High Pressure, high temperature water

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Outline

A new form of high pressure, high temperature ice.

Crystal Structure of Oxygen sub lattice **(Closed Pack ⟶ P21/c space-group)**

> **the phase diagram**

> **why this phase?**

> **why this phase diagram?**

> **connecting to T=0**

Computational details

**Electronic Structure:** **Ice rule ⟶ unimodal distribution**

> **Dynamical born charges**

What are the hydrogens doing? **anisotropic diffusion**

> **ionic conductivity**

Nuclear Quantum Effects

Closed Pack ⟶ P21/c space-group

2500 K | BCC-SI | CP-SI | P2₁/c-SI

increasing pressure
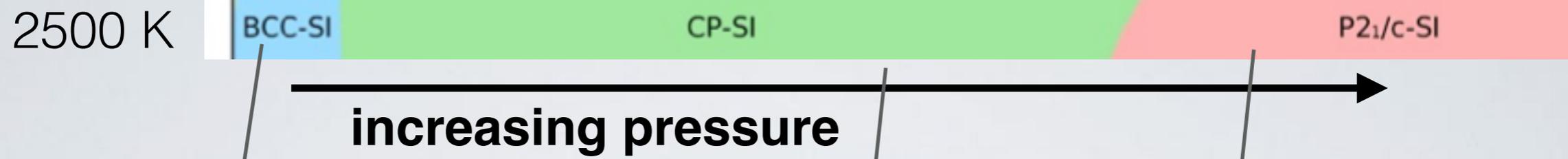
forever

Militzer, et. al
this work

this work
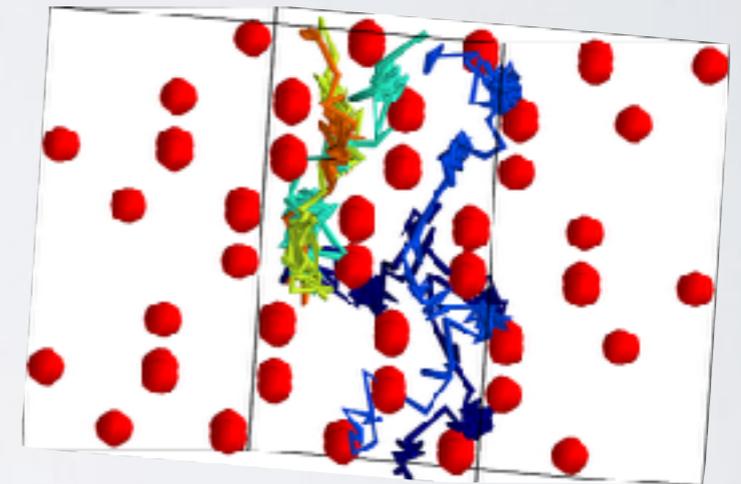
Superionic phases:

Say what a supersonic phase is

This is different then the ground state

same symmetry but less molecules/unit cell

Table 1 | Structural parameters of the oxygen sublattice of P2₁/c-SI.

Symmetry	P2₁/c
Molecules/unit cell	4
a(Å)	2.87
b(Å)	3.11
c(Å)	3.58
β(°)	151
O position	0.636, −0.077, 0.013

The structural parameters are calculated at 1.0 TPa and 1,600 K. a, a and c are the edges of the monoclinic unit cell. β is the angle between a and c. The position of one O atom in units of the cell parameters (a, b, c) is given in the last entry. The positions of the three other oxygens in the cell are obtained from the position in the table by symmetry operations.

the phase diagram
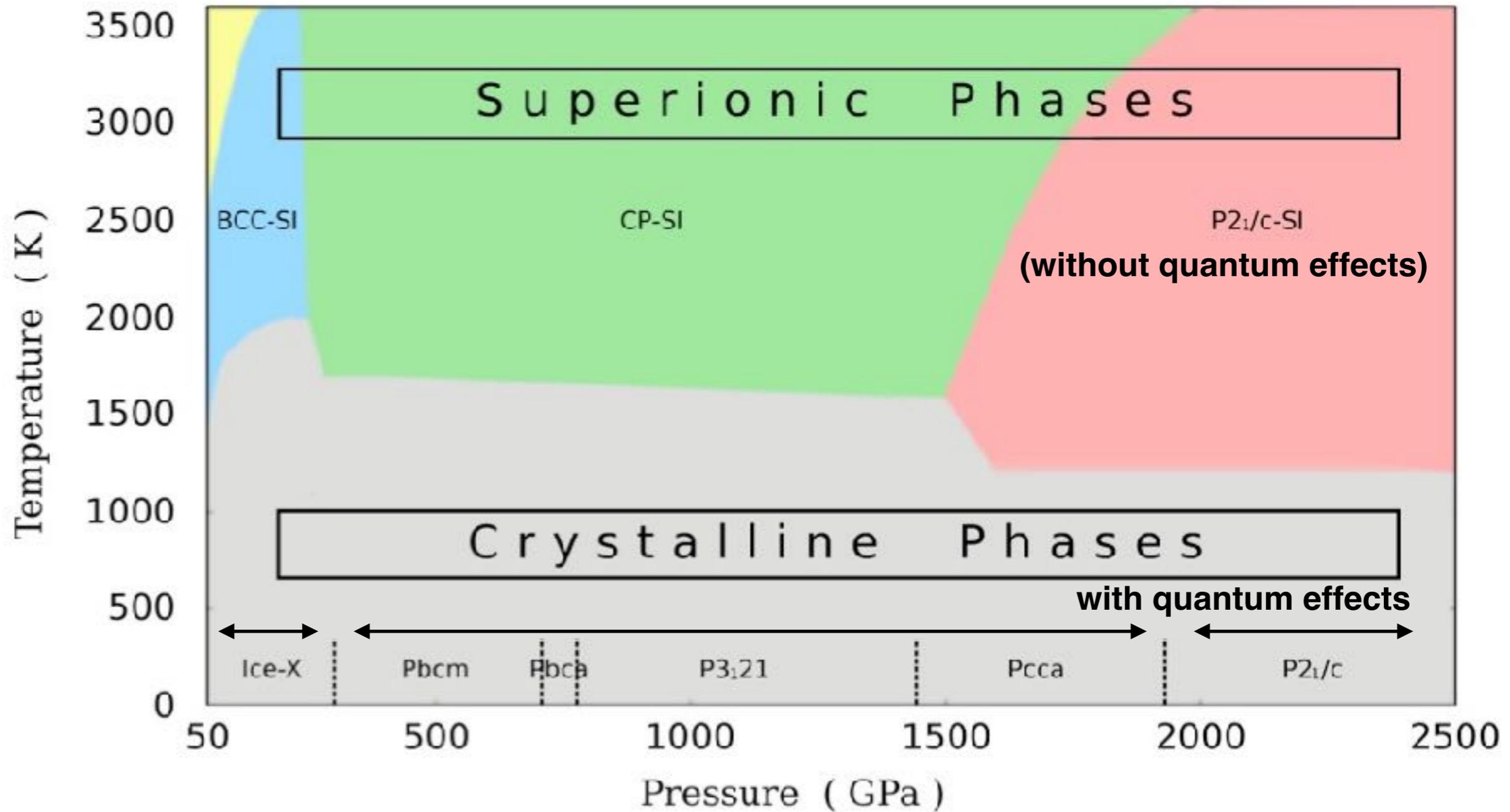
discuss crystalline phases here and simplification, etc?

1. *Decomposition and terapascal phases of water ice*
   C.J. Pickard, M. Martinez-Canales, and R.J. Needs
   Phys. Rev. Lett. **110**, 245701 (2013)
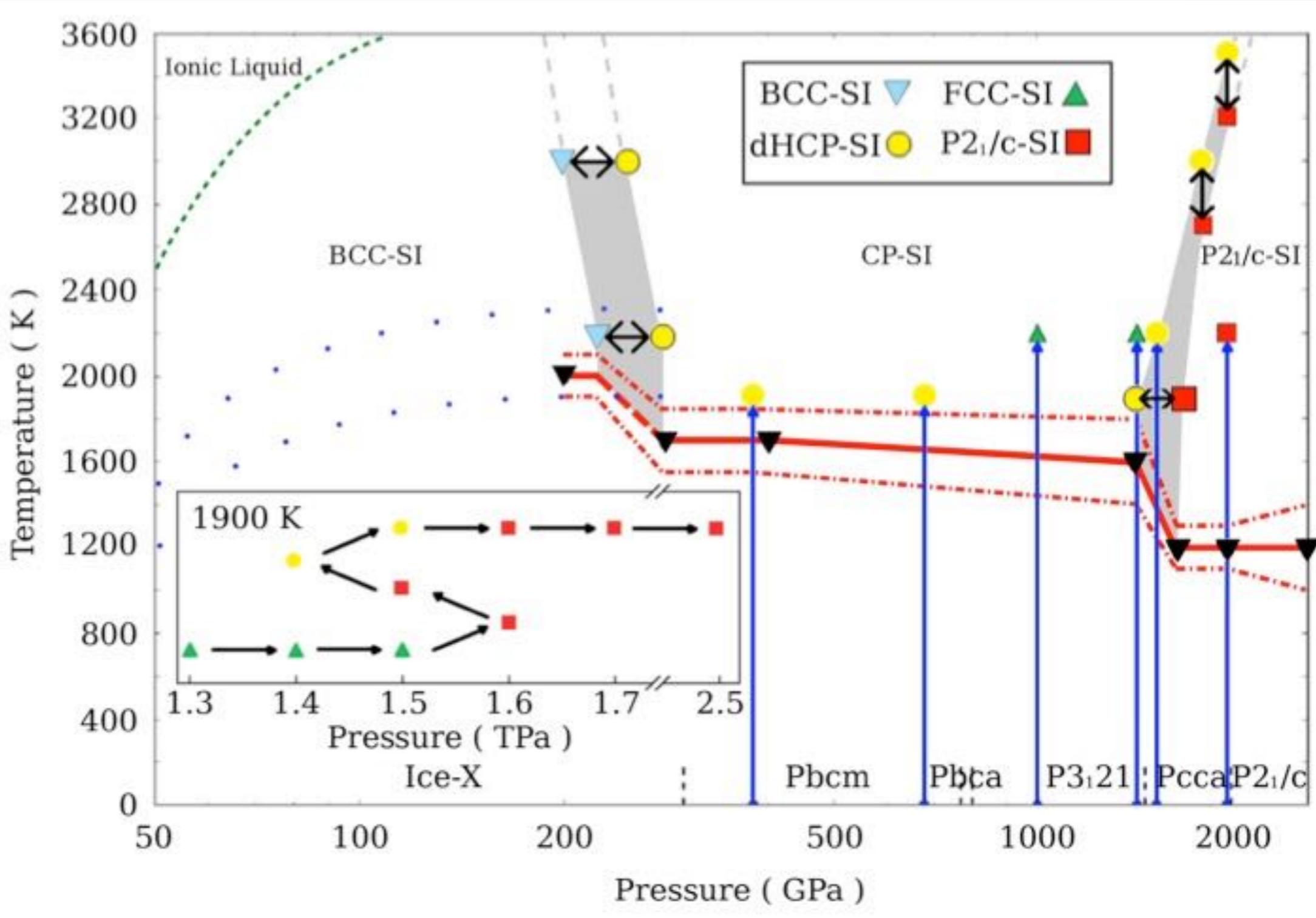
why this phase?

1900 K

| BCC-SI | CP-SI | P2₁/c-SI |
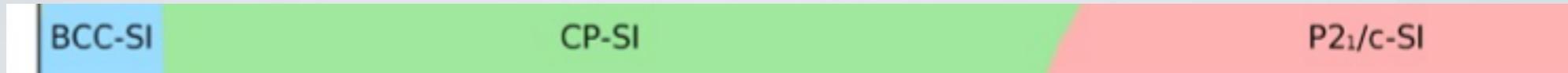
increasing pressure

Probably +PdV

$$\Delta H = \Delta U - P\Delta V - T\Delta S$$

FCC-SI ⟶ P21/c-SI

$\Delta U = +0.05\text{eV mol}^{-1}$

$\Delta V = -0.19 \text{ Bohr}^3 \text{ per mol}$

$P\Delta V = -0.28 \text{ eV mol}^{-1}$

How does density increase beyond a closed-packed structure?

The hydrogen allow for increased density

Table 2 | Change of thermodynamic properties in the FCC-SI to P2₁/c-SI transition.

|	
ΔH	−0.23 eV mol⁻¹
ΔV	−0.19 Bohr³ per mol
PΔV	−0.28 eV mol⁻¹
ΔU	+0.05 eV mol⁻¹

The change of specific enthalpy (H), volume (V) and internal energy (U) across the transition at P=1.6 TPa and T=1,900 K. The enthalpy difference is mainly due to the PΔV term, which in turn is due to the higher density in P2₁/c-SI.

why this phase diagram?
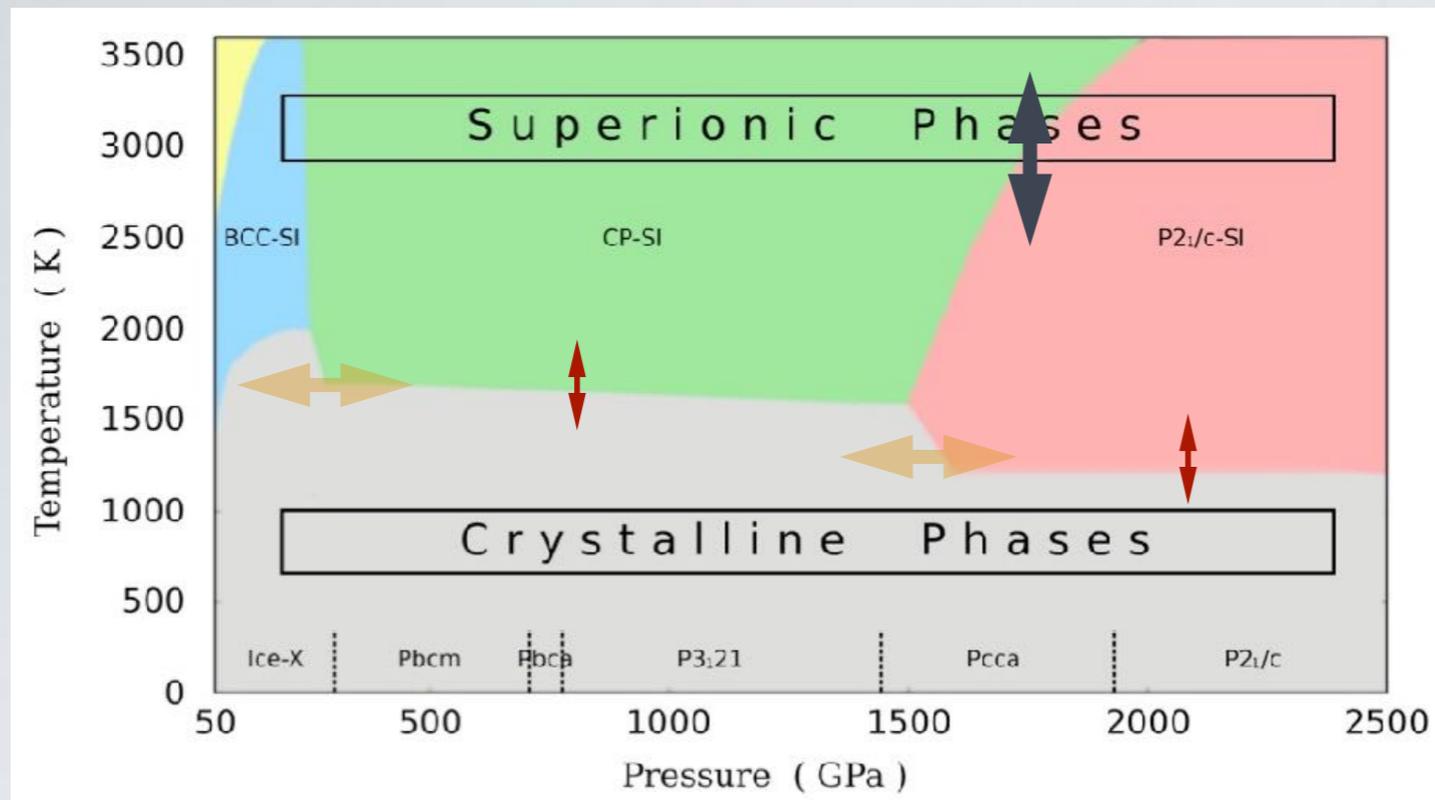
Melt P21 upon increasing T

$$\Delta H \approx -0.1 \text{ eV mol}^{-1}$$

ΔS favors closed-pack
  hydrogens higher diffusivity

melt upon increases pressure

Flat boundaries

Negative slopes

Clausius-Claperyon $\quad \dfrac{dT}{dP} = \dfrac{\Delta V}{\Delta S}$
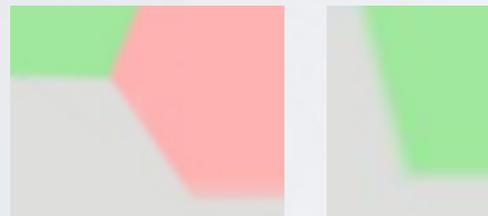
Superionic phase (presumably) higher entropy

Superionic smaller volume then nearby crystalline phase.

Superionic larger volume then nearby crystalline phase.

P21 denser and less entropy

BCC and CP same entropy
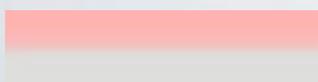
Crystalline and SI phases no volume change
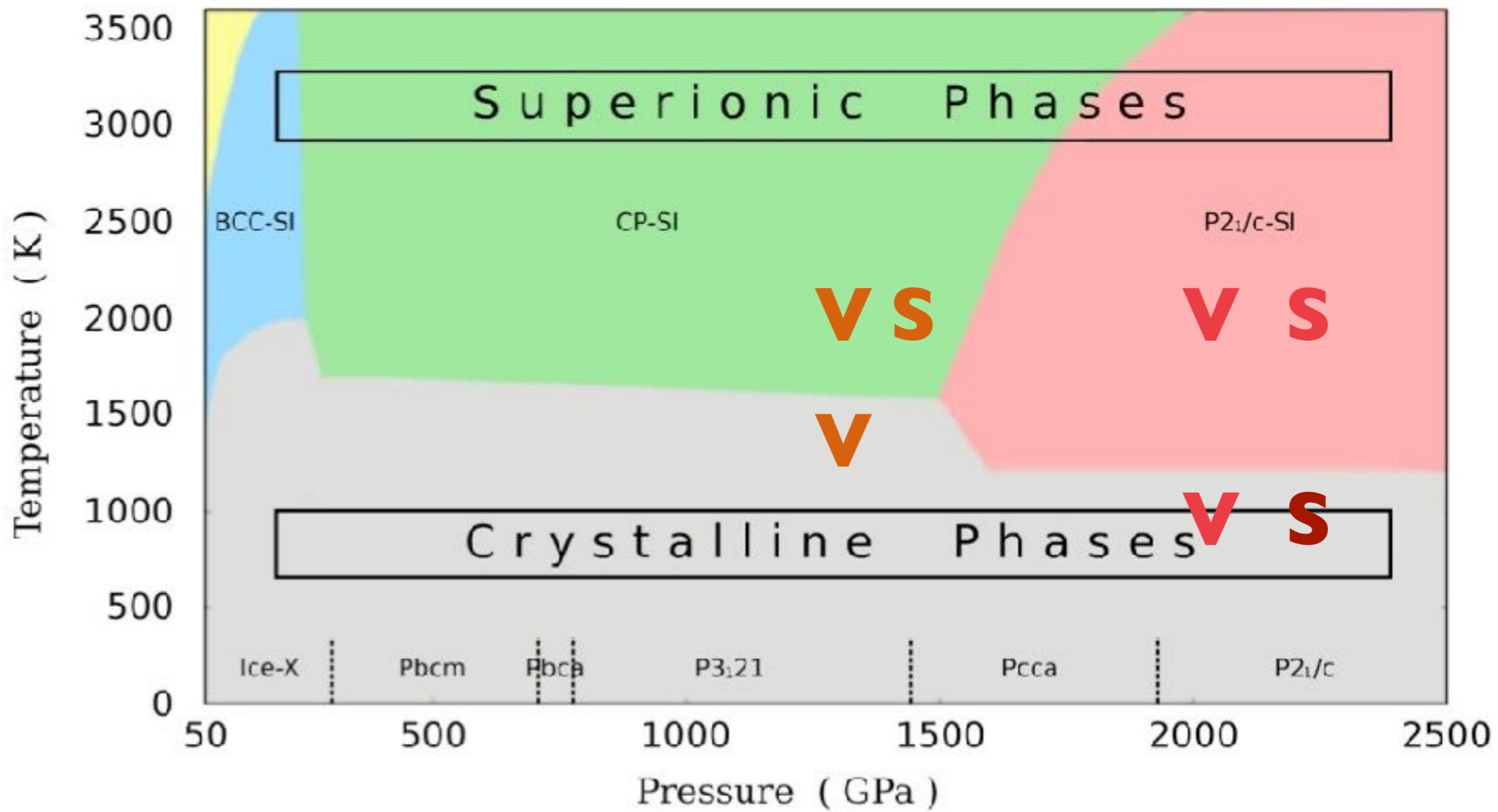
connecting to T=0
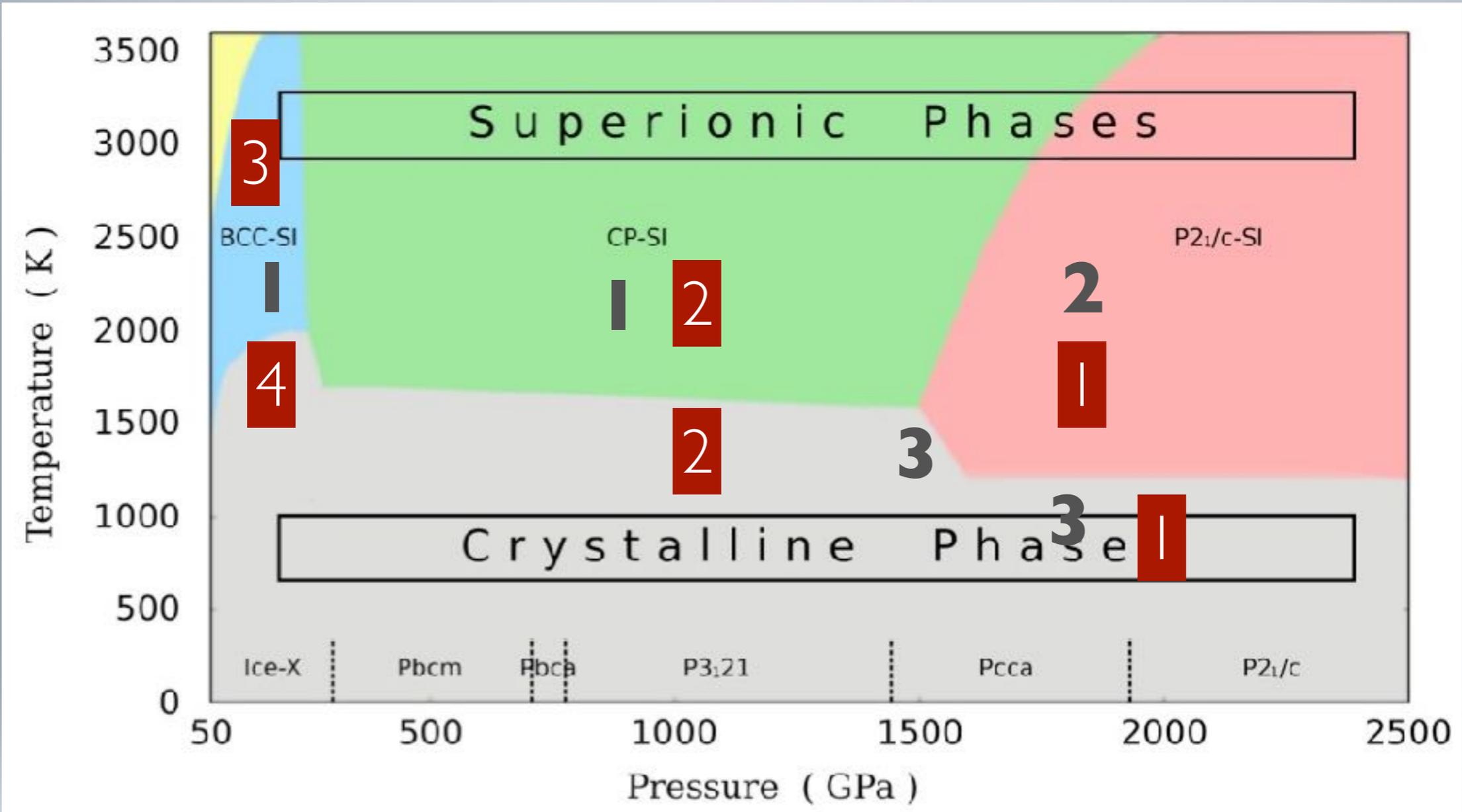
Electronic Structure: **Ice rule** $\longrightarrow$ **unimodal distribution**

electronic insulator; ionic conductor
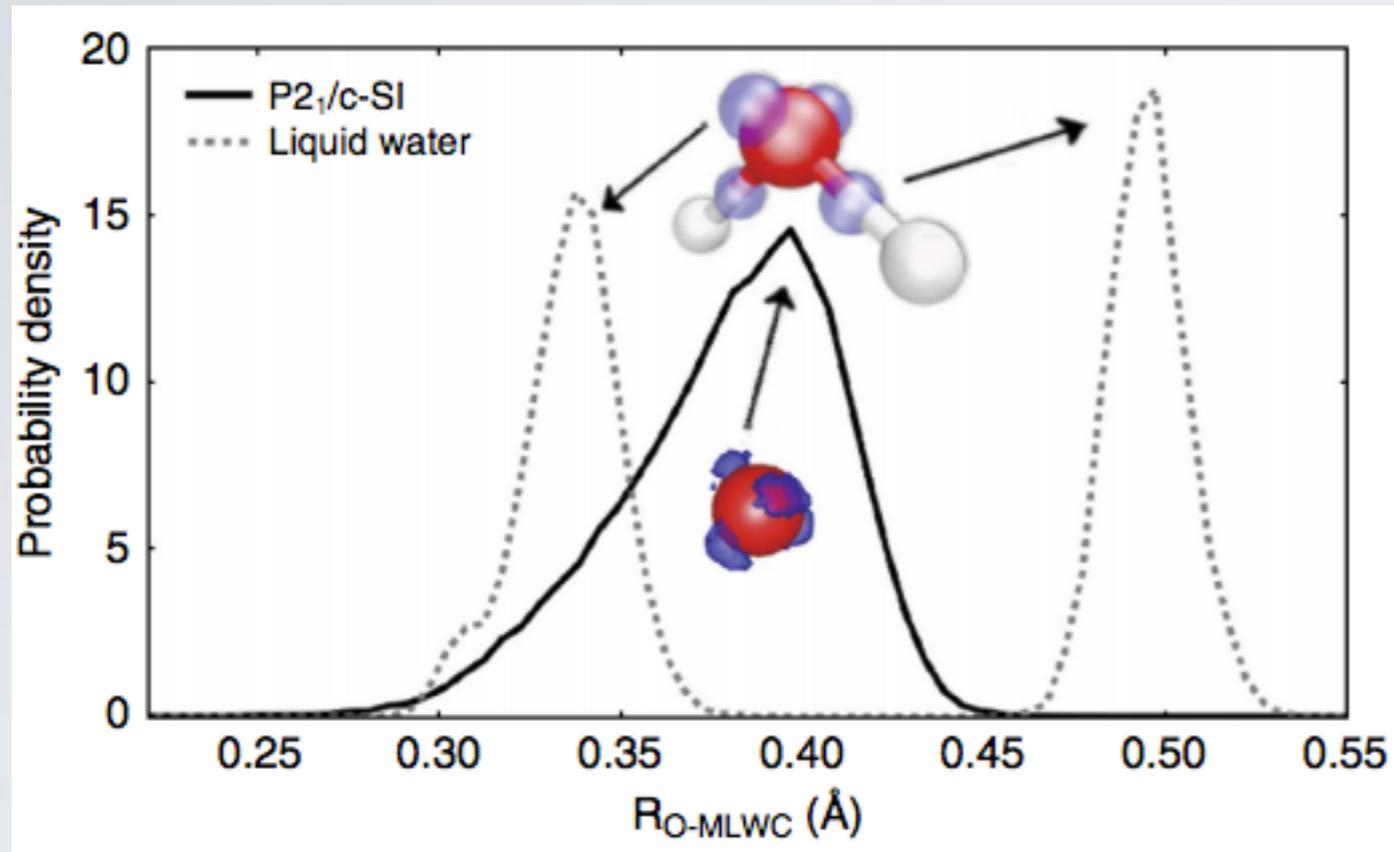

Dynamical born charges

$$Z_{i,\alpha\beta} = \frac{\partial F_{i,\alpha\beta}}{\partial E_\beta}$$

1.2   -2.4

What are the hydrogens doing?   anisotropic diffusion
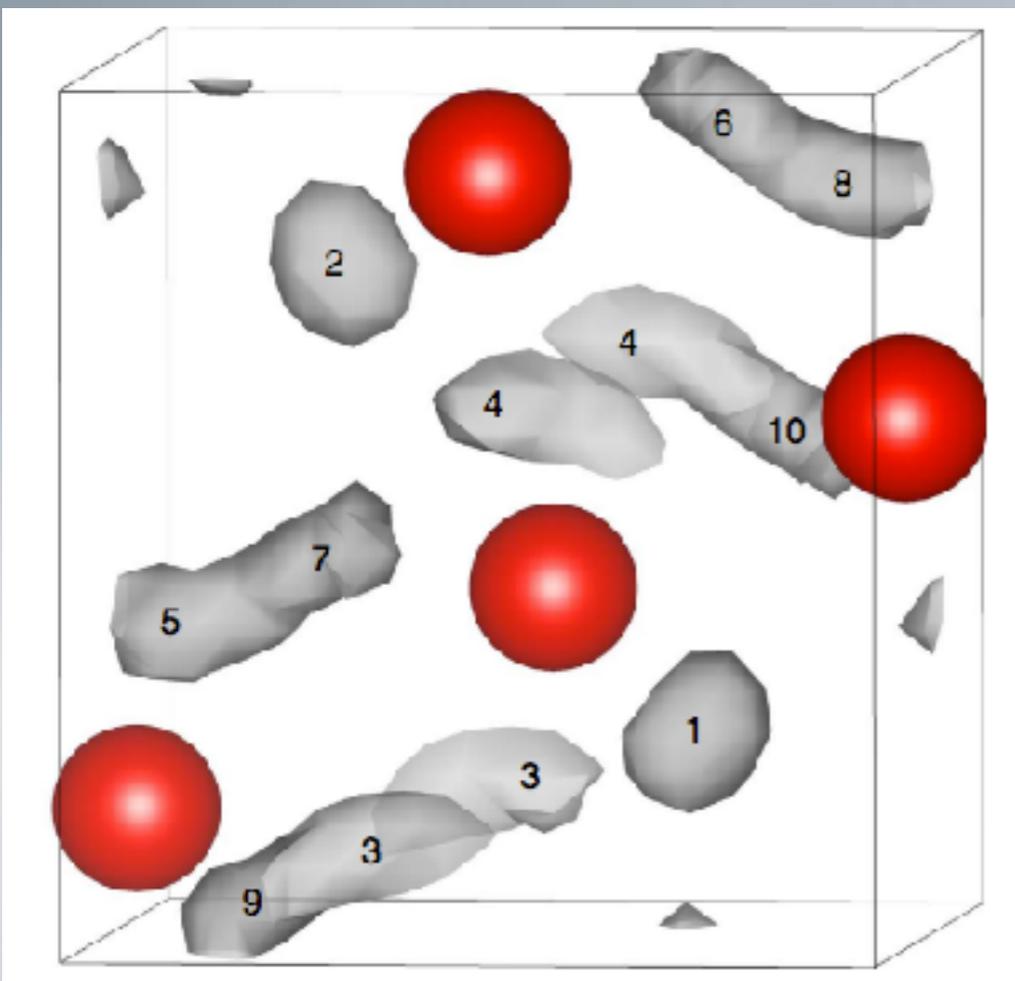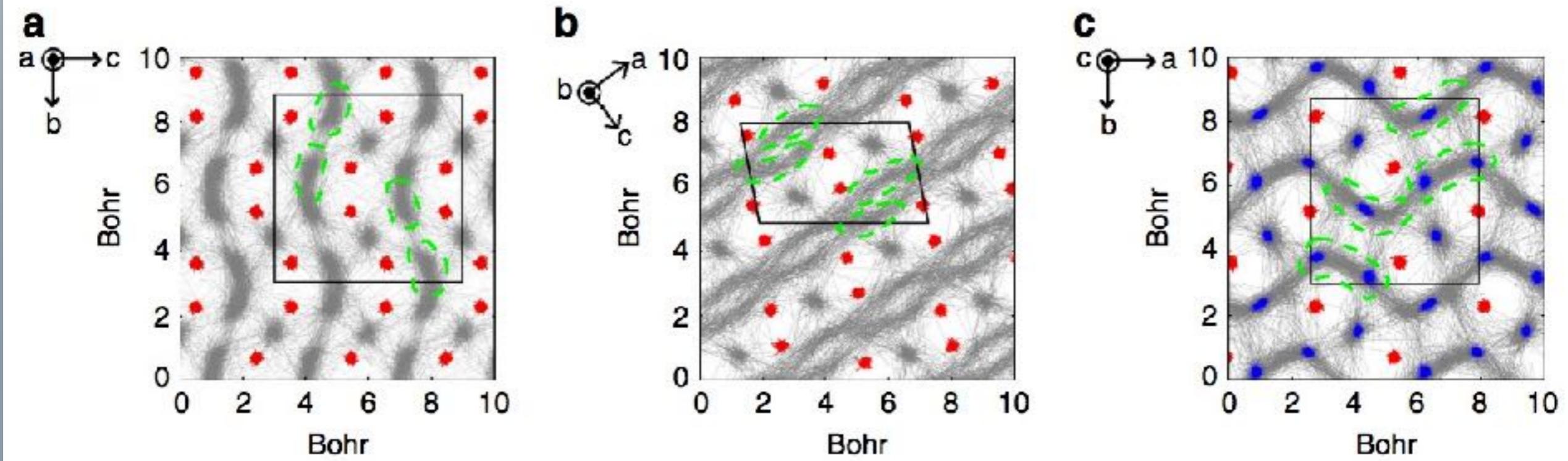
ionic conductivity

High pressure, high temperature ice

meta-dynamics
frozen oxygen; melted hydrogen
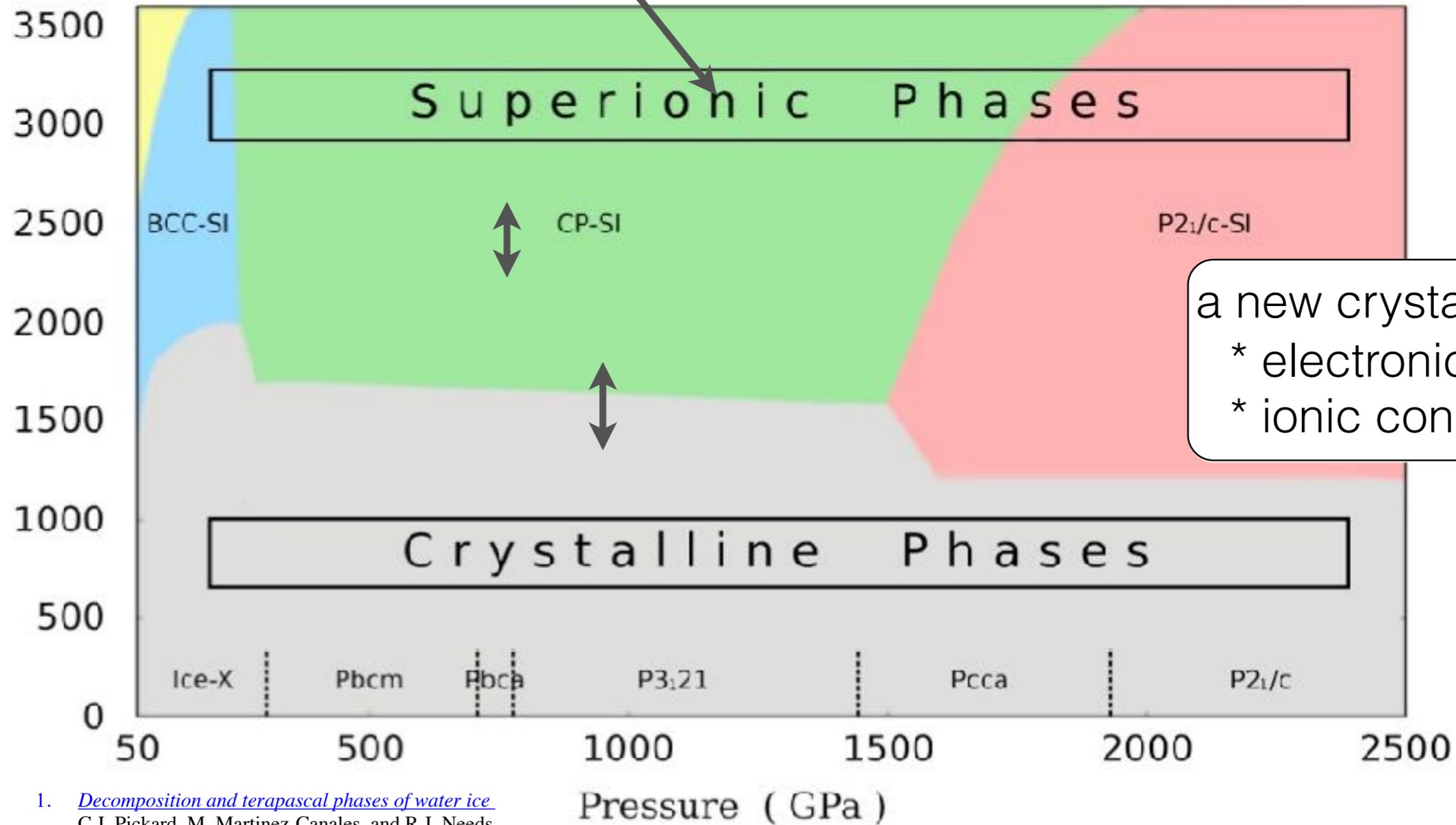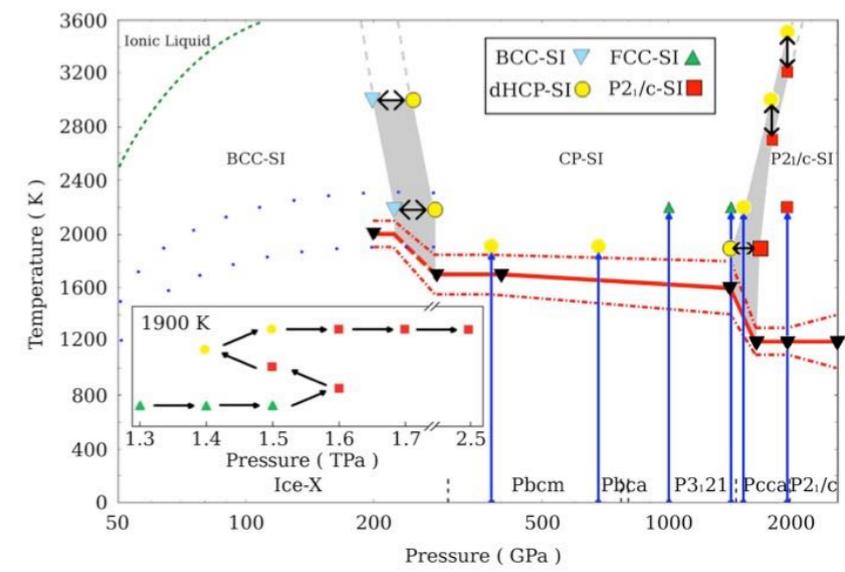
a new crystal phase
* electronic insulator
* ionic conductor

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b

c

a

goo

b

Noo

- Pbcm
- Pbca
- P3₁21
- Pcca
- P2₁/c

c

goo

d

Noo

- FCC
- P2₁ 0 K
- P2₁/c 0 K
- CP-SI (1.3 TPa, 1900 K)
- P2₁/c-SI (1.9 TPa, 1600 K)

a

Ionic Liquid

BCC-SI ▽   FCC-SI ▲

dHCP-SI ○   P2₁/c-SI ■

BCC-SI   CP-SI   P2₁/c-SI

Temperature (K)

b

1900 K

Ice-X   Pbcm   Pbca   P3₁21 Pcca P2₁/c

Pressure (TPa)

Pressure (GPa)

a — g_{OH} vs Radius (Bohr)

b — N_{OH} vs Radius (Bohr)

c — g_{OO} vs Radius (Bohr)

- FCC quenched
- P2$_1$/c quenched
- P3$_1$21 0 K
- P2$_1$ 0 K

d — N_{OO} vs Radius (Bohr)
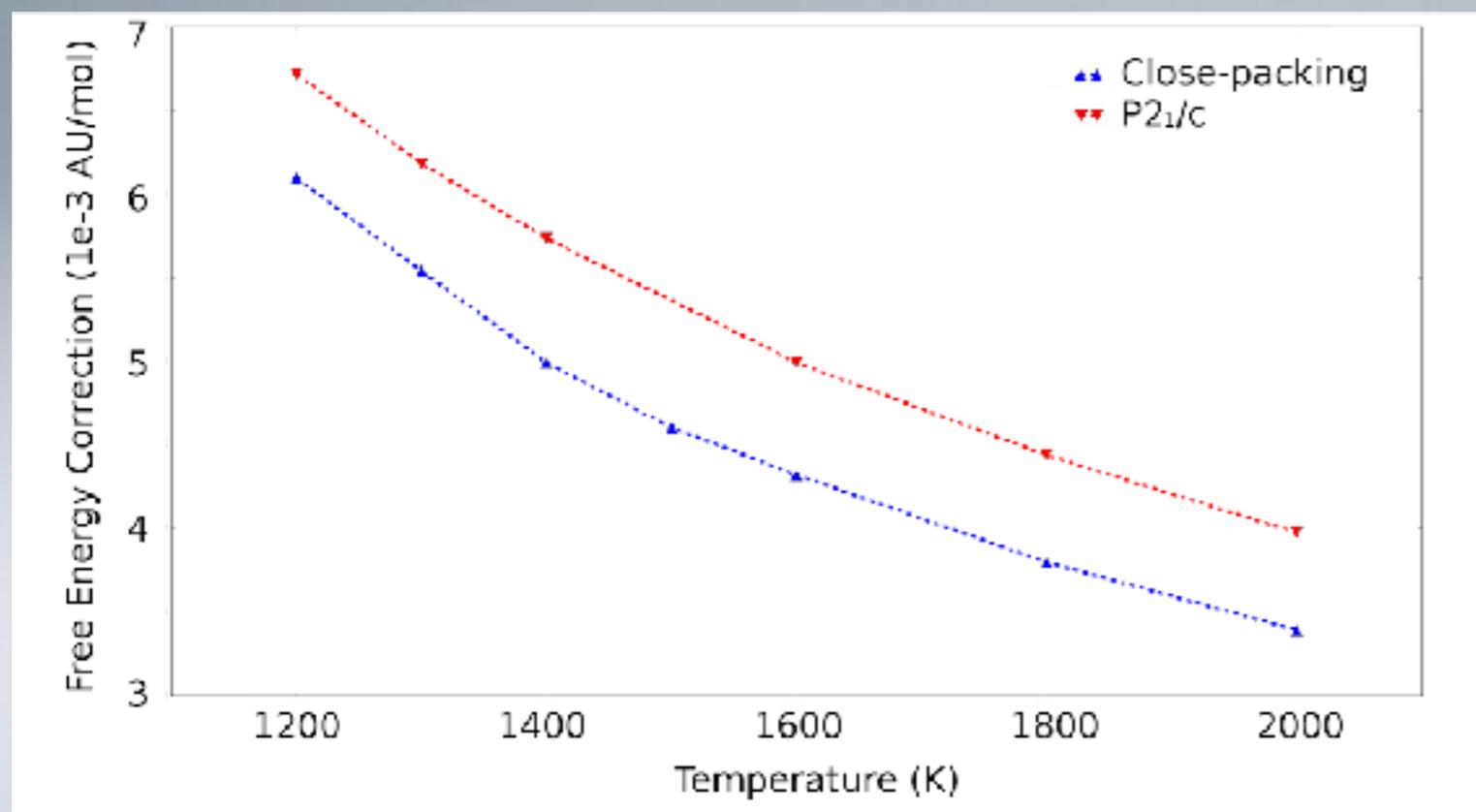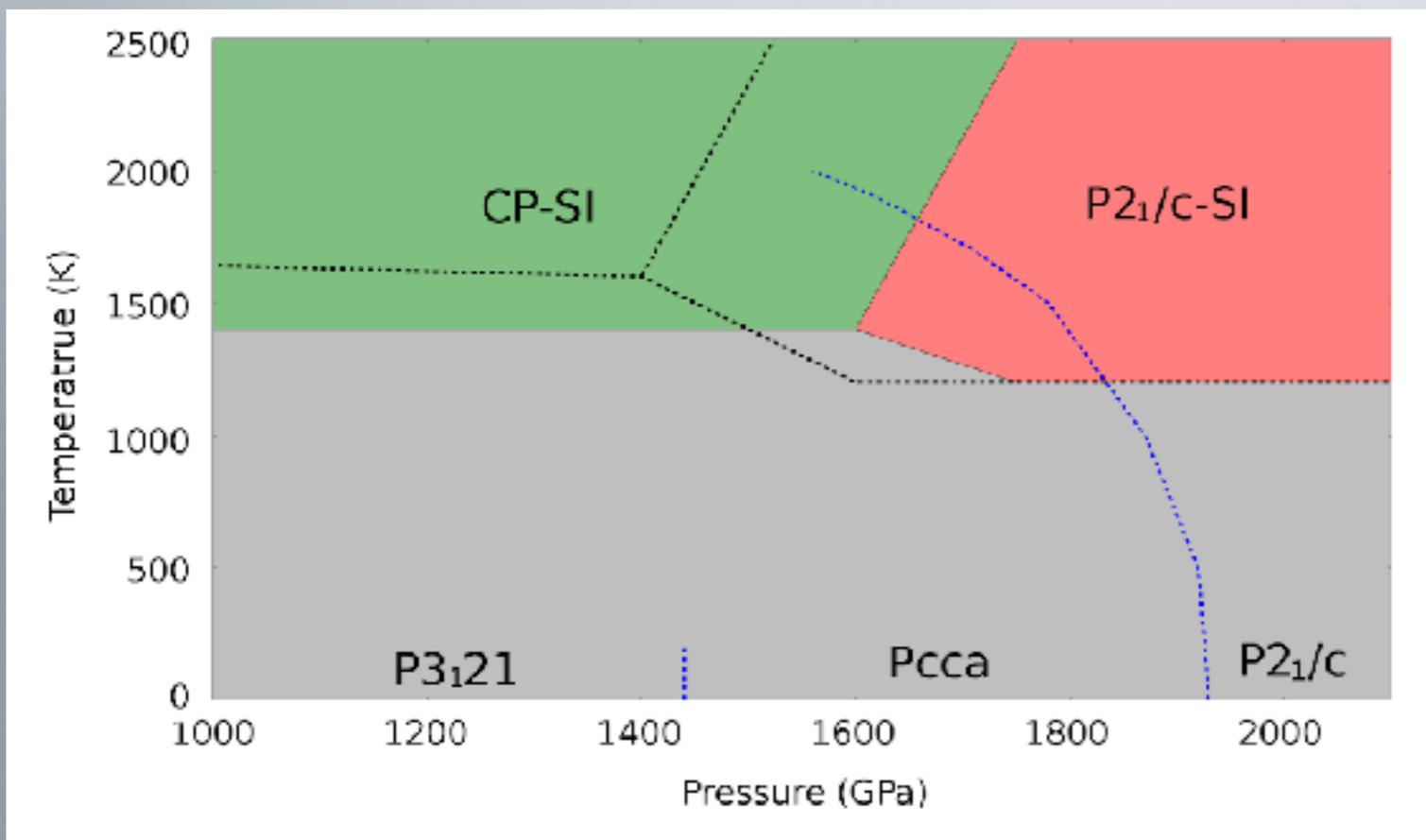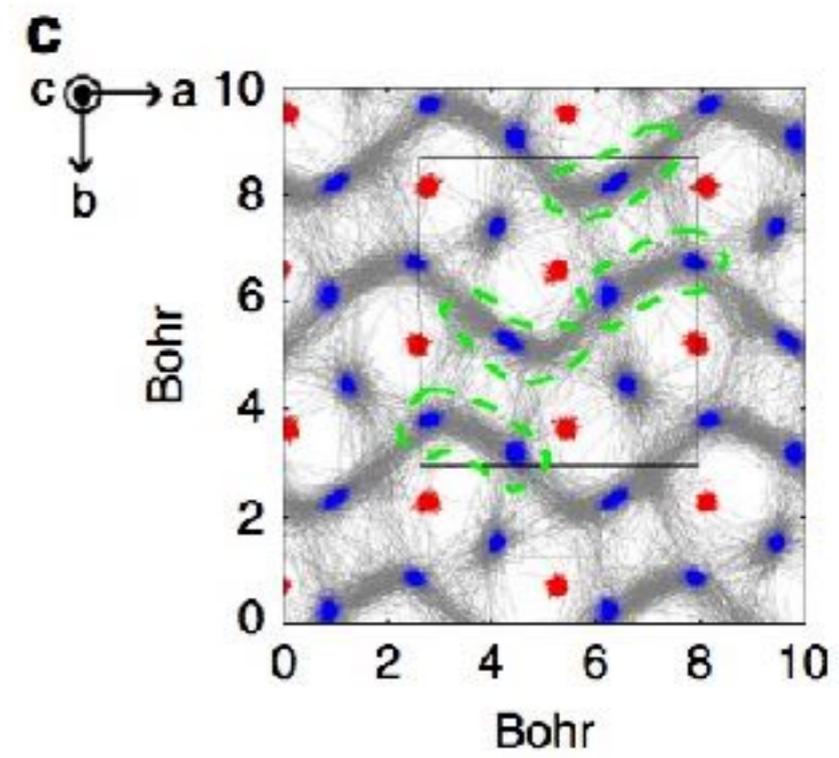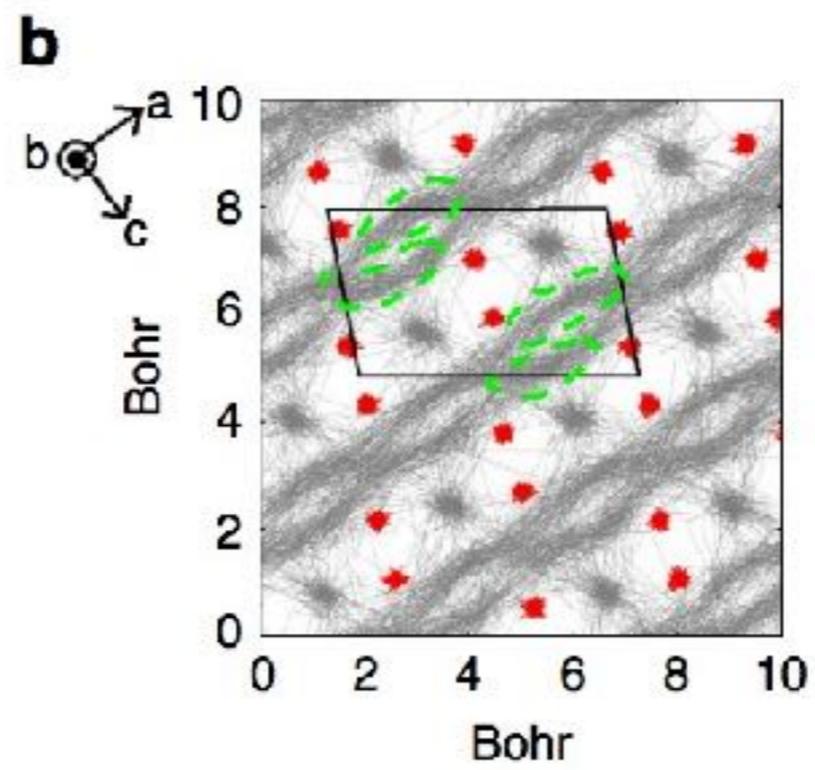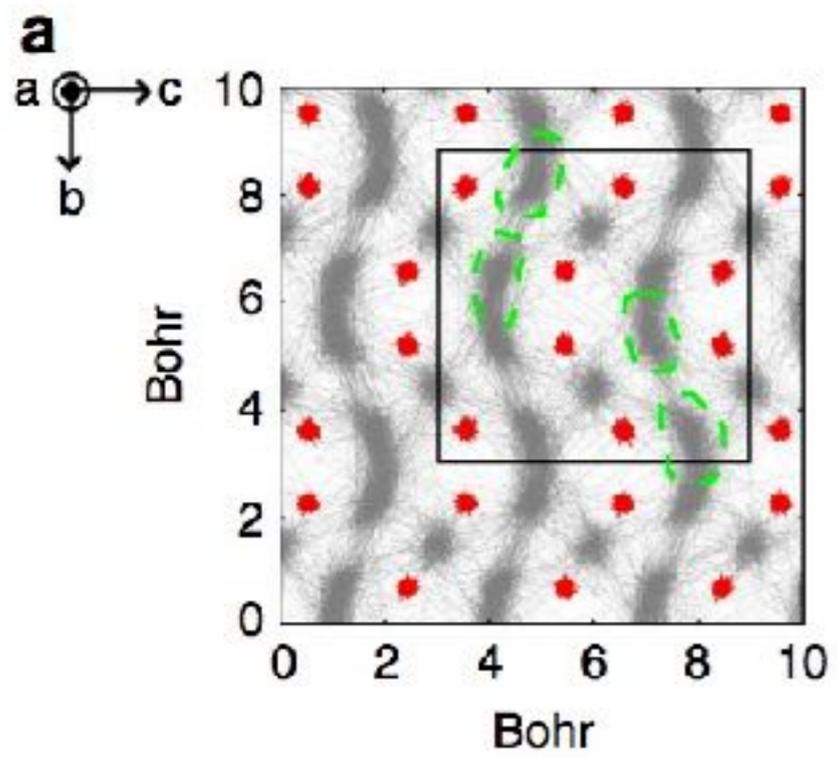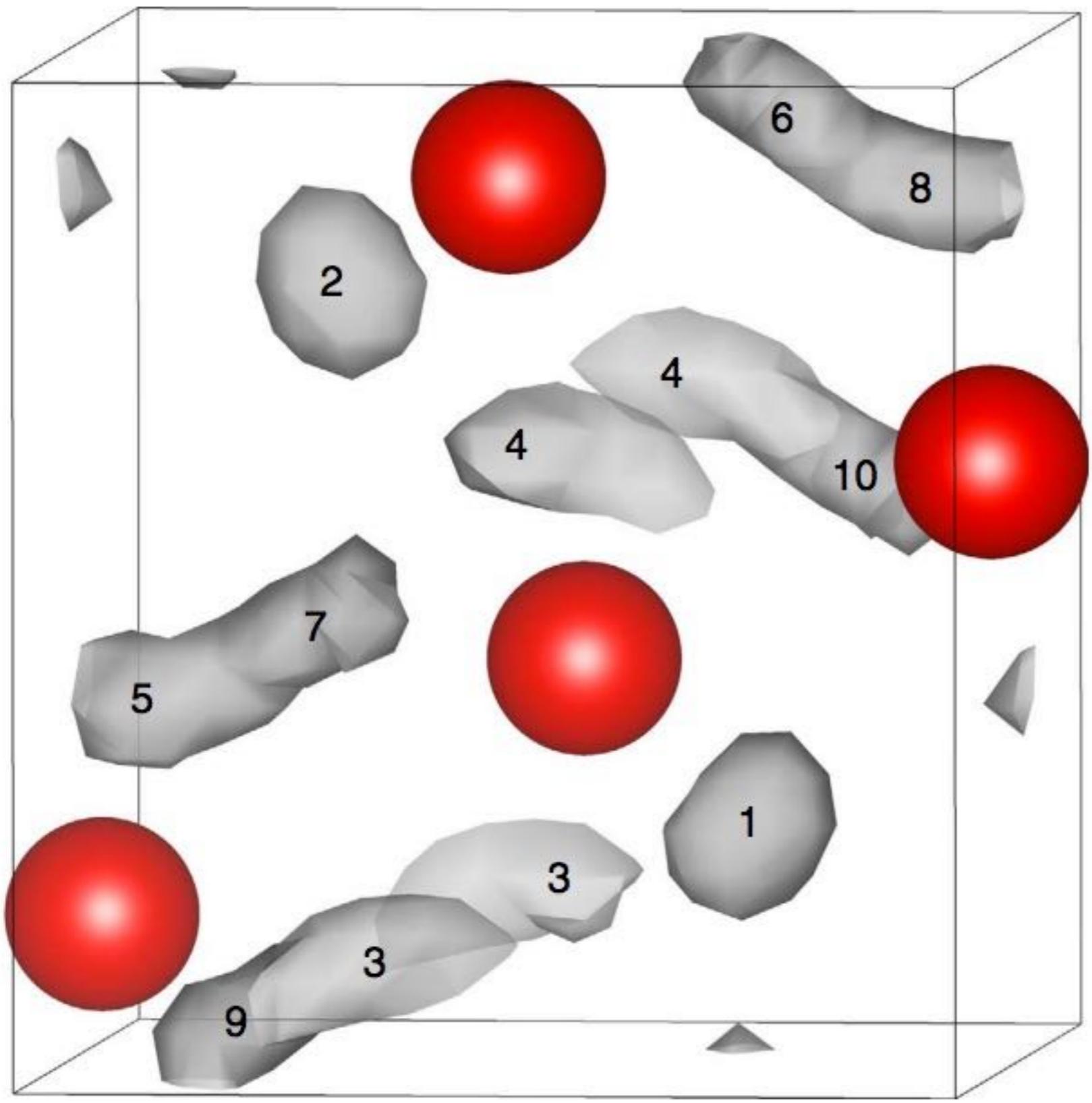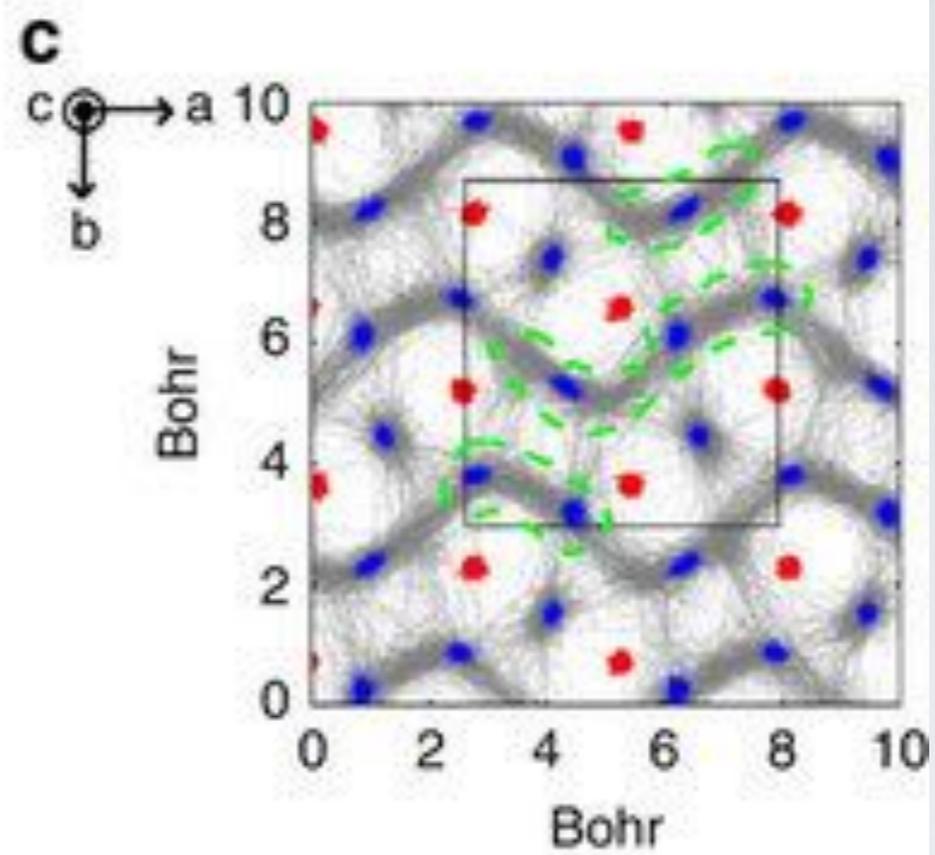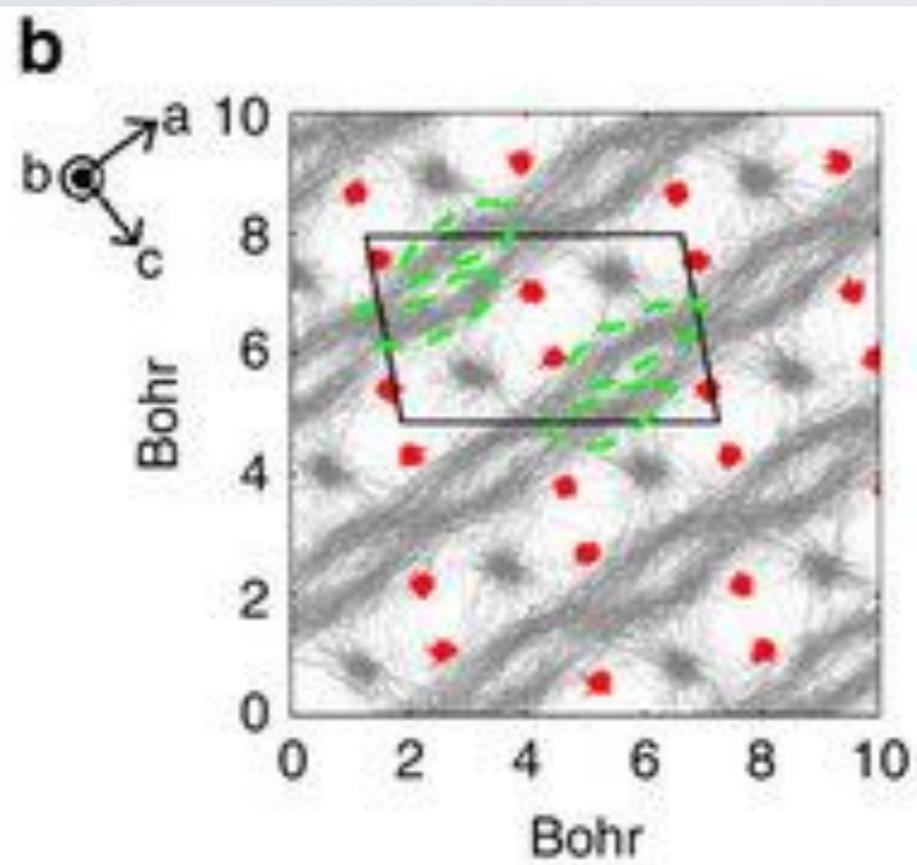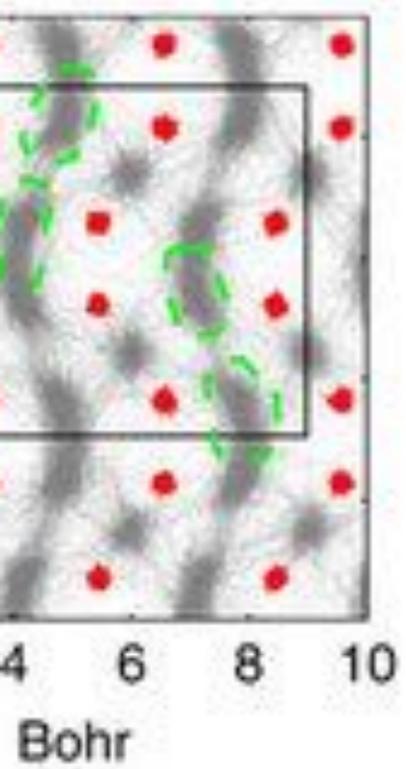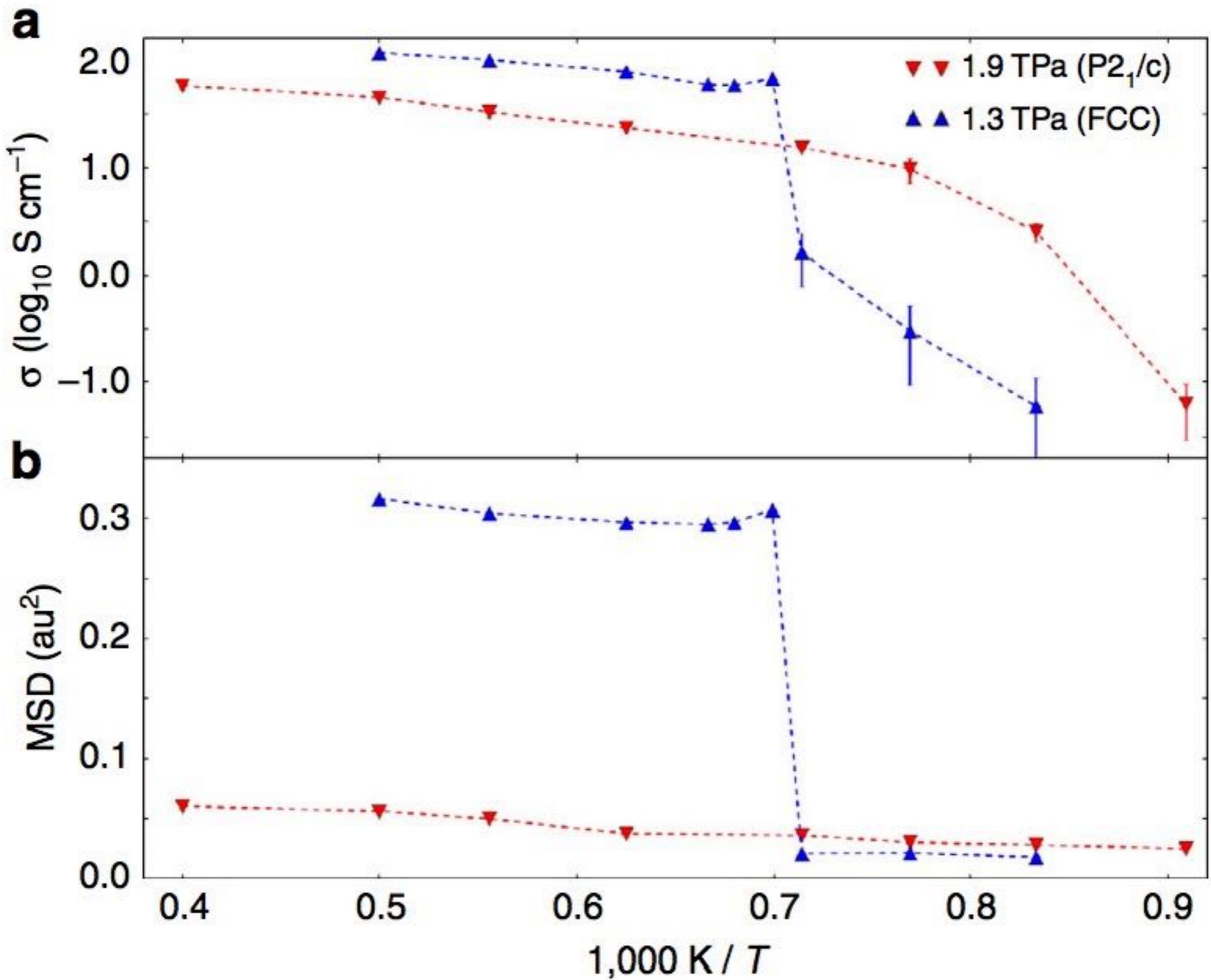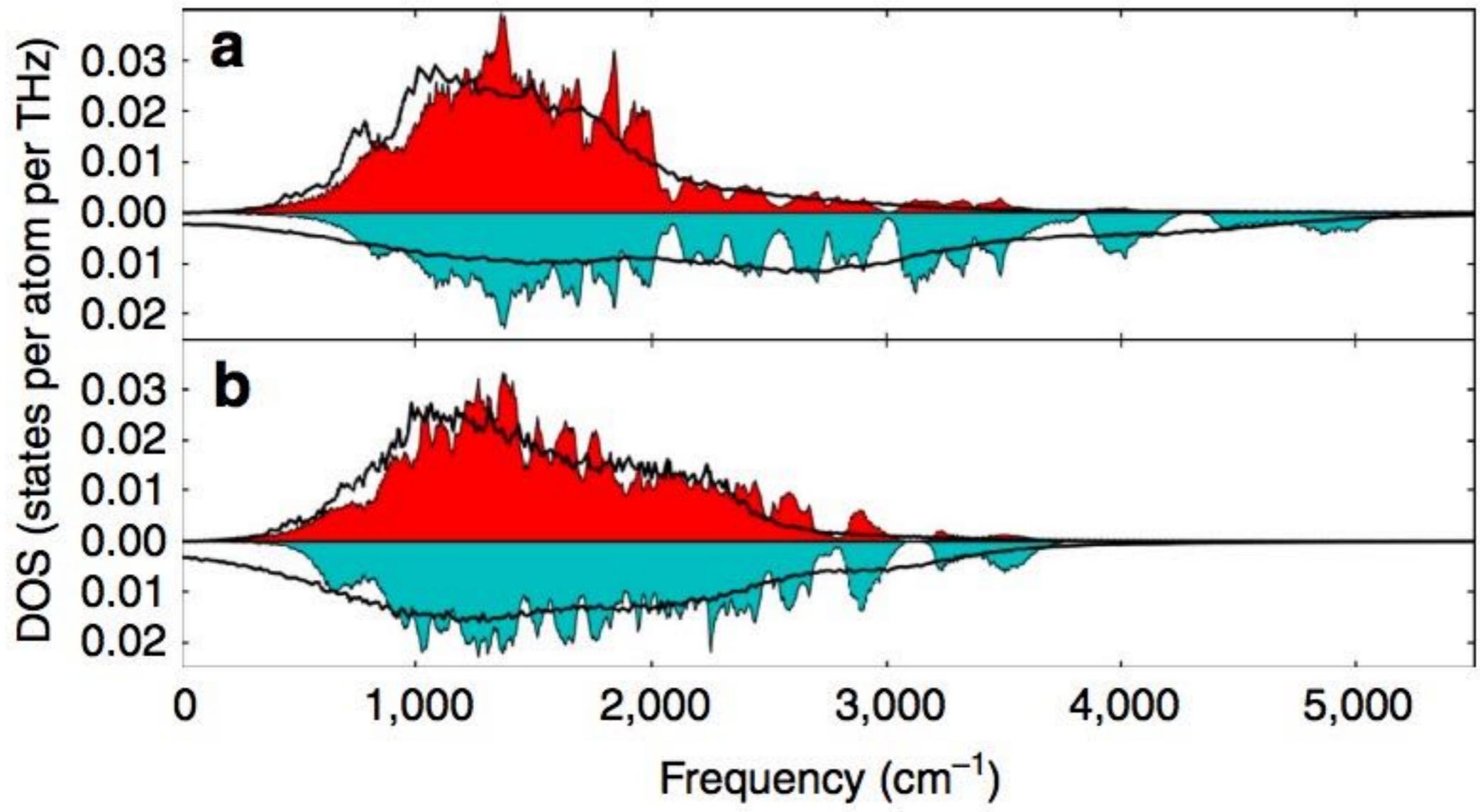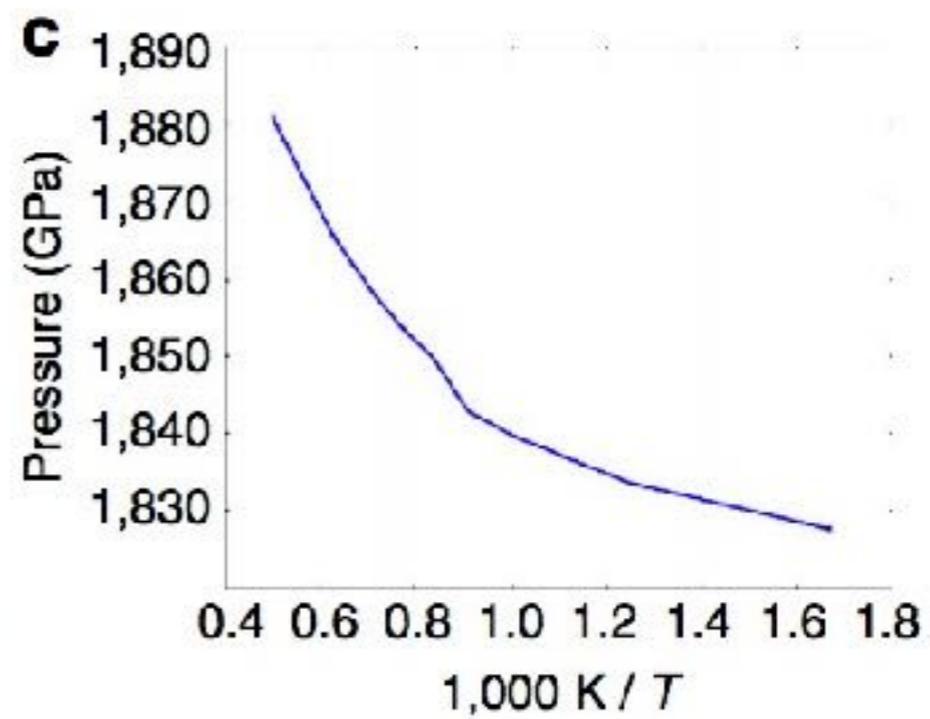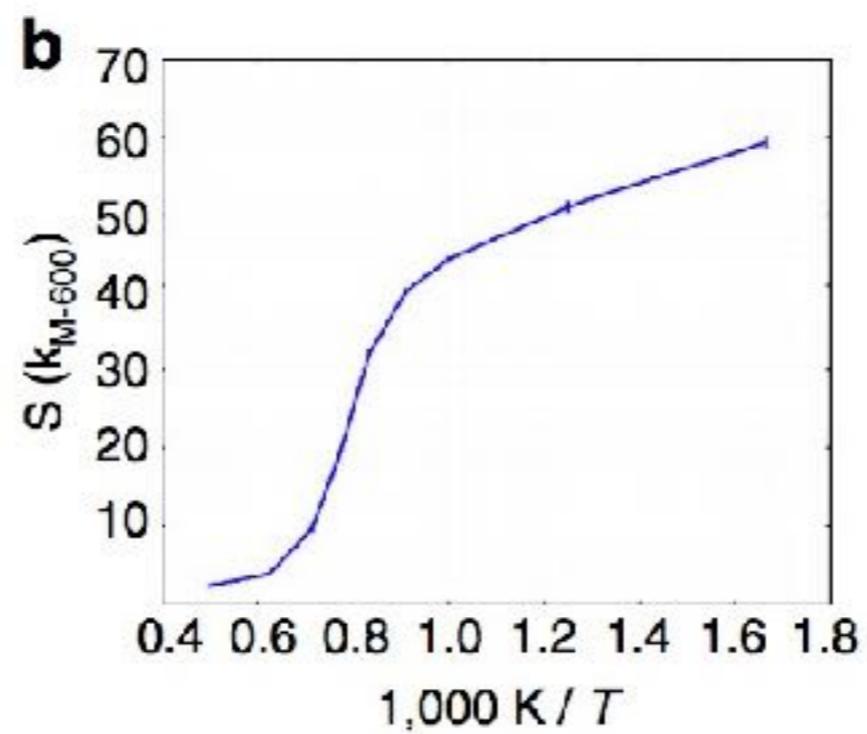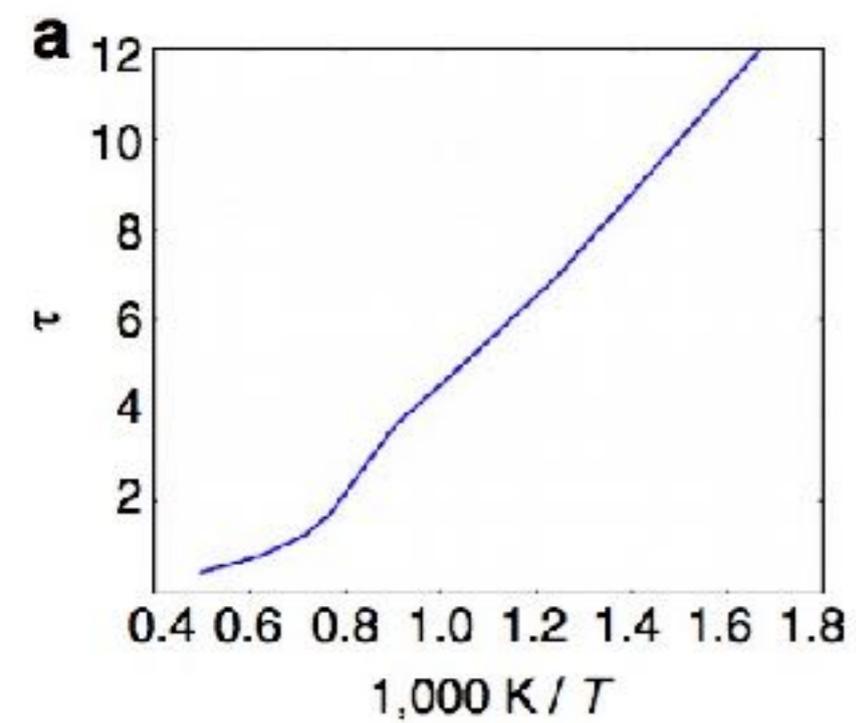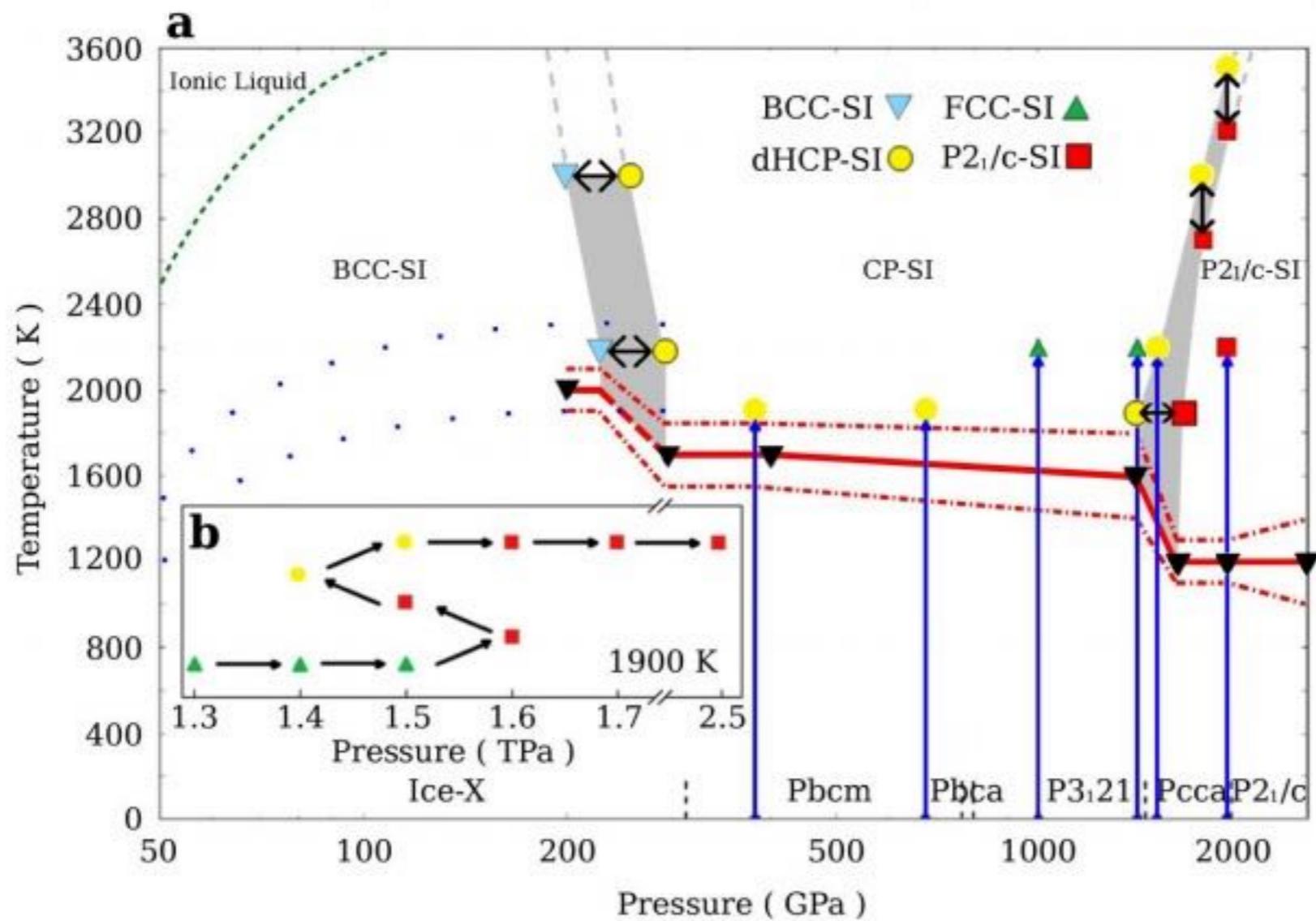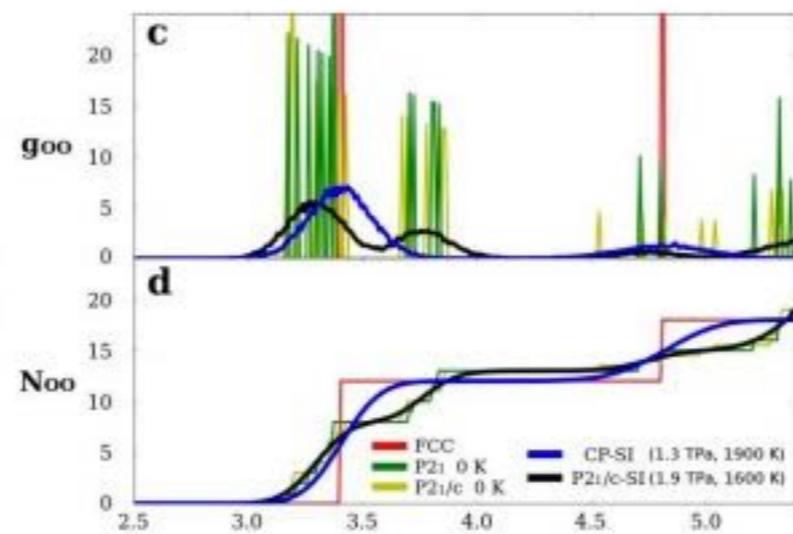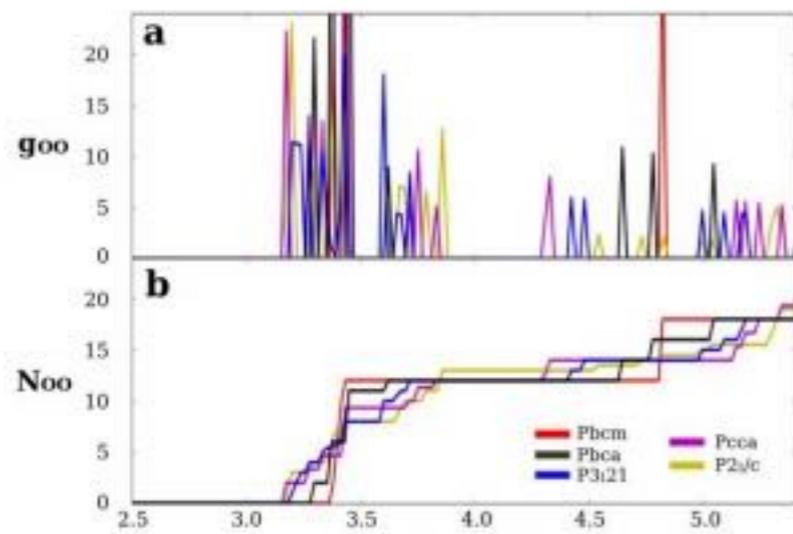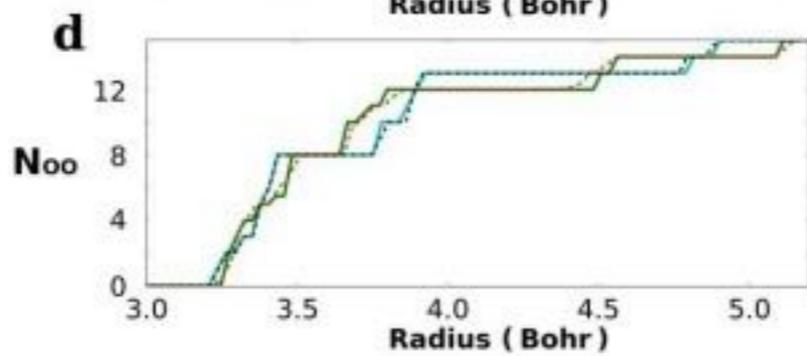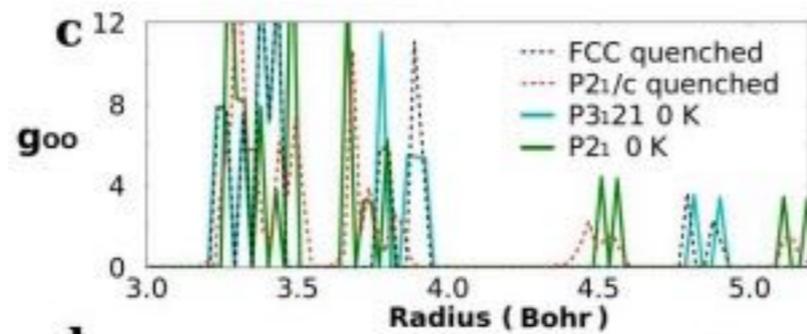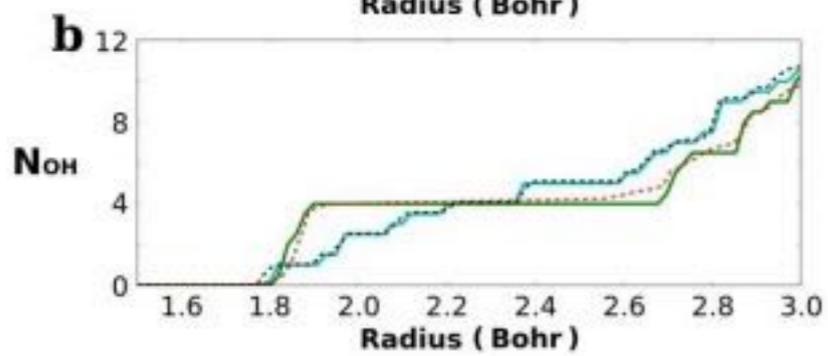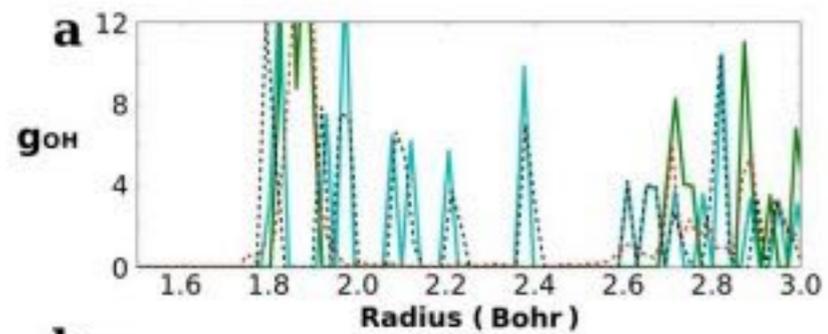
High pressure, high temperature ice

frozen oxygen; melted hydrogen
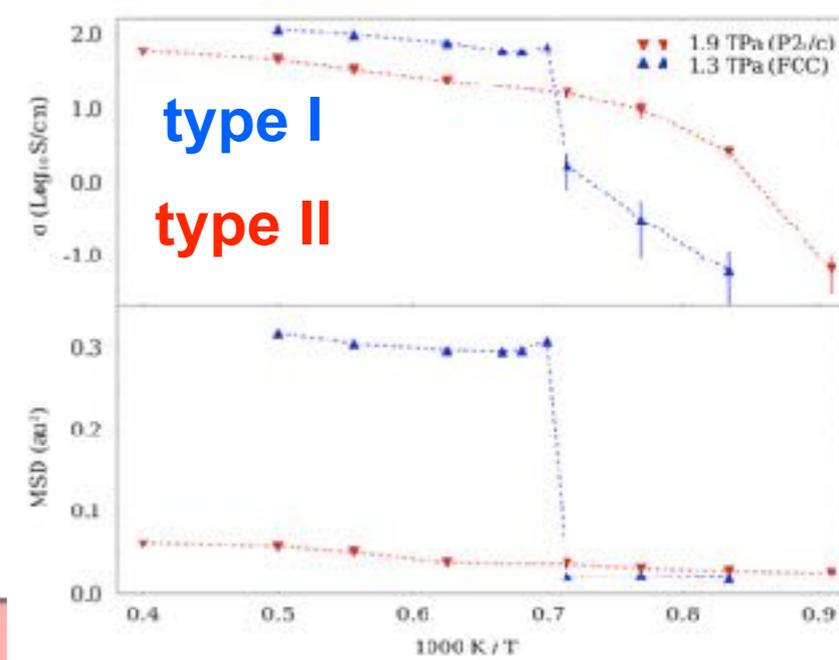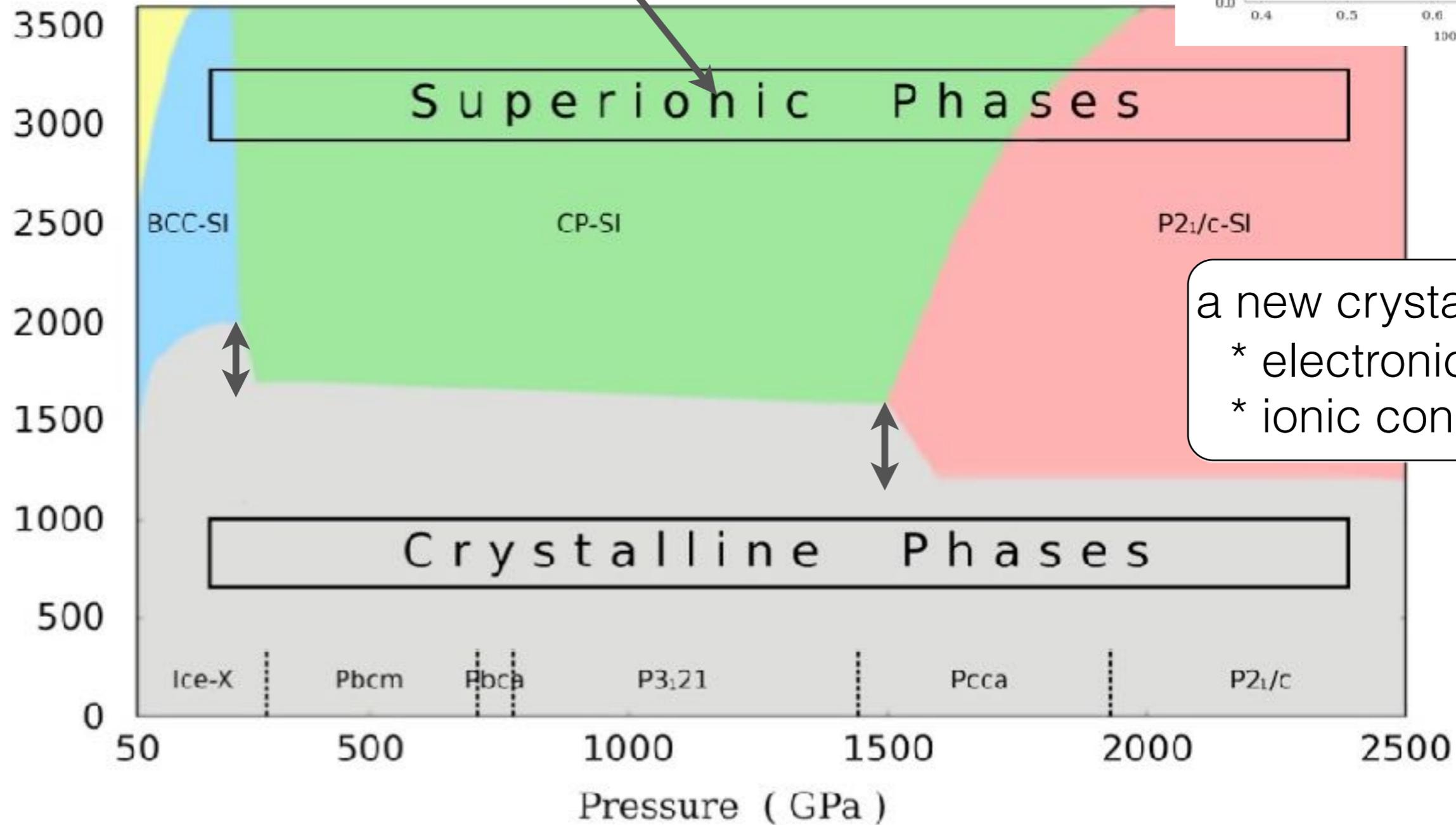
type I
type II

a new crystal phase
* electronic insulator
* ionic conductor

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   Hugh F. Wilson, Michael L. Wong1 and Burkhard Militzer
   Phys. Rev. Lett. **110**, 151102

Anisotropic diffusion
Anisotropic conductivity
  a quasi-2d ionic liquid!

1.9TPa, 1600K:
8 S/cm, 22 S/cm, 30 S/cm
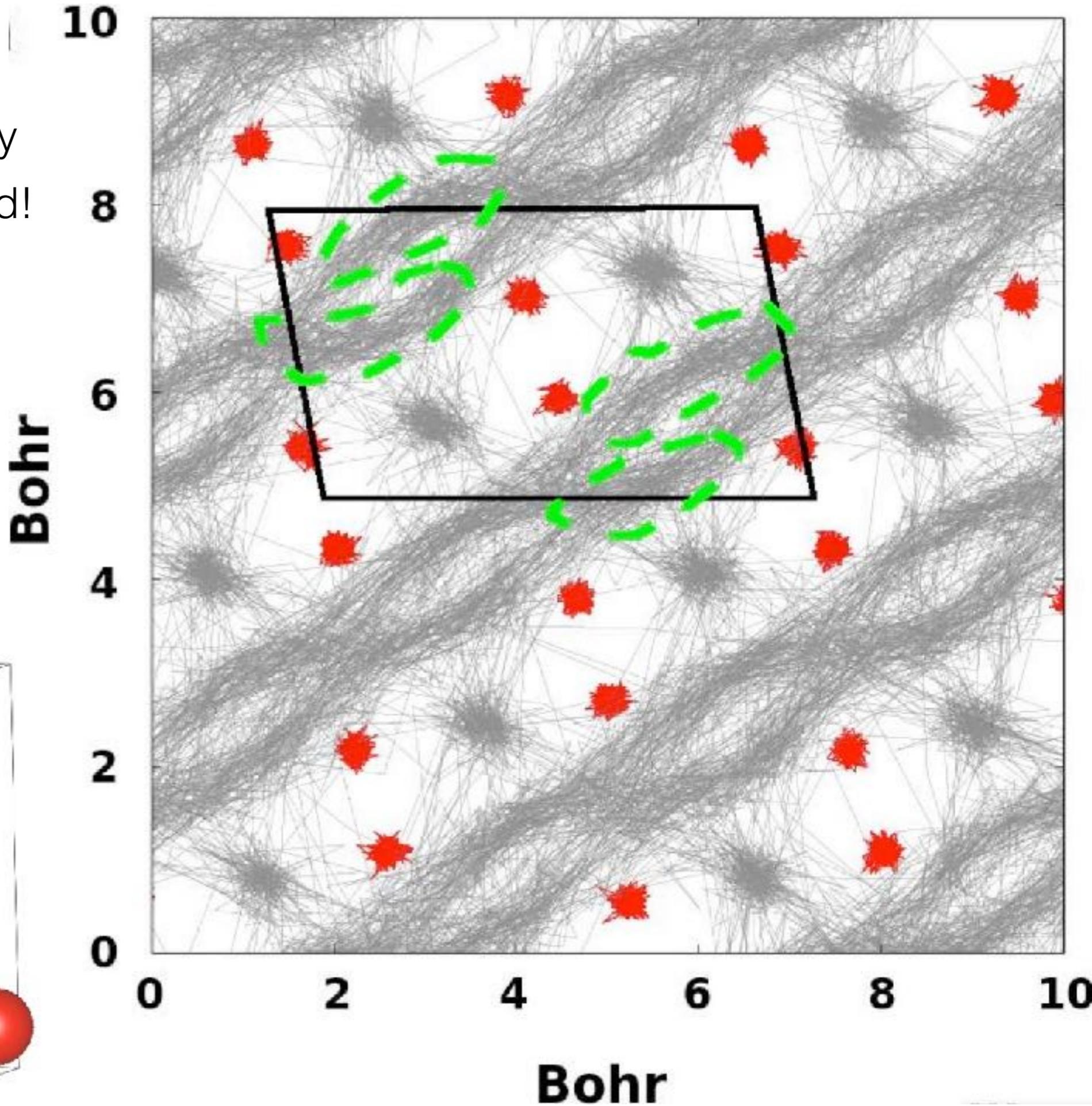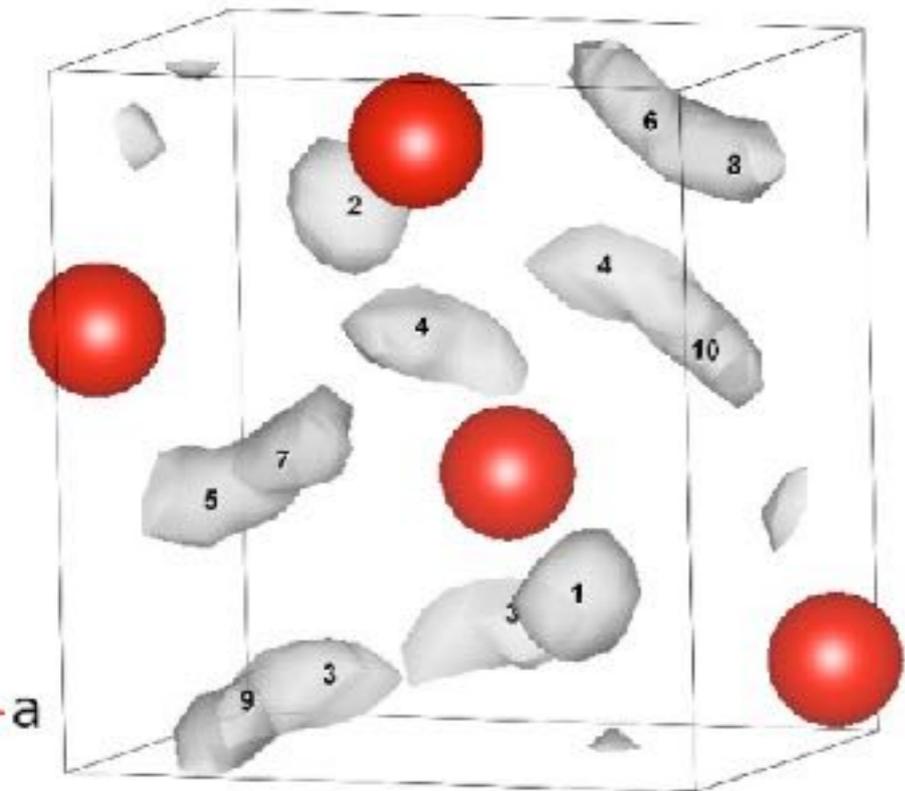
main story - methods for excited states
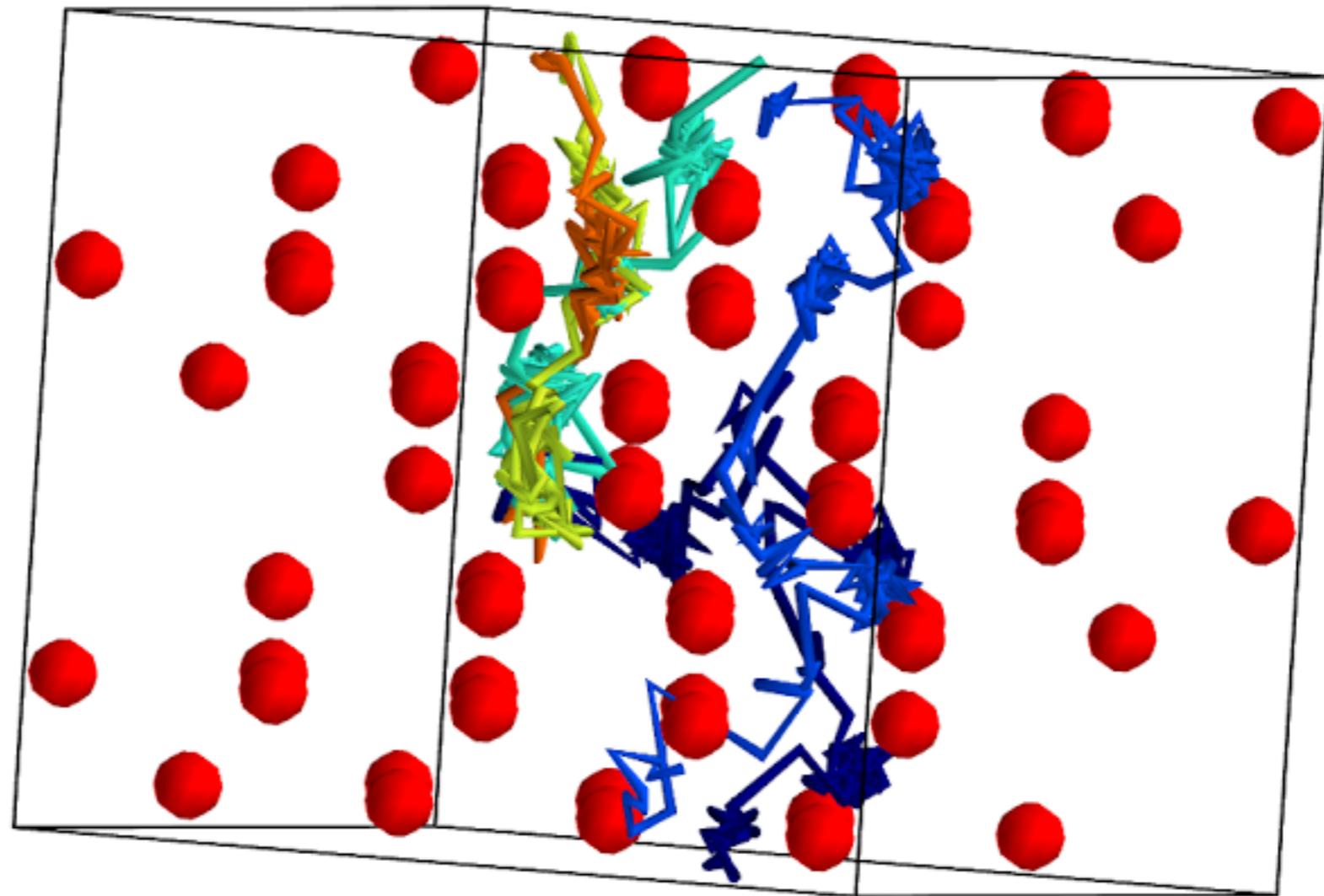
Real and "impressive" progress in finding excited states
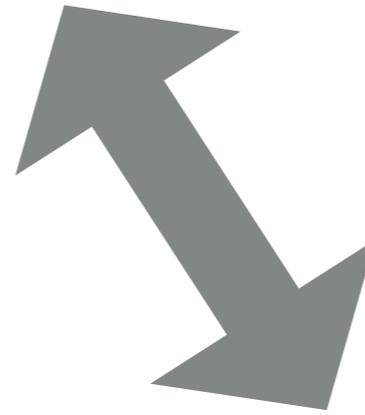
of a (physically very interesting) class of models which is somewhat distant from typical electronic structure problems

Goal: find (all) the excited states

> Given a Hamiltonian we would like some excited states...
>
> maybe in arbitrary parts of the spectrum....
>
> maybe many (even all -too greedy?) such states.

Seems to be a hard problem; are there any systems where we have good control over this?

Non-interacting systems....

Diagonalize single-body H. Create all many body sttes from s.p.o.

$$\left|\Psi_{\text{excited state}}\right\rangle = c_1^\dagger c_5^\dagger c_7^\dagger |0\rangle$$

Even simpler: Add some disorder and s.p.o all localized

We want to figure out how to do the same thing with interacting systems.

Anderson Insulator

Disorder

Localized single-particle orbitals

Many Body Localization

Disorder + Interactions

?
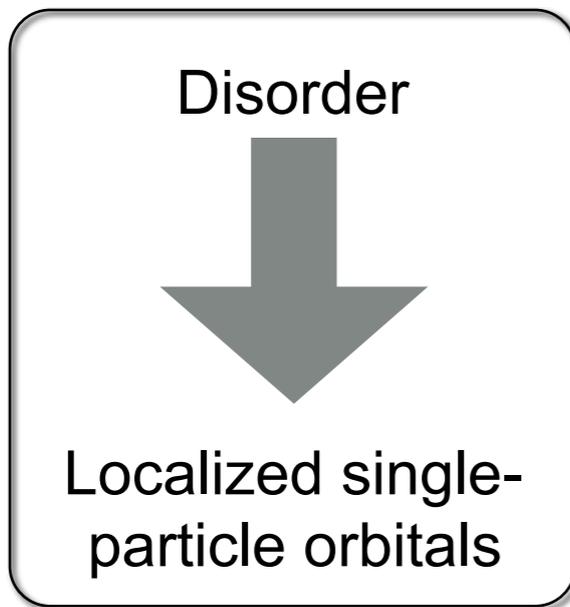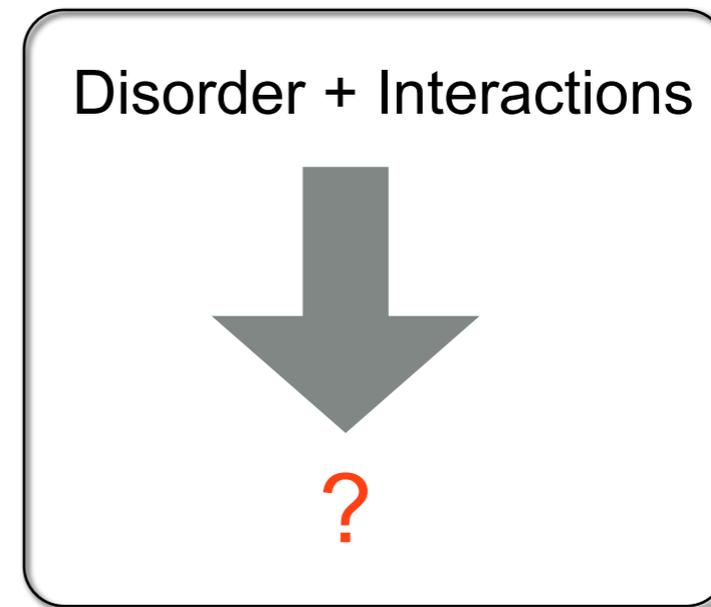
Many works

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Many Body Localization as the perfect insulator

Insulators that you know and love: **Arrhenius Equation**

$$\sigma(T) = (\sigma_0/T)\exp[-E_a/kT]$$

MBL Insulators:

$$\sigma(T) = 0$$

As you tune disorder there is a dynamic phase transition (not equilibrium!)

This is a quantum mechanical effect that is happening at infinite temperature!

At T=0, you identify phase transitions by their effect on the ground state.

At finite T, you identify phase transitions by their effect on the finite tempearture density matrix.

For dynamic transitions, you identify phase transitions by their effect on the excited states..

We need the excited states to learn about MBL!

Phenomenology of MBL

No conductivity even at infinite temperature

Failure of statistical mechanics - system doesn't act as own heat bath

No level repulsion of eigenstates

Eigenstates obey an area law

Quasi-localized in Hilbert Space

Conserved integrals of motion
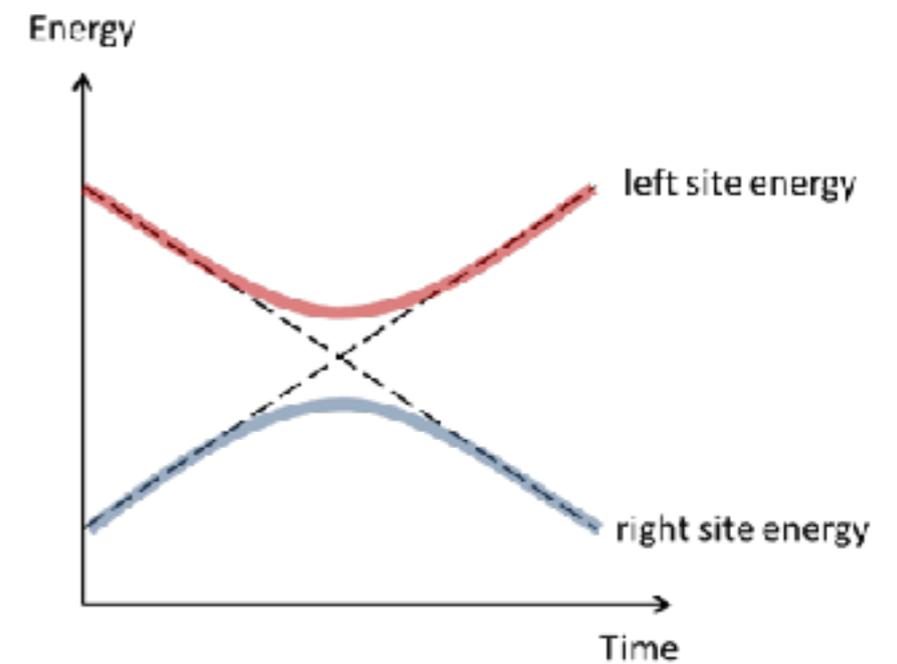
$$H = \sum_{i=1}^{L} [h_i S_i^z]$$

$$h_i \in [-W, W]$$

Ground State: ↑ ↓ ↓ ↓ ↑
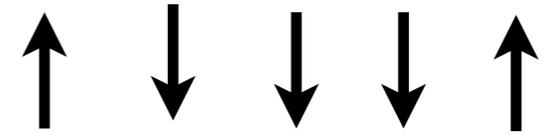
Excited State: ↑ ↓ ↓ ↑ ↑
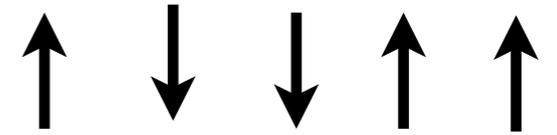
Highly Excited State: ↓ ↑ ↑ ↓ ↓

Is their a simple structure for the eigenstates
in a many-body localized phase?

$$H = \sum_{i=1}^{L} [h_i S_i^z + J \sum \hat{S}_i \cdot \hat{S}_{i+1}]$$

$$h_i \in [-W, W]$$

$$|\Psi_{\text{excited state}}\rangle = c_1^\dagger c_5^\dagger c_7^\dagger |0\rangle$$

Ground State: $\quad A^{1,\sigma_1} A^{2,\sigma_2} A^{3,\sigma_3} A^{4,\sigma_4} A^{5,\sigma_5}$

Excited State: $\quad A^{1,\sigma_1} B^{2,\sigma_2} A^{3,\sigma_3} A^{4,\sigma_4} A^{5,\sigma_5}$

Highly Excited State: $\quad B^{1,\sigma_1} B^{2,\sigma_2} A^{3,\sigma_3} B^{4,\sigma_4} A^{5,\sigma_5}$

The intuition....

$$UHU^{\dagger} = U_D$$

Represent U as a quantum circuit (tensor network)

Argue that this quantum circuit is compact.

Why compact?

excitations are made up of dressed interacting quasi-particles.

Identify the structure of eigenstates the circuit produces

Show that we can effeciently build the circuit that makes up U (build them up layer by layer).

4n matrices encode the whole spectrum

this is amazing!

eigenstates

this is a unitary operation

product states

$\{G_{\uparrow}^1, G_{\downarrow}^1\}$ $\{G_{\uparrow}^2, G_{\downarrow}^2\}$ $\{E_{\uparrow}^3, E_{\downarrow}^3\}$ $\{G_{\uparrow}^4, G_{\downarrow}^4\}$

U U U U
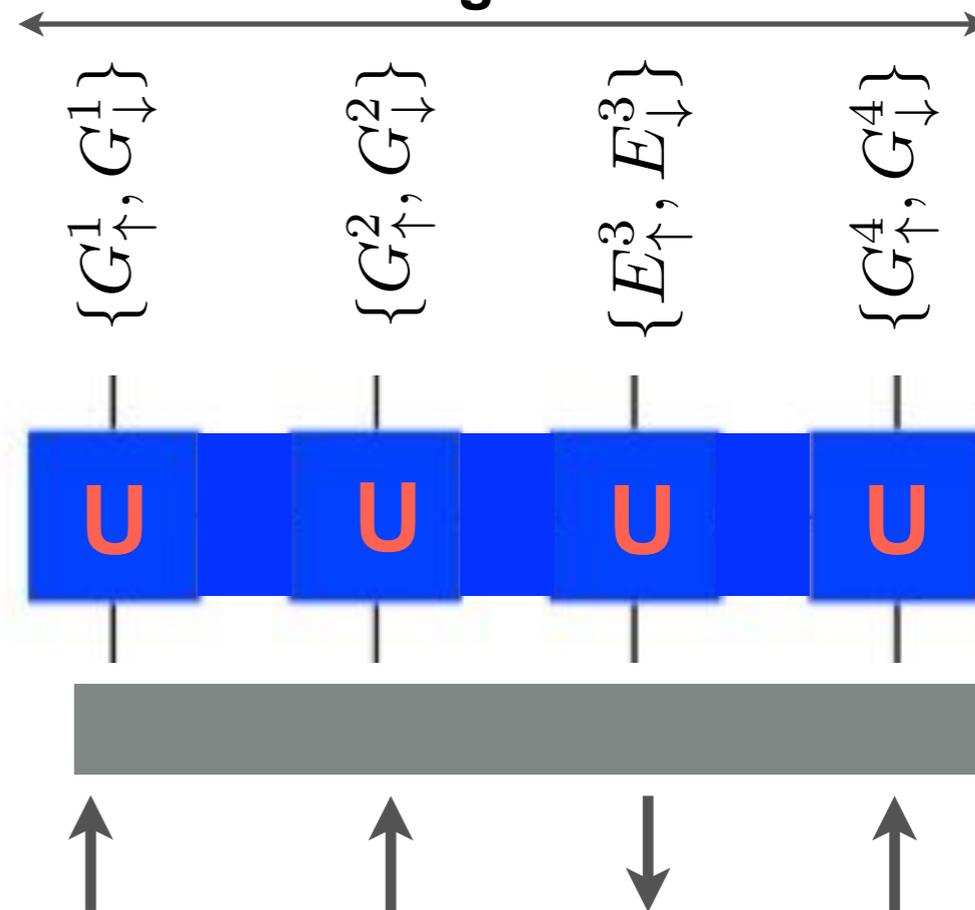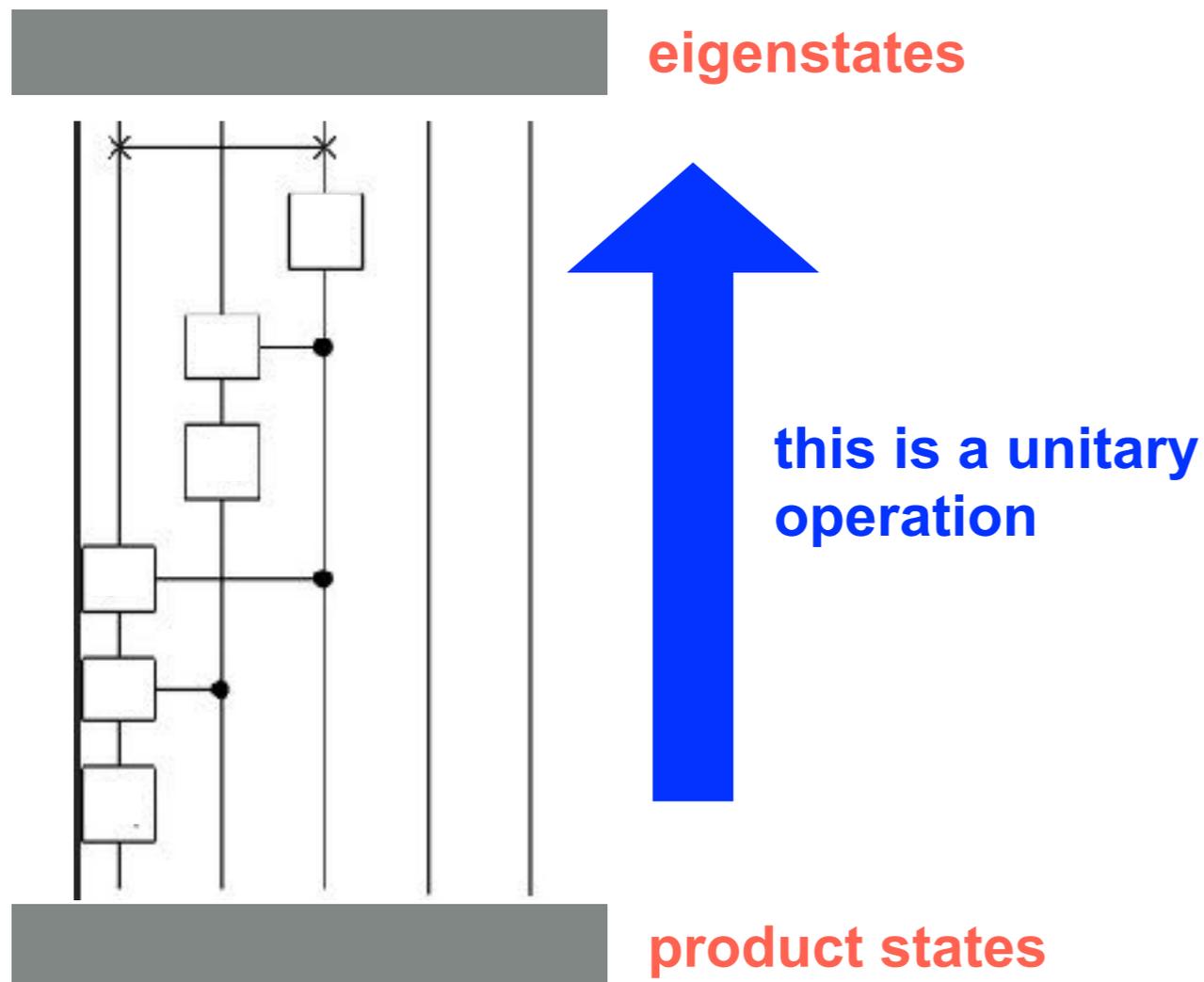
A *wave function* is an object that eats a configuration of spins and generates a number: $\Psi(\uparrow, \downarrow, \uparrow) = 0.3$

A *product state* eats a configuration of spins and generates a number by taking the product of complex numbers.

$$\Psi(\uparrow, \downarrow, \uparrow) = c^{1,\uparrow} c^{2,\downarrow} c^{3,\uparrow}$$

A *matrix product state (MPS)* eats a configuration of spins and generates a number by taking the product of matrices/vectors.

$$\Psi(\uparrow, \downarrow, \uparrow) = M_i^{1,\uparrow} M_{ij}^{2,\downarrow} M_j^{3,\uparrow}$$

2N matrices

Each of size DxD

$|i\rangle$
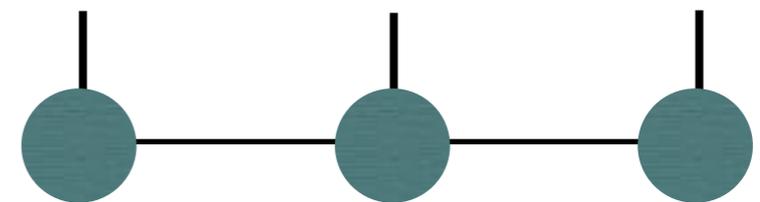
2N matrices

Each of size 1x1
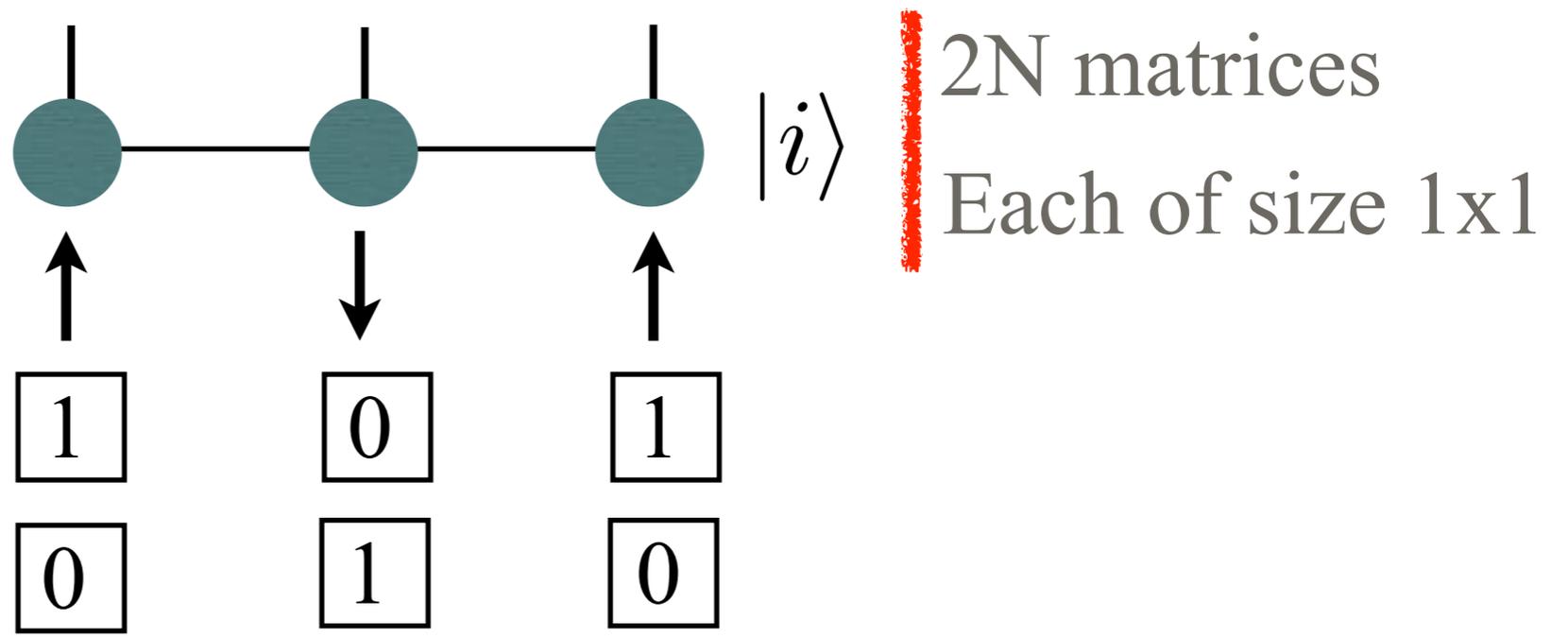
A product state is a very simple MPS

A *operator* is an object that eats two configuration of spins and generates a number: $\Psi(\uparrow\downarrow, \downarrow\uparrow, \uparrow\uparrow) = 0.9$

A *matrix product operator (MPO)* eats two configuration of spins and generates a number by taking the product of matrices/vectors. $\Psi(\uparrow\downarrow, \downarrow\uparrow, \uparrow\uparrow) = O_i^{1,\uparrow\downarrow} O_{ij}^{2,\downarrow\uparrow} O_j^{3,\uparrow\uparrow}$
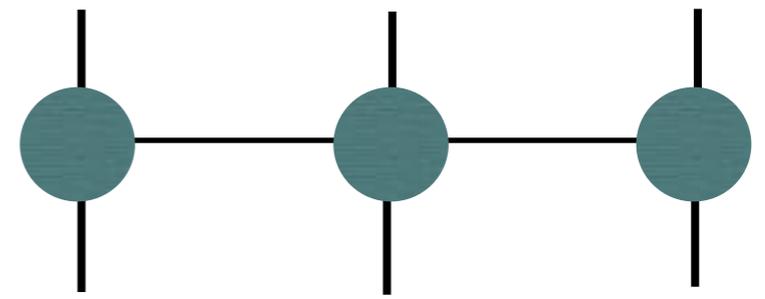
4N matrices

Each of size DxD

$$\sum_{\sigma_1}(O_1^{\sigma_1\sigma_1'} \otimes M_1^{\sigma_1}) \sum_{\sigma_2}(O_2^{\sigma_2\sigma_2'} \otimes M_2^{\sigma_2}) \sum_{\sigma_3}(O_3^{\sigma_3\sigma_3'} \otimes M_3^{\sigma_3})$$
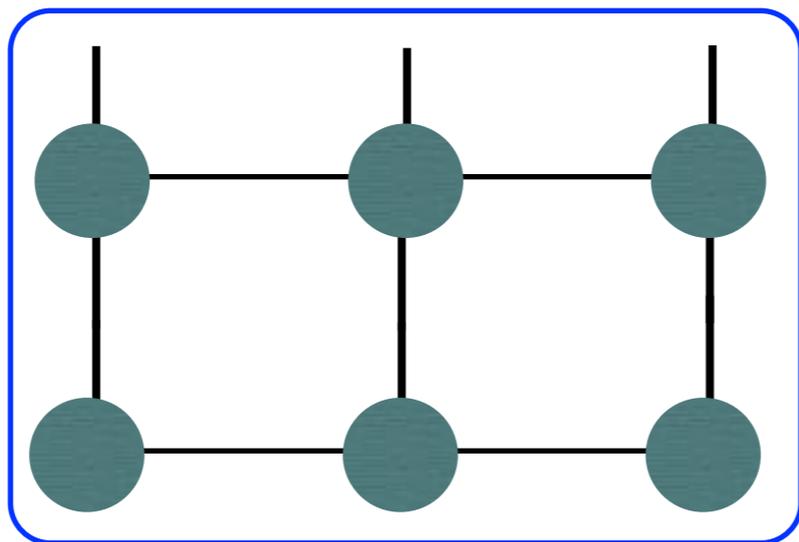
$$O_1^{\sigma_1\sigma_1'} O_2^{\sigma_2\sigma_2'} O_3^{\sigma_3\sigma_3'}$$

$$M_1^{\sigma_1} M_2^{\sigma_2} M_3^{\sigma_3}$$

$$O^{\uparrow\sigma_1'} O^{\downarrow\sigma_2'} O^{\uparrow\sigma_3'}$$

An operator applied to a product state picks out two of the four matrices (per site) from the operator.

$|i\rangle$

| 1 | 0 | 1 |
| 0 | 1 | 0 |

$$\sum_{\sigma_1}(O_1^{\sigma_1\sigma_1'} \otimes M_1^{\sigma_1})\sum_{\sigma_2}(O_2^{\sigma_2\sigma_2'} \otimes M_2^{\sigma_2})\sum_{\sigma_3}(O_3^{\sigma_3\sigma_3'} \otimes M_3^{\sigma_3})$$

$$O_1^{\sigma_1\sigma_1'}O_2^{\sigma_2\sigma_2'}O_3^{\sigma_3\sigma_3'}$$

$$M_1^{\sigma_1}M_2^{\sigma_2}M_3^{\sigma_3}$$

$$O^{\downarrow\sigma_1'}O^{\downarrow\sigma_2'}O^{\uparrow\sigma_3'}$$

$|i\rangle$
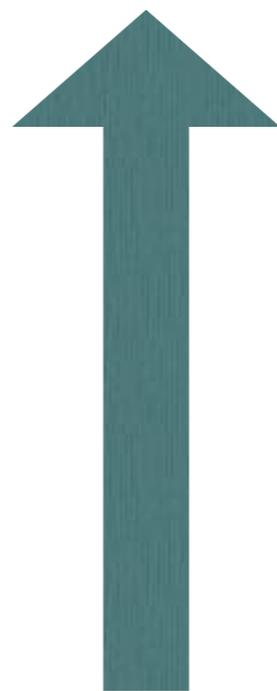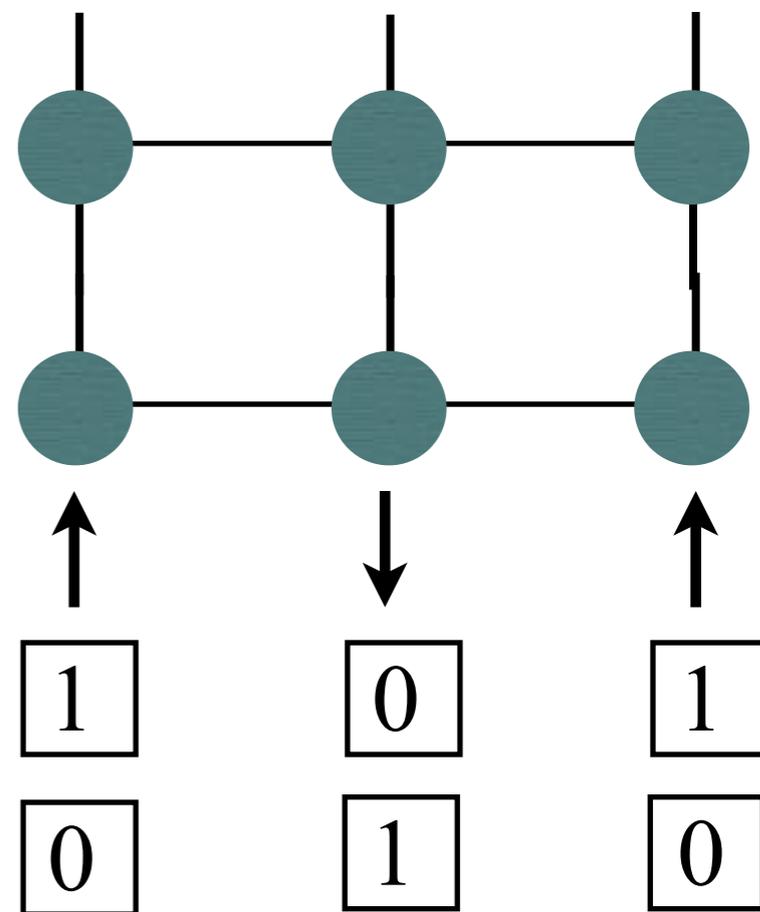
An operator applied to a product state picks out two of the four matrices (per site) from the operator.

Different product state - different matrices.
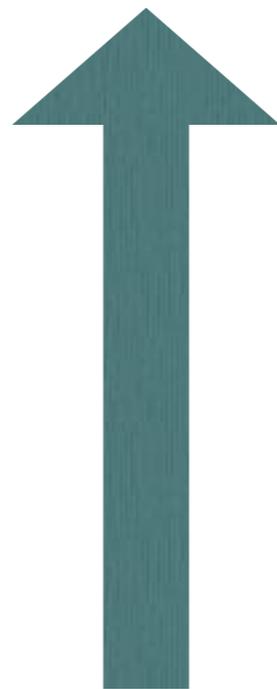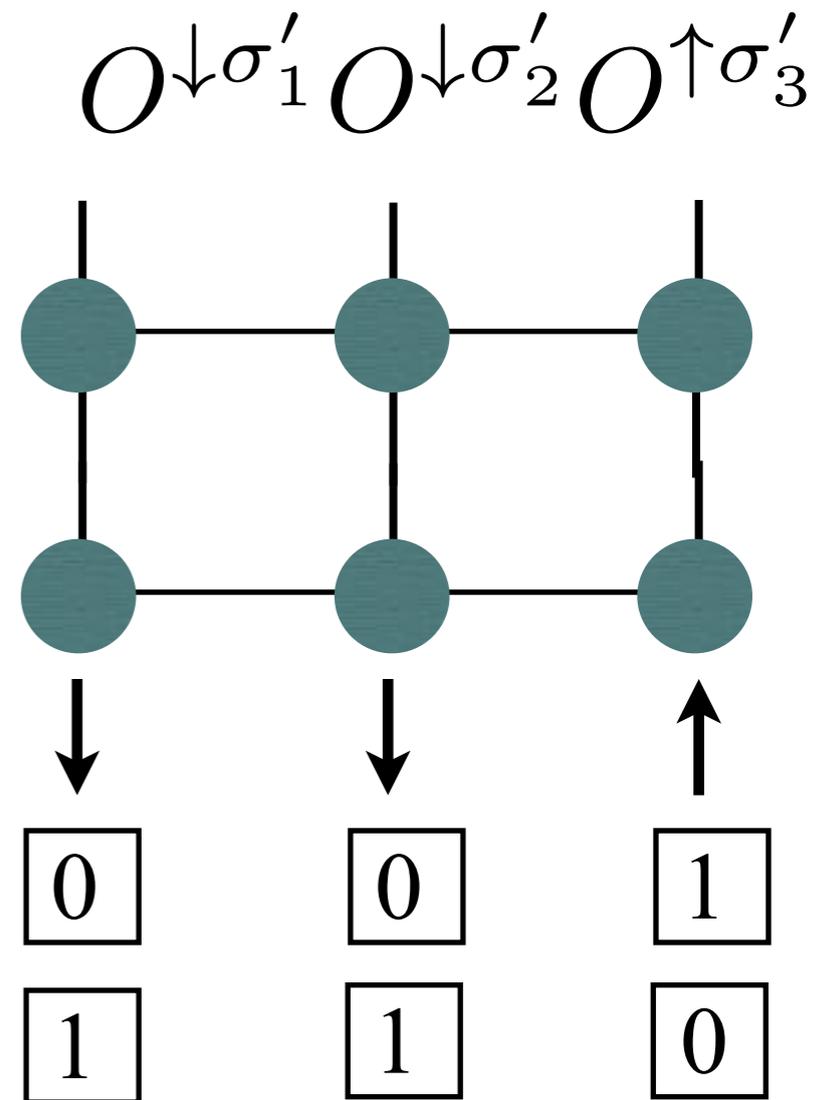
$$\hat{U}\hat{H}\hat{U}^\dagger = D$$

$$\hat{U}|i\rangle = |e_i\rangle$$

All the eigenstates are encoded with 4n matrices!

Ground State: $G_1 G_2 G_3 G_4 G_5$

Excited State: $E_1 E_2 G_3 E_4 G_5$

Key question: are the sizes of E and G constant with bond dimension?

Let's check this....

$$\hat{H} \longrightarrow \widehat{U} \longrightarrow MPO$$
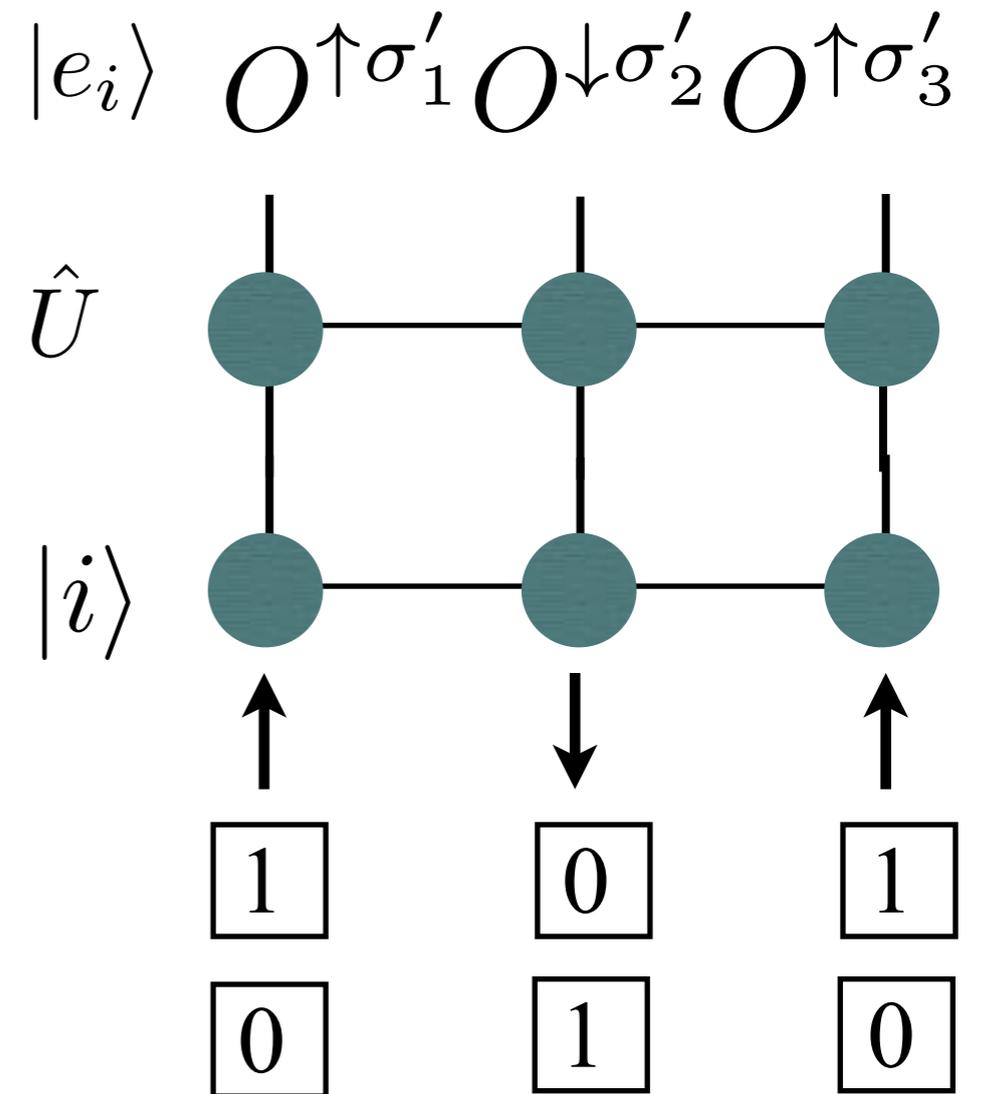
What's the bond dimension?

U maps product states to eigenstates.

Many such mappings

Which one we pick is important!

1

This is no good. Want to preserve locality in mapping.
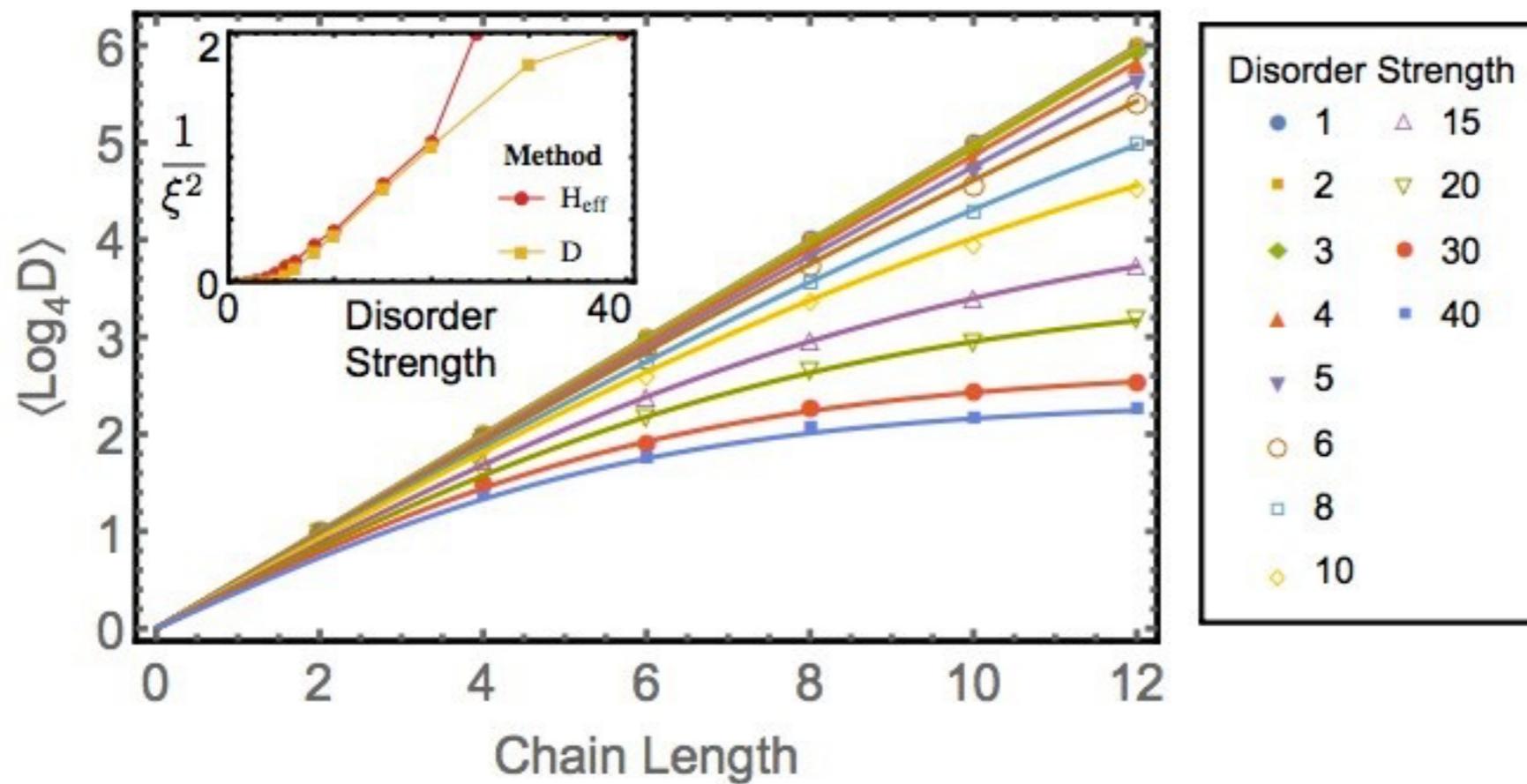
For large disorder, the bond dimension saturates.

A more refined look at the MPO bond dimension.
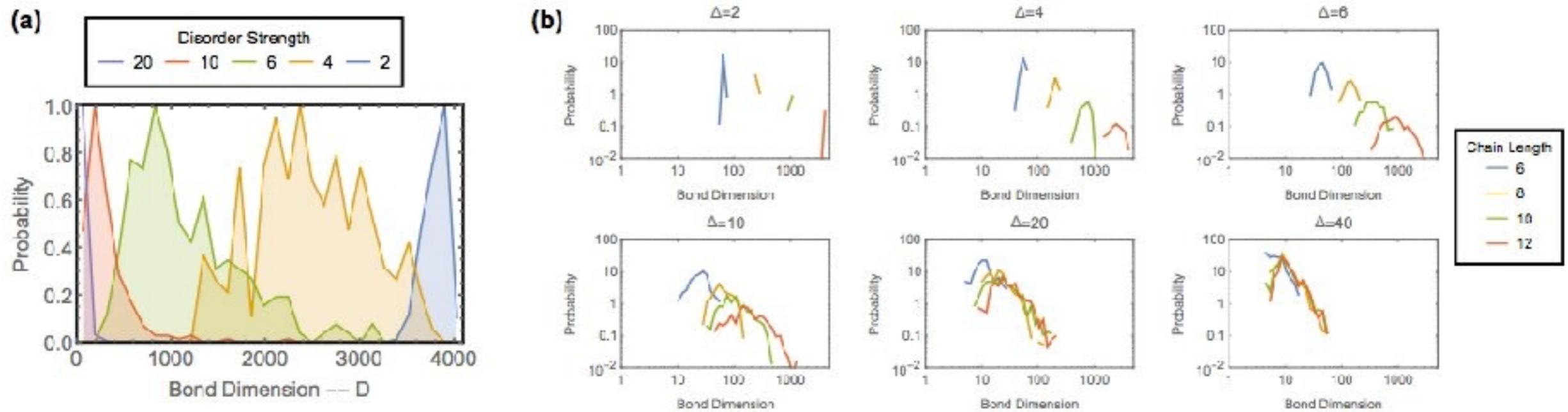
Large disorder ⟶ Low bond dimension

Low disorder ⟶ System-dependent bond dimension

Disorder near transition ⟶ Broad bond dimension

There exists a compact representation. Can we find it?
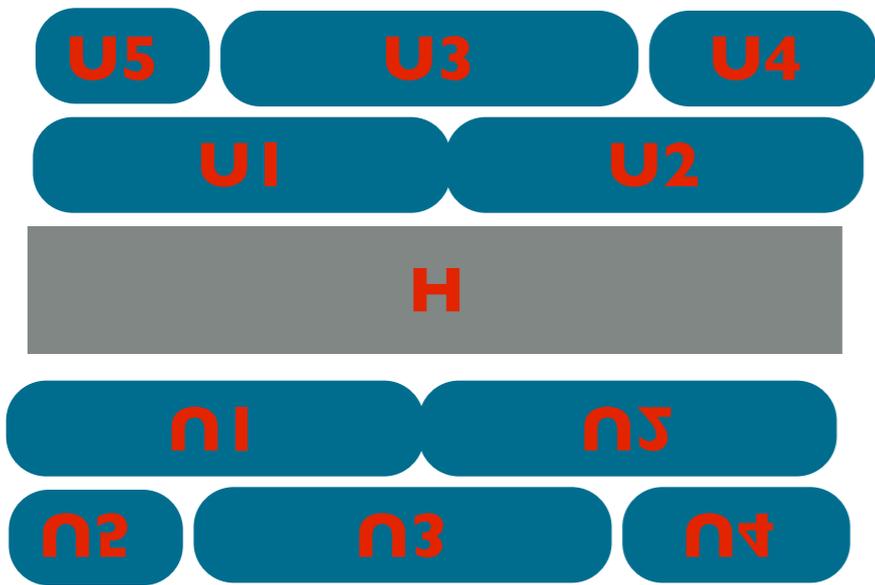
No (completely) free lunch.

Whole spectrum is powerful but hard.

$$\mathrm{Tr}\left(\text{[U1][H][U1]} \right)$$

$$\mathrm{Tr}\left(\text{[U1][U2][H][U1][U2]} \right)$$

L=12
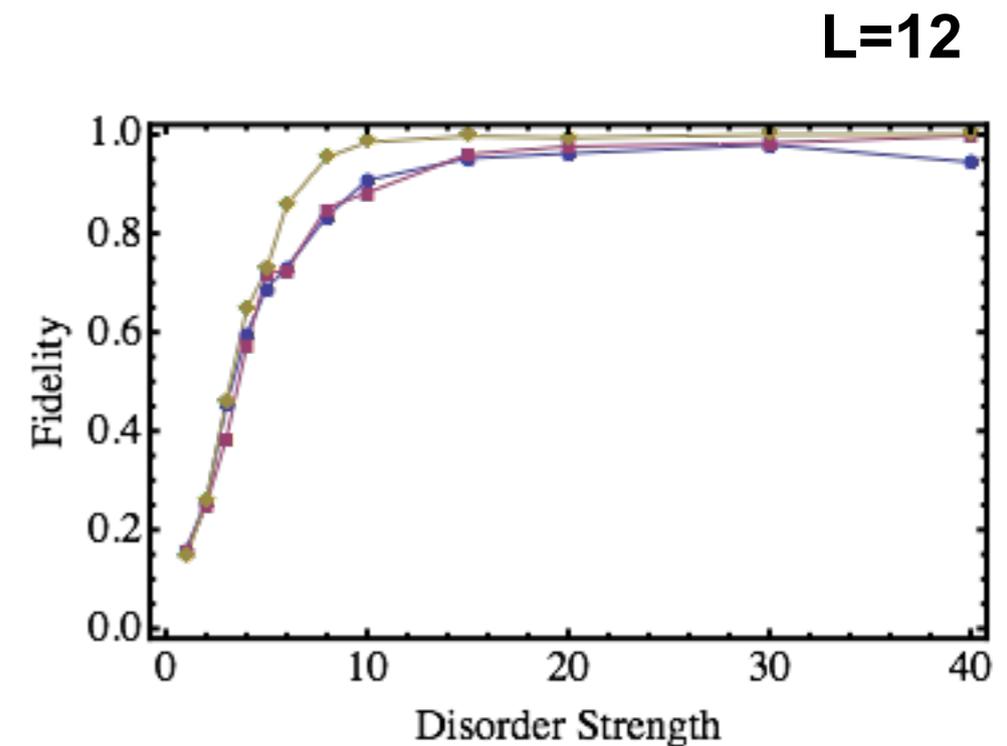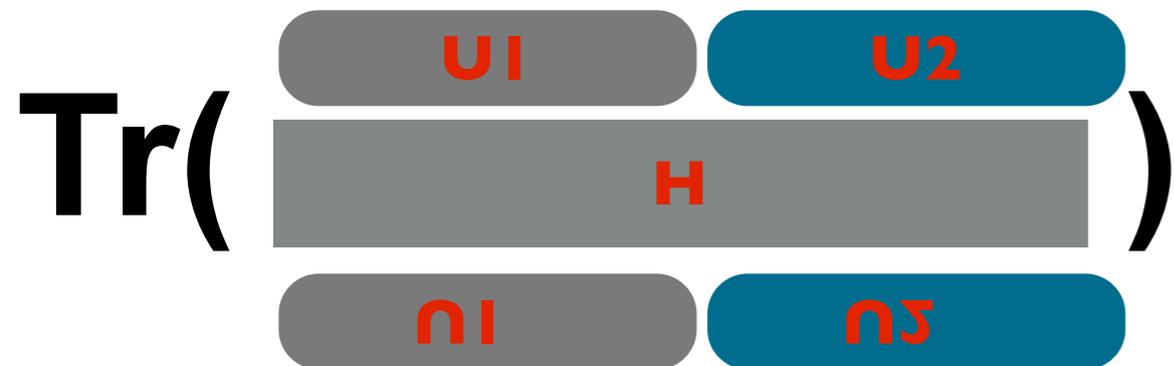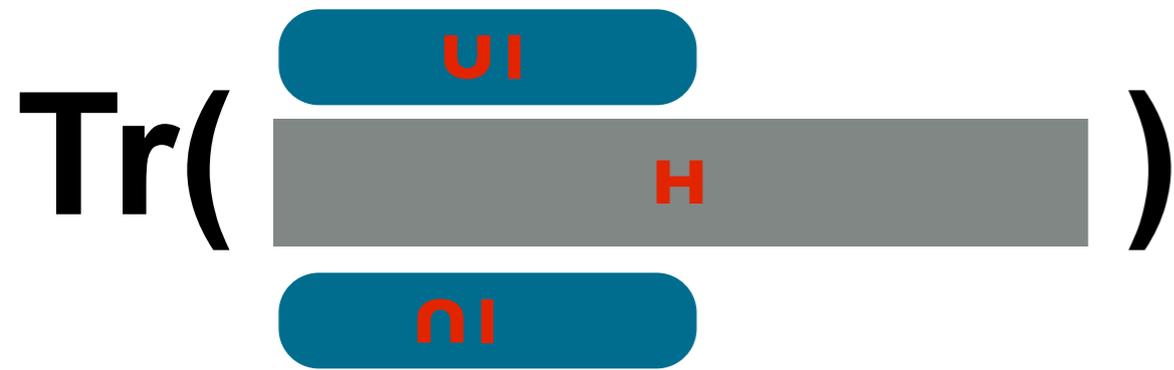
Suppose instead we want one state with very high fidelity

Problem: excited states very degenerate!

Solution 1: (H-E)$^{-1}$

Solution 2: KKR/Feast

$$-\frac{1}{2\pi i}\int_c dz(H-z)^{-1}v = P_{\text{subspace}}v$$

L=12, M=50, (H-λ)$^{-1}$ applied 4 times right after sweep 24

$\langle\varphi|$ $(H-\lambda)^\dagger$ $H-\lambda$ $|\varphi\rangle$

$=$

$\langle\varphi|$ $(H-\lambda)^\dagger$ $|\psi\rangle$

$\langle m \rangle$ vs L for different D's

Legend:
- D = 1
- D = 2
- D = 3
- D = 4
- D = 6
- D = 10
- D = 20
- D = 40

Axes: $\langle m \rangle$ (vertical), L (horizontal)
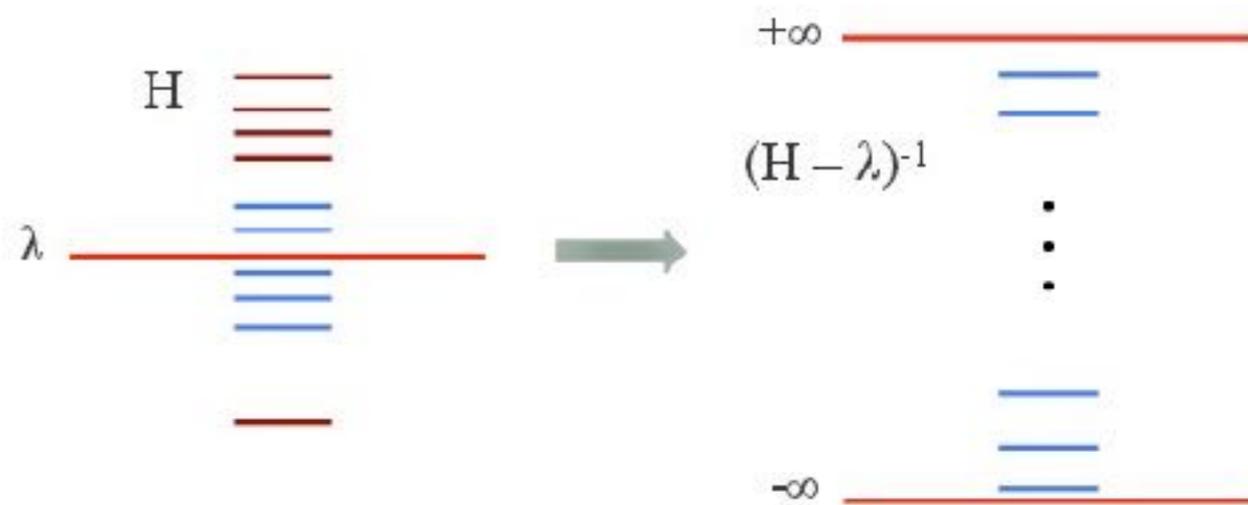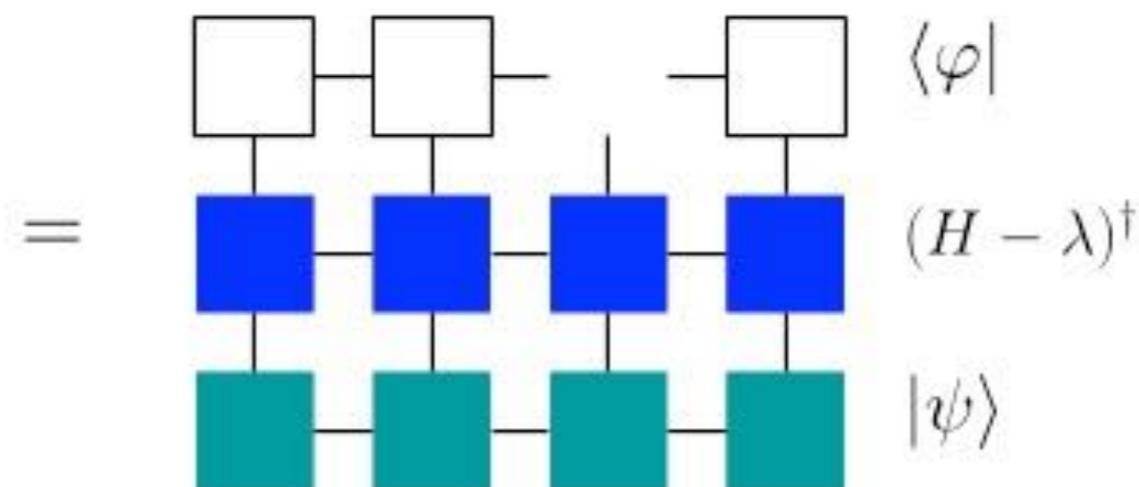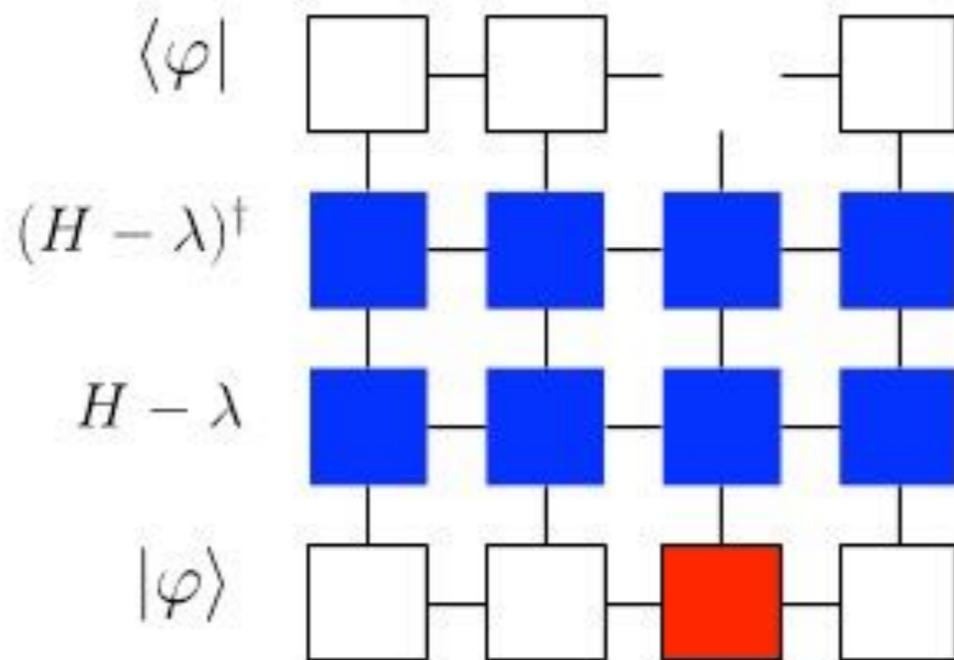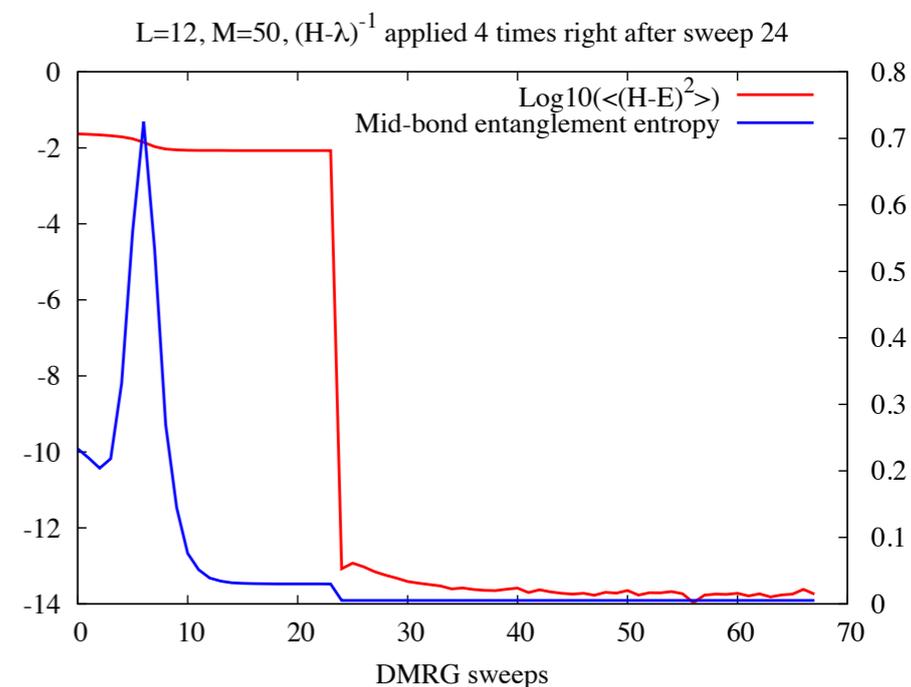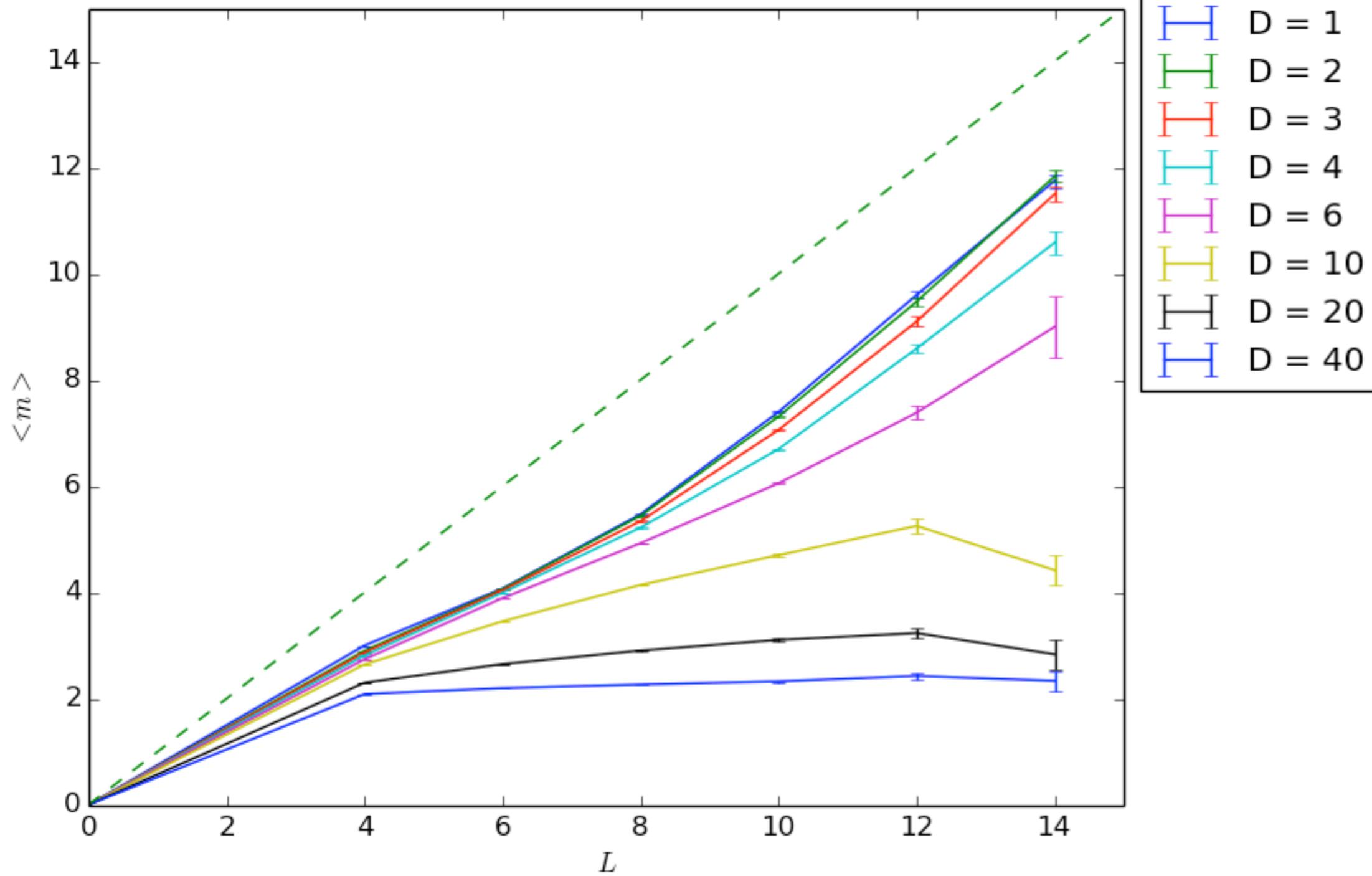
What, if any of this will generalize to clean, high-dimensional electronic structure?

Frozen liquid configurations look disordered... probably our techniques have plausibility of working here.

Need higher-d tensor networks... we have a MERA-like approach that should do this translation

The whole spectrum is going to be generically hard on clean systems, but .... we think these approaches will give us chunks of the spectrum. Study ongoing.

For electronic structure, we speculate we might get this to work in k-space around the fermi sea.

Conclusions
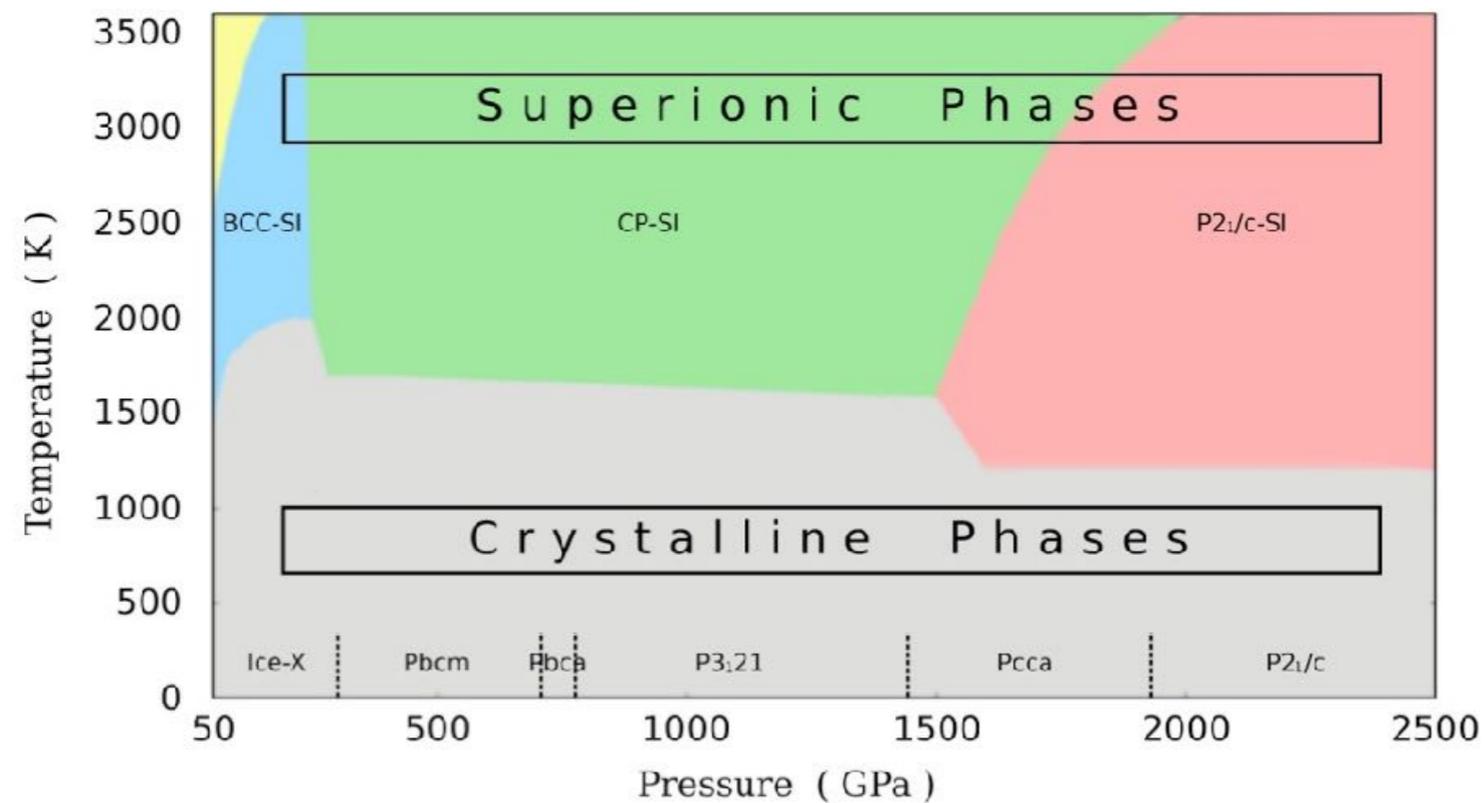
Superionic ice - quasi-2d liquid

Full spectrum of excited states in MBL
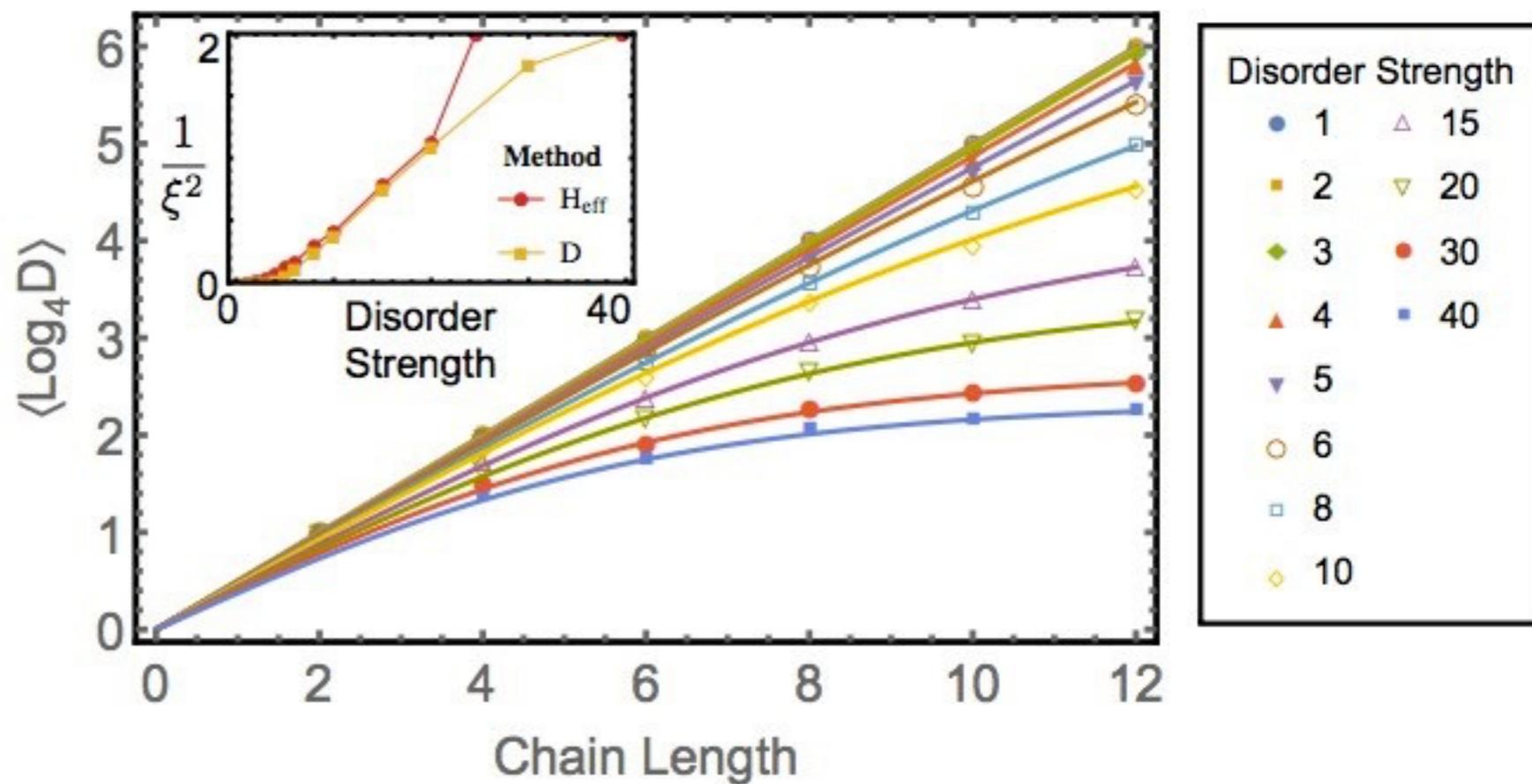
Many body localization

disorder + interaction + hopping

quantum mechanics at infinite temperature!
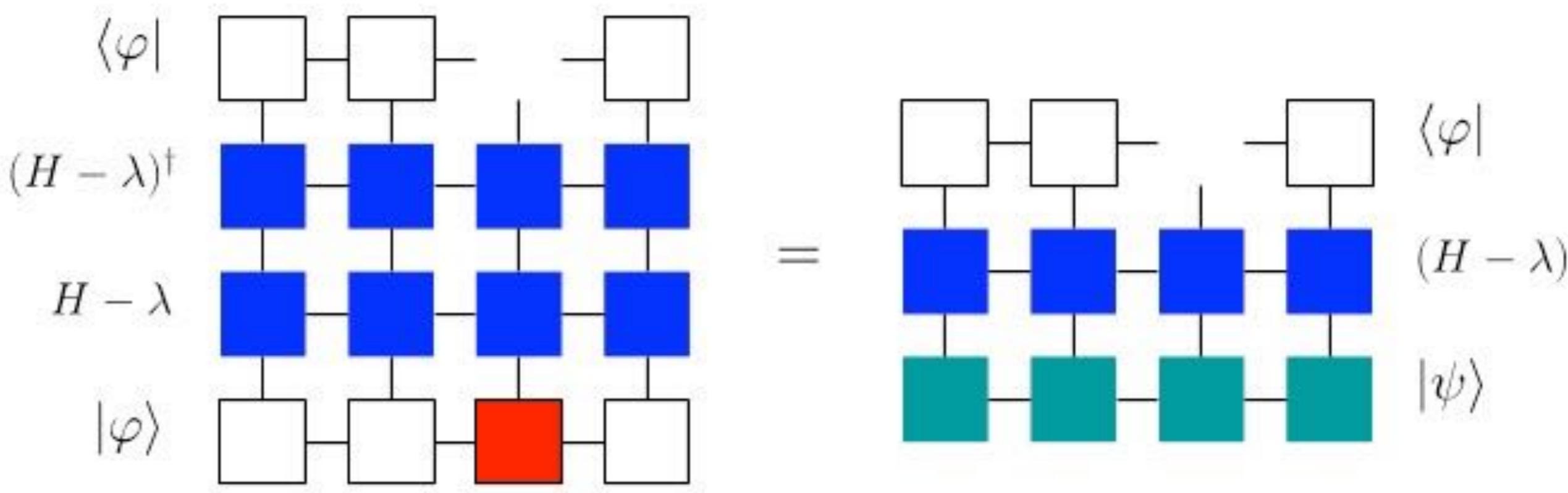
MBL IPR

Are you spread out over all of Hilbert space or just a little piece of it?

IPR $\dfrac{\sum_x |\Psi(x)|^4}{\sum_x |\Psi(x)|^2}$

MBL should be 'localized'

Let Φ map product state i to eigenstate $\Phi[i]$

Minimize $\sum_i |\langle i|\Phi[i]\rangle|^2$ over all functions Φ

This can be done with bipartite matching.
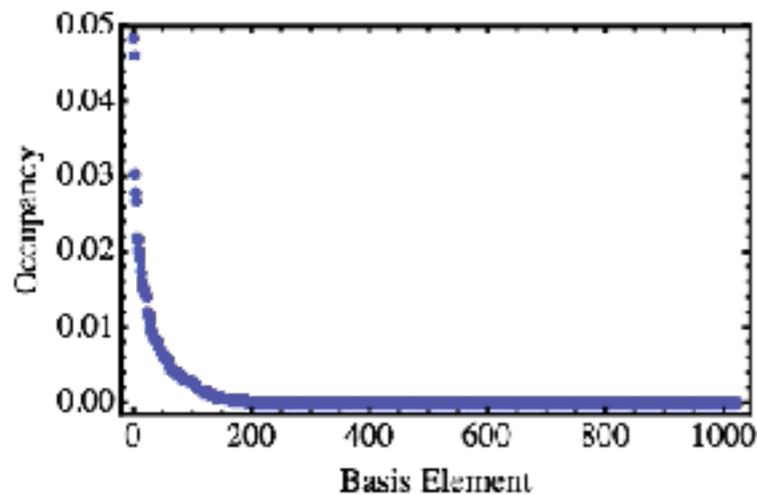
Low disorder
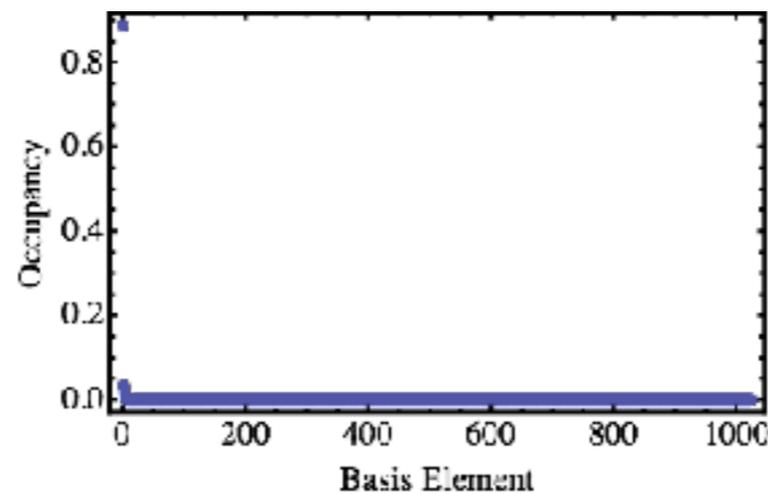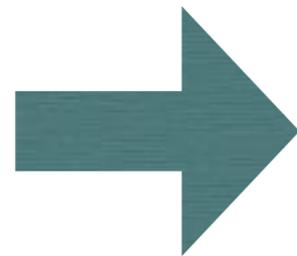
High disorder
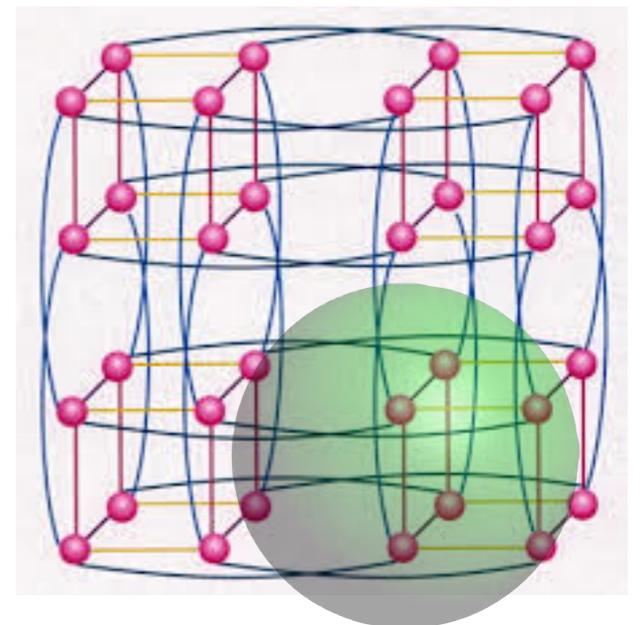
<u>Outline</u>   finding (all) the excited states in **perfect insulators**

* Exciting physical phenomenon: many body localization - no conductivity even at infinite T

* The relevant "order parameter" is the eigenstates.

* There exists a compact representation of the entire spectrum.

   * Which we can find:

       Each eigenstate of the form GEEGGEEGEGE

  * To find even better states, use many tricks + (a generalization of) KKR.

Discussion: Will any of this apply beyond this physical system to three-dimensional, electronic structure systems.

does this have anything to do with reality?

probably

other phenomenology

Q: Can we get an excited state in the middle of the spectrum?

Suppose we are exceedingly greedy. Can we get them all?

2^n eigenstates. Each with 2^n numbers.

We couldn't even write them down!

But we will see we can represent them in a compact way.

Inset axis: $\frac{1}{\xi^2}$ vs Disorder Strength

Method
H$_{eff}$
D

Main plot: $\langle Log_4 D \rangle$ vs Chain Length

Disorder Strength
1   15
2   20
3   30
4   40
5
6
8
10

(a)

Disorder Strength
20   10   6   4   2

Probability vs Bond Dimension — D

(b)

$\Delta=2$ $\Delta=4$ $\Delta=6$
$\Delta=10$ $\Delta=20$ $\Delta=40$

Probability vs Bond Dimension

Chain Length
6
8
10
12
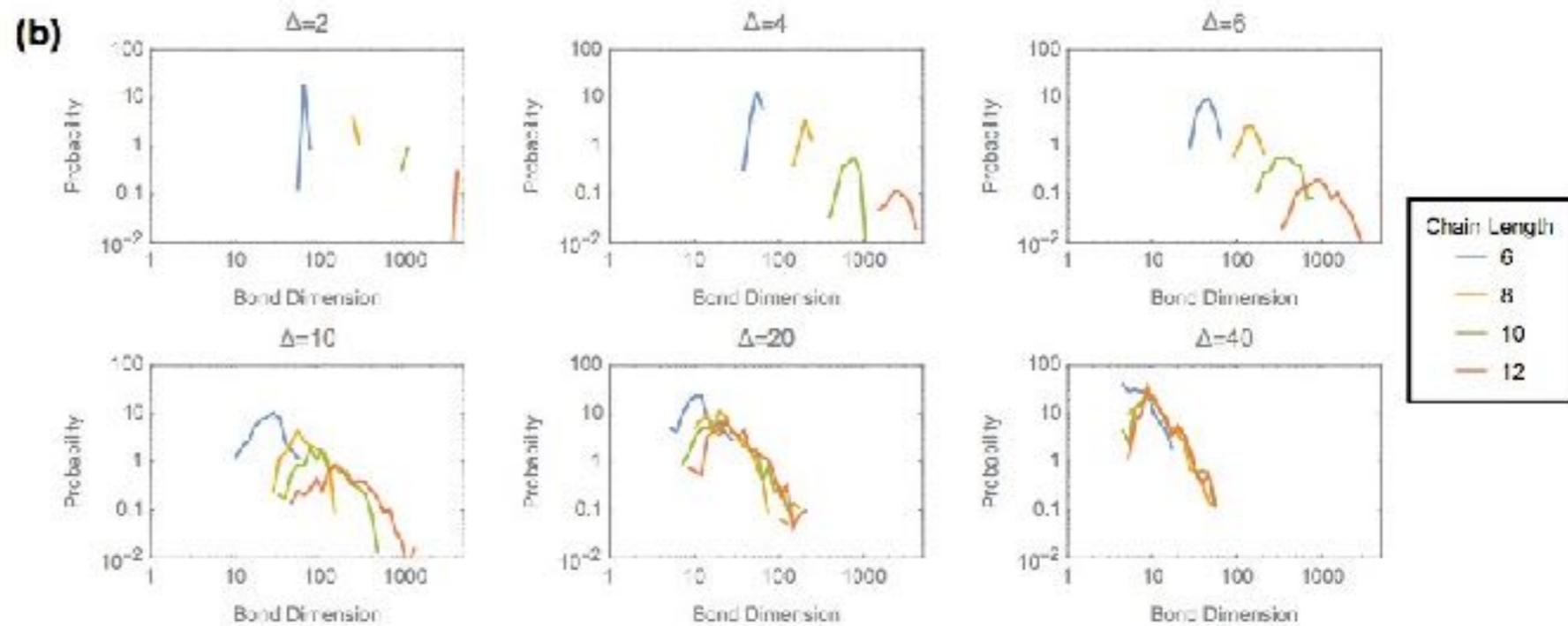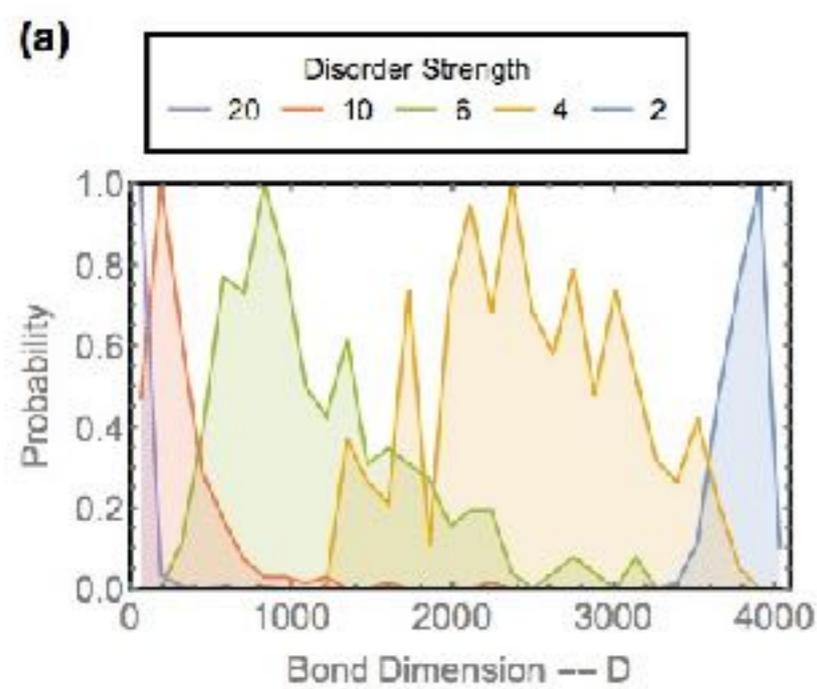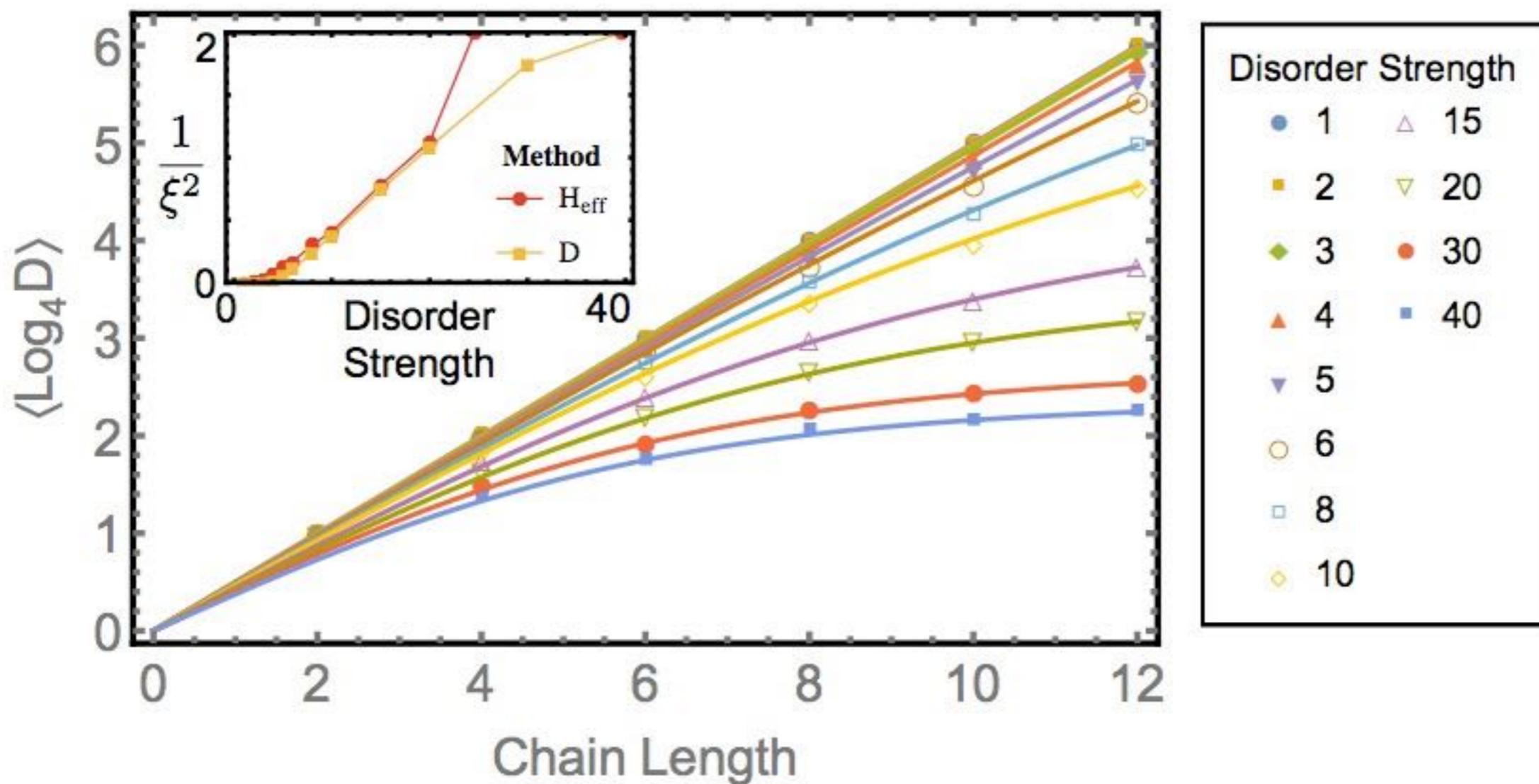
Matrix product states
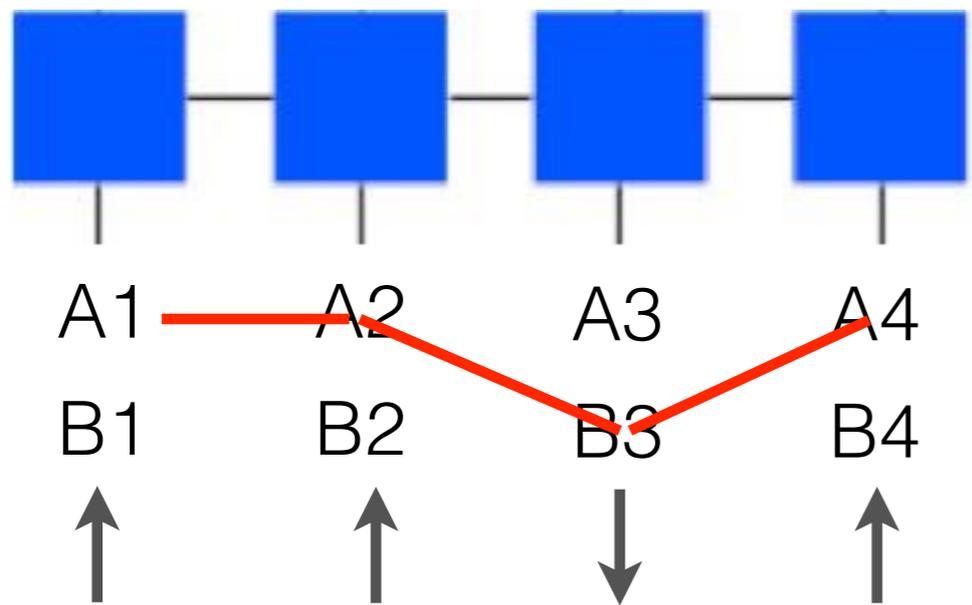
Dealing with electrons

Protons in water were at finite temperature: T=300 K

Electrons are on a ground state: T=0 K

(also fermions)

Aluminum: 136,000 Kelvin

Bosons   Fermions
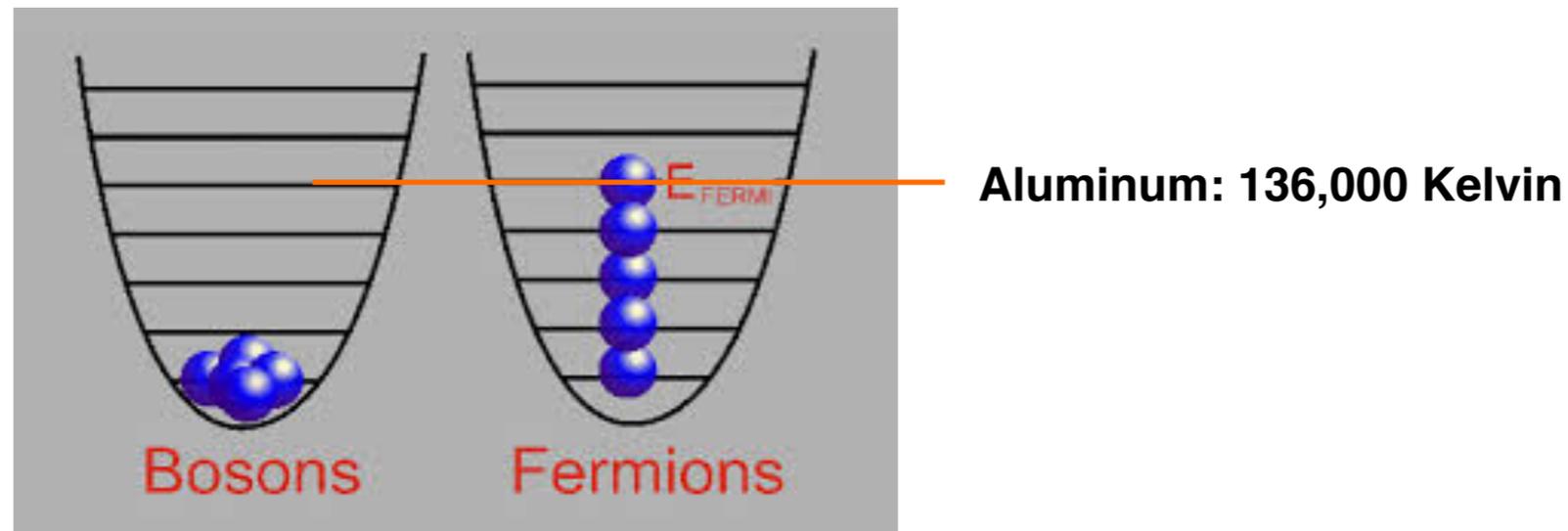
No point in doing path integrals.

Remember our whole goal: Given the ion locations R_I, what is the energy.

To get the energy, we could use the electronic wave-function.

$$E = \left[\int \Psi(R)[H\Psi](R)dR \right] / \left[\int \Psi(R)\Psi(R)dR \right]$$

The variational principle

$$E[\Psi(r_1, r_2, ...r_n)] \geq E_0$$
$$E[\Psi_0(r_1, r_2, ...r_n)] = E_0$$

Let's just guess the ground state.

More refined: Let's guess many states and assume the one with the lowest energy is the best guess.

Important steps:

1. How to compute energy?

2. What wave-functions?

3. How to optimize?

1. How to compute energy?

$$E = \frac{\int |\Psi(r_1, r_2, ..r_n)|^2 \frac{[H\Psi](R)}{\Psi(R)} dR}{\int |\Psi(r_1, r_2, ..r_n)|^2 dR}$$

Monte Carlo!!

Location of the electrons

Configuration Space: $\{R\}$
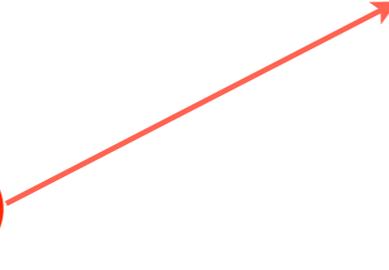
Probability: $|\Psi(R)|^2$

Algorithm

Start in location R for the electrons
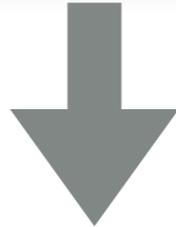
Choose a new location R'

If $|\Psi(R')|^2/|\Psi(R)|^2 > \mathrm{rand}()$

    use R'

else:

    keep R

Measure:

$$\frac{H\Psi(R)}{\Psi(R)}$$

$$\Psi = \det(M)$$
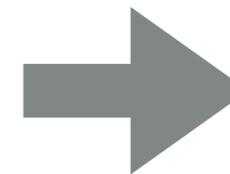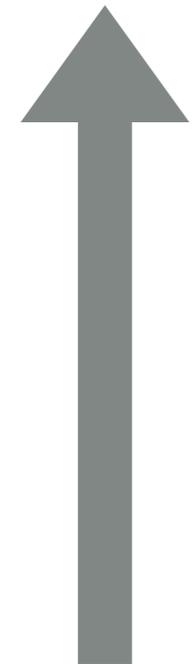
$$M_{ij} = \boxed{\phi_i}(r_j)$$

Slater Determinant

**Three dimensional function
N of them**

Hartree Fock: Minimize this ansatz
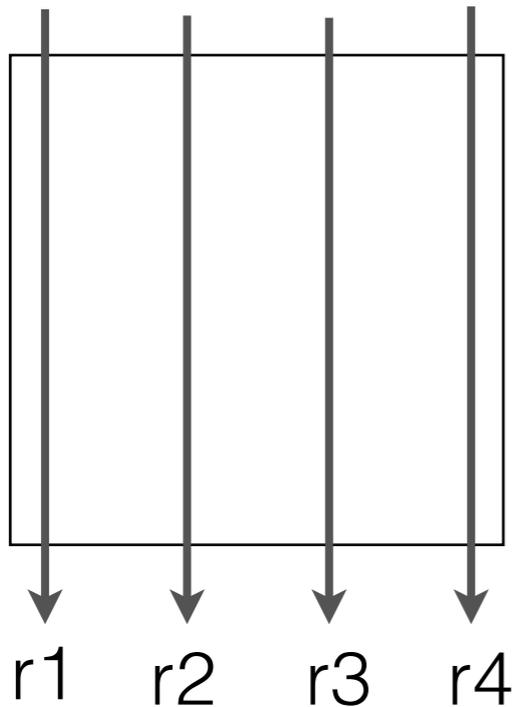
r1   r2   r3   r4

Notice: If you move one electron only one row of this matrix changes.

Need $\Psi(R')/\Psi(R)$

$$\frac{\det \begin{array}{cccc} \text{r1'} & \text{r2} & \text{r3} & \text{r4} \end{array}}{\det \begin{array}{cccc} \text{r1} & \text{r2} & \text{r3} & \text{r4} \end{array}} = (1 + v^T A^{-1} u)$$
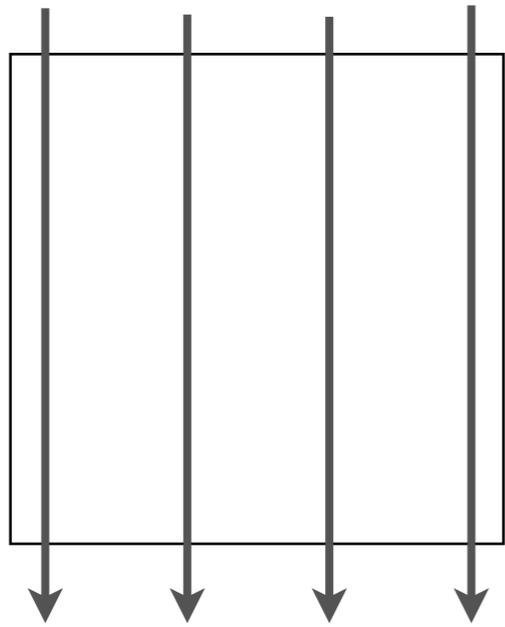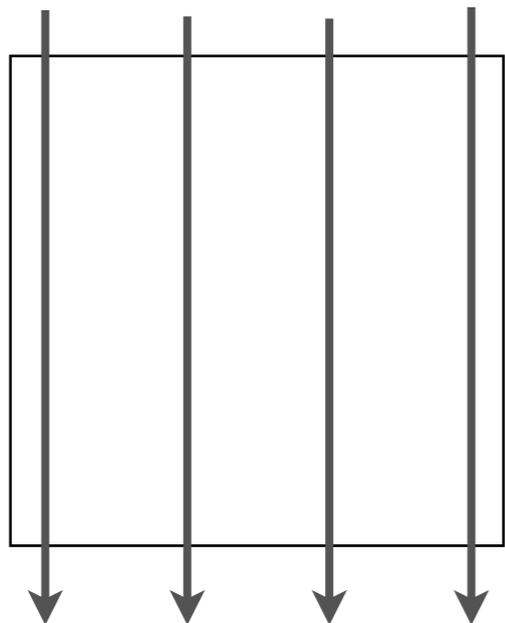
Must keep the inverse up to date.

Q: **Sanity Check**: Does this get the pauli principle correct?

$$\Psi = \det(M_\uparrow)$$

det

r1' r2   r3   r4
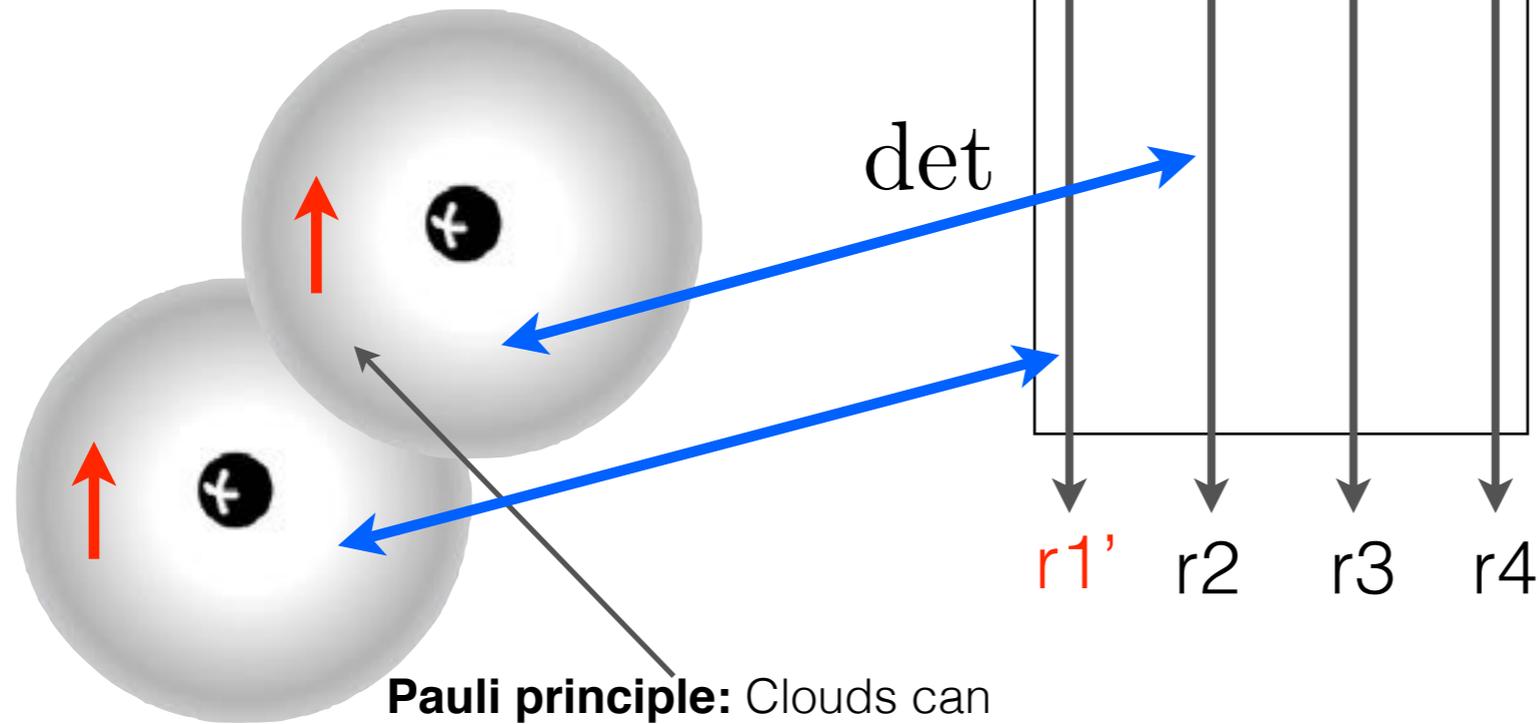
Pauli principle: Clouds can overlap but two electrons can't be in the same spot at the same time.

What happens when r1=r2?

Q: There are up and down electrons. What should I do with them?

$$\Psi = \det(M_\uparrow)\det(M_\downarrow)$$

Q: **What physics does Hartree Fock miss out on?**

$$\Psi = \det(M_\uparrow)\det(M_\downarrow)$$
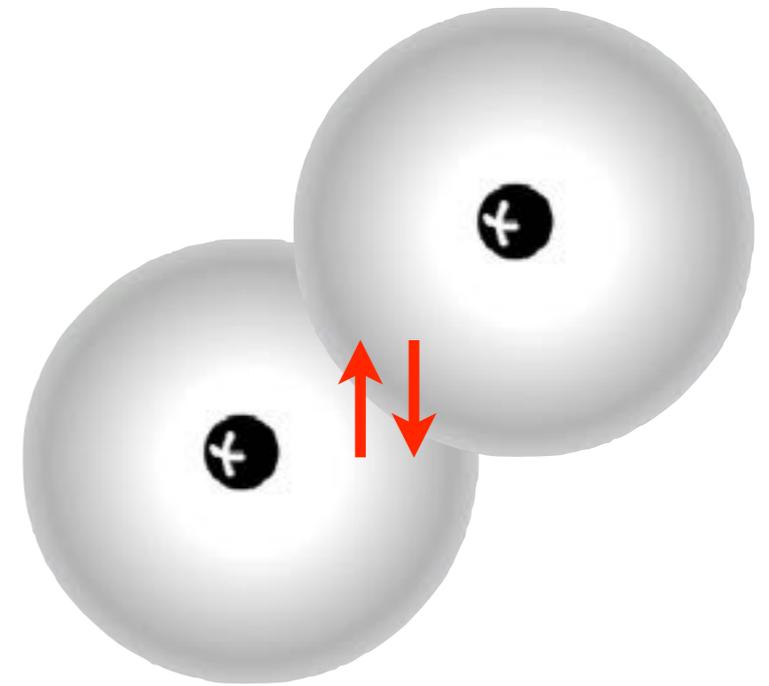
Q: What physics does Hartree Fock miss out on?

$$\Psi = \det(M_\uparrow)\det(M_\downarrow)$$

Q: How do we fix this?

Need some part of the wave-function which says, a spin up and spin down electron should stay away from each other.

Jastrow: $\exp\left[-\sum_{ij} \underline{u(|r_i - r_j|)}\right]$

One-dimensional function: get large as u->0

Nothing keeps an up and down electron from getting close. The probability an up electron is somewhere is independent of the down electron position.

We can get almost an exact two-body Jastrow.

Slater-Jastrow: $\Psi = \det(M_\uparrow)\det(M_\downarrow)\exp\left[-\sum_{ij} u(|r_i - r_j|)\right]$

Slater-Jastrow: $\Psi = \det(M_\uparrow)\det(M_\downarrow)\exp[-u(|r_i - r_j|)]$

This is what makes variational Monte Carlo more powerful then quantum chemistry.

Quantum Chemistry: $\sum_i \det(M_{i\uparrow})\det(M_{i\downarrow})$

Need thousands of these to get the electron-electron repulsion correct.

In quantum Monte Carlo, we get it essentially for free.

Q: **Is their a trade-off?**

A: **Yes. Quantum chemistry is mainly linear algebra. QMC requires randomness.**

Generalized Jastrow

$$\exp\left[-U(R)\right] = \exp\left[-\sum_{ij} u(|r_i - r_j|)\right] \exp\left[-\sum_{ijk} u(r_i, r_j, r_k)\right] \exp\left[-\sum_{ijkl} u(r_i, r_j, r_k, r_l)\right] \dots$$

two-body **three-body** **four-body**

Q: **What set of wave-functions does this include?**

Generalized Jastrow

$$\exp\left[-U(R)\right] = \exp\left[-\sum_{ij} u(|r_i - r_j|)\right] \exp\left[-\sum_{ijk} u(r_i, r_j, r_k)\right] \exp\left[-\sum_{ijkl} u(r_i, r_j, r_k, r_l)\right] \cdots$$

two-body　　　　**three-body**　　　　**four-body**

Q: **What set of wave-functions does this include?**

A: **All positive wave-functions**

$$\Psi = \det(M_\uparrow)\det(M_\downarrow)\exp\left[-U(R)\right]$$

Sets the sign-structure.　　　　**If we could optimize all the U's, we would have the best wave-function consistent with the signs of det's.**

You could imagine improving wave-functions, by expanding in higher-body Jastrows.

Aside: At the beginning of quantum mechanics, you might worry how should we write down a wave-function in quantum mechanics for a solid and for a liquid.

Q: What does this mean?

If you ask the quantum mechanical wave-function where the particles are, it tells you they are distributed like a liquid.

Q: What probability distribution looks like a liquid?

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Boltzmann Distribution:

$$Pr(R) \propto \exp[-\beta V(R)] \longleftrightarrow$$

Q: How can we write a wave-function that gives us this probability distribution?

Fact 1: $Pr(R) \propto |\Psi(R)|^2$

Fact 2:

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Boltzmann Distribution:

$$Pr(R) \propto \exp[-\beta V(R)] \longleftrightarrow \exp[-U(R)]$$

$$\beta V(R) \leftrightarrow U(R)$$

Q: How can we write a wave-function that gives us this probability distribution?

Fact 1: $Pr(R) \propto |\Psi(R)|^2$

Fact 2: Jastrow: $\exp[-U(R)]$

A simple quantum mechanical wave-function to give you a liquid.

Q: What about a quantum mechanical wave-function for a solid?

For the quantum-mechanical expert:

Q: What's wrong with this wave-function for the solid?

Hint: Think about superfluidity.

Slater-Jastrow: $\Psi = \det(M_\uparrow) \det(M_\downarrow) \exp\left[-\sum_{ij} u(|r_i - r_j|)\right]$

$$M_{ij} = \boxed{\phi_i}(r_j)$$

Three dimensional function
N of them

This is the bread and butter wave-function for VMC

In a second, we will see how we optimize. But before that, let's see what we optimize?

Optimize the Jastrow (a few one-d functions)

Optimize the phi's (N 3d functions)

Finding the **best** wave-function

Start in location R for the electrons
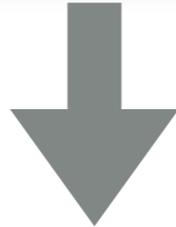
Choose a new location R'
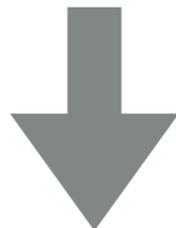
If $|\Psi(R')|^2/|\Psi(R)|^2 > \mathrm{rand}()$

    use R'

else:

    keep R
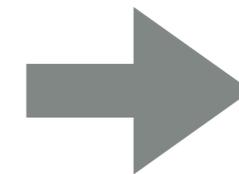
Measure:

$$\frac{H\Psi(R)}{\Psi(R)}$$

Finding the **best** wave-function

Try many guesses.

Choose the lowest one.

$$\Psi_{\text{guess}} \qquad E_{\text{guess}}$$

VMC
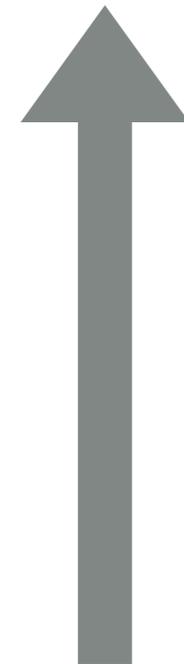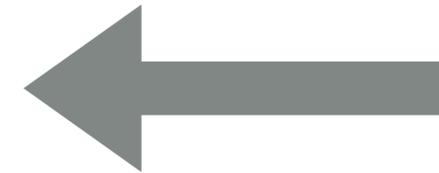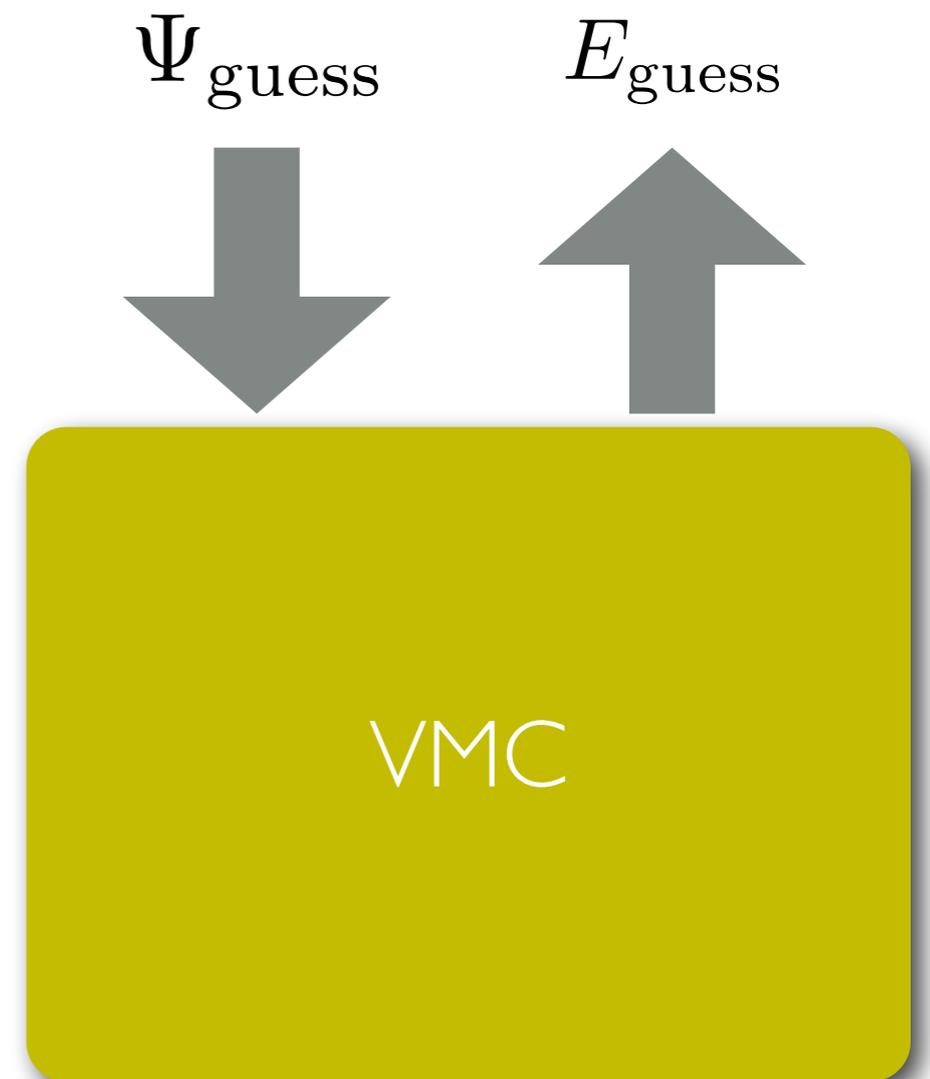
Finding the **best** wave-function

Try many guesses.

Choose the lowest one.

Better yet, tell some optimization package to find the minimum of this objective function.

Why this is hard

1. Global vs. local minima

2. Derivatives

3. Stochastic Errors
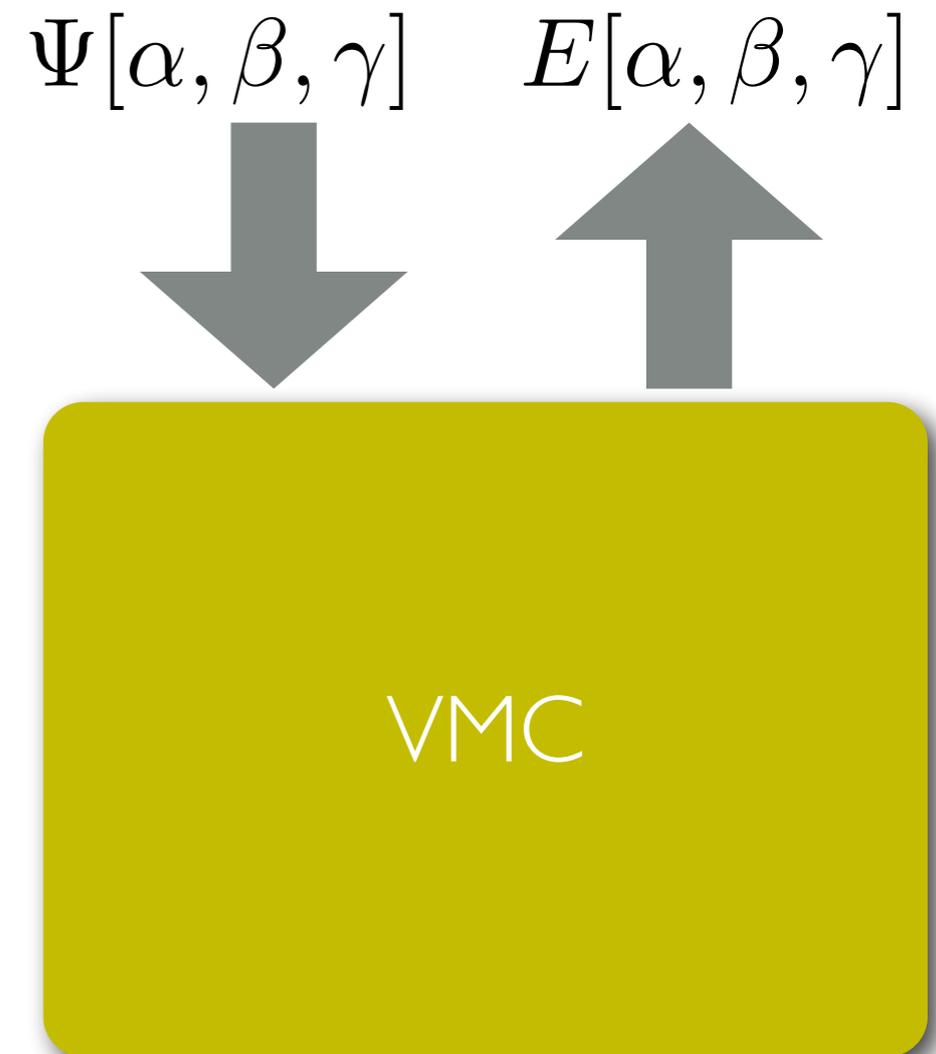
$$\Psi[\alpha, \beta, \gamma] \qquad E[\alpha, \beta, \gamma]$$

VMC

Q: Can we get an excited state in the middle of the spectrum?

Suppose we are exceedingly greedy. Can we get them all?

Derivatives

$$\frac{\partial E[\alpha, \beta, \gamma]}{\partial \alpha} = \frac{\partial}{\partial \alpha} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$= 2 \boxed{\frac{\langle \frac{\partial \Psi}{\partial \alpha} | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}} - 2 \boxed{\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}} \boxed{\frac{\langle \frac{\partial \Psi}{\partial \alpha} | \Psi \rangle}{\langle \Psi | \Psi \rangle}}$$

needs to be an integral   E   needs to be an integral

$$\frac{\int dR |\Psi(R)|^2 [\frac{\partial \Psi(R)}{\partial \alpha} / \Psi(R)]}{\int dR |\Psi(R)|^2}$$

**The first (and second) derivatives of the energy can be computed by a Monte Carlo integral.**

Need derivatives with respect to parameters living in a derivative...

Stochastic Errors

Can we fix this?

Two choices:

1. **Remove the stochasticity**

2. **Embrace the stochasticity**

These are noisy

$$\Psi[\alpha, \beta, \gamma] \qquad E[\alpha, \beta, \gamma] \qquad \partial E/\partial\alpha$$

VMC
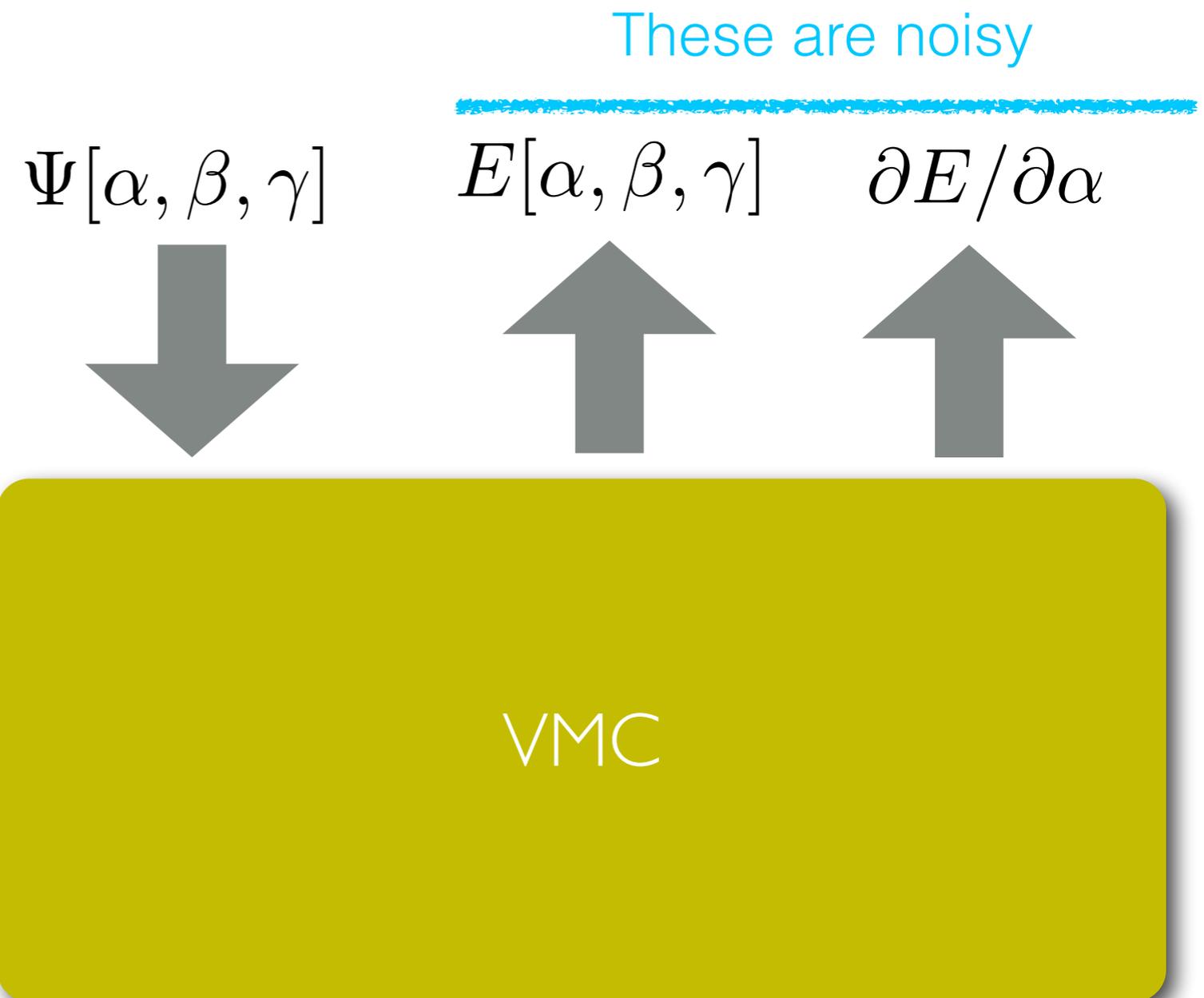
finding (all) the excited states in perfect insulators

back to model land....

Insulators that you know and love: **Arrhenius Equation**

$$\sigma = (\sigma_0/T)\exp[-E_a/kT]$$

Perfect Insulators:

$$\sigma = 0$$

The prototypical example: Anderson Insulator

Hopping + Disorder gives localized single particle orbitals.

   No conductivity

This is single particle physics. The many body generalization: many-body localization.
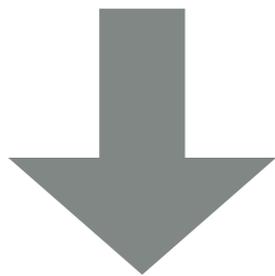
Disorder

Localized single-
particle orbitals

Disorder + Interactions
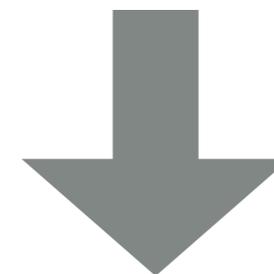
?

Remove the stochasticity

$\Psi[\alpha, \beta, \gamma]$ $E[\alpha, \beta, \gamma]$

VMC

$\Psi[\alpha, \beta, \gamma]$ $\{R_1, R_2, ...R_{1000}\}[\alpha, \beta, \gamma]$

VMC
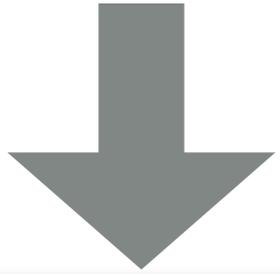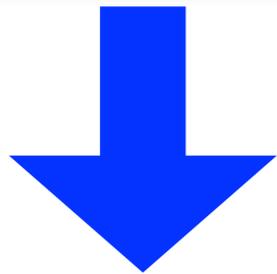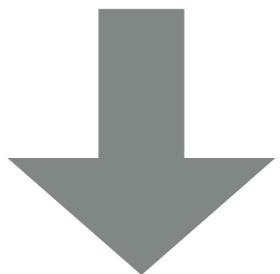
Q: If I give you this list of 1000 numbers can you evaluate $E[\alpha', \beta', \gamma']$

Remove the stochasticity

$$\Psi[\alpha, \beta, \gamma] \quad E[\alpha, \beta, \gamma]$$

VMC

$$\Psi[\alpha, \beta, \gamma] \quad \{R_1, R_2, ...R_{1000}\}[\alpha, \beta, \gamma]$$

VMC
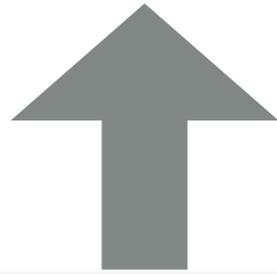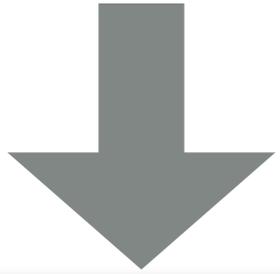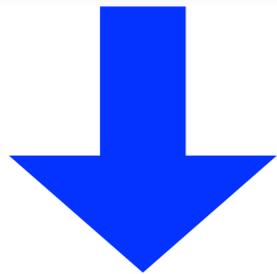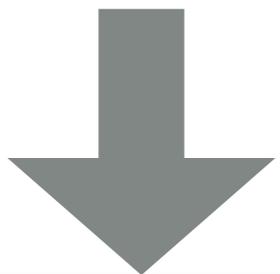
Q: If I give you this list of 1000 numbers can you evaluate $E[\alpha', \beta', \gamma']$

$$E[\alpha'] = \frac{\int |\Psi[\alpha']|^2 \frac{[H\Psi[\alpha']](R)}{\Psi(R)} dR}{\int |\Psi[\alpha']|^2 dR}$$

Then I've removed the stochasticity.

But there is an oversampling problem.

Removing the oversampling

A comment about the local energy: $\dfrac{H\Psi}{\Psi}$

Q: What happens if the Psi is a true eigenstate.

We could also optimize the variance of the local energy.

This avoid oversampling.

2. Embrace the stochasticity

Assume each objective function response is truly random.

Need a optimization method which is insensitive to this (not conjugate gradient!)

Stochastic gradient descent

Time evolution

Linear Method