Projector Augmented Wave-based Kohn-Sham Density Functional Theory in *OpenAtom* with N^2 *log N* scaling

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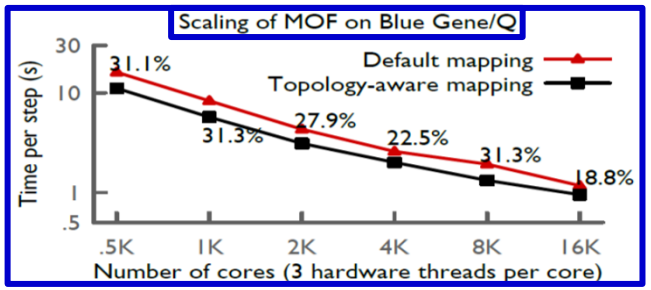
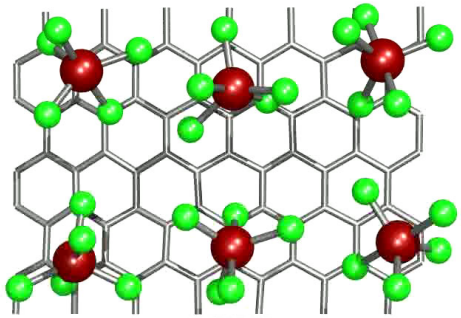
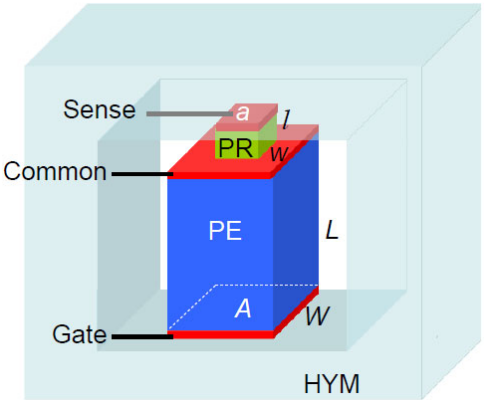
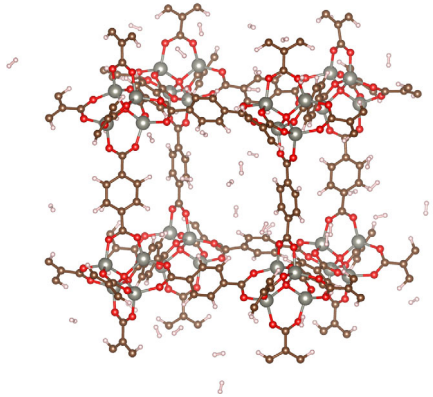
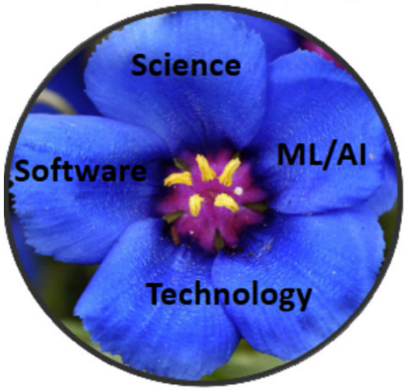


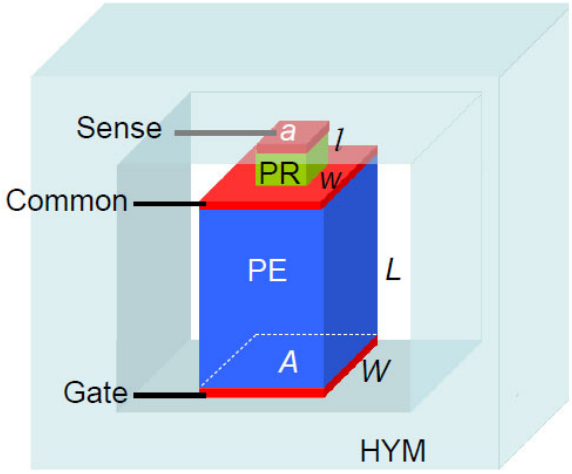


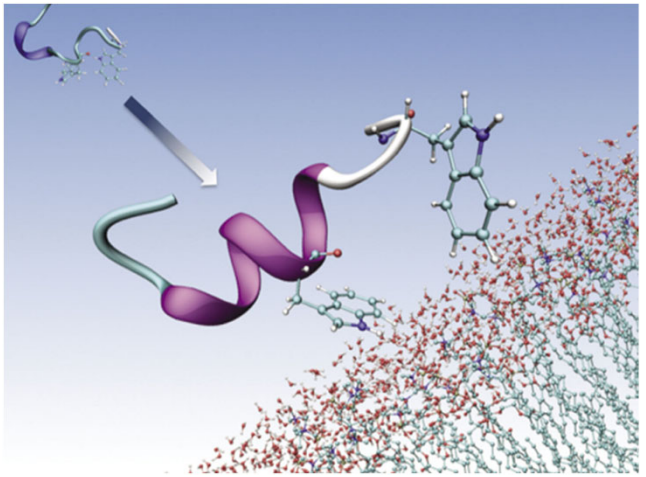


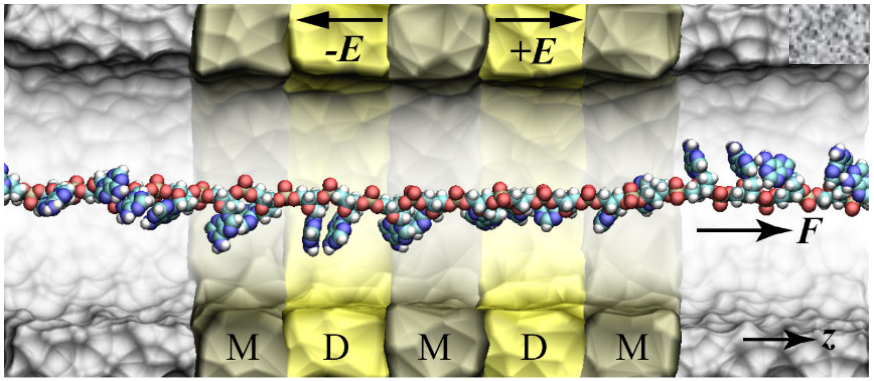




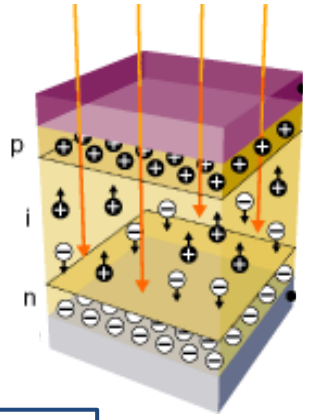
Goal: The study of complex heterogeneous systems to discern emergent and new physics and create impact



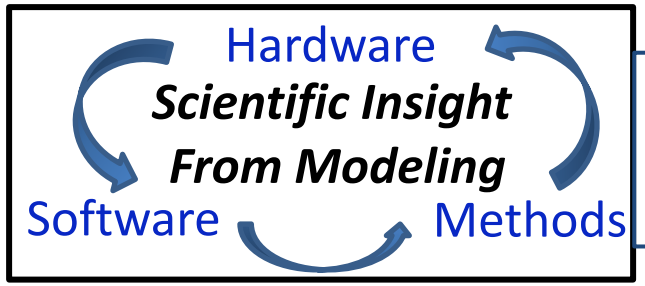




Light in



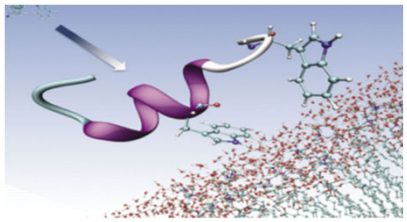
Approach:



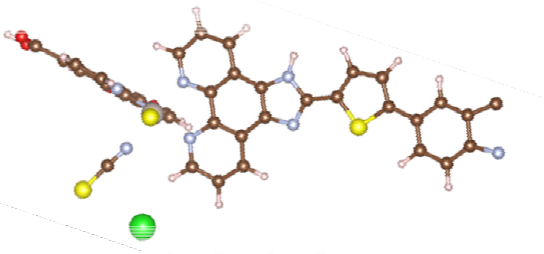
Physics-based solutions for complex systems

OpenAtom Concept: Statistical Sampling of Complex Environments is Key to Understanding many Physical Systems.

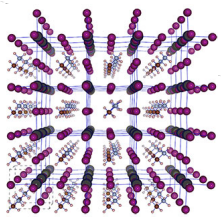
Biological function : enabled by fluctuations in both the environment and the biomolecules.



Pollutant detection: requires sampling complex aqueous systems and then exporting the results to a GW/GW-BSE app for computation of spectra.

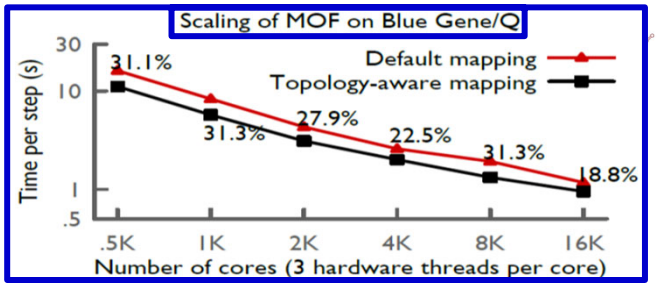


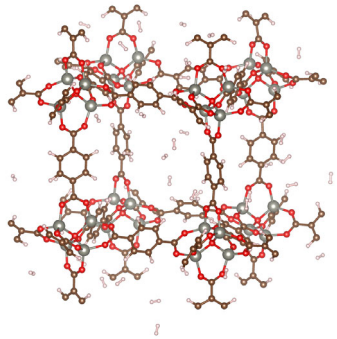
Understanding chemical reactions in dense arrays: requires non-trivial sampling of the full system due to complex many-body reaction paths.

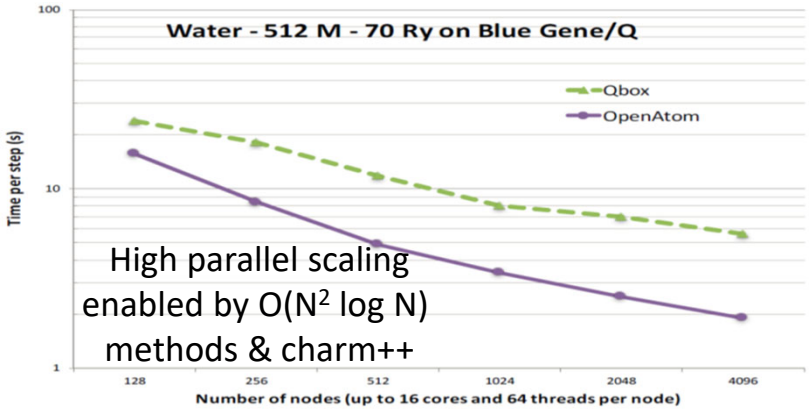


OpenAtom: Pimpernel (Martyna), UIUC (Kale) and Yale (Ismail-Beigi) collaborate to build the Electronic Ground and Excited State parallel software and methods including classical and quantum nuclear motion capabilities to realize this vision.

Key Project Accomplishments thus Far:





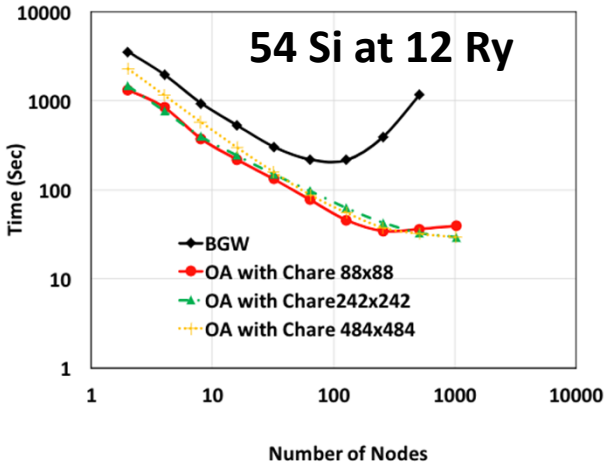


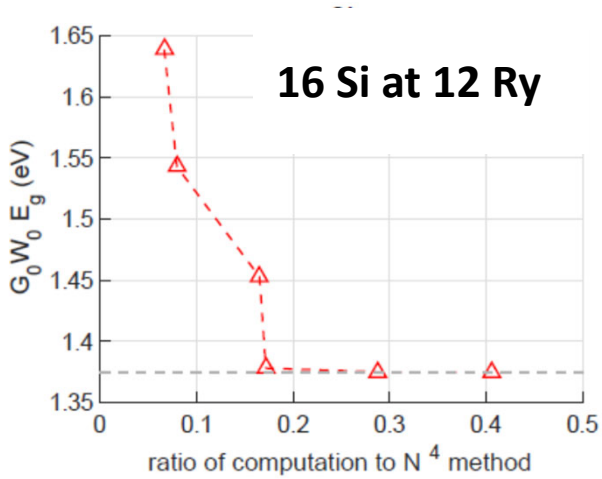
Electronic Ground State (charm++ parallelization):

1. High Parallel Scaling allows study of hydrogen storage in MOF's via Path Integral CPAIMD.

2. Exact Exchange N^2 $N^{1/3}$ log N (for metals & insulators): 10x speed 32 waters! (SIAM in prep).

3. *Projector Augmented Wave method in N^2 log N (new results!).*





Reduced order GW software soon to be released!

Electronic Excited States (charm++ parallelization)

1. High Parallel Scaling for O(N^4) GW

2. O(N^3) GW method based on a shredded propagator, complex time formalism

Kohn-Sham Density Functional Theory (KS-DFT):

A workhorse of computational science.

- **KS-DFT:** *Ground state electronic energy* expressed *exactly* as the *minimum of a functional of the zero temperature, 1-body density* written in terms of

$$\rho(\boldsymbol{r},\boldsymbol{r}') = \sum_{I=1}^{N_{KS}} \psi_I(\boldsymbol{r})\psi_I^*(\boldsymbol{r}')\,, \qquad n(\boldsymbol{r}) = \rho(\boldsymbol{r},\boldsymbol{r}), \qquad N_{KS} = (\#\,\text{electrons})/2$$

an *orthonormal set of KS states*, $< \psi_I \mid \psi_J > = 2\delta_{IJ}$.

Walter Kohn, Nobel Chemistry 1998

- **KS Density Functional:** *Sum of* the *kinetic energy* of non-interacting electrons, *Hartree energy, electron-ion/external energy* and an unknown correction term, *exchange correlation energy functional*,

$$E[n(\boldsymbol{r})] = -\frac{\hbar^2}{2m_e}\int d\boldsymbol{r}\,\left(\nabla^2\rho(\boldsymbol{r},\boldsymbol{r}')\right)\Big|_{\boldsymbol{r}'=\boldsymbol{r}} + \frac{e^2}{2}\int d\boldsymbol{r}d\boldsymbol{r}'\,\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

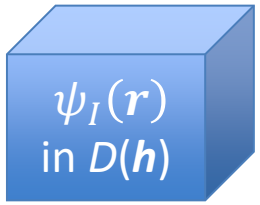
$$+e\int d\boldsymbol{r}\,n(\boldsymbol{r})V_{ext}(\boldsymbol{r};N) + E_{xc}[n(\boldsymbol{r})]\,, \qquad N = \#\,\text{ions},\ N_{KS}\sim N.$$

- **Generalized Gradient Approximation (GGA):** *Tractable approx. to* E_{xc}

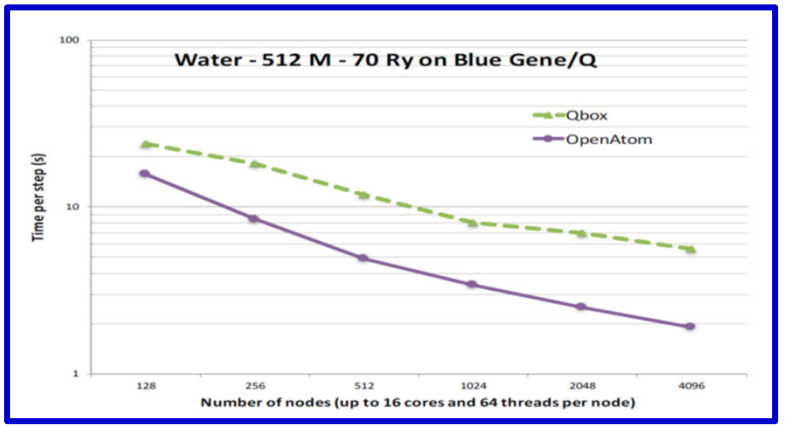
$$E_{xc}[n(\boldsymbol{r})] \approx \int d\boldsymbol{r}\,\varepsilon_{xc}\big(n(\boldsymbol{r}),\nabla n(\boldsymbol{r})\big)$$

KS-DFT in OpenAtom

- **OpenAtom:** *Plane-wave* (PW) based KS-DFT within the GGA – expand KS states in the delocalized PW basis.



- **PW-KS-DFT in OpenAtom - Advantages:**
  - $N^2 \log N$ or better scaling of interactions & derivatives - *Euler Exponential Spline (EES) Interpolation*.
  - Only orthogonalization is ~N^3 .
  - *High parallelism under charm++*.
  - k-points, path integrals, LSDA & tempering implemented.

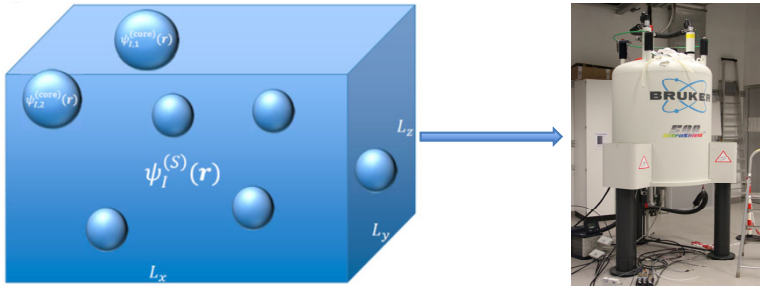


- **PW-KS-DFT in OpenAtom - Disadvantages:**
  - *Large basis set* required - millions and millions (*c.f.* Carl Sagan).
  - *Large memory* required – need large machines.
  - *Heavy atoms (impossibly) computationally intensive*.

Projector Augmented Wave Method (PAW)

P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)

- **Projector-Augmented Wave (PAW) :** *accurate* treatment of *heavy atoms* in KS-DFT with low computational cost.
- **PAW-KS-DFT Advantages**
  - KS states split into localized and delocalized/smooth parts – *small basis* possible even for *heavy atoms*.
  - *NMR* and some other linear response methods require the core – PAW makes it *easy.*
  - *Small memory* requirement.



- **PAW-KS-DFT Disadvantages**
  - Implemented with inefficient N^3 methods for interactions.
  - *Parallel performance* of standard implementations *poor.*
  - *Accuracy control poor.*

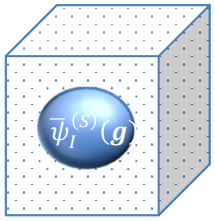
Goal: Implement $N^2 \log N$ EES-based PAW with high parallel efficiency in OpenAtom.

PAW Basics: KS states

- **KS states:** *delocalized/smooth part, (S), + localized/core part, (core).*
  Core localized within a sphere of radius R_{pc} around each ion:

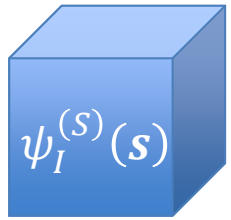
$$\psi_I(\boldsymbol{r}) = \psi_I^{(S)}(\boldsymbol{r}) + \sum_{J=1}^{N} \psi_{IJ}^{(\mathrm{core})}(\boldsymbol{r}), \qquad \psi_{IJ}^{(\mathrm{core})}(\boldsymbol{r}) = 0, |\boldsymbol{r} - \boldsymbol{R}_J| > R_{pc}$$

- **Smooth:** fills all spaces & varies, *expanded in plane-waves:*



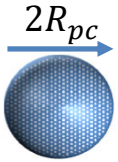
$$\psi_I^{(S)}(\boldsymbol{s}) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{g}}^{|\boldsymbol{g}|<G_c/2} \bar{\psi}_I^{(S)}(\boldsymbol{g}) \exp(i\hat{\boldsymbol{g}}\boldsymbol{s})$$

$\boldsymbol{r} = \boldsymbol{h}\boldsymbol{s}$, V = det $\boldsymbol{h}$, $\boldsymbol{g}$ =2π$\boldsymbol{h}^{-1}\hat{\boldsymbol{g}}$, $\hat{\boldsymbol{g}}$ ∈ integer



- **Core:** localized, written in *terms of fixed core projectors,* $\{\Delta p, p^{(S)}\}^*$:

$$\psi_{IJ}^{(\mathrm{core})}(\boldsymbol{r}) = \Delta p(\boldsymbol{r} - \boldsymbol{R}_J) Z_{IJ}^{(S)}, \qquad \Delta p(\boldsymbol{r} - \boldsymbol{R}_J) = 0, |\boldsymbol{r} - \boldsymbol{R}_J| > R_{pc}$$



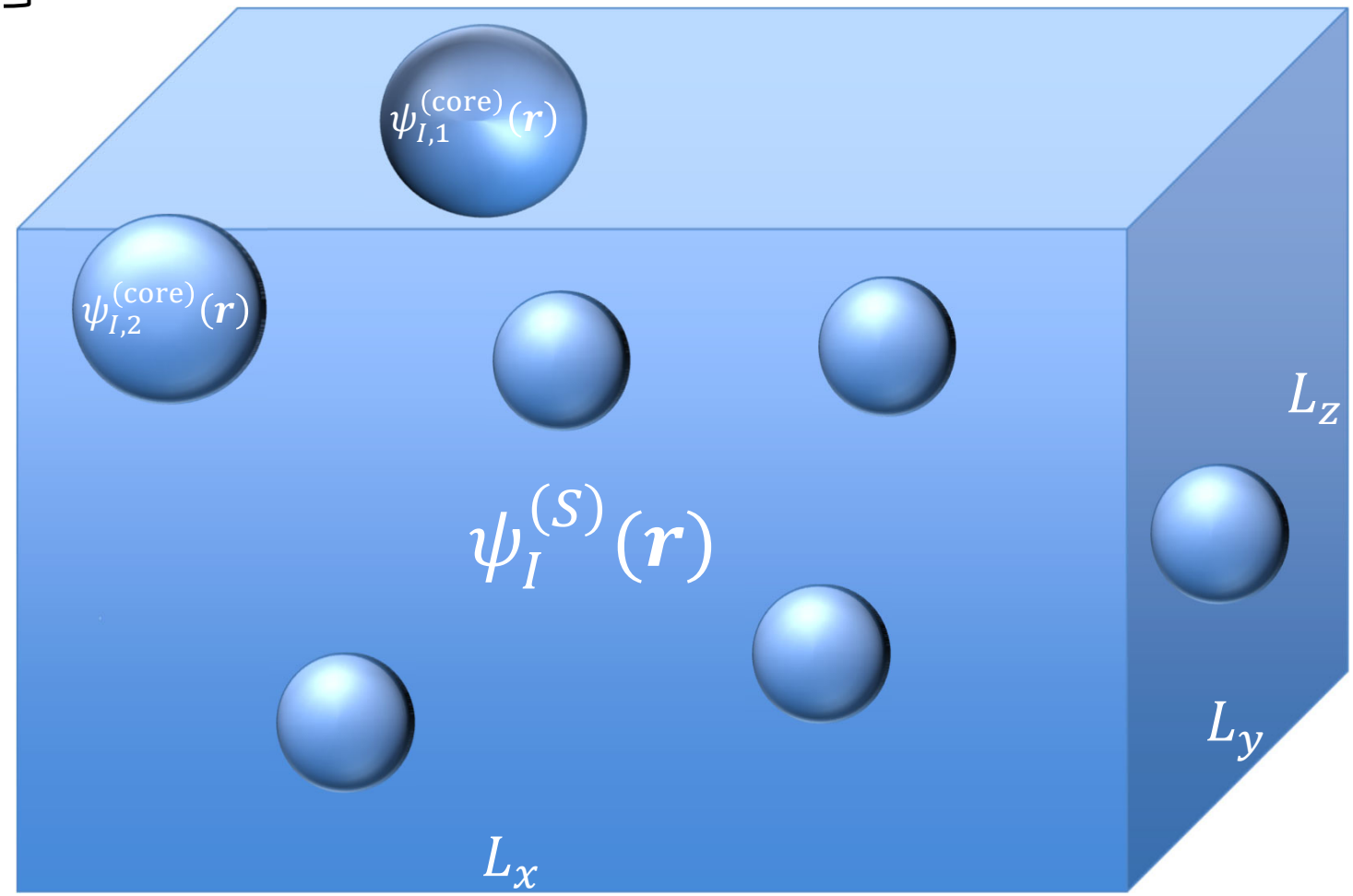
$$Z_{IJ}^{(S)} = < \mathrm{p}_\mathrm{J}^{(\mathrm{S})} | \psi_I^{(S)} > = \int dr^3 p^{(S)}(\boldsymbol{r} - \boldsymbol{R}_J)\, \psi_I^{(S)}(\boldsymbol{r}), \quad p^{(S)}(\boldsymbol{r} - \boldsymbol{R}_J) = 0, |\boldsymbol{r} - \boldsymbol{R}_J| > R_{pc}$$

∗ 1 ion type, 1 channel for simplicity

PAW Basics: Example KS state

$$\boldsymbol{h} = \begin{bmatrix} L_x & 0 & 0 \\ 0 & L_y & 0 \\ 0 & 0 & L_z \end{bmatrix}$$

Localized ion core states, $\psi_{IJ}^{(\mathrm{core})}(\boldsymbol{r})$ embedded



in the smooth part of the state, $\psi_I^{(S)}(\boldsymbol{r})$, that fills $D(\boldsymbol{h})$.

PAW Basics: KS-DFT within LDA under periodic boundary conditions at Γ

The whole enchilada:

$$E[n(\boldsymbol{r})] = E_{NIKE} + E_{ext} + E_H + E_{xc}$$

$$E_{NIKE} = -\frac{\hbar^2}{2m_e}\int_{D(\boldsymbol{h})} d\boldsymbol{r} \sum_I \langle\psi_I|\nabla^2|\psi_I\rangle \qquad E_{xc} = \int_{D(\boldsymbol{h})} d\boldsymbol{r}\, \varepsilon_{xc}(n(\boldsymbol{r}))$$

$$E_H = \frac{e^2}{2}\int_{D(\boldsymbol{h})} d\boldsymbol{r} \int_{D(\boldsymbol{h})} d\boldsymbol{r}\,' \sum_{\boldsymbol{m}} \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'+\boldsymbol{mh}|} \qquad E_{ext} = -\int_{D(\boldsymbol{h})} d\boldsymbol{r} \sum_J \sum_{\boldsymbol{m}} \frac{eQ_J n(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}_J+\boldsymbol{mh}|}$$

Non-interacting electron kinetic energy: Smooth and core terms

$$E_{NIKE} = E_{NIKE}^{(S)} + E_{NIKE}^{(core1)} + E_{NIKE}^{(core2)}$$

$$E_{NIKE}^{(S)} = -\frac{\hbar^2}{2m_e}\int_{D(\boldsymbol{h})} d\boldsymbol{r} \sum_I \left\langle \psi_I^{(S)} \middle| \nabla^2 \middle| \psi_I^{(S)} \right\rangle, \quad E_{NIKE}^{(core1)} = -\frac{\hbar^2}{2m_e}\sum_{IJ} Z_{IJ}^{(S)} Z_{IJ}^{(\nabla^2 S,\Delta)}, \quad E_{NIKE}^{(core2)} = -\frac{\hbar^2}{2m_e}\sum_J Z_J^{(S,2)} \langle \Delta p|\nabla^2|\Delta p\rangle$$

Exchange Correlation energy: Smooth and core terms

$$E_{xc} = E_{xc}^{(S)} + E_{xc}^{(core)} = \int_{D(\boldsymbol{h})} d\boldsymbol{r}\, \varepsilon_{xc}\left(n^{(S)}(\boldsymbol{r})\right) + \sum_J \int_{D(R_{pc})}^{\text{core}} d\boldsymbol{r} \left[\varepsilon_{xc}\left(n_J(\boldsymbol{r})\right) - \varepsilon_{xc}\left(n_J^{(S)}(\boldsymbol{r})\right)\right]$$

$$n^{(S)}(\boldsymbol{r}) = \sum_I |\psi_I^{(S)}(\boldsymbol{r})|^2, \quad \forall\, \boldsymbol{r} \text{ in } D(\boldsymbol{h}) \qquad n_J(\boldsymbol{r}) = n^{(S)}(\boldsymbol{r}-\boldsymbol{R}_J) + n^{(core1)}(\boldsymbol{r}-\boldsymbol{R}_J) + n^{(core2)}(\boldsymbol{r}-\boldsymbol{R}_J), \quad \forall\, |\boldsymbol{r}-\boldsymbol{R}_J| < R_{pc}$$

$$n_J^{(S)}(\boldsymbol{r}) = n^{(S)}(\boldsymbol{r}-\boldsymbol{R}_J), \quad \forall\, |\boldsymbol{r}-\boldsymbol{R}_J| < R_{pc}$$

PAW Basics: KS-DFT long/short-range decomposition

Due to the mixed localized and delocalized basis, there is no natural truncation scale for the long-range interactions of E_H and E_{ext} in ***g***-space or ***r***-space alone.

$$E_H = \frac{e^2}{2}\int_{D(\boldsymbol{h})} d\boldsymbol{r}\int_{D(\boldsymbol{h})} d\boldsymbol{r}'\sum_{\boldsymbol{m}}\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'+\boldsymbol{mh}|} \quad , \quad E_{ext} = -\int_{D(\boldsymbol{h})} d\boldsymbol{r}\, n(\boldsymbol{r})\sum_{J}\sum_{\boldsymbol{m}}\frac{eQ_J}{|\boldsymbol{r}-\boldsymbol{R}_J+\boldsymbol{mh}|}$$

Using Poisson summation and Ewald's decomposition of 1/r:

$$E_H = E_H^{(\text{short})} + E_H^{(\text{long})} \qquad E_{ext} = E_H^{(\text{short})} + E_H^{(\text{long})}$$

$$E_H^{(\text{short})} = \frac{e^2}{2}\int_{D(\boldsymbol{h})} d\boldsymbol{r}\int_{D(\boldsymbol{h})} d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')\,\text{erfc}(\alpha|\boldsymbol{r}-\boldsymbol{r}'|)}{|\boldsymbol{r}-\boldsymbol{r}'|} \qquad E_{ext}^{(\text{short})} = -e\int_{D(\boldsymbol{h})} d\boldsymbol{r}\, n(\boldsymbol{r})\sum_{J}\frac{\text{erfc}(\alpha|\boldsymbol{r}-\boldsymbol{R}_J|)}{|\boldsymbol{r}-\boldsymbol{R}_J|}$$

$$E_H^{(\text{long})} = \frac{e^2}{2V}\sum_{g\neq 0}^{|\boldsymbol{g}|^2<G_c}\frac{4\pi}{|\boldsymbol{g}|^2}\exp\left(-\frac{|\boldsymbol{g}|^2}{4\alpha^2}\right)|\bar{n}(\boldsymbol{g})|^2 - \frac{\pi e^2\,|\bar{n}(0)|^2}{2V\alpha^2}$$

$$E_{ext}^{(\text{long})} = -\frac{e}{V}\sum_{g\neq 0}^{|\boldsymbol{g}|^2<G_c}\frac{4\pi}{|\boldsymbol{g}|^2}\exp\left(-\frac{|\boldsymbol{g}|^2}{4\alpha^2}\right)\bar{n}(\boldsymbol{g})\bar{S}(\boldsymbol{g}) + \frac{\pi e\bar{n}(0)\bar{S}\,(0)}{V\alpha^2}$$

$$\bar{S}(\boldsymbol{g}) = \sum_J Q_J\exp(-i\boldsymbol{g}\cdot\boldsymbol{R}_J)$$

Choose α, such that the ***g-s***pace cutoff = G_c= pw *density* cutoff.

Ensure ***r***-space cutoff, $R_c = (3.5\ /\ \alpha) > R_{pc}$, confines the ***m***-sum to the 1st image.

Decompose short-range into smooth, core1 and core2 type terms, (not shown).

Accuracy of long/short decomposition

To approximately match long/short range accuracy: $\frac{G_c^2}{4} \approx \frac{\gamma^4}{R_c^2}$, $\gamma = \alpha R_c$

$R_c = 4$ bohr

PW cutoff: $(\hbar^2 G_c^2/2\mathrm{me})$ Ryd	$\gamma=\alpha R_c$	erfc(γ)
5.1	3.0	2.21e-05
9.4	3.5	7.43e-07
16	4.0	1.54e-08

$R_c = 2$ bohr

PW cutoff: $(\hbar^2 G_c^2/2\mathrm{me})$ Ryd	$\gamma=\alpha R_c$	erfc(γ)
20.3	3.0	2.21e-05
37.5	3.5	7.43e-07
64	4.0	1.54e-08

High accuracy can be obtained with both R_c and G_c small !

PAW Basics: Multi-Resolution, Grids, EES and N^2 log N scaling

How do we reduce scaling by one order in N and maintain accuracy?

1. Discrete real-space: Fourier Coefficients and FFTs

- Given a discrete, $\boldsymbol{g} = 2\pi \boldsymbol{h}^{-1}\hat{\boldsymbol{g}}$, finite g-space, $|g| < G_c$, the Fourier coefficients, $\bar{f}(\boldsymbol{g})$ of $f(\boldsymbol{r})$, can be converted to $\overline{f^m}(\boldsymbol{g})$ from $f^m(\boldsymbol{r})$ *exactly* using an equally spaced ***s***-space grid, ***r=hs***, of side $N_{FFT,\beta} > 2m\hat{g}_{\max,\beta}\,\Delta s_\beta = 1/N_{FFT,\beta}$. $\forall\, m \in Z > 0$

- Using FFTs, the $\overline{f^m}(\boldsymbol{g})$, can be computed *exactly* in $N \log N$ as:

$$f(\boldsymbol{s}) = \frac{1}{V} FFT^{(m,+)}\left[\bar{f}(\boldsymbol{g}), G_c\right], \quad \overline{f^m}(\boldsymbol{g}) = \frac{V}{N_{\mathrm{FFT}}} FFT^{(m,-)}\left[f^m(\boldsymbol{s}), mG_c\right], \; V = \det \boldsymbol{h}$$

2. Euler Exponential Spline Interpolation and FFTs

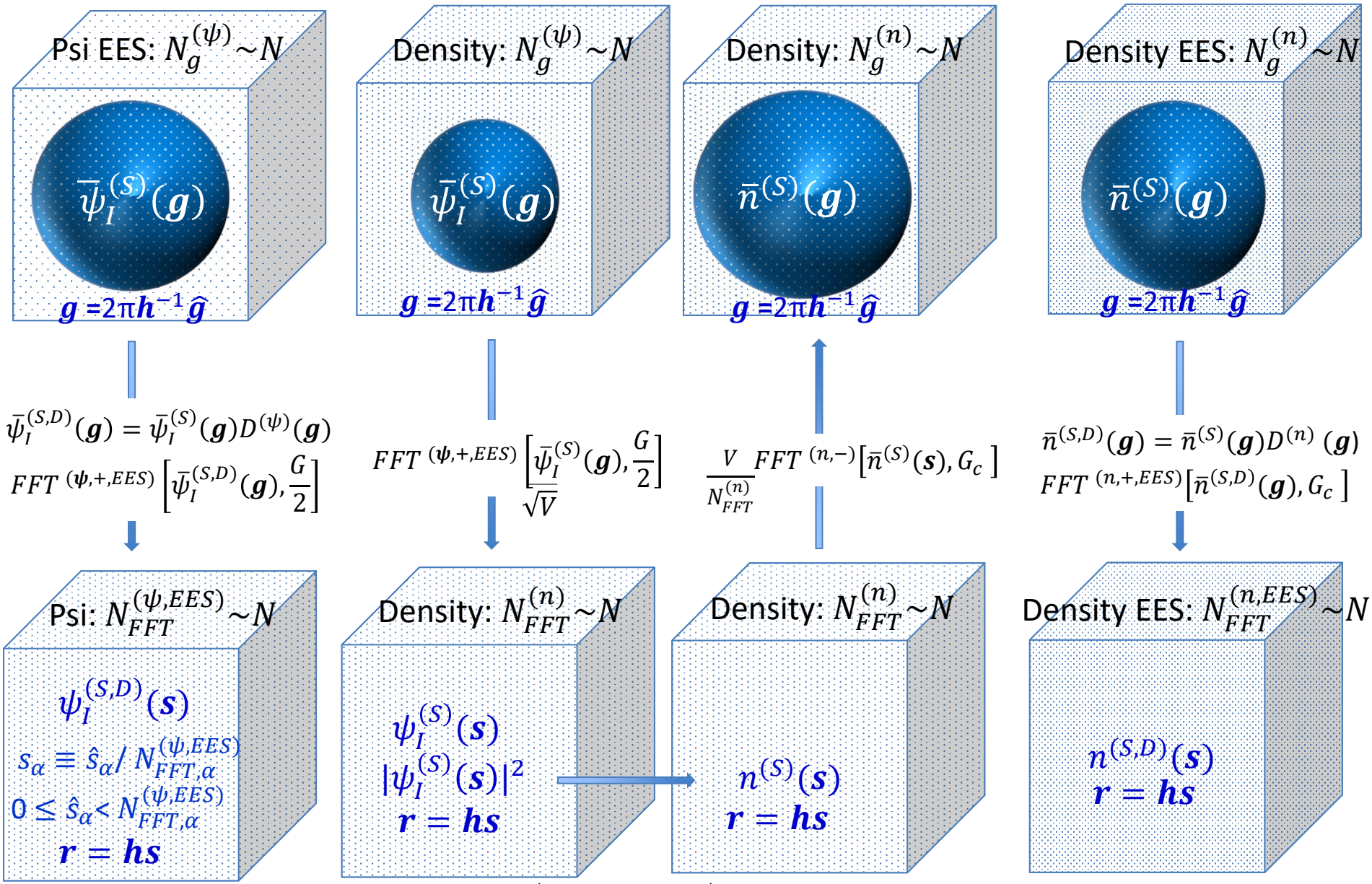
- To compute the *Z*-matrices, structure factors, $\bar{S}(\boldsymbol{g})$, and core functions, fast, it is useful develop a differentiable controlled approximation to $\exp(i\boldsymbol{g}\cdot\boldsymbol{r})$ on a discrete ***g***-space for all ***r=hs*** in D(***h***) via interpolation *from an equally spaced **s**-space grid*, enabling the use of *FFTs*.

- The Euler exponential spline (EES) delivers where M_p are the cardinal B-splines and p the spline order,

$$e^{2\pi i \hat{g} s} = D_p(\hat{g}, N_{\mathrm{FFT}}) \sum_{\hat{s}=0}^{N_{\mathrm{FFT}}} \sum_{j=1}^{p} M_p(u-\hat{s}) e^{\frac{2\pi i \hat{g}\hat{s}}{N_{FFT}}} \delta_{\hat{s},l-j} + \mathcal{O}\left(\frac{2\hat{g}}{N_{\mathrm{FFT}}}\right)^p, \qquad \begin{array}{l} M_p \text{ has compact supp.} \\ u = s N_{\mathrm{FFT}} \quad l = \operatorname{int} u \\ N_{\mathrm{FFT}} > 2\hat{g}_{\max} \approx 2.8\hat{g}_{\max} \end{array}$$

Using ***3 FFT grids***, (1) Psi EES, (2) Density, (3) Density EES, and ***1 discrete spherical polar grid*** around each ion, $|\boldsymbol{r}| < R_{pc}$, all PAW energy terms & their derivatives can be accurately computed in $N^2 \log N$.

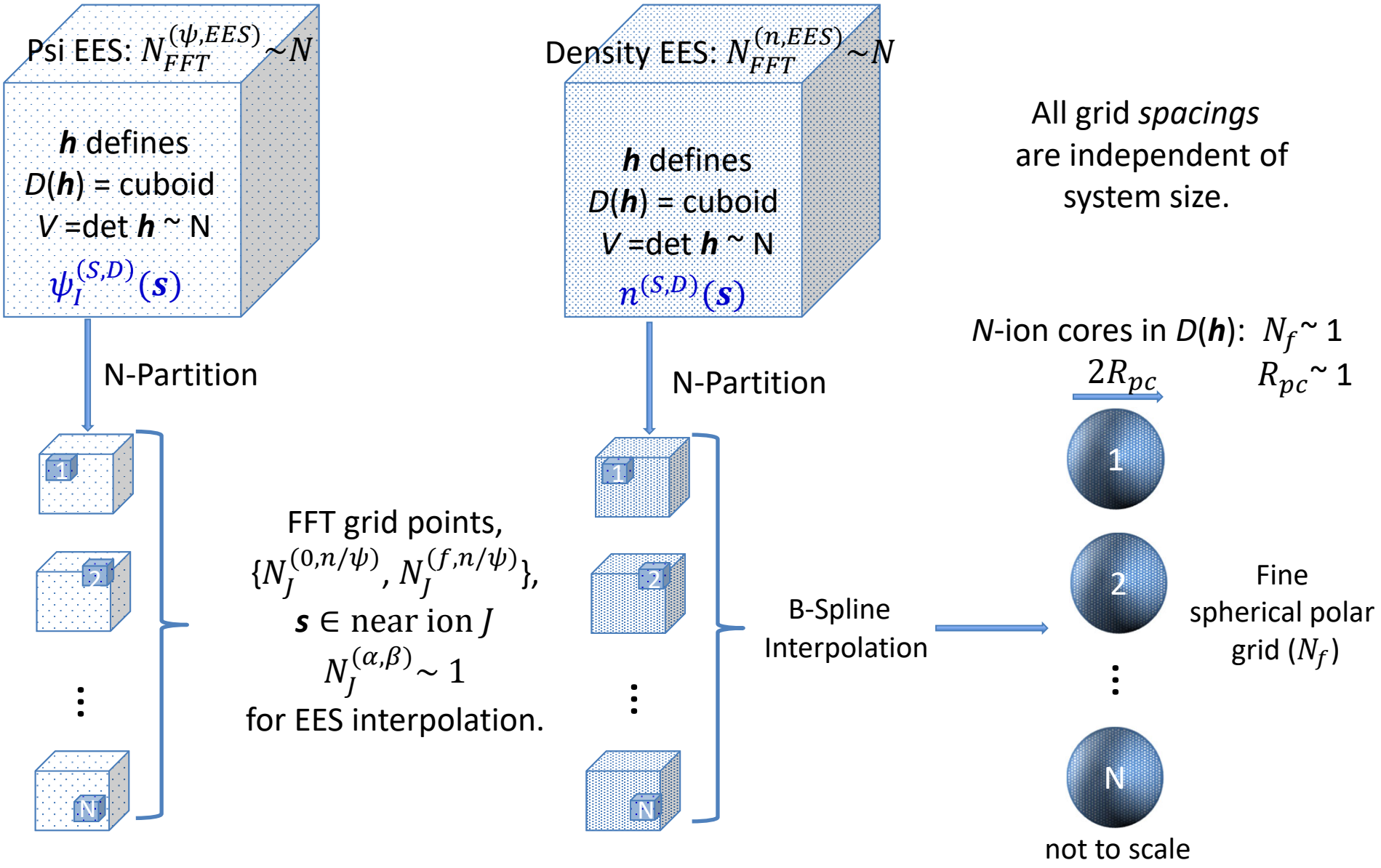
PAW Basics: $\boldsymbol{g}$-space to $\boldsymbol{s}$-space and back



The $D^{(\tau)}(\boldsymbol{g}) = \prod_\alpha D_p\left(\hat{g}_\alpha, N_{FFT,\alpha}^{(\tau,EES)}\right)$ enables B-spline interpolation

PAW Basics: *r*-space interpolation

EES provides an accurate, differentiable interpolation between the different resolutions and length scales of PAW



Creating the *r*-space representation of the e-density

In the following, the multi-length scale PAW method is used to construct the electron density in $N^2 \log N$ as a demonstration:

$$n_J^{(\mathrm{core})}(\boldsymbol{r}_f) = n_J^{(\mathrm{core\ 1})}(\boldsymbol{r}_f) + n_J^{(\mathrm{core\ 2})}(\boldsymbol{r}_f) + n_J^{(S)}(\boldsymbol{r}_f)\ \ J = 1..N$$

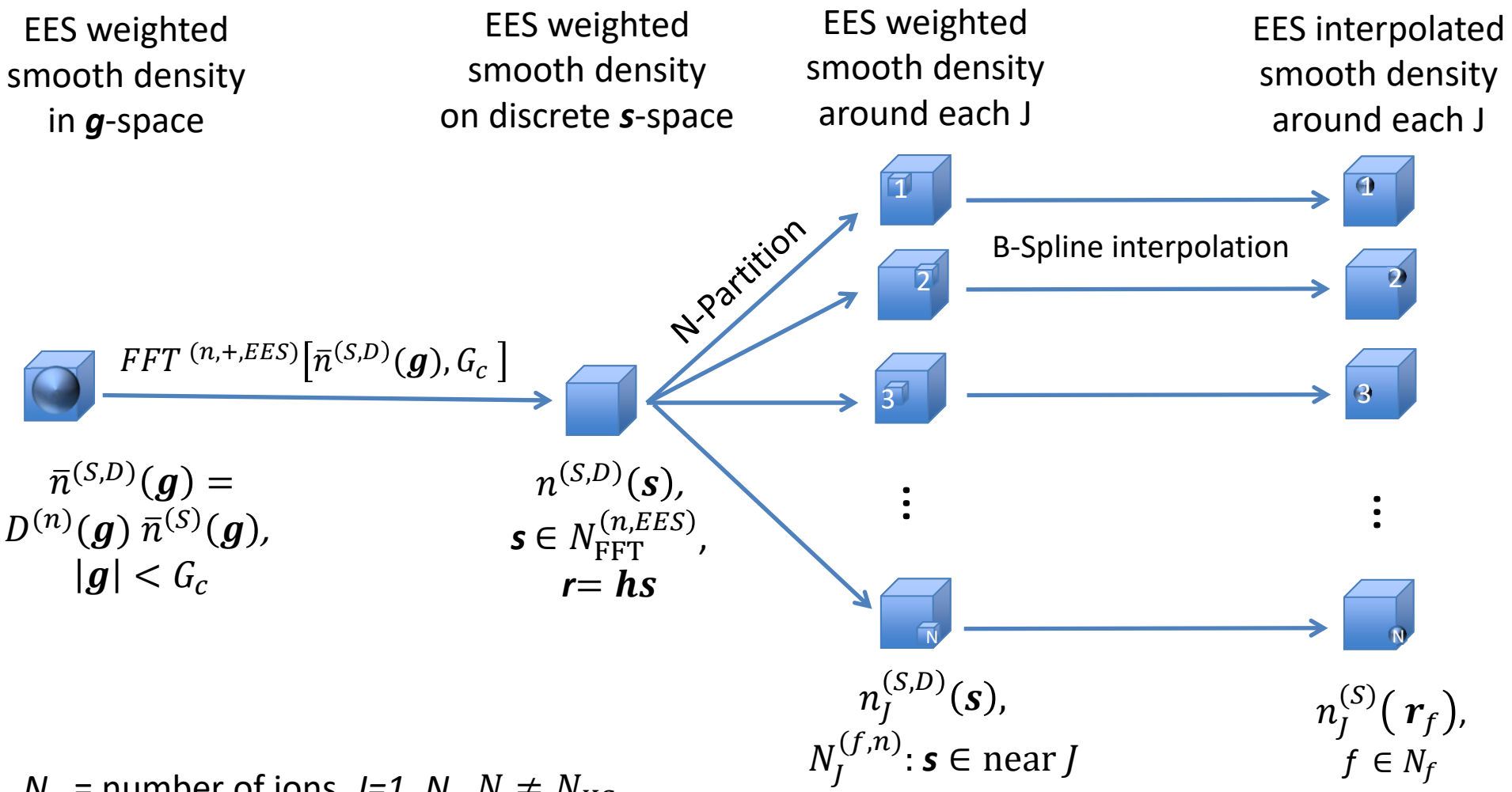
$n^{(S)}(\boldsymbol{r})$: outside of cores

(1) Create the smooth KS states in real space, $\psi_I^{(S)}(\boldsymbol{s})$: $N^2 \log N$.
(2) Create the smooth density in real space, $n^{(S)}(\boldsymbol{s})$: N^2.
(3) *Create the smooth density in the ion cores, $n_J^{(S)}(\boldsymbol{r}_f)$: $N \log N$.
(4) Create the smooth Z-matrix, $Z_{IJ}^{(S)}$: $N^2 \log N$.
(5) *Create the core-2 densities, $n_J^{(\mathrm{core2})}(\boldsymbol{r}_f)$: N^2.
(6) *Create the core-1 densities, $n_J^{(\mathrm{core1})}(\boldsymbol{r}_f)$: $N^2 \log N$.

* New terms.

Formulae for all other components of PAW-DFT have been derived including ionic and pw expansion coefficient derivatives.

3. Creating the smooth density, $n_J^{(S)}(\boldsymbol{r}_f)$ around each ion *J*, on the fine grid, $f \in N_f$



N = number of ions, *J*=1..*N*, $N \neq N_{KS}$

N_f = number points on spherical-polar grid around each ion.

N_f and $N_J^{(f,n)}(\boldsymbol{s} \in \text{near } J)$ independent system size .

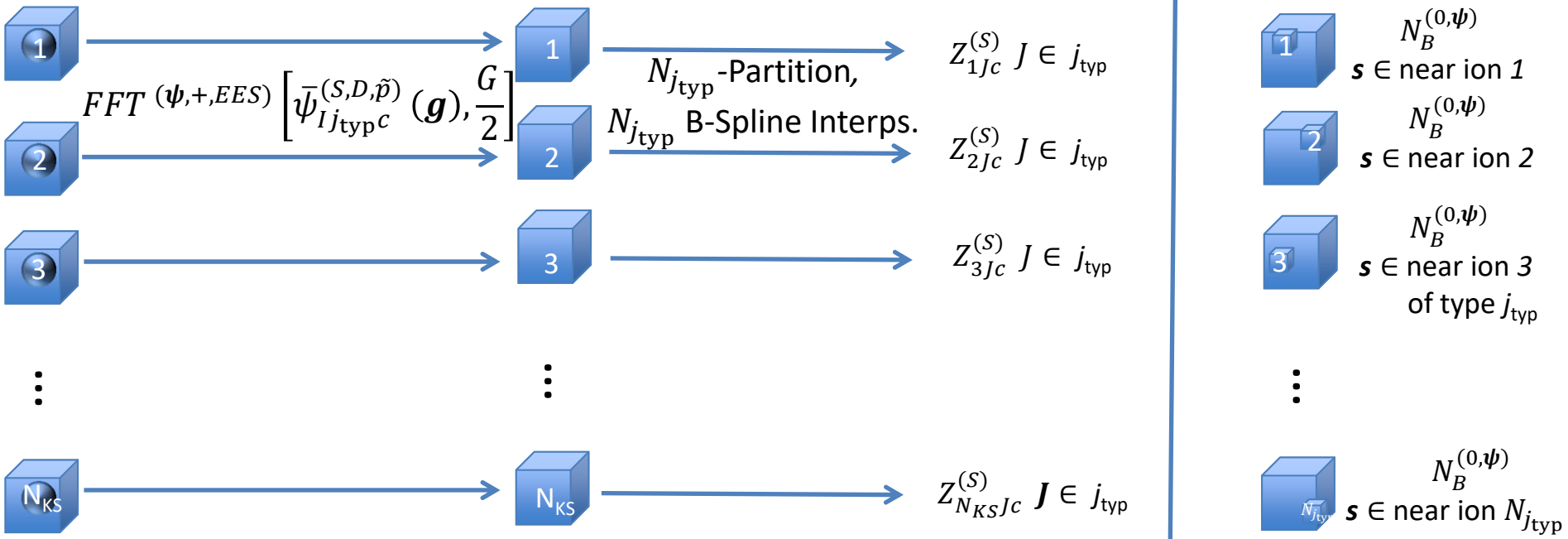
Creating the $Z_{IJc}^{(S)}$ matrix for all ions of type j_{typ} and channel c

$D^{(\psi)}(\boldsymbol{g})\,\tilde{p}^{(S)}_{j_{\text{typ}}c}(\boldsymbol{g})$
weighted KS states
in $\boldsymbol{g}$-space

EES x smooth projector
weighted KS states
in $\boldsymbol{s}$-space

Smooth Z-matrix
for ions of type j_{typ}
and channel, c

$N_{j_{\text{typ}}}$–Partition,
$N_{j_{\text{typ}}}$ B-Spline Interps
per KS state



$$\bar{\psi}^{(S,D,\tilde{p})}_{I j_{\text{typ}}c}(\boldsymbol{g}) = D^{(\psi)}(\boldsymbol{g})\,\bar{\psi}^{(S)}_{I}(\boldsymbol{g})\tilde{p}^{(\boldsymbol{S})}_{j_{\text{typ}}c} \quad |\boldsymbol{g}| < G_c/2$$

$$\psi^{(S,D,\tilde{p})}_{I j_{\text{typ}}c}(\boldsymbol{s}), \quad \boldsymbol{s} \in N^{(\boldsymbol{\psi},EES)}_{FFT}$$

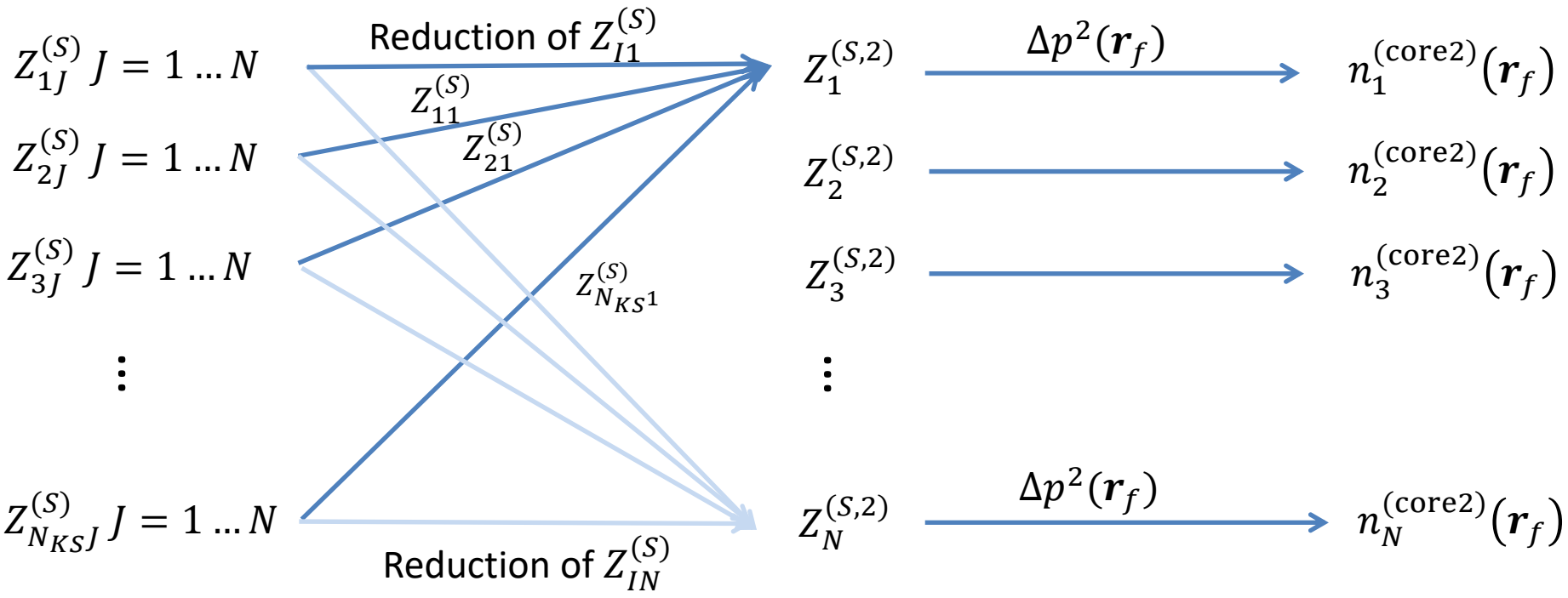
A set of points, $\boldsymbol{s}$ ∈ near ion J^*, of type j_{typ} interpolated to obtain $Z^{(S)}_{IJc}$ for all $I,J \in j_{\text{typ}}$ $(N_B^{(0,\boldsymbol{\psi})} \sim 1)$,

$$Z^{(S)}_{IJc} = \sum_{\boldsymbol{s}\,\in\,\text{near } J}^{N_B^{(0,\boldsymbol{\psi})}} \psi^{(S,D,\tilde{p})}_{I j_{\text{typ}}c}(\boldsymbol{s}) M^{(3)}_{J,p}(\boldsymbol{s})$$

$\boldsymbol{s}$ independent of I,c as are B splines, $M^{(3)}_{J,p}(\boldsymbol{s})$

*Note, index J need not be contiguous in list of all atoms

5. Creating the core density component, $n_J^{(\mathrm{core2})}(\boldsymbol{r}_f)$, around each ion *J*, on the fine grid, $f \in N_f$



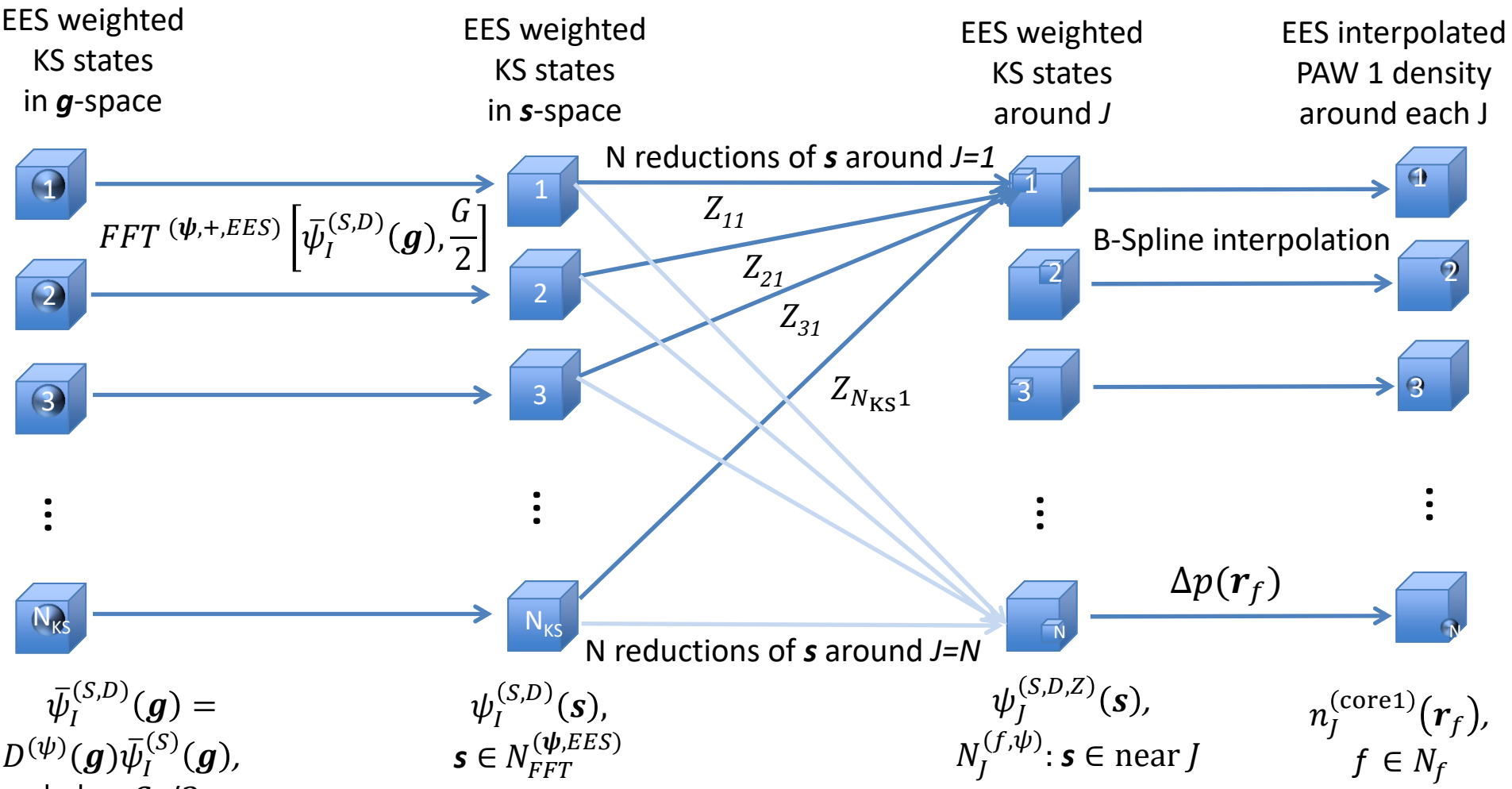
Each KS state contributes to N unique reductions

$$Z_J^{(S,2)} = \sum_I |Z_{IJ}^{(S)}|^2$$

In this example we have 1 projector

$$n_J^{(\mathrm{core2})}(\boldsymbol{r}_f) = Z_J^{(S,2)} \Delta p^2(\boldsymbol{r}_f) \ \forall\ f \in N_f$$

6. Creating the core density component, $n_J^{(\mathrm{core1})}(\boldsymbol{r}_f)$, around each ion *J*, on the fine grid, $f \in N_f$



Each KS state contributes to N unique reductions

$\psi_J^{(S,D,Z)}(\boldsymbol{s}) = \sum_I Z_{IJ}\psi_I^{(S,D)}(\boldsymbol{s}) \;\forall\; \boldsymbol{s} \in \text{near } J: N_B^{(f,\psi)}$

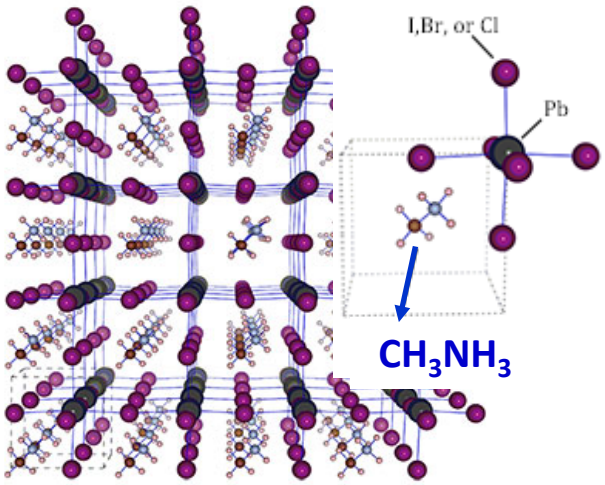
Z_{IJ} = weight for points $\boldsymbol{s} \in$ near J from KS state, *I*.

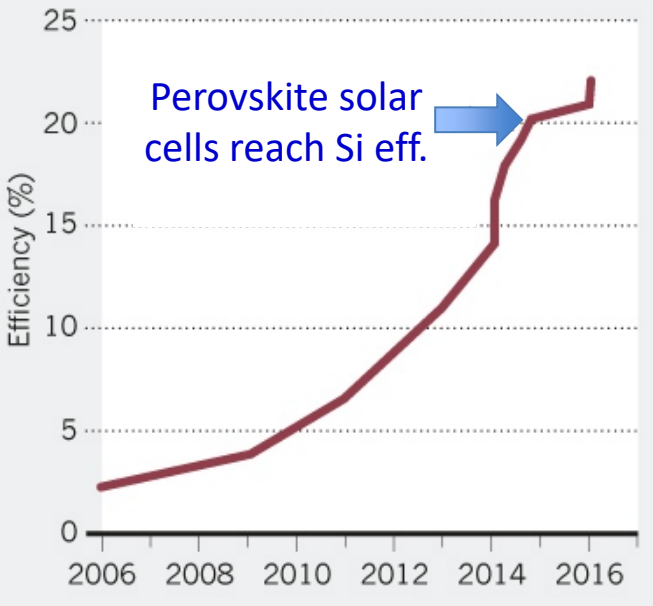
PAW Charm++ Implementation Progress:

- Chare arrays defined and communication patterns established in PowerPoint form.
- Full PAW-KS-DFT flow chart for energies. Forces in progress.
- Model Charm++ software outside of OpenAtom to test fine grid spacing, Coulomb cusp smoothing, convergence with real-space cutoff, ... Complete.
- N-partition and N-consolidation operations added to charmFFT. Periodic boundary conditions need to be added.
- Ready to begin integration into OpenAtom. Maybe with new funding.

Grand Challenge Application: Perovskite solar cells

$CH_3NH_3PbX_3$

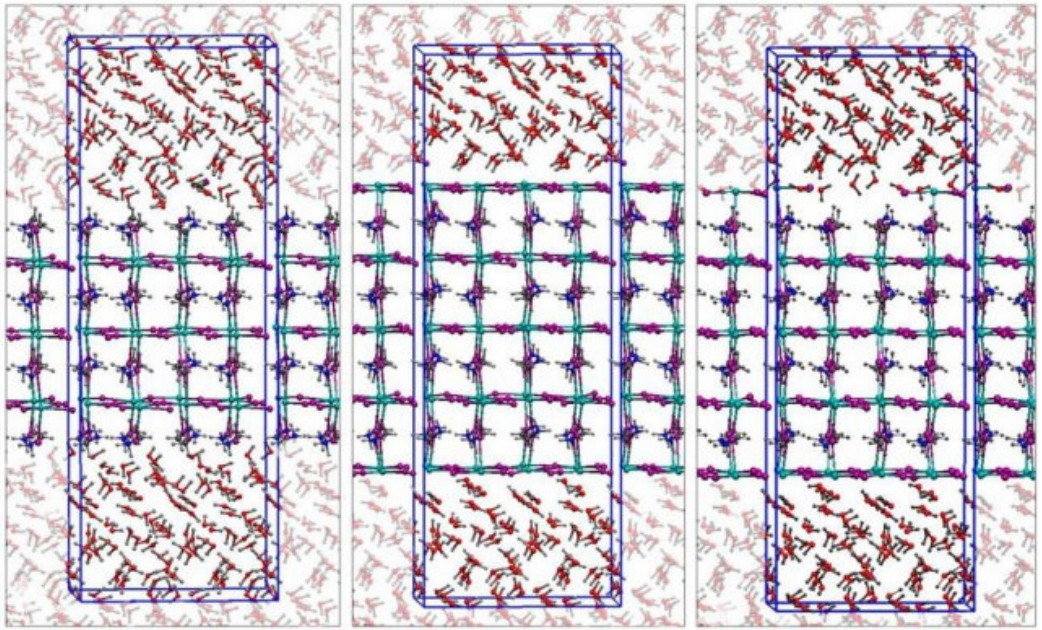




- **Pros:**
  High eff., low cost, tunable band gap (ABX_3)
- **Cons:**
  Instability: water, air, light, interface … & toxic compounds.

PAW in OpenAtom

MAI-term. **PbI_2-term.** **PbI_2-defect.**



- **Understand:** mechanism of instability/degradation.
- **Search:** non-toxic B^{2+} (Fe, Co, Ni,…) for new high perf. materials.
- **Design:** new interface/encapsulation for novel devices with long lifetime.
- **System size:** 512 atoms (4x4x2 $MAPbI_3$ +128 water), 1264 states

Conclusions

- PAW-KS-DFT is an important method in computational science that allows computations beyond PW-KS-DFT – heavy atoms.

- Using EES Interpolation, we have derived a multi-length scale PAW technique that scales as $N^2 \log N$ (all energy terms and all derivatives) – an important advance and 100 pages of latex.

- Charm++ parallel framework developed; communication scaling analysis complete. Currently implementing. New funding?