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QMCPACK for Solids

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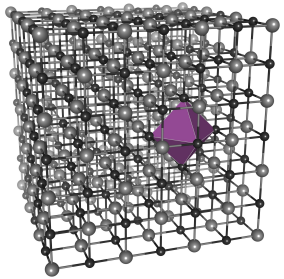

Slides: https://github.com/QMCPACK/qmcpack_workshop_2021

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CPSFM Center for Predictive Simulation of Functional Materials

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Topics Covered

1. Boundary conditions for solids & twist-averaging
2. Many-body wave functions for solids
3. Finite size effects
4. Laboratory exercises

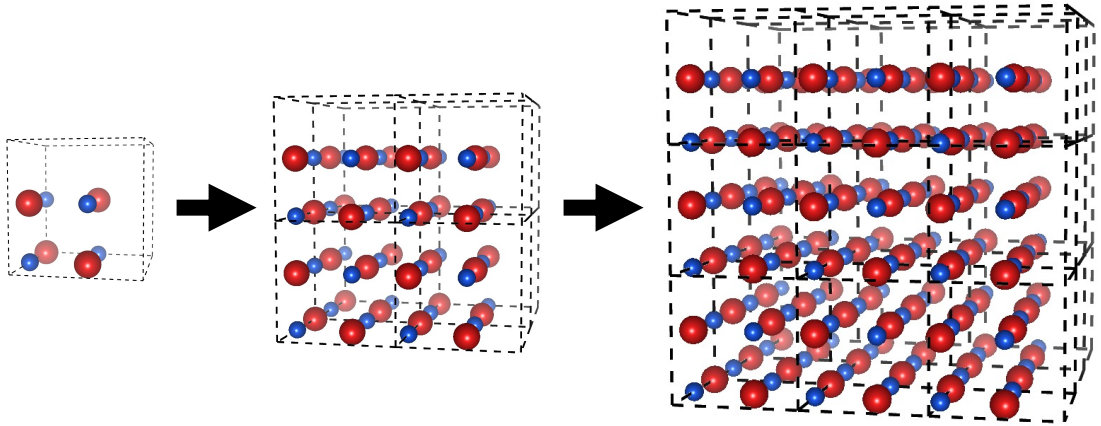
Topics Not Covered

1. QMC equilibration (covered in week 3)
2. DMC timestep extrapolation (covered in week 4)
3. DMC population bias (covered in week 4)
4. Mixed estimator bias (covered in week 6)
5. Pseudopotentials (covered in week 6)
6. Spins & magnetism (covered in week 8)
7. Systematic improvability (covered in week 4)

Topics Covered

1. **Boundary conditions for solids & twist-averaging**
2. Many-body wave functions for solids
3. Finite size effects
4. Laboratory exercises

From isolated molecules to bulk systems



- In open BC's surface effects spoil convergence of, e.g. energy/atom
- Means that you need *many* atoms to get accurate bulk properties
- For solids we use **twisted boundary conditions**
- Eliminates surfaces, need fewer atoms, but how to handle LR interactions?

Twist-Averaged Boundary Conditions

- Many-body version of Bloch's Theorem:

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

- The "twist", $\theta \equiv \mathbf{L} \cdot \mathbf{k}$
- Regular PBC's $\rightarrow \theta = 0$
- TABC = Many-body version of BZ integration
- Reduces finite size effects (more on this later)
- Faster convergence to thermodynamic limit

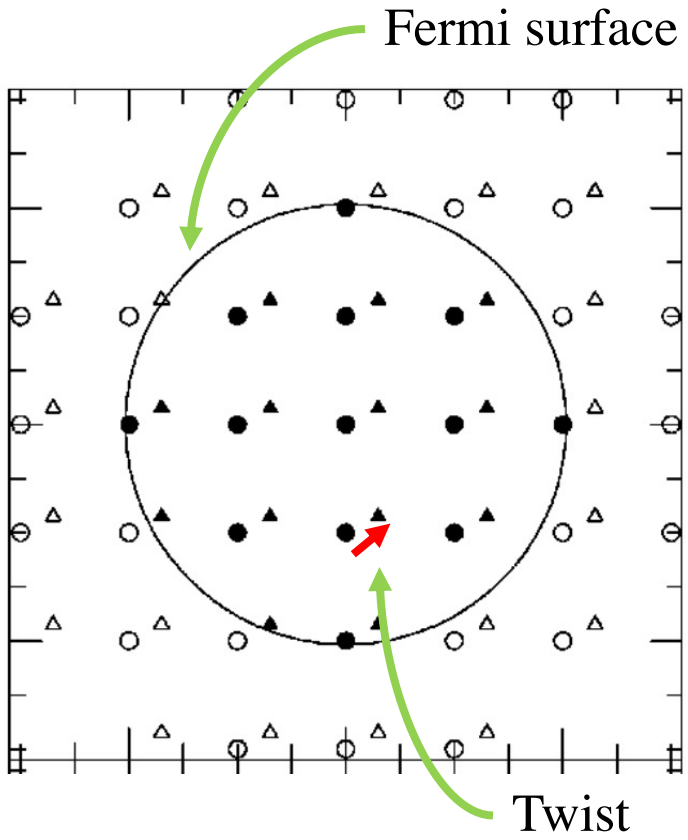


Fig from: Lin & Ceperley, PRE **64**, (2001)

Twist-Averaged Boundary Conditions

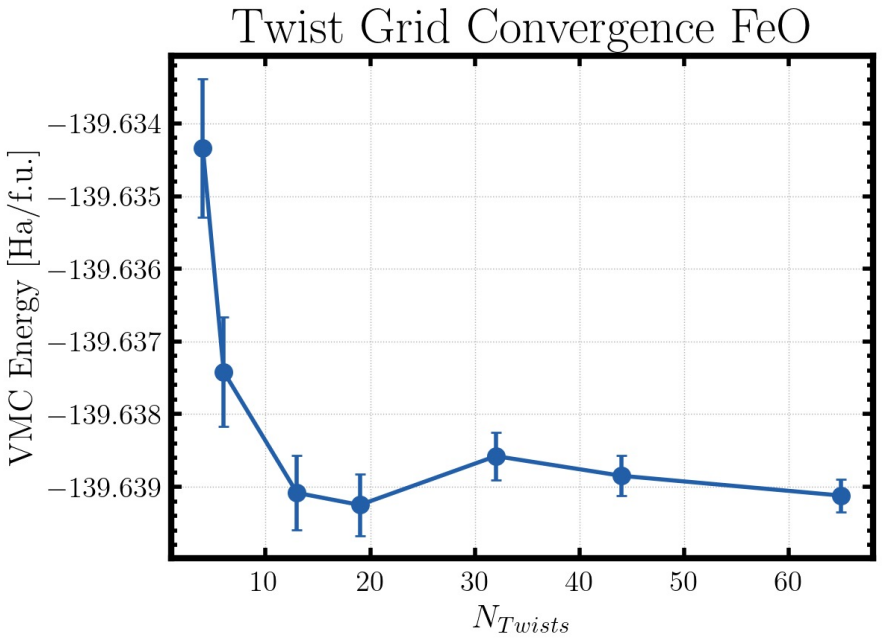
- Must apply TABC to all observables, not just energy!
- In general for TABC:

$$\langle A \rangle = \frac{1}{N_\theta} \sum_\theta A_\theta w_n$$

- A_θ is the usual MC average of A for a particular twist
- w_θ is the corresponding weight (just like a Monkhorst-Pack k-point mesh)

Twist Averaging – In Practice

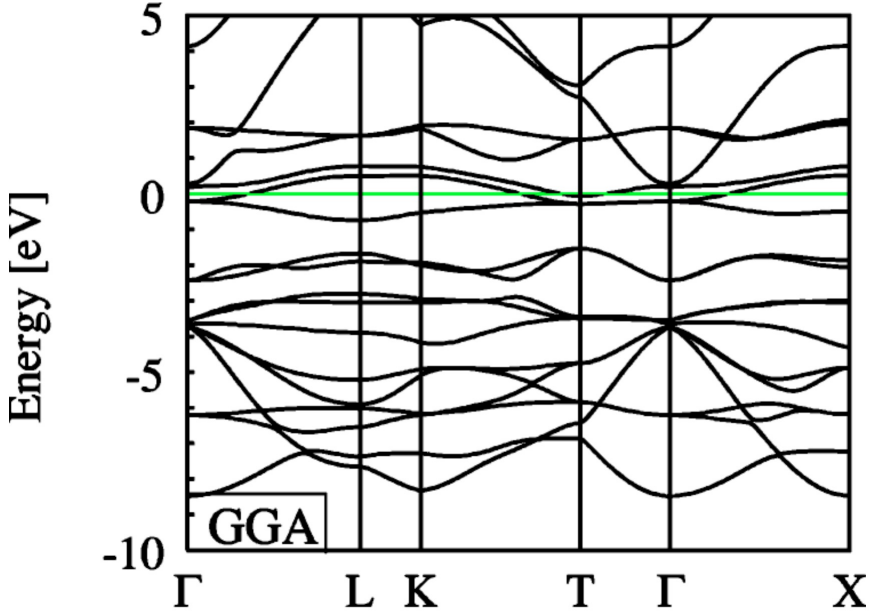
- Good news! Twists are independent
- Error reduction $\propto \frac{1}{\sqrt{N_{Twists}}}$
- How many twists are enough?
  - Depends on size, metallic vs insulating
  - You must check this yourself!
- Nexus can generate primitive cell k-point to supercell twist grid mapping for you



Grand Canonical Twist-Averaging

- In metals, N of occupied states depends on $\boldsymbol{k}$ due to bands crossing the Fermi surface
- Canonical TABC = Constant N for all twists
- GCTABC = N varies with twist
- Better energies, but more work and not always clear how to choose N in practice[2,3]

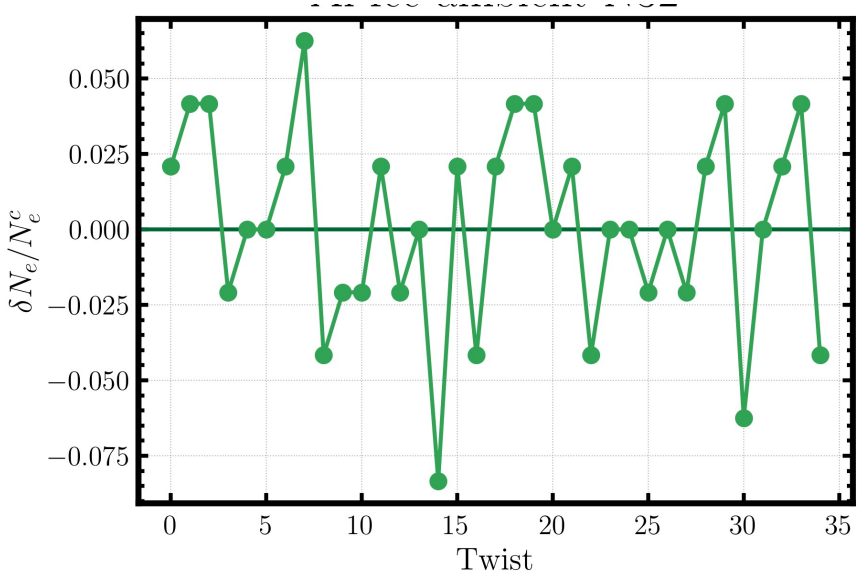
[1]Compare number of states below E_F:

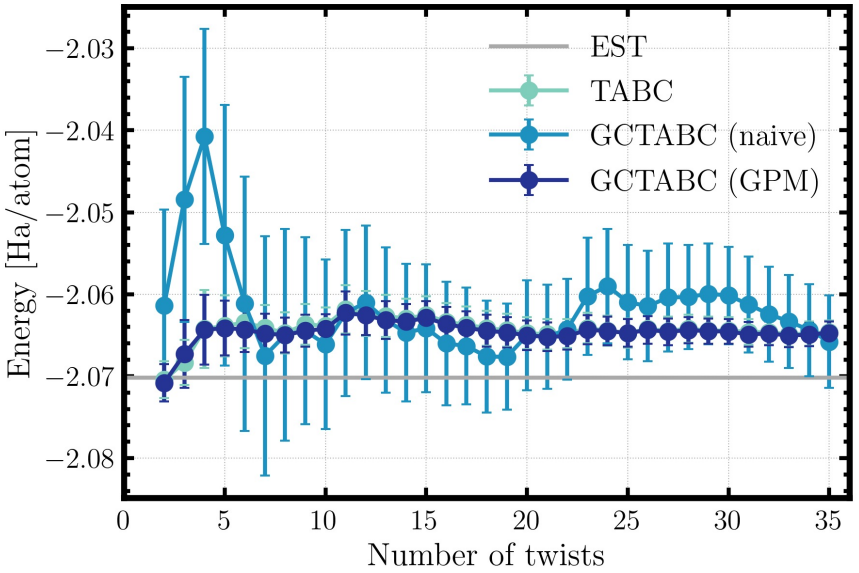


[1]Cococcioni et al, PRB **71**, (2005)
[2]Lin & Ceperley, PRE **64**, (2001)
[3]Azadi & Foulkes, PRB **100**, (2019)

Grand Canonical Twist-Averaging

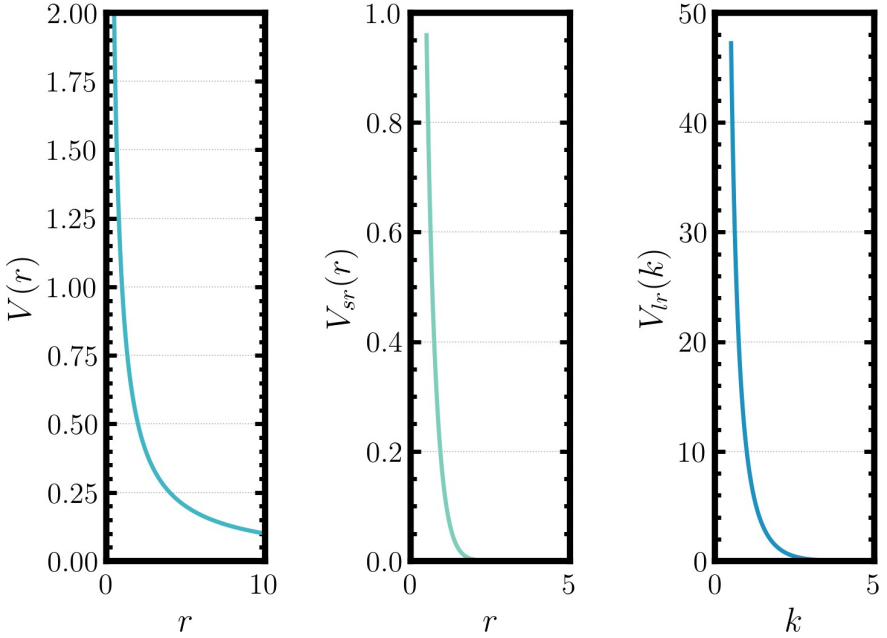
- Simple example of fcc aluminum:





Ewald Summation

- How to compute Coulomb interaction?
- Naively, it seems this term is conditionally convergent in PBC's
- Ewald summation provides rigorous value via breakup into LR and SR parts



Short-range r-space

Long-range k-space

$$V(\mathbf{r}) = \frac{1}{|\mathbf{r}|} = \sum_{\mathbf{L}} \frac{1}{|\mathbf{L}-\mathbf{r}|}\operatorname{erfc}(G|\mathbf{L}-\mathbf{r}|) + \frac{4\pi}{\Omega}\sum_{\mathbf{k}} \frac{e^{-|\mathbf{k}|^2/4G^2}}{|\mathbf{k}|^2} e^{i\mathbf{k}\cdot\mathbf{r}}$$

Ewald Summation

- How many times do we do Ewald in a typical QMC calculation?
  (Typical means ~100 electrons, ~1000 walkers, ~1000 steps)
  - For each MC step, propose a move for ~100 electrons
  - For each proposed move, evaluate ~100 interactions
  - Typically have O(1000) walkers
  - Typically take O(1000) steps
- Interaction calculated $\sim 10^{10}$ times!
- QMCPACK uses "optimized breakup" to maximize speed and minimize error[1]
  - Controlled via **`LR_DIM_CUTOFF`** in the input file.

[1]Natoli & Ceperley, JCP **117**, 171 (1995).

Topics Covered

1. Boundary conditions for solids & twist-averaging
2. **Many-body wave functions for solids**
3. Finite size effects
4. Laboratory exercises

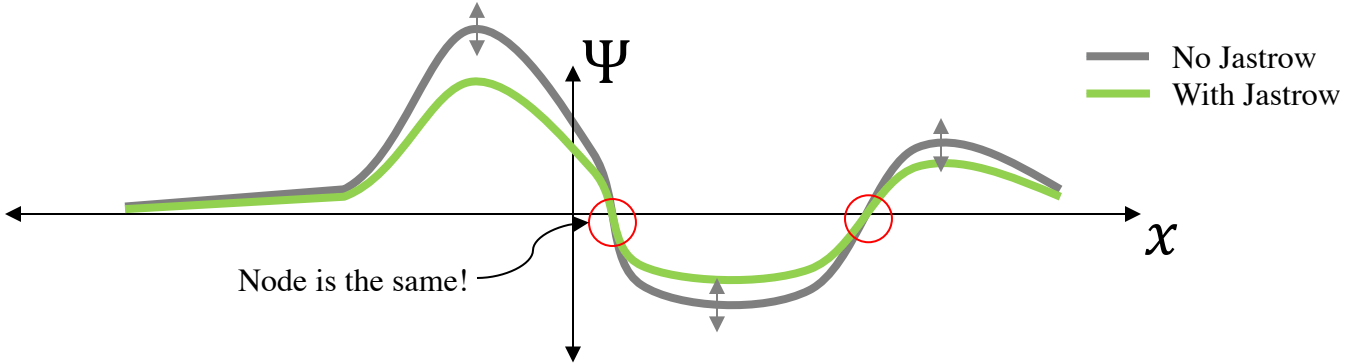
QMC Wave Functions for Solids

- Slater-Jastrow (SJ) is the simplest, most-compact, and most common many-body wave function ansatz:

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

- Explicitly incorporates (some but not all) electron correlations
- The determinant piece comes from outside QMC
  - E.g. DFT orbitals from Quantum ESPRESSO, RMG, PySCF…
- The Jastrow is constructed within QMC by VMC optimization

QMC Wave Functions for Solids – Jastrow

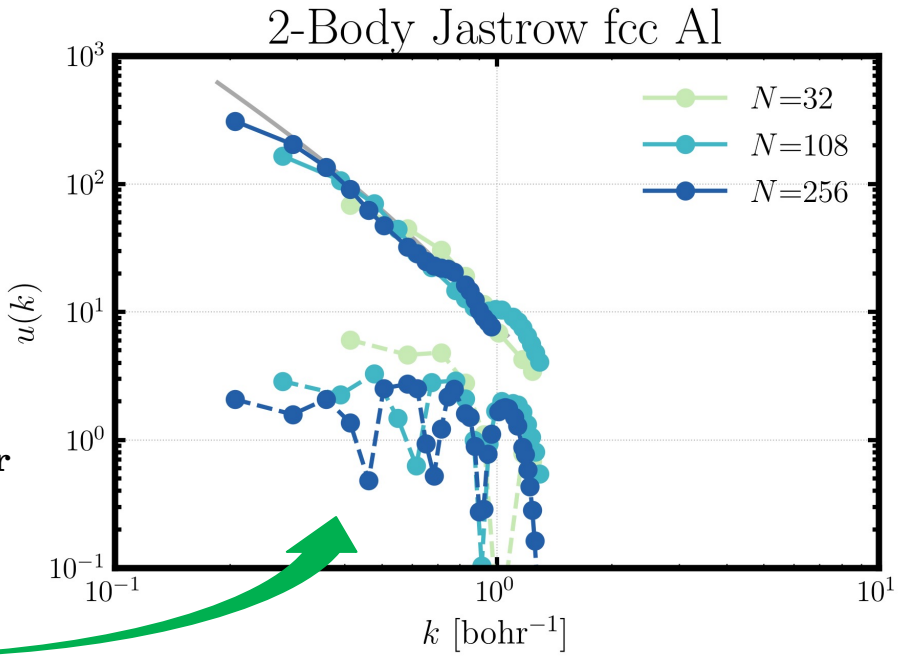


- 1B: Correlations between electron and atomic nucleus
- 2B: (Most important) Correlations between pairs of electrons
- 3B: (high Z semi-core states) Correlations between pairs of electrons and atomic nucleus
- K-space: (PBC's only) Restore long-range correlations in J2
- **Nodes** are not affected, only **amplitude** of Ψ!

QMC Wave Functions for Solids – Jastrow

- Correlation goes like 1/r, but truncated at cell boundary[1,2]
- Idea: Restore proper long-range behavior via 2-body Jastrow defined in k-space:

$$u(\mathbf{k}) = \sum_{\mathbf{k}} c(\mathbf{k}) \rho_{\mathbf{k}} \bar{\rho}_{\mathbf{k}}, \qquad \rho_{\mathbf{k}} \equiv \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}}$$



[1]Gaskell *Proc. Phys. Soc.* **77,** 1182 (1961)
2Becker et al., PRL **175,** (1968)

QMC Wave Functions for Solids - SPO's

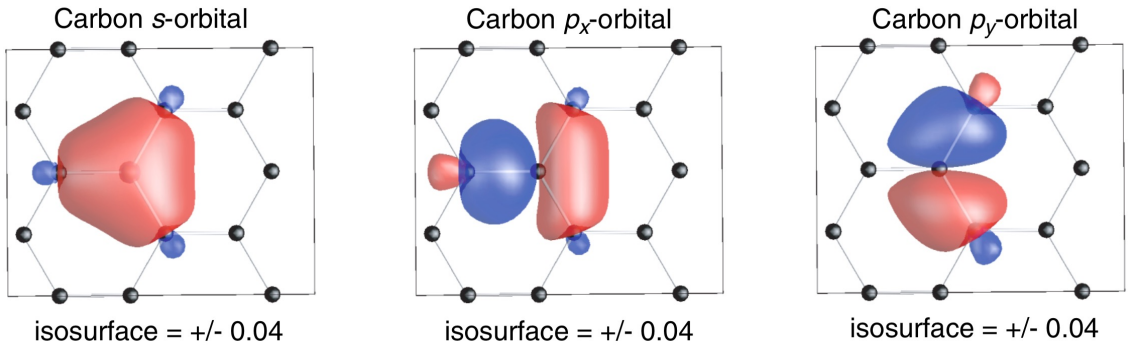
- DFT orbitals are commonly defined in a plane wave basis:

$$\phi_m(\mathbf{x}) = \sum_n c_{mn} e^{i\mathbf{k}_n \cdot \mathbf{x}}$$

- There are ~10^4 planewaves per orbital
- That's ~10^6 function calls *per move*
- That's ~10^8 function calls *per MC step*
- Quite expensive to call so many sin() & cos() !!!

QMC Wave Functions for Solids – SPO's

- Key idea: Use 3d b-splines to represent each orbital[1]

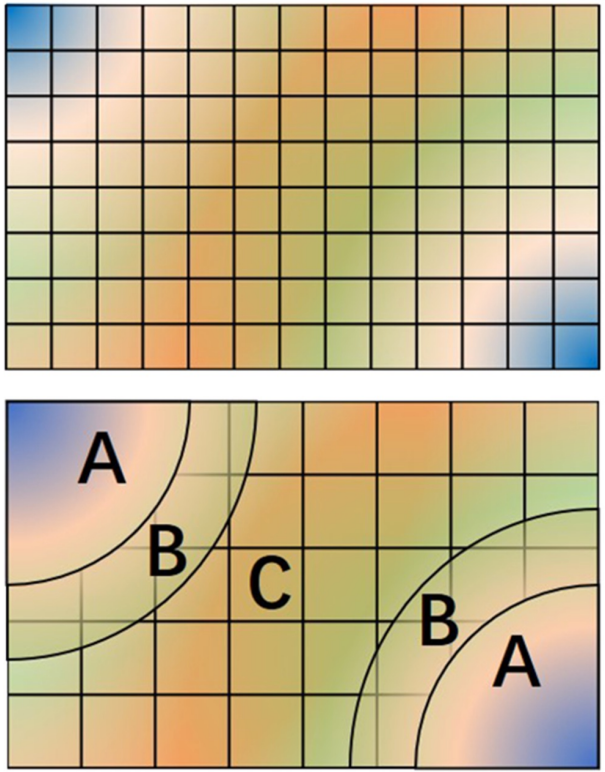


- Go from ~10^4 numbers to 64 numbers for wfn value at a point in 3d space
- Efficient routines transform DFT orbitals to splines automatically

[1]Alfe and Gillan, PRB 70, (2004)
Fig from: Marzari et al. RMP 84, (2012)

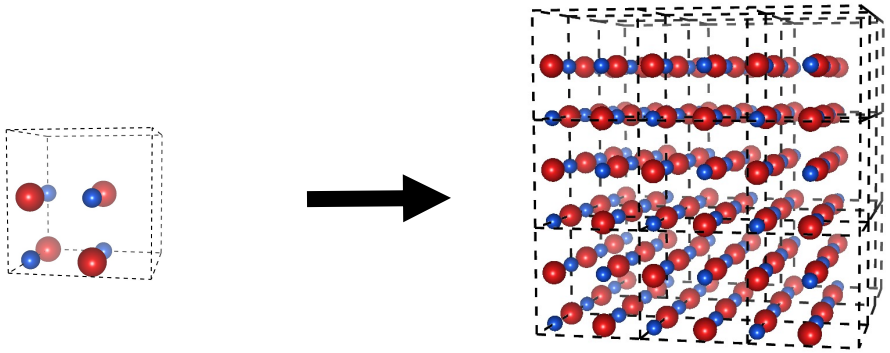
QMC Wave Functions for Solids – SPO's

- We can further reduce memory costs using a hybrid representation[1]
- Use spherical harmonics near nucleus (A)
- Smooth transition region (B)
- Normal 3d B-splines in intersitial space (C)
- Memory reduction of 4-8x possible!
- Controlled by **`hybridrep`** tag
  - Consult manual for details



[1]Luo et al. JCP 149, (2018)

QMC Wave Functions for Solids – k points



3x3x3 kpoint mesh here = 1x1x1 kpoint mesh here

- Another trick: Exploit crystal symmetry
- Generate SPOs in prim. cell with k-points, then tile into super cell
  - Straightforward application of Bloch's theorem
- This gets you an additional memory reduction of factor of N_{copies}

Topics Covered

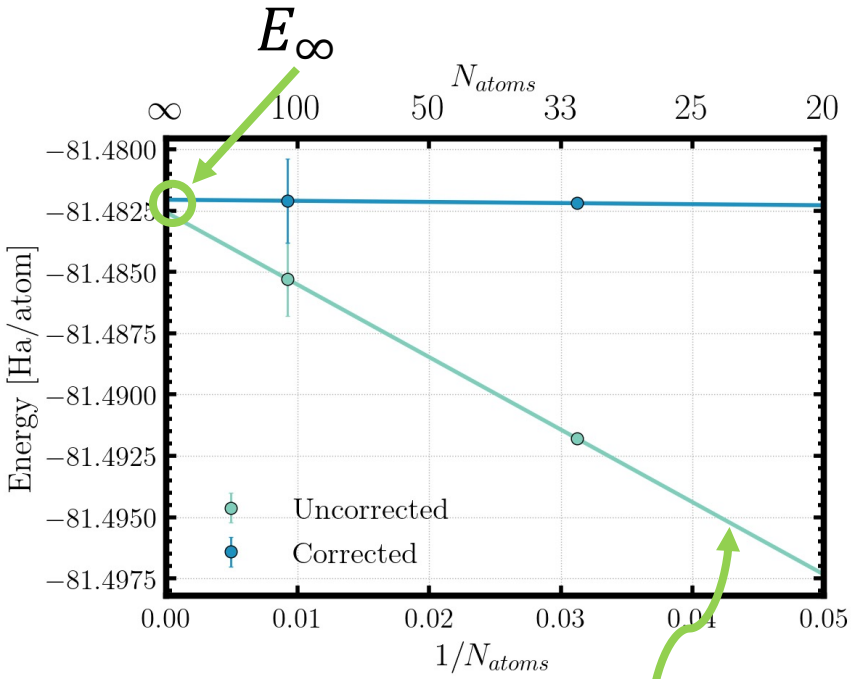
1. Boundary conditions for solids & twist-averaging
2. Many-body wave functions for solids
3. **Finite size effects**
4. Laboratory exercises

What Are Finite Size Effects?

- Most DFT functionals include finite size corrections
- For a QMC calculation on a solid, we directly simulate a finite number of electrons in a finite box
- Finite size errors arise because in PBC's space & momentum are restricted
  - Think discrete vs continuous set of points in BZ for finite cell
  - FSE exist *even if you had the exact* Ψ!
- So every QMC output (on solids, anyways) is biased when comparing to experiment because of FSE
- Two ways to get QMC estimates in thermodynamic limit:
  1. Extrapolate over system size
  2. Use finite size correction schemes

Finite Size Correction – Basic Idea

- In "big enough" cell, correction is an integration error
- Can derive expressions for corrections to kinetic and potential energy
- Must-read papers on FSC:
  - Chiesa et al. *PRL* **97**, 076404 (2006).
  - Drummond et al. *PRB* **78**, 125106 (2008).
  - Holzmann et al. *PRB* **94**, 035126 (2016).



$$E\left(\frac{1}{N}\right) = E_\infty + m\frac{1}{N}$$

Potential Energy Finite Size Corrections

- Ewald gets Hartree energy exact, but biases XC energy
- Model Periodic Coulomb (MPC) fixes that:

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

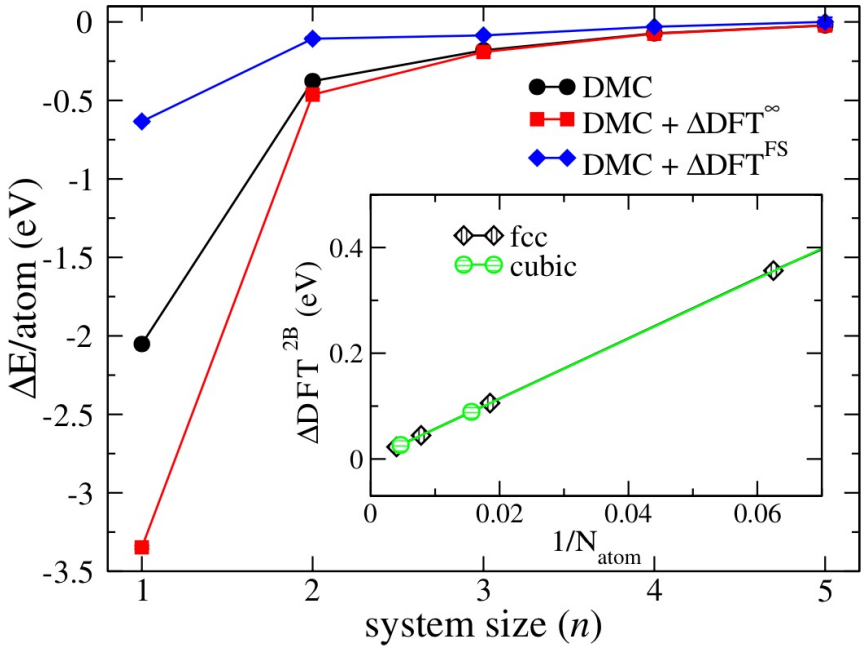
Normal Coulomb inside

Modified potential outside

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

Potential Energy Finite Size Corrections

- KZK correction[1]:
- 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



[1]Kwee et al. PRL **100**, (2008)

Potential Energy Finite Size Corrections

- **Gold standard**: Use structure factor[1,2,3]
- PE per particle is related to s(k) via:

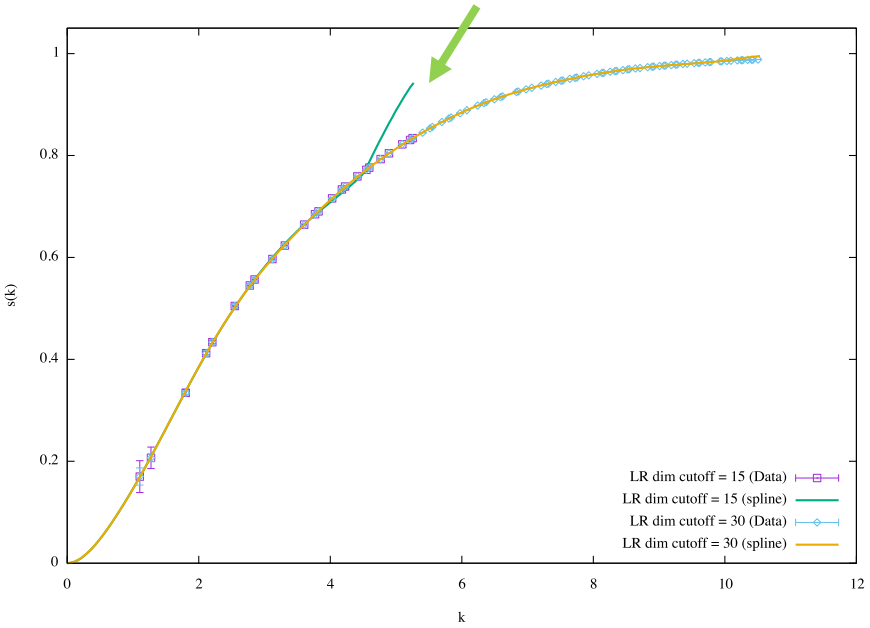
$$V_N = \frac{2\pi}{\Omega} \sum_{\mathbf{k}\neq 0} \frac{1}{k^2} \left(s(\mathbf{k}) - 1\right)$$

- 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

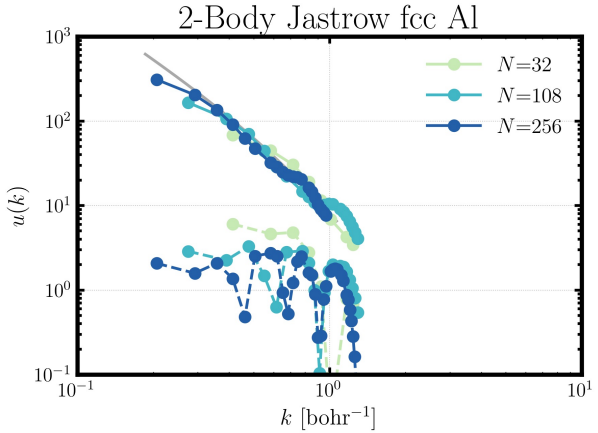
Change **`LR_dim_cutoff`**

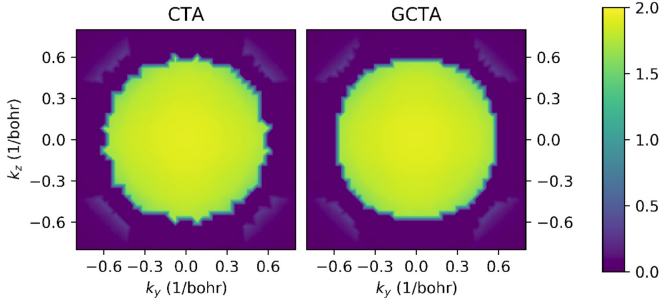


[1]Chiesa et al. PRL **97,** (2006)
[2]Drummond et al. *PRB* **78,** 125106 (2008)
[3]Holzmann et al. PRB **79,** (2016)

Kinetic Energy Finite Size Corrections

- Basically two ways to get a KE correction
- Examine LR behavior of J2:
  - See **`KECorr`** estimator in QMCPACK
  - Not guaranteed to be accurate – you must test!
- Momentum distribution:
  - See "nofk" estimator in QMCPACK
  - Done in post-processing. Must "roll your own"
- Excellent example of both can be found in Yang et al. PRB **101**, (2020)





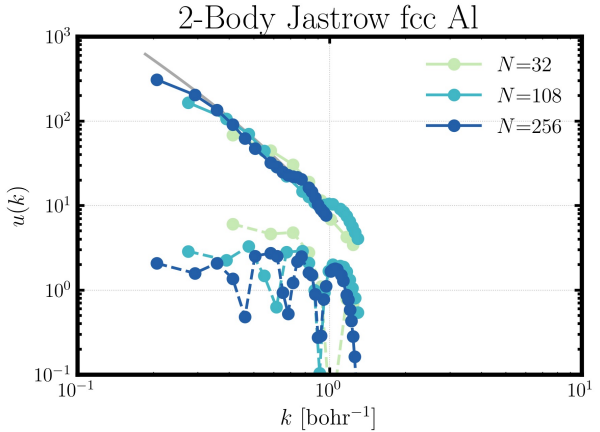
Kinetic Energy Finite Size Corrections

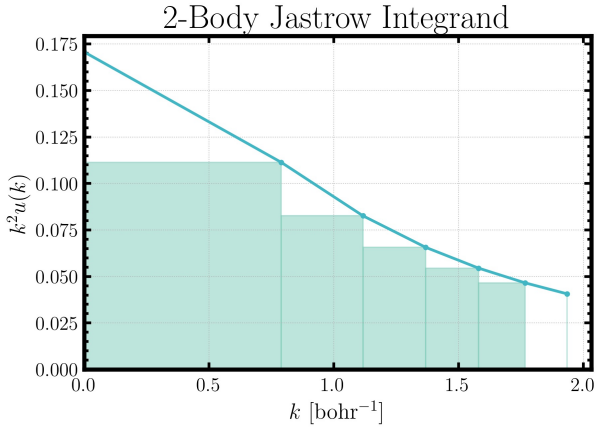
- Twist-averaging reduces kinetic finite size error, but often times further correction is needed
- Can obtain KE correction from long-ranged behavior of J2
- Ala Chiesa et al.:

$$\Delta T = \frac{N}{4(2\pi)^3}\int d\mathbf{k} k^2 u(\mathbf{k}) - \frac{N}{4\Omega}\sum_{\mathbf{k}\neq 0} k^2 u_N(\mathbf{k}) \approx \frac{\pi a N}{\Omega}$$

with "a" determined from LR piece of u(k):

$$u(\mathbf{k}) = 4\pi a\left[k^{-2} - (k^2 + a^{-1})^{-1}\right]$$



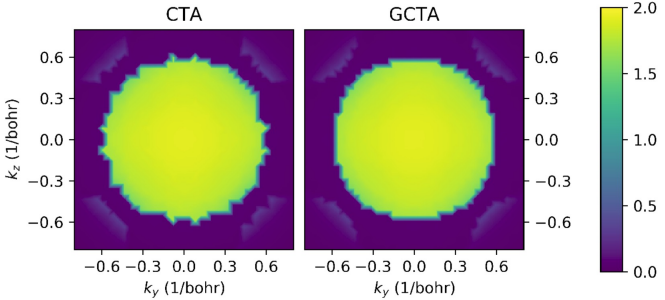


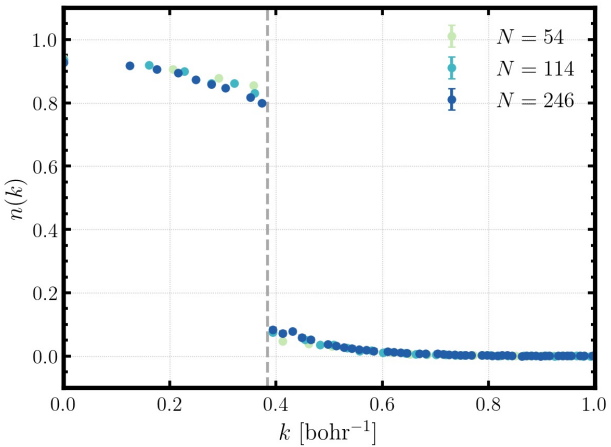
Kinetic Energy Finite Size Corrections

- **Gold standard**: Use momentum distribution[1]
- Independent of Jastrow
- GCTABC may be important
- Ala Holzmann et al.:

$$\Delta T = T_\infty - T_N = \frac{\Omega}{2N}\frac{1}{(2\pi)^3}\int d\mathbf{k} k^2 n_N(\mathbf{k}) - \frac{1}{2N}\sum_{\mathbf{k}} k^2 n_N(\mathbf{k})$$

- NB: $n(k)$ converges to "big enough" slowly!
  - Shape corrections may be important[2,3]





[1]Holzmann et al. PRB **79**, (2016)
[2]Yang et al. PRB 101, (2020)
[3]Holzmann et al. PRL **107**, (2011)

Finite Size Corrections – Final Words

- Many schemes, same physical quantities: $u(k)$, $s(k)$, $n(k)$
- QMCPACK provides all estimators, up to you to process correctly
- Different assumptions and approximations: Testing is required!

Topics Covered

1. Boundary conditions for solids & twist-averaging
2. Many-body wave functions for solids
3. Finite size effects
4. **Laboratory exercises**

Hands-On Tutorial Overview

- System: MgO in B1 structure
- Step 1: DFT & wave function generation in primitive cell with k-points
- Step 2: QMC Jastrow optimization in small supercell
- Step 3: QMC Twist grid convergence scan
- Step 4: Production DMC on 8-atom supercell
- Step 5: Analyze results