Metallic DFT

On Nanoparticles with Thousands of Atoms

UNIVERSITY OF Southampton
School of Chemistry

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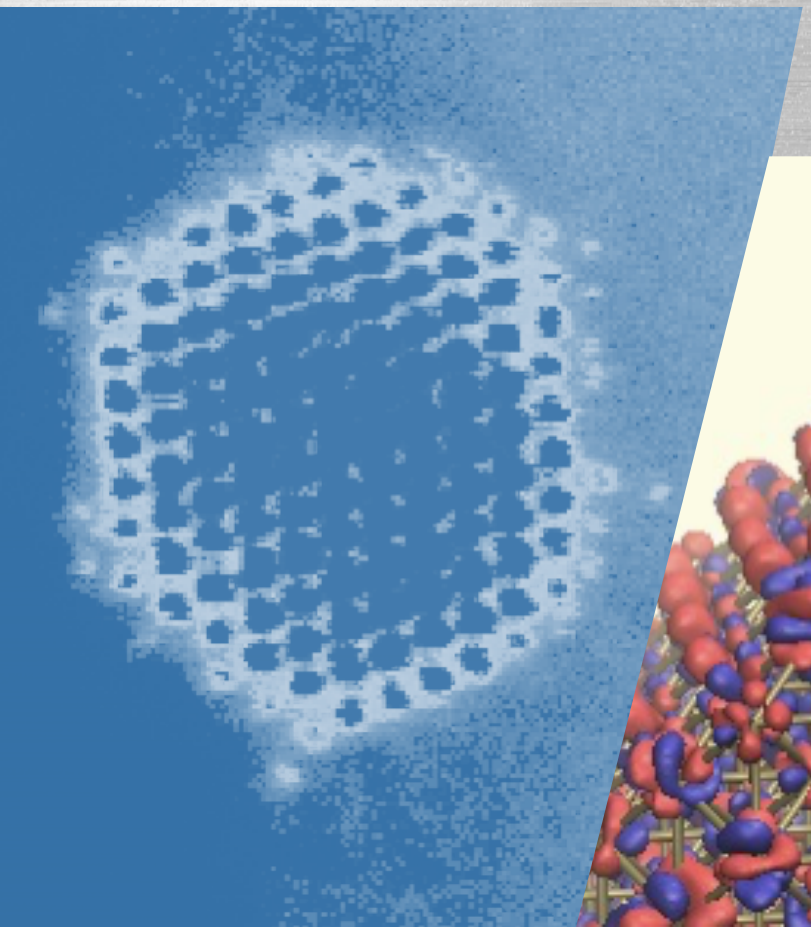
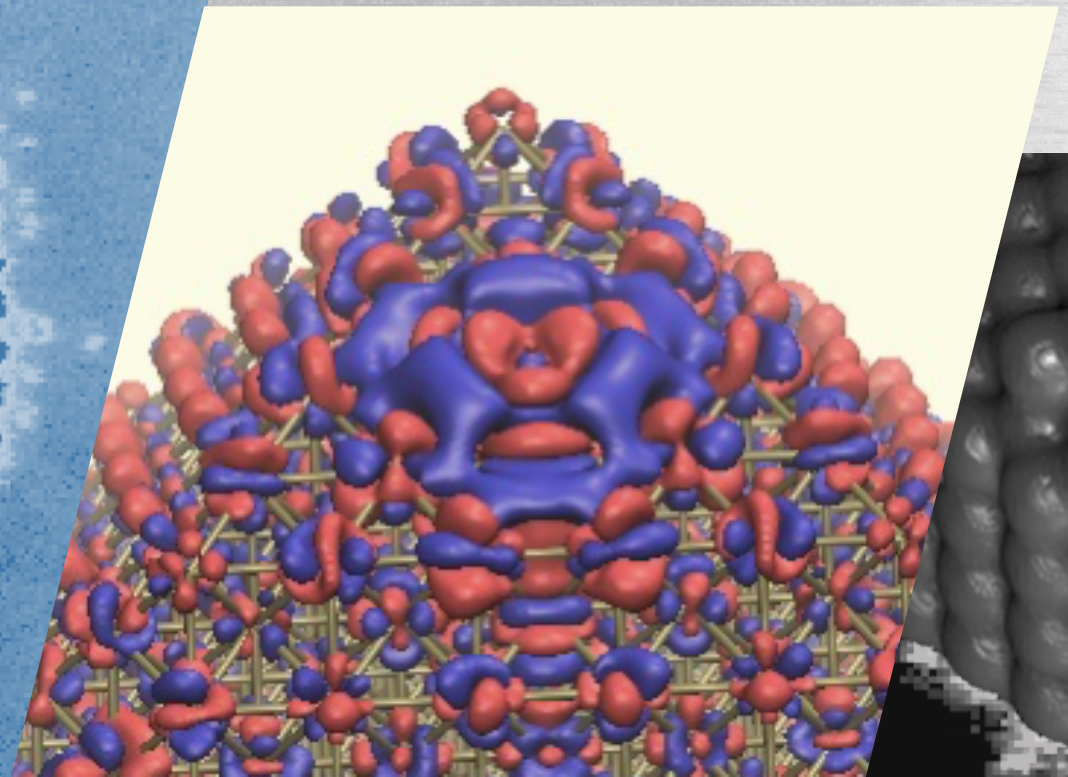
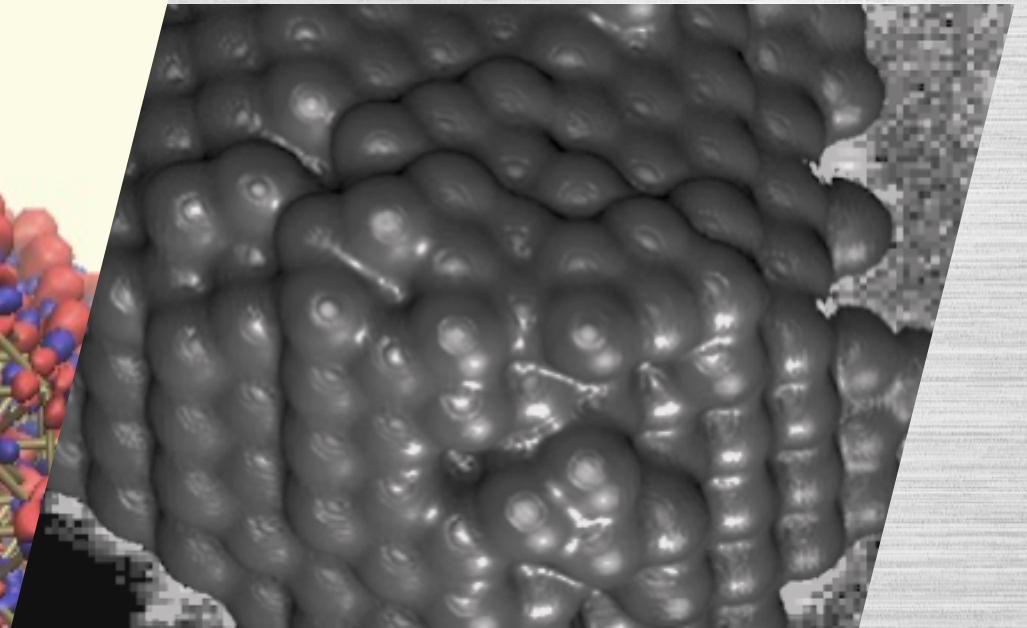
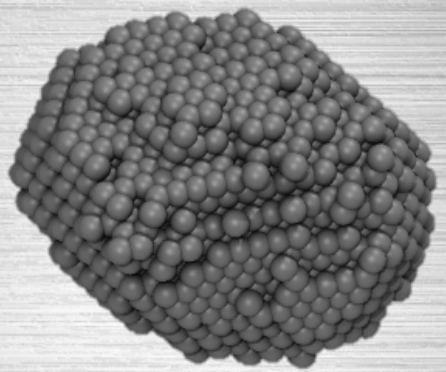






Motivation



- To simulate metal systems with thousands of atoms
  - Rough metal nanoparticles can have thousands of distinct binding sites
- Cubic scaling DFT is too expensive on systems with $\gtrapprox 1000$ atoms
- ONETEP is linear scaling for insulators, cubic scaling for metals
- Can we make it scale linearly for metals?

Nanoparticles in Catalysis

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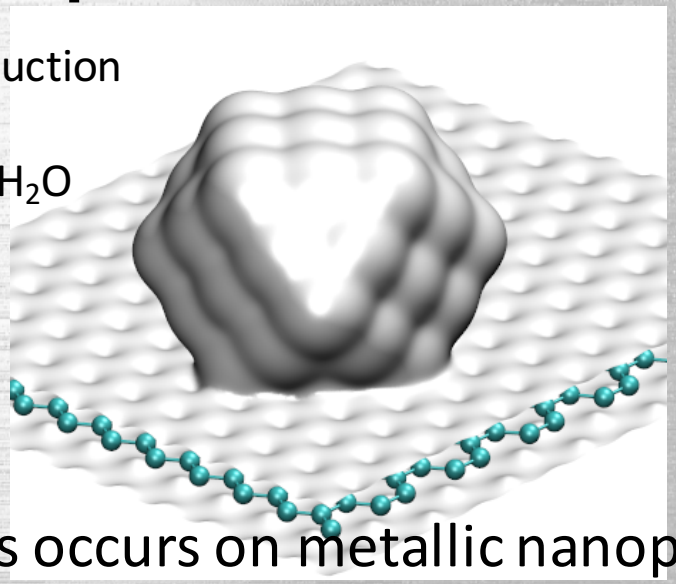
Oxygen Reduction Reaction:

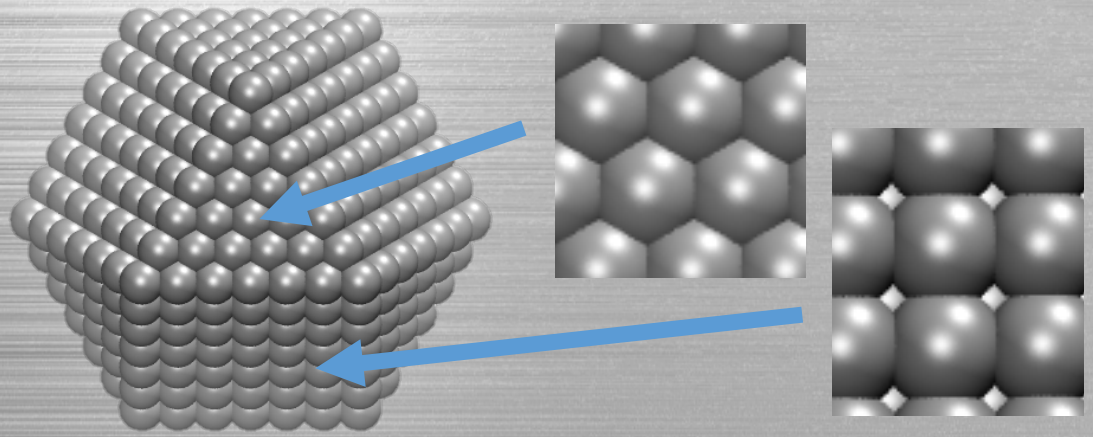
$O_2 + 2H_2 \rightarrow 2H_2O$



Real nanoparticles are not strongly faceted

OxfordMaterials

Catalysis occurs on metallic nanoparticles that are supported e.g. on an oxide

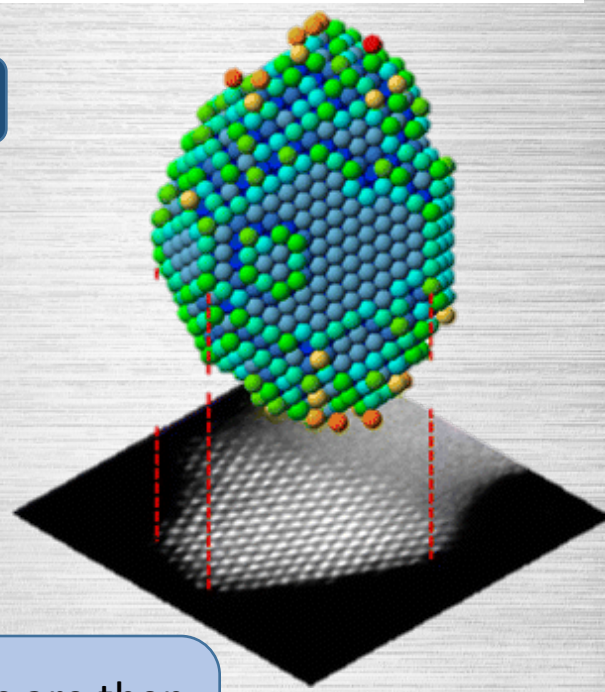


ADF STEM: 2.5D atomic coordinates

Z coordinates approximated by optimising force field model in 1D

Investigate NP using Molecular Dynamics simulations and annealing approach

These datasets are then passed to us for analysis in ONETEP

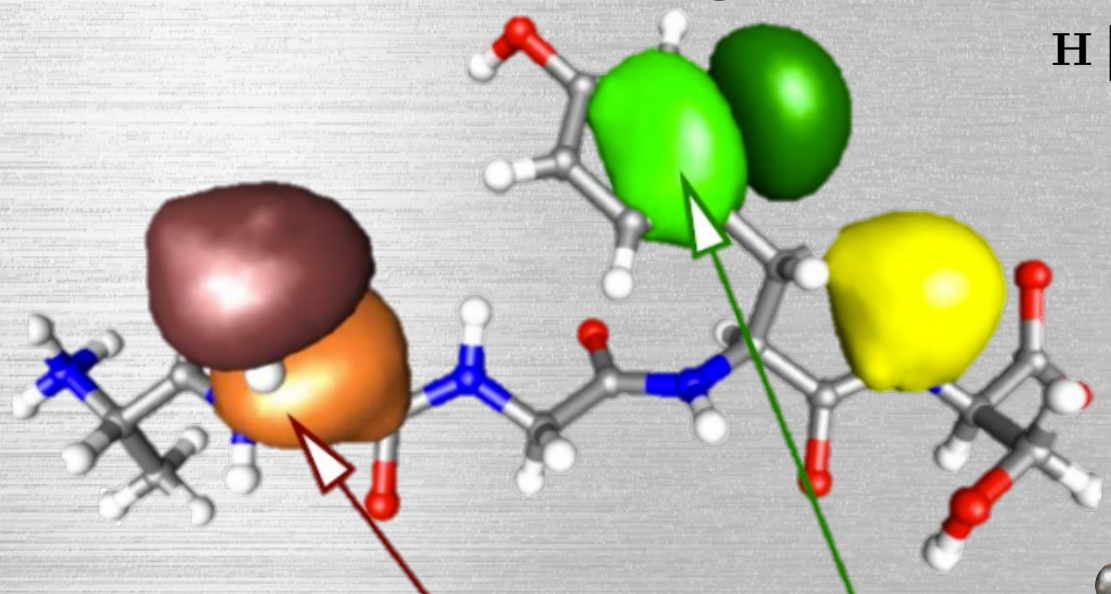


Conventionally, different facets are modelled individually using a slab model

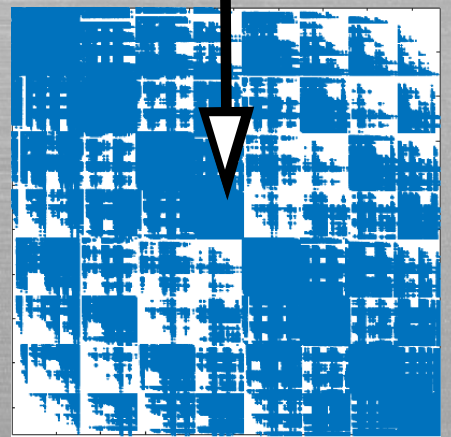
Predicting the Oxygen-Binding Properties of Platinum Nanoparticle Ensembles by Combining High-Precision Electron Microscopy and Density Functional Theory

J.Aarons *et al Nano Letters* **2017** *17* (7), 4003-4012

ONETEP in general



$$\rho(\mathbf{r},\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi^*_\beta(\mathbf{r}')$$



- Based on density matrix DFT

$$\mathbf{H}\left[\{\phi_\alpha(\mathbf{r})\}, K^{\alpha\beta}\right] = \mathbf{H}_{\mathrm{K}}\left[\{\phi_\alpha(\mathbf{r})\}\right] + \mathbf{H}_{\mathrm{NL}}\left[\{\phi_\alpha(\mathbf{r})\}\right] + \mathbf{H}_{\mathrm{L}}\left[\{\phi_\alpha(\mathbf{r})\}, K^{\alpha\beta}\right] + \mathbf{H}_{\mathrm{H}}\left[\{\phi_\alpha(\mathbf{r})\}, K^{\alpha\beta}\right] + \mathbf{H}_{\mathrm{XC}}\left[\{\phi_\alpha(\mathbf{r})\}, K^{\alpha\beta}\right]$$

  where every term in the Kohn-Sham equation is written as a functional of the Non-orthogonal Generalised Wannier Functions (NGWFs) and/or the "density kernel"

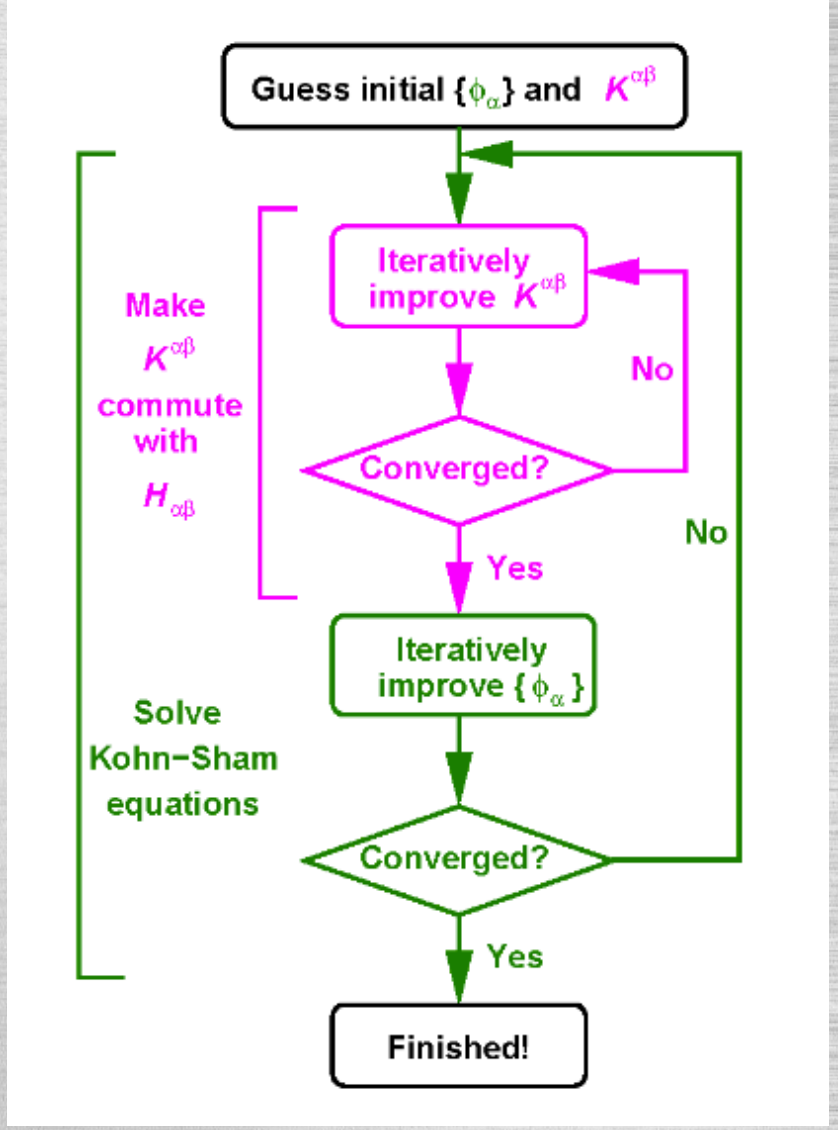
- The NGWFs are atom centric and local - leading to sparse overlap and Hamiltonian matrices

- The density kernel is made sparse through a spatial truncation

- Two loop approach → NGWFs optimised in outer loop, kernel in inner loop

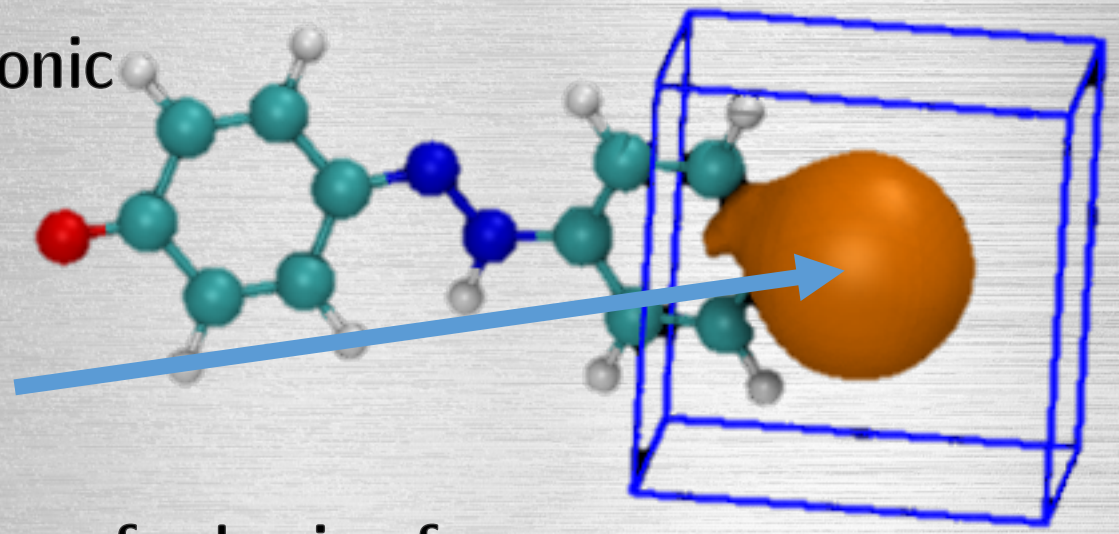
Insulators in ONETEP: Overall picture

- ONETEP's basis is non-orthogonal → Hamiltonian matrix and density matrix tensorial transformation properties become important
- Overlap matrix is the metric tensor → calculated by taking the overlap integrals of NGWFs with each other
- Integrals required to generate Hamiltonian matrix can be performed in linear scaling time

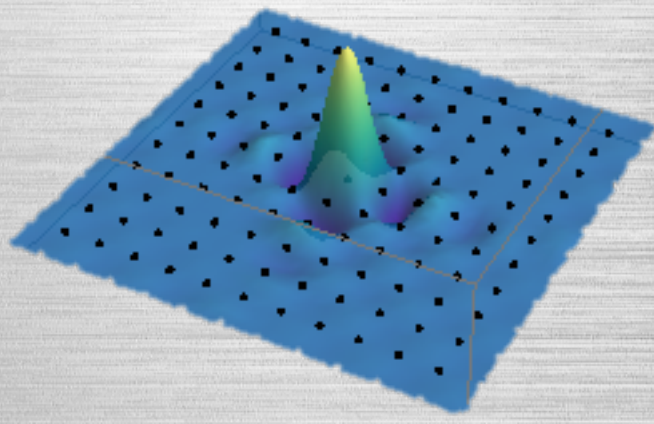


NGWFs

- ONETEP's NGWFs are effectively electronic support functions analogous to electron bands in plane-wave codes



- Local in space and atom centric
- Optimised *in situ* and represented in terms of a basis of cardinal sine (p-sinc) functions
- This basis set is equivalent to a plane-wave basis through a rotation
  - Like a plane-wave basis it is systematically improvable through a single parameter (kinetic energy cut-off)
  - Unlike a plane-wave basis, it is inherently localised



Density Kernel

- The density kernel ($K^{\alpha\beta}$) is a contravariant representation of the density matrix in terms of the NGWFs
- Eigenvalues of molecular orbital occupancy
- Idempotent for insulators → Heaviside step function occupancy distribution
- Can be produced by a "purification" transformation from an initial guess

$$\mathbf{K} \rightarrow 3\mathbf{KSK} - 2\mathbf{KSKSK}$$

- Or variationally through the LNV scheme, where a modified energy functional is minimised, which drives the density kernel towards idempotency

$$E_{\mathrm{LNV}} = \mathrm{tr}\left[(3\mathbf{LSL} - 2\mathbf{LSLSL})\mathbf{H}\right]$$

- The kernel can be made sparse...

Nearsightedness of Electronic Matter

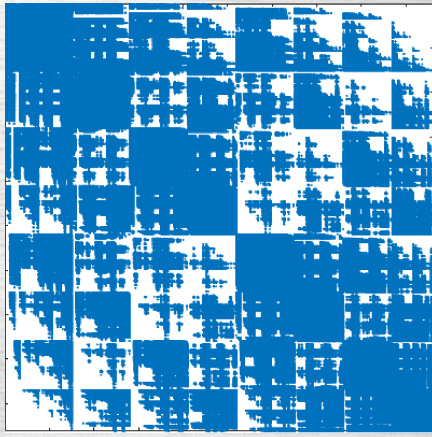
- Kohn-Sham DFT can be performed with linear scaling cost due to the principle of "Nearsightnedness of Electronic Matter" introduced by Kohn
- For insulators, elements of the density matrix decay exponentially with distance

$$\rho(\mathbf{r},\mathbf{r}') \sim e^{-\gamma|\mathbf{r}-\mathbf{r}'|} \to 0 \quad \text{as} \quad |\mathbf{r}-\mathbf{r}'| \to \infty$$

- We only calculate elements separated by $< r_{cut}$

$$\rho(\mathbf{r},\mathbf{r}') = 0 \quad \text{when} \quad |\mathbf{r}-\mathbf{r}'| > r_{\text{cut}}$$

- Goedecker : metals at finite temperature also exhibit exponential d



W. Kohn, *Phys. Rev. Lett.* **76**, 3168 (1996)

EDFT in ONETEP

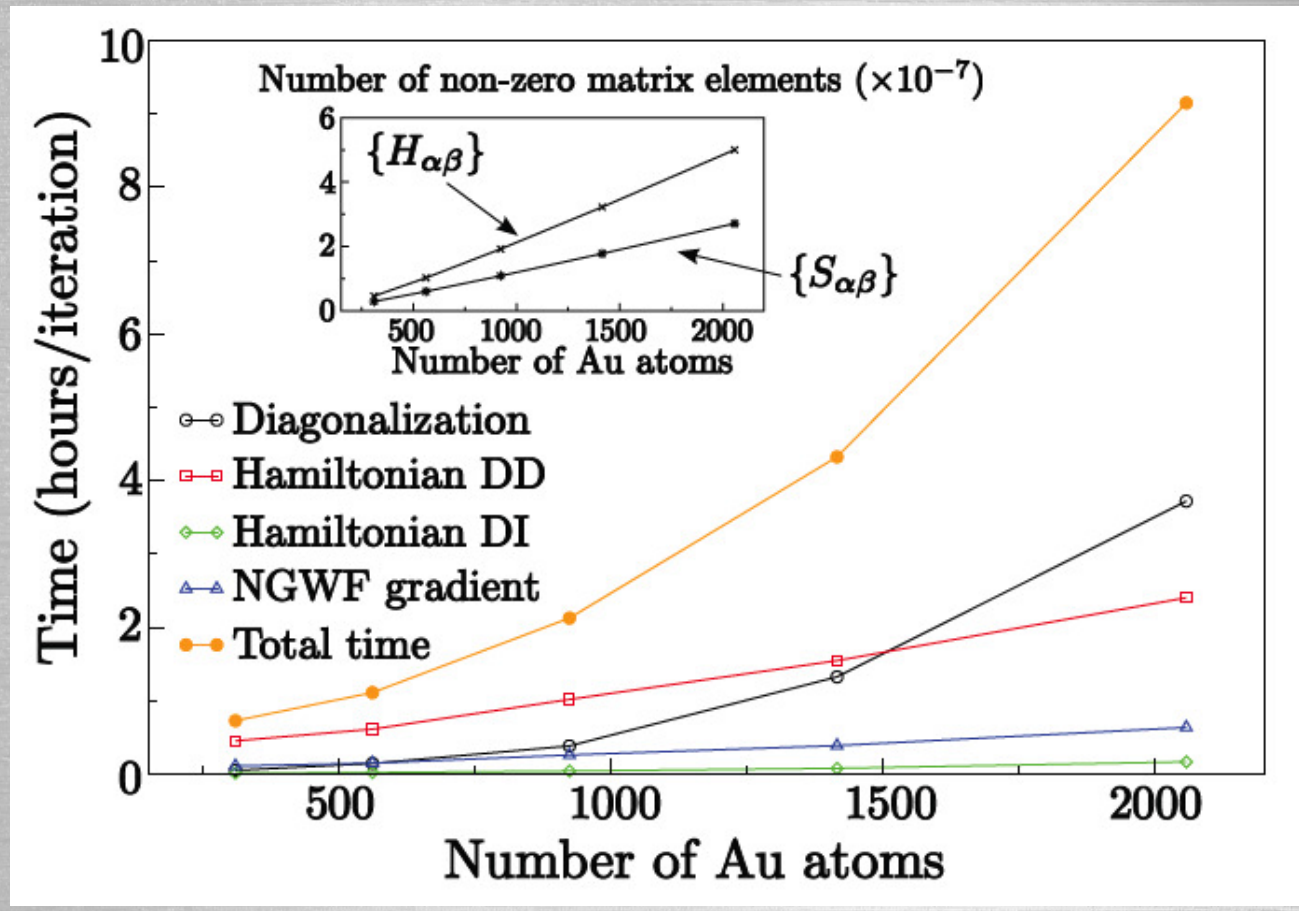
- Variational metals method implemented in ONETEP
- Outer loop the same
- Different inner loop: no longer doing LNV, K not idempotent
- Start from a guess H & diagonalise

$$H_{\alpha\beta}M^{\beta}{}_{i} = S_{\alpha\beta}M^{\beta}{}_{i}\,\varepsilon_i$$

- Eigs → new density kernel $K^{\alpha\beta} = \sum_{i}^{N} M^{\alpha}{}_{i} f(\varepsilon_i) M_i^{\dagger\,\beta}$
- Then build new H and line-search:

$$\Delta^{(n)}_{\alpha\beta} = H^{(n)}_{\alpha\beta} - H^{(n)}_{\alpha\beta}$$

$$H^{(n+1)}_{\alpha\beta} = H^{(n)}_{\alpha\beta} - \lambda\Delta^{(n)}_{\alpha\beta}$$



Some preliminaries...

- We need to have partially occupied conduction states → minimising Helmholtzfree energy $$A[T, \{\varepsilon_i\}, \{\psi_i\}] = \sum_i f_i \langle \psi_i | \hat{T} | \psi_i \rangle + \int \upsilon_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_H[n] + E_{xc}[n] - TS[\{f_i\}]$$
- Entropy and Smearing!
- Let's assume that we're dealing with contra-covariant quantities $\mathbf{K}^{\alpha}{}_{\beta}$ $\mathbf{H}^{\alpha}{}_{\beta}$
- Either multiply from the right by the metric / inverse metric or solve a linear equation – was shown to be representable with same sparsity patterns
- Eliminates the need for orthogonalization

FOE instead of Diagonalisation

- Write $f(\varepsilon, \mu, \beta) = \dfrac{1}{1 + e^{(\varepsilon - \mu)\beta}}$ in terms of matrices, not eigs
- And get:

$$\mathbf{K} = \left(\mathbf{I} + e^{(\mathbf{H} - \mu\mathbf{I})\beta} \right)^{-1}$$

- Extremely ill-conditioned if we were to do this directly with a matrix exponential technique and an inversion.
- Instead, expand the Fermi-Dirac function as a polynomial expansion, typically Chebyshevs:

$$f(\mathbf{X}) = \sum_{i=0}^{N} a_i \mathbf{T}_i(\mathbf{X})$$

$$\mathbf{T}_0(\mathbf{X}) = \mathbf{I}$$

$$\mathbf{T}_1(\mathbf{X}) = \mathbf{X}$$

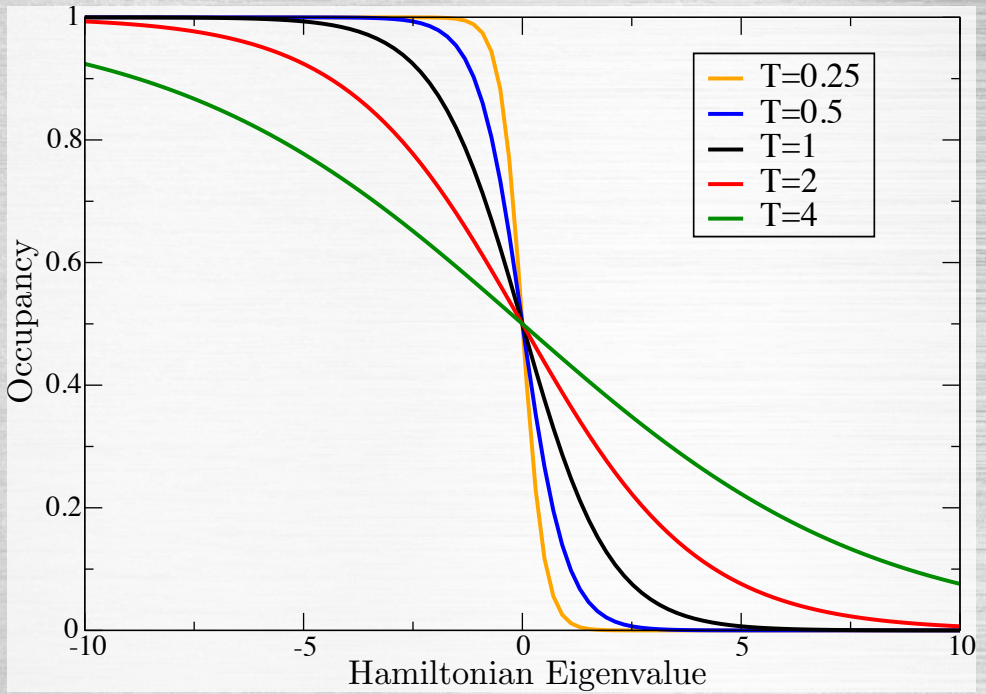
$$\mathbf{T}_{n+1}(\mathbf{X}) = 2\mathbf{X}\mathbf{T}_n(\mathbf{X}) - \mathbf{T}_{n-1}(\mathbf{X})$$

$$\{a_i\} = \mathrm{DCT}\left(\frac{1}{1 + e^{\cos(x)}} \right)$$

It gets easier with temperature...

$$f(\varepsilon) = \frac{1}{1 + e^{(\varepsilon - \mu)\beta}}$$

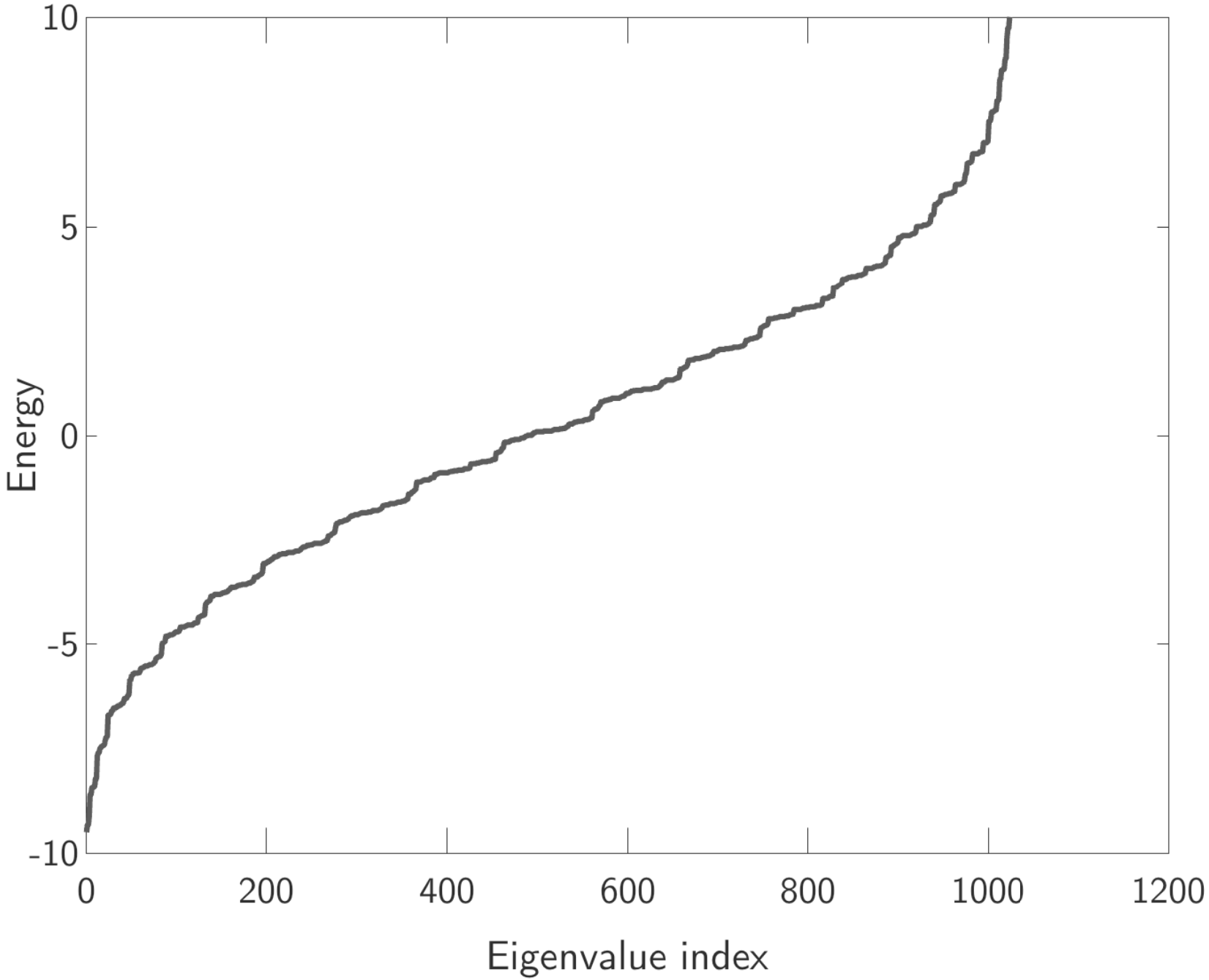
- Increased smearing → fewer terms in expansion → faster FOE
- But we probably don't want extremely hot electrons
- Is there a way to run the FOE at a hot temperature and recover the cold target result?

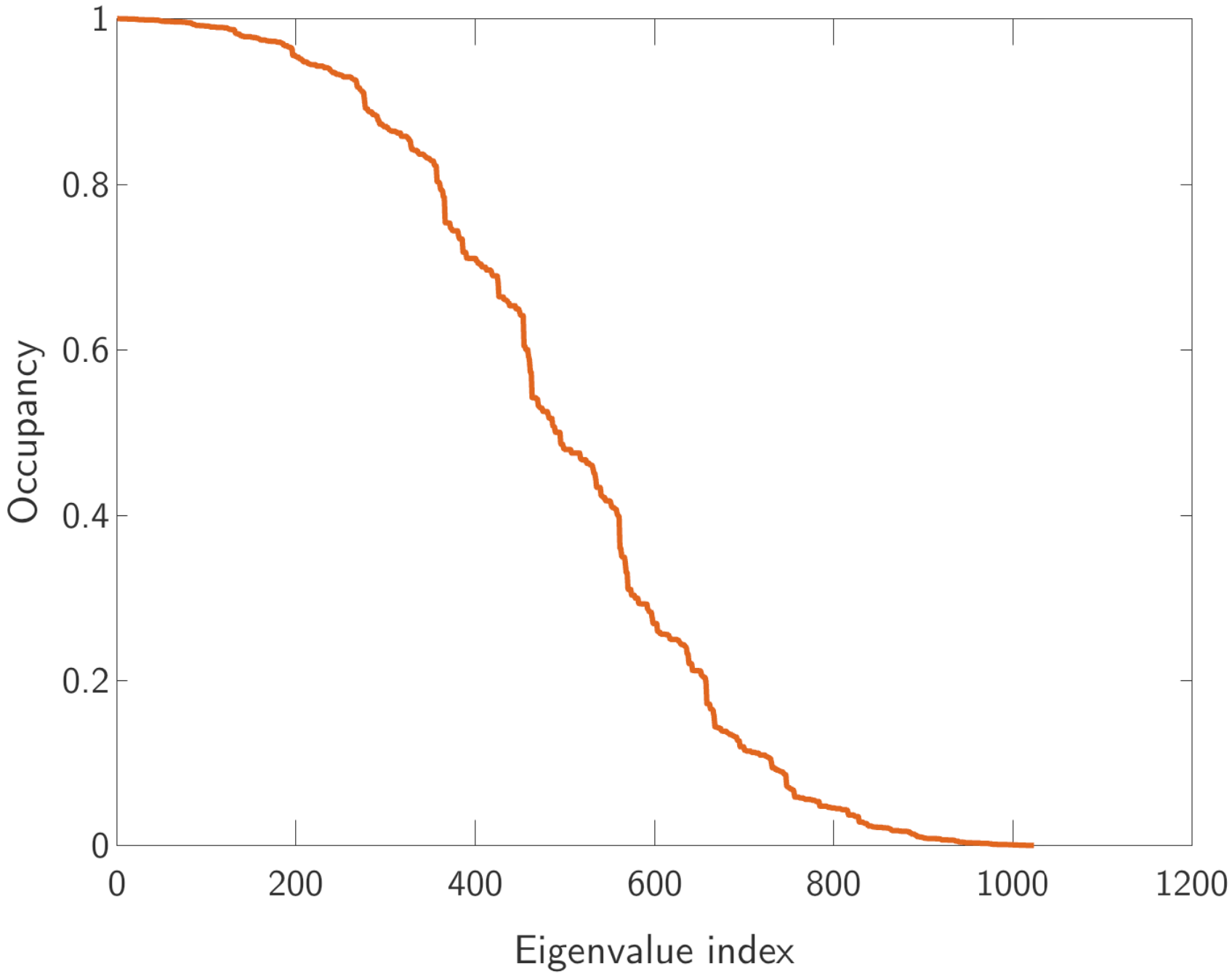


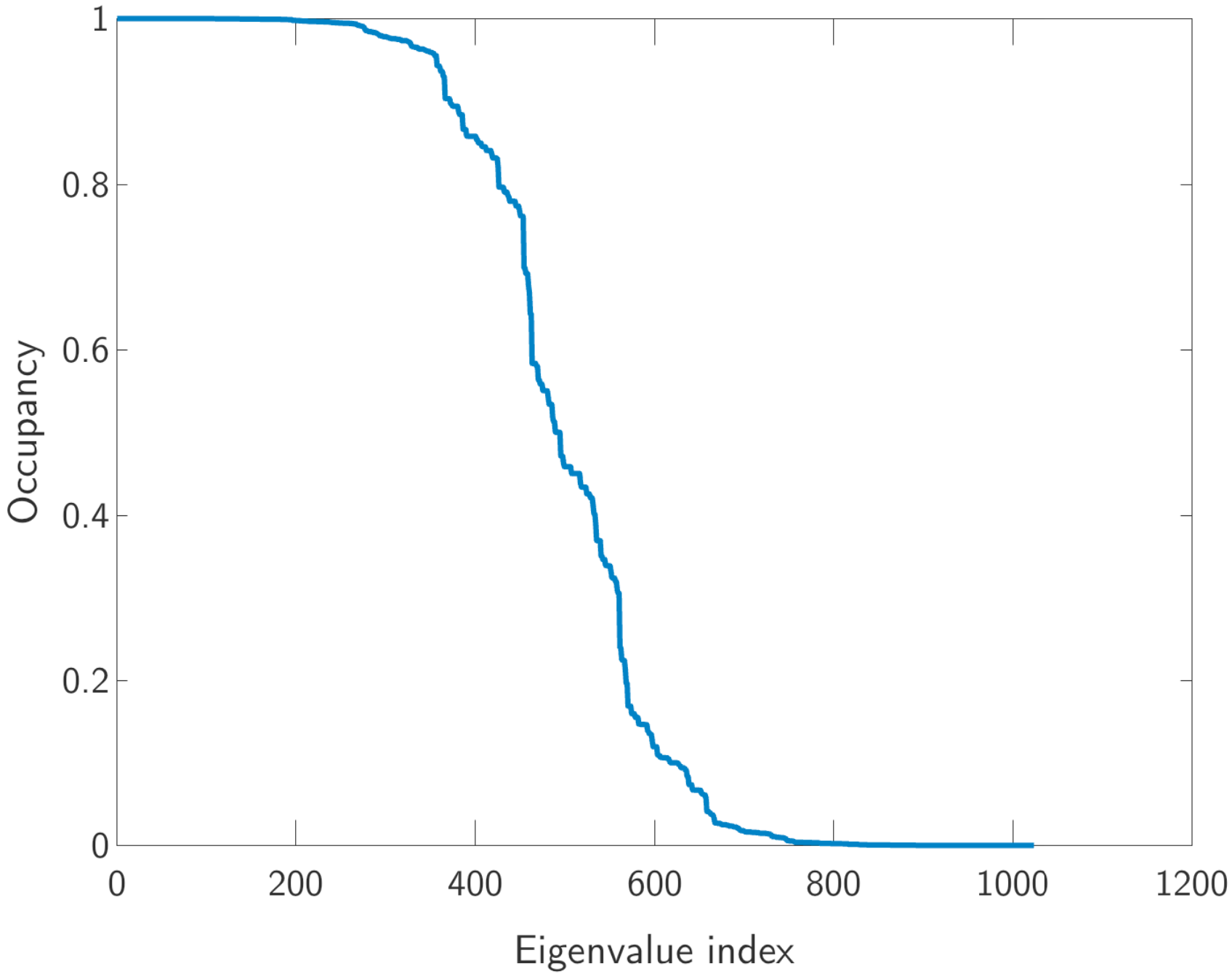
$$f(\varepsilon, \mu, \beta) = \frac{1}{1 + e^{(\varepsilon - \mu)\beta}} = \frac{1}{2}\left(1 + \tanh(\{\varepsilon - \mu\}\beta/2)\right)$$

- Hyperbolic double angle formula:

$$\tanh(2\mathbf{H}') = \frac{2\tanh(\mathbf{H}')}{\tanh^2(\mathbf{H}') + \mathbf{I}}$$


10
5
0
-5
-10
Energy
0
200
400
600
800
1000
1200
Eigenvalue index


1
0.8
0.6
0.4
0.2
0
Occupancy
0
200
400
600
800
1000
1200
Eigenvalue index


Occupancy
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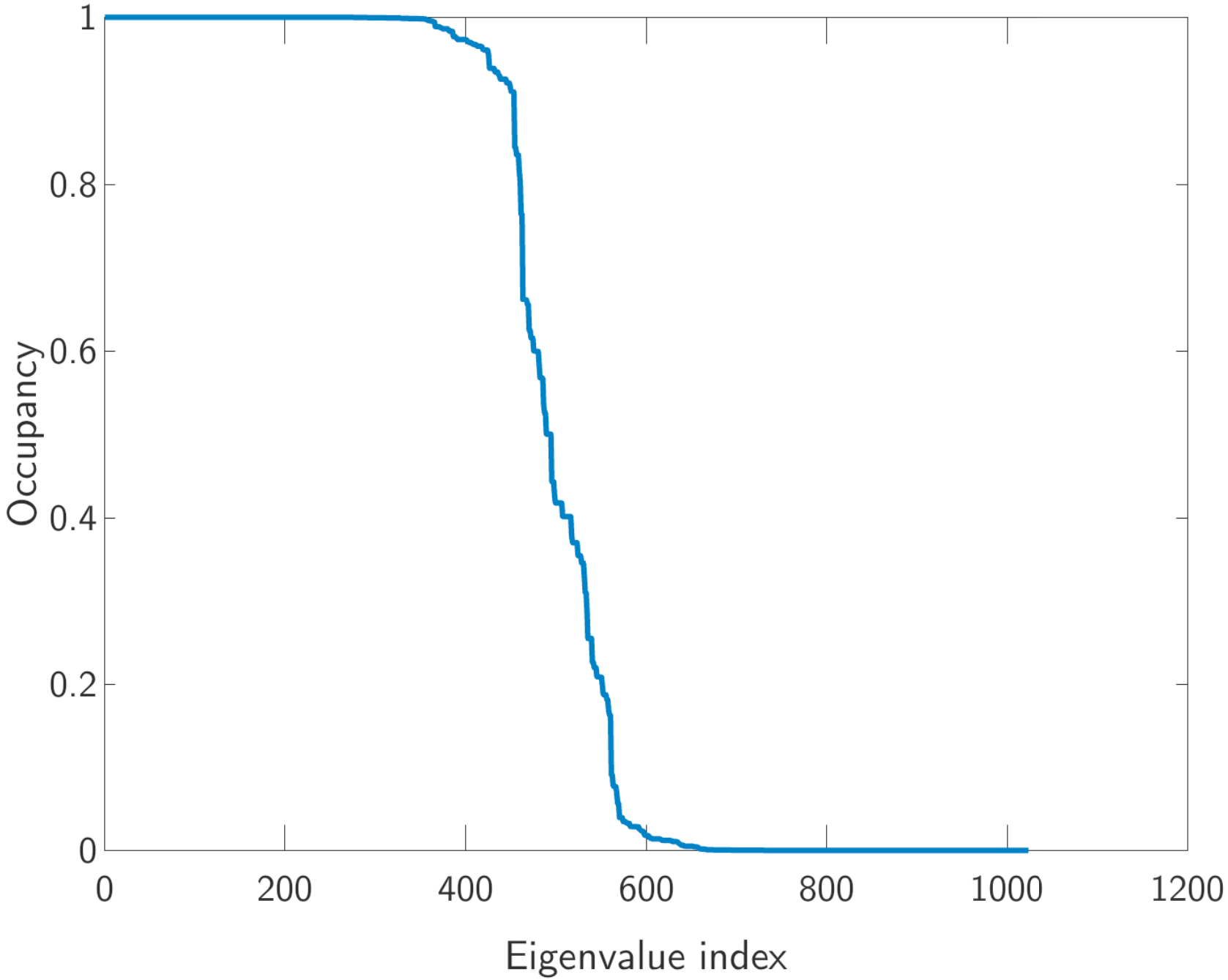
Eigenvalue index

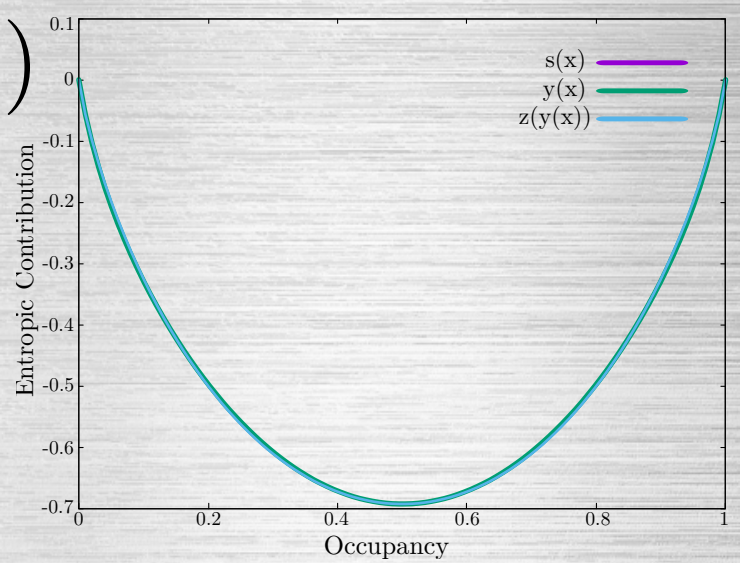

1
0.8
0.6
0.4
0.2
0
Occupancy
0
200
400
600
800
1000
1200
Eigenvalue index

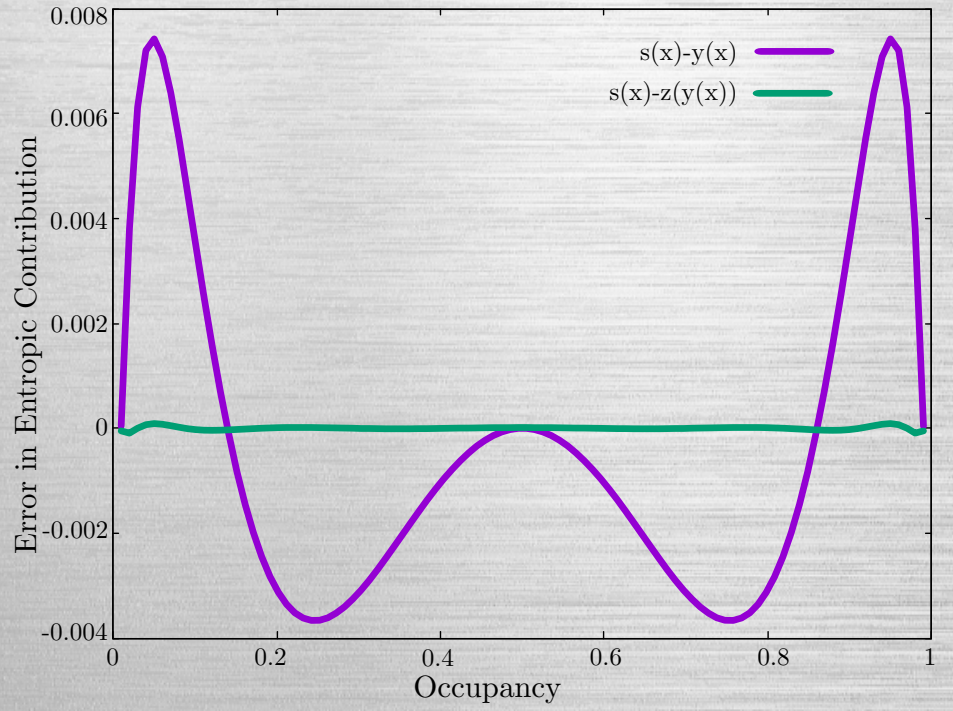
Entropy

- Cannot use $s_i = f_i \ln(f_i) + [1 - f_i] \ln(1 - f_i)$
- Matrix equivalent involves two logarithms of matrices:

$$\mathcal{S} = \mathrm{tr}[\mathbf{K}\ \ln(\mathbf{K}) + [\mathbf{I} - \mathbf{K}]\ \ln(\mathbf{I} - \mathbf{K})]$$

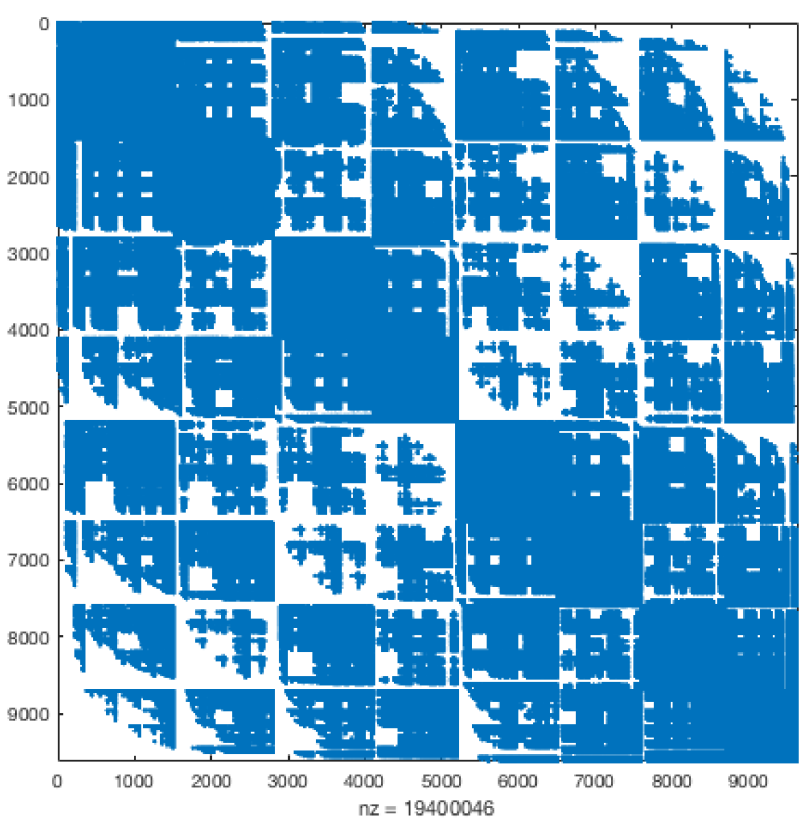
- Too expensive: expand again, this time its better conditioned → eigs all between 0 and 1. Any accuracy we like with few terms.

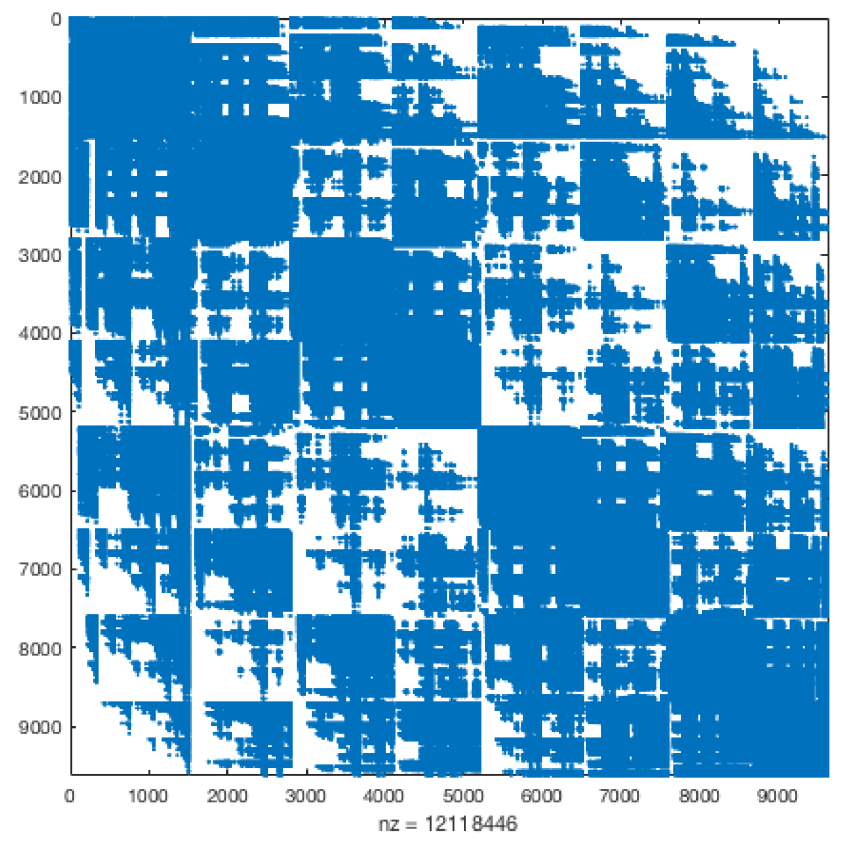


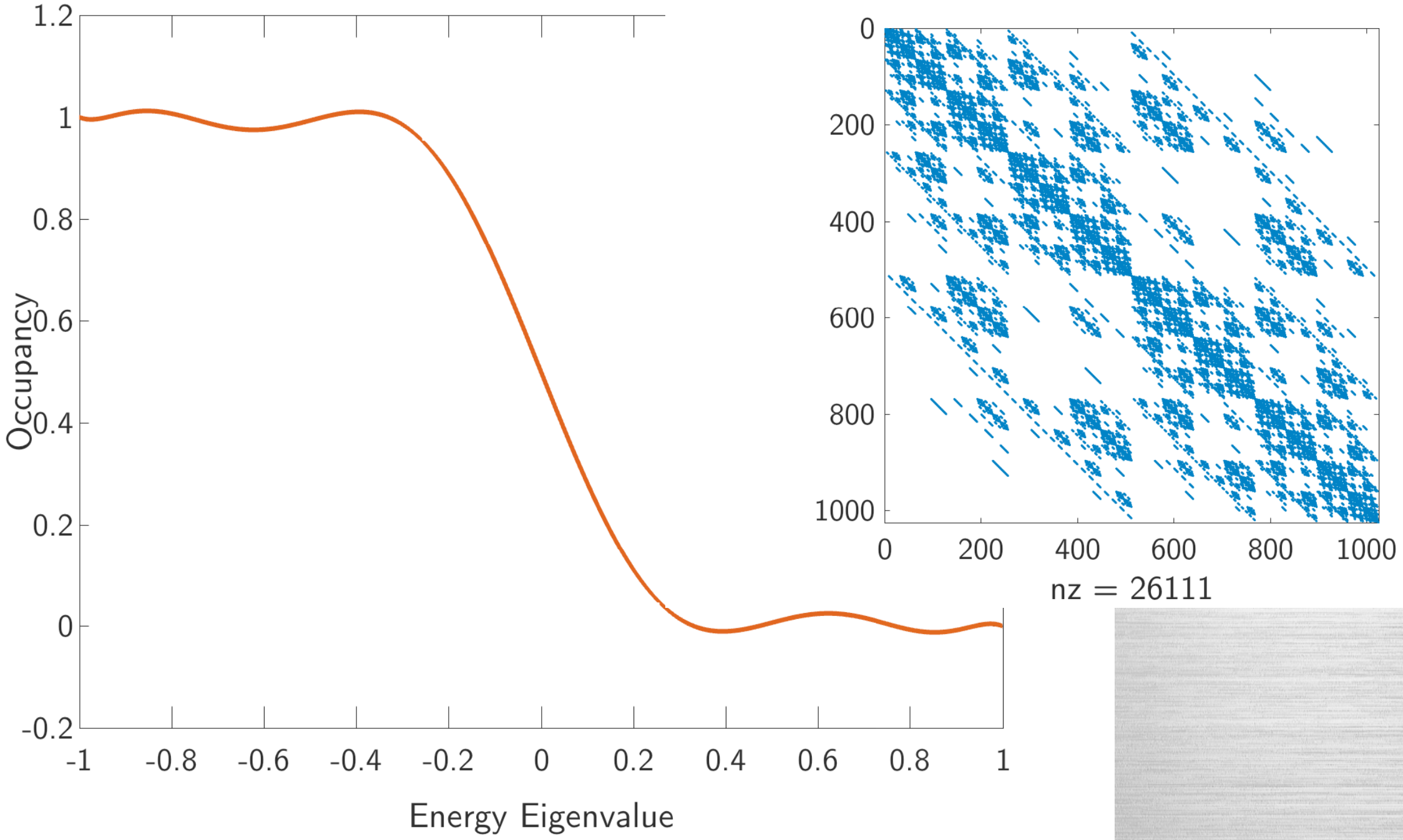


Density Kernel Sparsity

- Need kernel sparsity for linear-scaling, finite temperature metals
- Can we use the series expansion to inform our choice?
- Truncate the expansion early and use this sparsity pattern throughout



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0.8
0.6
0.4
0.2
0
-0.2
Occupancy
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
Energy Eigenvalue
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400
600
800
1000
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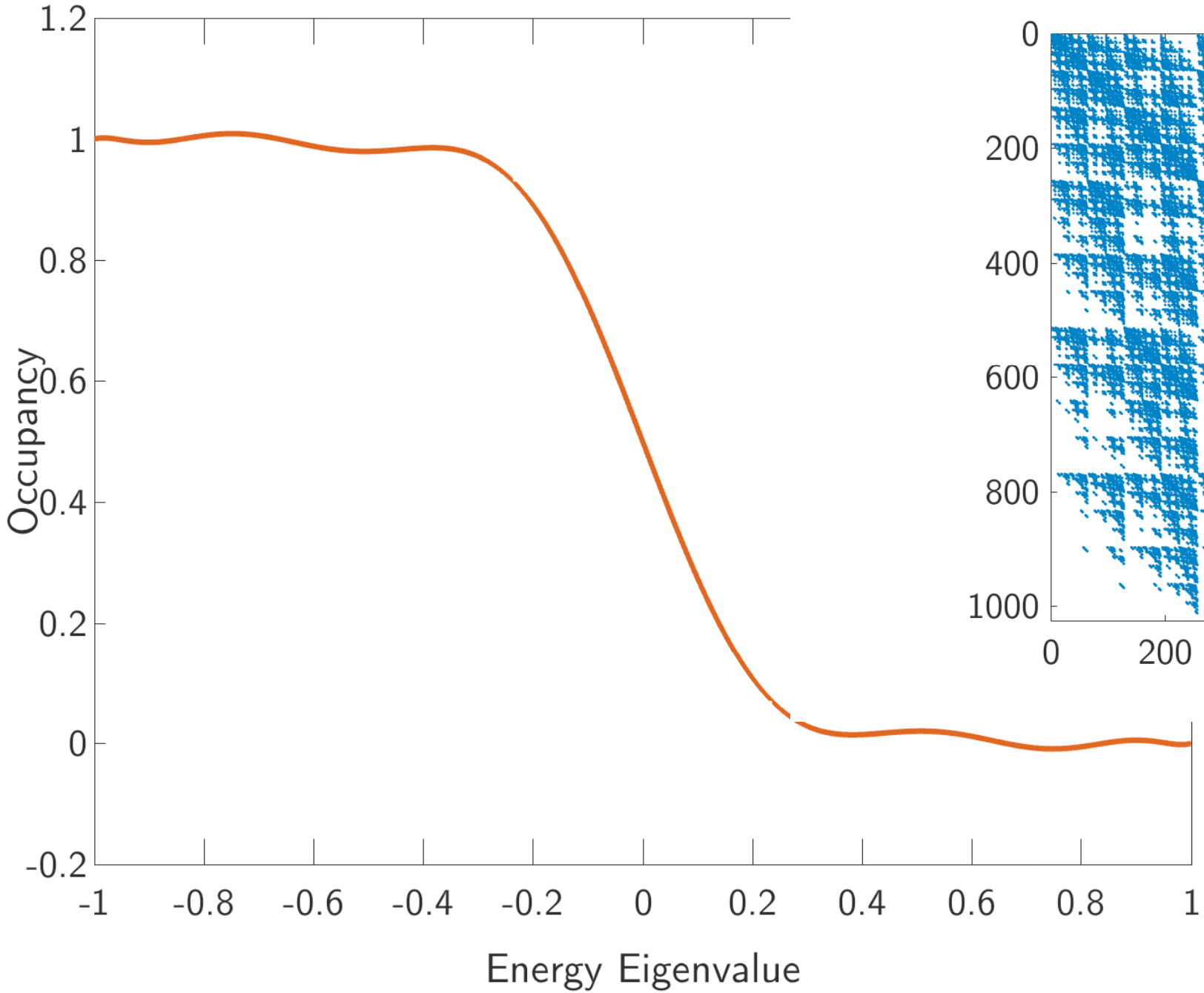
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Occupancy
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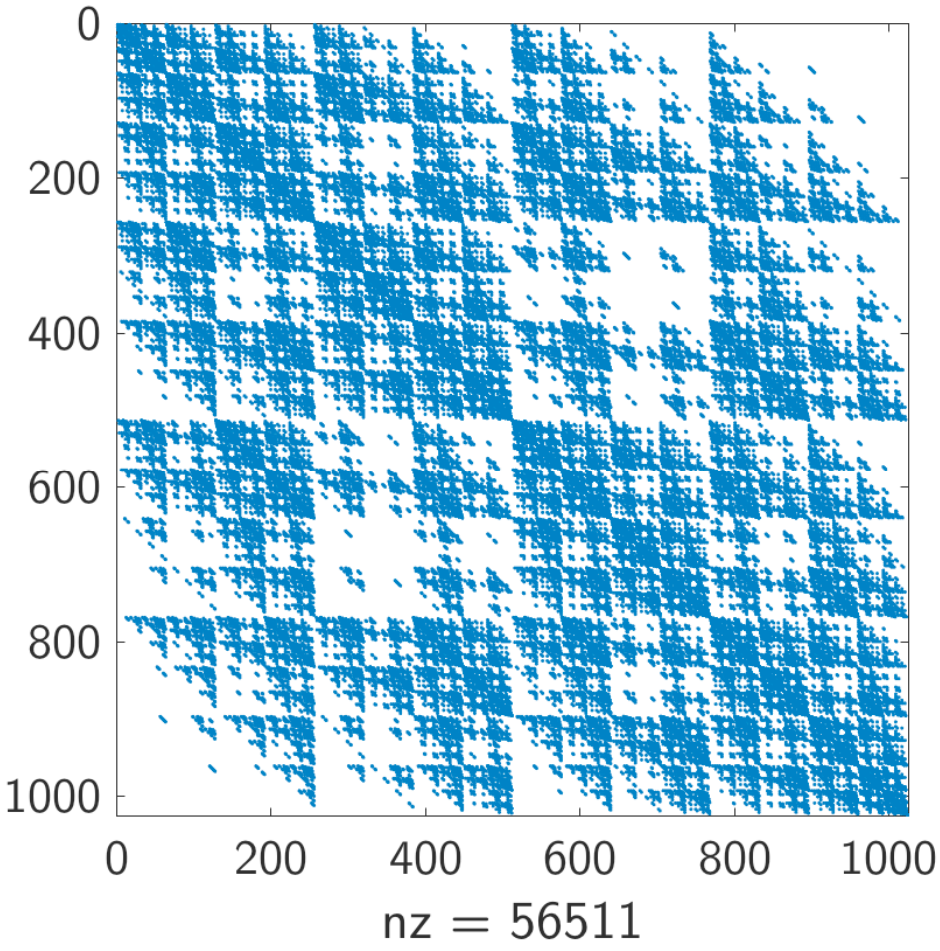
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
Energy Eigenvalue


0
200
400
600
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1000
0
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600
800
1000
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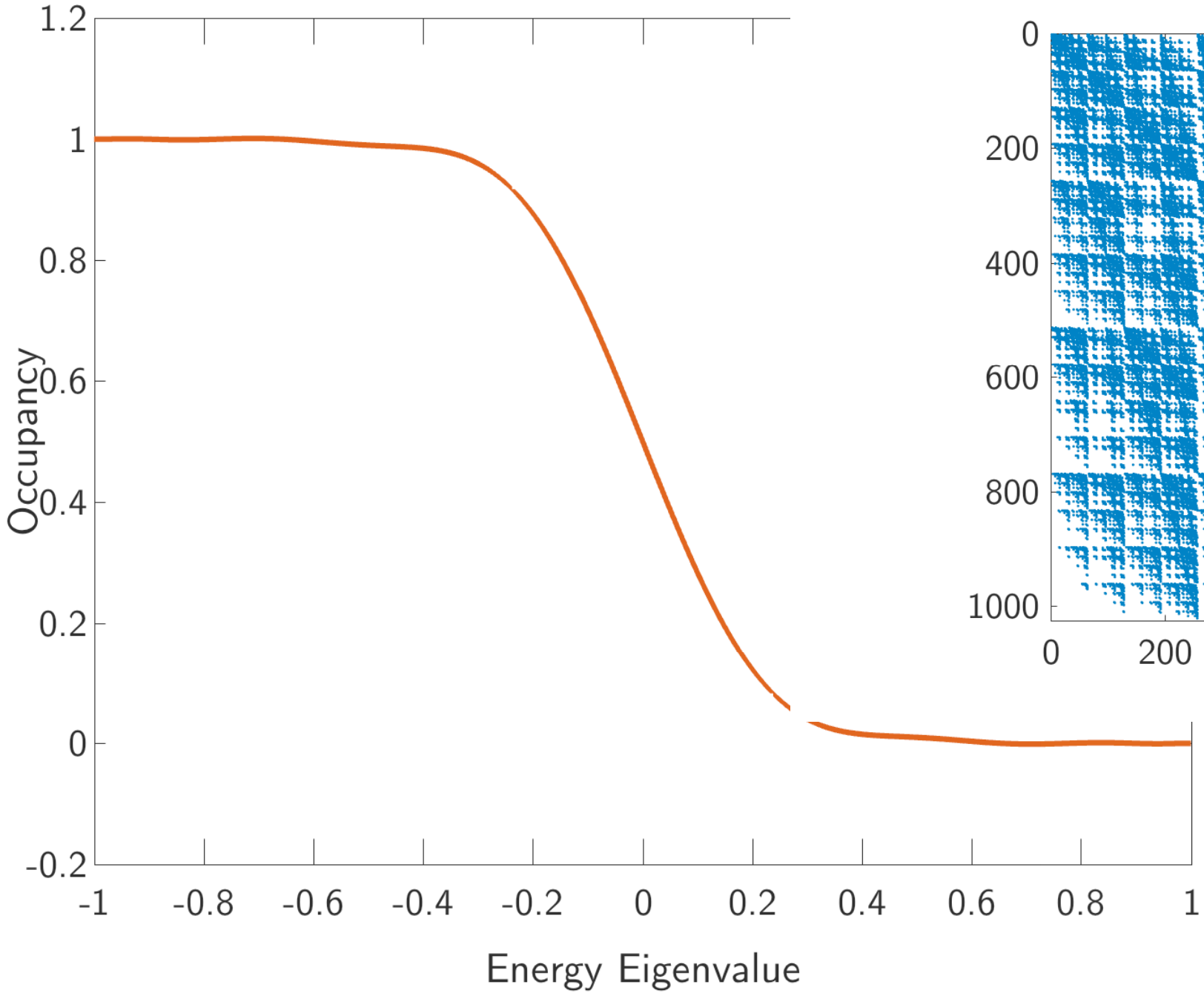
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Occupancy
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0
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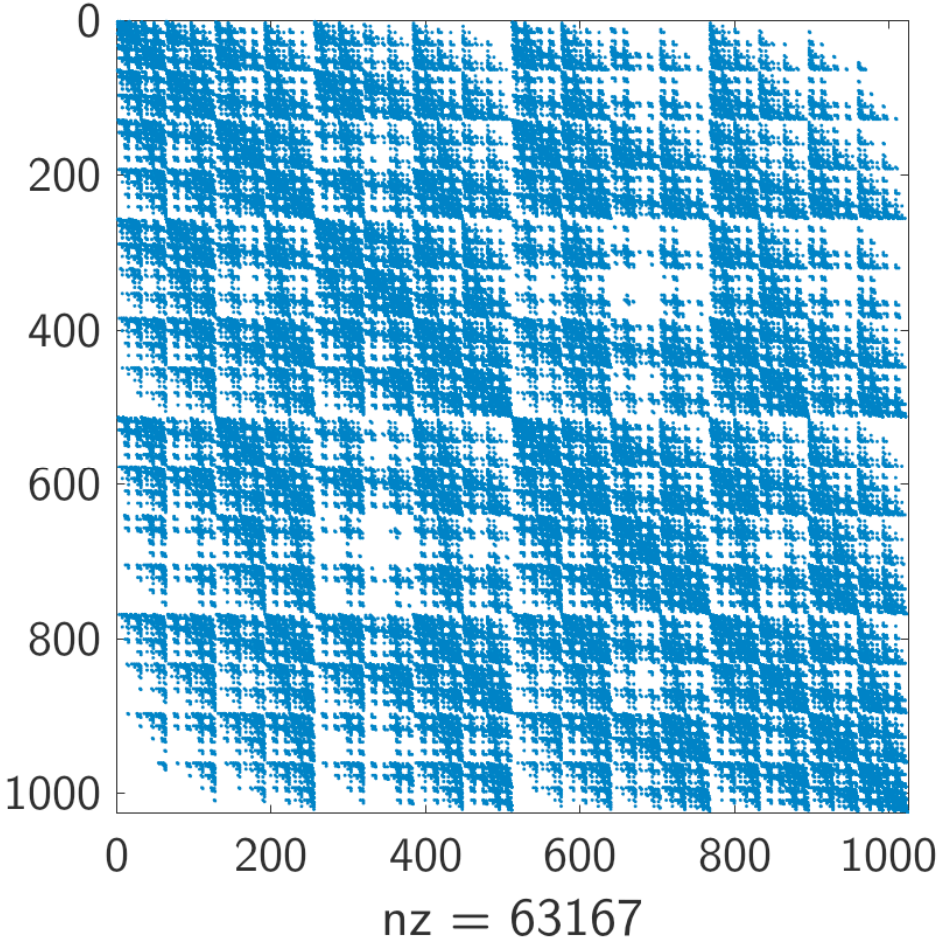
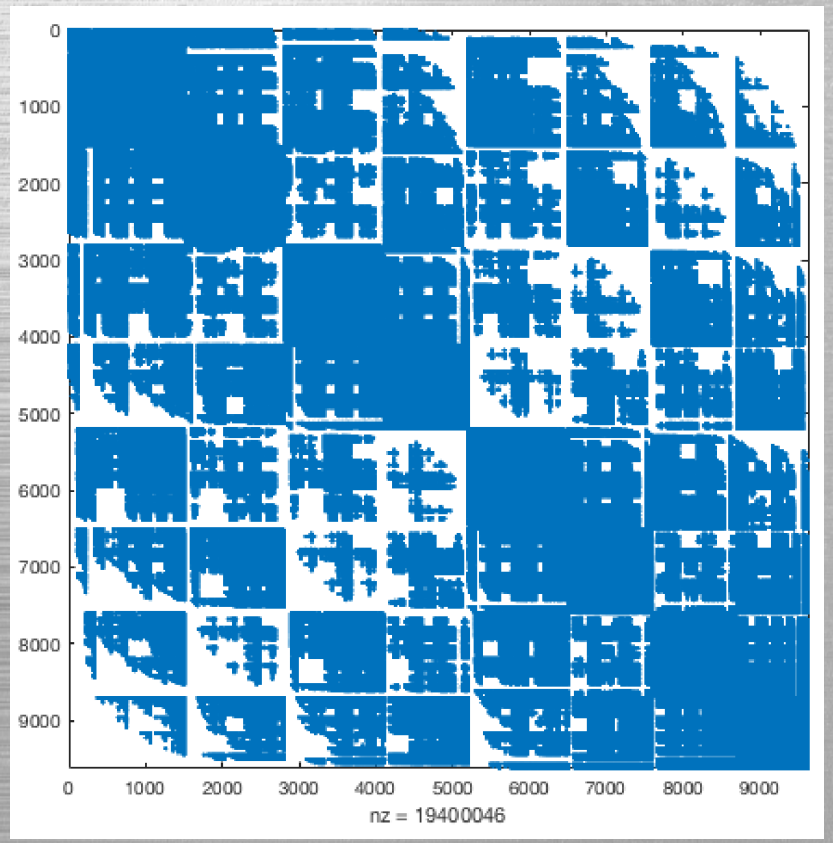
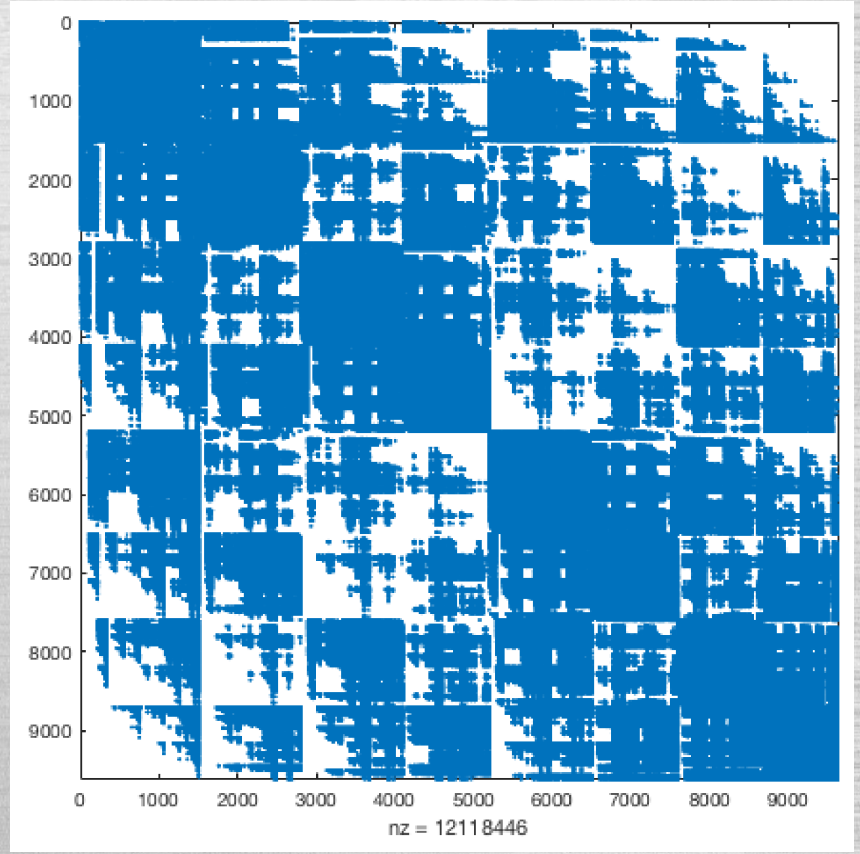
0.4
0.6
0.8
1
Energy Eigenvalue


0
200
400
600
800
1000
0
200
400
600
800
1000
nz = 63167

Density Kernel Sparsity

- Pattern derived from truncated polynomial expansion → a power of H
- Accuracy increases with power
- We used H^2 in our testing. H^3 may be necessary for production calculations





Finding the Chemical Potential

- Method for FOE → implemented in ONETEP + Entropy
- Need also to calculate electron number conserving chemical potential
- Starting from a guess we can root-find : $\Delta N_e = N_e - \mathrm{trace}\left(\frac{\mathbf{I}}{\mathbf{I} + e^{(\mathbf{H}-\mu\mathbf{I})\beta}}\right)$
- In a numerical root finder, we would have to calculate the FOE many times at different chemical potentials → expensive!
- We can use more matrix hyperbolic trigonometry to correct a density kernel for the chemical potential:

$$\tanh\left(\frac{((\mathbf{H}-\mu\mathbf{I})\beta)}{2} \pm \frac{\beta\Delta\mu\mathbf{I}}{2}\right) = \frac{\rho_{\mathbf{H},\mu,\beta} \pm \tanh(\frac{\beta\Delta\mu}{2})\mathbf{I}}{\mathbf{I} \pm \tanh(\frac{\beta\Delta\mu}{2})\rho_{\mathbf{H},\mu,\beta}}$$

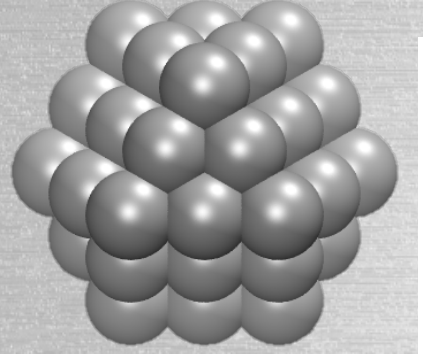
Finding the Chemical Potential 2

- This equation contains a matrix inversion.
- Instead, we again expand this expression as a Chebyshev series using the scalar equivalent: $q(x) = \frac{x+c}{1+xc}$ on the domain [-1:1]
- To speed up the root finding further, we can also use derivatives $\frac{\partial \rho}{\partial \mu} = -\frac{\beta}{4}\left(\mathbf{I} - \rho^2\right)$

$$\frac{\partial N_e}{\partial \mu} = -\frac{\beta}{4}\left(1 - \mathrm{trace}(\rho^2)\right)$$

- This gives the change in chemical potential necessary each step
- With this we can use a safeguarded Newton-Raphson method rather than a straight bisection method

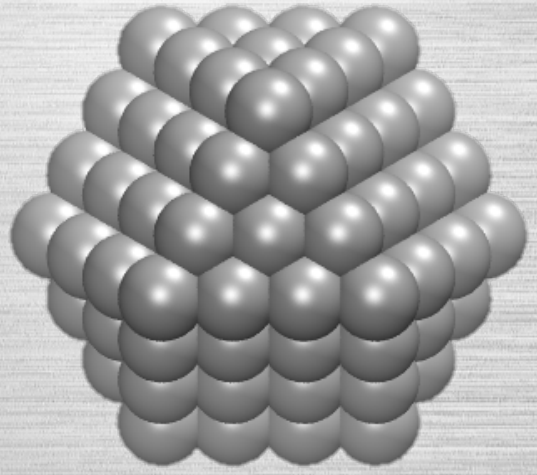
Validation



- Does it work?
- We tried running on cuboctahedral platinum

E_H	Pt_{55}	Pt_{147}
10^{-6}	-4914.74211	-13137.32070
10^{-7}	-4914.74475	-13137.33179
10^{-8}	-4914.74445	-13137.33169

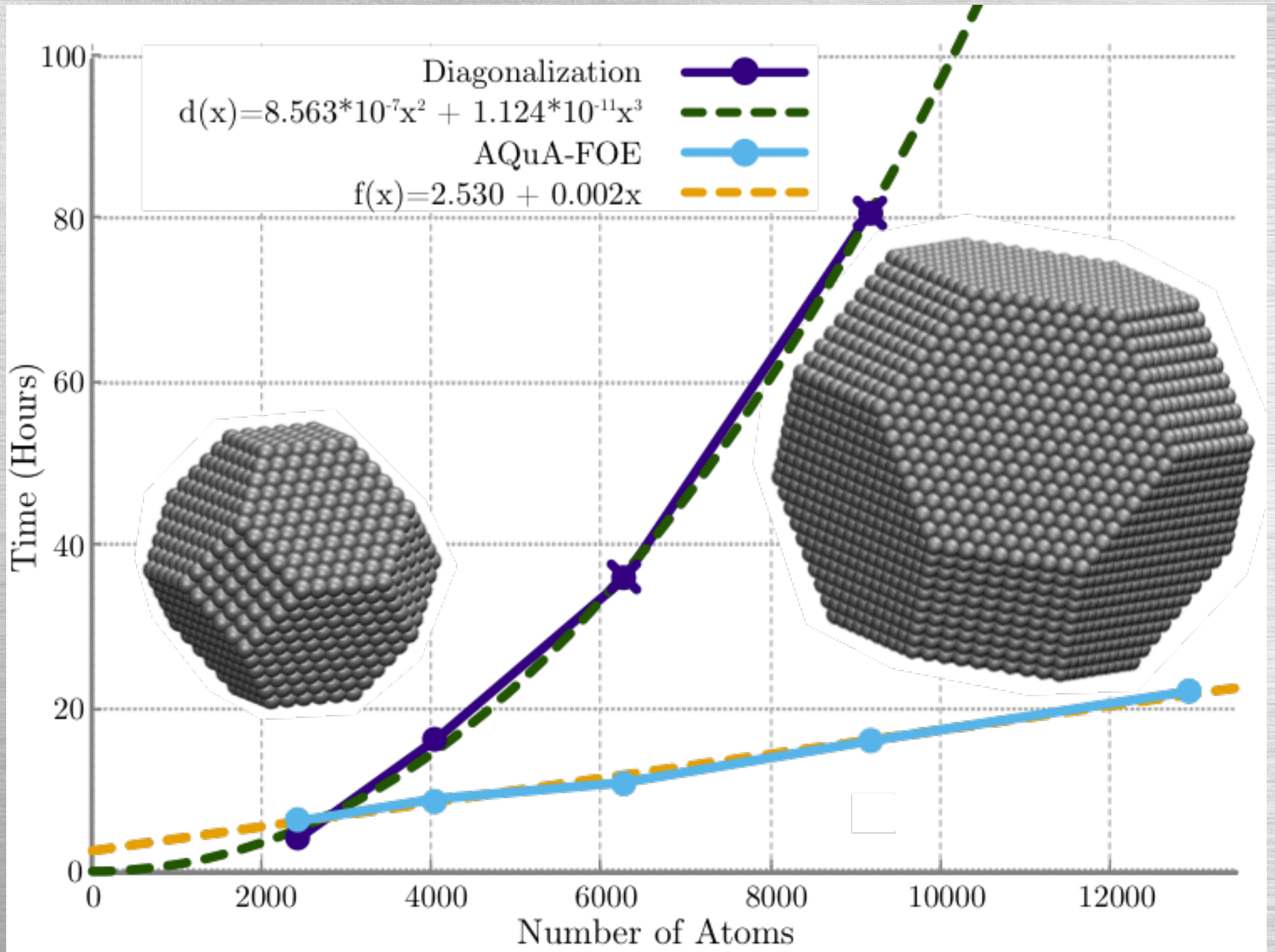
- Compared the convergence with chemical potential stopping criteria with EDFT with diagonalisation in ONETEP:
- With diagonalisation, we get -4914.74442 E_H for a Pt_{55} nanoparticle. With a 147-atom Pt nanoparticle we calculated an energy of -13137.33174 E_H with a diagonalization based technique.
- These tests were run without sparsity in the density kernel



Scaling

- To test scaling, we used the H^2 sparsity pattern for K
- We used truncated octahedral palladium nanoparticles of ~2000 to ~13000 atoms
- We could not test diagonalisation up to the larger sizes, so opted to run a single EDFT inner loop and multiply by the predicted number of steps to get the estimated timings
- We ran all tests 4 times and with 4 EDFT inner loop iterations to average the time per iteration

Scaling


Diagonalization
d(x)=8.563*10^-7x^2 + 1.124*10^-11x^3
AQuA-FOE
f(x)=2.530 + 0.002x
Time (Hours)
Number of Atoms
0
20
40
60
80
100
0
2000
4000
6000
8000
10000
12000

Conclusion

- Linear scaling metals calculations are possible now with ONETEP
- More work needs doing on the sparsity patterns
- Chris Skylaris (Southampton) is now planning to use these methods in anger to run production calculations
- There are many performance gains to be made