Thermodynamics of magnetic systems from first principles: WL-LSMS

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Motivation

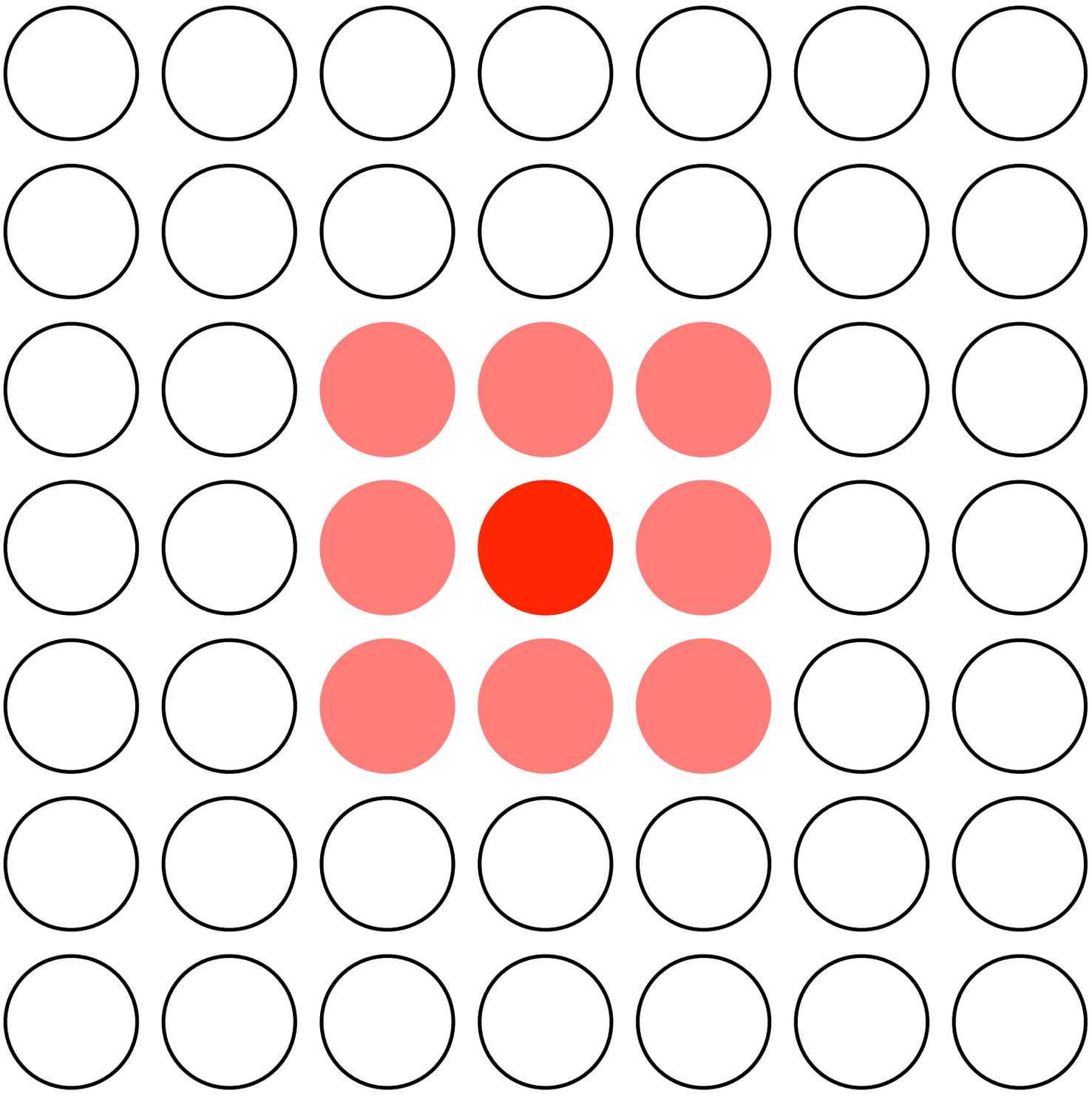
- Density Functional Calculations have proven to be a useful tool to study the ground state of many materials.

- For finite temperatures the situation is less ideal an one is often forced to rely on model calculation with parameters either fitted to first principles calculations or experimental results.

- Fitting to models is especially unsatisfactory in inhomogeneous systems, nanoparticles or other systems where the model parameters could vary significantly from one site to another.

Solution:
Combine First Principles calculations with statistical mechanics methods

Nearsightedness and the locally self-consistent multiple scattering (LSMS) method

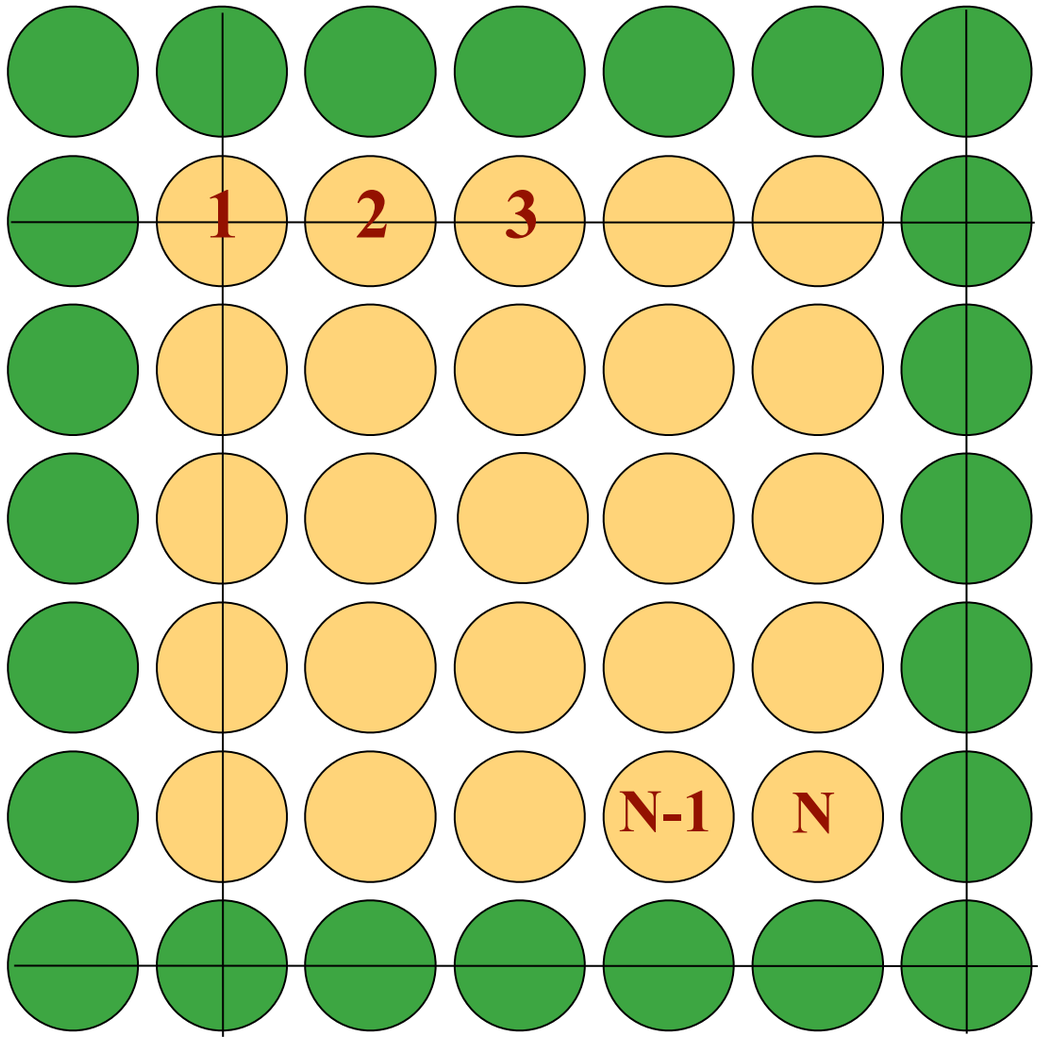


- Nearsightedness of electronic matter - Prodan & Kohn, PNAS **102**, 11635 (2005)
  - *Local electronic properties such as density depend on effective potential only at nearby points.*
- Locally self-consistent multiple scattering method - Wang et al., PRL **75**, 2867 (1995)
  - *Solve Kohn-Sham equation on a cluster of a few atomic shells around atom for which density is computed*
  - *Solve Poisson equation for entire system - long range of bare coulomb interaction*

Locally Self-consistent Multiple Scattering (LSMS) method

- Massively Parallel O[N] approach
  - Approximate total electron density by sum of locally determined site densities
  - At each at each site *i* approximate scattering path matrix for infinite sytem by that of a finite localiteraction zone (LIZ) comprising M-sites

$$\tau_M(\varepsilon)|_{ii} = \begin{pmatrix} \mathbf{t}_{11}^{-1}(\varepsilon) & \mathrm{K} & -\mathbf{G}^{1M}(\varepsilon) \\ \mathrm{M} & \mathrm{O} & \mathrm{M} \\ -\mathbf{G}_{M0}(\varepsilon) & \mathrm{L} & \mathbf{t}_{MM}^{-1}(\varepsilon) \end{pmatrix}^{-1}$$



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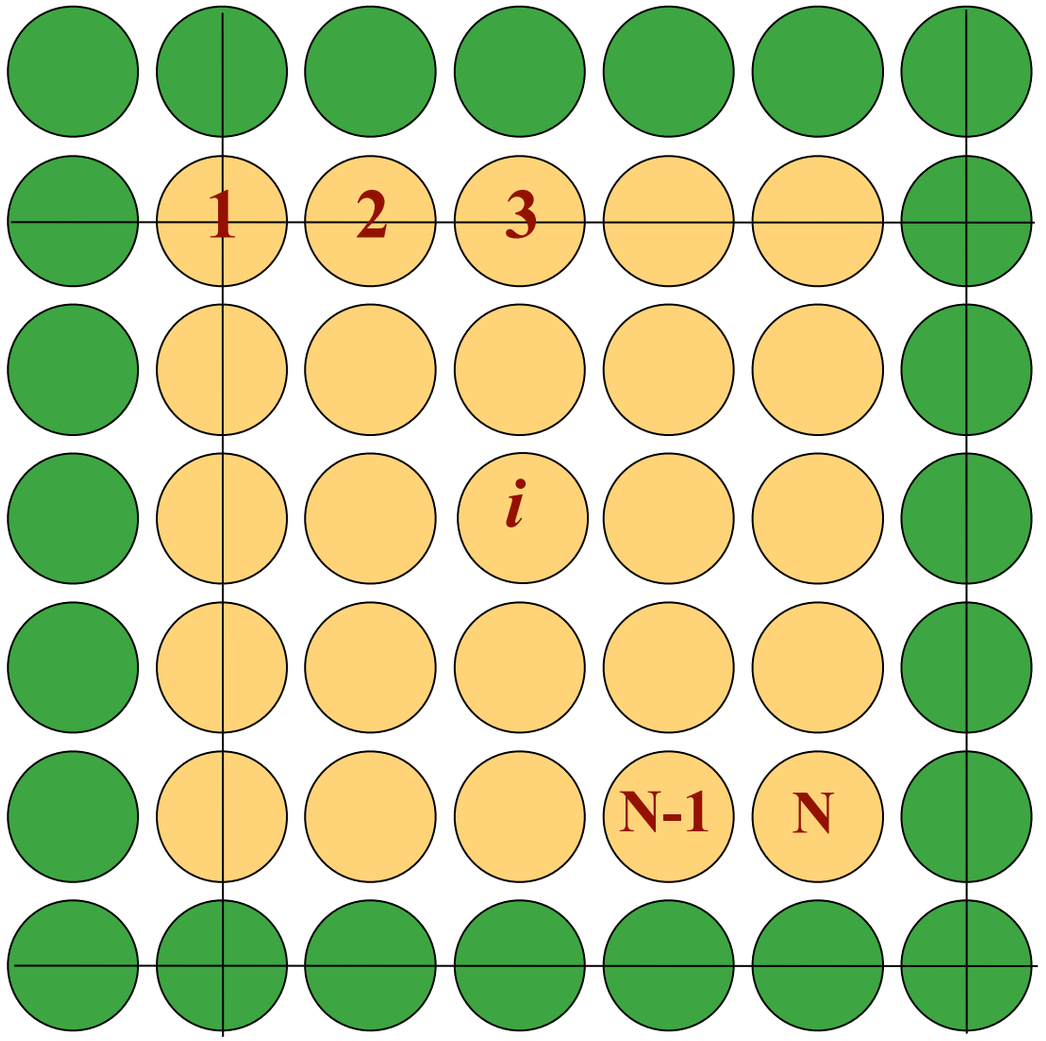

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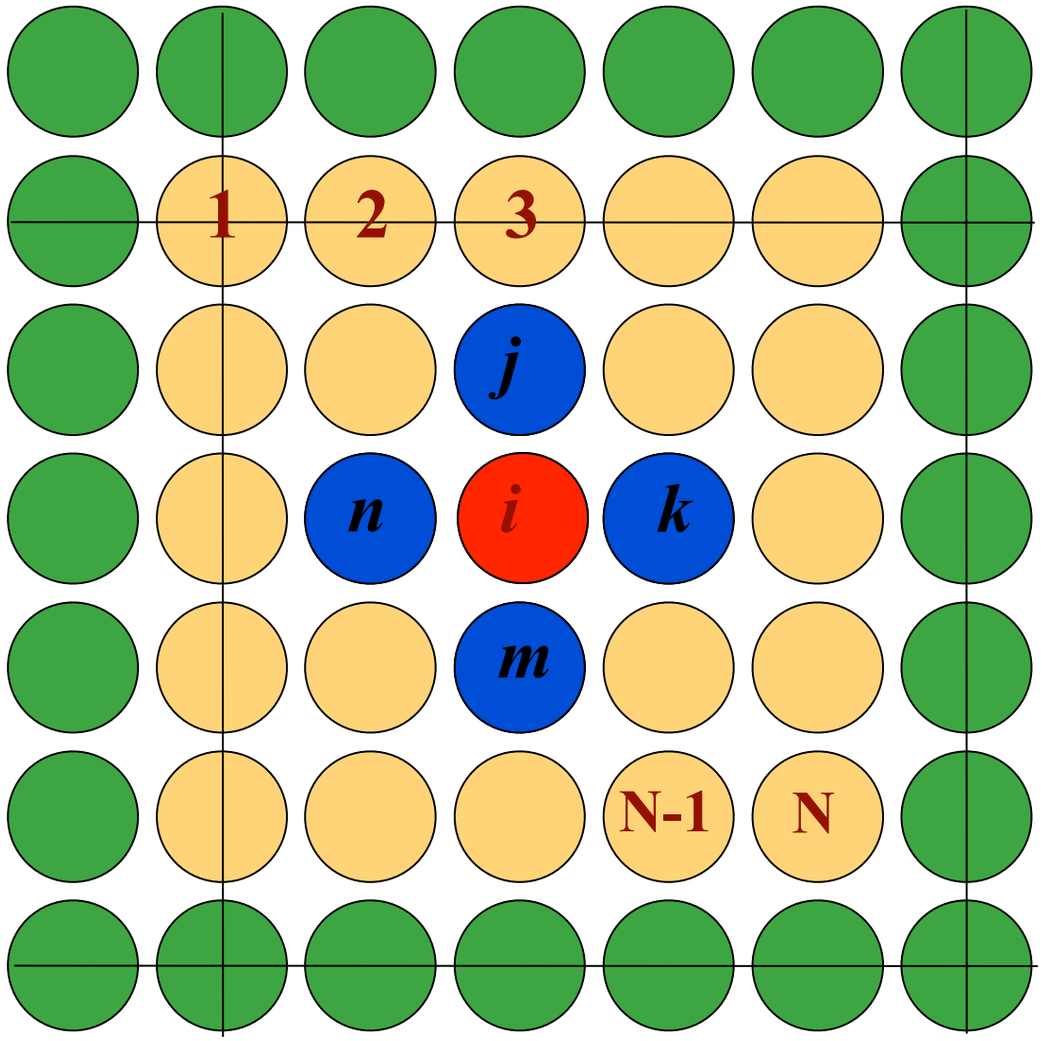

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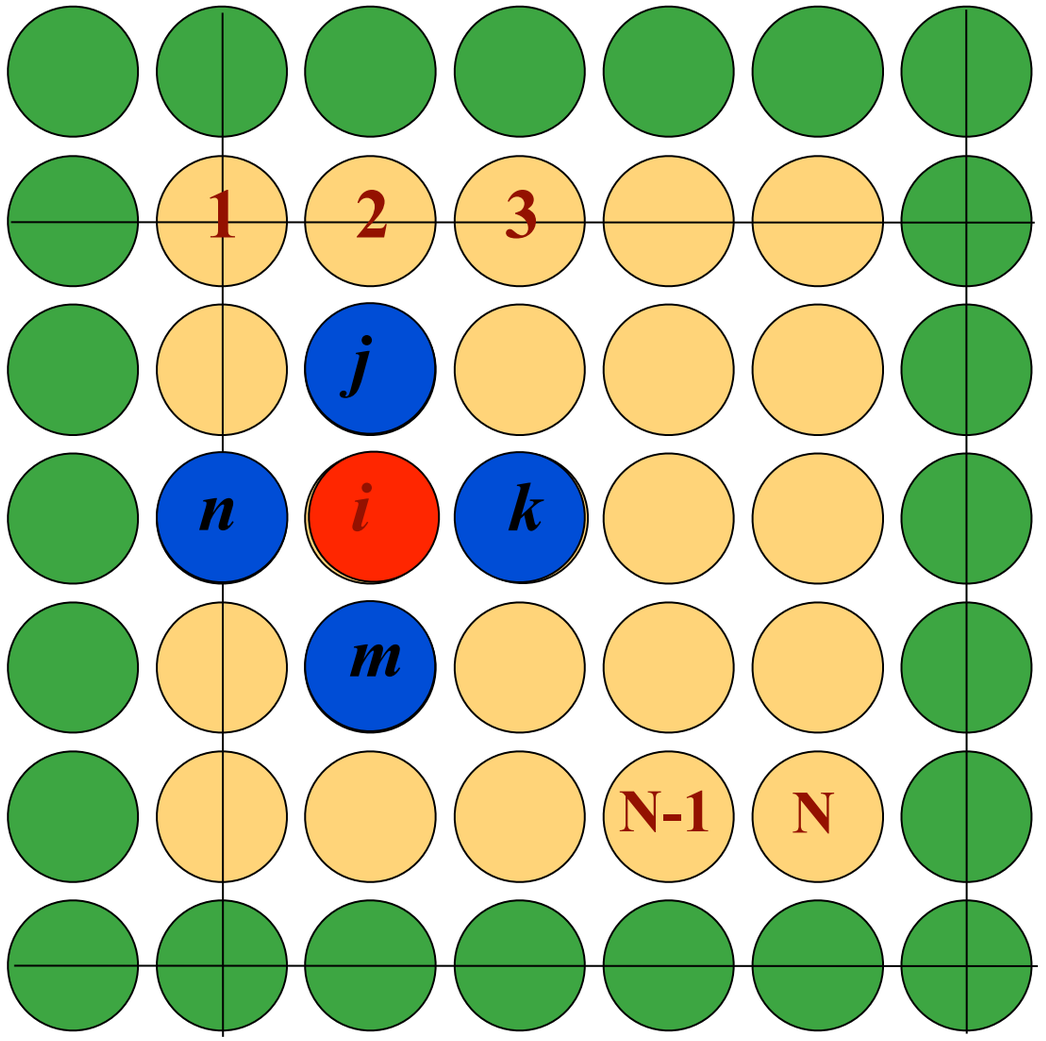

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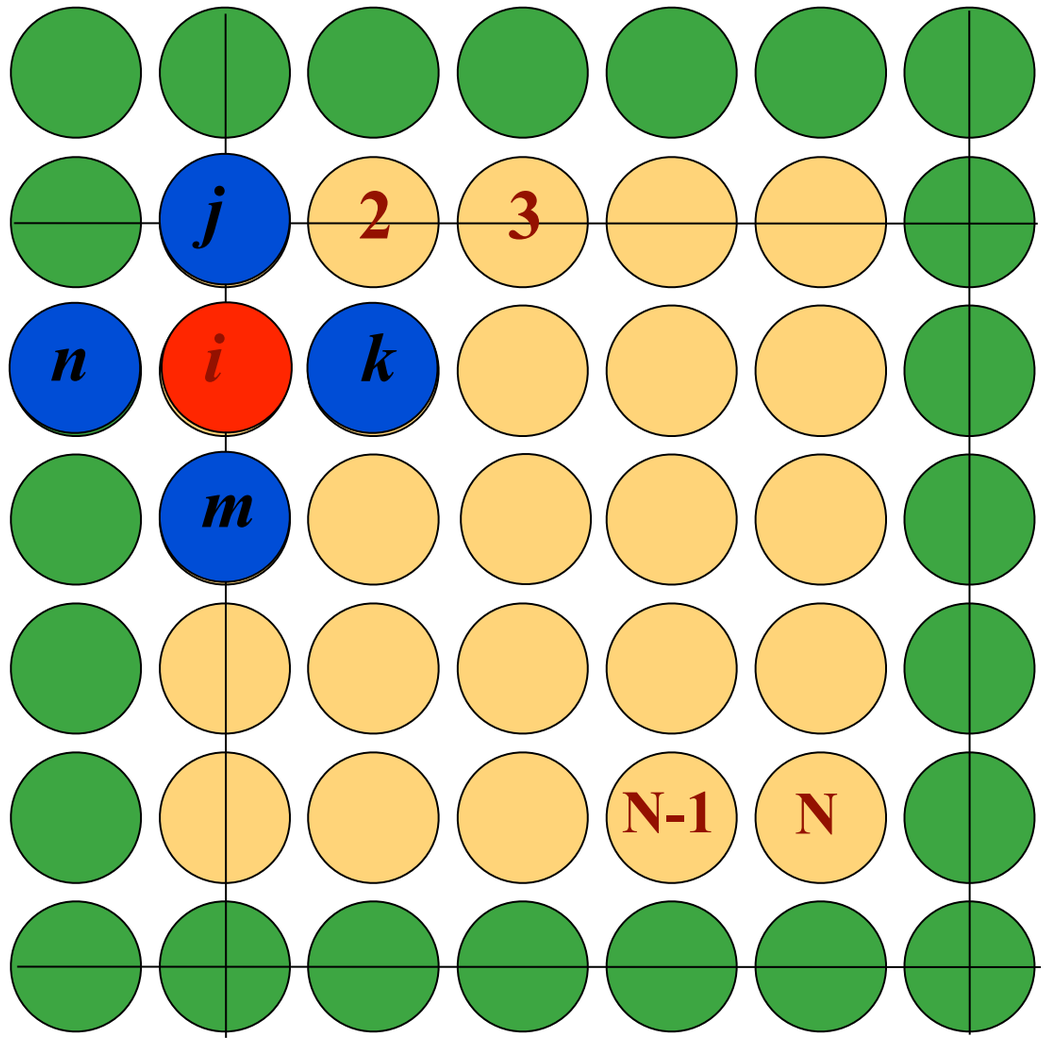

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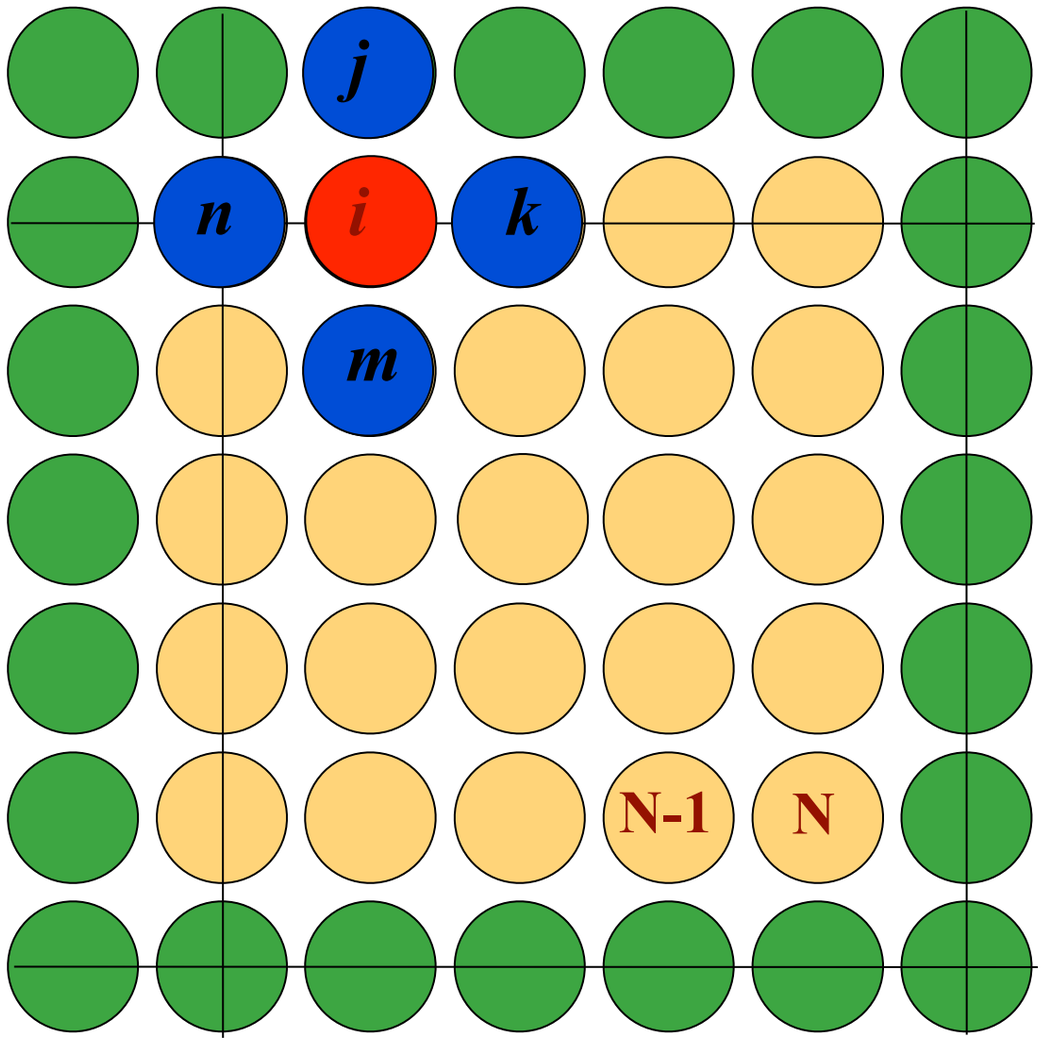

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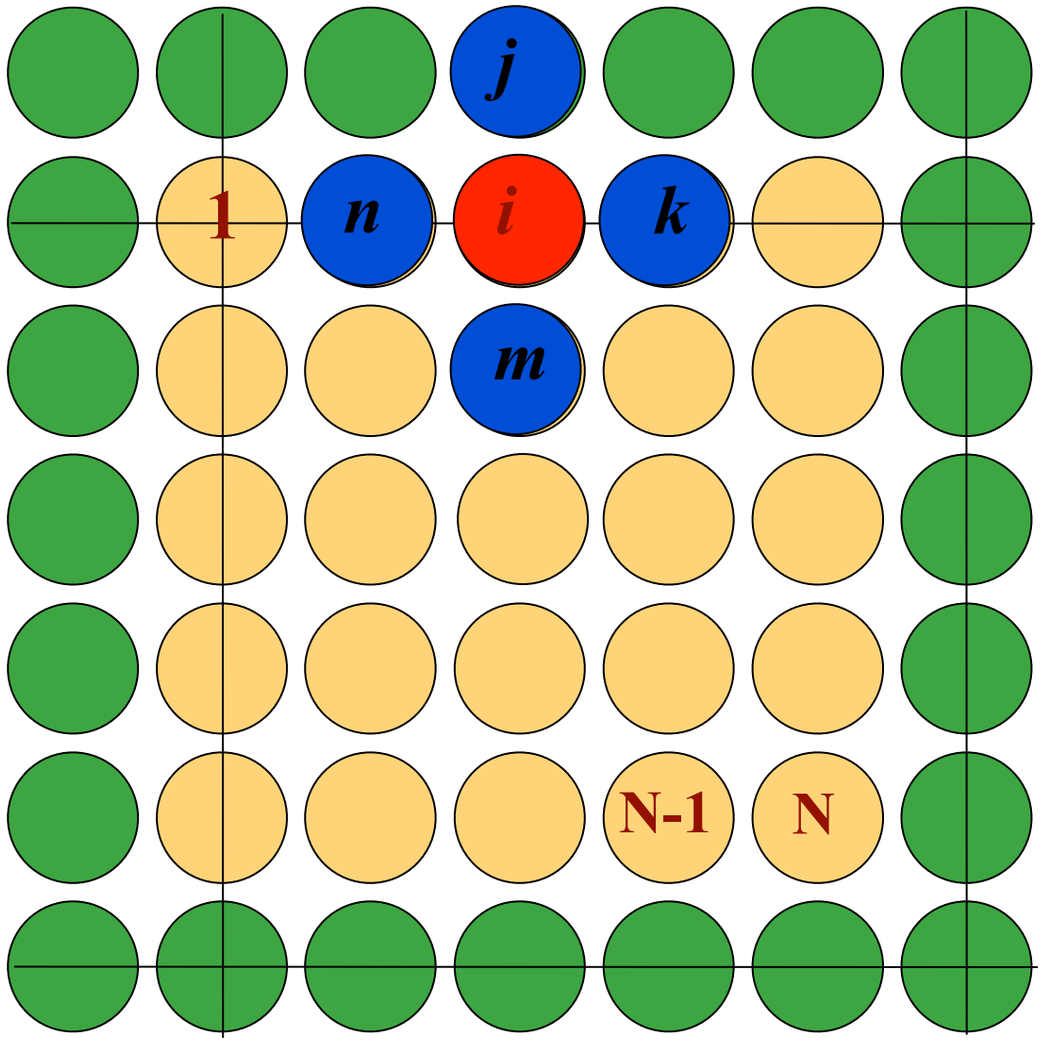

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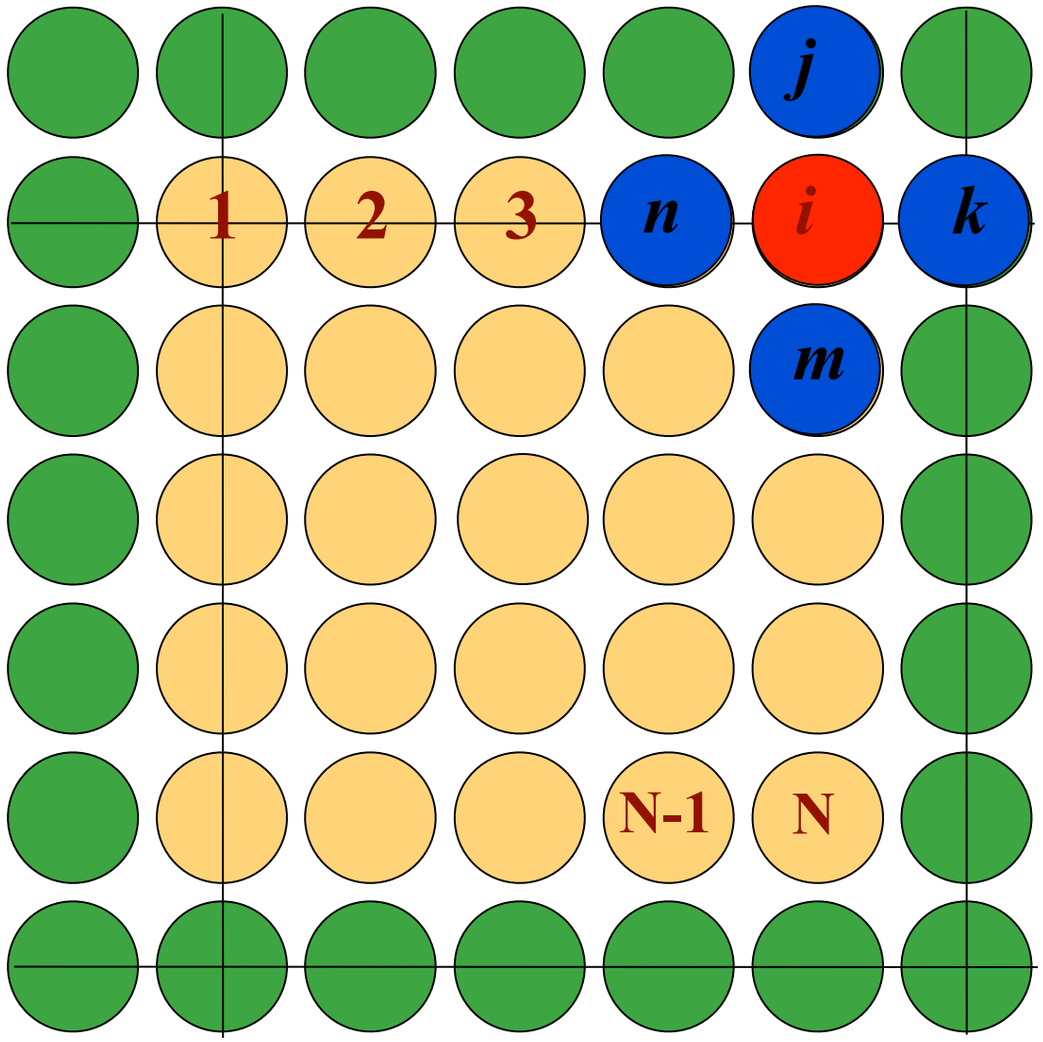

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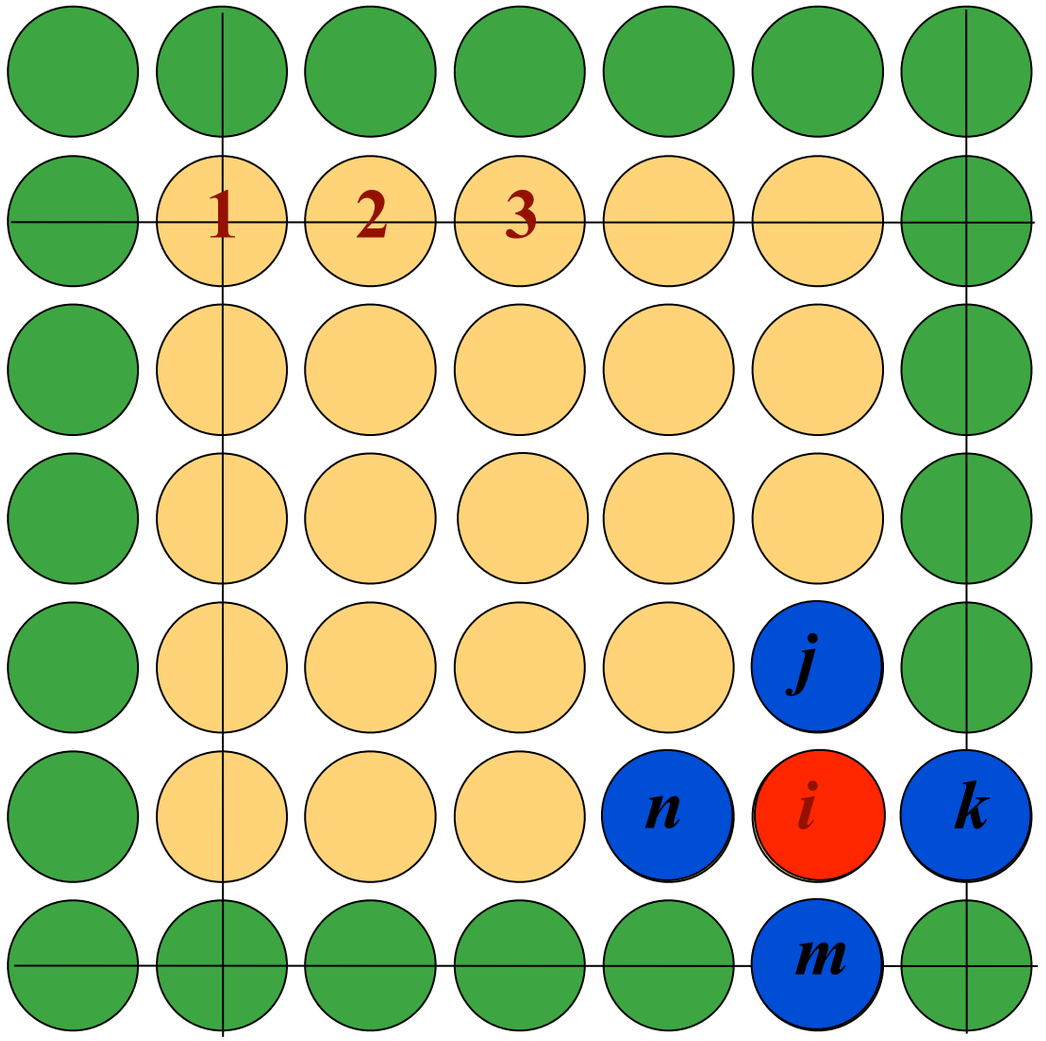

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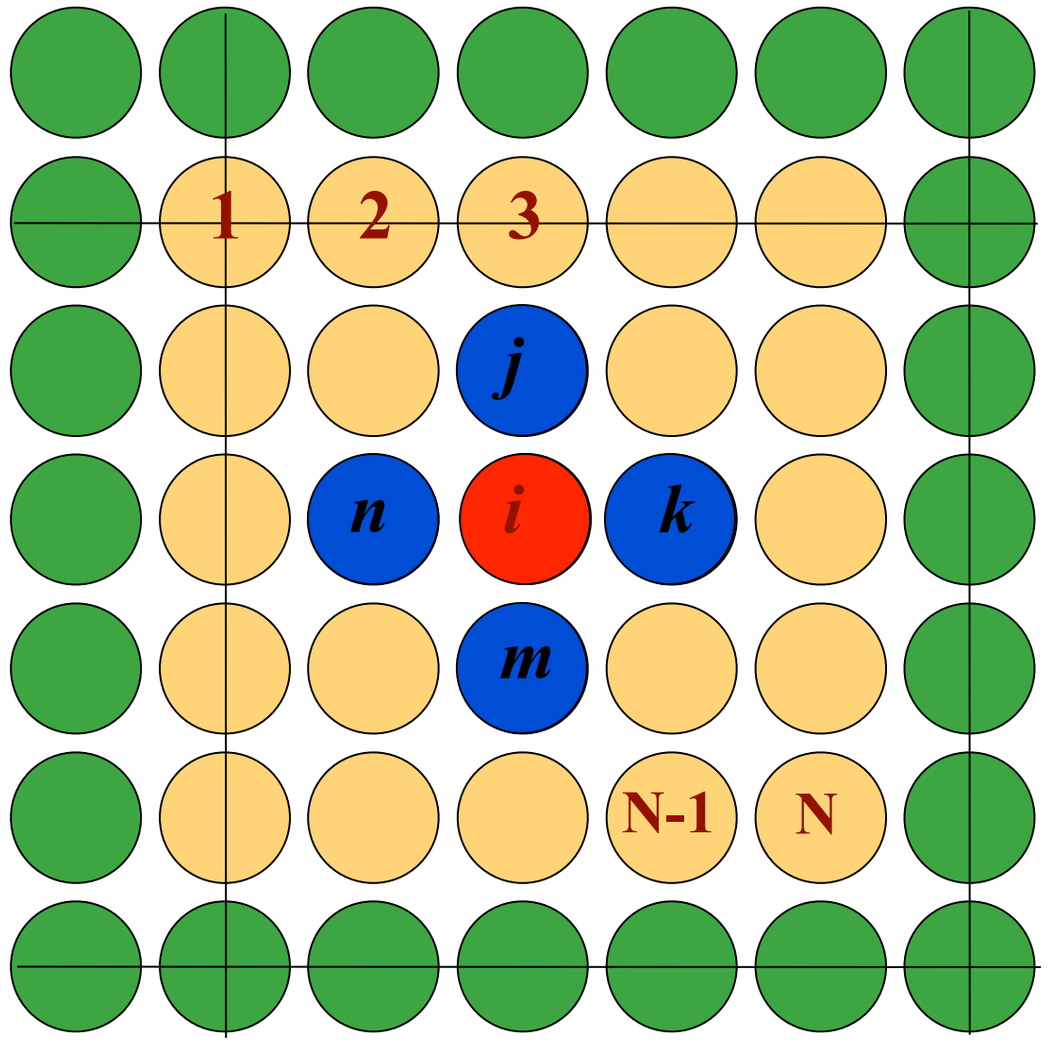

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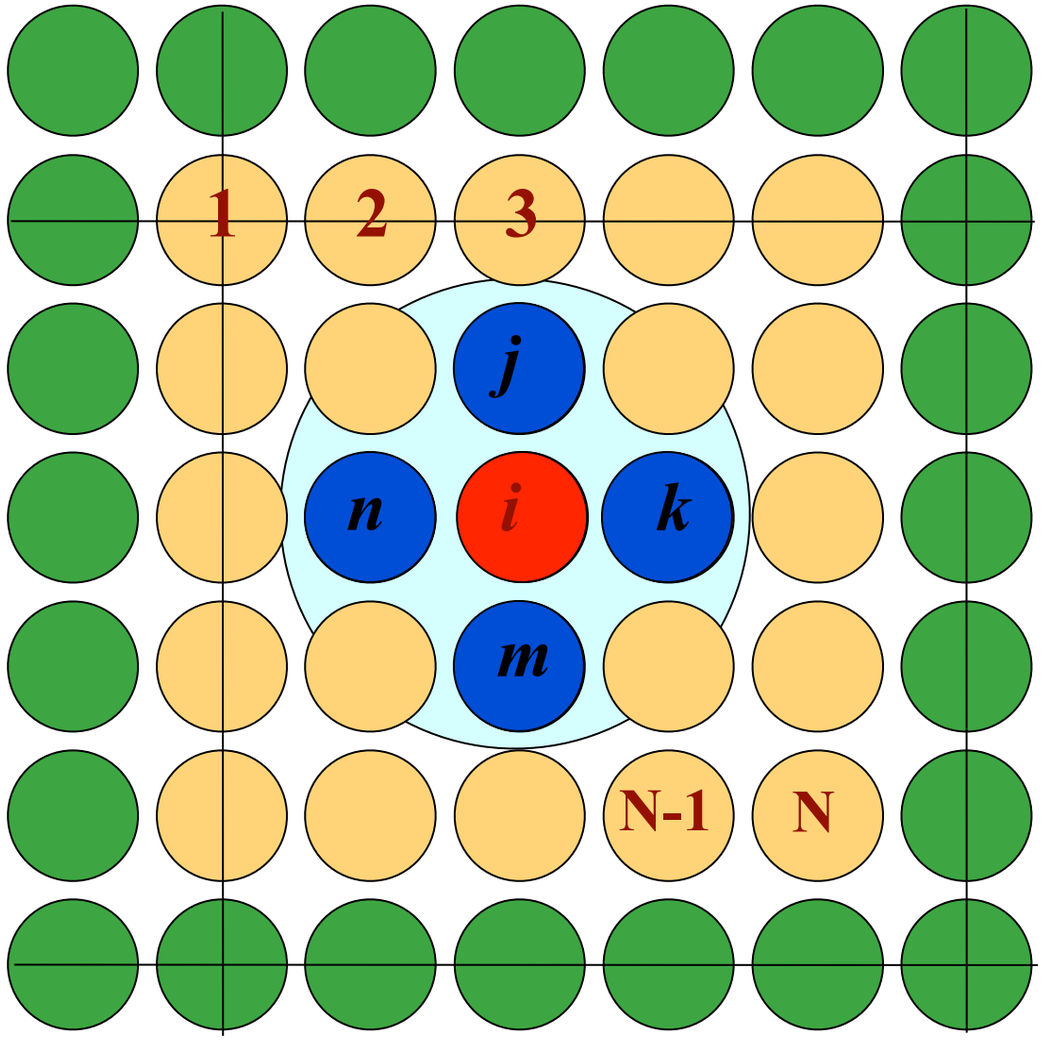

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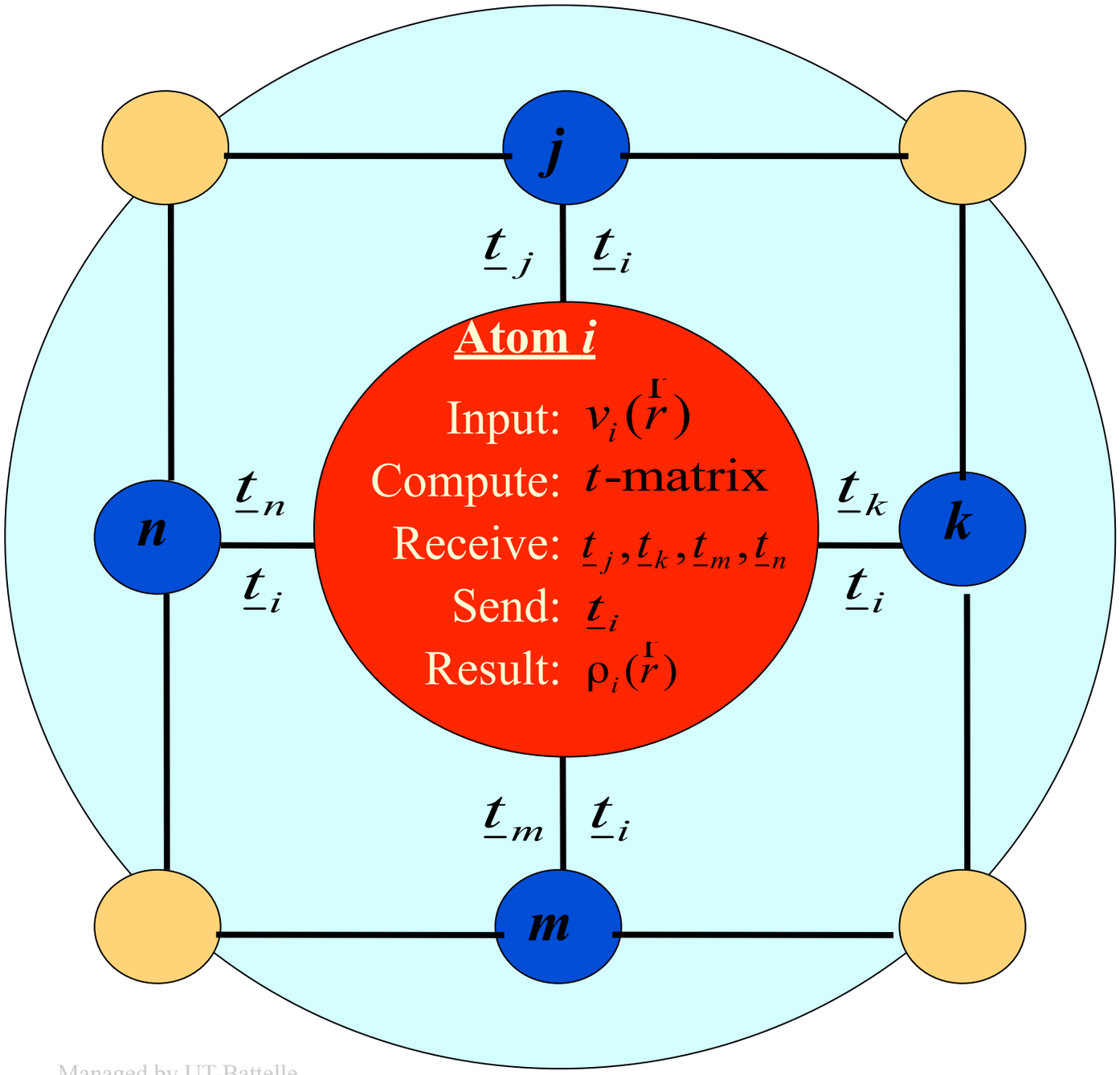
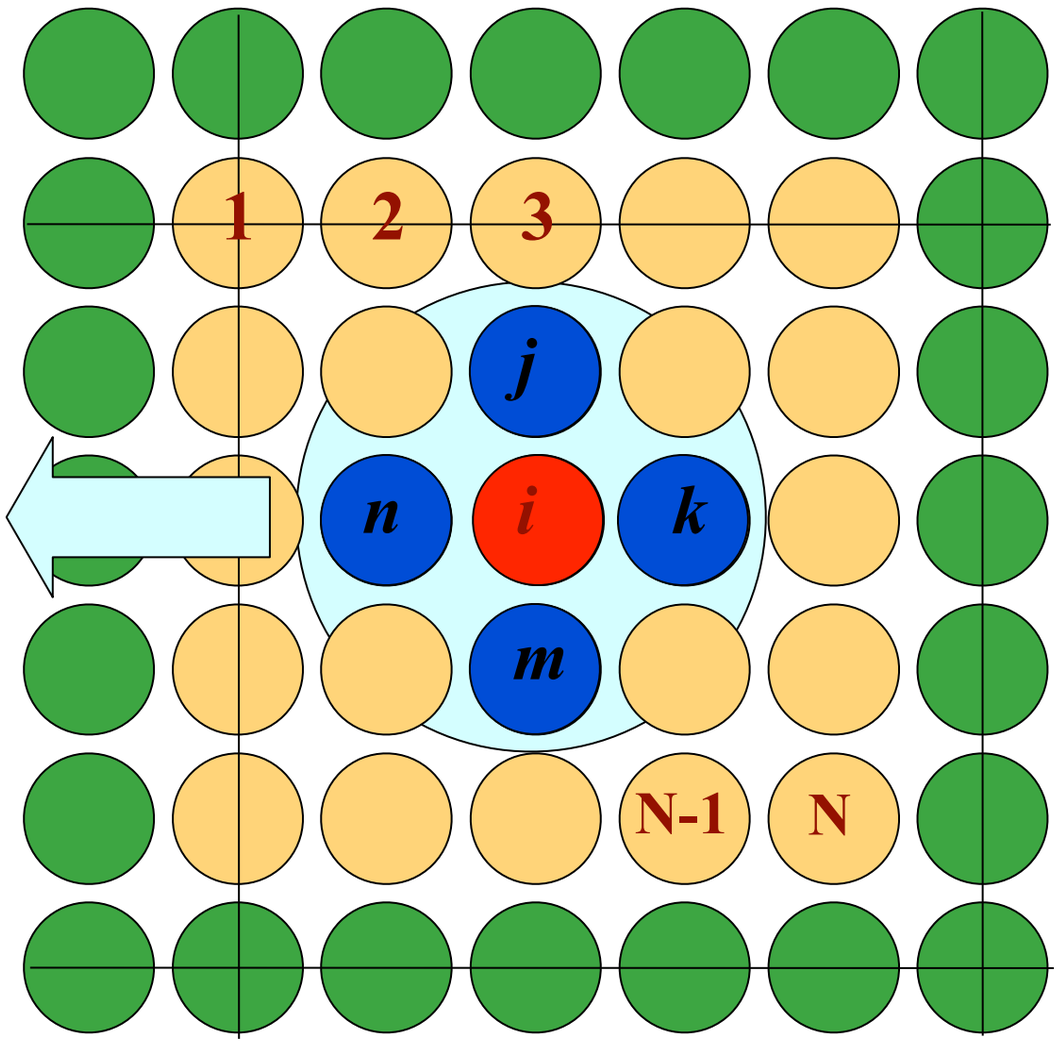
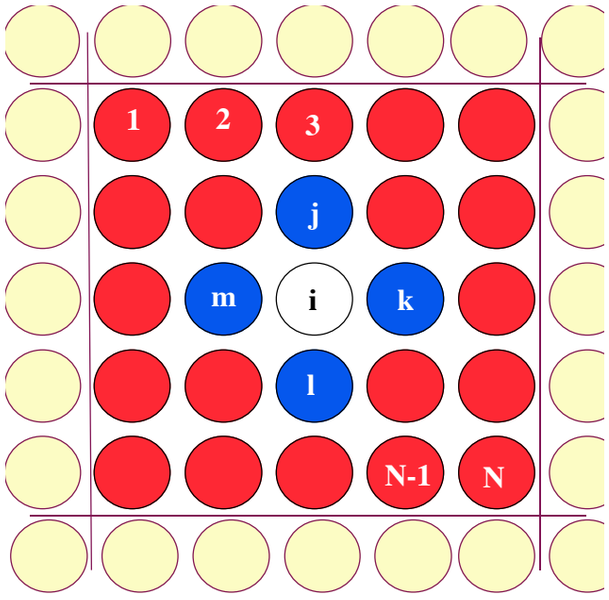
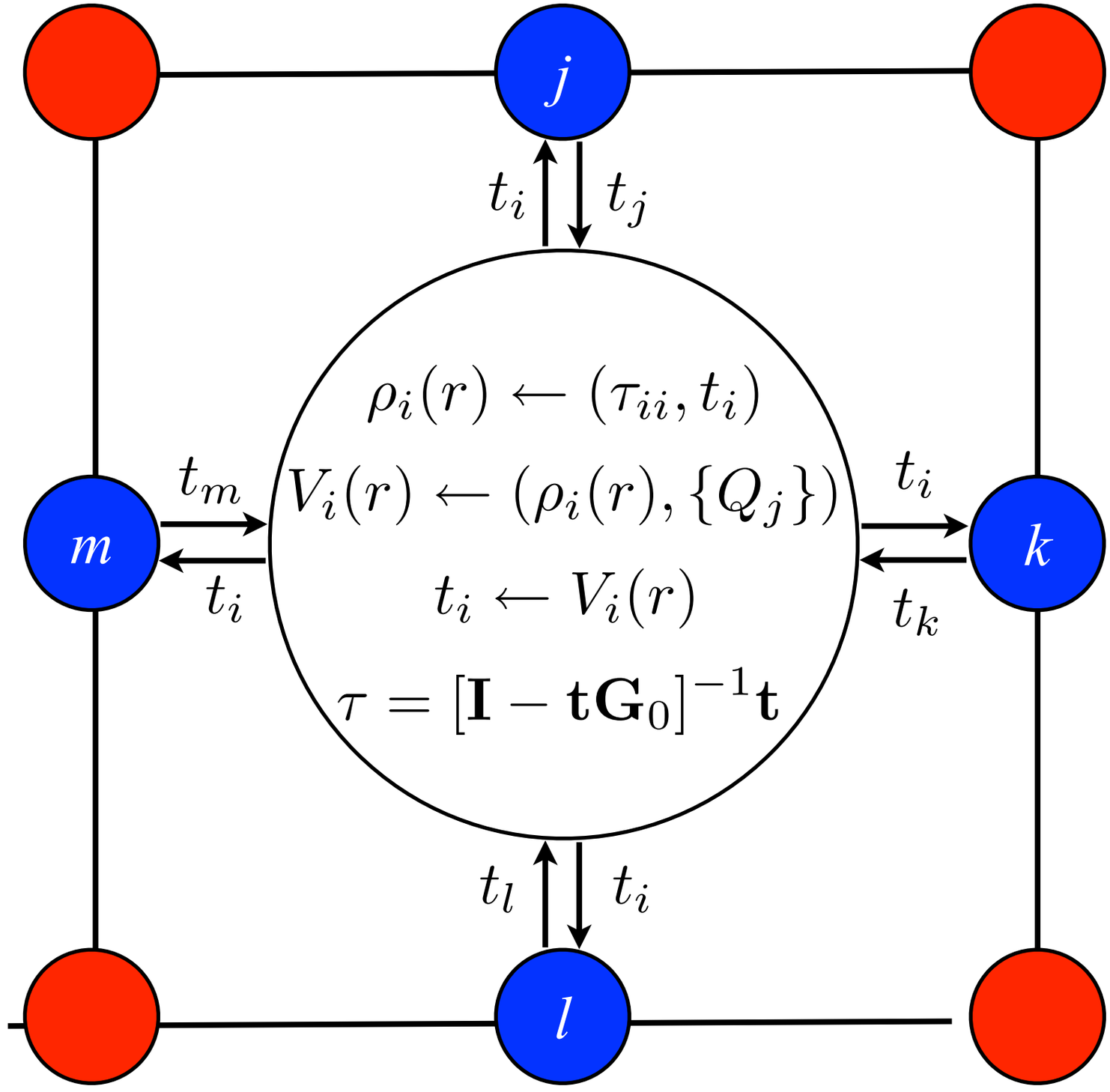




A parallel implementation and scaling of the LSMS method: perfectly scalable at high performance



- Need only block i of τ
- $\left(\begin{array}{c|c} A & B \\ \hline C & D \end{array}\right)^{-1} = \left(\begin{array}{c|c} (A - BD^{-1}C)^{-1} & * \\ \hline * & * \end{array}\right)$
- Calculation dominated by ZGEMM
- Sustained performance similar to Linpack



Block Inverse

The LSMS method requires only the first diagonal block of the inverse matrix

Recursively apply

$$\left(\begin{array}{c|c} A & B \\ \hline C & D \end{array}\right)^{-1} = \left(\begin{array}{c|c} (A - BD^{-1}C)^{-1} & * \\ \hline * & * \end{array}\right)$$

The block size is a performance tuning parameter:

- Smaller block size: less work
- Larger block size: higher performance of matrix-matrix multiply

Performance of LSMS dominated by double complex matrix matrix multiplication

`ZGEMM`

Thermodynamic Observables

- **Thermodynamic observables are related to the partition function Z and free energy F**

$$Z(\beta) = \sum_{\{\xi_i\}} e^{-\beta H(\{\xi_i\})}$$

$$F(T) = -k_B T \ln Z(1/k_B T)$$

- **If we can calculate Z(β) thermodynamic observables can be calculated as logarithmic derivatives.**

Wang-Landau Method

- Conventional Monte Carlo methods calculate expectation values by sampling with a weight given by the Bolzmann distribution
- In the Wang-Landau Method we rewrite the partition function in terms of the density of states which is calculated by this algorithm

$$Z(\beta) = \sum_{\{\xi_i\}} e^{-\beta H(\{\xi_i\})} = g_0 \int g(E) e^{-\beta E} dE$$

- To derive an algorithm to estimate g(E) we note that states are randomly generated with a probability proportional to 1/g(E) each energy interval is visited with the same frequency (flat histogram)

Metropolis Method

Metropolis et al, JCP **21**, 1087 (1953)

$$Z = \int e^{-E[\mathbf{x}]/k_{\mathrm{B}}T} d\mathbf{x}$$

Compute partition function and other averages with configurations that are weighted with a Boltzmann factor

Sample configuration where Boltz-mann factor is large.

1. Select configuration

$$E_i = E[\mathbf{x}_i]$$

2. Modify configuration (move)

$$E_f = E[\mathbf{x}_f]$$

3. Accept move with probability

$$A_{i\to f} = \min\{1, e^{\beta(E_i - E_f)}\}$$

Wand-Landau Method

Wang and Landau, PRL **86**, 2050 (2001)

$$Z = \int W(E) e^{-E/k_{\mathrm{B}}T} dE$$

If configurations are accepted with probability $1/W$ all energies are visited equally (flat histogram)

1. Begin with prior estimate, eg $W'(E) = 1$

2. Propose move, accepted with probability

$$A_{i\to f} = \min\{1, W'(E_i)/W'(E_f)\}$$

3. If move accepted increase DOS

$$W'(E_f) \to W'(E_f) \times f \qquad f > 1$$

4. Iterate 2 & 3 until histogram is flat

5. Reduce $f \to f = \sqrt{f}$ and go back to 1

Metropolis Method

$$Z = \int e^{-E[\mathbf{x}]/k_{\mathrm{B}}T} d\mathbf{x}$$

Sample configuration space with probability

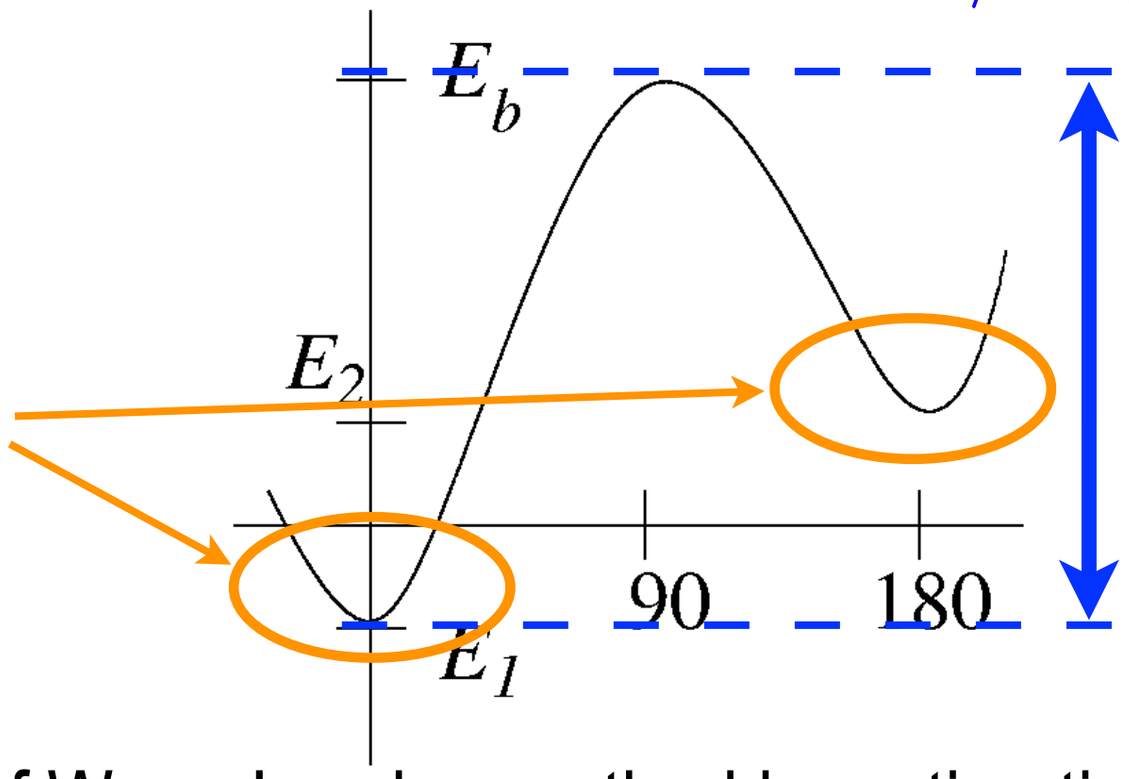
$$e^{-E[\mathbf{x}]/k_{\mathrm{B}}T}$$

Samples mainly regions around energy minima

Wand-Landau Method

$$Z = \int W(E) e^{-E/k_{\mathrm{B}}T} dE$$

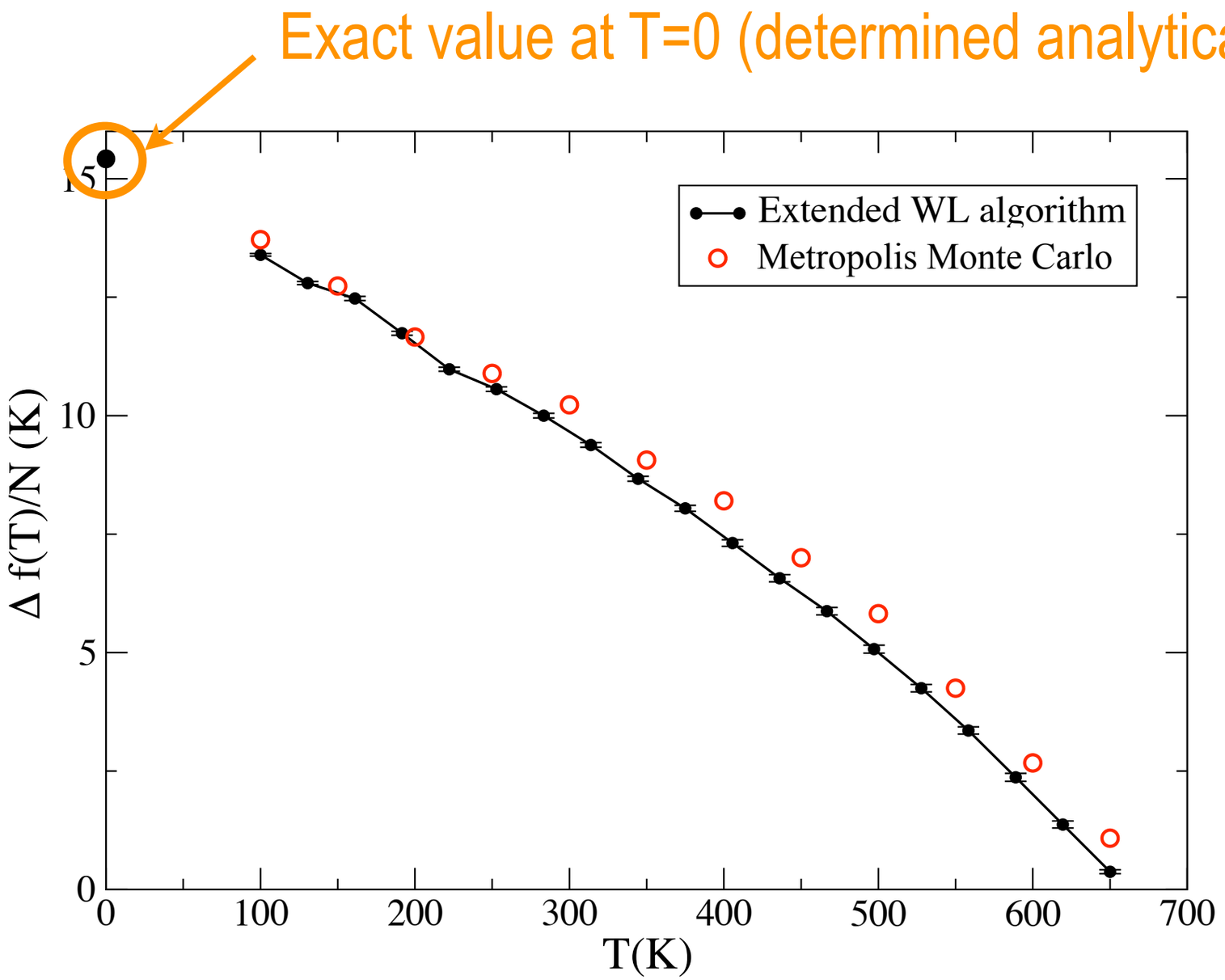
$$1/W(E[\mathbf{x}])$$



Samples all energies equally -

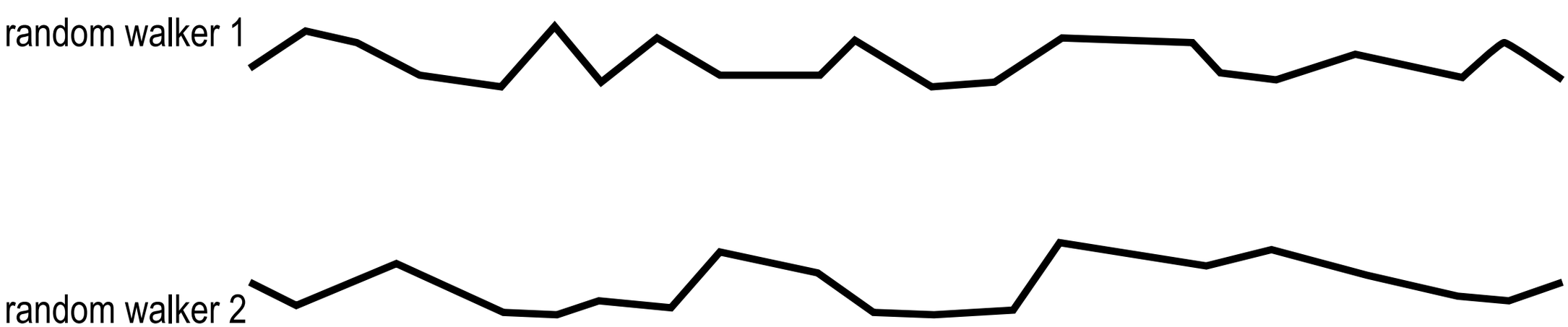
Check validity of Wang-Landau method by estimating barrier hight from Metropolis MC and fitting to $KV \sin^2 \Theta$

Quantitative test for bulk model of FePt



Not quite embarrassingly parallel

Metropolis MC acceptance: $$A_{i \to f} = \min\{1, e^{\beta(E_i - E_f)}\}$$



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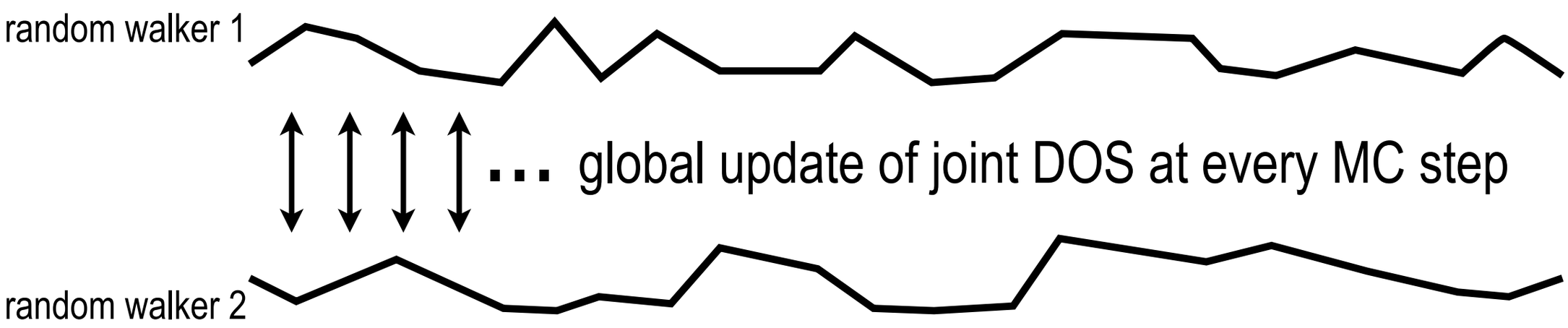

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Test problem: *ab initio* simulation of magnetism in Fe

- Robust local magnetic moment
  - Well reproduced by LDA calculation
- Ferromagnetic transition temperature T_c=1050K
  - LDA + mean field on magnetic fluctuations overestimates T_c
  - Adding Onsager cavity field corrections improves results
  - What would a full *ab initio* Monte Carlo simulation give for T_c?

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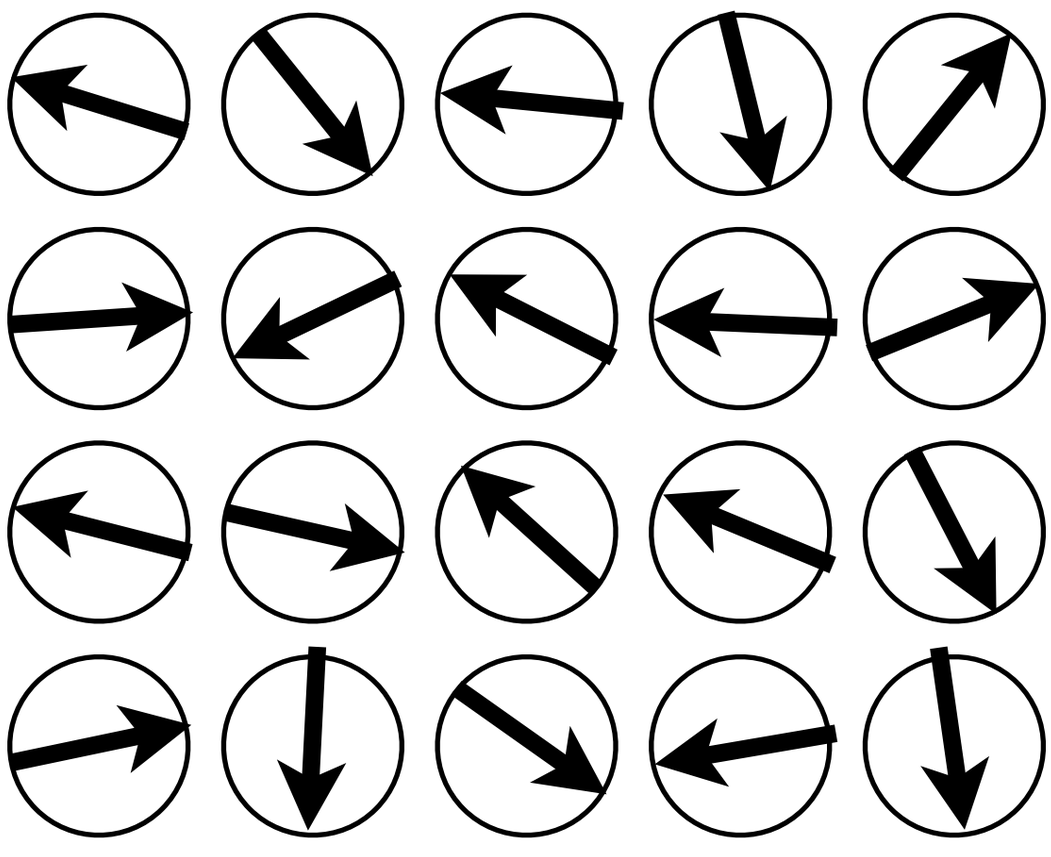
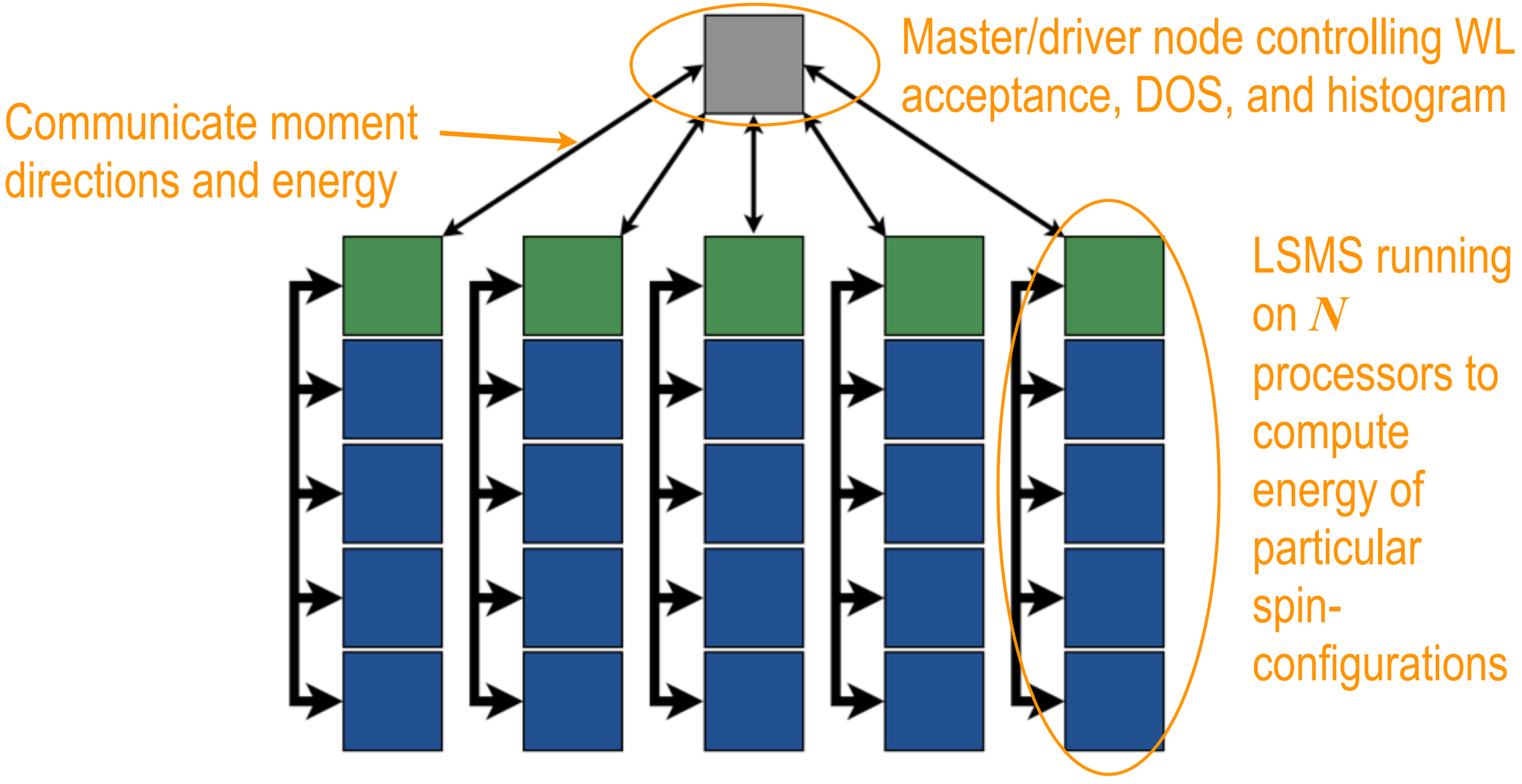


Excellent test for WL-LSMS method:

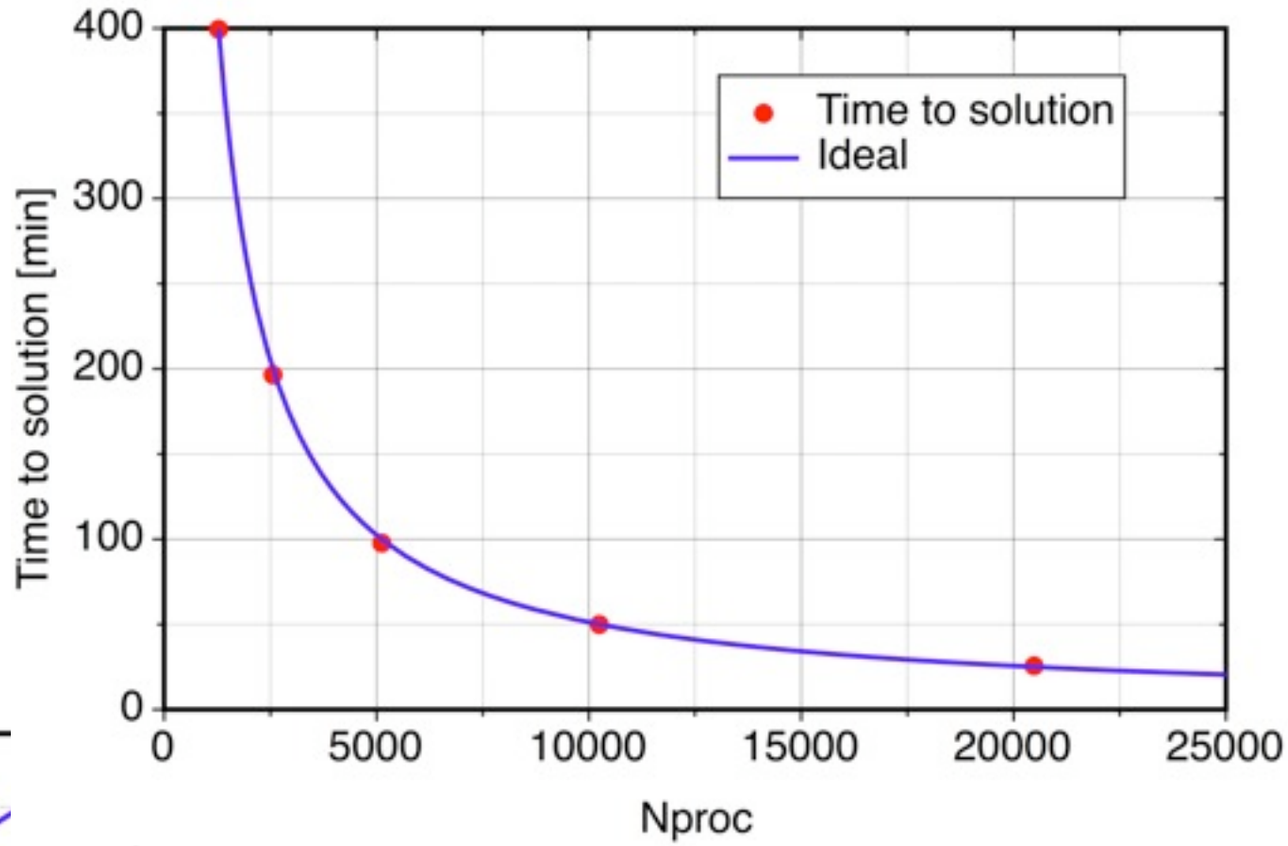
- Bulk Fe with N atoms (hundreds) in unit cell
- Sample non-collinear magnetic moment configurations $\{\vec{m}_1, \vec{m}_2, \ldots, \vec{m}_N\}$
- Compute energy with LSMS method using (LSDA) and frozen potential approx.
- Accumulate density of states with extended Wang Landau algorithm

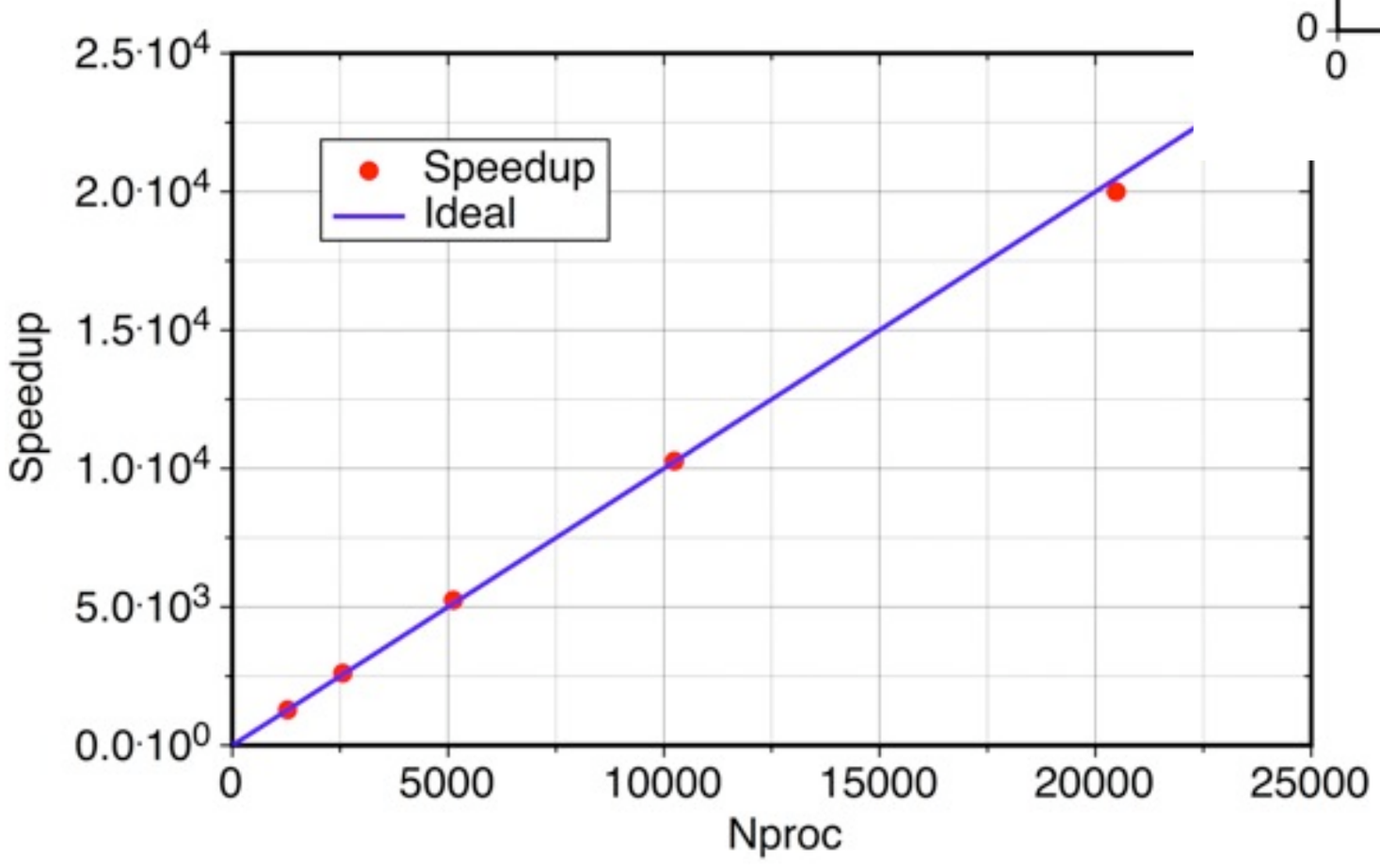
Organization of the WL-LSMS code using a master-slave approach



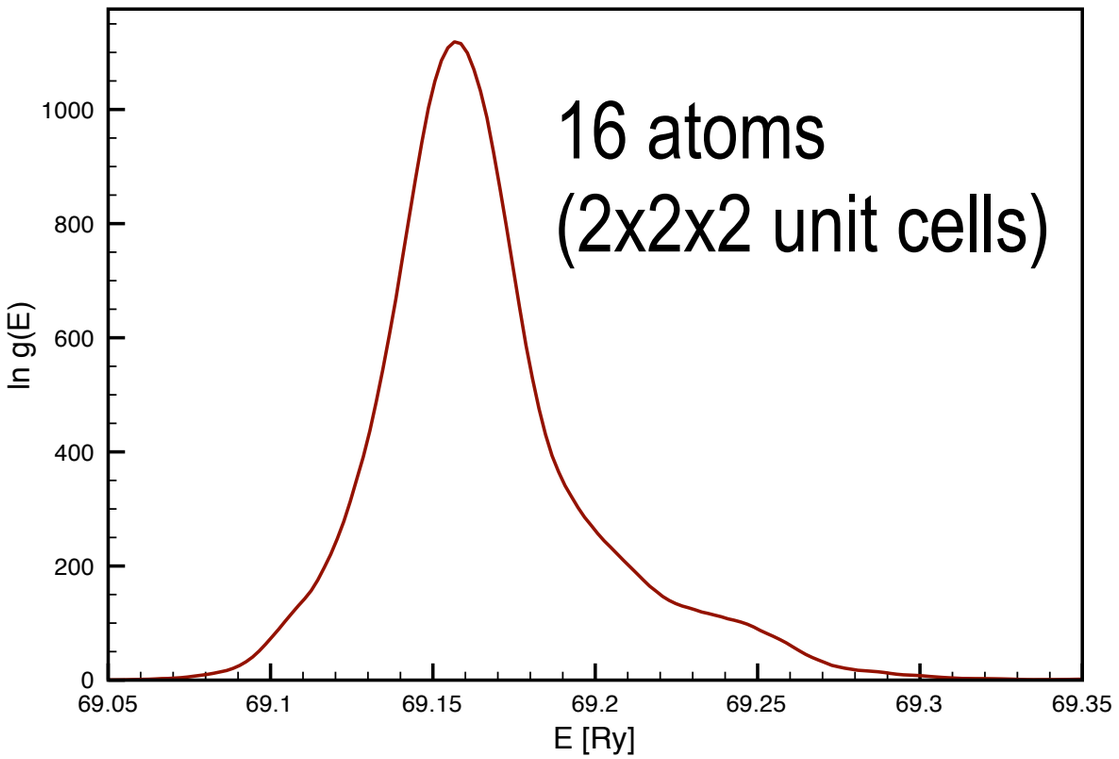
Scaling test with WL-LSMS code

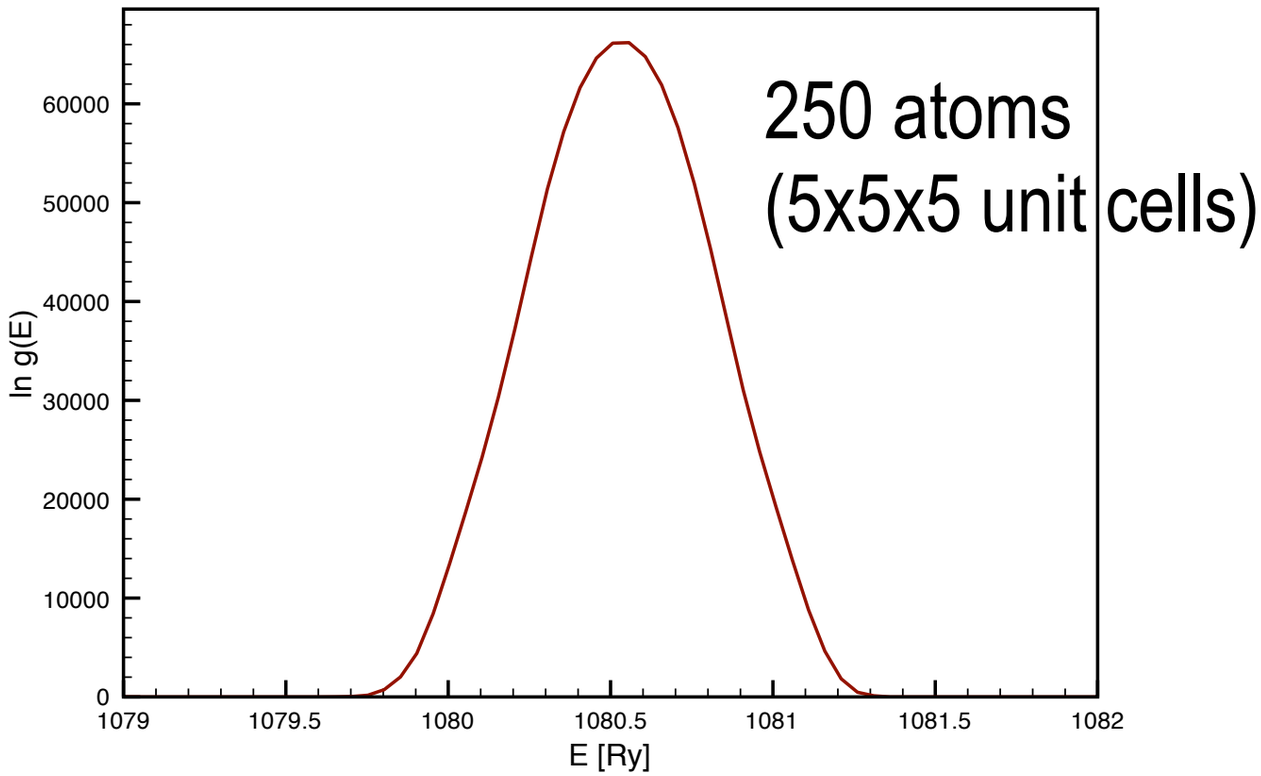
N = 128 Fe atoms and 800 Monte Carlo samples running on Cray XT4 (Jaguar)





What it takes to compute a converged DOS on a Cray XT5





	16 atoms	250 atoms
WL walkers	200	400
total cores	3,208	100,008
WL samples	23,200	590,000
CPU-core hours	12,300	4,885,720

Just 2 days!!!

Calculation of thermodynamic quantities

- Note: g(E) as calculated by the algorithm described has an unknown normalization factor

$$Z = g_0 Z'; \;\; Z'(\beta) = \int g(E) e^{-\beta E} dE$$

- Free Energy:

$$F = -k_B T \ln Z = k_B T \ln Z' - k_B T \ln g_0$$

- Internal Energy

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} = \frac{1}{Z'} \int E g(E) e^{-\beta E} dE$$

- Specific Heat

$$c = \frac{\partial U}{\partial T}$$

- Entropy

$$S = -\frac{\partial F}{\partial T} = \frac{1}{Z'T} \int E g(E) e^{-\beta E} dE + k_B \ln Z' + k_B \ln g_0$$

With the DOS we have the partition function and everything else!

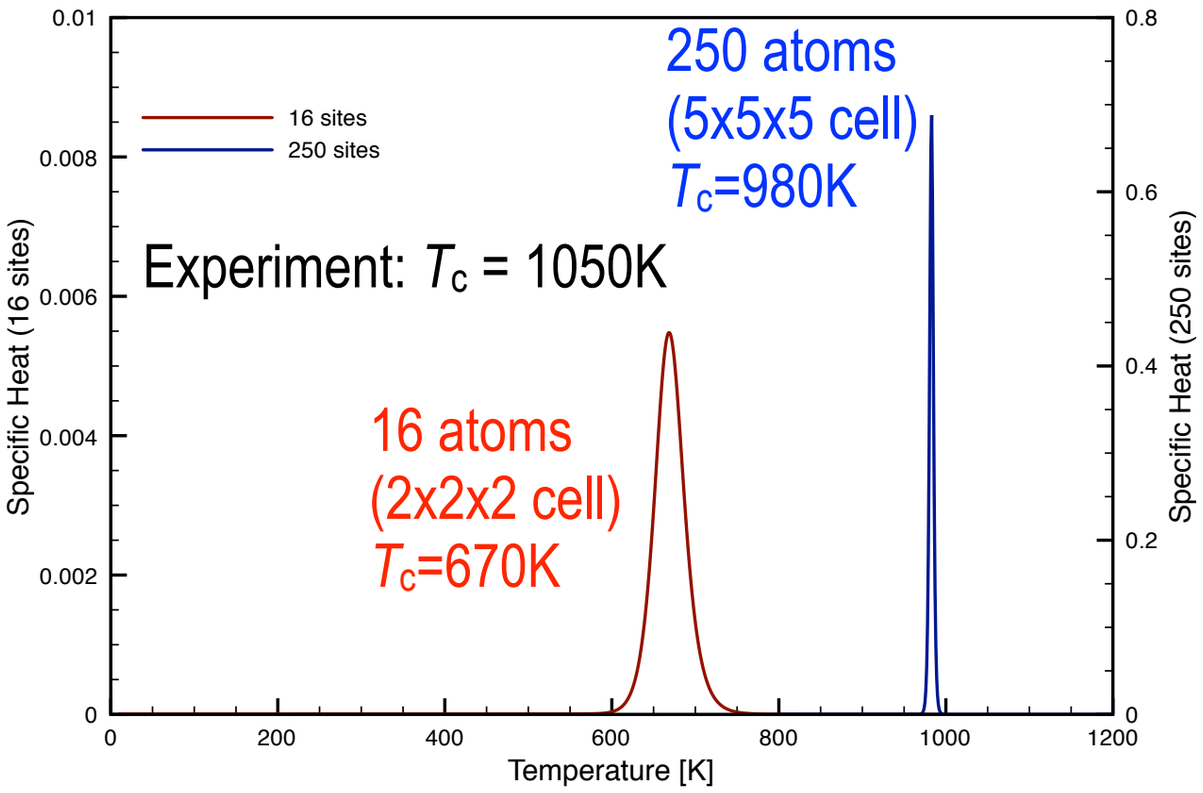
$$Z'(T) = g_0 \int g(E) e^{-E/(k_B T)} dE = g_0 Z$$

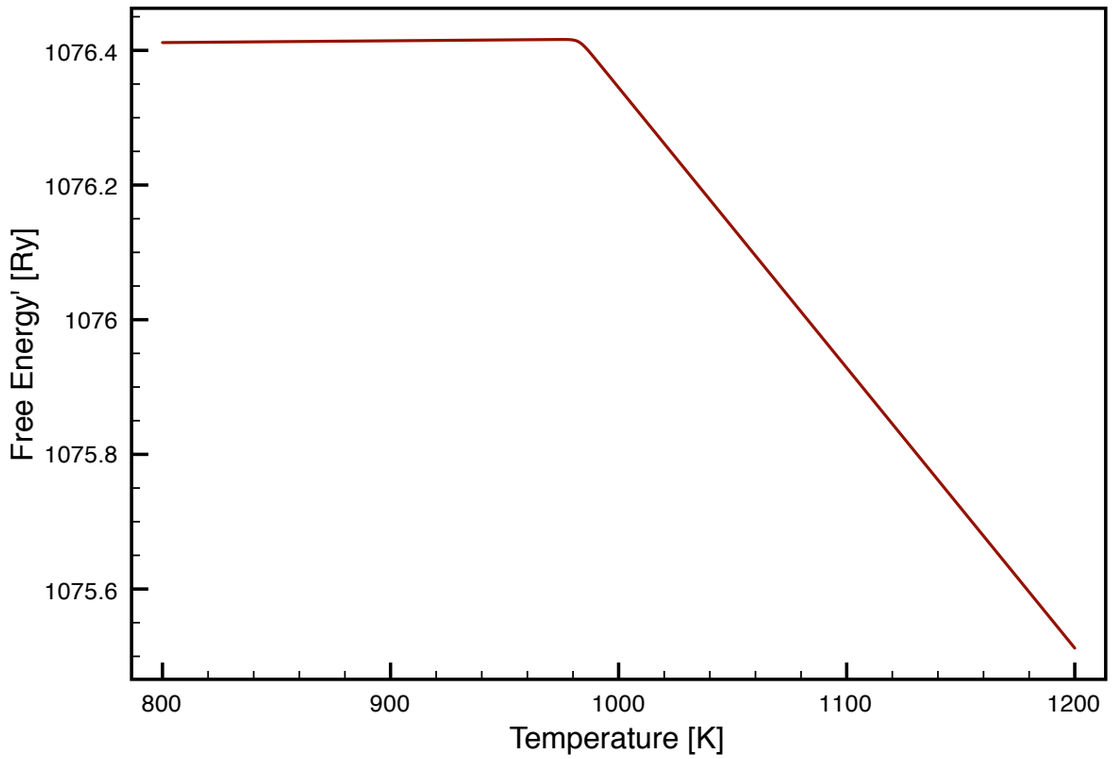
unknown normalization factor

$$F = -k_B T \ln Z \qquad S = -\frac{\partial F}{\partial T}$$

$$U = F + TS = F' + TS'$$

Specific heat $C = \frac{\partial U}{\partial T}$





WL simulations for cubic Heisenberg model

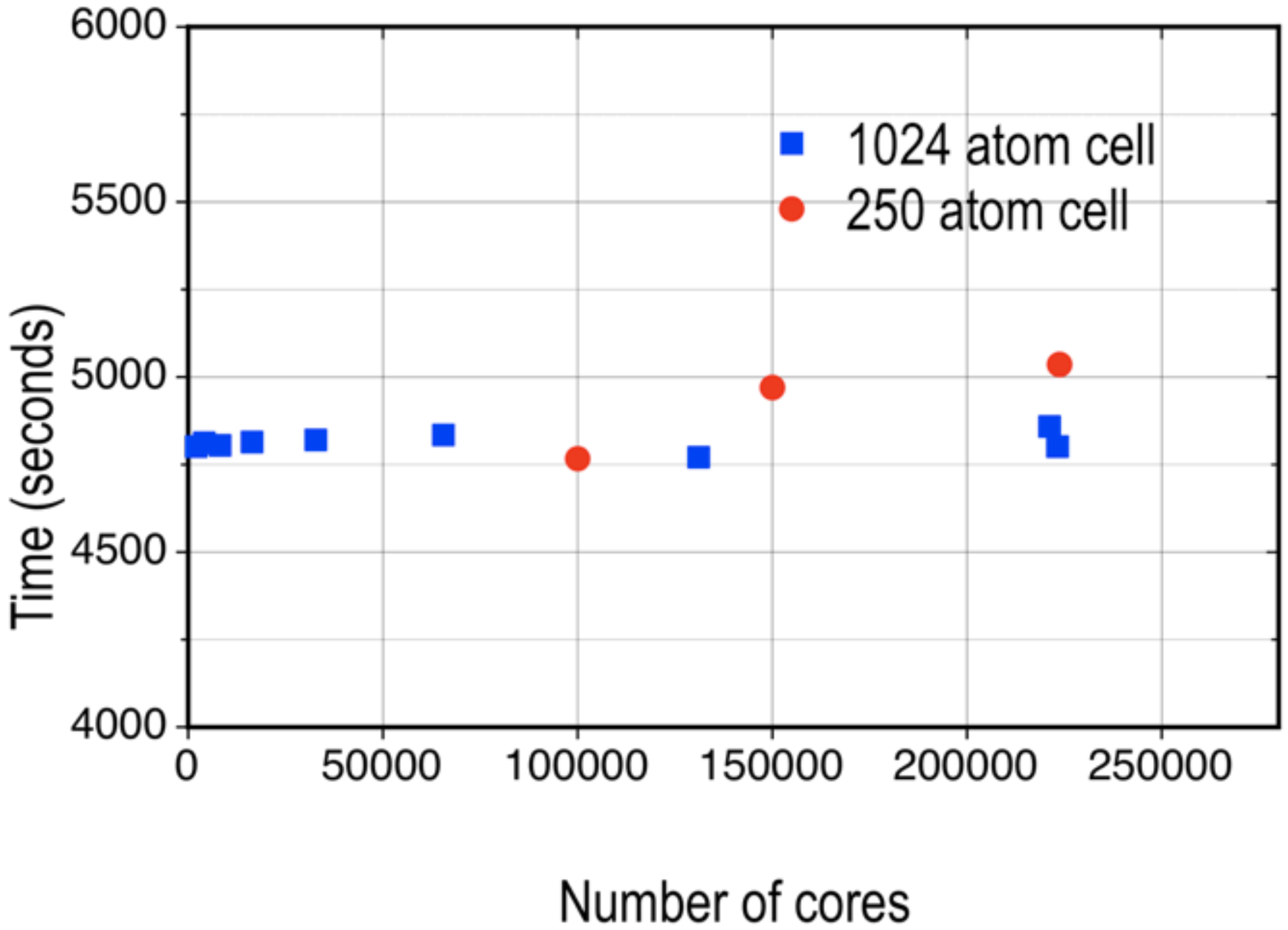
$$E(\{\vec{S}_i\}) = \sum_{i \neq j} J \vec{S}_i \vec{S}_j$$

L	T_c (J)
2	**1.105**
3	1.340
4	1.370
5	**1.420**
6	1.465
7	1.460
8	1.490
∞	1.44

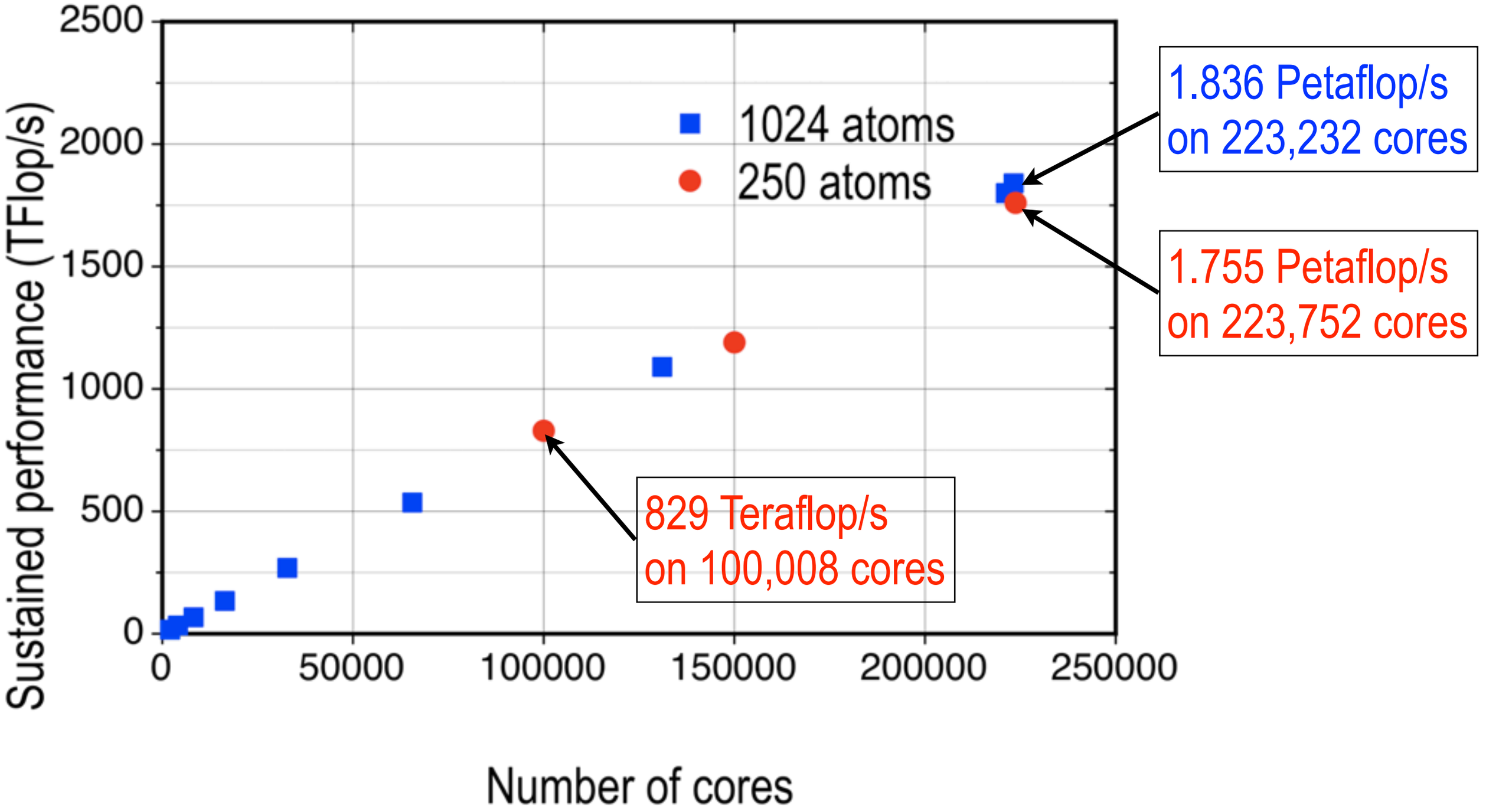
Cray XT5 portion of Jaguar @ NCCS

Peak: 2.331 PF/s
Hex-Core AMD
Freq.: 2.6 GHz
224,162 cores
Memory: 300 TB
For more details, go to
www.nccs.gov

Weak scaling on Cray XT5 (Jaguar)



Sustained performance of WL-LSMS on Cray XT5



Conclusions

- It is now possible to compute free energies in nanoscale systems
  - using ab initio methods based on Density Functional Theory
  - fully taking into account entropy
- First ab initio calculation of ferromagnetic transition temperature in Fe that does not rely on mean-field approximation
  - LDA answer based on WL-LSMS underestimate Tc by (only) 7%
- WL-LSMS code sustained 1.836 Petaflop/s (double precision) on 223,232 cores of the Cray XT5 system Jaguar