle = \varepsilon_n\,|\psi_n\rangle$$

where $|\psi_n\rangle$ and ε_n are the nth KS eigenstate and eigenvalue , ρ is the electron density, $\hat{H}_{\mathrm{KS}}$ is the Hamiltonian operator

Electron density:

$$\rho(\mathbf{r}) = \sum_n f_n\,|\psi_n(\mathbf{r})|^2$$

where f_n is the Fermi–Dirac occupation function
$\psi_n(\mathbf{r}) = \langle \mathbf{r}|\psi_n\rangle$ is the real-space wavefunction

Kohn–Sham Equation

Hamiltonian in the Kohn–Sham equation:

$$\hat{H}_{\mathrm{KS}}[\rho] = \hat{T} + \hat{V}_{\mathrm{ion}} + \hat{V}_{\mathrm{H}}[\rho] + \hat{V}_{\mathrm{XC}}[\rho]$$

$\hat{T}$: kinetic energy operator

$\hat{V}_{\mathrm{ion}}$: ionic potential

$\hat{V}_{\mathrm{H}}[\rho]$: Hartree potential

$\hat{V}_{\mathrm{XC}}[\rho]$: exchange–correlation potential

Self-consistent solution procedure: Iterate KS equations until both the electron density and the total energy are converged

Real–space KS-DFT

- KS wavefunctions, electron density, and potentials are represented directly on a spatial grid
- Accuracy is controlled by the real-space resolution (grid spacing)
- Naturally highly parallelizable across many CPU cores

Uniform Real–space Grid Representation

Wavefunction on a uniform grid:

$$|\psi_n\rangle \approx \sum_{\mu=1}^{N_b} \omega_\mu \, \psi_{n\mu} \, |\mathbf{r}_\mu\rangle$$

where $\psi_{n\mu} \equiv \psi_n(\mathbf{r}_\mu) = \langle \mathbf{r}_\mu | \psi_n \rangle$

$\{\mathbf{r}_\mu\}$: grid points ω_μ: volume weight of each point

Electron density on the grid:

$$\rho(\mathbf{r}_\mu) = \sum_n f_n \, |\psi_{n\mu}|^2$$

Discrete Kohn–Sham Equation

Discrete Kohn–Sham equation:

$$\mathbf{H}[\rho]\,\Psi_n = \epsilon_n\,\Psi_n$$

where $\Psi_n \equiv [\,\psi_{n1},\,\psi_{n2},\,\ldots,\,\psi_{nN_b}\,]^T$ is the nth discrete wavefunction (eigenvector).

Hamiltonian matrix elements:

$$\begin{aligned} H_{\mu\nu}[\rho] \equiv H[\rho](\mathbf{r}_\mu,\mathbf{r}_\nu) &= \langle \mathbf{r}_\mu \,|\, \hat{H}_{\mathrm{KS}}[\rho] \,|\, \mathbf{r}_\nu \rangle\, \omega_\nu \\ &= T(\mathbf{r}_\mu,\mathbf{r}_\nu) + V_H[\rho](\mathbf{r}_\mu)\delta_{\mu\nu} + V_{XC}[\rho](\mathbf{r}_\mu)\delta_{\mu\nu} \\ &\quad + \underbrace{V_{\mathrm{loc}}(\mathbf{r}_\mu)\delta_{\mu\nu} + V_{\mathrm{nl}}(\mathbf{r}_\mu,\mathbf{r}_\nu)}_{V_{\mathrm{ion}}(\mathbf{r}_\mu,\mathbf{r}_\nu)} \end{aligned}$$

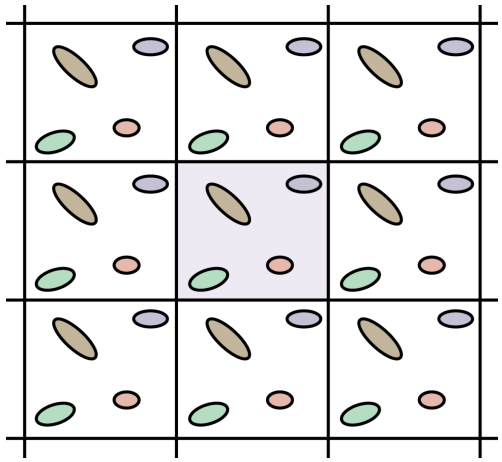
Uniform Grids in Real-space DFT

- A uniform 3D grid is constructed in the simulation cell
- Number of grid points is determined by lattice vectors $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ and the spacing h
- Grid points fill the entire simulation cell, including large vacuum regions
- Works for both boundary types:
  - PBC: periodic systems (solids, 2D materials, nanotubes)
  - DBC: isolated systems (molecules, clusters)

Boundary Conditions in Real–space DFT

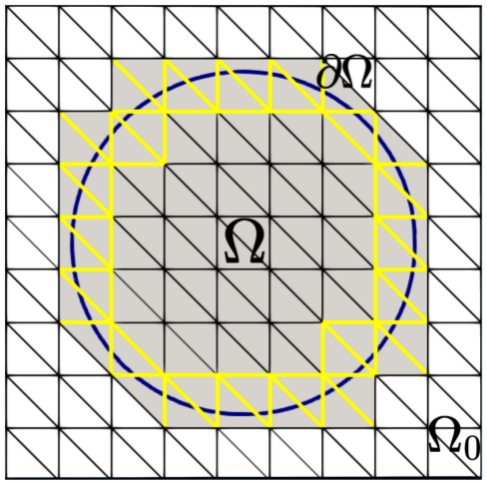
Periodic Boundary Condition (PBC)

- System repeats periodically (like an infinite crystal)
- $\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r})$
- Used for solids, 2D materials, nanotubes



Dirichlet Boundary Condition (DBC)

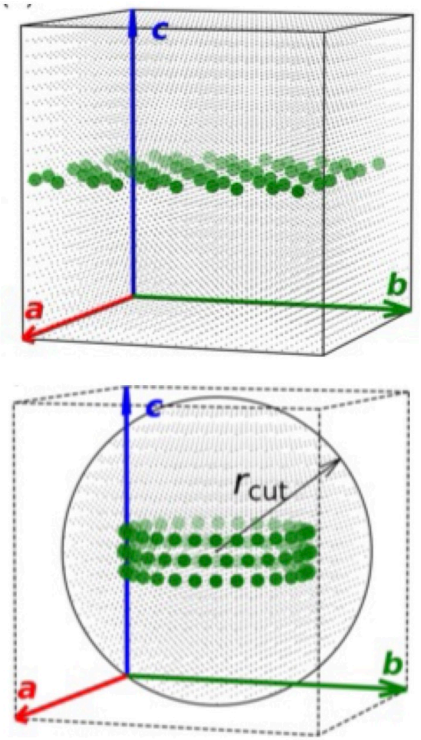
- Wavefunction is set to zero at the boundary
- Used for isolated systems: molecules, clusters



Uniform Grids Are Wasteful

Many materials contain large vacuum regions:

- 0D clusters (C_{60}, nanoparticles)
- 1D nanotubes (SWNT)
- 2D layers with vacuum (graphene, tBLG)
- 3D porous materials (MOFs, DSSCs)



Problem (atoms are not average distribution):

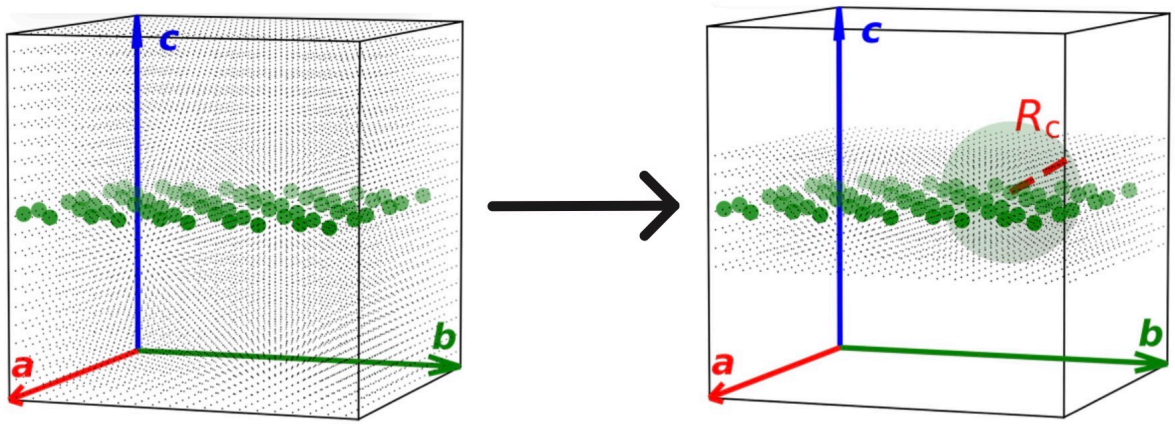
- Uniform grids waste many points in empty space
- Leads to slower computation and high memory usage

Outline

Atom-Sphere Truncation (AST)

Core concept: Electrons are mainly located around atoms

- Define a cutoff radius R_c around each atom
- Works for both PBC and DBC
- Fewer grid points and faster SCF steps
- Energy difference converges to within 2 meV/atom



AST definitions

AST grid set

$$\Omega_{\mathrm{AST}} = \bigcup_a \{\mathbf{r}_\mu : \|\mathbf{r}_\mu - \mathbf{R}_a\| \leq R_c\}\,.$$

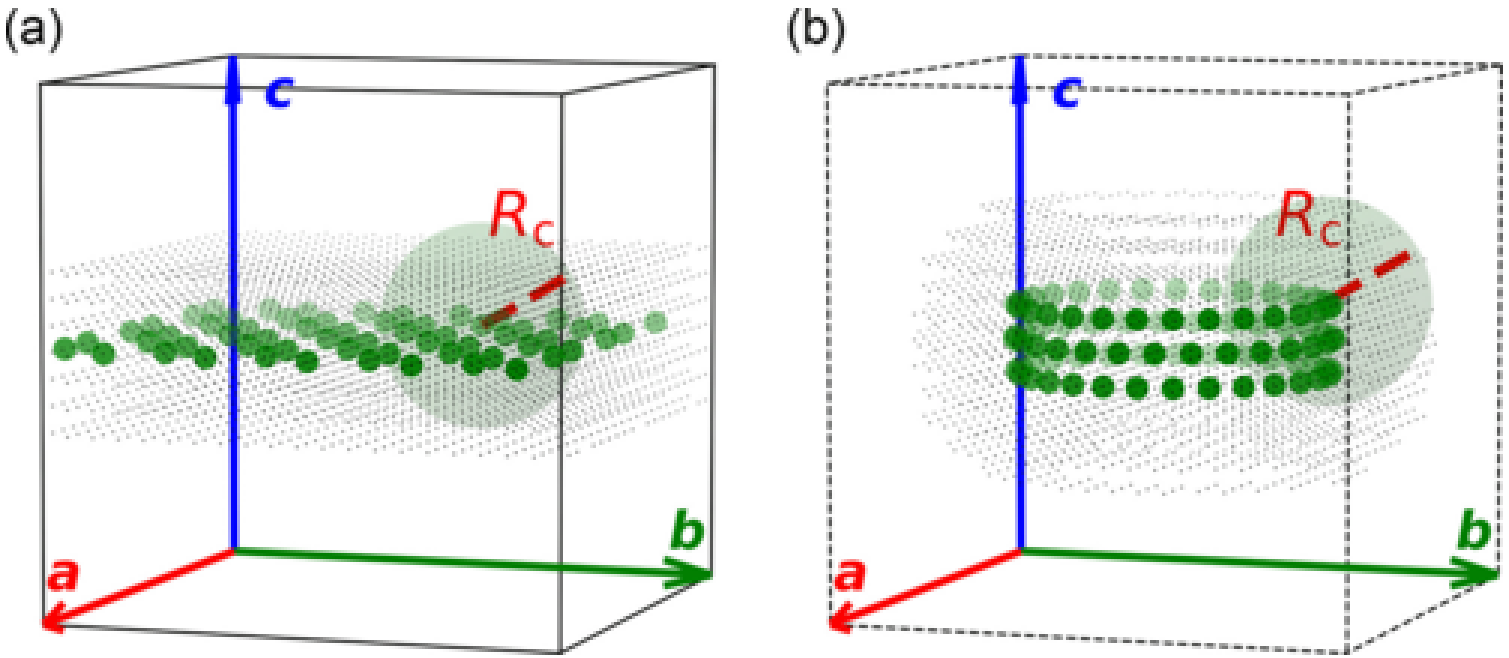
Truncated wavefunction

$$\psi_n^\mu = \begin{cases} \psi_n(\mathbf{r}_\mu) & \mathbf{r}_\mu \in \Omega_{\mathrm{AST}} \\ 0 & \text{otherwise} \end{cases}$$

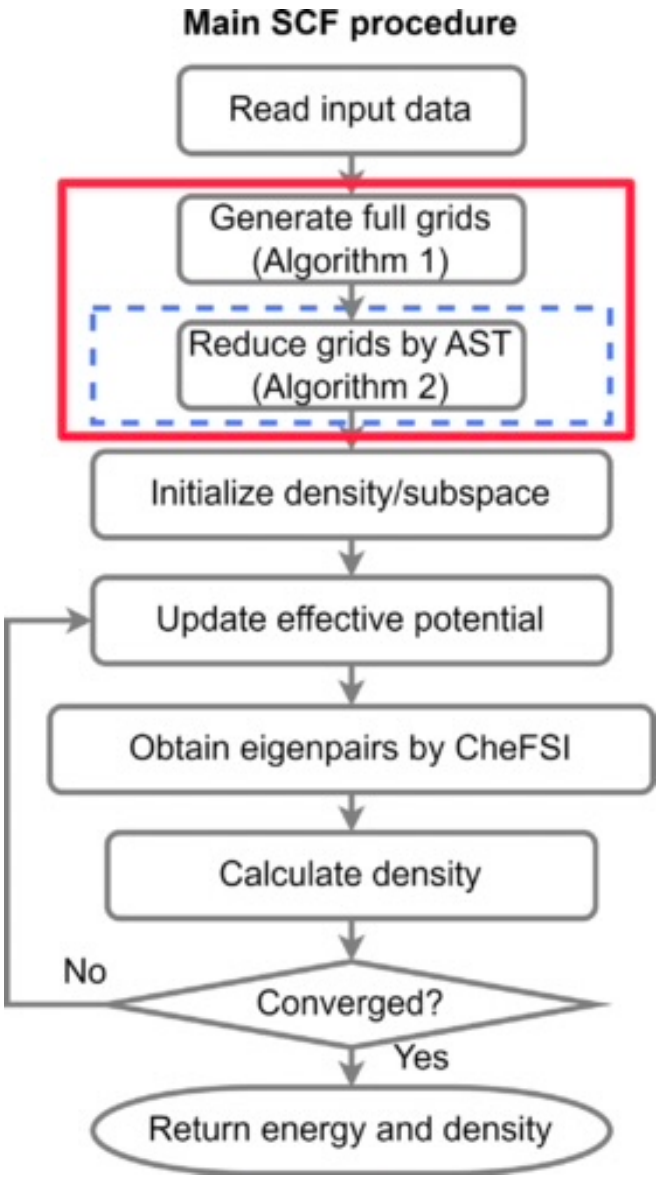
$\mathbf{r}_\mu$: grid point $\quad$ $\mathbf{R}_a$: atom position $\quad$ R_c: cutoff radius

AST Grids in Real Space

- The AST algorithm keeps only grid points within a cutoff radius R_c around each atom
- This removes most vacuum grid points and reduces the computational cost



Details of Algorithms and Implementation



- Exchange–correlation: PBE functional (via `libxc`)
- Eigenproblem solver: CheFSI

Algorithm 1: Generation of Full Uniform Grids

Data: Lattice vectors $(\mathbf{a}, \mathbf{b}, \mathbf{c})$, grid spacing h
Result: $N_b, N_x, N_y, N_z, h_x, h_y, h_z, \{\mathbf{r}_\mu\}$

// Calculate the number of full grids

$$N_x = \left\lfloor \frac{|\mathbf{a}|}{h} \right\rfloor, \quad N_y = \left\lfloor \frac{|\mathbf{b}|}{h} \right\rfloor, \quad N_z = \left\lfloor \frac{|\mathbf{c}|}{h} \right\rfloor$$

$$N_b = N_x N_y N_z$$

// Reset the grid spacings

$$h_x = |\mathbf{a}|/N_x, \quad h_y = |\mathbf{b}|/N_y, \quad h_z = |\mathbf{c}|/N_z$$

// Loop over 3D grid points

for $k = 1$ **to** N_z **do**
  for $j = 1$ **to** N_y **do**
    for $i = 1$ **to** N_x **do**
      // Map integer coordinates to in-memory index
      $\mu = i + N_x(j-1) + N_x N_y (k-1)$
      // Store grid position
      $\mathbf{r}_\mu = \left(\frac{\mathbf{a}}{N_x}, \frac{\mathbf{b}}{N_y}, \frac{\mathbf{c}}{N_z} \right) (i,j,k)^T$

return $N_b, N_x, N_y, N_z, h_x, h_y, h_z, \{\mathbf{r}_\mu\}$

Algorithm 2: Generation of the atom-sphere truncation (AST) grid size and coordinates.

Data: Full-grid count and positions N_b, $\{\mathbf{r}_\mu\}$; number of atoms N_a; atom positions $\mathbf{R}_a$; cutoff radius R_c

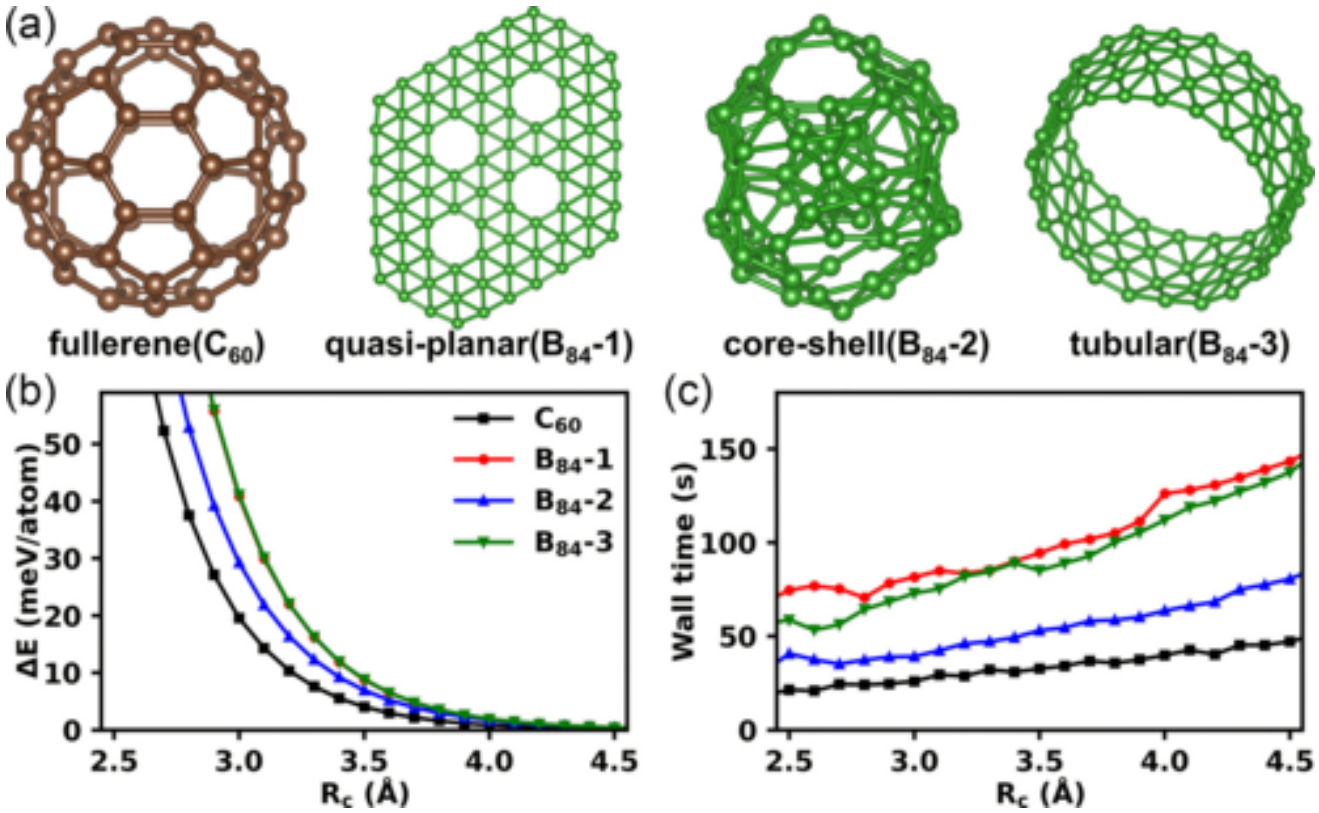
Result: Ω_{AST}, N_b^{AST}

```
// Initialize AST grids
Ω_AST = ∅
N_b^AST = 0
for μ = 1 to N_b do
    // Select the grid positions
    for a = 1 to N_a do
        if ||r_μ − R_a|| ≤ R_c then
            // Store grid point
            Ω_AST = Ω_AST ∪ {r_μ}
            N_b^AST = N_b^AST + 1
return Ω_AST, N_b^AST
```

Outline

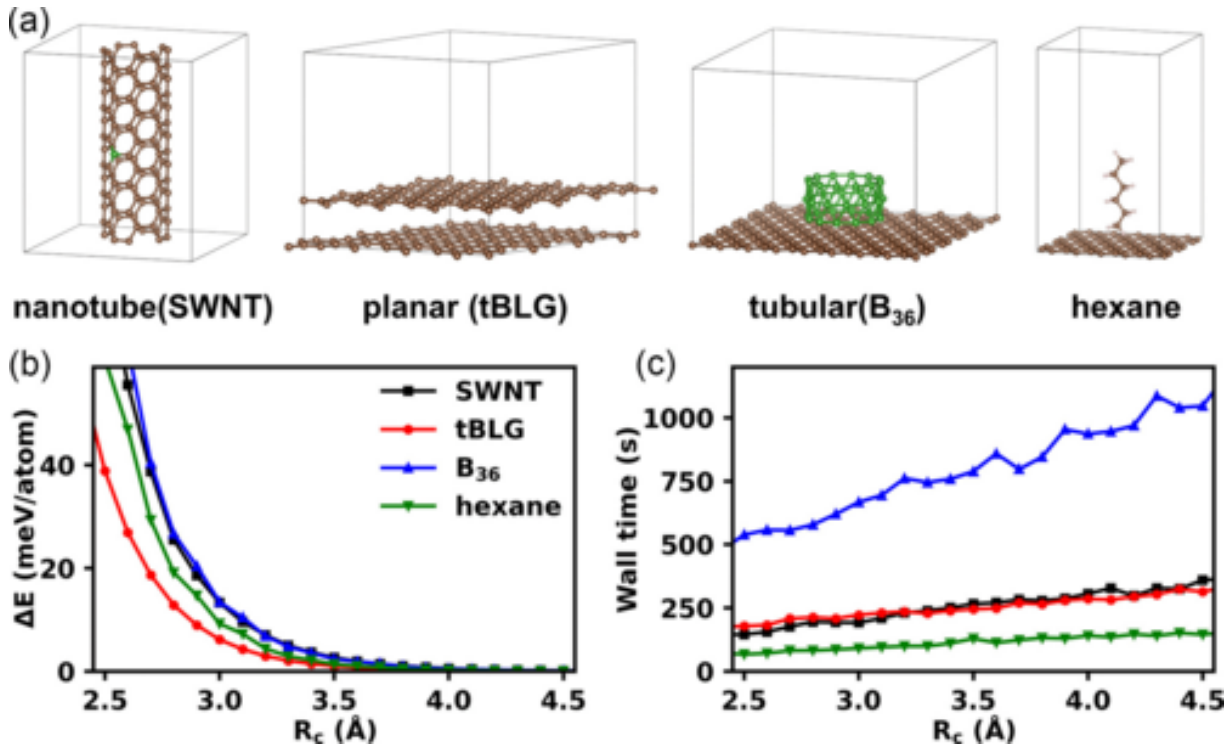
Isolated Cluster Systems

- Tested: C_{60} and three B_{84} structures
- Energy difference converges to within 2 meV at $R_c \approx 4.0$ Å
- Grid reduction: 35–73%
- Time reduction per SCF step: 41–71%



Low-dimensional and Adsorption Systems

- Tested: SWNT (1D), tBLG (2D), B_{36} cluster, hexane/graphene
- Energy difference converges to within 2 meV/atom at $R_c \approx 3.6$ Å
- Grid reduction: 30–46%
- Time reduction per SCF step: 37–52%



MOFs

- Systems: IRMOF-1(a) and IRMOF-10(b)
- Energy difference converges to within 2 meV/atom at $R_c \approx 3.6$ Å
- Grid reduction: 36% (a)& 50% (b)
- Time reduction per SCF step: 36% (a) & 47% (b)

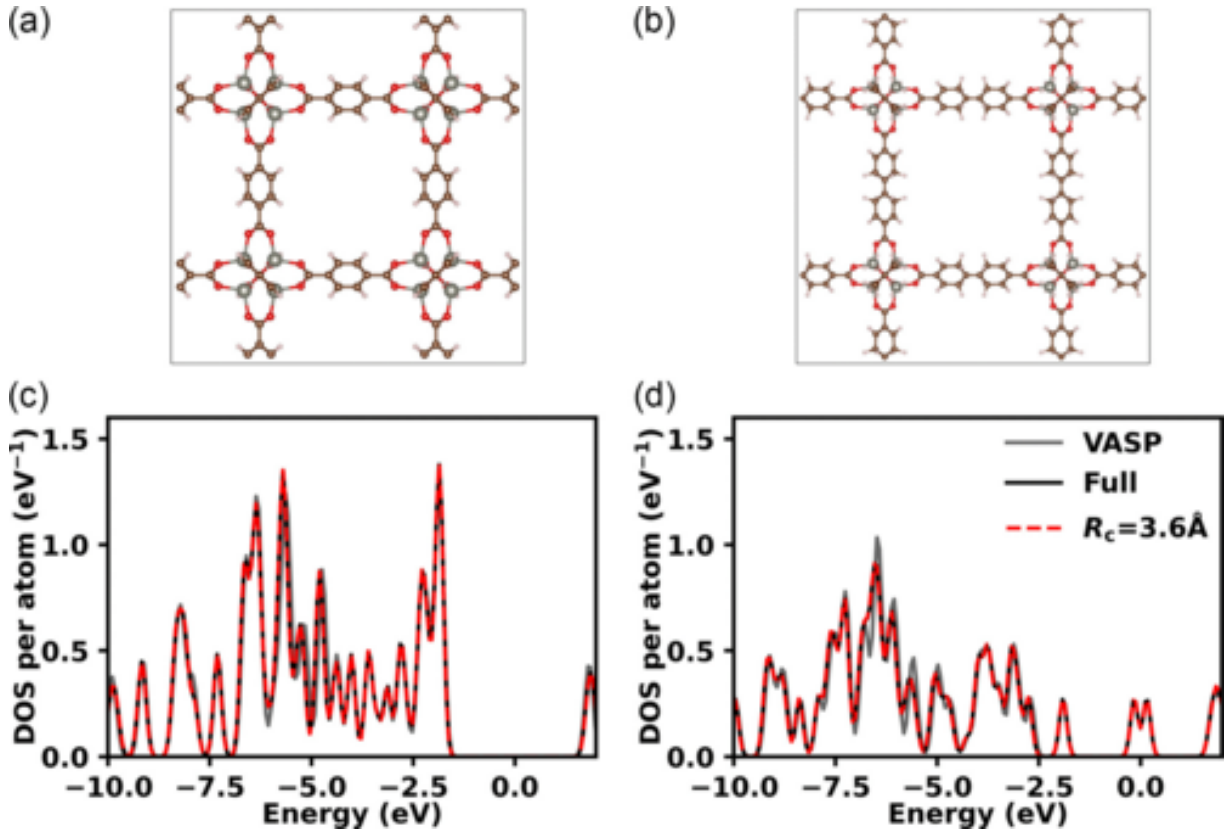


Table : Efficiency comparison of Full grids vs AST

Test system	Atoms	Number of grid points		SCF steps [time(s)/step]	
		Full	AST[a]	Full	AST[a]
C_{60}	60	449k	287k	30(2.2)	30(1.3)
B_{84}−1	84	1802k	484k	32(14.3)	31(4.1)
B_{84}−2	84	716k	366k	32(4.2)	28(2.3)
B_{84}−3	84	927k	496k	32(6.8)	31(3.6)
SWNT	112	677k	364k	41(12.0)	44(5.7)
tBLG	148	592k	413k	33(10.7)	32(6.6)
B_{36}	196	1109k	602k	44(35.7)	40(19.1)
Hexane	80	435k	293k	36(4.9)	34(3.1)
IRMOF-1	106	1161k	718k	85(39.2)	70(25.1)
IRMOF-10	190	2628k	1319k	81(80.3)	79(42.3)

[a]Absolute errors for AST are below 2 meV/atom.

Outline

Conclusion

The AST method improves real-space KS-DFT efficiency:

- Reduces 30−73% of real-space grid points by removing vacuum regions
- Accelerates SCF calculations by 36−71%, tested on clusters, nanotubes, 2D materials, and MOFs
- Maintains energy accuracy within 2 meV/atom using $R_c \approx 3.6$–4.0 Å

Thank you ！