



# Exploiting Sparsity, Symmetry, and Fourier Treatment of long-range Interactions in Quantum Chemistry

Mark Zanon



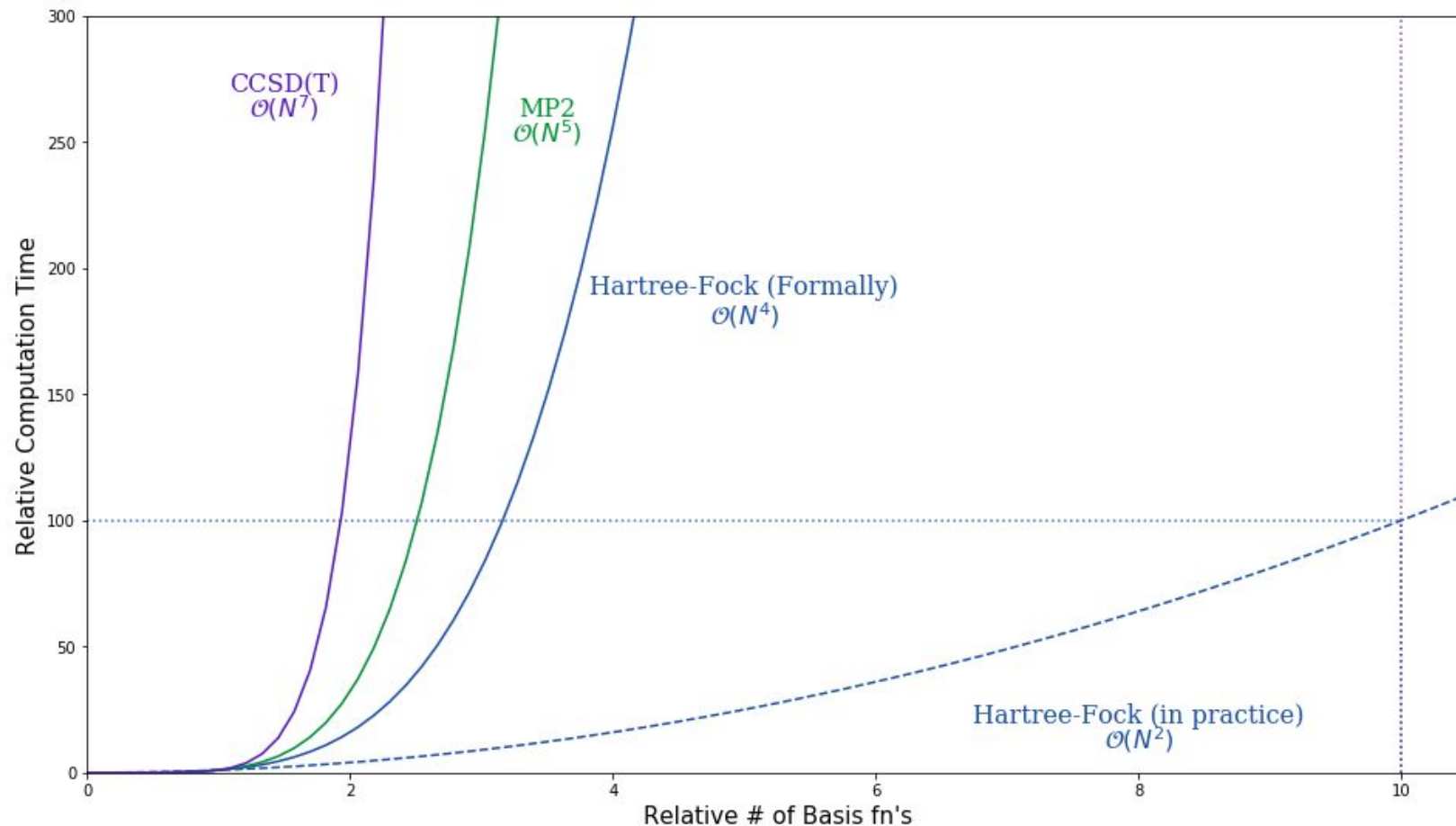
# Motivation

- Computational calculations can determine molecular properties:
  - Geometry
  - Thermochemistry\*
- 'Gold-standard': Coupled cluster singles, doubles, and perturbative triples (CCSD(T))
  - ~1 kcal/mol accuracy
  - Computationally expensive,  $O(N^7)$



# Computational Complexity

- Accuracy vs Complexity
  - How does the method scale for large inputs?





# Motivation

How can we improve coupled cluster methods for use in the solid state?

1. Use *congruent localized orbitals* (CLO's) to exploit symmetry and local correlation
2. Treat long-range interactions in the solid state via Fourier transform



# Motivation

How can we improve coupled cluster methods for use in the solid state?

1. Use *congruent localized orbitals* (CLO's) to exploit symmetry and local correlation

2. Treat long-range interactions in the solid state via Fourier transform



# Theory – Hartree-Fock (HF)

- $|\Psi\rangle$  is represented as a single Slater determinant of 1e functions

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_i(x_1) & \phi_j(x_1) & \cdots & \phi_n(x_1) \\ \phi_i(x_2) & \phi_j(x_2) & \cdots & \phi_n(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_i(x_n) & \phi_j(x_n) & \cdots & \phi_n(x_n) \end{vmatrix}$$

$$\begin{aligned} E_{HF} &= \langle \Psi | \hat{H} | \Psi \rangle \\ &= \underbrace{\sum_i \langle i | h | i \rangle}_{\text{1-e orbital energy}} + \underbrace{\sum_{j>i} \langle ij | ij \rangle - \langle ij | ji \rangle}_{\text{e-e repulsion and exchange}} \end{aligned}$$

- HF is accurate to 99% of the total electronic energy
- 1% error is due to **Electron Correlation**

$$|\Phi_{1s}\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}(x_1) & \bar{\phi}_{1s}(x_1) \\ \phi_{1s}(x_2) & \bar{\phi}_{1s}(x_2) \end{vmatrix} \Rightarrow \mathcal{P}(x_1, x_2) = ||\phi_{1s}(x_1)||^2 ||\bar{\phi}_{1s}(x_2)||^2$$



# Beyond HF – Coupled Cluster (CC)

- Introduce cluster functions

$$C_{ij}(x_m, x_n) = \sum t_{ij}^{ab} \phi_a(x_m) \phi_b(x_n)$$

- $|\Psi\rangle$  written as an exponential ansatz in terms of excitation operators and t-amplitudes

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle$$

$$\hat{T}_1 \equiv \sum_i \hat{t}_i = \sum_{ia} t_i^a a_a^\dagger a_i$$

$$\hat{T} \equiv \hat{T}_1 + \hat{T}_2 + \dots \hat{T}_n$$



# Beyond HF – Coupled Cluster (CC)

- CC equations use a similarity transformed Hamiltonian

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

$$\hat{H} e^{\hat{T}} |\Phi_0\rangle = e^{\hat{T}} E |\Phi_0\rangle$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle = E |\Phi_0\rangle$$

$$\langle \Phi_0 | e^{-T} \hat{H} e^T | \Phi_0 \rangle = E$$

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$\vdots$

$$\langle \Phi_{i\dots}^{a\dots} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$



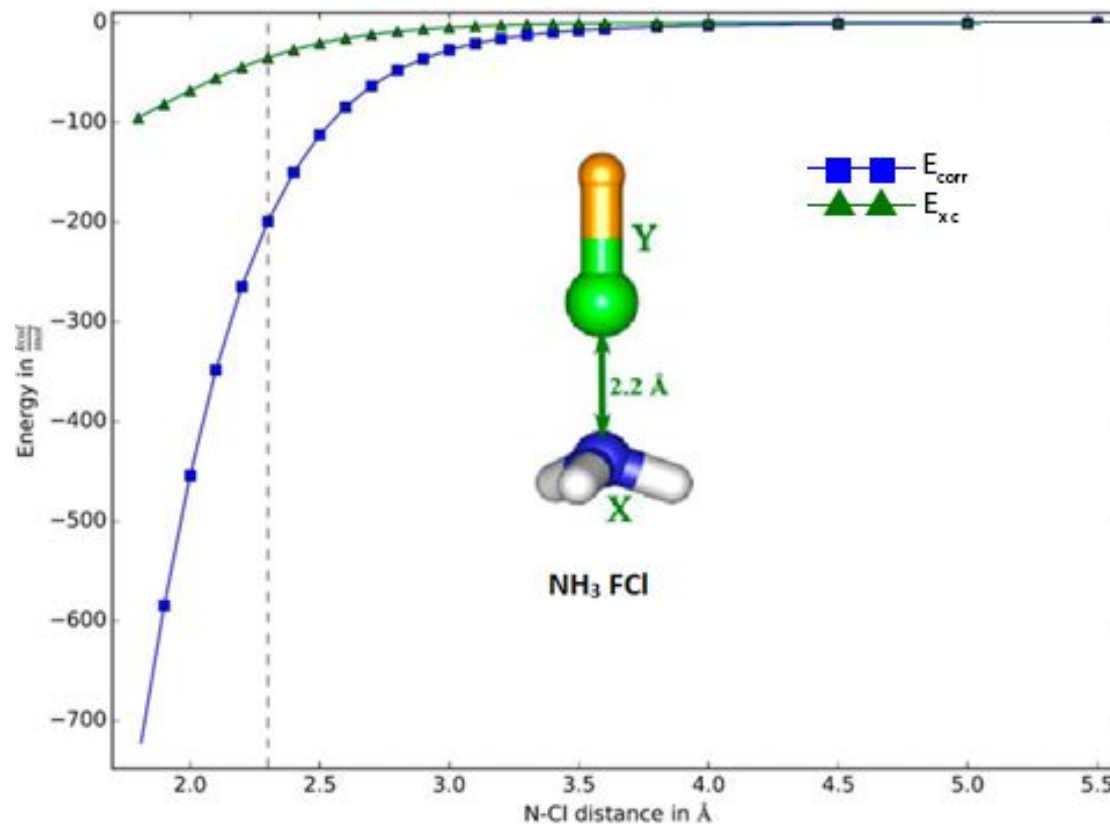


# Benefits of Coupled Cluster Methods

- Accuracy
  - CCSD(T) energies accurate to within 1 kcal/mol
- Truncation
  - Can truncate  $\hat{T}$  for any  $\hat{T}_n$ , CCSD truncates at  $\hat{T}_2$
  - Higher order excitations can be treated perturbatively (CCSD(T))
- Size-consistency for any level of truncation
  - $E(A) + E(B) = E(A+B)$

# Exploiting Sparsity - Orbital Localization

- Electron correlation increases complexity by  $O(N^4)$
- Falls with  $r^{-6}$





# Exploiting Sparsity - LPNO-CCSD(T)

- Local pair natural orbital implementation of CCSD(T) (LPNO-CCSD(T))
- Pair-natural orbitals (1973) used as a basis for localized orbitals

$$|\tilde{\mu}\rangle = (1 - \hat{P}) |\mu\rangle \qquad \hat{P} = \sum |i_L\rangle \langle i_L|$$

- Recent improvements to LPNO-CCSD(T) assign PNO's to explicit correlation domains (DLPNO-CC)

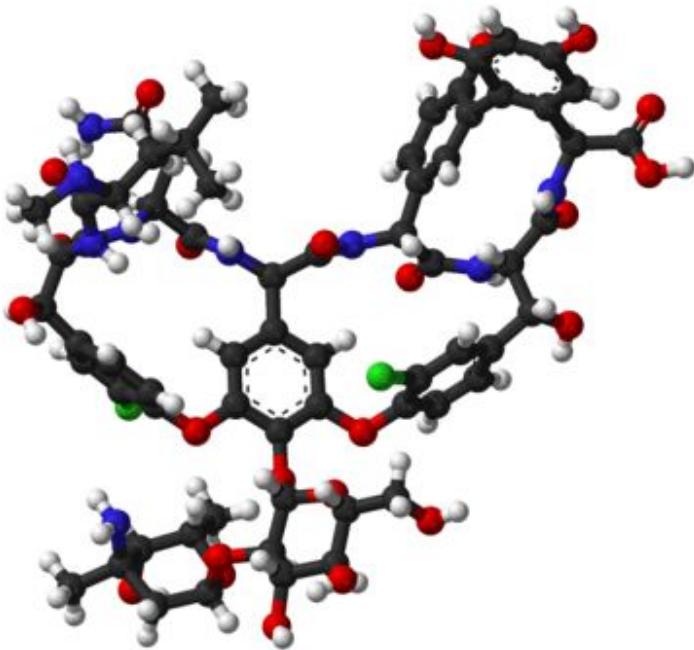


# Exploiting Sparsity - LPNO-CCSD(T)

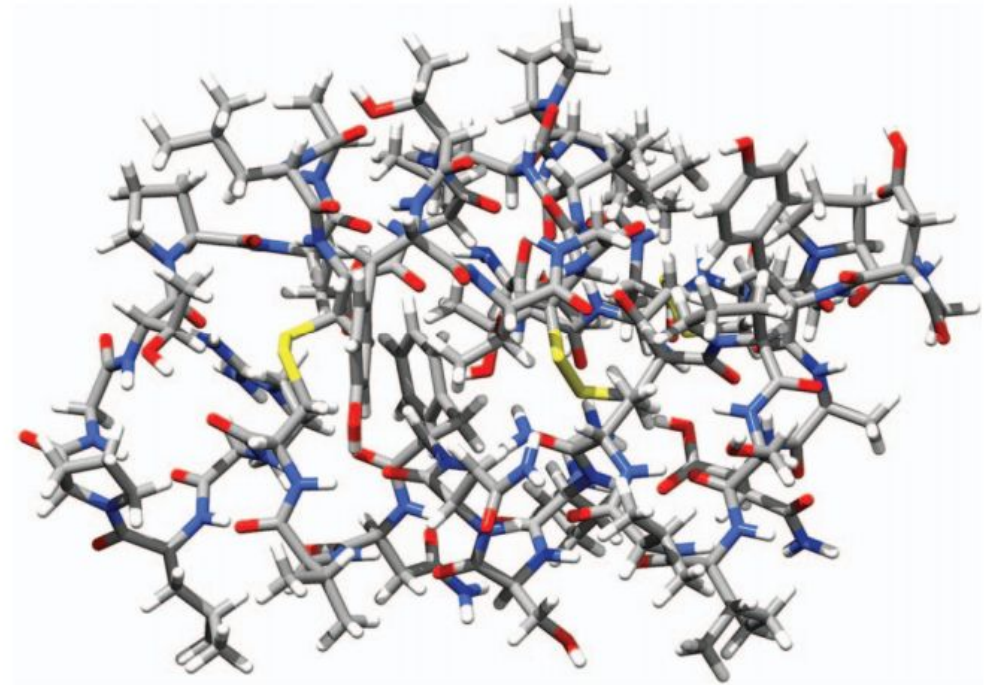
- Correlation energy treated hierarchically
  - Pairs are pre-screened via linearly scaling algorithm to estimate the correlation energy,  $\varepsilon_{ij}^{OSV}$
  - $\varepsilon_{ij}^{OSV} < 10^{-6} E_h$ , i,j are weakly correlated.
  - $\varepsilon_{ij}^{OSV} > 10^{-6} E_h$ , calculate  $\varepsilon_{ij}^{MP2}$
  - $\varepsilon_{ij}^{MP2} > 10^{-4} E_h$ , treat pair with CC
- Scales near-linearly for large systems

# Exploiting Sparsity - LPNO-CCSD(T)

- LPNO-CCSD captures >99% of the correlation energy while scaling like DFT.



Vancomycin: 176 atoms, 3593 basis functions  
J. Chem. Phys. 130:11408 (2009)



Crambin: 644 atoms, 6187 basis functions  
J. Chem. Phys. 139:134101 (2013)



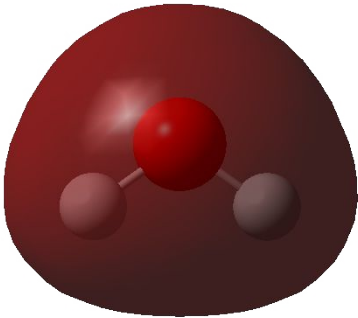
# Exploiting Sparsity - Improving LPNO-CCSD

How can we improve LPNO-CC?

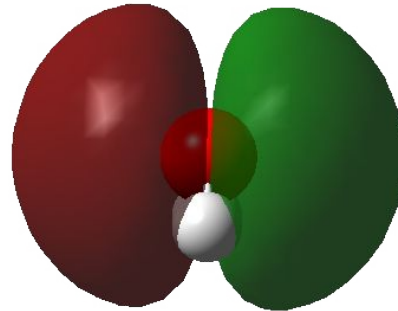
With Symmetry!

# Exploiting Molecular Symmetry

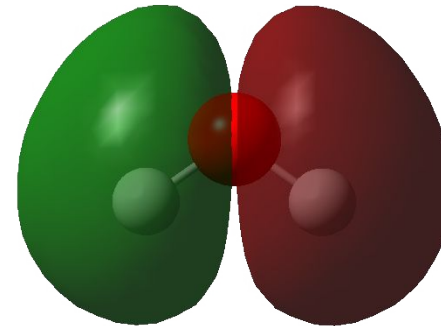
- Canonical orbitals transform according to their irreducible representations of the point group:



$A_1$



$B_2$



$B_1$

$$\Psi(\{\mathcal{R}\}, \hat{R}_i x) = e^{i\theta_i} \Psi(\{\mathcal{R}\}, x)$$

Finite molecules

$$\Psi_k(\{\mathcal{R}\}, (x + a)) = e^{ika} \Psi_k(\{\mathcal{R}\}, x)$$

Solids



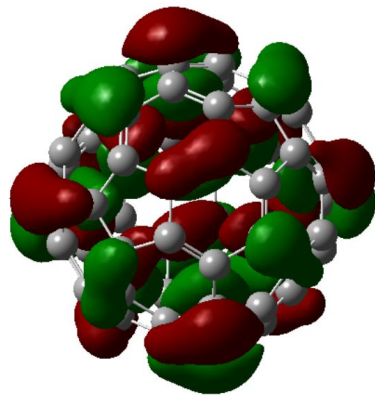
# Exploiting Molecular Symmetry

- Molecular symmetry simplifies calculations

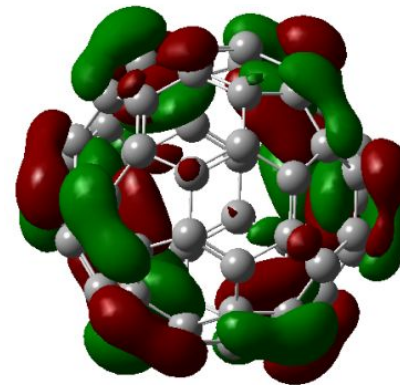
$$\hat{t}_{ij}^{ab} \neq 0 \text{ iff: } \Gamma_a \otimes \Gamma_b \otimes \cdots \Gamma_i \otimes \Gamma_j \otimes \cdots = A_1$$

	$A_1$	$\Gamma_2$	$\cdots$	$\Gamma_n$
$A_1$	$X_{11}$	0	$\cdots$	0
$\Gamma_2$	0	$X_{22}$	$\cdots$	0
$\vdots$	$\vdots$	$\vdots$	$\ddots$	0
$\Gamma_n$	0	0	$\cdots$	$X_{nn}$

- Canonical MO's are delocalized, cannot exploit sparsity



C60 HOMO

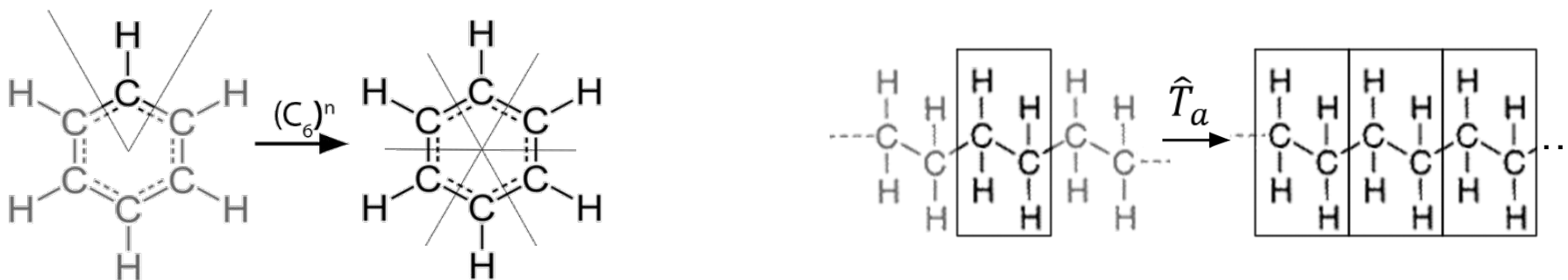


C60 LUMO

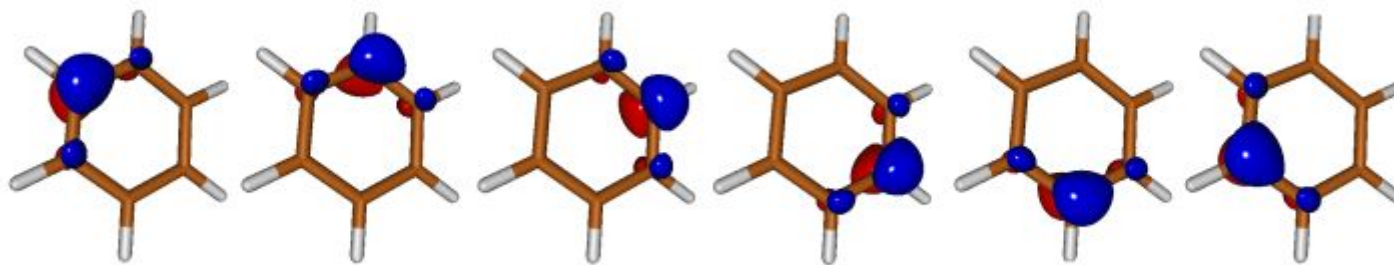


# Exploiting Molecular Symmetry – Alternative View

- Molecules can be broken up into 'unit cells' congruent through a subset of the point group



- To exploit symmetry, we need six *congruent localized orbitals* (CLO's)



# Building Congruent Localized Orbitals

- Atoms are divided into unit cells,  $\{B_n\}$
- Construct and diagonalize:

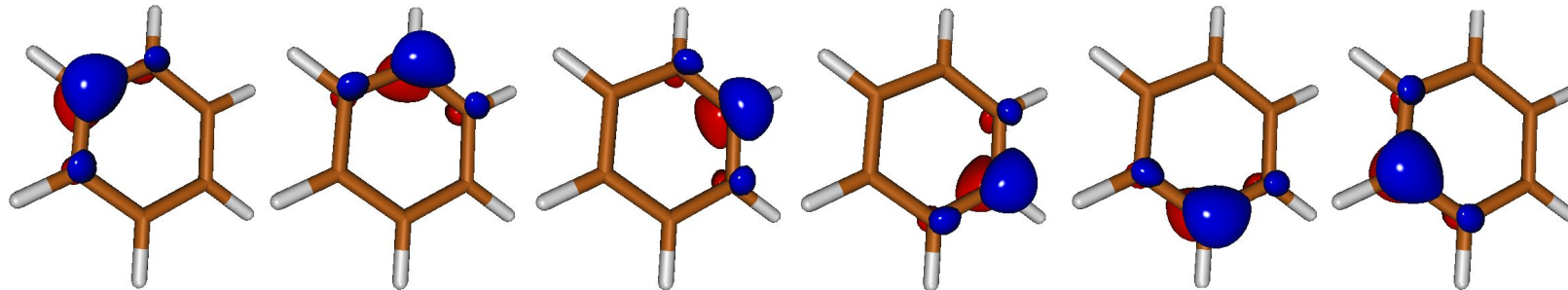
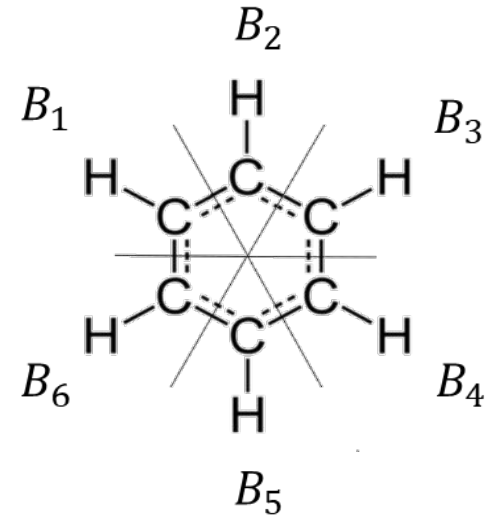
$$D_{\alpha\beta} = \sum c_{\alpha i} c_{\beta i}$$

$$S_{\alpha\beta} = \langle \alpha | \beta \rangle$$

$$(SDS)_{B_1} \tilde{u}^{B_1} = S_{B_1} \tilde{u}^{B_1}$$

- CLO's on  $B_n$  can then be constructed via symmetry:

$$\tilde{u}_{B_n} = \hat{C}_6^{n-1} \tilde{u}_{B_1}$$



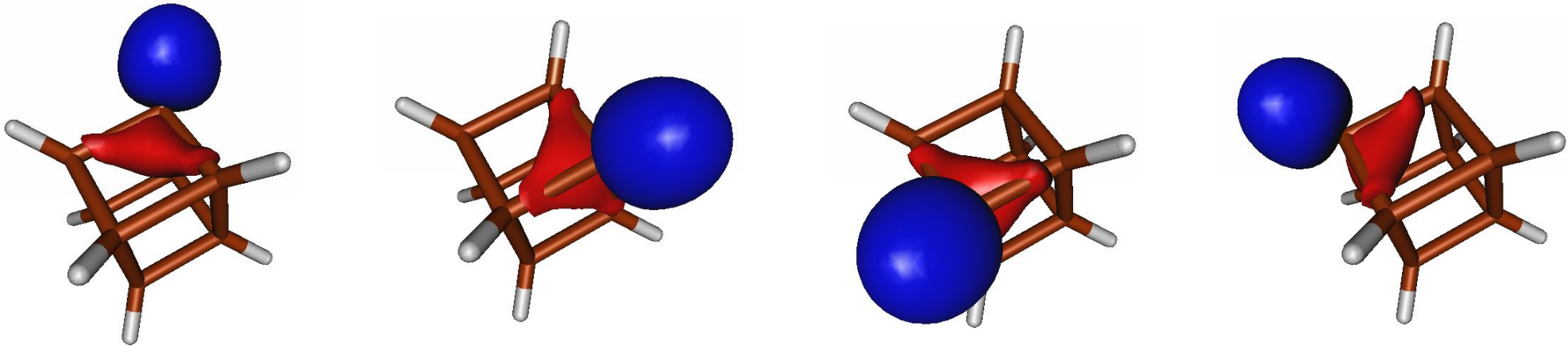
$i, j \dots \rightarrow$  Occupied MO's

$\alpha, \beta \dots \rightarrow$  AO's

$\mu, \nu \dots \rightarrow$  CLO's

# Building Congruent Localized Orbitals

- Symmetry of the CLO's can greatly simplify calculations
  - Only need to calculate unique quantities
- CLO's must meet two criteria:
  - 1) If linearly independent, orthonormal
  - 2) If linearly dependant,  $D_{CLO}$  must be idempotent:  $(D_{CLO})(D_{CLO}) = D_{CLO}$



- Construction of CLO's scales as  $O(1)$  with the overall system



# Motivation

How can we implement coupled cluster methods for use in the solid state?

1. Use *congruent localized orbitals* (CLO's) to exploit symmetry and local correlation

2. Treat long-range interactions in the solid state via Fourier transform

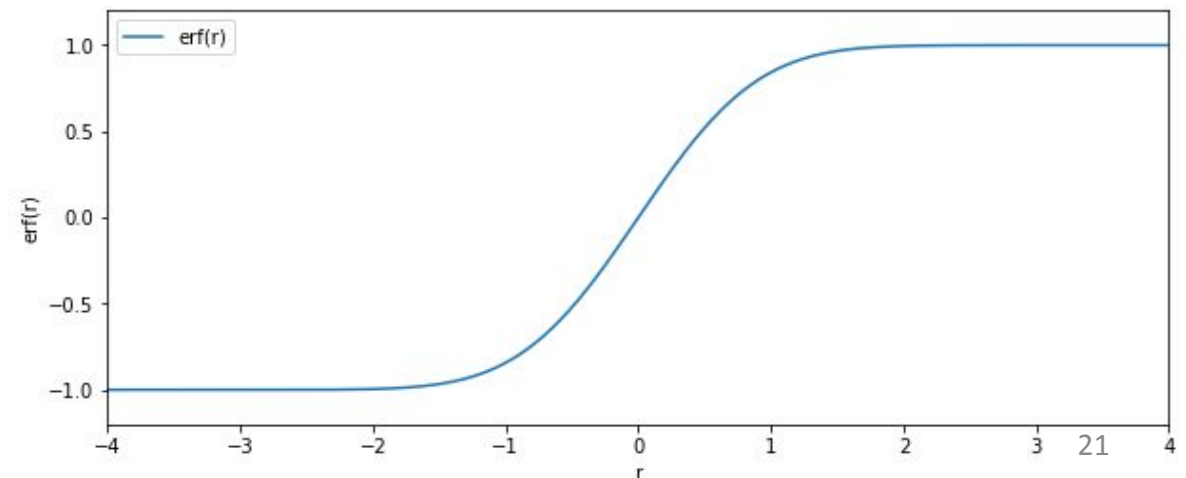
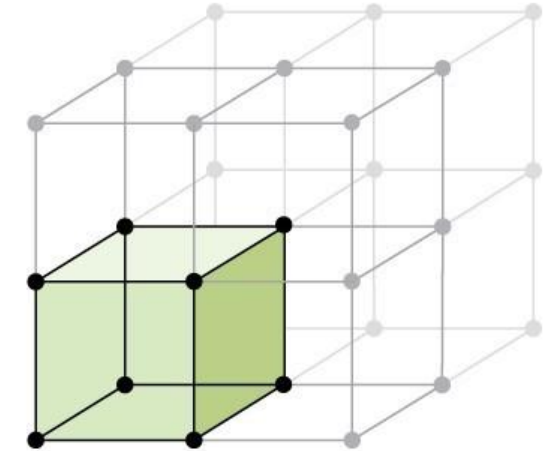


# Motivation – Long-range Interactions in Solids

$$E_{NN} = \frac{1}{2} \sum_{i,j} \frac{Z_i Z_j}{r_{IJ}}$$

- Trivial in finite systems
- Difficult in the solid state
  - $\frac{1}{r}$ , slow to converge
- Convenient to partition *all* coulombic interactions in to two bits:

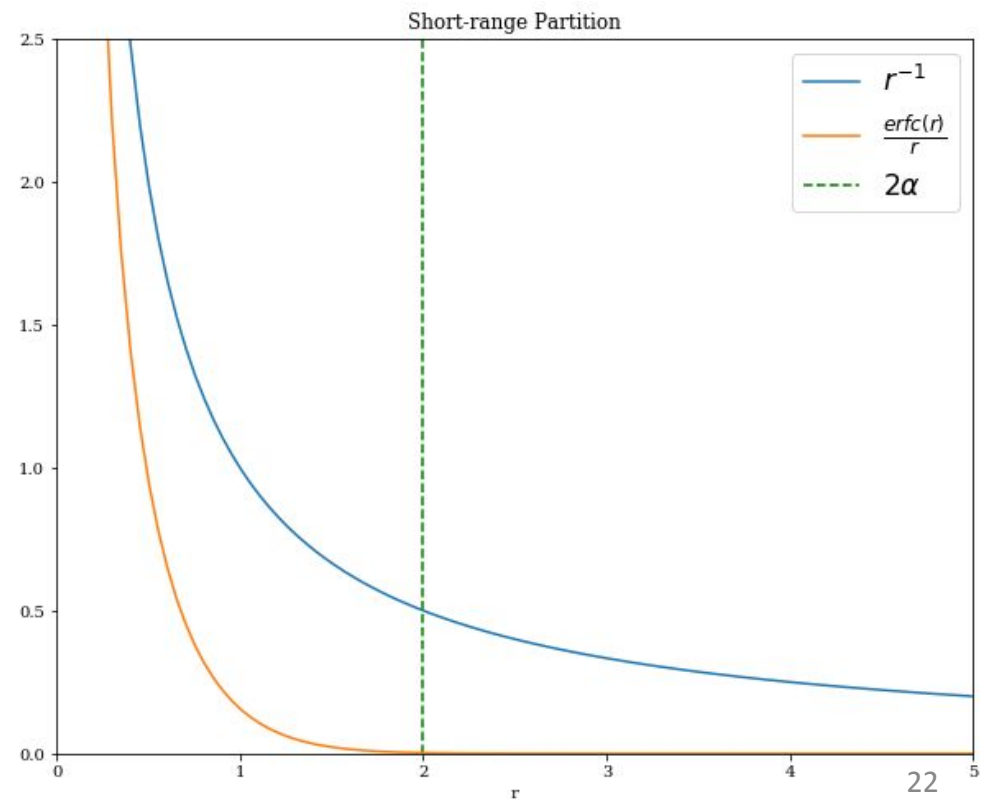
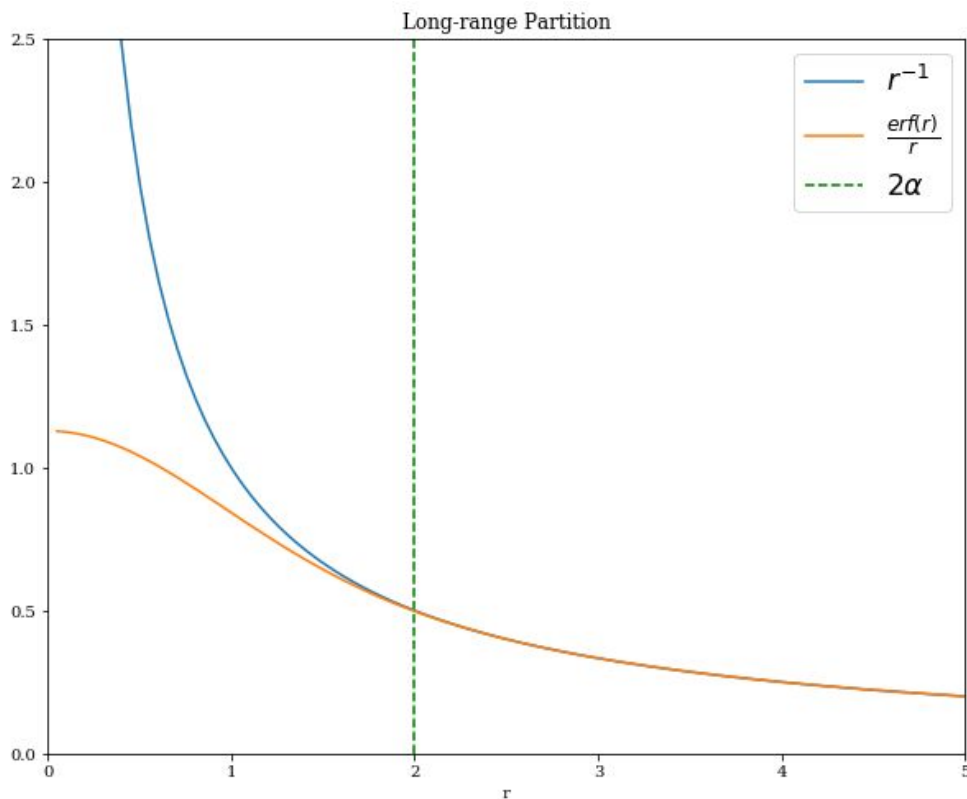
$$\frac{1}{r} = \underbrace{\frac{\text{erf}\left(\frac{r}{\alpha}\right)}{r}}_{\text{long-range}} + \underbrace{\frac{\text{erfc}\left(\frac{r}{\alpha}\right)}{r}}_{\text{short-range}}$$





# Motivation – Decomposing $\frac{1}{r}$

$$\frac{1}{r} = \overbrace{\frac{\text{erf}\left(\frac{r}{\alpha}\right)}{r}}^{\text{long-range}} + \overbrace{\frac{\text{erfc}\left(\frac{r}{\alpha}\right)}{r}}^{\text{short-range}}$$







# Motivation – Coulomb Potential in Solids

- Short range interactions calculated explicitly
- Long range potential evaluated via Fourier transform
  - Ewald Summation

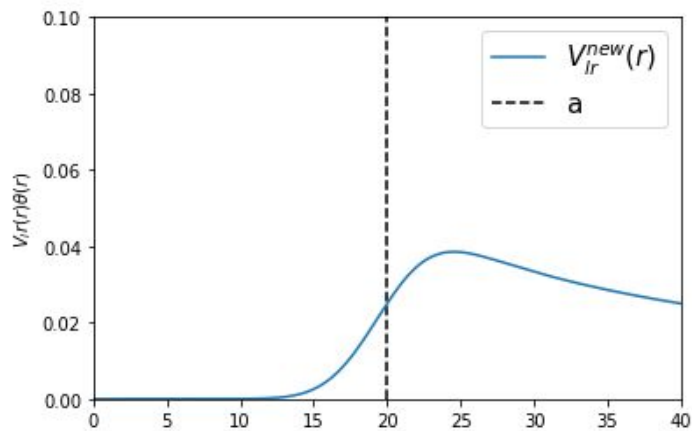
$$E_{NN} = \underbrace{Z_i Z_j \frac{1}{2} \sum_T \frac{\text{erfc}\left(\frac{|r_{ij}-T|}{\alpha}\right)}{|r_{ij}-T|}}_{\text{short-range in r-space}} - \underbrace{\frac{4\pi}{2\Omega} \sum_k |S_k|^2 \frac{e^{-k^2 \alpha^2}}{k^2}}_{\text{long-range in k-space}} - \underbrace{\frac{1}{\alpha \sqrt{\pi}} \sum_i Z_i^2}_{\text{lr "self" correction}}$$

- This partitioning can be used for any interaction in the solid state

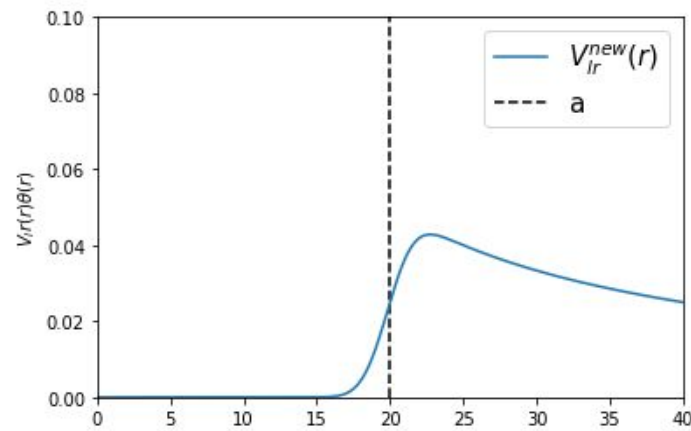
Can we improve this partitioning?

# Improved Partitioning of the Coulomb Potential

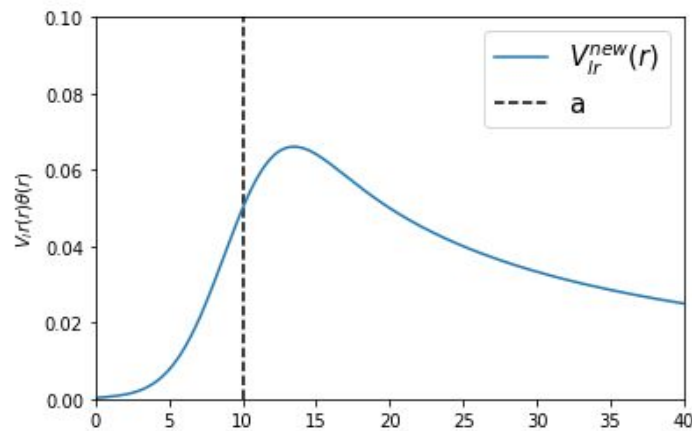
- New, adjustable potential,  $V_{lr}^{new}(r) = V_{lr}^{old}(r)\theta(r)$



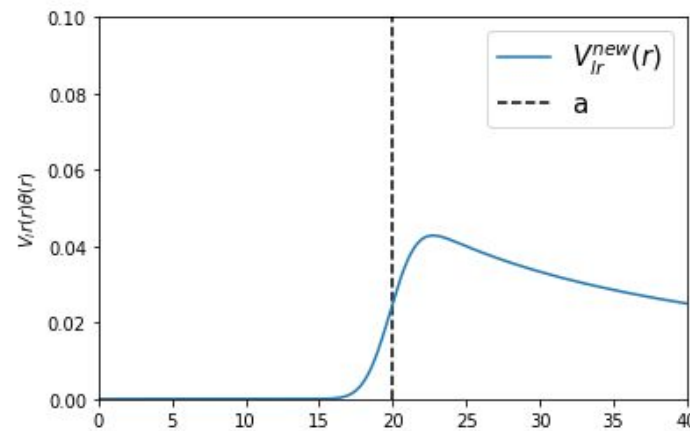
$a = 20, b = 5$



$a = 20, b = 2$

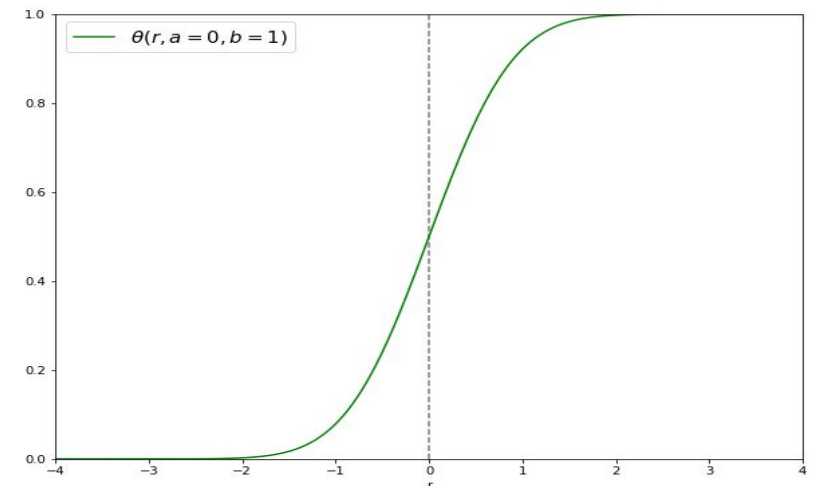


$a = 10, b = 5$



$a = 10, b = 2$

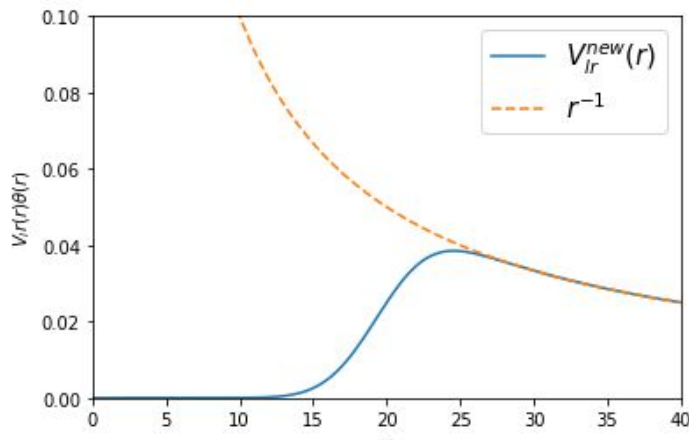
$$\theta(r) = \frac{1}{2} \left( 1 + \operatorname{erf} \left( \frac{r - a}{b} \right) \right)$$



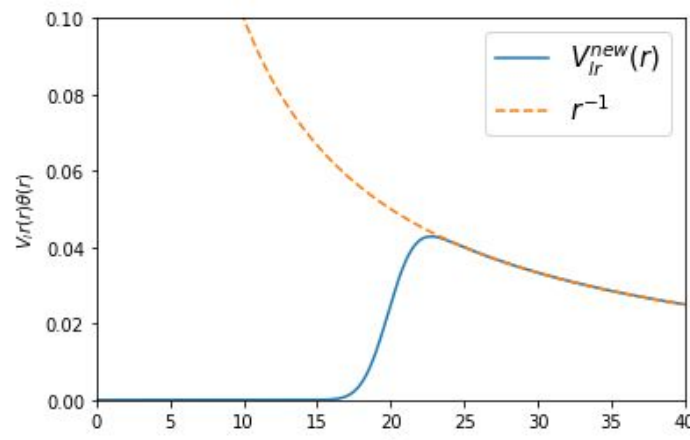


# Improved Partitioning of the Coulomb Potential

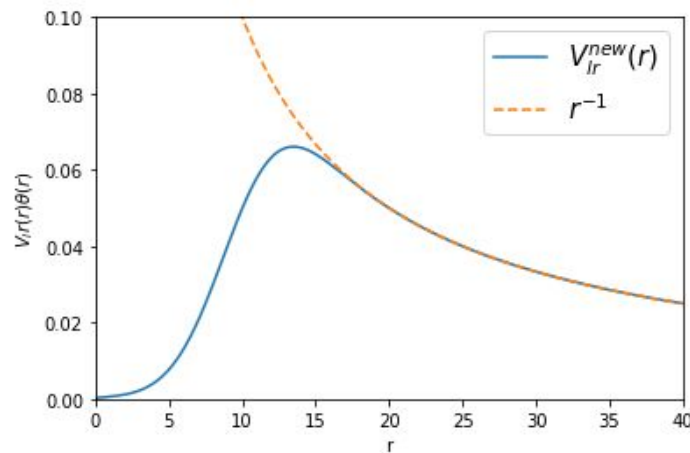
- New, adjustable potential,  $V_{lr}^{new}(r) = V_{lr}^{old}(r)\theta(r)$



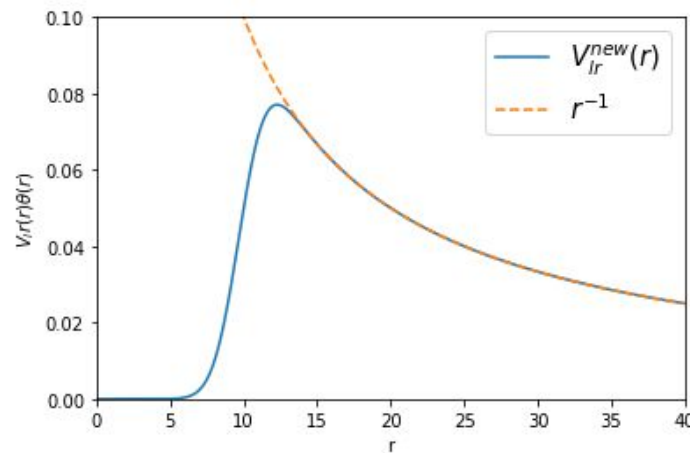
$a = 20, b = 5$



$a = 20, b = 2$

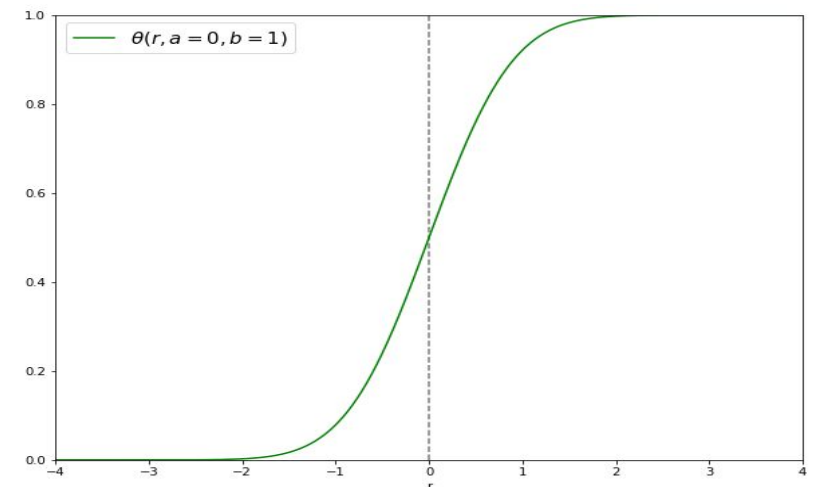


$a = 10, b = 5$



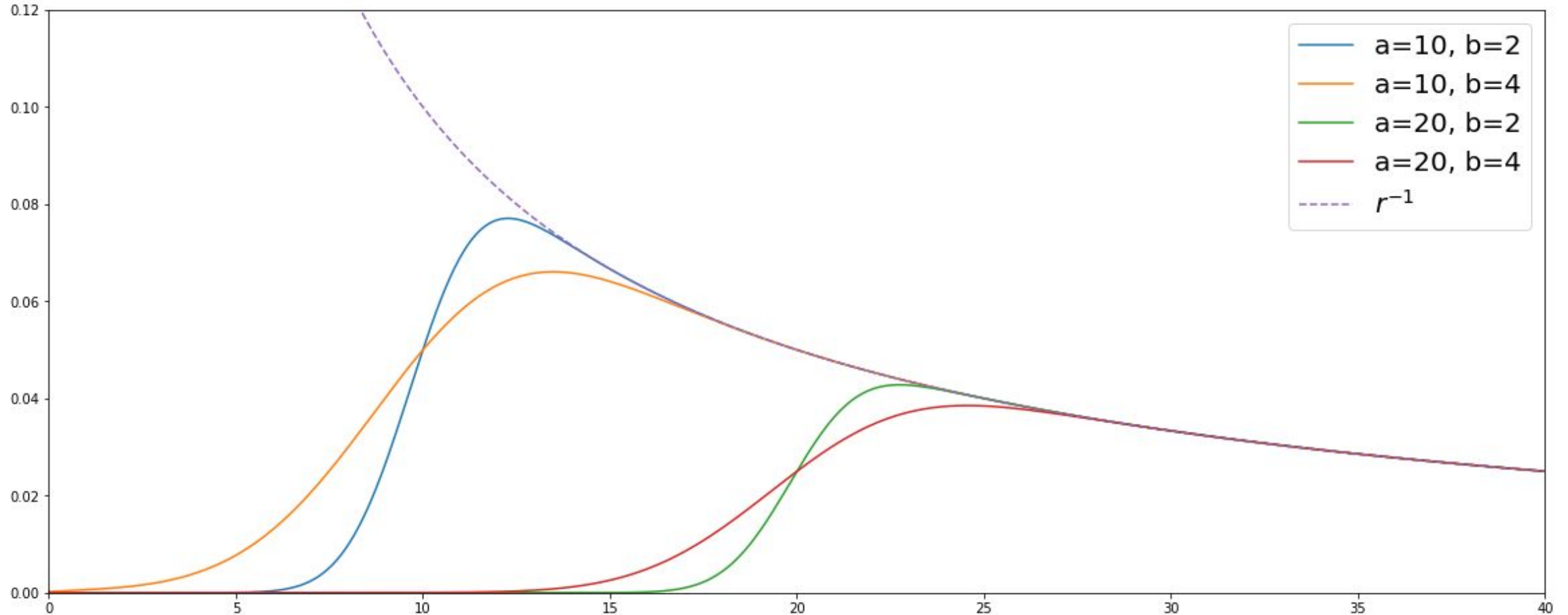
$a = 10, b = 2$

$$\theta(r) = \frac{1}{2} \left( 1 + \operatorname{erf} \left( \frac{r - a}{b} \right) \right)$$



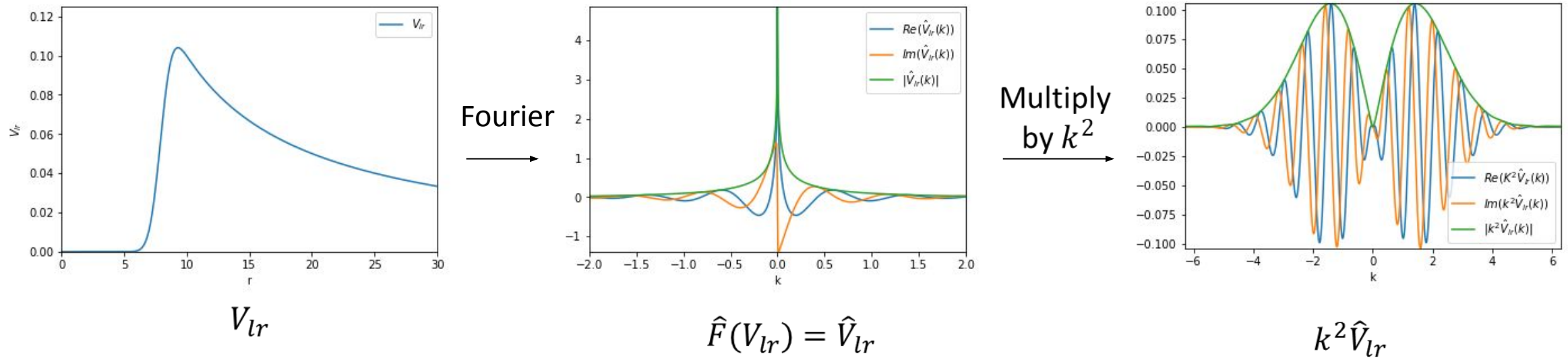


# Improved Partitioning of the Coulomb Potential



# Improved Partitioning of the Coulomb Potential

- Spatially disperse functions have localized counterparts in k-space



$$\int_{\Omega} \hat{V}_{lr}(k) dk = \int_{\phi} \int_{\theta} \int_k \hat{V}_{lr}(\theta, k, \phi) \underbrace{k^2 \sin(\theta) dk d\theta d\phi}_{\text{Volume element}}$$

$$\langle pq | \frac{1}{r} | rs \rangle_{lr} = \langle pq | \vec{k} \rangle \hat{V}_{lr}(\vec{k}, \theta, \phi) \langle \vec{k} | rs \rangle$$

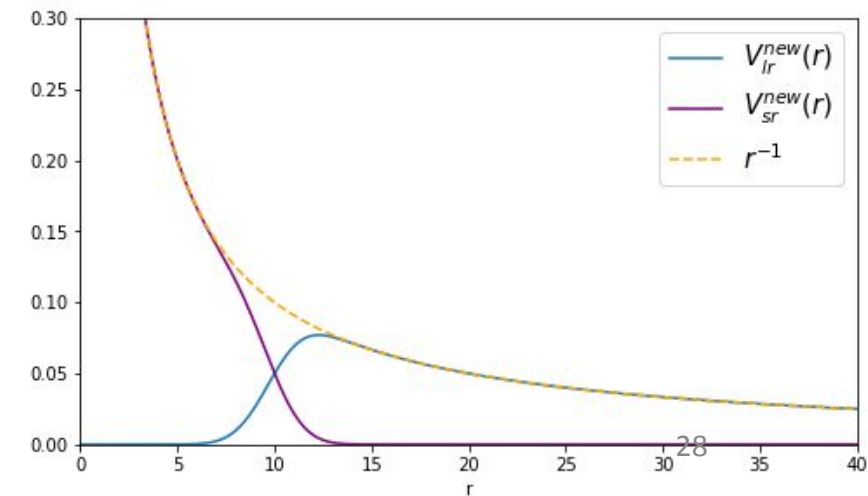
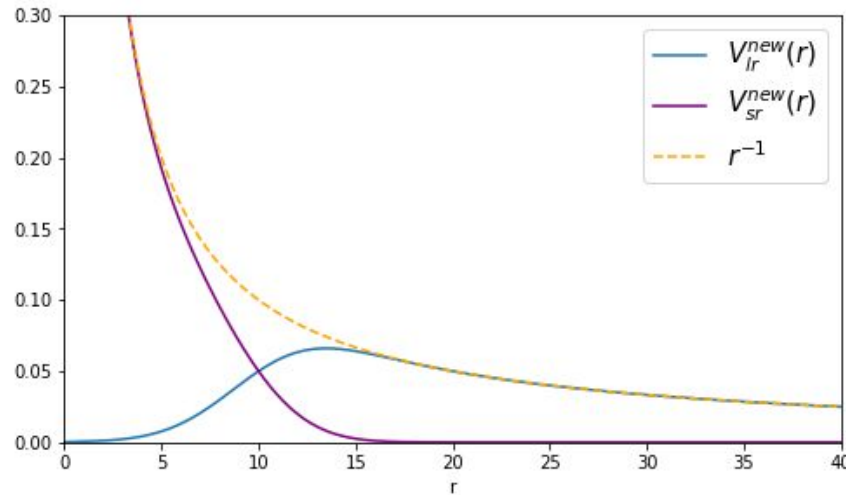
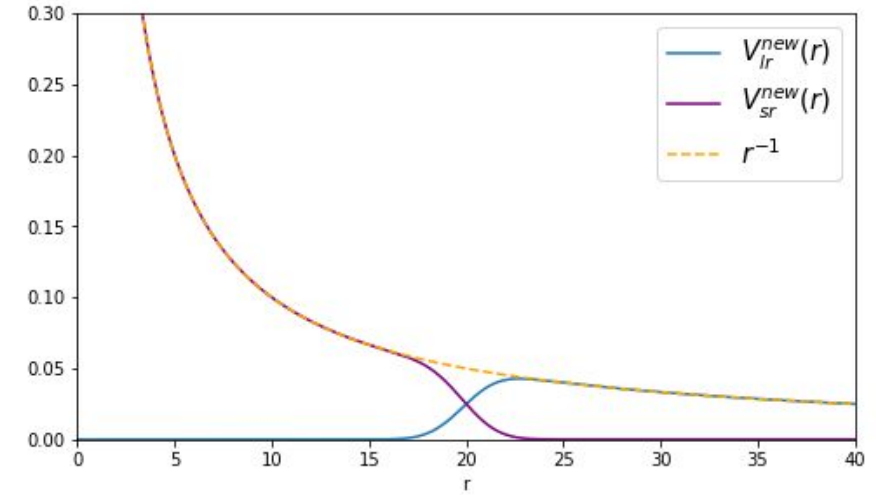
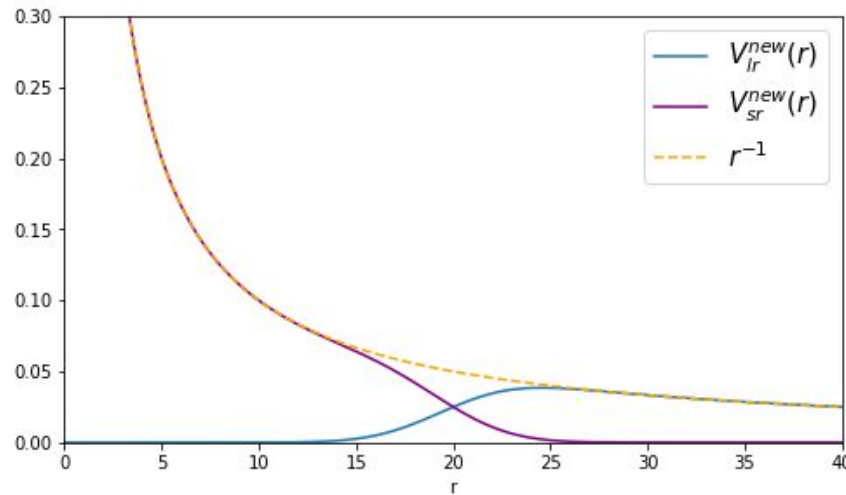


# The Short Range Partition

- $V_{sr}$  can be evaluated numerically

$$\frac{1}{r} = V_{sr}^{new} + V_{lr}^{new}$$

$$\frac{1}{r} - V_{lr}^{new} = V_{sr}^{new}$$





# Partitioning Contributions in CC calculations

- We should be able to partition t-amplitudes

$$^{\text{total}}t_{ij}^{ab} = {}^{sr}t_{ij}^{ab} + {}^{lr}t_{ij}^{ab}$$

$$E_{CC} = V_{\text{total}} \cdot T_{sr}^{CC} + V_{\text{total}} \cdot T_{lr}^{MP2}$$

- This does not work with conventional partitioning



# Long Term Goal: Solid State CC

- Partition calculations into short and long range
- Long range interactions via Fourier transform
- Short range interactions via CLO implementation of DLPNO-CC



# Next steps

- Implement CC calculations using CLO's in ACESII
  - Test CC equations using linearly dependent CLO's
  - Implement CLO version of DLPNO-CC in ORCA
  - Eventually use CLO's in solid state systems.
- Test 'pure' long range partitioning in solids
  - Implement Gauss-Lebedev integration scheme for integrals over  $\hat{F}[V_{lr}]$
  - Evaluate integrals of Gaussian products using PYSCF
  - Test partitioning of t-amplitudes using our adjustable potential





# Acknowledgements

- Dr. Marcel Nooijen
- Theoretical Chemistry Department
- Mike Lecours



**UNIVERSITY OF WATERLOO**  
FACULTY OF SCIENCE  
Department of Chemistry







Questions?