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# QMC WORKSHOP 2025 WORKFLOW FOR SOLID-STATE CALCULATIONS

**CPSFM** | Center for Predictive Simulation  
of Functional Materials



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July 15, 2025

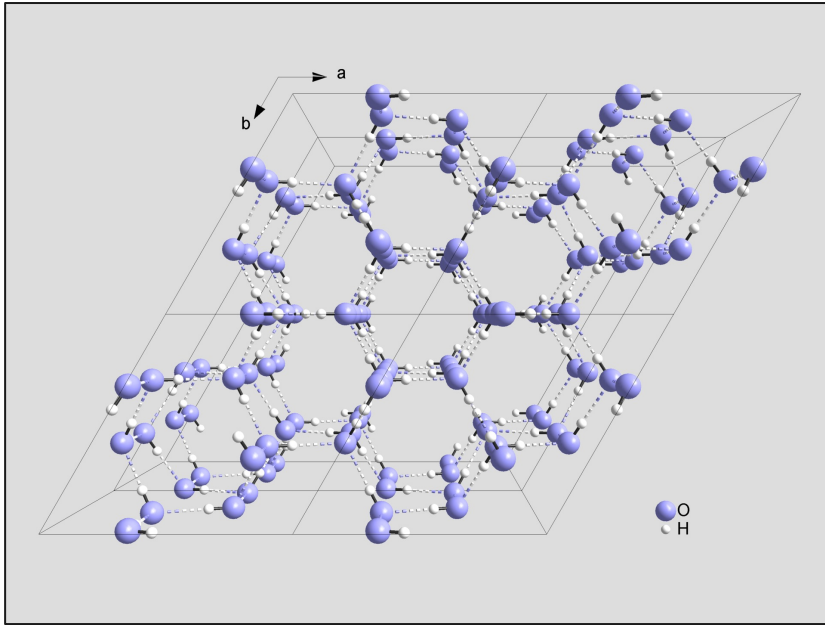
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# INTRODUCTION

# MODELLING MATERIALS



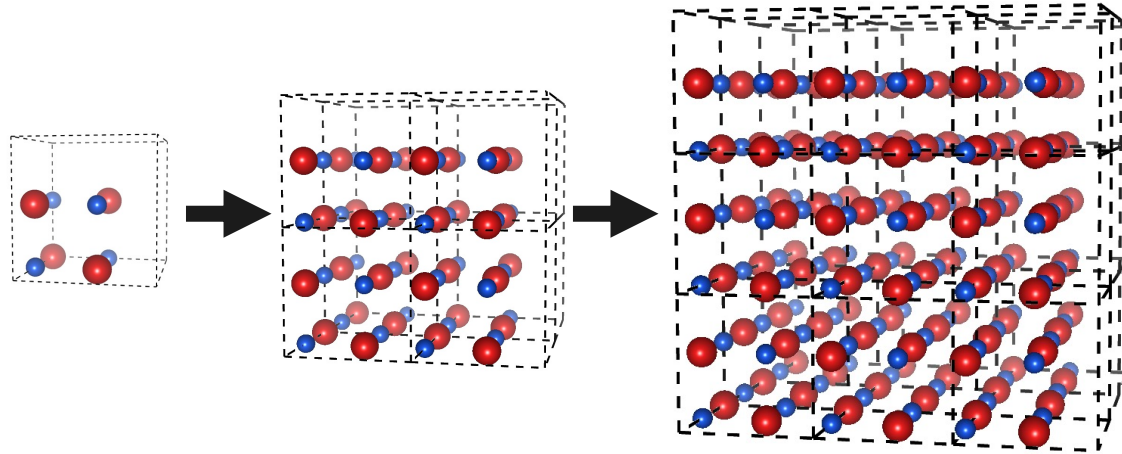
- In contrast to molecules, we are trying to determine properties of macroscopic objects.
- Micron or larger,  $\sim 10^{23}$  atoms.
- Consider an idealized scenario, the “thermodynamic limit” ( $L=\infty$ ,  $N=\infty$ )
- The challenge is how to predict these properties in the “thermodynamic limit” with only 10-1000 atoms.



# OVERVIEW

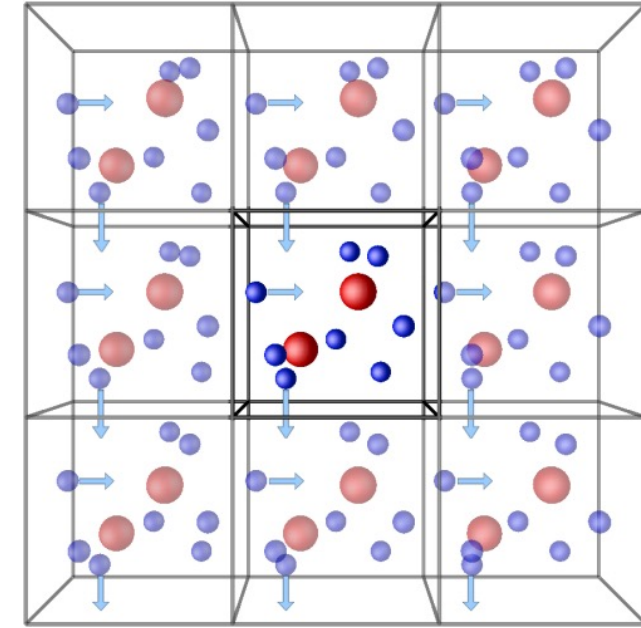
- Posing the problem—Boundary Conditions.
- Finite-size effects in DFT.
- One and two-body finite size effects for QMC.
- QMC wave functions for solids.
- Overview of Lab.

# PERIODIC BOUNDARY CONDITIONS



**Open boundary**

**VS**



**Periodic Boundary**

- For molecules, system is really straightforward to write down.
- If we try to build up a solid state system (left) using the same techniques, we introduce surfaces and surface physics. This is NOT reflective of bulk properties.
- Imagine instead a finite system, but instead of being surrounded by vacuum, we have an infinite lattice of copies of our unit cell.
- No surface. Atoms pass out of the box, they come in from the other side. They “wrap around”.
- This is what we mean by “periodic boundary conditions”. Converges way faster to TDL.



# FINITE-SIZE EFFECTS



## WHAT IS A “FINITE-SIZE EFFECT”?

- For otherwise converged calculations, a “finite-size effect” is any deviation from the infinite system answer (in almost all cases, the “right” answer).
- Examples: energy/cell, pressure, electron density, etc.
- If you plot a quantity vs. system size and see that it changes, it’s likely a finite-size effect that you need to control for.



# DFT AND BLOCH'S THEOREM

**Bloch's theorem**—For electrons in a perfect crystal, there is a **basis** of wave functions with the following two properties:

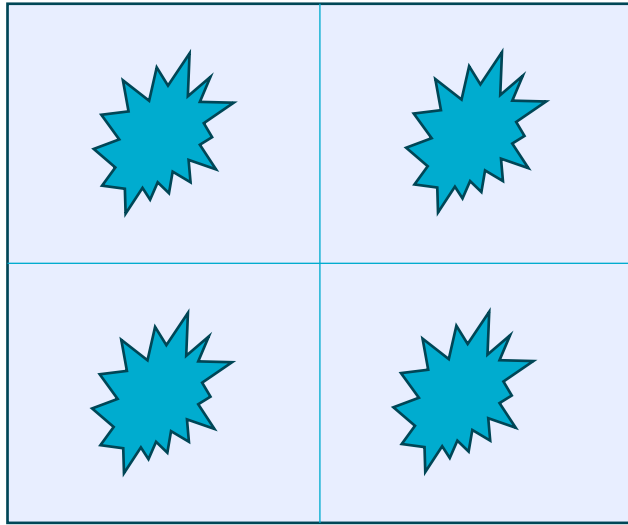
- each of these wave functions is an energy eigenstate,
- each of these wave functions is a Bloch state, meaning that this wave function  $\psi$  can be written in the form  $\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r})$ , where  $u(\mathbf{r})$  has the same periodicity as the atomic structure of the crystal, such that  $u_{\mathbf{k}}(\mathbf{x}) = u_{\mathbf{k}}(\mathbf{x} + \mathbf{n} \cdot \mathbf{a})$ .

$$\hat{H}_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) = \left[ \frac{\hbar^2}{2m} (-i\nabla + \mathbf{k})^2 + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})$$

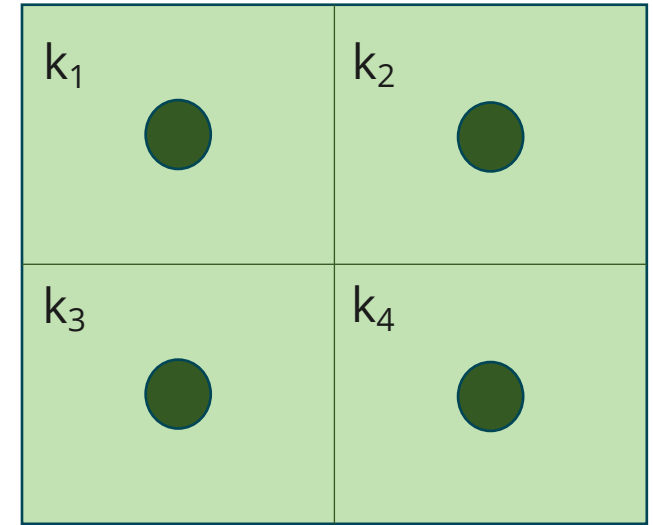
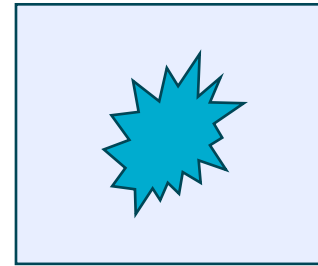
- Kohn-Sham DFT is a single-particle theory, so Bloch's theorem holds.
- Cool, but what does this mean in practice?
- \*\*STRONGLY RECOMMEND READING ASHCROFT & MERMIN OR RICHARD MARTIN'S "ELECTRONIC STRUCTURE THEORY" TO LOCK THIS DOWN IN YOUR BRAIN\*\*\*



# BLOCH'S THEOREM



One-to-one Mapping



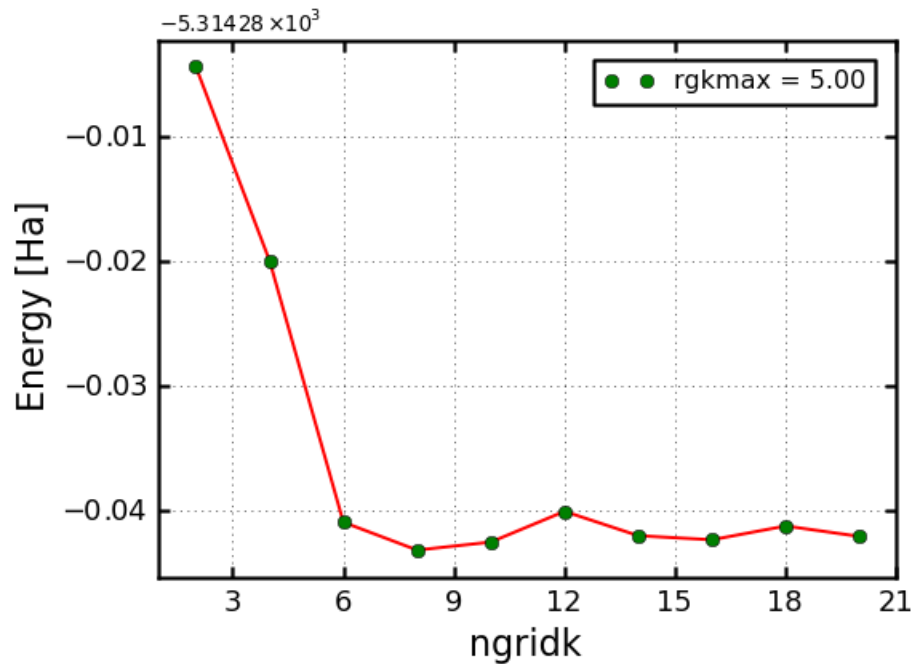
$$\hat{H}\psi(\mathbf{r}) = \left( -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \right) \psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$

$$\hat{H}_{\mathbf{k}}u_{\mathbf{k}}(\mathbf{r}) = \left[ \frac{\hbar^2}{2m}(-i\nabla + \mathbf{k})^2 + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}u_{\mathbf{k}}(\mathbf{r})$$

- One-to-one mapping between the two pictures.
- Instead of solving Schrodinger's equation for the whole cell (left), I can solve it the primitive cell at over a set of k-points.
- Significantly cheaper, because we work with way fewer orbitals in the primitive cell.
- For semi-local functionals (LDA, PBE), there is no coupling between k-points, and so I can do these calculations in parallel.



# FINITE SIZE EFFECTS IN DFT (ONE-BODY)

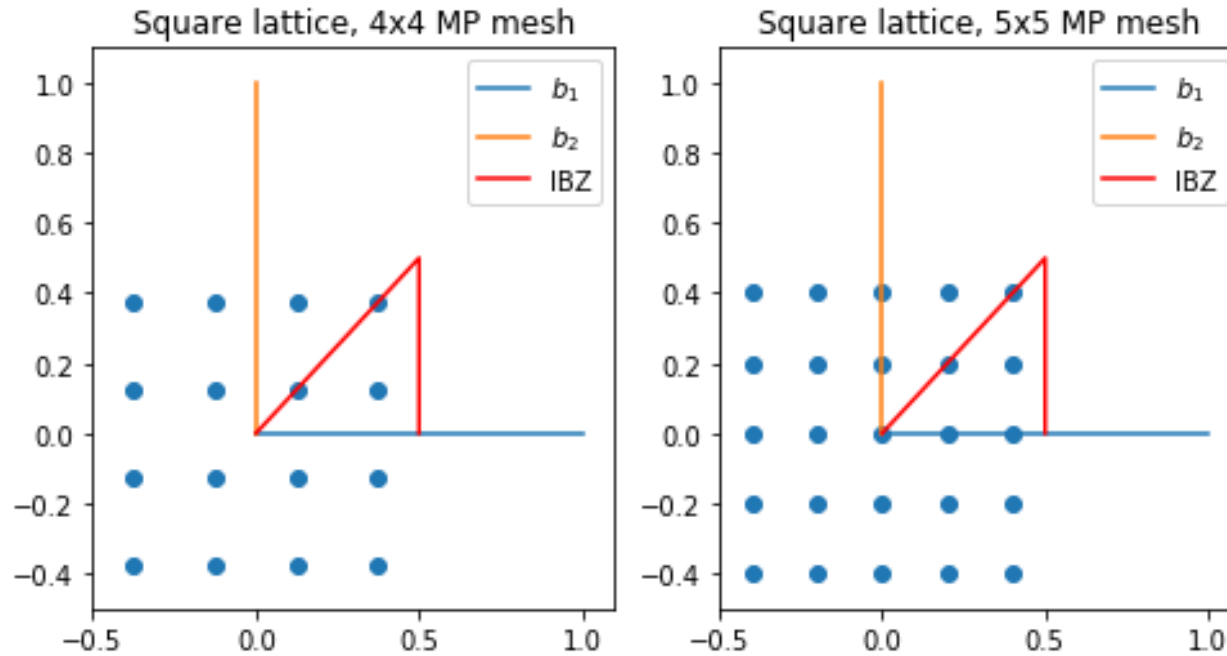


<http://exciting.wikidot.com/lithium-simple-convergence-tests>

- (Left) Convergence study of total energy w.r.t. k-point grid size (ngridk x ngridk x ngridk) for lithium.
- Once the density is converged (SCF step), there are many quantities that are expressible as  $I = \int d^3\mathbf{k} f(\mathbf{k})$ . The finite-size error here is an integration error caused by using a finite resolution grid. This can be fixed by using larger (finer) k-point grids.
- In effect, the standard SCF and NSCF convergence procedures you are already accustomed to completely eliminate electronic finite-size effects in DFT.



# FINAL NOTE ON BRILLOUIN ZONE INTEGRATION



<https://sites.psu.edu/dftap/2019/02/01/shifting-of-kpoints-in-hexagonal-lattices/>

- We can use space group symmetries to cut down the number of k-points we need to consider.
- The region outlined in red is the “irreducible Brillouin zone”. By symmetry, these are the only “unique” or irreducible k-points we need to describe to evaluate any integral over the entire Brillouin zone.
- If enabled, DFT codes will list these inequivalent k-points with “weights”, basically how many other k-points are related to it by symmetry. More on this coming soon.

# ONE-BODY FINITE SIZE EFFECTS IN QMC

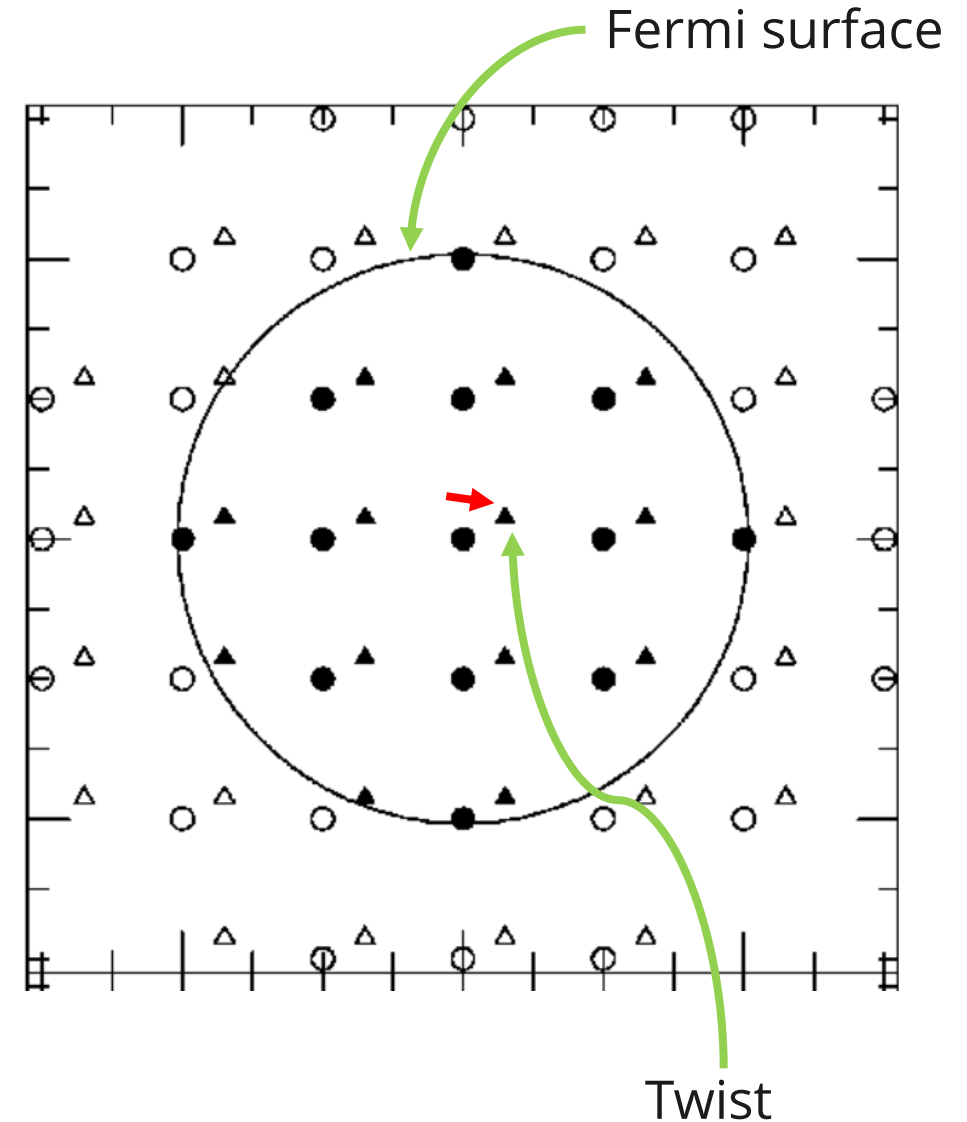
- Many-body wave functions spoil the power of Bloch's theorem, but we know that there are sizeable one-body finite size effects present, just from the mean field level.
- We will use a wave function ansatz as follows:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2 + \mathbf{L}, \dots, \mathbf{r}_N) = e^{i\mathbf{L} \cdot \mathbf{k}} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

- We define “twist-averaged” observables as follows:

$$\langle \hat{A} \rangle_{TABC} = \frac{\int d\mathbf{k} \int d\mathbf{R} \langle \Psi(\mathbf{R}, \mathbf{k}) | \hat{A} | \Psi(\mathbf{R}, \mathbf{k}) \rangle}{\int d\mathbf{k} \int d\mathbf{R} \langle \Psi(\mathbf{R}, \mathbf{k}) | \Psi(\mathbf{R}, \mathbf{k}) \rangle}$$

- Reduces finite size effects<sup>1</sup> (more on this later)
- Faster convergence to thermodynamic limit<sup>1</sup>



<sup>1</sup>Lin & Ceperley, PRE **64**, 016702 (2001)



## (CANONICAL) TWIST AVERAGING PROCEDURE

- Must apply TABC to all observables, not just energy!
- Note that the integral over the VMC/DMC random walk and twist vector is an average, and so can be discretely calculated like one.

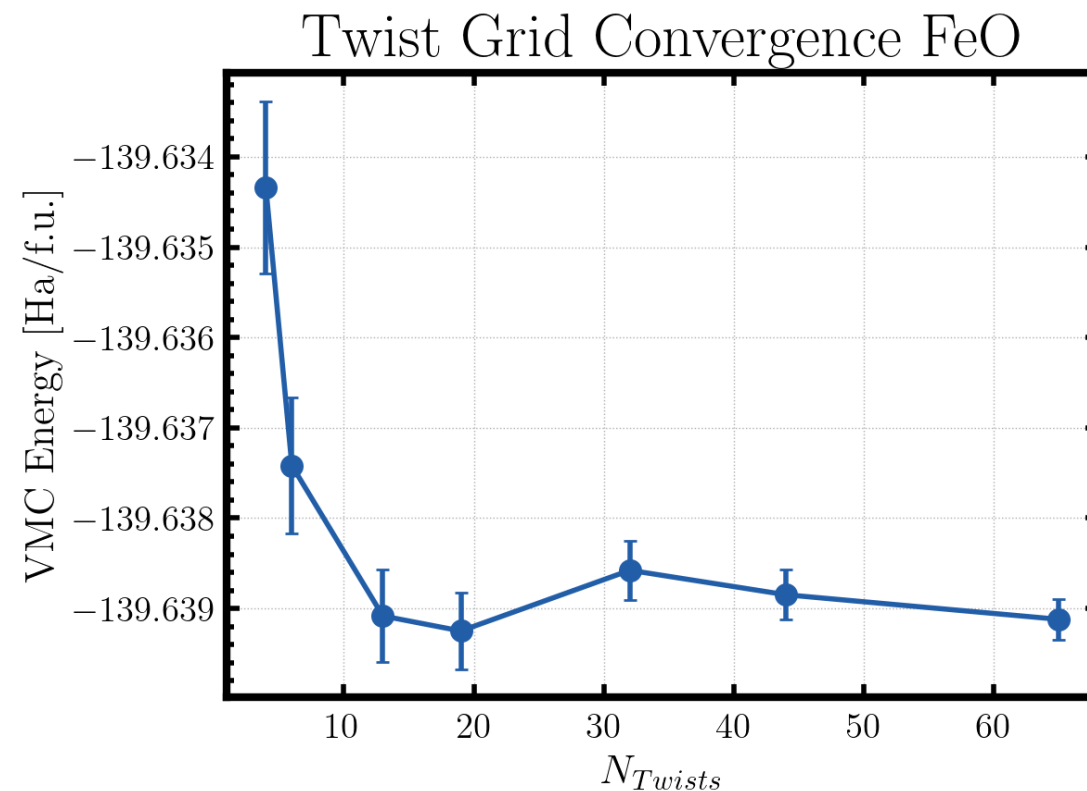
$$\langle \hat{A} \rangle_{TABC} = \sum_{\mathbf{k}} A(\mathbf{k}) w_{\mathbf{k}}$$

- $A(k)$  is the usual MC average of  $A$  for a particular twist
- $w_k$  is the corresponding weight (just like a  $k$ -point mesh in DFT). Above expression assumes sum of weights is 1. Alternatively, the weight is the multiplicity of that  $k$ -point divided by the total number of  $k$ points.



# TWIST-AVERAGED BOUNDARY CONDITIONS IN PRACTICE

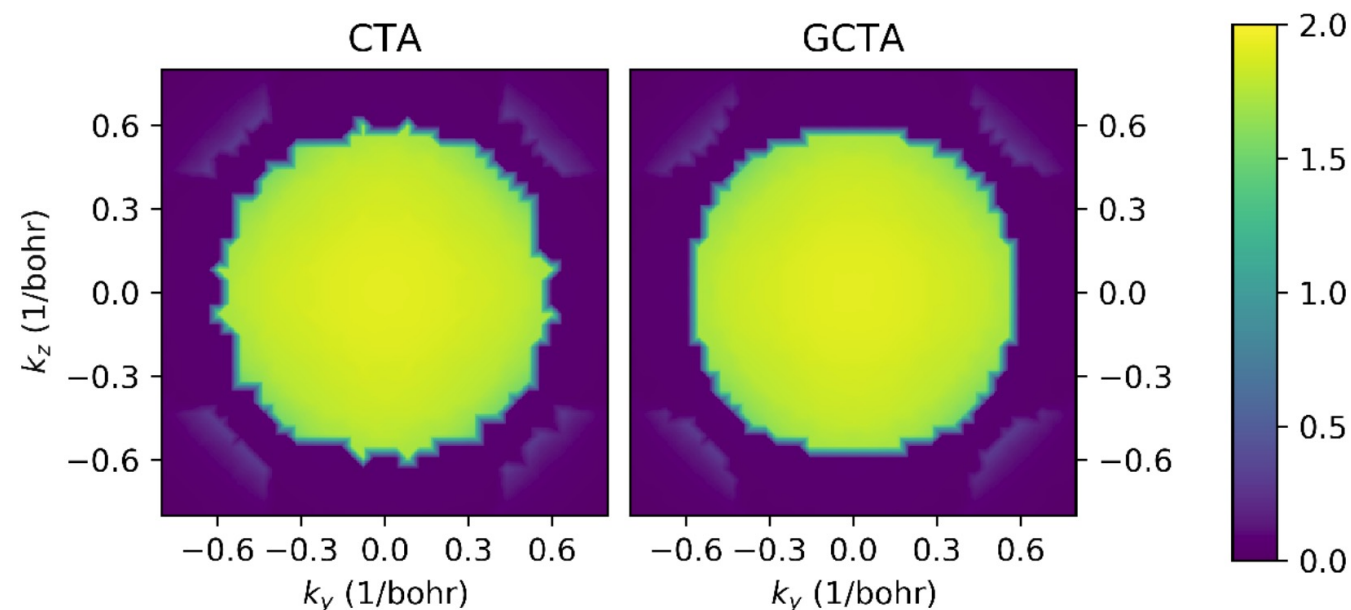
- Good news! Twists are independent. (Like in DFT)
- Error reduction  $\propto \frac{1}{\sqrt{N_{Twists}}}$
- How many twists are enough?
  - Depends on size, metallic vs insulating
  - You must check this yourself!
- Nexus can generate primitive cell k-point to supercell twist grid mapping for you







# GRAND-CANONICAL TWIST AVERAGING



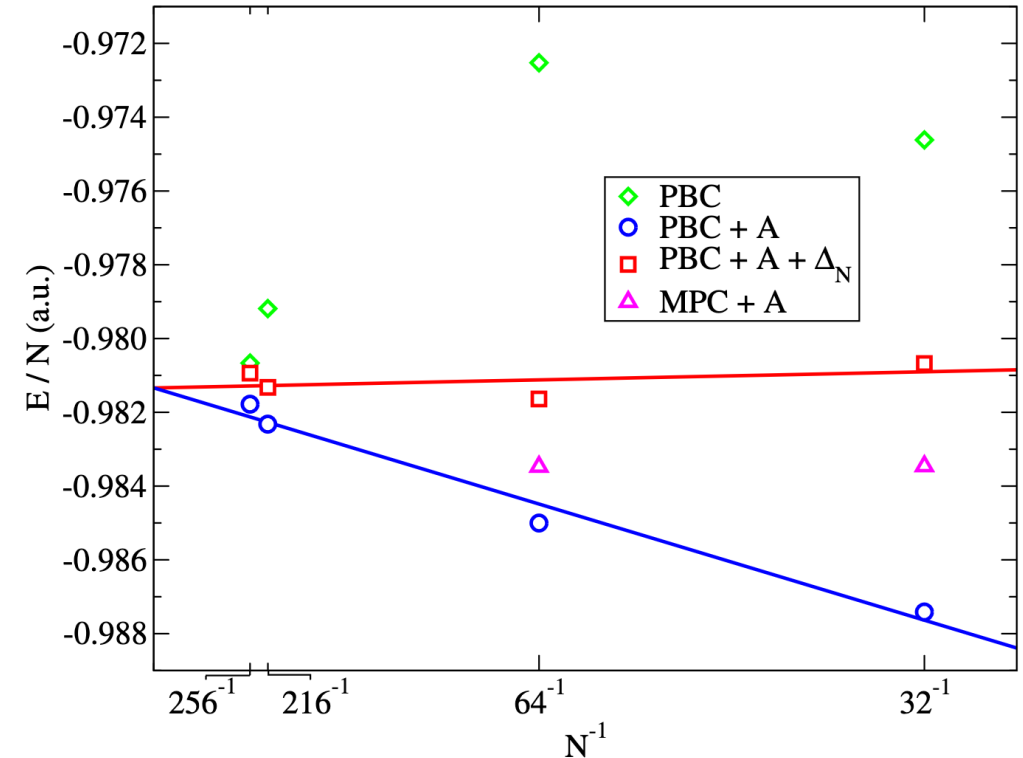
<sup>3</sup>Yang et al, PRB **101**, 165125 (2020)

- It's possible to do better than canonical twist averaging, both in terms of convergence rate w.r.t. twists, and with respect to biases.
- Canonical twist averaging occupies each with the actual number of electrons in the cell.
- Grand-canonical twist averaging sets the occupation based on the Fermi level.
- Does less violence to the Fermi surface. Try it out, find it in the manual.



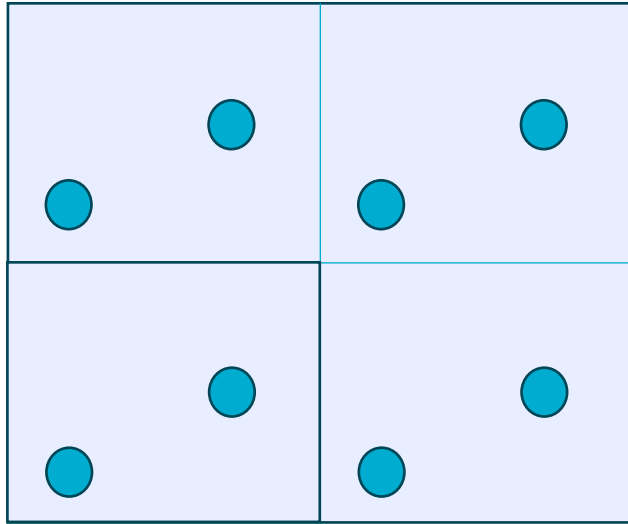
## ARE WE DONE?

- Unfortunately, no. This procedure mitigates single-particle finite size effects, but QMC is a many-body theory. So we have many-body finite size effects.
- Fortunately, the only ones we have to worry about for energetics are two-body finite size effects.
- Analytic results in 3D and ample empirical evidence confirms that the two-body finite size effect in bulk systems scales like  $1/N$  in the number of atoms.
- When in doubt, run several (twist averaged) supercells, fit to  $1/N$ , and extrapolate to  $1/N=0$  ( $N=\text{infinity}$ ).

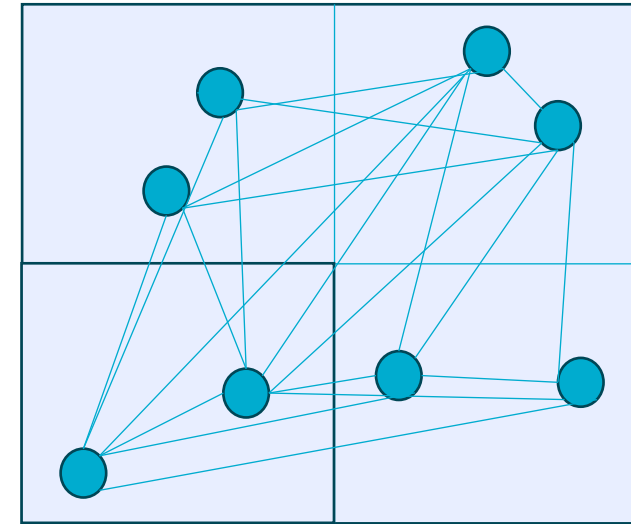


Diamond silicon energy/atom as a function of  $1/N$ . PBC+A is “twist averaging”. Difference between  $N=32$  and  $N=\text{infinity}$  is  $\sim 6\text{mHa/atom}$ , which is large.

## TWO-BODY FINITE SIZE EFFECTS



Bottom Left Cell in PBC's



Bottom Left Cell in 2x2 Supercell

- Electrons interact via a long range coulomb potential. This induces correlations between cells that cannot be captured in a Bloch picture. That is, they will redistribute according to the positions of other electrons in the supercell.
- Won't show up in density, but WILL show up in two-body correlation functions (  $g(r)$ ,  $S(k)$  ). These impact the energy significantly (as seen previously).



# HOW DO WE FIX TWO-BODY FINITE SIZE EFFECTS?

1. Extrapolate
  1. Already talked about.
  2. Gold standard, and easily validated. Will get really expensive.
2. Correct
  1. MPC (model periodic coulomb potential)
  2. Structure factor and Jastrow based corrections (Chiesa corrections)
  3. KZK (DFT Based)



# MODEL PERIODIC COULOMB POTENTIAL

- Ewald gets Hartree energy exact, but biases XC energy
- Model Periodic Coulomb (MPC) fixes that<sup>1</sup>:

$$V_{MPC} = \frac{1}{2} \sum_{i \neq j} f(r_i - r_j) + \sum_i \int_{\Omega} \rho(r) [V_e(r_i - r) - f(r_i - r)] dr - \frac{1}{2} \int_{\Omega} \rho(r) \rho(r') [V_e(r - r') - f(r - r')] dr dr'$$

Normal Coulomb inside

Modified potential outside

- Not a real FSC by itself, but sometimes used in that way
- See **MPC** potential for details

<sup>1</sup>Kent et al. PRB **59**, 1917 (1999)



# STRUCTURE FACTOR (CHIESA) CORRECTIONS

- **Gold standard**: Use structure factor<sup>1,2,3</sup>
- PE per particle is related to  $s(k)$  via:

$$V_N = \frac{2\pi}{\Omega} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} (s(\mathbf{k}) - 1)$$

- Correction is an integration error:

$$\Delta V_N = \frac{1}{4\pi^2} \int d\mathbf{k} \frac{s(\mathbf{k}) - 1}{k^2} - \frac{2\pi}{\Omega} \sum_{\mathbf{k} \neq 0} \frac{s_N(\mathbf{k}) - 1}{k^2}$$

- Use **SkAll** + qmcfinitesize in postprocessing

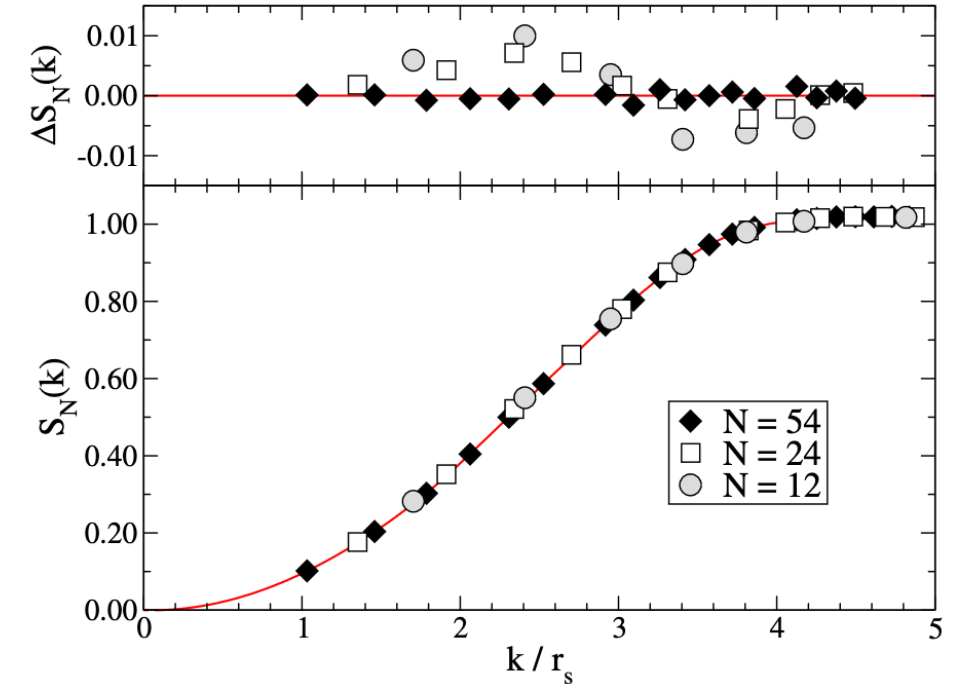


FIG. 1 (color online). Lower panel: static structure factor for the electron gas at  $r_s = 10$ . Upper panel:  $\Delta S_N = S_N(k) - S_{66}(k)$ . The difference is computed using a spline function interpolation of  $S_{66}$ .

<sup>1</sup>Chiesa et al. PRL **97**, 076404 (2006)

<sup>2</sup>Drummond et al. PRB **78**, 125106 (2008)

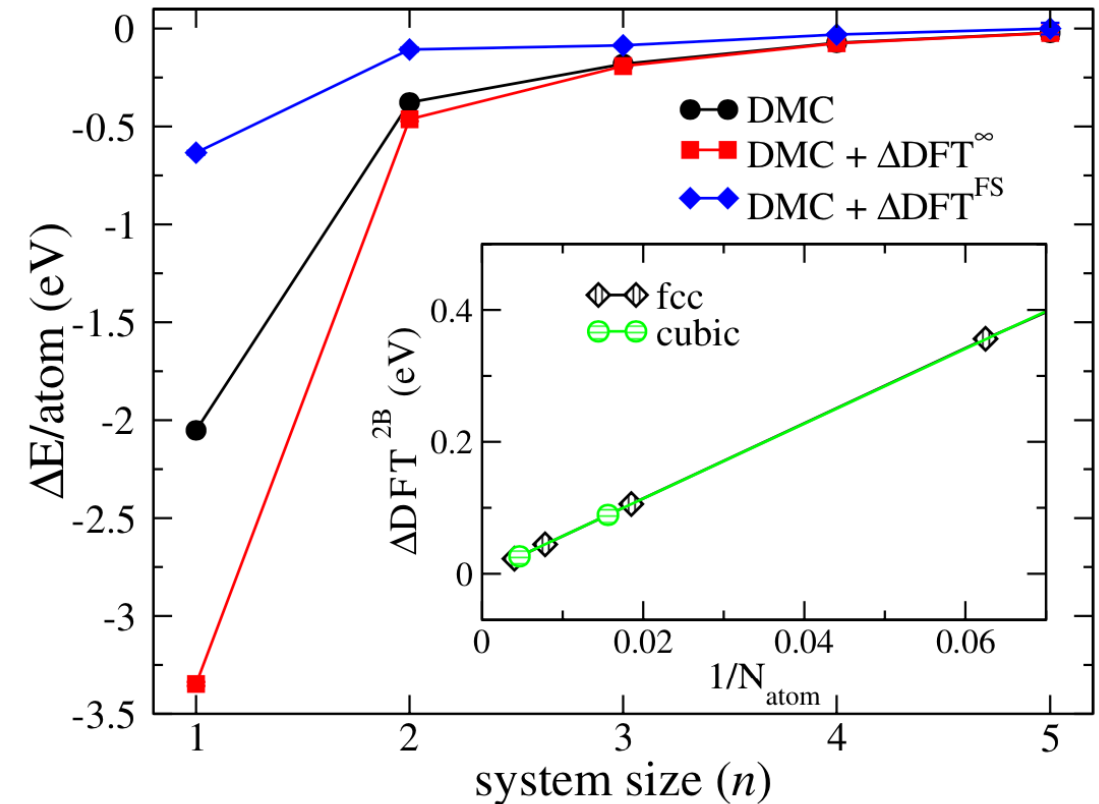
<sup>3</sup>Holzmann et al. PRB **94**, 035126 (2016)





# KZK CORRECTION

- KZK correction<sup>1</sup>:
- Take  $E_{XC}(N)$  from the HEG
- In ESPRESSO: **dft="kzk"**
  - LDA only by default
- Entirely independent of QMC
- Gives approximate 2-body KE & PE corrections



<sup>1</sup>Kwee et al. PRL **100**, (2008)

# WAVE FUNCTIONS FOR SOLIDS



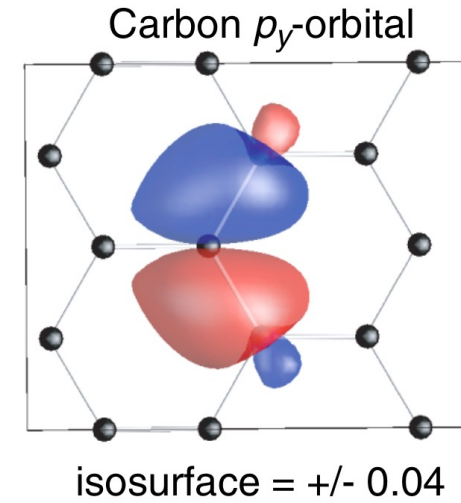
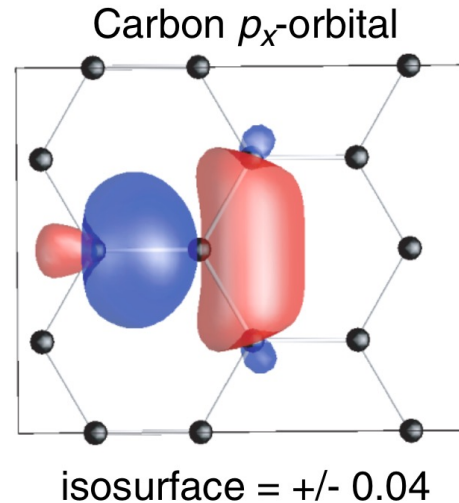
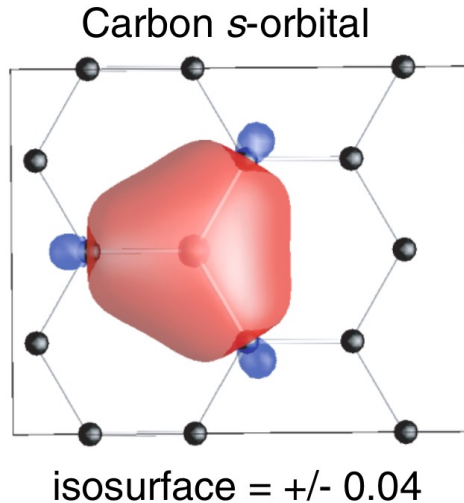
# QMC WAVE FUNCTIONS

$$\Psi^{SJ}(X) = e^{J(X)} \det \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_1(\mathbf{x}_2) & \cdots & \phi_1(\mathbf{x}_N) \\ \phi_2(\mathbf{x}_1) & \phi_2(\mathbf{x}_2) & \cdots & \phi_2(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{x}_1) & \phi_N(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix}$$

- At a very high level, this is the same ansatz and general workflow as for molecules, but solids pose interesting additional complications.
- Plane wave DFT codes are dominant in this space for many reasons.
- Systematically convergeable as we increase plane wave cutoff, but the memory requirements can become unwieldy as we increase system size.
- Heavy elements can also significantly increase plane wave cutoffs and thus overall cost of simulation.
- Speed is important too! Our team hits 1000's of electrons more frequently in solids than in molecules.

# QMC WAVE FUNCTIONS FOR SOLIDS -- ORBITALS

- Key idea: Use 3d b-splines to represent each orbital<sup>1</sup>



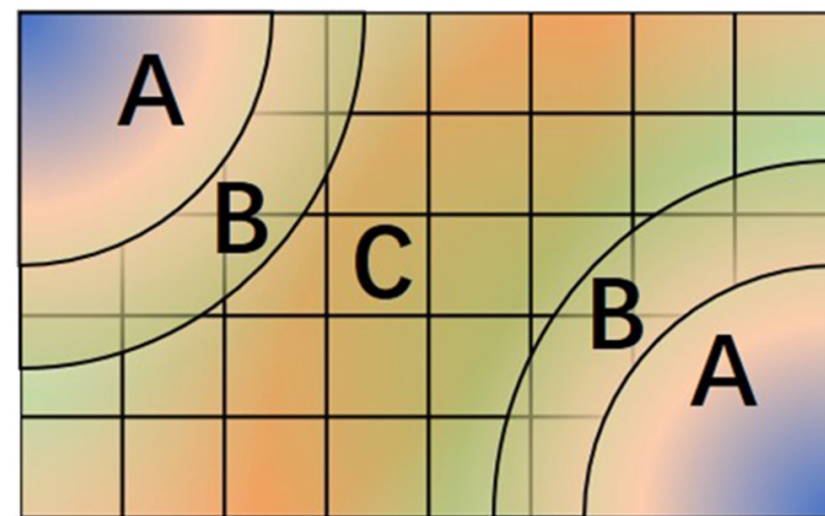
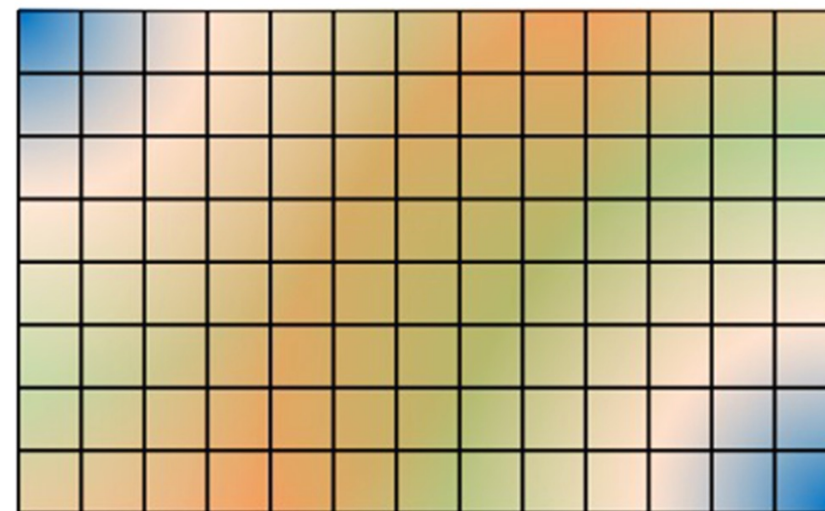
- Evaluate 64 grid points per orbital independent of system and basis set size
- Efficient routines transform DFT orbitals to splines automatically
- These get BIG. Using shared memory and proper batching is pretty much required for production calculations.

<sup>1</sup>Alfe and Gillan, PRB **70**, 161101 (2004)  
Fig from: Marzari et al. RMP **84**, (2012)



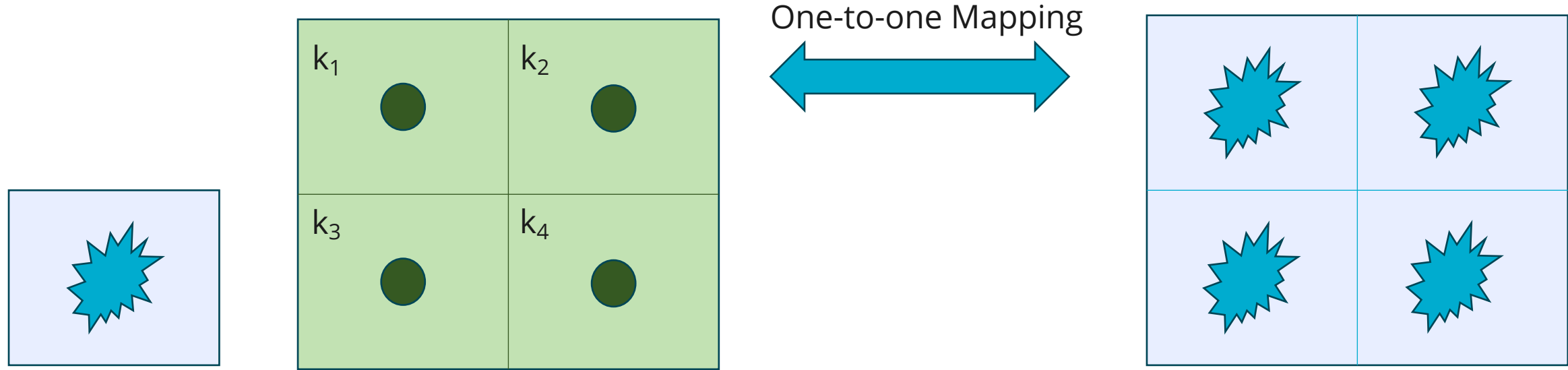
# QMC WAVE FUNCTIONS FOR SOLIDS – HYBRID REPRESENTATION

- We can further reduce memory costs using a hybrid representation<sup>1</sup>
- Use spherical harmonics near nucleus (A)
- Smooth transition region (B)
- Normal 3d B-splines in interstitial space (C)
- Memory reduction of 4-8x possible!
- Controlled by **hybridrep** tag



<sup>1</sup>Luo et al. JCP **149**, 084107 (2018)

# WAVE FUNCTION GENERATION



$$\hat{H}_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) = \left[ \frac{\hbar^2}{2m} (-i\nabla + \mathbf{k})^2 + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})$$

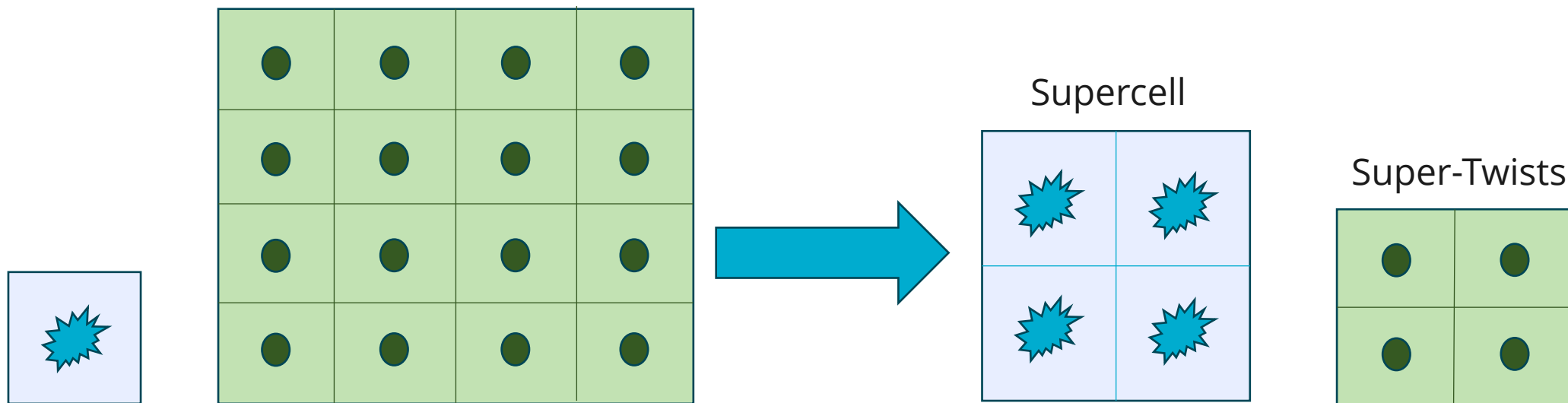
$$\hat{H} \psi(\mathbf{r}) = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$

- We typically use Bloch's theorem when possible to accelerate generation of single particle orbitals for use in the QMC supercell.
- We will run primitive (or small) cell calculations with a large number of k-points, and then "unfold" those by Bloch's theorem into the super cell.





## WAVE FUNCTION GENERATION—MORE REALISTIC USE CASE



- Remember, we need to do twist-averaging to take care of one-body finite size effects, but we also need to run multiple supercells to be able to extrapolate or correct the two-body finite size effects.
- Proper generation of primitive cell twists allows us to generate orbitals for a supercell with twists.
- Nexus is smart enough to do this, and you will do this in the lab.



## CHECKLIST FOR QMC ON SOLIDS

1. Converge twist grid
2. Exploit symmetry
3. Plan ahead for estimators/observables
4. Establish work required for desired accuracy in a small cell
5. Plan to quantify/mitigate finite size effects
6. When in doubt, get a bigger supercell!
7. Reach out to QMCPACK community: [qmcpack.slack.com](https://qmcpack.slack.com)

# OVERVIEW OF LAB



## LAB SUMMARY: DIAMOND

1. Generate converged scf density.
2. Use density to generate SPO's for 8 atom cell with NSCF procedure.
3. Optimize J1 and J2.
4. Perform VMC and DMC calculations for (1x1x1), (2x2x2), and (3x3x3) twist grids.
5. Twist-average the results of each grid calculation to determine the twist-averaged total energy for each grid.
6. Convergence figure for total energy including (4x4x4) and (6x6x6) grids.

